

Development of Metal-Matrix Composite Materials by Rapid Solidification Process

A

Thesis

Submitted for the award of degree of

DOCTOR OF PHILOSOPHY

By

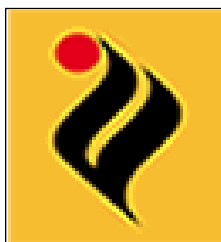
Kamalpreet Kaur

(Registration No. 90712007)

Under the Supervision of

Dr. O.P. Pandey

Senior Professor



School of Physics and Materials Science

Thapar University, Patiala – 147 004.

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CERTIFICATE

This is to certify that the thesis entitled “**Development of Metal-Matrix Composite Materials by Rapid Solidification Process**” which is being submitted by Ms. Kamalpreet Kaur to School of Physics and Materials Science, Thapar University, Patiala in fulfilment of the requirements for the award of the degree of Doctor of Philosophy, is a record of candidate’s own work carried out by her under my guidance and supervision. The matter presented in this thesis has not been submitted in part or full for the award of any degree in any other University or Institute.

Date: 10/07/2012

Place: Patiala



Dr. O.P. Pandey
Senior Professor
School of Physics and Materials Science
Thapar University
Patiala-147004 (India)

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PREFACE

The current demand of industries to develop high performance lightweight alloys for fuel saving is increasing day by day. Light weight Al-alloys which are used in structural applications like automotive, aerospace, defense industry and other fields of engineering requires further modification for better properties. Al-Si alloys which are used for structural purposes have wide range of composition and varies from hypoeutectic to hypereutectic compositions. However, eutectic and near eutectic Al-Si alloys with Si contents (≈ 12.6 wt% Si) exhibit better physical properties. Moreover, other reinforced particles like oxides, nitrides and carbides in various volume fractions are used in combination with Al-alloys to enhance their properties. The manufacturing methods of these composites are also important factor which causes variation in their properties.

There are two ways to modify the microstructures i.e. chemically or by rapid solidification processes. In the present study, the spray forming process has been adopted to develop MMC which is different from other rapid solidification processes. After studying the literature of Al-Si alloys, it has been found that a little information regarding particulate size and volume fraction related to abrasive or dry sliding wear processes is available. The data collected from the work done indicate that only two reinforcement types, mainly silicon carbide and alumina have been tried. The wear behavior of spray deposited alloys with other potential reinforcement materials such as TiC, TiB, ZrSiO₄, Si₃N₄ and SiO₂ are less studied systems. Only few publications are on the combined approach of immiscible elements like Pb, Bi, Sn and particle reinforced rapidly solidified AMCs i.e. spray forming techniques. Limited work has been reported on fabrication and characterization of zircon sand reinforced with aluminum metal matrix composites and none has used spray deposition technique to manufacture zircon sand reinforced AMCs. Considering these aspects we have planned to work on spray forming.

The main objective is to prepare the cost-effective AMCs by taking Al-Si alloy as matrix with immiscible elements like Sn and Bi and also some ceramic particulate like silicon carbide and zircon sand as reinforced phase using spray deposition technique. Further the

wear behavior of the developed composites has been analyzed with variation in load and temperature.

The **1st chapter** presents in brief the background of the composites and their classification. Various fabrication and processing techniques for their preparation with superiority of composites over monolithic alloys is also described. Further the advantages of rapid solidification process viz. spray forming are discussed. The fundamental characteristics of light weight Al-Si alloys and reinforcements are explained in light of their application for better mechanical properties. The concepts of rapid solidification have also been summarized. Chapter also describes about wear and related mechanisms for loss of materials during wear.

Chapter 2 gives a detailed account of the literature review. It was necessary to review the work done at national and international level before selecting any particular composition and reinforcement material. The near eutectic Al-Si composition (commercially grade LM13) and zircon sand, SiC as reinforcement are selected on the basis of gaps in the literature.

The **3rd chapter** contains the information about designing of the nozzle. The spray formed setup has been designed and fabricated in our metallurgical laboratory. In this chapter, the designs of convergent-divergent nozzle used for atomization has been described. The problem faced with the initial designs and details of modified nozzle is also documented. The chapter reveals different parts of spray set-up assembly and their drawings.

On the basis of literature study different samples have been prepared and detailed description is listed in **chapter 4**. This chapter describes the materials specifications used in present work and procedure adopted to prepare composites from these materials. A lot of experiments have been done to optimize the parameters before the fabrication of composites. The various characterization techniques; X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDX), Rockwell hardness testing and dry sliding wear with their parameter details are also elaborated. Further the whole methodology and the step-wise wear testing plan is shown in the form of flow charts.

In **chapter 5**, the experimental results of as received and spray formed LM13 alloy (containing around 12 wt.% Si) are presented. The samples were analyzed by optical and SEM along with EDS to study the difference in morphology of the alloy after spray forming. Further the samples were wear tested under various loads and temperatures. The worn surfaces and debris obtained were also analyzed by SEM and EDS to predict the mode of wear under different set of conditions.

The results and discussions part are presented in **chapter 6 and chapter 7** for zircon sand and silicon carbide reinforcement respectively.

In the **chapter 6**, the experimental results of zircon sand reinforced composites are presented. The chapter is subdivided in two parts on the basis of the size range of zircon sand particulates. The zircon sand reinforced composites have been prepared by spray deposition process where immiscible element Sn and Bi in varying quantity is added to achieve dense product. The prepared samples have been characterized by XRD, Optical microscope, SEM and EDS. Wear tests of spray formed samples have been done at different loads and temperatures. The analysis of worn surfaces has been done to predict the mode of wear for the prepared samples. **Chapter 7** describes the details of the experimental results of silicon carbide (SiC) reinforced composites. This chapter is also subdivided in two parts on the basis of the size range of SiC particulates. The characterization of the prepared samples has been done by XRD, SEM and EDS. The microstructural analysis of worn surfaces and wear debris has been done to predict the mode of wear in various tested specimens.

Chapter 8 summarizes the results of various experiments described in previous chapters. At the end, suggestions for future work are given on the basis of results obtained in this work.

At the end, the list of papers published, presented and communicated are also appended.

CHAPTER-1

Introduction

Overview

This chapter presents in brief the background of the composites and their classification. Various fabrication and processing techniques for their preparation along with superiority of composites over monolithic alloys is also described. Further the advantages of rapid solidification process viz. spray forming are discussed. The fundamental characteristics of light weight Al-Si alloys and reinforcements are explained in light of their application for better mechanical properties. The concepts of rapid solidification have also been summarized. Chapter also describes about wear and related mechanisms for loss of materials during wear.

Historically materials development and their application started about two million years ago when mankind started shaping and using the natural materials for the hunt of food and living. Prehistoric people have adapted the material around them such as wood, stone and some few metals like gold and silver, which are available on earth's crust as such. The process of smelting the mineral in 3500 BC has led to discovery of bronze metal and gave an idea about how to shape the metal into an object by casting. In 1700's awareness of better smelting processes expanded the use of iron for making machines, which led to the industrial revolution [1]. In the wake of the recent developments, several new demands are being placed in front of science and technology. People's demand for new materials and new ways of production is constantly increasing.

One of the new promising engineering materials is the combination of two or more different materials tailored specifically for its end application. The composites have been proving one of the best selections for such materials. The engineered materials made from two or more constituent materials which show significantly different physical and chemical properties yet remain separate and distinct on a macroscopic level with the finished structure is known as composite material. The constituents retain their identities in the composites and do not dissolve or otherwise merge completely into each other, although they act together [2]. Composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk properties significantly different from those of any of the constituents.

- a) **Matrix phase:** The primary phase, having a continuous character, is called matrix. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it.
- b) **Dispersed (reinforcing) phase:** The second phase (or phases) is embedded in the matrix in a discontinuous form. This secondary phase is called dispersed phase. Dispersed phase is usually stronger than the matrix, therefore it is sometimes called reinforcing phase.

Composite materials are usually classified based on physical or chemical nature of the matrix phase, e.g., polymer-matrix, metal-matrix and ceramic-matrix composites. Present

work is concerned with metal matrix composites and more specifically on the aluminium matrix composites (AMCs).

1.1 Aluminium Matrix Composites (AMC)

AMCs are composed of aluminium/aluminium alloy as matrix phase and dispersed ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum etc.) phase. AMCs exhibit the ability to withstand high tensile and compressive stresses by the transfer and distribution of the applied load from the ductile matrix to the reinforcement phase.

The current demand of industries to develop high performance lightweight alloys for fuel saving is increasing day by day. Light weight Al-alloys which are used in structural applications like automotive, aerospace, defense industry and other fields of engineering require further modification to achieve better properties [3, 4].

Aluminium (Al) and silicon (Si) having closer densities are the best suitable alloying elements for the development of light weight alloys. Al-Si alloys are one of the deserving candidates for this class due to their low coefficient of thermal expansion, good machinability and greater strength to weight ratio.

These alloys are most versatile materials, comprising 85% to 90% of the total aluminium cast parts produced for the automotive industry. Enhancement in performance can be attained with microstructural homogeneity of second phase. Depending on the Si concentration, the Al-Si alloy systems fall into three major categories: hypoeutectic (<12% Si), eutectic (12–13% Si) and hypereutectic (14–25% Si) [5]. However, the compositions and relative amounts of the two phases are limited to a narrow range (Fig. 1.1), controlled by growth kinetics and equilibrium conditions. Al containing Si above the solubility limit can be produced by rapid solidification processes. Al-Si alloys which are used for structural purposes have a wide range of composition, which varies from hypoeutectic to hypereutectic compositions. However, eutectic and near eutectic Al-Si alloys with Si contents (≈ 12.6 wt% Si) exhibit desirable physical properties. Moreover, other reinforced particles like oxides, nitrides and carbides with various volume fractions are used in aluminium metal combination to enhance their properties. The manufacturing methods of these composites are also important as it influences their properties.

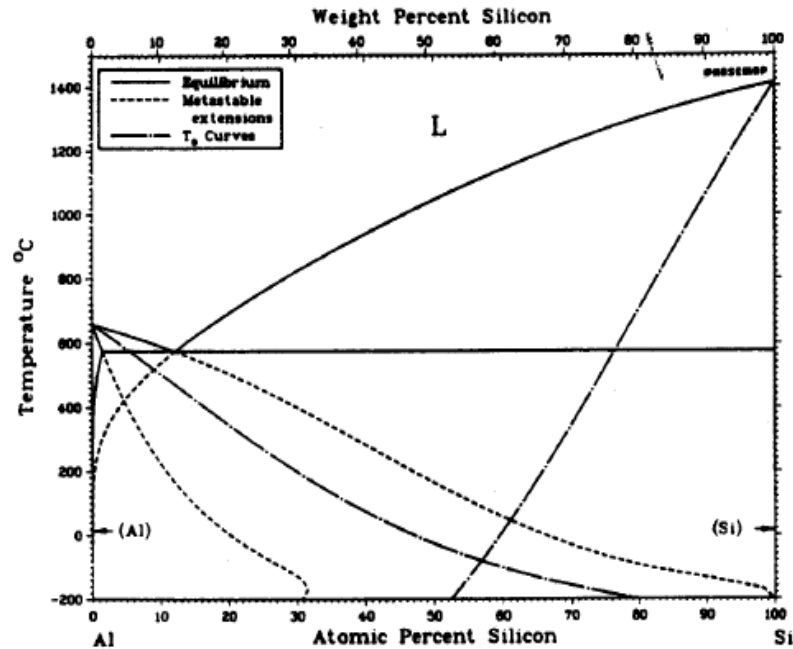


Figure 1.1: Phase diagram for the Al-Si system showing metastable extensions of liquidus and solidus lines [6].

On the other hand, other non-metallic constituents that are embedded in this Al/Al-alloy matrix serve as reinforcement. The major advantages of AMCs compared to unreinforced materials are as follows:

- Greater strength
- Improved stiffness
- Reduced density(weight)
- Improved high-temperature properties
- Controlled thermal expansion coefficient
- Thermal/heat management
- Enhanced and tailored electrical performance
- Improved abrasion and wear resistance
- Control of mass (especially in reciprocating applications)
- Improved damping capabilities.

Surappa [7] classified AMCs into four categories depending on the type of reinforcement:

1.1.1 Whisker and short fibre-reinforced aluminium matrix composites (SFAMCs)

SFAMCs contain discontinuous short fibres oriented in various directions having an aspect ratio greater than 5. These are one of the first and the most popular AMCs to be developed and used in pistons. These are produced by the squeeze infiltration process [8]. However, in the recent year's usage of whiskers as reinforcements in AMCs are fading due to perceived health hazards and hence of late commercial exploitation of whisker reinforced composites has been very limited. Short fibre reinforced AMCs display characteristics in between that of continuous fibre and particle reinforced AMCs.

1.1.2 Continuous fibre-reinforced aluminium matrix composites (CFAMCs)

CFAMCs contain the reinforcements in the form of continuous fibres (Al_2O_3 , SiC or carbon) having the diameter less than 20 μm . These long continuous fibres can be parallel or knitted prior to the production of the composite. AMCs having the fibre volume fraction up to 40% are produced by squeeze infiltration technique [8]. Alumina fibre (continuous fibre) reinforced composite having a tensile strength and elastic stiffness of 1500 MPa and 240 GPa respectively.

1.1.3 Mono filament reinforced aluminium matrix composites (MFAMCs)

Monofilaments are large diameter (100 to 150 μm) fibres, usually produced by chemical vapour deposition (CVD) of either SiC or B into a core of carbon fibre or W wire. Bending flexibility of monofilaments is low compared to multi filaments. Monofilament reinforced aluminium matrix composites are produced by diffusion bonding techniques, and is limited to super plastic forming aluminium alloy matrices [8].

1.1.4 Particle reinforced aluminium matrix composites (PAMCs)

These composites contain equiaxed ceramic reinforcements with an aspect ratio less than about 5. Ceramic reinforcements are generally oxides or carbides or borides (Al_2O_3 , ZrO_2 , SiC or TiB_2) and present in the volume fraction less than 30% when used for structural and wear resistance applications. However, in electronic packaging applications reinforcement volume fraction could be as high as 80%. In general, PAMCs are manufactured either by solid state (P/M processing) or liquid state (stir casting, infiltration and in-situ) processes. PAMCs are less expensive compared to CFAMCs. Mechanical properties of PAMCs are inferior compared to SFAMCs but far superior compared to unreinforced aluminium alloys.

These composites are isotropic in nature and can be subjected to a variety of secondary forming operations including extrusion, rolling and forging [8].

In CFAMCs and MFAMCs, the reinforcement is the principal load-bearing constituent and role of the aluminium matrix is to bond the reinforcement as well as transfer and distribute the load. In particle and whisker reinforced AMCs, the matrix is the major load-bearing constituent. The role of the reinforcement is to strengthen and stiffen the composite by preventing the matrix deformation due to mechanical restraint.

1.2 Modification of microstructure

Prasad et al. [9] have reported the wear behavior of the Al-Si alloys which was greatly influenced by the presence of primary Si particles and was a function of their size. For achieving better mechanical properties they have mentioned that the fine distribution of reinforced phases is required. There are two ways to modify the microstructures, i.e. chemically or by rapid solidification processes. In the chemically modified systems, some additives in the small amount at particular temperatures are added to refine the microstructure. However, in rapid solidification processes microstructure is controlled by higher cooling rates of the melts i.e. within the range of 10^3 to 10^6 Ks⁻¹, much faster than the conventional solidification rates which are 10^2 Ks⁻¹ or less [10, 11].

Silicon is introduced into the Al primarily to improve castability and flowability [12]. Silicon appears as thin plate-like structures (acicular). The morphology of the silicon is quite dependent on the cooling rate. With low cooling rates, silicon appears coarse but as the cooling rate increases silicon becomes finer. Modification of silicon can also be achieved by the addition of Sr, Ba, Yt, Na, Sb etc. These elements modify the Si morphology from coarse to lamellar (finer) thus enhancing the mechanical properties of the cast product.

Rapid quenching of metallic melts was first introduced by Duwez [13] in 1960. After that varieties of techniques have been developed to obtain alloys as well as composites produced by rapid solidification. Although, the effect of rapid solidification varies widely from system to system, the major effects include:

- (i) Decreased grain size
- (ii) Increased chemical homogeneity

- (iii) Extension of solid solubility limits
- (iv) Creation of metastable crystalline phases
- (v) Formation of metallic glasses [14–16]

A large number of devices designed for producing rapid solidification materials have been reported over the last three decades, and these can be classified in many different ways. Jones [17] classified them into three categories:

- (i) Surface methods: Laser surface treatment
- (ii) Chill methods: Melt spinning and Planar flow castings
- (iii) Spray methods: Atomization and deposition, Gun quenching

Laser processing involves three major steps heating, melting and resolidification to generate required topography. It particularly indicates the field of surface treatments. It allows to generate high-energy concentrations and attaining elevated skin temperatures in the fraction of seconds with small thermal alteration of the bulk material. Melt spinning is continuous casting technique given by Libermann and Gaham [18]. Conventionally casting and powder metallurgical processes are used for making Al/Al-alloy composites at large scales. However, the microstructural control by spray deposition of Al-matrix composites (AMCs) provides an exciting new opportunity for the development of materials with a superior wear property. Spray deposition techniques fall into two distinct classes, depending whether the droplet stream is produced from a molten bath (Osprey process) or by continuous feeding of cold metal into a zone of rapid heat injection (thermal spray process).

Spray forming is a direct, single-step forming process, which combines aspects of atomization and deposition of molten material for the bulk conversion of a liquid metal or alloy into a near net-shape [19]. It differs from conventional thermal spray processes (plasma spray, high-velocity oxygen fuel (HVOF) spray, arc spraying, etc.) where the deposition rates are considerably higher and free standing products up to several tonnes in weight can be produced in relatively short times. Originally proposed by Richard Singer [20] at University College Swansea, the process has developed into a global technology

attracting interest for the bulk and near net-shape processing of a broad range of conventional and advanced high performance monolithic and composite materials.

Thus, by utilizing near-net shape forming and selective-reinforcement techniques, AMCs can offer economically viable solutions for the wide variety of commercial applications.

1.3 Commercially used processing techniques

Currently considerable attention is being given for modification of microstructure by different processing routes. This leads to the development of the alloy for industrial applications. Here the comparison of the processing steps involved in spray deposition with that of casting and powder metallurgy methods are given in Fig. 1.2 [21].

1.3.1 Castings

A casting may be defined as a *"metal object obtained by allowing molten metal to solidify in a mould"*, the shape of the object being determined by the shape of the mould cavity. Several machining operations are required to make a finished part. Moreover, the assembly of various smaller parts is required for an intricate complex shape machine part. Pressure casting or die casting is far more suitable and economical for such products. This level of versatility has placed die castings among the highest volume products made in the metalworking industry.

Commercially, zinc and aluminium are used for die casting. These are usually not pure metals; rather are alloys, which have better physical characteristics. Thermal-mechanical processing refers to the design and control of the individual metal working and heat treatment steps in a manufacturing process in order to enhance final properties.

1.3.2 Variables/defects in castings

During solidification of liquid metals and crystals, alloy formation takes place. The resulting morphology has certain characteristics peculiar to cast structures. The morphology includes both macrostructure and microstructure.

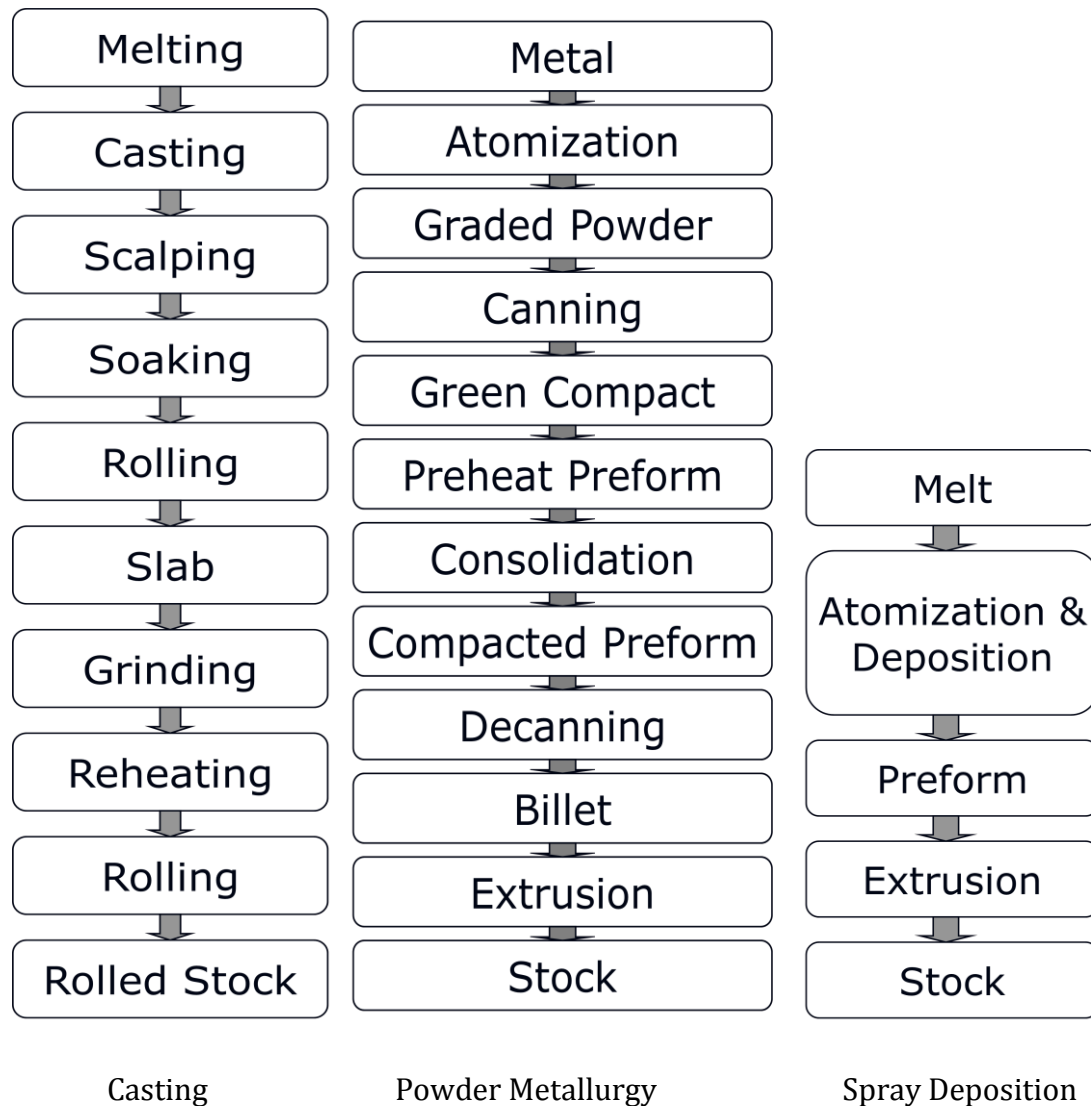


Figure 1.2: Comparison of production routes for high-grade materials [21].

- (a) *Grain size effect:* In castings grain size obtained is quite large in size during the solidification process. For better strength, the smaller grain size of the cast product is required.
- (b) *Grain boundary segregation:* Some alloying elements are added in the molten alloy to react with unwanted substances forming intermetallics. In some cases a fine distribution of these brittle phases helps in enhancing mechanical properties. However, if these get segregated along the grain boundaries it may lead to failure of the cast product.

(c) *Distribution in grain*: In certain cases, intermetallics are not finely distributed and get segregated as a thick molten liquid throughout the structure within the grains. This phase is brittle in nature and also has a different coefficient of thermal expansion as compared to the matrix. The existence of such segregation at a higher scale may cause severe type of damage. In almost all types of castings certain unwanted phases exist. Because of their different thermal expansions these phases may chip out easily and substance becomes weak at those areas.

1.3.3 Powder metallurgy

In the powder metallurgy process, metal powder is compacted by placing in a die under high pressure. The green compacted material is placed in the furnace and sintered in a controlled atmosphere at high temperatures. The metal powders coalesce and form a solid. The particle size, shape, structure and surface conditions also influence the final sintered part. The powders are obtained by atomizing molten metal using various types of atomization nozzles such as pressure nozzle, two fluid nozzle and centrifugal atomization. These atomization processes produce the broad particle size distribution except pressure nozzle, which confines the powders to narrow size regime. The process can be automated, and its advantages include control of porosity and grain size. The waste material can also be minimized depending upon the process parameters [22].

1.3.4 Limitations of powder metallurgy

A few limitations with P/M process are listed below:

1. The cost of powder production resulting in high tooling price.
2. There is always difficulty to handle and store the metal powder like degradable metal and fire hazards.
3. Large number of processing steps is involved.
4. The process restricts production of the complex shapes and features like radial holes in vertically pressed cylinders and re-entrant angles by die pressing.
5. The change in the resulted product is always observed after sintering, which depend upon the number of factors, e.g. powder size and shape, as pressed density [23].

1.4 Spray deposition technique

Spray forming or spray deposition is a new emerging technique in the field of metallurgy. Spray forming is different from powder metallurgical process within the strict definition because metal in powder form is not involved in this process. It consists of atomization of molten metal/alloys by high-velocity gas jets into micron size droplets, which are subsequently deposited on a substrate. The droplets get consolidated and solidified into a high density preform on the conductive substrate. The substrate motion can be rotating or stationary according to the requirement. The process inherits the benefits of rapid solidification effect through the generation of microstructure of preform with the desired level of properties. Its development has encompassed process design, process modeling, new materials and automatic control. The process of spray deposition involves the fundamental phenomena of atomization, fluid flow, heat flow, mass transport, solidification and microstructural development.

The solid thus produced has a structure similar to that of powder-based material with all the inherent advantages of fine grain, freedom from macro-segregation. In common with the P/M process, spray deposition facilitates the production of alloy compositions that are difficult if not impossible to produce conventionally, and in certain cases, the benefits that rapid solidification offers can be obtained also. Properties even superior to those of powder-based wrought products have been reported; for example, super alloys having a much lower inclusion count than that of its powder-based equivalent.

Extremely wide range of materials are being processed by this technique ranging from non-ferrous to ferrous metals, alloys and super alloys. The direct shapes that can be produced by spray forming are round billets, tubes, strip and discs and near-net shape preform. Other shapes like bearings, cylinder blocks can further be processed from round billets.

Grant [19] and Mathur et al. [24] reveals that the microstructure of the final deposit is related to the state of the droplets impinging on the top surface of the growing preform. In order to know the physical state of the droplets at the time of impingement, thermal history analysis of the droplets is inevitable. The atomized droplets lose heat, mostly by convection due to the surrounding gas. The droplets experience different cooling rates/heat transfer rates depending on their size and internal crystallization nuclei. The gas atomization may lead to

- (a) Fully solid droplet
- (b) Fully liquid droplet with a temperature above the liquidus
- (c) Partially solidified droplet with a temperature between the liquidus and solidus
- (d) Fully liquid droplet with a temperature below the liquidus (undercooled droplet)

The spray can contain the droplets with sizes between 20 and 500 μm and hence the largest droplets will be in conditions such as (b) and (c) while the smallest droplets can be in conditions such as (a) and (d) [25]. The momentum transfer occurs from atomizing gas to droplets, which governs the droplet velocity, the flight time and subsequent deformation behavior during the deposition stage. The droplets lose their heat to atomizing gas during the flight and solidify completely or partially depending on their size and velocity. The next stage in spray casting is the collection of these droplets on a substrate or platform to result in a deposit or preform.

1.4.1 Advantages of spray deposition

On comparing with conventional products such as stainless steel tubing, the benefit of spray deposition is mainly cost saving. Moreover, in other cases, there are significant property improvements. The various benefits [26] include:

- Near net shape preform.
- Shorter manufacturing time due to few processing steps.
- Low cost and high yield due to the direct conversion of liquid metal into compacted preform.
- Minimization of costly labor, materials and energy intensive thermo-mechanical processing operations.
- Fine chemically homogeneous microstructures (uniform distribution of fine grains, no macroscopic segregation and low oxide content), improved properties and better response to thermo-mechanical processing.
- High degree of freedom in choosing alloying elements regardless of their sensitivity towards intermetallic formation and segregation. Composites can also be

manufactured by this technique, which comprise poor formability in conventional cast techniques.

Among the materials that cannot be made conventionally, are rapidly solidified e.g. Al–Li alloys, Al–Sn alloys with high Zn content (11%), highly alloyed Cu–Ni–Sn and Cu–Cr, as well as some metal matrix compositions. In this last case, the reinforcing particles are injected into the metal stream during the atomization process. Spray deposition seems destined to have a very interesting future. For the composite materials comparison between the relative costs of the various manufacturing processes along with reinforcements is shown in Fig. 1.3.

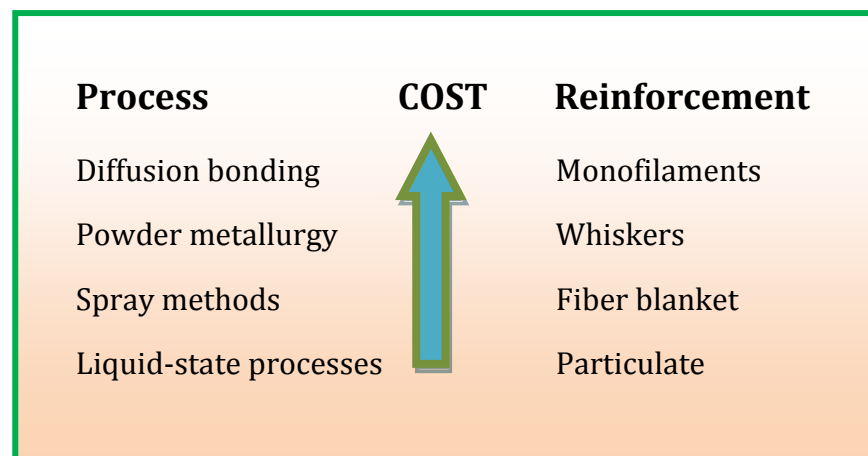


Figure 1.3: The relative cost of various processing methods and reinforcements [27].

Al–Zn–Mg–Cu alloys have traditionally been the highest strength alloys. However, further increase in strength is restricted by the occurrence of macro segregation in large ingots as well as difficulties in ingot casting when solute contents become too high. Spray forming overcomes these problems, and 7XXX alloys exhibiting the highest strength levels of wrought aluminium products with excellent fracture toughness and high cycle fatigue properties are being manufactured. Al–Cu–Mg–X alloys with improved elevated temperature strength coupled with good wear resistance in comparison to conventionally cast alloys have been demonstrated [28].

1.4.2 Demerits of the spray forming

Few demerits come along with the merits of the process which are listed below:

- Porosity is the major problem in spray formed preforms.
- The droplets which do not get impacted on the substrate and bounce off from the solid substrate get involved in the material loss.
- The machining loss occurring to produce out of specification component from preforms.

1.4.3 Applications

The spray formed alloys and composites contain the wide range of applications in automotive, electronic, structural, aerospace, packaging and electrical industries. Typical applications include:

- Spray forming has introduced a number of specially designed steel grades, which has industrial-scale usability in tool steel as screws, barrels (for plastic processing) as well as forged inserts and trimming dies. High wear resistant forming rolls are also well in demand.
- Spray formed Al-alloys have a broad range of applications in automotive engines as cylinder liners. Moreover, high-strength (Al-Zn), high-temperature (Al-Cu), and light-weight alloys (Al-Li) and metal-matrix composites (MMCs) are produced by spray forming process. Spray formed special Al-alloys are used as sputter target material. Si-Al alloys are used in electronic packages, heat sinks, and other applications where lightweight materials with a low coefficient of expansion are required.
- Spray formed Cu-alloys are used in high-tech telecommunication applications in the form of electronic connectors. Super alloy rings, seals and cases manufactured by this process are predominantly used in aircraft gas turbine engines.

1.4.4 Commercial viability

Spray forming was developed and subsequently licensed by Osprey Metals, Neath, Wales (U.K.). Many licensed companies under Osprey are Peak (Germany), Billiton (U.K.), Alcan

(U.K.), Special Melted Products (U.K.), Forged Rolls (U.K.) and British Rollmakers (U.K.). The full-scale commercial operations include successful commercial ventures such as high pressure diecast engine blocks with spray formed Al-Si cylinder liners, which are produced by M/S Peak (Germany) for Mercedes-Benz cars and pistons for racing application by M/S Swissmetal Boillat, Switzerland, etc. are currently in the market. Danspray (Denmark) is in producing tool steels; and Sandvik Steel producing stainless steel clad tubes for incinerator applications. Furthermore, spray-formed connectors produced by Swissmetall (Switzerland) are already starting to replace wrought Cu-Be alloys and P/M Cu-Ni-Sn alloys.

Spray technology found its commercialized application in automotive industry due to enhanced wear resistance of lightweight Al-Si alloys. The nature of wear is highly influenced by the method of processing, size, type, and amount of ceramic reinforcement. Moreover, spray technology enhanced its applications via MMCs where hard particulates in the soft metallic matrix help to reduce wear loss in comparison to base soft metal.

1.5 Wear

Wear is a process of gradual removal of a material from surfaces of solids. The detached material becomes loose wear debris. Wear of materials is the result of many mechanical, physical and chemical phenomena. Wear can further be characterized in various different types: Abrasive wear, adhesive wear, erosion wear, and oxidative wear depending upon their mechanisms – abrasion, adhesion, third body, fatigue, fretting and corrosion [29, 30]. The mechanism of wear is very complex. It should be understood that the real area of contact between two solid surfaces compared with the apparent area of contact is invariably very small, being limited to points of contact between surface asperities. The load applied to the surfaces is transferred through these points of contact, and the localized forces can be very large. The material intrinsic surface properties such as hardness, strength, ductility, work hardening, etc. are very important factors for wear resistance, but other factors like surface finish, lubrication, load, speed, corrosion, temperature and properties of the opposing surface, etc. are equally important. Al-Si alloys and Al-based metal-matrix composites have found application in the manufacture of various

automotive engine components such as cylinder blocks, pistons and piston insert rings where adhesive wear (or dry sliding wear) is a predominant process.

Adhesive wear is defined as the transfer of material from one surface to another during relative motion by a process of solid-phase welding or as a result of localised bonding between contacting surfaces. Particles that are removed from one surface are either permanently or temporarily attached to the other surface [31].

1.5.1 Archard wear law

The Archard wear equation is a simple model used to describe sliding wear and is based around the theory of asperity contact. Archard theory is based upon an earlier theory developed by Holm. It is also referred to as the Archard-Holm and Holm-Archard law. Holm published his theory of atoms being removed from the surface of a material in 1946. Archard improved upon the theory by using asperities (clusters of atoms) instead of individual atoms as the basis for his model in 1953 [32]. The most common form of the equation is shown below.

$$W = \frac{K}{H} \cdot F \cdot S$$

Where W is the wear volume lost, K is the non-dimensional wear coefficient, H is the surface hardness, F is the normal force, and S is the sliding distance.

1.5.2 Delamination wear theory

Suh [33] proposed a new theory based upon dislocations at the surface and sub-surface cracks. Suh analyzed that at low sliding speeds, wear debris formation could be described by a delamination wear theory. The theory predicts qualitatively that the wear particle shape is likely to be thin flake-like sheets. Moreover, the surface layer under wear investigation can undergo large plastic deformation. Wear processes such as adhesive wear, fretting and fatigues were all related to this same mechanism. Suh [33] stated that wear occurred by the following sequential steps:

1. Cyclic plastic deformation of surface layers by normal and tangential loads.
2. Crack or void nucleation in the deformed layers at inclusions or second-phase particles.

3. Crack growth nearly parallel to the surface.
4. Formation of thin, long wear debris particles and their removal by extension of cracks to the surface.

1.5.3 Wear mechanism maps for aluminium alloys

Wear data can be presented in many ways. The more common modes of presentation include the tabulation of wear rates and elucidation of the dominant mechanisms of wear observed under the sliding conditions of interest. The latter usually being accomplished through the presentation of micrographs showing features on the worn surfaces. However, these cover a relatively narrow range of sliding conditions. Tabor [34] suggested a more complete approach through the linking of the wear rates and wear mechanisms over a much wider range of sliding conditions in the form of a wear-mechanism map. These maps are the multi-dimensional representation of wear rates and wear mechanisms observed under certain set of sliding (or operating) conditions, and at the same time provide a framework for the overall wear behavior of the materials in relative motions. There are various wear-mechanism map designed for different systems like steels, aluminium alloys, ceramics, composites, polymers, cutting tools etc. depending upon the system in use.

Liu et al. [35] proposed a wear mechanism map for aluminium alloys (Fig. 1.6) in which the dominant wear regimes were constructed with reference to the wear mechanism. Fig.1.4 showed that there are predominantly four wear mechanisms acting in the Al-alloys and their respective wear constants were also listed from the empirical studies.

Oxidation dominated wear mechanism was reported at relatively low sliding velocities and loads. The two delamination wear and severe plastic deformation wear mechanisms were based on the delamination wear theory postulated by Suh [33]. Melt wear regime was stated to be predominant at high loads and sliding velocities, where a high wear rate was characterized by gross material transfer, due to severe plastic deformation or ejection of the melt.

However, seizure can occur at all the velocities depending upon the pressure applied between the sliding surfaces. In this wear regime, near surface temperatures are high enough to lower the shear strength in the sub-surface layer and promoted extensive material transfer from the wearing alloy.

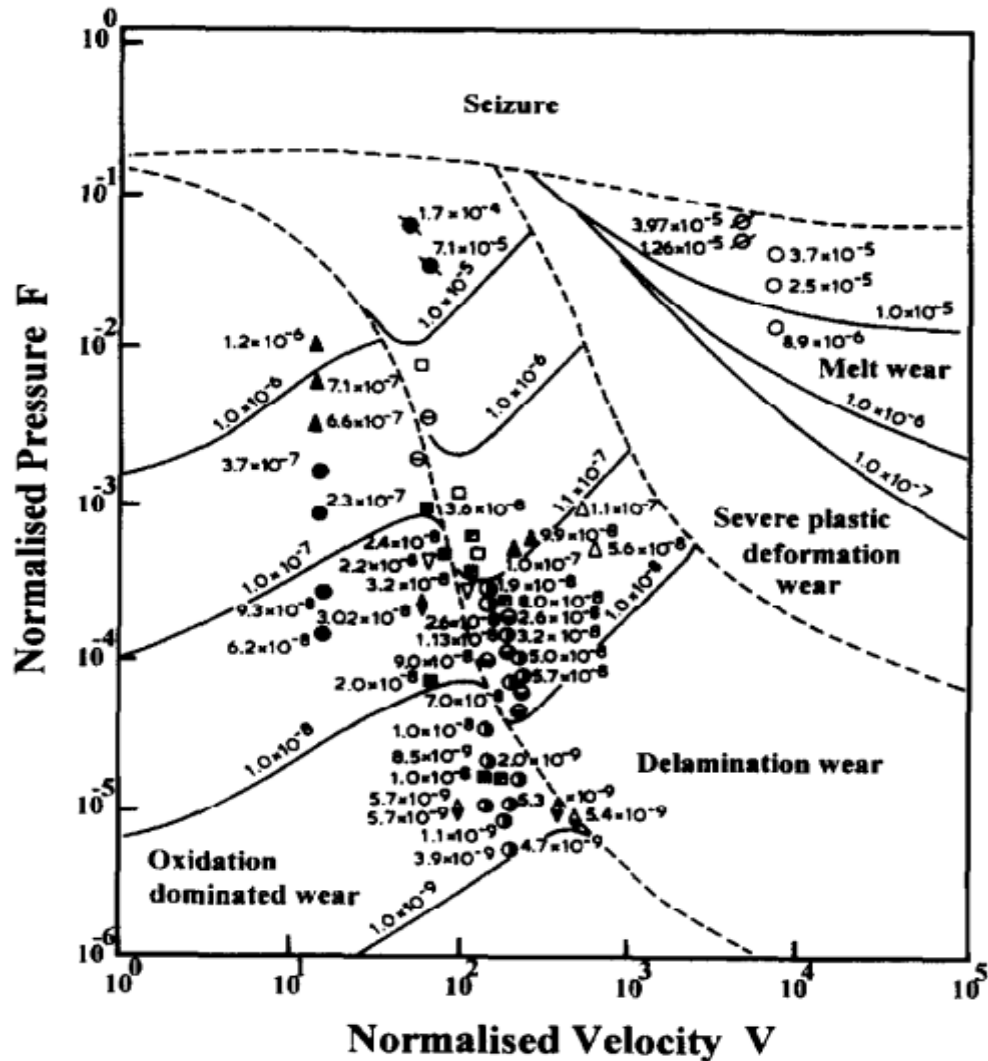


Figure 1.4: Wear mechanism map for aluminium alloys [35].

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LITERATURE REVIEW

Overview

The purpose of this section is to identify and review previous works that is relevant to the present study. In this chapter, the development in the field of spray forming, detailed study of the various Al-alloys and the effect of process variables on the mechanical properties have been reviewed. Published papers dealing with the applicability of the process in ceramic particulate reinforced metal matrix composites is discussed. The reinforcing particle type, volume fraction, size etc. and their effect on the manufacturing parameters which ultimately affect the properties including wear of composites have been described. The role of immiscible elements in the Al-alloy system and its effect on wear characteristics is also investigated thoroughly. Besides this recently published literature for spray formed Al-alloys studies have been documented to include the latest work in this field.

2.1 History

In 1960, Duwez [1] and his co-workers developed a novel technique to extend the solid solubility limit and to produce metastable crystalline [2] or amorphous [3] solid phase in some simple binary eutectic alloy systems. Further, the theory was materialized in commercial scale in University College Swansea by A.R.E. Singer [4]. In 1968, the spray rolling process was first selected for investigation using low melting point aluminium alloys. The spray forming concept was formulated after the successful exploration of spray rolling process [5]. The schematic cross-section diagram of spray rolling process is shown in Fig. 2.1. Spray rolling is suitable for making rapidly solidified products in strip form by using a low spray density followed by controlled densification.

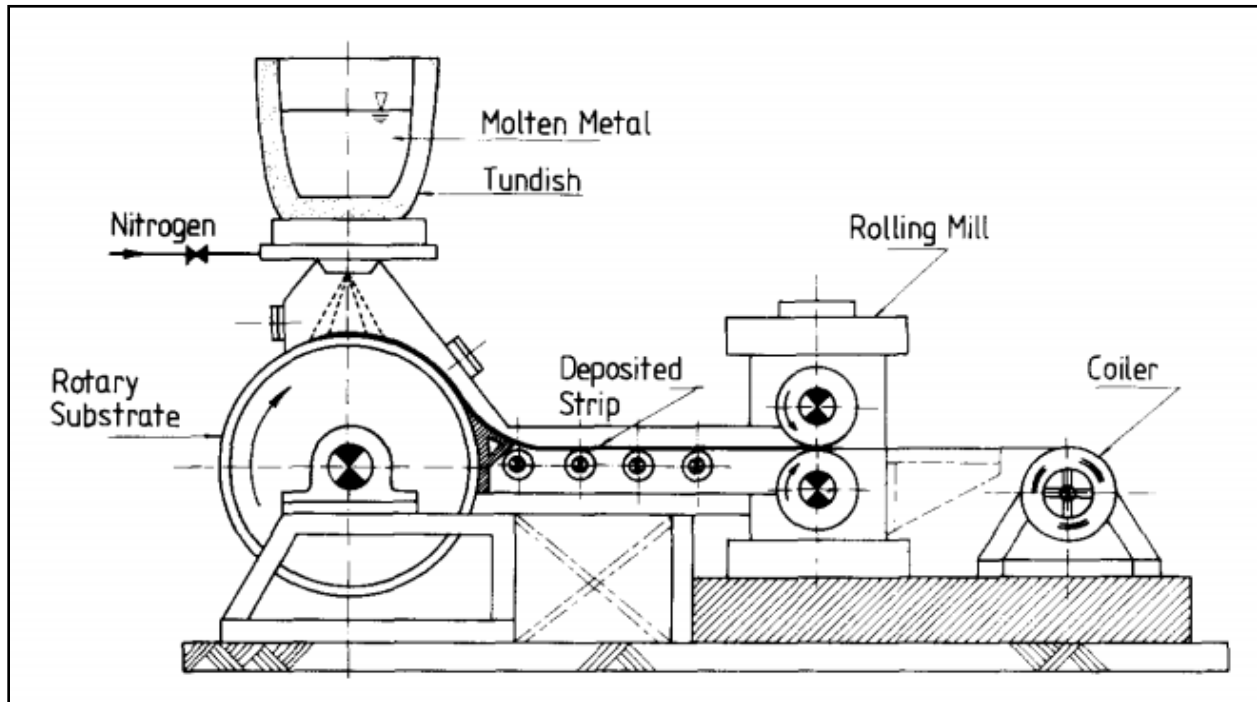


Figure 2.1: Schematic diagram of spray rolling equipment for producing strip [6].

The early work by Singer was confined to Al alloys only. Later on spray forming was further developed to other non-ferrous to ferrous alloys and metals. Afterward in early 1980s, the process was licensed by Osprey metals, Neath, Wales, and consequently spray forming is often referred to as the “Osprey process” [7–14]. Further Lavernia and Grant [15] developed liquid dynamic compaction (LDC) process in late 1980s which is similar to spray

forming. LDC, Osprey process, and sprays forming are the generic names of similar or related processes. In LDC, the melt was atomized at a high-gas pressure to generate the maximum yield of small size droplets in the spray. The cooling rate of a large fraction of droplets was well within the rapid solidification regime.

The spray forming process is extended or elaborated afterwards depending upon the end product application. The substrate motion in different directions can result to the various near net shapes. Different shapes like billets, tubes, strips and discs can be produced by this technique as shown in Fig. 2.2.

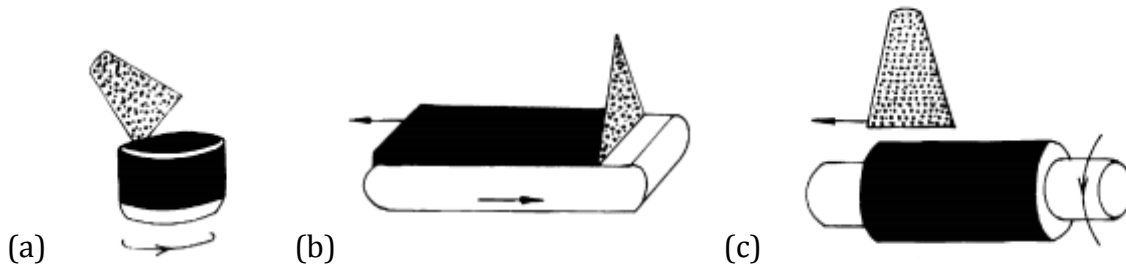


Figure 2.2: Illustration of various shapes **(a)** disc, **(b)** sheet and **(c)** tube produced by spray technology [16].

Presently this technique is also used to manufacture the composites. The detail of the published work is given as further.

2.2 Types of atomizers and process parameters

There are basically two types of gas atomizers depending upon the gas-melt interaction e.g. free fall gas atomizer and confined gas atomizer. In free fall design of atomization (Fig. 2.3a) the molten metal stream travels a certain distance before it interacts with the gas jets to precede atomization. Since gas jet strikes the molten metal stream after travelling a relatively larger distance, this leads to poor transfer of kinetic energy from the gas jet to liquid stream because the gas velocity decays rapidly from the nozzle exit. Whereas in confined gas atomization (Fig. 2.3b) the gas interacts with the liquid metal at the orifice of the tundish nozzle, and the liquid metal flow is influenced by the gas flow. In this case, the energy transfer from the gas to metal is more efficient and more uniform due to prefilming of the molten metal at the tip of the delivery tube as well as shorter distance between the

gas and metal stream before their interaction [17]. Thus the median droplet diameter is smaller in case of confined atomization than that of free fall [18–20].

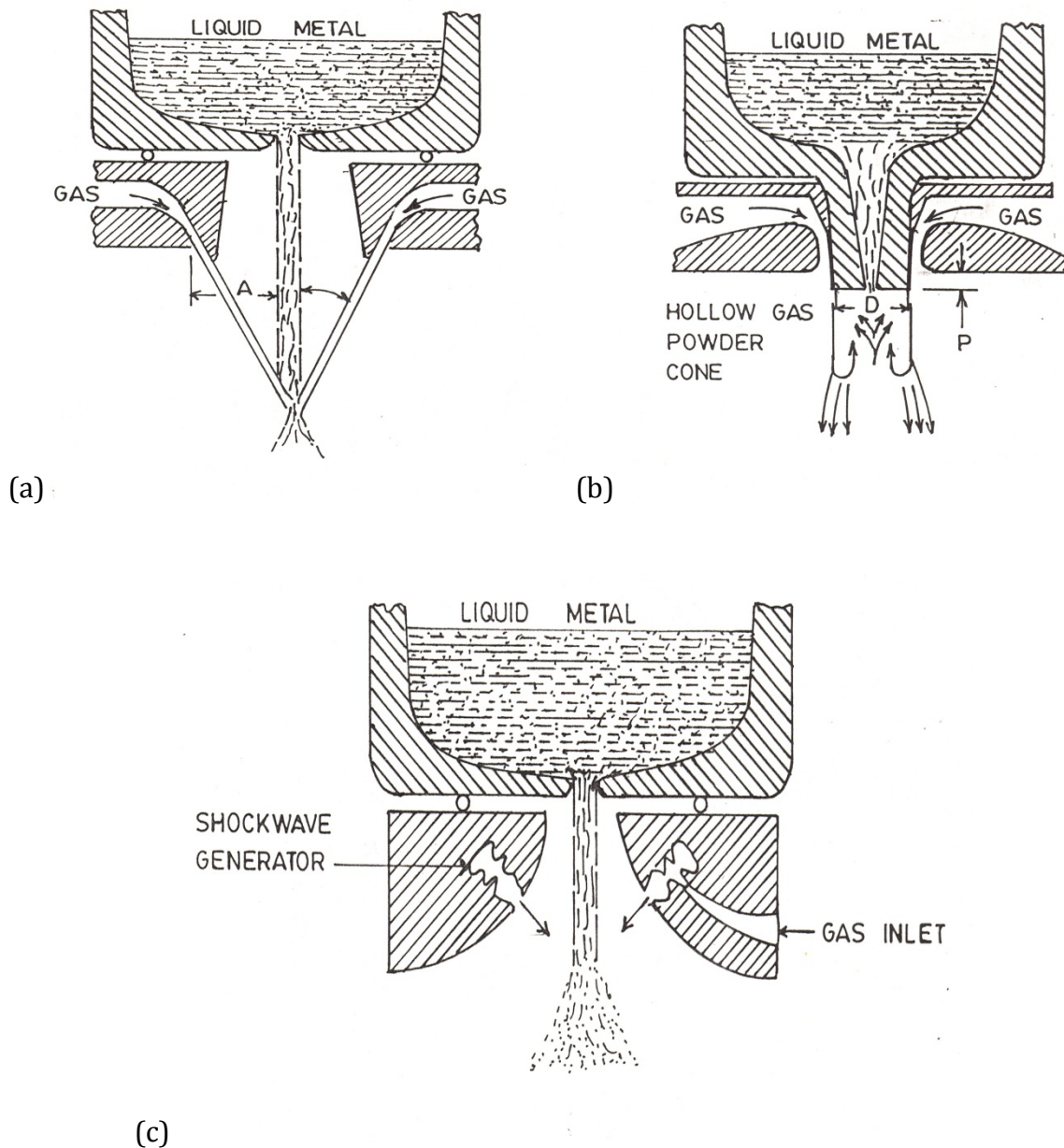


Figure 2.3: Different modes of gas-metal interaction in **(a)** free-fall, **(b)** confined gas atomization process, **(c)** ultrasonically superimposed gas atomization process [18–20].

However, confined gas atomizer is commonly used for low melting point materials to avoid the problem of freeze-up. In this situation, the melt freezes near the tip of the liquid delivery tube of the nozzle as atomizing gas interacts with melt at smaller distance from

nozzle tip and produces chilling effect. In free fall atomization, higher velocity is required to produce same velocity of atomization as in confined atomization. Thus the consumption of gas increases in the free fall. However, Singh et al. [20] reported a correlation of melt build up process with that of atomizer parameters. It has been observed that free fall atomization is safe upto certain limiting pressure. Atomization in the free fall atomizer is possible without metal build up below the certain velocity called limiting velocity. This limiting velocity V_L is a function of density of metal (ρ), free fall distance of the stream (L) and apex angle (α) of the atomizer, as given by the relation

$$V_L = 2.7 \times 10^3 \rho^{0.22} L^{0.62} \alpha^{-0.93}$$

In ultrasonic gas atomization as shown in Fig. 2.3c, a liquid stream is disintegrated by impact with multiple high-velocity gas pulses. The high-velocity gas pulse is generated on the principle of HARTMAN shock wave tubes arranged concentrically around and focused on metal stream. The gas is accelerated up to a speed of 2 mach at frequencies ranging from 60–120 kHz. The particles of gas traveling at extremely high velocities in pulse wave shear the molten metal stream into line of droplets.

The subdivision of the both free-fall and closed atomizer can be done depending upon their gas exit areas. There are many annular types e.g. continuous slit, ring of circular gas exit orifices as well as linear series of circular slits on either side of melt delivery slit to produce a metal sheet.

2.3 Mechanism governing atomization

In the atomization process, the exact interaction mechanism of atomizing fluid with liquid metal, which leads to breakup of liquid metal into fine droplets, is not fully understood yet. With the existing data, some mechanism for liquid break up is predicted by various scientists. Among these, work of See et al. [21] provides a better understanding of gas-metal stream interaction with their experiments with lead and tin metals. They suggested that the liquid metal break up in free fall atomization occurs in three different stages: primary disintegration, secondary disintegration and solidification. Initially primary breakup occurs, which leads to the formation of shed or ligaments. These ligaments further undergo secondary breakup resulting into droplets as they are still in the liquid state. At third stage these droplets spheroids and solidify to generate semi-solid/liquid droplets in

the spray. Various other models [22–26] given by other workers describe that actual atomization occurs above the point of focus of the gas jets on the melt stream. This is because of the vacuum created around the metal stream. The stream acceleration causes the liquid metal to expand into a series of hollow conical configuration. Later on the dynamic instability of the surface disturbances results in detachment of ligaments from the periphery of the cone. The assumption of these proposed models is that at initial stage, a sinus wave is generated at the surface of the molten metal stream which rapidly increases in amplitude as shown in Fig. 2.4. This wave is then detached from the bulk liquid depending on the wavelength during disintegration. In a similar way, the gas stream causes further disintegration of ligaments into droplets. The relative magnitude of freezing time and time of spherodisation of droplets control the shape of the atomized droplets.

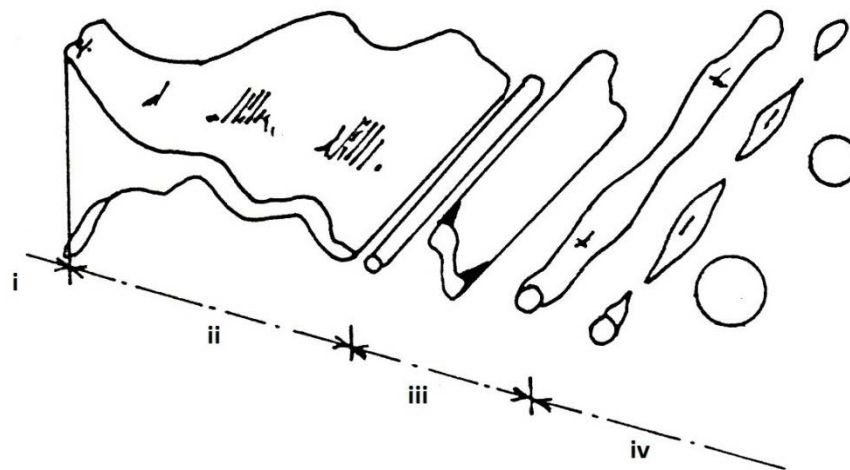


Figure 2.4: Disintegration of sheet showing various stages: **(i)** formation of sheet, **(ii)** growth of waves on the sheet, **(iii)** fragmentation and formation of ligaments and **(iv)** breakdown of ligaments into droplets [22].

For annular confined gas nozzle, in a series of experiments, Unal [26] described that the primary breakup takes place by prefiling mechanism. The secondary breakup depends on initial size of the droplets and gas flow condition around these droplets. If the relative velocity between gas and droplet is very high then this may lead to strip thin film from the side or the droplet which further breaks up from the edges (Fig. 2.5). This stripping action continues until the droplet attains a critical size. The critical size of the droplet is decided

by the Weber number, We criteria which is a ratio of internal forces to the surface tension of the melt i.e.

$$W_e = \frac{\rho_g v_g^2 d}{\gamma}$$

where ρ_g is the atomizing gas density, and v_g is the gas velocity. It has been suggested that at $We > 13$ droplets undergo second stage atomization [27].

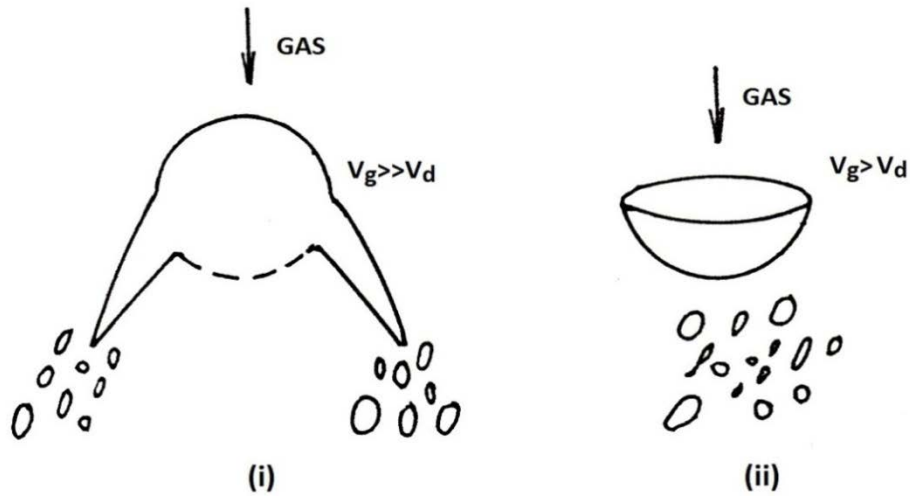


Figure 2.5: Secondary breakup mechanism during atomization **(i)** stripping action and **(ii)** inflated droplet [26, 27].

When relative velocity between gas and droplet becomes critical, the droplets may inflate like a parachute and still attached to a thick rim (Fig 2.5). At a critical pressure, the thin liquid film may burst into showers of line droplets, whereas the rim breakup may give coarse droplets. The bimodal distribution of atomized droplets in their study further verifies this model. This particular characteristic of atomized droplets using annular confined gas nozzle brings microstructural homogeneity throughout the section in the preform during spray deposition.

2.4 Microstructural features of spray deposited alloys

Spray deposition is a flexible process and the properties of these materials depend upon microstructure of the preform. Broadly speaking the spray deposited alloys exhibit two different types of microstructures. The first type contains a prior particles or splat

boundaries which amount to large porosity. This type of structure is mostly observed at the edges of the preform and at the substrate deposit interface. This is due to difference in distance traversed by the droplets toward the preform. There is a difference of distance travelled by each droplet within a spray cone which is quite significant. The droplets depositing at the edge travel a much longer distance than those depositing at the centre. Apart from this the periphery of the spray cone contains higher density of small sized droplets. The presence of prior particle structure at the substrate deposit interface is because of the conductive heat transfer through the substrate at the bottom section of the deposit leading to higher quenching rate of the splat. This restricts complete bonding among subsequent splats and gives birth to pores. Whereas the second type of microstructure consists of equiaxed grain morphology. As the thickness of deposit increases the heat extraction via substrate slows down and a steady-state condition is maintained between the heat flux added to the surface of the deposit in the form of spray and the heat flux absorbed by the deposit [28]. This results in a semi-liquid zone at the upper surface of the deposit which is essential for the development of fully dense deposit with minimum porosity [29–31]. The high velocity droplets transfer considerable momentum onto the surface of the deposit [32]. As a result of this the dendrites of the semi-solid droplets and semi-liquid zone on the top surface of the deposit got fragmented. The broken dendrite arms and the fine solid droplets provide a large number of nucleation centers for further crystallization of the melt. The rapid quenching of semi-liquid zone by a high velocity gas stream also induces sufficient kinetic undercooling of the melt and favour increased nucleation of new crystals [33, 34]. In addition to this, the momentum transfer from high velocity droplets causes turbulent fluid motion in the liquid film which develops on the growing surface of the preform [33]. This process generates sufficient shear forces in the semi-liquid film to continuously break the dendrites which are unstable during their initial growth. Subsequent growth of the crystal or second phase particles is then constrained, resulting in fine equiaxed grains of the deposit [35]. The deposition behaviour during various spray and preform conditions is listed in Table 2.1. The overall top surface solid fraction is determined by the relative rates of heat input into, and output from, the preform top surface.

Table 2.1: Relation between deposition behaviour of droplet, spray and preform conditions [17].

Preform condition	Spray condition		
	Solid	Mushy	Liquid
Solid	Bounce off	Partial Sticking	Good Sticking (Layered)
Mushy	Partial Sticking	Good Sticking	Good Sticking
Liquid	Surface ejected and whipped up	Surface ejected and whipped up	Surface ejected and whipped up

The ability of this process to generate equiaxed morphology is considered to be a major benefit which improves the workability of a material. Research is going on microstructural development for various alloys ranging from non-ferrous to ferrous. In the earlier study of ferrous alloy, Rickinson et al. [36] reported the structures and properties of controlled spray deposited highly alloyed tool and high speed steels. The secondary dendrite arm spacing measurement of the deposits indicated the achievement of cooling rates within the range 10^3 – 10^4 Ks⁻¹. The study reveals the microcellular carbide distribution in splatted M2 high speed steel. However, no change in chemical composition was observed during the atomization-splating cycle. Moreover, oxygen and nitrogen contents were reported to be similar to those for normal air melt ingot practices.

2.5 Al-Si alloys and composites

As described in earlier chapter Al-Si alloys offer wide range of properties available for the engineering applications. Many researchers [37–40] have worked on Al-Si alloys. Their work showed that there is considerable relation between morphology of Si particles in these alloys and manufacturing process parameters.

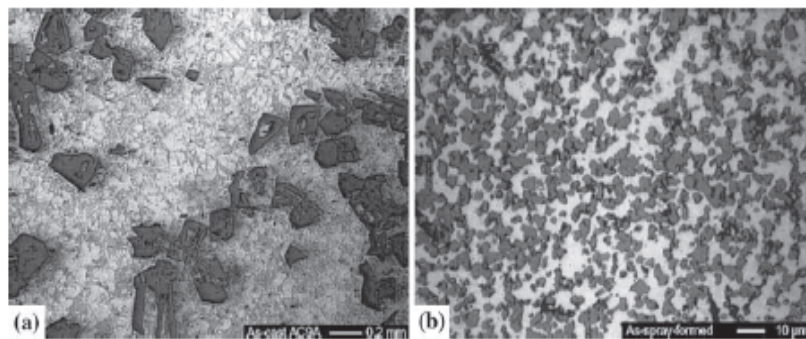


Figure 2.6: Microstructures of (a) as-cast and (b) as sprayed AC9A alloy [38].

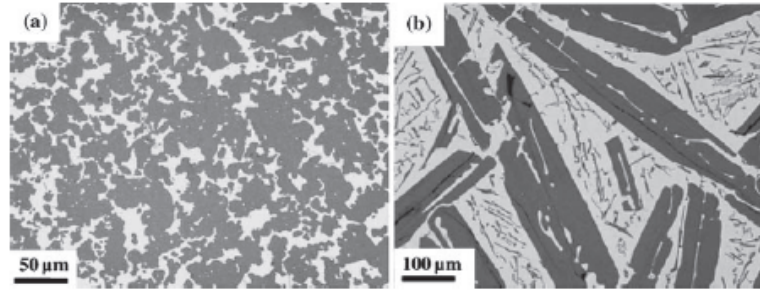


Figure 2.7: Microstructures of **(a)** as-sprayed and **(b)** as-cast Si-30%Al alloy [37].

As the result of this, mechanical and wear properties of Al-Si alloys get affected [41]. The difference between the microstructure of as cast and as-sprayed alloys has been shown in Fig. 2.6 and 2.7. Both hypo and hypereutectic Al-Si alloys have been studied by Srivastava et al. [42–44]. Their studies reveal that hypoeutectic Al-6.5%Si alloy exhibits spherical morphology of primary α -phase as shown in Fig. 2.8(a). The hypereutectic Al-18%Si alloy showed a fine Si particulate morphology in their microstructures (Fig. 2.8(b)). It has also been concluded that the microstructures, mechanical and wear properties of as-sprayed alloys showed better results than their as-cast counterparts. The comparison of the processing route and alloys with their mechanical properties are listed in Table 2.2.

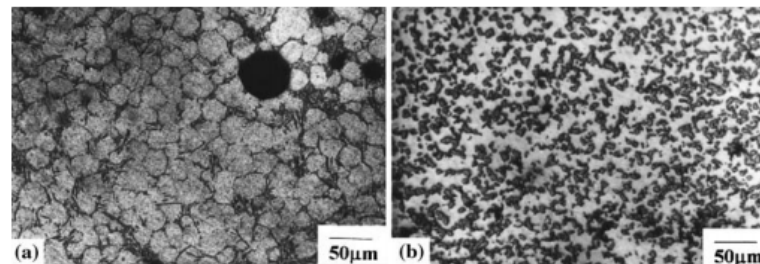


Figure 2.8: Microstructures sprayed alloys **(a)** Al-6.5%Si and **(b)** Al-18%Si alloy [44].

Table 2.2: Comparison of mechanical properties obtained with diffetent processing techniques of Al-Si alloys [44].

Alloy composition	Processing route	Tensile properties			Microhardness (H_v)
		YS(MPa)	UTS(MPa)	EI(%)	
Al-6.5Si	AC	77.2	130.9	9.0	31.54
Al-6.5Si	SD+Ext.	75.5	132	34.3	39.35
Al-18Si	AC+Ext.	97.5	129	6.7	41.10
Al-18Si	SD+Ext.	119.5	158	18.7	58.57

Note: AC, as cast; AC+Ext., ascast and hot extruded; SD+Ext., spray deposited and hot extruded; YS,yield strength;UTS,ultimate tensile strength.

As a result, there is a growing interest to understand the mechanism of microstructural evolution in spray deposition processing. The equiaxed grains observed in this process are relatively fine and uniform throughout the section of the deposit (Fig. 2.8(a)) whereas in a conventional casting process, the equiaxed grains are large and formed at the centre of the casting only. This feature in a conventional casting, is attributed either to constitutional supercooling of the melt or to an increased nucleation sites caused by chill crystals detached from the mould wall and get carried by convection towards the centre of the casting [45]. However, the spray deposition conditions are different from that of a conventional casting. Accordingly, several alternative models have been proposed to account for the origin of such microstructural features in atomized [46–50] and spray deposited alloys [51–55, 35].

Cui et al. [56] studied the effect of secondary processes on the microstructure and porosity of the hypereutectic alloys as shown in Fig. 2.9. The porosity in the AlSi35 alloy is significantly higher than lower content of silicon (Fig. 2.9 (c) and (f)). However, porosity also depends upon the thermal condition in spray forming. Hot spray condition leads to high amount of porosity. In contrast, very few pores have been observed in the relatively cold sprayed AlSi18 and AlSi25 billets (Fig. 2.9 (d) and (e)). There is a remarkable influence of thermal condition e.g. cooling and solidification conditions on the metallurgical quality of the spray formed Al–Si alloys. It has been investigated that on increasing cooling rate of the deposited materials, the size of primary silicon phase in the materials decreases. The flake type eutectic phase is also modified into short and blunted shape as the deposit solidifies rapidly. Also, interstitial pores appear instead of spherical gas pores if the thermal condition in spray forming is changed from hot condition to cold condition. The effect of the secondary processes like extrusion plays a role on the inter particles spacing depending upon the particle fragmentation mechanism. In extruded Al–Si alloys, Si particles are more homogenous and regular than in as deposited one. Along with that it presents a certain amount of anisotropy and tendency to preferred orientation [57, 58].

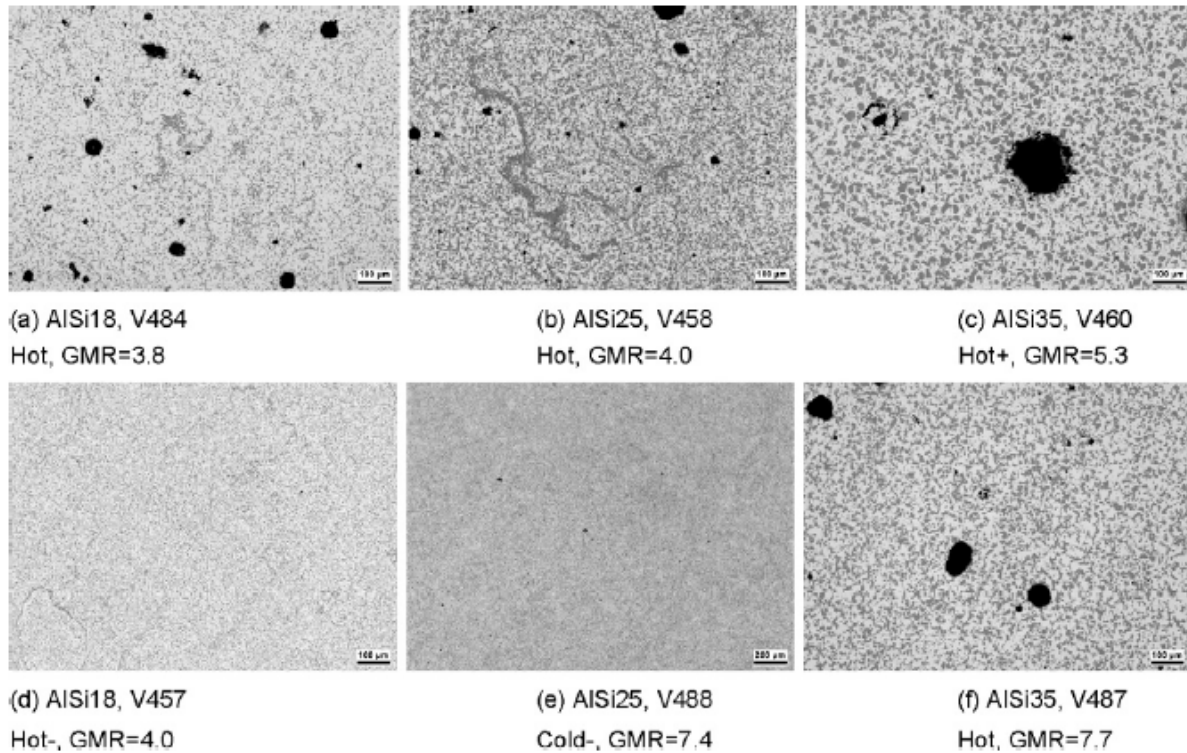


Figure 2.9: Porosity in spray formed hypereutectic Al-Si alloy billets. **(a)** AlSi18, V484 Hot, GMR= 3.8; **(b)** AlSi25, V458 Hot, GMR= 4.0; **(c)** AlSi35, V460 Hot+, GMR= 5.3; **(d)** AlSi18, V457 Hot-, GMR= 4.0; **(e)** AlSi25, V488 Cold-, GMR= 7.4 and **(f)** AlSi35, V487 Hot, GMR= 7.7 [56].

Anand et al. [59] synthesized and studied hypereutectic Al-Si alloy by spray atomization and deposition technique. At ambient and elevated temperature tensile tests reveal the spray-processed alloy to have better strength and ductility than a conventional ingot metallurgy processed alloy having the same chemical composition. The quasi-static fracture characteristics of the spray-processed alloy is presented and discussed in light of processing and intrinsic microstructural effects. Similarly, Ojha et al. [60] discussed the mechanism governing generation of spray of droplets, large undercooling and high heat exchange rate at the droplet-gas interface in light of models based on enthalpy considerations to account microstructural modification arising during spray deposition process.

Wang et al. [61] investigated Al-12Si, Al-20Si and Al-25Si (wt %) alloys synthesized by spray atomization and deposition technique. It has been found that the effect of Si content

on dry sliding wear of spray-deposited Al-Si alloy was associated with applied loads. At lower load (8.9 N), with increasing Si content, the wear rate of the alloy was decreased and dominant wear mechanism was oxidative mechanism. At higher load (35.6 N), spray-deposited Al-20Si alloy exhibited superior wear resistance to the Al-12Si and Al-25Si alloys, the dominant wear mechanism was delamination and third-body abrasion.

The modelling of spray deposition process has been developed by many researchers. An integrated, multiphysics numerical modelling of the spray forming process has been analyzed by Mi et al. [62]. The integrated model was further divided into four sub-models:

1. Atomization model: simulating the fragmentation of a continuous liquid metal stream into droplet spray during atomization.
2. Droplet spray model: simulating the droplet spray mass and enthalpy evolution in the gas flow field prior to deposition.
3. Droplet deposition model: simulating droplet deposition, splashing and redeposition behaviour and resulting preform shape and heat flow.
4. Porosity model: simulating the porosity distribution inside a spray formed ring perform.

This model shows good agreement with experimental measurements of the spray formed IN718 Ni superalloy.

In order to get better wear properties immiscible elements are added to Al-Si alloys which get segregated along the grain boundaries as well as inside the grain. Due to their lower melting points they form a film on the top of surface giving them good smearing properties. Pb and Sn are conventionally used as immiscible elements which are added to Al-Si alloys as bearing materials. These alloys provide good surface and mechanical properties and act as lubricant. However, macrosegregation is the main problem occurring in the directionally solidified Pb-Sb and Pb-Sn systems [63, 64]. Spray deposition process solved the problem of macrosegregation giving better microstructural features and low wear rate as compared to as-cast babbit alloy of Pb-Sn-Sb [65, 66]. Similarly, Pandey [33] analyzed spray formed Al-4.5Cu-5Pb system with sand and chill casting and observed equiaxed grains and lower wear in spray deposited alloy as compared to chill and sand cast alloys.

Rudrakshi et al. [67] analyzed the wear behaviour of spray formed Al-3.5Cu-10Si-20Pb (wt.%) alloy in different environmental conditions and inferred the results from the microstructural features of the alloy and the nature of the worn surfaces of the wear test specimen. The wear behaviour in air atmosphere clearly indicated the influence of surface oxidation on the mating surfaces. The nature of variation in wear with sliding distance, both in air and vacuum, remained similar showing two distinct wear regimes, viz., running in wear and steady state wear. A relatively lower running in period and a large reduction in the frictional force were observed in vacuum as compared to that obtained in air under same conditions of sliding speed and applied pressure. The wear rate increased with sliding speed in vacuum. On the other hand, in air atmosphere the wear rate decreased with increasing sliding speed, reaching a minimum at a critical sliding speed and then increasing with further increase in sliding speed. The coefficient of friction remained almost constant for different sliding speeds for both air and vacuum. However, under vacuum, the value of coefficient of friction was lower than that in air, throughout the range of sliding speed.

An et al. [68] analyzed the hot-extruded Al-Si-Cu-Pb bearing alloys and found that the wear rate decreases greatly with increasing lead content and wear rate-load curves took different form for extruded bearing alloys containing 20% and 25% lead. Optical observation revealed that the reason was formation of a black compact film of lubricant covering almost the entire worn surface of specimens at highly applied load level. This film is a mixture of different constituents containing the elements Al, Si, O, Fe and Pb.

Rudrakshi et al. [69] investigated a modified spray forming process to synthesize liquid immiscible alloys based on Al-Si-Pb system. The microstructure exhibited an equiaxed grain morphology of the primary α -phase with variation in grain size from 10 to 25 μm in addition to a uniform dispersion of ultra-fine particles of lead and globular silicon particles in Al-matrix. The size of Si particles varied from 0.5 to 5 μm and that of Pb particles from 0.1 to 25 μm with variation in deposition distance. The wear rate and the coefficient of friction of Al-Si-Pb alloy were observed to be lower than that of Al-Si alloy at loads varying from 10 to 90 N at a sliding velocity of 1.0 ms^{-1} . It has been discussed in the light of microstructural features of the alloy and the nature of the worn out surfaces. Again the

mode of solidification of liquid immiscible alloys i.e. Al-Pb and Cu-Pb system during spray forming process is discussed by Gouthama et al. [70]. The microstructure of spray formed Al-4Cu-20Pb alloy revealed a uniform distribution of ultrafine Pb particles in Al-matrix and Cu-20Pb alloy. It exhibited equiaxed grain morphology of the primary α -phase with dispersed Pb particles along the grain boundary and inter-granular region. Microstructural homogeneity was observed in both the atomized powders and spray formed alloys. The spray formed Cu-Pb alloy revealed a higher wear rate than Al-4Cu-20Pb alloy at low load and sliding velocity which changes to severe wear regime in high load and sliding velocity regime.

Friction and wear are of considerable importance in most of the structural components particularly in bearing applications. The tribological behaviour of steel backed Al-Sn strip via spray atomization-deposition-rolling route was evaluated against bearing steel under fretting contacts [71]. The typical structure of tough matrix with soft tin inclusions in Al-Sn alloy determines the tribological behaviour of the bearing. It has been found that the fretting wear of the warm rolled strips exhibit a decrease in wear rate with increasing amount of rolling.

Uyyuru et al. [72] studied the tribological behaviour of stir-cast Al-Si-SiC_p composites/automobile brake pad system under dry sliding conditions using pin-on-disc tribo-tester. During the wear test, formation of a heterogeneous tribo-layer was observed, presence of which can affect the wear behaviour, apart from acting as a source of wear debris.

Much of the literature is available on the particulate reinforced spray deposited composites that give better mechanical properties as compared to their cast counterparts. Ding et al. [73] fabricated and studied the spray deposited SiC_p/Al composites up to 15% volume fraction of SiC_p and obtained uniform distribution, good bonding between particle and matrix, high density matrix and low-segregation of SiC particulates. The composite could be manufactured with weight up to 150 kg or more with all of above properties if the operation was performed correctly. Thus, spray deposition process has the potential to utilize it to produce large particulate-reinforced metal matrix composite ingot.

Similarly, Gomes et al. [74] spray deposited AA7475 aluminium alloy with 20% volume fraction of SiC particles. The formed composite billets were hot extruded into round bars and heat treated (annealed, aged, and over-aged). SEM revealed an extensive Mg_2Si phase precipitation at the Al/SiC_p interface probably due to Mg segregation from the matrix to the interface during the heat treatments. Similarly, Zhenhua et al. [75] studied the wear of spray deposited Al-Si/SiC_p composites and found that the wear rate decreases with increase of hardness of composites due to increase in silicon content. The wear resistances of the composites improved dramatically through thermomechanical treatment, compared to as-sprayed composite, due to increasing hardness and elimination of porosity. The wear mechanisms of composites vary with silicon content from abrasive to oxidative wear.

Zhang et al. [76] spray deposited 6061Al/SiC/Gr hybrid metal matrix composites (MMCs). In their as-extruded condition it exhibits both relatively high damping and high elastic modulus, but a reduced strength in comparison with that of unreinforced 6061-T6A1 alloy. Both damping capacity and dynamic modulus were measured using a dynamic mechanical thermal analyzer at frequencies of 0.1, 1, and 10 Hz over a 30 to 250°C temperature range. Experimental results revealed that the 6061 Al/SiC/Gr MMCs, following T6 heat treatment, exhibit an optimum combination of room temperature mechanical properties along with an improved damping capacity in the intermediate testing temperature range. The operative damping mechanisms are discussed on the basis of microstructural analyses.

Srivastava et al. [77, 78] spray deposited the SiC_p reinforced 2014Al metal matrix composites with average particle sizes of 17, 30 and 58 μm in the range of 5–11 vol.%. The compressive flow behaviour of these composites at different strain rates in unlubricated condition were analyzed at temperatures of 150, 300 and 450 °C. The variation in flow behaviour has been attributed mainly due to particle fracture and debonding at particle/matrix interface, confirmed by microstructural features of the deformed samples. The major particle fracture events were recorded at low temperature and low strain rate of deformation. This deformation behaviour of the composites has been discussed in light of microstructural observations and the void formation during deformation. Moreover, microstructures of the over-sprayed powder particles showed that the collision of melt droplet and SiC particles is major mechanism for incorporation of small particles.

Composites with smaller particulate size show an early hardness peak than those with larger size particles.

AMC reinforced with zircon sand are more suitable because of its higher fracture toughness of zircon than SiC, high hardness, high modulus of elasticity and excellent thermal stability. Because of these characteristics, it is being studied for AMCs where contacting parts operate in relative (or opposing) motions. However, hardness of zircon sand particles is comparatively less than SiC particles. In most of the literature, zircon reinforced AMC had been prepared by die-casting or stir castings because zircon is relatively heavier than many ceramic particles and requires little or no vortex/ mixing before introduction into the alloy melt. Banerji et al. [79] produced die cast composite by simultaneously stirring and degassing N_2 in Al-11.8Si-3Mg superheated melt and introducing preheated zircon particles, using a bottom-pouring crucible. Al-alloy composites is being prepared by stirring zircon particles (40 to 200 μm size) in commercially pure Al (99.5 %) and Al-11.8% Si melts and subsequently casting these melts in permanent moulds. It was found to be necessary to alloy the above two melts with 3 % Mg to disperse substantial amounts of zircon particles (25 to 30 %). Further, it was possible to disperse up to 60 wt% zircon by adding up to 5 % Mg; however, the melts containing above 30 wt % zircon showed insufficient fluidity for gravity die-casting and had to be pressure die-cast. Microstructural studies of cast composites indicated the presence of a reaction zone at the periphery of zircon particles, and electron probe microanalysis showed concentrations of Mg and Si at the particle-matrix interface. Hardness, abrasive wear resistance, elastic modulus, 0.2 % proof stress, and tensile strength of cast Al-3% Mg alloy were found to improve with the dispersions of zircon particles. SEM of abraded and fractured surfaces did not show any evidence of particle pull-outs or voids at the particle matrix interface, indicating strong continuous bonding.

Ejiofor et al. [80] made an attempt to manufacture the conventional low-cost method of double compaction powder metallurgy route in the synthesis of Al-13.5Si-2.5 Mg alloy (wt%) reinforced with $ZrSiO_4$. The mechanical, physical and tribological properties were determined following the development of optimum conditions of compaction and sintering. At a critical volume fraction (0.03–0.05) of zircon a significant improvement in wear

resistance was observed. Further structural analysis showed that the improvement in mechanical properties is attributed largely to the load-bearing ability and intrinsic hardness of zircon than to particulate dispersion effects.

Jangg et al. [81] produced light and wear resistant Al camshaft belt pulleys for engines from standard Al powder mixtures with addition of 10 mass% ZrSiO_4 by pressing, sintering at optimized parameters, and sizing. Both dimensional and wear properties were found to be well comparable to those of conventional iron pulleys.

Satyanarayana et al. [82] analyzed the role played in wetting between the dispersoid and the matrix by Mg during the synthesis of Al–alloy matrix composites with dispersoids such as zircon (ZrSiO_4), zirconia (ZrO_2), titania (TiO_2), silica (SiO_2), graphite, aluminium oxide (Al_2O_3) and silicon carbide (SiC). It is the requirement during the preparation of MMC especially with the casting/liquid metal processing technique. The basic principles involved in improving wetting fall under three categories: (i) increasing the surface energies of the solids, (ii) decreasing the surface tension of the liquid matrix alloy, and (iii) decreasing the solid/liquid interfacial energy at the dispersoid matrix interface. The important role played by the magnesium during the composite synthesis is the scavenging of the oxygen from the dispersoid surface, thus thinning the gas layer and improving wetting and reaction-aided wetting with the surface of the dispersoid.

Das et al. [83] studied the ageing behavior of Al–4.5 wt% Cu matrix alloy reinforced with Al_2O_3 and ZrSiO_4 particulate with varying particle size manufactured by stir casting technique. Acceleration in age hardening was observed in the case of composite reinforced with ceramic particles compared to matrix alloy and in case of smaller particle sized reinforced composites as compared to larger particle reinforced composite. It was found that Al_2O_3 reinforced composite show high acceleration in age hardening as compared to ZrSiO_4 particulates, which is due to the breakage of Al_2O_3 particles during melting and stirring process. The comparative study on abrasive wear of AMC reinforced with aluminium and zircon sand particles shows that the alumina particle reinforced composite have relative poor wear resistance property compared to zircon–reinforced composite.

However, abrasive wear resistance of both of the composites improves with the decreased particle size [84].

Yang et al. [85] applied spray-deposition technique to produce in situ TiC/Al and TiC/Al-20Si-5Fe-3Cu-1Mg composites. This technique provides a new route to solve the problems of losses and agglomeration of the reinforcement particles when they are injected into the spray cone of molten droplets during spray forming process. The silicon particles in the spray-deposited 5 wt% TiC/Al-20Si-5Fe-3Cu-1Mg composite were much refined ($\sim 2 \mu\text{m}$) compared to those ($\sim 5 \mu\text{m}$) obtained in the matrix alloy without TiC addition. The modification of the microstructures in the spray-deposited Al-20Si-5Fe-3Cu-1Mg alloy can be interpreted in the light of the knowledge of atomic diffusion. The experimental results also showed that the ultimate tensile strength of the TiC/Al composites was improved over that of the unreinforced Al matrix.

Wang et al. [86] studied the TiC reinforced 7075 (Al-Zn-Mg-Cu) Al matrix composites fabricated by a melt in-situ reaction spray deposition. At a lower load (8.9 N), with increasing TiC content, the wear rate of the alloy was decreased. At a higher loads (26.7, 35.6 N), a spray-deposited 7075 Al alloy exhibited superior wear resistance to the 7075/TiC composites.

Hoskings et al. [87] reported a decrease in adhesive wear rate with increasing particle content (at constant particle size) and dimension (at constant volume fraction) for Al 2014 and 2024 alloys reinforced with Al_2O_3 and SiC_p (1–142 μm) of various weight fractions (2–30 %). SiC was shown to be more effective than alumina in resisting wear, when tested in a ball-on-disc rig. In general, the friction coefficient decreased with increased sliding velocity for all the composite combinations. For composites reinforced with >10% of SiC, TiC, Si_3N_4 , Al_2O_3 or silica sand, the wear rate was less than that of the unreinforced matrix. Composites containing TiC exhibited a high wear rate due to the existence of much lower shear strain at the TiC/matrix interface. The introduction of the reinforcing particles appeared to increase the load corresponding to transition from mild to severe wear [88].

2.6 Wear mechanism maps of Al-Si alloys and composites

Antoniou and Subramanian developed the wear mechanism map [89, 90] for aluminium alloys by observing the wearing surfaces of both the aluminium alloy and the steel counterface (Fig. 2.10). The wear tests were performed using a pin-on-disc rig. According to them wear can be subdivided to five different regions based upon the topography and microstructure of the wear debris and associated worn surfaces. The resulted microstructures of the different wear surfaces are shown in Fig. 2.11. The characteristics of the different regions are described as follows:

Region a. This region lies at low sliding speeds and applied pressures. Under such conditions, the worn surfaces exhibited a smooth surface interspersed with granular wear scars. The micrograph showed (Fig. 2.11(a)) the dark regions associated with high iron content came from the material transfer between the steel counterface and the aluminium. The wear debris under such condition are found to be a mixture of very fine equiaxed microstructure ($\sim 5 \mu\text{m}$) consisting of Al, Si and $\alpha\text{-Fe}$. The previous literature do reports the difference between the oxidation of aluminium from other metals. As very fine 2–5 nm thickness aluminium oxide has been formed at room temperature conditions. However, at higher temperatures it converts firstly to amorphous layer and later in eta and gamma aluminium oxide [91, 92].

Region b. The wear debris produced in this region exhibit flake-like morphology with a smooth upper surface and granular under surface (Fig. 2.11 (b, c)). This type of wear debris is supposed to be formed by compaction of the fine equiaxed particles into depressions of worn surface followed by the delamination mechanism which removes the compacted layer in the form of flakes. However, the composition of this wear debris reveals the similar mass transfer of both pin and counterface as in region a.

Region c. In this delamination mode, Al-Si alloy get delaminated with the increase of applied load and sliding velocity. The crack produced underneath sliding interface propagates to produce flake-type morphology. The flakes consist of smooth upper-surface and heavily scarred under-surfaces due to ductile shearing (Fig. 2.11 (c)). The material transfer was the distinguishable phenomenon under such conditions.

Region d. As the both load and sliding velocity were increased further, the gross material transfer between the sliding surfaces became prominent as shown in Fig. 2.11 (d). On further sliding, the transfer of material occurred until the counterface is significantly covered with the aluminium alloy. Such condition resulted in seizure of material.

Region e. Certainly at very high applied loads when the surface temperature exceeds the melting temperature, the material is removed by extrusion from the sliding interface. Such type of wear is called melt wear which is characterized by low coefficient of friction and removal of the material by the formation of an interfacial molten film between the sliding surfaces [93].

Howell et al. [94] also experienced the melt-wear in the aluminium alloy composite where a molten MMC layer got trapped between the surfaces of unmelted MMC and the counterface material. During the investigation wear rate is found to decrease and a stable friction coefficient is obtained which is not desirable from application point of view.

Thus, Fig. 2.10 represents the qualitative prediction of wear behaviour over a broad range of loads and sliding speeds divided by boundary of effective mechanisms. The mechanism boundaries for Regions a, b and c are justified by the findings of previous experimental data. However, limited literature is available for the boundary where melt-wear would be expected to dominate on the gross material removal. The researchers have positioned this boundary over the normalized pressure and velocity. As per the test findings under such conditions melting was thought to have occurred on the surfaces and is shown in Fig. 2.11(e).

In an Al-12.3%Si alloy system, Subramanian [95] reported formation of tribolayer on the wear surfaces sliding against a copper counterface at low speed (0.1 m s^{-1}) and high pressure ($>1.0 \text{ MPa}$). This layer was composed of a mechanical mixture of the Al-alloy and copper. He further concluded that the formation of the tribolayer is dependent on sliding wear parameters such as applied pressure and sliding speed. A tribolayer is favoured in the wear mechanism map as shown in Fig. 2.10 in regimes (a) and (b).

Sarkar et al. [96] reported that the Si content does not appear to be a dominant factor in wear resistance. Moreover, the eutectic alloy was the most wear resistant of the alloys studied. The predominant wear mechanism occurring on the surfaces are the surface work-hardening during sliding and further removal of these work hardened patches via crack

propagation. Moreover, Hertzian stress is reported as the crack or debris nucleation site below the sliding surface.

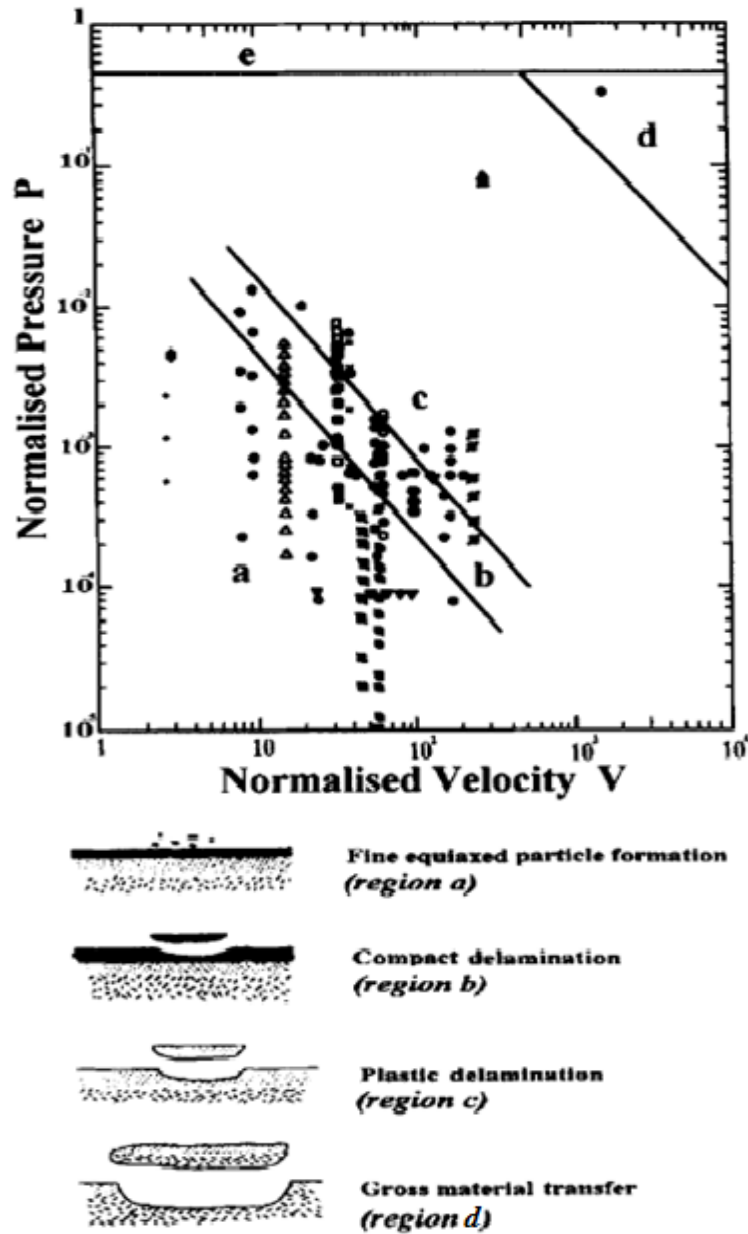


Figure 2.10: Wear mechanism map for aluminium alloys and schematic drawing of the sub-surface structure developed in Al-Si alloys as a result of different wear conditions depicted in this map [89, 90].

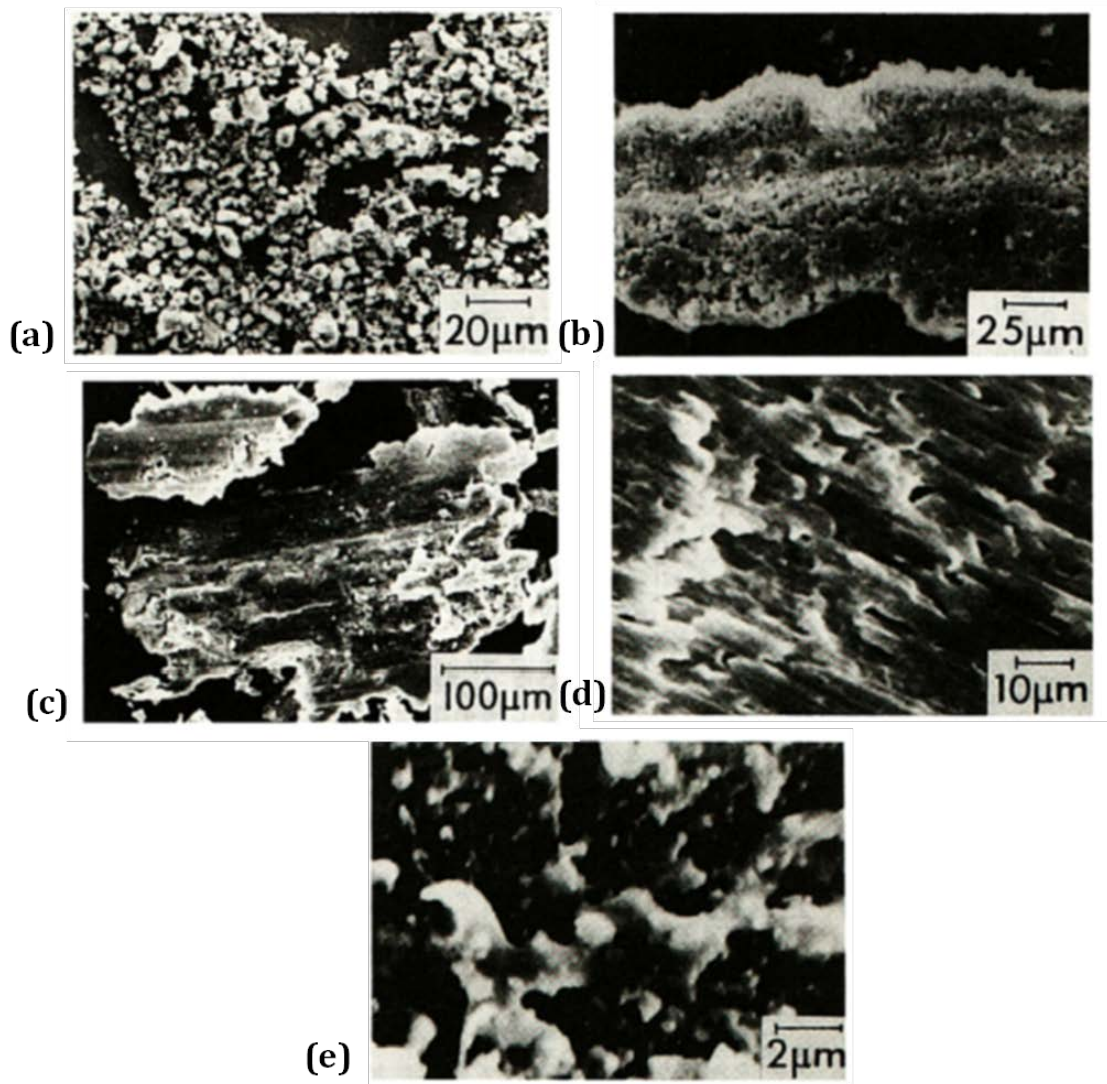


Figure 2.11: (a) Region a: equiaxed debris, (b) Region b: compacted equiaxed debris, (c) Region c: delamination debris (d) Region d: gross material transfer, (e) Region e: melt-wear [89].

As described above wear mechanism map for many monolithic metallic materials provide understanding of the processes by which the tailor-made materials or composites wear during dry sliding. However, still the wear mechanism maps of the composites are limited and in some cases these are contentious. Wang et al. [97] made the wear mechanism map corresponding to the dry sliding wear of an Al 6061/SiC_w (20 vol.%) with the regimes defined as a function of normal load and sliding speed (Fig. 2.12) [98].

Similar to the previous map, it is also reported that with the increase in sliding speed and/or normal load there is a transition in wear behaviour from mild wear to severe wear and ultimately to seizure. Moreover, it was found that at the lower loads (mild wear regime), the worn surface morphology was relatively smooth and wear debris were small and brittle. However, in contrast to the previous map oxidative wear was significantly considered in this wear mechanism. However, quantitative data regarding oxidation was not given. Also, the map showed that the adhesion and delamination arose under high load while abrasive wear occurs at relatively high velocity. Moreover, under the 20–50N load condition, the friction force was found to be less due to the compaction of the wear debris into the surfaces leading lower wear. Furthermore, enhanced load results in the removal of these compacted particles resulting plastic deformation or subsurface cracking. The delamination wear mode is prominent in the severe wear regime.

In the present scenario, these maps can only provide a guide to the nature of dry sliding wear in aluminium alloys under the stated operating conditions [99]. Application of such maps in the study of composite wear behaviour would have to incorporate the influence of intrinsic tribological factors, such as reinforcement volume fraction, morphology and size.

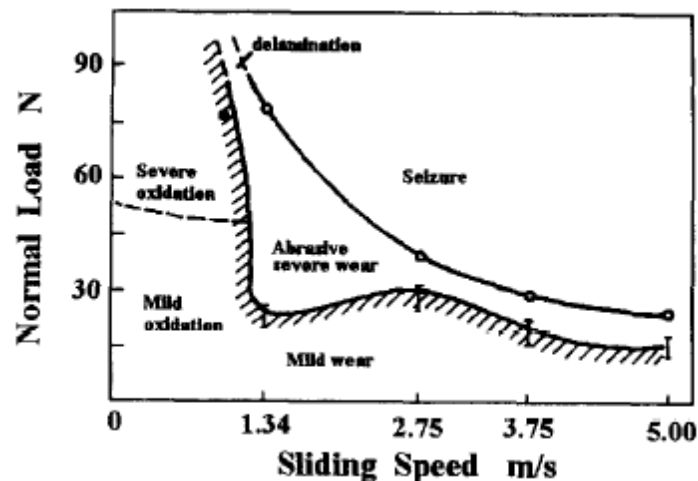


Figure 2.12: Dry sliding wear mechanism map for an as-cast Al 6061 alloy reinforced with SiC_w [98].

After studying the literature of Al–Si alloys and composites, it has been found that influence of reinforcement size, volume fraction and morphology on wear behaviour was

investigated by many researchers. However, none of these investigations were based on a systematic approach. A little information regarding particulate size and volume fraction related to abrasive or dry sliding wear processes is actually available. The data collected from the work done indicate that only two reinforcement types, mainly silicon carbide and alumina have been tried. Future research should incorporate the wear behaviour of spray deposited alloys with other potential reinforcement materials such as TiC, TiB, ZrSiO₄, Si₃N₄ and SiO₂.

Less work has been done on the combined approach of immiscible elements like Pb, Bi, Sn and particle reinforced rapidly solidified AMCs i.e. spray forming techniques. Limited work has been reported on fabrication and characterization of zircon sand reinforced with aluminium metal matrix composites and none has used spray deposition technique to manufacture zircon sand reinforced AMCs.

Therefore, the objectives of present work are

- a. To prepare the cost-effective MMC material by taking Al–Si alloy as matrix with immiscible elements like Sn & Bi and also some ceramic particulate like silicon carbide and zircon sand as reinforced phase using spray deposition technique.
- b. To analyze the microstructural characteristics of the as cast material.
- c. To study the feasibility of the material as bearing material by analyzing their wear and other related characteristics.
- d. To compare the properties of the so developed materials.

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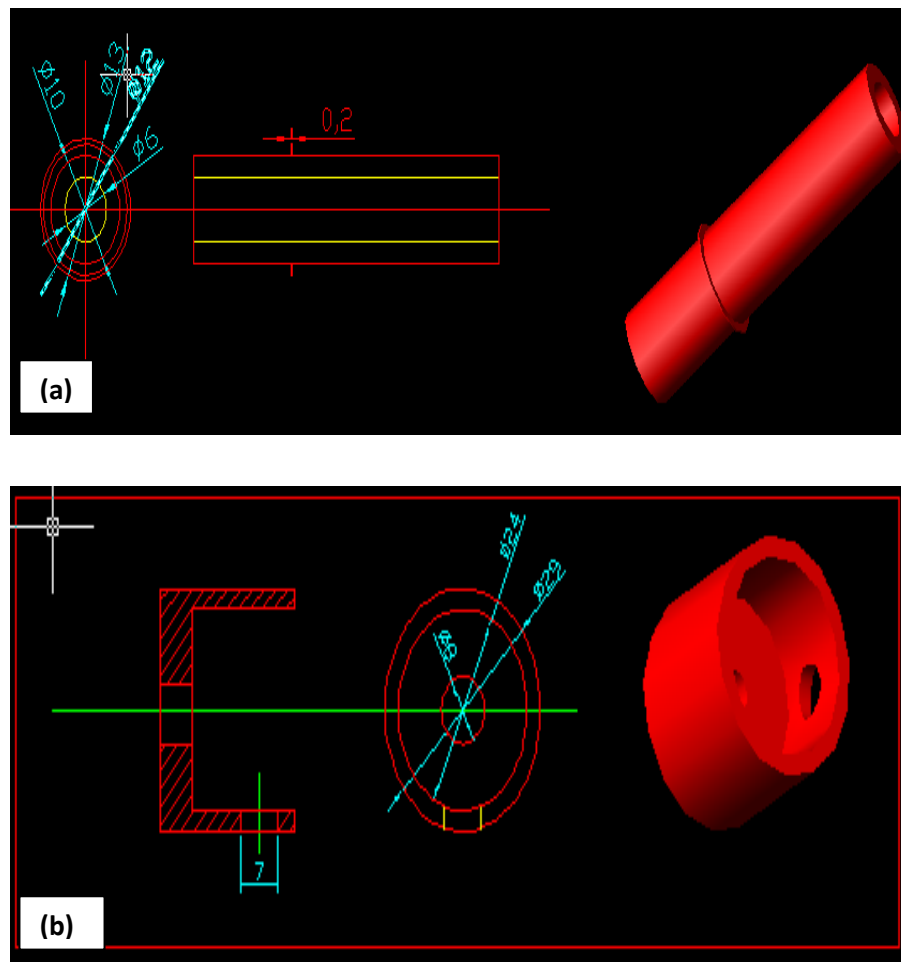
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Overview

In this chapter, the designs of convergent-divergent nozzle used for atomization has been described. The problem faced with the initial designs and details of modified nozzle is also documented. The chapter reveals the different parts of spray set-up assembly and their drawings.

3.1 Nozzle preparation and set up

During the preliminary experimentation, a spray forming set up has been designed and fabricated. The nozzle which has been used for the spray deposition is an annular convergent divergent nozzle where gas-metal interaction occurs at the tip of the melt delivery tube concentrically placed with the flow channel. The melt delivery tube, gas-pressure nut and the nozzle designs were prepared taking different parameters into consideration. The length, pitch of threading and radii of each component and other related design parameters are illustrated in Computer-Aided Design (CAD) as shown in Fig. 3.1.



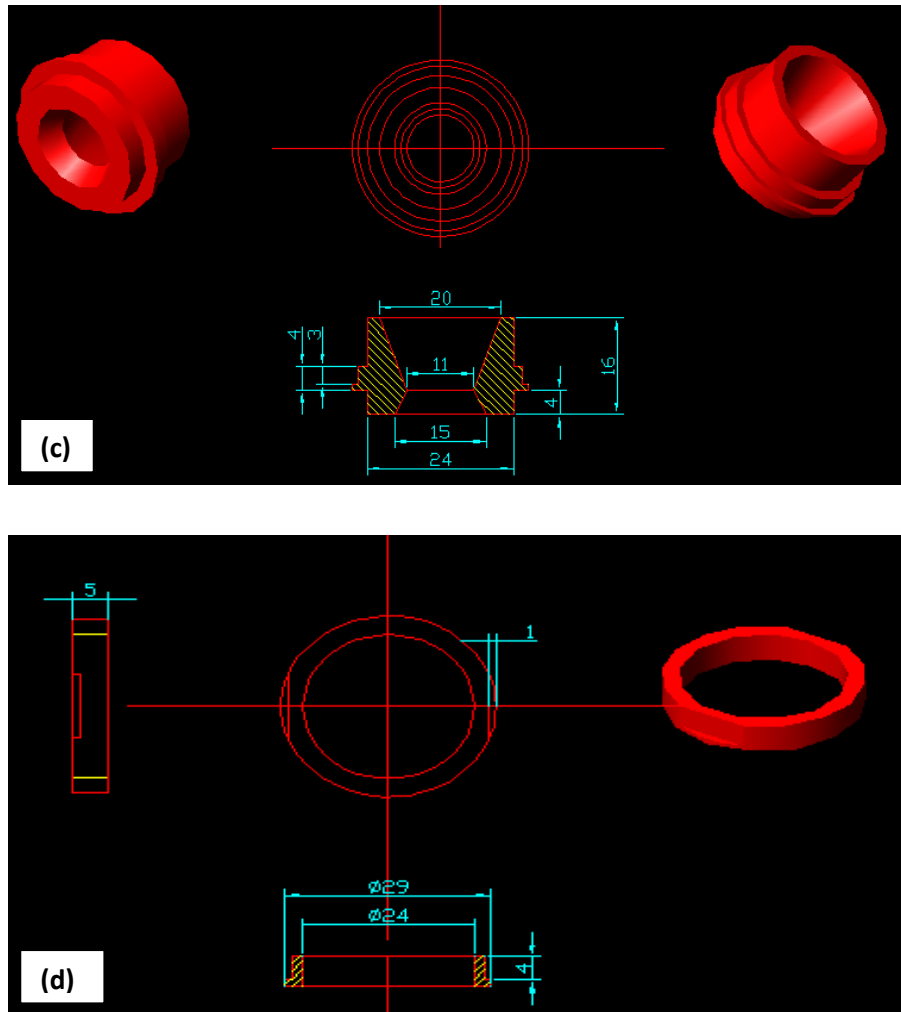


Figure 3.1: The design of the parts of the nozzle used for preliminary tests: **(a)** Melt delivery tube, **(b)** gas-pressure nut, **(c)** convergent-divergent nozzle and **(d)** shell to increase and decrease the distance.

The main problem in the design was freeze-up of the melt in the melt delivery tube of the nozzle. The photographs of the blocked nozzle taken after the spray deposition process are shown in Fig 3.2. The difficulties occurring in the first nozzle and assembly with the solutions are listed below:

1. The melt spray gets deflected with the high pressure in one side. However, it should be circular and evenly deposited on the substrate. The concentricity as well as the firmness of the nozzle with the whole apparatus can resolve this problem.

2. The choking of the melt which is taking place in the melt delivery tube during spray can also be resolved by preheating of the tundish before pouring the melt. Therefore a new tundish design with a band heater around this has been prepared to solve this freezing problem.
3. The outer diverging cone of the nozzle should be designed such that the spray should be confined in maximum 8 inches circular diameter, if the distance between the substrate and melt delivery tube should be changed from 25-45 cm apart.

To overcome these difficulties second nozzle was designed and the photographs of modified nozzle parts are shown in Fig. 3.3 and 3.4 respectively.

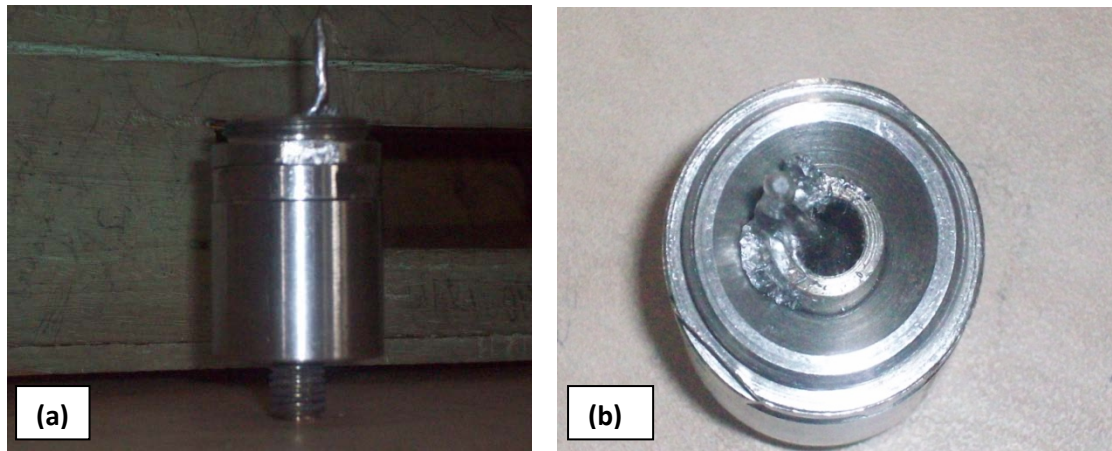
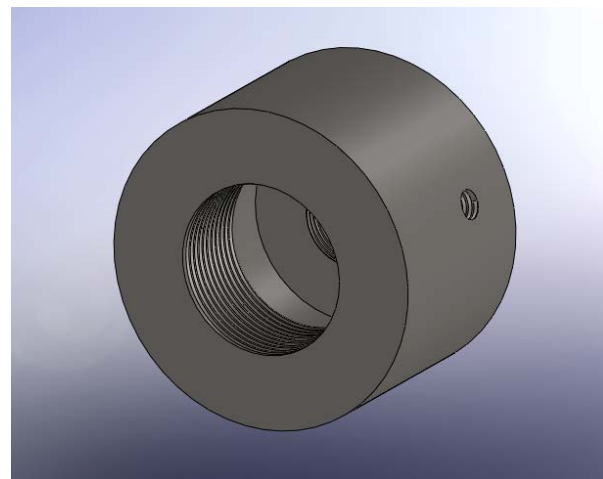
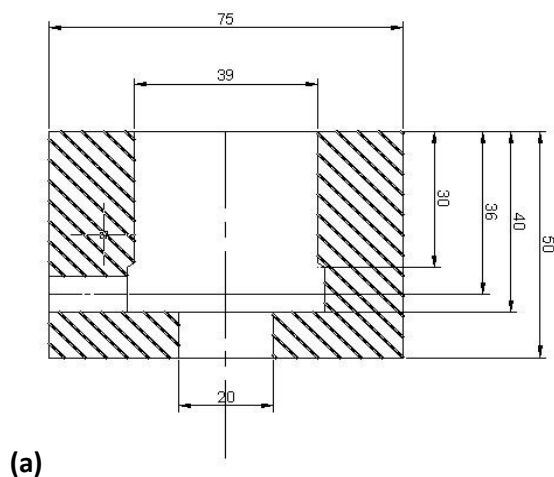


Figure 3.2: The nozzle freeze-up **(a)** lateral view and **(b)** top view.



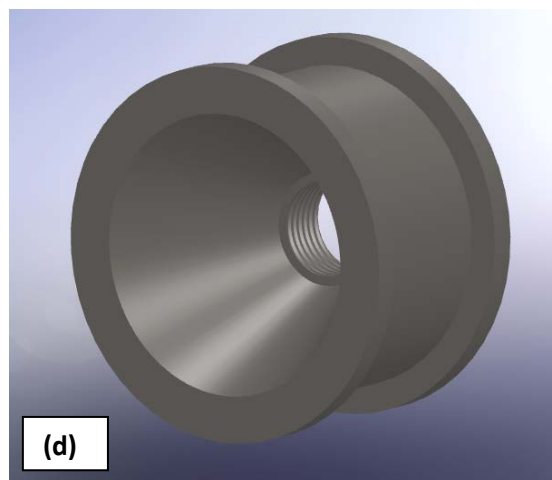
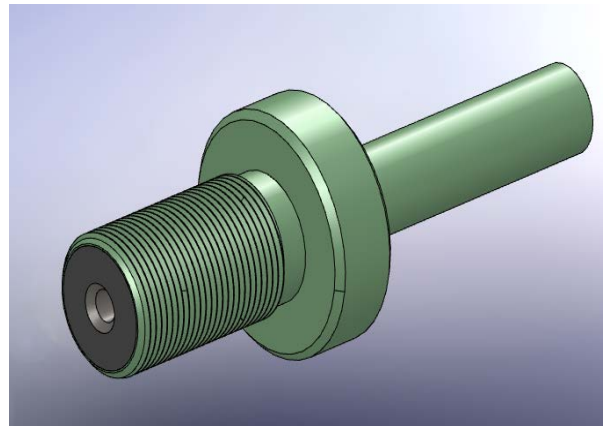
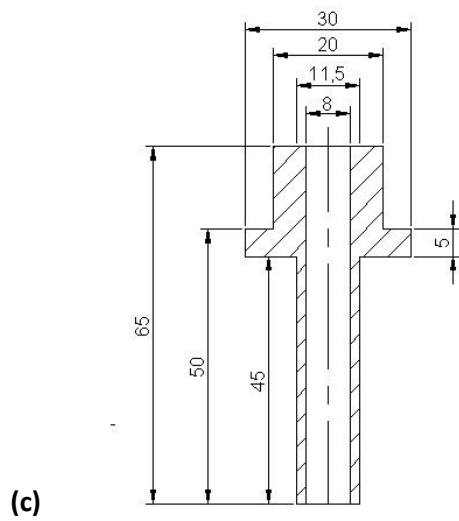
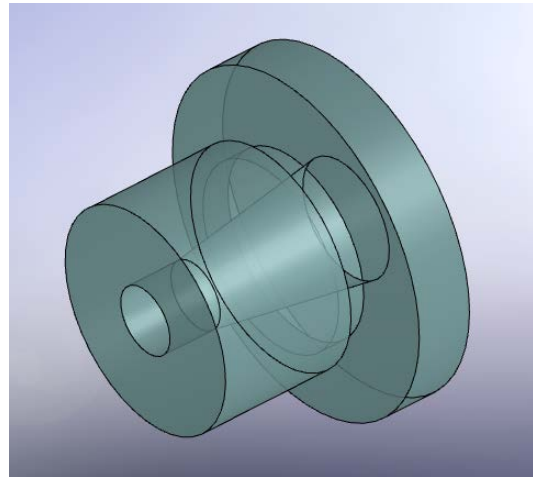
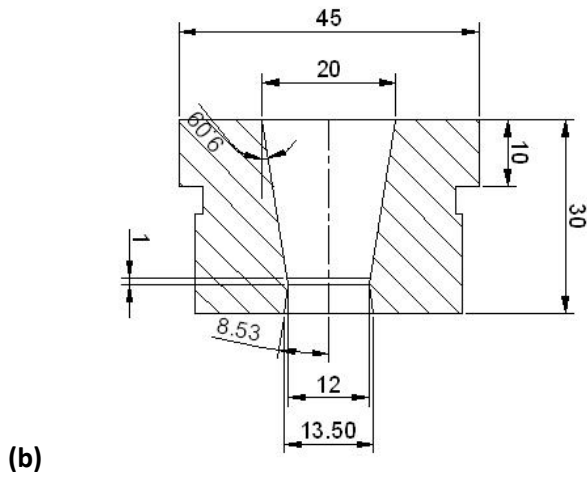


Figure 3.3: The line diagrams and designs of modified nozzle **(a)** pressure nut, **(b)** nozzle, **(c)** melt delivery tube and **(d)** tundish.

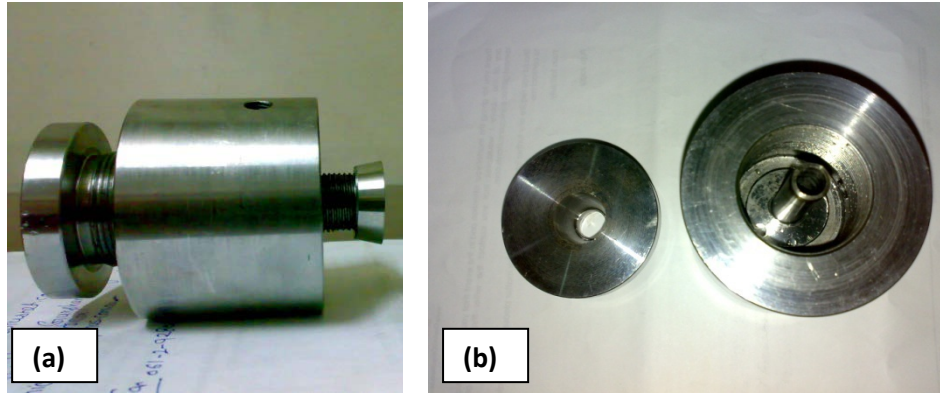


Figure 3.4: The modified nozzle **(a)** assembled and **(b)** showing different parts.

Moreover, the ceramic particulates are added in the atomization region near the spray nozzle with the help of two injectors. The different injector designs are used during spray atomization. The design and cross sectional view of primarily used injector is shown in Fig. 3.5. There are the two injectors used in the proximity of the melt delivery tube. It consists of the semicircular slit of 1mm for the particulate outcome. Since metal machining is hard for such type of design therefore afterwards an injector with round orifice as shown in Fig. 3.6 has been used. The experiments have been done with different injector orifice with four and two injectors near injection region. Finally 2mm injector orifice is used for the work.

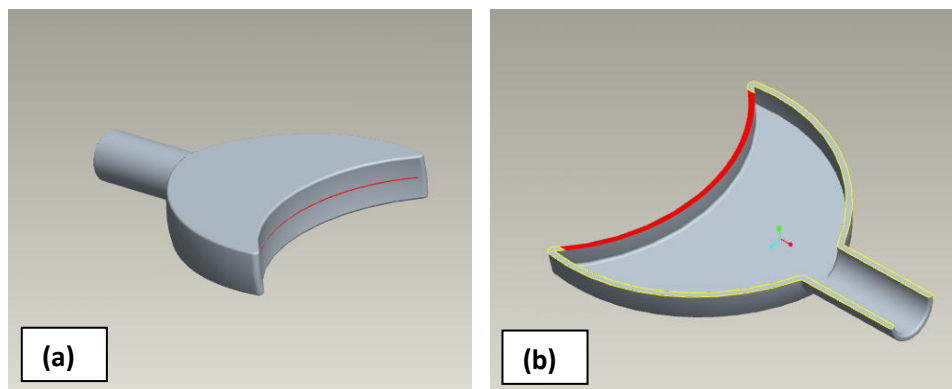


Figure 3.5: The modified injector **(a)** assembled and **(b)** lateral view.

The complete set up used for experimental work has also been modified and the assembly is shown in Fig 3.6. In the assembly, injectors are placed at diagonal position near the nozzle outlet. The melt delivery tube joins the tundish from the upside and the nozzle downside. Before melt pouring the tundish is heated with the help of band heater (red

colour) as shown in Fig. 3.6(b). The tundish and delivery tube are made from 304 stainless steel. The photograph of the setup is shown in Fig. 3.7.

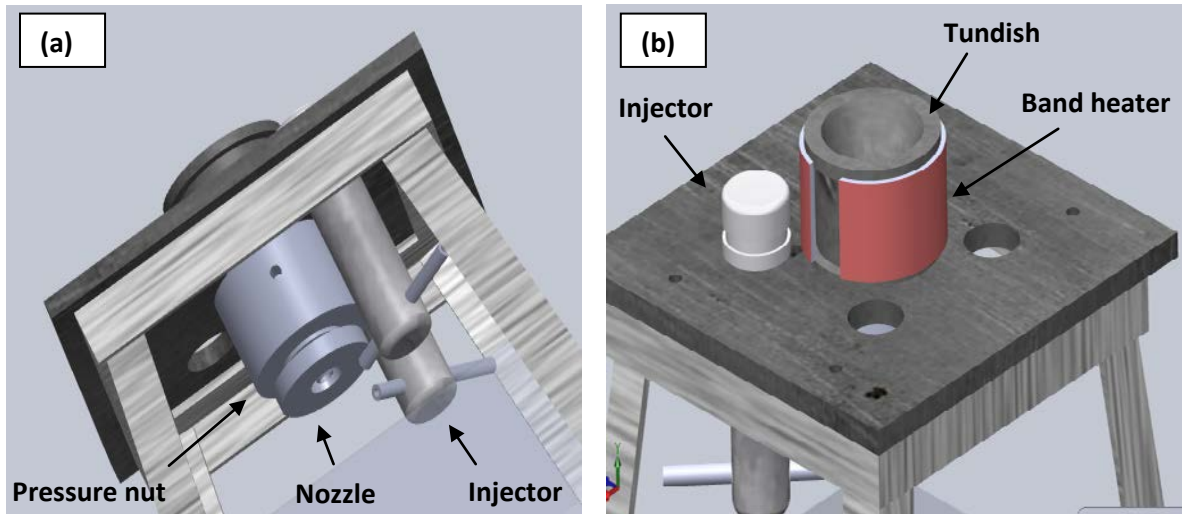


Figure 3.6: (a) The bottom and (b) the top view of the spray set up assembly.

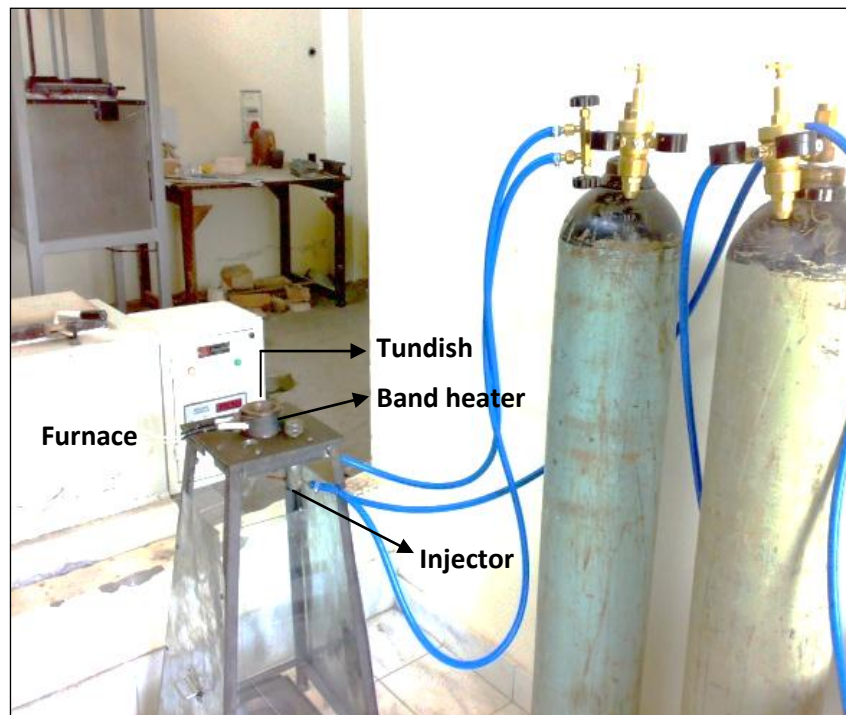


Figure 3.7: The experimental set-up.

EXPERIMENTAL PROCEDURE

Overview

In this chapter, the specifications of different materials used and procedure adopted to prepare composites from these materials is described. The various characterization techniques; X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDX), Rockwell hardness testing and dry sliding wear with their parameter details are also elaborated. Further the whole methodology and the step-wise wear testing plan is shown in the form of flow charts. The preliminary experimentation done to optimize the process parameters before the fabrication of composites is also documented.

4.1 Raw materials

In the present work the Al–Si alloy and reinforcements used to form the metal-matrix composite are described below.

4.1.1 Matrix material

Commercial grade near eutectic Al–Si alloy (LM13) was used in the present investigation. The composition of obtained Al–Si alloy was analyzed by wet chemical analysis and X-ray fluorescence technique as shown in Table 4.1. LM13 alloy contains around 1% Mg which is helpful for wetting the dispersoid in the matrix. LM13 alloy was obtained in the form of ingots which was further cut into small pieces by an electric power saw in order to feed into the crucible properly. The immiscible element (Sn or Bi) with 99.9% purity were added in the alloy in the form of granules.

Table 4.1: Composition of Al–Si alloy.

Alloy	Si	Fe	Cu	Mn	Mg	Zn	Ti	Ni	Pb	Sn	Al
Chemical analysis	11.800	0.365	1.230	0.411	0.94	0.21	0.025	0.940	0.029	0.005	Bal
XRF	11.166	0.332	1.247	0.598	0.849	0.25	0.026	0.868	0.001	0.002	Bal

4.1.2 Reinforcement materials

Two types of particulate ceramic reinforcements viz. zircon sand and silicon carbide (98% purity) were used as reinforcement material. The zircon sand is supplied by M/s Indian Rare Earths Ltd., Mineral Division, Chavara (Kerala). The particle size of as received particulates were in the wide range between 25–200 μm . The ceramic particles were sieved and two particle size ranges, 106–125 μm and 63–90 μm were selected for the experimentation. The composition analysis of the zircon sand is given in Table 4.2.

Table 4.2: Composition of the zircon sand (ZrSiO_4).

Elements	ZrO_2 (+ HfO_2)	SiO_2	TiO_2	Fe_2O_3
% in Bulk	65.30	32.80	0.27	0.12

4.2 Methodology

The methodology of the experimentation is given in the form of flow chart in Fig. 4.1.

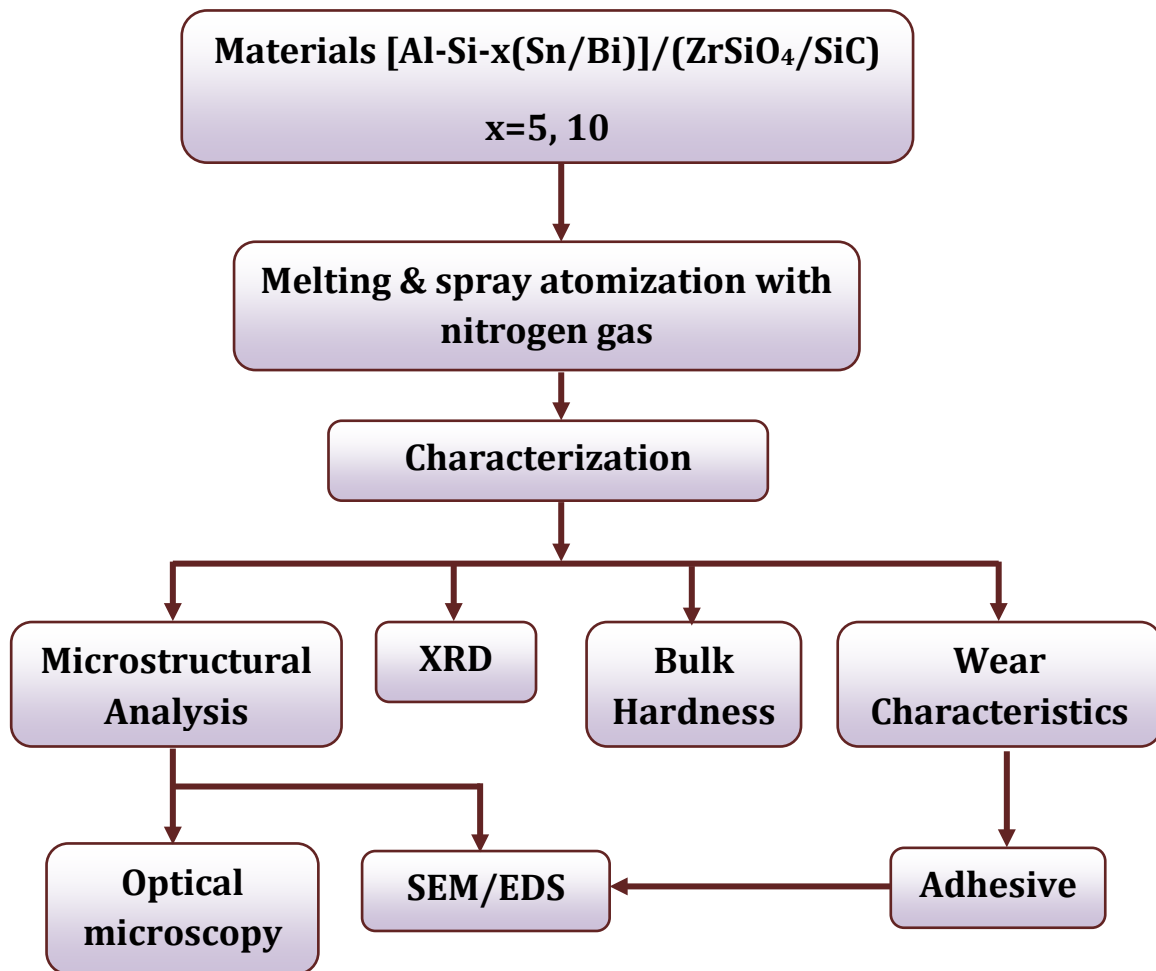


Figure 4.1: Flow chart of the methodology adopted.

The Al-Si reinforced composites have been prepared by the spray atomization and co-deposition process. The indigenously designed and fabricated convergent-divergent atomizer is used for gas atomization and spray deposition. For spray deposition, 1.5 kg charge of LM13 alloy was melted and superheated up to 730-750°C in a graphite crucible under nitrogen atmosphere in a resistance furnace. At this temperature, weighed granules of immiscible element (Sn/Bi) are added in the melt and stirred rigorously to homogenize the melt. The air was removed from atomization chamber by flushing argon gas in the chamber before pouring the melt to minimize the oxidation of the droplets. After cooling the melt to 700-730 °C, it is poured in the tundish attached above the atomizer

assembly. Before pouring the molten alloy high pressure (0.7 MPa) nitrogen gas was passed through the atomizer.

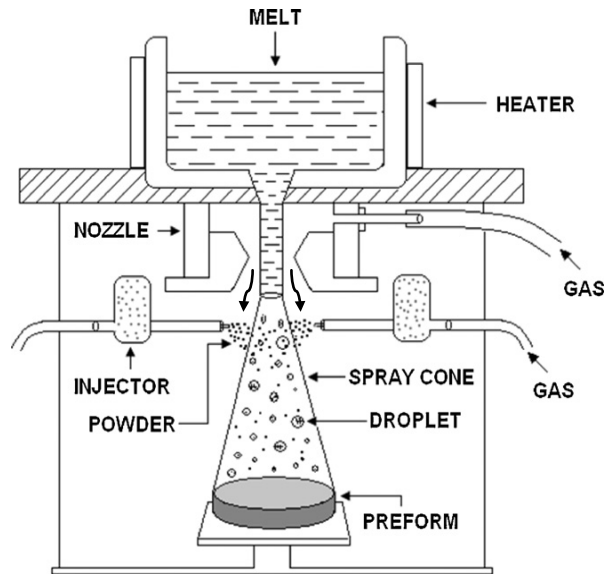


Figure 4.2: Schematic diagram of spray forming process.

The melt flows from the tundish to the melt delivery tube of inner diameter 8 mm concentrically fixed in the convergent-divergent atomizer. The schematic diagram of the atomizer assembly is shown in Fig. 4.2. In the atomization region, the molten metal stream is disintegrated into spray of droplets by gas jets. The droplets are cooled by the gas stream and accelerated towards a deposition substrate on which they impinge and consolidate to form a coherent deposit. The substrate is placed 300 mm below the nozzle assembly. Simultaneously for development of composite materials, preheated particles are fed into the spray cone with the help of two external powder injectors having orifice of 2 mm placed near the melt delivery tube in atomization section. The particles interact with the liquid droplets in the spray and travel towards the substrate. These are dragged by the droplets or pulled under the force of gravity. The atomized droplets get collected on the stationary copper substrate to make a solid preform of diameter 150 mm and thickness of 40–45 mm. The over-spray powders were also collected for the study of interaction behaviour of metal and dispersoid. The atomized droplets are collected on the stationary copper substrate to make a solid preform of diameter 150 mm and thickness of 40–45 mm. The substrate is placed straight perpendicular to the incoming droplets and is not preheated to achieve maximum cooling conditions on droplet striking.

4.3 Material characterization

4.3.1 Microstructural analysis

The samples of dimensions 25mm×15mm×15mm were cut from different areas of the preform for further characterization. The microstructural analysis has been done with the help of both optical (Eclipse MA-100, Nikon) and scanning electron microscope (JEOL, JSM-6510 LV, Japan) at various magnifications. The specimens for microstructural analysis were prepared following the standard metallographic procedure of polishing and grinding. Over sprayed powder particles were mounted with a cold setting acrylic resin to facilitate metallographic preparation. All the samples were etched in a Keller's reagent. The chemical composition of Keller's reagent is given in table 4.3.

Table 4.3: Chemical composition of Keller's reagent.

Composition	Dist. Water	HNO ₃	HCl	HF
Vol%	95ml	2.5ml	1.5ml	1ml

4.3.2 X-ray analysis

The X-ray diffraction patterns of the prepared samples were recorded on Panalytical X'pert Pro MPD, Netherland using Cu K_α radiation ($\lambda = 1.54\text{\AA}$). The collected data was matched with reference data for identification of different phases.

4.3.3 Hardness

The Rockwell hardness of the cast Al-Si alloy, spray formed Al-Si alloy and its composites reinforced with ZrSiO₄/SiC particles have been measured at digital Rockwell hardness tester (model TRSND, Fine Manufacturing Industries, India) machine using 1/16 inch ball indenter at 100 kg load. Each reading is an average of at least five separate measurements taken at random places on the surface of specimens.

4.3.4 Wear testing

The wear tests were performed on pin-on-disc tribometer. The as prepared samples were machined to 8mm diameter cylindrical pins from the middle section of the preform for the tests. The tribometer used for the present study is one of the industrial standard TR 20 series wear and friction monitor with facility to acquire data from room temperature to elevated temperature by data acquisition system (model: TR20 CH400) supplied by M/S Ducom Instruments Pvt. Ltd., Bangalore, India. The photograph of the tribometer is shown in Fig. 4.3. This instrument consists of a rotating disc against

which a test pin (sample) is pressed with a known force. The counterface disc is a hardened and polished EN-31 steel disc (0.9–1.2 wt.% C, 0.3–0.75 wt.% Mn, 0.1–0.35 wt.% Si, 0.04 wt.% S, 0.04 wt.% P, balance Fe) having hardness 65 HRC. The tests were carried out at a relative humidity of 36–56%. The load is applied on the sample pin, perpendicular to the rotating disc. The tests were conducted at five different loads of 1.5–5.5 kg (14.7N, 24.5N, 34.3N, 44.1N and 53.9N). Wear rates for the pin are calculated from the volume of material lost divided by the sliding distance during the test i.e.

$$W = \frac{\pi r^2 h}{S}$$

where W = wear rate (m^3m^{-1}), r = radius of the pin, h = loss of height during wear testing as measured by tribometer and S = sliding distance. The friction coefficient has been calculated as $\mu = \frac{F}{N}$; where F = frictional force measured by tribometer (N) and N = applied load (N). The wear characteristics have been noted down at four different temperatures (50°C, 75°C, 100°C and 150°C). The option for elevated temperature test has been provided by heating the chamber surrounding the rotating disc. The chamber temperature is set constant during each operation and is measured by Type K (Chromel–Alumel) thermocouple. This instrument is specifically designed to measure maximum 2mm wear of the pin height. For every experiment sliding velocity of the disc is kept constant at 1.6ms^{-1} . The wear test was performed for a maximum sliding distance of 2880m. The wear debris obtained after the 30 min of sliding of each test run were examined under SEM and EDS (JEOL, JSM-6510 VL, Japan). The worn surfaces of the samples were also examined under SEM to determine the wear mode.

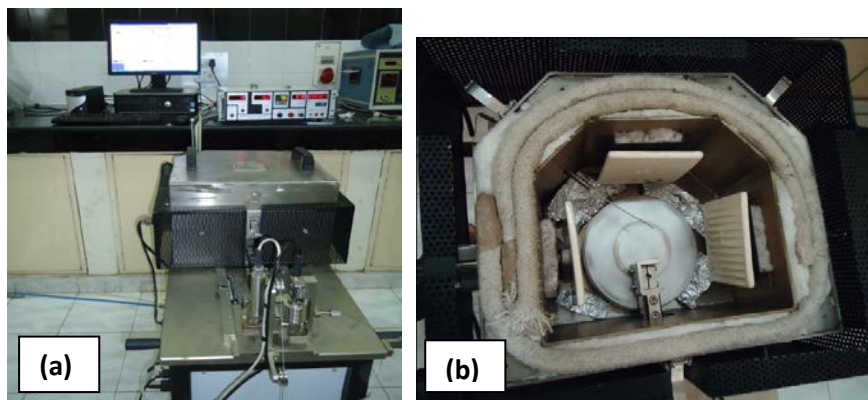


Figure 4.3: Wear testing machine **(a)** Wear and friction monitor, **(b)** mounting and heating chamber.

4.4 Optimization of process parameters

In order to get good quality spray formed alloys the preliminary experiments have been done on modified nozzle. The literature data has been utilized for the optimization of the process parameters. Accordingly the condition of nozzle to substrate distance was optimized by keeping the melt flow rate and pouring temperature constant. However the amount of porosity developed is different as the nozzle to substrate distance was varied. This is summarized in Table 3.1. After analyzing all data we kept nozzle to substrate distance 300 mm for each set of conditions. The obtained results for different other experimental conditions are presented in results and discussion sections of this thesis. The conditions were also optimized in order to achieve proper reinforcement of ceramic particulates in the alloy. For this the flow rate of reinforced particles of different size were calculated by noting down the time to get the flow rate at different injector pressure. For achieving 10 vol. % of the particulates in the overall composition, a finishing run was done at 0.7 MPa atomization pressure and the optimized injector pressure was varied from 0.15–0.2 MPa for different size of zircon sand and SiC particles. However, in the final spray formed composite the reinforcement has been achieved up to 6–12 vol. % in the composite. This variation was observed for the samples taken from different zones of the spray formed composites. Moreover in the central part it was around 8 vol. %. Also, the loss of reinforcement particles has occurred in the form of overspray powders. However, an average reinforcement of approx. 8 vol. % was observed in the formed composite containing $\text{ZrSiO}_4/\text{SiC}$ of different size. The length of the melt delivery tube is kept constant for entire experimentation. The position of the melt delivery tube was optimized as aspiration created near the tip of the melt delivery tube which varied with variation in atomizing pressure. The tip of the melt delivery tube was placed 2 mm below the gas ejection region (protrusion). For less than 2 mm length back pressure is generated inside the melt delivery tube causing chocking. After performing several trails, the conditions for atomization were fixed as follows:

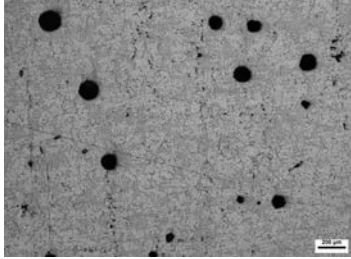
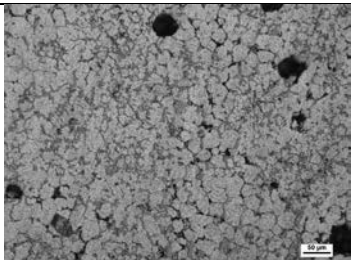
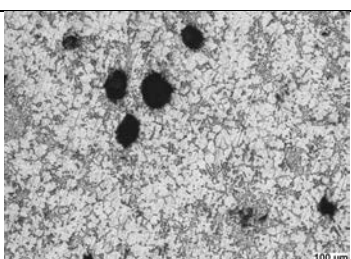
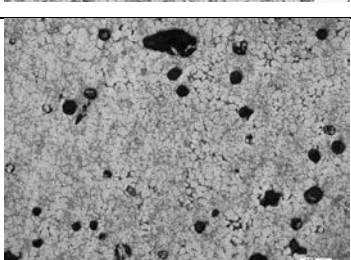
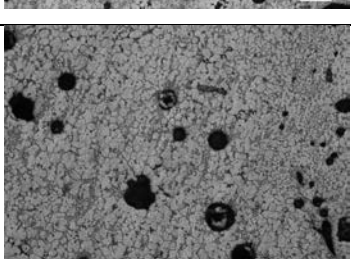
Atomizing gas pressure = 0.7 MPa

Protrusion length (beyond gas ejection region of divergent section) = 2 mm

However, beyond 3 mm length also fluctuating pressure was observed. The metallographic specimens are tested from the middle section of the preform. The samples do

show different porosity with respect to the composition of material yet the range in the middle section of the substrate is found to be 2.5-3.2% for 300 m. The optimization of porosity and process parameters is given in Table 4.4.

Table 4.4: Optimization of processing parameters for spray deposition.

Material	Melt flow rate ($\times 10^{-3}$ kgs $^{-1}$)	Pouring temperature ($^{\circ}$ C)	Nozzle to substrate distance (mm)	Porosity (%)	Micrograph
LM13	105.34	700	250	4.0-4.5%	
LM13	108.82	700	300	2.5-3.2%	
LM13	102.45	700	350	3.6-4.8%	
LM13	110.31	700	400	5.3-6.1%	
LM13	107.63	700	450	6.0-6.7%	

CHAPTER-5

RESULTS AND DISCUSSION

(MODALITY OF SPRAY FORMING)

Overview

In this chapter, the experimental results of as received and spray formed LM13 alloy (containing around 12 wt.% Si) are presented. The samples were analyzed microscopically to study the difference in morphology of the alloy after spray forming. Further the samples were wear tested under various loads and temperatures. The worn surfaces and debris obtained were also analyzed by SEM and EDS to predict the mode of wear under different set of conditions.

5.1 Microstructural analysis

The optical micrographs of as cast and spray formed Al-Si alloy are shown in Fig. 5.1. There is large difference between the microstructural features of the as cast and spray formed alloy. The optical micrograph of the as cast Al-Si alloy (Fig. 5.1(a)) shows the dendritic growth of α -Al grains (white phase) and eutectic phase in between the inter-dendritic arms. Spray formed Al-Si alloy exhibits homogeneous equiaxed α -Al grains with refined eutectic Al-Si phase as shown in Fig. 5.1(b). The equiaxed α -Al grains of 25–50 μ m size are observed in the spray formed Al-Si alloy. The equiaxed microstructural features have been reported widely in spray forming by other researchers [1] also and have been explained in the previous chapter 2.

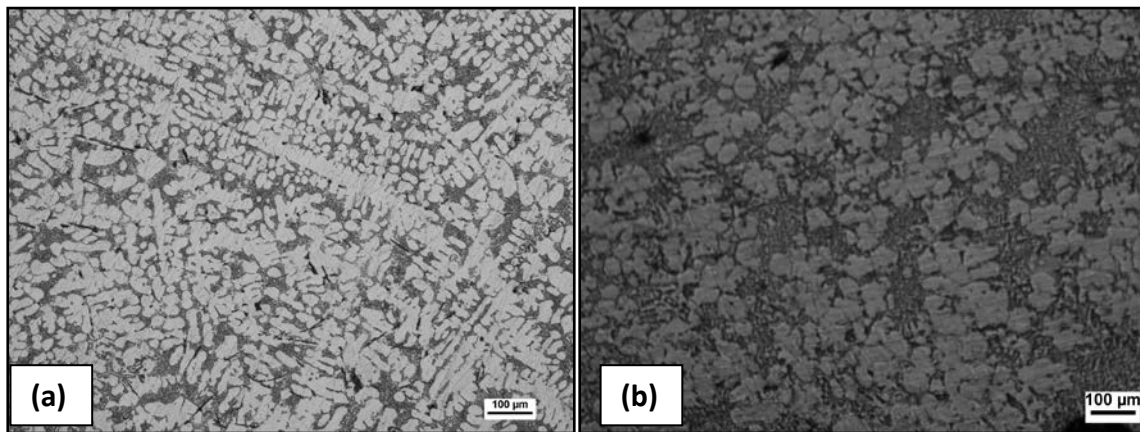


Figure 5.1: Optical micrographs of **(a)** as cast and **(b)** spray formed Al-Si alloy.

5.2 Hardness

The hardness of the materials has been measured on B-scale of the Rockwell hardness tester. The average hardness of as cast and spray formed Al-Si base alloy has been found to be 31.46 and 35.2 HRB respectively. There is little increase in the hardness of the alloy after spray forming. The increase in hardness of spray deposited alloy is due to inherent microstructural modification by spray forming technique. However, the spray formed alloy do contain large amount of porosity along with refined structure. The presence of porosity affects the mechanical properties of the material. Therefore while the microstructure

modification has been achieved as shown in earlier section yet hardness does not vary much.

5.3 Wear characteristics

Wear rate of the specimen as a function of sliding distance was measured. The wear rates of the as-cast and spray formed Al-Si alloy are shown in Fig. 5.2 to Fig. 5.3 respectively. The wear rate behavior of each sample is categorized depending upon the operating temperature and further subcategorized based on applied loads.

In general, it has been found that the wear rate is rising on increasing the applied load. The wear rate behavior shows the similar trends for lower loads (1.5, 2.5 and 3.5 kg). Under an applied load two different type of wear behavior can be predicted from the curves. Each curve corresponds to two main types of wear mechanism. First high increment in wear rate before 500 m sliding distance corresponds to the run-in wear. The run-in wear always represents the unstable fluctuations when the two surfaces come into contact on start of sliding. The mechanical welding of the plastically deformed material at the edges of the pin leads to rise in fluctuating wear rate in the plots. The constant wear rate has been established after initial sliding which is represented by the plateau in the wear rate curves.

The change of wear behavior is predicted as we progress from 3.5 kg to 4.5 kg for Al-Si alloy at 50 °C (Fig. 5.2(a)). However, as the temperature is increased wear rate gets stabilized for 4.5 kg load as shown in Fig. 5.2(b-d), still at higher load (5.5 kg) the alloy shows an abrupt increase in the wear rate limit of the tribometer. The instrument is specifically designed to measure maximum 2 mm wear of the pin height. The wear mechanism alters from mild to severe delaminating mode at higher loads.

Figure 5.3(a-d) illustrate that spray formed Al-Si alloy shows higher wear rate at load greater than 3.5 kg for all the temperatures. However, wear rate tries to get stabilized at 4.5 kg load at 100°C as shown in Fig. 5.3(c). It can be concluded that up to 3.5 kg load the spray formed alloy poses the mild wear regime which is further transformed to severe wear at higher loads irrespective of the wide temperature variation. The reason behind such phenomenon at higher loads is consequence of delamination of alloy which leads to severe

wear. The spray formed alloy contains pores that act as crack nucleating sites under the pressure of higher loads. The severe wear phenomenon guided by these crack growth under continuous loading leads to removal of chunk of material [2, 3].

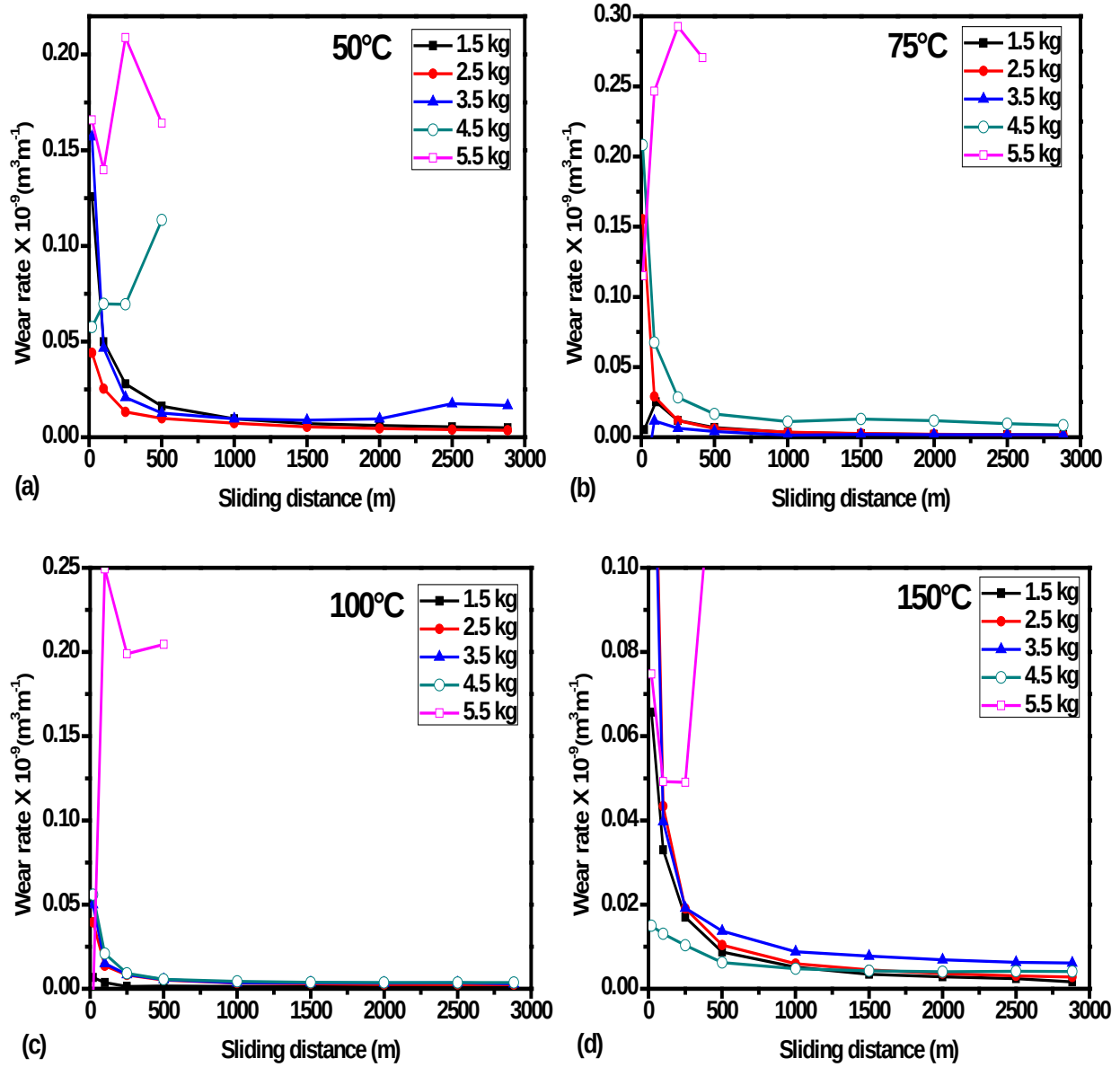


Figure 5.2: Wear rate of the as-cast Al-Si alloy under various loads at (a) 50 °C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

Average wear rate against various temperatures and applied loads for as cast and spray formed Al-Si alloy has been illustrated in Fig. 5.4. The average of the wear rate has been calculated after 500m run for each load to ensure presentation of the non-fluctuating wear regime. However, for severe wear average of fluctuating wear rate has been plotted. Figure 5.4 clearly depicts the transition load of 3.5 kg for both the materials as predicted earlier in Fig. 5.2 and 5.3.

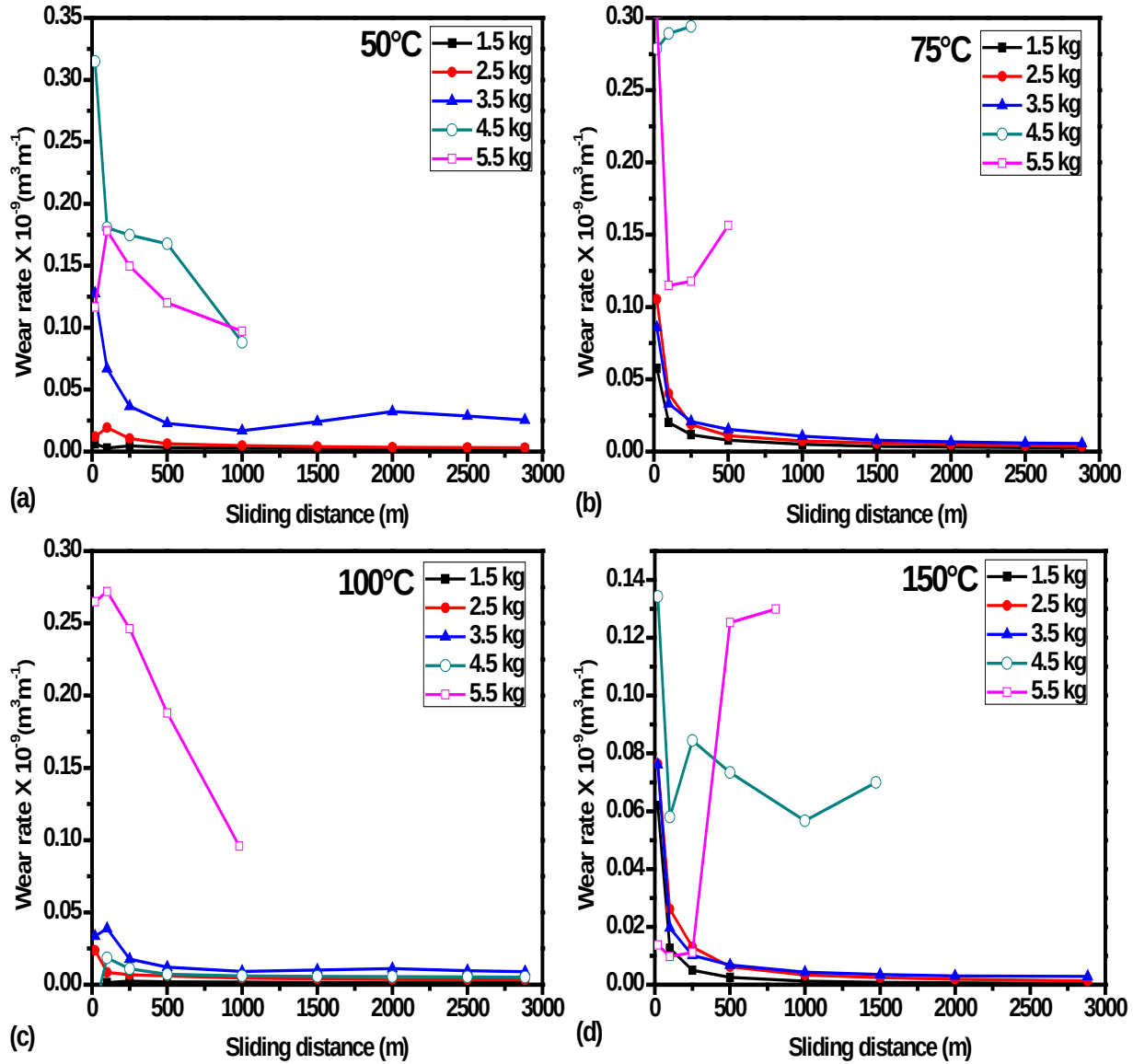


Figure 5.3: Wear rate of the spray formed Al-Si alloy under various loads at (a) 50°C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

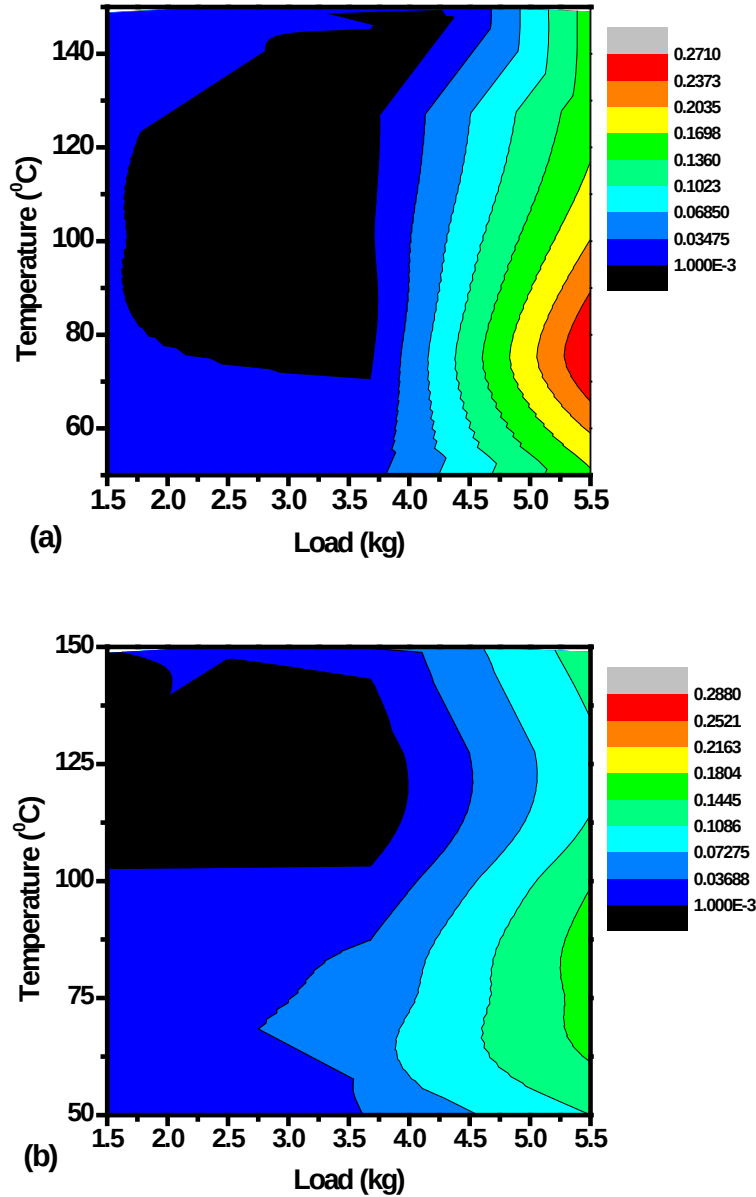


Figure 5.4: Averaged steady wear rate ($\times 10^{-9} \text{ m}^3 \text{ m}^{-1}$) against various temperatures and applied loads for **(a)** as-cast Al-Si alloy and **(b)** spray formed Al-Si-5Sn/ZrSiO₄.

5.4 Microstructural analysis of worn surfaces and wear debris

The morphology of the wear debris is of great interest due to its importance to know the mode of wear and its mechanism. The morphological analysis helps to understand how

material is crushed, redistributed and consolidated in a system. The details of analysis scheme of the worn surfaces and debris of spray formed samples is given in Fig. 5.5.

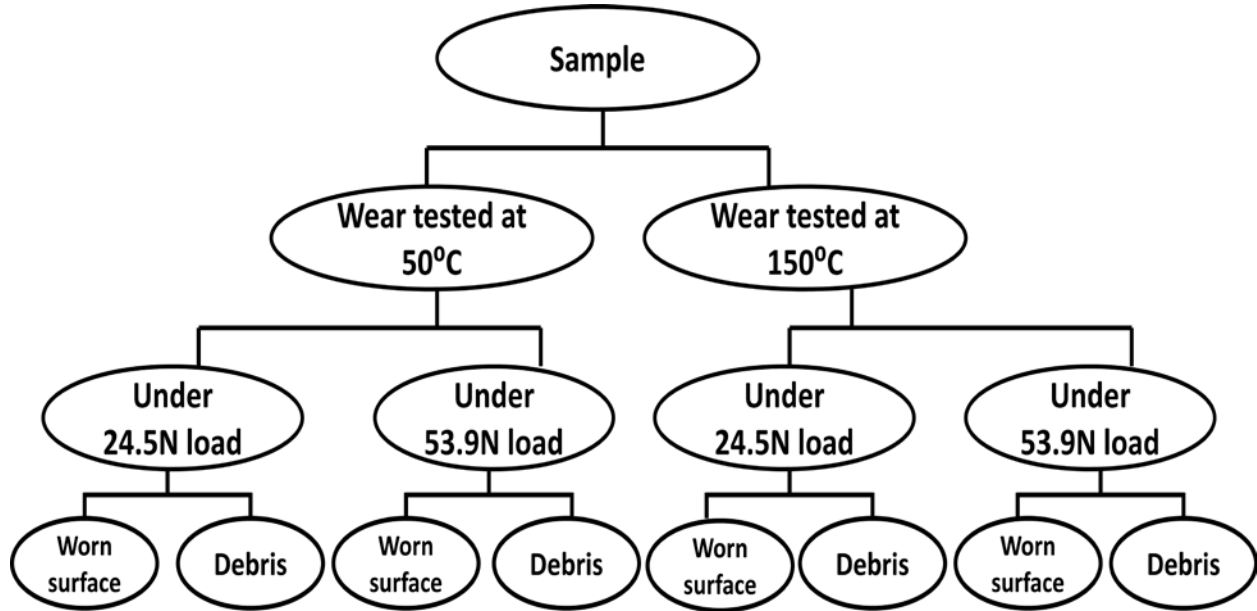


Figure 5.5: Details of analysis scheme of the worn surfaces and debris of samples.

SEM micrographs of worn pin surfaces and wear debris of as-cast Al–Si alloy are shown in Fig. 5.6 and 5.7 respectively. The grooves running parallel to the sliding direction can be seen in Fig. 5.6(a). At 150 °C and 2.5 kg load (Fig. 5.6 (c)) the continuous grooves get shallower at higher temperature. At 5.5 kg load (Fig. 5.6 (b)) along with grooves large amount of repetitive plowing marks are also present. At higher load and higher temperature conditions, Fig. 5.6 (d) shows the production of wear debris from the running surface due to deep grooving and microcutting. The plate like morphology has been observed from the debris collected at 2.5 kg load at both the temperatures as illustrated in Fig. 5.7(a, c). However, at higher load large forces are acting on the surfaces leading to removal of large chunks from the surfaces as shown in Fig. 5.7 (b, d). These debris also verify the presence of sever wear at high load conditions at both the extreme temperatures as shown in Fig. 5.2 (a, d).

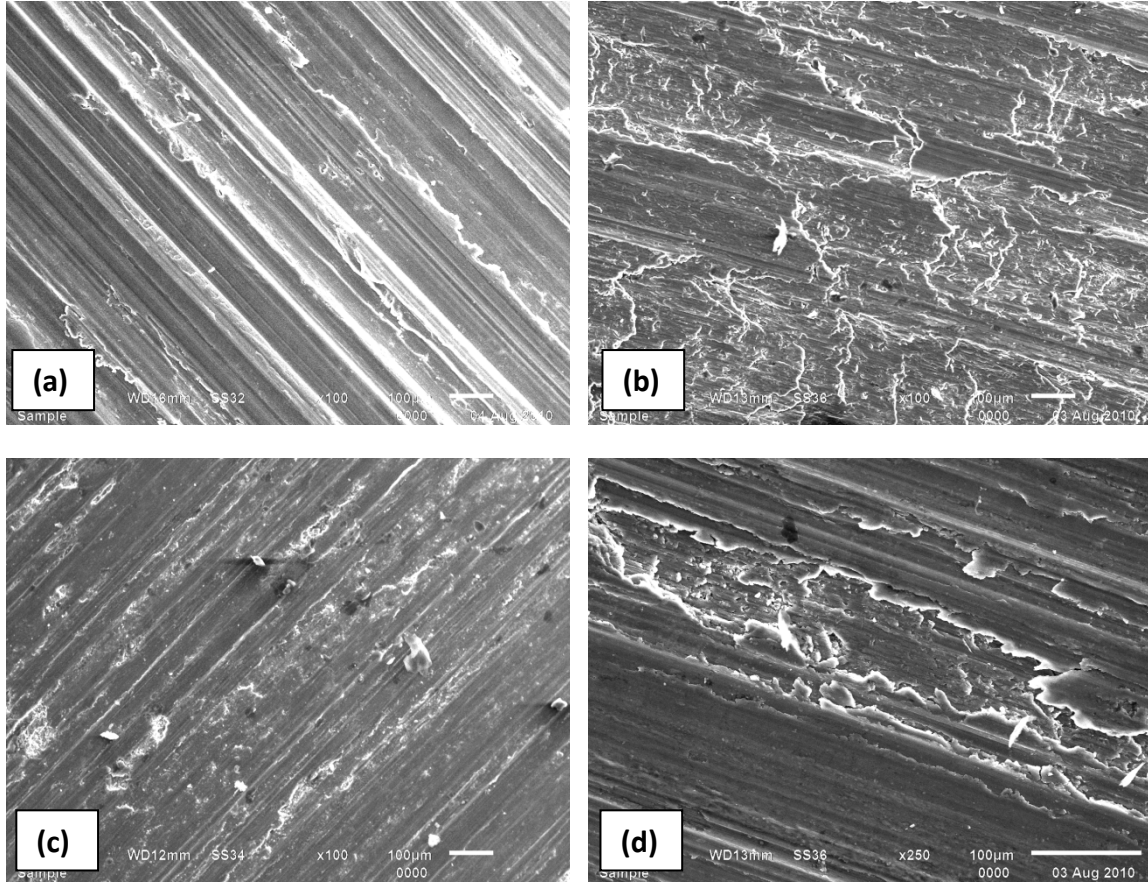
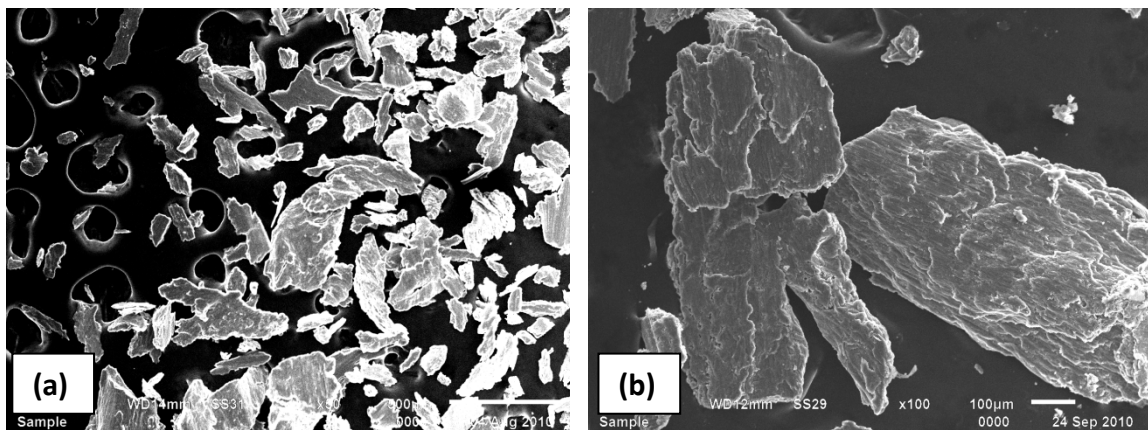


Figure 5.6: SEM micrographs of worn pin surfaces of as-cast Al-Si alloy at **(a)** 2.5 kg, 50°C; **(b)** 5.5 kg, 50°C; **(c)** 2.5 kg, 150°C; **(d)** 5.5 kg, 150°C.



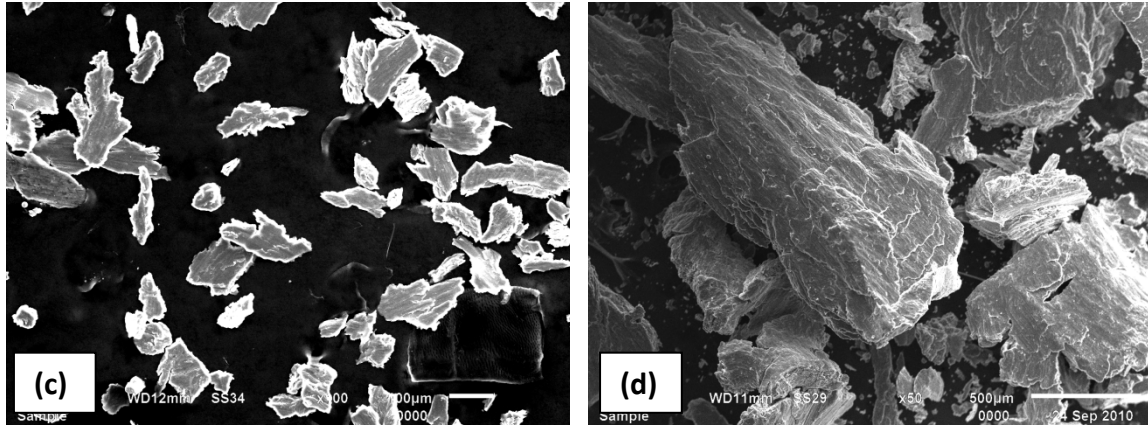
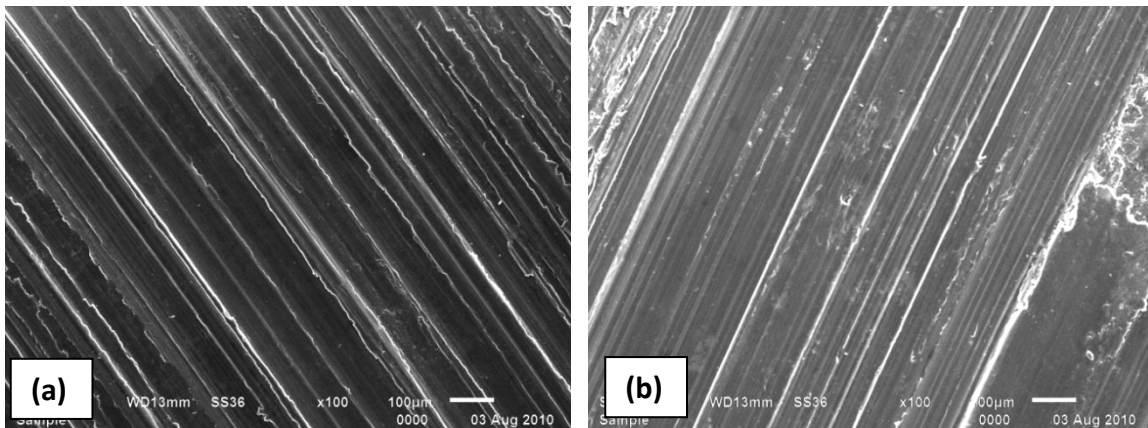


Figure 5.7: SEM micrographs of wear debris of as-cast Al-Si alloy at **(a)** 2.5 kg, 50 °C; **(b)** 5.5 kg, 50 °C; **(c)** 2.5 kg, 150 °C; **(d)** 5.5 kg, 150 °C.

Figure 5.8 shows the SEM micrographs of worn surfaces of spray formed Al-Si alloy at 2.5 kg load and 5.5 kg load under both lowest and highest temperature i.e., 50°C and 150°C. The adhesive continuous plowing marks are clearly visible on the sliding surface at 2.5 kg load as shown in Fig. 5.8 (a). The plowing marks got deeper on increasing the load to 5.5 kg (Fig. 5.8 (b)). The generation of debris and surface cracks is clearly visible at higher magnification with higher applied load as shown in Fig. 5.8 (c). As the temperature is increased from 50°C to 150°C, the worn pin surface shows the wear scars running parallel to the sliding direction as shown in Fig. 5.8 (d).



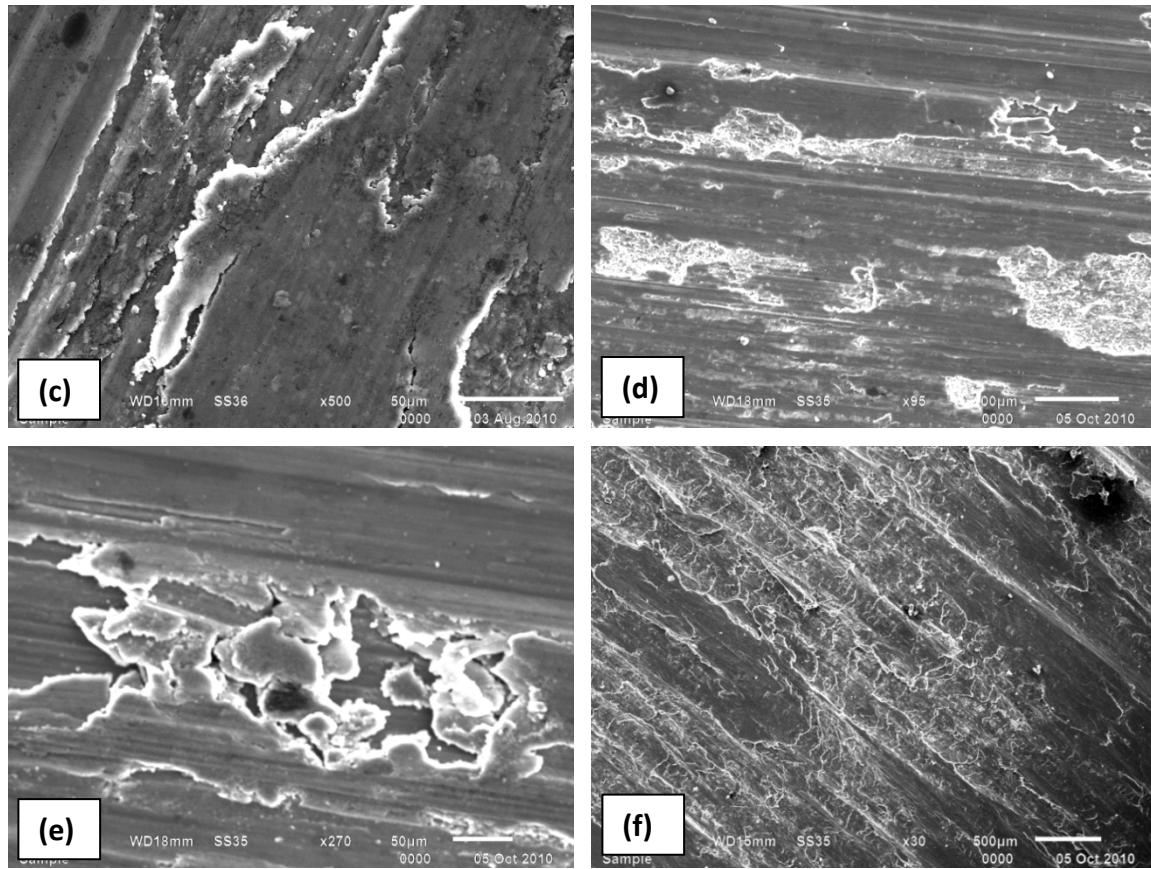
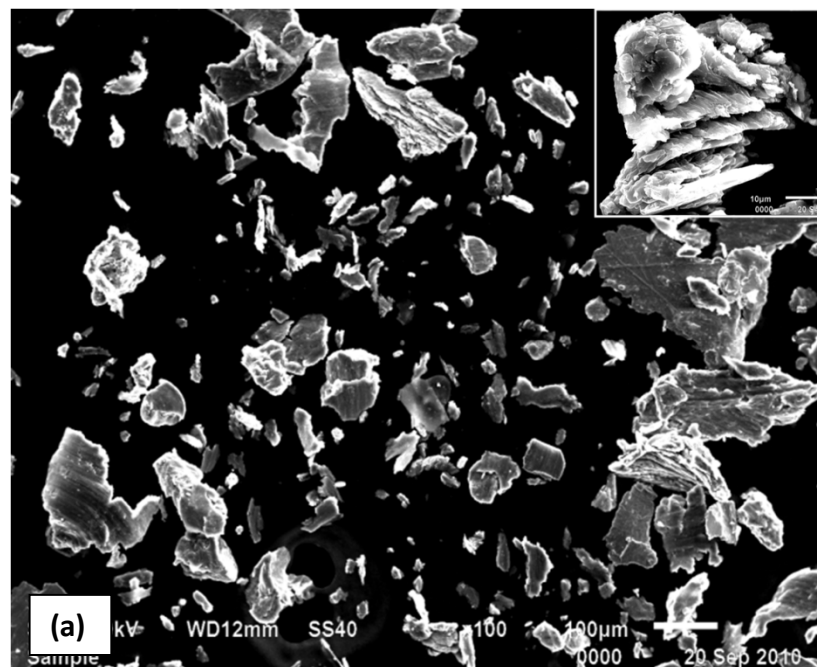


Figure 5.8:SEM micrographs of worn surfaces of spray formed Al-Si alloy at **(a)** 2.5 kg, 50°C; **(b,c)** 5.5 kg, 50 °C; **(d,e)** 2.5 kg load, 150 °C; **(f)** 5.5 kg load, 150 °C.

It has been observed that junctions have been formed by the asperities which appear to rupture the original interface (Fig. 5.8 (e)). The material of the pin adheres along the flat running surfaces causing adhesive sliding wear. However, at higher temperature and load conditions the pin material is found to be under gone through repetitive plowing as shown in Fig. 5.8 (f). Similar wear surface has been found by Kim et al. [4] at sliding speed of 1ms^{-1} indicating abrasive and adhesive wear phenomenon.

Different sizes of the debris has been observed in the spray formed Al-Si alloy at 2.5 kg load and 50°C temperature as shown in Fig. 5.9 (a, b). The size of the debris varies from 10–200µm. Mostly smaller debris are created due to the repetitive plowing action over the surface and these marks are clearly visible on the debris surface at higher magnification as shown in inset of Fig. 5.9 (a). At the same temperature sever wear is found to occur in the

alloy as we increase the load from 2.5 kg to 5.5 kg as shown in Fig. 5.9 (b). The size of the debris also increases and lies in the range of 300–1000 μm . The debris is formed like long flake type indicating delamination mechanism. Moreover, along the sliding direction the repetitive plowing marks are clearly seen in inset of Fig. 5.9 (b). Similar wear debris morphology has been studied by Wang et al. [5] at the load of 35.6 N for Al–12Si system. The flake type debris is seen in Fig. 5.9 (c, d). The roundness at the edges of the wear debris (Fig. 5.9 (d)) indicates that the reduction in the wear rate might be due to the small amount of oxidative wear prevailing in system. This is again in relevance to the lower wear found at 2.5 kg load in Fig. 5.3 (d) as compared to Fig. 5.3 (a). Figure 5.9 (e, f) shows the debris size is in wide range from the 50–500 μm with chunks of the material found to be formed as the wear transform to sever wear as shown in Fig. 5.3 (d). The EDS profiles of as-cast and spray formed alloy have been illustrated in Fig. 5.10 and 5.11 respectively. The presence of alloy's major elements peaks in the debris further verifies the gross metal removal at higher load by delamination.



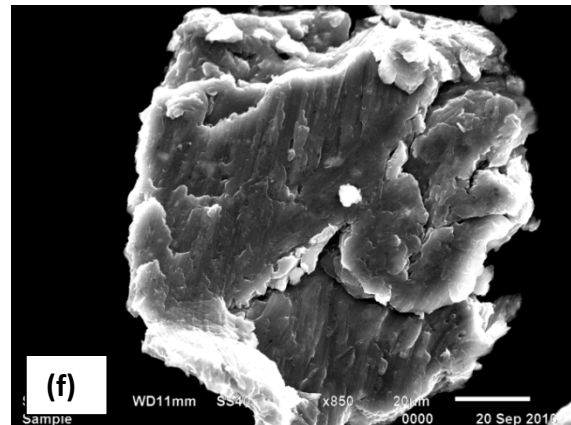
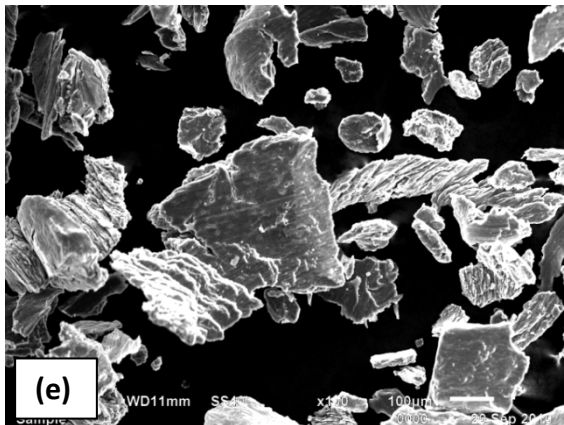
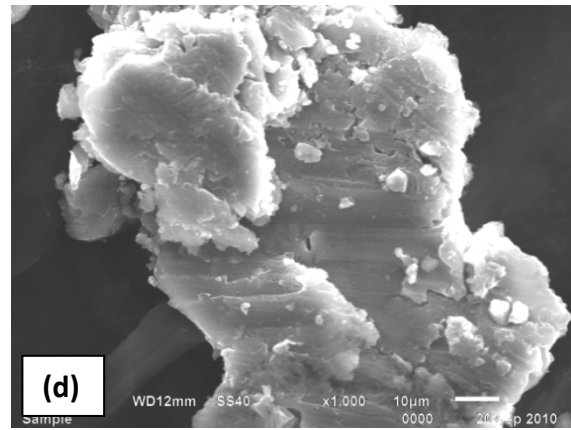
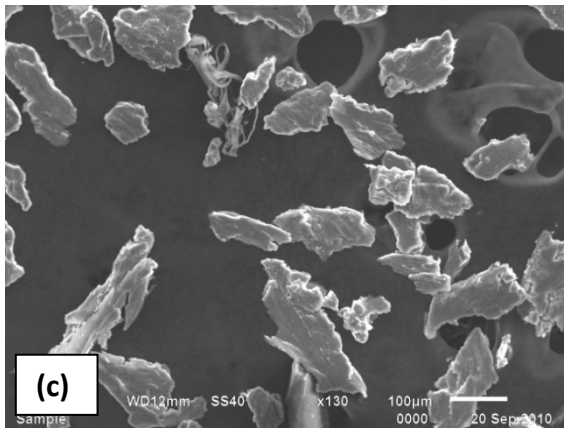
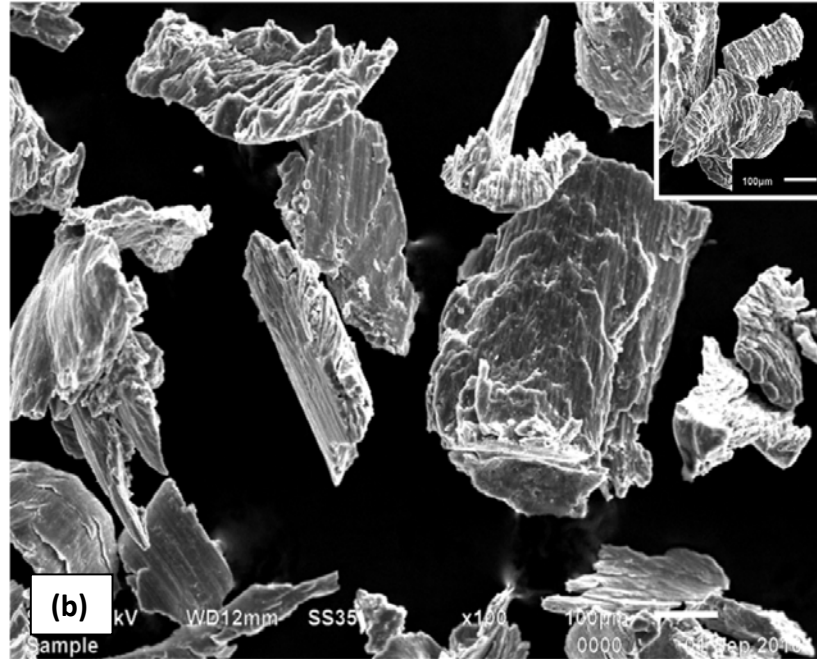


Figure 5.9: SEM micrographs of wear debris of spray formed Al-Si alloy at (a) 2.5 kg, 50 °C; (b) 5.5 kg, 50 °C; (c, d) 2.5 kg, 150 °C; (e, f) 5.5 kg, 150 °C.

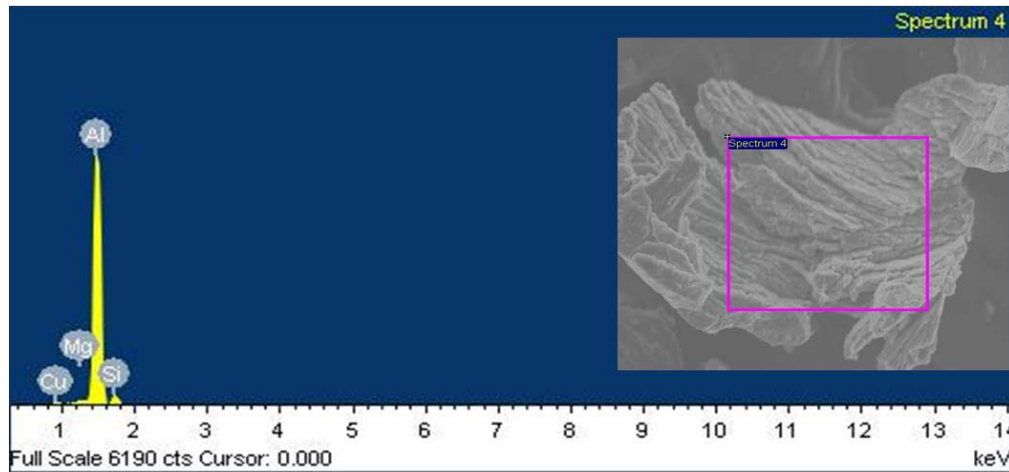


Figure 5.10: EDS profile of wear debris of as-cast Al-Si alloy at 5.5 kg load and 150°C temperature.

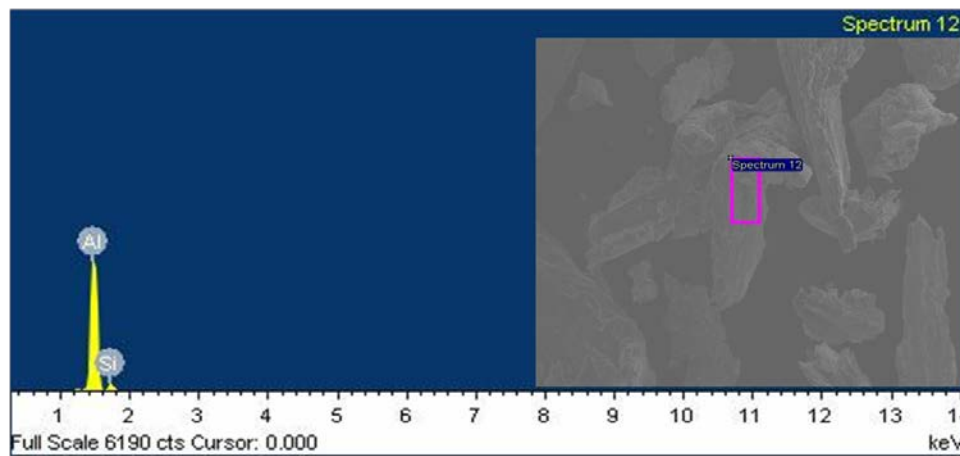


Figure 5.11: EDS profile of wear debris of spray formed Al-Si alloy at 5.5 kg load and 150°C temperature.

The drawback of the spray forming process is porosity which gives rise to the small cracks under dry sliding conditions and hence deteriorates the material properties [3]. In the spray forming process, atomized droplets of spray solidify partially and fully during the flight. The mushy droplets solidify completely on striking the preform due to extraction of heat by substrate and surroundings. However, there are some places left on the substrate surface which has not been filled by subsequent striking of droplets which lead to porosity. Porosity may also arise due to entrapment of gases during solidification. To increase the wear properties at higher temperature reinforcement of ceramic particles have been

doneto the alloy. In order to control the porosity in the material immiscible elements (Sn and Bi) are added to decrease the viscosity of the melt. The low melting point immiscible element solidifies later and tries to fill the pores created during spray forming. Italso gets decorated along the grain boundaries as well as within the matrix. Furthermore, the benefit of this addition favors the lubrication effect during wear testing. However, the effect of Sn has been studied by various researchers on wear properties at room temperature but the effect of temperature on wearcharacteristics has not been reported. Therefore, present study incorporates the study of wear mechanism at higher temperature which is described in subsequent chapters.

References:

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CHAPTER- 6

RESULTS AND DISCUSSION

(ZIRCON SAND SERIES)

Overview

In this chapter, the experimental results of zircon sand reinforced composites are presented. The chapter is subdivided in two parts on the basis of the size range of zircon sand particulates. The zircon sand reinforced composites have been prepared by spray deposition process where immiscible element Sn and Bi in varying quantity is added to achieve dense product. The prepared samples have been characterized by XRD (X-Ray Diffraction), Optical microscope, SEM (Scanning Electron Microscope), EDS (Energy dispersive spectrometer). Wear tests of spray formed samples have been done at different loads and temperatures. The analysis of worn surfaces has been done to predict the mode of wear for the prepared samples.

6.1 Introduction

This chapter comprises of two sections. In the first section the size of reinforced particulate (ZrSiO_4) is in the range of 106–125 μm whereas in the second section the size range of ZrSiO_4 is 63–90 μm .

Effect of zircon sand reinforcement of particulate size 106–125 μm

6.2 Samples prepared

In this section, the results of spray formed near eutectic aluminium alloy reinforced with zircon sand (ZrSiO_4) with particulate size 106–125 μm has been discussed. In the entire composition the volume fraction of reinforced zircon sand is kept constant i.e. 8 vol. %. As described in the earlier chapter, the addition of appropriate level of immiscible element in the matrix reduces the porosity and enhances the wear properties. Therefore, the amount of immiscible elements has been varied in the prepared composites. The composition of spray formed samples is as follow:

1. Al–Si/ ZrSiO_4 (106–125 μm)
2. Al–Si–5Sn/ ZrSiO_4 (106–125 μm)
3. Al–Si–10Sn/ ZrSiO_4 (106–125 μm)
4. Al–Si–5Bi/ ZrSiO_4 (106–125 μm)
5. Al–Si–10Bi/ ZrSiO_4 (106–125 μm)

6.3 X-ray diffraction analysis

The XRD pattern of spray formed Al–Si/ ZrSiO_4 , Al–Si–5Sn/ ZrSiO_4 , Al–Si–10Sn/ ZrSiO_4 , Al–Si–5Bi/ ZrSiO_4 and Al–Si–10Bi/ ZrSiO_4 is shown in Fig. 6.1. The data collected is matched with the reference peaks of Al (ICDD card no. 03–065–2869), Si (ICDD card no. 01–077–2109), Sn (ICDD card no. 00–004–0673), Bi (ICDD card no. 01–089–2387) and ZrSiO_4 (ICDD card no. 01–072–0402) which clearly depicts their presence in the material.

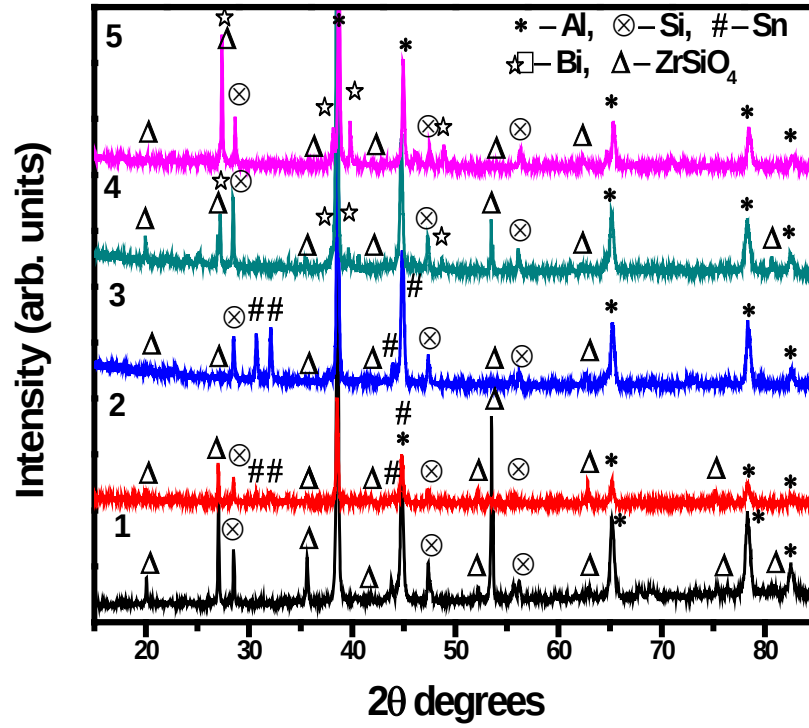


Figure 6.1: XRD pattern of (1) Al-Si/ZrSiO₄, (2) Al-Si-5Sn/ZrSiO₄, (3) Al-Si-10Sn/ZrSiO₄, (4) Al-Si-5Bi/ZrSiO₄ and (5) Al-Si-10Bi/ZrSiO₄ composites.

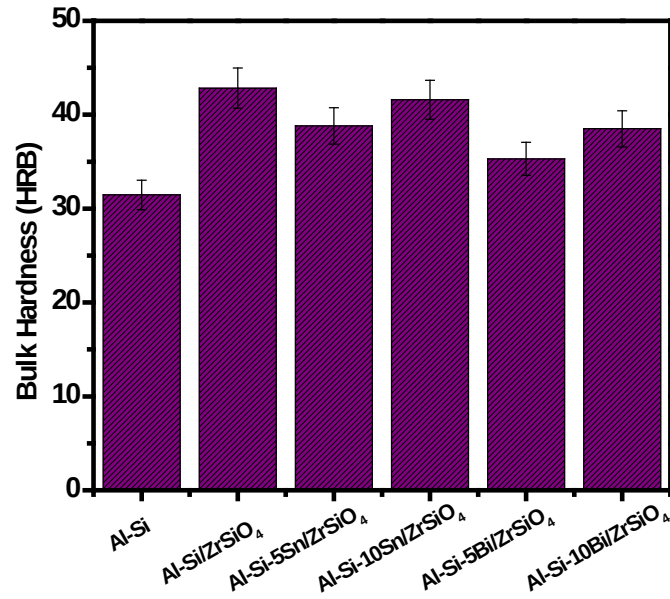


Figure 6.2: Bulk hardness of the composite of particulate size 106–125 μm.

6.4 Hardness

The hardness of the materials has been measured on B-scale of the Rockwell hardness tester. The average hardness values obtained are shown in Fig. 6.2. The steep rise in hardness of all composites as compared to spray formed Al-Si alloy (31.46 HRB) is due to the incorporation of zircon sand particles in the matrix. However, this increment is not abrupt for composite containing soft elements like Sn and Bi. This variation in hardness of composite is due to the incorporation of zircon sand and inherent microstructural modification by spray forming technique.

6.5 Microstructural analysis

Figure 6.3 (a-d) shows the microstructures of spray formed alloy with the reinforcement of zircon sand particulates in the Al-Si matrix. As can be seen in Fig. 6.3, the zircon sand particles are well embedded in the matrix with no porosity at the interfacial zone of particle and matrix (Fig. 6.3 (c, d)). The equiaxed α -Al grains of 25–50 μm size are observed in the Al-Si/ZrSiO₄ composite. The equiaxed features are widely reported in spray forming by other researchers [1]. The structural features indicate a good interfacial bonding of zircon sand with matrix. Zircon sand particles also provide nucleation sites for Si due to localized cooling. It is evident in Fig. 6.3 (c, d) that 3–10 μm sized globular Si particles are present all along the vicinity of the embedded zircon sand particle. As we proceed away from the interface of zircon sand particles the Si needles were observed to be elongated. The size variation of nearly 15–25 μm in the form of long thin Si needles in the matrix was observed. The localized cooling effect produced by zircon sand particles around its vicinity has led to such type of morphological changes. A large amount of thermal gradient exists between zircon sand particle (preheated up to 60 °C) and atomized droplets when zircon sand collides with the melt (heated up to 800 °C) in the atomization zone near the melt delivery tube. The particles get embedded in the molten alloy and extract heat at higher rates from the surrounding melt which give rise to localized rapid cooling effect during solidification. Because of this phenomenon the formation of small globular Si morphology in the vicinity of zircon sand particle is observed. The cooling rate away from the interface slows down and because of this effect the silicon morphology changes from globular to needle shape. There are two types of heat transfer phenomenon which occurs

during atomization. Firstly due to the convection cooling by the atomizing gas and secondly by conduction cooling by ceramic particles. Apart from this the conductive surface of substrate and preform also participate in heat extraction leading to non-equilibrium solidification. During strike of incoming high velocity gas jets and droplets a turbulent flow in the semi-solid liquid pool on the preform surface is produced that gives rise to kinetic undercooling. This lead to increase in nucleation centers, equiaxed morphology and decrease in size of primary Si. Moreover, it also helps in engulfing the zircon sand particles on the semi-liquid pool that do not get a chance to collide with liquid droplets in the atomization zone.

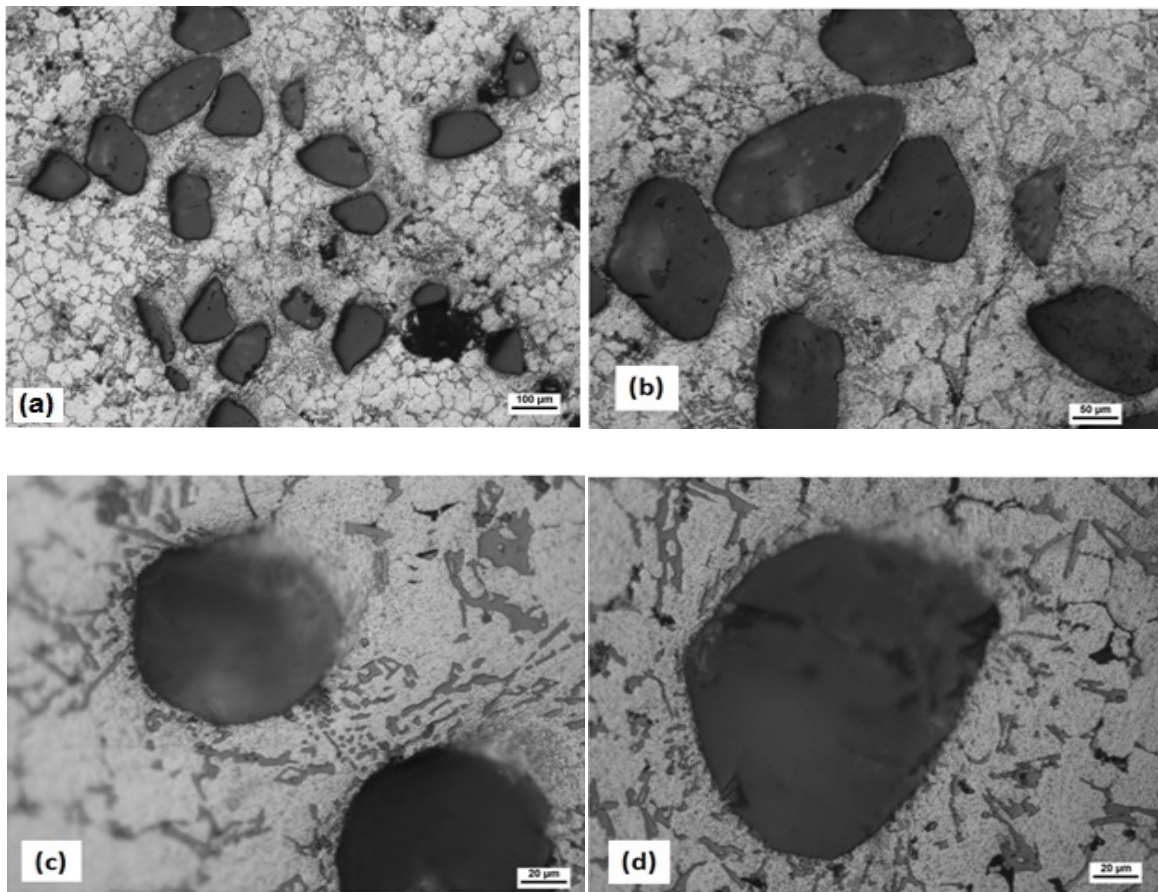


Figure 6.3: Optical micrographs of Al-Si/ZrSiO₄ composite at **(a)** 100X, **(b)** 200X and **(c, d)** 500X.

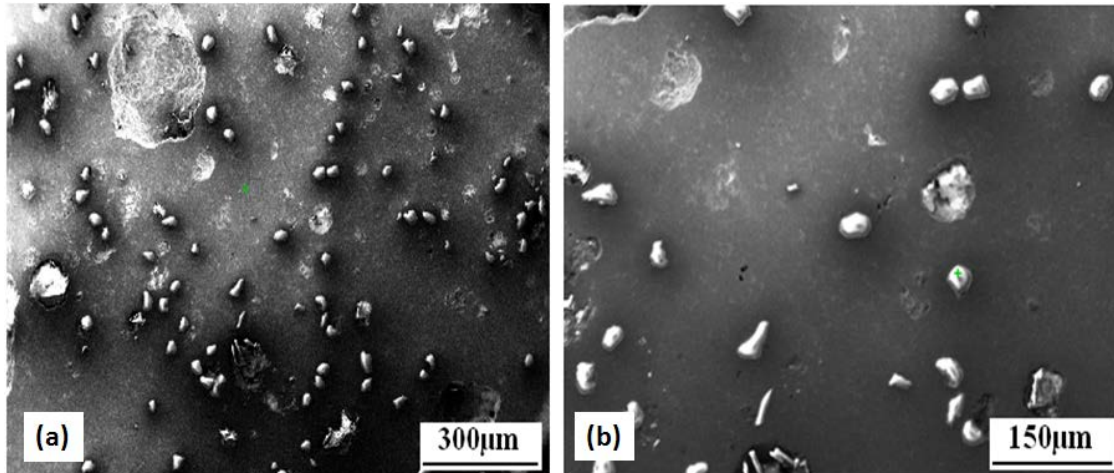


Figure 6.4: SEM micrographs of spray formed Al-Si/ZrSiO₄ composite at (a) 41X and (b) 92X.

SEM micrographs taken at different magnifications (Fig. 6.4) shows the uniformly distributed reinforced particles in the spray formed alloy. Hence, it is evident in both optical and SEM studies that the particles are well embedded in the matrix with good interfacial bonding showing no porosity at the interface of zircon sand particle and the matrix. This is further confirmed by energy dispersive spectroscopy (EDS) analysis along the interface and on the particle as shown in Fig. 6.5 and 6.6 respectively. The presence of all the four major elements (Al, Si, Zr, O) at the interface confirmed good bonding between particle and matrix phase. However, EDS on the zircon sand particle (Fig. 6.6) also confirmed the presence of Zr, O and Si elements as major constituents. However, the intensity of Al peak is less in this case as Al is absent in the zircon sand particle.

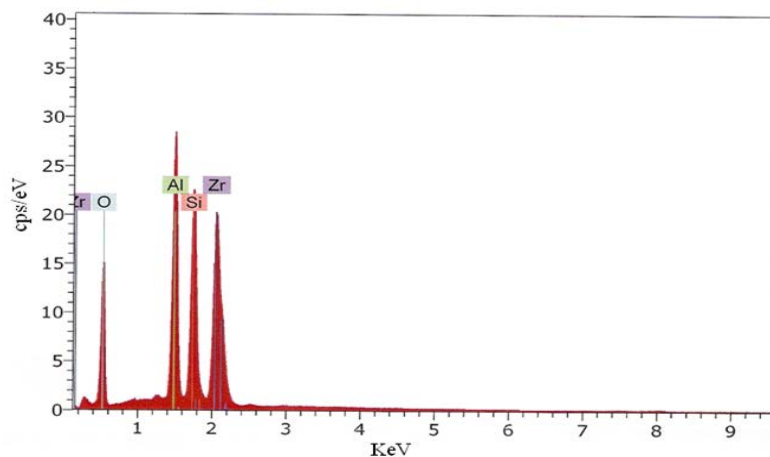


Figure 6.5: EDS analysis of the sample at the interface.

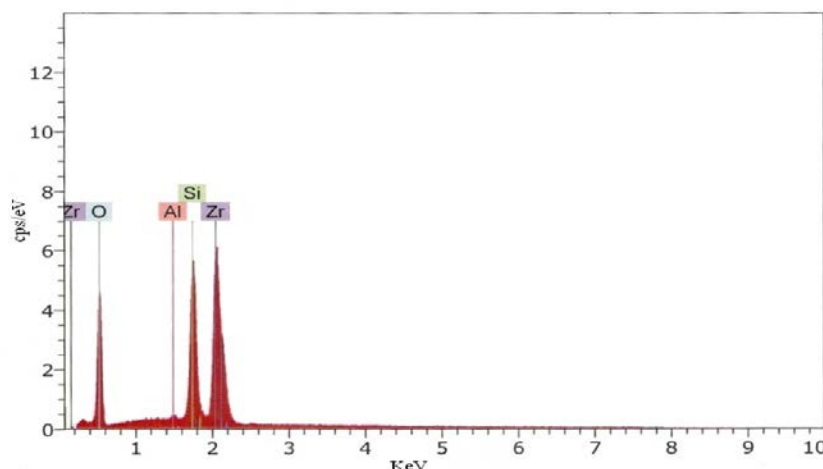
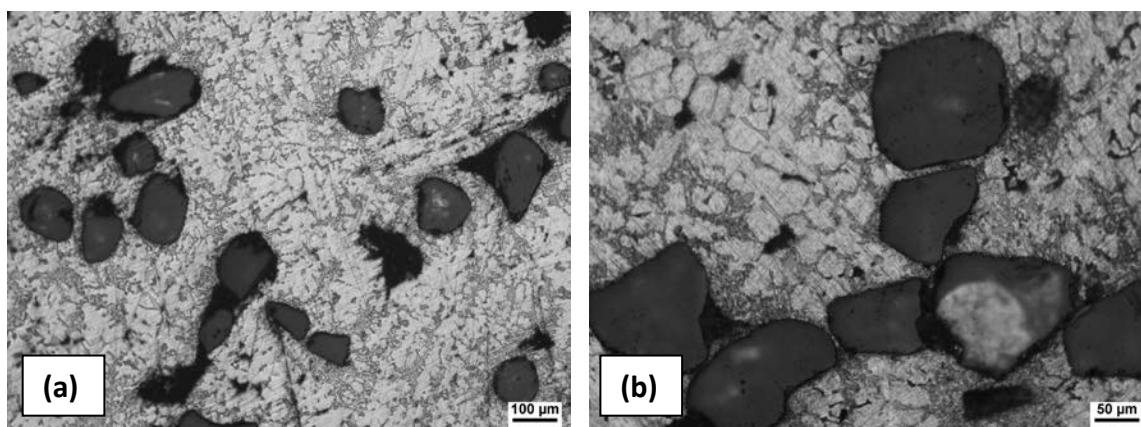


Figure 6.6: EDS analysis of the sample on the zircon sand particle.

The micrographs of polished samples of Al-Si-5Sn/ZrSiO₄, Al-Si-10Sn/ZrSiO₄, Al-Si-5Bi/ZrSiO₄ and Al-Si-10Bi/ZrSiO₄ are shown in Fig. 6.7 to 6.10 respectively. The zircon sand particles can be seen well distributed and firmly attached to the matrix on addition of 5wt. % and 10wt. % Sn in Al-Si alloy as shown in Fig 6.7 and Fig 6.8 respectively. The presence of different elements along the matrix and particle can be seen in the line profile as shown in Fig. 6.7 (d). At 500X, Fig. 6.9 (c) shows the refinement of eutectic Al-Si phase around the zircon sand particle. The needle like shape of the Si particles is changed to the globular. However, an addition of 5 wt. % Bi the eutectic phase get finer as observed in Fig. 6.9 (b) . With increasing the Bi content to 10 wt. % the phase does not refine much though the Si particles are short and evenly distributed throughout the Al matrix as shown in Fig. 6.10 (a, b).



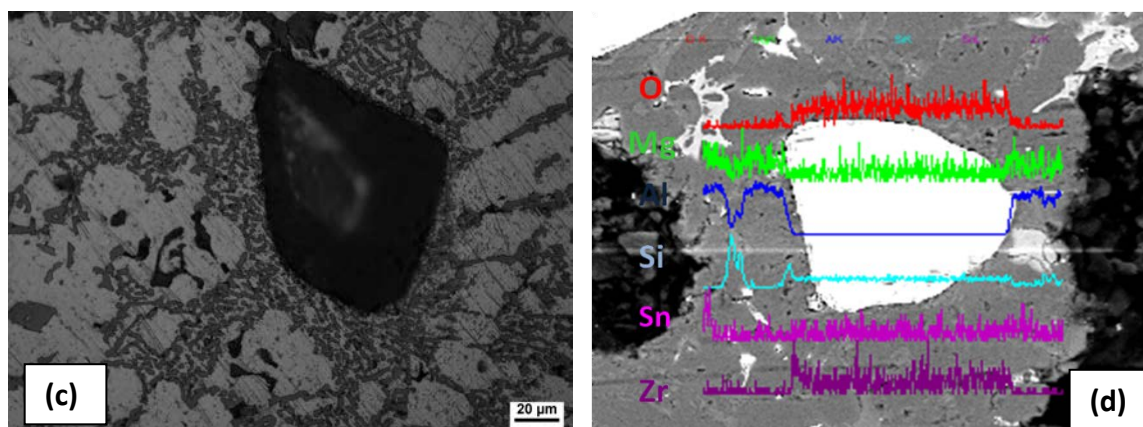


Figure 6.7: Optical micrographs of Al-Si-5Sn/ZrSiO₄ composite at **(a)** 100X, **(b)** 200X, **(c)** 500X and **(d)** line profile.

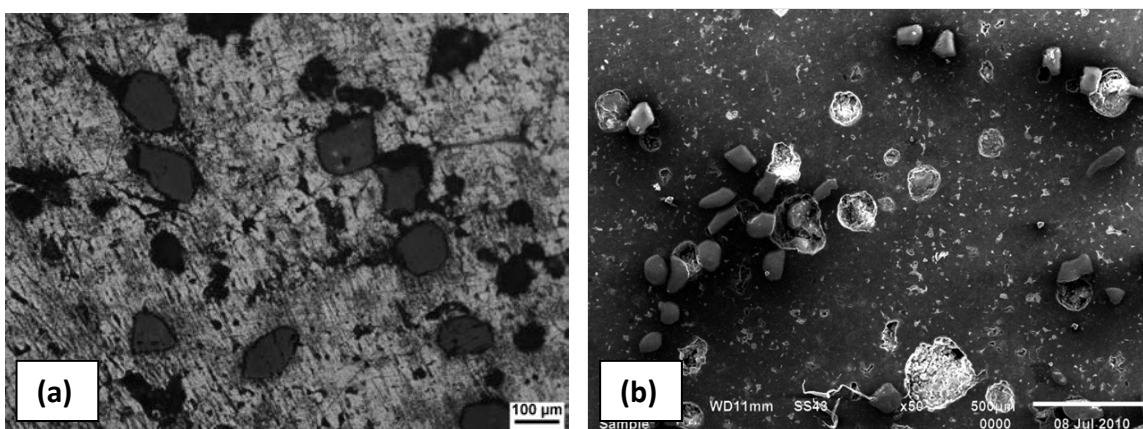


Figure 6.8: **(a)** Optical micrographs at 100X and **(b)** SEM micrograph of Al-Si-10Sn/ZrSiO₄ composite.

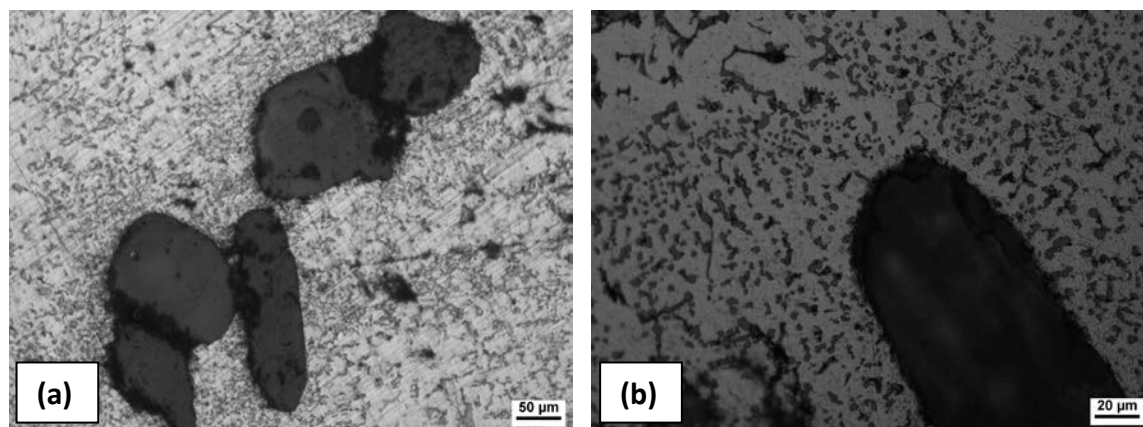


Figure 6.9: Optical micrographs of Al-Si-5Bi/ZrSiO₄ composite at **(a)** 200X and **(b)** 500X.

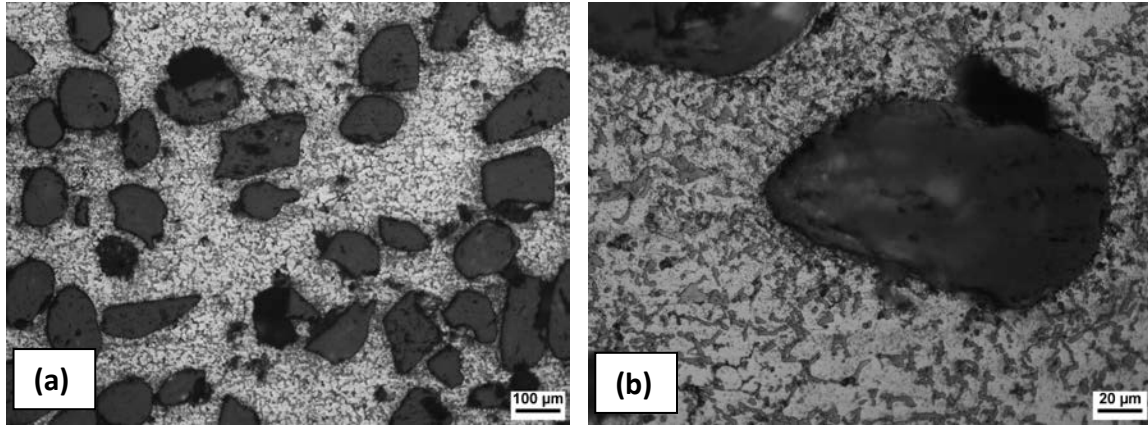
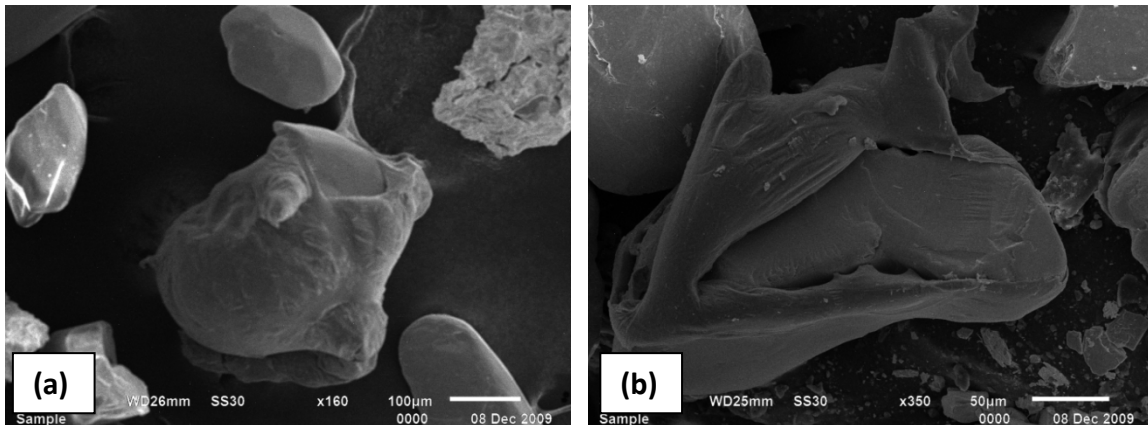


Figure 6.10: Optical micrographs of Al-Si-10Bi/ZrSiO₄ composite at **(a)** 100X and **(b)** 500X.

The interaction of the melt with zircon sand in the atomization zone has been studied by collecting the overspray powders. The SEM micrographs of the overspray powders are shown in Fig. 6.11. The various types of interactions are seen while the liquid droplets are in flight. Figure 6.11 (a) shows three particles collision where initially one zircon sand particle collide with semi-solid droplet and partly penetrate in the molten droplet. This duo further surrounds a fully solidified droplet in its flight path. The particle has been found to be fully engulfed in the melt drop (Fig. 6.11 (b)) if the particle velocity is greater than the droplet velocity in flight and the droplet is large enough to be in molten state.



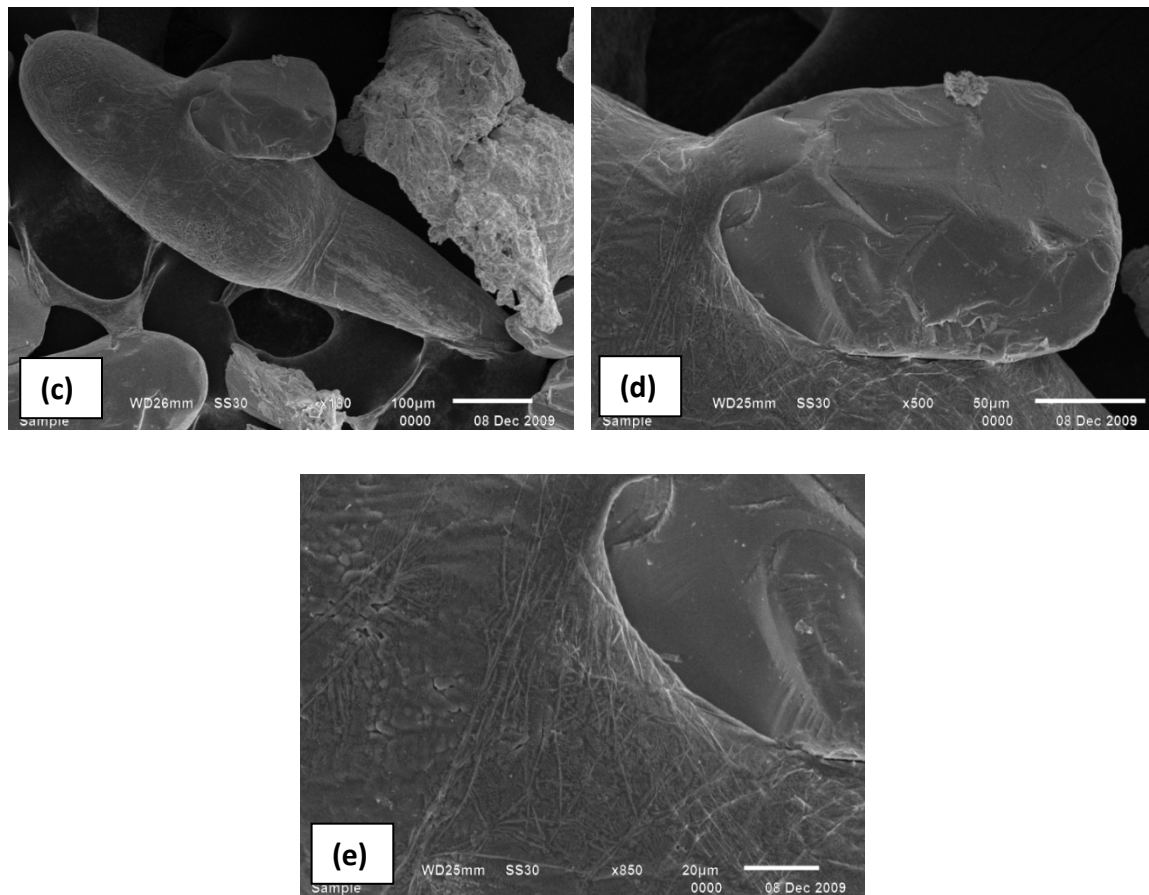
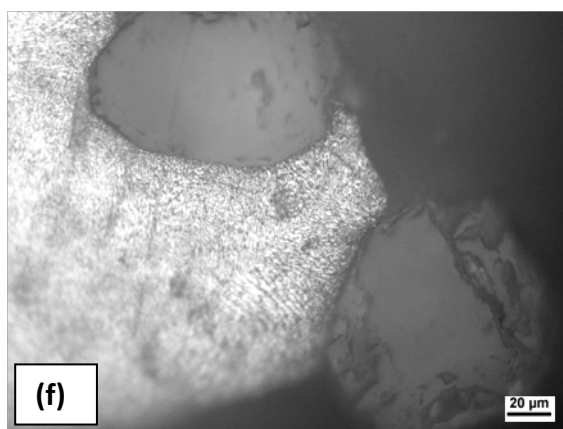
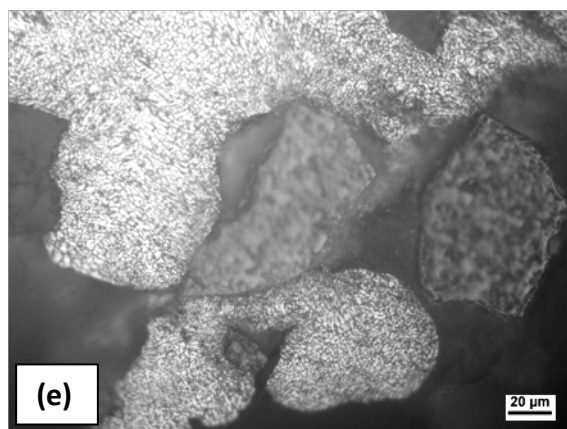
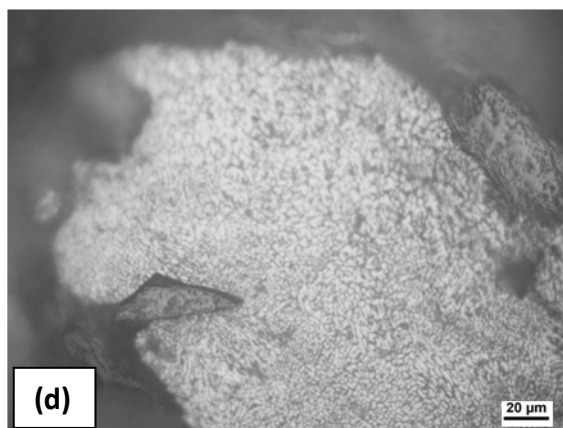
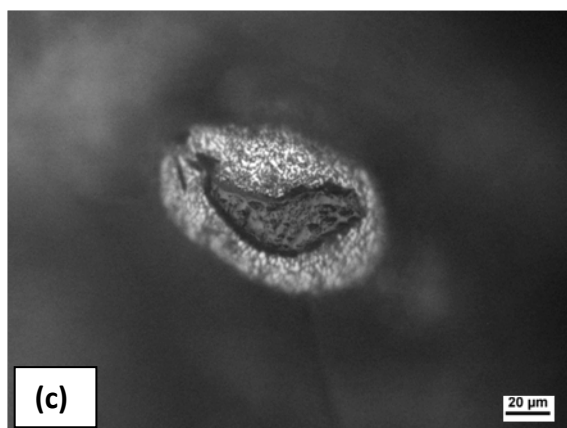
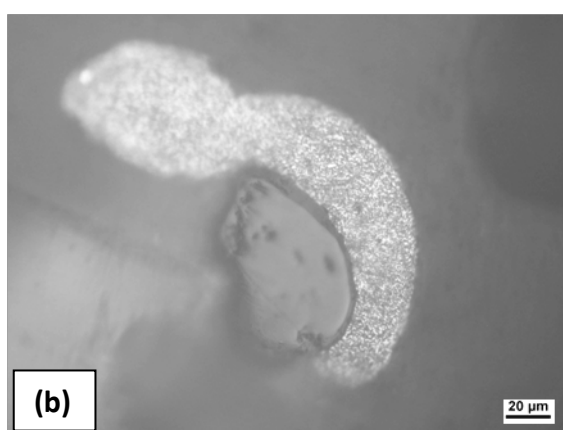
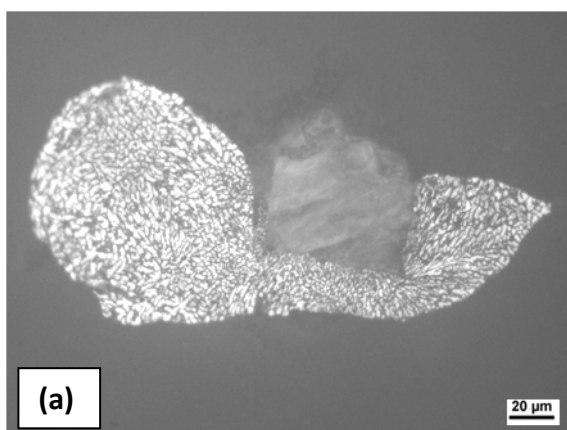


Figure 6.11: SEM micrographs of overspray powders.

Figure 6.11 (c–e) represents the adhering phenomenon of the particle with the ligament. The particle velocity is less than the ligament velocity therefore the collision resulted in the adhesion of the particle at the surface of the ligament. The localized cooling effect (as described earlier) produced by the particle in the ligament is illustrated in Fig. 6.11 (d, e). The dendritic arms originated from the particle ligament interface can be clearly seen in Fig. 6.11 (e). Similar morphology was also observed in optical micrographs taken for overspray powders which are shown in Fig. 6.12.



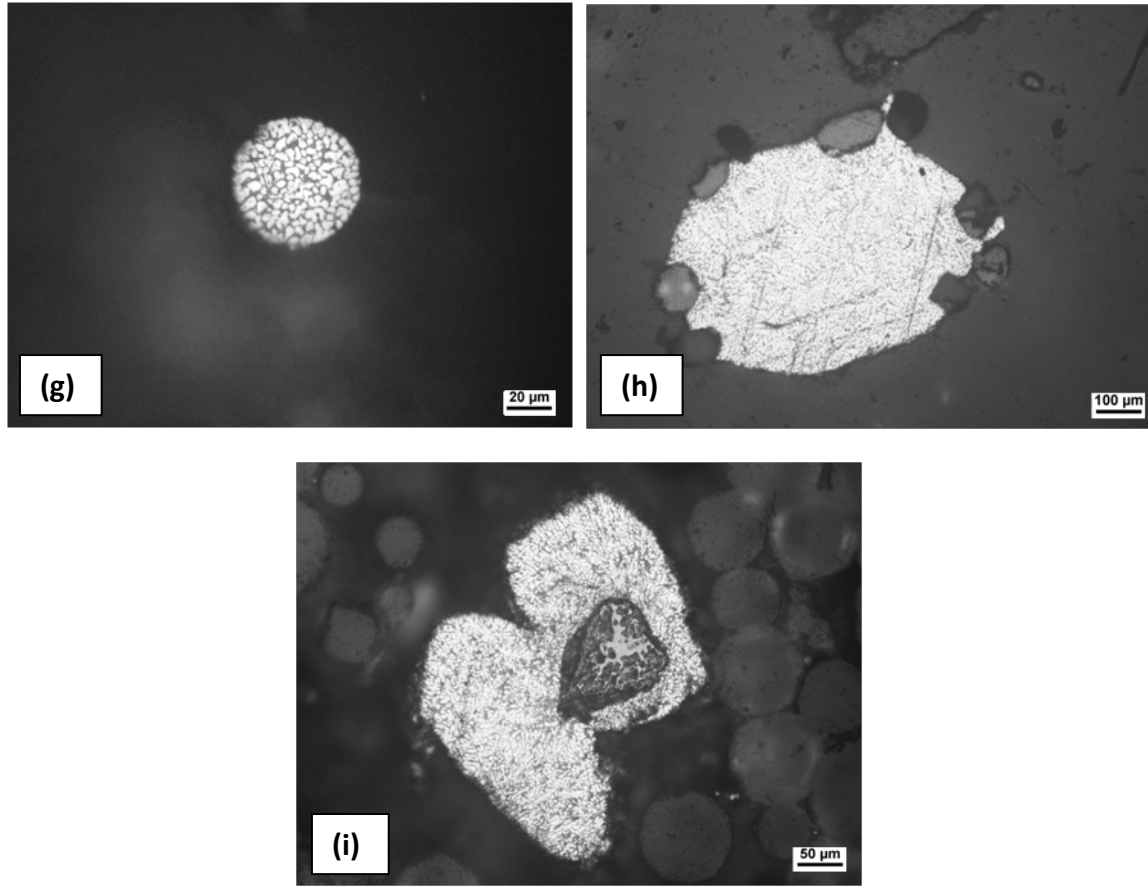


Figure 6.12: Optical micrographs of over sprayed powders showing **(a)** collision of bigger particle, **(b)** process of particle engulfment, **(c)** engulfed particle, **(d, e)** interaction of particles during atomization and development of cellular structure at the interface, **(f)** microcellular to cellular transformation from the interface, **(g)** undercooled droplet having cellular morphology, **(h)** collision of smaller reinforced particles with droplet, **(i)** collision of two droplets leading to complete engulfment of particle.

6. Wear characteristics

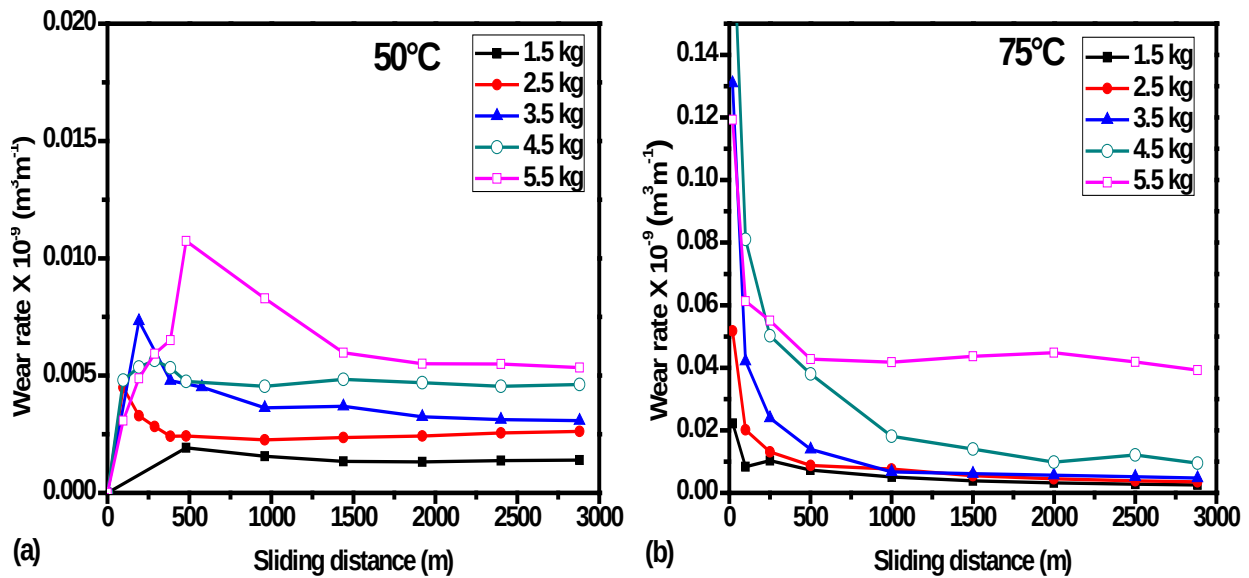
The wear characteristics of the spray formed composites are reported as variation in wear rate of the specimen as a function of sliding distance. The wear rates of the as-cast Al-Si alloy, spray formed Al-Si/ZrSiO₄, Al-Si-5Sn/ZrSiO₄, Al-Si-10Sn/ZrSiO₄, Al-Si-5Bi/ZrSiO₄ and Al-Si-10Bi/ZrSiO₄ composites are shown in Fig. 6.13 to Fig. 6.17 respectively. The wear rate behavior of each sample is categorized depending upon the operating temperature and further subcategorized based on applied loads.

6.6.1 Wear rate vs. sliding distance

For each wear rate curve, there are two distinct regions; initially run-in wear and later on a stable wear rate. Therefore, under an applied load two different types of wear behavior can be predicted from the curves. Fluctuating, unstable and greater wear at the initial stage corresponds to the run in wear. On the other hand, at later stage constant wear rate has been obtained corresponding to steady state wear. For both reinforced and unreinforced materials, a steady state is approachable after 500 m sliding distance for all applied loads and temperatures (Fig. 6.13–Fig. 6.17). These results are analogous to dry sliding block-on-ring wear test of squeeze cast A390 reinforced with 20% SiC at 45 N and 3.3ms^{-1} speed as observed by Ma et al. [2].

6.6.2 Effect of load

Wear rate has been measured with increasing load from 1.5 kg to 5.5 kg load. With increase in load wear rate increases. This clearly follows Archard's law of adhesive wear for metals [3]. The wear rate plot reveals that the composite material offers greater resistance to wear than base Al-Si alloy (given in the previous chapter). The most significant difference in wear rates of the cast alloy and spray formed composites has been found at higher loads.



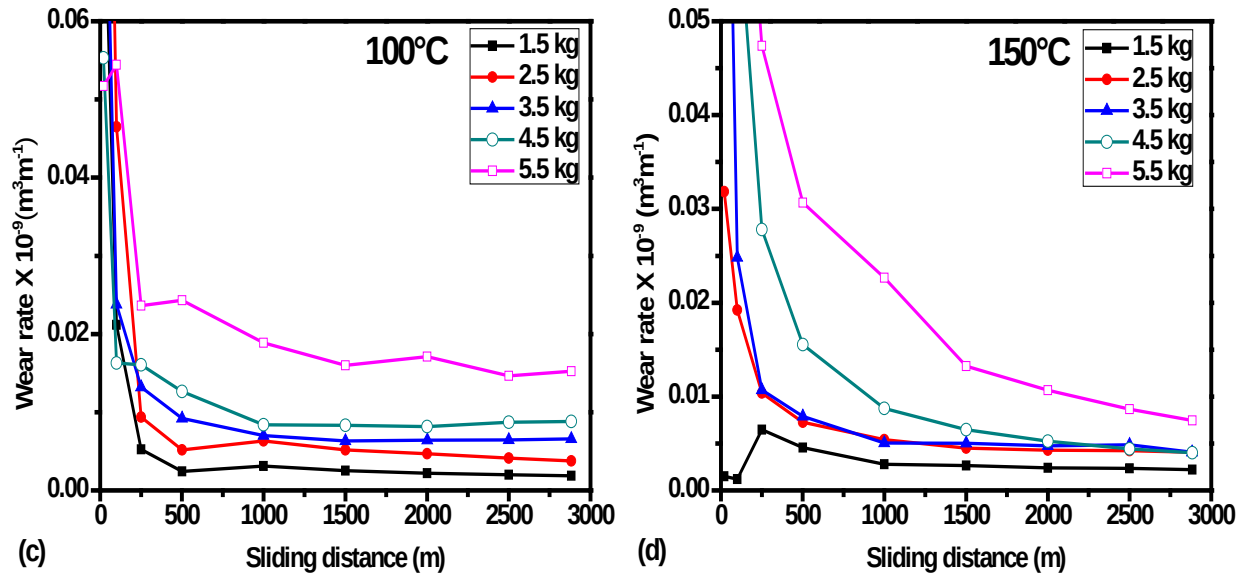
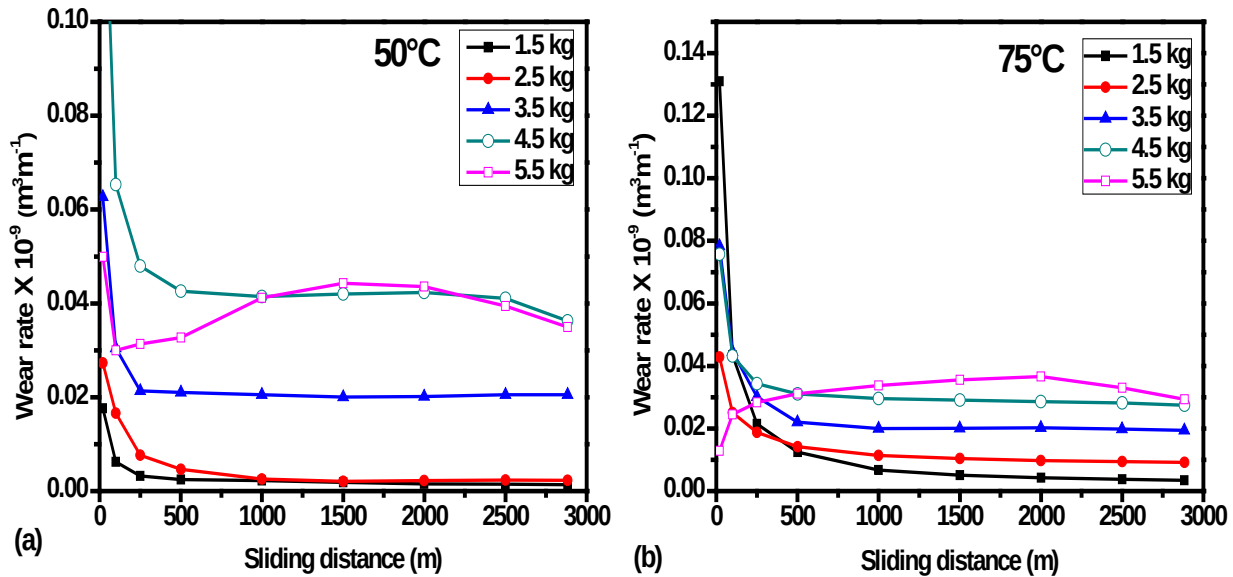


Figure 6.13: The wear rate of the spray formed Al-Si/ZrSiO₄ (106–125μm) composite under various loads at (a) 50 °C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

Figure 6.13 shows that at all the temperatures, the Al-Si/ZrSiO₄ composite offers greater wear resistance at 5.5 kg load. Whereas the alloy shows the severe wear rate as described in the previous chapter. The wear rate at the highest load further decreases with the addition of 5 wt. % Sn in the matrix as illustrated in Fig. 6.14.



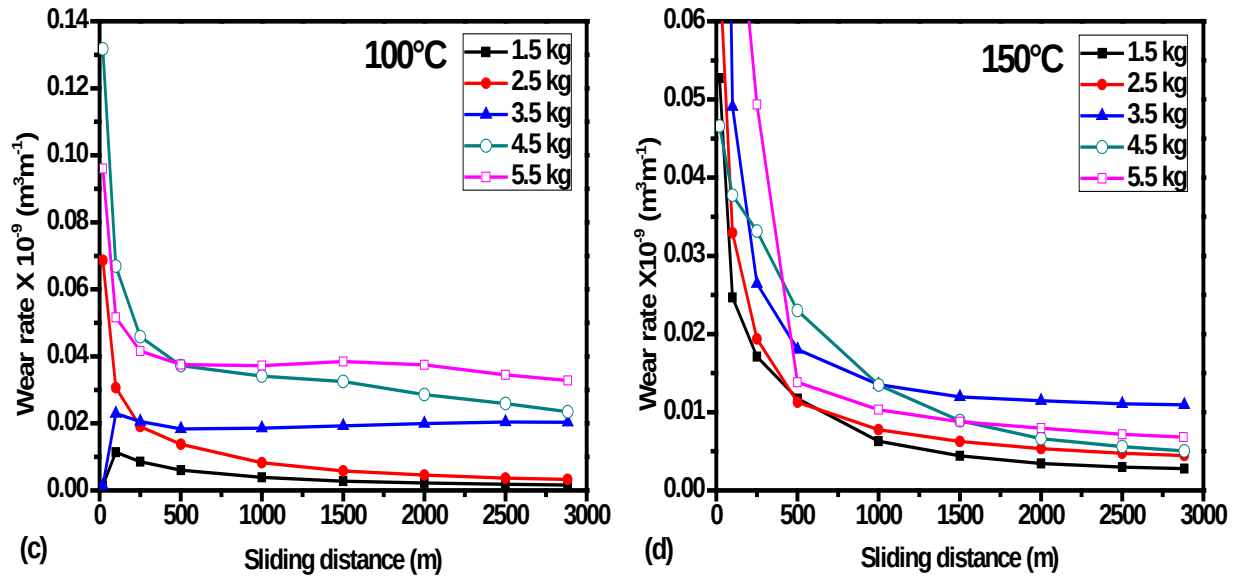
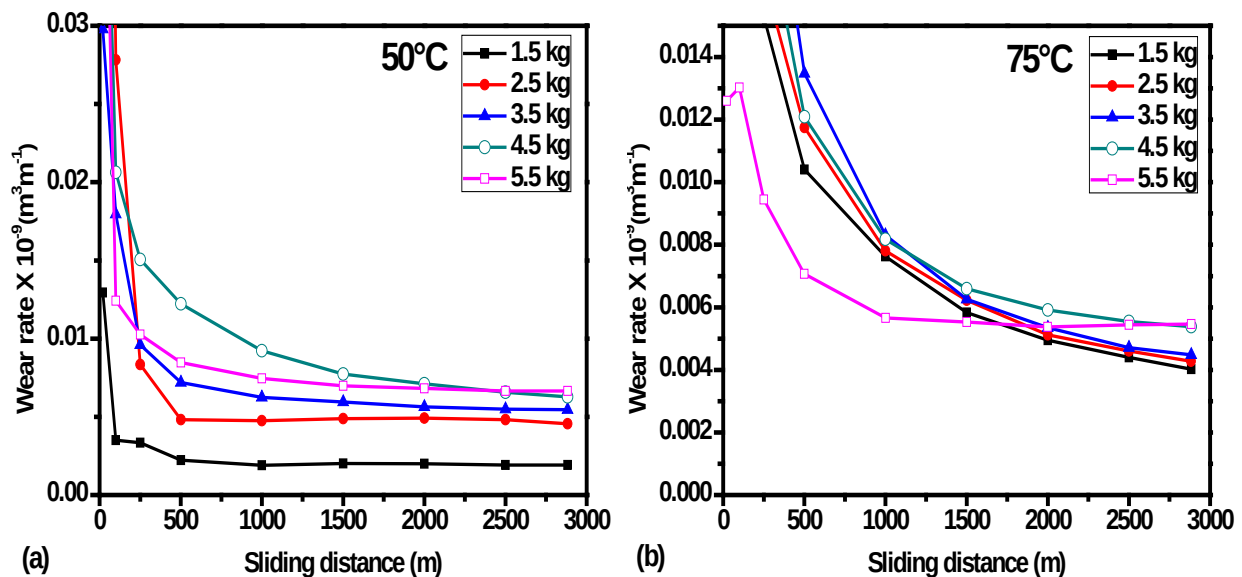


Figure 6.14: Wear rate of the spray formed Al-Si-5Sn/ZrSiO₄ (106–125 μm) composite under various loads at (a) 50°C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

The increased hardness of Al-Si-5Sn/ZrSiO₄ reported in earlier section completely rely the results of low volume loss and reduced wear rate at higher loads. However, best results of wear resistance have been found on addition of 10 wt. % Sn in the alloy. The wear rate has been found to be minimum under higher applied loads at all the temperatures in spray formed Al-Si-10Sn/ZrSiO₄ composite as shown in Fig. 6.15.



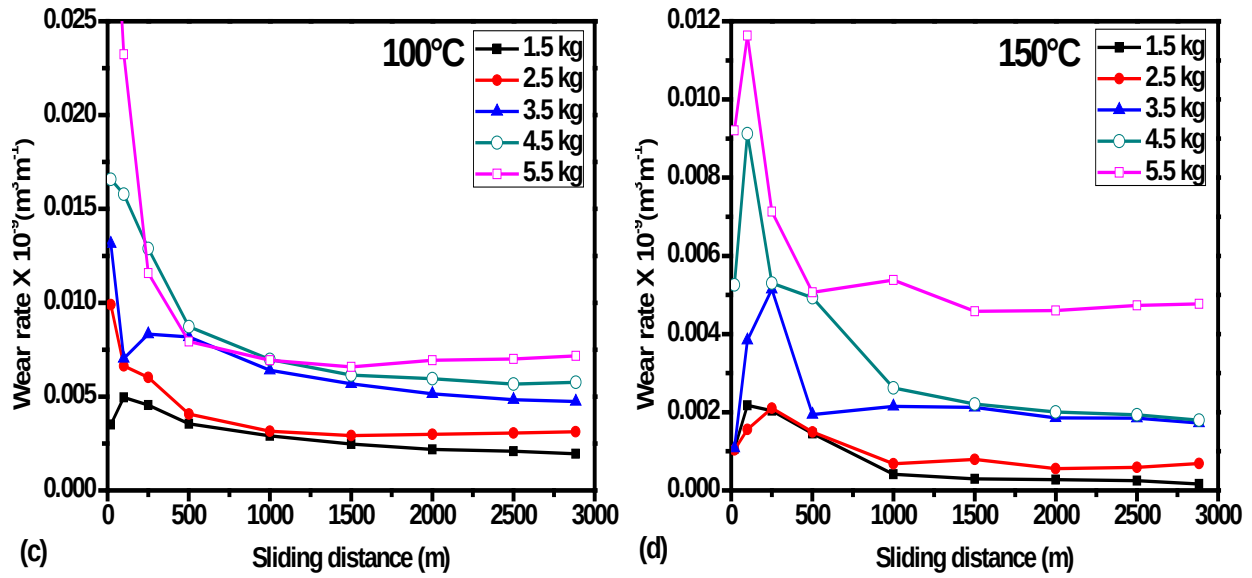
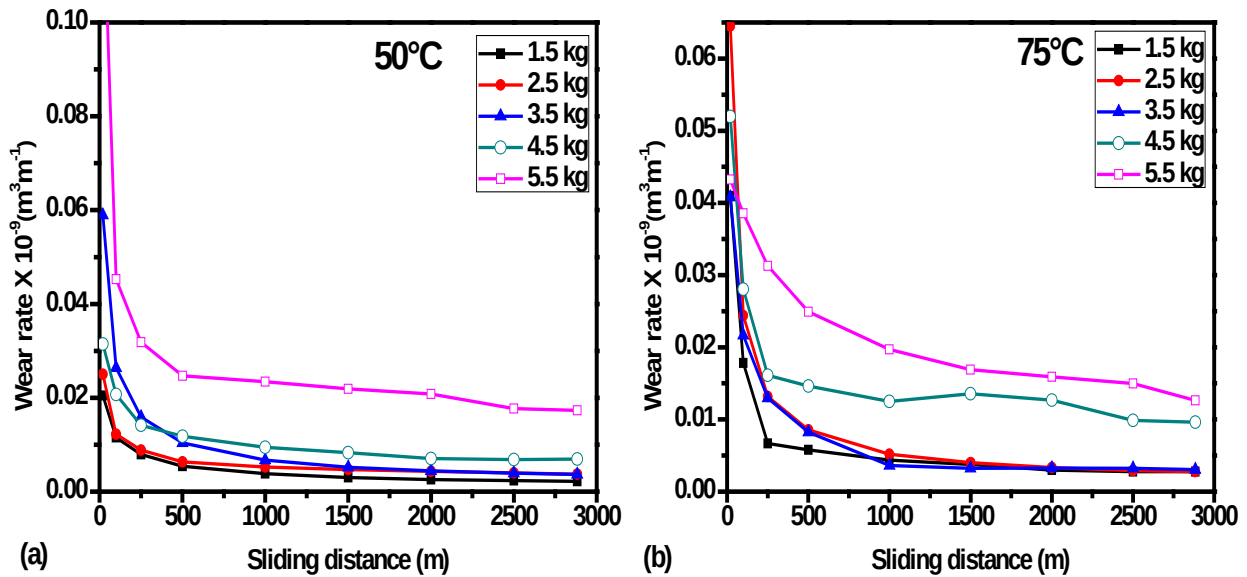


Figure 6.15: Wear rate of the spray formed Al-Si-10Sn/ZrSiO₄ (106–125μm) composite under various loads at (a) 50°C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

Figure 6.16 (a–d) represent the wear rate behavior of spray formed Al-Si-5Bi/ZrSiO₄ composite. The composite offers good resistance to wear at 5.5 kg load at 50°C as shown in Fig. 6.16 (a). The wear rate stabilization for the highest weight is delayed with increment in temperature (Fig. 6.16 (b–d)).



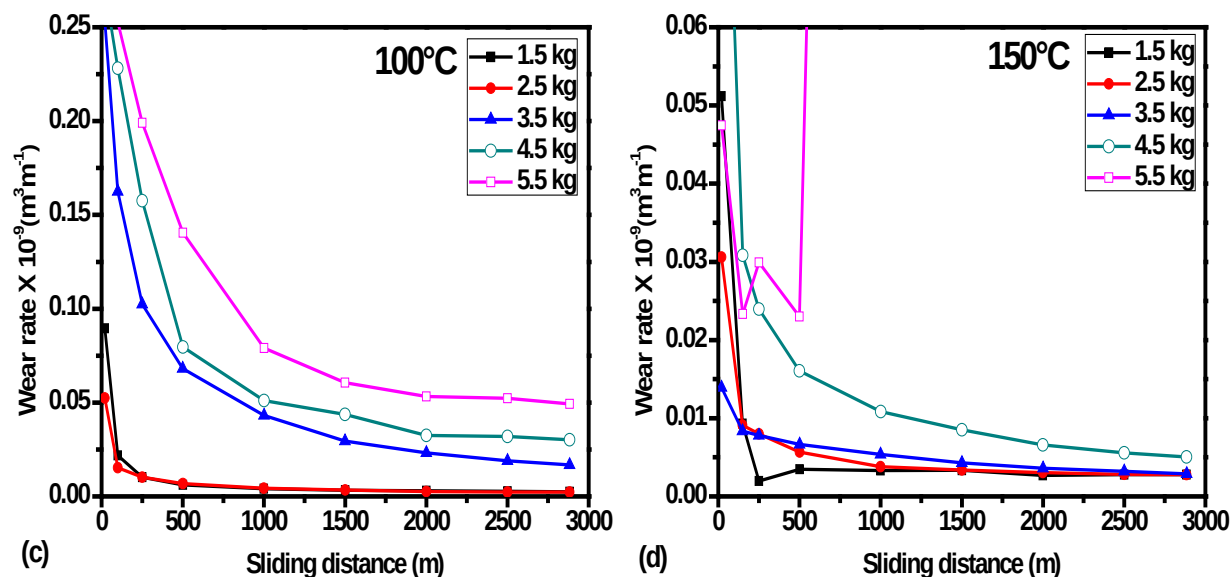


Figure 6.16: Wear rate of the spray formed Al-Si-5Bi/ZrSiO₄ (106–125μm) composite under various loads at **(a)** 50°C, **(b)** 75°C, **(c)** 100°C and **(d)** 150°C temperature.

At 150°C, the composite material shows the severe wear regime. Hence, it can be deduced that with addition of 5 wt. % Bi to the alloy enhances the wear resistance of the material even at high temperature test conditions. During the wear test frictional forces come into account and large amount of heat is generated due to dissipation of energy. The immiscible element Bi is deposited within the grain and along the grain boundaries in the matrix alloy. During sliding Bi having low melting point is smeared over the surface due to produced heat and provides good lubrication to the surface. However, in due course of time it gets oxidized and thus exposing fresh surface.

It has been found that at the highest temperature and load conditions (Fig. 6.16 (d)) the Al-Si-5Bi/ZrSiO₄ composite is unable to withstand the lubricated film due to its fast oxidation. The optimum amount of the lubricating material is required to provide better wear resistance and reducing the direct metal to metal contact. The removal of the lubricating film in Al-Si-5Bi/ZrSiO₄ composite with increase in load and temperature shows the delay in achieving steady state and hence severe wear occur at the extreme conditions. However, with the increase in Bi content to 10 wt. % in Al-Si-10Bi/ZrSiO₄ composite severe wear regime has not been observed at extreme conditions as shown in Fig. 6.17. It might be due

to the presence of higher Bi content in the matrix as well as the microstructure modifications achieved as shown in Fig. 6.9 and 6.10. The smearing off Bi at higher temperature and load conditions is continuously compensated by higher content over the surface. Therefore a stable lubricating film is always present over the surface and this has enhanced the wear resistance of the material.

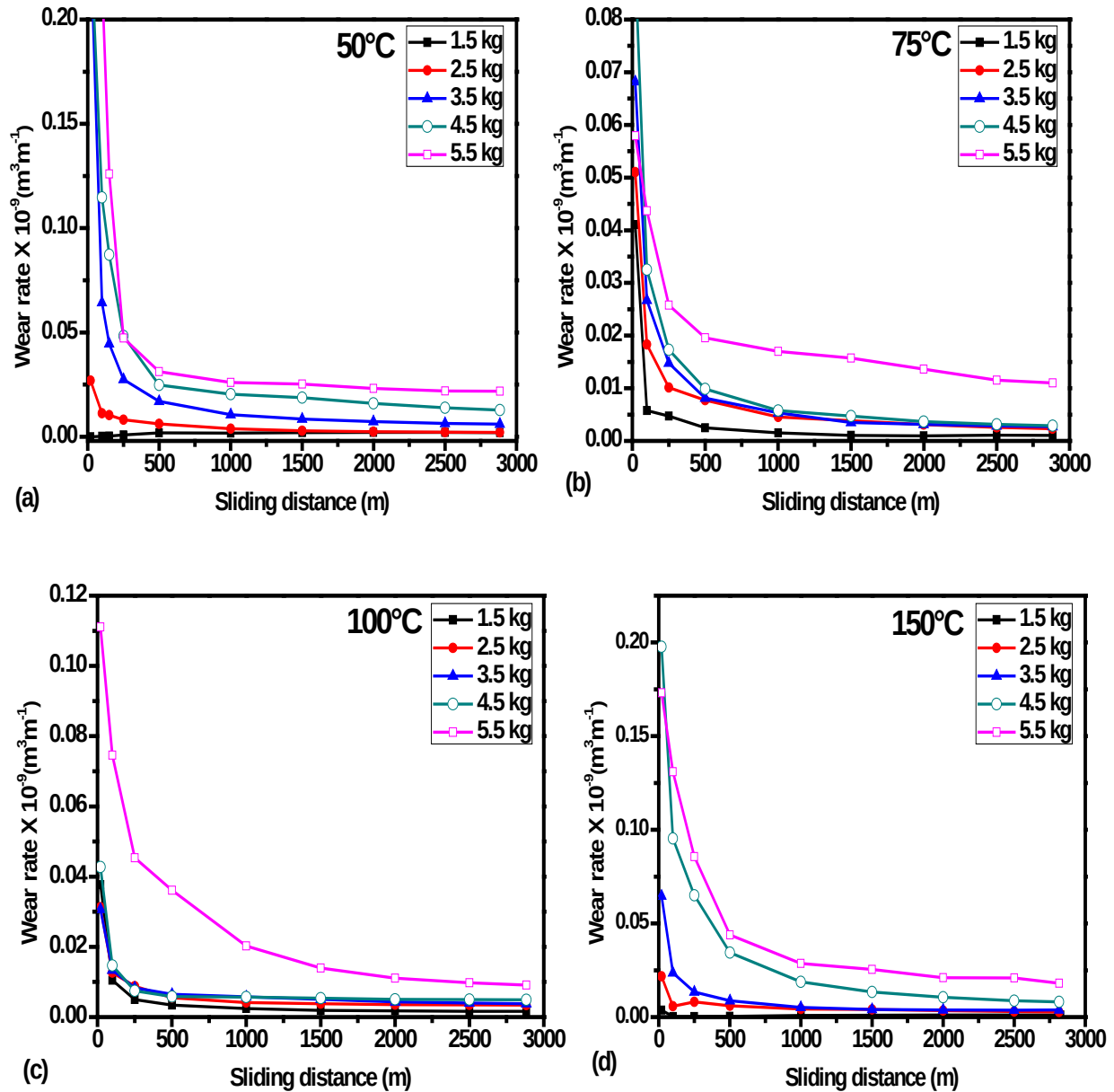
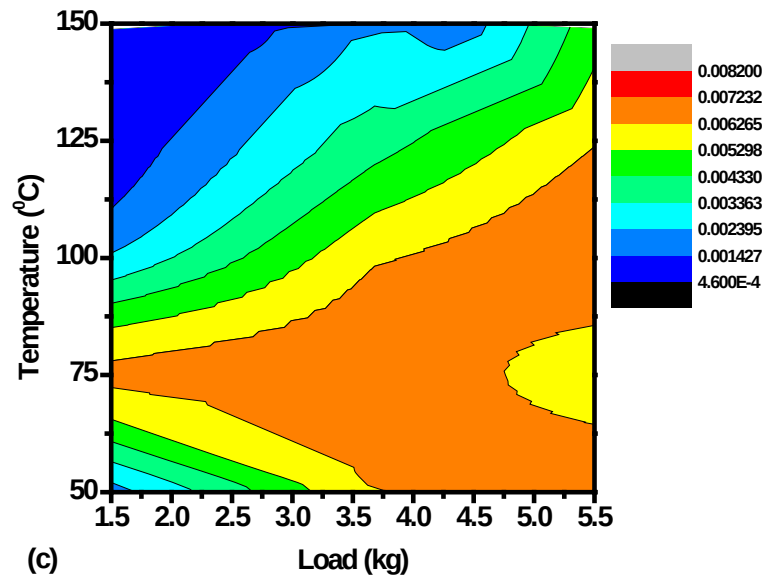
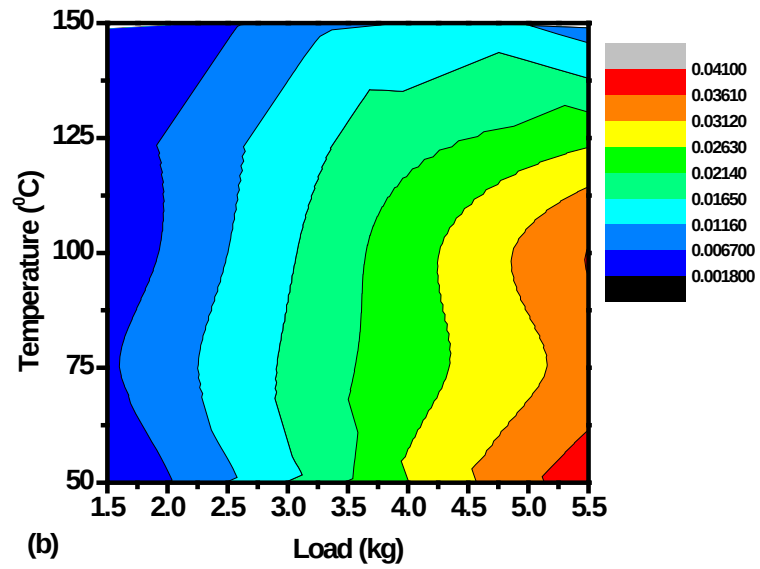
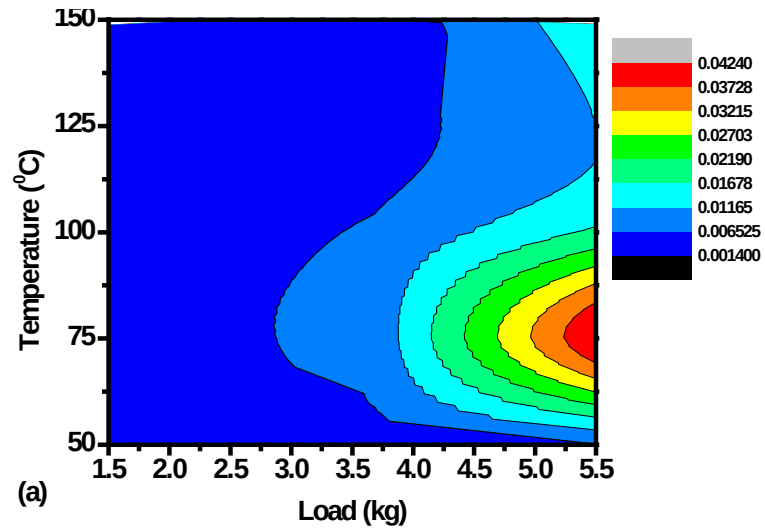


Figure 6.17: Wear rate of the spray formed Al-Si-10Bi/ZrSiO₄ (106–125 μm) composite under various loads at (a) 50°C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

6.6.3 Effect of temperature

Under steady state condition, the average wear rate for each sample has been plotted in contours with respect to the test temperatures and applied loads as shown in Fig. 6.18. As has been illustrated in Fig. 6.18 (a), Al-Si/ZrSiO₄ composite shows the higher wear rate at 75 °C and 5.5 kg load. However, with a rise in temperature the wear again decreases. The change in wear mode from low to the high temperature conditions has led to reduce the wear rate. The wear rate has been found to be greater at 50°C and 5.5 kg load which further got reduced at higher temperatures at the same load for Al-Si-5Sn/ZrSiO₄ composite as shown in Fig. 6.18 (b). On enhancing Sn concentration to 10 wt. %, the composite proved to be better wear resistant at all the loads and temperatures as shown in Fig. 6.18 (c). Figure 6.18 (d) represents wear plots of Al-Si-5Bi/ZrSiO₄ composite and depicts that higher wear regime lies on upper right end of the graph. It shows that the severe wear region lies at 5.5 kg and above 75 °C for Al-Si-5Bi/ZrSiO₄. In other words 5.5 kg is the critical transition load above 75 °C. However, for Al-Si-10Bi/ZrSiO₄ composite as shown in Fig. 6.18 (e), the wear mode changes after 3.5 kg load as shown by base Al-Si alloy though the severe wear mode has not reached at 5.5 kg load. Wear is greater at 50°C and decreases with increase in temperature for (75 and 100 °C). This indicate that temperature is operating parameter to change the wear mode at high load conditions in Al-Si-10Bi/ZrSiO₄ composite.

The steady state average wear rates at 2.5 kg for Al-Si-10Sn/ZrSiO₄ composite are 6.17×10^{-12} and $8.01 \times 10^{-13} \text{ m}^3\text{m}^{-1}$ at 50 °C and 150 °C respectively. At 5.5 kg applied load the average wear rate are found to be 7.17×10^{-12} and $4.85 \times 10^{-12} \text{ m}^3\text{m}^{-1}$ at 50 °C and 150°C respectively. At 50°C and 2.5 kg load, the wear rate results are comparable to the Chaudhary et al. [4] for Al-2Mg-TiO₂ composite at similar wear conditions. Moreover, the wear results are better than Al-4Cu-20Pb and Cu-20Pb bearing alloy systems at an ambient temperature under lower load conditions [5]. However, the zircon sand reinforced composite containing 10 wt. % (Sn/Bi) elements show much better wear resistance at 5.5 kg load even at 150 °C. The immiscible element used in present investigation solidified within the grains and along the grain boundaries during the spray forming process. The amount of heat generated during the wear process facilitates smearing of the immiscible element over the surface.



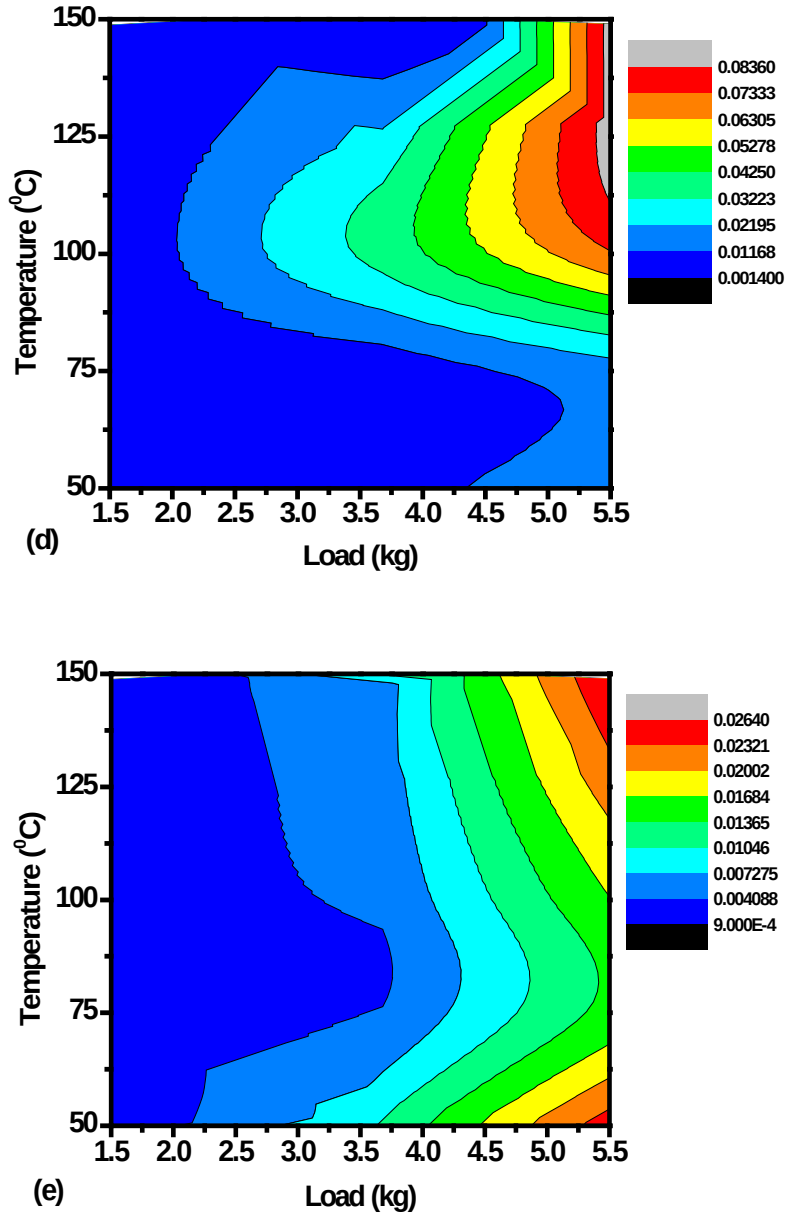


Figure 6.18: Averaged wear rate (X 10⁻⁹ m³m⁻¹) against various temperatures and applied loads for **(a)** Al-Si/ZrSiO₄, **(b)** Al-Si-5Sn/ZrSiO₄, **(c)** Al-Si-10Sn/ZrSiO₄, **(d)** Al-Si-5Bi/ZrSiO₄ and **(e)** Al-Si-10Bi/ZrSiO₄ composite.

Due to smearing action a thin lubricating film of Sn/Bi has been formed over the surface. This lubricating film reduces the probability of direct metal to metal contact between the sliding surfaces and hence reduces the wear. The results show the stability of the lubricating film even at high temperature. Moreover, under the high load the debris

generated during the process further get mechanically ground and form a mixed layer responsible for reducing wear rate.

The low wear rate at the higher temperature under similar load can be due to the change in wear mode from adhesive to oxidative wear mechanisms. At high temperature, there is higher probability of the surface under sliding to get oxidized easily leading to oxidative wear. Moreover, it is well known fact that oxidative wear mode is operative under a mild wear regime [6]. This can further be verified in light of microstructural analysis of the debris generated during the process.

The variation of the wear rate at higher temperature is better understood by comparing the average wear rate of all specimens at 5.5 kg test condition as shown in Fig. 6.19 and 6.20. It is clearly observed from Fig. 6.19 and 6.20 that the composites offer better wear resistance even at higher temperature test conditions than the base Al-Si alloy. Fig. 6.19 shows the variation of Al-Si alloy with zircon sand reinforced and Sn containing composites. It has been observed that Al-Si/ZrSiO₄ composite offer greater wear rate at lower temperature even at high load condition. However, an abrupt change in wear behavior is observed with rise in temperature from 50 to 75 °C. Further reduction in wear has been found with increase in temperature. This variation in wear rate is better explained on the basis of fact that at 50 °C the most of the load is carried by the reinforcing particles which are further distributed to the matrix. With increase in the temperature from 50 to 75 °C due to thermal softening large amount of soft metal is removed under the high load. Therefore, the matrix alloy is unable to hold the reinforcing particles strongly. Some of these insecurely held zircon sand particles are being largely dragged by the counterface which results in the abrasive wear and microcutting. Hence, at 75 °C the wear has been enhanced suddenly due to the change in wear mechanism. However, at higher temperatures large amount of metal oxides have been formed which provide a protective oxide layer over the surface. This oxide layer reduces the direct metal to metal contact and hence reduce wear rate with increase in temperature.

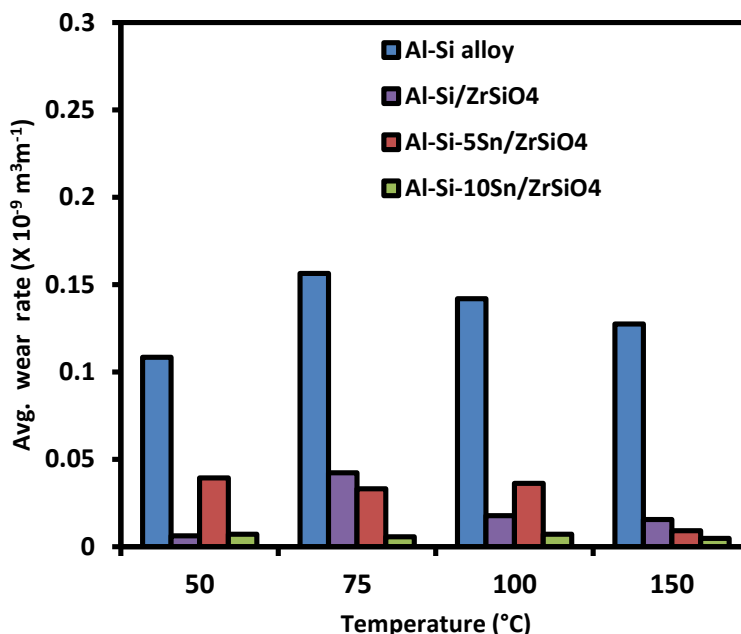


Figure 6.19: Comparison of the average wear rates against various temperatures at 5.5 kg applied load for zircon sand reinforced (106–125 μm) and Sn containing AMC.

Al-Si-5Sn/ZrSiO₄ composite does not show much difference in the average wear behavior with temperature rise from 50–100 °C. However, sudden reduced wear rate has been observed at highest temperature and load condition. At higher temperature, the oxidative wear helps to reduce the wear rate. Additionally, the lubricating Sn film along with oxide layer provides the smooth surface for sliding which reduces the wear. Al-Si-10Sn/ZrSiO₄ composite shows the similar wear rate irrespective to the temperature variation at 5.5 kg load. The higher amount of Sn in the matrix provides a smooth lubricating layer spread on the entire surface which has been replenished again and again even at higher load and higher temperature conditions. Moreover, at higher temperature the oxidative layer greatly helps to increase the wear resistance. Therefore Al-Si-10Sn/ZrSiO₄ composite shows the enhanced wear properties at all the test conditions.

Figure 6.20 presents the average wear rate of the composites containing Bi and zircon sand. The average wear rate of Al-Si-5Bi/ZrSiO₄ and Al-Si-10Bi/ZrSiO₄ composites is similar for lower temperature regime at 5.5 kg load as shown in Fig. 6.20. However, dissimilarity is found at higher temperature (100 and 150 °C) conditions. This can be better

explained on the basis of lubrication effect induced by the immiscible element Bi on the sliding surfaces as observed for Sn. The micron sized Bi which is distributed throughout the matrix form uniform lubricating film over the sliding surfaces. This helps in reducing the wear rate of the composites at lower temperature regions as described earlier. However, as the temperature increases the lubrication film of Bi is smeared off in large amounts which result in discontinuous lubrication effect over the surfaces. Therefore Al-Si-5Bi/ZrSiO₄ composite shows higher wear rate at higher temperature conditions. As soon as Bi content is enhanced in the matrix to 10 wt. % (Al-Si-10Bi/ZrSiO₄ composite) the smearing off Bi is continually fed by the matrix over the surface and hence the lubricating film does not get ruptured. Therefore, Al-Si-10Bi/ZrSiO₄ composite shows lower wear rate even at higher temperature as shown in Fig. 6.20. The lubrication effect has been studied earlier by other researchers also with increasing amount of Pb content in Al-10Si-3.5Cu alloy system [7]. It has been investigated that varying the Pb content from 10 to 20% improve the wear resistance at higher pressure regime for Al-10Si-3.5Cu alloy.

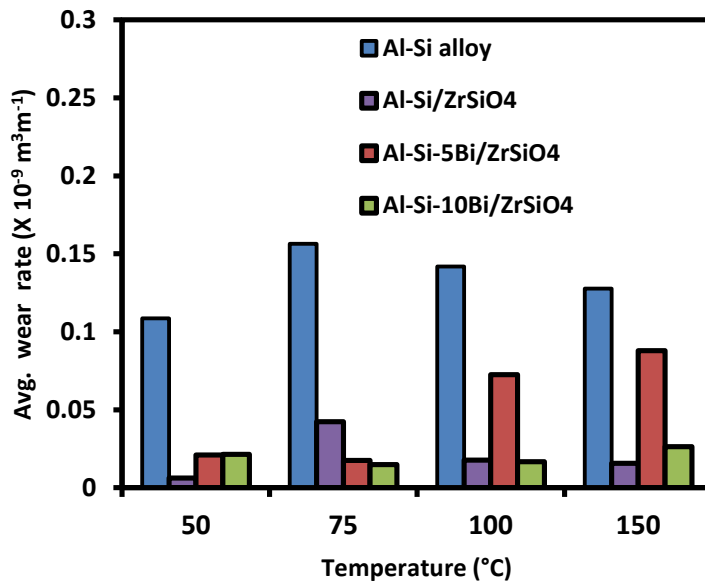


Figure 6.20: Comparison of the average wear rates against various temperatures at 5.5 kg applied load for zircon sand reinforced (106–125 μm) and Bi containing AMC.

The major difference between average wear rates of the prepared samples has been found at 150°C temperature for 5.5 kg. The average wear rate has been found to be 1.27×10^{-10} ,

1.56×10^{-11} , 9.15×10^{-12} , 4.85×10^{-12} , 8.78×10^{-11} and $2.63 \times 10^{-11} \text{ m}^3\text{m}^{-1}$ for Al-Si alloy, Al-Si/ZrSiO₄, Al-Si-5Sn/ZrSiO₄, Al-Si-10Sn/ZrSiO₄, Al-Si-5Bi/ZrSiO₄ and Al-Si-10Bi/ZrSiO₄ composite respectively. Sn containing composites exhibit higher wear resistance as compared to the Bi containing composites. Al-Si-5Sn/ZrSiO₄ and Al-Si-10Sn/ZrSiO₄ composites offer minimum wear at extreme test conditions. However, Al-Si-5Bi/ZrSiO₄, Al-Si-10Bi/ZrSiO₄ show highest wear resistivity at 75 °C under the highest applied load. Al-Si/ZrSiO₄ also offers good wear resistance at 50 and 150 °C.

6.6.4 Friction coefficient

Friction behavior of spray formed Al-Si alloy and composites have been examined by the variation in temperature for one of the three lower loads and the highest loads. Figures 6.21 and 6.22 represent the average friction coefficient of all the prepared samples at 2.5 and 5.5 kg. During dry sliding, friction forces rise initially (similar as wear rate) and then fluctuates around mean value with further sliding. Therefore average frictional coefficient has been calculated excluding initial higher values to account for steady state frictional forces acting on the surfaces.

Figure 6.21 illustrates the variation of average friction coefficient with temperature for zircon sand reinforced composites. At higher temperature, Al-Si alloy exhibits abrupt increase in frictional coefficient irrespective to the applied load. This is due to the metal softening and plastic deformation of the alloy at higher temperature. Moreover, at higher temperature the low hardness of Al-Si alloy increases the real area of contact and hence greater friction coefficient has been obtained. At lower load, Fig. 6.21 (a) shows that friction coefficient gradually increases with increase in temperature for Al-Si/ZrSiO₄ composite. Moreover, at the lower temperature (50 and 75 °C) friction coefficient is lower and beyond 75 °C friction coefficient is higher as compared to the monolithic Al-Si alloy. It has been reported that friction coefficient results from action of the adhesion and ploughing in metals during dry sliding. However, besides these two phenomena particle fracture also plays an important role in total frictional coefficient of the composite materials [8]. Therefore, it is expected that composite materials will show higher values of frictional coefficients during tests.

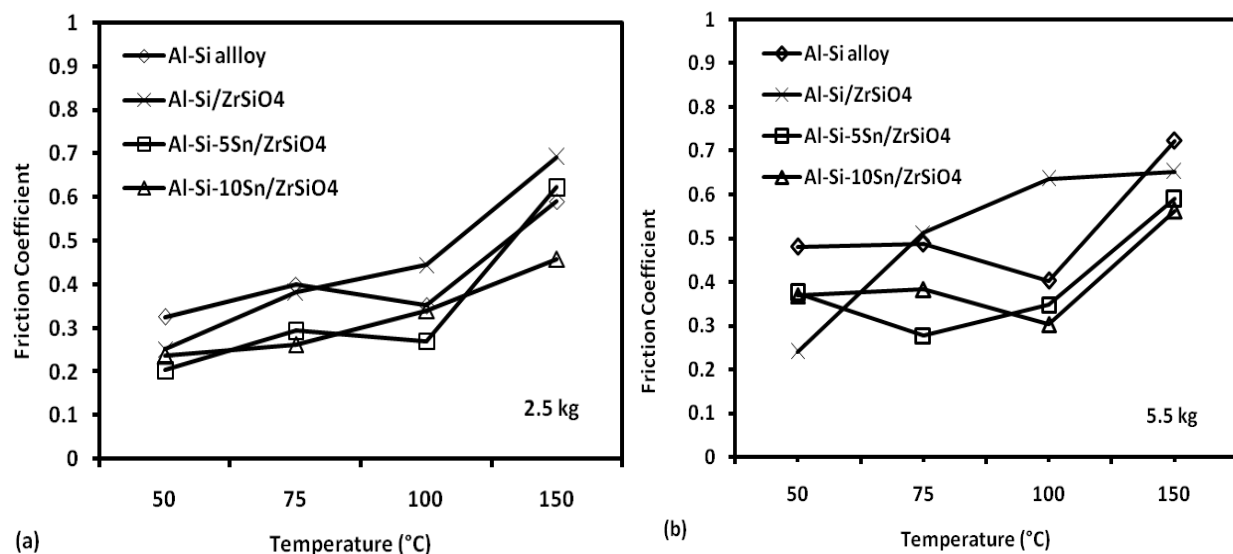


Figure 6.21: Variation of average friction coefficient with temperature of zircon sand reinforced and Sn containing composites at **(a)** 2.5 kg and **(b)** 5.5 kg load.

At the lower temperature the particles are well embedded in the matrix alloy and helps in reducing wear therefore the friction coefficient is lower. At higher temperatures, due to metal softening, particles matrix bonding gets loosen. The loose particles give supplement effect to the total friction coefficient which increases friction coefficient of Al-Si/ZrSiO₄ composite at higher temperature. Apart from this the solid lubricant present in composites provides lubricating film. The lubricating film helps in reducing the frictional coefficient if lubricating film is continuous and adhere the entire surface. Therefore Sn containing composites show the lower friction coefficient due to the presence of lubricating Sn film in the Al-Si-5Sn/ZrSiO₄ and Al-Si-10Sn/ZrSiO₄ composites as shown in Fig. 6.21 (a, b).

The comparison of the average friction coefficient of the Bi containing composites is shown in Fig. 6.22. Figure 6.22 (a) shows that at 2.5 kg the spray formed Al-Si alloy and Al-Si-5Bi/ZrSiO₄ exhibit similar frictional coefficient while Al-Si-10Bi/ZrSiO₄ composite shows lower values of friction coefficient. Therefore the trend of frictional curves shown in Fig 6.22 (a) can be explained on the basis of lubrication effect catered by immiscible element Bi in the composite materials. Addition of Bi in the matrix alloy provides a lubricating film over the surface which reduces direct metal to metal contact.

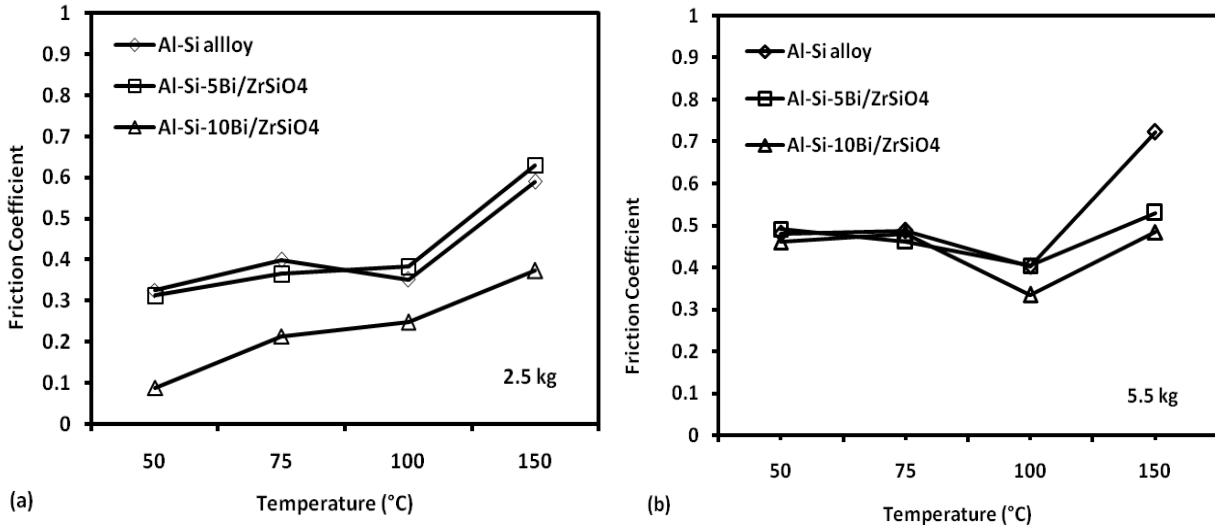


Figure 6.22: Variation of average friction coefficient with temperature of zircon sand reinforced and Bi containing composites at **(a)** 2.5 kg and **(b)** 5.5 kg load.

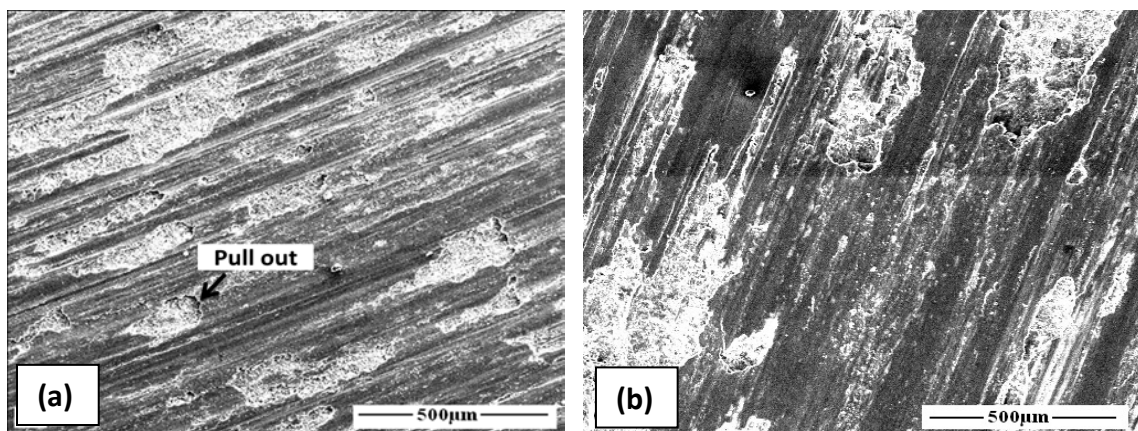
In Al-Si-5Bi/ZrSiO₄ composite the effect of particle fracture increases the frictional coefficient which is compensated by the lubrication effect given by Bi. However, it has been observed that friction coefficient increases with increase in temperature from 50 to 150 °C. In Al-Si-5Bi/ZrSiO₄ composite with increase in the temperature the lubricating film has been continually removed or oxidized which enhances the effect of particle fracture in the total frictional coefficient. However, in Al-Si-10Bi/ZrSiO₄ the continuous supply of Bi from the grains and grain boundaries does not lead the condition of removal of lubricating film from the surface and hence lower frictional coefficient has been obtained at 2.5 kg load. Figure 6.22 (b) shows that with increase in load (5.5 kg) higher frictional coefficients have been obtained in all the prepared samples. Moreover, all samples show similar frictional coefficient at lower temperature regime (50 and 75 °C) and depression in frictional coefficient at 100°C has been found. There is a steep rise in frictional coefficient at 150°C which is related to the softening of the alloy as described earlier. At higher load and higher temperature the frictional force increases leading to large heat dissipation at the contact areas. The higher temperature will lead to formation of more oxide layer which gets compacted under higher load [9]. This effect leads to decrease in friction coefficient at 100°C. However, with further rise in temperature an increase in frictional coefficient is observed which can be accounted from the plowing and three body wear in the composite

materials. However, this rise is not as much as found in Al-Si alloy which gets plastically deformed at extreme conditions.

6.7 Microstructural analysis of worn surfaces and wear debris

SEM micrographs of worn surfaces and wear debris of Al-Si/ZrSiO₄ composite are shown in Fig. 6.23 and 6.24 respectively. The morphological features of spray processed Al-Si/ZrSiO₄ composite shows completely different worn surfaces than Al-Si alloy. Large elongated dimple morphology can be seen along the sliding direction on the surface of composite material showing white patches along the grooves. Similar morphology has also been observed by other researchers in ceramic reinforced AMCs [10, 11]. The width of the grooves and elongation of dimples is more predominant as the load is increased from 2.5 kg to 5.5 kg as shown in Fig. 6.23 (a, b). A critical analysis of the dimple morphology indicates that the oxidative wear mechanism is operational in this case.

Such morphology indicates the formation of non-uniform tribo-layer on the worn surface. Also, the formed tribo-layer is heterogeneous in nature and morphology of craters predicts the formation of oxide debris. The repetitive sliding marks are clearly visible at high temperature conditions as shown in Fig. 6.23 (c, d). However, with the variation of load from 2.5 kg to 5.5 kg the marks are broadened. The wear mechanism is further correlated to the microstructure of loose debris of composite at 2.5 kg and 5.5 kg as shown in Fig. 6.24.



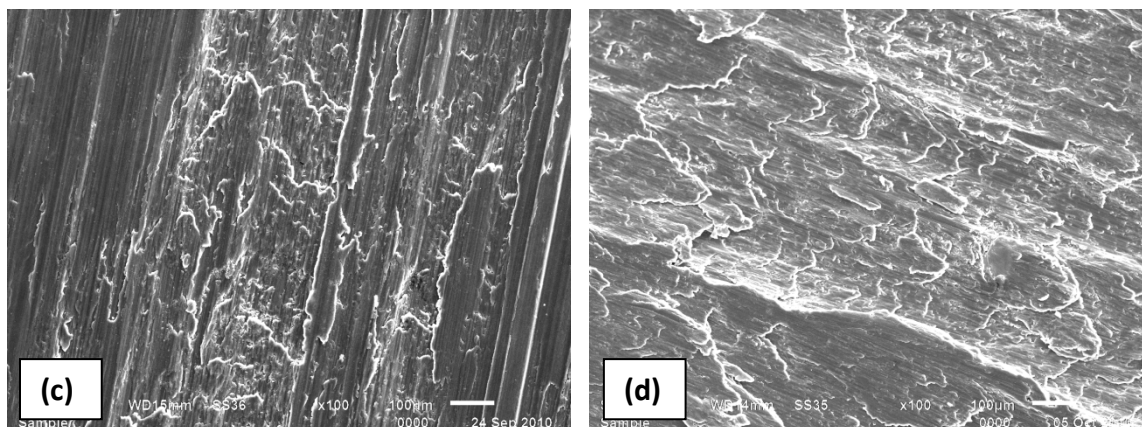
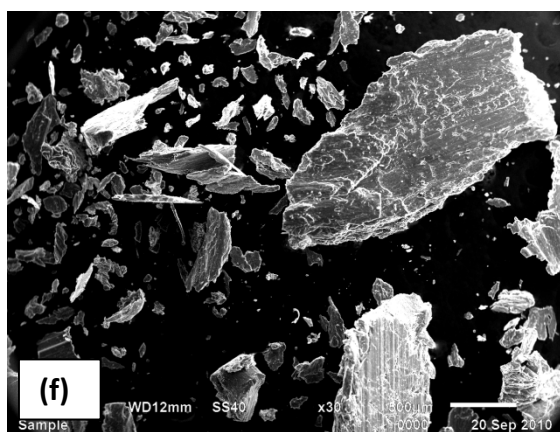
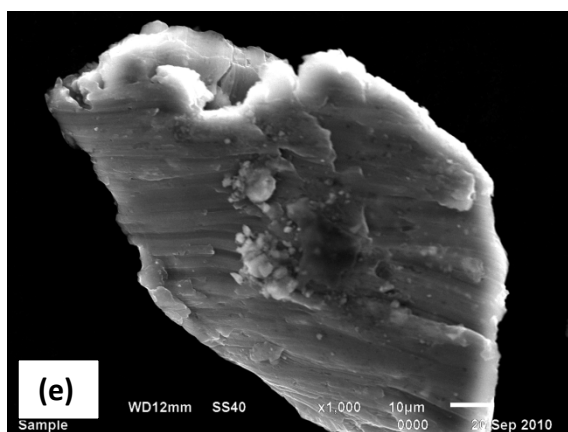
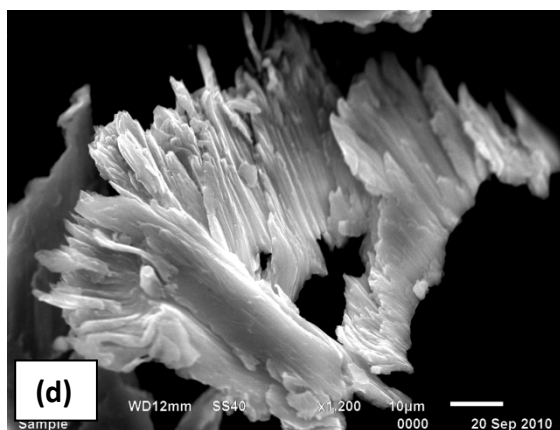
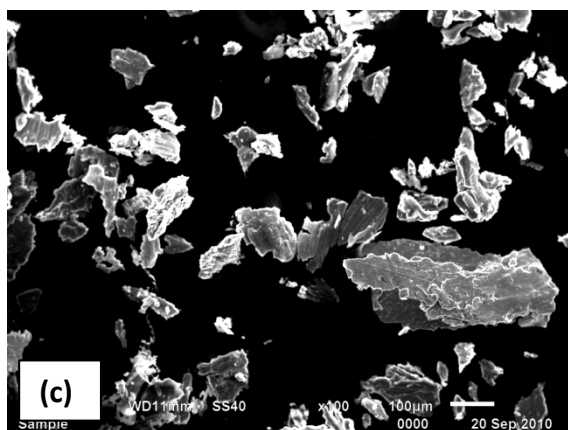
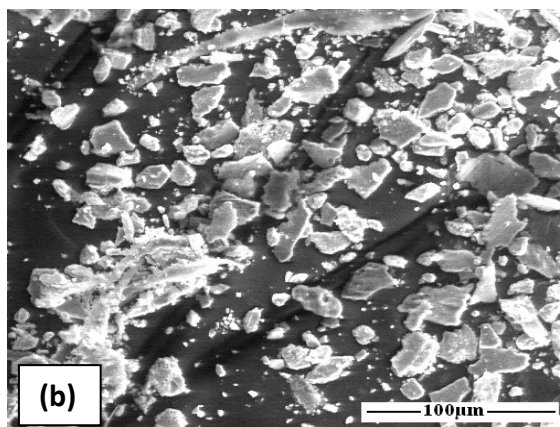
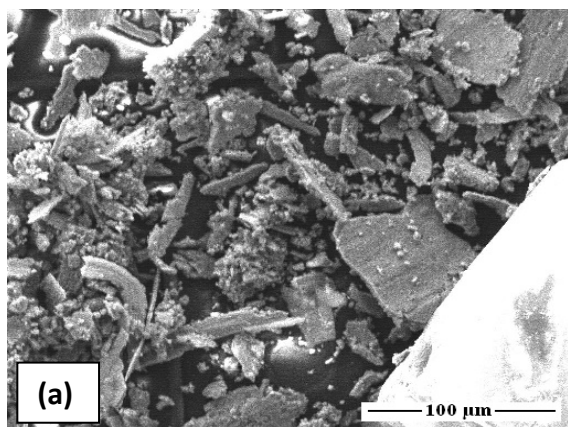


Figure 6.23: SEM micrographs of worn pin surfaces of Al-Si/ZrSiO₄ (106–125 μm) composite at **(a)** 2.5 kg, 50°C; **(b)** 5.5 kg, 50°C; **(c)** 2.5kg, 150°C and **(d)** 5.5kg, 150°C.

Both metallic as well as oxide wear debris can be found in Al-Si/ZrSiO₄ composite (Fig. 6.24). At applied load of 2.5 kg plate like morphology of debris can be seen in Fig. 6.24 (a). Also the formation of wear tracks on the loose debris has been observed. On analyzing Fig. 6.24 (b) it is observed that higher load favors the generation of finer debris. This may be due to mechanical grinding of wear debris between the sliding surfaces under the action of high normal load. This mechanism is comparable to the ball milling process in which fine particles are produced from large particles by the action of repetitive stress forces [12]. Also, under 5.5 kg load the reinforced composite shows the granular nature of small oxide wear debris (Fig. 6.24 (b)) as compared to base Al-Si alloy (Fig. 5.7 (b)). The morphology of the debris indicates the adhesive-cum-oxidative nature of wear as reported in earlier study [13]. Figure 6.24 (c) shows that at 2.5kg load and at highest studied temperature small size debris has been observed. On analyzing at higher magnification it reveals the repetitive plowing as can be seen on the worn surface that give rise to the wrinkled debris as shown in Fig. 6.24 (d). Along with this small round oxide debris has also been observed as illustrated in Fig. 6.24 (e). At 5.5 kg load both small and large debris has been observed (Fig. 6.24 (f)). The large debris seems to be generated during the run-in wear regime. The repetitive wear scars can be seen on the surface of wear debris as shown in Fig. 6.24 (g).



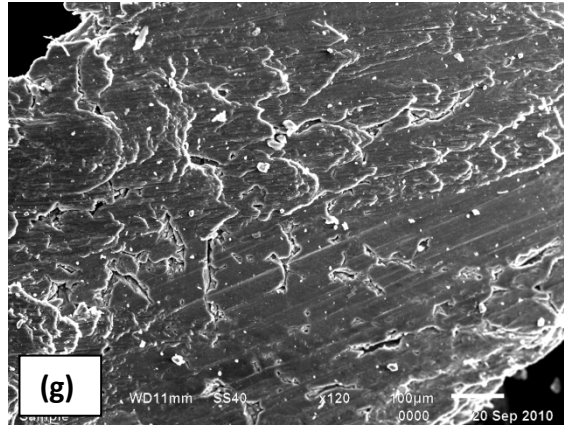


Figure 6.24: SEM micrographs of wear debris of Al-Si/ZrSiO₄ (106–125 µm) composite at (a) 2.5 kg, 50°C; (b) 5.5 kg, 50°C (c–e) 2.5kg, 150°C and (f, g) 5.5kg, 150°C.

The worn pin surfaces and debris of Al-Si-5Sn/ZrSiO₄ and Al-Si-10Sn/ZrSiO₄ composites are shown in Fig. 6.25 to 6.28. The pin surfaces (Fig. 6.25 and 6.27) illustrate the similar morphology of white patches and grooves running parallel to the sliding direction. A critical analysis of the white patches indicates the presence of mechanically mixed layer (MML) deposited over the entire surface. The MML has been formed from initially detached debris which got compacted under higher load and oxidized easily at higher temperature. The presence of a thin lubricating Sn layer can also be felt on the running surfaces in the composites. However, the amount of lubricating layer is more in Fig. 6.27 as compared to Fig. 6.25.

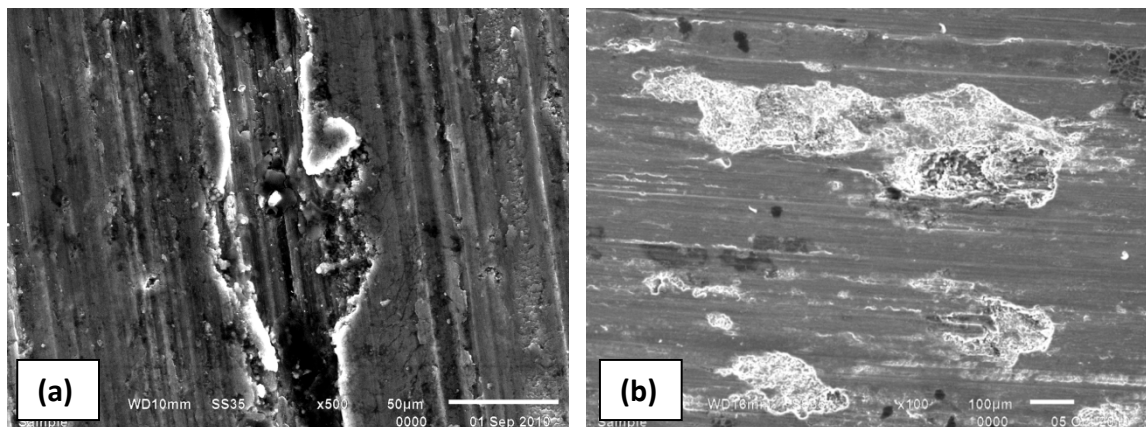


Figure 6.25: SEM micrographs of worn surface of Al-Si-5Sn/ZrSiO₄ (106–125 µm) composite at 150°C (a) 2.5kg and (b) 5.5 kg.

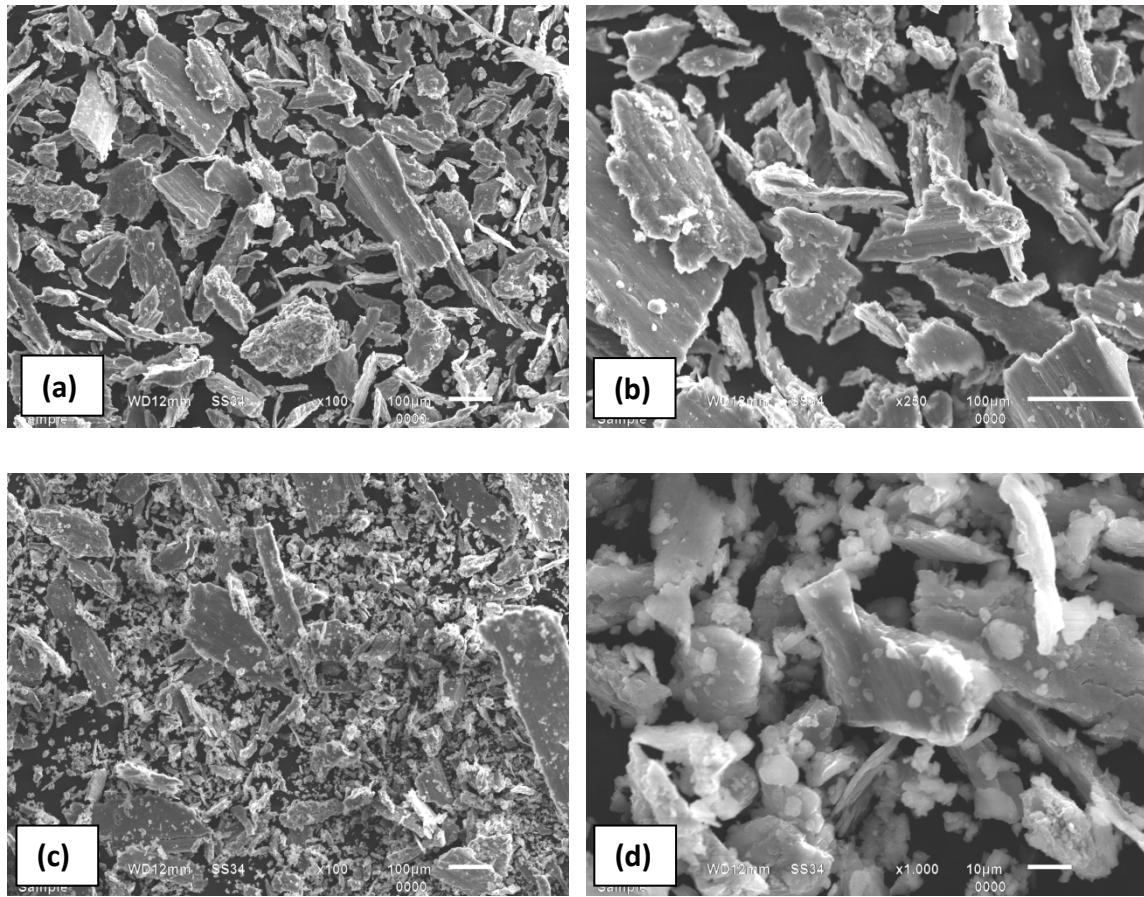


Figure 6.26: SEM micrographs of wear debris of Al-Si-5Sn/ZrSiO₄ (106–125 µm) composite at **(a, b)** 5.5kg, 50°C and **(c, d)** 5.5kg, 150°C.

Figure 6.26 and 6.28 show that the collected wear debris that exhibited two types of morphology e.g. (i) plate like flakes and (ii) fine sized debris. The plate like flakes seems to be generated during the run-in wear. On the other hand the finer ones are formed in the steady state wear regimes. Under the highest load and temperature conditions, both the amount and size of the collected debris for Al-Si-10Sn/ZrSiO₄ (Fig. 6.28 (c)) is less than that of Al-Si-5Sn/ZrSiO₄ (Fig. 6.26 (c)). It again verifies the wear rate results of Fig. 6.14 (d) and 6.15 (d) where the steady state average wear at 150 °C and 5.5 kg load is found to be 9.15×10^{-12} and $4.85 \times 10^{-12} \text{ m}^3\text{m}^{-1}$ for Al-Si-5Sn/ZrSiO₄ and Al-Si-10Sn/ZrSiO₄ respectively. However, Fig. 6.26 (a, b) shows that at similar load and lowest temperature most of the debris exhibit plate like morphology. Figures 6.26 (d) and 6.28 (b, d) show that some of the debris are very small, rounded and coagulated which clearly depict the oxidative wear mechanism. The generated debris are crushed between the rubbing surfaces, oxidized and

form a compact layer. This oxide layer poses a greater resistance to the sliding wear as oxide debris diminish the contacts between the matrix and the disc surface [14].

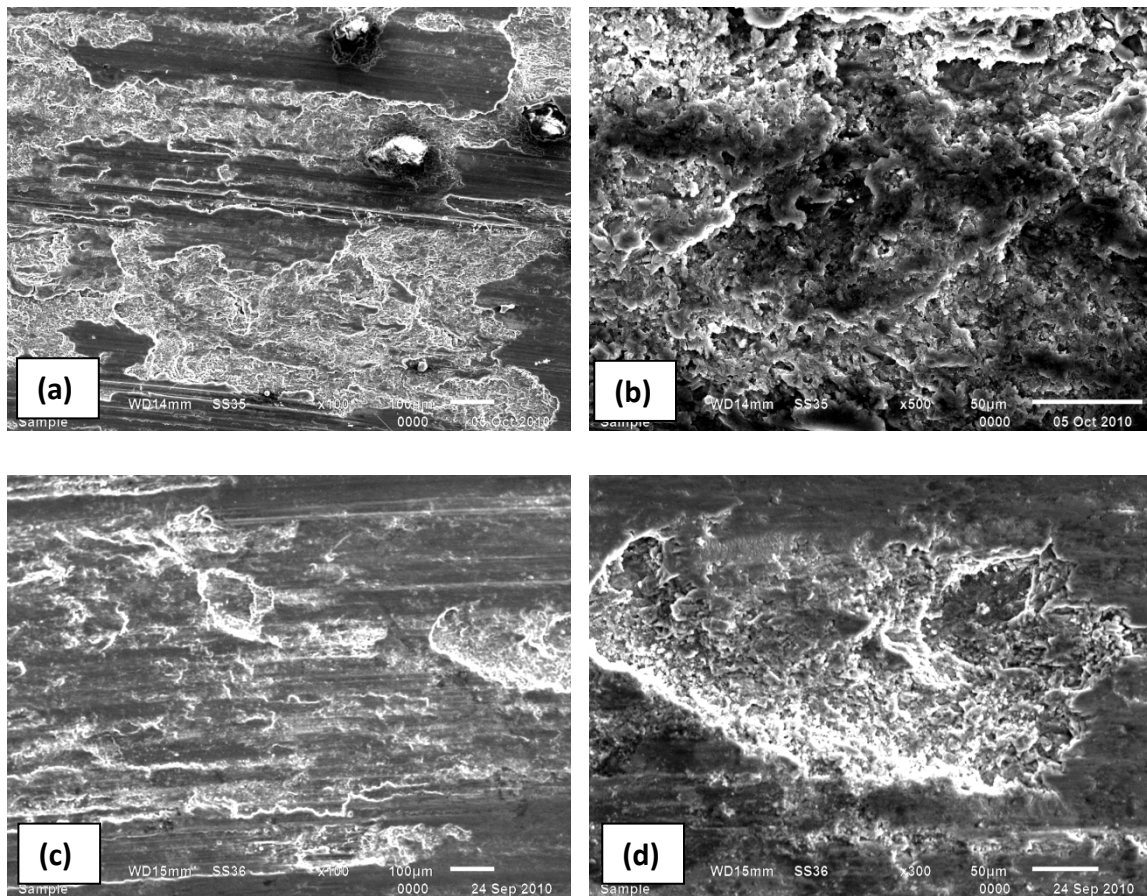
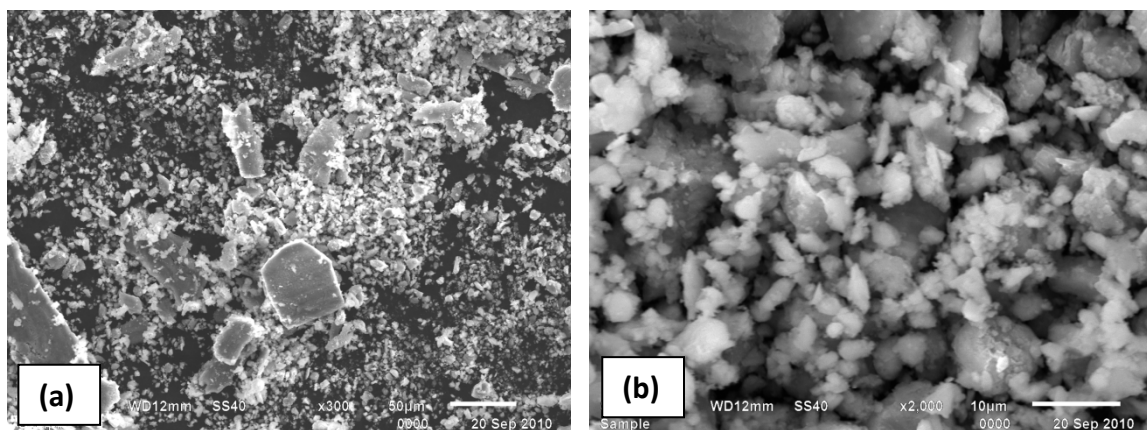


Figure 6.27: SEM micrographs of worn surface of Al-Si-10Sn/ZrSiO₄ (106–125 µm) composite at at 5.5 kg load **(a, b)** 50°C and **(c, d)** 150°C.



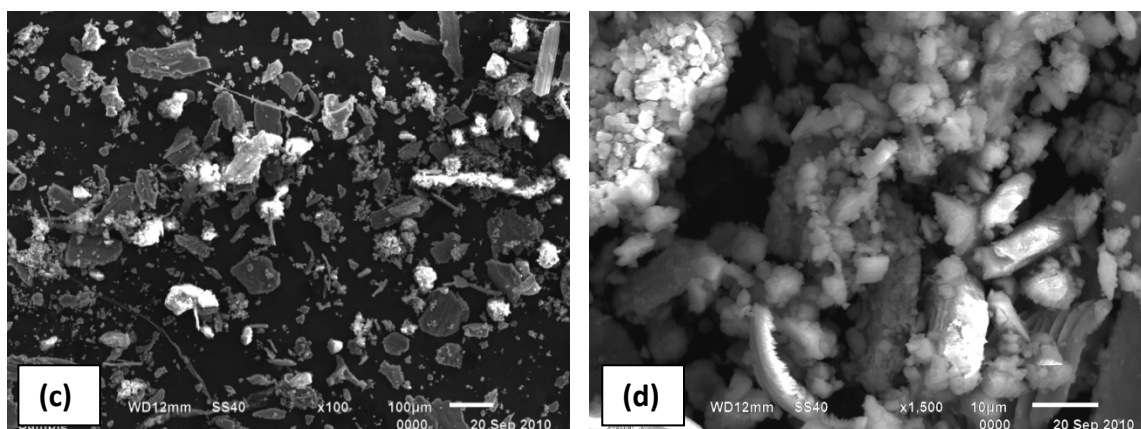


Figure 6.28: SEM micrographs of wear debris of Al-Si-10Sn/ZrSiO₄ (106–125 µm) composite at 5.5 kg, **(a, b)** 50°C and **(c, d)** 150°C.

The worn pin surfaces and debris of Al-Si-5Bi/ZrSiO₄ composite are shown in Fig. 6.29 and 6.30 respectively. Fig. 6.29 shows the presence of white patches along the grooves. The grooves get deeper and broader with the applied load as seen in Fig. 6.29 (c, d, f) as compared to 6.29 (a, b, e). Moreover, Bi provides homogenous lubricating film over the entire surface. The repetitive plowing marks are clearly visible in Fig. 6.29 (c, e). The large elongated white patches as shown in Fig. 6.29 (f) indicate highly ruptured mechanically mixed layer (MML) at 150°C and 5.5 kg load. This is a sign of the severe wear as indicated earlier by the wear rate in Fig. 6.14 (d). The discontinuous lubricating film can be seen over the worn surfaces at 150°C and 5.5 kg load. Small plate like debris has been observed at 50°C (Fig. 6.30 (a, b)) as compared to the large debris and a chunk of material obtained at 150°C as shown in Fig. 6.30 (c) under 5.5 kg load. Some repetitive marks and wrinkled debris has also been obtained at 150°C. The worn surface and debris analysis again verifies that Al-Si-5Bi/ZrSiO₄ composite show the severe wear at the extreme test conditions of temperature and load due to excessive rupture of MML. Also, the wrinkled debris indicates towards delaminating wear theory prevailing with repetitive sliding at 5.5 kg load. The cracks beneath the surface piled up and remove the large amount of MML layer from the sliding surface enhancing wear rate. Thus partially metal to metal direct contact due to discontinuous film enhances the wear rate. However, at lower loads and temperature MML seems to be stable and effective in reducing the wear rate.

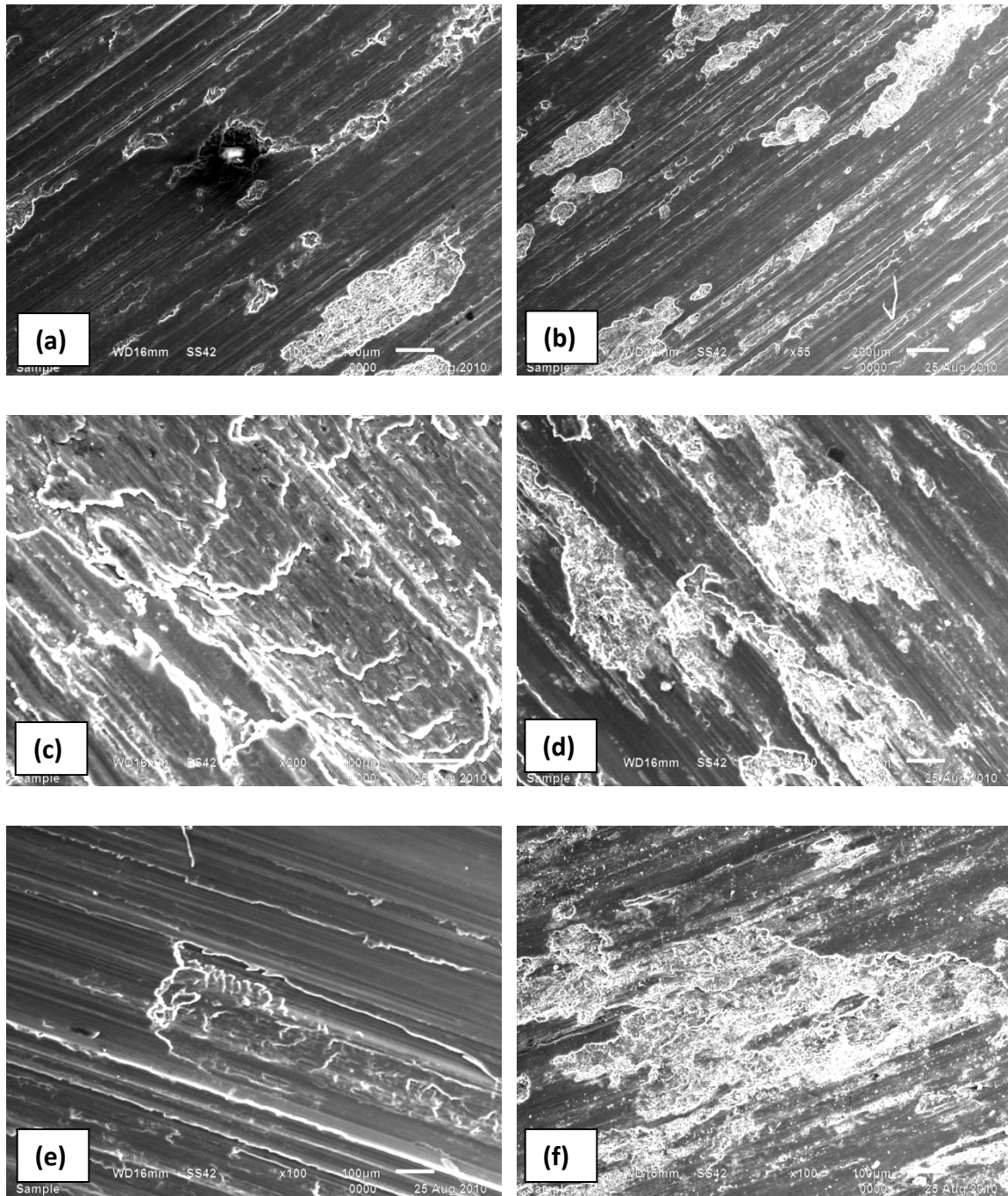


Figure 6.29: SEM micrographs of worn surfaces of Al-Si-5Bi/ZrSiO₄ (106–125 µm) composite **(a, b)** at 2.5kg, 50 °C ; **(c, d)** 5.5 kg, 50 °C ; **(e)** 2.5 kg, 150 °C and **(f)** 5.5 kg, 150 °C.

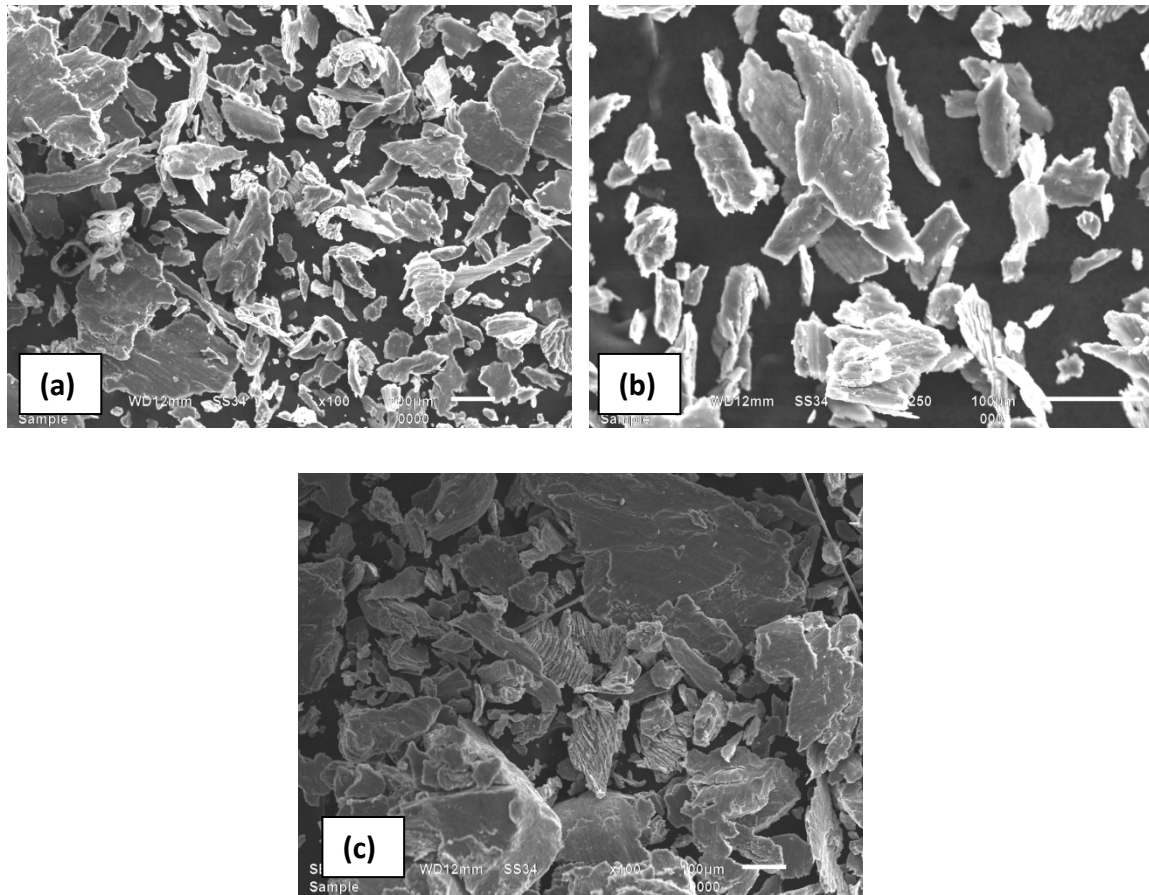


Figure 6.30: SEM micrographs of wear debris of Al-Si-5Bi/ZrSiO₄ (106–125 μm) composite at 5.5 kg load at **(a, b)** 50 °C; **(c)** 150 °C.

Fig. 6.31 and 6.32 represent the worn surfaces and wear debris of Al-Si-10Bi/ZrSiO₄ composite respectively. The shallow running grooves with white patches are observed over the surface as shown in Fig. 6.31 (a, c). A homogeneous lubricating film of Bi can be seen on the surface. The deeper grooves and small rupture in MML with repetitive marks at 5.5 kg load can be seen at both 50 °C and 150 °C temperatures (Fig. 6.31 (b, d)). At these test conditions the debris also depicts the similar morphology of metallic wear debris as shown in Fig. 6.32 (a, b).

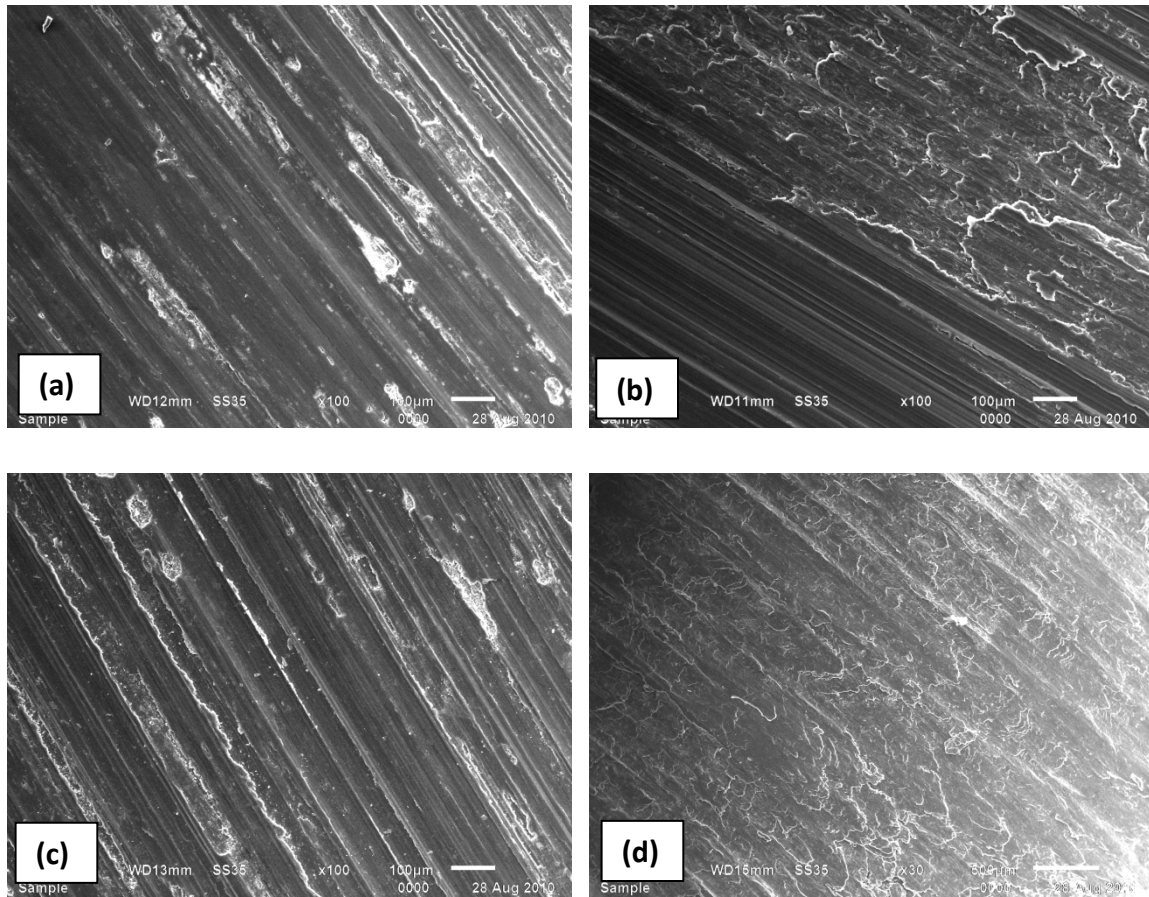


Figure 6.31: SEM micrographs of worn surfaces of Al-Si-10Bi/ZrSiO₄ (106–125 µm) composite at **(a)** 2.5 kg, 50 °C; **(b)** 5.5 kg, 50 °C; **(c)** 2.5 kg, 150 °C and **(d)** 5.5 kg, 150 °C.

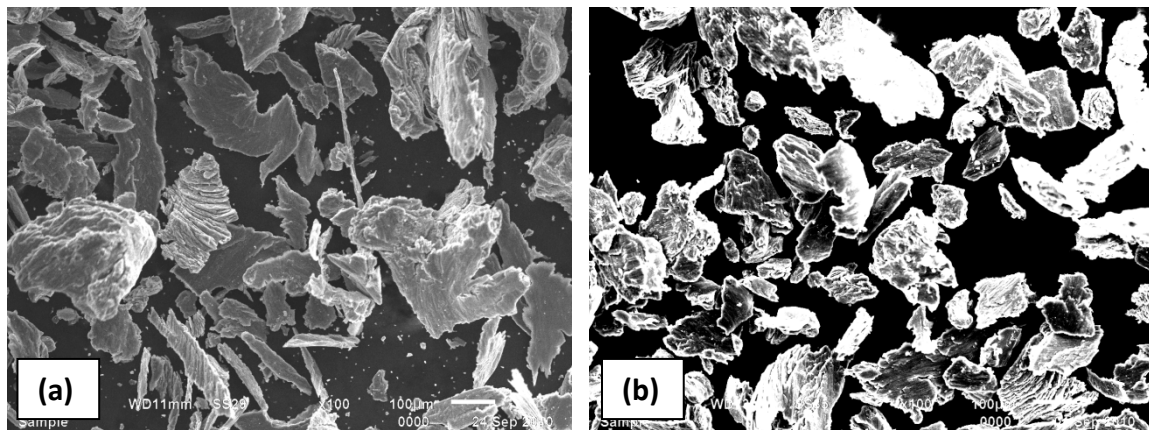


Figure 6.32: SEM micrographs of wear debris of Al-Si-10Bi/ZrSiO₄ (106–125 µm) composite at 5.5 kg load at **(a)** 50 °C and **(b)** 150 °C.

The wear scars of reinforced composite of white patches correspond to head and tail morphology of dimples along the sliding direction. The various stages illustrating the development of this type of morphology are shown in Fig. 6.33 (a–f). Fig. 6.33 (a) shows the various forces acting on the test pin surface where W represents the applied load, N is the normal force to applied load acting on the counterpart, F is the traction force acting due to sliding and F' is the frictional force developed against sliding. On initial sliding aluminium matrix being softer has been removed from the composite as illustrated in Fig. 6.33 (b). On further sliding the stress has been carried out by the particle only due to which the crack start propagating at the interface of zircon sand particle and matrix. This situation leads to the development of the head of the dimple depicted in Fig. 6.33 (c). The increase in the stress distribution promotes crack initiation on the matrix as well as particle (Fig. 6.33 (d)). The cracking of zircon sand particle abrades matrix around the particle in the sliding direction creating tail of the dimple as shown in Fig. 6.33 (e). The further sliding leads to the formation of smaller zircon sand particles causing lengthening of tail in the matrix which is shown as a tail growth in Fig. 6.33 (f).

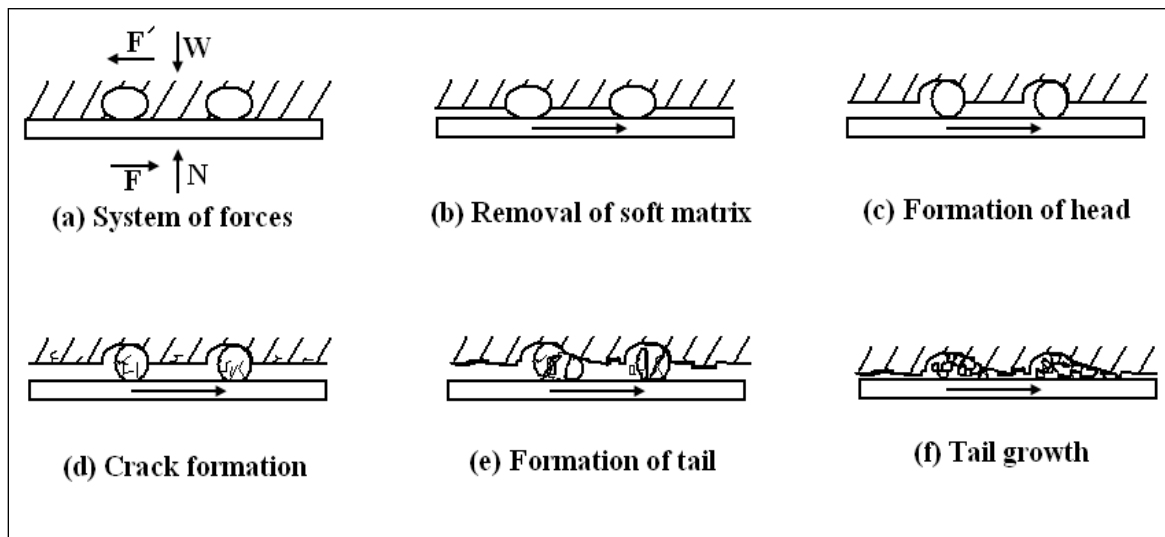


Figure 6.33: Schematic diagram indicating wear mechanism at various stages during the wear test.

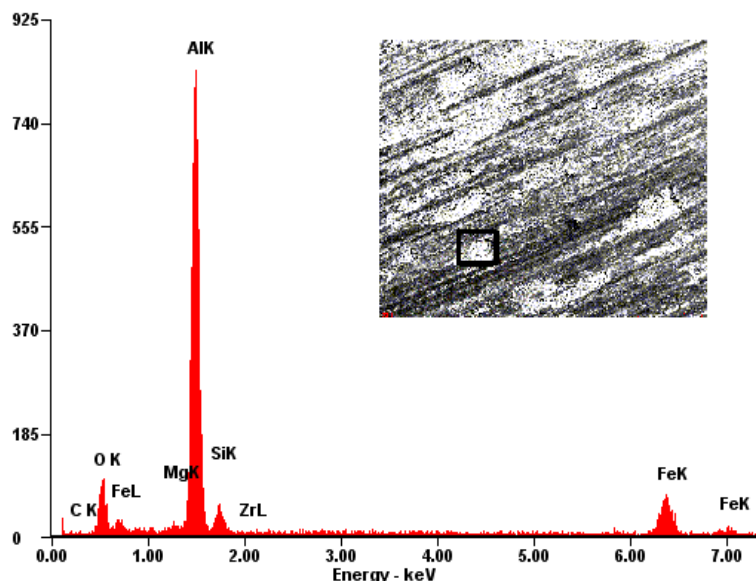


Figure 6.34: EDS of worn surface of the pin of Al-Si/ZrSiO₄ composite.

The chemical composition of dimple morphology on the worn surface of the Al-Si/ZrSiO₄ composite shows an oxidative wear mechanism indicated by the presence of Al, O, Si, Zr and Fe as given by EDS result in Fig. 6.34. On analyzing microstructural features and EDS of worn surfaces and debris of Al-Si/ZrSiO₄ composite it has been again verified that there is a formation of wear protective oxide layer on the load bearing surfaces. The oxide layer poses a greater resistance to the sliding wear and friction as oxide debris reduces the extent of direct metal to metal contact. The formation of chemically reacted oxide layer is resulted from the oxidation of the exposed metal surface in the relative motion. The rupture of the oxide layer during transversal and reoxidation of the exposed metal surface is called oxidation–delamination–reoxidation [15]. Moreover, the compaction and comminution of the debris between the sliding surfaces favored the development of wear protective oxide layer [6].

In addition, X-ray dot mapping of the worn surface (Fig 6.35) give the evidence of oxygen rich phases (Fig. 6.35 (e)) present all over the surface of composite material. Besides this a uniform distribution of zircon rich phase on the worn surface (Fig. 6.35 (d)) indicates the good particle/matrix bonding and confirms the proposed wear mechanism. Similar results are reported earlier in wear behavior of spray formed Al-2Mg-11TiO₂ composite [4].

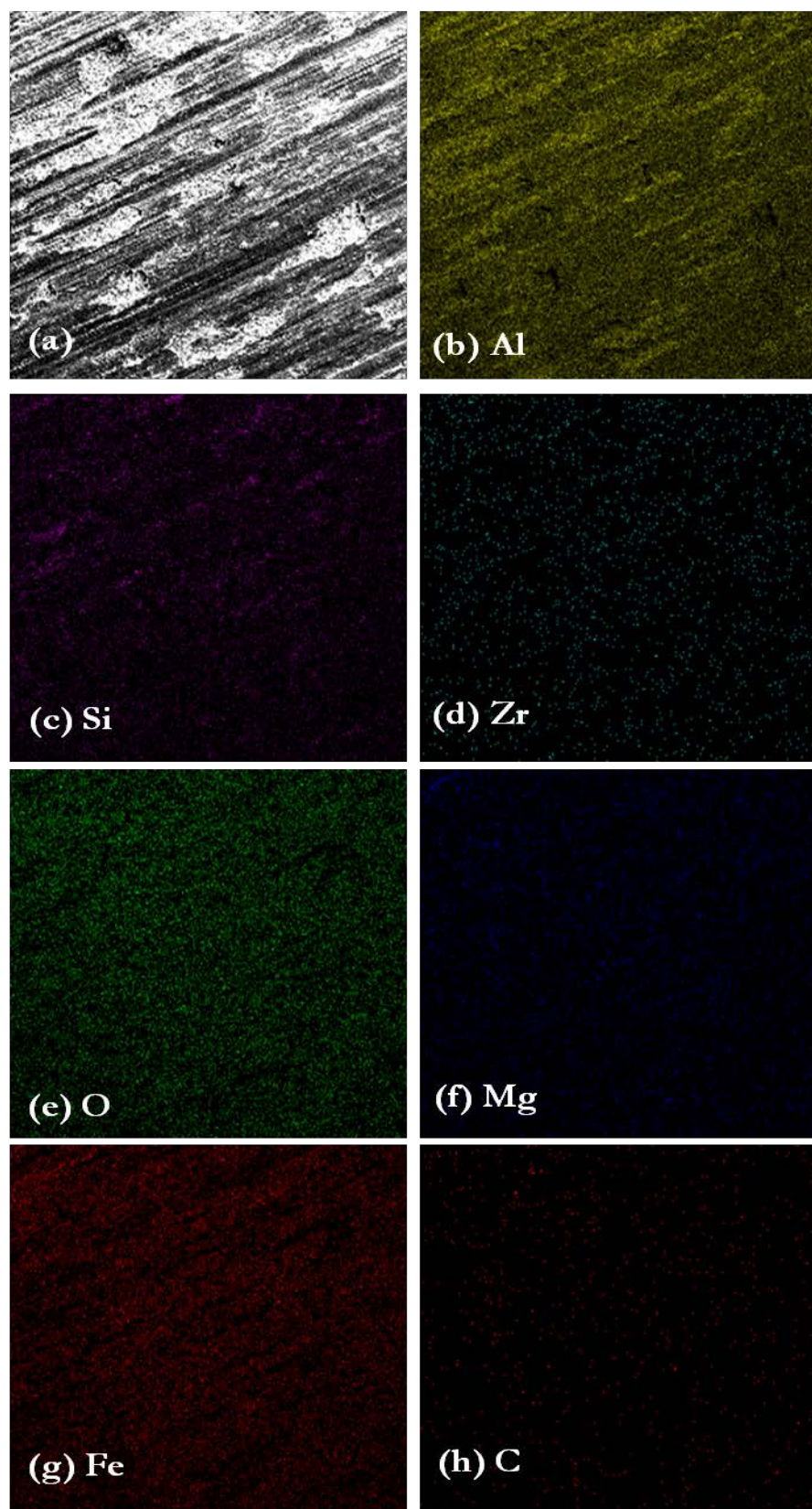


Figure 6.35: X-ray dot mapping of worn surface of Al-Si/ZrSiO₄ at 2.5 kg, 50 °C.

Moreover, the Fe mapping (Fig. 6.35 (g)) confirms the material transfer from steel counterpart disc has taken place.

The oxidative nature as described by wear debris and worn surface morphology of Al-Si-5Sn/ZrSiO₄ and Al-Si-10Sn/ZrSiO₄ composites is further confirmed from the presence of characteristic peak of oxygen in EDS of wear debris as shown in Fig. 6.36 to 6.38. Al-Si-10Sn/ZrSiO₄ composite even shows the oxidative wear nature at 50°C under 5.5 kg load as shown in Fig. 6.36. The EDS analysis clearly reveals the presence of Fe indicating the transfer of material from the steel counterface. Undoubtedly, Al-Si-10Sn/ZrSiO₄ (Fig. 6.37) illustrates the ultrafine, rounded and coagulated debris proving the higher amount of oxidative wear and greater wear resistance than Al-Si alloy and Al-Si-5Sn/ZrSiO₄ composite. Similar morphology of wear debris is also reported earlier by Li et al. [16] in Al-alloys and composites. Li et al. [16] also confirmed the MML formation on the rubbing surface and material transfer from the counterface. Li's findings show that the transfer behavior of the elemental iron in the Al-Si/SiC composite is greater than Al-Si alloy as illustrated in our results (Figs. 5.11 and 6.36–6.38).

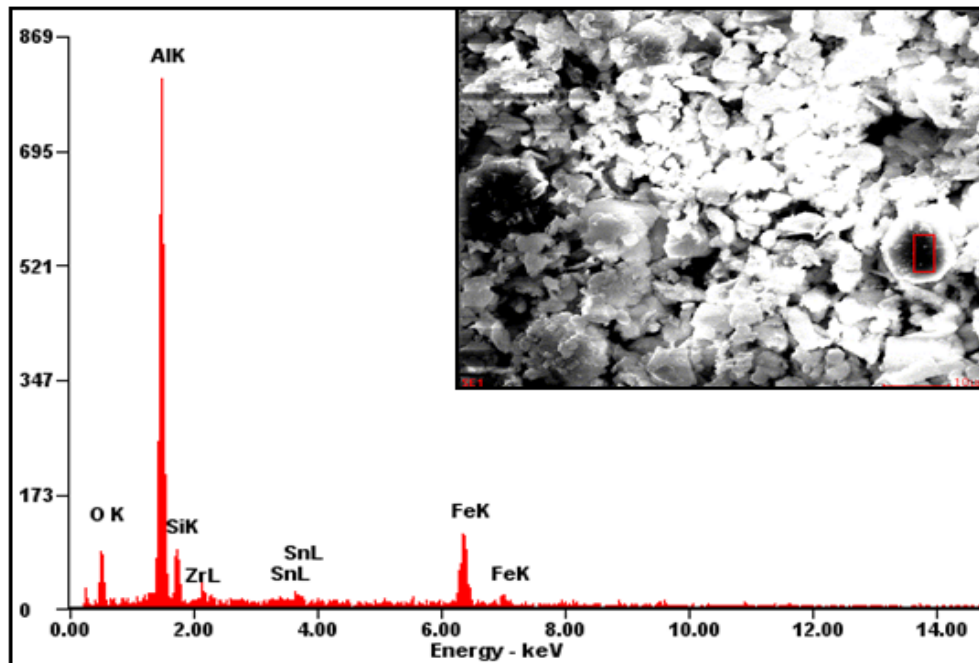


Figure 6.36: EDS profile and SEM micrograph of wear debris of spray formed Al-Si-5Sn/ZrSiO₄ composites under 5.5 kg applied load and 50°C temperature.

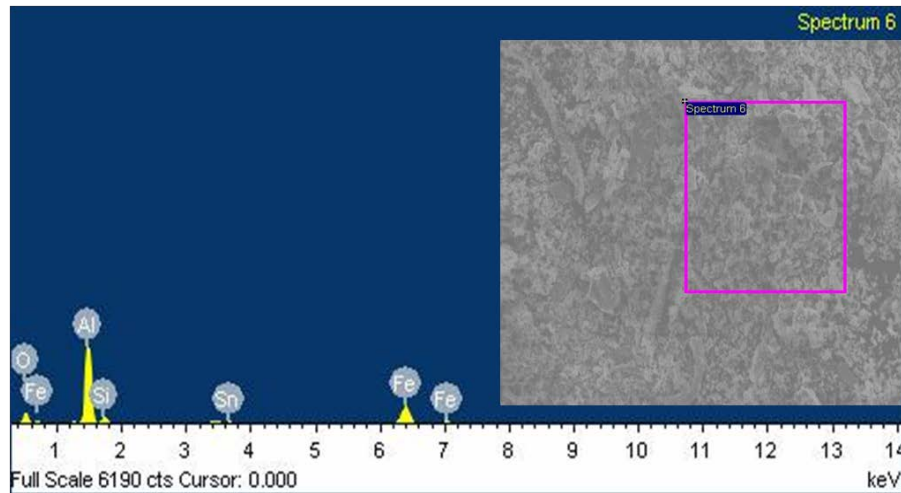


Figure 6.37: EDS profile and SEM micrograph of wear debris of spray formed Al-Si-10Sn/ZrSiO₄ composites under 5.5 kg applied load and 50°C temperature.

Furthermore, X-ray dot mapping of worn pin surface of Al-Si-10Sn/ZrSiO₄ composite proves the presence of uniform Sn lubricating film over the entire running surface as shown in Fig. 6.39. The presence of Fe, Zr, O and Sn shows the existing MML that helps in reducing the wear rate. EDS profile and SEM micrograph of wear debris of spray formed Al-Si-10Bi/ZrSiO₄ composite under 5.5 kg applied load at 50°C and 150°C temperature are shown in Fig. 6.40 and 6.41 respectively. Higher temperature conditions (Fig. 6.41) show greater oxidative nature and material transfer from counterface than at 50°C temperature conditions (Fig. 6.40).

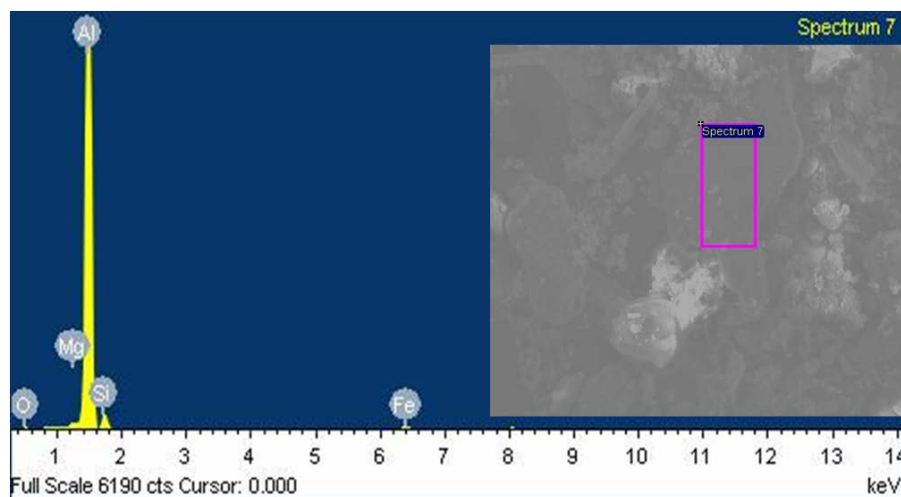


Figure 6.38: EDS profile and SEM micrograph of wear debris of spray formed Al-Si-10Sn/ZrSiO₄ composites 5.5 kg applied load and 150°C temperature.

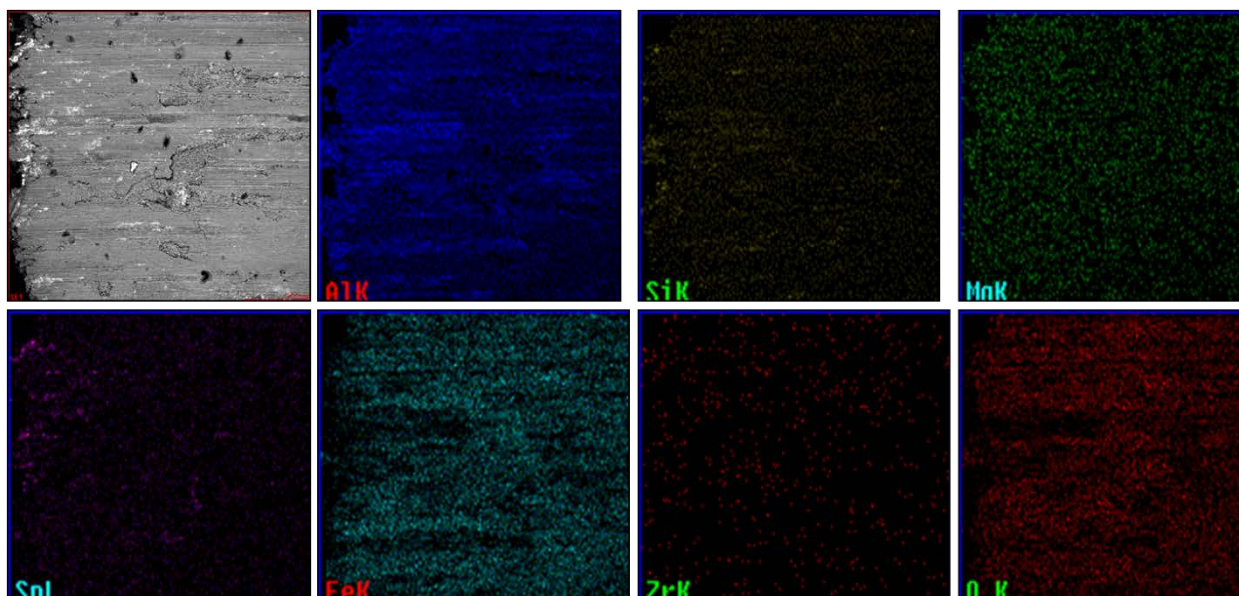


Figure 6.39: X-ray dot mapping of worn surface of spray formed Al-Si-10Sn/ZrSiO₄ composites 5.5 kg applied load and 50°C temperature.

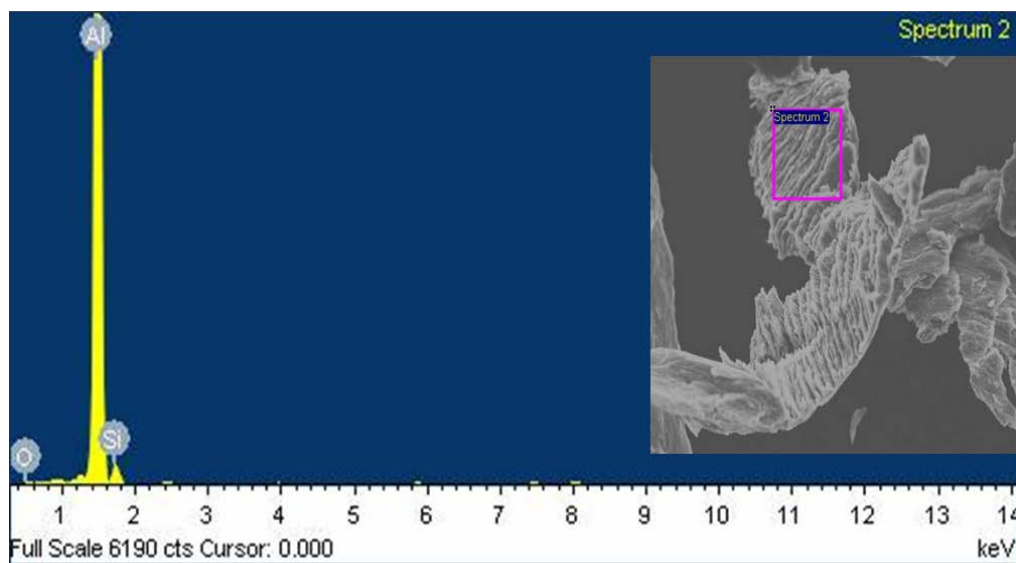


Figure 6.40: EDS profile and SEM micrograph of wear debris of spray formed Al-Si-10Bi/ZrSiO₄ composites 5.5 kg applied load and 50°C temperature.

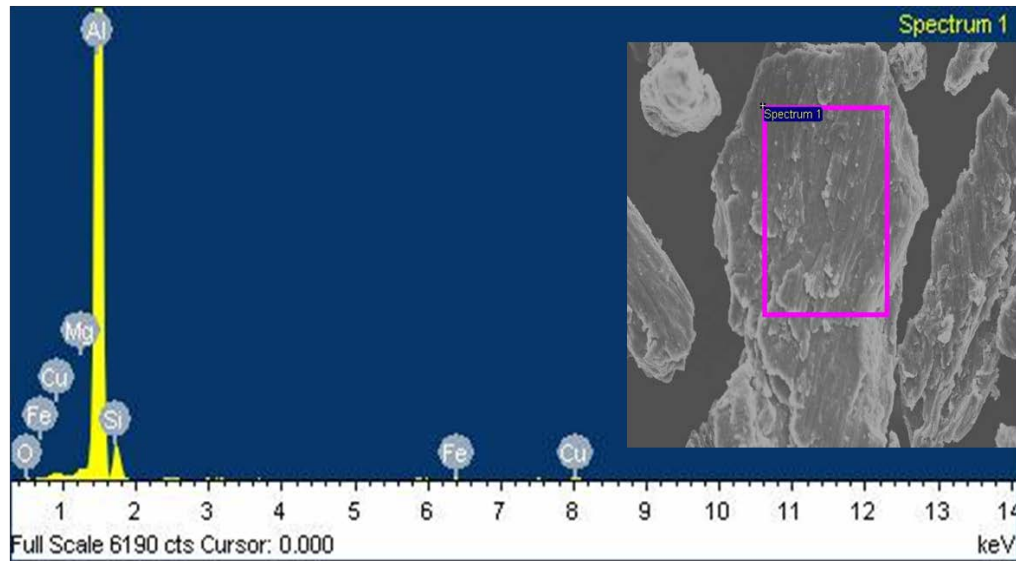


Figure 6.41: EDS profile and SEM micrograph of wear debris of spray formed Al-Si-10Bi/ZrSiO₄ composite 5.5 kg applied load and 150 °C temperature.

Effect of zircon sand reinforcement of particulate size 63–90 μm

6.8 Samples prepared

In this section, the results of spray formed near eutectic Al-Si alloy reinforced with 8 vol. % zircon sand (ZrSiO₄) having particulate size 63–90 μm has been discussed. The effect of immiscible element on the wear properties of zircon sand reinforced AMC has been discussed. The amount of immiscible elements has been varied in the prepared composites. The composition of spray formed samples is as follow:

1. Al-Si/ZrSiO₄ (63–90μm)
2. Al-Si-5Sn/ZrSiO₄ (63–90μm)
3. Al-Si-10Sn/ZrSiO₄ (63–90μm)
4. Al-Si-5Bi/ZrSiO₄ (63–90μm)
5. Al-Si-10Bi/ZrSiO₄ (63–90μm)

6.9 X-ray diffraction analysis

Figure 6.42 represents the XRD pattern of spray formed Al-Si/ZrSiO₄, Al-Si-5Sn/ZrSiO₄ and Al-Si-10Sn/ZrSiO₄ composites. The data collected is matched with the reference peaks of Al (ICDD card no. 03-065-2869), Si (ICDD card no. 01-077-2109), Sn (ICDD card no. 00-

004–0673), Bi (ICDD card no. 01–089–2387) and ZrSiO_4 (ICDD card no. 01–072–0402). It has been observed that on increasing the amount of Sn and Bi intensity of their respective peaks also get enhanced.

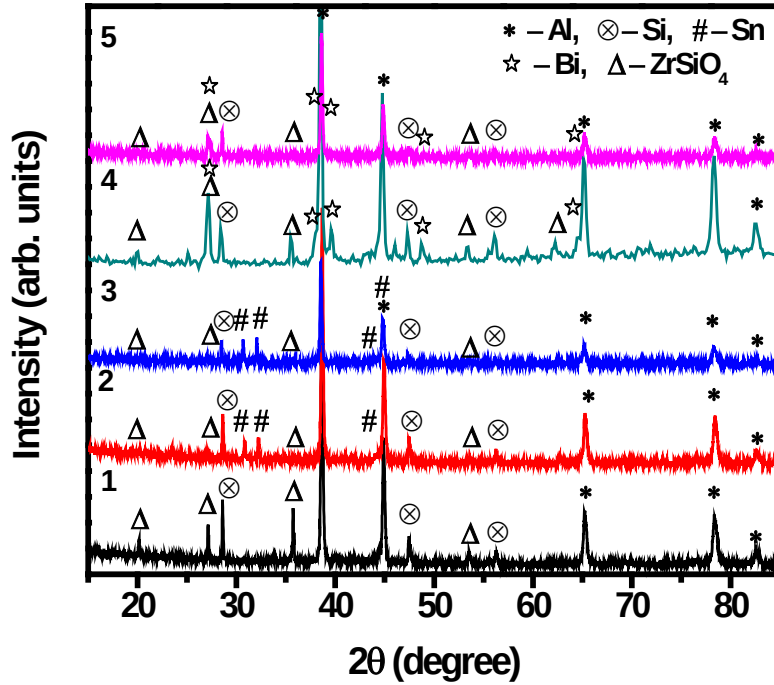


Figure 6.42: XRD pattern of (1) Al-Si/ ZrSiO_4 , (2) Al-Si-5Sn/ ZrSiO_4 , (3) Al-Si-10Sn/ ZrSiO_4 , (4) Al-Si-5Bi/ ZrSiO_4 and (5) Al-Si-10Bi/ ZrSiO_4 composites.

6.10 Hardness

The hardness of the materials has been measured on B-scale of the Rockwell hardness tester. The average hardness values of spray formed Al-Si alloy is 31.46 HRB and the averaged hardness values obtained for different composites are shown in a bar diagram (Fig. 6.43). On incorporation of zircon sand particles (63–90 μm) in the matrix a steep increase in the hardness has been found. However, it decreases further with the addition of 5 wt. % Sn and Bi. This is because of addition of soft material in the matrix alloy. Also, the modest enhancement is observed with increasing Sn and Bi content. The reason behind this enhancement would be the filling of pores (which is the inherent property of the spray forming process) by low melting point element e.g. Sn/Bi during solidification process. The increase in the hardness can be associated with the microstructure control by the spray deposition process.

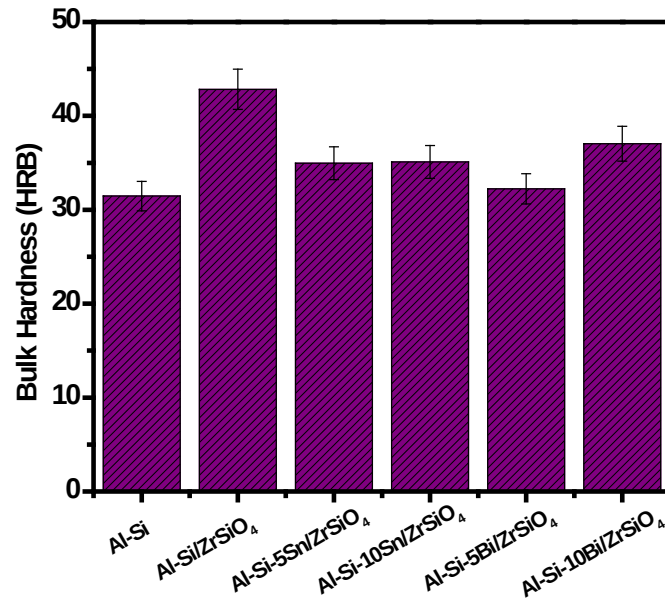
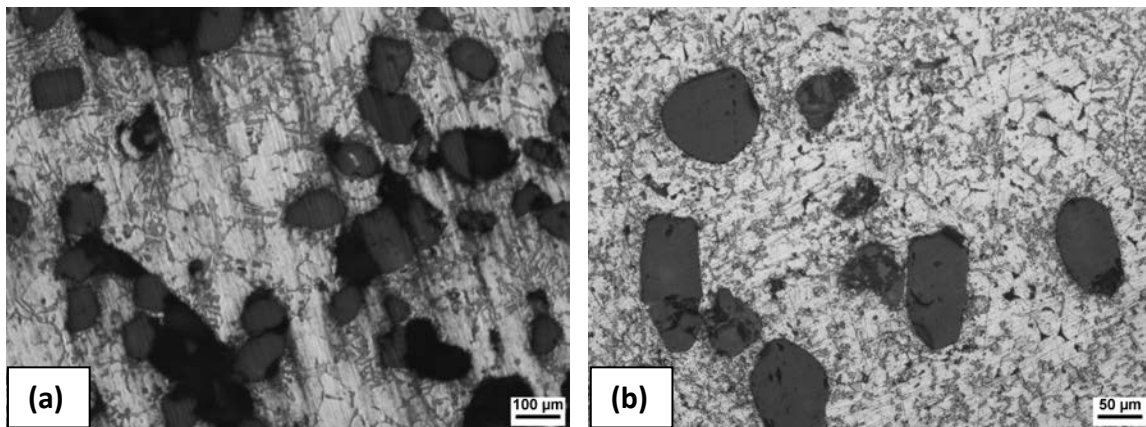


Figure 6.43: Bulk hardness of the prepared composites reinforced with zircon sand having particulate size 63–90 μm .

6.11 Microstructural analysis

Figure 6.44 represents the optical micrographs of Al-Si/ZrSiO₄, Al-Si-5Sn/ZrSiO₄, Al-Si-10Sn/ZrSiO₄, Al-Si-5Bi/ZrSiO₄ and Al-Si-10Bi/ZrSiO₄ respectively. The rapidly solidified matrix alloy represents the equiaxed α -Al grains as illustrated in Fig. 6.44 (a–f) instead of dendritic morphology of the conventionally cast alloys.



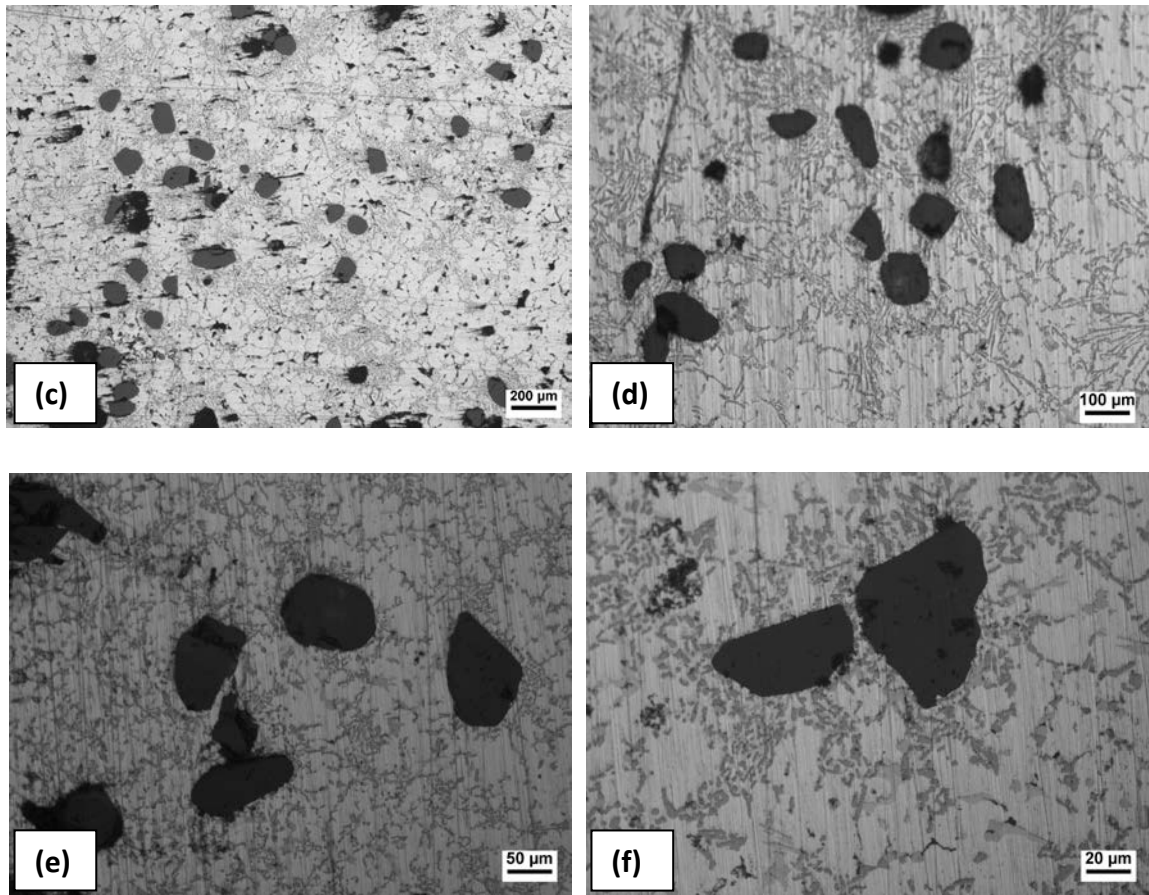


Figure 6.44: Optical micrographs of **(a)** Al-Si/ZrSiO₄, **(b)** Al-Si-5Sn/ZrSiO₄, **(c)** Al-Si-10Sn/ZrSiO₄, **(d)** Al-Si-5Bi/ZrSiO₄ and **(e, f)** Al-Si-10Bi/ZrSiO₄ composites having particulate size 63–90μm.

The particles are homogeneously distributed and well embedded throughout the prepared samples. Moreover, the spray forming process has led to the refined Si morphology. Therefore primary Si is not observed in any sample.

6.12 Wear characteristics

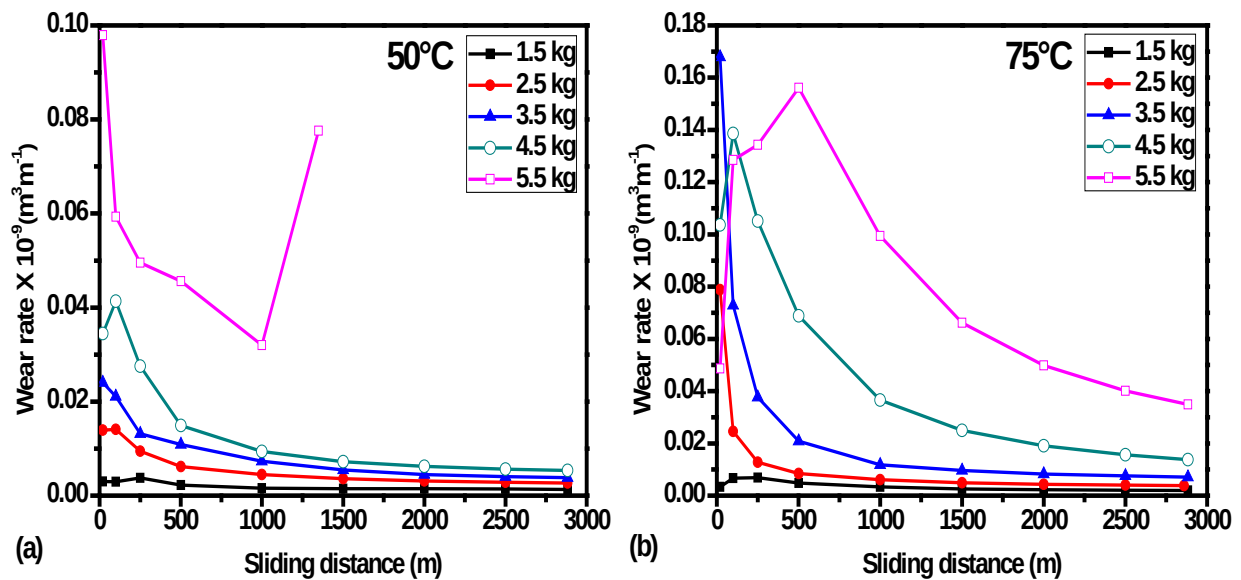
6.12.1 Wear rate vs. sliding distance

The variation in wear rate versus sliding distance for Al-Si/ZrSiO₄, Al-Si-5Sn/ZrSiO₄, Al-Si-10Sn/ZrSiO₄, Al-Si-5Bi/ZrSiO₄ and Al-Si-10Bi/ZrSiO₄ composites are illustrated in Fig. 6.45 to 6.49 respectively. Every specimen has been tested at four different temperatures. Wear rate at five different loads ranging from 1.5–5.5 kg has been complied for every temperature. The common trend found in all the wear rate curves shows that for each load there are two distinct types of wear rate depending upon the slope of the curve. The initial

higher slope is due to run-in wear indicating higher wear rate. However, with further sliding the slope of the curve diminishes representing steady state wear rate.

6.12.2 Effect of load

In general trend of the wear rate curve favors the Archard's law of adhesive wear [3] indicating an increase of wear rate with an increase in load. Figures 6.45 to 6.49 depict that the transition of mild to severe wear is delayed by incorporation of ZrSiO_4 sand and immiscible element (Sn, Bi) in the matrix alloy as compared to spray formed Al-Si alloy. Figure 6.45 (a) shows that for Al-Si/ ZrSiO_4 exhibits better wear resistance at 4.5 kg as compared to spray Al-Si alloy (Fig. 5.2 and 5.3). However, at 5.5 kg the pin has worn out suddenly after 1000 m sliding distance. This type of abrupt change in wear curve shows the delamination wear as stated by Suh [17]. Under normal and tangential load conditions the surface layers undergo cyclic deformation which causes nucleation of cracks and formation of voids at the junction of second phase particles. These cracks grow further parallel to the surface leading to plastic flow of the material which leads to detachment of surface in the form of long and thin wear debris.



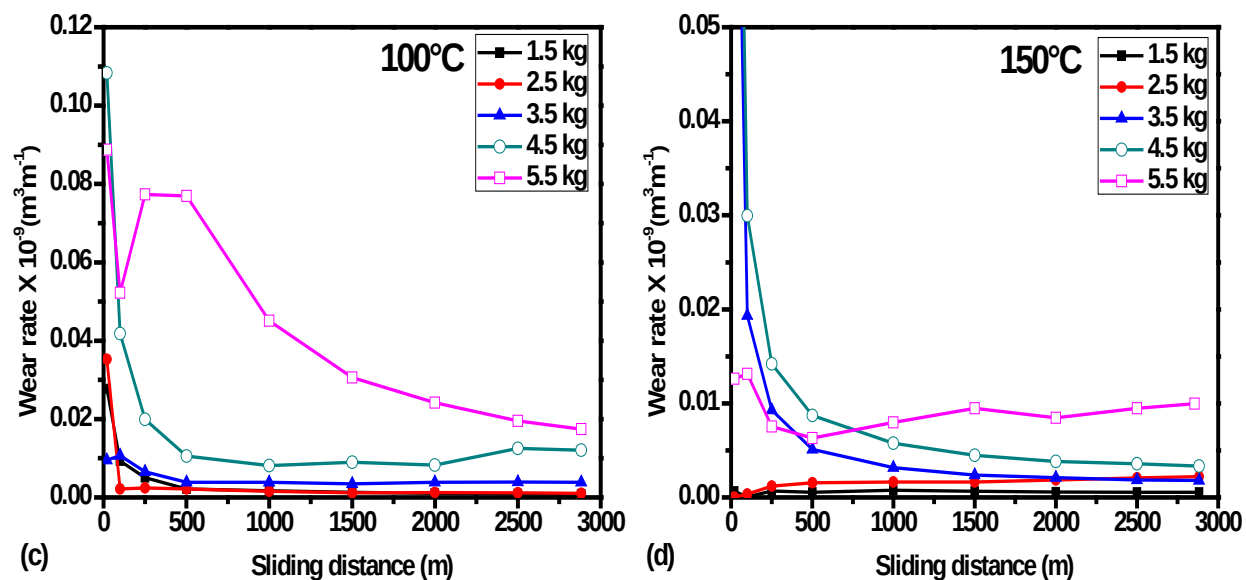


Figure 6.45: Wear rate of the spray formed Al-Si/ZrSiO₄ (63–90μm) composite under various loads at **(a)** 50 °C, **(b)** 75 °C, **(c)** 100 °C and **(d)** 150 °C temperature.

Figure 6.45 (b–d) shows that with rise in temperature the wear rate tries to get stabilize even at 5.5 kg load. The sliding distance covered to get steady state wear rate has been increased for 75 and 100 °C as shown in Fig 6.45 (b, c). However, the wear rate stabilizes easily at the highest temperature (Fig. 6.45 (d)).

An addition of 5 wt. % of Sn in the matrix alloy the wear rate become stable at every load and temperature as shown in Fig. 6.46 (a–d). The effect has been seen at 75 and 100 °C for 5.5 kg load (Fig. 6.46 (b, c)) where the steady state wear rate has been attained earlier. This indicates that Sn favors the earlier stabilization of the wear rate. However, at the highest temperature (Fig. 6.46 (d)) Sn is not effective in achieving the steady state wear rate earlier. As the temperature increases, more amount of Sn is leached out at the contact surface which is further smeared off at high loads. Therefore, an optimum amount of Sn is

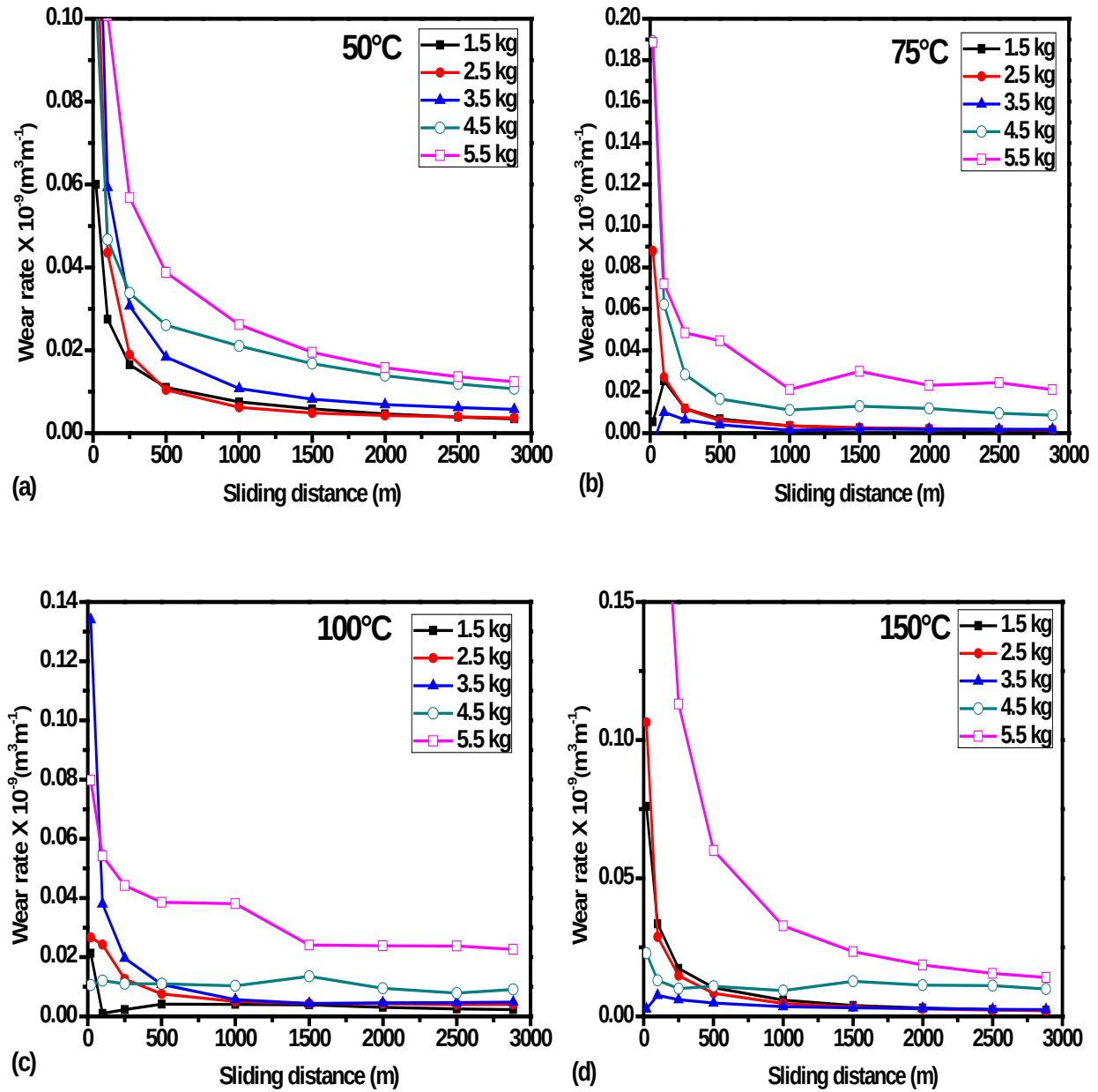


Figure 6.46: Wear rate of the spray formed Al-Si-5Sn/ZrSiO₄ (63–90 μm) composite under various loads at (a) 50 °C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

required to keep the lubricating film continuous [18, 19]. The composite poses much decreased wear rate with higher content of Sn (10 wt. %) in the matrix as shown in Fig. 6.47 (a–d). With the increase in the Sn content the lubricating film does not smear off with the rise in temperature and hence improves the wear resistance of the composite.

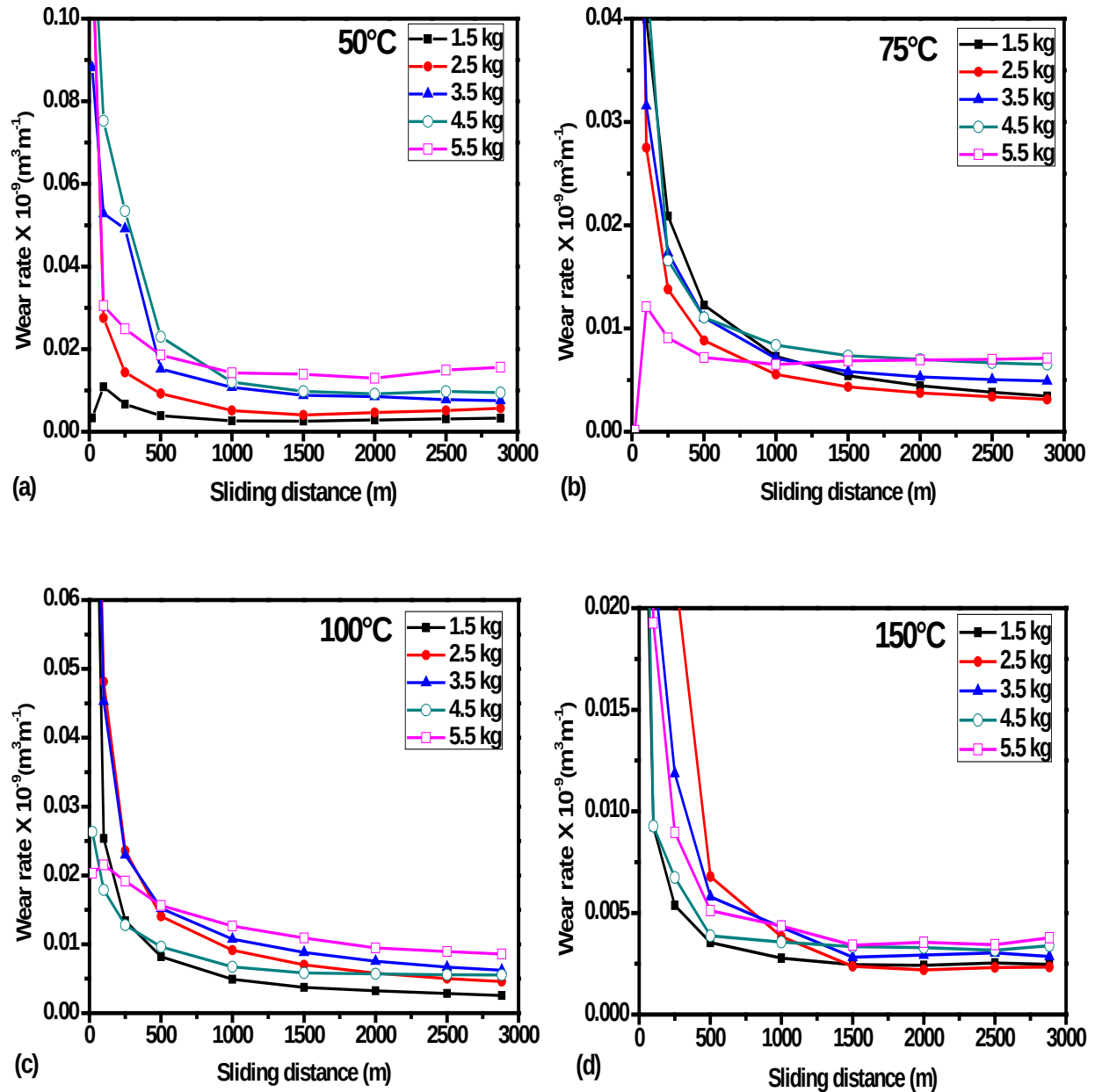


Figure 6.47: Wear rate of the spray formed Al-Si-10Sn/ZrSiO₄ (63–90 μm) composite under various loads at (a) 50 °C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

It has been observed in the previous chapter that 3.5 kg load acts as a critical transition load for spray formed Al-Si alloy. However, such transition is found to be delayed in spray formed composites at higher loads. Spray formed Al-Si-5Bi/ZrSiO₄ composite shows mild wear even at higher loads for 50 and 75 °C as illustrated in Fig. 6.48 (a, b).

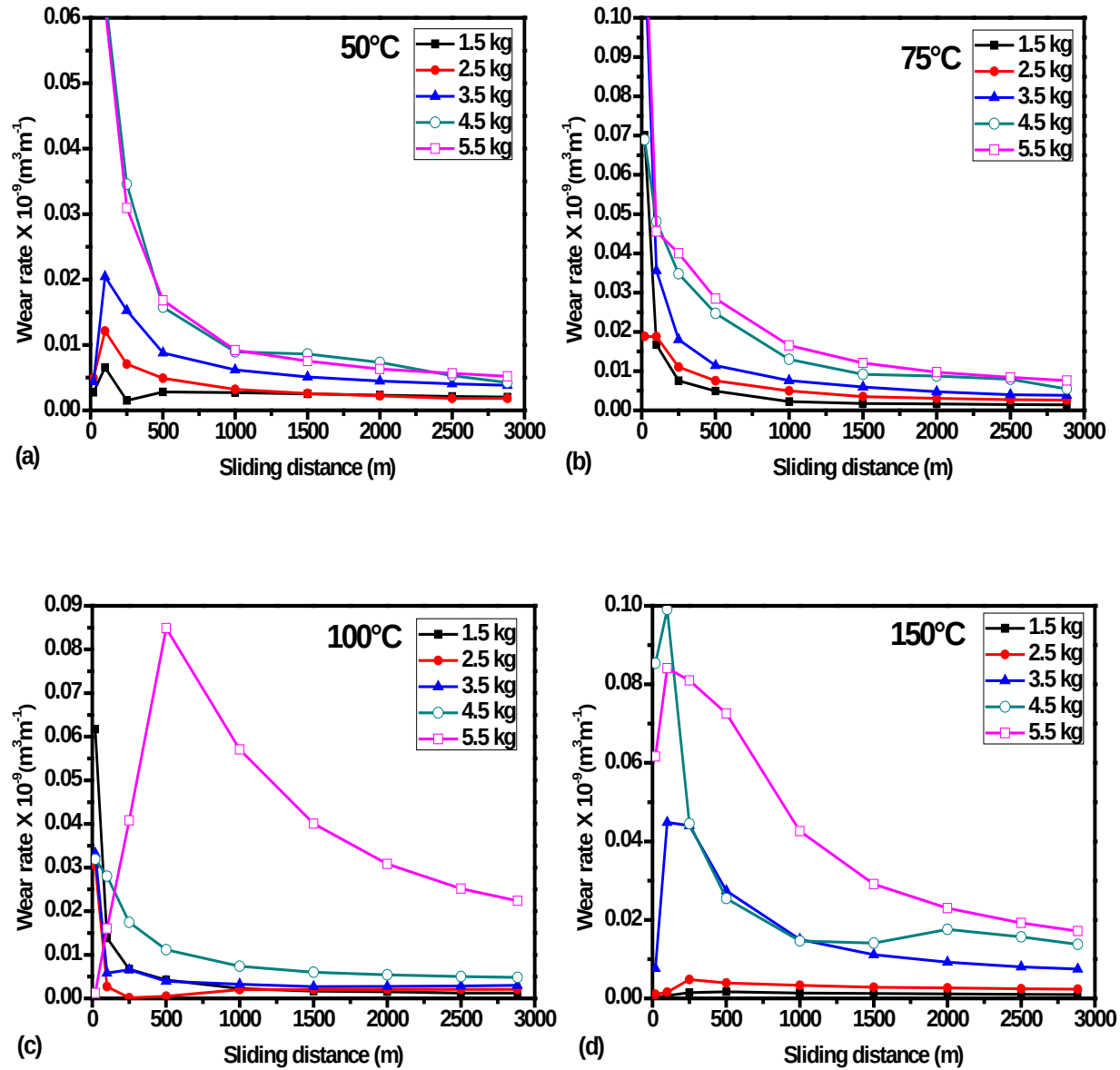


Figure 6.48: Wear rate of the spray formed Al-Si-5Bi/ZrSiO₄ (63–90 μm) composite under various loads at (a) 50 °C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

As the temperature increases (Fig. 6.48 (c)) the wear rate tries to get stabilize at 5.5 kg load and hence higher wear rate is observed. It can be predicted from such behavior that the sliding pin surface is being continuously removed under high load. Further, at 150 °C (Fig. 6.48 (d)) the wear rate shows the similar behavior as that for 4.5 kg load. At higher temperature, Bi does not play effective role in achieving the early steady state. The optimum amount of immiscible element is required which should not smeared off from the

surface at higher temperatures as discussed earlier [18, 20]. By increasing the amount of Bi to 10 wt. % in the matrix, the stabilization at the higher load has been achieved even at higher temperatures as shown in Fig. 6.49 (a-d).

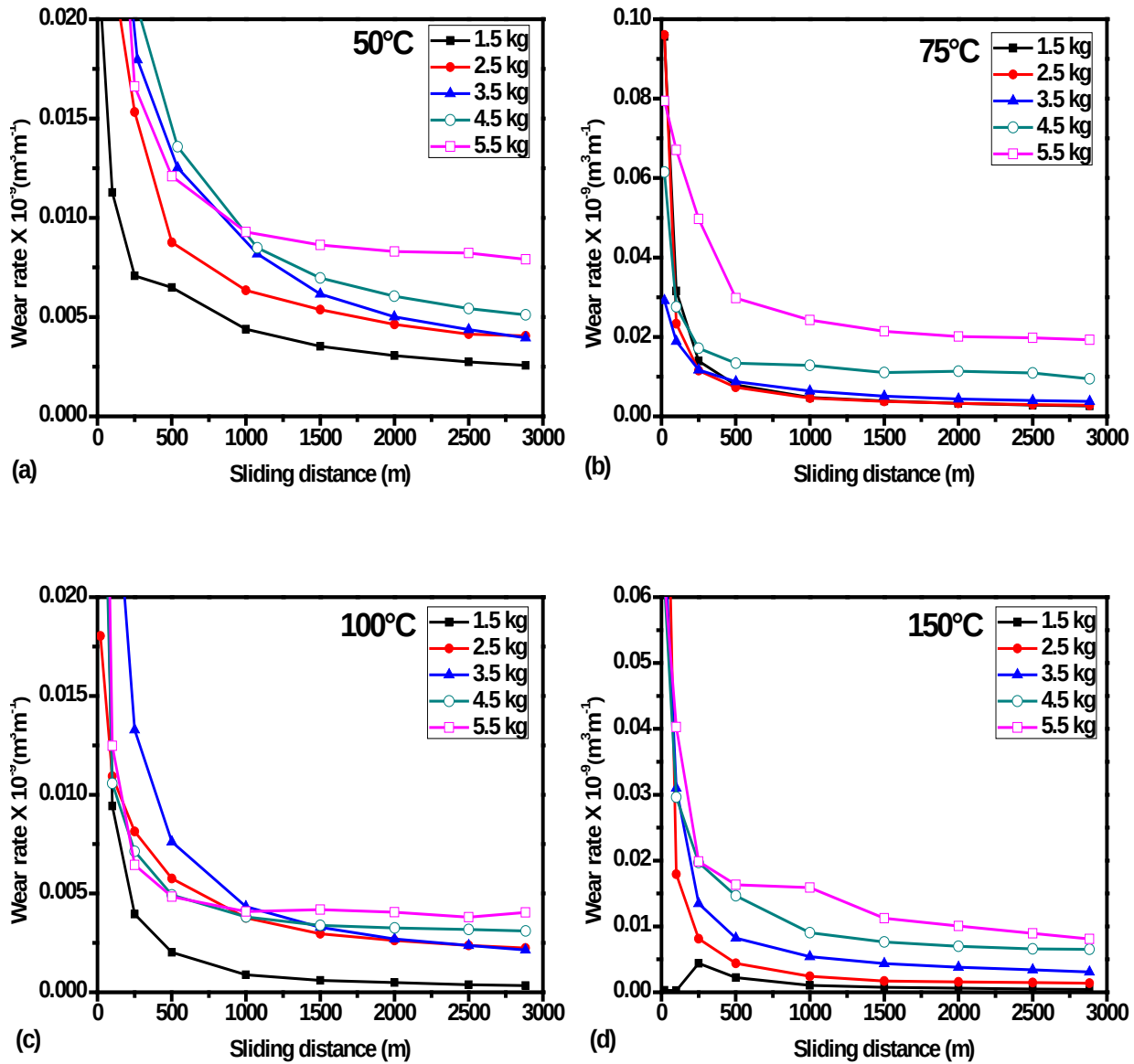
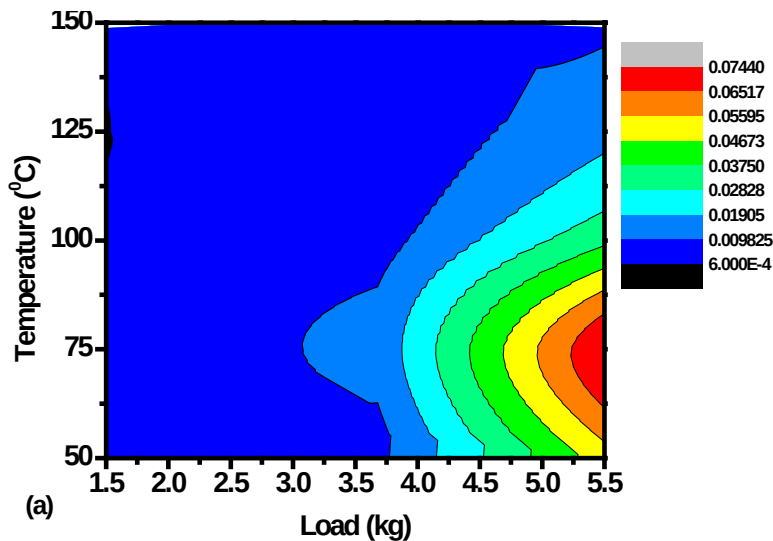
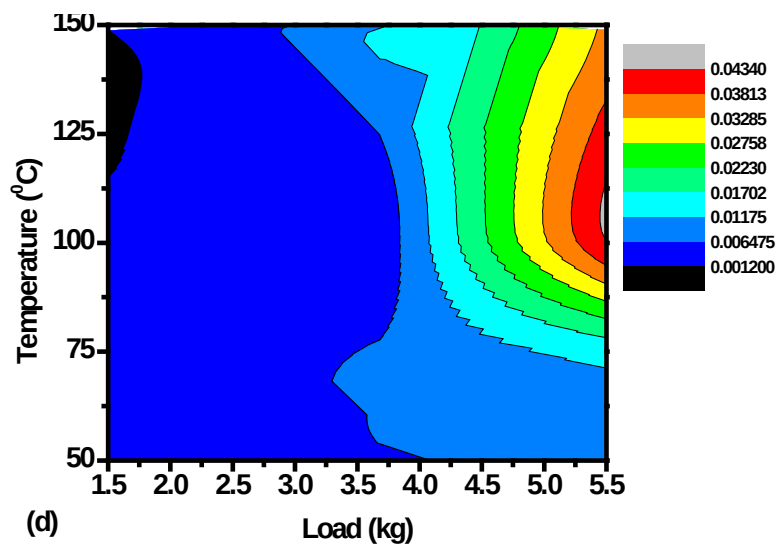
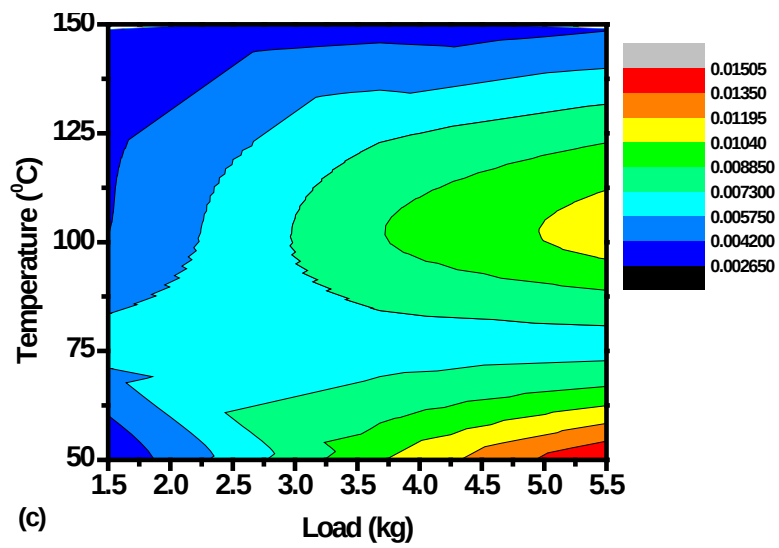
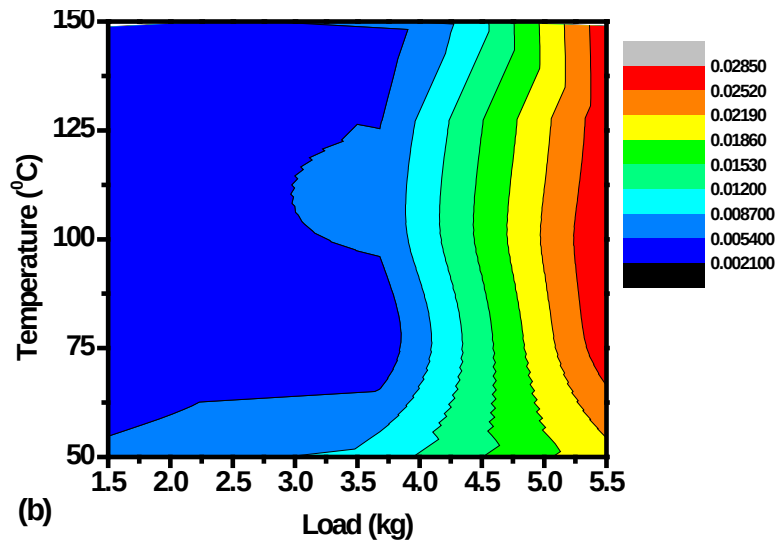


Figure 6.49: Wear rate of the spray formed Al-Si-10Bi/ZrSiO₄ (63–90 μm) composite under various loads at (a) 50 °C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

6.12.3 Effect of temperature

Average wear rate against various temperatures and applied loads for Al-Si/ZrSiO₄, Al-Si-5Sn/ZrSiO₄, Al-Si-10Sn/ZrSiO₄, Al-Si-5Bi/ZrSiO₄ and Al-Si-10Bi/ZrSiO₄ composites has been illustrated in Fig. 6.50 (a-e). The average of the wear rate has been calculated after the 500 m run for each load to ensure the presentation of the non-fluctuating wear regime. However, for severe wear average of fluctuating wear rate has been plotted. The load of 3.5 kg was the transition load for cast and spray formed Al-Si alloy as depicted from Fig 5.4 in the earlier chapter. On incorporation of ZrSiO₄ (63–90 μm) in the alloy, the wear transition only lies at higher load and lower temperature as shown in Fig. 6.50 (a). The wear contour depicts lower wear rate at the higher temperature region as compared to cast and spray formed Al-Si alloy. Therefore, temperature is the only factor which alters the wear mechanism at higher loads for Al-Si/ZrSiO₄ composite. Al-Si-5Sn/ZrSiO₄ (Figure 6.50 (b)) shows the similar transition behavior as that of alloy (Fig. 5.4) but with better wear rate. It indicates that Sn acts as solid lubricant at lower temperature, though at the higher temperature smearing off the lubricating film give rise to greater yet stabilized wear rate than Al-Si/ZrSiO₄ composite at higher temperature. The reduction in the wear rate is further achieved with the addition of 10 wt. % Sn in the matrix which enhances lubrication effect in the composite and gives rise to the better wear rate. Figure 6.50 (c) represents the wear contours of 10 wt. % of Sn and depicts that the wear is higher at 50 °C and 5.5 kg load and decreases with increase in temperature.





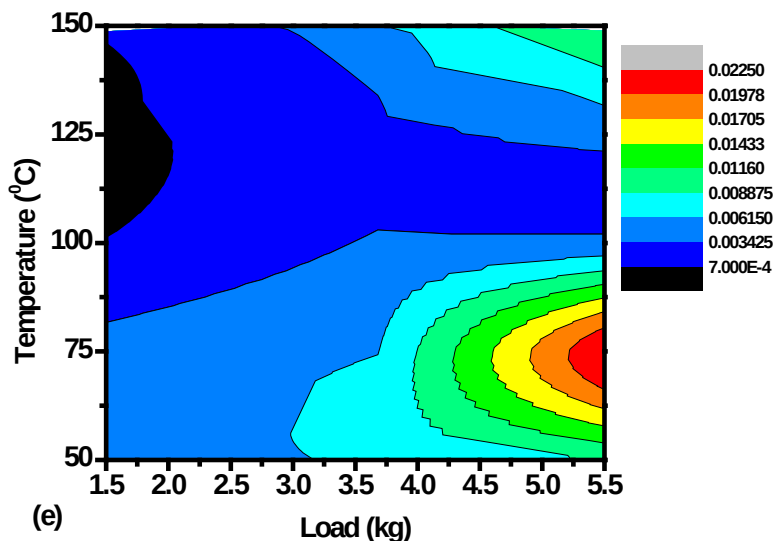


Figure 6.50: Averaged wear rate ($\times 10^{-9} \text{ m}^3\text{m}^{-1}$) against various temperatures and applied loads for **(a)** Al-Si/ZrSiO₄, **(b)** Al-Si-5Sn/ZrSiO₄, **(c)** Al-Si-10Sn/ZrSiO₄, **(d)** Al-Si-5Bi/ZrSiO₄ and **(e)** Al-Si-10Bi/ZrSiO₄ composite.

An addition of 5 wt. % Bi and ZrSiO₄ to the matrix the larger wear rate regime at higher loads shifted towards greater temperature region as shown in Fig. 6.50 (d). During dry sliding wear test Bi present in the matrix offers lubrication effect on the surface and helps in reducing the frictional force. The film further gets ruptured at higher temperature and pressure conditions. To enhance the effect of lubrication 10 wt. % Bi has been added in the matrix which shows that even at higher temperature composite exhibits good wear resistant (Fig. 6.50 (e)). Although the effect of these composite on wear resistant properties is comparable at lower loads yet at higher loads and higher temperature Al-Si-10Bi/ZrSiO₄ composite shows better results than Al-Si alloy. Similar effect has been studied by other researchers with increasing amount of Pb content in Al-10Si-3.5Cu alloy system. The improvement in wear resistance at higher pressure regime has been achieved with an increase in Pb content from 10 to 20% [7].

The comparative study of wear data can be further analyzed by plotting average wear rate with temperature at 150°C and 5.5 kg load conditions as shown in Fig. 6.51. It clearly shows that the Sn containing composites offer greater wear resistance than unreinforced and reinforced alloy at 50 and 75 °C. Also, with increase in the temperature at 100 and 150 °C the smearing off Sn from Al-Si-Sn/ZrSiO₄ composite leads to higher wear rate than

reinforced composite. However, further reduction in the wear rate at higher temperatures has been achieved with the enhanced amount of Sn in the composite.

The anomaly found at higher temperature is best understood by comparing the average wear rate of Bi containing composites at 5.5 kg test conditions as shown in Fig. 6.52. It clearly depicts that the composites offer better wear resistance even at higher temperature test conditions. Secondly, 5 wt. % Bi offers better wear results than 10 wt. % Bi at 50 and 75 °C. However, as the temperature is increased 10wt. % Bi offers greater resistance to wear than composite containing 5 wt. % Bi. At 100 and 150 °C temperature Bi get smeared off from Al-Si-5Bi/ZrSiO₄ composite leading to increased wear rate. However, further reduction in wear rate at higher temperatures has been achieved by enhancing Bi amount in the composite. The transition temperature for Al-Si-10Bi/ZrSiO₄ is found to be at 100 °C where it shows minimum wear rate which is 50 °C for Al-Si-5Bi/ZrSiO₄.

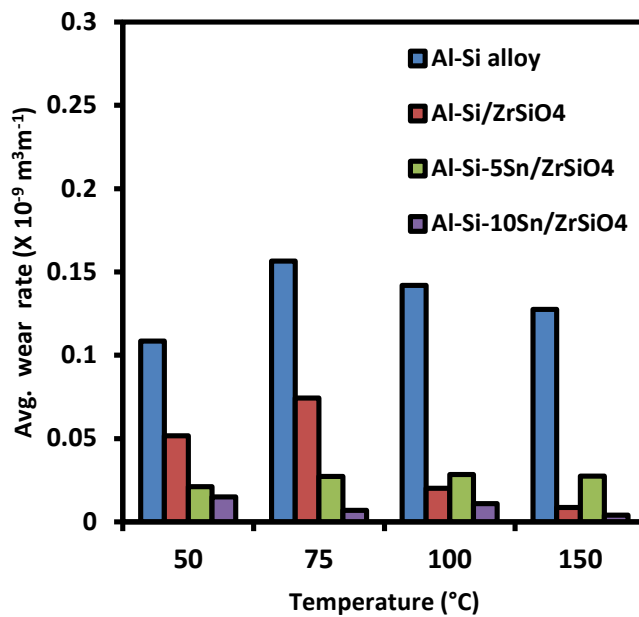


Figure 6.51: Average wear rate against various temperatures at 5.5 kg applied load for the prepared samples.

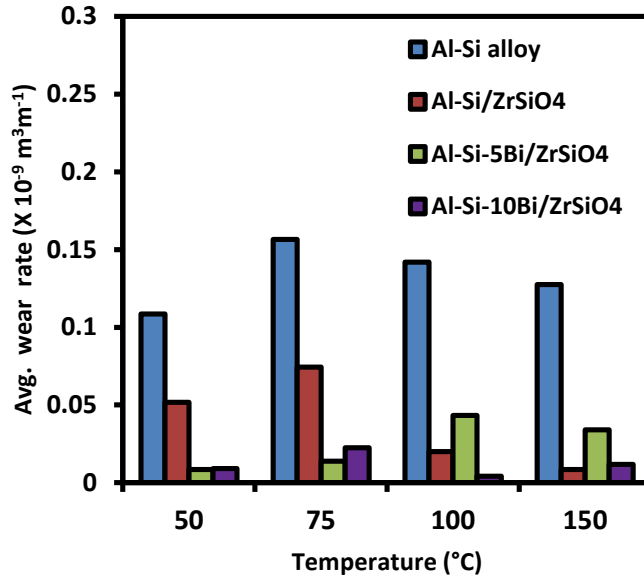


Figure 6.52: Average wear rate against various temperatures at 5.5 kg applied load for 63–90 µm particulate size prepared samples.

The average wear rate of Al-Si/ZrSiO₄, Al-Si-5Sn/ZrSiO₄, Al-Si-10Sn/ZrSiO₄, Al-Si-5Bi/ZrSiO₄ and Al-Si-10Bi/ZrSiO₄ composites are 8.61×10^{-12} , 2.74×10^{-11} , 3.94×10^{-12} , 3.39×10^{-11} and 1.18×10^{-11} m³m⁻¹ respectively. Al-Si-10Sn/ZrSiO₄ and Al-Si/ZrSiO₄ composites exhibit good wear resistance followed by Al-Si-10Bi/ZrSiO₄ at 5.5 kg load and 150 °C. Al-Si-5Sn/ZrSiO₄ and Al-Si-5Bi/ZrSiO₄ composites show minimum wear at 50 °C. Moreover, at 100 °C, Al-Si-10Bi/ZrSiO₄ composite offers higher wear resistance. On the other hand Al-Si-10Sn/ZrSiO₄ composite demonstrates good wear properties at 5.5 kg load irrespective to the temperature change.

6.12.4 Friction coefficient

Average friction coefficients of all the prepared samples at one of the three lower loads and the highest loads are given in Fig. 6.53 and 6.54. Figure 6.53 represents the variation of average friction coefficients for Al-Si/ZrSiO₄, Al-Si-5Sn/ZrSiO₄ and Al-Si-10Sn/ZrSiO₄ composites. It has been shown in Fig. 6.53 (a, b) that at 150 °C alloy and composite materials exhibit higher friction coefficient. The base Al-Si alloy shows steep rise in the friction coefficient as compared to lower temperatures. The reason behind this is the generation of frictional heating which gets further added to 150 °C environmental

temperature and causes a decrease in the strength of the material. Therefore large plastic deformation is introduced at the asperity contact at 150 °C as compared to the lower temperatures. Moreover, at higher temperature the low hardness of Al–Si alloy increases the real area of contact and hence greater friction coefficient is obtained. In metals friction coefficient is caused by adhesion and plowing only. Besides adhesion and plowing, particle reinforcement also plays an important role in total frictional force in composite materials [21]. Al–Si/ZrSiO₄ composite shows lower frictional coefficient at 50 and 75 °C than Al–Si alloy. However, as the temperature increases to 100 and 150 °C the matrix strength decreases as described above due to which the interfacial bonding between matrix and particle get loosen. Therefore, increased frictional coefficient at higher temperature has been obtained in Al–Si/ZrSiO₄ composite (Fig. 6.53 (a)).

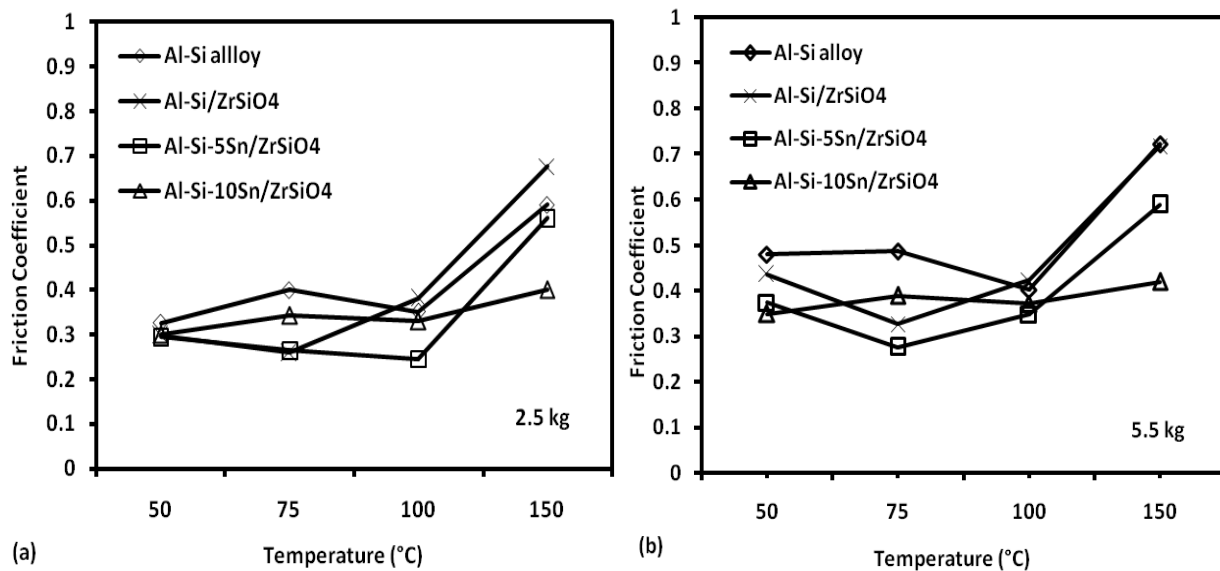


Figure 6.53: Variation of average friction coefficient with temperature at **(a)** 2.5 kg and **(b)** 5.5 kg load.

The composites containing immiscible element show lower friction coefficients as compared to unreinforced alloy at both lower and higher loads (Fig. 6.53 (a, b)). At higher load, the variation of the friction coefficient with temperature in Al–Si–5Sn/ZrSiO₄ is similar to Al–Si/ZrSiO₄ composite (Fig. 6.53 (b)) but with the lower values. Formation of lubricating Sn film over the sliding surface decreases the friction coefficients of Sn contained composites. However, this decrease is further dependable upon the stability and uniformity of the lubricating film. The higher amount of Sn gives higher probability of

stable and uniform lubricating film. Therefore Al-Si-10Sn/ZrSiO₄ composite shows lower frictional coefficients even at higher load and temperatures. Moreover, Al-Si-10Sn/ZrSiO₄ composite does not show much variation in the friction coefficients with temperature both at lower as well as at higher loads (Fig. 6.53 (a, b)).

The comparison of the friction coefficients at various temperatures for Al-Si alloy and Bi containing composites are shown in Fig. 6.54. At 2.5 kg load (Fig. 6.54 (a)) the friction coefficient for Al-Si-10Bi/ZrSiO₄ composite material is constant with respect to variation in temperature. However, it is found to increase for Al-Si-5Bi/ZrSiO₄ and spray formed alloy. The steep rise in friction coefficient has been found in Al-Si alloy at 150 °C. With an increase in load to 5.5 kg, the friction coefficient is different for different material as shown in Fig. 6.54 (b). The alloy show highest friction coefficient at all the temperatures on the contrary composite gives a lower value at 5.5 kg load. The change in the behavior has been found for Al-Si-10Bi/ZrSiO₄ composite which shows decrease in friction coefficient than Al-Si-5Bi/ZrSiO₄ at 100 °C. Wear rate data also depict the critical temperature 100 °C for Al-Si-10Bi/ZrSiO₄ related to the change in the wear mechanism. However, the friction coefficient of Al-Si-5Bi/ZrSiO₄ is increasing with increase in test temperature. Similar results of increased friction coefficient for composite have been found by L. Yao-hui et al. [20] for 12 vol. % Al₂O₃/Al-Si. The friction coefficient of Al-Si alloy increases suddenly at 150 °C owing to softening and plastic deformation of the alloy at this temperature.

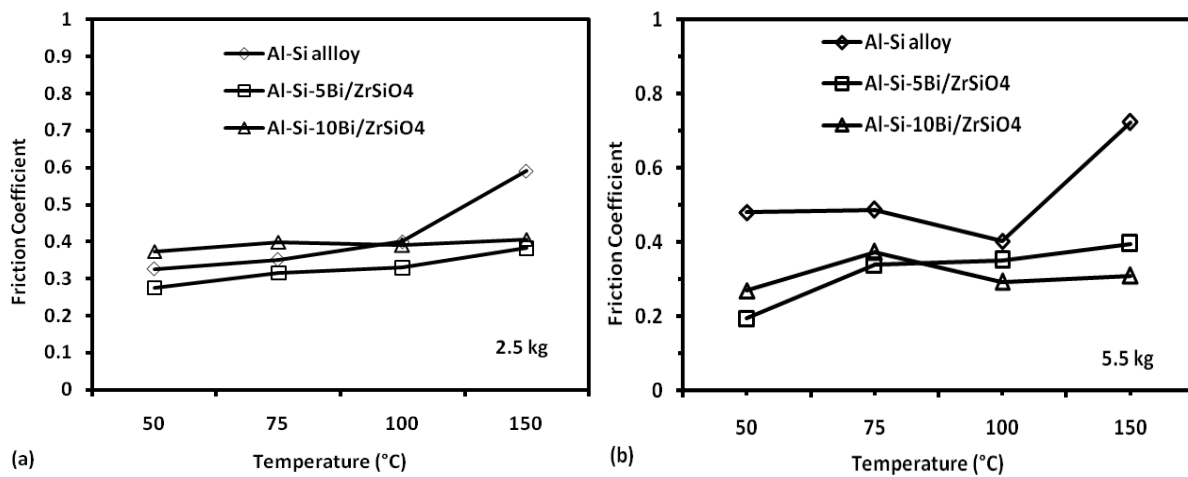


Figure 6.54: Variation of average friction coefficient with temperature at (a) 2.5 kg and (b) 5.5 kg load.

The friction coefficient does not show much change in Al-Si-10Bi/ZrSiO₄ with respect to temperature variation at lower load (Fig. 6.54 (a)). The contact characteristics of the tribosystem will change due to fracture of reinforcement. The complex mechanism of friction has been attributed to the force required to shear minute particles formed during rubbing surfaces over a soft surface. The real area of contact will decrease and so the adhesion between the counterparts gives rise to decrease in the friction coefficient. These abrading particles do behave like cutting tool resulting the formation of grooves and enhancing friction coefficient. Thus there is always a competition between these two phenomena which result in total friction coefficient. On the contrary, at higher load condition in self lubricating composite materials the soft matrix is worn out first and reinforcement protrude during successive sliding. The self lubricating film deposited over the surface overweighs the high friction coefficient due to hard reinforcing material. The self lubrication offered by matrix overcomes the minute particle abrasion that leads to decrease in friction coefficient. Moreover, with rise in temperature the effect of self lubricated Bi film gets deteriorated in Al-Si-5Bi/ZrSiO₄ as shown in Fig. 6.50 (d). This enhances the abrasion effect of minute particles and hence the friction coefficient. However, in Al-Si-10Bi/ZrSiO₄ due to the presence of large amount of Bi as lubricating substance the abrasion behavior of the fractured particles did not overcome at 100 and 150°C. The less friction coefficient at higher test temperature is attributed to the fact that the self-lubrication does not fail due to higher amount of Bi present in the matrix. Further the mode of mechanism acting at various test conditions can be better understood with the help of microstructural analysis of worn surfaces and collected debris.

6.13 Microstructural analysis of worn surfaces and wear debris

The microstructural features of the collected debris and worn surface help in predicting the wear mechanism. The SEM micrographs of the worn surfaces and wear debris are shown in Fig. 6.55 and 6.56 respectively. The micrographs of the worn surface also show lots of variation as revealed in Fig. 6.55. The deep grooves running parallel to sliding direction can be seen in Fig. 6.55 (a). The generation of plate like debris can also be observed from the subsequent sliding from Fig. 6.55 (b) at 50 °C. However, the worn surface at 150 °C appeared to have shallow grooves and white patches indicating small debris has been

detached from them which got compacted between sliding surfaces. A completely different wear mechanism is acting at both the conditions which give rise to difference in wear rate. Figure 6.56 (a) represents the plate like morphology of the wear debris leading higher wear as depicted earlier in Fig. 6.45 (a). However, at 150 °C two types of morphological features of the wear debris have been observed as shown in Fig. 6.56 (b, c). Firstly, the plate like debris which has a large aspect ratio seemed to be generated during the initial run in wear (highlighted as 1 in Fig. 6.56 (c)).

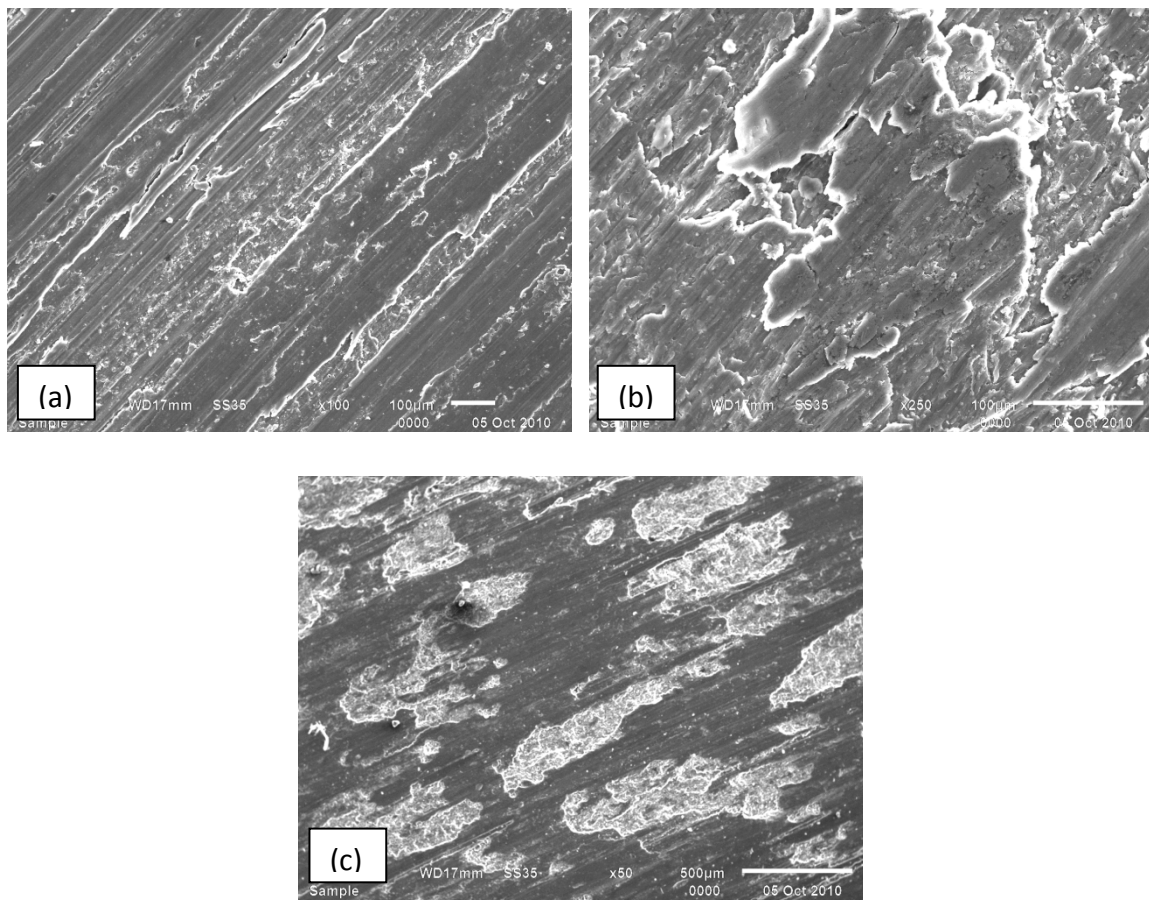


Figure 6.55: SEM micrograph of worn surfaces of Al-Si/ZrSiO₄ (63–90μm) composite under 5.5 kg load at **(a, b)** 50 °C and **(c)** 150 °C.

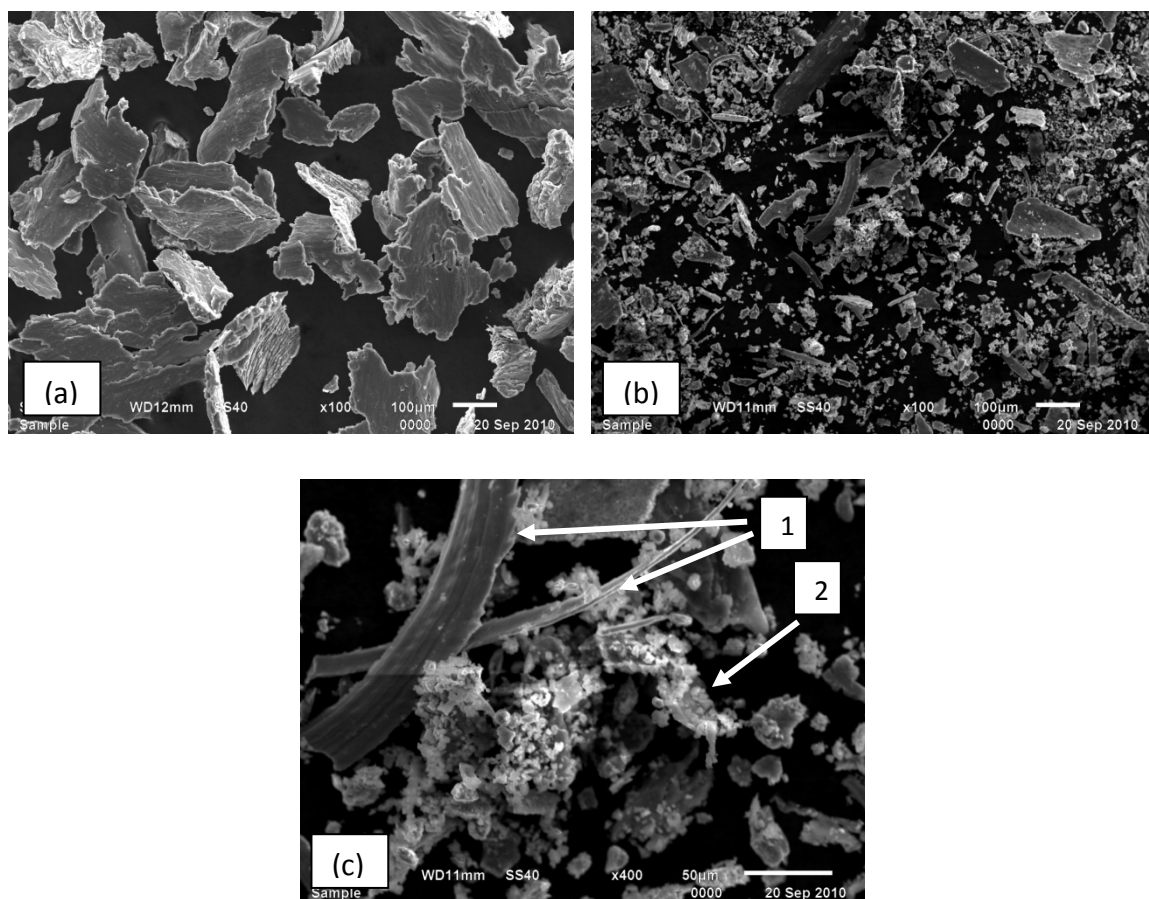


Figure 6.56: SEM micrograph of wear debris of Al-Si/ZrSiO₄ (63–90µm) composite under 5.5 kg load at **(a)** 50°C and **(b, c)** 150 °C.

Secondly, highlighted with arrow 2 in Fig. 6.56 (c) are smaller sized, rounded and rugged debris. These appeared to be created during steady state wear. The round shape of the debris depicts that along with adhesive wear, the oxidative wear mechanism is also acting which lead to enhancement in the wear resistance of the material. Thus, it can be deduced from all the results that wear is changing from delamination to adhesive-cum-oxidative mode with increase in temperature at higher load in Al-Si/ZrSiO₄ composite.

The micrographs of worn surface and wear debris of Al-Si-5Sn/ZrSiO₄ composite are shown in Fig. 6.57 and 6.58 respectively. The wear tracks as shown in Fig. 6.57 (a) shows the continuous lubricating Sn film over the entire surface which gets ruptured at higher temperature as shown in Fig. 6.57 (b, c). The smaller debris of size 10–60 µm (Figure 6.58 (a)) has been found at 50 °C as compared to long debris at 150 °C temperature (Fig. 6.58 (b)) at 5.5 kg load. Although, wear rate is found to be little increased from 50 °C to 150 °C

which is 2.103 and $2.742 \times 10^{-11} \text{ m}^3\text{m}^{-1}$ respectively. It again verifies the discontinuous lubricating film at higher temperature as described in the earlier section.

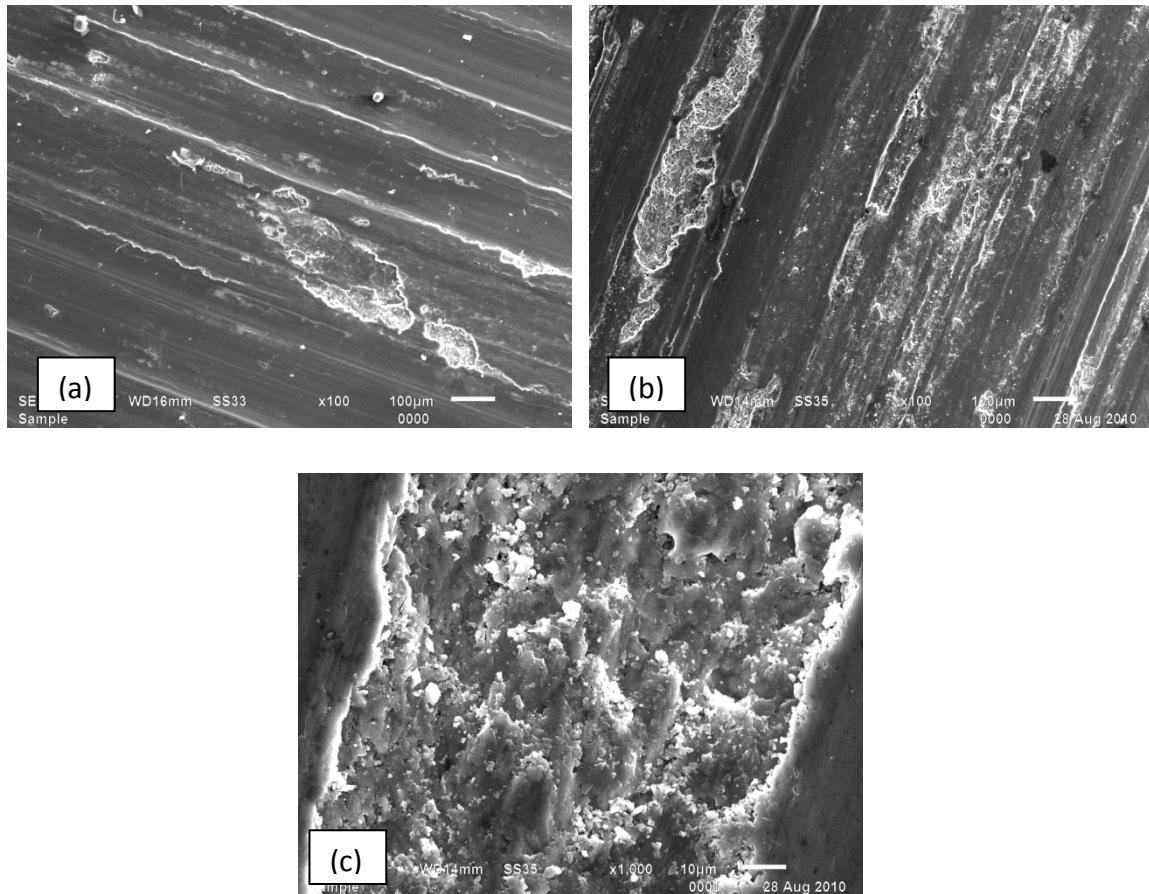


Figure 6.57: SEM micrograph of worn surfaces of Al-Si-5Sn/ZrSiO₄ (63–90μm) composite under 5.5 kg load at **(a)** 50°C and **(b, c)** 150°C.

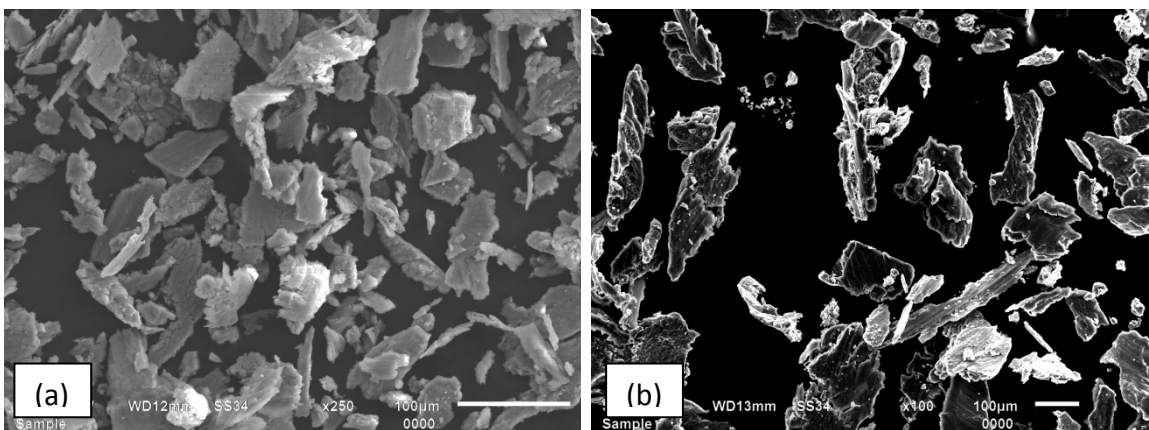


Figure 6.58: SEM micrograph of wear debris of Al-Si-5Sn/ZrSiO₄ (63–90μm) composite under 5.5 kg load at **(a)** 50 °C and **(b)** 150 °C.

Figures 6.59 and 6.60 show the worn surfaces and wear debris micrographs of Al-Si-10Sn/ZrSiO₄ composite respectively. The pin surface shows the similar morphology of white patches along grooves irrespective of the temperature difference as illustrated in Fig. 6.59 (a, b). The continuous lubricating film is also observed over the entire surface. Figure 6.60 (a, c) shows very fine debris collected at 50 °C and 150 °C temperature at 5.5 kg load. Higher magnification of the debris as shown in Fig. 6.60 (b, d) revealed that coagulated round debris have size less than 5 μm. The presence of MML is indicated by the surface and debris morphology. This confirms that the stability of the lubricating film continues up to a higher applied load and temperature in Al-Si-10Sn/ZrSiO₄ composite.

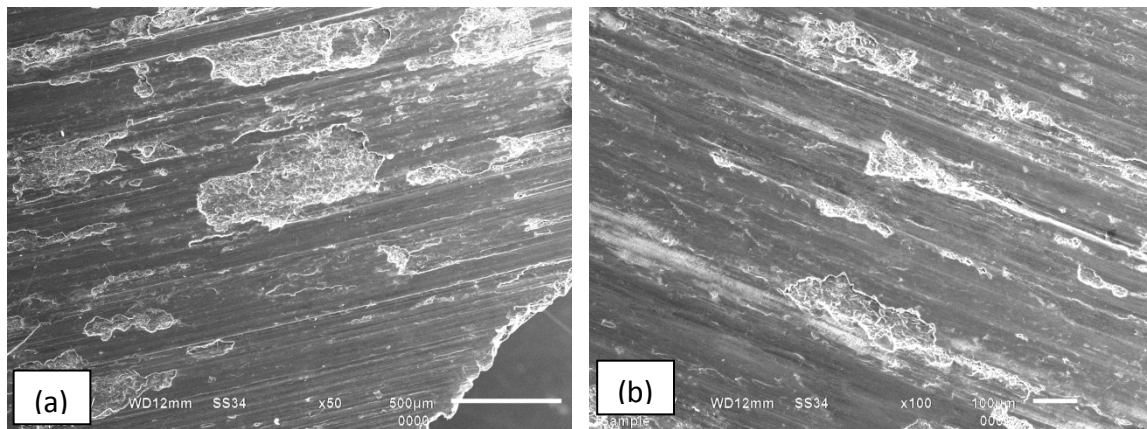
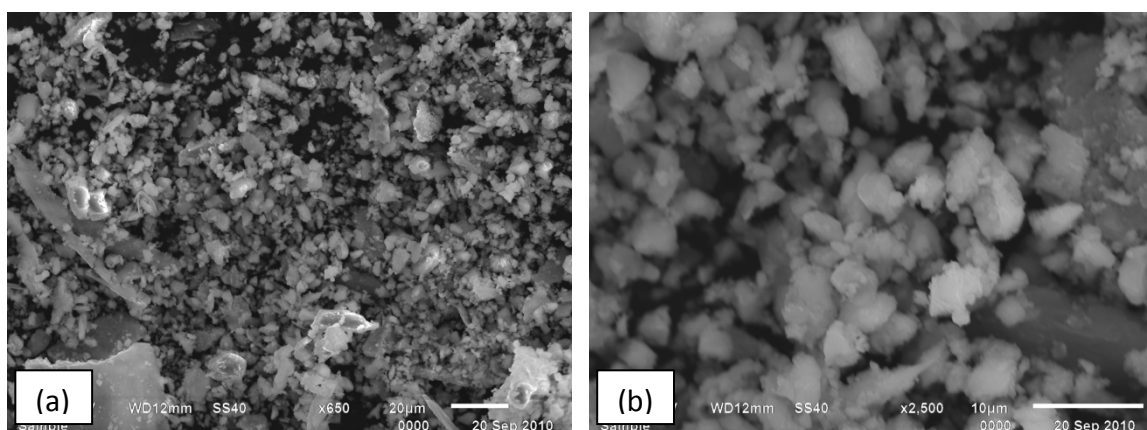


Figure 6.59: SEM micrograph of worn surface of Al-Si-10Sn/ZrSiO₄ (63–90μm) composite under 5.5 kg load at (a) 50°C and (b) 150 °C.



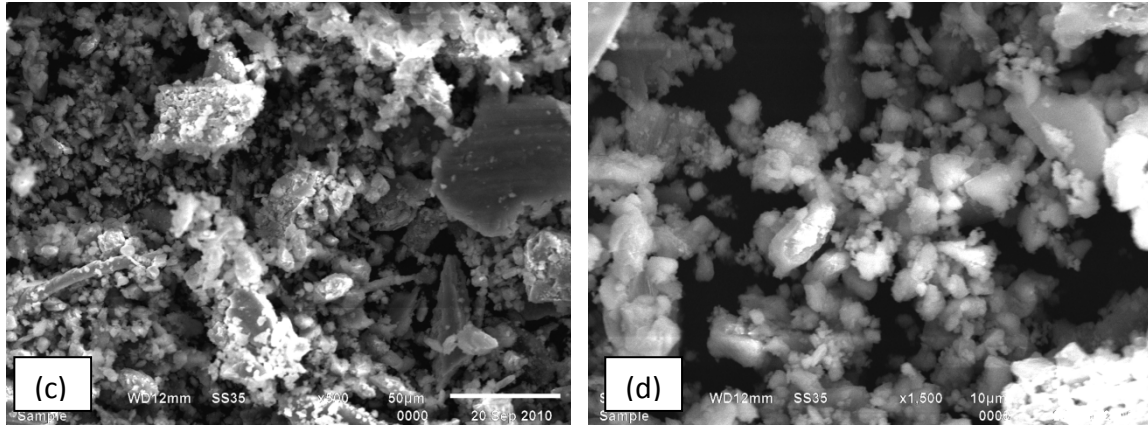


Figure 6.60: SEM micrograph of wear debris of Al-Si-10Sn/ZrSiO₄ (63–90μm) composite under 5.5 kg load at **(a, b)** 50 °C and **(c, d)** 150 °C.

The worn pin surfaces at both lower and higher temperatures of Al-Si-5Bi/ZrSiO₄ composite can be seen in Fig. 6.61. Figure 6.61 (a) shows continuous grooving marks on the surface of the pin that give rise to small debris. However, the repetitive shear wedge can be seen at 150 °C as shown in Fig. 6.61 (b). The wear debris of Al-Si-5Bi/ZrSiO₄ composite is shown in Fig. 6.62. At lower temperature both small (up to 10 μm) and long debris can be seen as shown in Fig. 6.62 (a) whereas at higher temperature large debris is generated (Fig. 6.62 (b)). This is analogous to the wear rate results found as per Fig. 6.48 (a, d).

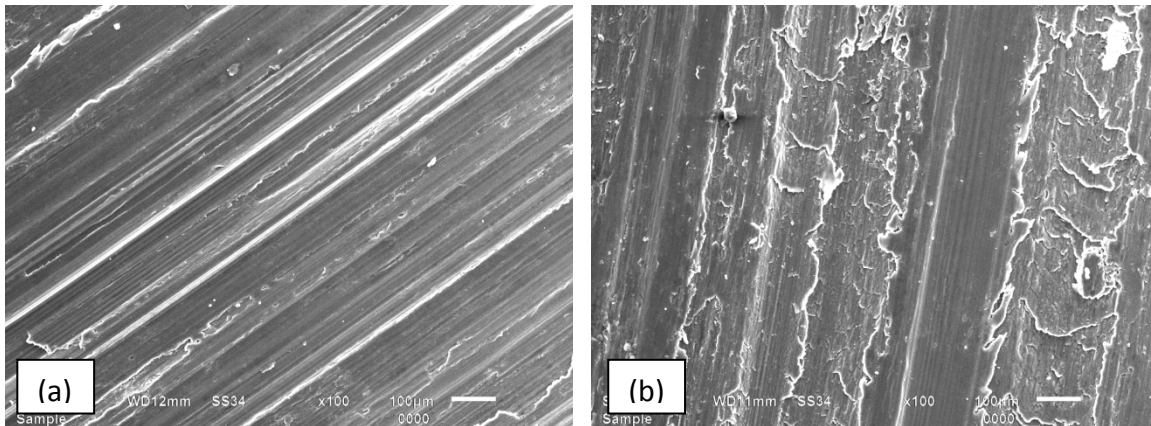


Figure 6.61: SEM micrographs of worn surfaces of Al-Si-5Bi/ZrSiO₄ (63–90 μm) composite under 5.5 kg load **(a)** 50 °C and **(b)** 150 °C.

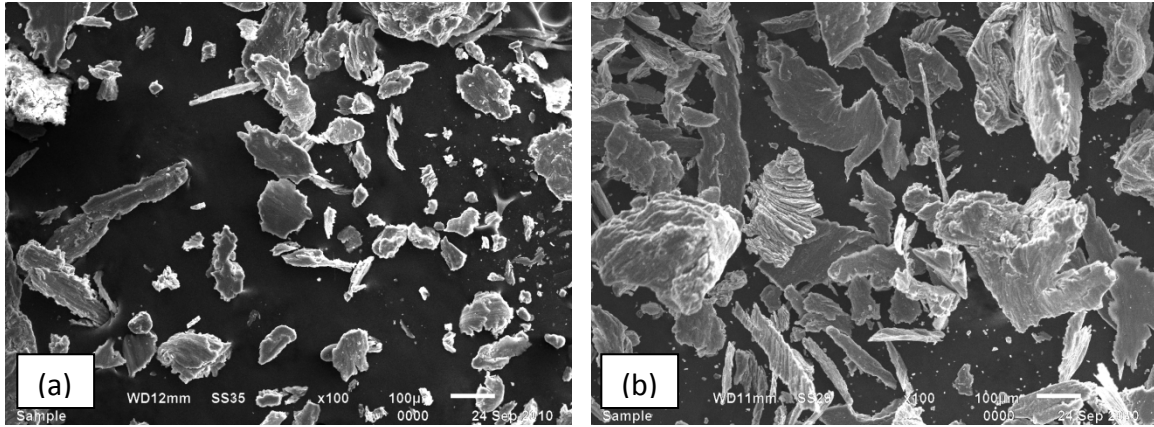
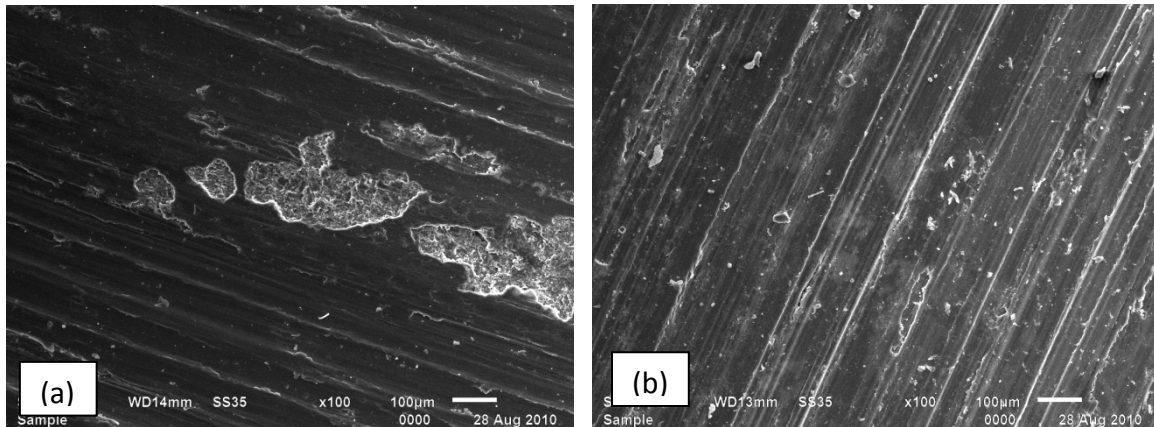


Figure 6.62: SEM micrographs of wear debris of Al-Si-5Bi/ZrSiO₄ (63–90 μm) composite under 5.5 kg load at **(a)** 50 °C and **(b)** 150 °C.

SEM micrographs of worn surface and wear debris of Al-Si-10Bi/ZrSiO₄ under 5.5 kg load generated at 50 °C and 150 °C are shown in Fig. 6.63 and 6.64 respectively. A continuous film can be seen over the worn pin surface of Al-Si-10Bi/ZrSiO₄ composite (Fig. 6.63). The morphological analysis of wear debris (Fig. 6.64) shows the mild metallic wear along with small oxidative wear on addition of 10 wt. % Bi irrespective of the temperature change.



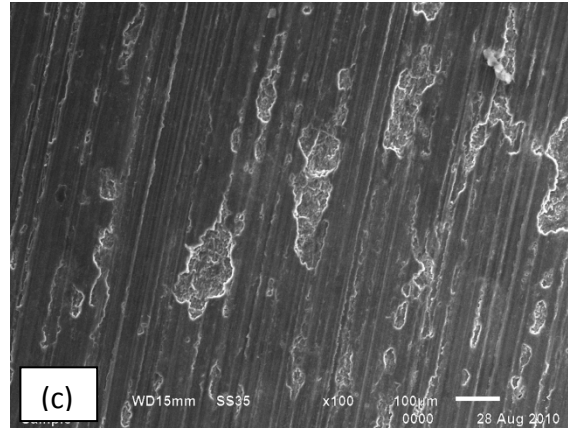


Figure 6.63: SEM micrographs of worn surfaces of Al-Si-10Bi/ZrSiO₄ (63–90 µm) composite under 5.5 kg load at **(a, b)** 50 °C and **(c)** 150 °C.

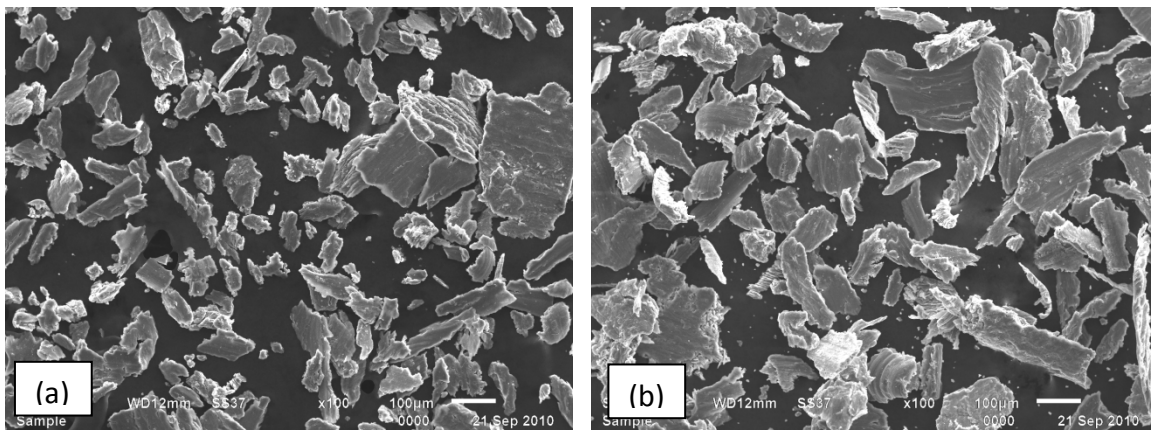


Figure 6.64: SEM micrographs of wear debris of Al-Si-10Bi/ZrSiO₄ (63–90 µm) composite under 5.5 kg load at **(a)** 50 °C and **(b)** 150 °C.

The EDS analysis of the wear debris for both Al-Si/ZrSiO₄ and Al-Si-10Sn/ZrSiO₄ composites are shown in Fig. 6.65 and 6.66 respectively. For both the EDS confirms the presence of oxygen and iron in the debris. It further confirms the presence of oxidative wear prevailing at higher temperature in zircon reinforced composite. The presence of iron also indicates the transfer of the material from counterface. The presence of high amount of Sn in the wear debris (Fig. 6.66) shows the optimum presence of lubrication on the surface giving rise to higher wear resistance offered by Al-Si-10Sn/ZrSiO₄. The EDS of wear debris (Fig. 6.67) shows the presence of Al and Si as major peaks indicating mild metallic wear up to 150 °C at 5.5 kg test conditions in Al-Si-5Bi/ZrSiO₄ composite.

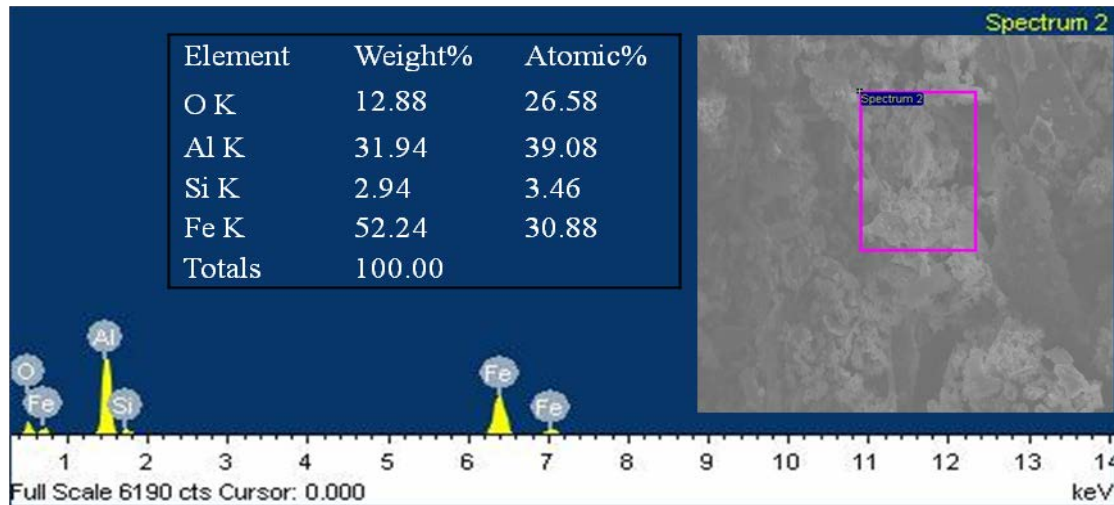


Figure 6.65: EDS profile and SEM micrograph of wear debris of spray formed Al-Si/ZrSiO₄ (63–90 μm) composite at 5.5 kg applied load and 150°C temperature.

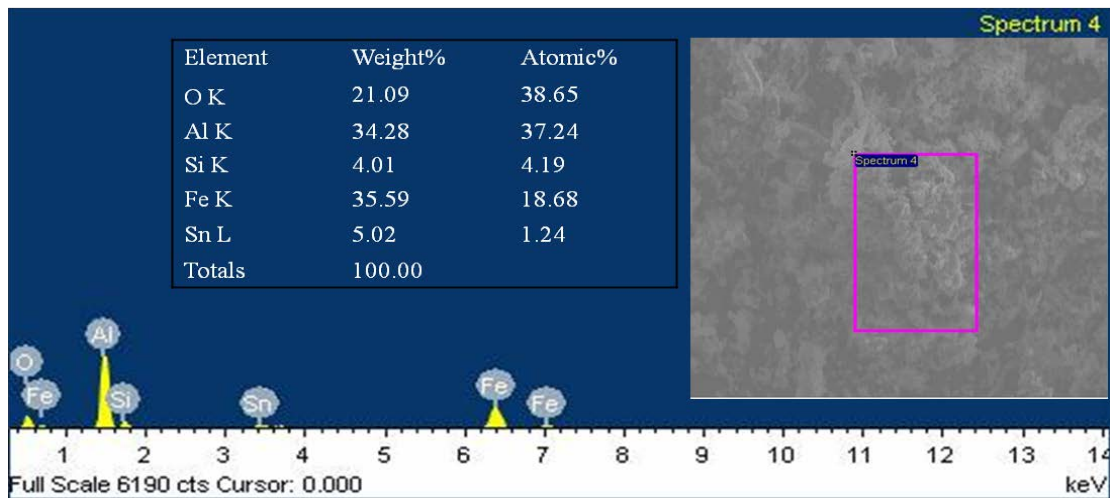


Figure 6.66: EDS profile and SEM micrograph of wear debris of spray formed Al-Si-10Sn/ZrSiO₄ (63–90 μm) composite at 5.5 kg applied load and 50°C temperature.

The composite containing reinforcing particles are successfully resisting the penetration and cutting of the soft surface. These are not cut by the slider due to their larger size and higher hardness. The particles protruding from the surface of the composite bear most of the wear load [22]. Thus, the wear mechanism under the sliding wear testing conditions is grinding instead of cutting for the composites containing large particles [23]. This grinding mechanism which also consists of transfer of material from counterface material give rise to mechanically mixed oxidative layer. This layer further helps in reducing the wear of

materials. The presence of such layer has been indicated by the worn pin surfaces (Figs. 6.55 (c), 6.57, 6.59, 6.63) of the composite material. Further enhancement in the wear resistance property is achieved by introducing solid lubrication effect (Sn, Bi) in the matrix that gave rise to decreased wear rate.

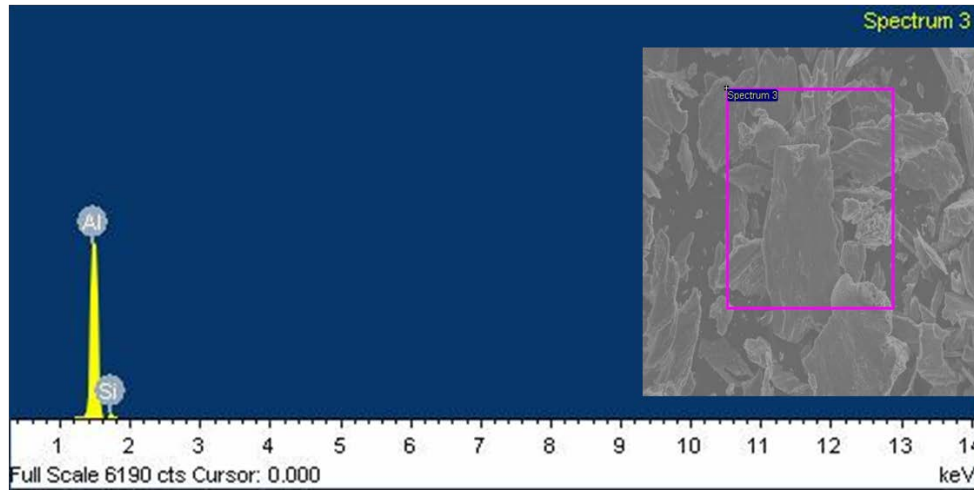


Figure 6.67: EDS profile and SEM micrograph of wear debris of spray formed Al-Si-5Bi/ZrSiO₄ (63–90 μm) composite at 5.5 kg applied load and 150°C temperature.

6.14 Comparative wear behavior according to the particulate size

Al-Si/ ZrSiO₄ (63–90 μm) offers higher wear resistance at extreme conditions than Al-Si/ZrSiO₄ (106–125 μm). On the other hand, bigger particulate size offers good wear resistance at 50°C and higher wear rate regime lies around only 75°C. In smaller particulate size at 50°C and 5.5 kg load higher wear regime lies. The composites containing less amount of immiscible elements irrespective to the particulate size show the severe wear at higher load conditions except Al-Si-5Sn/ZrSiO₄ (106–125 μm) which show stable and lower wear rate of $9.15 \times 10^{-12} \text{ m}^3\text{m}^{-1}$ at higher load and temperature conditions. Al-Si-10Sn/ZrSiO₄ (106–125 μm) composite offers stable wear rate at higher load irrespective to the temperature variation. However, Al-Si-10Sn/ZrSiO₄ (63–90 μm) composite exhibits higher wear resistance at extreme test conditions (5.5 kg load and 150 °C). Therefore, bigger sized zircon sand reinforcement and higher Sn containing composites offer stable wear rate with variation in temperature than smaller sized. In Bi containing composites, there is not much difference in wear rate behavior of smaller and bigger sized zircon sand

particulates. However, the temperature regime for higher and stable wear resistance lies at 100 and 150 °C whereas in smaller sized it is at 75 and 100 °C.

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RESULTS AND DISCUSSION

(SILICON CARBIDE SERIES)

Overview

In this chapter, the experimental results of silicon carbide (SiC) reinforced composites are presented. This chapter is also subdivided in two parts on the basis of the size range of SiC particulates. The SiC reinforced composites have been prepared by spray deposition process where immiscible element Sn and Bi in varying quantity is added to achieve denser product. The prepared samples were analyzed microscopically and also wear tests at four different temperatures and five different loads have been done. The characterization of the prepared samples has been done by XRD (X-Ray Diffraction), SEM (Scanning Electron Microscope), EDS (Energy dispersive spectrometer). The microstructural analysis of worn surfaces and wear debris has been done to predict the mode of wear in various tested specimens.

7.1 Introduction

The chapter comprises of two sections in which the first section contains the results of AMC reinforced with SiC particulates of size range 106–125 μm . In the second section, AMC reinforced with SiC particulates having particulate size 63–90 μm is described.

Effect of SiC reinforcement of particulate size 106–125 μm

7.2 Samples prepared

In this section, the results of spray formed near eutectic Al–Si alloy reinforced with silicon carbide (SiC) with particulate size 106–125 μm is discussed. In the entire composition the amount of reinforced SiC is kept constant i.e. 8 vol. %. Moreover, the addition of immiscible elements in amounts of 5 and 10 wt. % is incorporated to provide the solid lubricant effect in the composites. The immiscible element in the matrix also helps in reducing the porosity and enhances the wear properties. The composition of spray formed samples is as follow:

1. Al–Si/SiC (106–125 μm)
2. Al–Si–5Sn/SiC (106–125 μm)
3. Al–Si–10Sn/SiC (106–125 μm)
4. Al–Si–5Bi/SiC (106–125 μm)
5. Al–Si–10Bi/SiC (106–125 μm)

7.3 X-ray diffraction analysis

Figure 7.1 shows the XRD pattern of spray formed Al–Si/SiC, Al–Si–5Sn/SiC, Al–Si–10Sn/SiC, Al–Si–5Bi/SiC and Al–Si–10Bi/SiC composites respectively. The data collected is matched with the reference peaks of Al (ICDD card no. 03–065–2869), Si (ICDD card no. 01–077–2109), Sn (ICDD card no. 00–004–0673), Bi (ICDD card no. 01–089–2387) and SiC (ICDD card no. 01–089–2224) which clearly depicts their presence in the material. The peak intensity of Sn in Al–Si–10Sn/SiC is greater as compared to the Al–Si–5Sn/SiC due to higher amount of Sn addition in the composite. Similarly, it has been found that the peak intensity of Bi increases with increase in the Bi content from 5 to 10 wt. %.

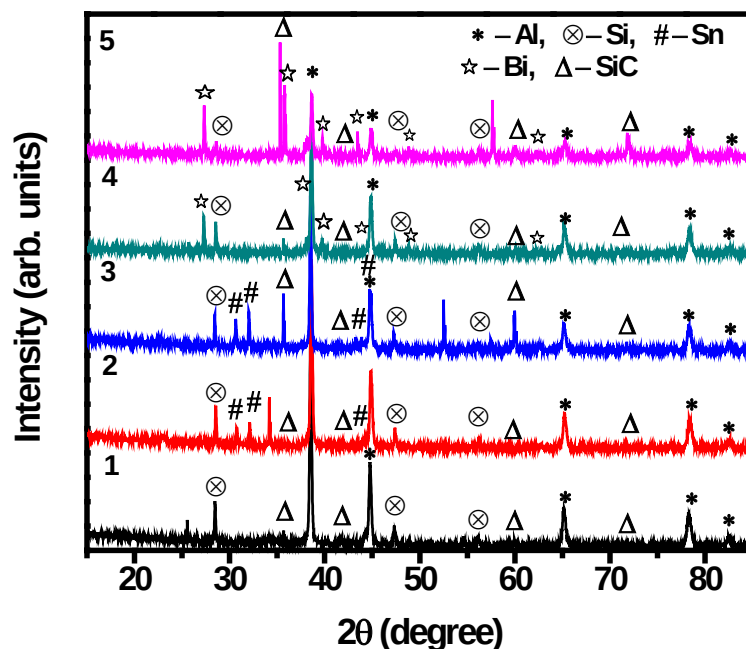


Figure 7.1: XRD pattern of **(1)** Al-Si/SiC, **(2)** Al-Si-5Sn/SiC, **(3)** Al-Si-10Sn/SiC, **(4)** Al-Si-5Bi/SiC and **(5)** Al-Si-10Bi/SiC composites.

7.4 Hardness

The hardness was measured on B-scale of Rockwell hardness tester for spray formed Al-Si alloy and its composites. Figure 7.2 shows the variation of average hardness of the base alloy with the prepared composites. The embedment of SiC particles increases the hardness of Al-Si/SiC composite. The hardness of the composite depends upon the hardness of embedded particle, matrix phase and their interfacial bonding. On addition of 5% and 10% Sn, the hardness further increases to 36.9HRB and 37.2HRB respectively. During spray forming immiscible element is distributed within the grains and along the grain boundary of Al-matrix. Moreover, Sn is working as a modifier of microstructure as Si needles transforms to globular with Sn addition. On incorporation of SiC particles and immiscible Bi in the matrix, the hardness is found to increase drastically. Small amount of porosity is always associated with the spray deposition process. The low melting point constituents Bi tries to fill these pores during preform solidification which ultimately increases the hardness of the material. Moreover, the microstructure refinement of Al-Si alloy with Bi and by the spray deposition process also contributes to the enhanced hardness of the composites.

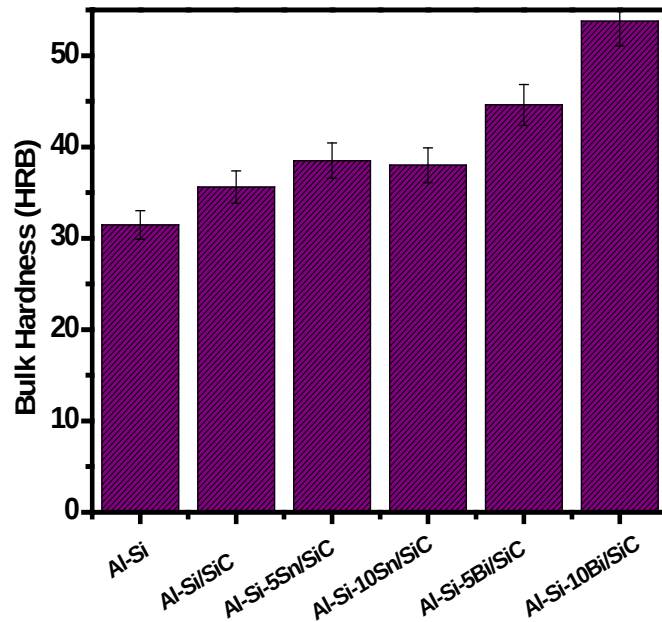


Figure 7.2: Bulk harness of Al-Si composite reinforced with SiC of particulate size 106–125 μ m.

7.5 Microstructural analysis

The microstructure of Al-Si/SiC, Al-Si-5Sn/SiC, Al-Si-10Sn/SiC Al-Si-5Bi/SiC and Al-Si-10Bi/SiC composites processed by spray forming technique is shown in Fig. 7.3 (a–e). The matrix alloy shows the equiaxed morphology of α -Al grains in which SiC particles of size range 106–125 μ m can be seen well embedded in the matrix as shown in Fig. 7.3. The equiaxed morphology has also been reported by the other researchers in Al-alloy systems [1, 2].

The particle-droplet interaction in the atomization zone and on the deposition surface plays a crucial role in evolution of microstructure during spray deposition. As the SiC particle collide with the melt, due to difference in the temperature of SiC particle and molten matrix a thermal gradient has been generated which give rise the splat quenching in the region around its deposition. The generation of small silicon globules around the SiC particle with fine network of Si is also visible in the micrographs (Fig. 7.3 (a–d)). These micrographs show the equally distributed SiC particle in matrix phase.

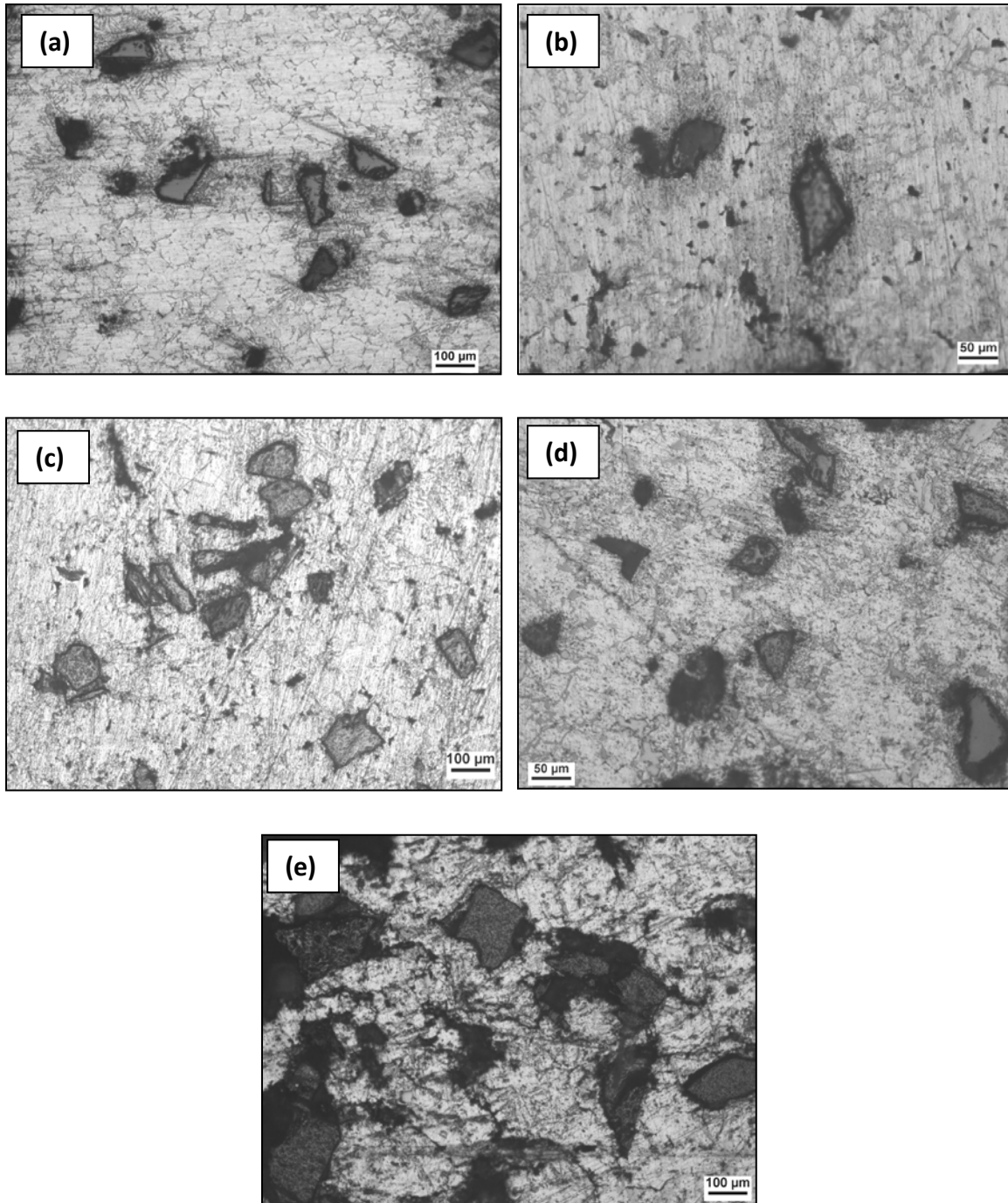


Figure 7.3: Optical micrographs of spray formed **(a)** Al-Si/SiC, **(b)** Al-Si-5Sn/SiC, **(c)** Al-Si-10Sn/SiC, **(d)** Al-Si-5Bi/SiC and **(e)** Al-Si-10Bi/SiC composites having particulates size 106–125 μm.

7.6 Wear characteristics

7.6.1 *Wear rate vs. sliding distance*

Tribological properties of the prepared samples have been studied at 50, 75, 100 and 150 °C and at five different loads (1.5–5.5 kg). Figures 7.4 to 7.8 illustrate the variation of wear rates with sliding distance for Al–Si/SiC, Al–Si–5Sn/SiC, Al–Si–10Sn/SiC, Al–Si–5Bi/SiC and Al–Si–10Bi/SiC composites. Wear rate curves show three wear regimes (i) run-in, (ii) steady state and (iii) seizure. The run-in wear always represents the unstable fluctuations when the two surfaces come into contact on start of sliding. The mechanical welding of the plastically deformed material at the edges of the pin leads to rise in fluctuating wear rate in the plots. The run-in distance range is found to be 500–1000 m for the composites (Fig. 7.4 to 7.8) depending upon the test conditions. The constant wear rate has been established after initial sliding which is represented by the plateau in the wear rate curves. Similar findings have been obtained in the Al–2Mg–TiO₂ system for spray and stir cast composites by Chaudhury et al. [3]. The steady state wear is acquired when the energy contributed during sliding is in equilibrium with the topographic modification of the surfaces in contact. At this stage, wear is proportional to the normal applied load [4]. However, seizure has been found to occur where the slope of the curve suddenly increases and further steady state is not achieved.

7.6.2 *Effect of load*

In general, it has been found that the wear rate is rising on increasing the applied load. This is analogous to Archard's equation which shows that wear volume loss is directly proportion to the applied normal load and inversely to the hardness of the material [5]. It has been found that in almost all the prepared samples and for first three loads the wear rate behavior is similar and exhibit mild wear (Fig. 7.4 to 7.8). The variation in the wear rates of the higher loads i.e. 4.5 and 5.5 kg are different for different specimens. This shows that the mode of wear changes at the higher loads. Therefore more fluctuations in wear rate are found at higher load conditions.

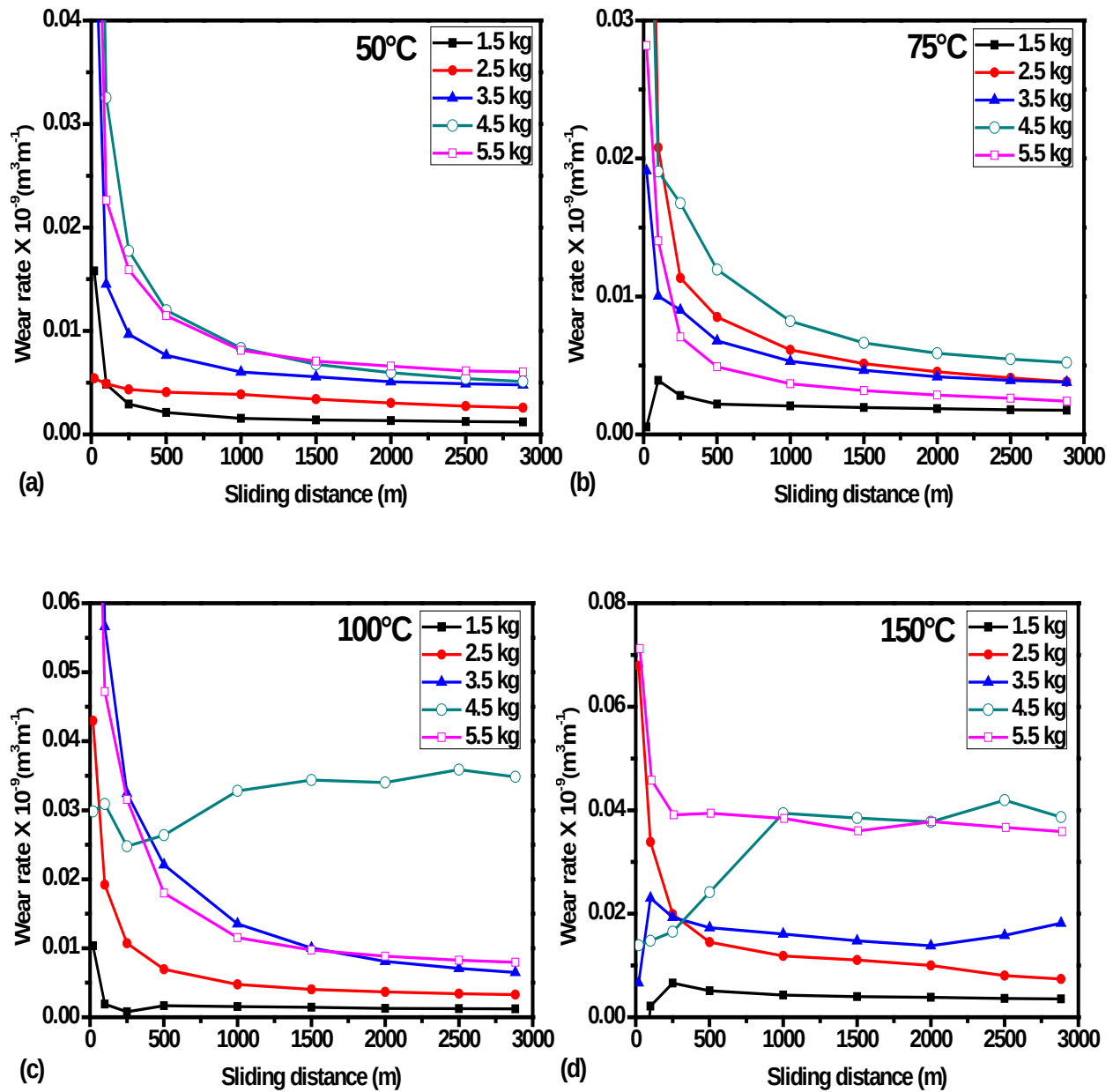


Figure 7.4: Wear rate of the spray formed Al-Si/SiC (106–125 μm) composite under various loads at (a) 50 °C, (b) 75 °C, (c) 100 °C and (d) 150 °C temperature.

Figure 7.4 represent the wear rate behavior of spray formed Al-Si/SiC composite. At 75°C and 5.5 kg load Al-Si/SiC composite shows the reduction in wear rate. Beyond 75 °C temperature, both 4.5 and 5.5 kg loads show fluctuating wear rates. It might be due to the change in wear mechanism from adhesive to oxidative wear. Wear rate fluctuations at 4.5 kg followed by wear rate stabilization at 5.5 kg can be understood due to the stabilization

of the oxide layer on the running surfaces. It seems that 4.5 kg load acts as the critical transition load after which oxidative wear is prevailing. Also the higher stability of the oxide layer contributes towards the lower wear rate even at 5.5 kg loads (Fig. 7.4 (b, c)).

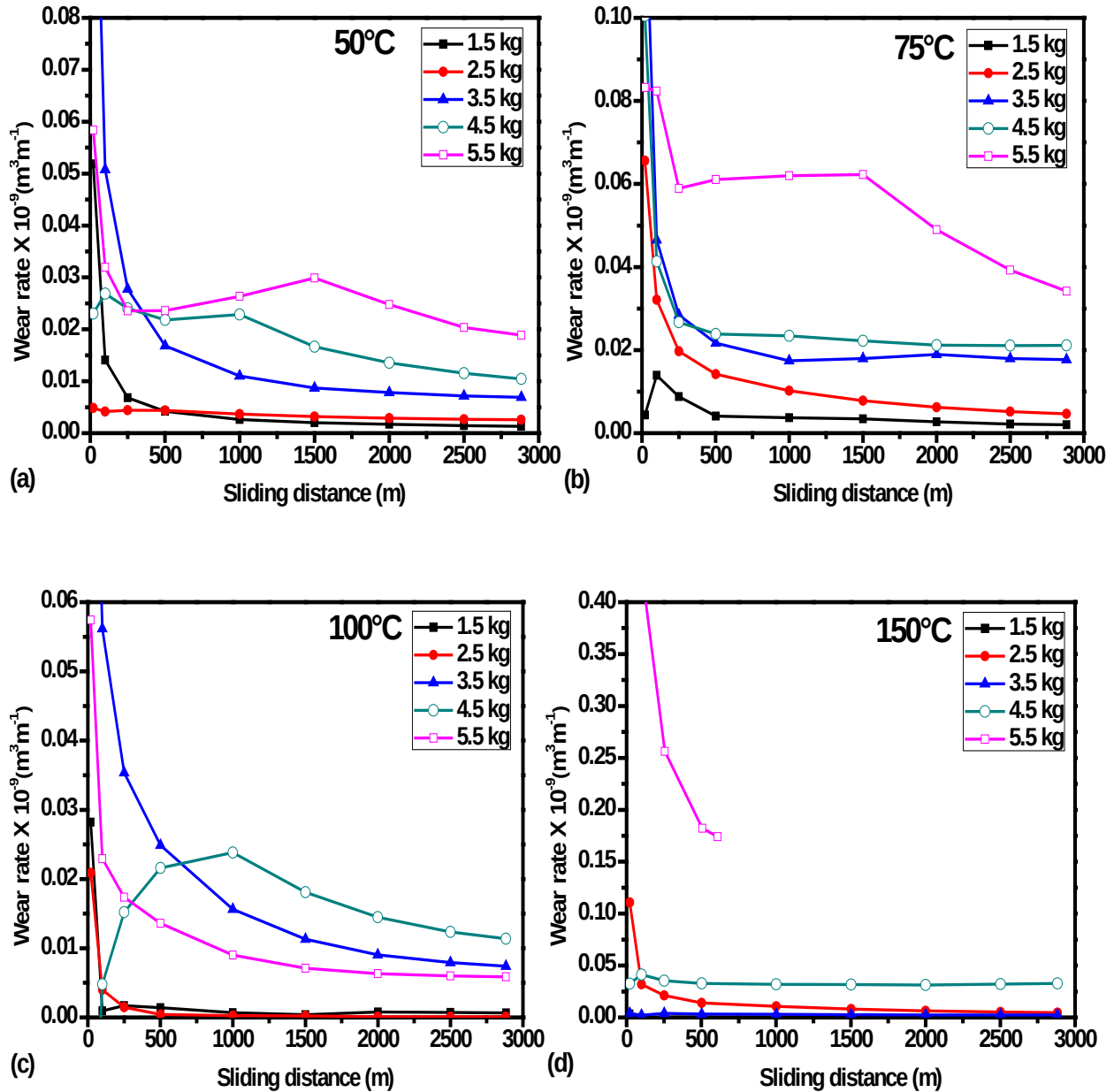
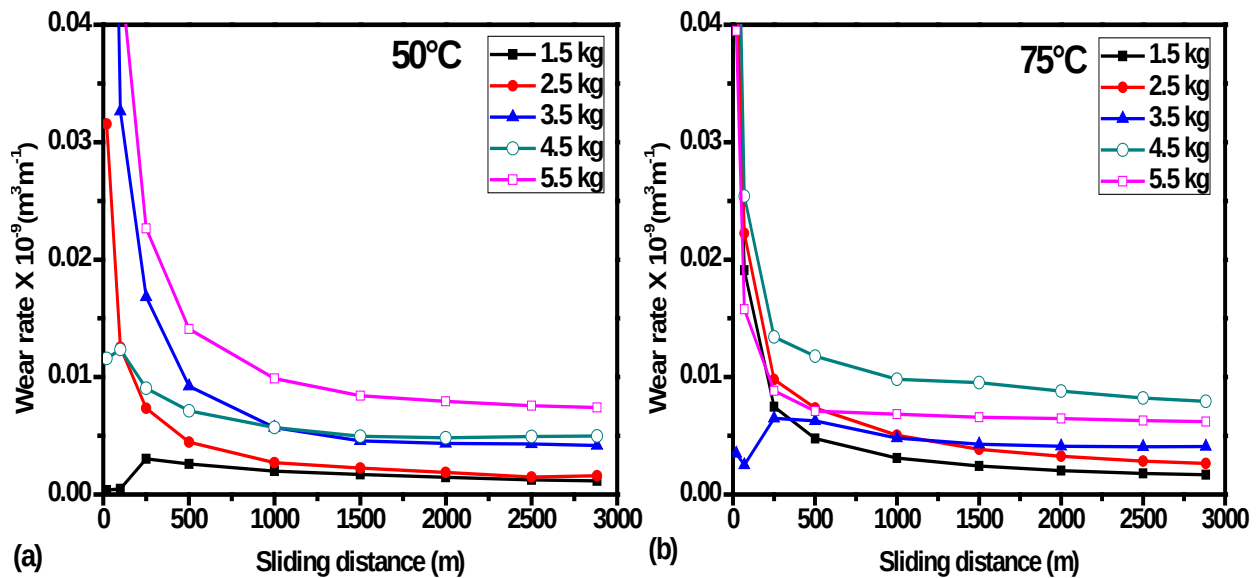


Figure 7.5: Wear rate of the spray formed Al-Si-5Sn/SiC (106–125 μm) composite under various loads at (a) 50 °C, (b) 75 °C, (c) 100 °C and (d) 150 °C temperature.

Figure 7.5 represents the wear rate behavior of spray formed Al-Si-5Sn/SiC composite under various applied loads and temperatures. The similar wear rate fluctuations at high

loads have been observed as shown in Fig. 7.5 (b–d) and also described earlier. At 50 °C, Al–Si–5Sn/SiC composite shows good wear resistance even at higher load condition. With increase in temperature, the wear rate increases at 5.5 kg load due to continuous formation and removal of oxide layer from the sliding surfaces. However, reduction in the wear rate at 5.5 kg load has been achieved at 100 °C due to greater stability of oxide layer. Additionally Sn present in the alloy matrix form thin lubricating film over the sliding surface which helps in smooth sliding and reducing friction. At 150 °C, 4.5 kg load the steady state wear rate is achieved though at 5.5 kg load the wear rate stabilization has not been achieved and the seizure occurs as shown in Fig. 7.5(d).

Wear rate behavior of Al–Si–10Sn/SiC composite is shown in Fig. 7.6 at different loads and temperatures. On comparing the wear rate at each load it has been found that the wear resistance offered by spray formed Al–Si–10Sn/SiC composite is higher than as-cast Al–Si alloy (Fig. 5.2), spray formed Al–Si alloy (Fig. 5.3) and SiC reinforced composites as shown in Fig. 7.4–7.5 (a–d). This shows the good interfacial bonding of SiC particle and matrix phase. Also, wear rate in Al–Si–10Sn/SiC composite (Fig. 7.6) is found to be lower than Al–Si–5Sn/SiC composite (Fig. 7.5).



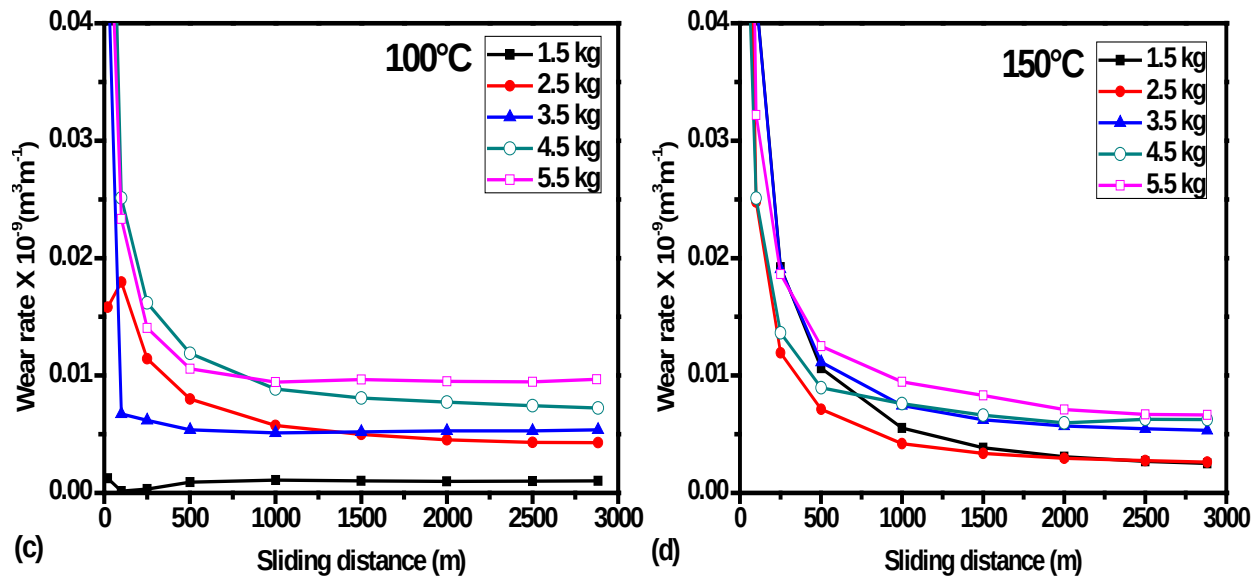


Figure 7.6: Wear rate of the spray formed Al-Si-10Sn/SiC (106–125 μm) composite under various loads at (a) 50 °C, (b) 75 °C, (c) 100 °C and (d) 150 °C temperature.

This might be due to the increase in the lubrication effect provided by Sn between the rubbing surfaces. In Al-Si-10Sn/SiC composite, large amount of Sn solidified within the grains and grain boundaries and get smeared over the surface while sliding. This provides a protective, stable and uniform lubricating film over the sliding surface even at higher load and temperature. Additionally, probability of oxide layer formation is greater at higher test temperatures. The combination of both the oxide layer and lubrication effect drastically decreased the wear rate of material.

With addition of immiscible element Bi in the matrix alloy and SiC particles the seizure condition has been delayed at 50 and 75 °C in Al-Si-5Bi/SiC composites as shown in Fig. 7.7 (a, b). This can be attributed to the higher hardness of the composite as described in the previous section which is endorsed by the Archard's equation [5]. Moreover, immiscible element Bi present in matrix acts as solid lubricant which helps in reducing the wear rate of the material. The tiny amount of Bi is uniformly distributed in the grain and grain boundaries of the alloy during spray forming. While sliding Bi smears on the contact surfaces and form a thin lubricating film which is effective in enhancing wear resistance. The stable and continuous thin film decreases the direct metal to metal contact and hence removal of material from the surface is inhibited.

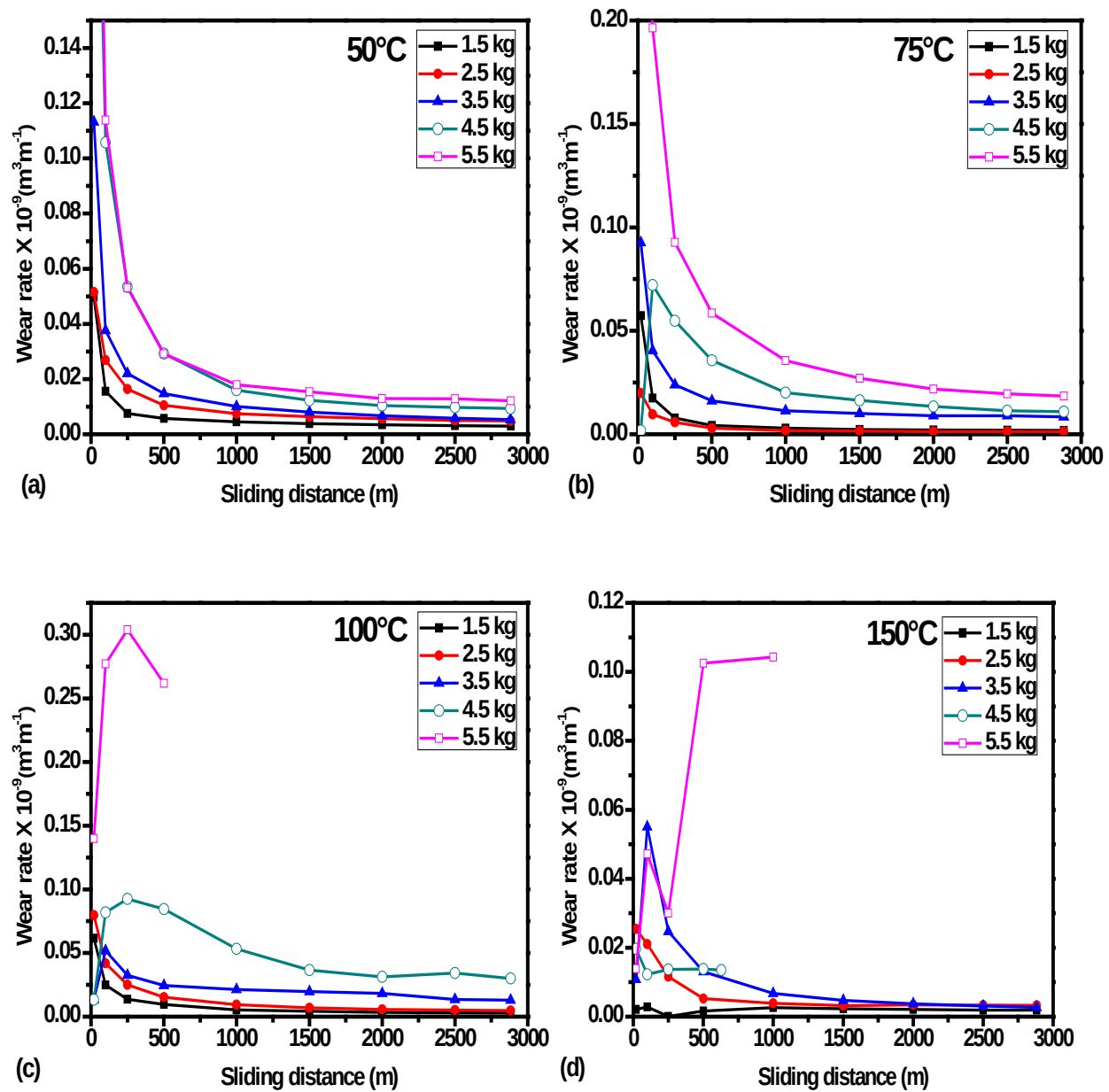


Figure 7.7: Wear rate of the spray formed Al-Si-5Bi/SiC (106–125 μm) composite under various loads at (a) 50 °C, (b) 75 °C, (c) 100 °C and (d) 150 °C temperature.

Therefore at 50 and 75 °C even at high load conditions (Fig. 7.7 (a, b)) the higher wear has not been found. However, with rise in temperature the film gets oxidized and the contact surfaces again come in the direct contact. At higher temperature and higher load the wear did not get stabilize (Fig. 7.7 (c, d)) as the Bi fails to lubricate the surface. However, with

increase in the amount of Bi in the alloy such situations have not been encountered as depicted from Fig. 7.8.

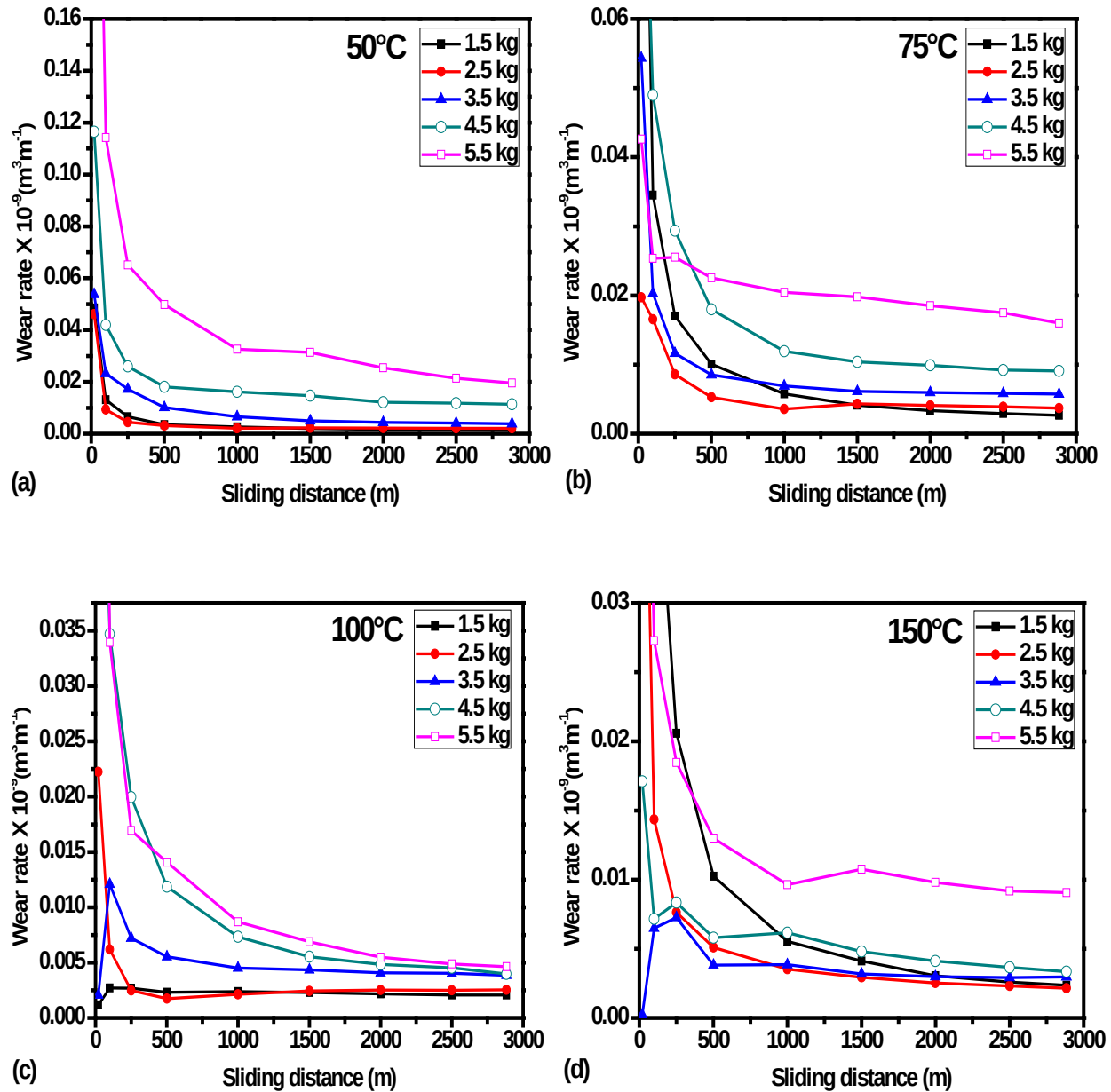


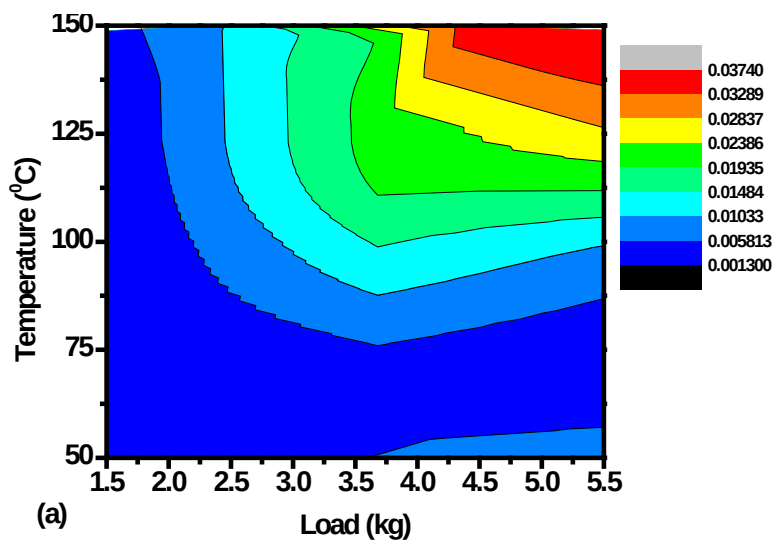
Figure 7.8: Wear rate of the spray formed Al-Si-10Bi/SiC (106–125 μm) composite under various loads at (a) 50 °C, (b) 75 °C, (c) 100 °C and (d) 150 °C temperature.

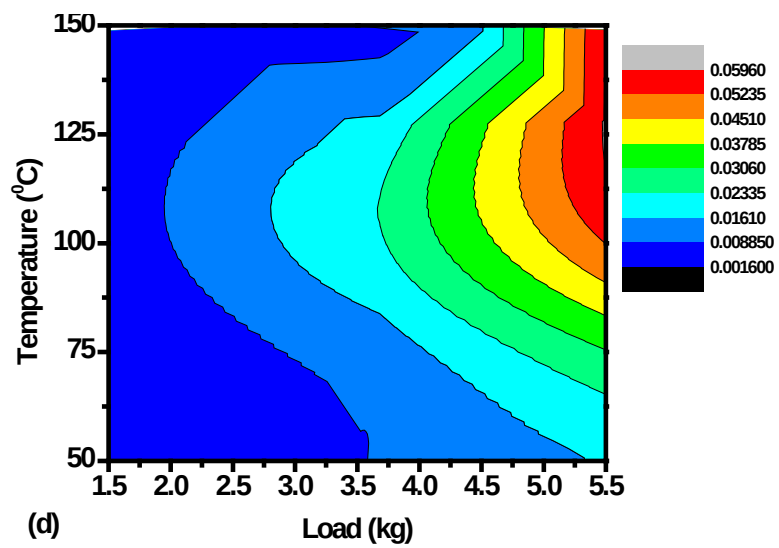
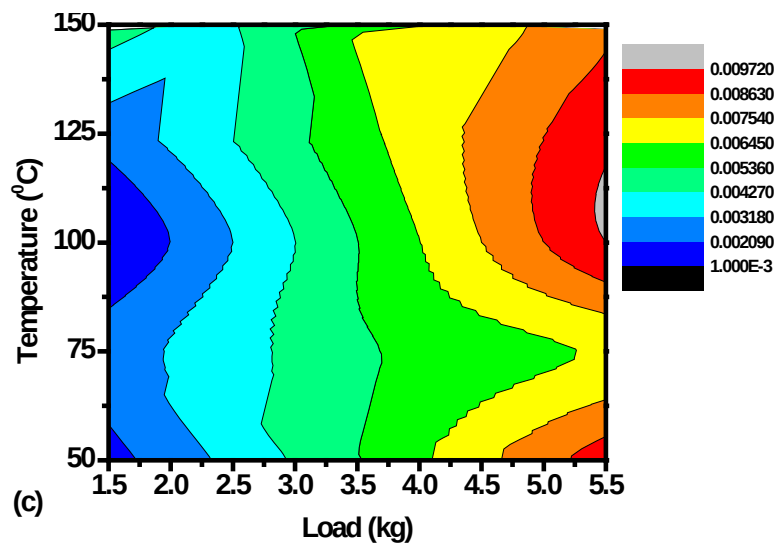
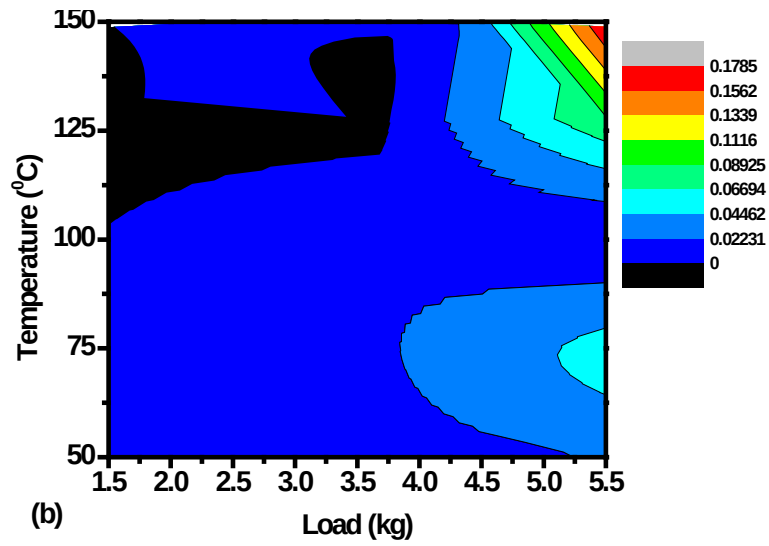
The result is also appropriate with the highest hardness obtained in Al-Si-10Bi/SiC composite. Moreover, higher Bi content present in the matrix holds the optimum requirement of Bi on the surface for lubrication. Therefore, even at higher temperature and

load conditions the Al-Si-10Bi/SiC show mild wear. Similar results have also been reported by An et al. [6] in the hot-extruded Al-Si-Cu-Pb bearing alloys and found that the wear rate decreases greatly with increasing Pb content. The reason for such behavior was found to be the formation of a black compact film of lubricant which is mixture of Al, Si, O, Fe and Pb elements. The film was found to cover almost the entire worn surface of specimens at highly applied load level.

7.6.3 Effect of temperature

Effect of temperature on wear has been explored by plotting wear contours at different temperatures and loads as shown in Fig. 7.9. Figure 7.9 (a) clearly indicates the change in the wear mechanism beyond 100 °C in Al-Si/SiC composite. The critical transition temperature of 100 °C distinguishes between the mild and severe wear regimes. It has been found from the wear contours that in Al-Si-5Sn/SiC (Fig. 7.9 (b)) at lower loads (1.5–3.5 kg) greater wear resistance is attained at higher temperatures. The abrupt change in the wear rate has been found at 5.5 kg load and 150 °C where oxide layer is unstable at higher load and lubricating film is also uneven due to less amount of Sn in matrix. On enhancing the amount of Sn in the matrix alloy, lower and stable wear rates have been achieved (Fig. 7.9 (c)).





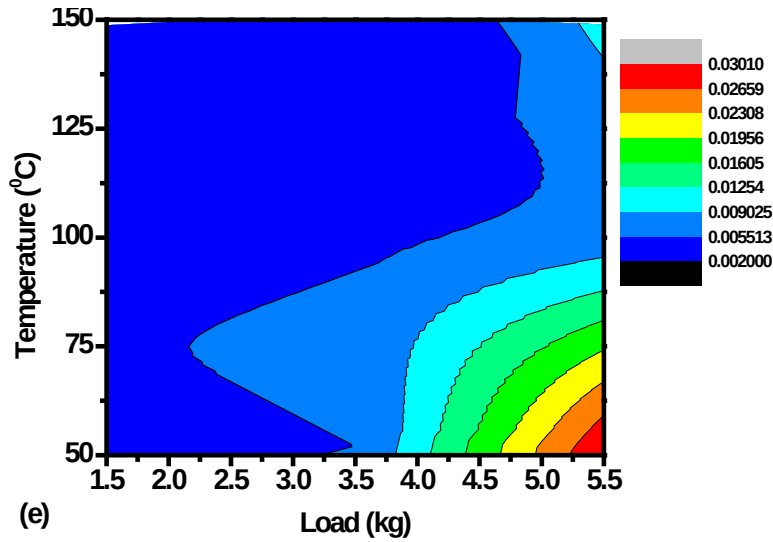


Figure 7.9: Averaged wear rate ($\times 10^{-9} \text{ m}^3\text{m}^{-1}$) against various temperatures and applied loads for **(a)** Al-Si/SiC, **(b)** Al-Si-5Sn/SiC, **(c)** Al-Si-10Sn/SiC, **(d)** Al-Si-5Bi/SiC and **(e)** Al-Si-10Bi/SiC composite.

Al-Si-10Sn shows gradual increase in the wear rate with load in mild wear regime which is not much affected by the change in temperature. The higher wear regimes are shifted towards higher temperature in Al-Si-5Bi/SiC composite as shown in Fig. 7.9 (d). On contrary, in Al-Si-10Bi/SiC composite higher though stable wear has been found at 50 °C and 5.5 kg as shown in Fig. 7.9 (e). It further decreases with increase in the temperature as additional Bi comes out at the contact surfaces and reduces the wear [6].

The comparison of average wear rates at the extreme test conditions is shown in Fig. 7.10 and 7.11. The average wear rate has been calculated after initial 500 m sliding to ensure the presentation of steady state wear rate unless the seizure occurs in run-in wear regime. Figure 7.10 represents the average wear rate of Al-Si alloy, Al-Si/SiC, Al-Si-5Sn/SiC and Al-Si-10Sn/SiC composites. It is clear that at lower temperatures the composites offer better resistance to wear as compared to the Al-Si alloy. Al-Si/SiC shows good wear resistance below 150 °C temperature while it seizes suddenly at 150 °C. Al-Si-5Sn/SiC composite shows unsteadiness in the average wear rates at different temperatures. This variation in wear rate is due to the instability of the oxide layer and the lubricating film. At 100 °C, the stability of the oxide layer and the lubricating film is the highest. Therefore maximum resistance to wear has been offered by Al-Si-5Sn/SiC composite at this

temperature. However, Al-Si-10Sn/SiC shows highest stability of lubricating film and oxidative wear with temperature. Therefore it does not show much variation in wear rate with respect to temperature.

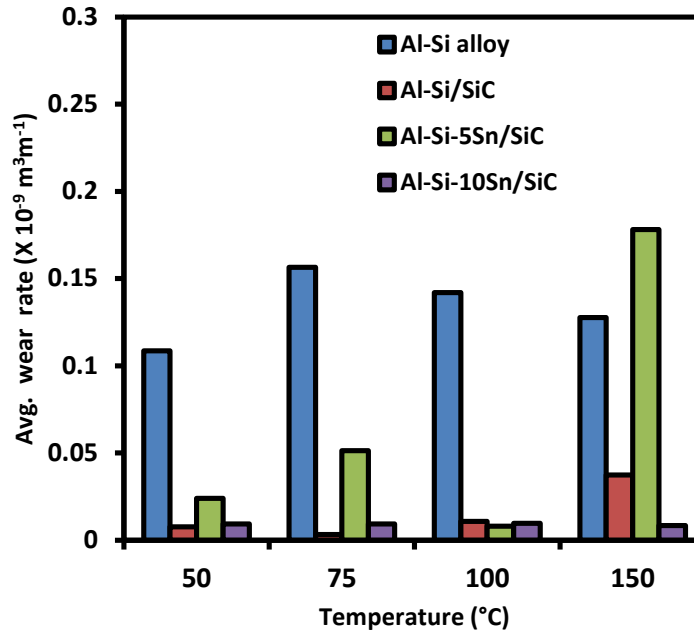


Figure 7.10: Average wear rate against various temperatures at 5.5 kg applied load for SiC (106–125 μm) and Sn containing composites.

The average wear rates against various temperatures for Al-Si alloy, Al-Si/SiC, Al-Si-5Bi/SiC and Al-Si-10Bi/SiC composites are shown in Fig. 7.11. It has been clearly indicated in Fig. 7.11 that both the composites show the higher resistance to wear in comparison to the Al-Si alloy. The wear rate is found to be in ascending trend with temperature at 5.5 kg load in Al-Si-5Bi/SiC composite. At 100 and 150 °C, Al-Si-5Bi/SiC composite exhibit seizure condition due to which its average wear rate has been evaluated from run-in wear rate. The wear has been found to be greater in Al-Si-5Bi/SiC than Al-Si/SiC composite at higher temperatures due to seizure. However, in Al-Si-10Bi/SiC composite wear rate was found to decrease with temperature. The lowest wear rate exhibited by Al-Si-10Bi/SiC composite under 5.5 kg load at 100 °C is $7.44 \times 10^{-12} \text{ m}^3\text{m}^{-1}$.

At 150 °C and 5.5 kg load, the average wear rate of Al-Si alloy, Al-Si/SiC, Al-Si-5Sn/SiC, Al-Si-10Sn/SiC, Al-Si-5Bi/SiC and Al-Si-10Bi/SiC composite is 1.28×10^{-10} , 3.74×10^{-11} ,

1.78×10^{-10} , 8.45×10^{-12} , 5.96×10^{-11} and 1.02×10^{-11} respectively. The average wear rate shows that Al-Si/SiC composite offers good wear resistance at the lower temperatures (Fig. 7.10 and 7.11). For Al-Si-5Sn/SiC and Al-Si-5Bi/SiC composites seizure occur at extreme conditions. The Al-Si-5Sn/SiC and Al-Si-5Bi/SiC composites show lowest wear rate at 100 and 50 °C respectively under 5.5 kg load. Also, under the severe test conditions, Al-Si-10Sn/SiC and Al-Si-10Bi/SiC composites offer better wear resistance as compared to other composites. Moreover, Al-Si-10Sn/SiC composite exhibits wear resistant in SiC (106–125 μm) reinforced AMCs.

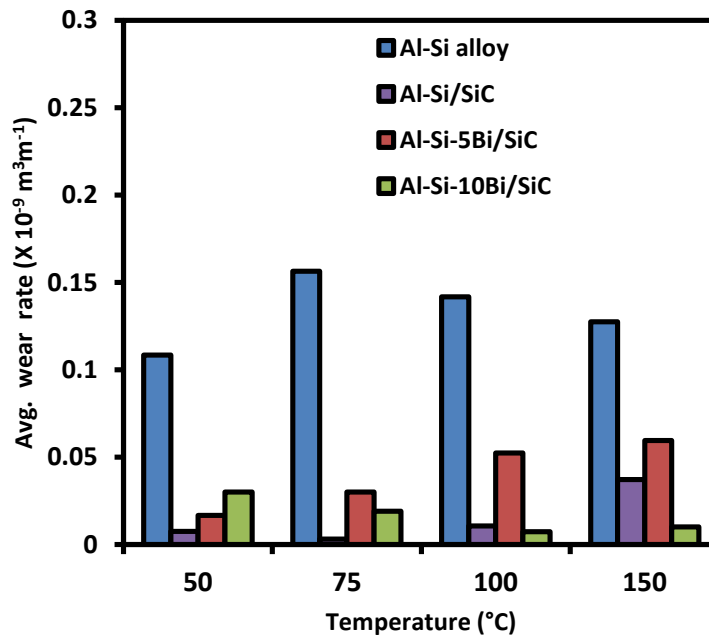


Figure 7.11: Average wear rate against various temperatures at 5.5 kg applied load for SiC (106–125 μm) and Bi containing composites.

7.6.4 Friction coefficient

Average friction coefficients for spray formed alloy and composites are presented at one of the three lower loads i.e. 2.5 kg and at the highest load 5.5 kg in Fig. 7.12 and 7.13 respectively. The average has been taken after 500 m sliding distance to account for the friction coefficient of the steady state wear. At 2.5 kg load, Al-Si/SiC composite exhibits higher frictional coefficient than Al-Si alloys at 75 and 100 °C as shown in Fig. 7.12 (a). However, at highest test temperature the lower frictional coefficients have been measured for composites than alloy. At lower load and lower temperature, the frictional heat

dissipation is large in alloys as compared to the composites. Therefore, higher friction coefficient is observed for composite at these test conditions. However, the lubrication effect also helps in reducing the frictional coefficient of Sn containing composites (Fig. 7.12 (a)). It depends upon the stability of the lubricating film over the sliding surfaces.

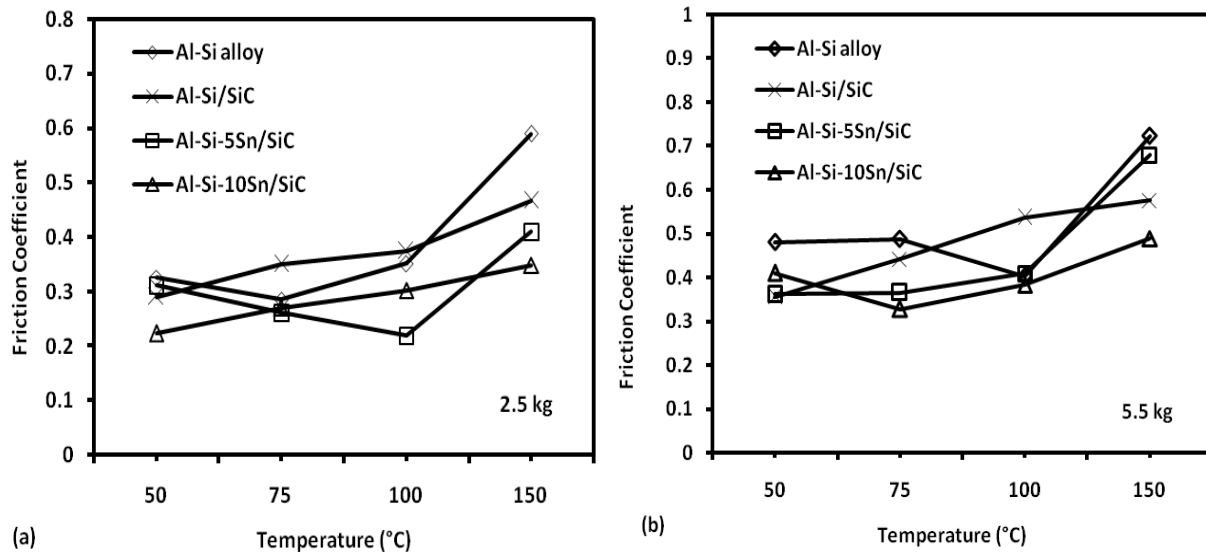


Figure 7.12: Variation of average friction coefficient with temperature at (a) 2.5 kg and (b) 5.5 kg load.

Figure 7.12 (b) illustrates the variation of the frictional coefficients with respect to test temperatures at 5.5 kg load. Al-Si/SiC composite exhibits ascending values of friction coefficient with temperature as shown in Fig. 7.12 (b). Also, Sn lubricating composites exhibit less friction coefficients than the base Al-Si alloys. However, Al-Si-5Sn/SiC composite exhibits similar friction coefficient as unreinforced alloy at 150 °C at 5.5 kg load. The seizure at extreme test conditions increases the frictional coefficient of the Al-Si-5Sn/SiC composite.

Figure 7.13 (a) shows that at 2.5 kg load Al-Si alloy and Al-Si-5Bi/SiC composite exhibit similar friction coefficients. However, Al-Si-10Bi/SiC shows the lower friction coefficients at all the temperatures. It has been found that up to 100 °C temperature there is not much variation in the friction coefficient. The abrupt rise in friction coefficient of all the materials has been found at 150 °C. During sliding, large amount of energy has been dissipated to overcome the disparity in contact with the asperity. The higher energy is dissipated in the

form of heat as the frictional forces are acting in the opposite direction to the sliding. It raises the localized temperature of the contact surface of the pin. In addition to this extra heat is added to the system by the environment at test temperature of 150 °C. With increase in the temperature at the contact, the material gets soften as the strength decreases [7]. Therefore, frictional coefficient rises at 150 °C temperature in monolithic alloy. However, it has been reported that frictional coefficients of the composites are greater as compared to the monolithic alloys.

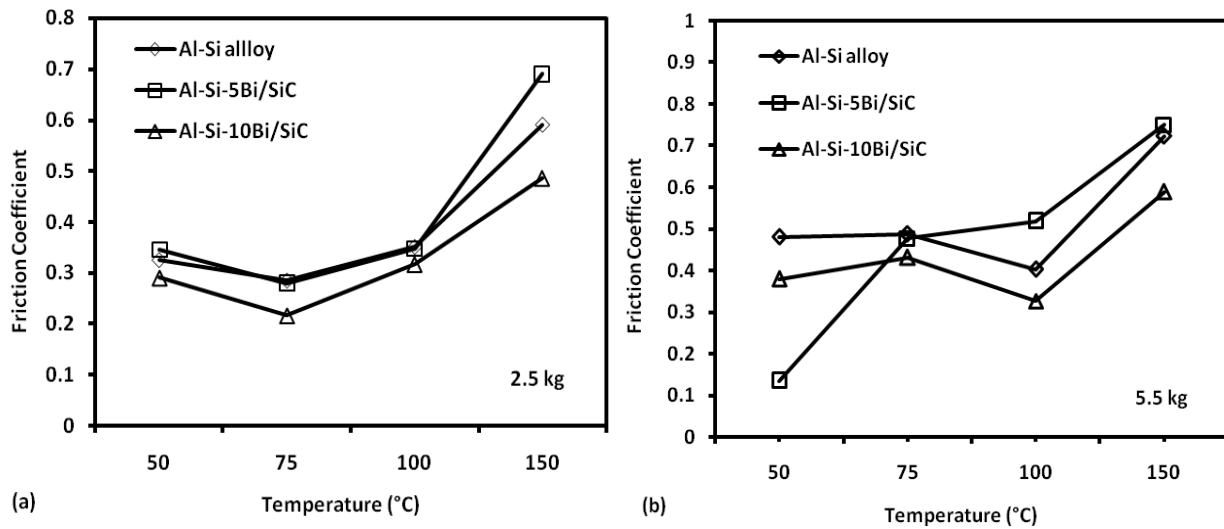


Figure 7.13: Variation of average friction coefficient with temperature at (a) 2.5 kg and (b) 5.5 kg load.

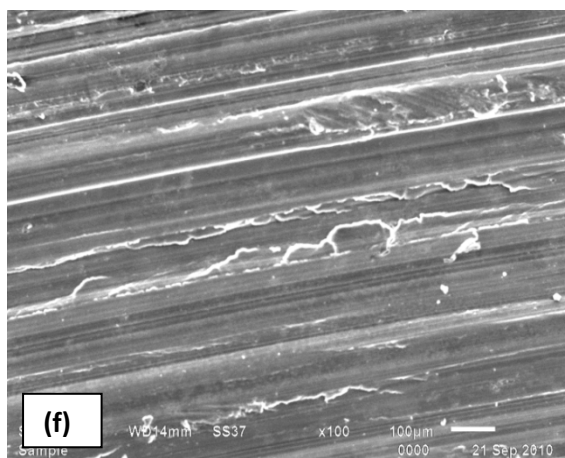
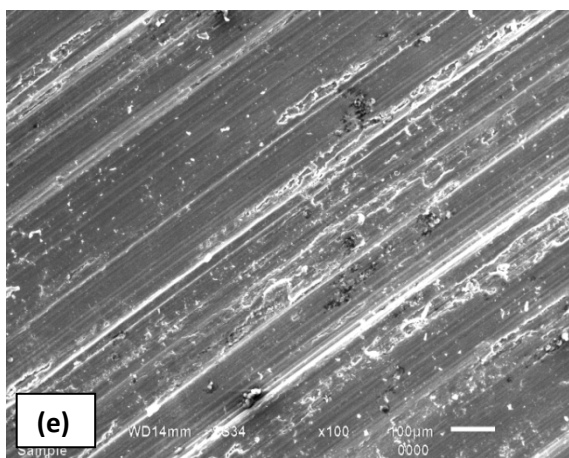
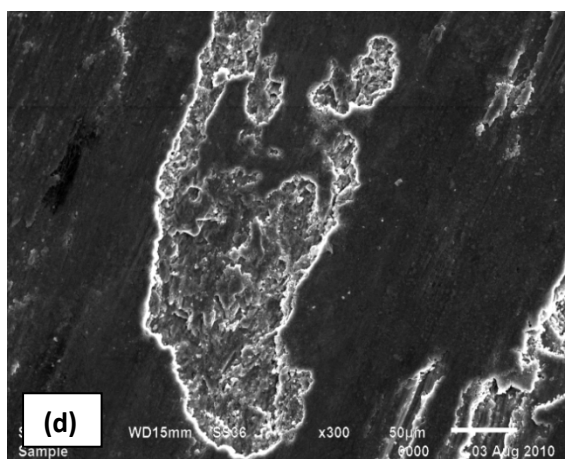
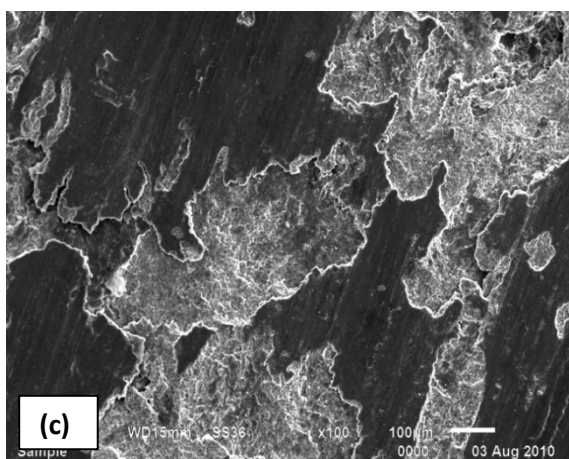
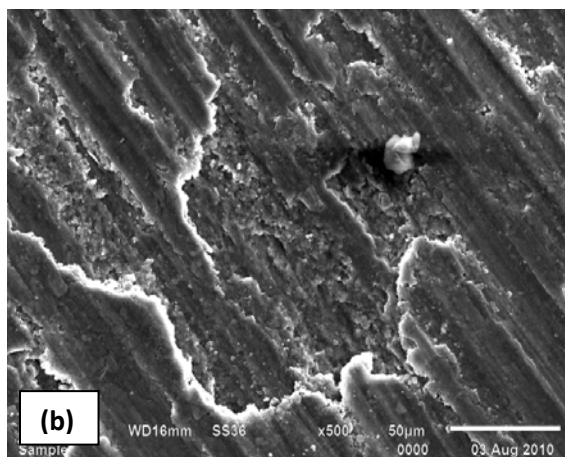
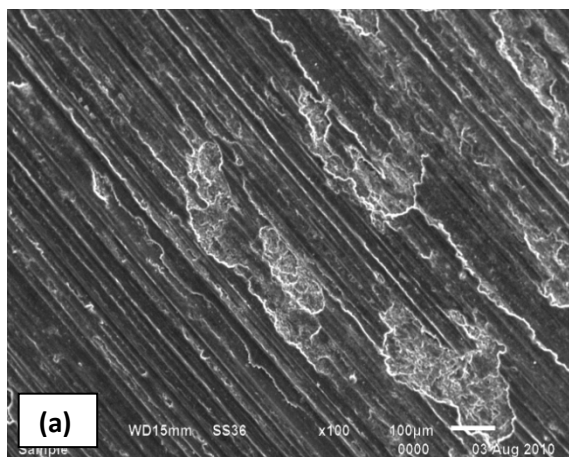
The total frictional coefficient of the composites is the sum of plowing, adhesion and particle fracture [8]. But in self-lubricated composites the friction coefficients are lower than that of the monolithic alloy as lubrication decreases the effect of adhesion. At higher load, as shown in Fig. 7.13 (b) the friction coefficients keep rising with temperature for Al-Si-5Bi/SiC composite. With increase in temperature the lubricating film of Bi is getting oxidized and more wear rate has been experienced in the absence of lubrication. However, Al-Si-10Bi/SiC composite offers lower friction coefficients as the enhanced lubrication effect decreases and the direct metal to metal contact increases causing low friction coefficient that has been experienced as compared to the Al-Si alloy.

7.7 Microstructural analysis of worn surfaces and wear debris

The morphology of the wear debris is of great interest due to its importance to know the mode of wear and its mechanism. The morphological analysis helps to understand how material is crushed, redistributed and consolidated in a system. The present wear study is done to understand the effect of SiC particle reinforcement and lubrication effect catered by Sn/Bi in the spray formed Al-Si matrix.

The morphology of worn surface and debris of Al-Si/SiC composite is shown in the Fig. 7.14 and 7.15 respectively. At 50 °C temperature, for both at lower and higher loads the composites show white patches running along the plowing marks on the sliding surfaces as shown in Fig. 7.14 (a-d). However, the white patches are found to be bigger in size at higher load as shown in Fig. 7.14 (c). At higher magnification (Fig. 7.14 (b, d)) it seems that a layer got compacted on the sliding surface indicating oxidative wear which can be further analyzed from the debris morphology. At lower load and higher temperature the worn pin surface shows the sliding wear scars consisting of small debris sticking on the surface shown in Fig. 7.14(e). These scars become deeper on increasing the load up to 5.5 kg (Fig. 7.14 (f-h)). The surface crack on the edges of the groove leading to formation of debris is clearly seen in Fig. 7.14(h).

Fig. 7.15 shows the morphology of wear debris of Al-Si/SiC composite. At lower load and lower temperature two types of debris are found as shown in Fig. 7.15 (a). The large flakes seem to be generated during the run-in-wear. The perturbation in the wear rate behavior before 500 m sliding distance (Fig. 7.4 (a)) also indicates the large size material removal from surface. However, very small sized debris are also present at 2.5 kg load and 50 °C. The small rounded and coagulated debris indicate the oxidative wear mechanism. As the sliding distance increases large flakes are crushed between the sliding surfaces and converted into smaller debris. Oxidative wear always enhances the wear resistance of the material [9]. This is the reason why on addition of SiC particles the material does not undergo delamination wear at higher loads as in the as-cast base and spray formed Al-Si alloy (Fig. 5.3, 5.4 and 7.4).



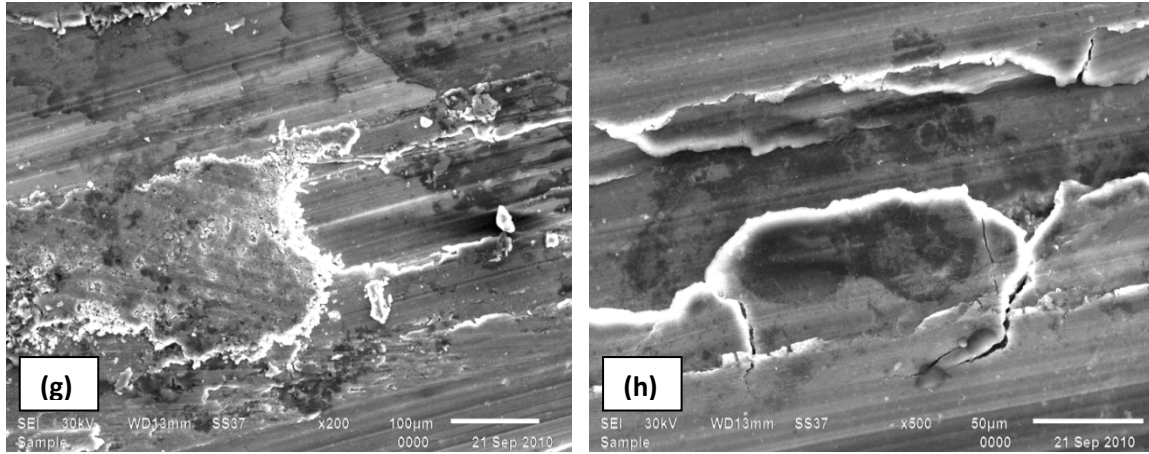


Figure 7.14: SEM micrographs of worn surfaces of spray formed Al-Si/SiC at 5.5 kg load at (a, b) 2.5 kg, 50 °C; (c, d) 5.5 kg, 50 °C; (e) 2.5 kg, 150 °C and (f-h) 5.5 kg, 150 °C.

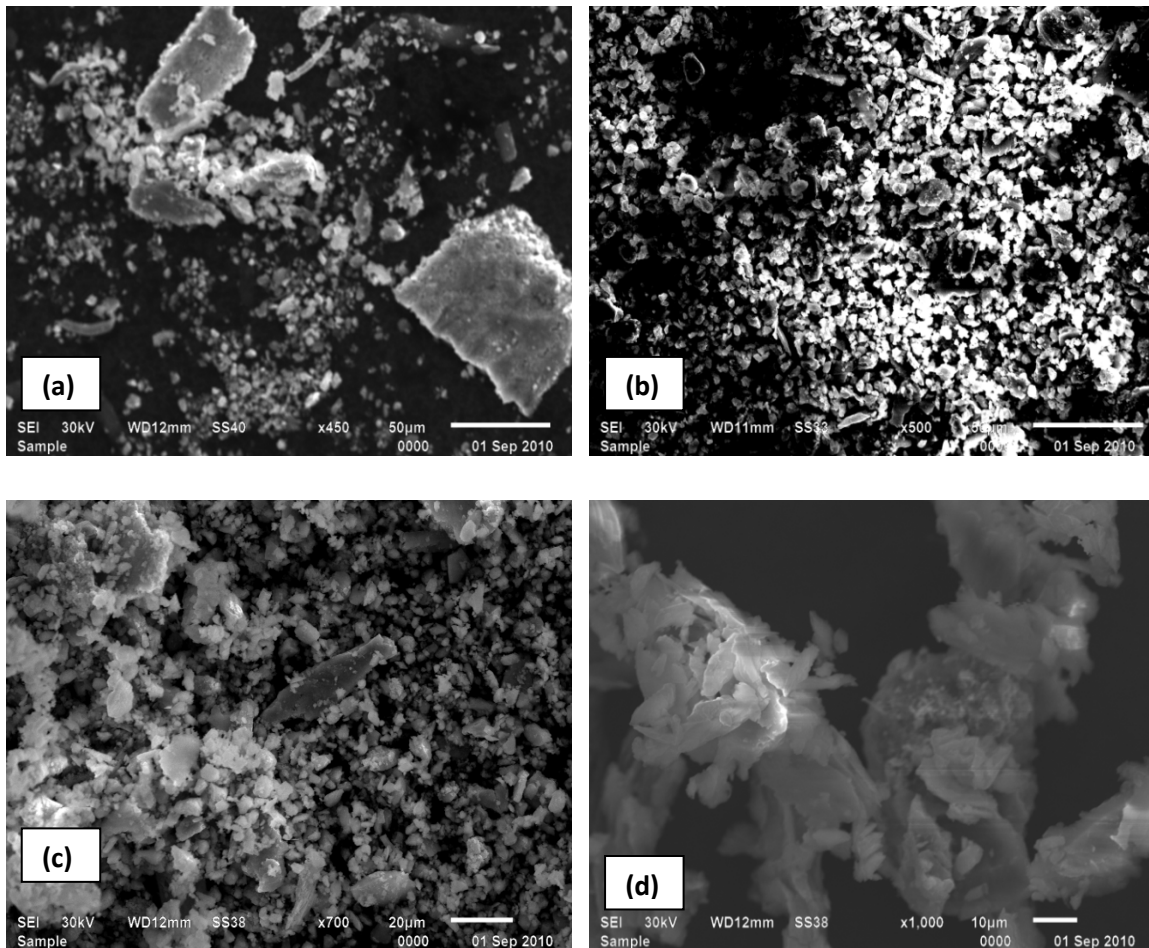


Figure 7.15: SEM micrographs of wear debris of spray formed Al-Si/SiC at 5.5 kg load at (a) 2.5 kg, 50°C; (b) 5.5 kg, 50°C; (c) 2.5 kg, 150°C and (d) 5.5 kg, 150°C.

Moreover, the results confirm that composite exhibit better wear resistance as compared to the unreinforced alloy as reported by other researchers [10]. The size of the debris further reduces to 2–20 μm as the applied load is increased to 5.5 kg at same temperature as shown in Fig. 7.15 (b). No large metallic flakes have been observed at lower load. On increasing the temperature from 50 °C to 150 °C even at lower load debris are much smaller in size as shown in Fig. 7.15 (c). This indicates oxidative wear that prevails even at lower applied load and higher temperature. However, at higher load the debris stick together to form coagulative mass and the size of the debris are also larger at 2.5 kg load as shown in Fig. 7.15(d). This is because of repetitive welding of debris.

Figure 7.16 shows the pin surface morphology of Al–Si–5Sn/SiC composite. The grooves and craters are present all over the pin surface along sliding direction as shown in Fig. 7.16(a). At 5.5 kg load and 50° C temperatures the grooves and crater become rougher in direction of sliding as shown in Fig. 7.16 (b). The grooves and small craters have also been observed at 150 °C (Fig. 7.16 (c)) which became larger at higher load i.e. 5.5 kg (Fig. 7.16 (d)). Large craters and plastic flow observed at surface are also visible on the surface (Fig. 7.16 (d)). This plastic flow leads to wear out the pin with increment in wear rate as shown in Fig. 7.5 (d). Moreover, the oxidative–cum–adhesive wear prevailing at lower load and lower temperature, is confirmed by the wear debris morphology (Fig. 7.17 (a)). A beautiful feathery morphology of debris exhibited the phenomena of delamination followed by cutting through is also spotted out under SEM (Fig. 7.17 (b)). The curve shape and sliding marks on the debris illustrate that the material is removed from the pin surface along sliding direction. The lower surface of the debris consists of the crack might be due to the repetitive plowing of the material. The morphological features of debris (Fig. 7.17 (c, d)) consist of metallic flakes indicating adhesive wear that dominates as compared to oxidative wear. Large chunk is also seen in the Fig. 7.17 (c) indicating more wear than Al–Si/SiC composite. However, at 2.5 kg load and 150°C temperature metallic large flakes have been observed in Fig. 7.17 (e). The repetitive plowing marks are clearly seen on large sized debris surface at higher load and higher temperature (Fig. 7.17 (f)).

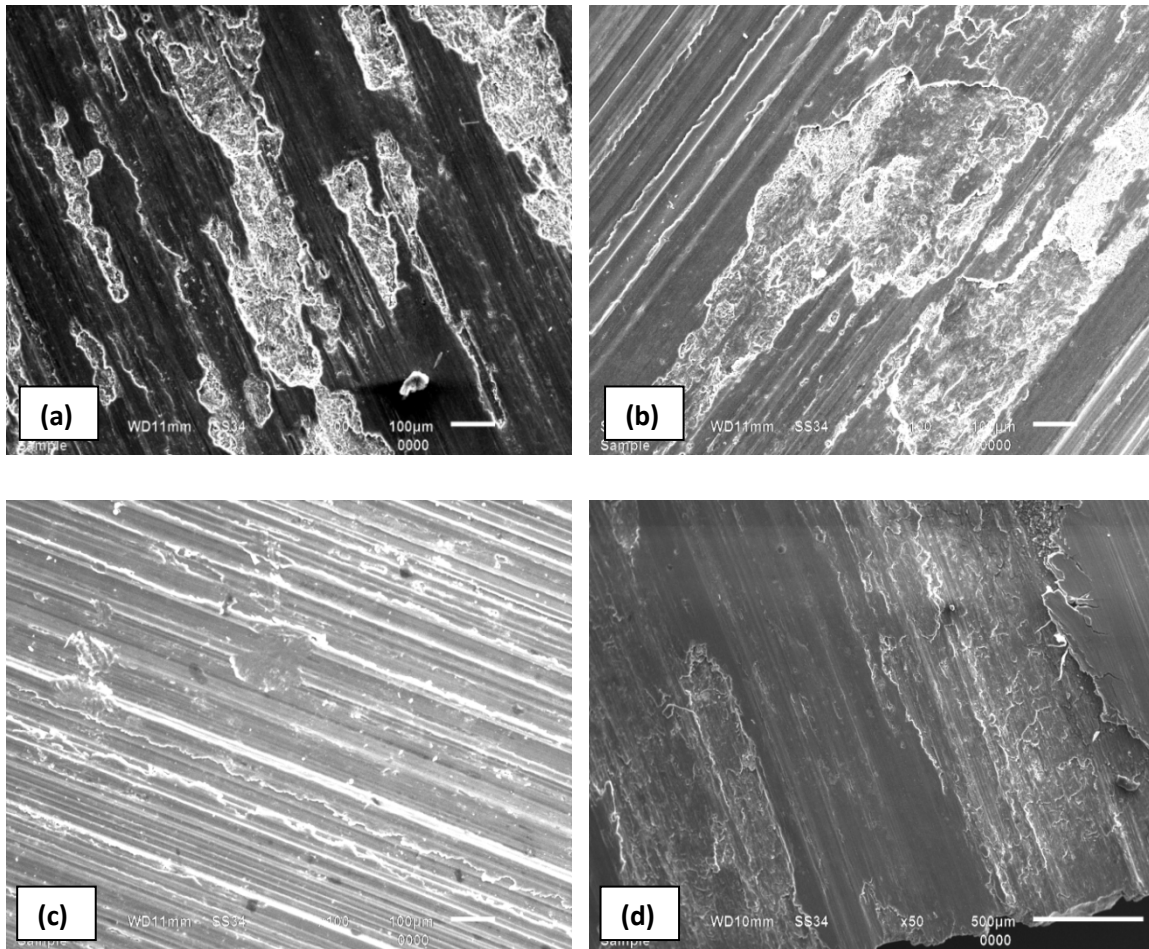
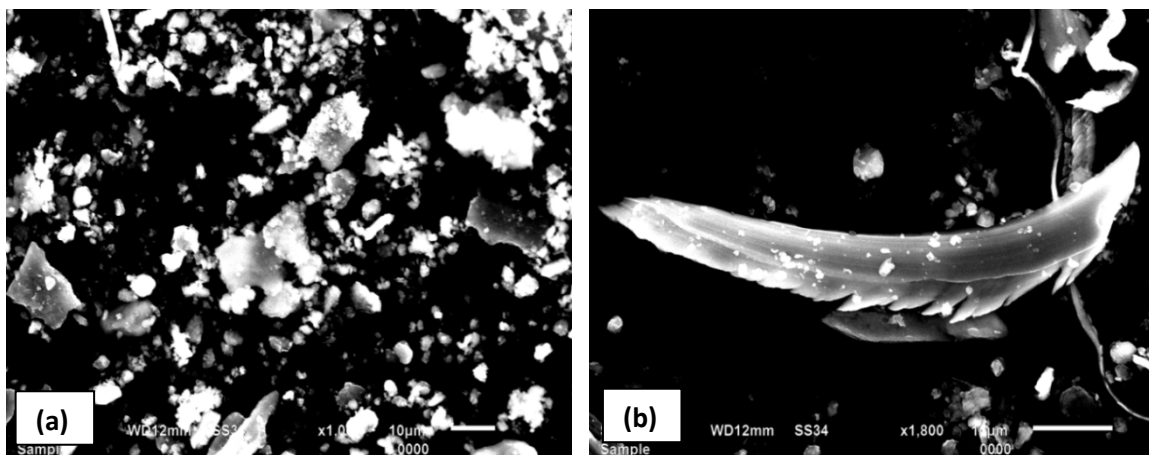


Figure 7.16: SEM micrographs of worn surfaces of spray formed Al-Si-5Sn/SiC at **(a)** 2.5 kg, 50 °C; **(b)** 5.5 kg, 50 °C; **(c)** 2.5 kg, 150 °C and **(d)** 5.5 kg, 150 °C.



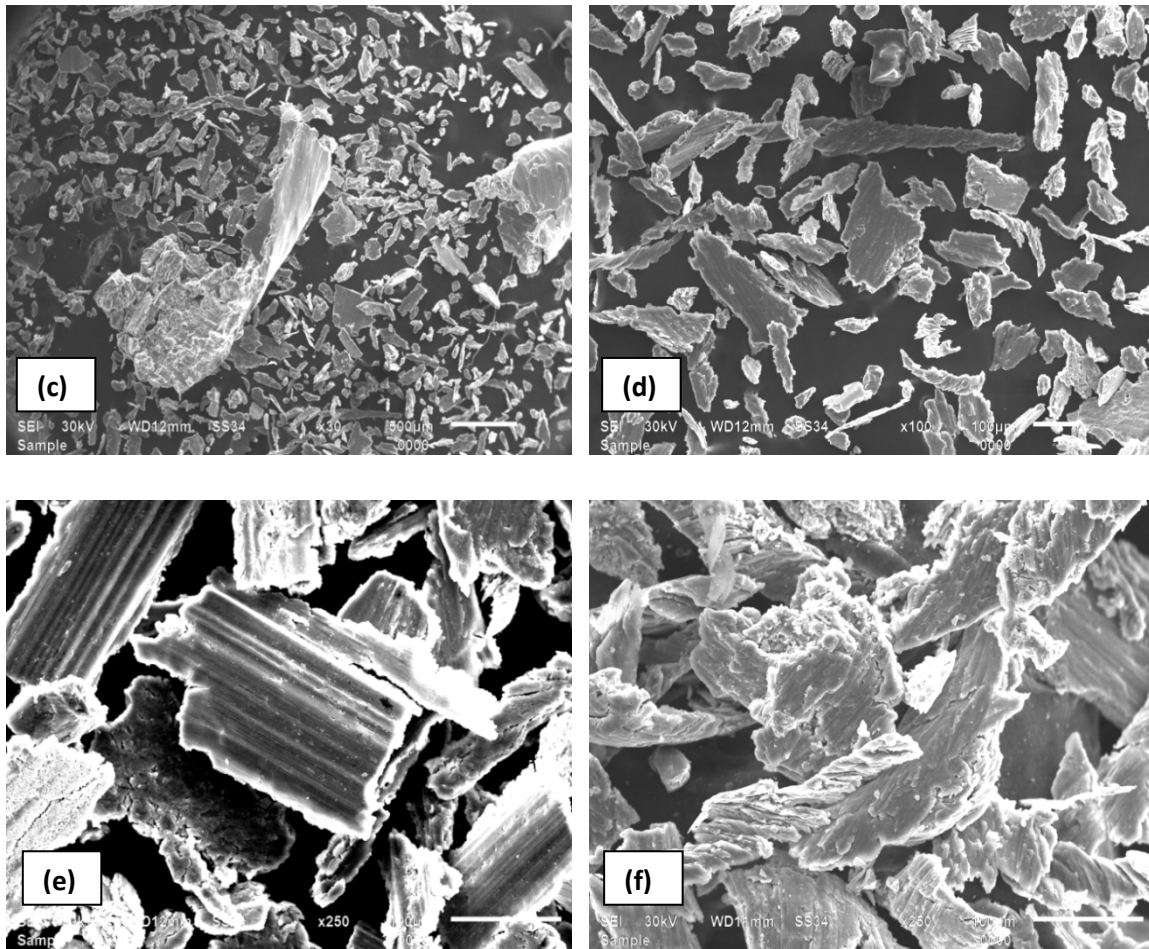
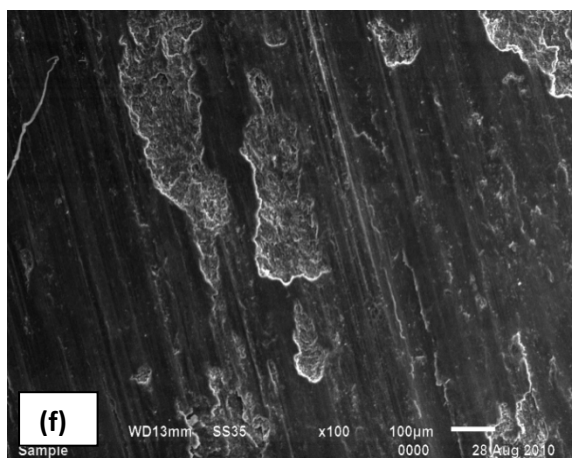
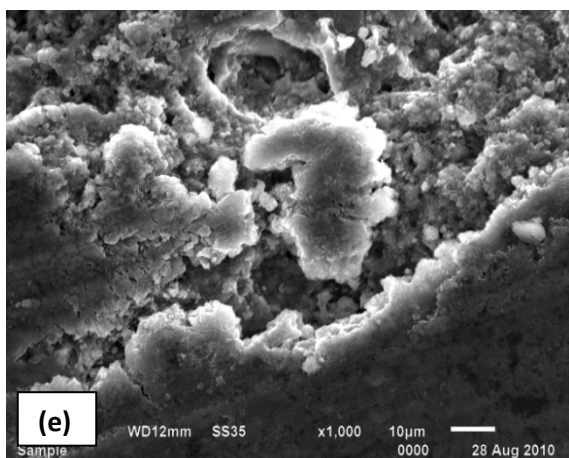
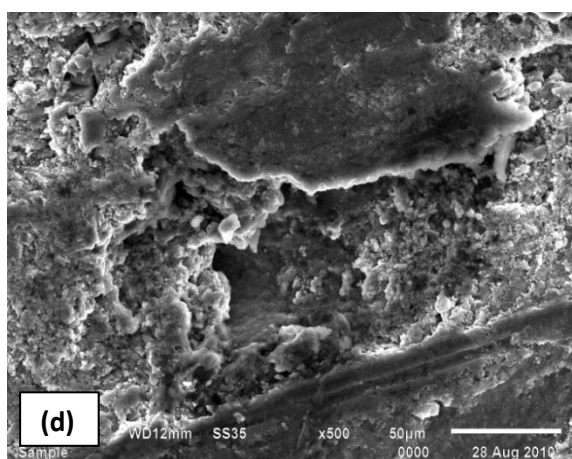
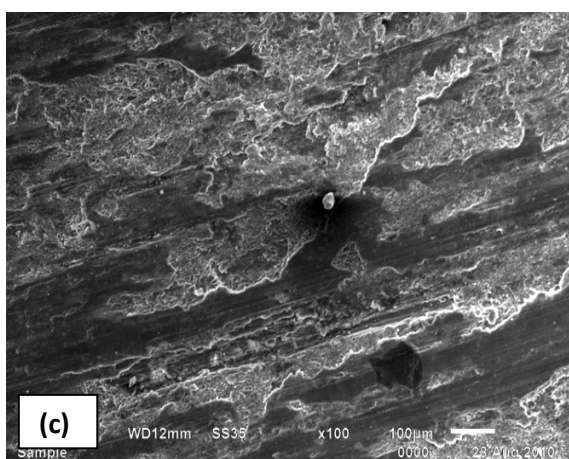
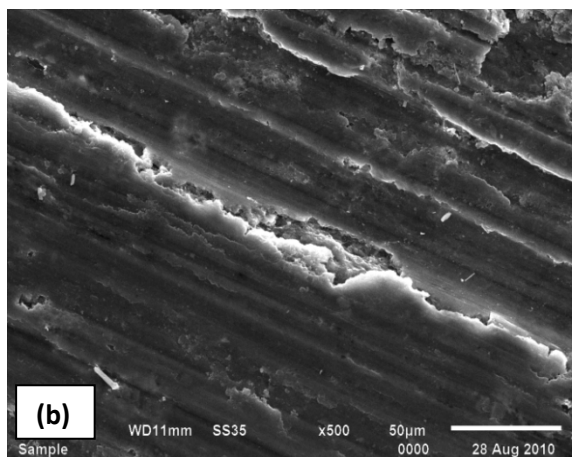
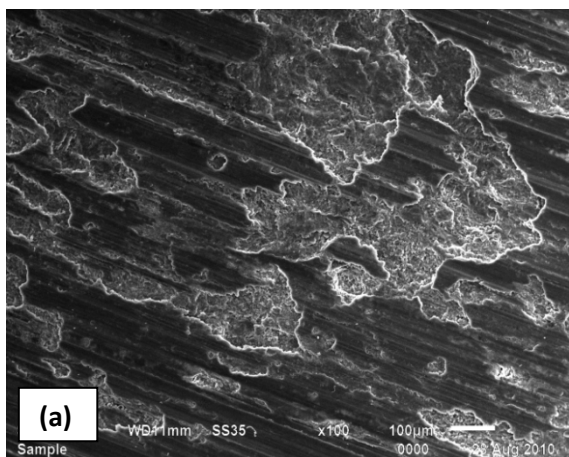


Figure 7.17: SEM micrographs of wear debris of spray formed Al-Si-5Sn/SiC at **(a, b)** 2.5 kg, 50 °C; **(c, d)** 5.5 kg, 50 °C; **(e)** 2.5 kg, 150 °C and **(f)** 5.5 kg, 150 °C.

The worn pins of Al-Si-10Sn/SiC composite at both temperatures and loads are shown in Fig. 7.18. Similar morphology of craters and grooves are seen on the worn surface of the pins except the Sn forming lubricating film over the surface as shown in Fig. 7.18 (a, b). The grooves and craters get deeper on increasing load at same temperature as illustrated in Fig. 7.18 (c-e). However, at higher magnification Fig. 7.18 (e) the craters seem to be formed from the rupture of mechanically mixed layer (MML). On increasing the temperature at 2.5 kg load the worn pin surface exhibits shallow grooves and less deep craters as compared to lower temperature shown in Fig. 7.18 (f). On further enhancement of load the number of craters and white patches increases over the surface in the vicinity of SiC particles as shown in Fig. 7.18 (g).



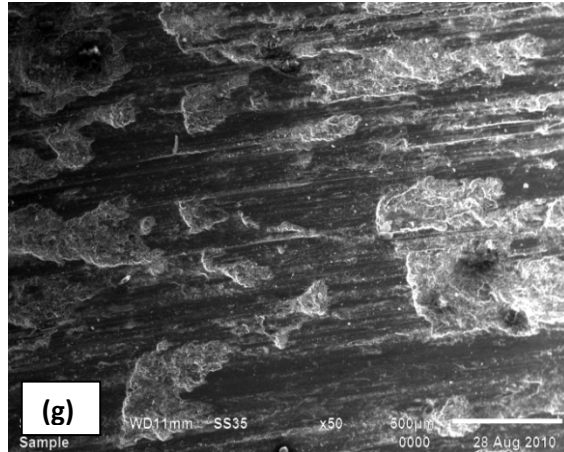


Figure 7.18: SEM micrographs of worn surfaces of Al-Si-10Sn/SiC at **(a, b)** 2.5 kg, 50 °C; **(c-e)** 5.5 kg, 50 °C; **(f)** 2.5 kg, 150 °C and **(g)** 5.5 kg, 150 °C.

Fig. 7.19 shows the wear debris morphology of Al-Si-5Sn/SiC composite. The wear debris is collected for 2.5 kg applied load and 50°C test temperature which is quite small in size i.e. 2–20 μm (Fig. 7.19 (a, b)). The debris appeared to be generated from the craters or edges of the grooves as shown in Fig. 7.19 (b). The rupture process generates oxide debris of quite fine size at higher applied loads (Fig. 7.19 (c)). The wear rate behavior is also analogous to the results found at higher loads described earlier in Fig. 7.6. Moreover, the craters are also shallow which depicts the stable MML over the surface. Wear debris formed under such conditions are quite small in quantity. The chunks formed during run-in-wear are observed with very small amount of oxide debris as shown in Fig. 7.19 (d). The homogeneous lubricating Sn film can be seen on the surface of the flake with some cracks running both parallel and perpendicular to the sliding direction as shown in Fig. 7.19 (d). The lubricating Sn layer is more uniform on the surface at higher temperature and lower load which corresponds to the minimum wear loss. The coagulation of the small debris is also observed in Fig. 7.19 (e) which seems to be generated from material loss of the MML. Moreover, wear rate in Al-Si-10Sn/SiC reinforced composite (Fig. 7.6) is lower than Al-Si-5Sn/SiC reinforced composite (Fig. 7.5). This might be due to the increase in the lubrication effect provided by Sn between the rubbing surfaces. The results are similar to the findings of Rudrakshi et al. [11] in Al-Si-Pb alloys showing smearing of Pb particles at 50N load.

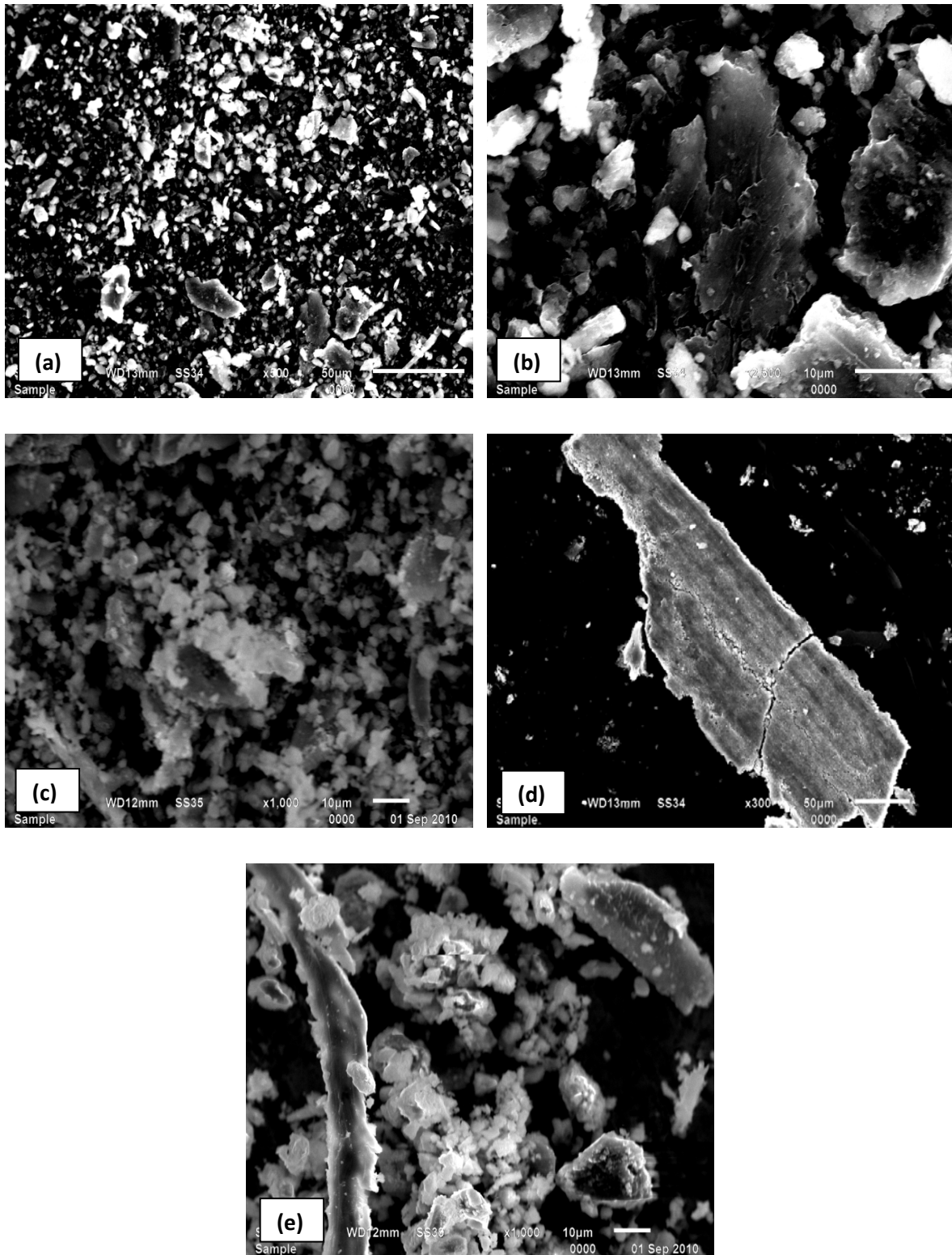


Figure 7.19: SEM micrographs of wear debris of spray formed Al-Si-10Sn/SiC at **(a, b)** 2.5 kg, 50 °C; **(c)** 5.5 kg, 50 °C; **(d)** 2.5 kg, 150 °C and **(e)** 5.5 kg, 150 °C.

The worn surfaces and debris of Al-Si-5Bi/SiC composite are shown in Fig. 7.20 and 7.21 respectively. Fig. 7.20 (a) shows that at higher load debris have been generated from edges of the grooves. However, a thin lubricating layer is also found on the surface. The morphology of the debris generated under such conditions consists of small flakes detaching from the edges of grooves as shown in Fig. 7.21(a).

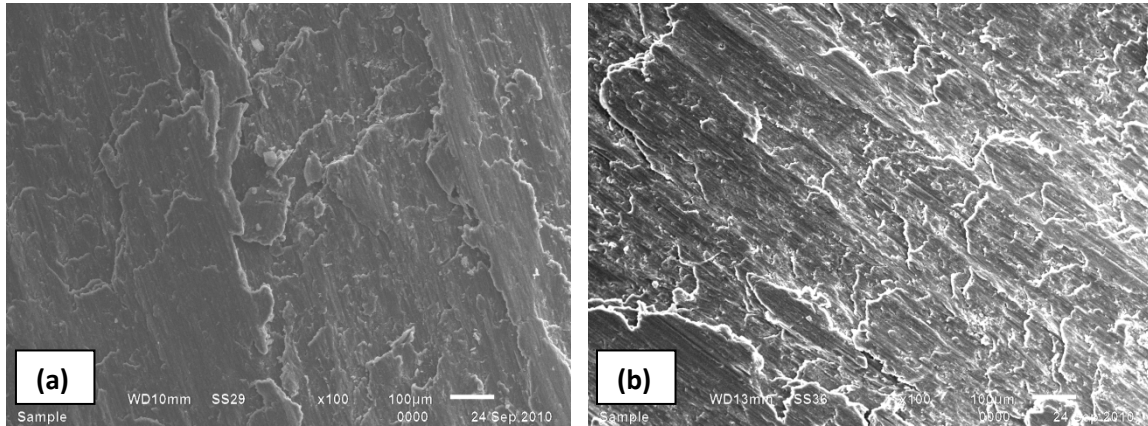


Figure 7.20: SEM micrographs of worn surfaces of spray formed Al-Si-5Bi/SiC (106–125 µm) composite under 5.5 kg load at (a) 50 °C and (b) 150 °C.

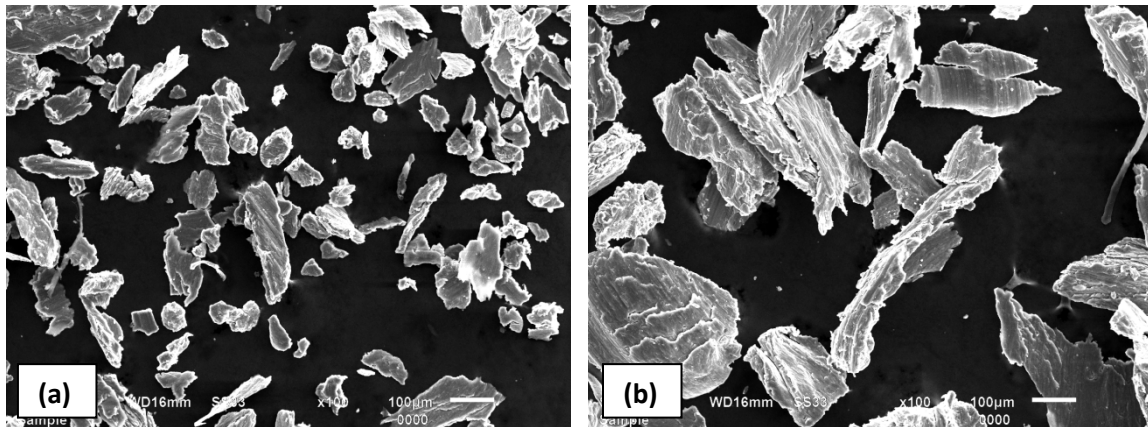


Figure 7.21: SEM micrographs of wear debris of spray formed Al-Si-5Bi/SiC (106–125 µm) composite under 5.5 kg load at (a) 50 °C and (b) 150 °C.

At higher temperature, continuous loading marks on the sliding surface of Al-Si-5Bi/SiC composite can be seen in Fig. 7.20 (b). Such morphology has resulted from severe adhesion as the steel counterface plastically deforms the soft metal surface. The relatively large size flakes has been removed from the surface as shown in Fig. 7.21(b). Yao-hui et al. [7]

reported such type of worn surface morphology in Al-alloys and composites and called it shear-wedge pattern.

The worn surfaces and wear debris of Al-Si-10Bi/SiC composites have been shown in Fig. 7.22 and 7.23 respectively. The worn surface shows the oxidative compact layer deposited over the surface of the composite along with the lubricating film of Bi. The worn surface topography as shown in Fig. 7.22(a) indicates that grooves are deep where as at higher temperature the groove depth decreases and become broader (Fig. 7.22 (b)).

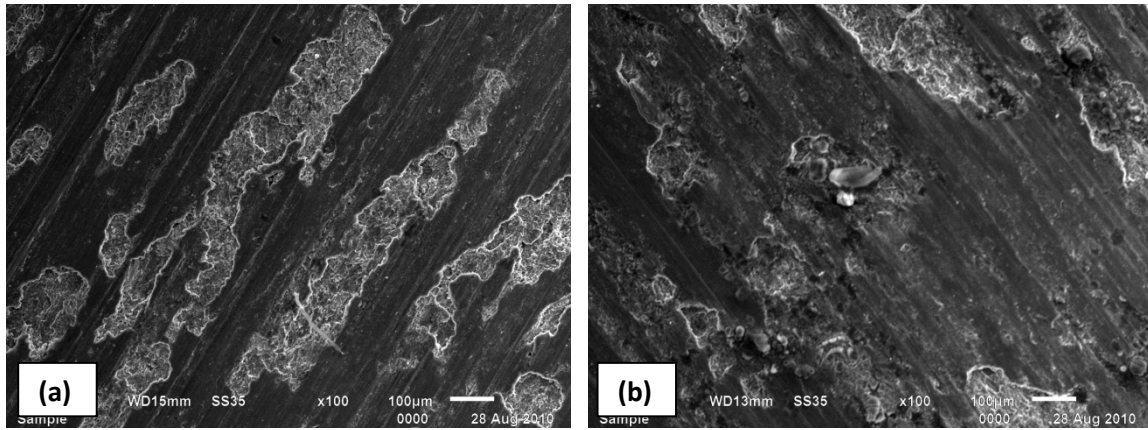


Figure 7.22: SEM micrographs of worn surface of spray formed Al-Si-10Bi/SiC (106–125 μm) composite at 5.5 kg load **(a)** 50 °C and **(b)** 150 °C.

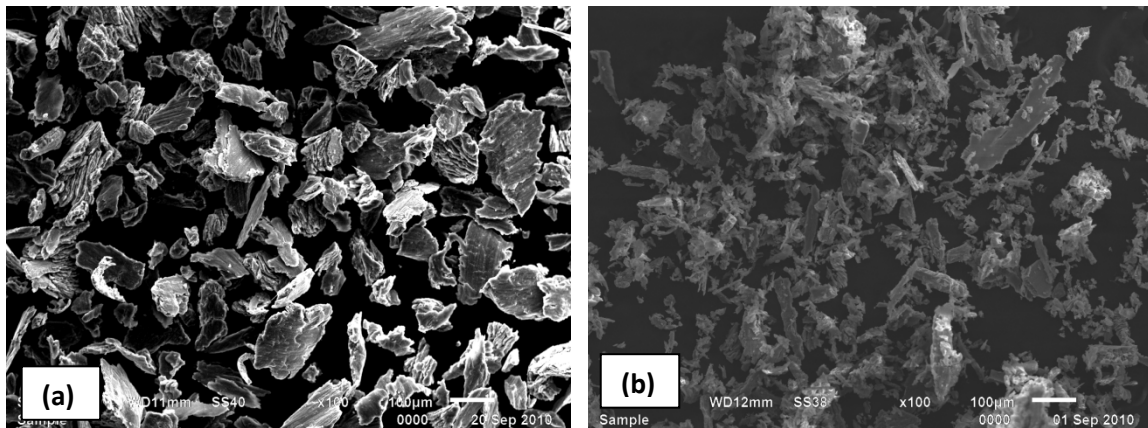


Figure 7.23: SEM micrographs of wear debris of Al-Si-10Bi/SiC (106–125 μm) composite under 5.5 kg load at **(a)** 50 °C and **(b)** 150 °C.

Also at higher temperature the length of white patches has decreased and more uniform layer has been deposited over the entire surface which reduces the direct adhesion

between steel counterface and composite material. Moreover, higher amount of Bi present in the composite get mixed with the oxide layer which further help in smoothening the surface. The morphology of the debris (Fig. 7.23) also indicates that at higher temperature smaller debris have been generated as compared to lower temperature.

The mode of wear mechanism is further verified by the EDS analysis of the worn debris of the alloys and composite. The debris morphology is found to be quite different on addition of SiC particulates in the matrix alloy and their EDS analysis is shown in Fig. 7.24. At 5.5 kg load and 50 °C temperature, Fig. 7.24 (a) confirms the presence of MML on the worn surface as the debris contains large amount of counterpart material. Again at higher temperature and higher load the debris do not get oxidized easily as shown in Fig 7.24 (b). However, the counterpart elements are clearly seen at higher loads.

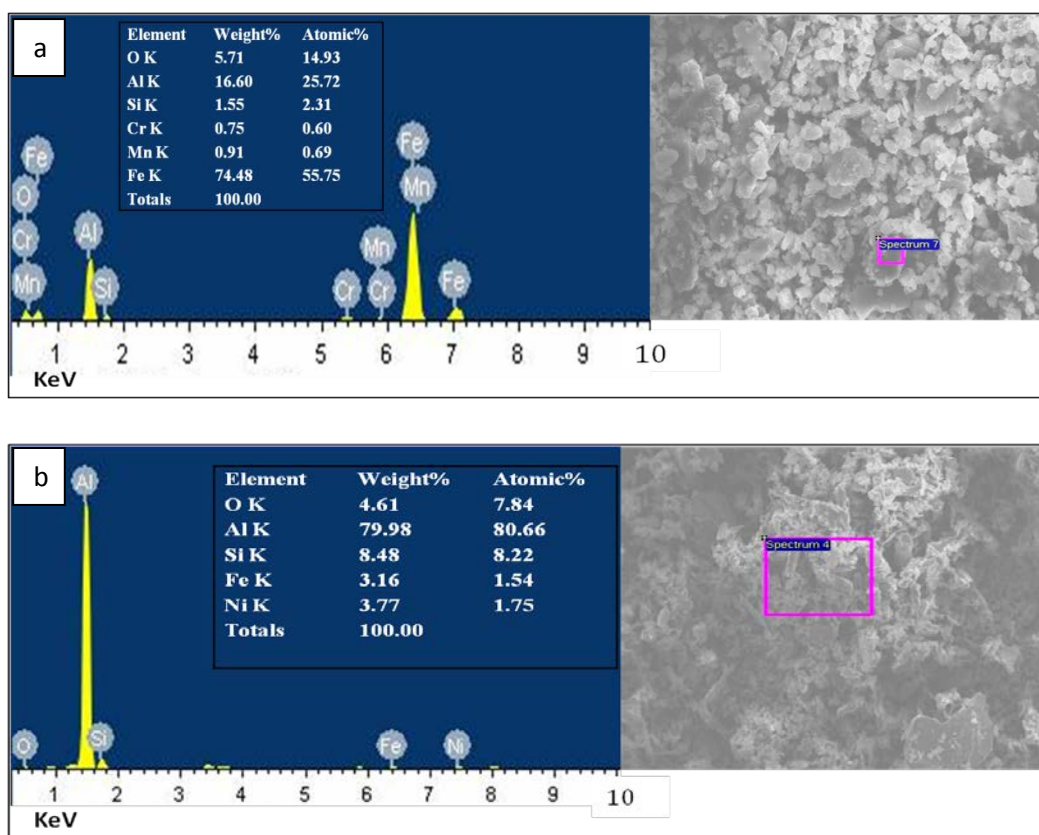


Figure 7.24: The EDS of spray formed Al-Si/SiC (106–125 μm) composite under 5.5 kg at **(a)** 50 °C and **(b)** 150 °C.

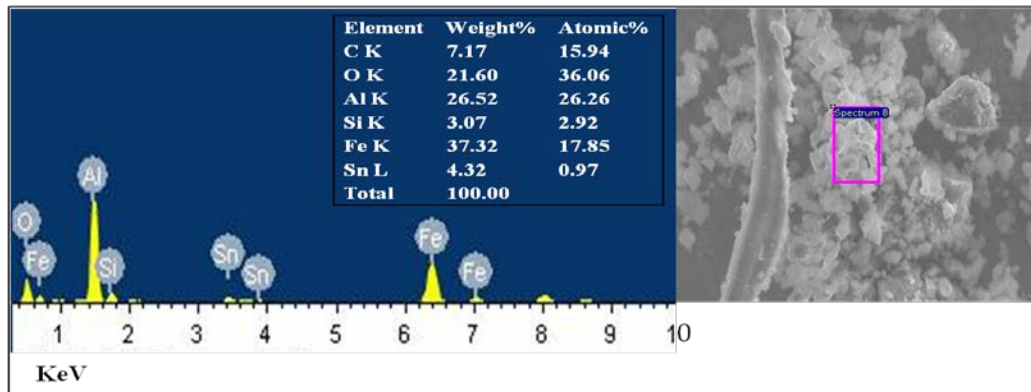


Figure 7.25: The EDS of spray formed Al-Si-10Sn/SiC (106–125 μm) composite at 5.5 kg and 50 $^{\circ}\text{C}$.

Figure 7.25 clearly indicates the presence of oxidative and iron rich contents in Al-Si-10Sn/SiC composite even at higher loads. It again confirms the oxidative wear and presence of MML. This kind of wear mechanism is analogous to the morphological features (Fig. 7.18 and Fig. 7.19), and wear behavior (Fig. 7.6).

Effect of SiC reinforcement of particulate size 63–90 μm

7.8 Samples prepared

This section comprises of the results of spray formed near eutectic Al-Si alloy reinforced with 8 vol. % SiC particles having particulate size 63–90 μm . Also the immiscible elements are added in varied amount to the AMCs. The effect of immiscible element (Sn and Bi) addition on the wear behavior of the composites has been analyzed at various loads and temperatures. The series of the spray formed samples is as follow:

1. Al-Si/SiC (63–90 μm)
2. Al-Si-5Sn/SiC (63–90 μm)
3. Al-Si-10Sn/SiC (63–90 μm)
4. Al-Si-5Bi/SiC (63–90 μm)
5. Al-Si-10Bi/SiC (63–90 μm)

7.9 X-ray diffraction analysis

The XRD pattern of spray formed Al-Si/SiC, Al-Si-5Sn/SiC, Al-Si-10Sn/SiC, Al-Si-5Bi/SiC and Al-Si-10Bi/SiC composites are shown in Fig. 7.26. The presence of major elements in the alloy (Al, Si, Sn/Bi) and the reinforced SiC can be seen. The presence of elements is confirmed by matching the peaks with the reference data of Al (ICDD card no. 03-065-2869), Si (ICDD card no. 01-077-2109), Sn (ICDD card no. 00-004-0673) and SiC (ICDD card no. 01-089-2224). It has been found that the intensity of the Sn/Bi peaks has been enhanced with increasing the Sn/Bi content from 5 to 10 wt. % as shown in Fig. 7.26.

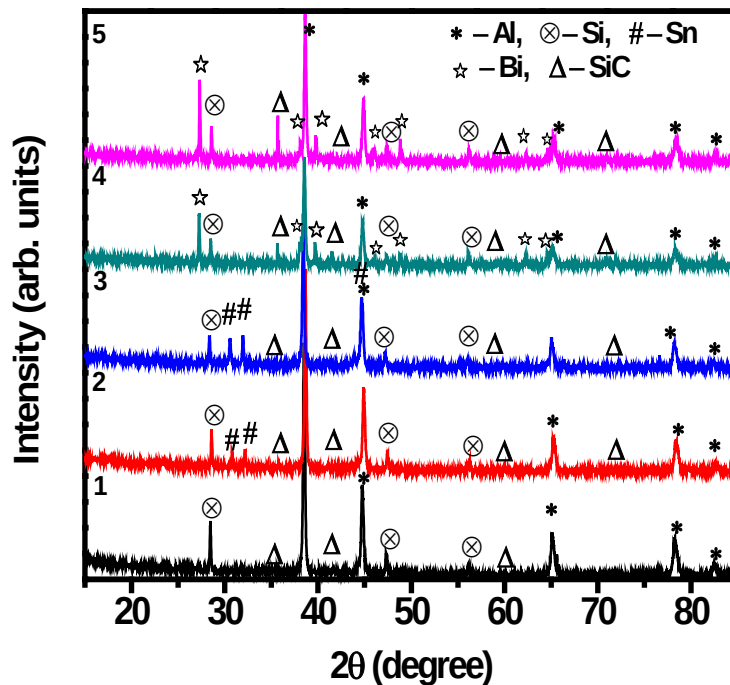


Figure 7.26: XRD pattern of (1) Al-Si/SiC, (2) Al-Si-5Sn/SiC, (3) Al-Si-10Sn/SiC, (4) Al-Si-5Bi/SiC and (5) Al-Si-10Bi/SiC composites.

7.10 Hardness

Hardness of the materials has been measured on B-scale of the Rockwell hardness tester. The average hardness values obtained for spray formed Al-Si alloy, Al-Si-5Sn/SiC, Al-Si-10Sn/SiC, Al-Si-5Bi/SiC and Al-Si-10Bi/SiC composites are shown in Fig. 7.27. The hardness has been found to increase on incorporation of SiC particles in the Al-Si alloy. Further increment in hardness has been obtained with addition of immiscible element

(Sn/Bi) in the matrix alloy. Moreover, microstructure refinement by the spray deposition process also leads to the enhancement of hardness but it is always associated with small amount of porosity. The composites containing low melting point constituent (e.g., Sn/Bi) fills the pores and increases the hardness.

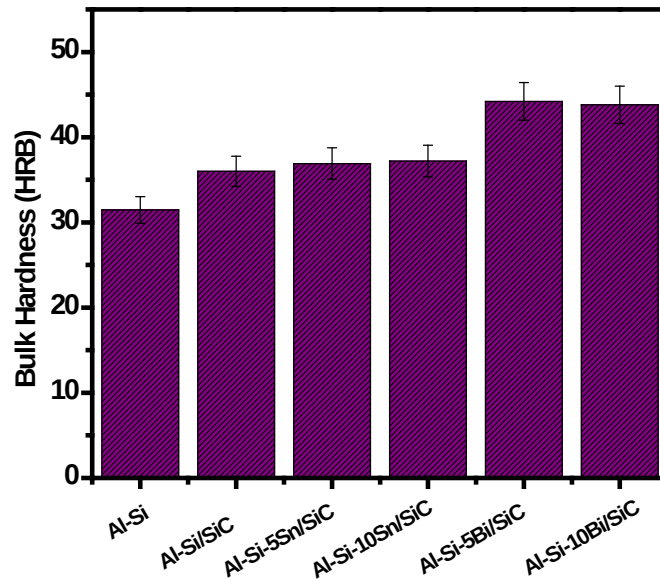
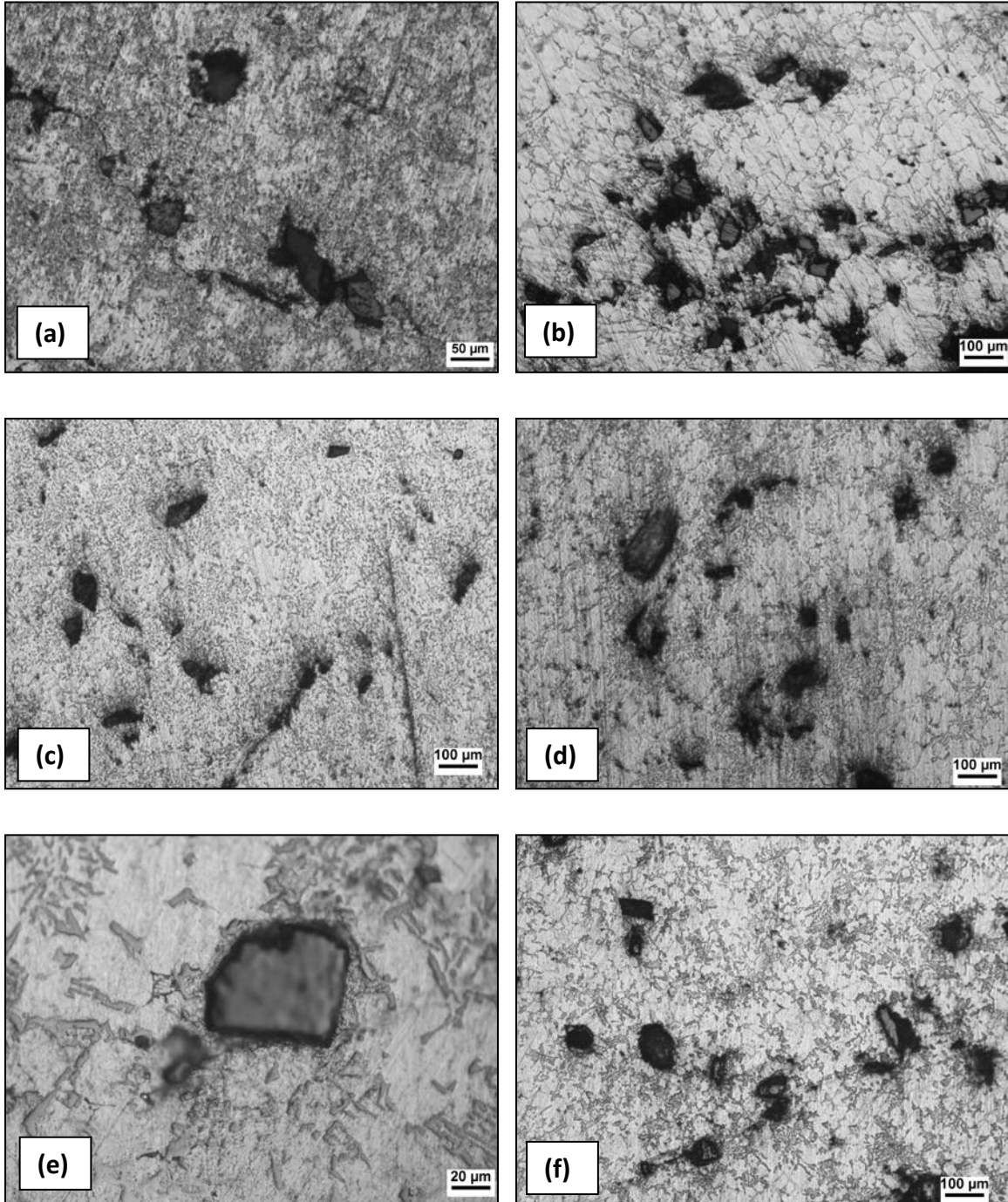


Figure 7.27: Bulk hardness of the prepared composites reinforced with SiC having particulate size 63–90 μm .

7.11 Microstructural analysis

Optical micrographs of spray formed alloy and composites are shown in Fig. 7.28. Figure 7.28 illustrates the refined eutectic morphology of Al–Si matrix along with equiaxed α -Al grain. The evolution of microstructure in spray formed alloys depends upon three sequential steps consisting of droplet deposition, thermal equilibrium and microstructure coarsening. It has been reported that the optimum condition for deposited preform is that the solid fraction of the preform should be equal or lower than the solid fraction of the droplet [12]. This condition makes sure that mushy or liquid droplet impinges onto the mushy preform surface which exhibits good sticking. The initial droplets impinging on the substrate and transfer large amount of heat to the substrate resulting in small equiaxed grains at the bottom of the preform. However, the heat extraction by the substrate slows down as the thickness of the preform increases. Therefore thermal equilibrium is

generated between the heat flux added to the surface by incoming droplets and the heat flux absorbed by the deposit. This condition gives rise to the semi-liquid pool over the surface of the preform.



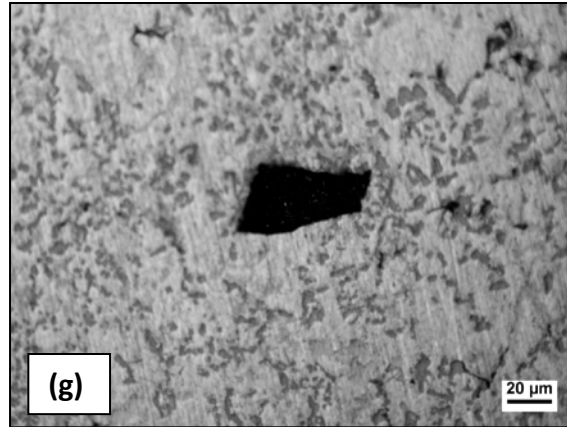


Figure 7.28: Optical micrographs of **(a)** Al-Si/SiC, **(b)** Al-Si-5Sn/SiC, **(c)** Al-Si-10Sn/SiC, **(d, e)** Al-Si-5Bi/SiC and **(f, g)** Al-Si-10Bi/SiC composites having particulate size 63–90μm.

This semi-liquid pool contains floating dendrite network at nucleation sites created by the high velocity gas. The approaching semi-solid droplets impinge on the pool with high velocities which result in breakup of the dendrite network present in semi-liquid pool and semi-solid droplets. The broken dendrite arms acts as fresh nucleating centre for further crystallization. The high velocity gas solidify the preform surface having large nucleation sites and result in the equiaxed microstructure of the grains [13, 14]. Such morphology has been extensively reported by the other researchers also [1, 2]. The SiC particles of size range 63–90 μm can be seen well embedded in the matrix alloy as shown in Fig. 7.28 (a–g). Moreover, primary Si has not been found in any of the sample due to rapid solidification of the melt with N₂ gas jets. In SiC reinforced composite modification in Si morphology is observed as shown in Fig. 2 (d–g). However, the refinement is on higher side with increase in Bi content from 5 to 10%.

7.12 Wear testing

7.12.1 Wear rate vs. sliding distance

Figures 7.29 to 7.33 represent the basic wear curves (wear rate as a function of sliding distance) obtained for Al-Si/SiC, Al-Si-5Sn/SiC, Al-Si-10Sn/SiC, Al-Si-5Bi/SiC and Al-Si-10Bi/SiC composites respectively. The wear behavior has been presented at four different temperatures 50, 75, 100, 150°C and five different loads (1.5–5.5 kg). Initial run-in wear has higher and unstable wear rate which is observed for all the specimens. Such behavior is

obtained when two different surfaces come in contact during sliding and their relative asperities hinder each other. However, on further sliding the shape of the asperities changes and adjusts according to the mating surfaces. The steady state is reached at this point in which wear is stable. In most of the samples steady state is reached after 500–1000 m sliding distance depending upon the wear behavior of material unless seizure has occurred in the run in wear regime.

7.12.2 Effect of load

In general, wear rate is found to increase with increase in the applied load. This can be correlated with the widely used quantitative relationship for adhesive wear rate given by Archard [5]. According to which the wear volume is directly proportional to the applied load and inversely proportional to the hardness of the material. As studied in previous chapter 5 that beyond 3.5 kg load, seizure is observed in base Al–Si alloy and wear rate do not get stabilize for higher loads as pin worn out up to the maximum limit of the tribometer. Similar wear rate variation is presented by Al–Si/SiC composite as shown in Fig. 7.29 (a) at 5.5 kg load and 50 °C. However, Al–Si/SiC composite do not exhibit seizure at the higher loads and higher temperatures (Fig. 7.29 (b–d)). Also little fluctuations in the wear rate can be seen at the higher load conditions owing to detachment of the welded wear debris from the pin surface. Therefore, due to incorporation of the hard particles in the soft Al–Si alloy the seizure wear is delayed for higher loads and temperatures. It has been reported that when the SiC particles are strongly bonded with the Al–Si matrix they protect the surface from severe distortion. The strong interfacial bonding helps to transfer load from matrix to the hard reinforced particles [15]. On the other hand, cracks have nucleated at the area of poor interfacial bonding which lead to pull out the particle from the surface. The wear rate of the material further enhances as the loosen particle contribute to abrade the sliding surface. The prepared samples show good particle matrix bonding therefore wear rate is found to decrease at higher load and temperature conditions.

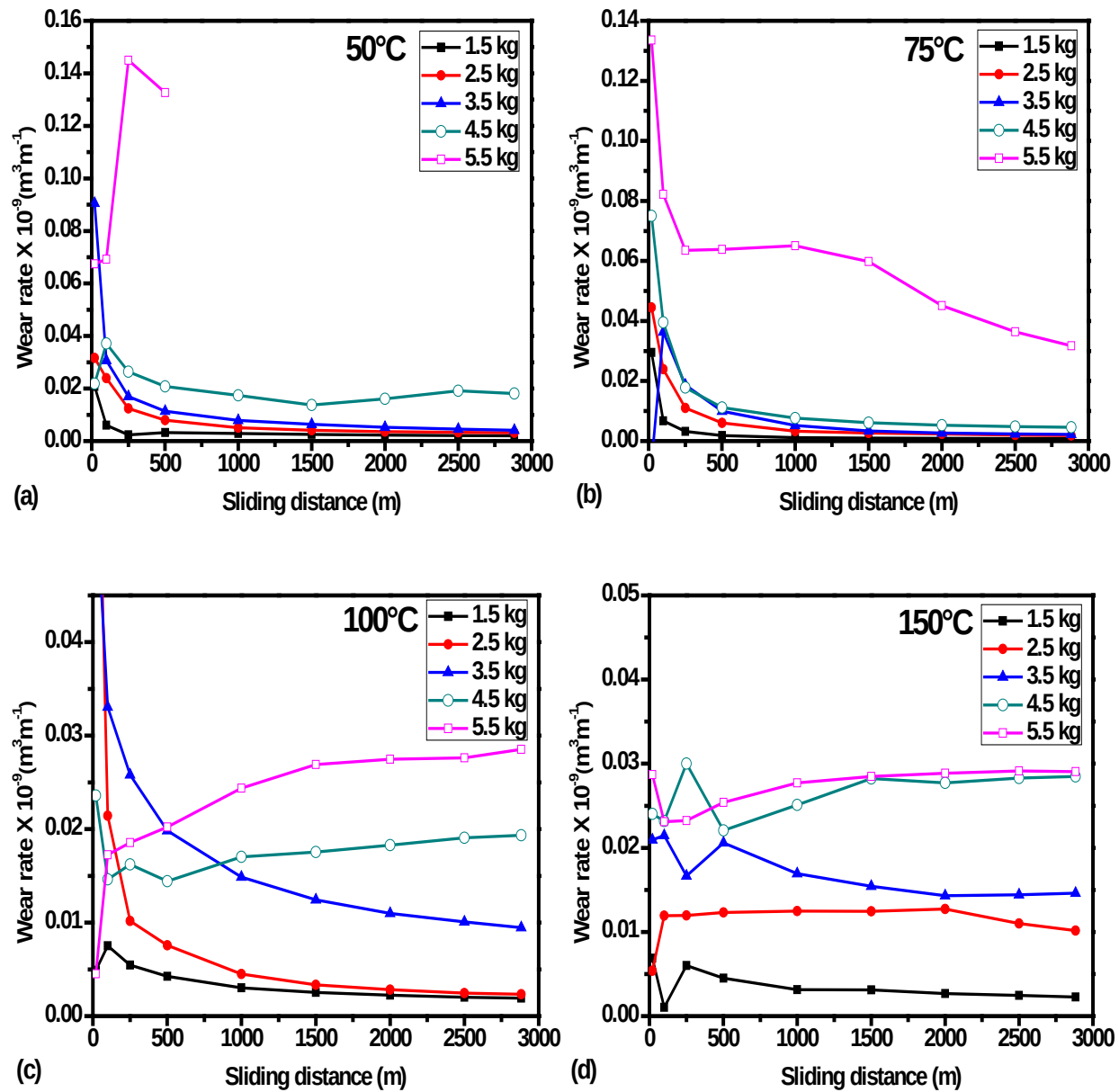


Figure 7.29: Wear rate of the spray formed Al-Si/SiC (63–90 μm) composite under various loads at (a) 50°C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

Supplementary reduction in the wear rate is achieved with addition of low melting point constituent Sn in the matrix alloy as shown in Fig. 7.30. The exceptional behavior has been found at 50 °C and 5.5 kg load (Fig. 7.30 (a)) where lesser wear rate has been obtained as compared to the wear rate exhibited by lower loads. At higher load debris are continuously ground in between the sliding surface and get compacted over the surface. This diminishes the chance of the direct metal to metal contact and hence reduces the wear rate of the

material to a greater extent. Additionally, Sn provides a lubricating film over the sliding surfaces which further helps in wear reduction. Therefore, the stable lubricating Sn film formed by crushed debris decrease the wear exceptionally at high load condition. The temperature plays an important role in stability of lubricating Sn film.

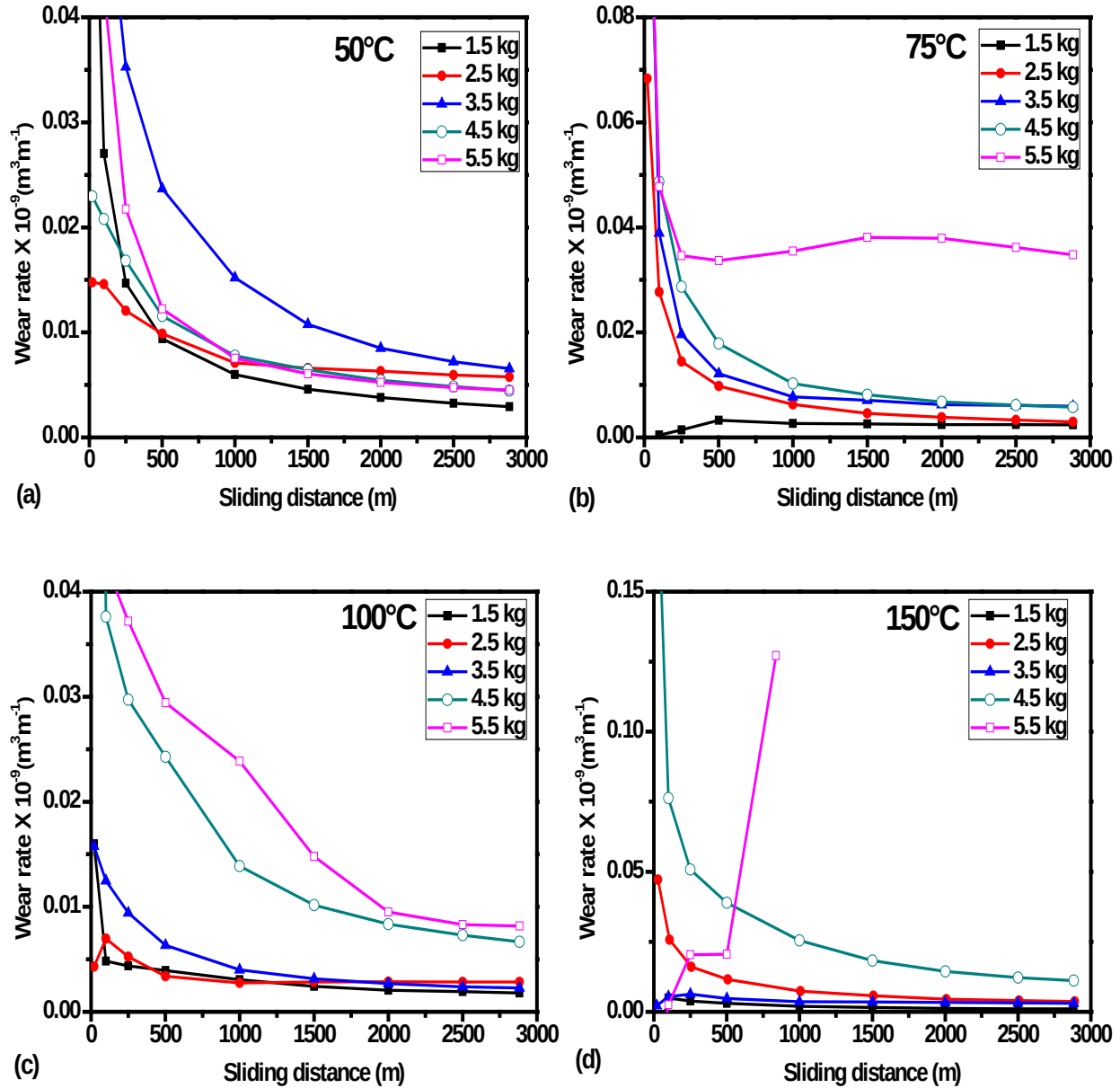


Figure 7.30: Wear rate of the spray formed Al-Si-5Sn/SiC (63–90 μm) composite under various loads at (a) 50°C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

The film is stable and continuous at lower temperature and hence reduces the wear rate remarkably at 5.5 kg load and 50 °C. However, at the same load with temperature

increment the time to get steady state wear rate condition increases as shown in Fig. 7.30 (c) at 100 °C which ultimately lead to seizure at 150 °C (Fig. 7.30 (d)).

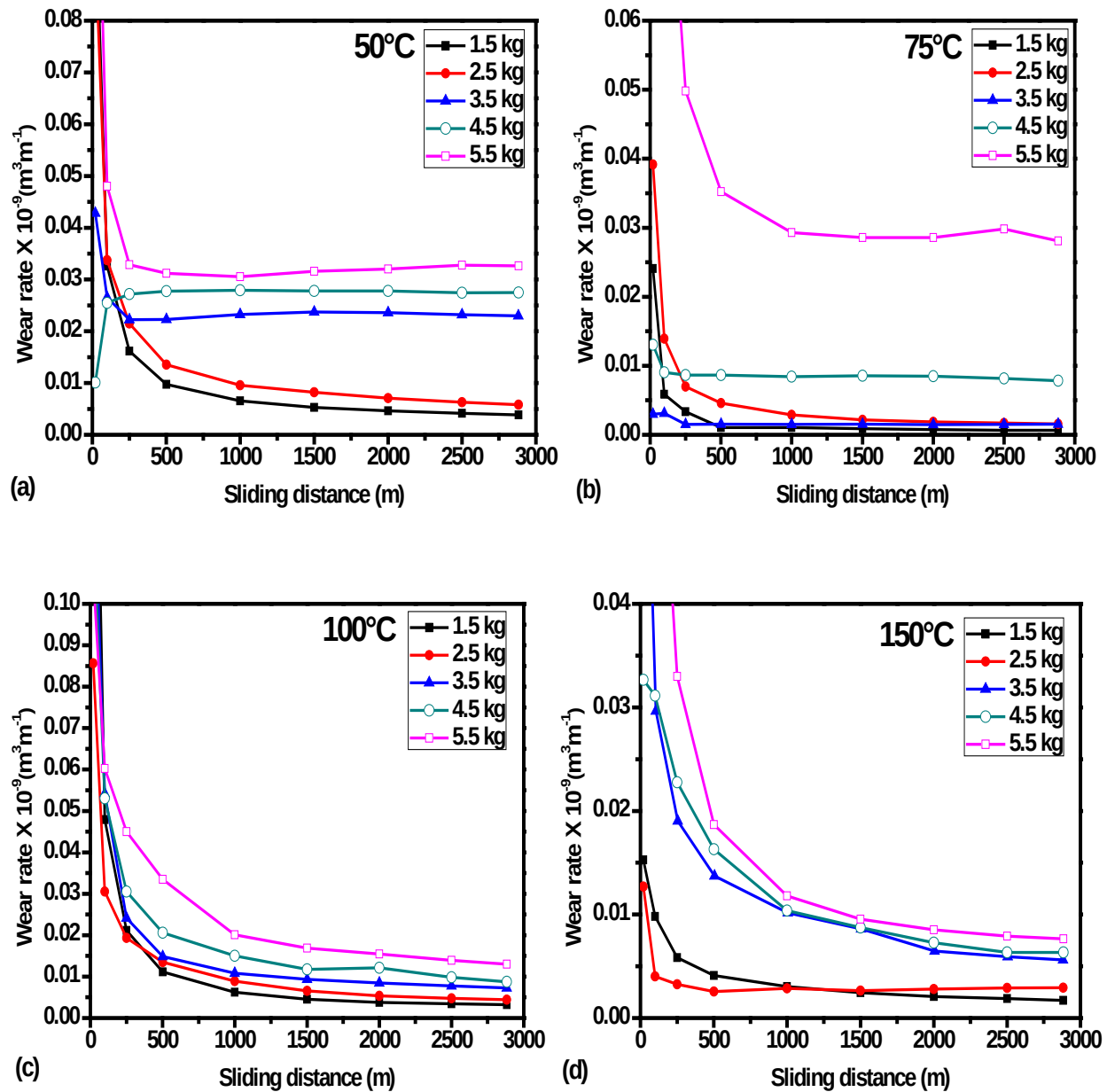


Figure 7.31: Wear rate of the spray formed Al-Si-10Sn/SiC (63–90 μm) composite under various loads at (a) 50°C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

The seizure occurs as the lubricating film gets oxidized at the higher temperature. The critical amount of Sn is required to feed the sliding surfaces continuously for stable lubricating film at higher temperature. This has been achieved with 10 wt. % Sn addition in

the matrix alloy as shown in Fig. 7.31 (a-d) for Al-Si-10Sn/SiC composite. The mild wear has been found in Al-Si-10Sn/SiC composite irrespective of the higher loads and temperatures owing to stability of continuous lubrication film. Higher content of Sn in the alloy offer a stable lubricating film, as once the film is worn through or oxidized it is simultaneously replenished by other Sn present in the grains and grain boundaries of the composite.

Figure 7.32 (a-d) represents the wear rate behavior of spray formed Al-Si-5Bi/SiC composite. Addition of 8 vol. % SiC and Bi play important role in enhancing the wear rate properties of the composite material. The immiscible Bi having low melting point tries to cover the entire sliding surface during smearing action. However, at 5.5 kg and 150 °C test condition (Fig. 7.32 (d)) wear rate does not get stabilize and shows the abrupt increase in wear for Al-Si-5Bi/SiC composite. Under lower temperatures, the wear has been stabilized even at higher applied loads (Fig. 7.32 (a-c)). Therefore, with increase in temperature wear rate seems to be increasing. Even the lower loads are imposing higher wear with increment in temperature. It could be best understood by oxidative and lubrication phenomena that occur during the wear test conditions. The heat is generated from frictional forces, due to which low melting point Bi comes out from the grains and grain boundaries at the surface and provides lubrication effect. However, with increase in the test temperature the lubricating film of Bi itself oxidizes and smears off from the surface leading to direct metal to metal contact. Also at lower loads, the surfaces do not get excessive heating as compared to higher load and higher temperature conditions. Therefore, at higher temperature wear, larger amount of Bi is required to get continuous thin film on the sliding surfaces. Figure 7.33 shows the wear rate of Al-Si-10Bi/SiC composite at various temperatures. It has been observed that an addition of 10 wt. % Bi in composite, severe wear regime has not been observed even for extreme conditions as shown in Fig. 7.33 (a-d).

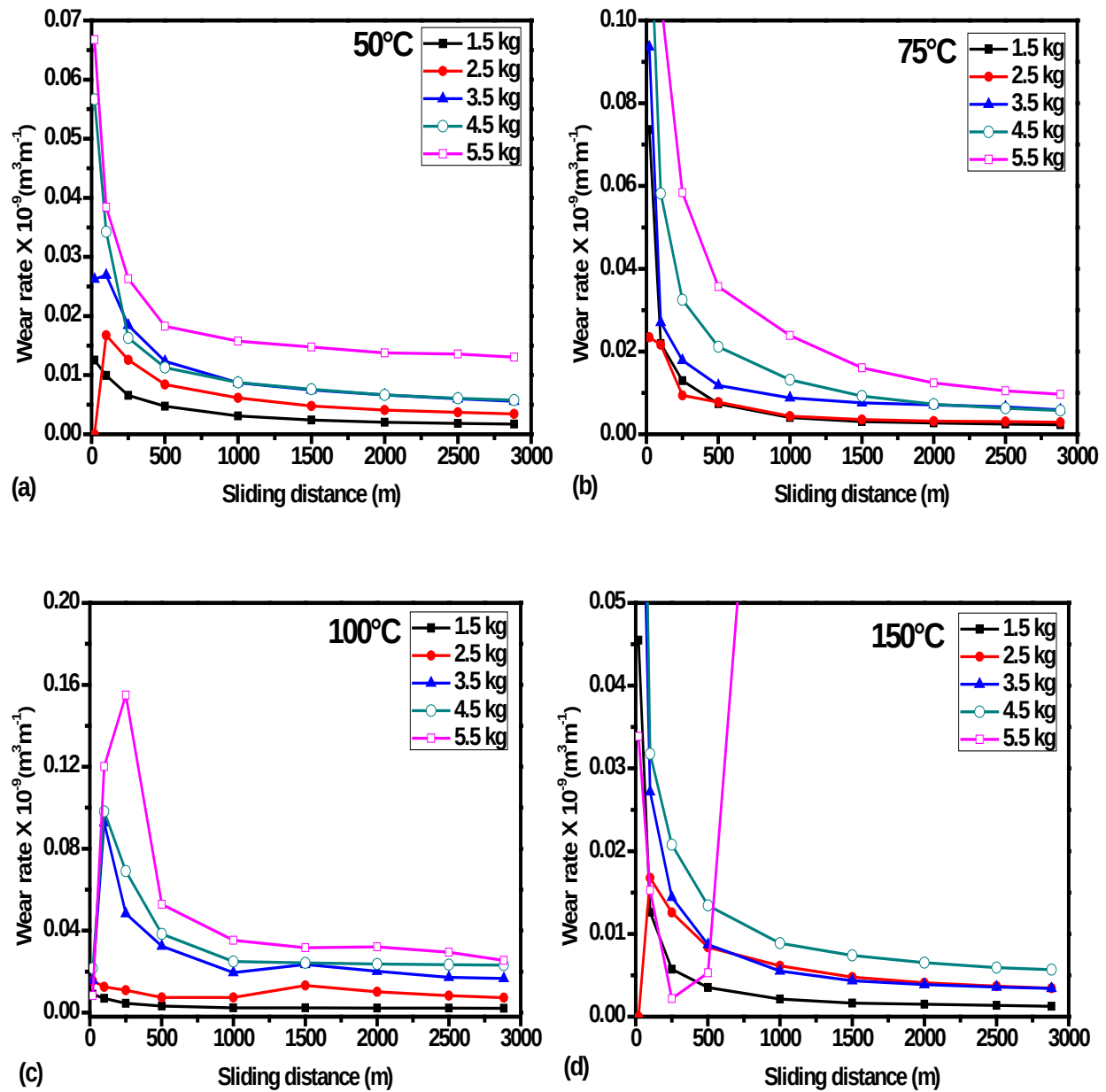


Figure 7.32: Wear rate of the spray formed Al-Si-5Bi/SiC (63–90 μm) composite under various loads at (a) 50°C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

The continuous feeding of Bi in the form of the lubricating film between the sliding surfaces decreases direct metal to metal contact. Even at higher temperature the stable wear rate has been obtained as shown in Fig. 7.33 (d). It has been reported that the improvement in wear resistance at higher pressure can be obtained by increasing the amount of immiscible

Pb content in the Al-base alloy [16]. Similar results have been found in our case where increment in Bi content lowers the wear rate even at high temperature.

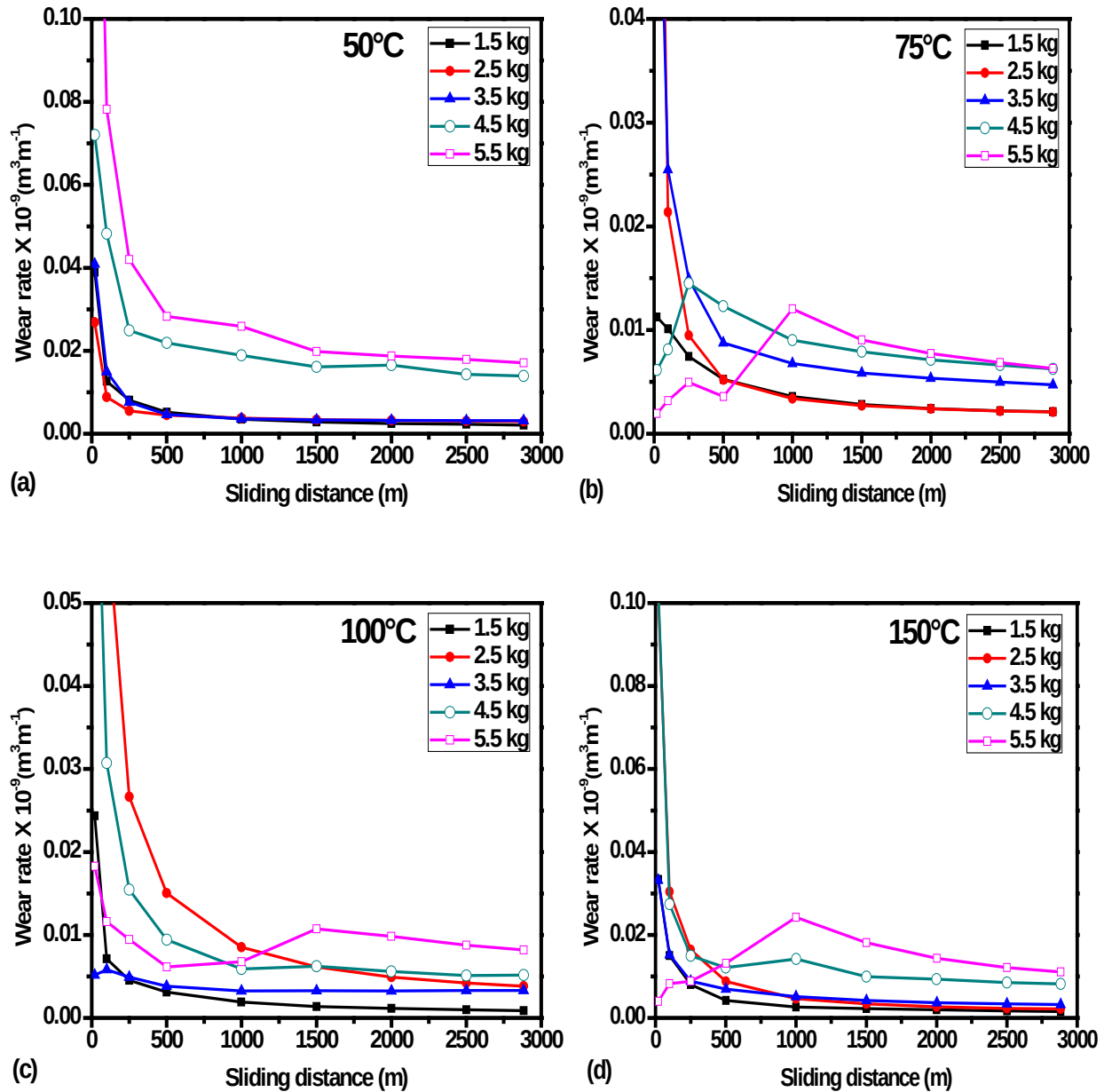


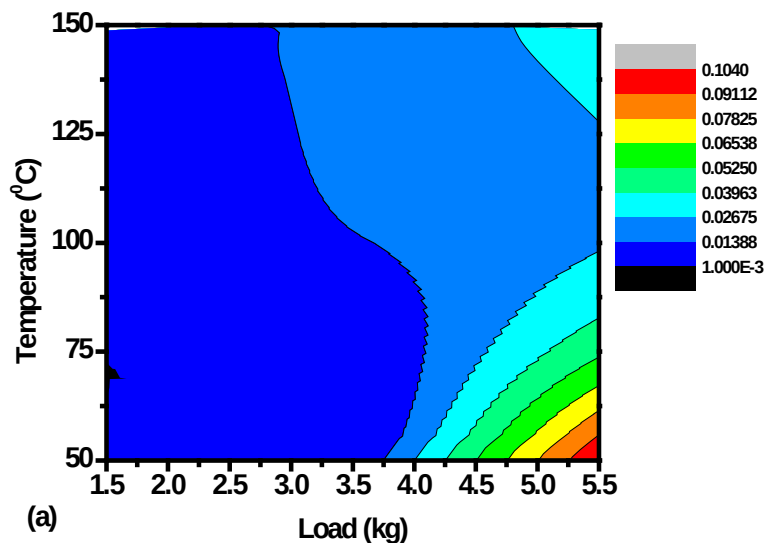
Figure 7.33: Wear rate of the spray formed Al-Si-10Bi/SiC (63–90 μm) composite under various loads at (a) 50°C, (b) 75°C, (c) 100°C and (d) 150°C temperature.

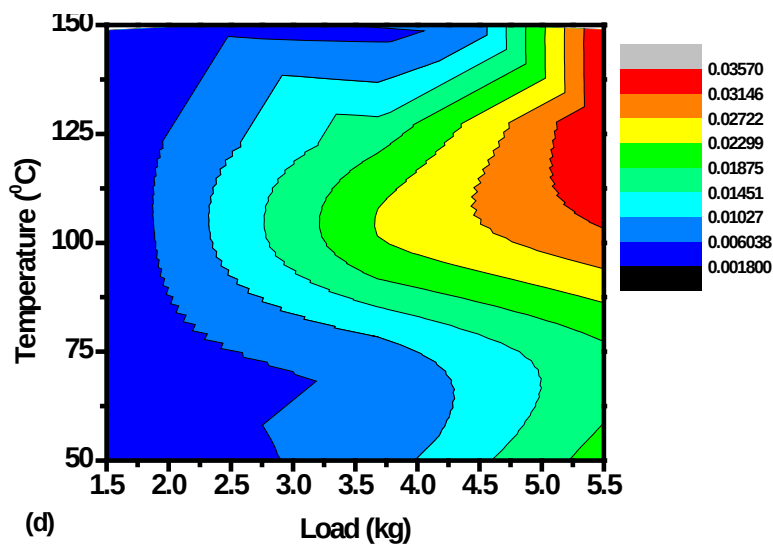
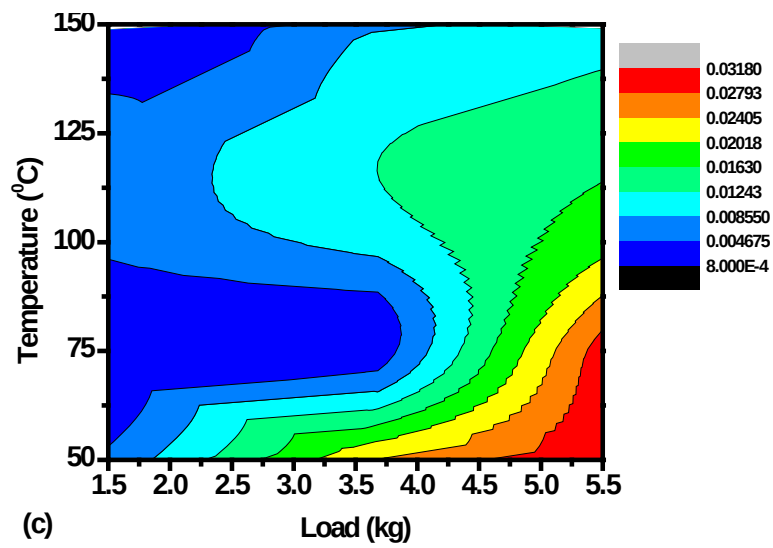
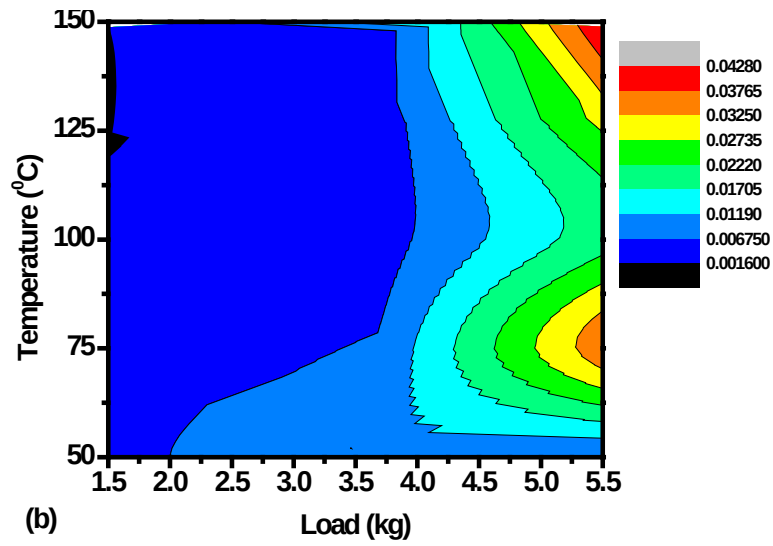
7.12.3 Effect of temperature

The steady state average wear rate contours have been plotted against various temperatures and applied loads to analyze the effect of variation in test parameters on the

wear. Figure 7.34 (a–e) represents the wear contours of spray formed Al–Si/SiC, Al–Si–5Sn/SiC, Al–Si–10Sn/SiC, Al–Si–5Bi/SiC and Al–Si–10Bi/SiC composites respectively. As depicted from the wear rate behavior, Fig. 7.34 (a) shows that the higher wear rate regime lies at the right bottom where severe wear occur at 50 °C and 5.5 kg load. The temperature helps in reducing the wear rate at higher load in Al–Si/SiC composite. The higher temperature results the formation of oxides which ultimately reduces the direct metal to metal contact and hence wear rate. However, further reduction in the wear rate is found with addition of Sn in the alloy as shown Fig. 7.34 (b). The reverse temperature effect on wear rate is found in Al–Si–5Sn/SiC composite. With increase in temperature an increase in the wear owing to the oxidation of the lubricating film at higher temperature is seen. Figure 7.34 (c) illustrates the wear contours of Al–Si–10Sn/SiC composite. The higher though stable wear rate has been found at lower temperature region at higher loads. The stable wear rate has been obtained with increase in the temperature even at 5.5 kg load. This is because both the oxidative layer and lubrication film facilitate greater wear resistance.

Figure 7.34 (d) represents average wear rate of Al–Si–5Bi/SiC composite at different test temperatures and loads. The wear contours show that the average wear rate at lower loads increases gradually with temperature though the increment lies in the mild wear regime. However, at higher load and at temperature greater than 100 °C the increment in wear rate is larger. Therefore severe wear has been delayed up to 100 °C in Al–Si–5Bi/SiC composite as compared to the base alloy.





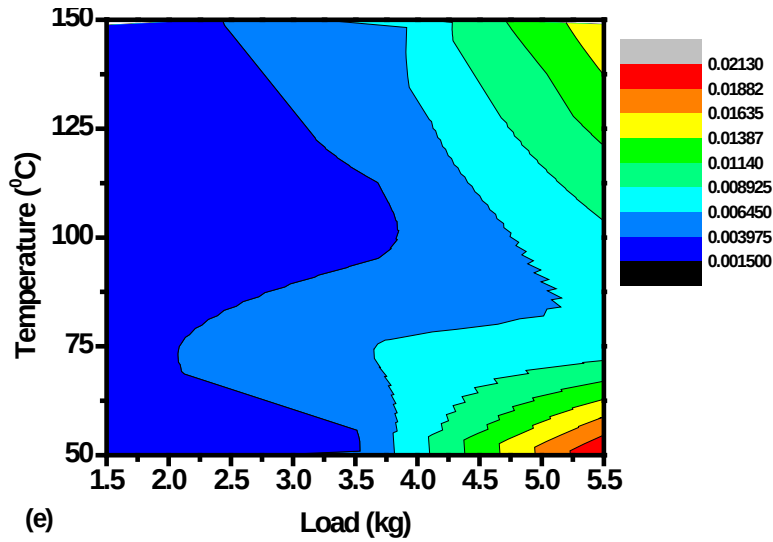


Figure 7.34: Averaged wear rate ($\times 10^{-9} \text{ m}^3\text{m}^{-1}$) against various temperatures and applied loads for **(a)** Al-Si/SiC, **(b)** Al-Si-5Sn/SiC, **(c)** Al-Si-10Sn/SiC, **(d)** Al-Si-5Bi/SiC and **(e)** Al-Si-10Bi/SiC composite.

Figure 7.34 (e) shows the average wear contours of Al-Si-10Bi/SiC composite. The composite shows higher wear at 5.5 kg load at lower temperatures. With increase in temperature (75 and 100 °C) the wear rate decreases which further increases at 150 °C test temperature though this increment does not lead the pin to wear out. This can be better understood on the basis of higher amount of Bi in the matrix which imparts continuous and steady lubrication film even at higher temperature. Additionally, at the higher temperature the probability of formation of oxides is increased. Therefore these oxides form a stable oxidative layer on the sliding surfaces. This oxide layer further combines with lubricating Bi as well as counterface elements during high temperature sliding. It ultimately leads to the formation of mechanically mixed layer (MML) over the surface which reduces the wear rate of the material.

The comparison of wear rate of the different specimens at the extreme test conditions is shown in Fig. 7.35. At 50 °C temperature Al-Si-5Sn/SiC composite shows the lowest wear rate where Al-Si alloy and Al-Si/SiC composite shows the highest wear due to seizure of the material. However, at higher temperatures (75 °C and 100 °C) the Al-Si alloy, Al-Si/SiC, Al-Si-5Sn/SiC and Al-Si-10Sn/SiC show the descending trend of wear rates as illustrated in Fig. 7.35. In brief, wear rate reduces with increase in temperature for Al-Si/SiC due to

oxidative wear. In Al-Si-5Sn/SiC composite both oxidative layer as well as lubricating film effect the tribological behavior of the material. However, at 150 °C the oxidation of the lubricating layer provides discontinuity on the sliding surface which enhances the wear rate in Al-Si-5Sn/SiC composite. However, the higher content of Sn in Al-Si-10Sn/SiC composite provides continuous lubricating film over the surface even at higher temperature. Thus in Al-Si-10Sn/SiC composite offers lowest wear rate at 150 °C.

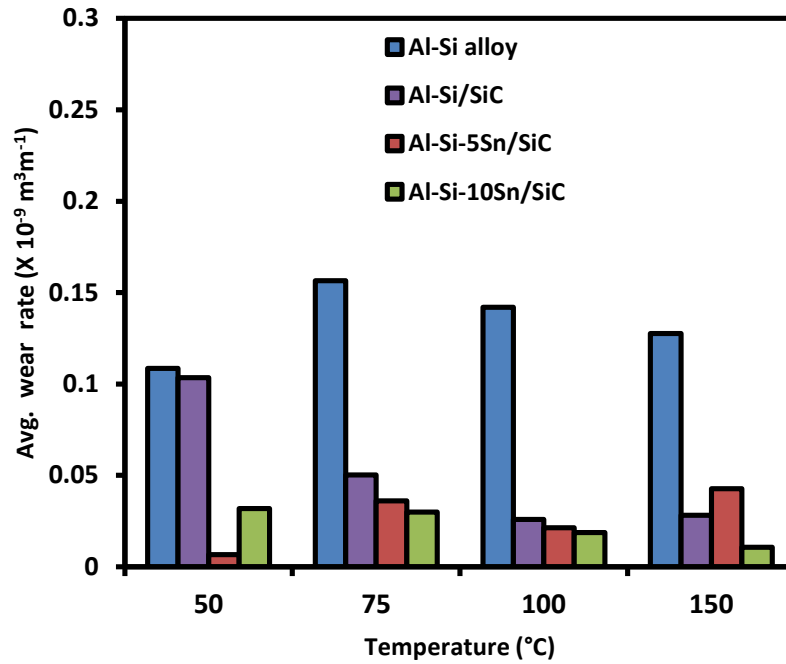


Figure 7.35: Comparison of the average wear rates against various temperatures at 5.5 kg applied load for SiC reinforced (63–90 μm) and Sn containing AMC.

Figure 7.36 illustrates the average wear rate at extreme test condition of Al-Si alloy, Al-Si/SiC, Al-Si-5Bi/SiC and Al-Si-10Bi/SiC composites. At each temperature, Al-Si alloy shows higher wear as compared to the composite materials. At lower temperature, both Al-Si-5Bi/SiC and Al-Si-10Bi/SiC shows similar behavior irrespective to the variation in Bi content. However, as temperature is increased Al-Si-5Bi/SiC composite shows gradual increase in the wear rate. This increment is due to metallic wear that occurs due to direct metal to metal contact. The lower Bi content fails to provide continuous lubrication over the entire sliding surface at the higher temperature. On the other hand, Al-Si-10Bi/SiC exhibits the minimum wear rate ($7.6 \times 10^{-12} \text{ m}^3\text{m}^{-1}$) at 75 °C as shown in Fig. 7.36. The wear

rate further enhances from 8.4 to $15.5 \times 10^{-12} \text{ m}^3\text{m}^{-1}$ with temperature though this increment does not lead to severe wear.

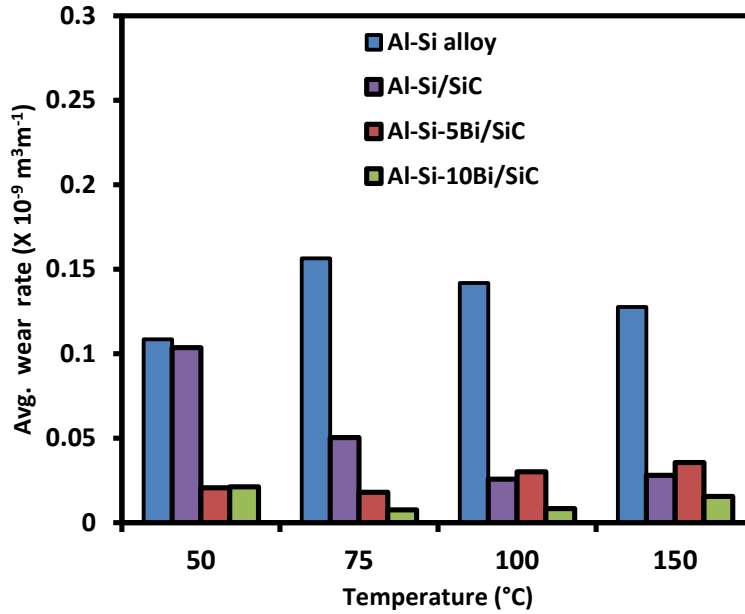


Figure 7.36: Comparison of the average wear rates against various temperatures at 5.5 kg applied load for SiC reinforced (63–90 μm) and Bi containing AMC.

As discussed earlier, at higher temperature both the lubrication and oxidation effect comes into existence. The higher content of Bi continuously provides the lubrication even at 75 °C whereas with further increment in temperature the chances of oxide formation are greater. Therefore a competition between lubricating film and oxide layer led to increase yet stable wear rate at higher temperature in Al–Si–10Bi/SiC composite.

At 150 °C and 5.5 kg load, the average wear rate of Al–Si/SiC, Al–Si–5Sn/SiC, Al–Si–10Sn/SiC, Al–Si–5Bi/SiC and Al–Si–10Bi/SiC (63–90 μm) composites is 2.81×10^{-11} , 4.26×10^{-11} , 1.07×10^{-11} , 3.57×10^{-11} and 1.55×10^{-11} respectively. The average wear rate shows that Al–Si/SiC composite offer good wear resistance at the highest temperatures due to higher stability of oxide layer. Al–Si–5Sn/SiC and Al–Si–5Bi/SiC composites show the greater wear resistance at 50 and 75 °C respectively at 5.5 kg load (Fig. 7.35 and 7.36). Also, under the severe test conditions, Al–Si–10Sn/SiC and Al–Si–10Bi/SiC composite offer better wear resistance as compared to other composites. It can be concluded from the

average steady state wear rate that Al–Si–10Sn/SiC composite is the best wear resistant in SiC (63–90 μm) reinforced AMCs.

7.12.4 Friction Coefficient

The variation in friction coefficient against temperatures at 2.5 and 5.5 kg load is presented in Fig. 7.37 and 7.38. It is worth to be noted that the data given is average values of friction coefficients in steady state unless seizure occurs for the material during run-in wear. The friction coefficient does not follow any regular trend. Figure 7.37 represents the comparison of frictional coefficients of Al–Si alloy, Al–Si/SiC and Sn containing composites. In general, frictional coefficient for the composites increases with increase in temperature as shown in Fig. 7.37 (a). During sliding, the energy is transformed in various actions. Large amount of energy is dissipated in overcoming frictional forces which ultimately rise the pin temperature due to generation of heat. Some part of energy is spent on plastic deformation of the asperities and subsequent material removal [17].

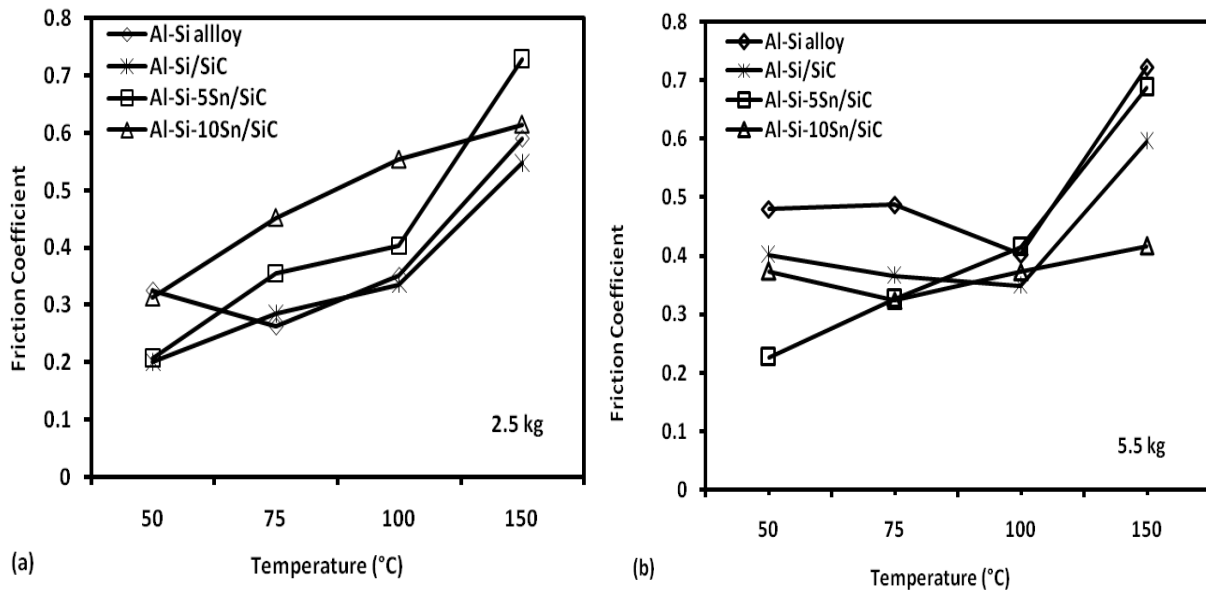


Figure 7.37: Variation of average friction coefficient with temperature of SiC and Sn containing composites at (a) 2.5 kg and (b) 5.5 kg load.

The Al–Si alloy at 150 °C and at both lower and higher loads show higher frictional coefficients as compared to lower temperature. This is due to large amount of heat generated at higher temperatures which soften the alloy and material is removed

plastically from sliding surface. It raises the friction and hence frictional coefficient of the alloy at higher temperature. The composite materials offer greater friction coefficient than the unreinforced alloy at 2.5 kg load as shown in Fig. 7.37 (a). The friction coefficient is the sum of adhesion and plowing action for the alloys [18]. For the composite materials, in addition to the previous actions particle fracture also contributes to the total friction coefficient. Thus it is obvious to find enhanced friction coefficient in the composites as observed above. In contrast to this, at higher load Fig. 7.37 (b) shows that friction coefficient of composites is lower as compared to the unreinforced alloy below 100 °C. At higher load, the composite containing lubricating Sn film over the surface show lower friction coefficient. Therefore a continuous lubricating film helps in reducing the friction coefficient of the composites. In Al-Si-5Sn/SiC composite, the lubricating film become discontinuous and unstable at higher temperature therefore friction coefficient becomes higher.

The above dissimilarities at the both loads can be explained on the basis of thermal conductivity of the material. Rohtagi et al. [19] studied the frictional heating parameter for alloys as well as composites and found that at 10 N load the composite exhibit higher frictional heating parameter than unreinforced alloy. Therefore, at lower loads more energy is dissipated during sliding in composites which increases their frictional coefficient. However, at 50 N load there is a small difference in the frictional heating parameter of composites and alloys. The findings are similar to our results as at lower loads, composites offer higher friction coefficients than alloys. This may be attributed to the low thermal conductivity of the composite material due to SiC addition as compared to the unreinforced alloy.

The average friction coefficients of spray formed Al-Si alloy and Bi containing composites has been presented in Fig. 7.38 at one of three lower and the highest loads. The curves of the Fig. 7.38 (a, b) shows that wear rate increases with the increase in normal load from 2.5 to 5.5 kg. This is explained as higher frictional heat is generated at the contact surfaces under higher normal load. This further decreases the strength of the material and lead to higher friction coefficients. In case of Al-Si alloy the metal was in direct contact with the counterface. Therefore at high load the heat generated during sliding and test temperature

softens the material. Due to increased surface temperature material sticking took place leading to higher friction, friction coefficient and wear rate as shown in Fig. 7.38 (a, b) at 5.5 kg and 150 °C [17].

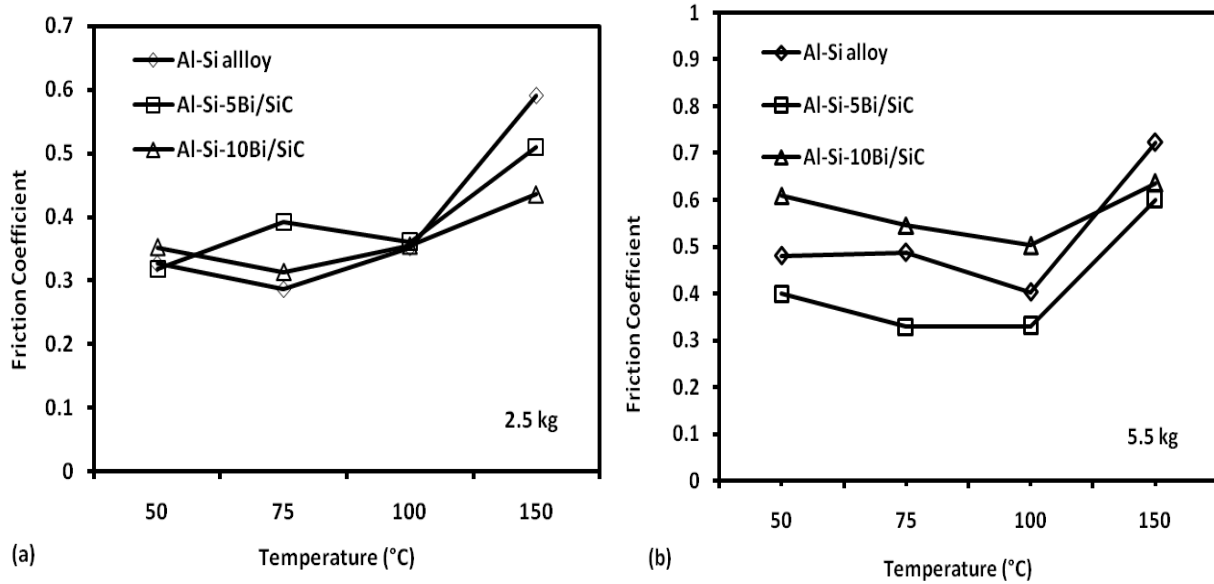


Figure 7.38: Variation of average friction coefficient with temperature of SiC and Bi containing composites at (a) 2.5 kg and (b) 5.5 kg load.

Also, in composites at higher load, large amount of heat is generated at the surface which enhances the oxidation process and reduces the friction. However, this is counteracted by continuous fracture of the particles under such conditions [20]. It has been reported that in composites the total friction coefficient is the sum of adhesion, plowing and particle fracture [18]. Therefore it has been found that Al-Si-5Bi/SiC and Al-Si-10Bi/SiC composite show higher friction coefficient than the alloy below 100 °C temperature at 2.5 kg load as shown in Fig. 7.38 (a). This can be due to the fact that particle fracture enhances the friction coefficient of composite material. However, at higher load Al-Si-10Bi/SiC composite shows lower friction coefficient at every temperature as the lubrication effect over ride the particle fracture in the composite.

7.13 Microstructural analysis of worn surfaces and wear debris

Wear debris generated during the wear were collected at the end of the wear tests and examined microscopically to analyze the mode of wear at different test conditions. The

worn surfaces of the Al-Si/SiC composite are shown in Fig. 7.39. At 50 °C, Fig. 7.39 (a) shows the deep grooves running parallel to the sliding direction along with small amount of the microcutting of the material at 5.5 kg load. At the same load and 150 °C the deep grooves have not been observed. The shallow sliding marks along with white patches can be seen in Fig. 7.39 (b). The magnified view of the patch (Fig. 7.39 (c)) indicates that the compact oxide layer has been formed over the surface which helps in reducing direct metal to metal contact. Therefore, the wear rate is decreasing with temperature in Al-Si/SiC composite as shown in Fig. 7.29 (d) in previous section.

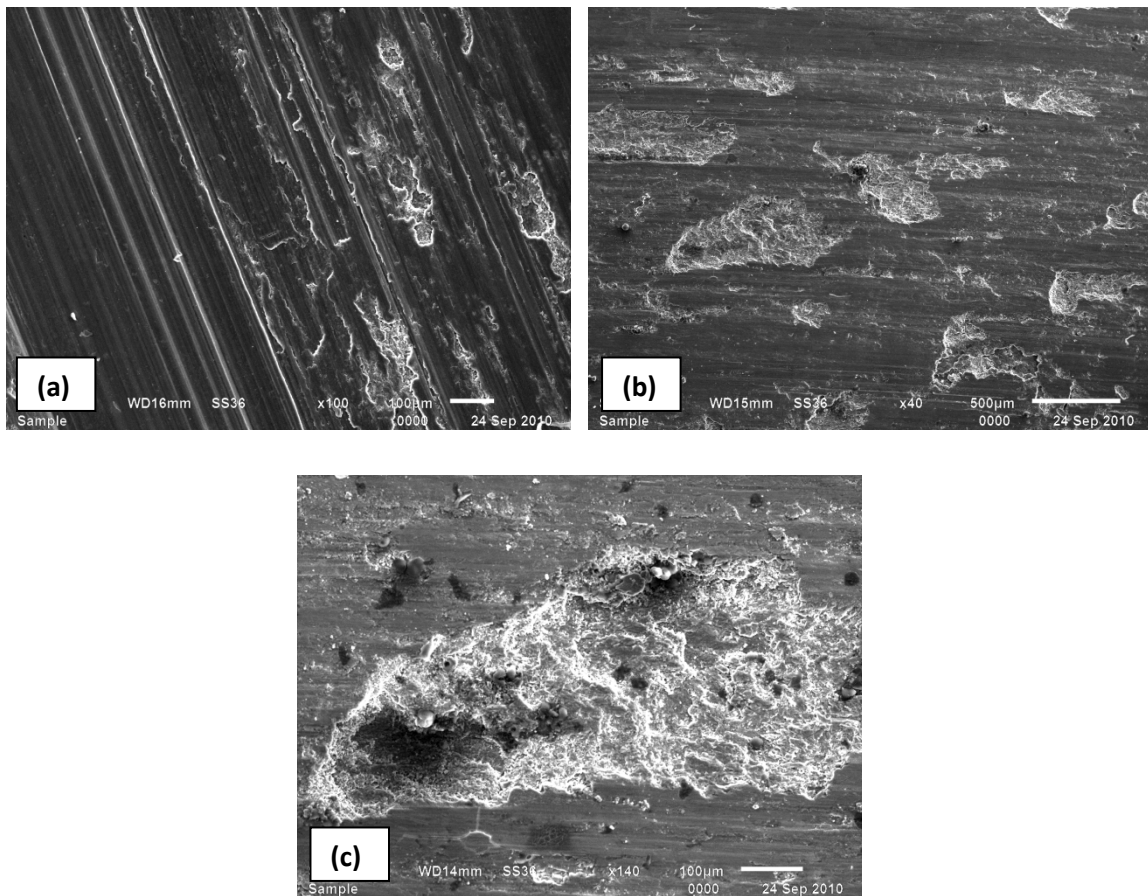


Figure 7.39: SEM micrographs of worn surface of Al-Si/SiC (63–90 µm) composite under 5.5 kg load at **(a)** 50 °C and **(b, c)** 150 °C.

SEM micrographs of wear debris of Al-Si/SiC at 5.5 kg are shown in Fig. 7.40. At 50°C, the debris show large flake morphology (Fig. 7.40 (a)). The debris are removed due to accumulative deformation of the material. The ratchet marks on the wear debris are the evidence of the cyclic deformation as shown in Fig. 7.40 (b). However, at same load and

higher temperature, Fig. 7.40 (c) shows two different types of debris morphology for Al-Si/SiC composite. Firstly, higher aspect ratio flakes are found to be generated during run-in wear regime. Secondly, small, rounded and very fine wear debris have been generated from the oxide layer formed on the wearing surface during steady state wear.

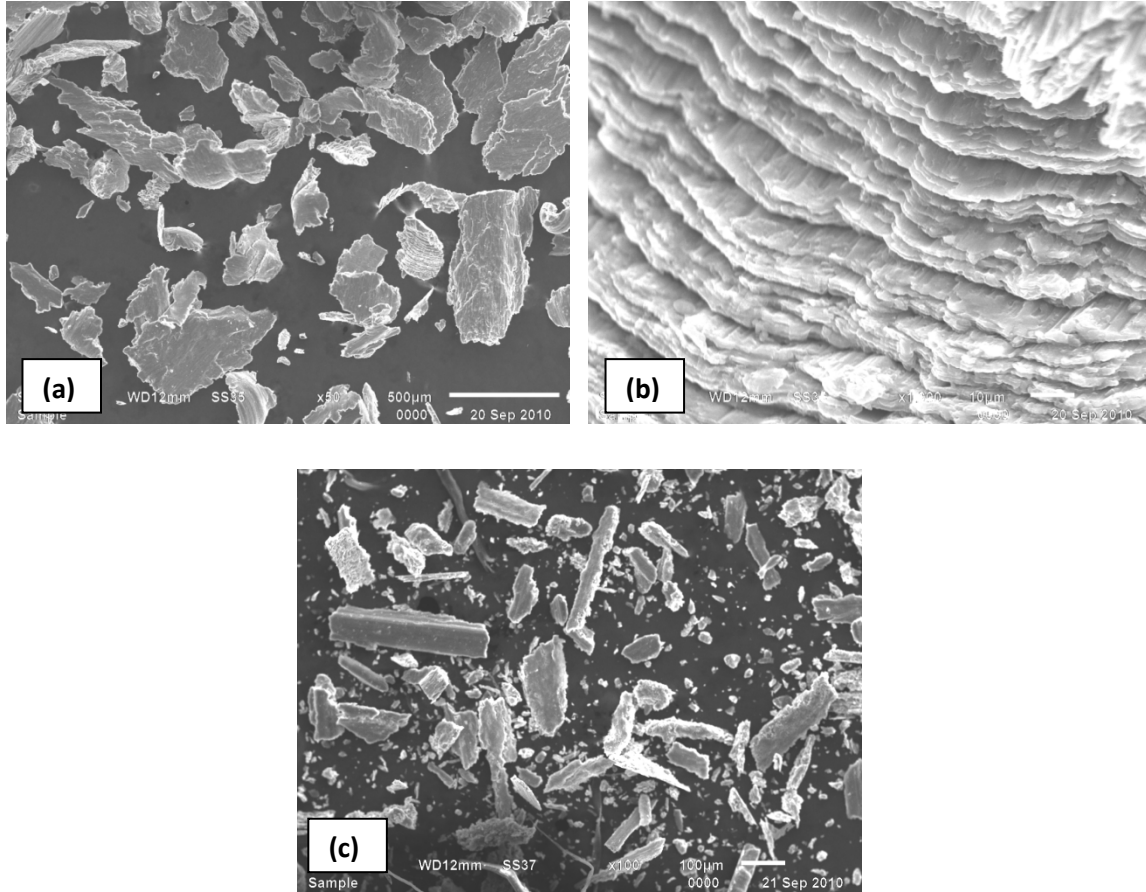


Figure 7.40: SEM micrographs of wear debris of Al-Si/SiC (63–90 µm) composite under 5.5 kg load at **(a, b)** 50 °C and **(c)** 150 °C.

The worn surfaces of lower and higher loads of spray formed Al-Si-5Sn/SiC composite are shown in Fig. 7.41. At 50 °C and 2.5 kg load (Fig. 7.41 (a)) shallow grooves along with lubricating film over the surface has been seen. Some areas do show small amount of microcutting on the surface. Though at higher load and same temperature the worn surface illustrate broader grooves along with the lubricating layer on the entire surface (Fig. 7.41 (b)). At lower load and high temperature adhesive wear with lubricating film on the surface has been observed in Fig. 7.41 (c). Small amount of oxidative wear is also prevailing at these conditions as compared to lower temperature and load (Fig. 7.41 (a)). However, at

higher load large amount of repetitive shearing marks have been found indicating the plastic deformation occurring at the surfaces (Fig. 7.41 (d)). Similar shear wedge morphology is reported by Yao-hui et al. for Al-Si and 4 vol. % C/Al-Si composite [7].

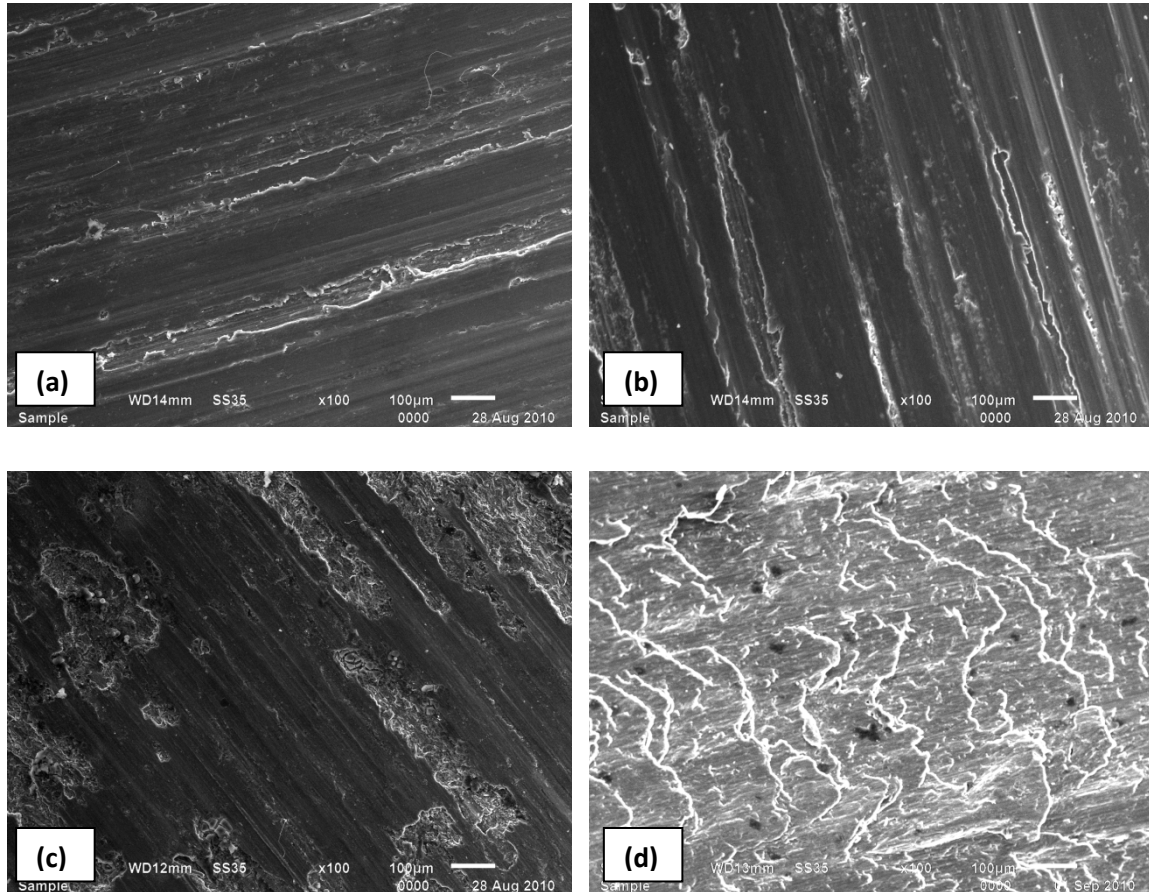
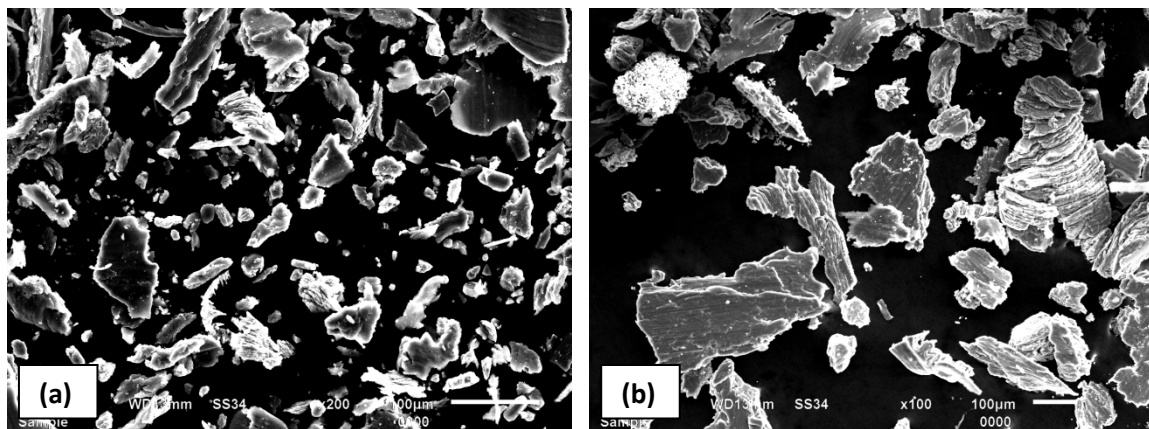


Figure 7.41: SEM micrographs of worn surface of Al-Si-5Sn/SiC (63–90 μm) composite at (a) 2.5 kg, 50 °C, (b) 5.5 kg, 50 °C, (c) 2.5 kg, 150 °C and (d) 5.5 kg, 150 °C.



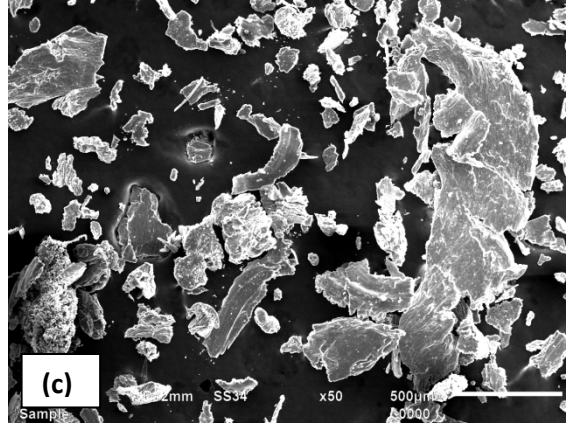


Figure 7.42: SEM micrographs of wear debris of Al-Si-5Sn/SiC (63–90 μm) composite under 5.5 kg load at **(a)** 50 °C and **(b, c)** 150 °C.

Moreover, continuous lubricating film has not been observed over the surface. The small wear debris at 5.5 kg load and 50 °C temperatures (Fig. 7.42 (a)) depict the grinding of the debris between sliding surfaces at the higher normal applied load. Moreover, the lubricating film can be seen on the debris surface. At higher load, small as well as large flakes of debris (Fig. 7.42 (b, c)) can be seen. It can be analyzed that seizure occurred due to discontinuous lubrication of film and the repetitive distortions produced over the surface at higher load and higher temperature.

The topographic features of worn surfaces and wear debris of Al-Si-10Sn/SiC composites can be seen in Fig. 7.43 and 7.44 respectively. At lower load a continuous lubricating layer has been observed at both higher and lower temperature as shown in Fig. 7.43 (a, c). However, at higher load and low temperature, the longitudinal and transverse crack propagation on the sliding surface that lead to the detachment of the wear debris (Fig. 7.43 (b)) can be seen. The morphology of the detaching debris is similar to the debris found in Fig. 7.44 (a). The debris have small as well as roughed morphology depicting the crushing of debris at higher frictional forces. Fig. 7.43 (d) shows the lubricating film along with oxide compact layer over the surface. The debris which have been generated during the sliding process at higher load get crushed between the running surfaces. These debris get mechanically mixed with the pin surface and counterface. The debris produced under such conditions are shown in Fig. 7.44 (c, d). Very fine ($< 2 \mu\text{m}$) and spherical shaped morphology of debris having bright contrast has been observed. These further indicate the

oxide compacted layer with greater lubricating Sn film. Similar morphological features have been reported earlier in spray formed Al-12.5Si-25Sn alloys under dry sliding conditions [4].

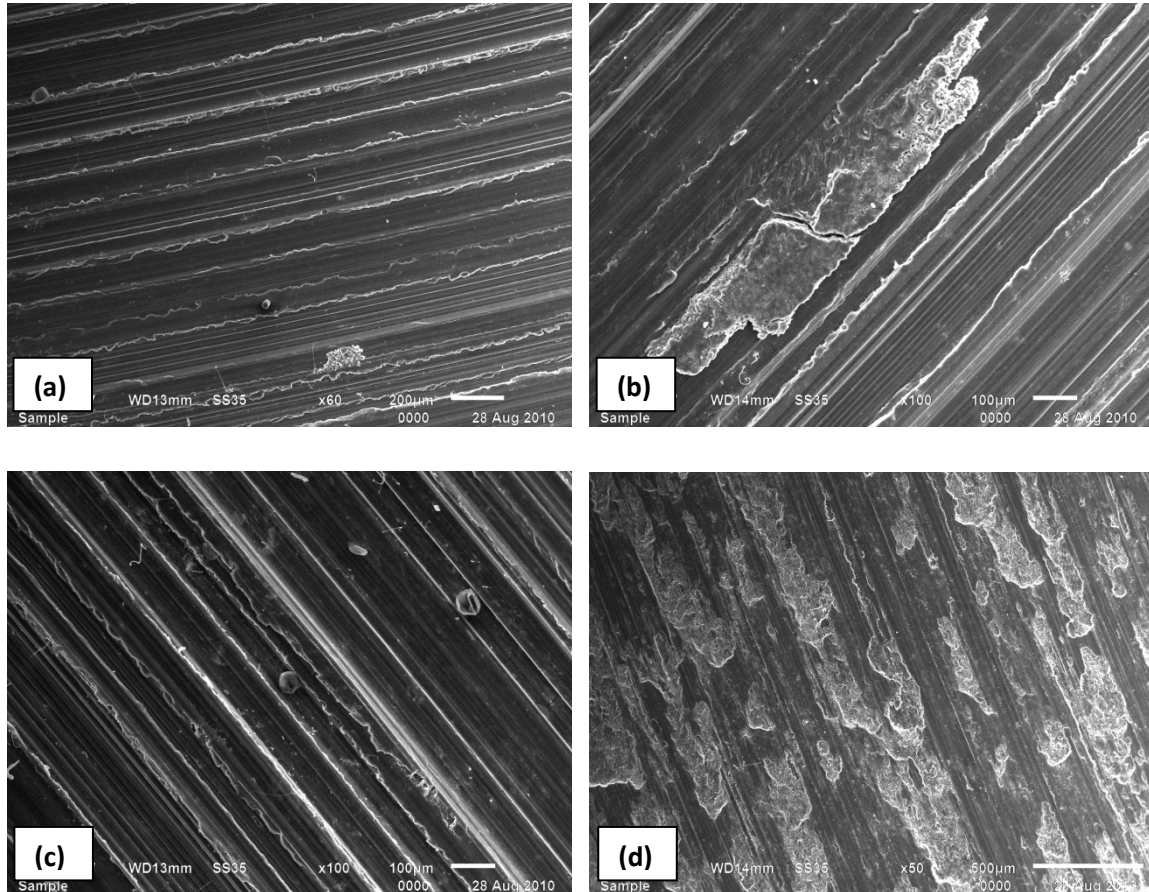
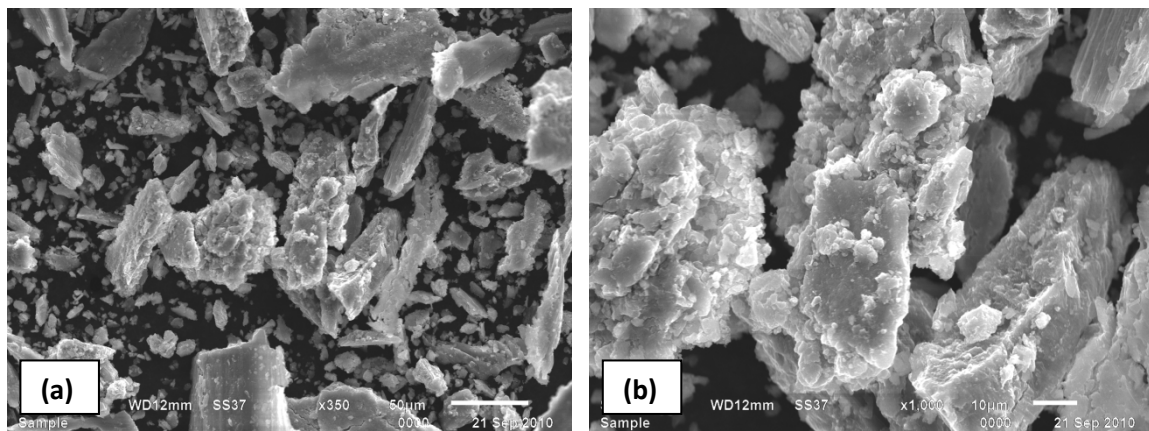


Figure 7.43: SEM micrographs of worn surface of Al-Si-10Sn/SiC (63–90 μm) composite at (a) 2.5 kg, 50 °C, (b) 5.5 kg, 50 °C, (c) 2.5 kg, 150 °C and (d) 5.5 kg, 150 °C.



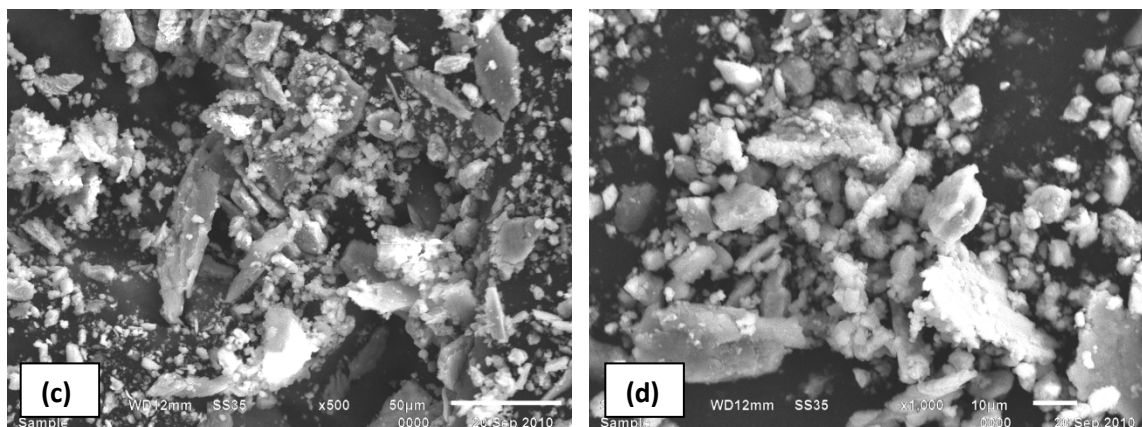


Figure 7.44: SEM micrographs of wear debris of Al-Si-10Sn/SiC (63–90 μm) composite under 5.5 kg load at **(a, b)** 50 °C and **(c, d)** 150 °C.

Figure 7.45 illustrates the worn surfaces of Al-Si-5Bi/SiC composite at 50 °C and 150 °C under 5.5 kg. The uniform lubricating film can be seen in Fig. 7.45 (a) over the entire sliding surface at 50 °C. The formation of wear debris at the edge of the pins can also be seen. Due to repetitive sliding the shear wedge pattern (Fig. 7.45 (b)) has been formed over the surface of Al-Si-5Bi/SiC composite at 150 °C. Similar morphology has also been reported by Yao-hui et al. [7] in Al-12 Si and 4 vol. % C/Al-12Si composite at 200°C. At 5.5 kg load and 150 °C, the material is removed under higher shear conditions resulting increased wear rate as shown in Fig. 7.7 (d) in previous section. Moreover, the surface morphology verifies the discontinuous lubricating film over the entire surface at high temperature as explained earlier.

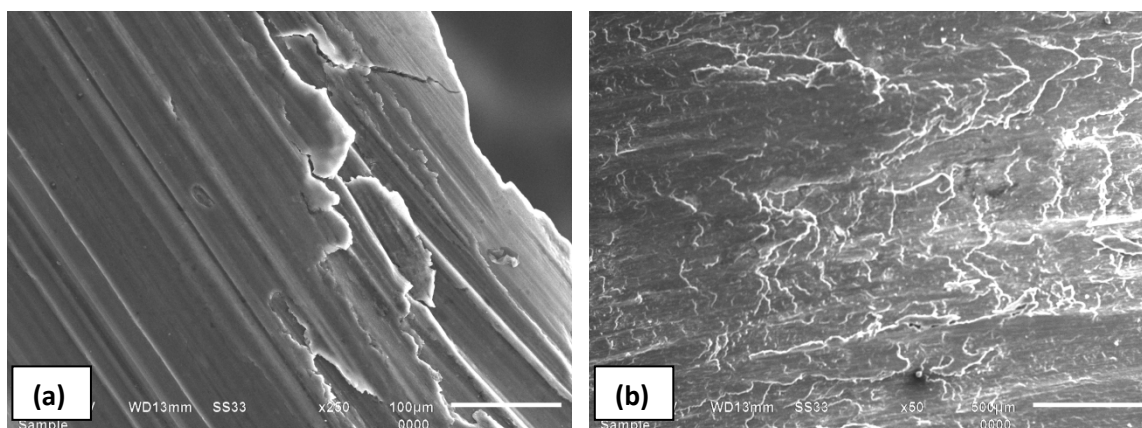


Figure 7.45: SEM micrographs of worn surface of Al-Si-5Bi/SiC (63–90 μm) composite under 5.5 kg load at **(a)** 50 °C and **(b)** 150 °C.

SEM micrographs of wear debris of Al-Si-5Bi/SiC at 5.5 kg and extreme temperatures are given in Fig. 7.46. The wear debris at lower temperature consists of long as well as small flake type morphology (Fig. 7.46 (a)). At higher loads, fine accumulative deformations appear beneath the sliding surface of the debris. Small amount of debris has been found to exhibit these ratchet marks and the magnified view of which is shown in Fig. 7.46 (b). Fine deformation lines of the material under high load have been observed which got closely compacted in due course of time. On the other hand, large chunk of the material removal can be seen in Fig. 7.46 (c) at higher load and temperature.

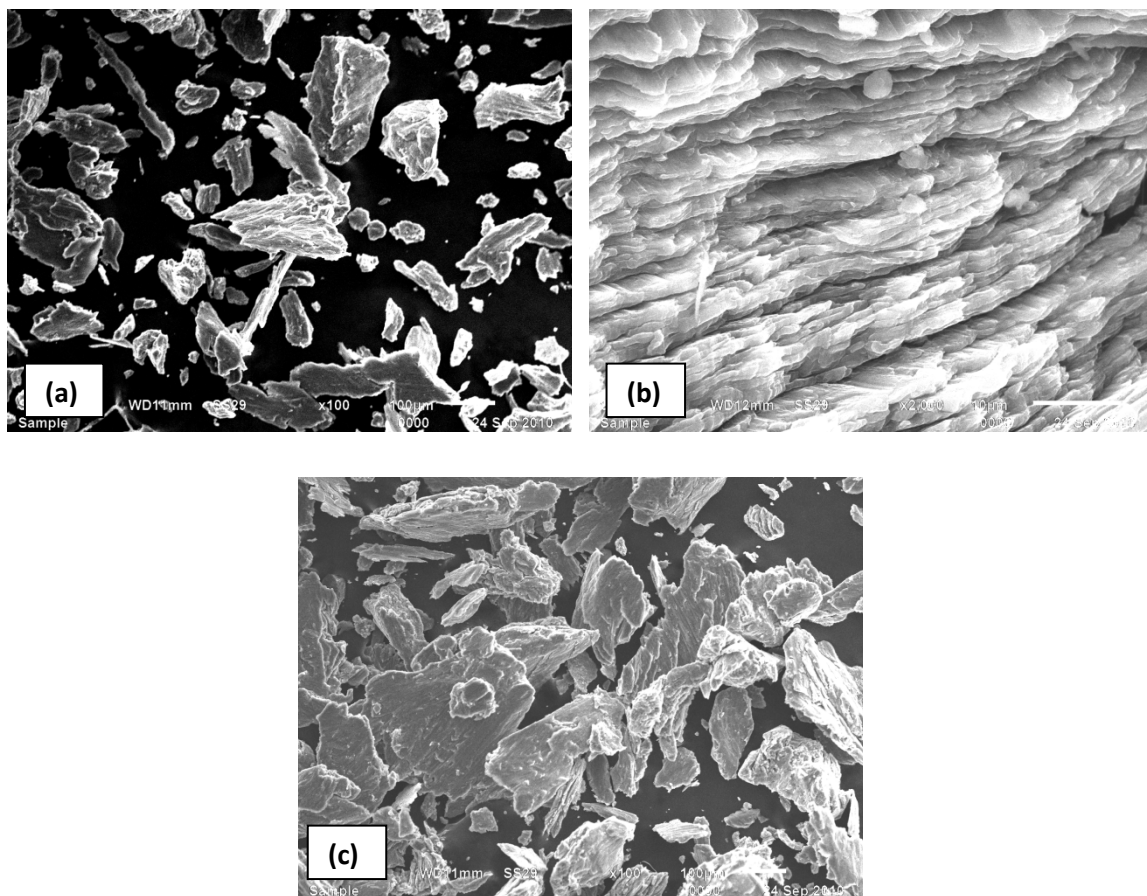


Figure 7.46: SEM micrographs of wear debris of Al-Si-5Bi/SiC (63–90 μm) composite under 5.5 kg load at **(a, b)** 50 °C and **(c)** 150 °C.

The worn surfaces of Al-Si-10Bi/SiC composite at 50 °C and 150 °C under 5.5 kg (Fig. 7.47) shows the formation of mechanically mixed layer (MML) compacted under the effect of higher load. Along with MML, the lubricating film is also present over the surface which reduces the direct metal to metal contact and hence reduces the wear rate. Similar MML

formation has also been reported by Liu [17] for short carbon fibre (SCF) reinforced Al system. The results concluded that SCF has the function of lubricating, counteracting the plastic deformation, supporting and load bearing. The worn debris as shown in Fig. 7.48 shows that debris came out of the MML formed over the surface of Al-Si-10Bi/SiC composite at both lower and higher temperature.

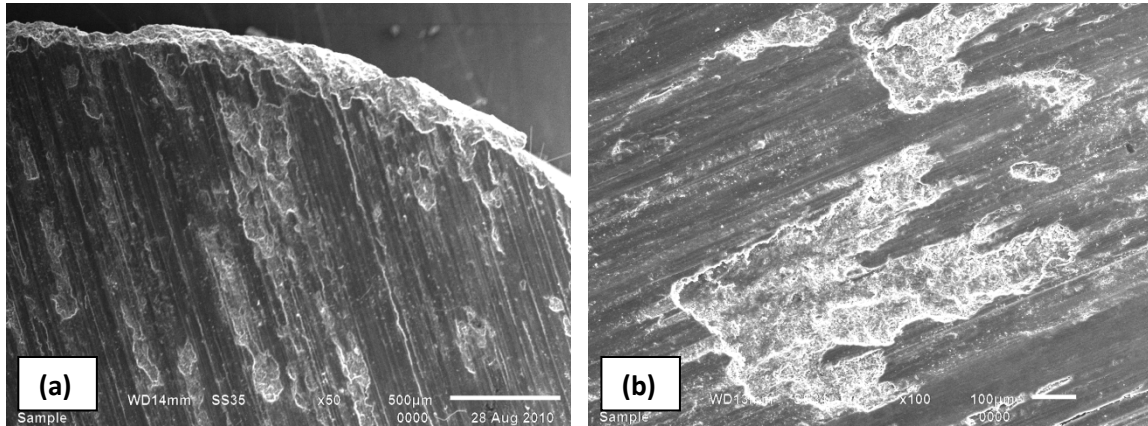


Figure 7.47: SEM micrographs of worn surface of Al-Si-10Bi/SiC (63–90 μm) composite under 5.5 kg load at **(a)** 50 °C and **(b)** 150 °C.

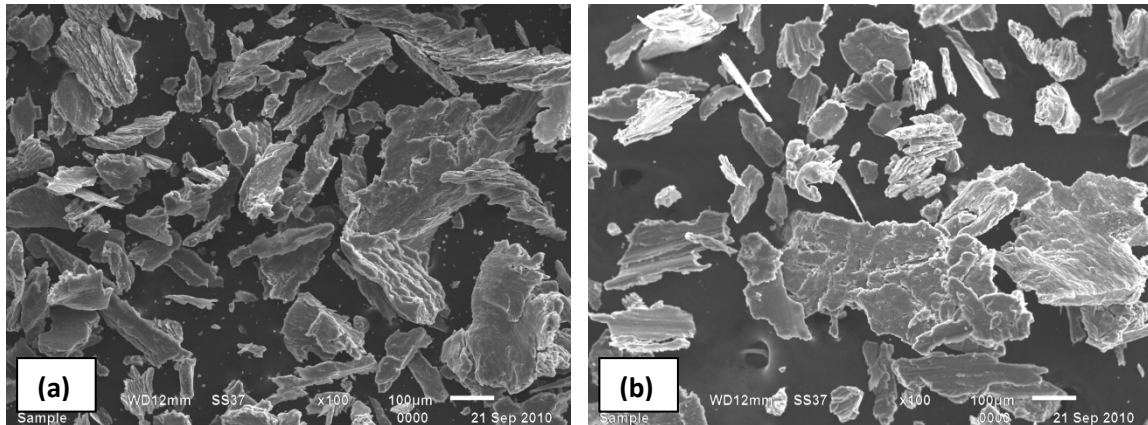


Figure 7.48: SEM micrographs of wear debris of Al-Si-10Bi/SiC (63–90 μm) composite under 5.5 kg load at **(a)** 50 °C and **(b)** 150 °C.

The wear mechanism for material removal for immiscible element and hard particulate reinforced composite is schematically represented in Fig. 7.49 (a–e). Figure 7.49 (a) presents the pin surface before sliding which contains large ceramic particulates and small white immiscible element dispersed throughout the specimen. The sliding direction is presented by the arrow above the pin surface. Figure 7.49 (b) presents the smearing

process of low melting point immiscible constituent with the sliding. It has been found that during sliding soft matrix alloy also get deformed. Third stage illustrated in Fig. 7.49 (c) presents the formation of lubricating film over the surface due to smearing action. On further sliding, shearing with the counterface results in the formation of MML as shown in Fig. 7.49 (d). MML consists of material from the matrix and counterface which reduces the metal to metal direct contact. The third and fourth stages help to reduce the wear rate of the material by preventing the surface from delamination. However, on excessive sliding or load conditions leads to development of cracks in the MML itself and the material from MML is detached in the form of debris as shown in Fig. 7.49 (e).

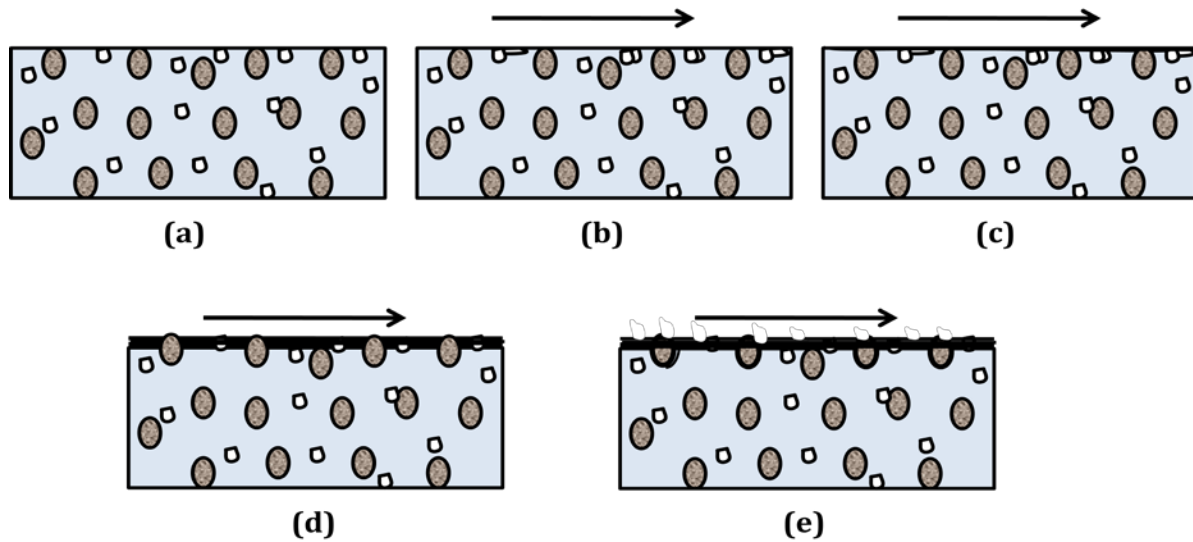


Figure 7.49: The proposed wear mechanism in immiscible composite.

7.14 Comparative wear behavior according to the particulate size

The bigger particulate size SiC reinforced Al-Si alloy exhibit higher wear resistance up to 100 °C than smaller size. On the other hand, Al-Si/SiC composite offers lower wear rate at 150 °C and 5.5 kg. Al-Si-5Sn/SiC (63–90 μm) composite shows higher wear resistance at 50 °C and larger particulate size offers good wear rate at 75 °C at 5.5 kg load. In 10 wt. % Sn containing composites larger particulates offer higher and stable wear behavior w.r.t. temperature variation at the highest load. Composites containing both the particulate sizes alongwith Bi offer good wear resistance up to 75 °C. The composite containing 10 wt. % Bi

with larger particulate size offer greater wear rate at higher temperature. Whereas smaller particulate type offers better wear rate at 75 and 100 °C.

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CONCLUSIONS AND FUTURE SCOPE

Overview

The present chapter summarizes the results of various experiments described in previous chapters. The effect of different immiscible elements on the tribological properties of the composites has been summarized. Apart from this, the results of different series are also concluded in this chapter. At the end, suggestions for future work are given on the basis of results obtained in this work.

8.1 Conclusions

In order to get good spray formed composite, a spray forming set up has been designed and fabricated. For it different designing parameters have been studied to get the molten metal atomized at low pressure through convergent-divergent nozzle. The atomized melt droplets are deposited on the copper substrate placed vertically below the atomizer. The spray atomization apparatus consists of four major units i.e. melting furnace, nozzle assembly, injector assembly and deposition surface.

In the present study, cost effective zircon sand and SiC reinforced Al-Si alloy composite is successfully prepared with spray deposition technique. The interaction of the ceramic particulates with the atomized droplets has also been analyzed by analyzing the over sprayed particles under SEM and optical microscope. The interaction between ligament and particles shows the collisions, engulfment of ceramic particulate in the melt droplet and adhesion of ceramic particle on the surface of the ligament. These interactions result in localized cooling effect in the melt droplets.

Composites have been spray formed under different conditions to optimize the porosity level. In order to reduce the porosity level further the addition of soft immiscible elements Sn and Bi has been done along with ceramic particulates. Their influence on the wear resistance of Al-Si alloys has been analyzed. The wear tests of each set of composite have been conducted up to 2880m run at a constant sliding velocity of 1.6ms^{-1} and under five different loads (1.5–5.5 kg) for both reinforced and unreinforced alloy. Moreover, the wear characteristics have also been studied at four different temperatures (50°C, 75°C, 100°C and 150°C) to analyze the change in wear mechanism. The wear characteristics of both reinforced and unreinforced alloy confirmed that spray formed Al-Si/ZrSiO₄ and Al-Si/SiC composites exhibit superior wear properties as compared to base Al-Si (LM13) alloy and also delay the transition to severe wear at higher loads. This behavior is further analyzed in light of microstructural features of worn surfaces and wear debris by SEM and EDS.

The X-ray diffraction analysis shows the presence of all elements in the prepared alloy and composites. The microstructural analysis of polished samples shows that the ceramic particulates are well distributed inside the preform and firmly attached to the matrix. The equiaxed α -Al grains have been observed along with refined Al-Si eutectic in the spray

formed alloy and composites. However, dendrites of Al are observed in the as-cast alloy. Also, the macrosegregation of the immiscible elements has not been observed on addition of 5wt. % and 10wt. % of Sn/Bi in Al-Si alloy.

The bulk hardness of the prepared samples depict that hardness got enhanced with incorporation of ZrSiO_4 and SiC particulates in the composites. The hardness of Al-Si/ ZrSiO_4 composites is greater than Al-Si/SiC composites irrespective of the change in particulate size. The change in hardness has been observed after the addition of soft immiscible elements in the composites. In zircon sand reinforced composites small decrement in the hardness has been found on addition of 5 wt. % Sn and Bi. However, the hardness increases further on increasing the amount of immiscible elements. The composites reinforced with SiC shows increment in hardness on addition of Sn and Bi. Also, SiC reinforced composites containing Bi shows higher hardness than Sn containing composites.

In most of the samples, steady state wear is reached after 500–1000 m sliding distance depending upon the wear behavior of material unless seizure has occurred in the run in wear regime. For spray formed Al-Si alloy, applied load of 3.5 kg is found to be the critical transition load. At all the test temperatures above the critical transition load, severe wear is dominating due to delamination wear mechanism. The wear rate behavior shows that the three lower loads (1.5–3.5 kg) behave similarly as compared to the two higher ones (4.5, 5.5 kg). The wear results show that the spray formed ZrSiO_4 and SiC reinforced composites are better wear resistant than unreinforced alloy even at higher loads.

The three different types of wear mechanisms are dominating in reinforced and unreinforced alloy i.e. adhesive, oxidative and abrasive. The adhesive cum oxidative wear mechanisms have been found in reinforced alloy. The basic wear mechanism is the adhesive wear illustrated by the presence of grooves and transfer of material from disc to load bearing surfaces. The oxidative wear is more predominant in reinforced composite, which is revealed by morphology and EDS analysis of worn surfaces and debris. The oxidative mechanism is the most effective in reducing the wear rate and friction in Al-Si/ ZrSiO_4 composite for both in lower and higher particulate sized composites. The wear results show that the spray formed self-lubricating Al-Si/ ZrSiO_4 (106–125 μm) composites containing Sn and Bi are better wear resistant than unreinforced alloy, especially at higher

load. The self-lubricating Al-Si-10Sn/ZrSiO₄ (106–125 μm) composite shows the stable wear resistance irrespective of temperature variation at 5.5 kg loads. Al-Si-10Bi/ZrSiO₄ (106–125 μm) composite shows transition in wear mechanism after 3.5 kg load though the severe wear mode has not reached at 5.5 kg load and lower wear rate has been obtained at extreme conditions. The wear results of Al-Si-5Bi/ZrSiO₄ composite shows that 5.5 kg load acts as the critical transition load above 75 °C. Friction coefficient values of Al-Si-10Bi/ZrSiO₄ (106–125 μm) composite are found to be lower due to the continuous as well as stable MML and lubricating Bi film over the sliding surfaces. The more uniform lubricating film has been found on increasing the amount of the immiscible element, even at higher temperature conditions. The wear rate behaviour is also analogous as depicted from the morphological features. The EDS analysis further confirms the wear mechanism observed during tests. At higher loads early stabilization of wear has been achieved with higher immiscible Bi content in the matrix.

The wear contours show that Al-Si/ZrSiO₄ (63–90 μm) composite offers greater wear resistance at higher temperature and the wear transition shifts towards higher load and lower temperature. The oxidative wear mechanism is significantly diminishing the effect of adhesive mechanism during this transition. The significant effect on wear rate stabilization at every load and temperature has been found on Sn addition in the matrix. The utmost reduction in the wear rate at 150 °C temperature is achieved with addition of 10 wt.% Sn in the matrix. Also, the wear contours show that Al-Si-5Bi/ZrSiO₄ (63–90 μm) composite offers greater wear resistance at 50 and 75 °C temperature. Although the wear rate results of Al-Si-10Bi/ZrSiO₄ (63–90 μm) composite are similar to Al-Si-5Bi/ZrSiO₄ (63–90 μm) at lower temperature yet it shows the reduced wear rate at higher temperatures (100 and 150 °C). The lowest wear rate at the highest load is found at 100 °C temperature attained by the addition of 10 wt. % Bi in the matrix.

In SiC (106–125 μm) reinforced composites, Al-Si/SiC composite possesses higher wear resistance up to 100 °C at 5.5 kg load. Al-Si-5Sn/SiC (106–125 μm) exhibits minimum wear rate ($7.99 \times 10^{-12} \text{ m}^3\text{m}^{-1}$) at 100 °C after which seizure occurs at 150 °C. Al-Si-10Sn/SiC (106–125 μm) offers stability in wear rate behavior up to 150 °C. Primarily oxidative wear mechanism is revealed from the analysis of its worn surface and wear debris. A uniform Sn lubricating film has been found to be stable at lower load and higher

temperature conditions in this system. The wear rate behaviour is also analogous as depicted from the morphological features. The EDS analysis further confirms the finding of wear rate behavior and morphological features. The wear contours portrays that with addition of SiC and 5 wt. % Bi in the alloy the higher wear regime shift above 100 °C as the lubricating film get oxidized at higher temperatures. However, with addition of 10 wt. % Bi much lower wear rates has been obtained as the lubricating film has not been replenished at extreme test conditions. Al-Si-10Bi/SiC (106–125 µm) composite offers minimum wear rate ($7.44 \times 10^{-12} \text{ m}^3\text{m}^{-1}$) at 100 °C and 5.5 kg load. Additionally, the frictional coefficient is found to be less in the lubricated composite due to higher Bi content.

In Al-Si/SiC (63–90 µm) composite, the severe wear regime occurs around 5.5 kg load and at 50 °C which shifts to mild wear regime with increase in temperature due to oxidative wear. The wear contours depicts that on addition of 5 wt. % Sn in the matrix, the composite offer good resistance to wear at low temperatures only as the stability of the lubricating Sn film decreases above 100 °C. With increment in the immiscible element Sn, the composite offers higher wear resistance at higher temperatures. At 150 °C under 4.5 and 5.5 kg applied load, Al-Si-10Sn/SiC (63–90 µm) composite exhibits wear rate of 9.23×10^{-12} and $1.07 \times 10^{-11} \text{ m}^3\text{m}^{-1}$ respectively. At higher temperature, morphology of the debris indicate the presence of oxidative wear along with lubrication effect induced by higher amount of Sn. Frictional coefficient is also found to be less in Al-Si-10Sn/SiC (63–90 µm) composite. In Al-Si-5Bi/SiC (63–90 µm) composite the higher wear regime shifts above 5 kg load and at 100 °C. The higher though stable wear regime for Al-Si-10Bi/SiC (63–90 µm) composite has been observed at 5.5 kg load and 50 °C and wear rate was found to decrease with further increase in temperature. The minimum wear rate at 5.5 kg load has been exhibited by Al-Si-10Bi/SiC (63–90 µm) composite at 75 °C. Also, Al-Si-10Bi/SiC composite shows the lowest wear rate among the prepared samples at 150 °C. The lubrication effect induced by higher amount of Bi and SiC particulates help to form MML over the surface of Al-Si-10Bi/SiC (63–90 µm) which enhances the wear resistance of the material even at higher temperature and load condition.

The composites containing 5 wt.% of immiscible elements irrespective to the particulate size and reinforcement show severe wear at higher load conditions except Al-Si-5Sn/ZrSiO₄ (106–125

μm) which shows stable and lower wear rate at higher load and temperature conditions. In 10 wt.% Sn containing composites larger particulates offer higher and stable wear behavior w.r.t. temperature variation at the highest load irrespective of the reinforcement type. However, 10 wt.% Bi and zircon sand reinforced composite shows wear transition at every temperature under 3.5 kg load as compared to SiC reinforcement where higher wear rate is obtained at lower temperature 50°C and higher load conditions.

Al–Si/ZrSiO₄ and Al–Si/SiC (63–90 μm) show wear resistant properties up to 4.5 kg load at 50 °C and severe wear occurs at 5.5 kg load. The decrease in wear rate has been observed with increasing temperature which is better in ZrSiO₄ reinforced composite than SiC. With addition of 5wt.% Sn, both reinforcements show wear transition after 3.5 kg load. The change is similar with increasing temperature in ZrSiO₄ sand reinforced composite. However, in SiC reinforced composite wear rate is lesser at 100 °C. With 10 wt.% Sn addition, ZrSiO₄ shows better wear resistance than SiC. Moreover, addition of 10wt.% Bi, ZrSiO₄ reinforced composite shows better wear resistance at extreme condition than SiC composite. The higher wear rate regimes are found to be at 75 °C, 5.5 kg load in ZrSiO₄. SiC reinforced composite shows higher wear at 50 °C, 5.5 kg condition and wear transition after 100 °C. From the above detail of conclusions following points are derived:

- The reinforcement of zircon sand in different alloys can be analyzed.
- Further the possibility of reinforcing smaller sized (< 50 μm) zircon sand and SiC particulates can be examined with different nozzle design.
- The wear behavior of reinforced composites can be analyzed with varying sliding velocity and V_f of the reinforcement.
- Enhancement of mechanical properties with different heat treatments and secondary processes can be investigated.

8.2 Future scope

After analyzing the data presented in the thesis, the possible avenues of further investigations are as follow:

- The reinforcement of zircon sand in different alloys can be analyzed.
- Further the possibility of reinforcing smaller sized ($< 50 \mu\text{m}$) zircon sand and SiC particulates can be examined with different nozzle design.
- The wear behavior of reinforced composites can be analyzed with varying sliding velocity and V_f of the reinforcement.
- Enhancement of mechanical properties with different heat treatments and secondary processes can be investigated.

Moreover, for military applications fine size reinforced composites which offer better wear properties can also be tested for bullet impact as armor materials.