SYNTHESIS AND CHARACTERIZATION OF TANTALUM CARBIDE NANOPARTICLES

Thesis submitted in partial fulfillment of the requirement for

The award of the degree of

Master of Science

In

PHYSICS

Submitted by

NAVJOT KAUR

Roll No**.-301004008**

Under the supervision of

Dr. O.P Pandey

School of Physics and Materials Science

Thapar University, Patiala (Punjab)

JUNE-2012

Dedicated to

my

Loving Parents

&

Brother Kamal Dhindsa

CERTIFICATE

This is to certify that Miss NAVJOT KAUR, Roll no. 301004008 has worked on this thesis report entitled "SYNTHESIS AND CHARACTERIZATION OF TANTALUM CARBIDE NANOPARTICLES" in partial fulfillment for award of the degree of MASTER OF SCIENCE in PHYSICS in THAPAR UNIVERSITY, PATIALA. This report is an authentic record of her own work carried out under the supervision of Dr. O.P.PANDEY. The matter embodied in this report is one of the candidate's own record and not submitted to any other University in any part or full form for the award of such kind of degree.

Dr. O. P. Pandey
Senior professor
Supervisor
School of Physics and Material Science
Thapar University, Patiala

Countersigned by:

Dr. Kulvir Singh
Associate Prof. & Head
School of Physics and Material Science

Thapar University,Patiala.

Dr. S. K. Mohapatra
Dean of academic affairs

ACNOWLEDGEMENT

Learning is creating knowledge. I would have never succeeded in completing my task without cooperation, encouragement and help provided to me by our faculty members. This thesis represents not only my work at the keyboard, it is a milestone in more than one semester of work at SYNTHESIS OF TANTALUM CARBIDE and specifically within the Material Science Laboratory. My experience has been nothing short of amazing.

Foremost, I would like to express my sincere gratitude to my esteemed and worthy supervisor Dr. O. P. Pandey for the continuous support of my M.Sc thesis, for his patience, keen interest, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I am greatful to Dr. Kulvir Singh, Associate Professor & Head for his constant source of inspiration and infrastructural facilities which he extended to me to execute this work.

I owe sincere thanks to Mr. Gaurav Singla who made me believe in myself and guided me through the whole process of dissertation writing and experimental work. I am sure that this dissertation would not have been possible without his support, timely help and valuable discussions. I extend my sincere thanks to all the staff members of School of Physics and Material Science for their support and encouragement. I thank my friends for the stimulating discussions, for the sleepless nights we were working together before deadlines, and for all the fun we have had in the last two years.

Last but not the least, I would like to thank my family: my parents Mr. Charan Singh Dhindsa & Mrs. Rajinder Kaur Dhindsa, for giving birth to me at the first place, taught me, loved me and supporting me spiritually throughout my life. To them I dedicate this thesis. Above all, hidden force by Almighty God steered me in the right direction to achieve the goal.

Navjot Kaur
NAVJOT KAUR
Roll No. 301004008

Abstract

Transition metal carbides are in demand for their unique properties resembling with metal and ceramic constituents. These carbides have high hardness, high melting temperature, high-temperature strength. They have been used as hard constituents in metal matrix composites for high temperature applications and as coatings on cutting tools. Among these carbides, tantalum carbide is a very important and promising example for industrial applications. Therefore in the present study tantalum carbide (TaC) nanoparticles were synthesized through a reduction-carburization route by using tantalum pentaoxide and acetone (C_3H_6O) as Ta and C sources along with metallic Mg as the reductant at 600 °C and 800 °C in an autoclave. The as-prepared TaC nanopowders were characterized and studied by X-ray powder diffraction, Scanning electron microscope at room temperature. The thermal stability of synthesized powder was investigated by DTA/TGA. The XRD results indicate that optimum reaction condition for the formation of nanocrystalline TaC was 600 °C for 10 h carburization at high pressure. The TaC nanoparticles produced from the present route typically have an average size below 50 nm. The influencing factors of the formation of the TaC nanopowder have been discussed in present work.

LIST OF CONTENTS

CHAPTER 1

CHAPTER 2

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.2. CHARACTERIZATION TECHNIQUES

CHAPTER 4

RESULTS AND DISCUSSIONS

CHAPTER 5

LIST OF TABLE

LIST OF FIGURES

LIST OF ABBREVIATIONS

TaC	Tantalum carbide
XRD	X-ray Diffraction
DTA	Differential thermal analysis
TGA	Thermal gravitational analysis
SEM	Scanning electron microscope

Chapter 1

1.1 Background

Nanoscale particle research has recently become an important field of materials science. Nanoscale particles (1 to 100 nm) usually have physical properties different from those of large particles. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed [1]. Thus, the properties of materials change as their size approach to the nanoscale. Recent experiments have shown that consolidated nano-materials have improved mechanical properties, such as increased hardness of metals and increased ductility and plasticity of ceramics. In nanoscale, the number of atoms at the surface and/or grain boundaries is comparable to that of the atoms located in the crystal lattice, thus the chemical and physical properties are increasingly dominated by the atoms at these locations. Nanoparticles present possible dangers, both medically and environmentally [2]. Most of these are due to the high surface to volume ratio, which can make the particles very reactive or catalytic [3].

The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the bulk materials. The high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperature and hence sintering can take place at lower temperatures, over shorter time scales than for larger particles. This theoretical approach does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate complicates the matters.

As mentioned above that nanotechnology offers potential solutions to many problems using emerging nanotechniques; like surface coating with a nanometer thickness of nanomaterial can be used to improve properties like wear and scratch-resistant properties. Similarly, current cutting tools (e.g mill machine tools) are made using a sort of metal nanocomposites such as tungsten carbide, tantalum carbide and titanium carbide that have more wear and erosion-resistant, and last longer than their other conventional (large-grained) materials.

1.2 Carbides

Carbide is a compound composed of carbon and a less electronegative element. The carbides of group IV (Ti, Zr, Hf) and group V (V, Nb, Ta) elements have metal-like properties, such as high thermal and electrical conductivity. They are opaque and have a metallic luster [4]. Transition metal carbides are important materials because they possess some desired properties such as corrosion and wear resistance, electronic, magnetic and catalytic characteristics [5-9]. They have extremely high melting points and are therefore referred to collectively as the “refractory carbides”.

In addition to their stability at high temperatures, these compounds are extremely hard and find different industrial applications in cutting tools and wear-resistant parts. Their hardness is retained even at very high temperatures and they have low chemical reactivity. They are attacked only by concentrated acid or base in the presence of oxidizing agents at room temperature and retain good corrosion resistance at high temperatures.

The refractory carbides have good thermal shock resistance and good thermal conductivity, permitting heat to be drawn away from the working surface of the tool. This gives them a benefit over other refractory materials, which do not conduct heat so well. Carbides materials are supplied in a variety of shapes, sizes, and forms.

The group IV−V transition metal mono carbides (MC) have wide homogeneous regions within which the content of carbon can be varied, while the FCC lattice of MC_x carbide phases remains unchanged. At the same time, vacancies in the carbon sublattice of carbides lead to change all their properties. The temperature dependence of resistivity, thermoelectric coefficient, and Hall effect shows that electron conduction prevails in the carbides of interest. The mobility of carriers for carbides of groups IV and V decreases with carbon content. The temperature dependence of the hardness of titanium and hafnium carbides increases with higher carbon content, but the difference in the hardness of carbides with different carbon contents at higher temperatures becomes smaller. The presence of carbon vacancies does not influence the temperature dependence of hardness. The electroerosion resistance of carbides also changes with different carbon contents within the homogeneity region. These changes are such that the erosion rate for group IV metal carbides decreases with smaller carbon deficiency and is extreme for group V metal carbides. To determine the extent to which the plasticity of carbides can be increased, the substructure of titanium, zirconium, and niobium carbides was examined within their homogeneity regions by changing the number of vacancies in the carbon sublattice after equivalent deformation of carbide phases.

The plasticity of TiC_x and ZrC_x monotonically increases with smaller carbon content and is extreme within the homogeneity region of niobium carbide and has a minimum at $x \sim 0.85$. Many physical properties of solids are known to depend not only on the arrangement of atoms at ideal lattice points but often (and largely) on the deviation from this arrangement. In this regard, not only the dynamic displacements of carbon and metal atoms is formed in the lattice but also assessed the static displacements caused by carbon sublattice imperfection; static displacements monotonically increase with greater carbon-related lattice imperfection. Titanium carbide phases have greatest static displacements among group IV metal carbides. These displacements decrease toward zirconium and hafnium carbides. The thermal vibrations of atoms monotonically increase with smaller carbon content in group IV transition metal carbides, while there are minimum thermal vibrations of niobium and tantalum atoms in their carbide phases. Since carbides are used in high-temperature materials so their recrystallization is especially significant.

Since, refractory carbides have a large reserve of grain-boundary energy, so recrystallization becomes collective after cold surface hardening. The activation energy of this process is commensurable with that of boundary self-diffusion. The activation energy becomes lower within the homogeneity region of group IV and V carbides as the number of vacancies in the carbon sublattice increases. The heat capacity isotherms for the carbide phases of group IV transition metals are linear, while those for the carbide phases of other group V metals (niobium and tantalum) have extremes between $x = 0.8$ and 0.9. The lower carbon content in group VI transition metal carbides within their homogeneity regions does not affect the exchange between localized and nonlocalized electrons and only insignificantly intensifies M–M interaction. The M–C interaction becomes weaker with increasing temperature as the stability of sp^3 configurations decreases but the M–M interaction that prevails in these conditions. However, the weak M–M interaction in NbC and TaC which was mentioned above, decreases the total bonding energy. The high-temperature redistribution of bonds in carbides is especially well seen from the temperature dependence of microhardness. The higher lattice stability near the stoichiometric compositions of group IV metal carbides may be due to the increasing influence of lattice completeness at high temperatures [10]. Tungsten carbide, WC, is the most commonly used for fabrication as “cemented carbide” tools for cutting steel in which the carbide is bonded in a metal matrix, usually cobalt. Cobalt is used because it wets the carbide particles and behaves as a good binder without having ability to dissolve the carbide, so that the carbide is left pure in the bound form. WC shows excellent catalytic properties similar to platinum [11]. Mixed-metal carbides have been examined for their melting point and hot-hardness behavior as well. In all cases the hot hardness decreased with increasing temperature Applications of transition metal carbides are limited due to their inherent brittleness, catastrophic failure mode and gathering [12].

Table 1.1 Comparative studies of different carbides properties

PROPERTY	**WC**	**TaC**	**MoC**	**NbC**
Crystal structure	BCC	BCC	BCC	BCC
Melting point, ºC	3407	3014	2917	2467
Density, g/cm^3	19.3	16.6	10.2	8.6
Thermal expansion, ppm/°C	4.5	6.3	4.8	7.3
Thermal conductivity, W/cm.°C	1.70	0.52	1.40	0.54
Specific heat J/g. °C	0.13	0.14	0.25	0.26
Electrical resistivity µ ohm-cm	5.3	13.1	5.4	14.4
Tensile strength at 20ºC GPa	0.7-3.5	0.2-0.5	0.7-1.4	0.4-0.7
Young’s modulus at 20º GPa	410	185	330	130

1.3 Applications of refractory carbides

Some major applications of refractory carbides are as follows:

- These are used in those structures at high temperatures that exceed the capability of conventional steels and superalloys and that require greater toughness and ductility than ceramics.
- Combustion chambers and hot-gas-path components (e.g. valves and tubing).
- Textured high emittance coatings for significantly increased heat transfer away from or to the coated component, as needed.
- High reflectivity coatings.
- Thermocouple sheaths with a platinum-group surface coating for high corrosion resistance.
- Crucibles for crystal growing.
- Radiology identification components for human implant devices (e.g. catheter bands and pacemaker tags).
- Bonding dissimilar metals or ceramics to metals in which welding or brazing is not possible.

1.4 Crystal structure and bonding of transition metal carbides:

Most of the compounds of transition metal carbides have close-packed or nearly close-packed arrangements of metal atoms with smaller carbon atoms placed into the interstitial sites. Based on Hagg rules, the structure of transition metal compounds should have a simple structure if the radius ratio $r = r_x/r_m$ (where r_x and r_m are the radius of the nonmetal and transition metal atoms, respectively) is less than 0.59. Most transition metal carbides have values of “r” less than 0.59 as mentioned in table 1.2. Metal atoms in carbides often form simple fcc, hcp, or simple hexagonal lattices. Occupation of all the octahedral interstitial sites by carbon in the fcc lattice results in the **(**NaCl**)** structure which is common among monocarbides. Simultaneous contributions of metallic, covalent, and ionic bonding to the cohesive energy are involved in all transition metal carbides. Unlike the boride structures, transition metal carbides do not exhibit apparent carbon-carbon localized interactions within the structures. Instead they show metal-carbon as well as metal-metal interactions. Theories have been proposed to determine the relative importance of metal-metal versus metal-carbon interactions. The strong metal-carbon bonding theories are based on the crystallographic evidence of the strong preference for the octahedral coordination.

Table 1.2 Radius ratios for transition metal carbides.

GROUP 4 $r = r_c/r_m$	Ti 0.526	V 0.576	Cr 0.609
GROUP 5 $r = r_c/r_m$	Zr 0.483	Nb 0.530	Mo 0.556
GROUP 6 $r = r_c/r_m$	Hf 0.486	Ta 0.529	W 0.553

The distance between transition metal atoms in octahedral sites is greater than in the pure transition metal. The increased metal-metal distance greatly decreases the importance of metal-metal bonding.

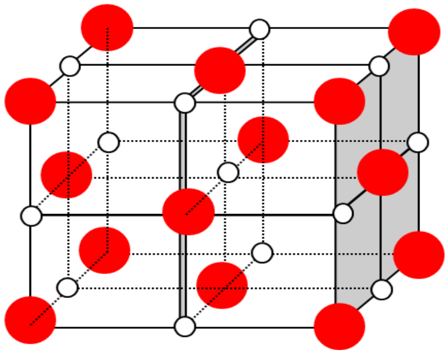


Figure 1.1 Crystal structure of MC compounds.

The strong metal-carbon bonding theories support the idea of predominantly covalent bonding which is used to explain the high hardness and brittleness of these compounds. On the other hand, strong metal-metal bonding theories are based on the interstitial nature of carbon and the role of carbon as a donator of electrons of the metal atoms. The theory has been used to explain the metallic nature of these compounds, and the wide range of compositions over which these phases are stable. This approach accounts for the high melting points of the compounds and the wide composition ranges over which individual phases are stable.

1.5 Types of carbides

1.5.1 Tungsten carbide

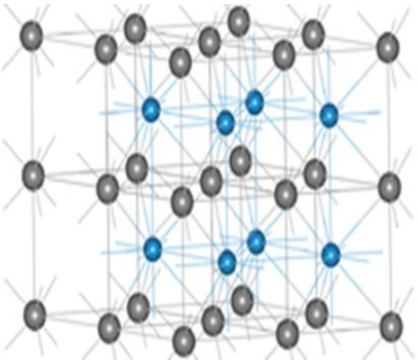


Figure 1.2 α -WC structure, carbon atoms are gray [13].

There are two forms of WC, a hexagonal form, α-WC and a cubic high-temperature form, WC_{1-x}, which has the rock salt structure [14]. BothWC and W_2C may be present in coating and the proportion can depend on coating material [15]. Tungsten carbide (WC) is an inorganic chemical compound containing equal parts of tungsten and carbon atoms. In its most basic form, it is a fine gray powder, but it can be pressed and formed into shapes for use in industrial machinery, tools, abrasives. Tungsten carbide is approximately three times stiffer than steel, with a Young's modulus of approximately 550 Gpa [16] and is much denser than steel or titanium. TiC are also used with tungsten carbide in cutting tools [17]. It is comparable with corundum (α-Al_2O_3) or sapphire in hardness and can only be polished and finished by material with superior hardness such as cubic boron nitride and diamond in the form of powder and compound. Nano crystalline ceramic materials were found to have higher hardness fracture toughness and ductility and are sintered at lower temperature and pressure than coarse-grained powder [18].

WC is readily wetted by both molten nickel and cobalt. Investigation of the phase diagram of the W-C-Co system shows that WC and Co form a pseudo binary eutectic phase. The phase diagram also shows that there are so-called η-carbides with composition $(W,Co)_6C$ also formed which is brittle in nature and affect the mechanical properties. Almost 50% of the total production of cemented carbides is now used for nonmetal cutting applications such as drill bits and components for mining, oil and gas drilling, transportation and construction, metal forming, structural and fluid-handling components, and forestry tools [19].

1.5.2 Titanium carbide

Titanium carbide is an extremely hard refractory ceramic material, similar to tungsten carbide. It is commercially used in tool bits. It has the appearance of black powder with NaCl-type face cubic crystal structure. It is mainly used in preparation of cermets, which are frequently used in machine steel materials at high cutting speed. The resistance to wear, corrosion, and oxidation of a tungsten carbide-cobalt material can be increased by adding 6-30% of titanium carbide to tungsten carbide. This forms a solid solution that is more brittle and susceptible to breakage than the original material. Tool bits without tungsten content can be made of titanium carbide in nickel-cobalt matrix cermet which can enhance the cutting speed, precision, and smoothness of the work-piece. This material is sometimes called high-tech ceramics and is used as a heat shield for atmospheric reentry of spacecraft. TiC coating was one of the first category giving lusture and shining surface followed by Ti(C,N) and TiN coating [20]. A surprisingly stable cluster with formula $Ti_8C_{12}^+$, was detected in 1992 [20, 21]. The 20 atoms were conjectured to be arranged as the vertices of a dodecahedron, with the titanium atoms at the corners of a cube. However, this claim was soon disputed by Linus Pauling [22] who proposed an alternative arrangement with the Ti atoms still at the corners of a cube, but with the carbon atoms pushed inwards so as to be nearly coplanar with the faces of that cube.

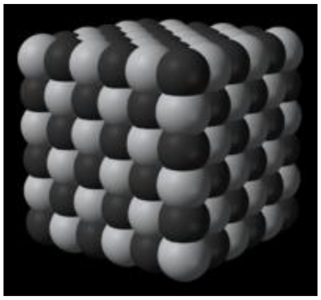


Figure 1.3 Titanium carbide

High titanium carbides (TiC) with nickel as the binder have high red hardness and good wear qualities. The machine steel in the very high speed ranges, providing good surface finishes and size control. They have low strength values and are recommended for light cuts only. Titanium carbide gives "lubricity" to the carbide so that the chip slides across the face of the cutter with less heat and friction. Titanium carbide additives permit the carbide to maintain high hardness at elevated temperatures.

1.5.3 Vanadium carbide

Vanadium carbide, VC, is an extremely hard refractory ceramic material. It also has the appearance of gray metallic powder with a cubic crystal structure. Vanadium carbide is chemically stable and has excellent high-temperature property. Vanadium carbide (VC) is a thermodynamically stable ceramic. It can be used as an additive to tungsten carbide to improve the property of the cermet. Vanadium carbide can be formed as thin film in the (111) orientation, when formed by R.F. Magnetron Sputtering. Vanadium incorporation is a well-known way to control the mechanical properties of the alloy in Interstital Free (IF) steels. Carbonitride precipitation traps C and N atoms out of the solid solution, thus improving the formability. In High-Strength Low-Alloyed (HSLA) steels, the grain size is controlled by a fine dispersion of carbonitride precipitates [23].

1.5.4 Tantalum carbide

Tantalum carbides form a family of binary chemical compounds of tantalum and carbon with the empirical formula TaC_x, where x usually varies between 0.4 and 1. TaC is extremely hard, brittle, gold colored metalloid which is of considerable interest because of high melting point (4150°C) [24]. It is refractory ceramic materials with metallic electrical conductivity. The melting points of tantalum carbides peak at about 3880 °C depending on the purity and measurement conditions. This value is among the highest for binary compounds. Only tantalum hafnium carbide has a distinctly higher melting point of about 4215 °C. Being important cermet materials, tantalum carbides are commercially used in tool bits for cutting applications and are sometimes added to tungsten carbide alloys as grain growth inhibitors. Tantalum carbide is frequently used in materials engineering due to its high corrosion resistance in aqueous solutions at temperatures up to 247°C [25]. Carburizing of tantalum is usually performed in two stages: direct carburizing followed by a diffusion process at temperatures above 1597ºC. The carburizing process of tantalum and the carburizing mechanism is discussed in radio-frequency (rf) plasma-enhanced chemical vapor deposition (PECVD) [26, 27].

The bonding between tantalum and carbon atoms in tantalum carbides is a complex mixture of ionic, metallic and covalent contributions, and because of the strong covalent component these carbides are very hard and brittle. TaC has a micro hardness of 1800 kg/mm^2 and an elastic modulus of 285 GPa, whereas the corresponding values for tantalum are 110 kg/mm^2 and 186 GPa. The given data show that the hardness and elastic modulus increase with the increase in carbon content in TaC_x. Tantalum carbides have metallic electrical conductivity, both in terms of its magnitude and temperature dependence. TaC is a superconductor with a relatively high transition temperature of T_C = 10.35 K. The magnetic properties of TaC_x change from diamagnetic for $x \leq 0.9$ to paramagnetic at larger x. An inverse behavior (para-diamagnetic transition with increasing x) is observed for HfC_x, despite it has the same crystal structure as TaC_x. The graded structure and composition lead to a significant improvement of corrosion resistance compared to untreated metal [28, 29].

1.6 Ta-C phase diagram

The melting point of tantalum is lowered from 3000 ºC to 2825 ºC by adding Ta_2C. The eutectic formed is characterized by composition containing 12.5 atomic percent carbon. The Ta_2C phase is apparently formed by a peritectic reaction at 3240 ºC from tantalum rich- liquid and TaC. No experimental evidence could be found for the eutectic reaction between Ta_2C and TaC, but the microstructure of melted Ta_2C specimens suggests congruent melting. The homogeneous limits of Ta_2C are approximately 29 and 33 atomic percent carbon within the temperature range 2850 to 3150 ºC. The low carbon boundary is variant above and below 2850°C; the high carbon boundary remains unchanged from stoichiometries value. At 3150°C the Ta_2C / Ta_2C + liquid boundary corresponds to the carbon content of slightly greater than 29 atomic percent. Homogeneous TaC has a boundary limits of 41.7 and 49.5 atomic percent carbon at 2250 ºC. Fussion experiment at 3300 ºC to 3400 ºC suggests that the low carbon boundary in this temperature region contains less than 39.5 atomic percent carbon. The existence of eutectic between TaC and C has been verified, but the particulars on temperature and composition are currently lacking. The melting temperature of these high carbon alloys appear to be substantially higher than 3300 ºC. The TaC-C eutectic corresponds to a 3375°C and composition containing 61.2 atomic percent carbon.

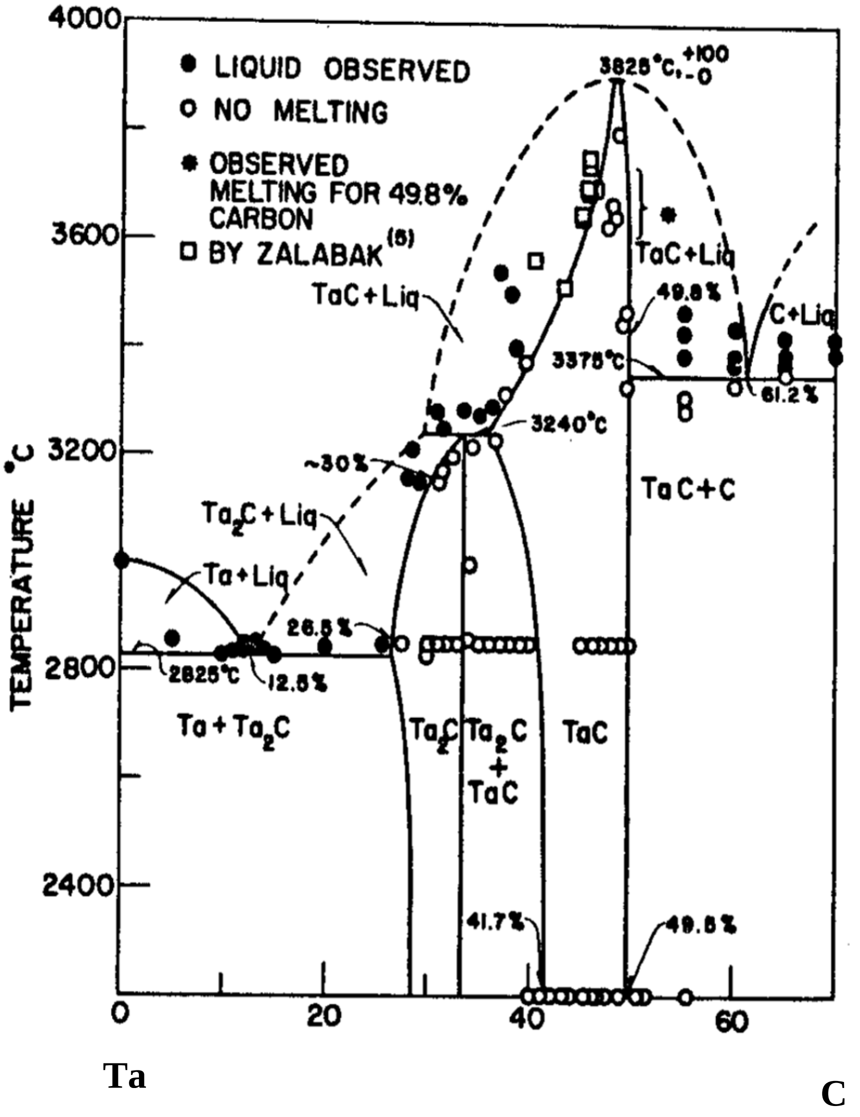


Figure 1.4 Phase diagram of TaC

The TaC melting point is above 3800°C, when carbon content is approximately 48.5 atomic percent carbon. The near stoichiometric TaC composition (49.8 atomic percent carbon) formed liquid in the temperature range of 3610°C to 3735°C according to resistance heating experiment. The melting at 3700°C containing composition 46.6 atomic percent carbon. Liquid formation takes place below 3700°C. The original measurement of 3800°C to 3900°C were unfortunately unaccompanied by chemical analysis.

1.7 Properties of tantalum carbide (TaC)

Tantalum carbide (TaC) has high hardness, high melting point, high chemical stability, good resistance to chemical attack and thermal shock, and excellent oxidation resistance and corrosion resistance [30], which makes it very attractive for anti-ablation applications. It is found that the ablation mechanism of throat materials could be divided into three categories: sublimation, oxidation and mechanical abrasion [31]. Addition of TaC into throat materials can effectively depress the oxidation reaction during the ablation process by means of forming tantalum oxides (Ta_xO_y) to make up for the defects of materials and inhibit further oxidation damage. With the proper interface bond between TaC particles and matrix, the addition of TaC can greatly improve the resistance and the corrosion withstanding properties of the matrix, which will ultimately improve the anti-ablation properties of the material. Because TaC has resistance to chemical attack and oxidation, which leads to catalytic properties and good thermal and excellent electronic conductivity. TaC are the contesting materials because they possess a low coefficient of thermal expansion, low vapor pressure at elevated temperatures, high modulus (537GPa) and good creep and fatigue properties.

On an industrial scale, tantalum carbide has primarily been produced by the carbothermal reduction of Ta_2O_5 with carbon due to the low cost of raw materials. It has been reported that tantalum carbides can be obtained by heating Ta_2O_5 at high temperature under high vacuum, and higher temperatures for long time [32]. A fast and complete reaction takes place due to high temperature treatment of TaC, so it also causes coarsening of the carbide grains. The reduction of carbide size generally gives a significant improvement of the mechanical properties [33]. The toughness of ceramics can be increased considerably without sacrificing the hardness by reducing the grain size [34]. Tantalum carbide is added to some grades of cemented carbides to make hard carbide cutting tools which have a low coefficient of friction and a high resistance to mechanical shock.

Over the past few years, several studies have been made on producing ultrafine and nanocrystalline WC and WC–Co powders [35,36], but little is known about research of ultrafine TaC for alloying element in WC–TaC–TiC–Co alloys. Tantalum carbide is often added to tungsten carbide/cobalt (WC/Co) powder attritions to enhance the physical properties of the sintered structure. It also acts as grain growth inhibitors preventing the formation of large grains, thus producing a material of optimal hardness. It is also used as a coating for steel moulds in the injection moulding of aluminium alloys. While providing a hard, wear resistant surface, it also provides a low friction mould surface.

Hot isostatic pressing, direct metal oxidation, extrusion, and hot pressing, have been widely used for the densification and near net shape (NNS) forming of ceramic materials. These techniques lack the capability to fabricate contoured and thin wall structures owing to high melting temperature and brittleness of the ceramics [37]. NNS processing of ultrahigh- temperature ceramics (UHTC) as free-standing structures becomes a problem when following conventional processing route [38,39].TaC formed by vacuum plasma spray provides an alternative to overcome fabrication hurdle of high melting point materials and their brittleness. Plasma plume reaches temperatures in excess of 10000 K and impacts the powders in molten or semi-molten states generating typical mechanically bonded layered structure [40,41 ,42] It is important to emphasize that much of the literature research material for the applications of TaC, because of military applications [40, 43, 44].

1.8 Applications of tantalum carbide (TaC)

They are suitable to cut a variety of materials such as gray cast iron, ductile nodular iron, austenitic stainless steel, nickel-base alloys, titanium alloys, aluminum, free-machining steels, plain carbon steels, alloy steels, and martensitic and ferrite stainless steels. Tantalum and molybdenum carbide coatings are used industrially for wear protection of steel moulds employed in injection cast molding of aluminum and aluminum alloys.

High speed steel tools for machining were coated with TaC by chemical vapor deposition (CVD), and were used in a high speed milling machine. The coating made from TaC resist higher attrition than that of made by WC. TaC is desirable for market applications such applications as boost rocket motor nozzles that require high thermal-shock resistance. In the commercial sector, TaC has potential application as a material used for cutting tools and wear parts. Tantalum carbide has wide application in biomedical, corrosion, aerospace and electro-technology. TaC stands as a candidate material for next generation thermal heat protection, space aircrafts, automotive wear resistant liners, and propulsion-exposed components. Due to their optical, electronic and magnetic properties, tantalum carbides have been used for optical coatings, electrical contacts and diffusion barriers. Though tantalum carbide (TaC) has been proposed for use as wound filaments in the form of wires, it is prohibited due to the low strength of TaC wires. In the industrial world, it can be used in machining-tool materials to reduce the tendency of welding between steel chips and tool material.

1.9 Nanocarbides

Nanocarbide has high purity, small diameters, even distribution, large specific surface area, high surface activity and low apparent density, as well as the excellent mechanics, electricity and chemical properties. It has higher hardness, melting point, wear resistance and low thermal expansion coefficient, high elevated-temperature strength etc. Nanoparticles exhibit superior mechanical properties and their tailored particle size and shape is for improved sintering and densification. The general formula of Nano carbides is M_xC_y representing a family of compounds. Nano carbides developed mainly include nano TiC , nano ZrC , nano SiC and nano BC.

The cemented carbide cutting tool industry suffers with the problem of higher mechanical properties for their cutting tools. As nanoparticles possess high strength, high hardness, high ductility and toughness, so the properties of these materials can be improved by reducing the average particle size of the hard carbides as the mean free path between carbide particles is reduced. These effects limit the cost-effective mechanical milling reduction of particle size. The most striking is the abrasion resistance, with finer grain composites (still in micron range) having much better abrasion resistance.

Chapter 2

2.1 Literature review

The study of tantalum, its compounds and alloys, first began in Melbourne in 1942. It was undertaken as part of a program to investigate the effect of adding the hard, high melting point metallic carbides, e.g. tantalum carbide. The early stages involved the development of a method for separating tantalum oxide and columbium (niobium) oxide from an ore which occurred abundantly in the Western States of Australia. This work gave the results of an investigation into a method of preparing pure tantalum carbide.

Traditionally, transition metal carbides have been made by high temperature powder metallurgical techniques [45]. These methods, however, are energy intensive and result in large grains with low specific surface area, which limits their promise to allow the consolidation of fully dense solids with excellent fracture resistance, use in high stress and temperature application [46]. Therefore, new and efficient solid-state routes are still desired to synthesize transition metal carbide nanoparticles. In this work, a facile solid-state reaction was utilized to prepare TaC nanoparticles at moderate temperature.

According to Nartowski et al. [47] the synthesis of transition metal carbides from metal oxides can also be carried out by solid state metathesis (SSM). Solid state metathesis reactions are not restricted to the use of transition metal halides as the metal source; metal oxides can also be used in certain circumstances. The reactions do not support a solid flame synthesis wave like conventional metathesis reactions, but do support the passage of a dark wave in which transformation of reactants to products occurs. Acquisition of crystalline materials from the SSM reaction using oxide precursors required annealing at 1000 °C for at least 6 h and formed the most thermodynamically stable transition metal carbide.

Chen et al. [48] in 2001 proposed that tantalum carbide (TaC_x) whiskers were successfully synthesized by Ta_2O_5–NaCl–C–Ni, Ta_2O_5– NaF–C–$C_{12}H_{22}O_{11}$ (sucrose) and Ta_2O_5–KCl–C–Ni system in the presence of Ni powder via a vapor–liquid–solid (VLS) mechanism. According to them the whiskers grew and exhibit fairly straight fiber morphology. Some whiskers grew with a zig zag shape tip and conical shaped morphology. All whiskers were grown under similar reaction conditions at temperatures which range from 1150 ºC to 1350 ºC in a nitrogen ambient atmosphere.

Kwon et al. [49] in 2004 proposed ultrafine synthesis of TaC by mechano-chemical process (MCP) by ball milling of spray dried Ta_2O_5 powder which was calcined at 500 °C with carbon. The carbothermal reaction occur in the presence of hydrogen gas at temperature 1050 °C for 6 h and found complete TaC powder with aprticle size less than 200 nm.

Xiang et al. [50] in 2006 prepared liquid tantalum carbide polymer precursors by using tantalum chloride, hydrofluoric acid and furan resin. It has been found that with the increase of the molar ratio of C/Ta, the solidification time of liquid precursors decreased. Carbonization at high temperature under an inert atmosphere yield cubic TaC and thus the formed composite was comprised of TaC particles and carbon matrix. TaC particles were dispersed relatively uniformly throughout the matrix, but the grain size distribution was inhomogeneous and diverse.

Leib et al. [51] in 2007 proposed the synthesis of fine TaC nanoparticles by using C_3N_4 as carbonizing reagent by highly efficient solid-state reaction which occur at the low temperature

(1150 °C). In this solid state reaction g-C_3N_4 as a precursor is proven to be a highly efficient carbonizing reagent, and the oxide Ta_2O_5 is completely converted into the corresponding carbide. The average particle size of TaC is of the order of 35 nm. A striking feature of this facile solid-state reaction is that g-C_3N_4 plays double roles in the reaction: carbothermal reduction reagent as well as act as carbonizing reagent. This novel route may provide new insights into the synthesis of other transition metal carbides.

Li et al. [52] in 2008 proposed synthesis of TaC by using CN_2H_2 and found that CN_2H_2 exhibits powerful carburization abilities to completely convert the metal oxides into the corresponding carbides at relatively low temperatures. During the formation of the transition metal carbides, the reaction process is proposed to involve the steps of condensations of CN_2H_2, reduction of the metal oxides and subsequent carburization of the reactive metal atoms.

Yinxiao et al. [53] in 2008 proposed synthesis of cubic TaC nanoparticles by a novel solid-state reaction process using amorphous C_3N_4 and transition metal oxides as starting reagents at 1150 ℃. The experimental results show that a-C_3N_4 is a highly efficient carburation reagent and the transition metal oxides are completely transformed into the corresponding metal carbide nanoparticles at 1150 ℃. The TaC, nanoparticles are found to have an average particle size of 10 nm.

Sevast'yanov et al. [54] in 2008 proposed synthesis of tantalum monocarbide via the carbothermic reduction of tantalum(V) oxide and it shows that TaC synthesized at a temperature below 750°C and in pressures range from 1×10^{-5} to 1×10^{-4}MPa. Using a $Ta(OC_5H_{11})_5$ solution in n-pentanol, prepared a transparent tantalum–carbon containing gel and then a fine-particle Ta_2O_5 + C mixture, which was used to synthesize tantalum monocarbide at temperatures from

850 to 1200°C and pressures from 10^{-5} to 10^{-4}MPa. According to TEM results, the particles are almost spherical in shape and uniform in size. The average size of the particles synthesized at 1050 and 1200°C is 20 ± 10 and 30 ± 15 nm, respectively.

Massot et al. [55] reported a new work of synthesized tantalum carbides by the electrochemical route over a moderate temperature range (700 – 900°C) and found an alternative to chemical vapor deposition (CVD) which occurs at higher temperatures (1300°C). The result of this work shows that the diffusion of reactive carbon occurs too rapidly as compared to the reaction within the tantalum grains. This conclusion can be extended to the possible preparation of other refractory metal carbides (Nb, Mo, and W). In this way, this methodology seems to be promising for the synthesis of such compounds.

In 2009 a new process has been given by Massot et al. [56] in which solid diffusion of an electrochemically tantalum into the bulk of another carbon occurs spontaneously to yield a thermodynamically stable product. This product transforms the porous surface of the carbon material into a tightly sealed, highly resistant layer of tantalum carbide. The most obvious applications of the product obtained from this process will be the protection of carbon electrodes and of carbon linings of nuclear reactors which are prone to surface crumbling and erosion.

Ma et al. [57] also reported the synthesis of TaC nanopowders by liquid precursor route. The liquid precursor was a mixture of tantalum ethylate and activated carbon nanopowders, prepared by ultrasonic equipment. The products had the cubic TaC structure. It consisted of particles with an average size less than 50 nm and specific surface area 28.399 m^2/g.

A new approach to solvothermal synthesis by using both thermal and chemical ignition techniques has been demonstrated by Ma et al. [58]. In this method, nano crystalline tantalum carbide (TaC) has been successfully prepared by the reaction of metallic magnesium with sodium carbonate and tantalum pentachloride in an autoclave at 600 °C. The obtained product has the cubic TaC structure. It consists of particle with an average size of 40 nm. The product obtained from this route had good thermal stability and oxidation resistance below 450 °C in air as investigated by TGA.

The characterization of the TaC powders obtained by solvothermal method demonstrates that this technique is attributed to the fast reaction kinetics. Furthermore, the figures of merit that were obtained relating to particle dispersion indicate that the level of hard agglomeration of the samples is low in this method. This unique approach will aid in the development of nanocrystalline ultra-high-temperature ceramics, and composites of them, and has the potential to satisfy other applications that require nanocrystalline and unagglomerated powders.

Lithium and calcium were found to be suitable reductants for this process. Since the reaction is very rapid and therefore is likely to be controlled by kinetics rather than thermodynamic equilibrium conditions. So, pure phase of obtained tantalum carbide (TaC) could be achieved by controlling the reaction temperature and reactant concentrations, which control diffusion, crystallization, and growth processes [59]. More understanding of the powder surfaces after using this synthesis method and analysis of oxygen and residual carbon are necessary.

2.2 Proposed Work

Since, the carbides of the transition metals are a special group of compounds. The physical and chemical properties of transition metal carbides are of interest for basic research and several technological applications. They exhibit some extraordinary properties which obviously differ from other common ceramics and metal and they have been applied widely as abrasives in cutting and grinding tools owing to their high hardness.

Tantalum carbide (TaC) is an undoubtedly promising material among transition metal carbides. It is characterized by high hardness, high melting point (approximately 3880 °C), excellent electronic conductivity (at 25 °C) , good resistance to chemical attack and thermal shock and high resistance to oxidation , which makes it very attractive for high-temperature and electronic applications. Thus the second part of the study is to focus on the synthesis process of synthesized TaC particles by new route (solvothermal). These prepared samples will be characterized by different techniques as given and discussed in Chapter 3.

Chapter 3

Experimental techniques

3.1 Methodology

In the present study Tantalum carbide (TaC) nanopowder will be synthesized by solvothermal route by taking tantalum pentaoxide (Ta_2O_5) and acetone (C_3H_6O) were used as tantalum and carbon source respectively, whereas Mg powder was used as reductant. The most probable reaction that can be carried out is given below:

$$Ta_2O_5+C_3H_6O+3Mg \rightarrow 2TaC+CO_2+H_2O+3MgO+2H_2 \qquad (1)$$

All the reactants were put in the specially designed autoclave. Then, the autoclave was sealed and put into a resistance heating furnace. The temperature of the furnace was increased to 800ºC in 3 hours and maintained at 600ºC and 800 ºC respectively for different time as mentioned in the table 3.1 given below. Then, it was allowed to cool down to room temperature. The dark solid powder was collected and dissolved in HCl to remove the MgO powder.

Table 3.1 Samples at different time and temperature:

SAMPLE	**TEMPERATURE(^{o}C)**	**REACTION TIME(h)**
S1	800	05
S2	800	10
S3	800	15
S4	800	20
S5	600	05
S6	600	10
S7	600	15
S8	600	20

Flow chart

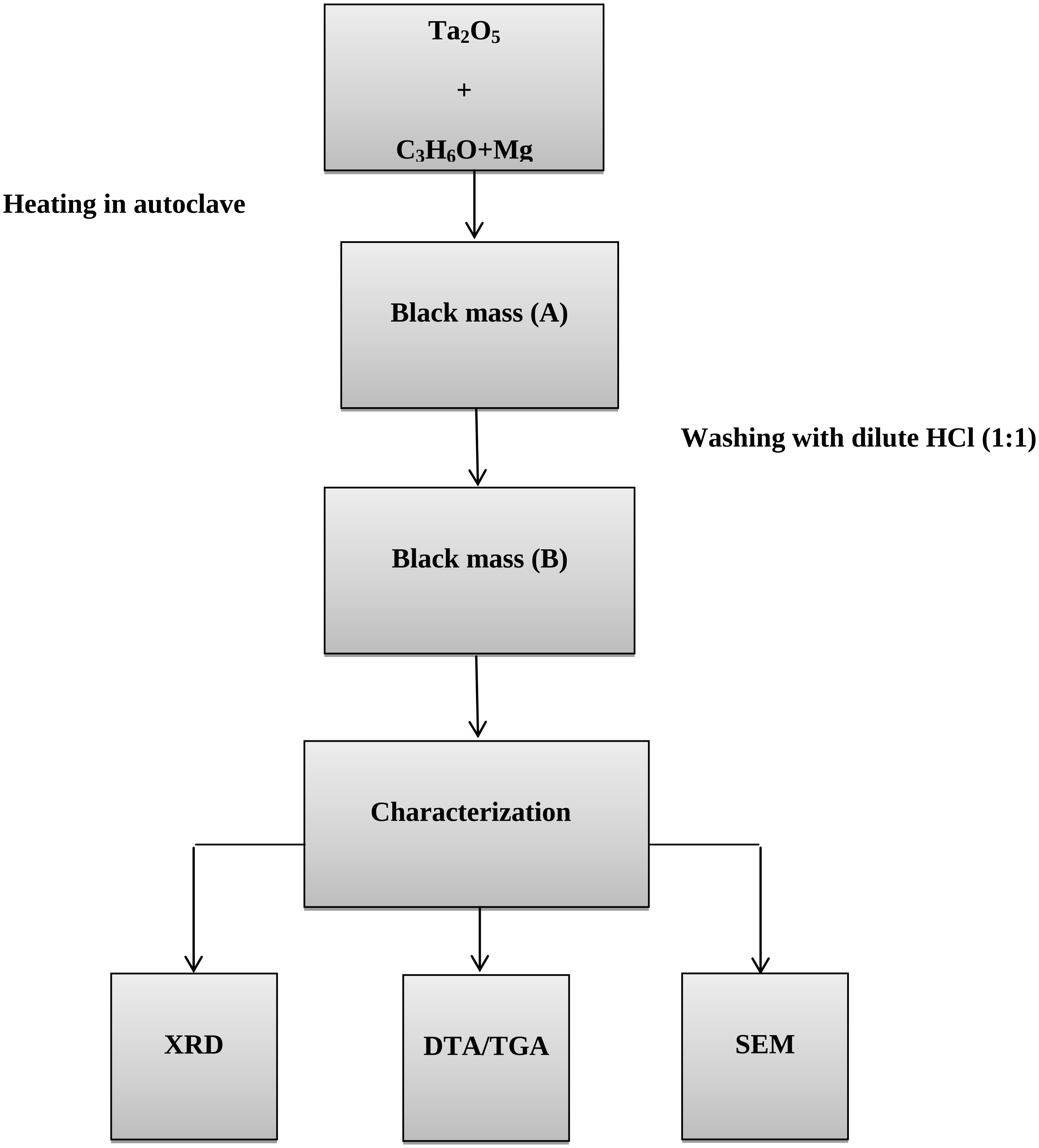


Figure 3.1: Flow chart showing the process of synthesis and techniques used for characterization of synthesized nano powders**.**

3.2 Characterization techniques

The synthesized carbides were characterized using X-ray diffraction, SEM for phase identification and morphological studies. The stability of compound was checked by DTA/TGA techniques. These are described below:

3.2.1 X-ray diffraction:

X-ray diffraction is versatile, non-destructive analytical techniques which reveals the information about the crystallographic structure, chemical composition and physical properties of materials and thin films. This technique is used to identify and characterize unknown crystalline material. These techniques are based upon observing the scattered intensity of X-ray beam hitting a sample, as a function of incident and scattered angle, polarization and wavelength or energy. Monochromatic X-rays are used to determine the interplaner spacing of the unknown material. Powder samples used for X-ray diffraction provide all possible peaks as grains are in random orientations that insures that all crystallographic directions are “sampled” by the beam.

In 1912 W.L Braggs recognized a predicable relationship among several factors. These factors are combined in Bragg’s law as described below:

$$2d\sin\theta = n\,\lambda \qquad (1)$$

Where d is interplaner spacing and λ is wavelength of incident x-ray, θ is diffraction angle, n is integer.

3.2.2 Differential thermal analysis (DTA)/Thermal gravimetric (TGA):

Differential thermal analysis (DTA) detects the release or absorption of heat, which is associated with chemical and physical changes in materials as they are heated or cooled. Such information is essential for understanding thermal properties of materials. Analysis of decomposition of materials, crystalline phase changes (phase transition), chemical reactions and glass transition temperature are some of the properties measured with DTA.

When the sample undergoes a transformation, it will either absorb (endothermic) or release (exothermic) heat. In differential thermal analysis, the T ºC difference between a reactive sample and a non-reactive reference is determined as a function of time, providing useful information about the temperatures, thermodynamics and kinetics of reactions. Thermo gravimetric analysis (TGA) determines the weight gain or loss of a condensed phase due to gas release or absorption as a function of temperature.

3.2.3 Scanning Electron Microscope:

Scanning electron microscope is an important tool for microstructural analysis. The microstructural characteristics of a sample correlate the effect of different processing condition with properties and behavior of materials that involve their micro structural changes. SEM provides the information relating to topographical features, morphology, phase distribution, compositional differences, crystal orientation, and presence of defects and their locations. The strength of SEM lies in its inherent versatility due to multiple signal generated, simple image formation process, wide magnification range and excellent depth of field. The SEM micrographs could be taken in two modes i.e. secondary emission and back scattered.

Chapter 4

Results and Discussions

4.1 X-Ray Diffraction Analysis

The X-ray powder diffraction data were collected for all samples at room temperature in the range of 20°≤2θ≤70° at the scan speed of 5°/ min using monochromatic Cu Kα radiation having 1.54 Å wavelength.

Product composition was investigated using X-ray diffraction. A typical XRD traces for sample synthesized at 800°C and 600 °C are shown in figure. 4.1 before acid treatment respectively. The XRD patterns exhibit prominent, broad peaks at 2θ values of 2θ≈ 34.856°, 40.461°, 58.561°,70.005°,73.611° corresponding to [111], [200], [220], [311] and [222] planes of TaC. Peaks marked match well with cubic structure of TaC with having lattice constants a=4.435 which is much closer to the remarkable value (a=4.456) given in PCPDF (35-0801).

It is clear from the X-Ray diffraction pattern of samples done before acid leaching, that with the increasing in synthesis time the intensity peak of byproduct MgO decreases and peak intensity of another yield products increases. It indicates that with increasing synthesis time the reactivity of the reactent increases. The MgO in the product was easily removed by leaching with HCl solution (1:1) at room temperature for 30 minutes. All final product samples indexed to tantalum carbide with some intermediate products such as tantalum sub-carbide (Ta_2C, an intermediate species in the Ta/C system), tantalum, unreacted tantalum oxide (Ta_2O_5, TaO). Unreacted carbon black would not appear in the XRD analysis may be due to the amorphous structure. The phase identification is done according to PCPDF (32-1280) for Ta_2C.

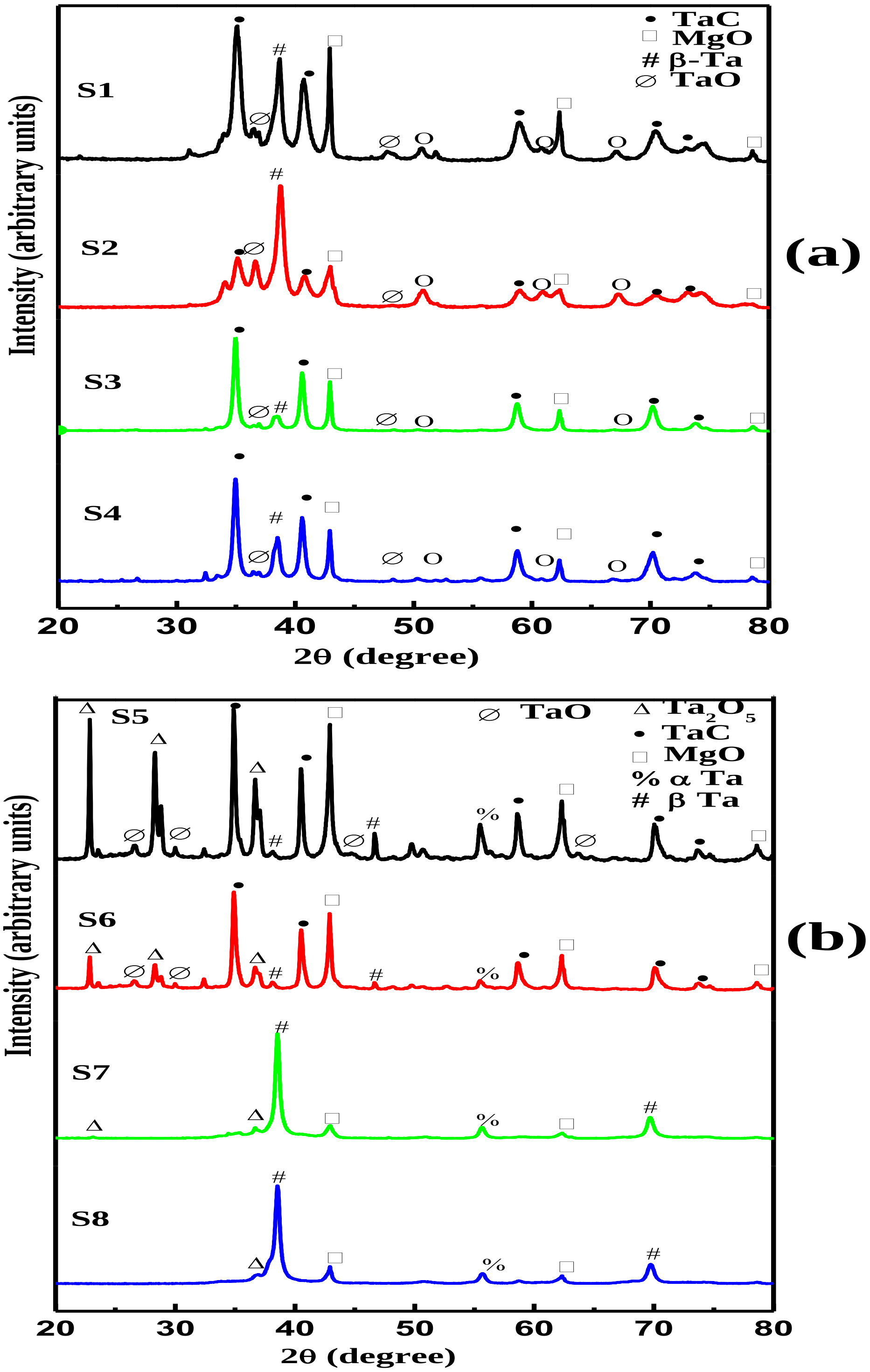


Figure 4.1 X-ray diffraction patterns of the prepared product before acid leaching at 800^{o}C and (b) at600^{o}C.

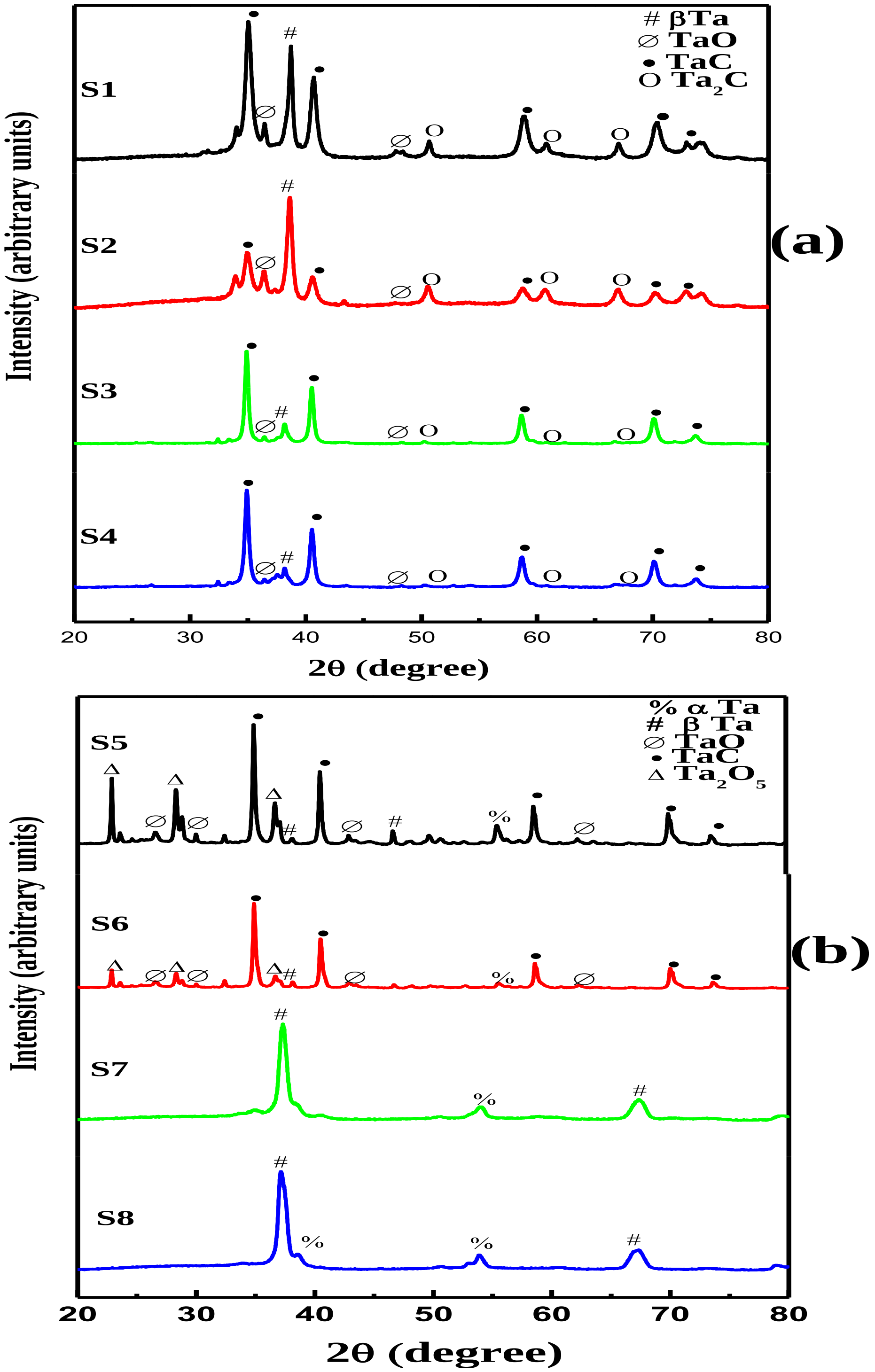


Figure 4.2 X-ray diffraction patterns of the product prepared after acid leaching (a) 800°C and (b) 600°C

The main peaks for [101], [102] and [103] reflections originate at 2θ≈ 38.067°, 50.07°, and 66.495°. Similarly phase assignment is done according to JCPDS (79-1375) and JCPDS (04-

0788) for Ta_2O_5 and Ta respectively. The main peaks for [010], [411], [1211] for 2θ≈ 22.819°, 28.244° and 36.614°,corresponds to planes of Ta_2O_5 as well as [202], [200] and [513] for 2θ≈38.2°, 55.546 and 71.028° corresponds to Ta. After leaching MgO the XRD pattern shown in figure 4.2 which indicates that for sample synthesized at 800 °C the phase percentage of TaC increases with increasing time. The details of this transformation are given below:

In sample S1, as the reaction time is very less (5h) so this sample shows the presence of Ta, TaC, and TaO peaks. The presence of Ta indicates that there is not sufficient time for tantalum to react with carbon. But in the case of sample S3 where reaction time has been increased to15 h shows the presence of TaC and Ta peaks, indicates that the reactivity of Ta with C increases and to see the effect of synthesis time we have increased the time up to 20 h in sample S4. In sample S4, we have found a saturation stage is reached where Ta_2O_5 powder carburized into ultrafine TaC particles with small amount of tantalum as well as lower tantalum oxide (TaO). In intermediate timing 10 h for sample S2, there is an abrupt change in result has been found. It shows a decrease in TaC peak intensity which means a reversible reaction may occur in this condition. The XRD results of samples synthesized at 800 °C clearly indicate one major point that the amount of Ta_2C remains almost constant. Considering Ta–C phase diagram, as well as simple diffusion couple reaction fronts, it seems that the reaction proceed through reduction process where Ta_2C phase forms followed by TaC through interfacial diffusion.

But in the case of samples synthesized at temperature 600 °C the amount of TaC increases with increasing time as mentioned in table 4.1. In case of sample S5 reaction time is 5h and this sample shows the presence of TaC with Ta_2O_5 and Ta peaks. This indicates that this timing and temperature is not enough for complete reduction/carburization of Ta_2O_5.

In sample S6 where the synthesis time has been increased to10 h, TaC and Ta_2O_5 has formed, which indicate that at this reaction time Ta_2O_5 is still present but in small amount along with its of lower oxide (TaO). But as the reaction time increased to 15 h complete reduction of Ta_2O_5 has taken place and finally formed TaC undergoes reverse reaction with the formation of Ta. Hence at the higher synthesis time (15 h and 20 h) α-Ta and β-Ta has formed.

All this results of XRD conclude that the influences of reaction temperature and time on the formation of the TaC nanopowder must be taken into account. It was found that a suitable reaction temperature was a key factor for the formation of TaC nanopowder. The reaction time should be sufficient enough to ensure the reduction/carburization of Ta_2O_5 powders. For a higher yield of the TaC nanopowder, a treatment time longer than 10 h at 800 °C was needed but for samples treated at 600 °C the reaction time should not be higher than 10 h.

Table 4.1 Presence of different phases along with %age for different reactions.

Sample	TaC phase (%)	Ta_2O_5 phase (%)	Ta_2C phase (%)	Ta phase (%)	TaO phase (%)
S1	27.78	-	15.52	41.15	15.52
S2	24.23	-	14.11	47.78	33.20
S3	61.39	-	14.45	14.48	12.66
S4	42.75	-	12.66	27.95	16.57
S5	32.14	14.11	-	40.67	13.06
S6	71.28	14.03	-	-	14.67
S7	-	-	-	100	-
S8	-	-	-	100	-

The average particle size of the sample mentioned in table 1.2 is determined from the full width at half maximum of the most intense peak making use of the Scherrer's equation, $D = 0.94\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray radiation, β is the FWHM in radians of the XRD peak and θ is the angle of diffraction.

Table 4.2 Particle size of TaC powder

Sample	Crystallite size (nm)
S1	17.29
S2	07.45
S3	13.41
S4	12.71
S5	23.24
S6	15.52

4.2 Thermal analysis

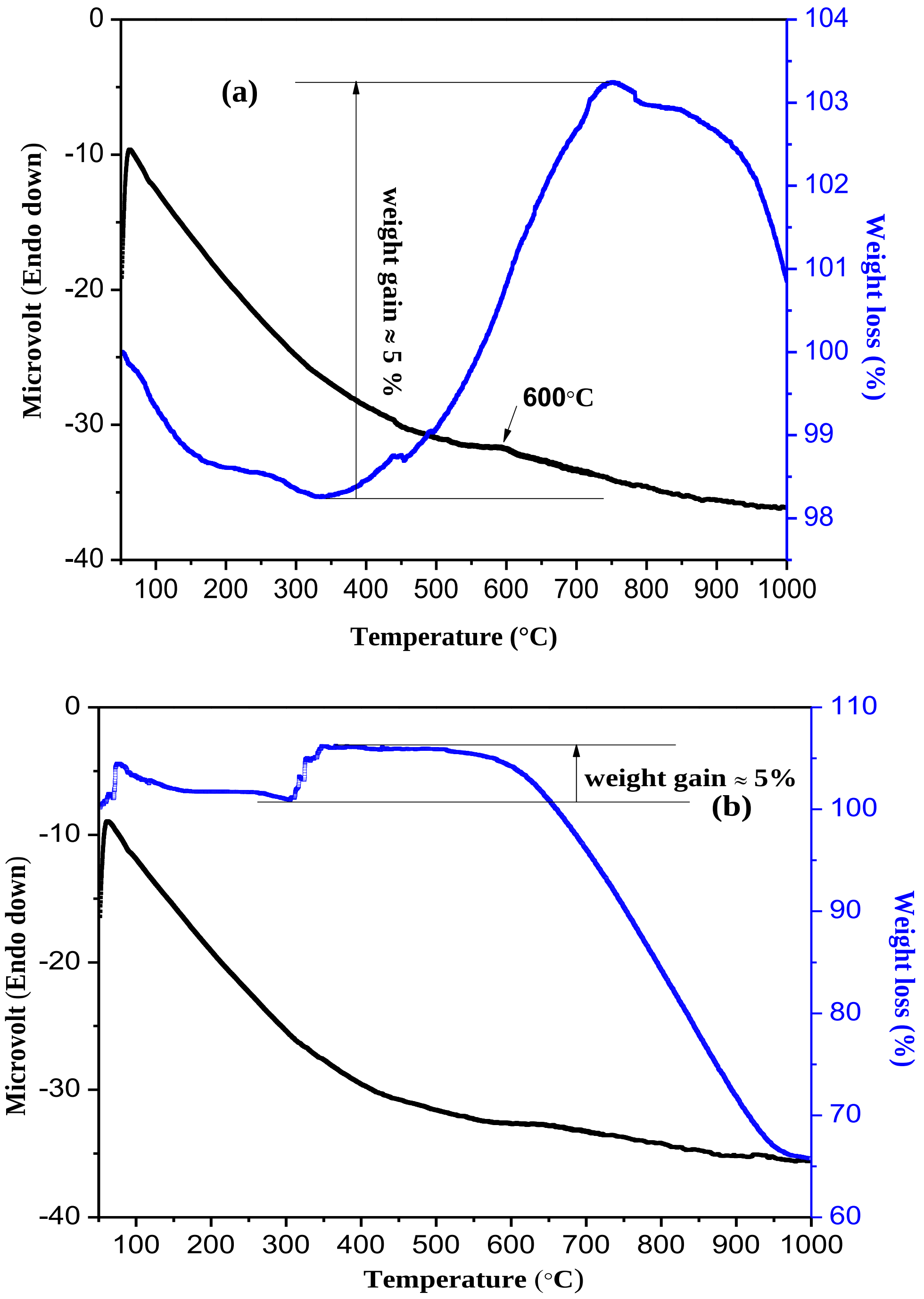
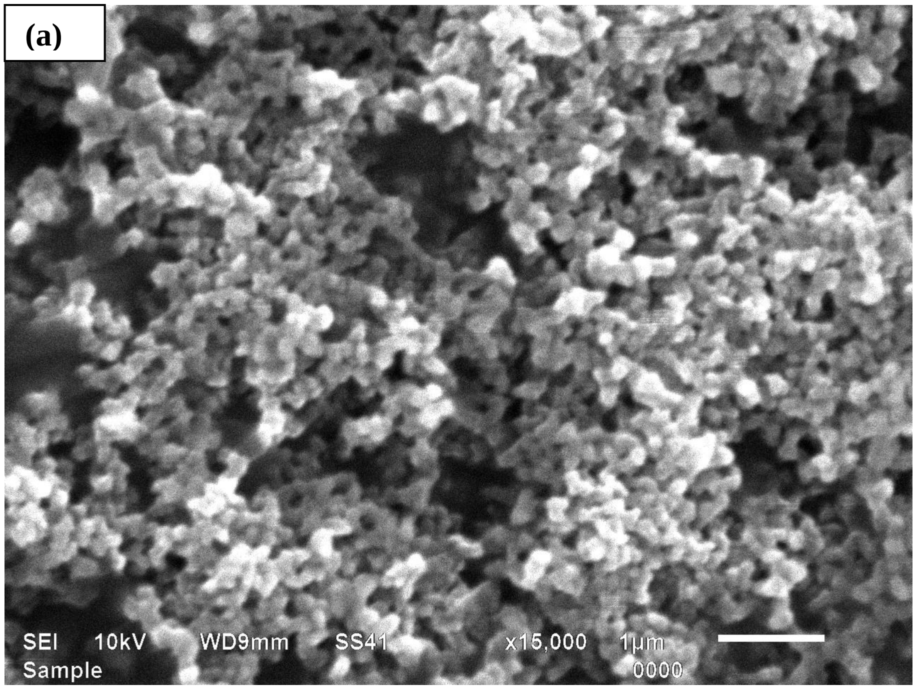
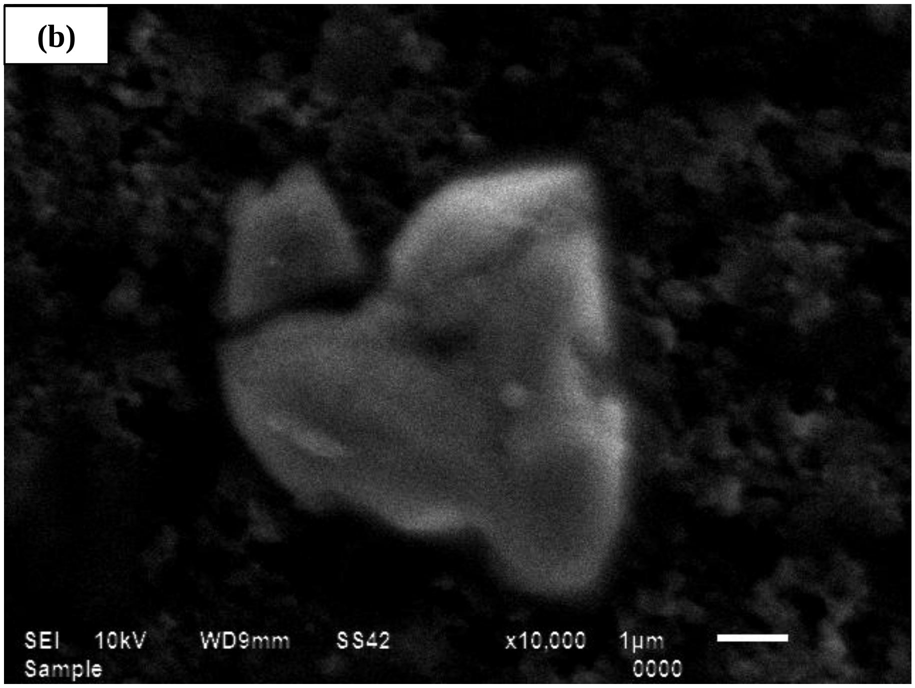


Figure 4.3: DTA/TGA curves of samples (a) S3 and (b) S6

The thermal stability of the synthesized nanosized powders has been investigated in nitrogen from 50 to 1000 ^{o}C. A slight weight loss indicates that this may arise from the evaporation of absorbed water on the surface of the sample. But the quantity of the adsorbed water is very small. From the TGA curve, we can find that the weight gain of the sample is not significant below 350 °C. It implies that the both the sample has good thermal stability below 350 °C. The weight gain (about 5 %) for both samples shows the presence of oxide of lower valance which further oxidized with increased temperature. It has been found that the onset of the oxidation of the synthesized powder was found to begin at about ≈350 °C for sample S3 and S6, which indicates that the sample is oxidized to form Ta_2O_5. As the temperature rises, the amount of the formed Ta_2O_5 is on higher ride, suggesting that the oxidation rate of the sample becomes faster. Finally, the formed Ta_2O_5 becomes an oxide layer on the surface of the sample grain. But the weight gain curves indicate clearly that, there may be lower oxide of tantalum TaO exists which is confirmed by XRD data. Since the formed Ta_2O_5 on the surface of the grains is protective at this temperature, so this oxide layer could prevent further oxidation of the underlying material. From the TGA curve, we can see that the oxidation process becomes weaker at about 450 ^{o}C in S3 and S6. With further increase in temperature from 450 °C for S3 weight gain shows a significant increase. This may originate from that the formed protective oxide layer is destroyed and the oxidation rate increases rapidly again. Above 600 °C in S6 the weight gain remains almost constant on the TGA curve, indicating no weight change. The DTA curves for S3 sample shows an exothermic peak at 600 °C indicates the presence of carbon which has not been detected by XRD.

4.3 SEM observation





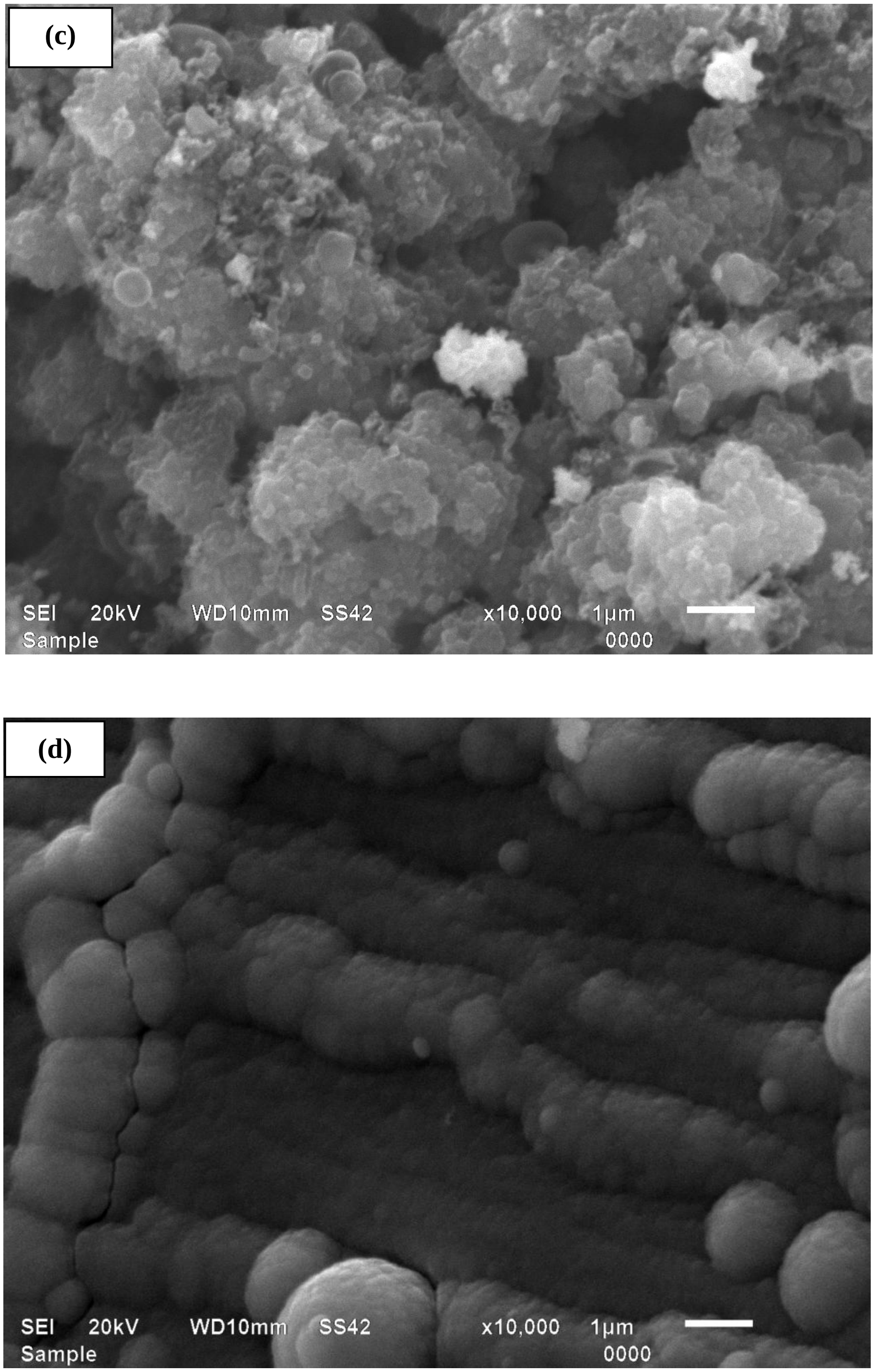


Figure 4.4 SEM micrograph of sample (a) S3 (800°C/15 h), (b) S4(800°C/20h), (c) S6(600°C/10h) and (d) S7(600°C/ 15h)

Figure 4.4 shows the SEM micrograph of the powders prepared at 600 °C and 800 °C for different time mentioned in table 3.1. The sizes of agglomerated particles with rounded and irregular shapes are below 50 nm but not uniform which suggests that the formation of TaC particles is via the solvothermal route. From XRD analysis it was found that both reaction temperature and time have significant influence on the formation of TaC. The structural features of synthesized powders are shown in figure (4.4 (a-d)). The structure shows the fine morphology of all synthesized powders having agglomerated characteristic. The agglomerate is on higher for condition (c) (600^{o}C/10h). Good transformation of the agglomerated particles of carbide to its element (Ta) is seen in figure (d). The structural features developed in exhibiting systematic transformation characteristics.

Chapter 5

Conclusion and Future Scope

In summary, nanocrystalline tantalum carbide (TaC) has been successfully prepared via a simple chemical reaction route by using acetone and tantalum pentaoxide. XRD analysis suggests that both reaction temperature and time have significant influence on the formation of TaC. It means the reaction time must be sufficient to ensure the reduction/carburization of Ta_2O_5 powders. Also the absence of Ta_2O_5 synthesised provides at 800 °C gives an idea that this temperature is suitable to reduce Ta_2O_5 to lower oxide which enhances the reaction rate for the formation of TaC. The product has the cubic TaC structure. It consists of particle with an average size below 50 nm. The product was also studied by TGA. It had good thermal stability and oxidation resistance below 350 °C in N_2. The morphology from SEM also confirms the formation of TaC particles via the solvothermal route and there was an aggregation phenomenon occurring in the systems studied.

Future scope

The lower synthesis temperature of tantalum carbide (TaC) by this route can be investigated which can be improved by varying the amount of tantalum oxide as well as carbon sources. It can also be optimised by using different carbon sources as well as different tantalum sources.

References

[1]. H. J. Scussel, ASM Int: **18** (1992) 796.

[2]. A. Mnyusiwalla, A. S. Daar, P. A. Singer, Nanotechnology: **14** (2003) 9.

[3]. Ying, Jackie, Nanostructured Materials: (2001).

[4]. B. Winkler, A. Friendich, L. Bayarjargal, E.A. Juarez. Arellano, Toth L. E, Science: **32** (2010) 397.

[5]. S.T. Oyama (Ed.), The Chemistry of Transition Metal Carbidesand Nitrides, Blackie Academic and Professional, London: (1996).

[6]. C. Charles Yu, S. Ramanathan, B. Dhandapani, J.G. Chen, S. Ted Oyama, J Phys Chem: B **101** (1997) 512.

[7]. D.R. Sadoway, J Miner Met Mater: **47** (1991) 15.

[8]. S. Niu, M.-B. Hall, Chem Rev: **100** (2000) 353.

[9]. M.-M. Rohmer, M. Benard, J.-M. Poblet, Chem Rev: **100** (2000) 495.

[10]. G. V. Samsonov, Powder Metallurgy and Metal Ceramics: **47(1-2)** (2008)

[11]. F.H. Riberio, R.A. Dalla Betta, M. Baumgartner, E. Iglesia, J Catal: **130** (1991) 86-105.

[12]. A. Biedunkiewics, N.Gordon, J Thermal Analysis and Calorimetry : **88** (2007) 717.

[13]. Krawitz, D. Aaron. Reichel, G. Daniel, Hitterman, Richard, J Am Ceram Soc: **72 (3)** (1989) 515.

[14]. R. V Sara, J Am Ceram Soc: **48 (5)** (1965) 251.

[15]. L. Jacob, M. M Hyland, M. Debonte, J Thermal spray technology: **7(2)** (1998) 213.

[16]. J. Nerz, B. Kushner, A. Rotolico, J Thermal Spray Technology: **1(2)** (1992) 147.

[17]. V. K. Sarin, Advances in powder Technology. Ed. D. Y. Chin, ASM: (1981) 253.

[18]. H. Kolaska, J Powder Metallurgical Int: **24(5)** (1992) 311.

[19]. A. T. Santhanam, P. Tierney, J. L. Hu, ASM Int: **2(10)** (1990) 950.

[20]. Jeans-Petter Palmquish, J Thin film synthesis: **930** (2004) 70.

[21]. Bc Guo, S. Wei, J. Purnell, S. Buzza, Castleman, Aw, Jr Science: **256(5056)** (1992) 515.

[22]. L. Pauling, Proc. Natl. Acad. Sci. USA: **89 (17)** (1992) 8175.

[23]. T. Epicier, D. Acevedo, M. Perez, J Philosophical Magazine: **88(1)** (2008) 31.

[24]. B. H. Eukstein, R. Forman, J App. Physics: **33(1)** (1962) 82.

[25]. C. R. Bishop, J Corrosion: **19** (1963) 308.

[26]. A. Rubinshtein, R. Shneck, A. Raveh, J.E. Klemberg-Sapieha, L. Martinu, J Vac Sci Technol, A, Vac Surf Films: **18(4)** (2000) 2017.

[27]. A. Raveh, A. Danon, J. Hayon, A. Rubinshtein, R. Shneck, J.E. Klemberg-Sapieha, L. Martinu, J Thin Solid Films: **392** (2001) 56.

[28]. A. Robin, J. L. Rosa, Int J Refract Met Hard Mater: **18** (2000) 13.

[29]. D. Lupton, W. Schiffmann, F. Scheiber, E. Heitz, Proceedings of the Eighth Inter. Congress on Metallic Corrosion, Dechema Mainz **2** (1981) 1441.

[30]. N. Ahle´n, M. Johnsson, M. Nygren, Thermochim Acta: **336** (1999) 111.

[31]. Cui Hong, Su Junming, Li Ruizhen, Li Hejun, Kang Mokuang, J Northwestern Polytechnical Uni: **18** (2000) 669.

[32]. E.K. Storms, The Refractory Carbides, Academic Press, New York: (1967) 61.

[33]. J. Gurland, Trans Metall Soc AIME: **227** (1963) 1146.

[34]. E.A. Brandles, Smithels Metal Reference Book, 6th edn., Butterworths, Boston, (1983).

[35]. W.D. Schubert, A. Bock, B. Lux, Int J Refract Hard Met: **13** (1995) 281.

[36]. G.E. Spriggs, Int J Refract Hard Met: **13** (1995) 241.

[37]. W. B. Einssen, B. L. Ferguson, and R. M. Germas, Materials Park, OH **7** (1999).

[38]. K. Upadhyay, J. M. Yang, W. P. Hoffmann, J Am Ceram Soc Bull: **76** (1997) 51.

[39]. K. Balani, G. Gonzalez, A. Agarwal, R. Hickman, S. O. Dell, J Materials Science: **3** (2005) 241.

[40]. R. Hickman, T. McKechnie, A. Agarwal, AIAA: **37** (2001)3435.

[41]. T. Laha, K. Balani, A. Agarwal, S. Patil, S. Seal, Metall Mater Trans A: **36A** (2005) 301.

[42]. L. L. Shaw, D. Goberman, R. Ren, M. Gell, S. Jiang, Y. Wang, T. D. Xiao, P. R. Strutt, Surf Coat Technol: **130** (2000) 1.

[43]. A. Agarwal, T. Mc Kechnie, S. Straett, M. M. Opeka, Elevated Temperature Coatings: Science and Technology: **4** (2001)310.

[44]. T. Nguyentat, K. T. Dommer, K. T. Bowen: (1992) 321.

[45]. J. A. Nelson, M. J. Wagner, J Chem Mater: **14(10)** (2002) 1639.

[46]. J. Y. Chan, S. M. Kauzlarich, J Chem Mater: **9 (2)** (1997) 531.

[47]. A. M. Nartowski, I. P. Parkin, M. Mackenzieb, A. J. Cravenb, Material Chemistry: **11** (2001) 3116.

[48]. Y. J. Chen, J. B. Li, Q. M. Wei, H. Z. Zhai, J Crystal Growth: **224** (2001) 244.

[49]. D. H. Kwon, S. H. Hong, B. K. Kim, Materials Letters: **58** (2004) 3863.

[50]. Xiang, YongdongXu, Litong Zhang, Laifei Cheng, J Scripta Materialia: **55** (2006) 339.

[51]. M. Leib, Z.B. Sunb, L.Z. Caob, Y.F. Guob, X. Guob, W.H. Tang, J Alloys and Cmpds: **430** (2007) 237.

[52]. P.G. Li, M. Lei, W.H. Tang, J Materials Research Bulletin: **43** (2008) 3621.

[53]. DU Yinxiao, LEI Ming, YANG Hui, WANG Xuefei; Journal of Wuhan University of Technology-Mater. Sci. Ed.: **23(6)** (2008) 779.

[54]. V. G. Sevast’yanov, E. P. Simonenko, N. A. Ignatov, Yu. S. Ezhov, N. T. Kuznetsov; Inorganic Materials: **46(5)** (2010) 495.

[55]. L. Massot, P. Chamelot, P. Taxil, J Alloys and Cmpds: **471 (1-2)** (2009) 561.

[56]. L. Massot, P. Chamelot, P. Winterton, P. Taxil, J Alloys and Cmpds: **471** (2009) 561.

[57]. M. M. W. Shen, P. Zhang, J. Zhang, Q. Wang, Changchun, J Materials Letters: **65** (2011) 96.

[58]. J. Ma, Y. Du, M. Wu, M. Pan, J Materials Letters: (2007) 3658.

[59]. J. P. Kelly, O. A. Graeve, J Am Ceram Soc: **2(2)** (2011) 1.