

Synthesis and Characterization of Vanadium Carbide Nanoparticles

A

Thesis

Submitted in partial fulfilment of the
requirements for the award of degree of

DOCTOR OF PHILOSOPHY

By

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Dedicated to My Parents

CERTIFICATE

This is to certify that this thesis entitled “**Synthesis and Characterization of Vanadium Carbide Nanoparticles**” which is being submitted by **Ms. Mani Mahajan** in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in the School of Physics and Materials Science, Thapar University, Patiala, Punjab, India is an exclusive record of candidate’s own research work under our supervision. The thesis in part or in full has not been submitted in any other university or institute for the award of any degree. The thesis is fit to be considered for the award of degree of Doctor of Philosophy.



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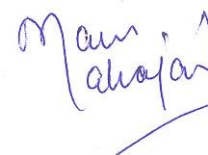
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- [4] **Mani Mahajan**, Gourav Singla, K. Singh, O.P. Pandey, “Synthesis of grape-like carbon nanospheres and their application as photocatalyst and electrocatalyst”. **J. Solid State Chem.**, 232 (2015) 108-117.
- [5] **Mani Mahajan**, K. Singh, O.P. Pandey, “Structural investigation of catalytically grown carbon nanotubes”. **Mater. Manuf. Processes**, 31 (2016), 989-994.
- [6] **Mani Mahajan**, Shalini Rajpoot, O.P. Pandey, “In-situ synthesis of chromium carbide (Cr_3C_2) nanopowders by chemical-reduction route”. **Int. J. Refract. Met. Hard Mater.**, 50 (2015) 113-119.

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Preface

Research on nanomaterials is a step towards miniaturization of technology that contributes significantly towards a sustainable usage of raw materials and energy. Properties of nanoparticles are different than bulk and often superior to their conventional polycrystalline form. The variation in properties is because of microstructure which is determined by the chemical composition, grain size, atomic structure and crystallographic orientation. Nanoparticles, due to their smaller size and large surface to volume ratio, exhibit interesting novel properties which include nonlinear optical behaviour, increased mechanical strength, enhanced diffusivity, high specific heat, magnetic behaviour and electric resistivity etc. Therefore, more emphasis is being given on the development of new processes for the synthesis of nano materials on large scale. It is well known fact that use of vanadium carbide in nano range enhances its mechanical, chemical and physical properties. Other than the conventional types, nano VC finds its applications as catalyst in many devices. Currently, synthesis of vanadium carbide is done at high temperatures ($> 1000\text{ }^{\circ}\text{C}$) and involves many intermediate steps. Therefore, there is a need to develop new synthesis routes to obtain the product at relatively lower temperature than the reported ones.

Literature review gives an idea on the work done on direct synthesis of nanocrystalline vanadium carbide from different precursors, which include the formation of mixed/impure phases also (VC and V_2C). Keeping in view these technological challenges, the present work is undertaken to synthesize pure nano vanadium carbide from V_2O_5 as precursor at relatively lower temperature by thermo-chemical/mechano-chemical route. The work reported here is innovative in nature to obtain pure phase (VC or V_8C_7) using these techniques. The techniques adopted for their synthesis are mild and of industrial importance as the processes developed are economical in nature. The as-synthesized vanadium carbide nano powders were mixed with WC and Co followed by consolidation and sintering at different temperatures. The control in the grain growth of WC-Co-VC composite has been observed during sintering. The variation in microstructure and hardness with variation in sintering temperature has been observed.

The present work deals with the synthesis and characterization of nano vanadium carbide(s) by thermo-chemical/mechano-chemical route. Also, suitability of the obtained vanadium

carbide has been checked in WC-Co cermets as grain growth inhibitor (GGI). The entire work of the thesis is divided into six chapters.

- In **Chapter 1**, the brief history and development of vanadium carbide, its different stoichiometric compositions (VC , V_8C_7 , V_6C_5 and V_2C), their crystal structures, properties and phase diagram is discussed. Different applications of vanadium carbide have been given. The role of VC in these applications has also been described. Different synthesis routes developed to get pure VC phase are given in brief.
- **Chapter 2** presents the detailed literature review on synthesis of different carbides of vanadium as VC, V_8C_7 and V_2C . The literature review indicated that only few reports on low temperature synthesis are available for the nano vanadium carbide that resulted in micron sized and/or mixed/impure phase formation. The reported methods require the reduction temperature in the range of 1000 to 1300 °C. After reviewing all segments of literature, need was felt to develop single-step synthesis route at lower temperature. Based on these gaps, the aims and objectives of the thesis work were decided.
- **Chapter 3** describes about the experimental procedures adopted in the present work. On the basis of literature survey, two routes were used for the synthesis of nano VC from vanadium pentoxide (V_2O_5) precursor at mild conditions. Synthesis of nano vanadium carbide was done via thermo-chemical (solvothermal) and mechano-chemical route at low temperature (600-800 °C) and room temperature, respectively. For thermo-chemical method, specially designed autoclave was used, while, mechano-chemical synthesis was carried out in a planetary ball mill (Retsch PM 100) at room temperature. The details of synthesis and characterization techniques are described in this chapter.
- **Chapter 4** deals with the results and discussion part of the present work. This chapter is divided into two sections; first one describes the results of thermo-chemical route. The second one describes the results of mechano-chemical route. In the first section, the details of systematic experiments conducted using V_2O_5 precursor with acetone for different time periods and at different temperatures are described. Reduction/carburization of V_2O_5 was done by using Mg as a reducing agent and acetone as carbon source in an autoclave. The raw materials were heated in autoclave

at different temperatures (600, 700 and 800 °C) and for different time intervals at the heating rate of 5 °C/min. The results showed that the reduction of V_2O_5 occurs into its lower oxides, followed by the carburization as shown in following path: $V_2O_5 \rightarrow VO_2 \rightarrow V_2O_3 \rightarrow V_8C_7 \rightarrow VC$. The synthesis of single phase V_8C_7 or VC depends on the experimental conditions employed viz. reaction time and temperature. Further experiments were carried out with the aim to synthesize single phase carbon-coated nano VC. The impurities in the as-obtained samples were removed by acid leaching in (1:1) HCl followed by its washing and then drying at 120 °C. After removal of impurities, single phase nano VC was obtained. The structural, thermal and microstructural analysis on as-obtained products was done using different characterization techniques.

- In the second section of the experiment, synthesis of nano vanadium carbide (VC) was done using mechano-chemical route at room temperature. In this section, the mixture of V_2O_5 , Mg and activated charcoal was milled in a planetary ball mill at room temperature. The reaction was carried out using tungsten carbide (WC) vial of 250 mL capacity and hardened tungsten carbide balls as milling media. The milling parameters such as rotation speed (rpm), milling time and the amount of reducing agent (Mg) were optimized in order to obtain single phase VC. The resultant as-milled powders were leached by dilute HCl (1:1) followed by its washing and then drying at 120 °C. The samples milled for 15 h reaction time showed complete transformation of V_2O_5 to VC. The as-milled powders were characterized using different techniques for its structural, microstructural and thermal analysis.
- **Chapter 5** deals with the discussion on the results related to the suitability of the obtained product as GGI used in WC-Co composite during sintering. The sintering behaviour of these composites at different temperatures (1250, 1350 and 1400 °C) in argon atmosphere is discussed in detail.
- In **chapter 6**, the entire work of the present study is summarized and concluded. The present work shows that single phase nano vanadium carbide(s) of different sizes can be synthesized from V_2O_5 directly by single-step method. Also, the reaction mechanism for the synthesis of vanadium carbide has been discussed in detail. The synthesized product acts as GGI in WC-Co composite, which enhances its mechanical properties.

CHAPTER 1

INTRODUCTION

Overview

This chapter presents a brief historical background of vanadium carbide. The details of its different forms (VC, V_4C_3 , V_8C_7), their crystal structures and properties has been presented. A brief idea about the V-C phase diagram and the existing phases has also been given. A comparison of bulk and nano vanadium carbide has been described. Further, the applications of nano vanadium carbide in WC-Co nanocomposite as grain growth inhibitor, hard protective coating and a catalyst are discussed.

1.1 Background

Among different transition metal carbides, vanadium carbide (VC) is well known for its unique physical and chemical properties [1-5]. It has significant industrial application as a hard refractory ceramic. It is known for its high hardness (2900 HV), high melting point (2810 °C) and high Young's modulus (434 GPa) [1-11]. Because of its unique properties, VC is extensively used in cutting tools, functional coatings, grain refiners, electronic components, sensing, catalysis, high-temperature structural materials, corrosion protection and binders [2-11]. Figure 1.1 shows the different applications of vanadium carbide in engineering and various other fields.

Vanadium carbide was first synthesized by Moissan in 1893 by heating the mixture of V_2O_5 with charcoal in an electric furnace [12, 13]. Further, Zhelankin et al. [14] in 1958 synthesized oxygen-free VC at 2300 °C and 133-200 Pa pressure (1–1.5 torr). Meerson and Krein [15] in 1960 studied the reduction of V_2O_3 with carbon to get oxygen free VC at around 1700-1800 °C in a CO atmosphere at 133-1333 Pa pressure (1–10 torr).

1.2 Structure and Phase Diagram

As shown in fig. 1.2, vanadium carbide exists in many forms viz. VC, V_2C , V_8C_7 , V_6C_5 and V_4C_3 . Among the different forms of vanadium carbides, V_6C_5 and V_8C_7 are most stable forms and are of great interest because of their high hardness. According to Rempel et al. [16] nonstoichiometric carbides MC_y ($0.5 - 0.7 < y < 1.0$) of group IV and V of transition metals are the second only hardest materials next to diamond and cubic boron nitride. These carbides contain 0-50% structural vacancies in their sublattice [16, 17]. Carbides of vanadium come under the category of non-stoichiometric (MC_y and M_2C_y) interstitial compounds where diffusion of carbon atoms is in the octahedral interstitial sites of the metallic lattice [18]. Interestingly, only a fraction of the interstitial sites are occupied by carbon atoms [18]. The ordering and disordering of the sublattice strongly depends on the distribution of carbon lattice and structural vacancies [16, 18]. At high temperatures (> 1227 °C), the carbon atoms and unfilled interstitial sites (structural vacancies $\square$) are distributed in the $MC_y\square_{1-y}$ carbide lattice and possess a cubic structure [16, 18]. By decreasing the temperature to 1227 °C, redistribution of non-metallic interstitial atoms and structural vacancies occur, which results in a disorder-order phase transition and form ordered structures [17-20].

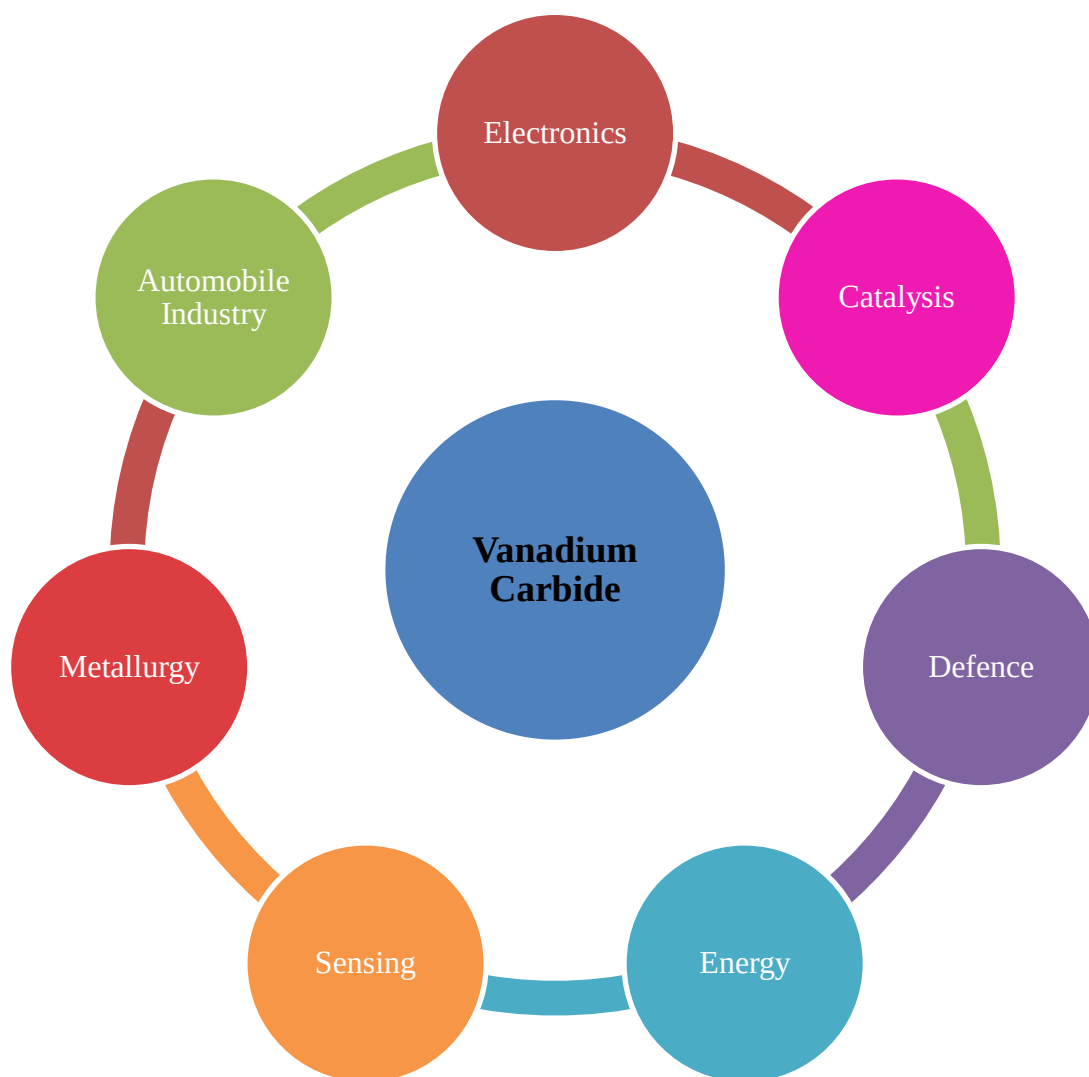


Figure 1.1: Applications of vanadium carbide in various fields.

In VC_y carbide, ordered V_8C_7 possess a cubic structure in the range of $VC_{0.86} - VC_{0.88}$ with the double lattice spacing than that of the disordered carbide with space group $P4_332$ (or $P4_132$) [18, 21, 22]. The other ordered phase V_6C_5 possesses trigonal or monoclinic structure with space group $P3_1$ or $C2$ or $C2/m$ in VC_y carbide in the range of $0.76 \leq y \leq 0.86$ [18, 23, 25]. Another carbide phase V_2C_y having rhombic structure forms as a result of the annealing with lowering the temperature from 1327-1527 °C [26, 27].

Other forms of vanadium carbide are VC and V_4C_3 having cubic crystal structure with space group $Fm3m$ [28]. In spite of different space groups and lattice parameters, the structure of VC, V_4C_3 and V_8C_7 is same if position of carbon atoms is neglected [29]. V_8C_7 crystal belongs to the space group $P4_332$ with the positions of vanadium atoms slightly off the ideal fcc positions having the ordered arrangement of carbon atoms on the interstitial sites [28, 29].

However, V_4C_3 has only one carbon vacancy per unit cell. The unit cell structures of these carbides are shown in fig. 1.3.

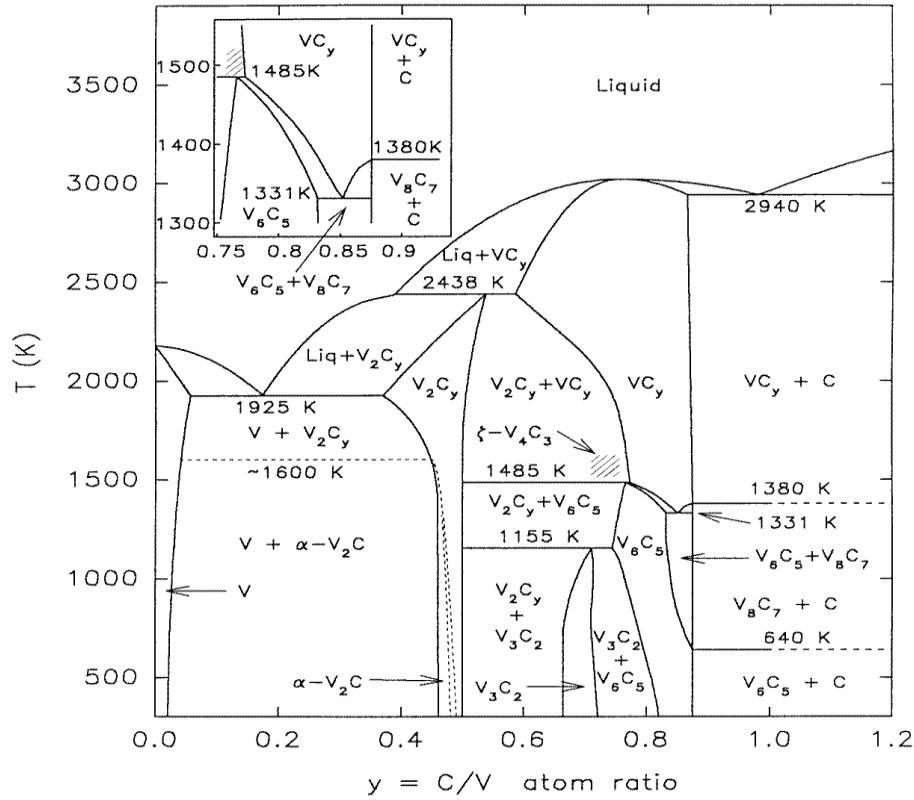


Figure 1.2: Phase diagram of V-C system [18].

VC is a metastable structure of NaCl type. Heat of formation and cohesive energy values of different forms of vanadium carbide (table 1.1) shows the feasibility of formation of non-stoichiometric carbides (V_8C_7 , V_4C_3) than stoichiometric (VC) [28]. More negative value of formation energy and cohesive energies indicate the favourable conditions for the formation of VC, V_4C_3 and V_8C_7 phases [28]. Therefore, V_8C_7 is more stable than VC and V_4C_3 . It may be because of the difference of the symmetry (VC, Fm3m and V_8C_7 , P4₃32) of these carbides. Moreover, pure VC is highly air-sensitive, therefore, it is more difficult to obtain VC than V_8C_7 .

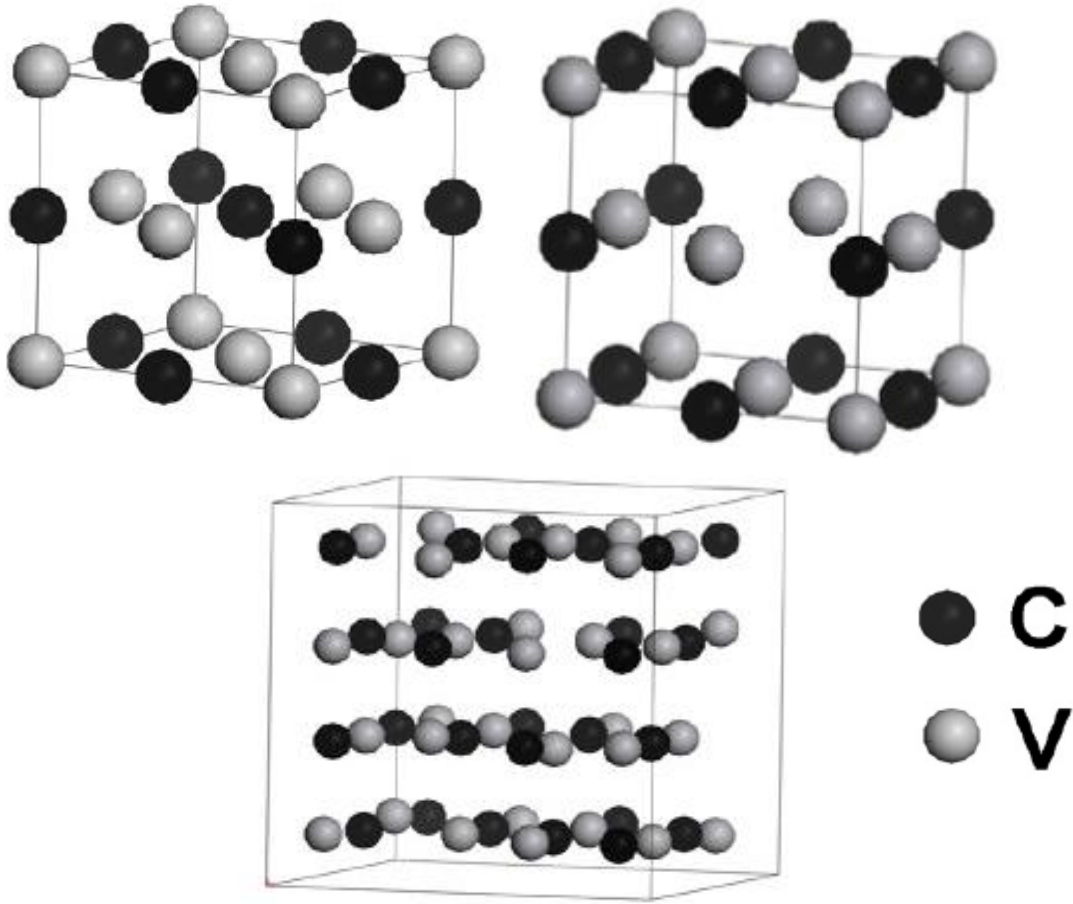


Figure 1.3: The unit cell structures of (a) VC (b) V_4C_3 and (c) V_8C_7 [28].

Table 1.1: Total energy (keV), formation energy ΔE_f (eV atom⁻¹) and cohesive energy E_{coh} (eV atom⁻¹) of VC, V_4C_3 and V_8C_7 phases [28].

Phases	Total Energy (keV)	ΔE_f (eV atom ⁻¹)	E_{coh} (eV atom ⁻¹)
VC	− 8.5	− 0.494	− 9.138
V_4C_3	− 8.4	− 0.413	− 8.988
V_8C_7	− 67.6	− 0.607	− 9.219

1.3 Nanostructured Vanadium Carbide

Nanotechnology is a multidisciplinary science as it covers a broad area of expertise in materials science, chemistry, biomedicine, electrical/mechanical/chemical engineering and energy science [30]. The development of new materials with smaller yet, stronger having designer properties and well-defined morphology is the key factor of nanotechnology [30-33]. Today, nanophase engineering is rapidly growing field, both in inorganic and organic materials in order to manipulate their mechanical, biomedical, catalytic, electric, magnetic, optical and electronic properties [30, 33-37]. The factors which differentiate the nanomaterials from bulk materials are the high relative surface area and quantum effects which are responsible for the enhancement of the properties of nanomaterials [30]. So, tailoring materials in the nanorange open up the new ways to study a material.

The strength or mechanical properties of the cutting tools materials strongly depend upon the grain size. It is associated with the microstructure as explained by Hall-Patch (H-P) relationship [38]. Strength of materials increases by decreasing the mean grain size between 100-20 nm. Below 20 nm, yield strength decreases with decreasing grain size, exhibiting softening behaviour. This is known as H-P breakdown where transition in deformation modes of metals occurs with the decrease in the grain size from nanocrystalline range to very low level [38]. With the reduction of the grain size in nanomaterials over conventional materials, fatigue life of the material is increased [39]. Nano grained cutting tools made of nanocrystalline materials of tungsten carbide, vanadium carbide, tantalum carbide and titanium carbide, are much harder, much more wear-resistant, erosion-resistant and last longer than their conventional (large-grained) counterparts. Because of their good mechanical properties, nanocrystalline carbides are currently used in microdrills (drill bits having a diameter less than the thickness of an average human hair or 100 μm) [39].

Because of the large grain boundaries relative to their grain size of the nanocrystalline materials, they are very active in terms of their chemical and physical properties. Therefore, these materials are also used as catalysts in automobile catalytic converters and power generation equipment in order to prevent environmental pollution arising from burning fuel [39].

1.4 Applications of Vanadium Carbide Nanopowder

The applications of the vanadium carbide nanopowders for the industrial and commercial purposes are increasing day-by-day. These applications include, but are not limited to, the following:

1.4.1 Grain growth inhibitor

In the WC-Co nanocomposites, fine grained structure of the composite with homogeneous distribution of grains is preferred. But due to abnormal grain growth (AGG), the presence of some larger grains than the average is undesirable. In the liquid-phase sintering (LPS), AGG is observed where the grain structure is angular or faceted [40, 41]. AGG leads to the formation of heterogeneous microstructure where few grains grow faster than the rest. High local rates of interface migration and localized formation of liquid at grain boundaries plays an important role in the AGG phenomenon [42, 43].

To avoid this AGG, VC as grain growth inhibitor (GGI) is added in WC-Co nanocomposite. WC crystals have triangular prism shape with truncated corners [40]. Adding VC as GGI in WC-Co, triangular prism shape of WC crystals without truncation was obtained [40, 44]. It was observed that the VC controls the coarsening process by increasing the edge energy for 2-D nucleation, which in turn increases the energy barrier [40, 44]. Therefore, with the addition of VC in WC-Co composite, AGG is inhibited and grains of fine and uniform matrix was obtained [44]. Moreover, when nano VC is added to the WC-Co nanocomposite, it exhibits high solubility and diffusivity in cobalt matrix because of its high surface reactivity [45, 46]. It leads to the suppression of solution reprecipitation of the WC-Co composite and preventing the coarsening of grains, which is the sole factor responsible for the grain growth.

1.4.2. Hard protective coated material

With the advancement of the manufacturing industries, sustainable processes and new materials have gained importance. Contrary to this, it is difficult to control the destructive process of corrosion of the new materials also. Much work has been done to control or slow down the rusting process. Mechanical tools, hard steel alloys, defence tools, metal wires and sheets have been the target of corrodant species and whenever conducive atmosphere exists, rusting initiates [47]. Department of defence has a long history against corrosion and according to the survey, more than \$20 billion per year have been spent by United States military in corrosion-related expenses [47]. In order to improve the corrosion resistance and

to increase its life span of forming dies and machining tools, corrosion inhibitors in the form of hard coatings have been used in the materials [48, 49].

Thermo-reactive diffusion (TRD) is the most widely used method for coating and is extensively used in industries including sheet metal, cold forging, aluminium and magnesium die casting, forming stainless steel, high strength alloys, galvanized steels [50]. In the TRD process, material is coated with hard and dense carbide materials. It is easily bonded to the substrate surface and provides wear-resistant property [50-52]. The capacity of a material to withstand high loads depends on the hardness and thickness of the coated material [53]. Vanadium carbide coatings have a thickness of 5-7 μm with a hardness of 3500-3800 HV. Because of the high hardness with sufficient ductility and superior tribological properties of nano VC, an extremely fine grain dispersion of thin film coatings could be achieved [54-56]. It is also observed that the VC coatings show some extra distinguishing properties in cutting tool applications than other carbides [55, 57]. Vanadium carbide layer is diffused onto the surface of the material being coated, creates an incredible bond which is much stronger than any other deposited coating that results in a longer tool life. Single coating of VC that has high hardness of ~ 3059 HV can resolve many tooling problems. It is reported by Ferro et al. [57] that high hardness of ~ 2549 HV was achieved by cubic VC coating deposited by electron beam from a carbide target. During the coating of vanadium carbide at higher temperatures, carbon migrates from tetrahedral to stable octahedral interstitial sites and results to lower the accessibility of reactive carbon in tetrahedral positions. Hence, decreases the transport of corrosive species and enhance the corrosion prevention [55, 58].

By using the coating material in the nanorange, a sufficient enhancement in the hardness of the material is also achieved in which carbide phase is precipitated along the grain boundaries of the material being coated [48]. However, the formation of carbide phase between the grain boundaries is very likely considered as a high risk of intergranular corrosion attack on stainless steel [48]. With the reduction of the particle size to nanorange, the risk of such attack is minimized which increases the corrosion resistance of the material [48].

1.4.3 Catalysis

Apart from mechanical properties, the recent applications of VC in electro-catalysis have also been observed by many researchers. Recently, Pt/Pd-based electrocatalysts in fuel cell applications have been paid much attention because of its higher activity in alkaline media [10, 59-61]. But because of the slow kinetics of oxygen reduction reaction (ORR), the output

voltage of fuel cells is limited [10]. Therefore, to improve the electrocatalytic properties of cathode electrocatalyst, there is a need to develop platinum alloys with other metals as Pd, Au, Co or to develop a new material which supports Pt to generate synergistic effect [10, 62]. The basic approach to choose the material for electrochemical applications is that the catalyst should not only be electrically conductive and resistant to corrosion in the extreme electrochemical environment but also should have low cost, high stability and small size [60, 63, 64]. In catalysis, assisting or retarding the reaction rate depend on the surface reactivity of the catalyst material used which facilitate the gas transport and provide good electronic conductance. Because of the corrosion resistance, high conductivity and high surface reactivity of VC nanopowder, it exhibits catalytic properties in electrochemical applications [10, 60, 61, 64]. Moreover, the electronic structure of VC is similar to the noble metals like Pt, Pd and Au etc., and therefore, has the potential to replace, or to support these metals [8, 65]. Among the transition metal carbides of group V, the stability order of catalytic activity is Vanadium > Niobium > Tantalum [11]. Therefore, extensive work is going on to use the metal carbides for as an electrode material for low temperature fuel cells and in energy devices for significant performance.

1.5 Synthesis of Vanadium Carbide Nanopowder

Synthesis of vanadium carbide nanopowder generally involves high temperature processes. From last few decades, there has been much interest in the synthesis routes of the inorganic solids, which generate product at relatively lower temperature. Here, we have adopted a different but most useful technique to synthesize nano vanadium carbide which is described in subsequent chapters. Additionally, the as-synthesized powder is characterized using various techniques to check the applicability in different applications.

The details of the synthesis methods alongwith work done till date is given in the next chapter of this thesis (Literature review).

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CHAPTER 2

LITERATURE REVIEW

Overview

In this chapter, the earlier reports on the synthesis of nano vanadium carbide and its properties have been reviewed. The literature review is divided into two parts; the first part deals with the recent advances in the synthesis routes for the formation of vanadium carbide nanopowder (VC/V₈C₇). The second part deals with the effect of addition of VC during sintering and consolidation of WC-Co nanopowder at high temperatures. Literature review includes all efforts and challenges for the synthesis of single phase vanadium carbide nanopowder. Apart from this, the control over the grain size of WC-Co nanopowder which is a technological challenge, has been reviewed thoroughly. On the basis of literature survey, the basic objectives of the present work has been formulated and given at the end of the chapter.

In this chapter, complete literature work pertaining to synthesis and application of nano vanadium carbide is presented.

2.1 Synthesis of Vanadium Carbide Nanopowder

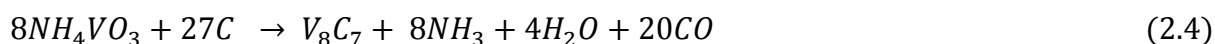
According to the literature, vanadium carbide (VC) was synthesized by heating the mixture of V_2O_5 with charcoal in an electric arc furnace in 1893 [1, 2]. Since then, various efforts have been made to search the new synthesis routes of the vanadium carbide. Further, in 1958 and 1960, oxygen free vanadium carbide (VC) was produced by reduction of V_2O_3 with carbon at the temperature range of 1700-2300 °C [3, 4]. However, the particle size and temperature was too high. Therefore, in order to reduce the particle size to nano scale, different procedures have been adopted for synthesis of VC. This includes direct current (DC) arc plasma method, temperature-programmed reaction, mechanical milling and thermo-chemical method. The details of these synthesis methods are given below:

2.2 Conventional Synthesis Processes of Vanadium Carbide

2.2.1 Direct carburization reactions

Synthesis of vanadium carbide (VC/ V_8C_7) by direct carburization is expensive and high temperature process. Conventionally, vanadium carbide is synthesized by various high temperature reactions, including reduction of vanadium hydride with carbon at low pressure and high temperature (2000 °C), direct elemental reaction of vanadium (V) and carbon at the temperature of 1000-1500 °C in protective atmosphere or in vacuum [5-7]. Moreover, for the reactions with carbon, different vanadium precursors are also used such as ammonium vanadate and oxides of vanadium [8-11]. This technique is exceptionally known for producing pure compounds. But the high temperature or high vacuum conditions or highly purified gas atmosphere are the main requirements of these processes. Moreover, particle size obtained in these processes is in the range of few micrometers because of the agglomeration at high temperatures. These reactions are time consuming, multi-steps and expensive. Also, the powder obtained by this method cannot be used in industries for potential applications because of mixed and agglomerated carbides [11]. The reactions involving the synthesis of vanadium carbide by direct carburization are given below:





2.3 Progressive upgradation of Synthesis Processes

Because of the various shortcomings in the conventional synthesis routes of vanadium carbide, progress in the processes has been made by adopting different techniques. The advancement in the synthesis process along with the modifications to get the better product has taken place. A brief review of these processes is discussed below:

2.3.1 DC thermal plasma method

The use of DC thermal plasma for the synthesis of nano refractory carbides is one of the promising routes. In this synthesis route, various types of plasma generators such as DC arc, radio frequency (RF) and super high frequency (SHF) plasmas are used to generate plasma jet at the input power of upto 20 kW. Earlier, metal carbides were synthesized by the arc plasma reaction of metal halides with hydrocarbons and nitrogen [12, 13]. But the need of secondary heat treatment for the removal of by-products is the major disadvantage of this method. In 1981, this method was modified by using pure metal or metal oxide precursor, which leads to the direct conversion to metal carbides in the presence of methane [14]. In this method, metal oxide precursor along with methane as carrier gas was transported by nitrogen and injected into plasma jet confined by water-cooled reactor walls [15]. The experimental set up for the synthesis of nano carbides is shown in fig. 2.1. The process of evaporation, reaction and condensation occurs due to the high temperature of the plasma flow which results to form nanopowder clusters.

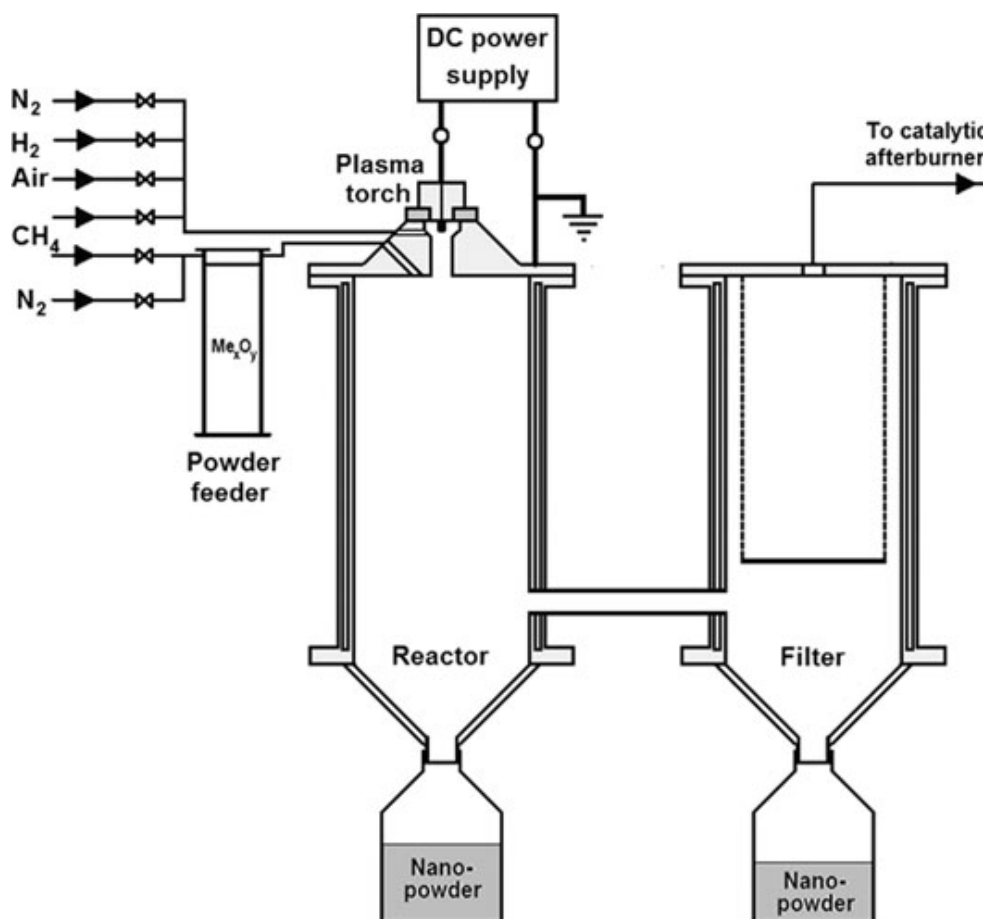


Figure 2.1: Plasma setup for carbide nanopowders synthesis [15].

2.3.2 Temperature-programmed reactions

Volpe and Boudart [16] proposed a new method for the synthesis of high surface area metal carbides by temperature-programmed reactions (TPR). In this method, metal oxides were heated in the presence of hydrocarbon under the flow of reactant gases as CH₄/H₂ or C₂H₆/H₂ with uniform increase in the temperature. An optimal balance between synthesis and sintering rates could be obtained by TPR method which helps to study the kinetics of the reaction products. After the reaction takes place, the prepared samples were quenched to room temperature under argon flow.

This method was further used by Oyama and his group [17] for the synthesis of VC having high surface area. In this method, the heating of vanadium precursor was done in the reactor in the presence of reactant gas mixture (CH₄/H₂) as per the temperature program. In such type of programmed controlled heating process, the mixture is heated initially upto a level where the initiation of solid-state transformation occurs. Due to the disruption of metal-oxygen bond, this method has been proved to be superior to the conventional isothermal method. The

space velocity of the synthesis gas is varied to obtain high surface area product which is highly favourable for the use in catalytic applications. This method proceeds in two steps: first V_2O_5 is reduced to V_2O_3 and then transformed to VC at around 1100 °C. The reduction in first step is highly exothermic leading to substantial rise in temperature in the reactor. The experimental set up used in this method is shown in fig. 2.2.

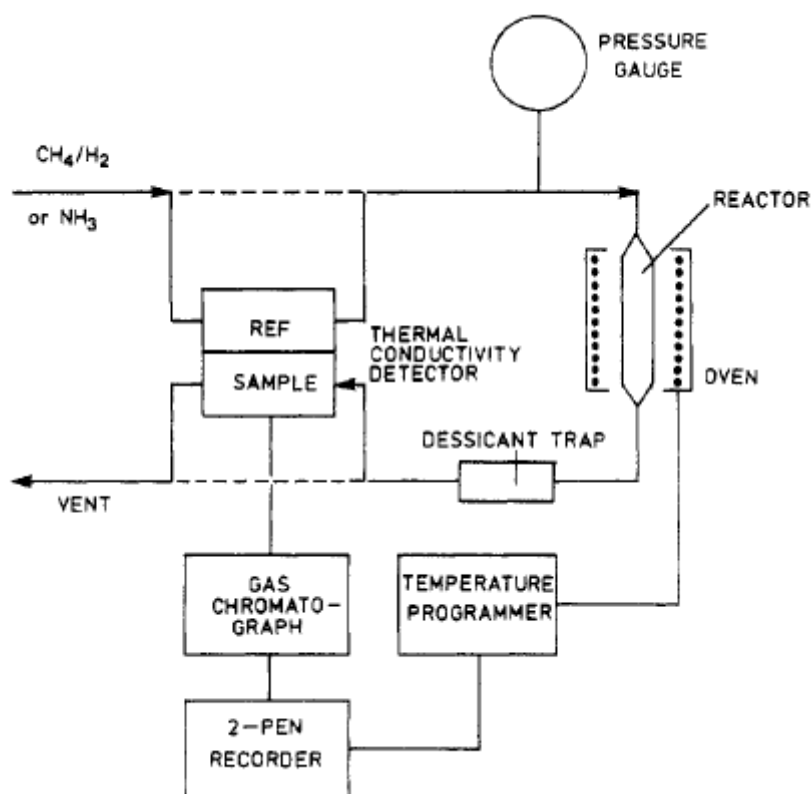


Figure 2.2: Schematic diagram of the VC synthesis process [17].

2.3.3 Mechano-chemical synthesis

Another process for the synthesis of vanadium carbide nanopowder is mechano-chemical route. It is a simple and facile route for the synthesis of various inorganic compounds, nanocrystalline materials and particle reinforced composites [18-23]. Although, it is the simple procedure but hard to establish a common mechanism for the reaction products because ball milling involves number of parameters viz. rotation per minute (rpm), reaction time, ball-to-powder ratio, ball diameter and type of mill used [22, 23]. In ball milling process, milled material gain kinetic energy from the moving balls and produce fresh surfaces by breaking the chemical bonds and fracturing the material [21, 24]. Thus, dangling bonds created on these surfaces are highly reactive which undergo further reactions [24]. Also, the

high amount of local pressure and temperature generated during these collision processes in the ball mill leads to the particles diffusion and hence formation of new phases without any external heat treatment [24-26]. Reports have shown the impact of high energy collision during milling can create a local high temperature and pressure of about 1000 °C and several GPa, respectively for short periods [18, 27]. As a result, chemical reactions, which occurs at high temperature can take place at room temperature in ball mill without any further heating [26]. Multiple collisions among powder, balls and vial walls of the grinding media significantly improve the structural properties of the nanocrystalline materials and also reduce the grain size [28].

In general, mechano-chemical synthesis of vanadium carbide nanopowder involves the reaction between elemental vanadium and graphite/active carbon powder followed by the subsequent heat treatment [23, 29]. Further modifications in the milling process have also been done by using reducing agent for the reduction of oxide precursor (V_2O_5) to enhance the reaction rate [30].

2.3.4 Thermo-chemical route

In general, the thermo-chemical process for the synthesis of nano particles is used to refine the nanostructure. Apart from this, control over the size, shape and compositions of product is achieved by this process. Hence, after looking its advantageous effect on the synthesis of nano particles, this route has been adopted for the production of homogeneous vanadium carbide powder. For the synthesis of vanadium carbide, the solution of reactants at specific conditions with heating at lower temperature is prepared [10]. This is done by adding reducing agent along with reactants in the presence of organic solvent in a closed vessel called autoclave. This method is also known as solvothermal method or reduction/carburization method. In this method, reduction and carburization of the vanadium precursor occurs simultaneously at relatively lower temperature than the conventional one because of the mixing of reactants at molecular level [31, 32]. One of the major advantages of this method is that the pressure inside the vessel increases drastically with the small increase in the temperature. The autogenous pressure of gases generated by the pyrolysis of liquid carbon source at lower temperature in autoclave helps to enhance the reaction rate, which shortens the diffusion distance and hence time. Moreover, the resultant product obtained by this method has high purity and small size.

Typically, synthesis of vanadium carbide nanopowder by solvothermal method involves the reaction between vanadium precursor (V_2O_5/VCl_4), carbon source and a reducing agent in a closed sealed vessel, heated at different temperature range (500-800 °C) [32-36]. The general reaction process during synthesis can be represented as below:



Details of work done for synthesis of vanadium carbide(s) using above mentioned techniques are described below:

Mitrofanov et al. [14] used DC arc plasma method for the preparation of vanadium carbide by reacting CH_4 with pure vanadium metal/metal oxide (V_2O_5) under argon flow. Samokhin et al. [15] modified the DC plasma method using air-methane and nitrogen-hydrogen gas mixtures as plasma-forming gas during the synthesis of vanadium carbide nanopowder. The effect of reaction parameters on the particle size, crystallographic phase compositions and morphology was investigated by the authors. The product obtained in this process was of high surface area and has particle size in the range of 40-80 nm.

Oyama et al. [17] synthesized VC nanoparticles of particle size, 100-200 nm using TPR technique. In this method, V_2O_5 as raw material was heated at 1080 °C in the presence of CH_4/H_2 gas mixture. They have concluded that the synthesis of high surface area material is affected by non-uniform temperature in the reactor and variant speed of the synthesis gas in the chamber. Kapoor and Oyama [37] considered these variations and modified the technique for the synthesis of high surface area VC nanopowder (17 nm). This is two step synthesis process, where in first step, V_2O_5 is reduced to V_2O_3 by hydrogen at 527 °C followed by the complete carburization of V_2O_3 in the presence of methane at 1047 °C. Choi et al. [38] have optimized the reaction conditions for synthesis of vanadium carbide by the same technique and obtained V_8C_7 at 1050 °C. They have also investigated the effect of heating rate and space velocity of synthesis gas mixture on structural properties viz. surface area and particle size. Authors have further evaluated the catalytic activity of obtained V_8C_7 for the ammonia decomposition. Kwon et al. [39] have also prepared and evaluated the catalytic properties of V_8C_7 for dehydrogenation of n-Butane prepared by TPR at 910 °C. They have also followed the high temperature H_2 post-treatment to remove the bound oxygen on synthesized V_8C_7 which results to lower its surface area and carbon content. Claridge et al. [40] modified the TPR process by substituting C_2H_6/H_2 instead of CH_4/H_2 in the gas mixture during TPR reaction. They have observed the lower carbide formation temperature of 750 °C with high

surface area by using C_2H_6/H_2 mixture rather than CH_4/H_2 . Pinto et al. [41] have prepared V_8C_7 by same process after mixing VCl_3 -3THF in acetic acid. They have heated the mixture at 800 °C in the presence of LPG/ H_2 as carburizing agent passed with space velocity of 6000 h^{-1} in the reactor.

Matteazzi and Caer [42] explored a new method for the synthesis of VC/ VC_x powder by mechano-chemical method at room-temperature. The starting powder in this case was the elemental powder of vanadium and graphite. The synthesis was carried out in WC vial and hardened steel balls as milling media. Milling was performed for 24 h in the nitrogen atmosphere. The particle size obtained in this process was of the order of 20 nm. Calka et al. [20] studied the effect of milling conditions on the formation of vanadium carbide (VC) nanostructures in planetary ball mill. The raw materials used in this study were vanadium and graphite powders. It has been found that using high energy milling, single phase (VC or V_2C) can be obtained in 70 h. However, in medium energy milling, no transformation of raw material into VC or V_2C even after the milling time of 1000 h could be obtained. The main drawback of mechanical alloying is long milling time required to refine the powder, microstructure and to form compound phases. Meunier et al. [43] have prepared V_8C_7 by post heat treatment of mechanical mixture of V_2O_5 and activated carbon. In this method, the formation of V_8C_7 takes place by successively reduction of V_2O_5 in lower oxide by following the reaction path ($V_2O_5 \rightarrow VO_2 \rightarrow V_2O_3 \rightarrow VO_{0.9} \rightarrow V_2C \rightarrow V_8C_7$) with the emission of CO at higher temperature (1290 °C). The average particle size of the obtained powder after complete reduction/carburization was found to be about 65 nm. Zhang and Li [29] modified the route by adding Mg as reducing agent to enhance the reaction rate. They have ball milled the V_2O_5 , Mg and graphite powders at room temperature at the rotation speed of 300 rpm with high purity argon. The results indicated that the reaction in a ball mill is a self-sustained process in which complete transformation from reactants to products (VC_x) takes place in 36 h. Further, the as-milled product (VC_x) was transformed to V_8C_7 , when annealed at 950 °C. Dai et al. [44] explored the synthesis of ultrafine vanadium carbide (VC) by dielectric barrier discharge plasma (DBDP) assisted milling. In this method, a mixture of V_2O_5 -graphite powder was milled in DBDP followed by their carburization at 1200 °C. The powder mixture milled in DBDP milling was highly activated and hence contains more effective sites for the nucleation and formation of VC nanoparticles. The powder obtained in this process has particle size of 50-200 nm. Hossein et al. [30] synthesized nanocrystalline vanadium carbide (V_8C_7) in planetary ball mill using V_2O_5 , Ca and C as the reacting materials. Studies showed

that V_8C_7 phase was obtained by milling for 15 h followed by subsequently microwave heating at 800 °C. Hassanzadeh et al. [45] obtained mixed phase of VC and V_2C nanopowders by mechano-chemical combustion method at 600 rpm under high purity argon gas. The raw materials used were V_2O_5 , Mg and active carbon. It was found that with the milling of 80 min, the transformation of reactant into VC and V_2C occurs without further heat treatment. This transformation is attributed to the mechanically induced self-sustaining reaction.

Artur et al. [46, 47] have prepared V_8C_7 nano powder via rapid, solid-state metathesis (SSM) route by heating the different vanadium precursors ($VCl_3/V_2O_3/NaVO_3$) with different carbiding reagents ($CaC_2/Al_4C_3/SrC_2$) at temperature upto 1000 °C. They have found that CaC_2 offers a fast, convenient carbide product at relatively low temperature with shorter reaction time. Apart from these, VC nanopowders were also produced by same technique using different organic reagents melamine and cyanamide as carbon source with V_2O_5 [48, 49]. These organic reagents have proved highly efficient carburization source to obtain nano powder in the range of 5-12 nm at 1200 °C.

Gusev and his co-workers [50-52] have reported the synthesis of nonstoichiometric vanadium carbide, VC_y ($0.66 < y < 0.88$) nanopowder in their different reports. They have followed different synthesis routes viz. carbothermal reduction and hot pressing method by using V_2O_5 and V, respectively as a vanadium source. The authors have discussed the effect of non-stoichiometry as well as structural vacancy on the heat capacity, particle size and microstructure of the synthesized VC_y carbide. Moreover, Gusev and his co-workers [53-55] have also discussed the microstrain anisotropy and homogeneity interval of non-stoichiometric vanadium carbide $VC_{0.875}$ powders.

Preiss et al. [31] have proposed a new method for the synthesis of V_8C_7 by making solutions of tartaric acid and V_2O_5 . In this method, the prepared solutions leads to the formation of porous composite of reactive carbon and V_2O_3 , which finally convert into VC at 1500 °C under the flow of argon. Lianwu et al. [10] have obtained V_8C_7 powder by heating the organically prepared mixture of V_2O_5 and carbon at temperature 700-1300 °C. They have obtained the orderly arranged V_8C_7 phase at 1100 °C. The particle size of obtained product was in the range of 100-200 nm. However, Zhao et al. [56] have also prepared V_8C_7 nano powder by thermal processing of ingredient mixture at 1100 °C. They have used ammonium vanadate (NH_4VO_3) and carbon black as starting materials. The obtained product consists of

uniform size particles with the diameter of about 50-100 nm. The effect of carbon content on the synthesis of V_8C_7 by same method has also been discussed [57]. Results showed that single phase diffraction peaks of V_8C_7 nanopowder (~ 200 nm) have been obtained with carbon content of 36 wt% at 1100 °C. Synthesis temperature of V_8C_7 was lowered to 1000 °C using glucose ($C_6H_{12}O_6$) and urea alongwith NH_4VO_3 [58]. It was observed that glucose and urea have lowered the reaction temperature by decomposing easily, which helps in formation of single phase V_8C_7 powders with the particle size of ~ 200 nm. Synthesis of V_8C_7 nano powder at lower temperature by same method has been reported by Zhao et al. [59] using different additives (CaF_2 , $CeCl_3 \cdot 7H_2O$ and $LaCl_3 \cdot 7H_2O$). The results showed that additives, especially CaF_2 enhances the solid state reaction rate during synthesis of V_8C_7 (particle size, 50 nm), which lowers the reaction temperature to 950 °C. Moreover, Ye et al. [9] have also studied the effect of CaF_2 addition on the synthesis of single phase V_8C_7 (40 nm) at 950 °C by using same route and base materials. Single phase VC nanoparticles (20-50 nm) are also synthesized by thermal refluxing-derived precursors using n-dodecane and hydrous V_2O_5 as starting materials at ~ 1200 °C [60]. Lin et al. [11] explored novel precursor, vanadium oxyoxalate (VOC_2O_4)/sucrose for the preparation of V_8C_7 nanopowders at the reaction temperature of 900 °C. The particle size of obtained powder by using this new vanadium source precursor is in the range of 30-50 nm.

Venugopalan and Sathiyamoorthy [33] investigated novel method for the preparation of vanadium carbide nano powder via aluminothermic reduction method. They heated the mixture of V_2O_5 , Al and C in the cylindrical vessel at high temperature. The authors have studied the effect of interacting reactants and their significance on the final yield of vanadium carbide powder. Li et al. [34] synthesized nanocrystalline VC by chemical co-reduction route using VCl_4 , CCl_4 and Na as vanadium, carbon and reductant sources, respectively. The reaction was carried out in an autoclave at the temperature of 500 °C for 12 h. The results showed that the particles of VC nanopowder were 10-40 nm in size. Ma et al. [35] have also followed the same route for the synthesis of nanocrystalline VC using different reactants. In this route, reaction of V_2O_5 and magnesium carbonate was carried out in an autoclave at 650 °C. The obtained product was cubic VC (particle size, 60 nm), showing good thermal stability upto 350 °C. Flower-like V_8C_7 hierarchical nanocrystals are prepared by Ma et al. [61] by hydrothermal method using a mixture of V_2O_5 and diethanolamine ($HN(C_2H_4OH)_2$ DEA). The resulting single-crystalline V_8C_7 phase has the morphology of flower-like and consists of thin sheets with the average thickness of 10 nm. Chen et al. [32] have opted citric acid

($C_6H_8O_7$) and potassium acetate (CH_3COOK) as carbon sources and Mg powder with V_2O_5 for the preparation of VC nano powder at 650 °C and 500 °C, respectively, in an autoclave. The particle size of obtained powder by this reaction was in the range of 50-80 nm. Wang and his group [36, 62] synthesised VC and V_2C nanoparticles in a stainless steel autoclave at 600 °C using different carbon sources and reducing agents with V_2O_5 precursor. Hu et al. [63] synthesized vanadium carbide of size 5-15 nm dispersed on carbon matrix (VC@C) at 1000 °C by hydrothermal method in the presence of nitrogen. The authors have also studied the electrocatalytic property of synthesized product for oxygen reduction reaction (ORR). They have observed 2.4 times better activity of Pt/VC@C as compared to that of Pt/C electrocatalyst. Zhang et al. [64] introduced multistep synthesis process of core-shell nano composite of vanadium carbide encapsulated into carbon nanotubes (VC@C). The authors have prepared $V_3O_7.H_2O@C$ nanobelts in autoclave by using glucose solution which was heated at 700-1000 °C in argon gas to get VC@C.

The other aspects of the synthesis for VC nano powder have been highlighted by many groups. They have followed multi-steps route and high temperatures. Li et al. [65] have synthesized vanadium carbide nanofibres via templated reactions on carbon nanotubes. They have used vanadium metal and multi-walled carbon nanotubes (MWCNTs) as carbon source in the reaction media of LiCl-KCl-KF at temperature of 950 °C. The final product formed in this work has similar morphology and length as that of MWCNTs having diameter 40-90 nm. Yan and his group have followed an ion exchange route for the preparation of vanadium carbide on carbon (C- VC_x) [66], on graphitized resin (GC- V_8C_7) [67] and on carbon matrix (C- V_8C_7) [68] in nitrogen atmosphere. The particle size of obtained materials is in the range of 2-4 nm. The authors have found better methanol oxidation property of Pt/C- VC_x and Pt/C- V_8C_7 than commercial Pt/C electrocatalyst [66, 68]. Moreover, same group have also showed the improved catalytic performance for ethanol oxidation of the synthesized Pd/GC- V_8C_7 than Pd supported carbon (Pd/C) [67]. Naguib et al. [69] have synthesized V_2C by selective etching of V_2AlC , at room temperature. The authors have also revealed that synthesized material shows better capability to handle high charge-discharge rates in Li-ion batteries. Li et al. [70] have synthesized mesoporous vanadium carbide incorporated on resorcinol-formaldehyde resin carbon ($V_8C_7@RFC$) by pyrolysis method at 900 °C in argon atmosphere. The results showed that Pt supported synthesized $V_8C_7@RFC$ (Pt/ $V_8C_7@RFC$) exhibited better activity with more negative oxidation potential for methanol oxidation reactions

(MOR) than pure Pt/RFC. Moreover, this catalyst shows higher stability as compared to conventional catalyst (Pt/C).

2.4 Application of VC in Sintering Process

WC-Co cermets are made by high temperature sintering of WC and Co powder, where Co acts as binder. During sintering, porosity decreases and density of product phase increases [71]. Moreover, it is observed that high temperature sintering may also lead to abnormal grain growth (AGG) of WC-Co composite [72]. The sintering process initiate the WC particles growth through solution re-precipitation process and metal binder becomes liquid during actual sintering process called liquid-phase sintering (LPS) [73]. The rapid grain growth occurs in WC-Co composite as a result of coalescence of grains during sintering via elimination of common grain boundary [71-74]. For high performance of cermet as cutting tool, this AGG has to be checked. Efforts made in this direction are described below:

2.5 Methods to Control Grain Growth

2.5.1 Sintering techniques

The control over the grain growth in the composite during sintering and the production of nanocrystalline WC-Co is a technological challenge for the material scientists as the average grain size has critical effect on the mechanical properties of the composite [73, 74]. Therefore, much research efforts have been made to optimize the conditions for obtaining high density sintered material with lower grain size. In order to control the grain growth, sintering techniques as pressure assisted sintering and field assisted sintering technique (FAST) have been used [73]. In pressure assisted sintering technique, nanorange grain size after sintering can be achieved by ultrahigh pressure processes in hot isostatic pressing (HIP) using ultrahigh pressure cells with different methods [73, 75]. It has been reported in the studies that finest grain size of about 100-200 nm is achieved, even after the sintering of the material under high pressure [73]. While, in FAST, pulsed electric current (PEC) also called Spark plasma sintering (SPS), generate very rapid heating and short processing cycles, because of which granular growth is suppressed [73]. As a result of SPS, materials with unique properties and size of submicron or in nanoscale are obtained. It has been reported by many authors that by using fast sintering techniques, grain size of the material comes out to be 50-800 nm [73, 76, 77].

2.5.2 Addition of dopants

Another approach to control the grain growth is the addition of various dopants/hard carbides like vanadium carbide (VC), chromium carbide (Cr_3C_2), titanium carbide (TiC), tantalum carbide (TaC) and niobium carbide (NbC) as grain growth inhibitors (GGI) in the WC-Co cermets during sintering [73, 78]. The first coating on the WC-Co was of the titanium carbide of $\sim 5 \mu\text{m}$ thickness which improves the life span of the material by 2 to 5 times. This was further improved by doping of the different hard metals by which the life time was further improved by 5-10 times. However, the overall effectiveness order of the inhibitors is $\text{VC} > \text{Cr}_3\text{C}_2 > \text{NbC} > \text{TaC} > \text{TiC} > \text{Zr/HfC}$ [73]. Among all dopants, VC is the most commonly used GGI in the cemented carbide industry because of their high solubility in Co phase at lower temperatures [72, 73, 78-80]. Due to the higher solubility of VC (8.19 wt%) in Co matrix, the amount of VC in WC-Co composite should be kept at 0.7 wt%. The higher amount of VC causes the precipitation of (V, W)C phase at the interface of the composite which results in increasing the embrittlement [81, 82]. Also, the combination of VC with one of the other GGI gives the best results to control the grain growth [73, 80, 83]. Moreover, with the reduction of the particle size from $30 \mu\text{m}$ to 10 nm, the sintering temperature also reduces as observed by Maheshwari et al. [84].

Sadangi et al. [85] investigated the effect of VC and Cr_3C_2 addition on grain growth of WC/Co alloys. The authors have revealed that because of the higher solubility and diffusivity in Co binder phase, VC and Cr_3C_2 are the most efficient inhibitors in inhibiting the grain growth of WC-Co composite. The effect on AGG by adding small amount of VC during the heat treatment of WC-Co alloys has been investigated by Choi et al. [86]. By adding VC, the grain was significantly retarded and suppressed which is attributed to the change in edge energy of WC crystals. The role of vanadium carbide additive during the sintering of WC-Co prepared by ball milling was studied by Lee et al. [72]. Authors have also elucidated the mechanism of grain growth inhibition during sintering. The findings suggested that only small amount of VC addition in WC-Co retarded the grain growth of the composite. The inhibition of grain growth is related to the change in the shape of WC crystals with VC addition. As a result of which, energy barrier for 2-D nucleation increases and retards the grain growth. Zhu et al. [79] compared the relative densities and grain size of WC-10Co-0.8VC nanocomposite prepared by mechanical alloying followed by sintering at 1200 and 1300 °C. Significant grain growth is observed in the WC grains sintered at 1300 °C, whereas at 1200 °C, small grains with more uniform and finer microstructure have been observed.

Kim et al. [87] compared the effect of dopants VC/TaC on the nanophase WC/Co added either by mechanical/chemical doping method. They have observed the absence of abnormal grain growth in WC/Co composite prepared by chemical doping method. In order to understand the inhibition mechanism in grain growth, structural analysis of VC/VC-Cr₃C₂ doped WC-Co composite was done by Lay et al. [88]. Findings reveal that V addition forms a thin coating of (V,W)C_x layers on the surface of WC crystals during sintering, which plays a major part in the grain growth inhibition. Also, segregation of Cr at the interface contributes to the resistance of W diffusion across WC layers and hence, inhibits the grain growth. Lan et al. [89] studied the effect of VC addition on the hardness and grain size of WC-Co composite. The results indicated that with the 0.5 wt% of VC addition, grain size of WC decreased from 540 to 380 nm and hardness also increased from 1828 to 1902 HV₃₀. But, the effect is reversed with further increasing the VC amount. Effect of VC during the early stage of sintering of WC-Co powder was also studied by Wang et al. [74]. The findings revealed the formation of multi-faceted characteristics of doped WC grains, while fully develop prism shaped grains has been observed in undoped WC. It concludes that VC delayed the aggregation of nanosized particles and has been proved to be the most effective GGI. Hashe et al. [90] studied the grain growth of WC-VC-Co composite in nitrogen atmosphere. The authors have found better results in materials sintered in nitrogen atmosphere than sintered in vacuum. The sintering atmosphere facilitate the suppression of cubic carbonitride (W,V)(C,N) grain growth. Dai et al. [91] studied the effect of GGI (VC/NbC) on the microstructure and properties of ultrafine WC-10Co cemented carbides. The results indicated that the addition of VC/NbC increases the hardness and toughness of the material by refining the WC grains and decreasing the volume fraction of Co₃W₃C phase in cemented carbides. Bonny et al. [80] investigated the impact of VC/Cr₃C₂ addition on the sliding friction and wear behaviour of WC-Co cemented carbides. Correlations between wear volume, wear rate and coefficient of friction shows a significant influence of VC/Cr₃C₂ on friction and wear characteristics of the base alloys. Espinosa et al. [92] studied the effect of additives VC/Cr₃C₂ or mixture of both on the friction and wear behaviour of cemented carbides. The results showed the significant reduction in wear rates by adding VC which increases the wear resistance of the specimen by 90%. Microstructure and mechanical properties of WC-based W-C-B ceramics containing VC were studied by Sugiyama and Taimatsu [93]. They have observed the suppressive effect of VC on the growth of WC grains. Mahmoodan et al. [94] investigated the effect of VC and TaC on sintering behaviour, microstructure, physical and mechanical properties of the WC-10%Co. The findings have showed 24% increase in

hardness and 35% increase in fracture toughness in the doped sample than the undoped one. Wang et al. [78] studied the effect of VC/V₂O₅ addition on the microstructure of WC-Co cemented carbides prepared by dielectric barrier discharge plasma (DBDP). It is observed that VC showed greater inhibiting effect on cemented carbides and leads to the ultrafine-grained microstructure of the material. Aqeeli et al. [83] studied the effect of GGI (VC/Cr₃C₂) on the mechanical properties of WC-Co composite. The results showed that addition of inhibitors refines the grain size of WC-Co composite to 131 nm with the hardness of 1592 HV₃₀ and fracture toughness of 9.23 M_{pam}^{1/2}. Effectivity of VC and Cr₃C₂ as GGI on sintering of binderless tungsten carbide was studied by Poetschke et al. [95]. The absence of AGG and fine microstructure was observed with higher content of VC [91, 95].

2.6 Goal of this Work

Despite of the importance of stoichiometric vanadium carbide (VC) on the basis of literature survey, its synthesis routes have not been explored much. It was also observed that precursor plays a very important role in shape, size and yield of the final product. However, these parameters are also influenced by temperature and carbon source. Many of the existing techniques require high temperature (> 1100 °C). Although sufficient work has been done for the synthesis of non-stoichiometric vanadium carbide (V₈C₇), but it lacks in analysis of reaction mechanism. Moreover, the effect of VC (C@VC) nanopowder on the consolidation of WC-Co composite has not been reported yet.

The goal of this work is to optimize the conditions for the synthesis of nano vanadium carbide at relatively lower temperature using thermo-chemical and mechano-chemical methods and check their thermal stability. Both of these routes are economical and better than any other method. The basic understanding of the mechanism based on the experimental results has been studied in detail in this work. Also, the effect of various reaction parameters viz. time, temperature, and pressure has been studied to get the final product. The approach of this work was also to check the suitability of the as-synthesized product as catalyst and GGI in WC-Co cermets.

The synthesis and characterization details of nano vanadium carbide(s) are given in next chapter of this thesis (Experimental procedure).

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CHAPTER 3

EXPERIMENTAL PROCEDURE

Overview

In this chapter, the details of the experimental procedure followed to synthesize nano vanadium carbide(s) from raw materials have been given. Two different routes for the synthesis of nano vanadium carbide viz. thermo-chemical and mechano-chemical synthesis route have been followed. For thermo-chemical synthesis route, self-designed and fabricated autoclave was used, whereas high energy planetary ball mill was used in mechano-chemical synthesis route. The details of the apparatus and chemicals used for the synthesis are described in detail. The obtained product was characterized using different characterization techniques. The characterization techniques along with instrument details are given in this chapter.

3.1 Raw Materials

The raw materials used for preparing the nano vanadium carbide were vanadium pentoxide, V_2O_5 (99%, Loba Chemie), magnesium metal powder, Mg (99%, Loba Chemie), acetone (99%, Merck Germany), activated charcoal (99%, S.D. fine chemicals), tungsten carbide, WC (US Research Nanomaterials, Inc.) and cobalt, Co (99.8%, Sigma-Aldrich). All these materials were used without any further purification.

3.2 Synthesis of Vanadium Carbide(s)

For the synthesis of vanadium carbide(s) nanoparticles, two types of routes have been adopted in the present work. These are:

- Thermo-chemical route (solvothermal)
- Mechano-chemical route

3.2.1 Synthesis of vanadium carbide(s) nanoparticles by thermo-chemical route

Thermo-chemical route is a simple and convenient chemical route to synthesize nanomaterials [1]. In order to facilitate the reduction process, some of the reactions are done at high temperature and high pressure which has been followed here. The reaction was carried out in a specially designed steel pressure vessel called 'autoclave' [1]. The gases generated inside the autoclave generate pressure during heating, which helps to carry out the complete reaction at relatively lower temperature.

Synthesis of nano vanadium carbide(s) was done by solvothermal route using vanadium pentoxide (V_2O_5) as precursor and organic solvent (acetone) in an autoclave. Magnesium turnings were used as a reducing agent in this method. The appropriate amount of raw materials was put in specially designed autoclave of 50 ml capacity. After proper sealing, the autoclave was put in an electric furnace at room temperature. The temperature was then increased from room temperature to desired temperatures for different holding time durations at the heating rate of 5 °C/min followed by furnace cooling. After cooling, the dark solid powder was taken out from the autoclave and leached with (1:1) HCl to remove the impurities. The acid treated product was then washed several times with distilled water followed by acetone washing and its drying at 120 °C for 20 h.

3.2.2 Synthesis of vanadium carbide nanoparticles by mechano-chemical route

Mechano-chemical synthesis is a simple and facile route for the synthesis of various inorganic compounds and nanocrystalline materials [2, 3].

For the synthesis of vanadium carbide nanopowders, raw materials V_2O_5 , Mg powder and activated charcoal was used as the reactants. Milling was carried out using a planetary ball mill (Retsch PM 100) at room temperature in a tungsten carbide (WC) jar of 250 ml capacity. Tungsten carbide (WC) balls of diameter 10 mm and weight 7.7 gm was used as a milling media. The ball-to-powder weight ratio was kept fixed 20:1 for all the experiments. The atomic ratio of reactants and milling variables are given in the chapter 4 (results and discussion). The milling was interrupted at the selected intervals of time and small amount of powder was taken out from the milling jar to evaluate the product phases as the milling progresses. Finally, the as-milled powders were treated with (1:1) HCl to remove the by-product. The obtained powder was washed several times with distilled water to maintain the neutrality of the solution. The final powder was washed with acetone and dried in the oven at 120 °C for 20 h.

3.3 Preparation of WC-Co-VC Nanocomposite

In order to check the suitability of the as-obtained vanadium carbide nanopowder, the synthesized powder was used as GGI in WC-Co composite. For the preparation of WC-Co-VC nanocomposite, the amount of Co binder (2 μ m) used was 10 and 20 wt% along with the variable VC content in commercially purchased WC nanopowder (55 nm). The known weight of powders was ground in an agate mortar pestle for 2 h in wet media. To this mixture, few drops of 10 mole% polyvinyl alcohol (PVA) was added and ground again for few minutes and dried.

3.3.1 Pellets preparation and sintering

For pellets preparation, known weight of dried powders was transferred into a 10 mm hardened steel die and pressed slowly in hydraulic press at a compaction load of 12 tons. After holding for five minutes, the pressure was released and pellet was taken out from the die. These pellets were then sintered in a calibrated resistance heating furnace at different temperatures under the flow of argon for 1 h. The methodology adopted for the experimental procedure is given below:

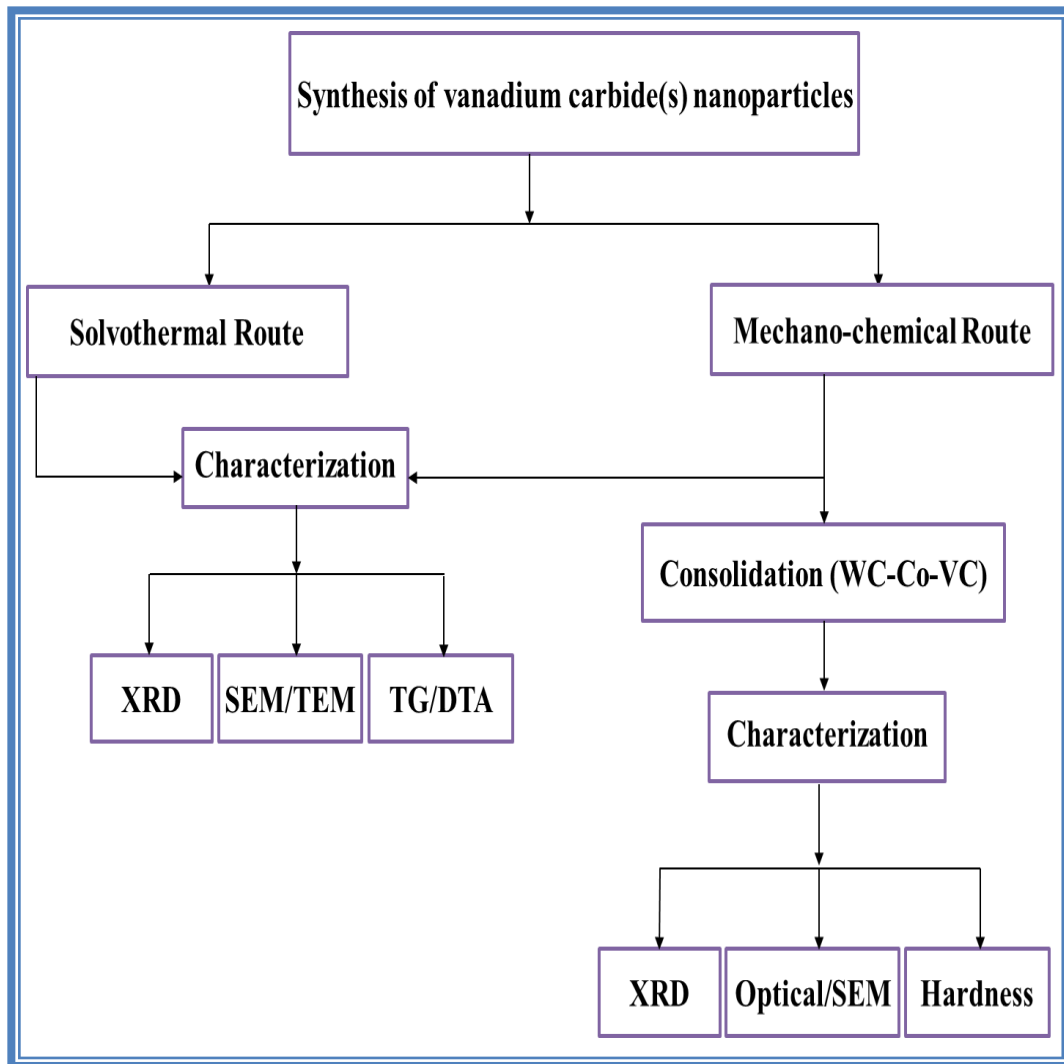


Figure 3.1: Methodology for the experimental procedure.

3.4 Characterization of Materials

In order to characterize the as-obtained product for their structural, morphological and physical properties, different characterization techniques have been used. The details of these are given below:

3.4.1 X-ray powder diffraction

Identification of phases obtained in the samples was done by X-ray powder diffraction (XRD) technique using Panalytical X'pert Pro diffractometer with Cu K α radiation, $\lambda=1.5418$ Å and an applied voltage and current 45 kV, 40 mA, respectively. All samples were scanned in the 2θ range of 20-80 with step size of 0.0131 degrees at room temperature. Moreover, before the analysis of sample the powders were ground in the mortar for similar particle size

distribution. Identical sample preparation techniques and data collection conditions were used for absolute comparison of peak intensities between different samples. The results of XRD data are analyzed and indexed by standard powder diffraction files provided by International centre for Diffraction Data (ICDD) [4]. Direct comparison method was used to calculate the volume fraction of the obtained phases.

3.4.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is an analytical technique used for the examination and analysis of sample's surface topography and chemical composition at magnifications of 10x to 100,000x [5]. In order to enhance the quality of the image taken, field emission SEM (FESEM) was used at the magnifications of 10x to 300,000x. SEM micrographs of the prepared samples were taken by using scanning electron microscope JSM-6510 LV (JEOL) and Zeiss Supra 55 field emission scanning electron microscopy (FESEM). Before SEM analysis of powder samples, the obtained samples were ground and coated with an ultrathin coating of electrically conducting material (gold), by low-vacuum sputter coating. In case of pellets, the polished samples were etched by Murakami's reagent in order to enhance the microstructural features followed by gold coating. Moreover, in order to identify the elemental composition of the material, Energy-dispersive X-ray spectroscopy (EDS or EDX) is used. Energy dispersive spectroscopy (EDS) was done by Oxford Instruments INCA-Act Energy 200.

3.4.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique which uses high energy electrons to penetrate through a thin (≤ 100 nm) sample to study the internal structure of specimens down to the atomic level [6]. Except the microstructure study, TEM analysis also provides information about the selected area diffraction pattern (SAED), which helps to identify the texture and discriminate nanocrystalline from amorphous phases. In the current work, microstructural features were examined by using a JEOL JSM 2100-F transmission electron microscope (TEM) at an applied voltage of 200 kV and TECHMAI G transmission electron microscope (TEM) at an applied voltage of 300 kV. For TEM study, the synthesized samples were suspended in ethanol by ultrasonic agitation. One drop of suspension was dropped on carbon-coated copper grid and ethanol was then allowed to evaporate.

3.4.4 Thermal analysis

Thermal analysis of the samples is done by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques with variation in temperature at different heating rates. DTA/DSC gives information about the phase transformation behaviour, crystallization, melting and phase stability of the sample [7]. TGA provides quantitative measurement of weight changes in the material associated with transition and thermal degradation of sample. TGA/DTA and DSC analyses were carried out in the heating mode at a rate of 5 °C/min using Perkin-Elmer, diamond TG thermal analyser and NETZSCH STA 449 F3, respectively. The spectrum was obtained in the temperature range of 50–800 °C in N₂/air atmosphere using alumina Al₂O₃ as a reference sample.

3.4.5 BET analysis

In material science, the surface area as well as porosity of sample is the important factor which affects the behaviour of a solid sample in any reaction. However, the true surface area, including surface irregularities and pore interiors is determined at the atomic level by the adsorption of an inert gas which corresponds to a monomolecular layer on the surface [8]. Among all the readily available gases and vapors, nitrogen gas has been used as adsorbate due to its easy availability and high purity in liquid form which provides strong interaction with most solid surfaces.

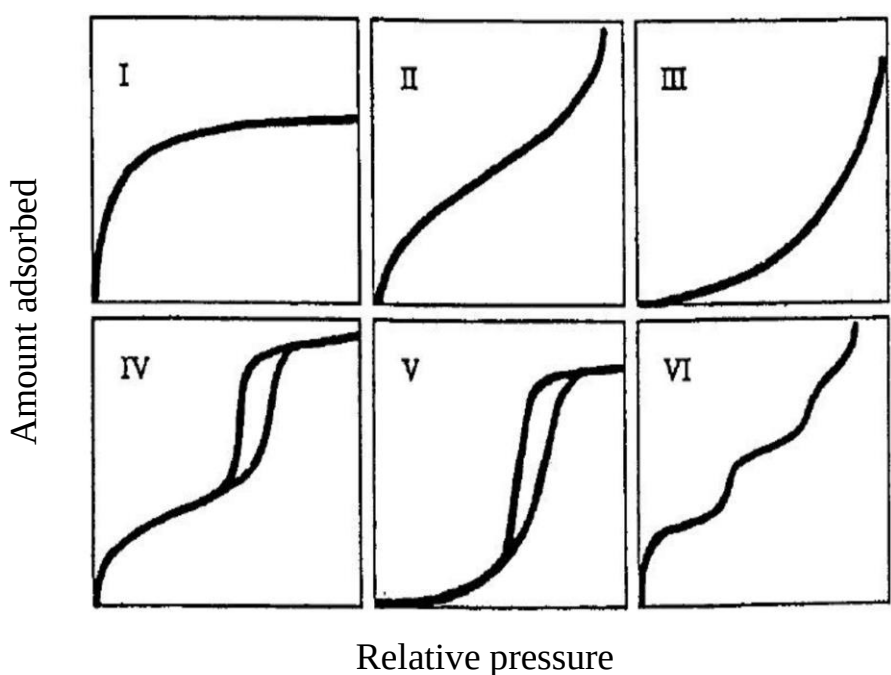


Figure 3.2: Types of sorption isotherms [9].

The data collected is presented in the form of BET isotherm which shows the plot between adsorbed gas and relative pressure. Referring to the IUPAC [9] conventions, porous materials can be described by six isotherms as shown in fig. 3.2. Type I isotherm is obtained for micro porous materials having pore size less than 2 nm. Type II isotherm shows the characteristics for materials which are not porous, or possibly macroporous and have a high energy of adsorption. In this isotherm, the nitrogen gas fills in the micropores at low pressure and monolayer formation starts at medium pressure. Type III isotherm is obtained for materials which are not porous, or possibly macroporous with low energy of adsorption. It shows the formation of multilayer with no asymptote in the curve but this isotherm is not applicable for BET. Type IV isotherm is obtained for mesoporous materials having high energy of adsorption and pore diameter 2-50 nm. In this isotherm, capillary condensation occurs which results to formed monolayer followed by multilayer. Type V isotherm is also obtained for mesoporous materials but it has low energy of adsorption. So, it is similar to type IV isotherm and is not applicable for BET analysis. Type VI isotherm is obtained only for those sample which have multiple pore size distribution. The specific surface area and porosity of the obtained product were examined by Brunauer–Emmett–Teller (BET) N₂ adsorption/desorption isotherm at 77 K by Micromeritics Gas Adsorption Analyser (Model: Tristar 3000).

3.4.6 Raman spectroscopy

Raman spectroscopy is a powerful molecular spectroscopic technique used for the identification of chemical and structural information of the molecules. This technique is based on the interaction of radiation with matter. When light radiation falls on the substance, inelastic scattering of monochromatic radiation takes place, in which light scatters in all directions [10, 11]. Energy is exchanged between the photon and the molecule such that the scattered photon is of higher or lower energy than the incident photon. The shift in wavelength (Raman shift) of the inelastically scattered radiation gives the fingerprint of the molecule to be detected. Raman shifts are reported in wavenumbers, which have units of inverse length, as this value is directly related to energy. In order to convert between spectral wavelength and wavenumbers of shift in the Raman spectrum, the following formula can be used:

$$\Delta\omega = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right) \quad (3.1)$$

Where $\Delta\omega$ is the Raman shift expressed in wavenumber, λ_0 is the excitation wavelength, and λ_1 is the Raman spectrum wavelength and is measured in cm^{-1} .

If the energy of the scattered radiation is less than the incident radiation, it is called Stokes lines and more than incident radiation for anti-Stokes lines. Some of the radiations may scatter off the sample with the same wavelength as that of incident, called Rayleigh scattering. The intensity of the scattered radiation depends on the chemical structure of the molecule [11]. Raman spectra have been most widely used to study carbon in its various crystallographic forms as the vibrations of non-polar functional groups are strong in Raman spectra. Raman spectra of the samples were recorded by Renishaw Raman spectrometer with Ar ion laser of 514.5 nm wavelength at 20 mW power and Labram-HR800 micro-Raman spectrometer equipped with 50 x objective, appropriate edge filter, and Peltier cooled detector.

3.4.7 Microhardness testing

Hardness measurement is widely used in laboratory and industry as a tool to characterize the mechanical properties of materials. The hardness is also related to wear resistance and abrasion of material, so there is a necessity to measure the hardness after selecting the appropriate hardness test. Moreover, measurements of hardness over small area are done with micro hardness tester where load up to 1 kg by Vickers and Knoop testers is applied. These two methods have been found to be used everywhere from research labs to quality control laboratories. These proved to be valuable tools in determining surface hardness, coating hardness, and case depth. The measurement of hardness has been done by pressing a hard indenter into the surface of the specimen to be tested under a specific load for a definite interval of time. Further the size or the depth of the indentation is to be used to determine the hardness by using the formula given below:

In Vickers, $\text{VHN} = \frac{1.8544 \times F}{d^2}$; where the F is in kgf and the average diagonal d is in mm.

In Knoop, $\text{KHN} = \frac{P}{L^2 \times C}$; where P is applied load in kgf, L is length of long diagonal (mm) and C is a constant for each indenter supplied by manufacturer. In the present investigation, Vickers microhardness tester (Mitutoyo, Japan) using diamond pyramid indenter is used for measuring micro hardness of the composites prepared.

3.4.8 Optical microscopy

Optical micrographs of the sintered WC-Co-VC nanocomposite were taken using optical microscope (Model: Eclipse MA-100, Nikon). Before taking the micrographs, the samples were mechanically polished using standard procedures and etched by Murakami's reagent in order to enhance the microstructural features.

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CHAPTER 4

RESULTS AND DISCUSSION-I

(Synthesis of Vanadium Carbide(s) Nanoparticles)

Overview

This chapter describes the details of work done for the synthesis of vanadium carbide using different techniques. The present work is further divided in three different parts. Since liquid hydrocarbon acetone is taken as source material for carburization, so first its dissociation behaviour has been studied which is described in the first section where the formation of carbon nanospheres is reported. On the basis of experimental results, the mechanism for the formation of CNS has been developed. Different applications of synthesized CNS have also been demonstrated. The second section of this chapter describes the effect of various processing parameters on vanadium carbide(s) nanopowder synthesized by thermo-chemical route. The kinetics of formation mechanism, thermal stability and morphology of the synthesized product has been studied in this section. In the third section, results obtained by mechano-chemical route have been presented and discussed. The effect of milling parameters has also been discussed in this section.

In the present section, results of the experiments carried out for the synthesis of vanadium carbide(s) nanoparticles are discussed in detail. The synthesis of vanadium carbide(s) has been done by two routes viz. thermo-chemical and mechano-chemical route. In order to study the morphology of carbon produced in solvothermal (thermo-chemical) route which also influences the synthesis parameters of vanadium carbide, decomposition behaviour of acetone in a sealed cylindrical vessel has been studied. The decomposition behaviour of acetone at low temperature was done using Mg as a reducing agent.

4.1 Decomposition of Acetone under High Pressure

Decomposition of acetone was done in a sealed cylindrical vessel called autoclave. In this experiment, autoclave was charged with acetone (20 mL) and Mg (1.5 g) and put in an electric furnace at 600 °C. The temperature of the furnace was raised from room temperature to 600 °C with the heating rate of 5 °C/min and held at this temperature for 5 h followed by furnace cooling. After completion of the reaction, the dark solid powder was washed with (1:1) HCl to remove impurities from the product. The powder was washed several times with high purity water to remove remaining HCl followed by drying at 100 °C for 20 h.

4.1.1 XRD analysis

In order to determine the structure of the obtained product after leaching and drying, XRD analysis was done as shown in fig. 4.1. The main peak at $2\theta = 25.6^\circ$ corresponds to the (002) diffraction plane of hexagonal graphite [1, 2]. The broadening of the peaks in X-ray diffraction pattern indicates the disorder and turbostratic structure of the graphite [2]. Moreover, the indistinguishability of the (100) and (101) peaks centred at 43.7° also reflects the presence of disorder in the structure [2]. This can also be associated with the presence of some oxygen atoms, which are not detected in XRD because of the negligible amount (< 5%) in the powder sample.

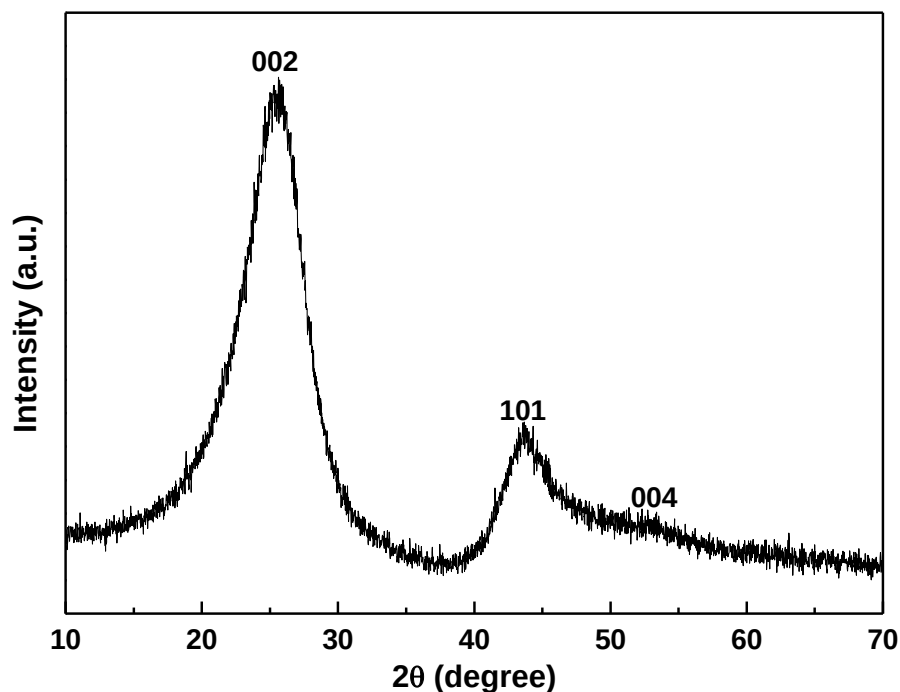


Figure 4.1: XRD pattern of the product phase after dissociation of acetone showing the presence of graphitic carbon.

4.1.2 Microstructural analysis and formation mechanism

The microstructural features of the above synthesized carbon was studied using FESEM and is shown in fig. 4.2. Low magnification micrograph shows the nearly uniform size of carbon nanospheres (CNS) having spherical morphology (fig. 4.2(a)). However, it also shows the agglomeration of the CNS. The high magnification image shows slight variation in size and formation of the chain of carbon spheres linked together as shown by an arrow in fig. 4.2(b).

In order to study the formation mechanism of CNS, it is necessary to understand the processes that take place in the sealed autoclave. In the beginning of the experiment, magnesium being the highly reactive element absorbs oxygen from the reaction atmosphere of the autoclave to form MgO, which acts as a catalyst for the decomposition of acetone [3]. The pyrolysis of acetone occurs in temperature range of about 300-400 °C, providing carbon containing intermediate species and hydrogen. It is difficult to say about the intermediate product at such a low-temperature range. Because of the H₂ gas generated as a by-product in reaction, high pressure is generated inside the autoclave, which further enhances the

reduction process and large quantities of carbon are produced. The reaction pressure generated inside the autoclave is calculated theoretically by the following equation:

$$\log_{10} p = A - \frac{B}{C + T} \quad (4.1)$$

where ‘p’ is the pressure, ‘T’ is temperature and A, B, and C are component-specific constants taken for acetone.

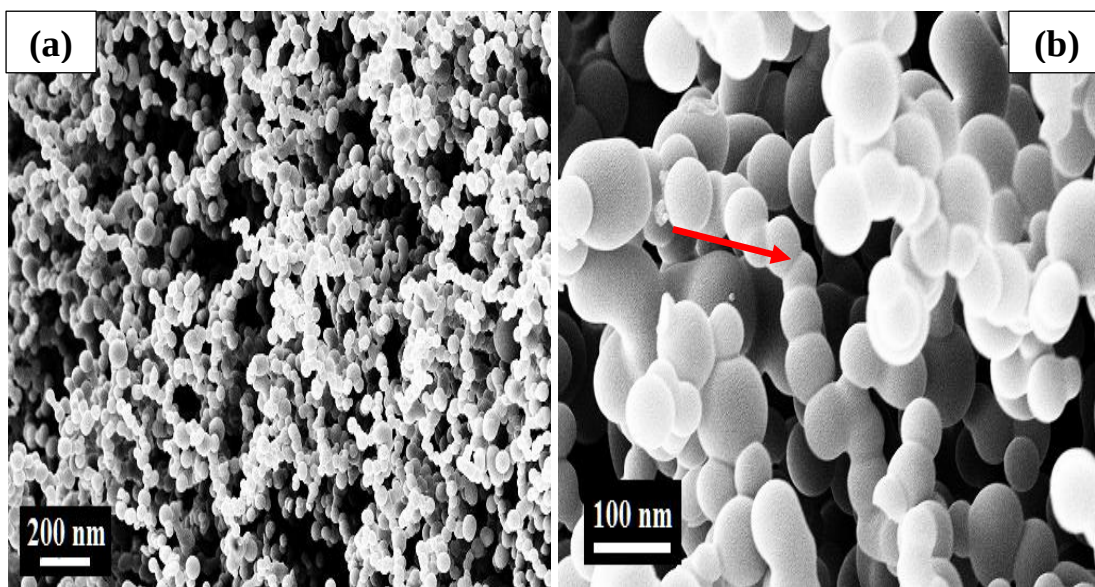


Figure 4.2: FESEM micrographs of CNS at different magnifications.

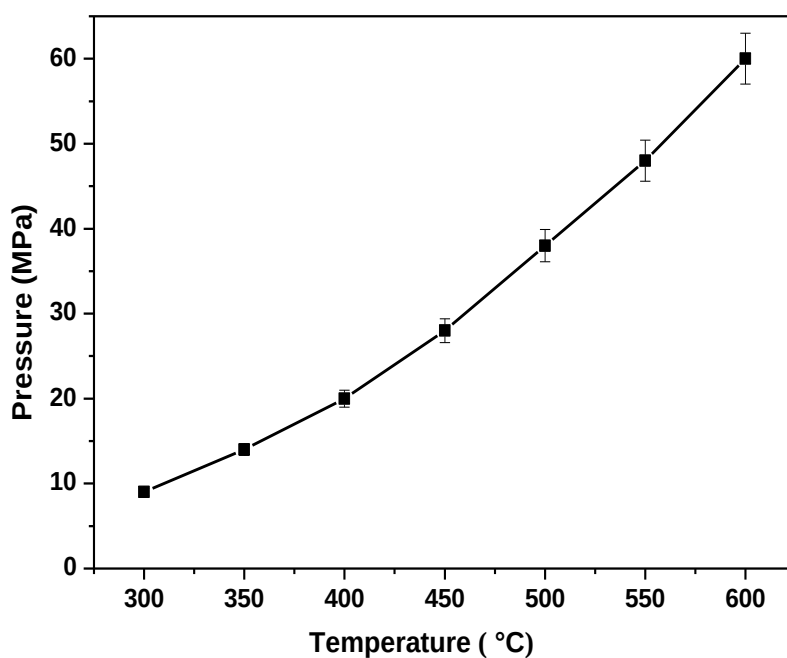


Figure 4.3: Pressure vs. Temperature curve of acetone.

The pressure vs. temperature graph is shown in fig. 4.3. It shows the amount of pressure that increases with the increasing temperature and at 600 °C, the value of pressure generated is 60 MPa.

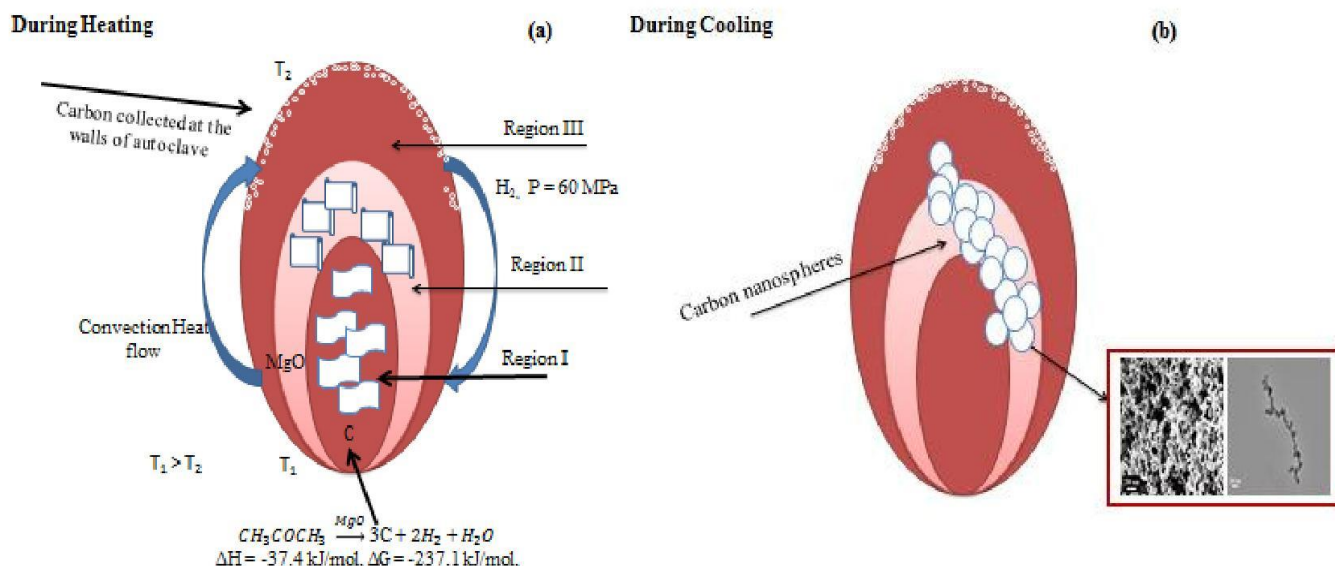


Figure 4.4: Schematic representation of formation of CNS during heating and cooling cycle.

It is well known that hydrogen is necessary for the growth of carbon nanostructured materials [4]. Also, MgO catalyses the nucleation and growth of carbon nanostructures and promotes the graphitization [5]. Consequently, under the catalysis of MgO, carbon atoms so generated will grow into graphite flakes as shown in the Region I of fig. 4.4(a). The graphite flakes are nothing but the pentagonal and heptagonal structure of carbon that follows the curvature of a sphere. At high temperature and pressure it is possible that a turbulent situation in the autoclave may exist because of which there is a possibility of the temperature gradient within the system. Therefore, heat flow from high to low temperature region within the autoclave and high-temperature high pressure is created as displayed in the Region II of fig. 4.4(a). With the continuous rise in temperature and high pressure, these graphene flakes aggregates into spherical graphitic shells, according to the free-energy minimization theory which results in the formation of CNS [2, 6, 7]. According to this theory, spherical shape of carbon with multi-shell structure is more energetically favourable and hence stable than a single or tubular shell [2]. Moreover, wrapping of graphene flakes into spherical shells eliminates the dangling bonds at the edge of the sphere which lowers the energy of the system. However, the presence of some defects or oxygen atoms on the surface of CNS acts as the nucleation sites

for further deposition of carbon atoms on the surface which might generate amorphous carbon [2].

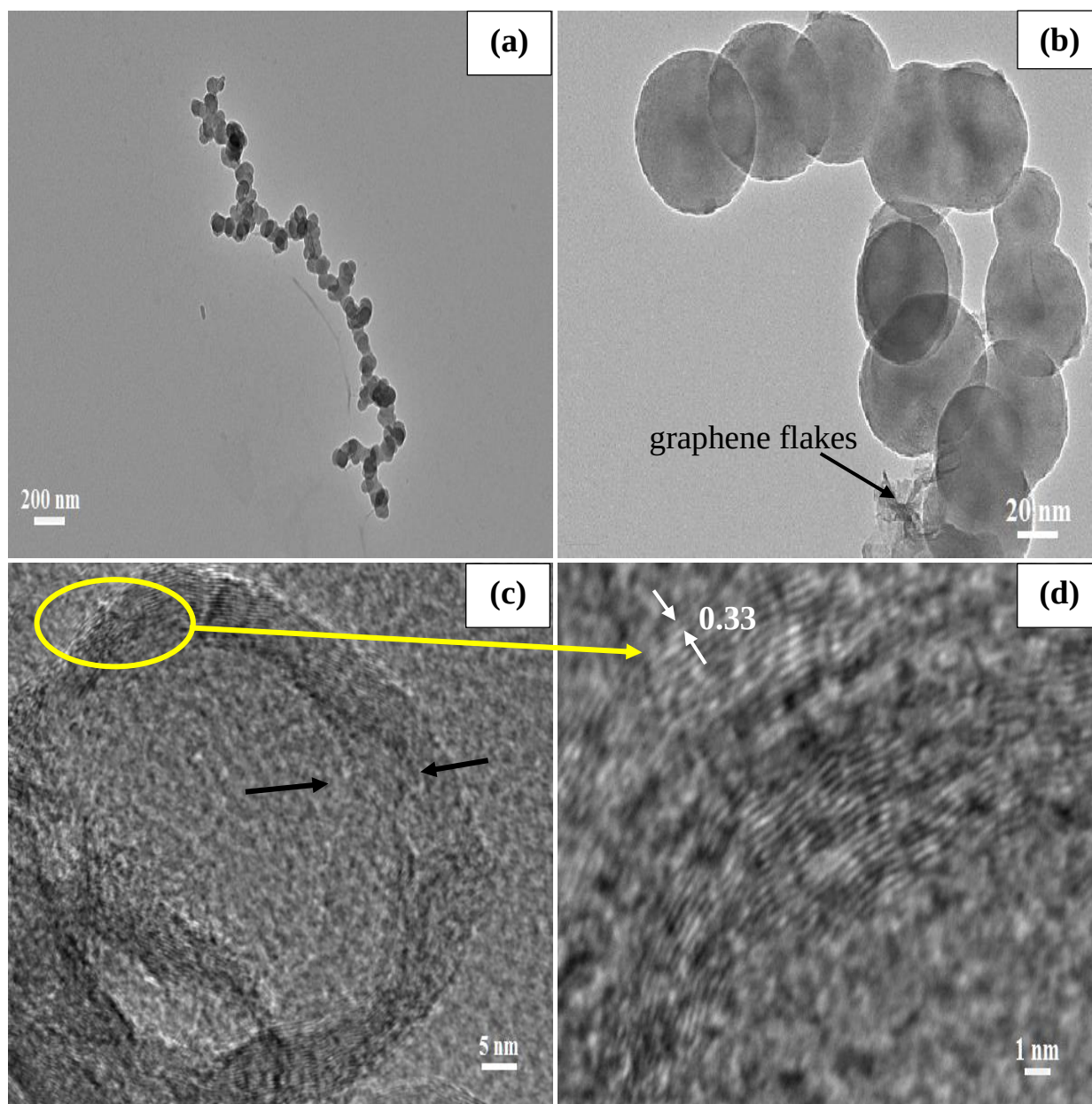


Figure 4.5: (a & b) TEM images and (c & d) HRTEM images of CNS.

The generated carbon spheres stuck to the walls of the autoclave in the agglomerated form because of the light weight as shown in the Region III of fig. 4.4(a). The agglomeration of the CNS can be explained based on the diffusion-limited aggregation (DLA) process during cooling [8]. It is a process by which particles undergo random walk because of Brownian motion and connect through Vander wall's forces into a network and form the interconnected grape bunch-like morphology, which is shown in fig. 4.4(b). The synthesized powder sample with the average size of 40-50 nm can be seen in fig. 4.5(a, b). The interplanar spacing shown

in HRTEM image (fig. 4.5(c)) corresponds to 0.33 nm which clearly matches with the (002) plane of graphite [2]. However, disorderness can also be seen on the surface of the sphere as marked by arrows (in black) in fig. 4.5(c) which accounts for the defects (explained earlier), which is also discussed in X-ray analysis. These interconnected structures, which are a unique feature of CNS ensures better performance as an electrode material in fuel cells and lithium-ion batteries [9].

EDS analysis of the marked area in fig. 4.6(a) is shown in fig. 4.6(b) to estimate the amount of oxygen present on the surface of the CNS. It shows the presence of 97.3% carbon with the little amount of oxygen (2.7%). X-ray dot mapping in fig. 4.6(c & d) also shows that the as-obtained product is rich in carbon with traces of oxygen present in it.

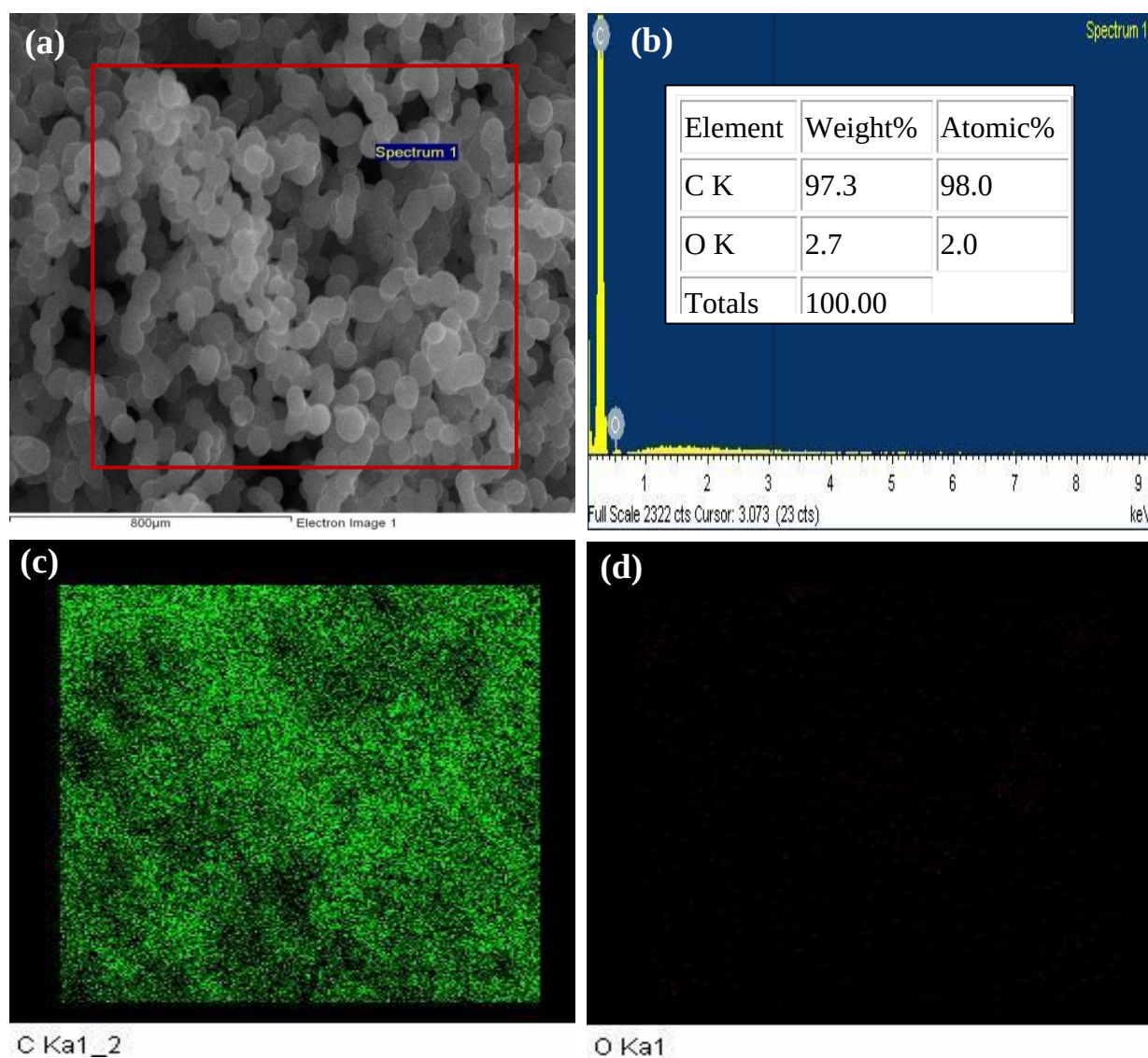


Figure 4.6: (a & b) EDS spectrum and (c & d) X-ray dot mapping of marked area in (a).

Assuming that the morphology of the nanoparticle is spherical, the average diameter of nanoparticles is estimated to be about 43 nm by averaging its diameters measured in several directions. It is observed from SEM images that the particle size measurement done by using AxioVision Rel. 4.8 software, follows the log-normal distribution shown in fig. 4.7.

$$f(d) = \frac{1}{\sqrt{2\pi} d \log \sigma_g} \exp \left\{ -\frac{(\log d - \log \mu_g)^2}{2(\log \sigma_g)^2} \right\} \quad (4.2)$$

$$\log \sigma_g = \sqrt{\frac{\Sigma(\log d_i - \log \mu_g)^2}{\Sigma n_i}} \quad (4.3)$$

$$\log \mu_g = \frac{\Sigma \log d_i}{\Sigma n_i} \quad (4.4)$$

where $f(d)$ corresponds to the log-normal distribution, d the particle diameter, n_i denotes the number of particles with diameter $d_i \pm 1$, $\log \mu_g$ the mean diameter and σ_g is the geometrical standard deviation, respectively.

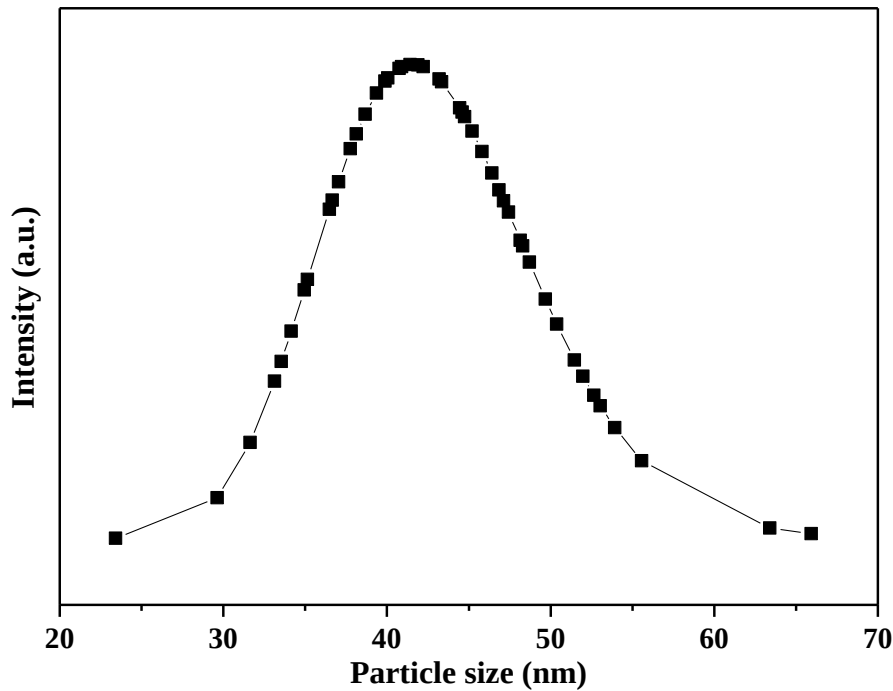


Figure 4.7: Particle size distribution of CNS.

4.1.3 TG/DTA analysis of CNS

The thermal stability of the sample was investigated by TG/DTA analyses in air as shown in fig. 4.8. The TGA curve does not show any change below 600 °C. Above 600 °C, the oxidation of carbon began which accelerates with the rise in temperature by the evolution of large heat at 675 °C ($\Delta H = -108.84$ kJ/mol) and decreases the sample weight continuously. The increase in oxidation as well as existence of declination of curve at ~ 629 °C as observed from TGA (shown in inset) indicates the onset of rapid oxidation reaction. Such kind of behaviour in TGA curve shows the presence of structural defects or dangling bonds at the edge of CNS, which enables oxygen to readily diffuse into the spheres facilitating rapid oxidative degradation [10].

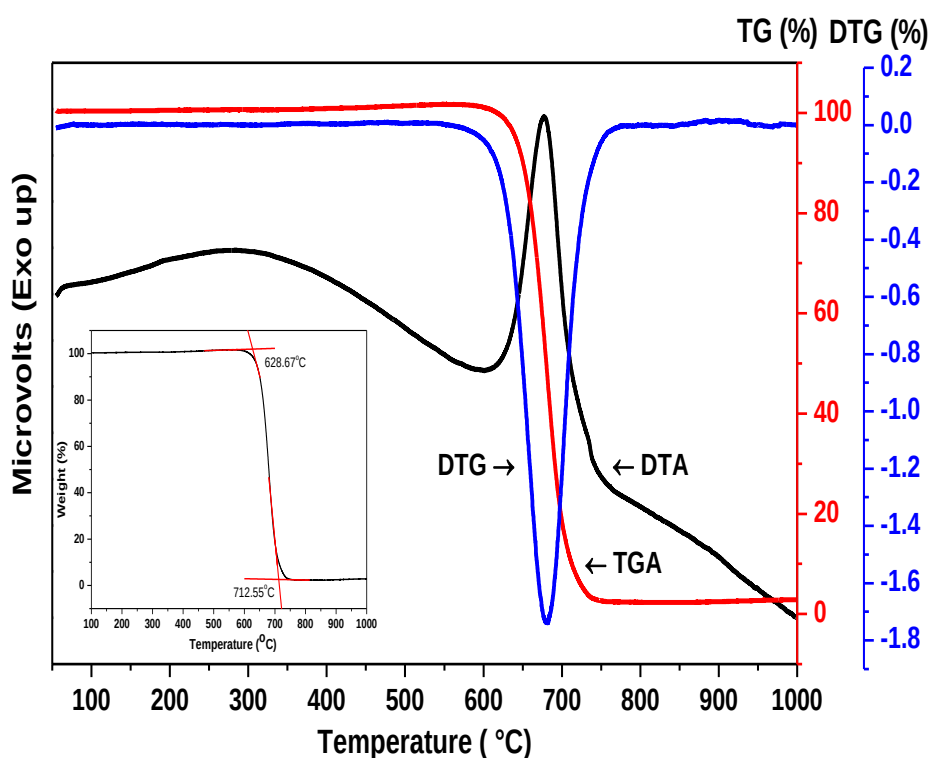


Figure 4.8: TG/DTA plot of CNS.

A sharp peak in DTG at 679 °C indicates the maximum oxidation rate at which CNS converts into CO/CO₂. Moreover, a broad exothermic peak in DTA curve at ~ 675 °C also confirms the formation of CO/CO₂ from CNS at this temperature. The possible formation of CO/CO₂ has been calculated by the thermodynamic data at high temperatures according to the equations below:



According to the thermodynamic values, the feasibility of formation of CO at higher temperatures of ~ 700 °C is more than of CO₂. It is because of the comparable value of heat of formation (ΔH_f) calculated from the DTA graph with the standard value of ΔH_f of CO ($\Delta H = -110.51$ kJ/mol) obtained at this temperature. The release of CO continues upto 738 °C, leaving the residue which is 2.7%. Such kind of behaviour of TGA curve has also been observed by Li et al. [11] in which the weight loss of CNS occurred in the temperature range of 500-760 °C. The residue may be due to the presence of oxide impurities that was not detected from XRD analysis. The high onset decomposition temperature of CNS than the reported ones shows the higher thermal resistance of the obtained product [11-13].

4.1.4 Raman spectroscopy

Raman spectrum of the as-obtained CNS is shown in fig. 4.9. The two major peaks at ~ 1339.5 and 1571.8 cm⁻¹ correspond to the D and G-bands of graphite, respectively [11]. D-band is associated with the amorphous carbon or edges that can break the symmetry i.e. disorder in the carbon structure because of strain-induced effects [11]. The G-band is related to the vibrations of sp²-bonded carbon atoms in a two-dimensional hexagonal lattice i.e. diagnostic of the structural order [11].

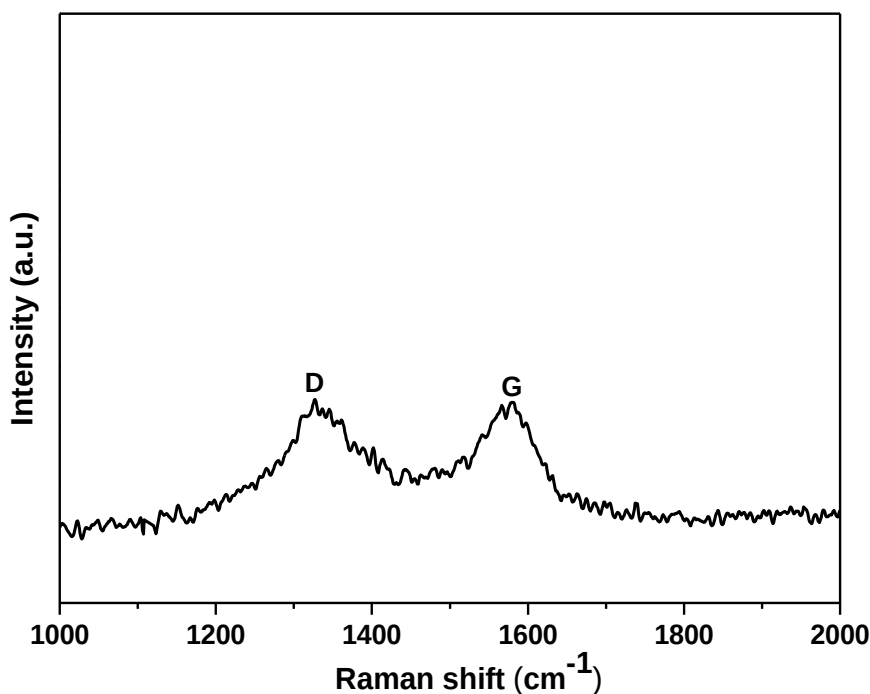


Figure 4.9: Raman spectra of CNS.

The broad D-band in the Raman spectrum indicates the presence of amorphous carbon or defects arising from disordered carbon layers or the incorporation of hydrogen or oxygen atoms within the graphite layer [14, 15] which matches well with the TEM/EDS results also. The intensity ratio of I_D to I_G is also used to estimate the disorder in the structure. Higher the value of I_D/I_G ratio indicates the presence of oxygen atoms in the carbonaceous core or on the surface leading to the disordered structure [16]. The calculated I_D/I_G value of 1.06 for the obtained CNS shows the presence of disorder in the structure and lower degree of graphitization [2, 16] which is in well agreement with the XRD and HRTEM results.

4.1.5 Optical studies

Optical properties of the CNS were investigated by UV-Vis spectroscopy as shown in fig. 4.10. Inset of fig. 4.10 shows the UV-Vis absorption spectroscopy of CNS in the range of 200-500 nm.

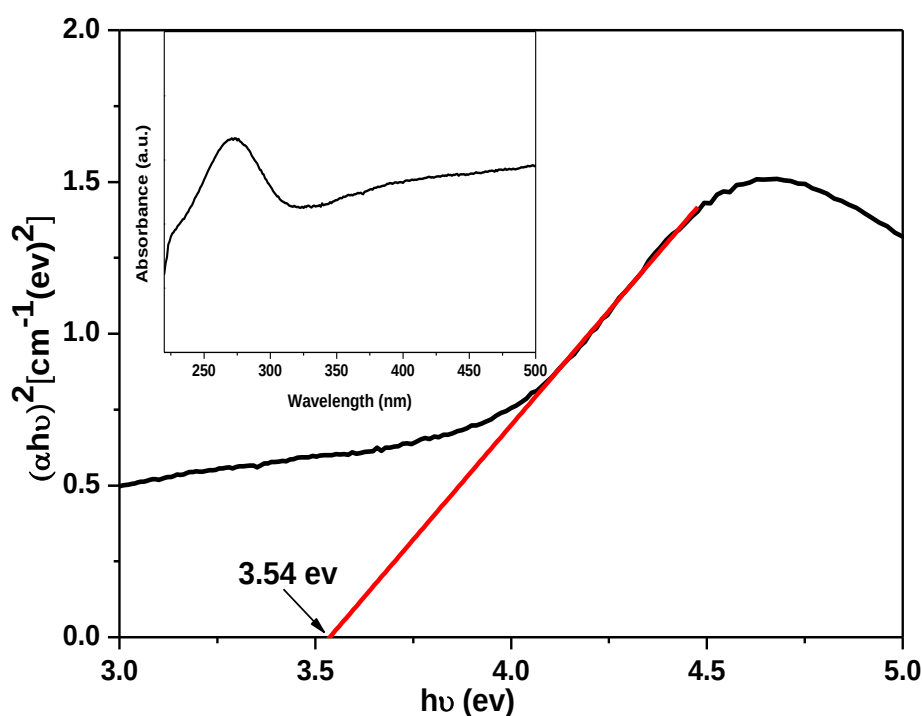


Figure 4.10: Band gap graph and absorption spectrum (inset) of the as-obtained CNS.

It exhibits a broad absorption band in UV-region with maxima centred at ~ 274 nm, which is associated with the $n-\pi^*$ transition of C=O bonds [17]. In the present work, this band is slightly blue shifted as compared to the reported one which is because of the quantum confinement effects or the presence of oxygen defects, which has also been confirmed from the EDS results (fig. 4.6). The band gap is calculated by using the ‘‘Tauc law’’ as [18]:

$$\alpha h\nu = B^2 (h\nu - E_g)^n \quad (4.7)$$

where, $h\nu$ is the photon energy, E_g is the optical band gap, n is the index which has different values (2, 3, 1/2, 3/2) depending on the different interband transition and B is constant called band tailing parameter. From the absorption data, the band gap energy was calculated by extrapolating the linear portion of $(\alpha h\nu)^2$ vs. $h\nu$ curve to absorption equal to zero as shown in fig. 4.10. Band gap value for direct transitions is 3.54 eV. Thus, this direct and wide band-gap material has the potential to be used in the various applications as in photo-catalysis, sensors, photo-electrocatalysis and opto-electronic devices etc.

4.1.6 Photocatalytic activity

The photocatalytic properties of the CNS have been checked for the degradation of methylene blue (MB) as a model organic pollutant. Photocatalytic degradation of the MB using CNS as a catalyst in the presence of UV light has been studied for different time intervals. Figure 4.11(a) shows the changes in the absorption spectra of MB during UV exposure in the presence of CNS as the catalyst. The MB solution has a major absorption band at the wavelength of 664 nm. The decreasing absorption intensity of MB solution with increasing UV irradiation time indicates the photocatalytic degradation of MB. The time-course graph for the decomposition of MB is shown in fig. 4.11(b). The degradation efficiency can be calculated using the following equation [19]:

$$D (\%) = (C_0 - C_t)/C_0 \times 100 \quad (4.8)$$

where, C_0 and C_t represent the concentration of MB at time = 0 and t , respectively. Photocatalytic degradation efficiency of CNS for MB is 65% in 300 min. However, the degradation efficiency of bare CNS is low, but it is much higher than that of reported for carbon nanoparticles (CNPs) [20].

After four hours of UV-light irradiation, about 43% of MB was degraded by CNS while only little activity was observed by Lin et al. [20] for CNPs under same conditions. The higher photo-reactivity of CNS was attributed due to the existing defects on the surface of sphere, generated during the synthesis as discussed in earlier section [1]. Moreover, it has been reported by Gala et al. [21] that the materials having band gap value (E_g) < 4 eV can be treated as photoactive materials under UV light, which is 3.54 eV in the present case. Additionally, higher graphitization in the present case also enhances the photocatalytic activity of as-synthesized CNS [20]. After the irradiation of UV-light on CNS, the

photogenerated electrons reduce the molecular oxygen (O_2) into superoxide radicals ($O_2^{\bullet -}$), which will react with the water molecule and activate the formation of oxidizing radical species that will interact with the organic pollutant, contributing to its degradation [21, 22].

The positive response of CNS towards the degradation of MB gives a new direction to use it as a support material for the conventional catalyst (TiO_2 , ZnO , CdS etc.) to enhance its photocatalysis.

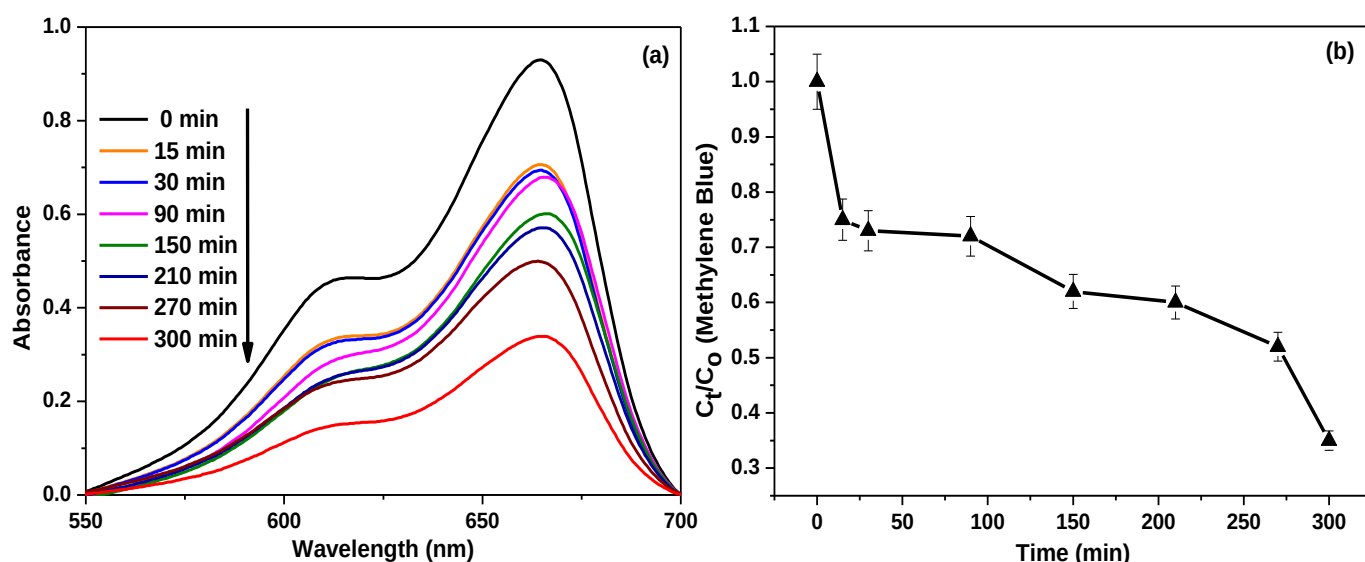


Figure 4.11: (a) Absorbance spectra of MB degraded under UV-light and (b) Time-course graph for the degradation of MB.

4.1.7 Electrocatalytic properties

In order to investigate the electrochemical stability of pure CNS for oxygen reduction reaction (ORR), potential opening experiments have been done in between -0.2 and 1.0 V in 0.5 M H_2SO_4 electrolyte (fig. 4.12). First, the potential was cycled between -0.2 and 0.8 V (scan rate 50 mV/sec) for pure CNS. Following the hydrogen region (-0.2 to 0.2 V), the CNS exhibited capacitive behaviour until the onset of a strong oxidation current at around 0.59 V. Here, the presence of oxidation peak at 0.59 V vs SCE and reduction peak at 0.25 V vs SCE (fig. 4.12(a)) on the CV curves are mainly due to the reversible redox reactions of oxygen functional group [23]. Hence, the obtained rectangular-shaped CV curves with broad humps in these CV curves owe to combined effects of electric double layer capacitance and pseudo capacitance [24, 25]. These types of characteristics imply the fast charge-discharge property of the active materials which is essential for the high-energy supercapacitors in the presence of the ionic liquid as the electrolyte [26]. However, a deviation in terms of decrement in the intensity of redox peaks with the increase in scan count has been observed in this potential

range (–0.2 to 0.8 V), which designates the instability of the sample. To optimize the potential range for ORR, the positive end of the potential window was extended by 0.2 V to the threshold potential 1.0 V. As compared to last potential range (–0.2 to 0.8 V), the decrease in the peak intensities as well as a negative shift in the CNS oxidation (fig. 4.12(b)) has been observed in the current potential range. In this case, the intensities of both cathodic and anodic peaks are increased with CV cycling. This is likely due to the increase in the fresh acting surface area of CNS [27]. But the absence of ORR peak at higher potential as observed from the CV curve confirms that the pure CNS has no activity for oxygen reduction in acidic solution in these potential ranges. It means that the pure CNS could not be used for oxygen reduction reactions (ORR). Hence, based on the observation of the electrochemical performance of pure CNS in this potential range (–0.2 to 1.0 V), CNS powders have been modified by platinum deposition. Figure 4.13 shows the XRD pattern of Pt deposited CNS powder sample. The broad diffraction peak at an angle 2θ around 25.5° is due to the (002) plane of carbon. The other broad diffraction peaks around 40° , 46° , 67° and 81° are due to Pt (111), Pt (200), Pt (220) and Pt (311), respectively [28] which clearly indicates that the platinum precursor has been successfully reduced to Pt nano particles. The broadened nature of XRD peaks designates the high dispersion of the Pt nano particles which have small size ~ 4 nm as calculated by using Debye Scherrer formula. Figure 4.14(a) shows the CV curve of Pt/CNS electrocatalyst at the different scan count. The amount of Pt loading on the CNS surface was 49 μg . The mechanism of electrochemical reactions on the Pt/CNS surface may take place by three stages. In the potential range –0.2 to 0.2 V, the peaks express the adsorptions and desorption of hydrogen atoms on Pt surface during the cathodic and anodic sweep, respectively [28]. During the forward scan, the potential range from 0.2 to 0.6 V vs SCE corresponds to the charge double layer by the oxygenated groups on the carbon support surface [29]. At the potential 0.65 V vs SCE, the oxidation process on Pt metal occurs to form Pt oxides. Corresponding with this process, a reduction peak in the range of about 0.43–0.5 V vs SCE of the reduction of Pt–O in the reverse scan [28, 29] has been observed.

The hydrogen adsorption/desorption in the CV curve depends on the particle size of platinum [30]. As shown in fig. 4.14(a), peaks (–0.2 to 0.2 V) corresponds to the bonded hydrogen for Pt/CNSs that did not appear clearly in initial scans. This may be due to the fact that after 1st cycle onwards, hydrogen penetrated into the CNSs, ensuring its electrochemical contribution, which is also observed by Li et al. [31] during the lithiation on Si/CNS sample. However, new cathodic (–0.025 V vs. SCE) and anodic peak (–0.011 V vs. SCE) after successive scans

have been observed. This is attributed to the strongly bonded hydrogen atom on platinum, which may be due to the smaller particle size of platinum [30]. The intensity of the characteristic peaks did not change much throughout 50 cycles, demonstrating that the CNS substrate was highly conductive and accommodated the volume expansion of hydrogen, and thus quite stable electrochemical performance was delivered.

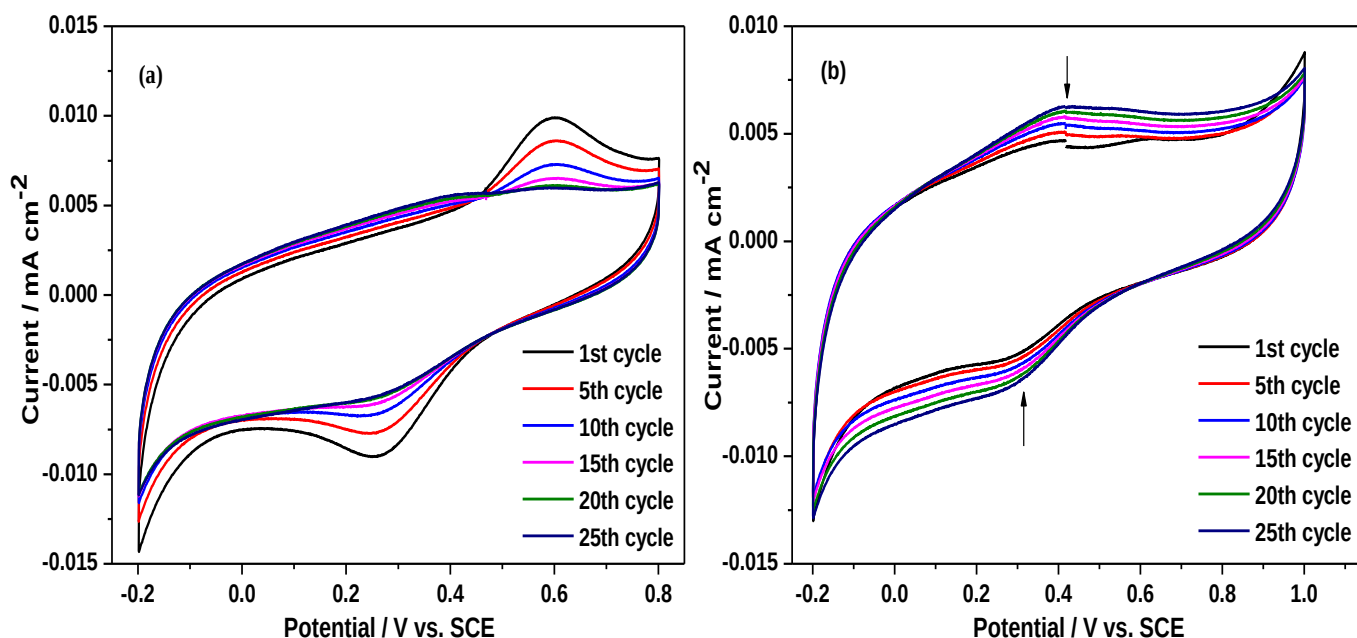


Figure 4.12: Cyclic voltammograms between (a) -0.2 and 0.8 V and (b) -0.2 and 1.0 V of as-obtained CNS in 0.5 M H_2SO_4 ; scan rate 50 mV/sec.

Furthermore, the nature of peak for ORR has also been analysed with electrochemical cycles for observing the sample stability. The decrement in the peak area as well as peak intensity with increasing number of scans (fig. 4.14(a)), suggested that Pt electrochemically active sites, on which oxygen species are adsorbed were decreasing, which result to decrease the ORR activity [32]. This is because of the loss of the top layer of Pt/CNS electrocatalyst. Moreover, the shifting of peak after 1st cycle towards positive potential during oxide formation-reduction peak has also been observed in fig. 4.14(a). According to Ross [33], this is due to the participation of two different plane of platinum viz Pt (111) and Pt (100). The appearance of reduction peak at 0.43 V is attributed due to the Pt (111) and at 0.50 V due to the Pt (100). For two different ordered surfaces of platinum, the process of reduction being much more reversible on Pt (100) as compared to Pt (111) which is also observed from the CV curve.

In order to understand the kinetic parameters of the synthesized powder sample, a plot of $\log I$ vs η for Pt/CNS is shown in fig. 4.14(b). The plot shows two linear regions for Pt/CNS electrocatalyst. The slope at the low current density (region 1) is -69 mV/decade and -122 mV/decade at the high-current density region (region 2). These two slopes are attributed to the formation and adsorption of surface oxides (Pt–O) on the Pt surface [32, 34]. According to Liu et al. [32] these oxides inhibit the ORR and influence the performance of electrocatalyst directly. But from this voltammograms, it is also clear that the magnitude of cathodic peak observed at about $0.43\text{--}0.5$ V vs SCE is caused by the reduction of platinum oxide. The value of exchange current density obtained by extrapolation of the Tafel line to the equilibrium potential [34] corresponding to each Tafel slope are 2.8×10^{-6} and 4.89×10^{-6} Acm^{-2} . From the calculated value of exchange current density, it was observed that with 49 μg Pt loading on electrode, the exchange current density increased by 4 orders of magnitude at the higher potential region than that reported by Shen et al. [34] for Pt/C system with 80 μg Pt loading. The enhanced electrocatalytic activity of CNS is related to its spherical morphology and unique interconnected structure (fig. 4.5(a & b)). Hence, the formation of interconnected structure due to the joining of CNS during cooling creates well-ordered channels throughout the spheres [35, 36] as shown in fig. 4.15. According to researchers [35, 36], these channels reduce the liquid sealing effect and not only allow the liquid to diffuse inside easily but also facilitate the reaction species transport at higher rates. Also, high degree of graphitization in the present route during synthesis helps to prevent the electrochemical corrosion which is low in case of carbon black due to its amorphous nature [36]. Additionally, irrespective to carbon black, due to the defects on the surface of CNS, its narrow size distribution and uniform morphology, Pt nanoparticles are uniformly distributed over the whole surface of CNS. As a result of it, the accessibility of reactants to Pt nanoparticles enhanced which increases the Pt utilisation. Hence this kind of system decreases the transfer resistance of the reactants and intermediate products which provide better charge transport phenomena and more effective active sites for catalytic reactions [1, 36, 37].

Hence, by platinizing the CNS to Pt/CNS, the ORR performance is significantly improved and it enhances the power output of energy storage devices, which is limited on the cathode side.

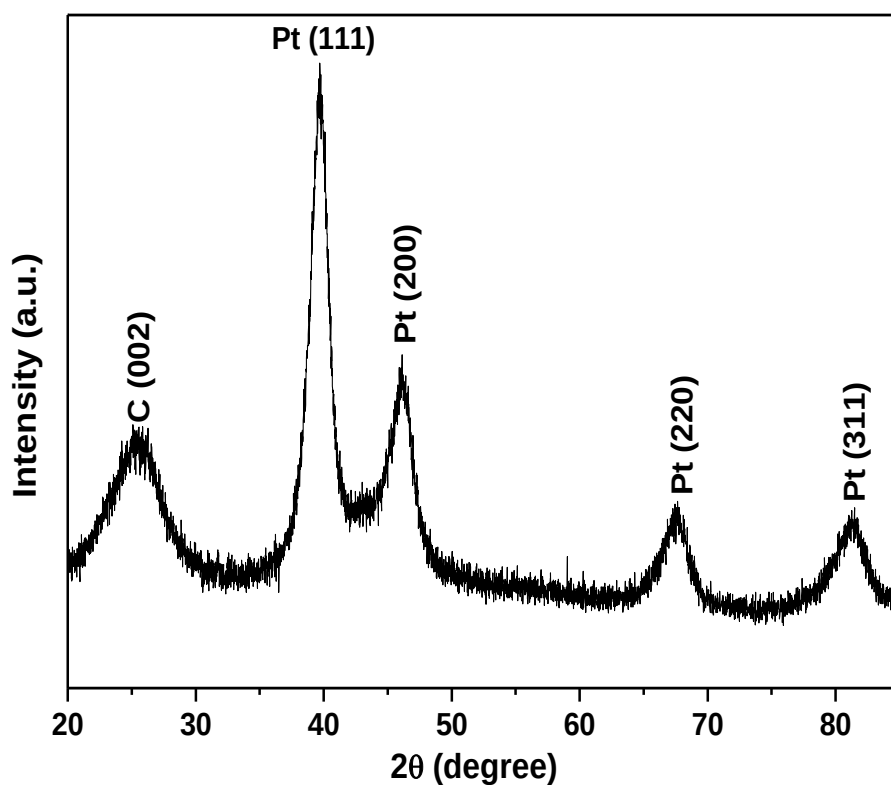


Figure 4.13: XRD pattern of as-obtained Pt/CNS.

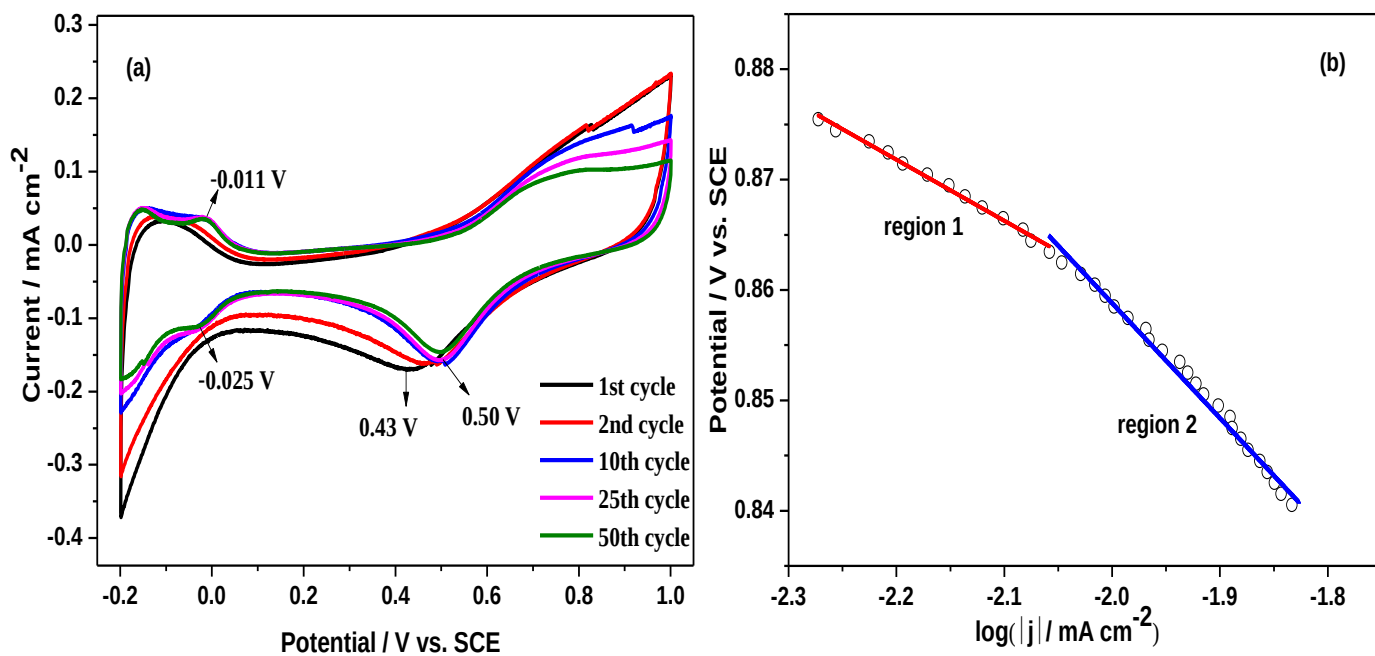


Figure 4.14: (a) Cyclic voltammograms of Pt/CNS in 0.5 M H₂SO₄ between -0.2 and 1.0 V and (b) Tafel slope for ORR on Pt/CNS electrocatalyst.

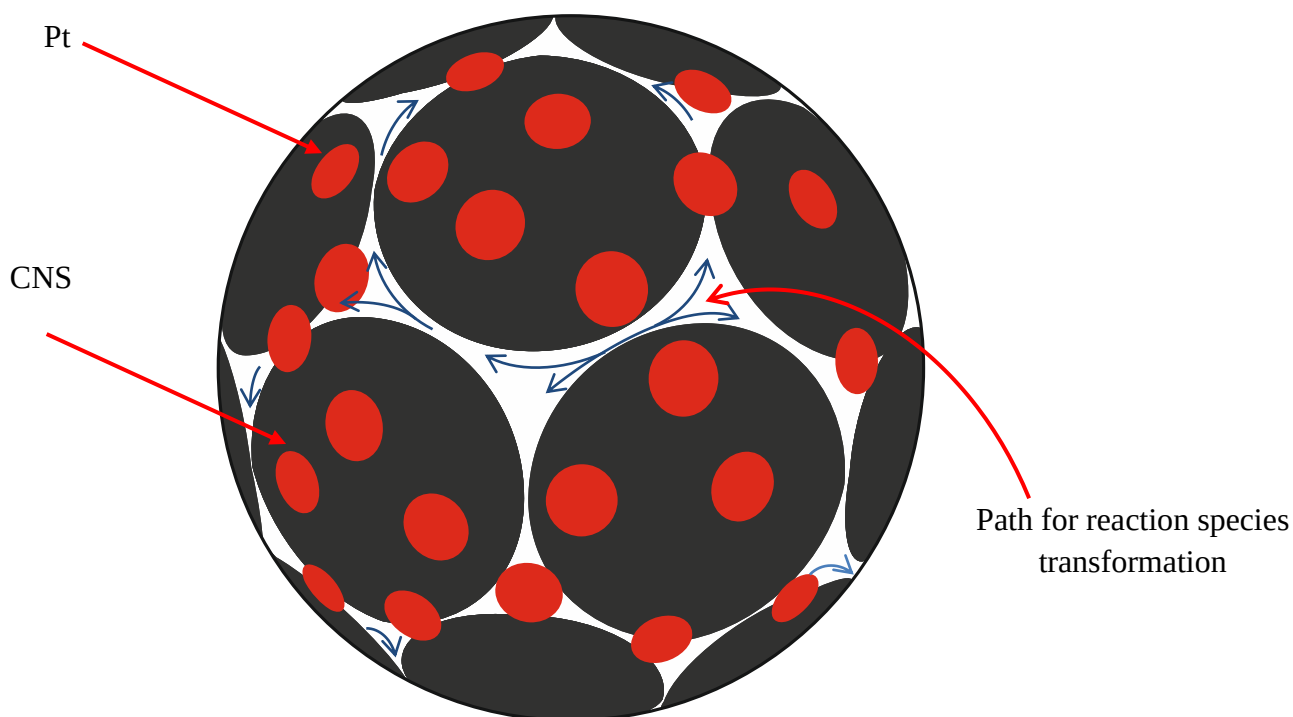


Figure 4.15: Schematic representation of Pt deposited CNS with increased reaction species transformation.

Above study demonstrated that acetone can be used as carbon source for the reduction of V_2O_5 followed by its carburization as CNS produced during decomposition of acetone have high surface activity. Details of this are presented in the following section:

4.2 Vanadium Carbide(s) Nanoparticles by Thermo-chemical Route

In this study, processing parameters have been optimized to obtain single phase vanadium carbide(s) (V_8C_7 , VC) at relatively lower temperature. For the formation of the vanadium carbide(s) nanoparticles, vanadium pentoxide (V_2O_5) as a precursor, magnesium (Mg) as a reducing agent and hydrocarbon acetone (CH_3COCH_3) as a carbon source were used as starting materials. In order to optimize the reaction parameters for the synthesis of single phase nano vanadium carbide(s), the role of different processing variables have been studied.

4.2.1 Effect of carbon amount

Amount of carbon plays a major role for the synthesis of vanadium carbide(s) nanoparticles. The variation in the amount of carbon source results in the change in pressure in the autoclave that affects the synthesis process. Therefore, amount of carbon content for the synthesis of vanadium carbide(s) nanoparticles has been varied in order to get the desired product at a constant temperature (800 °C). The details of the initial ingredients taken are shown in table 4.1.

Table 4.1: Initial ingredients and reaction parameters at 800 °C for the synthesis of V_8C_7 .

Sample	V_2O_5 (g)	Mg (g)	Acetone (mL)	M/C*	Reaction time (h)
AC-1	3	6	36	1:12	10
AC-2	3	6	36	1:12	12
AC-3	3	6	36	1:12	16
AC-4	3	6	40	1:13	16

* M/C = amount of V_2O_5 (g) / acetone (mL)

4.2.1.1 XRD analysis

Figure 4.16 shows the XRD patterns of synthesized samples after acid leaching. There are five main diffraction peaks observed for V_8C_7 phase for the planes (222), (400), (440), (622) and (444) (ICDD Card No. 01-077-2003) in all these XRD patterns. These peaks belong to cubic structure with space group $P4_332$ [38]. The XRD results of all set of reactions shown in fig. 4.16 indicate that the intensity and sharpness of the diffraction peaks of sample AC-4 is higher as compared to other samples. It corresponds to single phase V_8C_7 . However, in samples AC-1, AC-2 and AC-3, V_8C_7 along with VO_2 is also present. In these samples, amount of carbon is not sufficient as VO_2 phase is still present even after increased reaction time from 10 to 16 h (fig. 4.16(a-c)). However, the intensity of VO_2 peaks decreased with higher time but the complete conversion of VO_2 to V_8C_7 has not occurred. So, in the next AC-4 reaction, the M/C ratio was increased from 1:12 to 1:13 keeping the reaction time constant for 16 h which enabled the transformation of VO_2 to single phase V_8C_7 (fig. 4.16(d)). This is because of the increased amount of acetone, which decomposes to give H_2 in the autoclave. As a result, pressure inside the system increases, which helps in further reduction and also decreases the particle size of the synthesized product (table 4.2).

In order to get single phase VC, reaction was carried out for 20 h with same M/C ratio as in sample AC-4 (table 4.3). The XRD (fig. 4.17(a)) shows the diffraction peaks of VC phase alongwith semi carbide (V_2C) as well as lower oxide (VO_2). These results indicate that the reaction gets reversed at this condition [39].

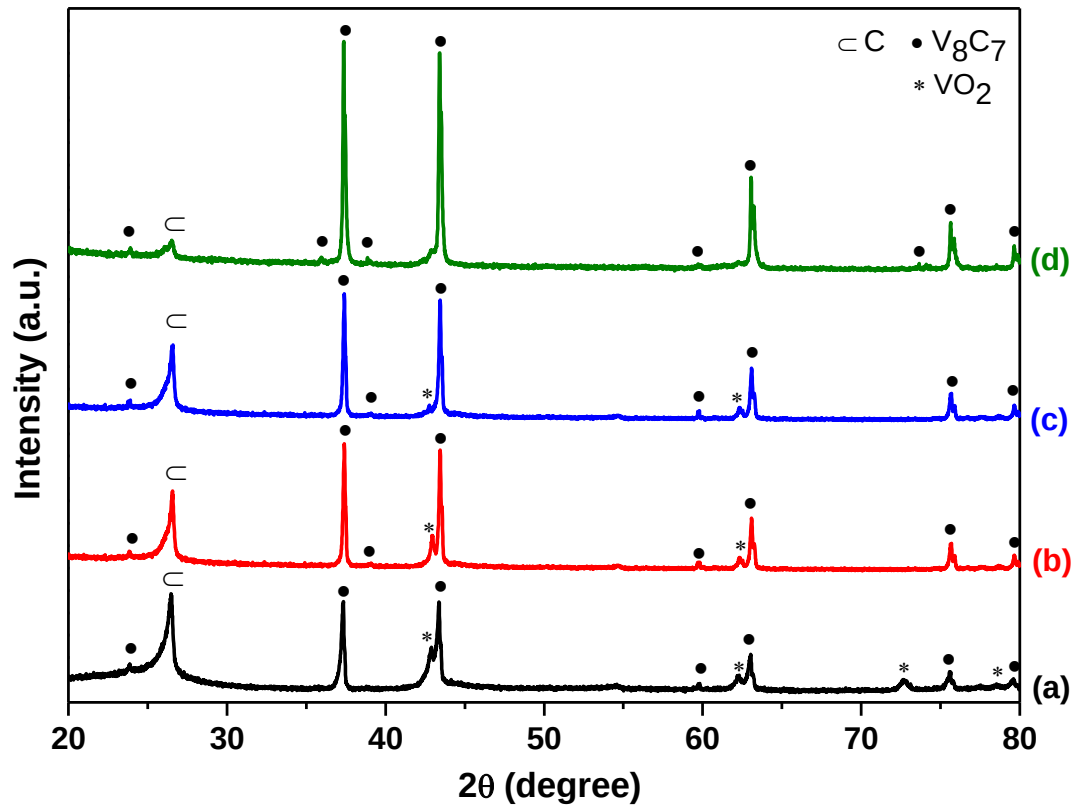


Figure 4.16: XRD pattern of samples (a) AC-1 (b) AC-2 (c) AC-3 and (d) AC-4.

Table 4.2: Crystallite size of vanadium carbide nanoparticles, strain produced and volume fraction of the obtained phases.

Sample	M/C ratio	Crystallite size (nm)	Strain ($\times 10^{-3}$)	Volume fraction of phases (%)				
				V_8C_7	VC	V_2C	VO_2	C
AC-1	1:12	34	0.567	70	-----	-----	8	25
AC-2	1:12	45	-2.11	83	-----	-----	5	15
AC-3	1:12	47	0.069	85	-----	-----	2	13
AC-4	1:13	28	2.25	92	-----	-----	-----	8
AC-5	1:13	37	1.58	-----	77.6	11	11.4	-----
AC-6	1:14	32	2.69	-----	92	8	-----	-----
AC-7	1:20	56	-0.27	-----	97.5	-----	-----	2.5

With the increase of M/C ratio in sample AC-6 and AC-7, pressure inside the system also increased and additional carbon in the system got enough thermal activation to enter into the octahedral interstitial sites of VC. Consequently, complete reduction as well as carburization of the oxide(s) takes place and single phase of VC (ICDD Card No. 01-073-0476) is formed in sample AC-7 as shown in fig. 4.17(c). The presence of carbon peak at $\sim 26.5^\circ$ shows the formation of nanocomposite VC@C (fig. 4.17(c)).

Overall reaction parameters indicate that the carbon source (acetone) plays an important role on the reduction of oxide precursor and then carburization. With the increase of the carbon content, the volume fraction of vanadium carbide(s) nanoparticles increases and that of free carbon decreases (table 4.2).

Table 4.3: Initial ingredients and reaction parameters at 800 °C for the synthesis of VC.

Sample	V ₂ O ₅ (g)	Mg (g)	Acetone (mL)	M/C	Reaction time (h)
AC-5	3	6	40	1:13	20
AC-6	3	6	42	1:14	20
AC-7	1	1.5	20	1:20	20

The crystallite size and strain for the samples synthesized at different reaction conditions was calculated using Williamson-Hall (W-H) plot analysis and the results are given in table 4.2. Compressive and tensile strain was observed for the sample with different carbon content. The observed positive value of strain in sample AC-1 indicates the tensile strain in the system, which is because of the transformation of lower ionic radii ion V⁵⁺ (0.54 nm) to higher ionic radii ion V⁴⁺ (0.58 nm) during the reduction and carburization of V₂O₅ to VC [40]. Also, the crystal defects which rise in the structure during cooling, produces tensile strain in the lattice [41]. The negative value of strain corresponds to compressive strain in the system, which is because of some interstitial sites that are still occupied by the oxygen instead of carbon atoms (AC-2) [42]. Further, the tensile strain in the system increases with increasing the carbon content (AC-4 and AC-6). It may be because of the diffusion of more carbon atoms into V₈C₇ lattice to convert into stoichiometric VC [40]. Again, the presence of compressive strain in sample AC-7 might be because of the presence of non-detectable oxygen atoms in the interstitial sites of VC lattice even with increasing the amount of carbon source. The variable role of oxygen in variation of strain is due to the fact that with increased content of acetone, oxygen content is also increased. The compressive strain leads to lower

the values of surface energy and increases the stability of the carbide sample [40, 43]. Therefore, the presence of compressive strain in sample AC-7 attributes to higher stability of the sample after the conversion into single phase VC nanoparticles.

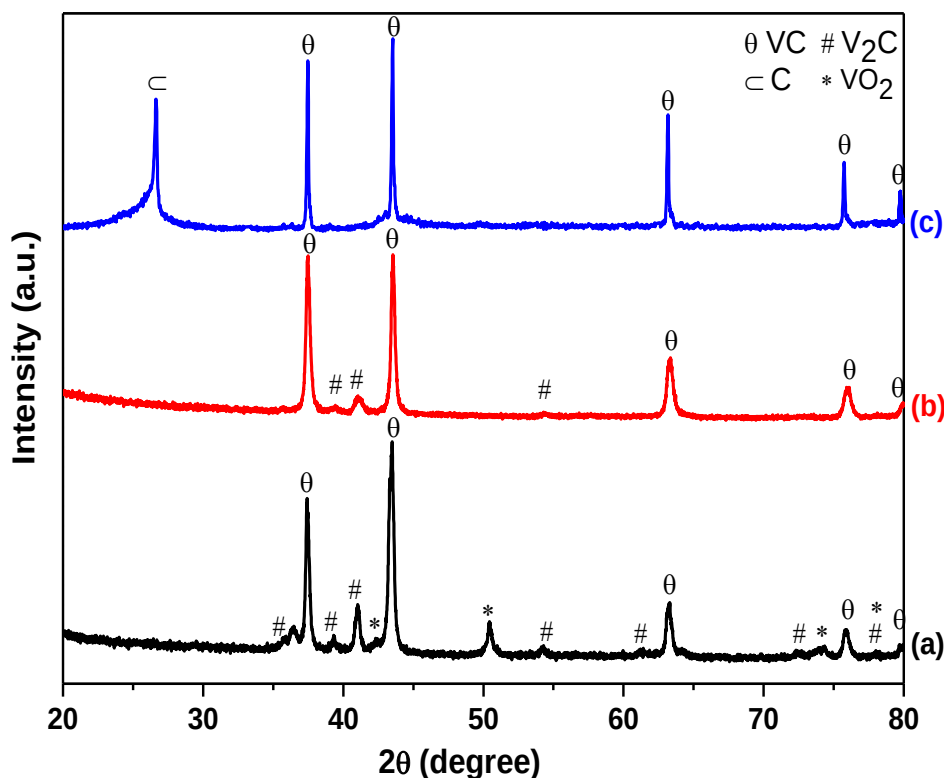


Figure 4.17: XRD pattern of samples (a) AC-5 (b) AC-6 and (c) AC-7.

4.2.1.2 Microstructure analysis

Morphological and structural details of the samples obtained at different reaction conditions were investigated by TEM/HRTEM. Figure 4.18(a) shows the TEM image of sample AC-1, where the reaction was allowed to occur for 10 h at 800 °C. The micrograph clearly shows the presence of two different features. One where particles have fibre like morphology and the other exhibiting spherical type feature. The interesting feature observed within almost all spheres is that there is some structural growth. Another interesting feature observed is marked with double arrow where rectangular phase is growing (fig. 4.18(a)).

In fig. 4.18(b), a typical TEM picture of the phases formed in sample AC-2 shows fibre like structure corresponding to V_8C_7 phase which is perhaps transforming stage of faceted morphology. These structural features are similar to those reported for the synthesis of V_8C_7 phase by the hydrothermal route also [44]. Once the reaction time and amount of carbon is

increased, these fibres try to acquire faceted feature as can be seen in fig. 4.18(c) for sample AC-4.

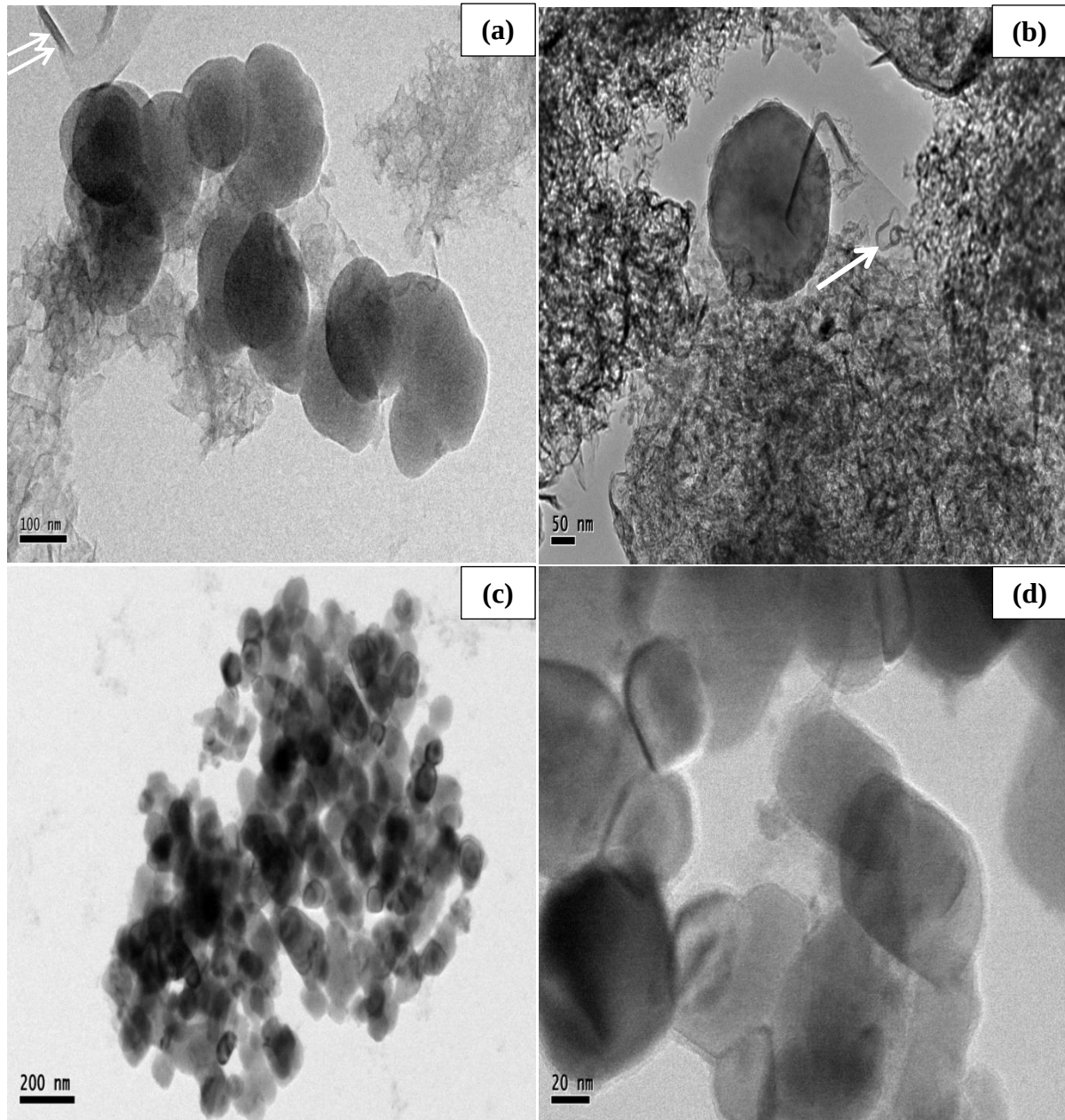


Figure 4.18: TEM micrographs of sample (a) AC-1 (b) AC-2 and (c & d) AC-4.

The faceted structure corresponds to V_8C_7 phase. However, when analyzed carefully the fibres like features start forming square loop that can be seen in the structure as has been also reported for Tantalum [45]. This clearly shows that the formation of these crystals occurs as fibres first which get collected as square mesh as shown by arrow in fig. 4.18(b) and finally grow like faceted morphology as shown in fig. 4.18(c). Clear faceted crystals of V_8C_7 having average diameter of 43 nm can be seen in fig. 4.18(d).

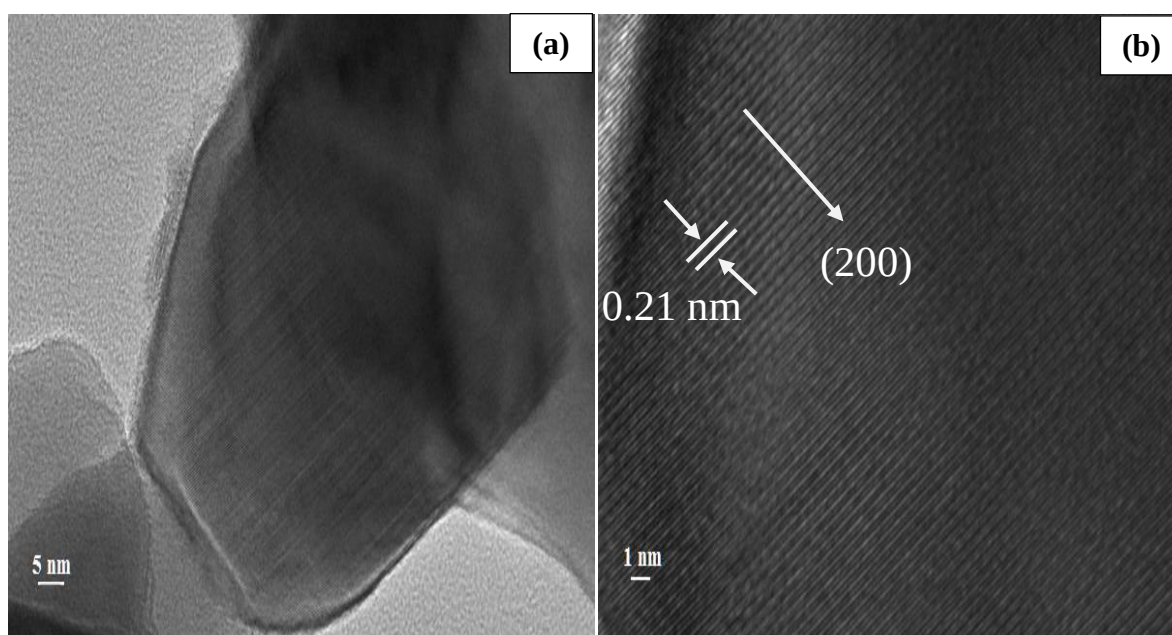


Figure 4.19: TEM micrographs of sample AC-6.

In another set of experiments also faceted morphology of sample AC-6 is observed as shown in fig. 4.19(a). As the reaction proceeds, more and more vanadium and carbon adhere to the surface of VC nanoparticles and most of them move to the lowest energy plane of VC when supersaturated. The surface energy of (200) plane of VC is smaller than other crystal planes, therefore (200) oriented nanostructures are obtained. Figure 4.19(b) shows the high resolution TEM image of fig. 4.19(a) with d-spacing 0.21 nm corresponding to the (200) plane of VC. Similar types of structural features were also reported by Dai et al. [46] for the synthesis of VC.

The HRTEM micrographs of the carbon coated vanadium carbide (VC@C) of sample AC-7 are shown in figure 4.20. In fig. 4.20(a), core-shell morphology is clearly visible and high resolution HRTEM image of 4.20 (a) is shown in fig. 4.20(b). It shows that VC nanoparticles of average size of 30-40 nm which are encapsulated by 20-22 layers of carbon.

In TEM micrographs of sample AC-4, AC-6, AC-7, the particle morphology is similar. We can see the faceted type structure of vanadium carbide(s) nanoparticles in all these samples. The only difference is the amount of free carbon or the coating of carbon which engulfs the VC nanoparticles.

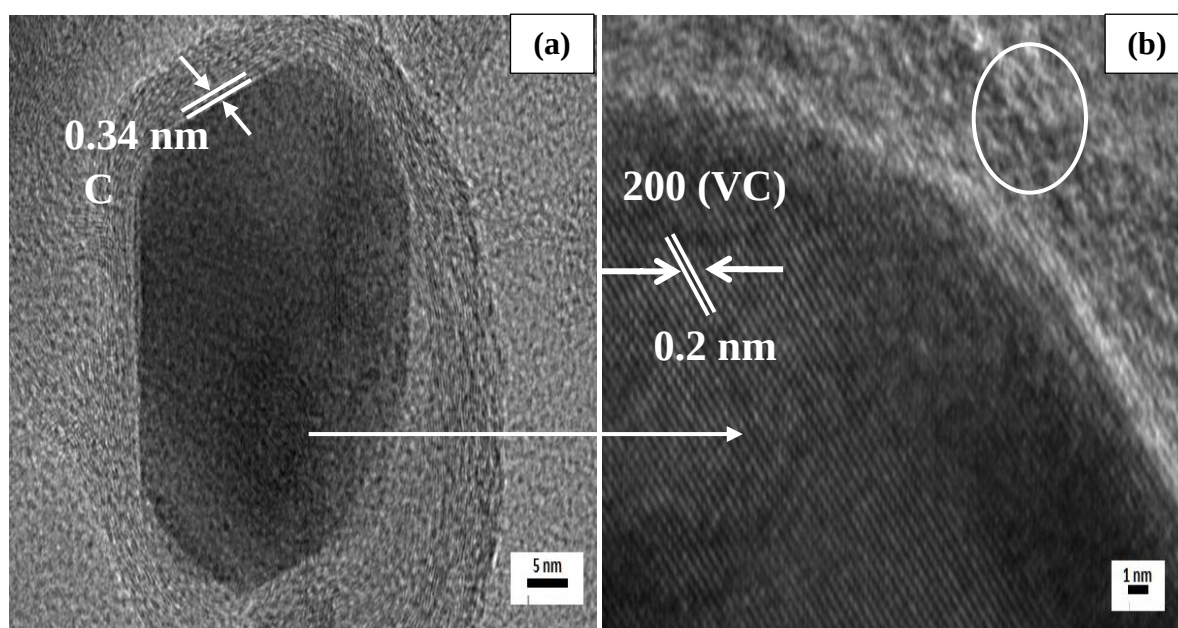


Figure 4.20: HRTEM micrographs of sample AC-7.

4.2.1.3 TG/DTA analysis

To check the thermal stability of the synthesized samples at different temperatures, TG/DTA of the samples was done in air and the results are shown in fig. 4.21. From the TGA curve, it is clear that there is a continuous decrease in the sample weight during heating. Initially, at around 300-350 °C, around ~ 5% weight loss corresponds to the oxidation of amorphous or very fine free carbon layer. However, the weak exothermic peaks in this range also confirm that the amount of free carbon is very small in the synthesized sample especially in the sample AC-1 and AC-2. The sudden weight loss from 350-700 °C is due to the oxidation of outer graphitic carbon layer of VC forming CO_x ($x=1, 2$) after the reaction with oxygen, which contribute in the decrease of the sample weight [47]. Pure VC is highly air sensitive and gets oxidised easily in air which results in increase in the sample weight. So, in spite of lower content of VC in sample AC-6 as compared to sample AC-7, it shows weight gain at lower temperature due to the reaction of oxygen at the surface of VC particles forming an adhering layer of vanadium oxide [48, 49].



whereas in case of sample AC-7, increased adherent carbon coating on outer surface of VC nanoparticles restricts the material from being oxidised. So, the TGA analysis of the samples

synthesized by proposed route shows that the carbon coating restricts the VC nano particles from oxidation and maintains its thermal stability up to higher temperatures.

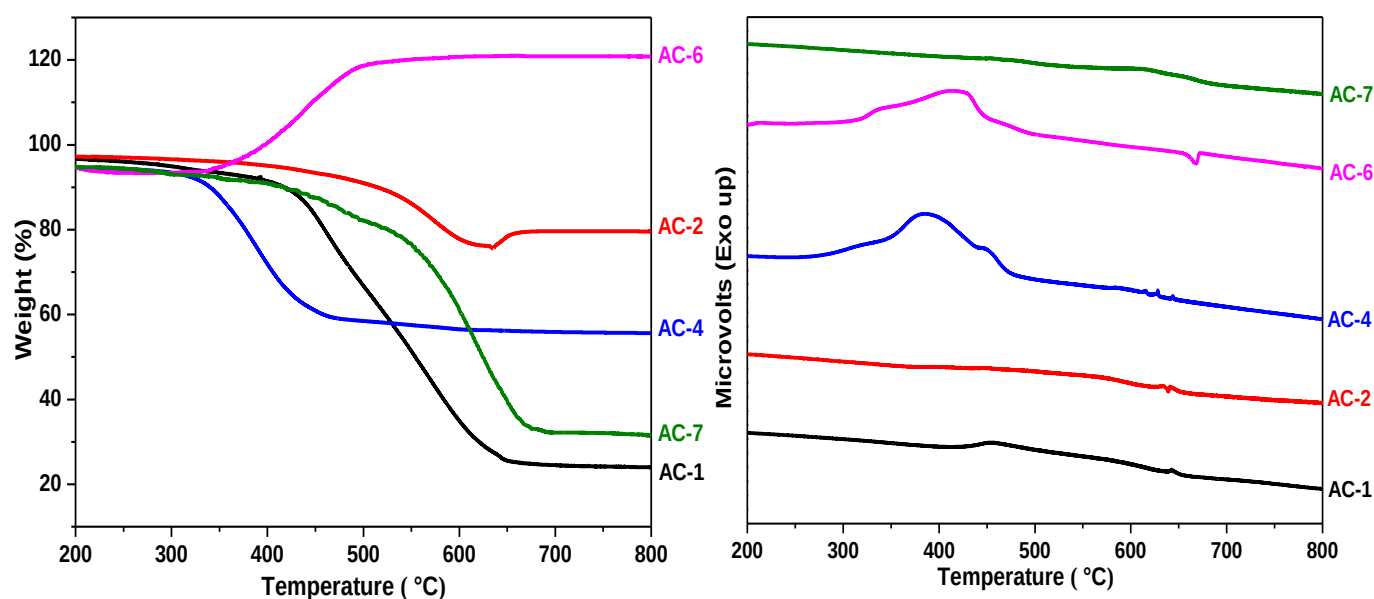


Figure 4.21: (a) TGA and (b) DTA plots of the synthesized samples.

Initially, the samples synthesized with lower amount of acetone (AC-1 and AC-2) have oxide which restricts it to get further oxidized and shift the oxidation temperature in the range of 400-500 °C. But with further increase in acetone amount, the formed non-stoichiometric carbide (V_8C_7 , V_2C) in sample AC-4 and AC-6 enhanced the oxidation and shifts the oxidation process directly at lower temperature in the range of 325-375 °C. While, the further shifting of onset temperature for oxidation on the higher side for sample AC-7 obtained at higher acetone amount (20 mL) seems to be more thermally stable as compared to other synthesized samples. It may be due to the strong Me-C bonding or the presence of oxide/carbon content on sample surface in the form of undetectable limit of thick/thin layer which restrict the oxidation further and delaying the oxidation process. Moreover, the absence of sharp weight loss in TG curve for all the synthesized samples indicates the formation of oxide layer during heating, which may act as a protective layer against further oxidation. The oxide protective layer prevents the powder from further oxidation but the carbide is gradually dissolved by formed oxide through a process of oxygen transfer [50]. However, the plateau after ~ 650 °C indicates that all free carbon and carbon in VC@C have been oxidized completely leaving only stable metal oxide, which has also been observed by many authors in their respective systems [47, 51, 52]. The appearance of endothermic peak at

~ 640-667 °C in DTA curve of sample AC-2 indicates the melting of formed oxide, (V_2O_5) [52] which shifts to higher temperature (~ 666 °C) in AC-6 depending upon the formation of $V_8C_7/V_2C/VC$ phase(s).

4.2.1.4 Raman analysis

The graphitic carbon on the surface was further confirmed from the Raman spectra of the samples as shown in fig. 4.22.

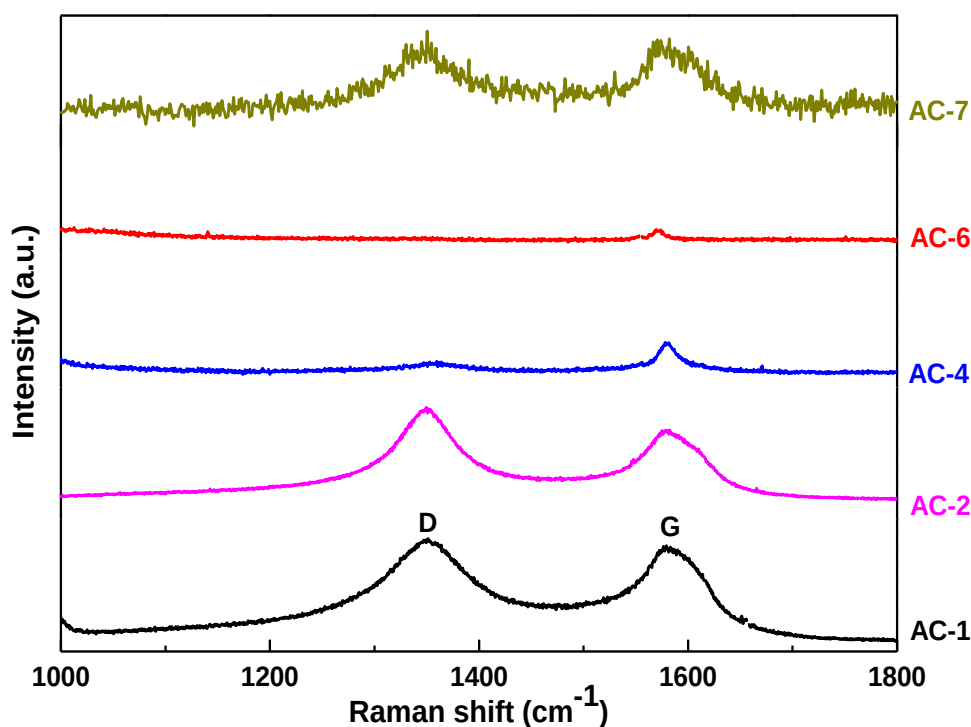


Figure 4.22: Raman spectra of the synthesized samples.

Raman spectra of the synthesized samples are characterized by two main bands called D (disordered) and G (graphitic) bands at ~ 1351 and 1578 cm^{-1} , respectively [11]. The G-band is associated with the first-order scattering of the E_{2g} mode of graphite and is related to the vibrations of sp^2 – bonded carbon atoms i.e. diagnostic of the structural order. The broad D-band is related to the structural defects or amorphous carbon or the incorporation of oxygen atoms within the graphite layer [11]. The intensity ratio of I_D/I_G is used to measure the content of defects in the sample. According to the calculated values (table 4.4), the highest I_D/I_G ratio is obtained for sample AC-2 (1.19), in which case, reaction time and amount of carbon is not sufficient enough to diffuse into the vanadium carbide (V_8C_7) and unreacted carbon remain as free carbon. It shows the presence of disorder in the structure and lower degree of graphitization. Further, I_D/I_G ratio decreases in sample AC-4 and AC-6 with

increasing carbon content. It is because of the diffusion of more carbon atoms into V_8C_7 . Similarly, in sample AC-6, formation of VC leads to the lesser yield of unreacted carbon and therefore, disorder. I_D/I_G ratio further increases in sample AC-7 because of the abrupt increase in the carbon content in this case.

Table 4.4: Calculated values of I_D/I_G ratio.

Sample	D-band (cm^{-1})	G-band (cm^{-1})	I_D/I_G ratio
AC-1	1351.1	1579.3	1.02
AC-2	1350.9	1579.5	1.19
AC-4	1357.7	1580.5	0.28
AC-6	1351.2	1571.5	0.17
AC-7	1350.0	1582.7	0.86

4.2.1.5 BET surface area and pore size distribution

In order to study the textural characteristics of synthesized samples, nitrogen adsorption/desorption measurements were carried out at 77 K. All adsorption/desorption curves are shown in fig. 4.23. Figure 4.23(a) shows the typical type IV isotherm profile. According to IUPAC classifications, this type of hysteresis loop corresponds to mesoporous materials [53-55]. The adsorption capacity increases with increasing relative pressures from 0.4 to 1.0. It directly indicates the presence of mesopores in the nanocomposite [54]. The shape of the hysteresis loops is of type H3 which is related to the slit-like pores present in the synthesized samples [55, 56]. The isotherms exhibit adsorption and desorption with hysteresis that shows capillary condensation and evaporation, which also indicate the hierarchical arrangement of the pores [57]. The highest surface area value is observed for sample AC-2 and it further decreases with the increase of the carbon content (AC-4 and AC-6). This is related to the diffusion of more carbon atoms into V_8C_7 which fills the pores and reduced the surface area. In case of sample AC-7 where surface area further increases because of the abrupt increase in the carbon content causes deposition of more carbon onto VC nanoparticles which results to form carbon coated VC (VC@C) as discussed earlier. These results are in good agreement with Raman results.

The pore size distribution (PSD) obtained from the desorption isotherm using Barrett-Joyner-Halenda (BJH) method is shown in fig. 4.23(b). The pore size distribution in all samples shows narrow peak distribution with mean pore diameter ranging from ~ 3 -3.9 nm which

indicates mesoporous structure. The PSD curve is shifted to the direction of larger mesopores because of the increase in the reaction time. The specific surface area, pore diameter and total pore volume of the synthesized samples are shown in table 4.5. Pore volume is maximum for sample AC-2 ($0.50 \text{ cm}^3 \text{ g}^{-1}$) and further it shows the similar trend as in case of surface area with the increase of carbon content.

The hierarchical arrangement of mesopores, high surface area and pore volume of the VC@C structure, indicates its better potential applications in electrocatalysis, energy storage and in sensors.

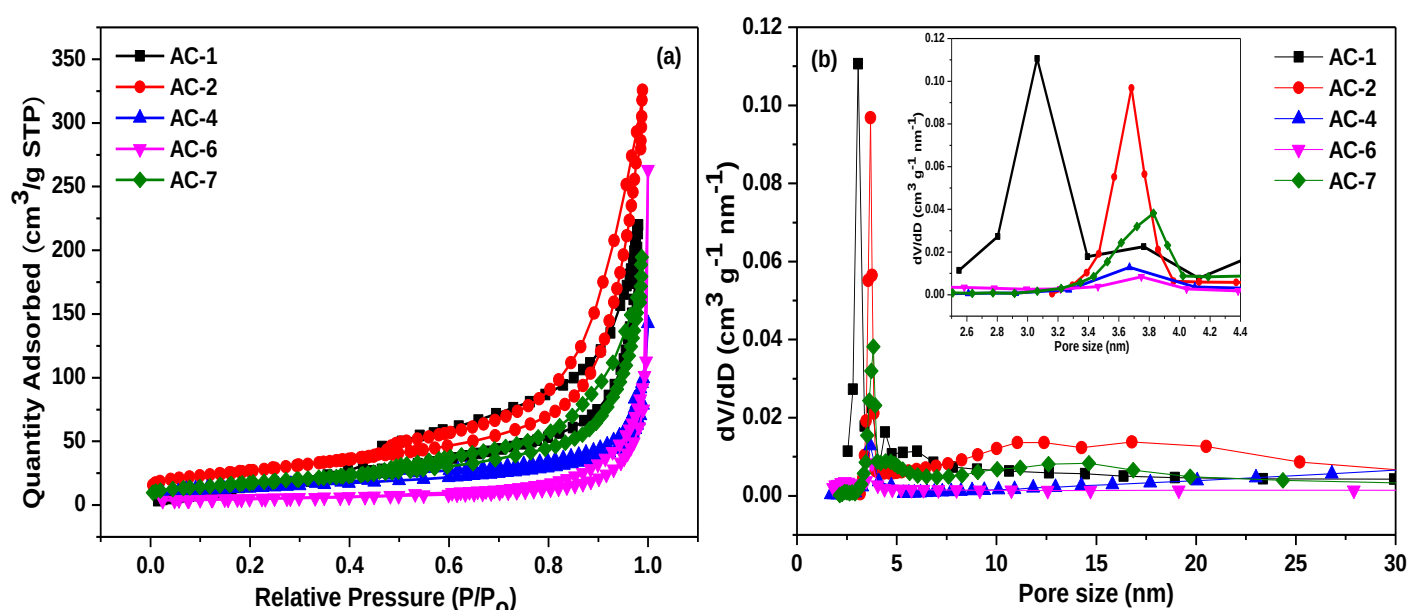


Figure 4.23: (a) N_2 adsorption-desorption isotherms and (b) Pore size distribution curve of the desorption branch of the synthesized samples.

Table 4.5: Texture properties of the synthesized samples.

Sample	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Peak pore size (nm)	Total pore volume ($\text{cm}^3 \text{ g}^{-1}$)
AC-1	75.1	3.06	0.34
AC-2	98.1	3.68	0.50
AC-4	48.1	3.66	0.15
AC-6	20.2	3.87	0.11
AC-7	62.5	3.83	0.30

4.2.2 Effect of temperature

From the above analysis, it is clear that M/C ratio have strong influence on the synthesis of vanadium carbide nanoparticles. Single phase of VC was obtained at M/C ratio of 1:20 at 800 °C. Therefore, keeping this ratio constant, effect of temperature was studied. Same proportion of starting materials V_2O_5 , Mg and acetone (1 g: 1.5 g: 20 mL) was put into stainless steel autoclave of 35 mL capacity and heated at different temperatures (500-800 °C). In the present set of experiments, all the initial ingredients were kept constant with variation in the reaction temperature only. The details are given in table 4.6.

Table 4.6: Initial ingredients and reaction parameters.

Sample	Reaction time (h)	Reaction Temperature (°C)
AT-1	20	500
AT-2	20	600
AT-3	20	700
AC-7	20	800

4.2.2.1 XRD analysis

Figure 4.24(b-e) shows the XRD pattern of the samples synthesized at different temperatures using V_2O_5 as vanadium precursor. The XRD pattern clearly shows the presence of different phases as V_2O_3 , C along with VC. Figure 4.24(a) shows the XRD pattern of V_2O_5 precursor of particle size ~ 50 nm. In sample AT-1, where reaction temperature was 500 °C, reduction of V_2O_5 occurs which otherwise starts at higher temperature (> 700 °C) [58, 59] and gives lower oxide (V_2O_3) of particle size ~ 35 nm (fig. 4.24(b)). All the diffraction peaks at 500 °C corresponds to V_2O_3 only.

It is observed that there is complete reduction of V_2O_5 at this temperature. But the absence of any carbide peak shows that the temperature is not high enough for the diffusion of carbon to occur to form vanadium carbide. With the increase of the reaction temperature to 600 °C in sample AT-2, the pressure continues to increase within the system and carbon started to diffuse inside the V_2O_3 lattice by fragmenting it into smaller size. The variation of pressure with increasing temperature is shown in fig. 4.25. It is observed that with increasing temperature, the intensity of V_2O_3 peaks started to decrease with simultaneous increase in VC peaks.

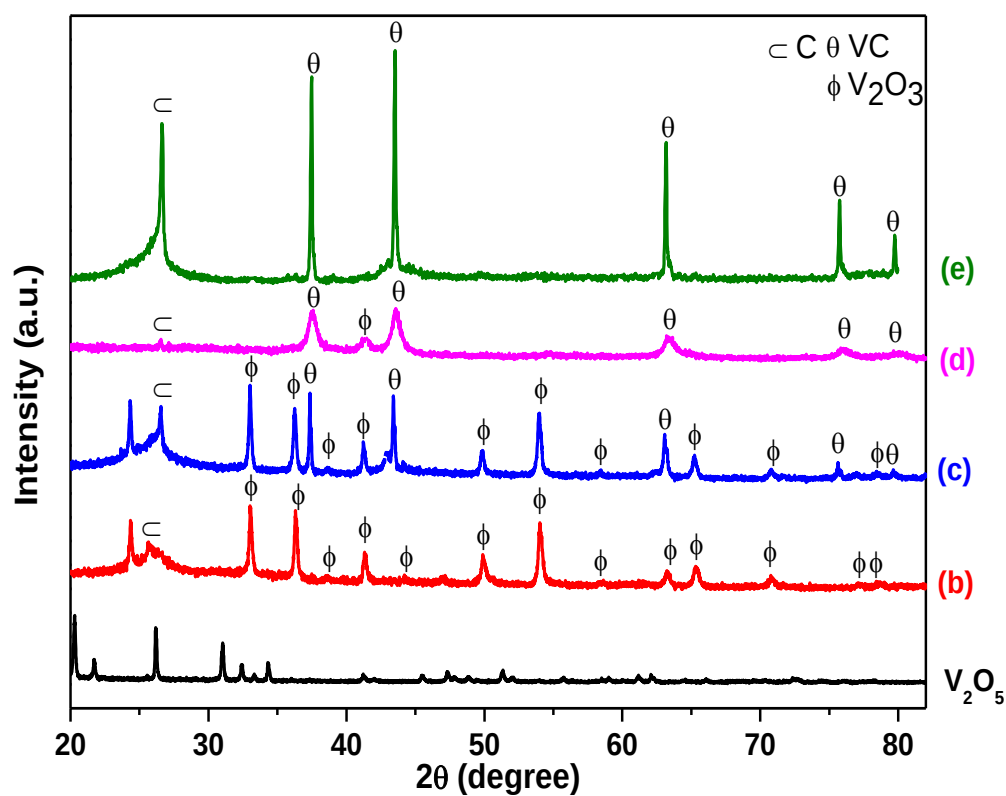


Figure 4.24: XRD pattern of samples (a) V_2O_5 (b) AT-1 (c) AT-2 (d) AT-3 and (e) AC-7.

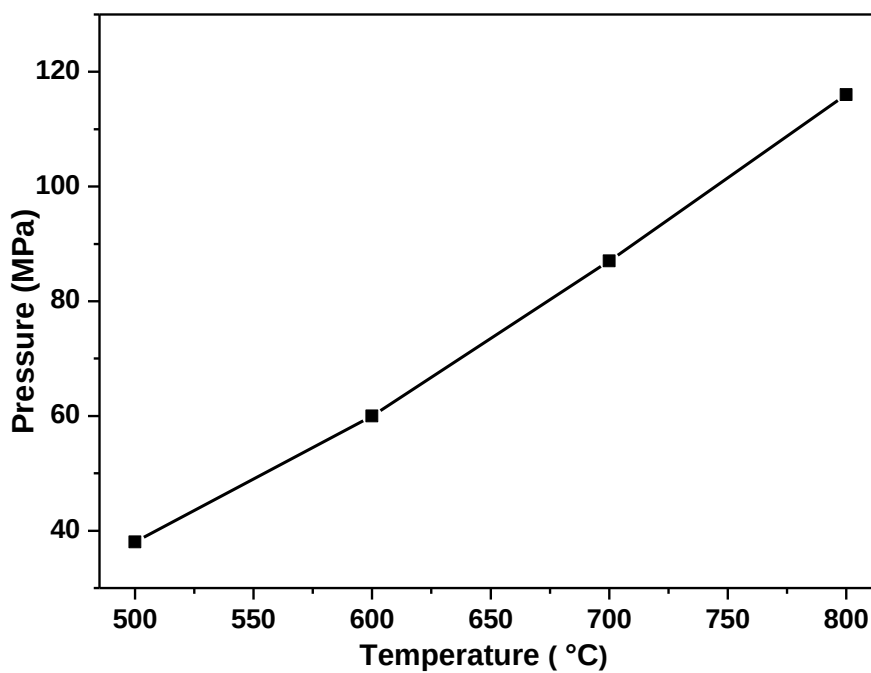


Figure 4.25: Graph of pressure generated with increasing temperature (estimated using equation 4.1).

The reduction process leads to transformation of V_2O_5 to V_2O_3 followed by carburization to VC phase (AT-2 & AT-3). Figure 4.24 (c) shows that all the five diffraction peaks corresponds to VC phase for the planes (111), (200), (220), (311) and (222) (ICDD Card No. 01 – 073 – 0476) at 600 °C. However, the presence of V_2O_3 peaks at 600 °C (AT-2) indicates that the temperature is not high enough to convert the entire V_2O_3 into VC. In case of sample AT-3, where reaction temperature is increased to 700 °C, the volume fraction of V_2O_3 phase remained only 10% (table 4.7). At the reaction temperature of 800 °C, a stage is reached where entire V_2O_3 is converted into VC with excess carbon. A substantial increase in the intensity of VC peaks is observed at this temperature (fig. 4.24(e)).

The crystallite size and strain produced in the synthesized samples are shown in table 4.7. The observed positive value of strain in sample AT-2 indicated the tensile strain in the system, which is because of the transformation of lower ionic radii ion (0.54 nm) V^{5+} to higher ionic radii ion (0.58 nm) V^{4+} during the reduction and carburization of V_2O_5 to VC [40]. With the increased reaction temperature to 700 °C (AT-3), the diffusion of more carbon atoms into VC lattice increases tensile strain. Also, the crystal defects which arise in the structure during cooling, produces tensile strain in the lattice [41] and size of VC nanoparticles decreased to 30 nm. At 800 °C (as discussed in section 4.2.1.1), system attains stability as is also clear from the negative value of strain (compressive strain) and increased particle size.

From the XRD analysis, it is clear that reaction temperature affects the reduction/carburization process and also the particle size. The variation in particle size and volume fraction of obtained phases is shown in table 4.7.

Table 4.7: Crystallite size of vanadium carbide nanoparticles, strain produced and volume fraction of the obtained phases.

Sample	Temperature (°C)	Particle size (nm)	Strain (*10 ⁻³)	Volume fraction of phases (%)		
				VC	V_2O_3	C
AT-1	500	-----	-----	-----	94	6
AT-2	600	50	0.877	35	59	6
AT-3	700	30	5.11	86	10	4
AC-7	800	56	-0.27	97.5	-----	2.5

4.2.2.2 Microstructure analysis

FESEM micrographs of sample AT-3 and AC-7 obtained at the reaction temperature of 700 and 800 °C, respectively show the presence of VC nanoparticles engulfed by carbon shell (fig. 4.26 and 4.27).

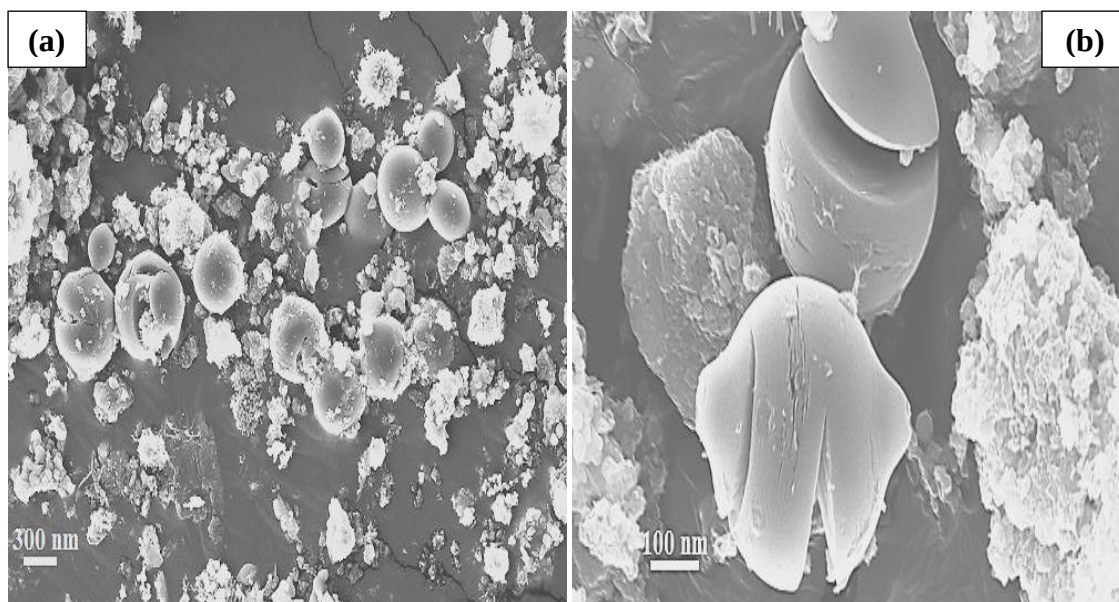


Figure 4.26: FESEM images of sample AT-3 (700 °C) showing the core-shell structure of VC nanoparticles.

These figures show the core-shell morphology of synthesized VC coated by carbon shell. The formation mechanism of these core-shell structures will be explained in the next sections.

TEM analysis was done for the selected samples in which VC was present. TEM images of all the samples show the presence of excess carbon that exists in the reaction product. But the form of carbon is different in all these samples. TEM image of sample AT-2 shows different features, in which reaction temperature was 600 °C (fig. 4.28). It is clear from our previous results that decomposition of acetone at high temperature (600 °C) generates carbon in the form of spheres (fig. 4.28(a)). These carbon spheres rearrange themselves with the rise in temperature and time and facilitate the formation of bamboo-like tubular structures creating knots at each end (fig. 4.28(b)). These knots with time get elongated and leads to the formation of carbon nanotubes (CNTs) (fig. 4.28(c)). Oxide particle got entrapped in these CNTs which can be seen in fig. 4.28(d). In fig. 4.28(d), vanadium oxide (V_2O_3) particles of spherical morphology are engulfed by carbon (shown by arrow).

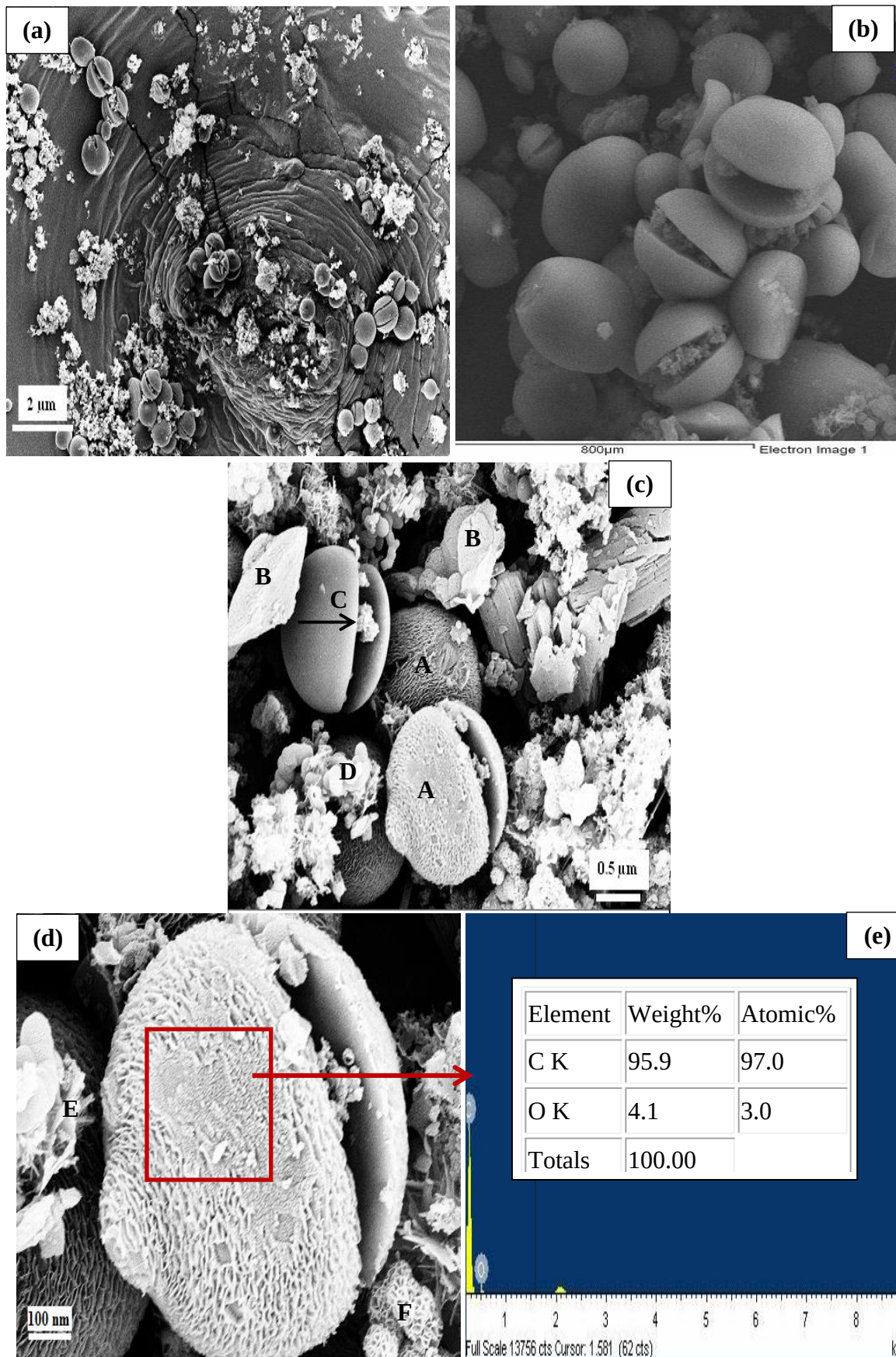


Figure 4.27: (a-d) FESEM images for sample AC-7 (800 °C) showing core-shell structure of VC particles and **(e)** EDS spectra of marked portion in **(d)**.

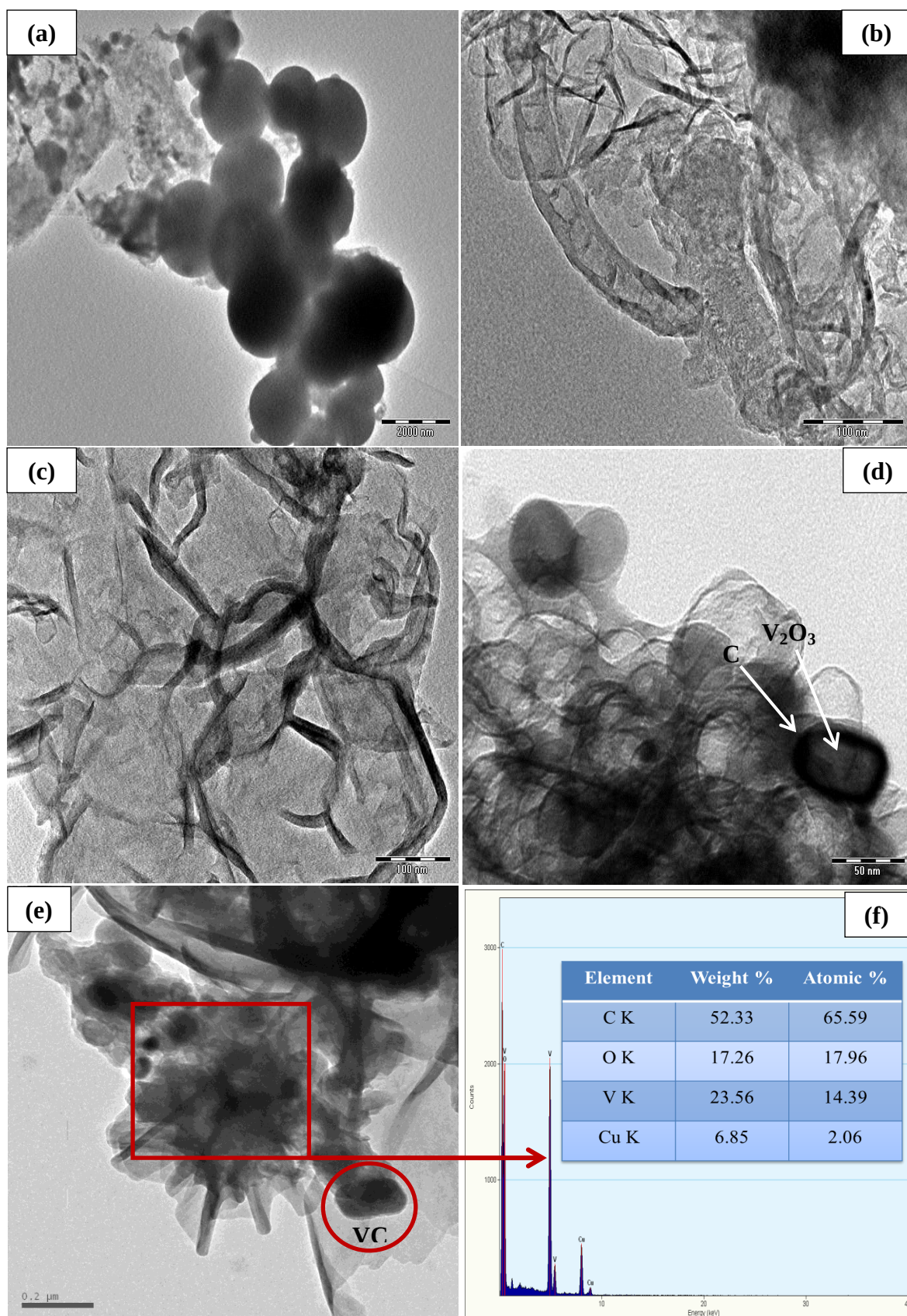


Figure 4.28: TEM micrographs of sample AT-2 (600 °C) showing presence of different features.

With time, more and more carbon starts to deposit on the oxide surface (V_2O_3) that leads to the formation of carbide. This theory is based on the fact that vanadium has strong affinity for carbon and therefore, carbon starts diffusing inside the lattice from the surface to the inner core and reduces the V_2O_3 and carburizes it into VC. In fig. 4.28(e), one can see the faceted morphology of VC particles (marked in circle) also. Therefore, at 600 °C, formation of VC nanoparticles has started along with mixed phase as is also clear from XRD results. This reduction/carburization process by carbon further increased in sample AT-3, where reaction temperature has been increased to 700 °C and more and more carbon started to diffuse inside the V_2O_3 lattice and carburizes it.

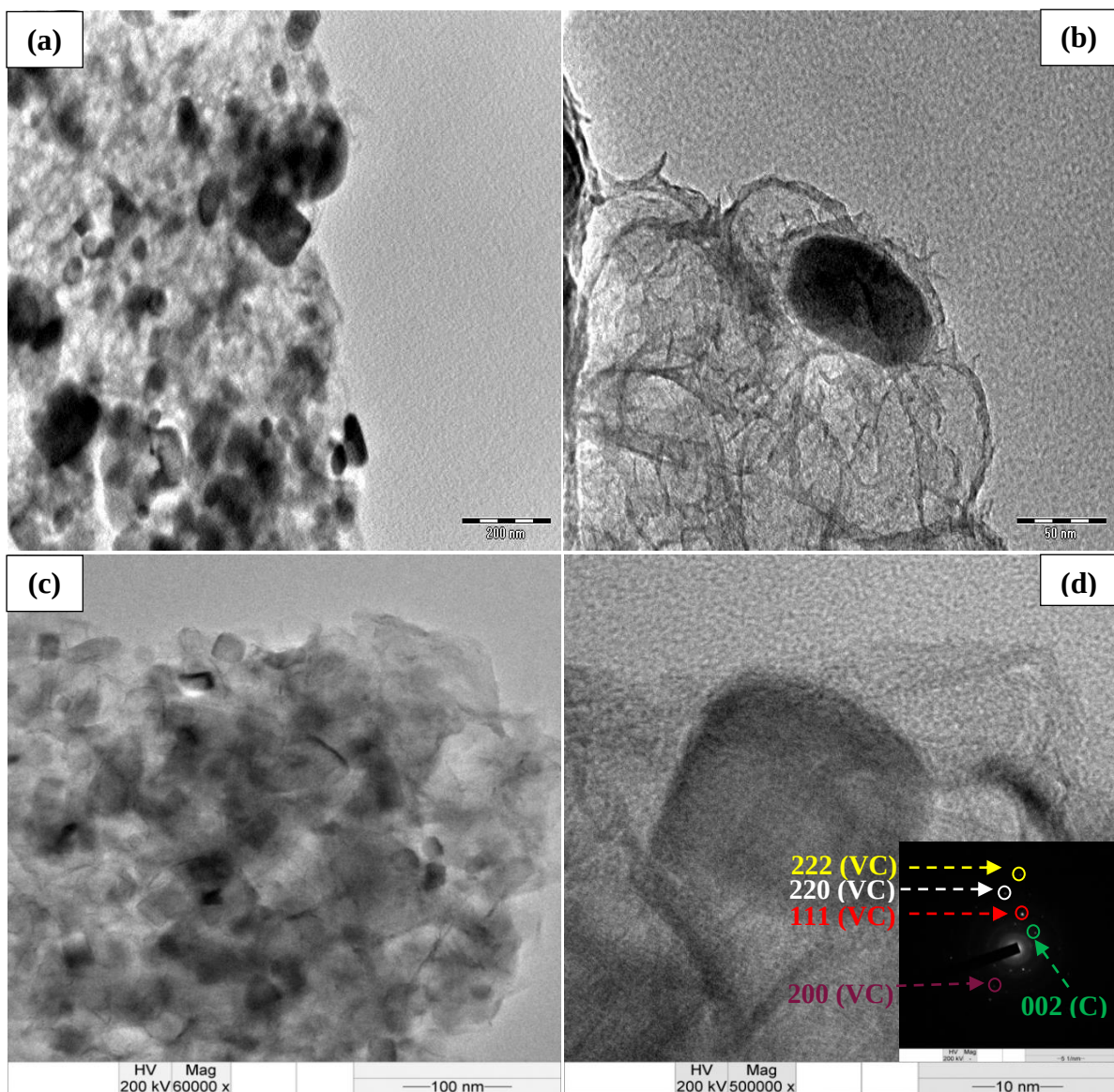


Figure 4.29: TEM micrographs of sample AT-3 (700 °C) showing the VC particles embedded in carbon matrix.

The faceted VC particles embedded in carbon layers can be seen in fig. 4.29. The SAED pattern shown in the inset of fig. 4.29(d) indexed with planes of VC (ICDD Card No. 01-073-0476) and (002) plane of carbon (ICDD Card No. 00-041-1487).

In TEM images of sample AC-7 synthesized at 800 °C, one can see the complete faceted morphology of VC nanoparticles covered by carbon layers (fig. 4.20). Since the growth of carbides occurs as faceted type to have high stability as predicted by Jackson and Hunt model [39, 60], these structures get aligned because of high surface area and acquire large facets. However, with due course of time or temperature, all fine crystal structures existing within the boundary merge with each other and finally grow as single particle as shown in fig. 4.20(a) where a faceted morphology of fully grown crystal embedded in the carbon matrix can be seen. The HRTEM image reveals that carbon shell contains about 20-22 layers with an average thickness of 6-7 nm containing fully grown core particle with an average size of 32 nm (fig. 4.20(b)). The D-spacing (0.34 nm) of these layers corresponds to the (002) plane of the graphitic carbon and that of the core particle corresponds to the (200) plane of VC. However, the carbon is not purely graphitic. It contains some amorphous character as has been marked as a circle in fig. 4.20(b). The reason of it might be the presence of some oxygen atoms in the graphite layer which creates defects in the structure. This observation is well in agreement with the EDS analysis (shown in fig. 4.27(e)).

Therefore, TEM analysis shows that the increasing temperature affects the reduction/carburization process as well as the amount of carbon coating on the VC nanoparticles.

4.2.2.3 TG/DTA analysis

In order to check the effect of synthesis temperature on the thermal stability of the synthesized samples using constant amount of acetone (20 mL), TG/DTA was done in air and the result is shown in fig. 4.30.

Similar to our earlier discussions, it has been observed from the TGA curves that there is a continuous decrease in the sample weight during heating at around 300-350 °C. It arises due to the oxidation of available free amorphous carbon. The sudden weight loss after 350 °C is due to the oxidation of outer graphitic carbon layer of VC and VC nano particles which after the reaction with oxygen forms CO_x ($x=1, 2$) [47].

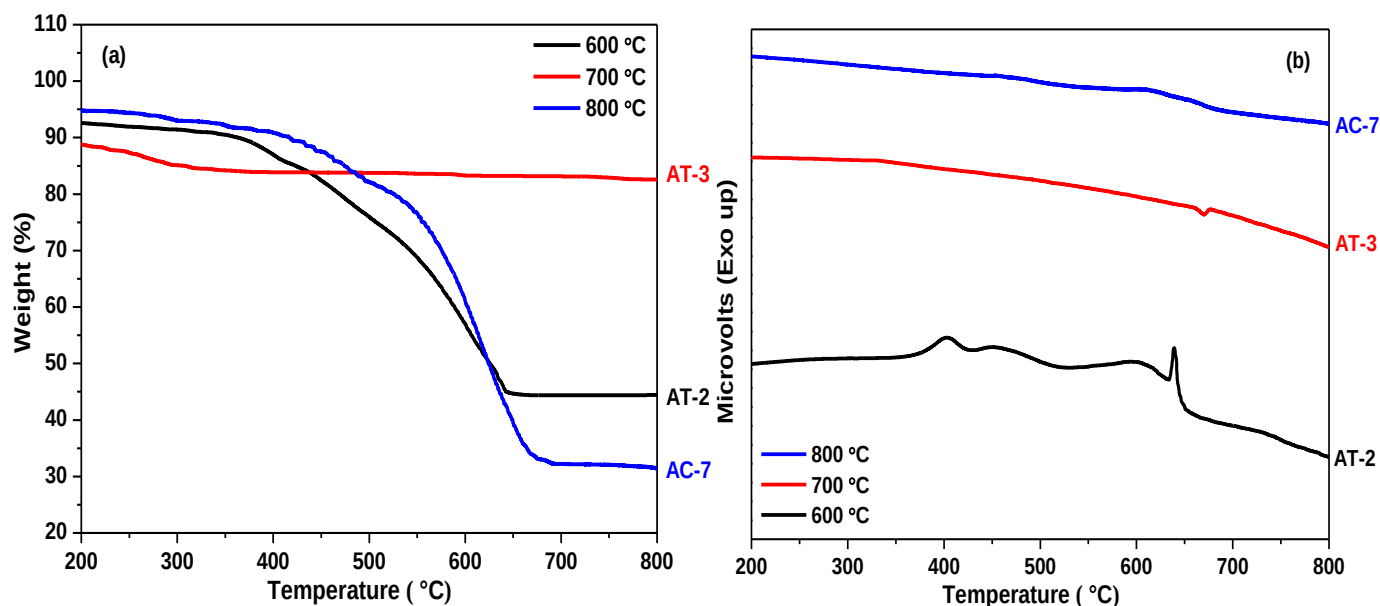


Figure 4.30: (a) TGA and (b) DTA plots of samples synthesized at different temperatures.

As observed in fig. 4.30(b), the exothermic peaks in the range of 400-600 °C arise during the heating in sample synthesized at 600 °C corresponds to the oxidation of different forms of carbon [39]. These results are in good agreement with TEM results (fig. 4.28). On the other hand, formation of very fine carbon in the sample synthesized at 700 °C promotes the oxidation of sample at lower temperature, which indicates its lower thermal stability. The overall minimum weight loss at higher temperature may be due to the presence of oxide content in the sample synthesized at 700 °C which is also confirmed from XRD analysis. However, because of the graphitization of carbon at higher temperature and its coating on the VC nano particles, the onset temperature shifts to higher side for sample obtained at 800 °C. The endothermic peak in the DTA curve at ~ 670 °C in the sample AT-3 corresponds to the melting of V_2O_5 formed as a result of oxidation of VC particles or the oxidation of remaining lower oxide (V_2O_3) as detected by XRD [52].

4.2.2.4 Raman analysis

Raman spectra of the synthesized samples are shown in fig. 4.31. It exhibits two main bands called D (disordered) and G (graphitic) bands at ~ 1349 and 1590 cm^{-1} , respectively. The G-band is related to the vibrations of sp^2 – bonded carbon atoms i.e. diagnostic of the structural order. The proportional values of I_D/I_G are calculated to estimate the defect ratio in the synthesized samples and results are shown in table 4.8.

According to the calculated values, the I_D/I_G ratio decreases with increasing temperature from 600 to 700 °C for sample AT-3. It is attributed to the graphitization of carbon at high temperatures i.e. conversion of sp^3 – to sp^2 – bonded carbon. Moreover, diffusion of more carbon atoms into VC decreases the yield of unreacted carbon at high temperatures. It shows the presence of order in the structure and higher degree of graphitization with the increase of temperature which is in good agreement with the XRD and TEM results. Also, I_D/I_G ratio decreases with increasing reaction temperature (sample AT-3). I_D/I_G ratio further increases in sample AC-7 at the reaction temperature of 800 °C. It might be because of the disordered carbon or the presence of oxygen or hydrogen atoms into the graphite layer [14, 15].

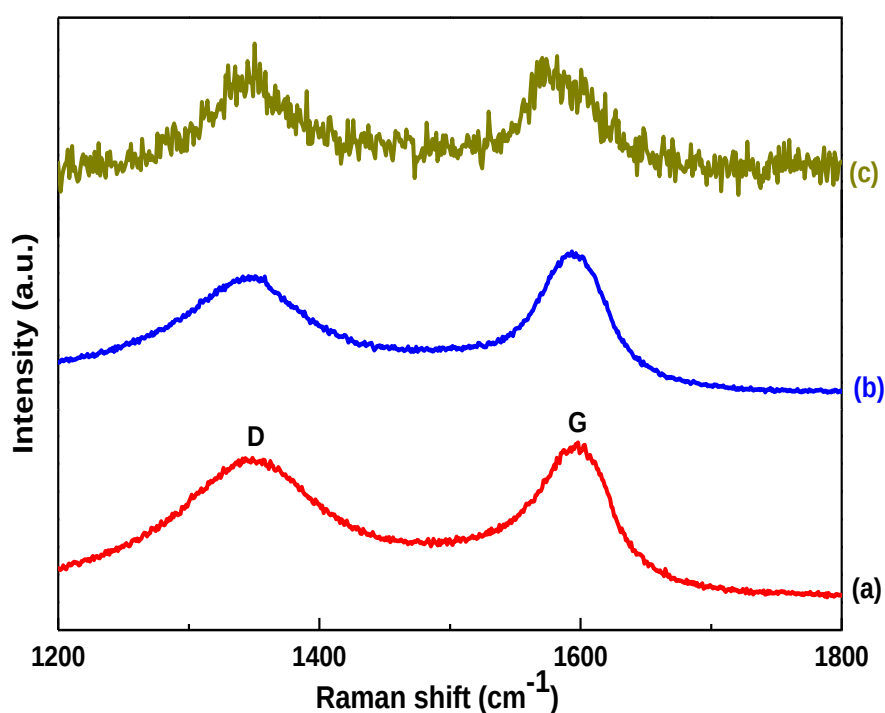


Figure 4.31: Raman spectra of sample (a) AT-2 (b) AT-3 and (c) AC-7.

Table 4.8: Calculated values of I_D/I_G ratio.

Sample	D-band (cm^{-1})	G-band (cm^{-1})	I_D/I_G ratio
AT-2	1349.1	1592.8	0.87
AT-3	1343.3	1591.3	0.63
AC-7	1350.0	1582.7	0.86

4.2.2.5 BET surface area and pore size distribution

Figure 4.32(a) shows the nitrogen adsorption/desorption measurements of the samples obtained at different temperatures. All adsorption/desorption curves show typical type IV hysteresis in the range of 0.4 to 1.0 P/P_0 indicating the presence of mesopores [54]. The shape of the hysteresis loops is of type H3 which is related to the slit-like pores present in the synthesized samples [56]. The PSD obtained from the desorption isotherm using BJH method is shown in fig. 4.32(b).

The isotherms and PSD curve show that reaction temperature has remarkable effect on the surface area and pore volume of the synthesized product. PSD curve of all samples shows narrow peak distribution with mean pore diameter ranging from 3.5-3.9 nm which indicates mesoporous structure. It is observed that the N_2 adsorption capacity increases with the increase of reaction temperature. The lesser surface area and pore volume is observed for the sample AT-2 at 600 °C whereas, highest is exhibited by the sample AC-7 at 800 °C (table 4.9). This is related to the collapse of the micropore wall and development of mesopores at higher temperature [54, 61]. This is also confirmed from the shifting of pore diameter at higher side with the increase of the reaction temperature (inset of fig. 4.32(b)). Formation of large mesopores at higher temperature is directly related to the deposition of more carbon during the carburization process [61].

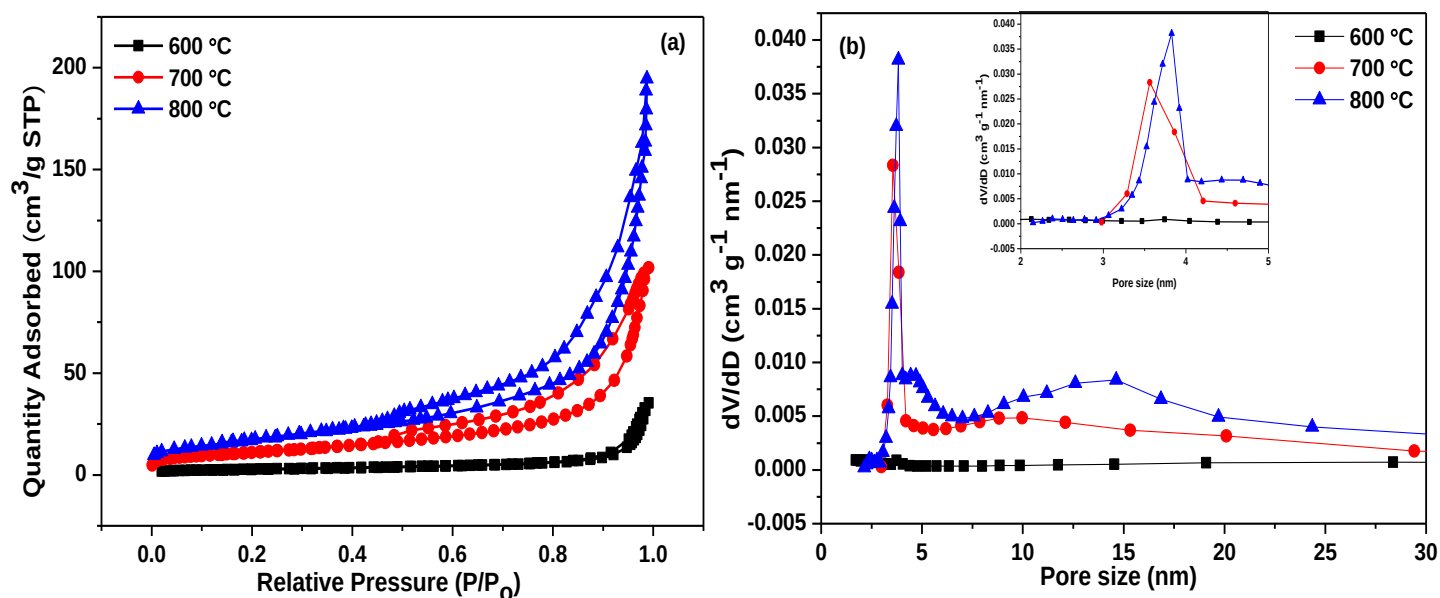


Figure 4.32: (a) N_2 adsorption-desorption isotherms and (b) Pore size distribution curve of the desorption branch of samples AT-2, AT-3 and AC-7.

Table 4.9: Texture properties of the synthesized samples.

Sample	Temperature (°C)	BET surface area (m ² g ⁻¹)	Peak pore size (nm)	Total Pore Volume (cm ³ g ⁻¹)
AT-2	600	9.9	-----	0.05
AT-3	700	39.4	3.59	0.15
AC-7	800	62.5	3.83	0.30

4.2.3 Effect of time

From the above analysis, it is clear that the optimum condition for the synthesis of desired product is for sample AC-7. In order to study the effect of time on the synthesis of nano VC, reaction time was varied with a constant proportion of V₂O₅, Mg and acetone at constant temperature (800 °C). The variation in the reaction time at constant temperature lead to the formation of different phases, which gives an idea about the reaction mechanism of the reduction/carburization processes taking place inside the autoclave. Appropriate amount of starting materials were put into stainless steel autoclave of 35 mL capacity and heated at different time durations. The initial ingredients, reaction temperature and time are given in table 4.10.

Table 4.10: Initial ingredients and reaction parameters.

Sample	Reaction time (h)	Reaction Temperature (°C)
At-1	5	800
At-2	10	800
At-3	15	800
AC-7	20	800
At-4	25	800

4.2.3.1 XRD analysis

In order to obtain the reaction mechanism, XRD pattern of the sample heated for different time intervals before acid treatment is shown in fig. 4.33. It shows the presence of VC, VO₂, V₂O₃, V₂C, MgO and C phases. From the XRD patterns, it is clear that reduction of V₂O₅ is not a direct process. It follows the multi-steps as per the following equation [62]:



Because of the continuous reduction phenomenon at high pressure, other intermediate phases do not appear in this reaction. There is some amount of VO_2 that remained in the reaction which could not be reduced to V_2O_3 . In order to remove the small impurities and by-products that are produced in the reduction process, all samples were acid treated with (1:1) HCl. Figure 4.34 shows the XRD pattern of the samples after acid treatment. It was observed that the intensity of V_2O_3 peaks got further increased after acid treatment. It might be possible that during acid treatment, the remained V^{4+} is further reduced to lower oxides (V^{3+}) which is further confirmed by changes in color of the samples as shown in fig. 4.35.

It is clear from fig. 4.34(a) that V_2O_5 reduced to V_2O_3 after 5 h and also carburized to some extent. There are only small peaks of VC showing the initiation of carburization after 5 h. With the increase in reaction time to 10 h, there is no noticeable change in the formation of VC and further reduction of lower oxides. The percentage of VC has increased with the increase in reaction time to 15 h, where the intensity of VC peaks increases and V_2O_3 decreases. However, the presence of V_2O_3 peaks showed that reaction time is not sufficient enough to convert entire V_2O_3 to VC. With the further increase in reaction time to 20 h, a stage is reached where entire V_2O_3 is converted to VC phase with no other impurities (fig. 4.34(d)). There are five diffraction peaks observed in VC phase for the planes (111), (200), (220), (311) and (222) (ICDD Card No. 01 – 073 – 0476). These peaks belong to cubic structure with the space group Fm-3m [63]. Instead of VC peaks, a broadened crystalline peak at 26.5° corresponds to the graphitic carbon (ICDD Card No. 00 – 041 – 1487). These results clearly showed that the composite of vanadium carbide nanoparticles on carbon matrix have been successfully synthesized with the optimized reaction conditions. With the further increase of reaction time to 25 h, intensity of V_2O_3 peaks further increased with decreased intensity of VC. Also, another extra peak of V_2C appeared in the system, which shows that with the increase of reaction time, a reverse reaction occurs in which VC is converted to V, which reacts with other VC particles to form V_2C phase and also V_2O_3 [39]. Therefore, XRD analysis indicates that the formation of VC@C is a time-dependent phenomenon where the increase of reaction time facilitates the reduction phenomenon and hence formation of VC. Crystallite size and strain analysis of the sample are done using W-H plot analysis and results are shown in table 4.11. The negative value of the strain corresponds to compressive strain in VC lattice, which is due to some interstitial sites occupied by the oxygen instead of carbon [42]. It decreases with increasing the reaction time from 15 to 20 h showing the stability of the obtained product.

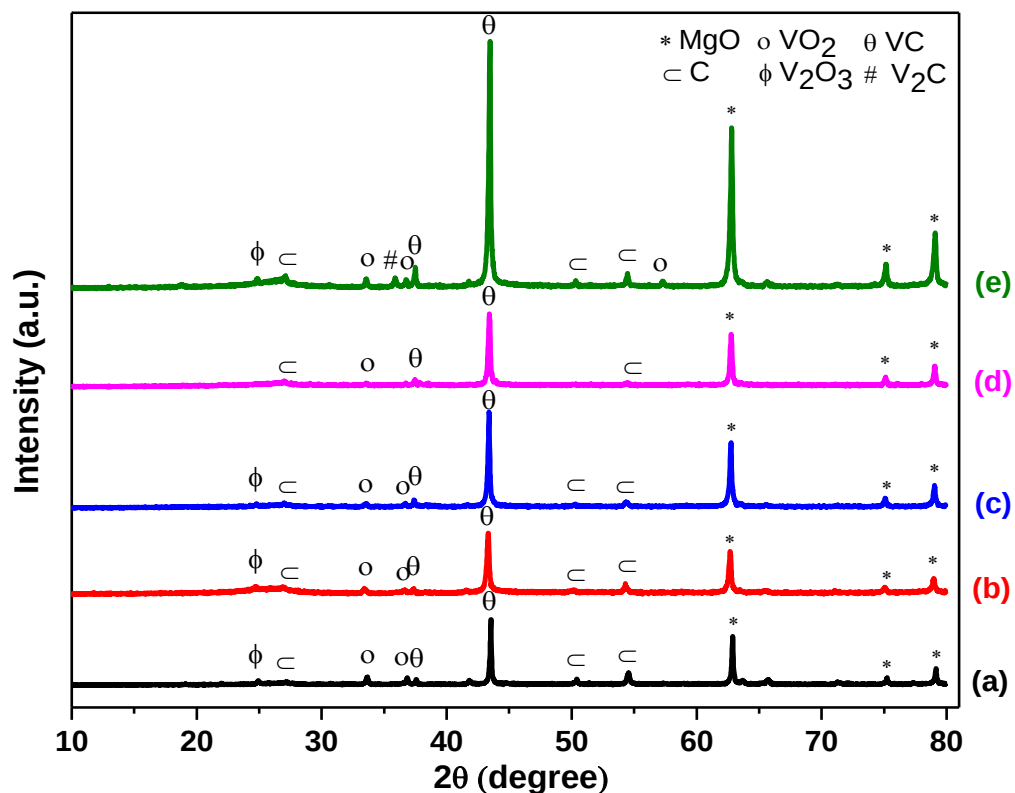


Figure 4.33: XRD pattern of samples (a) At-1 (b) At-2 (c) At-3 (d) AC-7 and (e) At-4 before acid treatment.

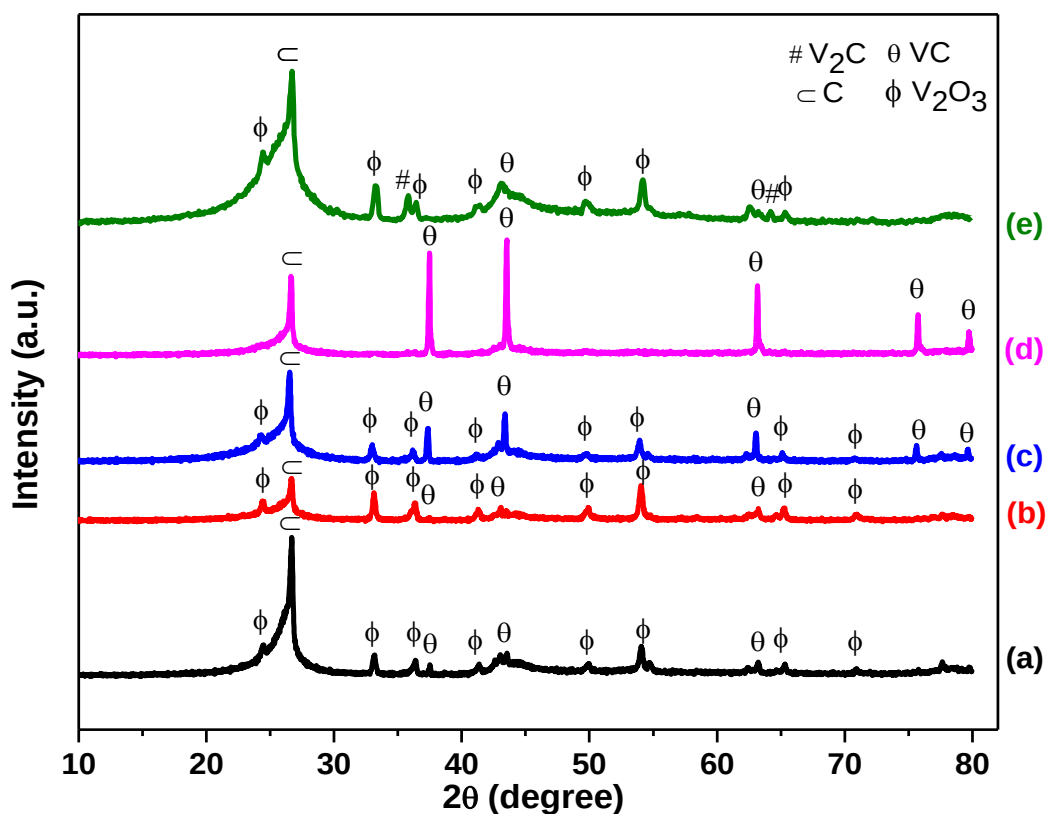


Figure 4.34: XRD pattern of samples (a) At-1 (b) At-2 (c) At-3 (d) AC-7 and (e) At-4 after acid treatment.

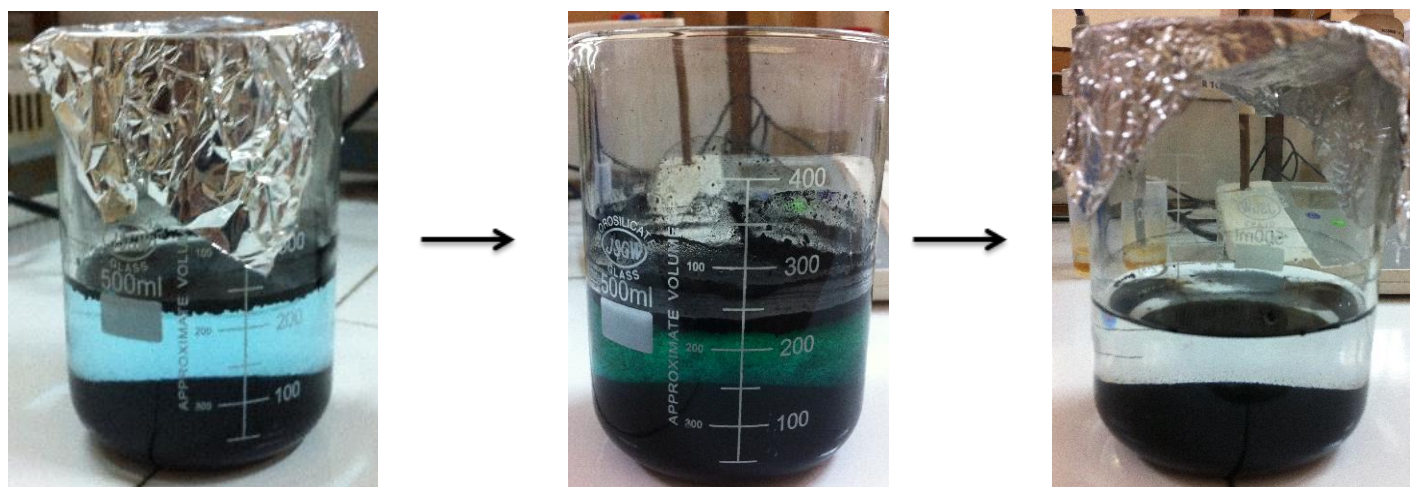


Figure 4.35: Change in colour of the sample during acid treatment.

Table 4.11: Crystallite size of VC nanoparticles, strain produced and volume fraction of the obtained phases.

Sample	Reaction time (h)	Particle size (nm)	Strain ($\times 10^{-3}$)	Volume fraction of phases (%)			
				VC	V ₂ O ₃	V ₂ C	C
At-1	5	56	-----	7.5	44.5	-----	48
At-2	10	44	-----	12.5	69	-----	18.5
At-3	15	47	-0.651	51.2	21.8	-----	27
AC-7	20	56	-0.27	97.5	-----	-----	2.5
At-4	25	3	-----	11	38.1	8.7	42.2

4.2.3.2 Microstructure analysis

Microstructural analysis of the selected samples was done in which VC was formed. FESEM of the sample obtained with 20 h (AC-7) is shown in fig. 4.27. Figure 4.27(a) shows two distinct morphological features. One corresponds to agglomerated nanoparticles and other appears like cocoon or eggs. Its feature is similar to the onion also. The important feature observed is that most of these structures are fractured. Careful examination of the surface reveals the growth of cellular structure on the surface of these spherical particles which in some cases are detached also.

In order to understand the reaction mechanism for the formation of these structures, it is essential to consider the various reactions that take place during heating and cooling of the

autoclave. Formation mechanism of m-VC@C involves the solid-state reaction by the interface reaction between vanadium oxide and carbon. Being a highly reactive substance, Mg takes oxygen from the reaction atmosphere of the autoclave and form MgO, which acts as a catalyst for further reaction [3].

Decomposition of acetone occurs in the presence of MgO generating carbon, oxygen, hydrogen ions/atoms, along with $\text{CH}_3\text{-CO}$, CH_3 and CO radicals [15, 64].



Further, these two methyl radicals combine and form methane, ethane and hydrogen. At a temperature above 400 °C, decomposition of hydrocarbon ethane leads to the formation of carbon and hydrogen [65].



Because of these gases, vigorous chemical reactions occur which further increases the local temperature of the system and facilitate the reduction process even at a low temperature. Consequently, the pressure inside the system also increases with temperature as shown in fig. 4.25. At 800 °C the value of pressure generated is 116 MPa. Being the lighter element and of the high diffusion coefficient of hydrogen, it first penetrates inside V_2O_5 and reduces it into VO_2 followed by the fragmentation to small pieces [47, 66]. This fragmentation process continues till the entire V_2O_5 is converted to VO_2 . Moreover, CO and H_2 so generated will always act as reducing agents. Under the influence of high pressure and active catalyst, reduction of V_2O_5 occurs at a low temperature in between 400-500 °C which generally occurs at about 700 °C. Because of the high surface area of these fragmented particles, they further react with unreacted Mg to form lower intermediate oxides [47, 63] according to the following equation:



$$\Delta\text{H} = -870.68 \text{ kJ/mole}, \Delta\text{G} = -912.27 \text{ kJ/mole}$$

Thermodynamically, the negative value of ΔH and ΔG shows that the reaction is spontaneous and exothermic due to which reaction occurs at a faster rate than before. So, these intermediate lower valence metal oxides play an important role in further propagating the reaction by reducing the synthesis temperature. These lower valence metal oxides have

defective sites which act as active centres for the nucleation and growth of carbide by the adsorption of carbon on its surface, and encapsulate it.

It is also found from literature that oxidation – reduction reaction between V_2O_3 and carbon takes place at ~ 1000 °C [58, 59], which occur at the lower temperature in our case because of high pressure inside the autoclave. The V_2O_3 thus formed is further reduced by carbon as per the following equation:



In the present process, inter-diffusion is a dominating factor, and carbon diffuses from high to low concentration leading to the reduction of V_2O_3 to V and its further carburization to VC. This would result in the formation of VC. Formation of carbide thus acts as a driving force for the inter-diffusion of carbon on its surface by blocking the further diffusion of carbon after saturation [67]. Thus excess carbon layers tend to grow on the saturated carbide core and finally form VC@C composite as marked as A in fig. 4.27(c). During the reduction process because of variation in thermal expansion, this layer chip out as marked as B in fig. 4.27(c) and consequently, the shell cracks. Also, gases like H_2 that are entrapped inside the shell combine with oxygen and create steam, which causes stress and expands at high temperature and pressure, and helps in shell cracking. The onion like structure grows on the top layer because the entire particle is under agitation in the autoclave which keeps them rotating like spinning top. After cracking, the encapsulated VC comes out from the shell as marked as C in fig. 4.27(c). This process of reduction and carburization continues till it acquires a critical size as marked as D in fig. 4.27(c). The nano VC so produced will have both types of morphology as spherical and also as rod like marked as D and E in fig. 4.27(c) and 4.27(d), respectively. Since the surface area of nano VC rod is high, these may be further associate with each other and form dahlia like mesoporous network with average size of 40-50 nm as has been marked as F in fig. 4.27(d). These observations indicate that the transition metal compounds not only help in the graphitization of carbon but also act as a catalyst for the formation of mesoporous structure [68].

EDS analysis on the surface of the shell as well as on other areas marked in fig. 4.27 and 4.36 has been done. The analysis indicates that spherical shells (A) are of carbon containing little oxygen (3%) as shown in fig. 4.27(e). Other areas (E & F) show the presence of V and C both. Apart from V and C, little amount of oxygen is also present. EDS analysis and X-ray dot mapping of the marked area in fig. 4.36(a) is shown in fig. 4.36(b-d). It shows the presence of vanadium and carbon almost in an equal amount.

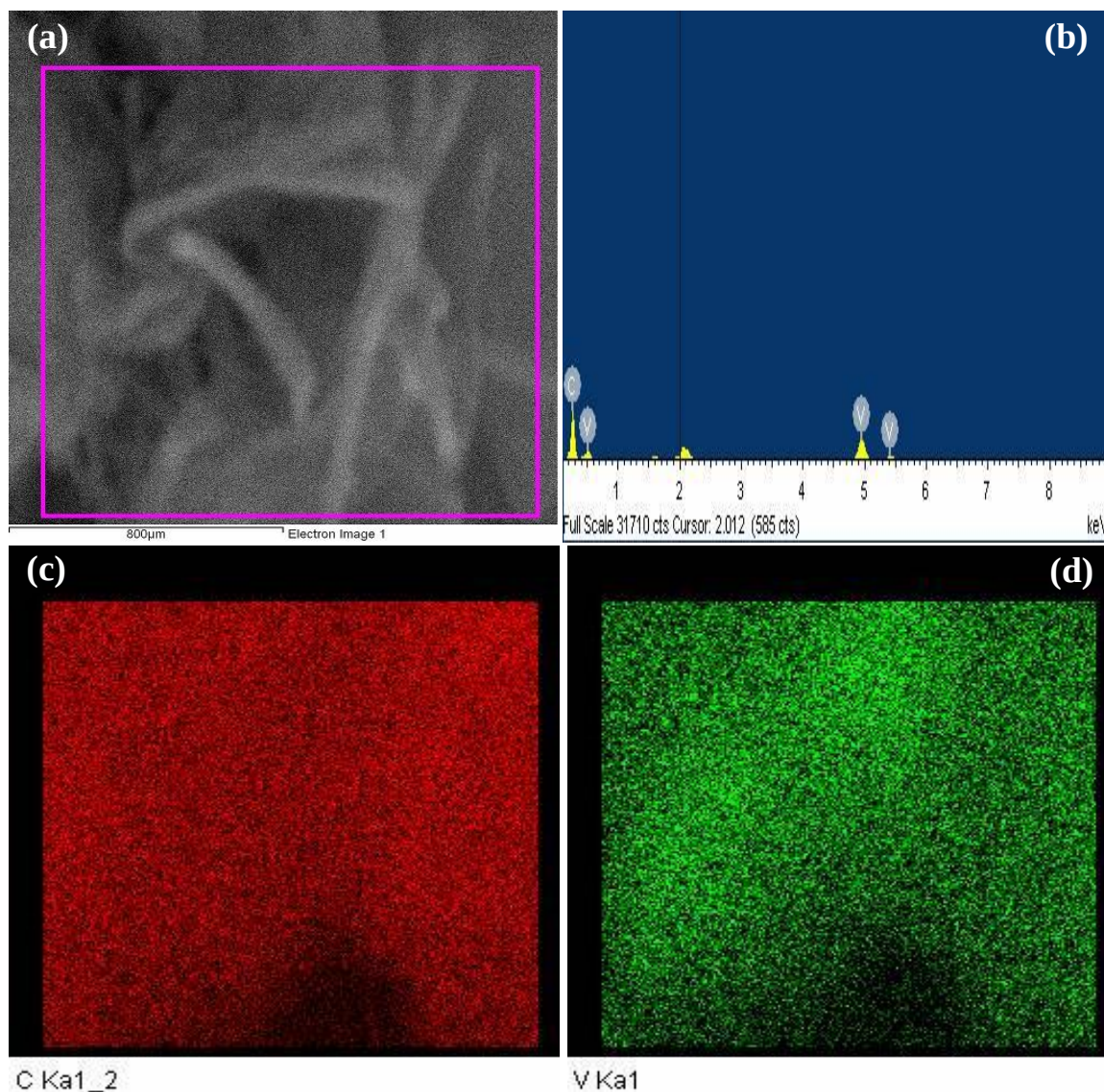


Figure 4.36: (a & b) EDX spectra and (c & d) X-ray dot mapping of the marked area of sample AC-7.

Figure 4.37 shows the effect of reaction time on the morphology of the obtained product. Figure 4.37(a) shows the formation of vanadium carbide having spherical morphology encapsulated by amorphous carbon. With the increase of the reaction time to 15 h, particle morphology was observed to change from spherical to faceted type as shown by arrows in fig. 4.37(b). However, it has not acquired full faceted structure. Also, the conversion of amorphous carbon to crystalline carbon has been observed with the increasing reaction time. HRTEM image of one of the particles of fig. 4.37(b) is shown in fig. 4.37(c). It shows the presence of vanadium carbide coated by carbon layers. However, the outer carbon is still amorphous. With the further increase in the reaction time to 20 h, the structure of the

vanadium carbide becomes completely faceted and the encapsulated carbon changes from amorphous to crystalline carbon as shown in fig. 4.20.

Two type of morphology have been detected in TEM micrographs of sample AC-7 shown in fig. 4.20 and 4.38. Figure 4.38(a) shows the rod like morphology of the obtained sample coated by carbon layer. Dark contrast shown in fig. 4.38(a) corresponds to the VC and that of light contrast corresponds to carbon. Figure 4.38(b) shows the corresponding dark field fringe image. The corresponding selective area electron diffraction (SAED) pattern is also shown in the inset of fig. 4.38(b) and confirms the presence of VC.

The structural features reveal that this entire process is very fast and occurs in segments. The support of the above-mentioned reduction process is based on observation of the structural features as shown in these micrographs. Schematic representation of the formation mechanism of VC@C has been shown in fig. 4.39.

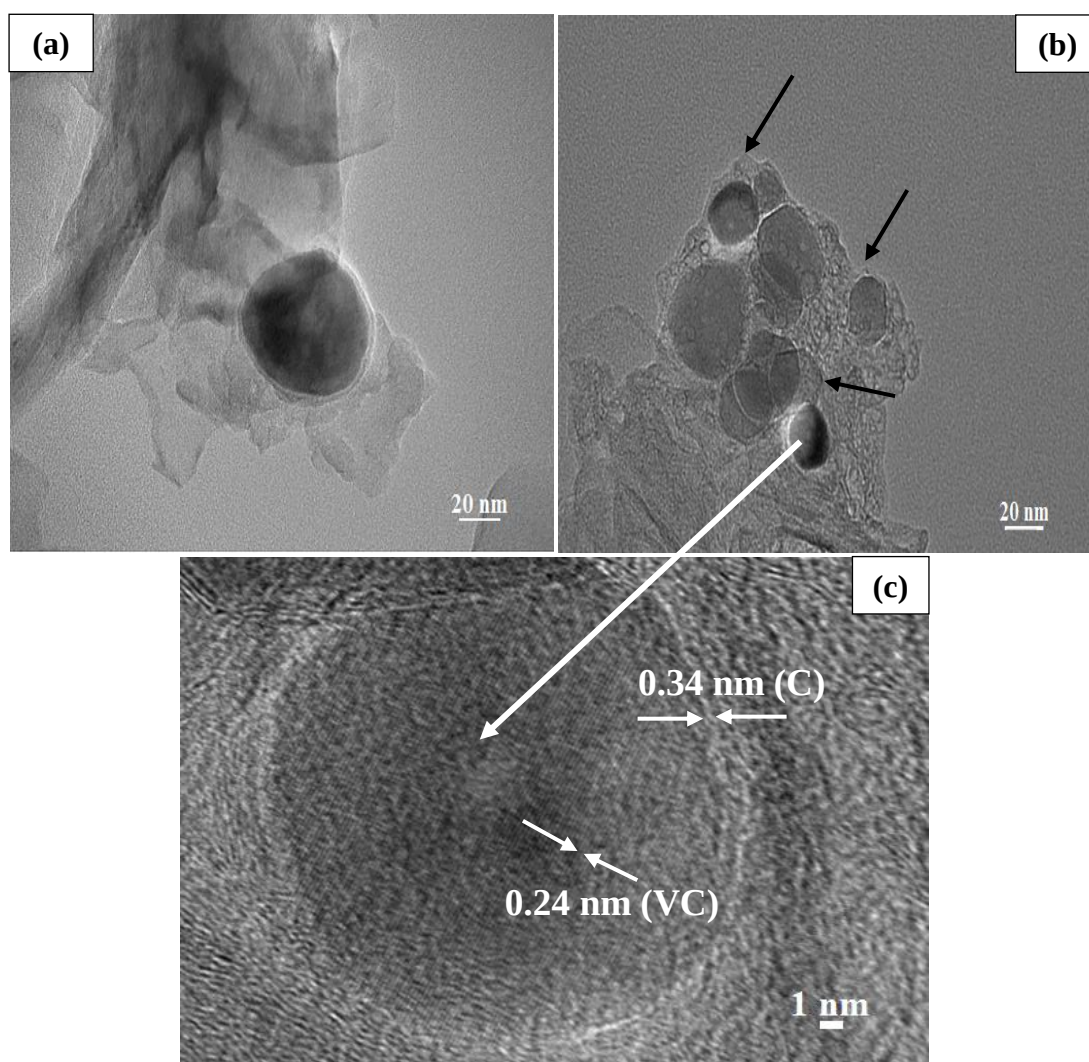


Figure 4.37: TEM images of vanadium carbide obtained for samples (a) At-1 (b) At-3 and (c) HRTEM of (b) showing the lattice fringes VC@C.

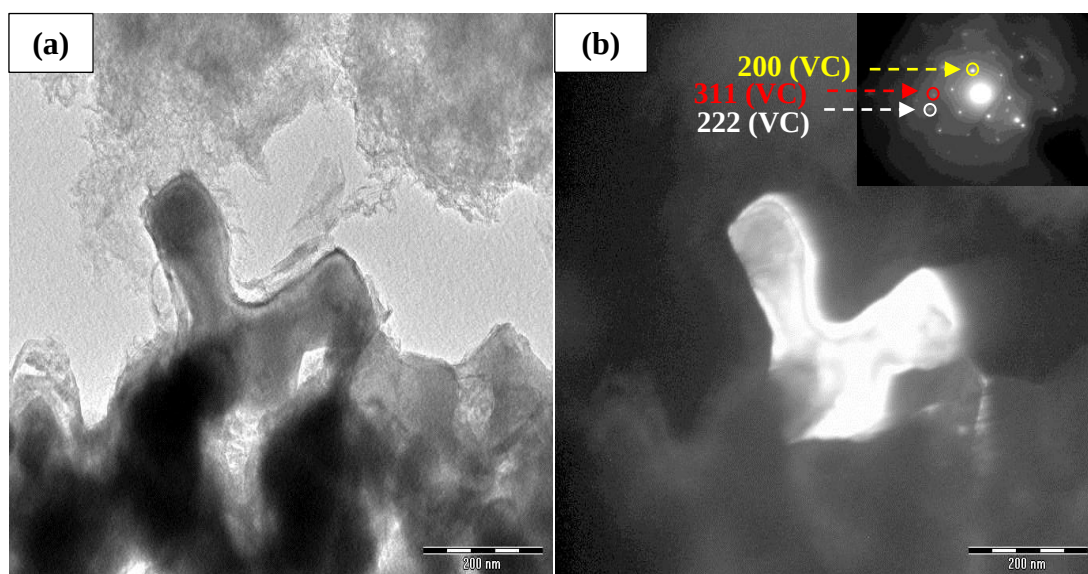


Figure 4.38: TEM images of sample AC-7 (VC@C) showing (a) rod-like morphology and (b) corresponding dark field TEM image of (a).

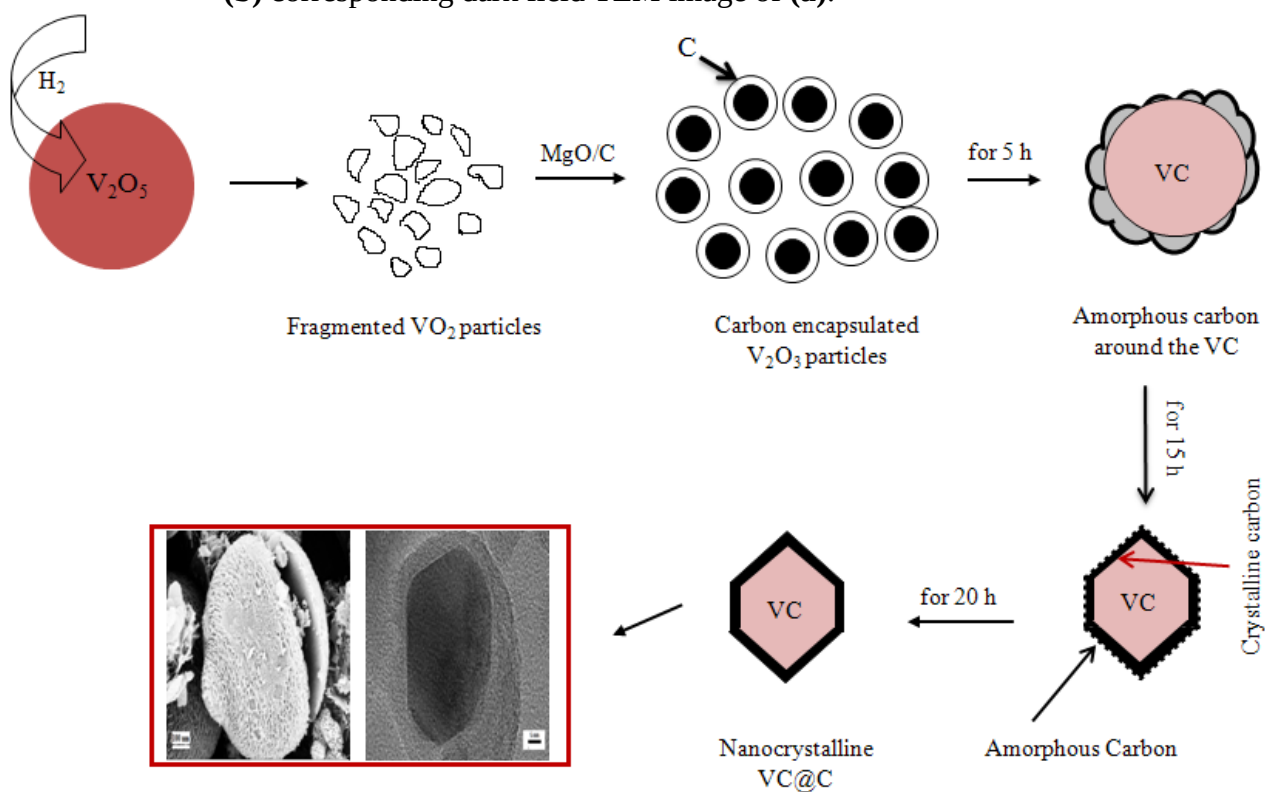


Figure 4.39: Schematic representation of formation mechanism of VC@C.

4.2.3.3 Raman analysis

Raman spectra of the obtained samples are shown in fig. 4.40. It exhibit two common bands called D (disordered) and G (graphitic) at ~ 1355 and 1578 cm^{-1} , which are the D and G band of graphite [11].

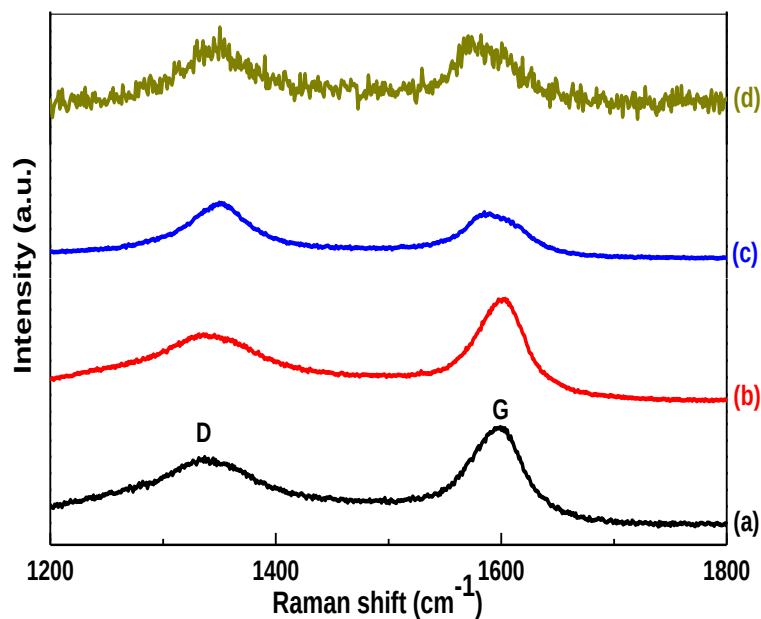


Figure 4.40: Raman spectra of samples (a) At-1 (b) At-2 (c) At-3 and (d) AC-7.

The I_D/I_G ratio for the obtained samples is given in table 4.12. With the increase of the reaction time (upto 15 h), the I_D/I_G ratio increases and at 20 h, it decreases because of the formation of single phase of VC.

Table 4.12: Calculated values of I_D/I_G ratio.

Sample	D-band (cm^{-1})	G-band (cm^{-1})	I_D/I_G ratio
At-1	1338.3	1593.8	0.48
At-2	1339.3	1597.9	0.50
At-3	1349.2	1590.4	1.01
AC-7	1350.0	1582.7	0.86

4.3 Synthesis of VC by Mechano-chemical Route

In order to synthesize vanadium carbide (VC) through mechano-chemical route, the ingredients taken was vanadium pentoxide (V_2O_5) and activated charcoal. The amount of the reactants and the milling variables are given in table 4.13. The milling was carried out in planetary ball mill (Retsch PM 100) using tungsten carbide (WC) jar of 250 mL capacity at 300 rotations per minute (RPM). WC balls of diameter 10 mm and weight 7.7 g was used as a milling media. The ball-to-powder ratio (B:P) was kept fixed (20:1) for all the experiments. The milling was interrupted at selected intervals of time and small amount of powder was taken out from the milling jar to evaluate the product phase(s) during the progress of milling.

The samples obtained at different RPM, milling time and with different Mg amount are denoted as B-R-t-M, where, R, t and M corresponds to RPM, milling time and amount of Mg, respectively.

Table 4.13: Amount of initial reactants and milling parameters.

Sample	V ₂ O ₅ (g)	Activated charcoal (g)	RPM	Milling time (h)
B-300-5-0	3	3	300	5
B-300-10-0	3	3	300	10
B-300-20-0	3	3	300	20
B-300-30-0	3	3	300	30
B-300-40-0	3	3	300	40
B-300-50-0	3	3	300	50
B-300-70-0	3	3	300	70

4.3.1 XRD analysis

For the synthesis of VC by mechano-chemical route, the experiments were conducted without adding any reducing agent in the milling jar (fig. 4.41). Figure 4.41(a) shows the presence of different phases after 5 h.

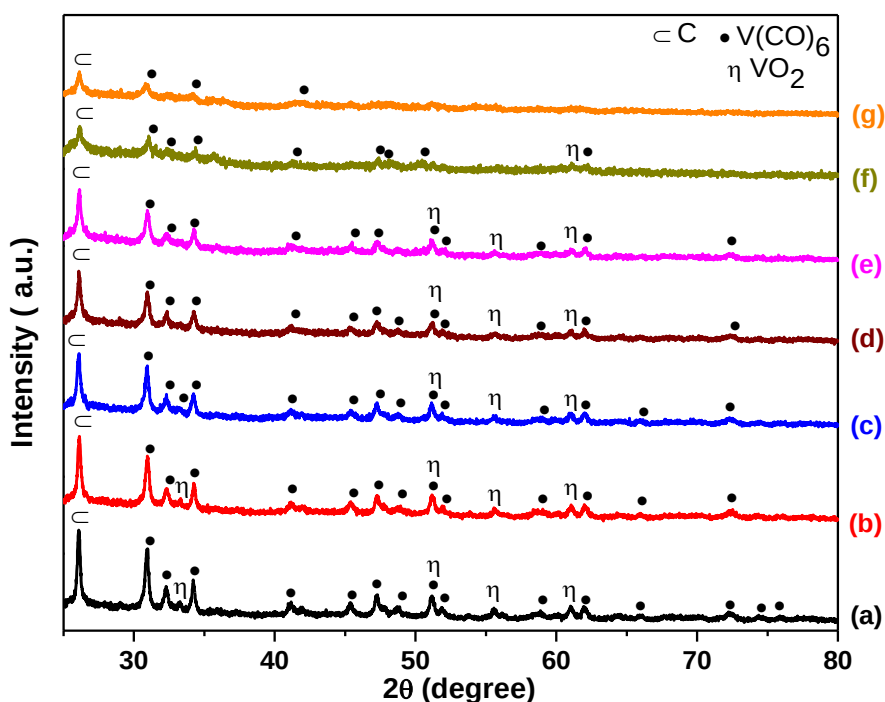


Figure 4.41: XRD pattern for samples (a) B-300-5-0 (b) B-300-10-0 (c) B-300-20-0 (d) B-300-30-0 (e) B-300-40-0 (f) B-300-50-0 and (g) B-300-70-0.

The XRD analysis shows that the reduction of V_2O_5 to its lower oxide(s) started after 5 h milling. With further increase in milling time to 10 h, the intensity of intermediate oxides peaks $V(CO)_6$ and VO_2 decreases but no new peak appears in the XRD pattern. However, on further increase in milling time to 20-70 h, some of the lower oxide peaks disappeared but no peak of vanadium carbide (VC) was detected in XRD pattern. The disappearance of the carbide peaks could be the result of amorphization because metastable phases easily turn into amorphous phase during intense milling [69, 70].

Hence, it was observed that with the increase of milling time to 70 h, no significant reduction/carburization has occurred. Therefore, it can be said that the selected milling parameters did not provide enough energy to reduce as well as carburize the oxide(s).

Table 4.14: Amount of reactants and milling parameters.

Sample	V_2O_5 (g)	Mg (g)	Activated charcoal (g)	RPM	Milling time (h)
B-450-5-1.34	2	1.34	1	450	5
B-450-10-1.34	2	1.34	1	450	10
B-450-15-1.34	2	1.34	1	450	15
B-450-20-1.34	2	1.34	1	450	20
B-450-25-1.34	2	1.34	1	450	25

So, in the next set of experiments, we added Mg in the ball mill with higher RPM, by keeping B:P (20:1) ratio same. The amount of initial ingredients and milling variables are given in table 4.14. Figure 4.42 shows the XRD pattern of the resultant product obtained after the addition of Mg. The XRD pattern shows that even after the addition of 1.34 g Mg as reducing agent along with the increment in milling speed, no peak of carbide(s) appeared. However, the intensity of formed $V(CO)_6$ phase has decreased with increasing milling time. This is related to the fact that lower amount of Mg could not generate sufficient amount of thermal energy for reaction to start. Considering this, the amount of Mg was increased to 2.5 g for the complete reduction/carburization of V_2O_5 . The details of reaction parameter along with the amount of ingredient are shown in table 4.15.

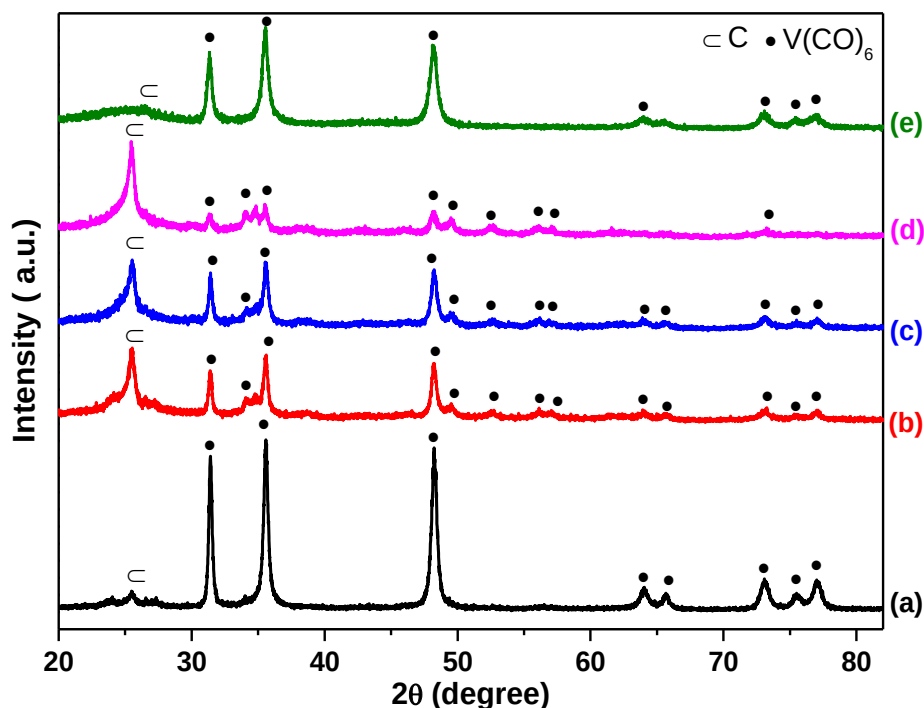


Figure 4.42: XRD pattern for samples (a) B-450-5-1.34 (b) B-450-10-1.34 (c) B-450-15-1.34 (d) B-450-20-1.34 and (e) B-450-25-1.34.

Table 4.15: Amount of initial ingredients and milling parameters.

Sample	V ₂ O ₅ (g)	Mg (g)	Activated charcoal (g)	RPM	Milling time (h)
B-450-5-2.5	2	2.5	1	450	5
B-450-10-2.5	2	2.5	1	450	10
B-450-15-2.5	2	2.5	1	450	15
B-450-20-2.5	2	2.5	1	450	20
B-450-25-2.5	2	2.5	1	450	25

Figure 4.43 is the XRD pattern of the product phase(s) obtained after milling for different durations. It shows that Mg plays an important role in the reduction/carburization of V₂O₅ precursor as significant changes in the XRD pattern are observed. With the milling time of 5 h, the reduction as well as carburization of V₂O₅ has occurred which is attributed by the appearance of broad peak of VC at $\sim 43.4^\circ$ (2θ) along with V(CO)₆ and C phases. The lower intensity and volume fraction of VC phase in the XRD pattern indicates the lack of sufficient time for the diffusion of carbon into the reduced oxide(s).

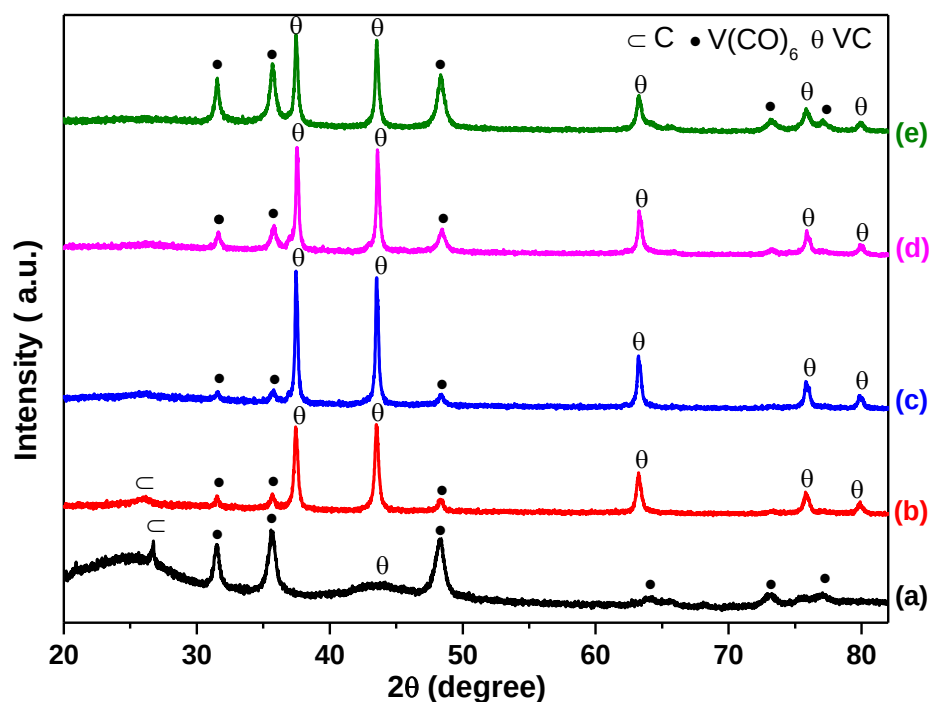


Figure 4.43: XRD pattern for samples (a) B-450-5-2.5 (b) B-450-10-2.5 (c) B-450-15-2.5 (d) B-450-20-2.5 and (e) B-450-25-2.5.

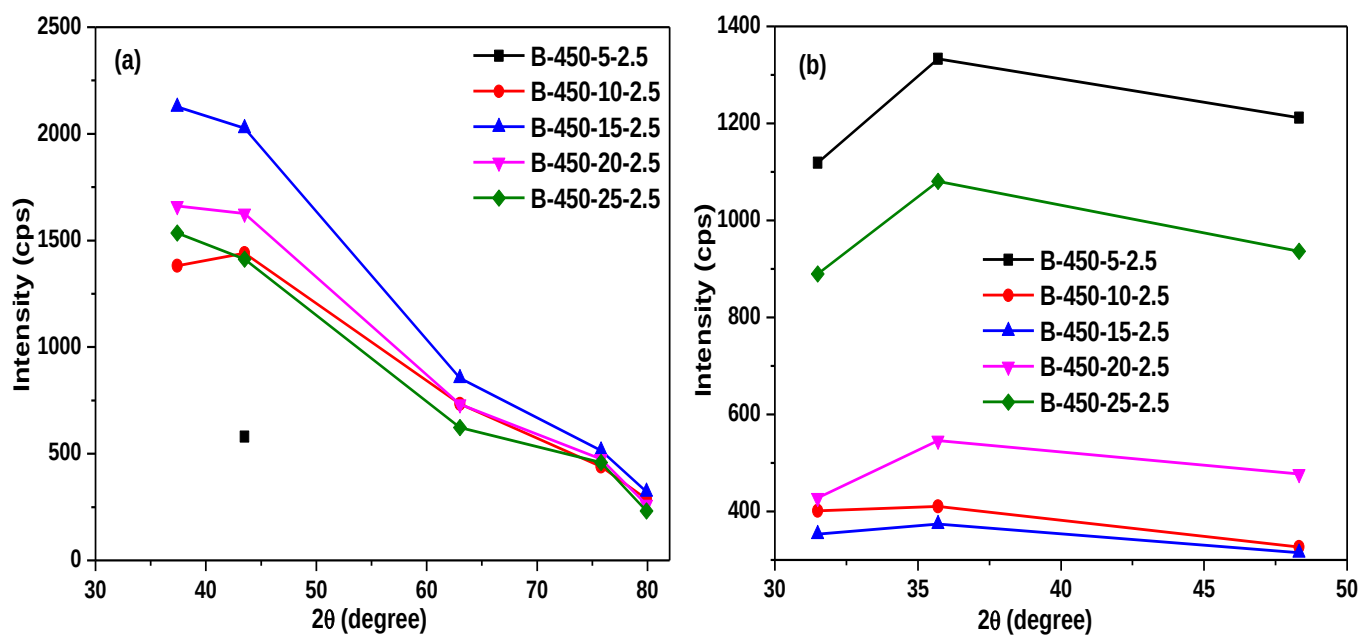


Figure 4.44: Intensity plot of diffraction peaks of (a) VC and (b) $V(CO)_6$ obtained with Mg (2.5 g) for different milling intervals at 450 RPM.

The broad peak of VC at 5 h milling time designates its amorphous nature. However, with increase in the milling time to 10 h, crystalline nature of VC peaks was observed in the XRD pattern (fig. 4.43(b)). The peak intensity of VC increased by the decrease in $V(CO)_6$ phase at

milling time of 15 h, which attributes higher content of VC in the obtained powder sample (table 4.16). On the contrary, the further increase of milling time from 20 to 25 h leads to the decrease in the intensity of VC phase with a gradual increase of $V(CO)_6$ phase intensity (fig. 4.43(d-e)). This is because of the fact that after a critical milling time, the moving balls do not generate any impact energy and hence the heating and efficiency of milling decreases [70]. As a result, ease of formation of low-temperature (160-200 °C) phase $V(CO)_6$ is more than that of high-temperature phase (VC).

Table 4.16: Crystallite size of VC nanoparticles, strain produced and volume fraction of the obtained phases.

Sample	Reaction time (h)	Crystallite size (nm)	Strain ($\times 10^{-3}$)	Volume fraction of phases (%)		
				VC	$V(CO)_6$	C
B-450-5-2.5	5	1.38	-----	4.50	58.80	36.7
B-450-10-2.5	10	35.09	0.999	85.1	12.0	2.90
B-450-15-2.5	15	92.4	1.75	92.65	6.4	0.95
B-450-20-2.5	20	106.61	1.92	82.54	16.71	0.75
B-450-25-2.5	25	111.77	2.5	58.17	41.38	0.45

The crystallite size of VC nanoparticles and strain produced in the samples during milling are calculated using W-H analysis and are given in table 4.16. The results reveal that the crystallite size and strain increases with the increase of the milling time. Moreover, the positive value of the strain shows the existence of tensile strain in the system which is because of the diffusion of more carbon atoms inside the VC.

From the XRD results, it is observed that 15 h milling at 450 RPM leads to maximum volume fraction of VC phase with minimum content of $V(CO)_6$ phase as shown in fig. 4.44. Therefore, by keeping the milling time constant (15 h), the effect of RPM was analysed for the synthesis of VC nanopowder which is given in table 4.17.

Figure 4.45 shows the XRD pattern of the obtained samples at different RPMs. It is observed that complete reduction of V_2O_5 has occurred even at 150 RPM as no peak of V_2O_5 is observed (fig. 4.45(b)). The broad peak observed at $2\theta \sim 43.5^\circ$ corresponds to the diffraction peak of cubic VC (200) (ICDD Card No. 01-073-0476) of NaCl type structure [63]. While on the other hand, the broad band from 20° to 29.5° belongs to the amorphous carbon or turbostratic carbon.

Table 4.17: Amount of initial reactants and milling parameters.

Sample	V ₂ O ₅ (g)	Mg (g)	Activated charcoal (g)	Reaction time (h)	RPM
B-150-15-2.5	2	2.5	1	15	150
B-175-15-2.5	2	2.5	1	15	175
B-200-15-2.5	2	2.5	1	15	200
B-225-15-2.5	2	2.5	1	15	225
B-250-15-2.5	2	2.5	1	15	250
B-275-15-2.5	2	2.5	1	15	275
B-300-15-2.5	2	2.5	1	15	300
B-350-15-2.5	2	2.5	1	15	350
B-375-15-2.5	2	2.5	1	15	375
B-400-15-2.5	2	2.5	1	15	400
B-450-15-2.5	2	2.5	1	15	450

The volume fraction of carbon at 150 RPM is maximum in this case also (table 4.18). The impact energy generated even at 150 RPM is sufficient enough to deform the material and allow the reaction to occur through newly generated surfaces sequentially with passage of time [70]. During this process, grain refinement followed by fragmentation occurs and internal stresses are built up which reduces the particle size also [71, 72]. The crystallite size of VC powder obtained after the milling at 150 RPM was 1.57 nm. The reduction in crystallite size during early stages of milling was because of the formation of high dislocation density regions within the grains created by of large numbers of linear defects, particularly dislocations [73]. With slight increase in RPM to 175 RPM, a low intensity peak at $2\theta \sim 35.82^\circ$ corresponding to V(CO)₆ appears (fig. 4.45(c)). On the other hand, VC peak becomes more intense. Apart from this, the carbon peak changes from amorphous to crystalline. Moreover, the decrement in the volume fraction of carbon with increased RPM corresponds to high affinity of vanadium and carbon at high RPM, which facilitate more carbon to diffuse inside the VC lattice and leads to the growth of VC phase. At 200 RPM, the peaks corresponding to carbon and V(CO)₆ disappeared (fig. 4.45(d)). This milling condition is optimum required condition for obtaining nanocrystalline VC powder. The continuous milling of powder causes the welding and fracture of the powder due to which fresh VC

surfaces become the nucleation sites for the diffusion of more carbon into VC lattice and lead to the growth of other planes of VC.

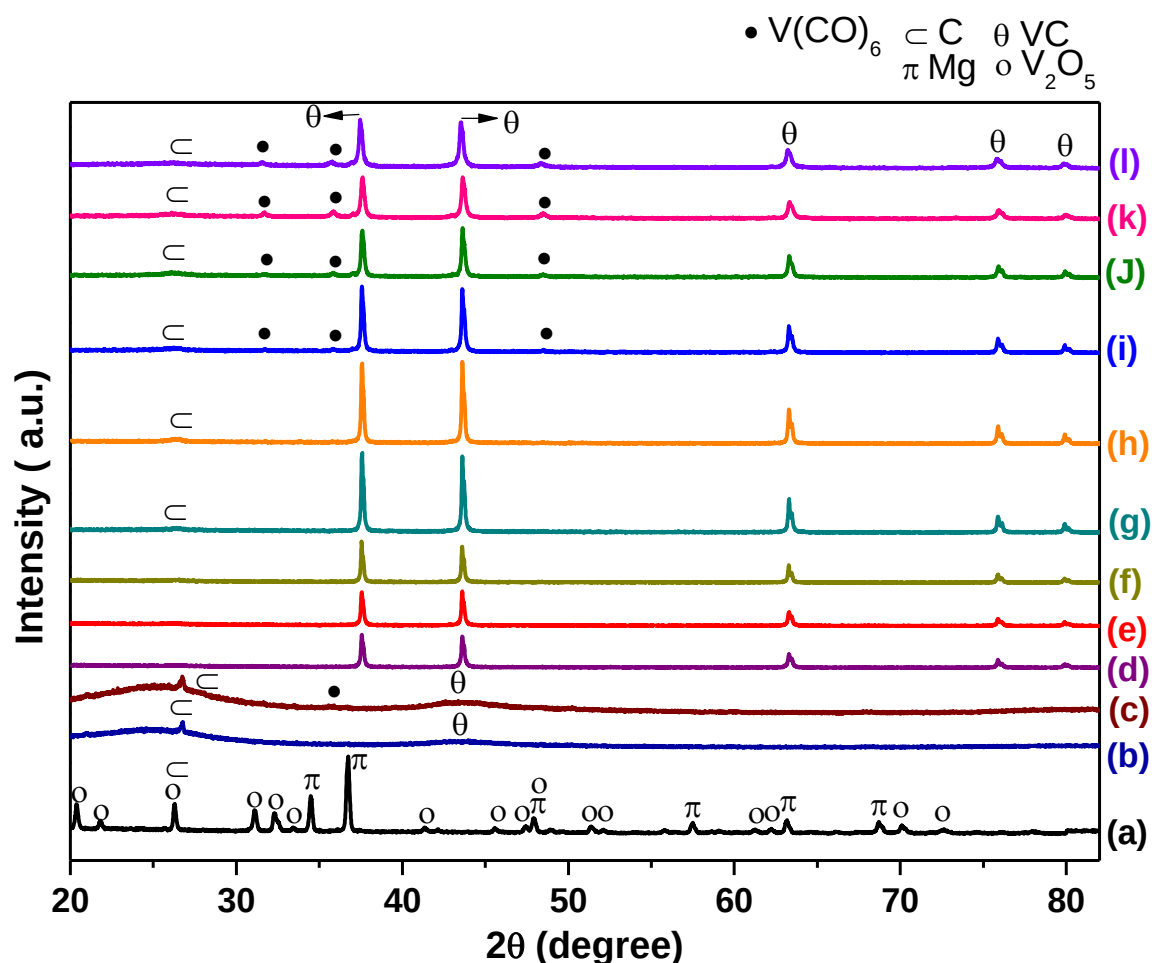


Figure 4.45: XRD pattern for samples (a) Raw material (b) B-150-15-2.5 (c) B-175-15-2.5 (d) B-200-15-2.5 (e) B-225-15-2.5 (f) B-250-15-2.5 (g) B-275-15-2.5 (h) B-300-15-2.5 (i) B-350-15-2.5 (j) B-375-15-2.5 (k) B-400-15-2.5 (l) B-450-15-2.5.

Further milling of the powder by increasing the RPM does not provide any structural changes upto 300 RPM (fig. 4.45(e)-(h)) except the increase in the intensity of VC peaks. The presence of higher intensity of VC peaks at 300 RPM confirmed the best milling speed for the formation of nanocrystalline VC (fig. 4.46). After the 300 RPM milling, a stage is reached where the volume fraction of VC again decreases with simultaneous formation of $V(CO)_6$ phase as shown in the XRD pattern, though its intensity is low (fig. 4.45(i)). Such kind of change is related to the fact that at higher RPM (200-300), more heat is generated inside the container due to collisions between the grinding media and milling container. It leads to transformation of $V(CO)_6$ to VC. However, at higher milling speed (350-450), the milling balls don't fall down to generate any impact energy and pinned to the inner walls of

the milling jar which reduces the heating and efficiency of the milling [70]. It has been observed that the rotation speed should be such that the milling balls should fall from the maximum height to generate maximum collision energy. Therefore, after the optimum speed of 300 RPM, enough energy is not imparted to the powder being milled, which lead to incomplete conversion of $V(CO)_6$ into VC. It indicates that after the increment in the speed (> 300 RPM), the milling speed gives adverse effects on the formation of VC phase. As a result, the volume fraction of $V(CO)_6$ increases and of VC decreases (table 4.18). It clearly indicates that formation of VC phase occurs at intermediate optimum milling speeds. While the formation of intermediate phase, $V(CO)_6$ occurs at relatively lower and higher speed where the effect of mechanical activation of the material is low.

The crystallite size and strain produced in the powder during milling at different RPMs were calculated by using W-H plot analysis and is shown in table 4.18. Results indicate that crystallite size first increases with the increase in the rotation speed and then decreases. The increment in the crystallite size indicates the occurrence of welding between the particles. With increasing RPM, the deformations and fragmentation of particles is more. With the decrease of particle size of fragmented particles, the agglomeration starts, this increases the fracture resistance due to cohesion between the particles [74].

Table 4.18: Crystallite size of VC nanoparticles, strain produced and volume fraction of the obtained phases.

Sample	RPM	Cryatallite size (nm)	Strain ($\times 10^{-3}$)	Volume fraction of phases (%)		
				VC	$V(CO)_6$	C
B-150-15-2.5	150	1.57	-----	7.51	-----	92.49
B-175-15-2.5	175	1.70	-----	18.43	3.27	78.30
B-200-15-2.5	200	101.91	1.28	99.01	-----	0.99
B-225-15-2.5	225	213.56	1.67	98.73	-----	1.27
B-250-15-2.5	250	140.0	1.28	99.08	-----	0.92
B-275-15-2.5	275	81.0	0.827	98.99	-----	1.01
B-300-15-2.5	300	84.51	0.814	98.90	-----	1.10
B-350-15-2.5	350	101.91	1.25	96.22	2.53	1.25
B-375-15-2.5	375	77.86	1.15	93.98	4.47	1.55
B-400-15-2.5	400	73.33	1.39	87.61	10.62	1.77
B-450-15-2.5	450	99.0	1.81	92.24	4.23	1.11

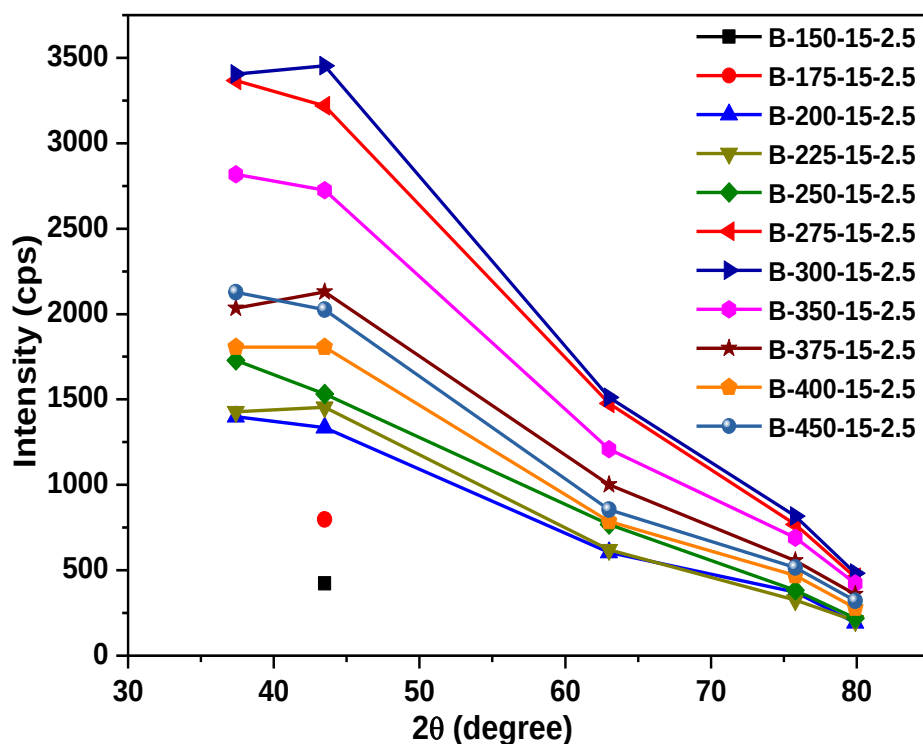


Figure 4.46: Intensity plot of diffraction peaks of VC obtained at different RPM.

Almost similar behaviour has been observed in case of strain with the variation in rotation speed. The positive value of strain attributes the tensile strain inside the lattice, which is because of the diffusion of carbon atoms into VC. During the complete formation of VC, the reactions become exothermic in nature, which releases the stress within the system by producing heat. Therefore, minimum value of strain was observed for the sample obtained at 300 RPM, where high intense peak of nanocrystalline VC is achieved.

The results of XRD analysis with the variation in RPM clearly show that an optimum milling speed is essential for the mechano-chemical synthesis which is 300 RPM in this case. Considering this, milling time has been optimized by keeping all the parameters constant as shown in table 4.19.

Table 4.19: Amount of initial reactants and milling parameters.

Sample	V ₂ O ₅ (g)	Mg (g)	Activated charcoal (g)	Reaction time (h)	RPM
B-300-5-2.5	2	2.5	1	5	300
B-300-10-2.5	2	2.5	1	10	300
B-300-12-2.5	2	2.5	1	12	300
B-300-14-2.5	2	2.5	1	14	300
B-300-15-2.5	2	2.5	1	15	300

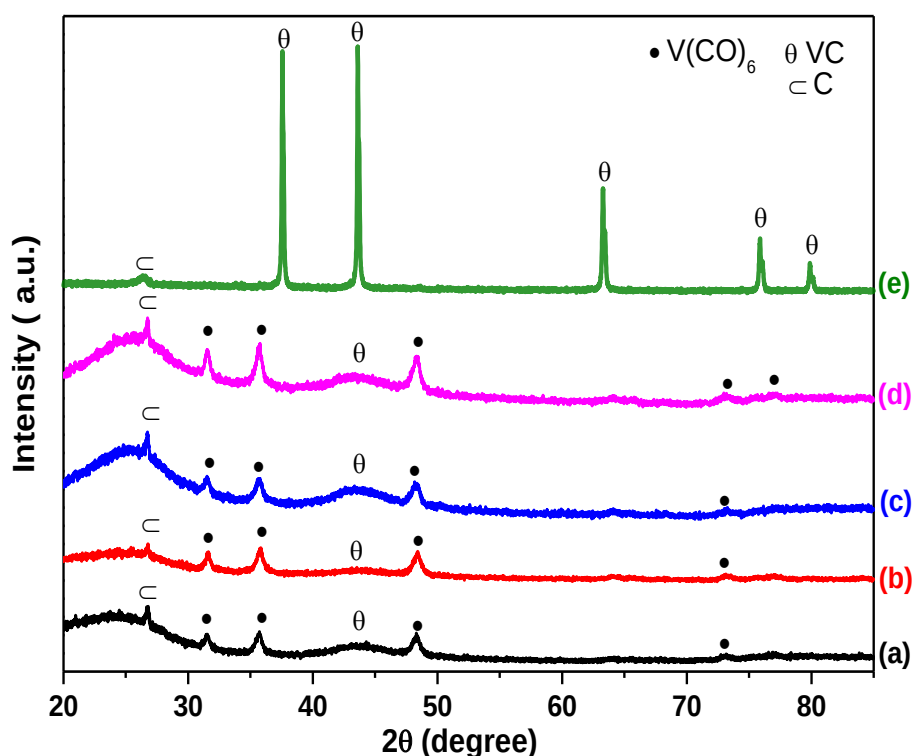
**Figure 4.47:** XRD pattern for samples (a) B-300-5-2.5 (b) B-300-10-2.5 (c) B-300-12-2.5 (d) B-300-14-2.5 and (e) B-300-15-2.5.

Figure 4.47 shows the XRD pattern of the samples milled for different milling time (5-15 h) at 300 RPM. As clearly seen in fig. 4.47, no changes have been observed in the XRD pattern of samples prepared by milling time upto 14 h. While, with successively increment in the milling time to 15 h leads to the instant transformation of $V(CO)_6$ into VC through mechanically induced self-sustaining reactions [70].

Moreover, after getting the specific milling speed and time, another important parameter is to maintain the minimum amount of reducing agent for good product. So, in order to optimize

the amount of Mg for the synthesis of single phase VC, the amount of Mg was varied in the next set of experiments for 15 h at 300 RPM (table 4.20).

Table 4.20: Amount of initial reactants and milling parameters.

Sample	V ₂ O ₅ (g)	Mg (g)	Activated charcoal (g)	Reaction time (h)	RPM
B-300-15-2.0	2	2.0	1	15	300
B-300-15-2.10	2	2.10	1	15	300
B-300-15-2.15	2	2.15	1	15	300
B-300-15-2.20	2	2.20	1	15	300
B-300-15-2.25	2	2.25	1	15	300
B-300-15-2.5	2	2.5	1	15	300
B-300-15-3.0	2	3.0	1	15	300

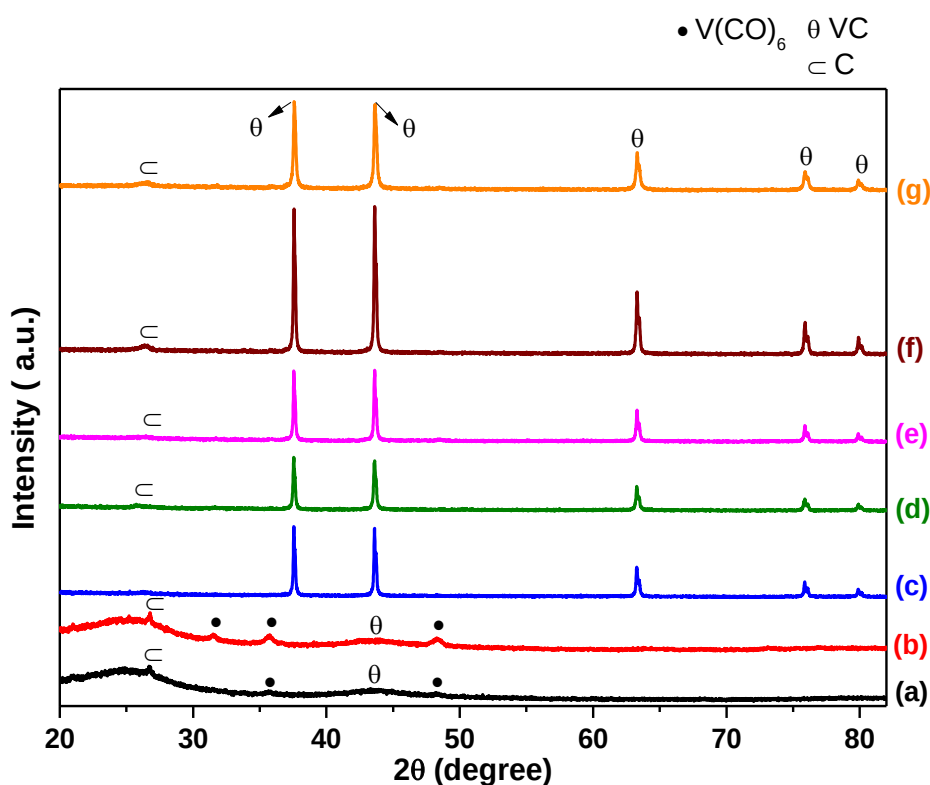


Figure 4.48: XRD pattern for samples (a) B-300-15-2.0 (b) B-300-15-2.10 (c) B-300-15-2.15 (d) B-300-15-2.20 (e) B-300-15-2.25 (f) B-300-15-2.5 and (g) B-300-15-3.0.

Figure 4.48 shows the effect of Mg on the synthesis of VC nanopowder obtained by mechano-chemical route. As observed from the XRD pattern, the intensity of the VC peaks

increases with the increase of Mg amount upto 2.5 g and then decreases for 3 g of Mg. Maximum intensity of VC peaks was observed with 2.5 g of Mg (fig. 4.49).

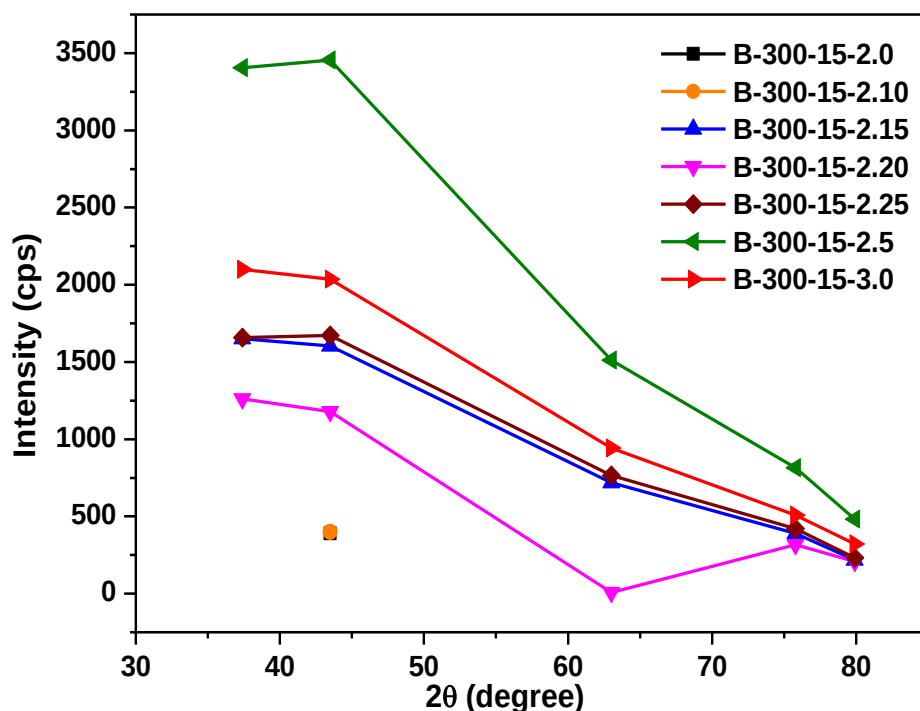


Figure 4.49: Intensity plot of diffraction peaks of VC obtained with different amount of Mg.

Table 4.21: Crystallite size of VC nanoparticles, strain produced and volume fraction of the obtained phases.

Sample	Mg (g)	Cryatallite size (nm)	Strain (*10 ⁻³)	Volume fraction of phases (%)		
				VC	V(CO) ₆	C
B-300-15-2.0	2.0	1.61	-----	4.84	4.35	90.81
B-300-15-2.10	2.10	1.90	-----	7.48	32.83	59.69
B-300-15-2.15	2.15	77.86	0.742	98.04	-----	1.96
B-300-15-2.20	2.20	96.25	1.11	98.58	-----	1.42
B-300-15-2.25	2.25	110.88	1.12	98.69	-----	1.31
B-300-15-2.5	2.5	84.51	0.814	98.90	-----	1.10
B-300-15-3.0	3.0	121.58	1.59	98.51	-----	1.49

The crystallite size and strain in the VC produced by varying the Mg content was calculated by W-H plot and the data is given in table 4.21. The crystallite size of the VC nanopowder increases with the increase of the amount of Mg up to 2.25 g and then decreases for 2.5 g. This behaviour of crystallite size is in reverse order where Mg content was sequencely increased upto 3 g. The similar behaviour in the variation of strain value was also observed.

It is evident from our previous XRD results that single phase high intensity VC nanopowder could be obtained at 300 RPM for 15 h milling with 2.5 g of Mg. But, it is very difficult to assess the energy evolved during milling which leads to increase in temperature inside the ball mill. In order to estimate the synthesis temperature generated in the ball mill for the formation of VC nanoparticles, the same composition was charged in autoclave and heated for same time as in milling (15 h) but at different temperatures (table 4.22).

Table 4.22: Amount of initial reactants and autoclave parameters.

Sample	V ₂ O ₅ (g)	Mg (g)	Activated charcoal (g)	Reaction time (h)	Temperature (°C)
AC-600-15-2.5	2	2.5	1	15	600
AC-700-15-2.5	2	2.5	1	15	700
AC-800-15-2.5	2	2.5	1	15	800
AC-900-15-2.5	2	2.5	1	15	900

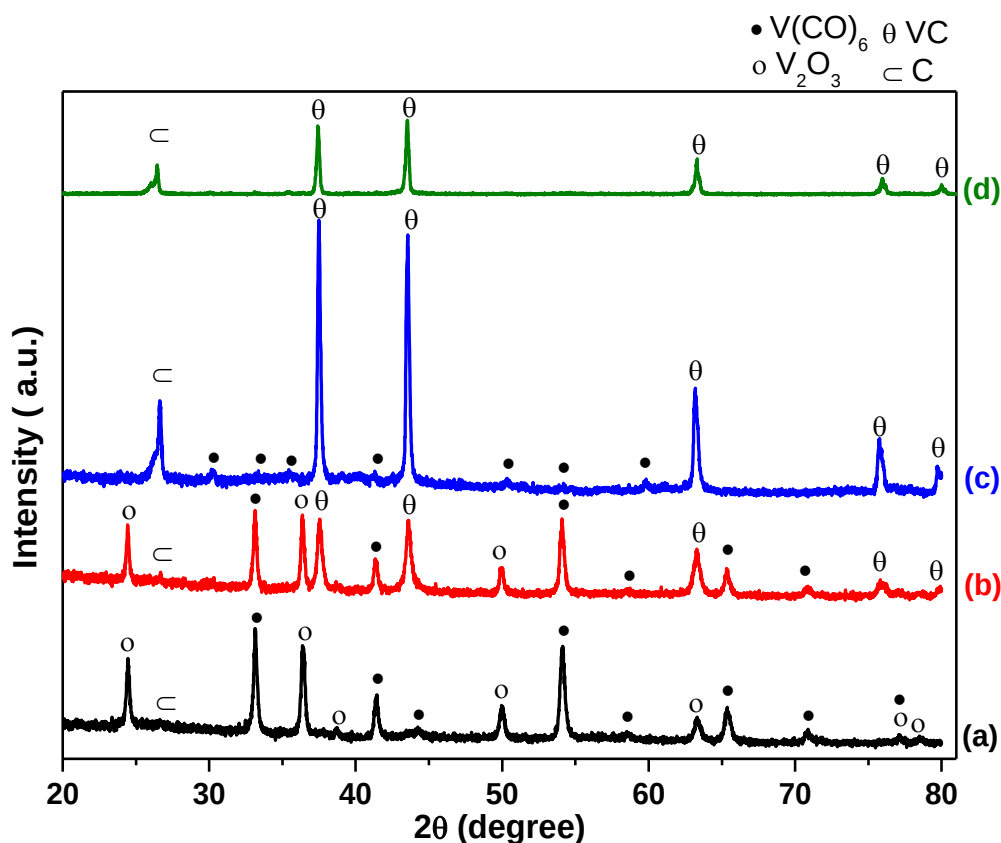


Figure 4.50: XRD pattern for samples (a) AC-600-15-2.5 (b) AC-700-15-2.5 (c) AC-800-15-2.5 and (d) AC-900-15-2.5.

Figure 4.50 shows the XRD pattern of the product phase(s) having same ingredient as used in milling but heated at different temperature in autoclave. At 600 °C, the appearance of

$V(CO)_6$, V_2O_3 and C in the XRD pattern indicates the reduction of V_2O_5 into lower oxides at this temperature. By increasing the temperature of autoclave to 700 °C, the diffraction peaks of VC appeared along with the reduction in peak intensity of intermediate oxides in XRD pattern. However, the XRD pattern clearly revealed that temperature between 700 and 900 °C ($700 < T_{\text{autoclave}} < 900$ °C) did not reduce completely the intermediate oxides though the intensity of the oxide peaks decreased (fig. 4.50(c)). But after getting the temperature of 900 °C, the complete transformation and formation of single phase VC has been obtained (fig. 4.50(d)). Therefore, it is clear that formation of VC in an autoclave is a self-propagating high-temperature synthesis, in which conversion of products gradually occurs as a diffusional solid-state reaction between the starting phases [70]. But in case of mechanical milling, the reactants instantly transformed into products after critical milling parameters as a result of mechanically induced self-sustaining reactions (MSR). During this instant transformation, the temperature generated inside the milling container was around ~ 900 °C for a very short period of time because of the high energy collisions inside it. Moreover, local high temperature and pressure of above 1000 °C and several GPa, respectively was also created for short time periods as a result of impact of high energy collision during milling [70, 75, 76]. During this process, highly exothermic magnesio-thermic reactions occur during milling, generates high local pressures and temperatures which result in the phase transformation of the solid [70]. As a result of this, chemical reactions, which occur at high temperatures can occur at room temperature without any further heating.

4.3.2 Microstructure analysis

4.3.2.1 FESEM analysis

In order to investigate the microstructures of the ball-milled powder, FESEM and TEM/HRTEM are employed. Figure 4.51 shows the effect of rotation speeds on the morphology of the milled sample at different magnifications. Samples milled at 150 RPM exhibited well faceted morphology with sharp edges having size distribution ranging from 1-2 μm in diameter containing small pores between the particles (fig. 4.51(a)). However, the agglomeration of bigger size particles leads to less porosity, which can be seen in the samples milled at higher RPM (fig. 4.51(b-d)). This is because of the continuous high-energy collisions between grinding media and container. As a result, continuous fracture and welding of the particles at high RPM occur and particle shape changes from well faceted to irregular with large aggregates. Consequently, decrease in the surface area and pore volume takes place at high RPM, which is also clear from the BET analysis (discussed later). Therefore, in

contrast to later stages of milling, the powder at early stages tends to have well-faceted shape with narrow size distribution.

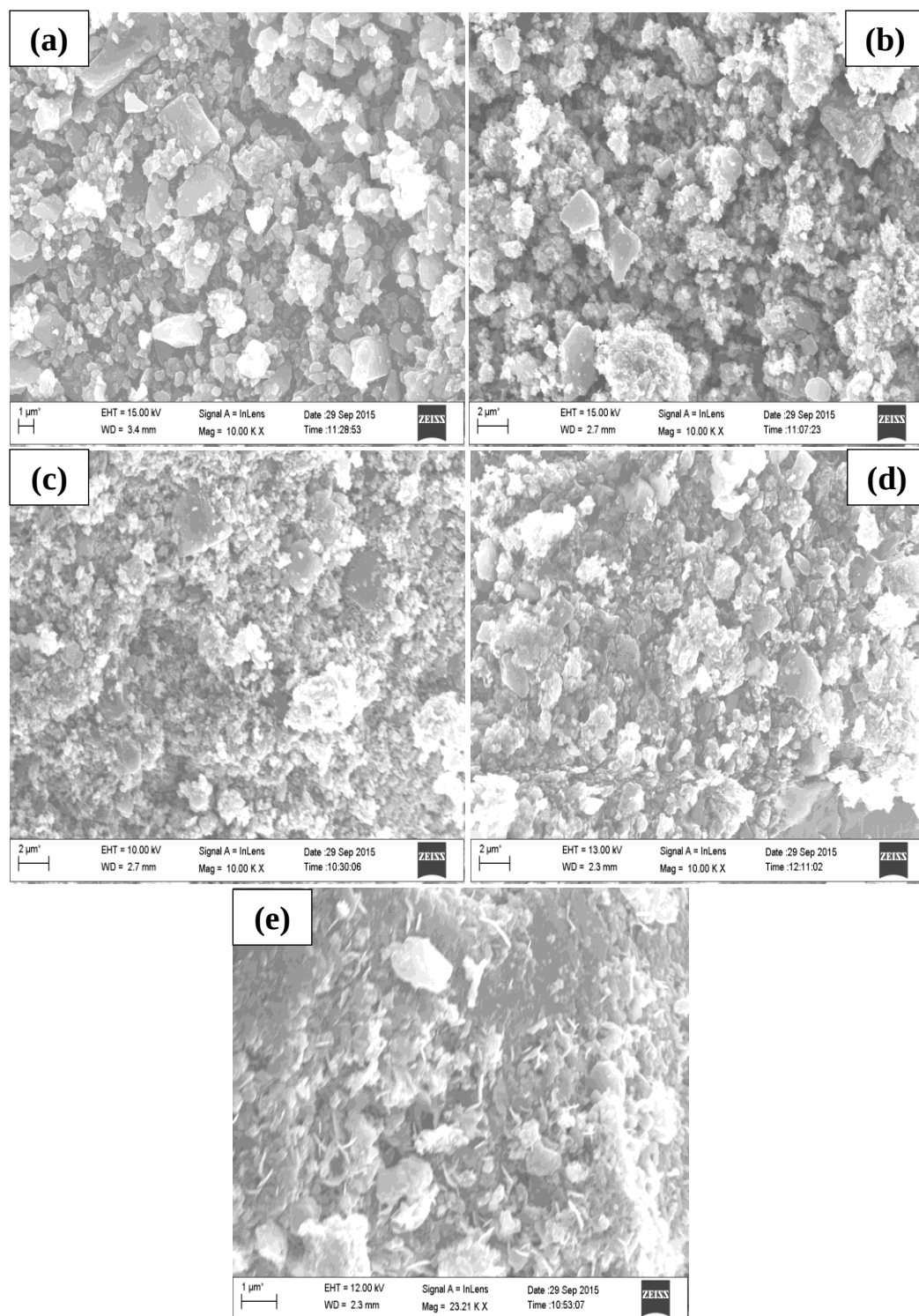


Figure 4.51: FESEM images of samples (a) B-150-15-2.5 (b) B-200-15-2.5 (c) B-275-15-2.5 (d) B-300-15-2.5 and (e) B-450-15-2.5.

On contrary to others, two types of features appeared in the sample milled at 450 RPM (fig. 4.51(e)). One is faceted morphology, which is of VC particles and other is sharp needle shape morphology. The needle-shaped morphology could be because of vanadium hexacarbonyl $V(CO)_6$ which is also evidenced from the XRD results. The size of these needles is several micrometers in length and few nanometers in diameter.

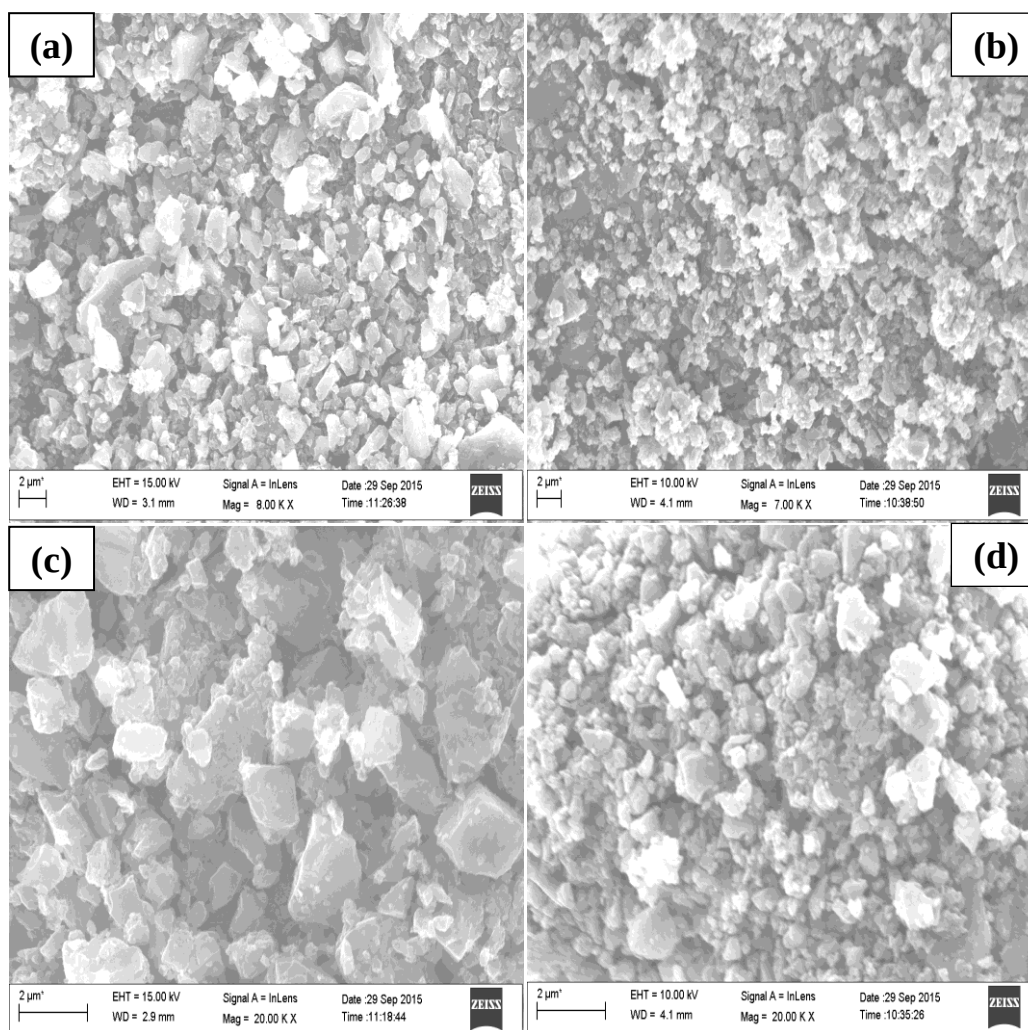


Figure 4.52: FESEM images of samples (a & c) B-300-5-2.5 and (b & d) B-300-14-2.5.

Sample milled for 14 h (B-300-14-2.5) shows more agglomeration of upto few micrometers in size as compared to that milled for 5 h (B-300-14-2.5) (fig. 4.52)). Careful examination of the microstructure reveals the larger particles (fig. 4.52(b, d)) having same morphology and are the agglomerates of smaller ones, which are formed because of the continuous impact that occurs during intense milling [77]. With the reaction time of 15 h, more agglomeration can be seen in fig. 4.51(d), which also fills the pores and reduces the surface area of the material as has been also observed from the BET analysis which is discussed later (section 4.3.6).

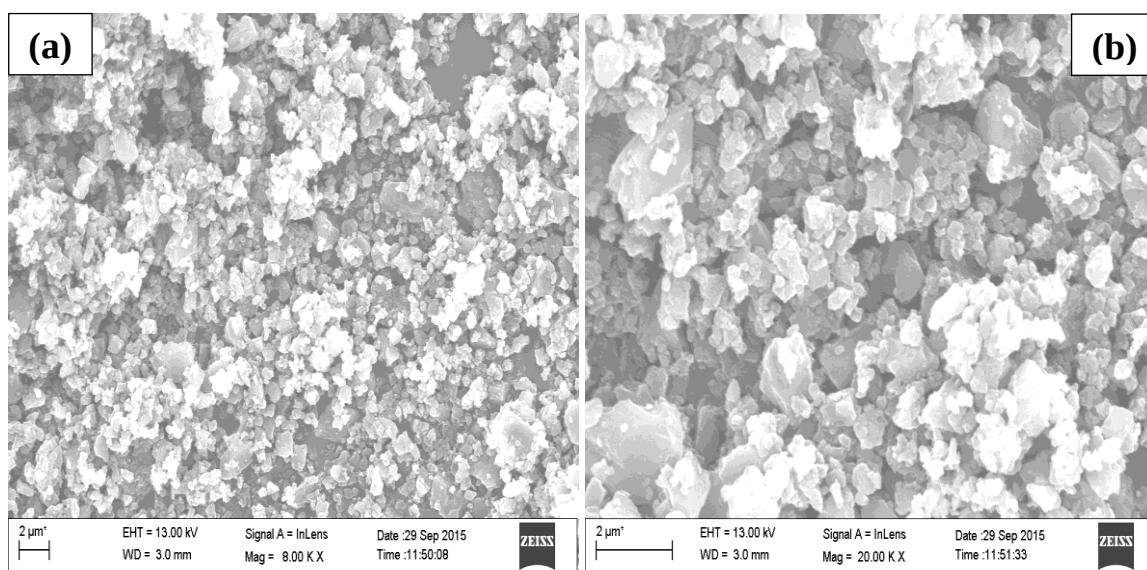


Figure 4.53: FESEM images of B-300-15-2.10 at different magnifications.

Also, in case of varying the amount of Mg, the variation in size of obtained VC nanoparticles has been observed as shown in fig. 4.51(d) and fig. 4.53. With increasing the amount of Mg, the amount of heat generated inside the milling container would be more which provides enough thermal activation for the diffusion of more carbon atoms into interstitial sites of VC. As a result, growth of highly crystalline VC nanostructure takes place with high Mg content.

4.3.2.2 TEM/HRTEM analysis

Morphological characteristics of the samples obtained at different milling parameters were analysed by TEM/HRTEM analysis. TEM analysis for the formation of VC nanoparticles indicates the presence of free carbon in all the reaction products. The TEM micrographs of the samples milled at 200 RPM are shown in fig. 4.54. Particles with nearly faceted morphology of size in the range of 50-80 nm can be seen in these micrographs. The selected area electron diffraction pattern (SAED) taken from the fig. 4.54(a) is shown in fig. 4.54(b). The clear spots in SAED pattern indexed with VC and C suggesting the nanocrystalline nature of VC in the carbon matrix which is in well agreement with XRD results.

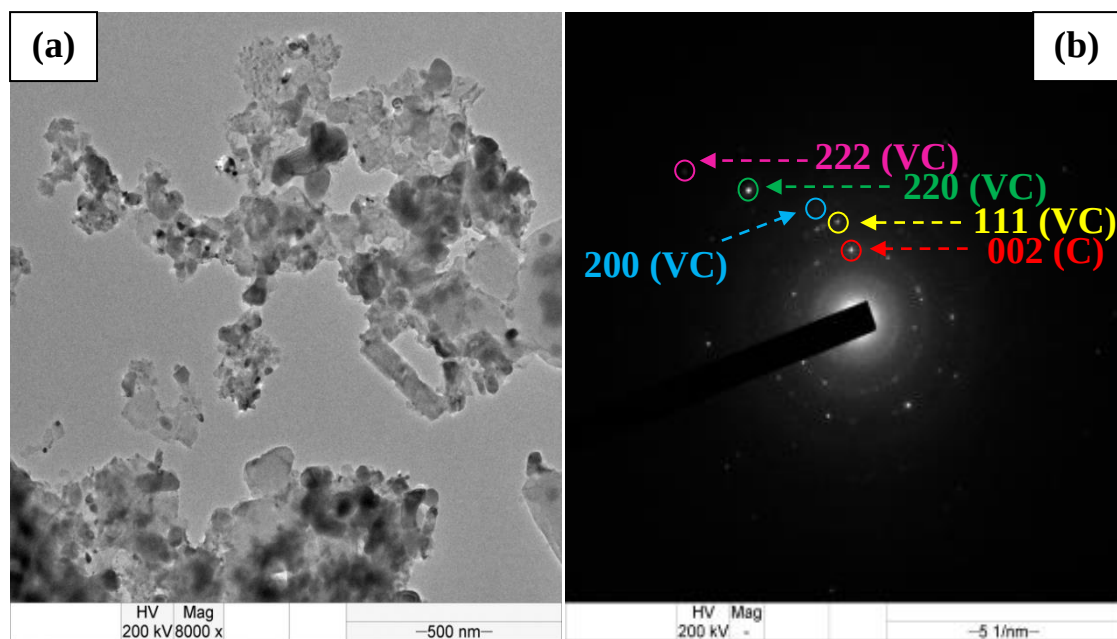


Figure 4.54: (a) TEM micrograph and **(b)** corresponding SAED pattern of B-200-15-2.5.

VC particles of average diameter of 114 nm embedded in carbon layers can be seen in fig. 4.55(a) for sample B-300-15-2.5. Inset of fig. 4.55(a) shows the HRTEM image of the stacking of graphene layers with d-spacing 0.35 nm of carbon. The appearance of graphene layers in HRTEM shows that the system remains stable during mechanical impact [78]. The particles of VC tend to join with each other because of the agglomeration, which occurs at high RPM due to the intense milling. Figure 4.55(b) shows the HRTEM image in which agglomeration of VC particles coated by outer carbon layers can be seen. The outer carbon shell contains about 19-21 layers with an average thickness of 6-7 nm. The D-spacing (0.34 nm) of these layers corresponds to the (002) plane of the graphitic carbon and that of the core particle (0.21) corresponds to the (200) plane of VC (fig. 4.55(c)). The SAED pattern taken from the nanocrystalline region is shown in fig. 4.55(d). It shows the reflections of crystalline phase of cubic VC and C which is in agreement with the XRD results.

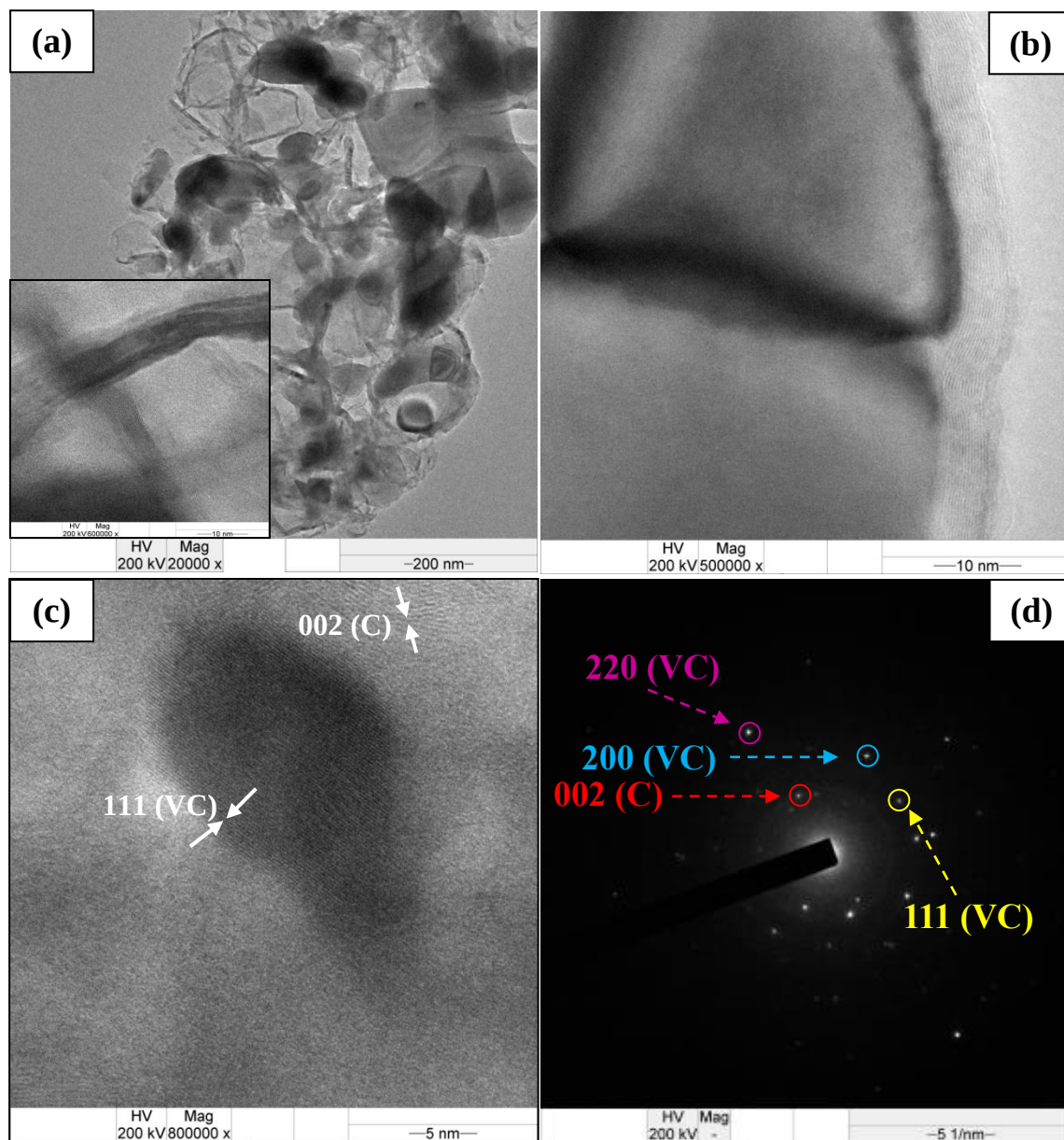


Figure 4.55: (a) TEM (b & c) HRTEM images and (d) corresponding SAED pattern of B-300-15-2.5.

Figure 4.56 shows the TEM image of the sample milled at 450 RPM. As compared to the TEM images of sample obtained at 300 RPM, the sample obtained at 450 RPM contains more amorphous carbon as is clear from TEM images (fig. 4.55(a) and 4.56(a)). However, HRTEM analysis also reveals the coating of amorphous carbon over the VC particles (fig. 4.56(b, c)). It might be because of the presence of some oxygen atoms in the graphite layer which creates defects in the structure as has been also observed in XRD analysis. However, mechanical

impact at intense milling also causes high density of defects and stacking faults that caused amorphization of the material [79].

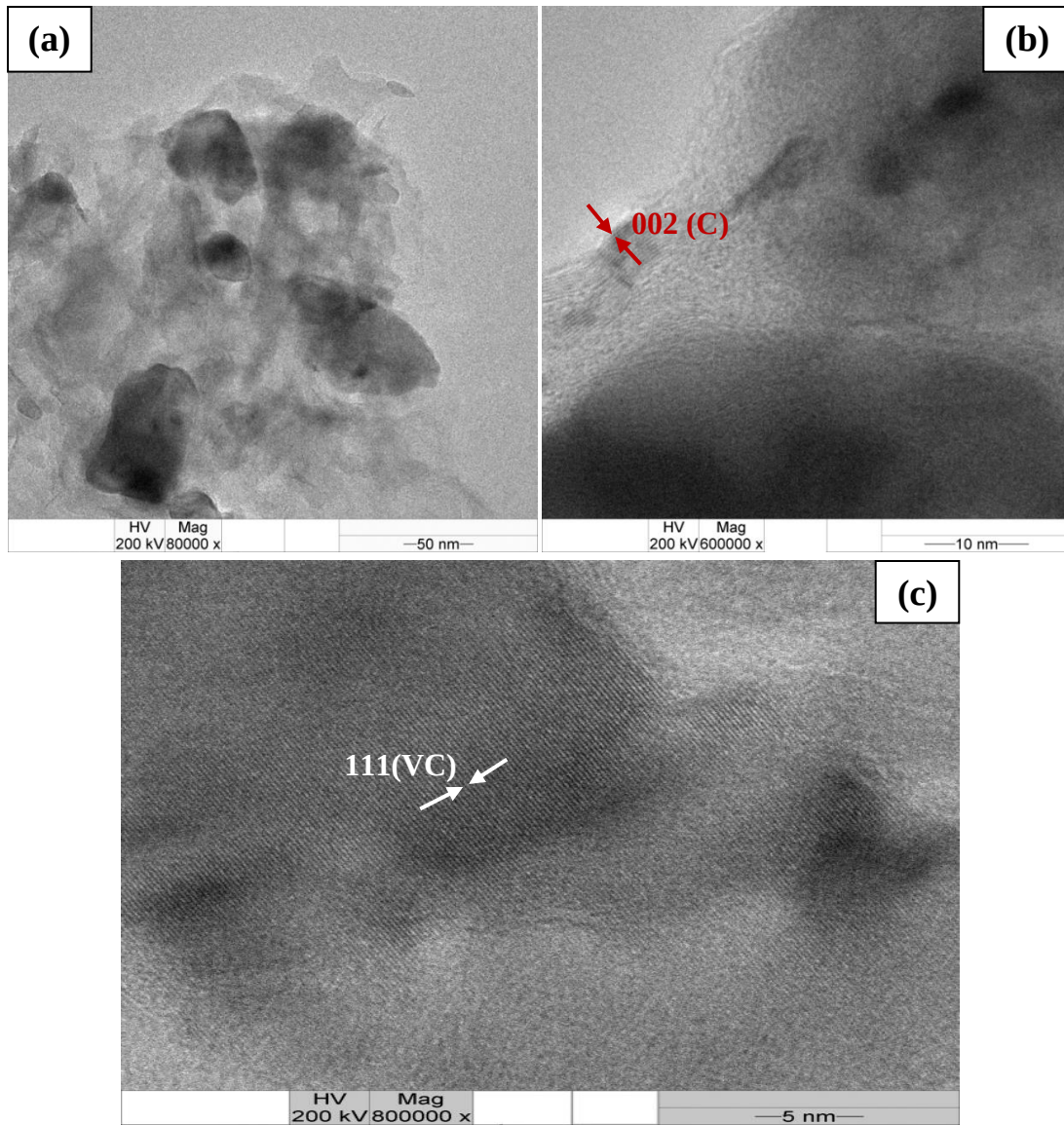


Figure 4.56: (a) TEM and (b & c) HRTEM micrographs of sample B-450-15-2.5.

In case of variation in the amount of Mg, the particles obtained with less amount of Mg show clear faceted morphology (fig. 4.57). HRTEM micrograph shows well-dispersed particles in nanometer range (fig. 4.57(b, d)). The reduction in the particle size was obtained with lower Mg amount. With the increase of milling parameters, the particles become coarser. Similar behaviour was also reported in the literature during milling at high milling time and speed [79, 80].

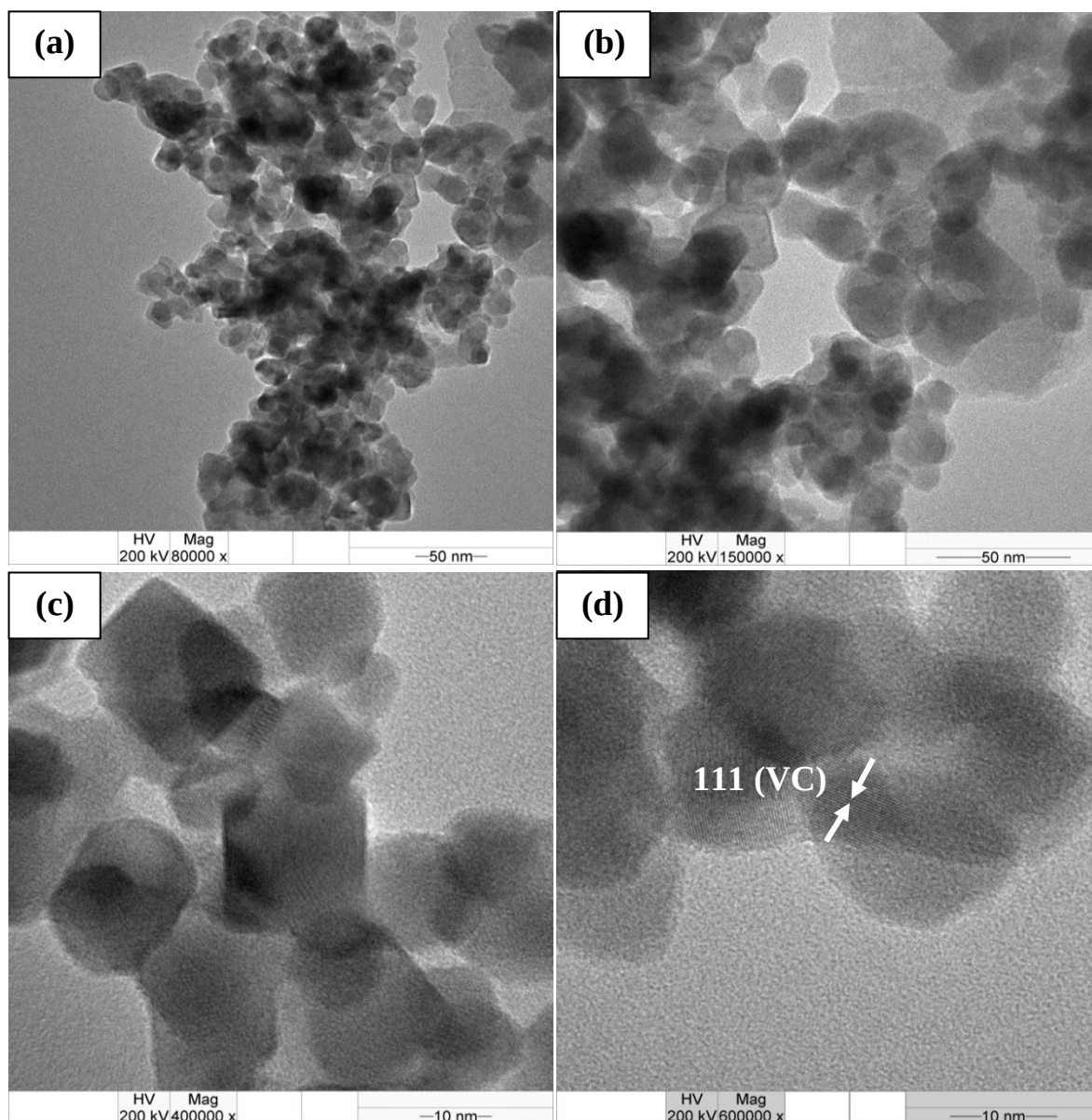


Figure 4.57: (a & b) TEM and (c & d) HRTEM micrographs of sample B-300-15-2.15.

4.3.3 Proposed Reaction Mechanism

The formation of VC-C nanocomposite during mechano-chemical synthesis can be divided into three parts. At initial stage, continuous fragmentation of reactants (V_2O_5 and Carbon) into smaller particles at lower milling parameters (RPM, milling time and amount of Mg) occurs. These fragmented particles having higher surface area, react with unreacted Mg to form lower intermediate oxides. These magnesio-thermic reductions are highly exothermic and generally evolves high amount of heat. The heat generated would be considered as the driving force for the phase transformations. Since the reaction takes place in a very short

period of time so it is difficult to predict the nature of the intermediate products during reduction. The XRD results show the formation of only one phase, $V(CO)_6$ at all the milling parameters before the formation of VC in almost all milling conditions. However, at critical parameter, $V(CO)_6$ is instantaneously converted to VC indicating that milling introduces mechanically induced self-sustaining reaction (MSR) during which local temperature of the system was around ~ 1000 °C for a short period of time [75] and reactants readily transformed into products [70]. MSR is a self-propagating high temperature synthesis in which reactants abruptly transforms into products after critical milling conditions (RPM, milling time, etc.). $V(CO)_6$ is highly reactive compound and it can explode at high temperatures by releasing carbon monoxide (CO) and vanadium (V) as product phases. The reaction between V and C is thermodynamically favourable and activated by high-energy ball collisions. Therefore, because of the high affinity of vanadium and carbon, there is surface interaction of carbon with vanadium in the second stage with the increase in milling parameters. At this stage, the milled powder attains sufficient energy and a stage is reached, where extra carbon started to accumulate over the surface of VC. As a result, formation of VC-C nanocomposite takes place in which VC nanoparticles are covered by carbon layers and molecular-dense compaction of mixture takes place which leads to the significant decrease in the surface area of the powder. In the third stage, almost all atoms participate in the chemical interaction of metal with carbon leading to the crystallization of the synthesized product. As a result, homogeneous distribution of strengthening phase in metal matrix takes place during milling [71].

4.3.4 Thermal analysis

In order to study the thermal stability of the obtained product during milling, thermal analysis was done on samples by heating them in air with heating rate of 5 °C/min. Figure 4.58 shows the TG/DSC curves of the samples obtained by the variation in RPM of milling. The TG curve shows that maximum weight loss has occurred in sample obtained at higher RPM (B-450-15-2.5) which is improved by decreasing RPM. This weight loss in the samples arises due to the availability of free carbon in the synthesized powder samples whose loss in terms of CO_x ($x=1, 2$) contributed in the overall loss. However, the weight gain revealed by the samples obtained at lower RPM (250 and 300) may be due to oxidation of pure VC nano powder. But due to the lower crystallite size of synthesized powder at 300 RPM, it ascribed to the oxidation process through single peak.

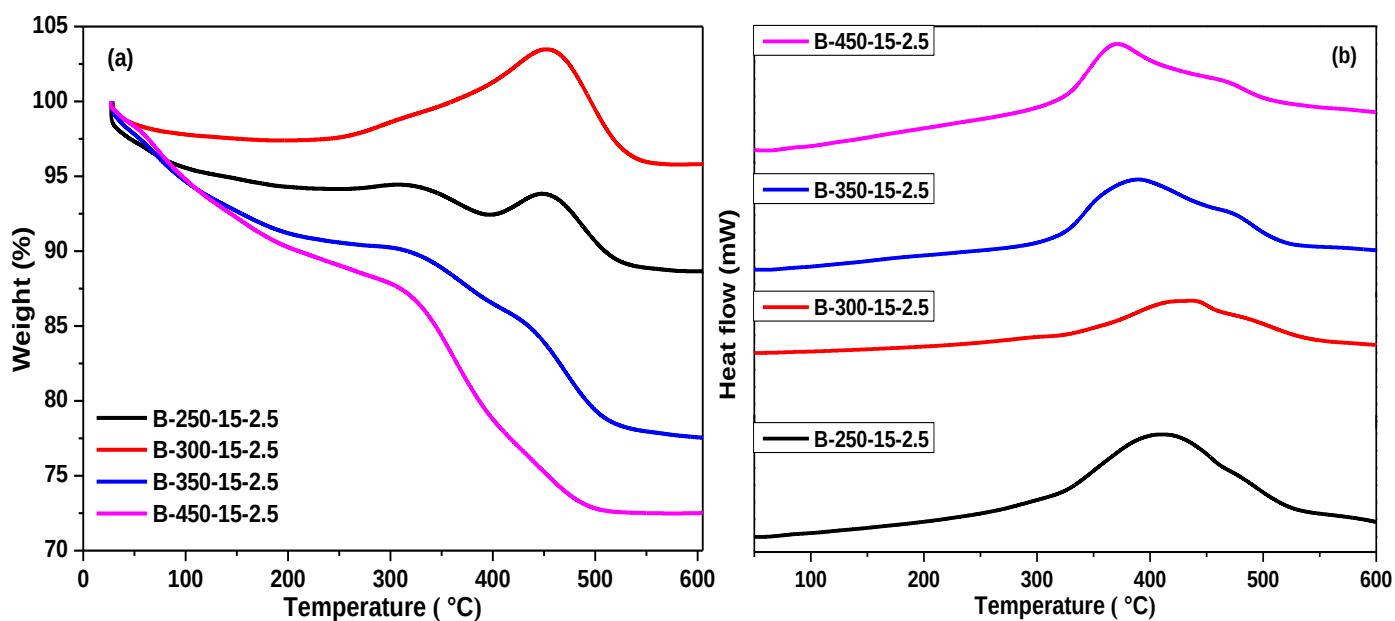


Figure 4.58: (a) TGA and (b) DSC plots of samples obtained at different RPMs.

Moreover, DSC analysis also correlates the process of oxidation of the synthesized samples by showing exothermic peaks at lower temperature range 300-400 °C. The shifting in the peak towards lower temperature at higher RPM (350 and 450) shows the lower thermal stability of the obtained product. One of the aspects in the shifting of DSC peaks towards lower temperature may be due to the fine size of carbonaceous species which is obtained as a result of consistently extensive milling at higher RPM.

The effect of milling time on the thermal property of obtained samples have been clearly observed from TGA curve (fig. 4.59(a)) which attribute the minimum weight loss in the powder samples obtained with the increase in milling time. It may be due to the formation of VC phase at higher milling time which stabilizes the sample against weight loss. Moreover, at higher milling time, the diffusivity of carbon is high which tends to convert oxide into carbide and decreases the amount of free carbon. In DSC curve, shifting of the oxidation peak towards lower temperature with the increase of milling time shows the low thermal stability of the obtained product. Moreover, the higher milling time also promote to the fineness of the carbonaceous species and results to shift in the DSC peak at lower temperature as discussed earlier.

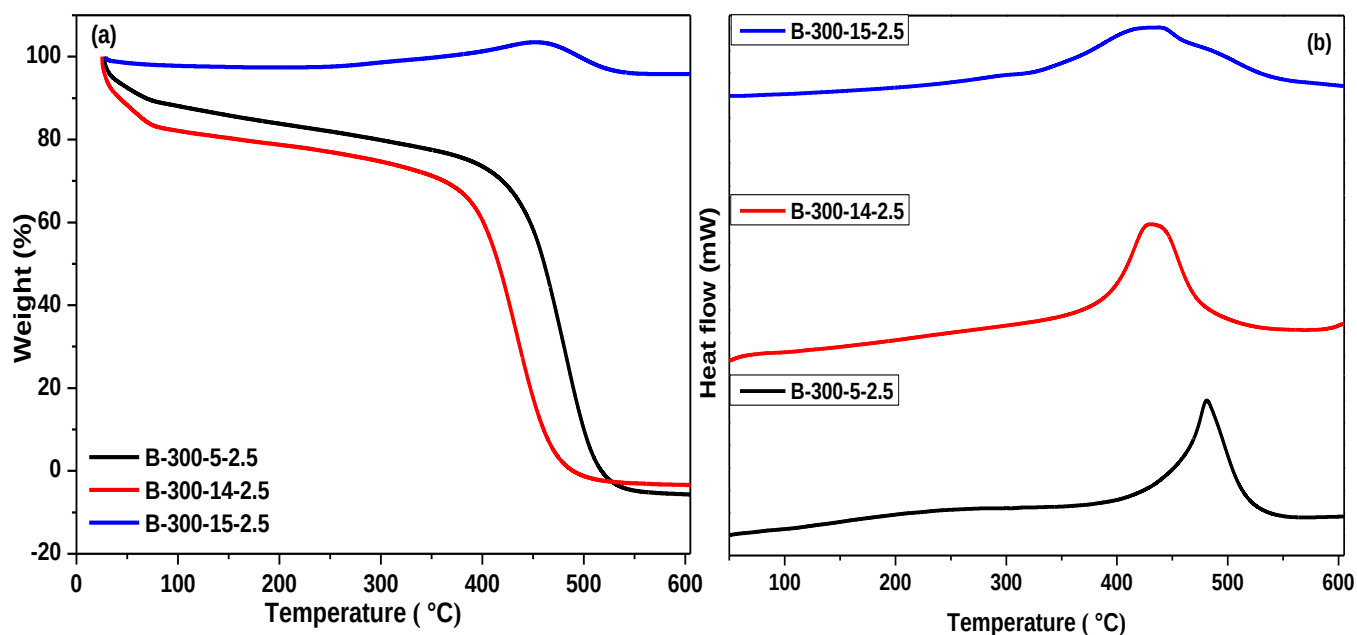


Figure 4.59: (a) TGA and (b) DSC plots of samples obtained for different milling time at 300 RPM.

As discussed in the XRD analysis, after getting single phase at 300 RPM in 15 h by using 2.5 g of Mg as reducing agent, the next optimization have been done on the amount of reducing agent (Mg). Hence, in order to study the thermal effect on the samples obtained with different amount of reducing agent, TGA/DSC analyses was done and is shown in fig. 4.60. Among all samples, the sample obtained with lower Mg content (2 g) shows maximum weight loss which corresponds to oxidation of free carbon as well as in-situ produced carbon due to the decomposition of $V(CO)_6$. With the increasing amount of reducing agent, the %age of VC content increases and correspondingly minimum weight losses in the powder samples has been observed. Such kind of features in the obtained behaviour reflects the formation of single phase VC nano powder. Moreover, the shifting in the oxidation peak in DSC curve towards higher temperature in B-300-15-2.25 and B-300-15-2.5 than B-300-15-2.15 ascribed to the higher thermal stability of VC synthesized with higher amount of reducing agent. It may be due to the enhancement in crystallinity in the carbonaceous species with high reducing agent which is also observed in Raman analysis (discussed later).

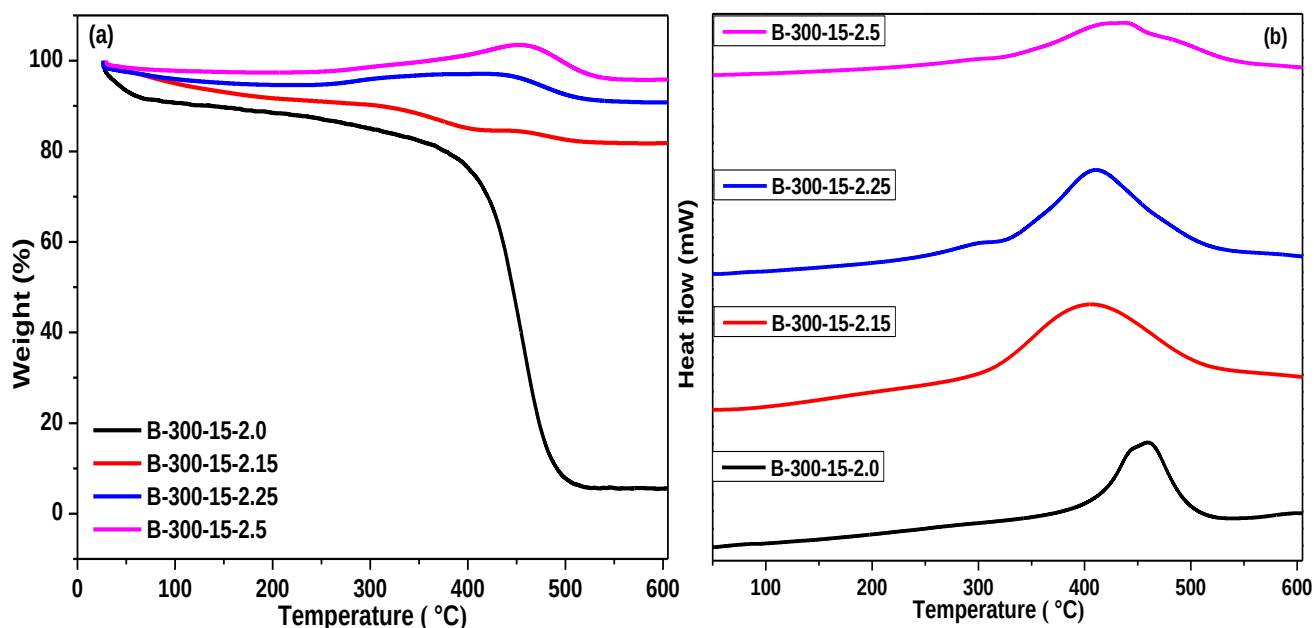


Figure 4.60: (a) TGA and (b) DSC plots of samples obtained with different amount of Mg at 300 RPM for 15 h.

4.3.5 Raman spectroscopy

Raman spectroscopy is an effective method to investigate the degree of graphitization and defect density of the carbon materials. Raman spectra of the ball-milled powders are shown in fig. 4.61. It exhibits two main bands called D (disordered) and G (graphitic) bands at ~ 1349 and 1588 cm^{-1} , respectively [11]. The G-band is associated with the vibrations of sp^2 -bonded carbon atoms. The broad D-band is related to the structural defects or amorphous carbon or the incorporation of oxygen atoms within the graphite layer. The intensity ratio of I_D/I_G is used to estimate relative content of defects. The calculated value of I_D/I_G ratio for the synthesized samples is shown in table 4.23.

According to the calculated values, the higher I_D/I_G ratio for B-150-15-2.5 is directly related to the decrease in the average size of the sp^2 graphene domains at lower milling conditions [81]. With the increase of RPM to 300, the I_D/I_G ratio decreases and again increases with the increase in RPM to 450. This is because of the disordered carbon or the incorporation of oxygen atoms within the graphite layer at higher RPM [14, 15]. It shows the presence of disorder in the structure and lower degree of graphitization. These results are well in agreement with the XRD results, where appearance of $\text{V}(\text{CO})_6$ phase started to increase after 300 RPM and maximum at 450 RPM.

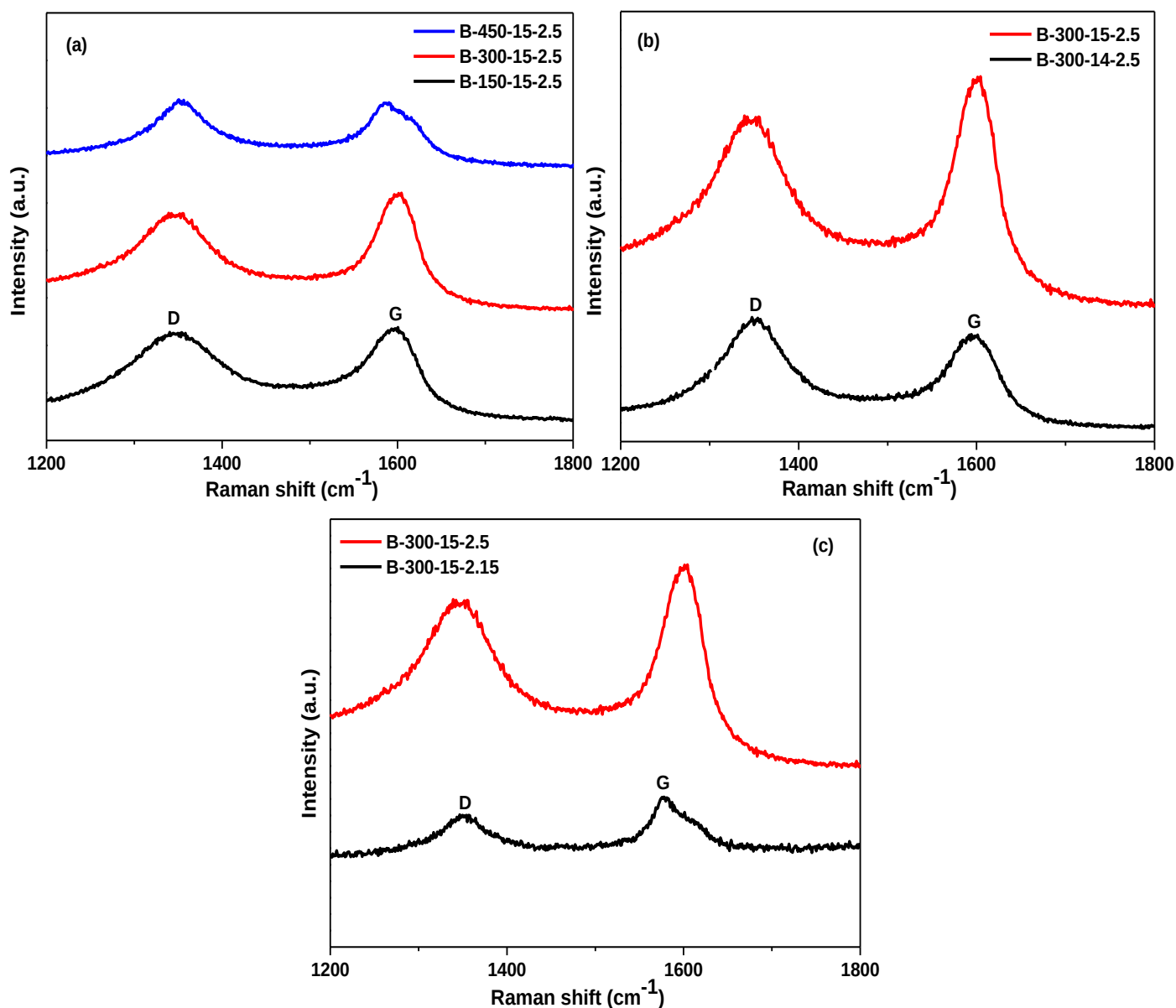


Figure 4.61: Raman spectra of the samples obtained with variation in (a) RPM (b) milling time and (c) amount of Mg.

Moreover, with the effect of increasing milling time from 14 to 15 h and the amount of Mg from 2.15 to 2.5 g, I_D/I_G ratio decreases, indicating the increase in the crystallinity of the synthesized product at higher milling parameters. In addition, the diffusion of more carbon atoms into the lattice to convert an oxide into VC nano particle with the effect of higher milling parameters (RPM, milling time and amount of Mg) reduces the amount of unreacted carbon and therefore, content of defects. These results are in well agreement with XRD, TGA and BET results (discussed later).

Table 4.23: Calculated values of I_D/I_G ratio.

Sample	D-band (cm^{-1})	G-band (cm^{-1})	I_D/I_G ratio
B-150-15-2.5	1349.2	1588.3	0.98
B-300-15-2.5	1344.4	1596.7	0.71
B-450-15-2.5	1353.6	1588.6	0.86
B-300-14-2.5	1349.8	1590.6	1.02
B-300-15-2.15	1352.2	1584.0	0.76

4.3.6 BET surface area and pore size distribution

In mechano-chemical synthesis, the textural properties of the milled particles mainly depend on the secondary processes as aggregation and agglomeration [79]. The surface area and pore size distribution of the selected samples was investigated by nitrogen adsorption/desorption measurements carried out at 77 K. All adsorption/desorption curves are shown in fig. 4.70. As shown in fig. 4.70, typical type IV isotherm profile along with hysteresis (indicative of narrow distribution of mesopores) was observed [54]. The adsorption capacity increases with increasing relative pressures from 0.4 to 1.0, which directly shows the presence of mesopores in the material. The shape of the hysteresis loops is of type H3, which is related to the slit-like pores present in the synthesized samples [55, 56]. The increase in adsorption at relative pressures lower than 0.1 also shows the presence of micropores in the material milled at low milling parameters [53]. The capillary condensation and evaporation at a medium relative pressure indicate the hierarchical arrangement of the pores [57].

On comparing the surface area of powder samples obtained by varying RPM, highest surface area ($S_A = 608.84 \text{ m}^2\text{g}^{-1}$) was obtained with lowest RPM for sample B-150-15-2.5 (table 4.24). While, on the other hand, after increasing the RPM from 150 to 300, the surface area of the powder samples is decreased from 608.84 to $32.43 \text{ m}^2\text{g}^{-1}$. The value of surface area is again going to increase for the sample which is prepared at milling speed of 450 RPM (B-450-15-2.5). Similar behaviour was also observed in the samples prepared by varying milling time (5-14 h) and amount of Mg (2.10-2.5 g). The decrement in surface area is related to the enhanced diffusion process with the increase of milling parameters which fill the pores and reduced the surface area. Also, during extensive milling of the powder, the surface area of the particles increases as a result of the reduction in size. This will increase the surface energy of the material being milled.

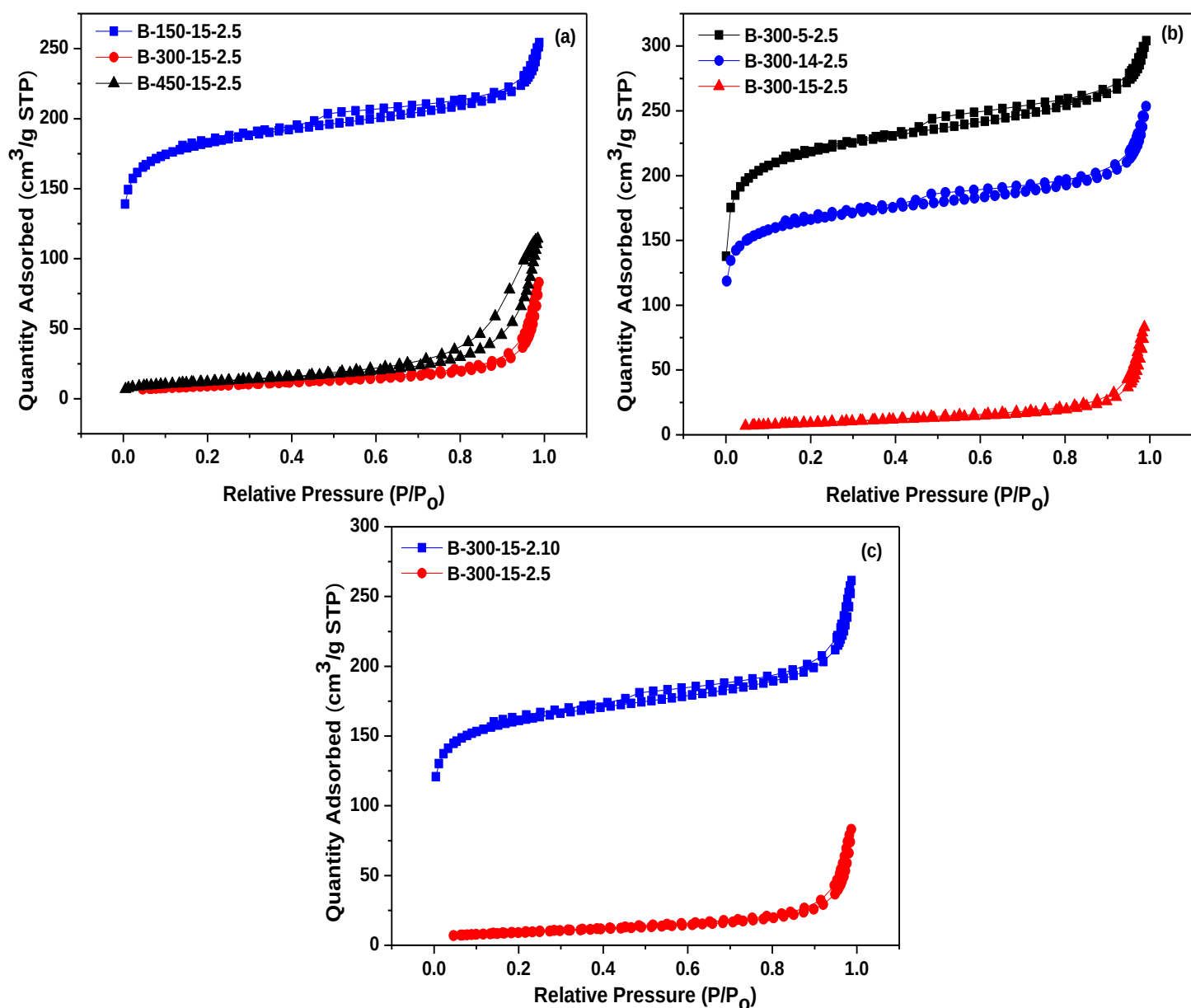


Figure 4.62: N₂ adsorption-desorption isotherms of the samples obtained with variation in (a) RPM (b) milling time and (c) amount of Mg.

Therefore, in order to release the excess free surface energy, particles started to agglomerate which results to decrease the surface area. Similar behaviour was also observed by many authors during high intensity dry grinding of materials [79, 80]. This is in accordance with the XRD results, where at lower milling work, broad XRD diffraction peaks were observed, which corresponds to higher surface area of the milled samples. FESEM micrographs also show the large aggregates having no definite shape at higher milling speed and time (fig 4.51 and fig. 4.52).

Table 4.24: Texture properties of the synthesized samples.

Sample	BET surface area (m^2g^{-1})	Peak pore size (nm)	Total pore volume (cm^3g^{-1})
B-150-15-2.5	608.8	3.76	0.15
B-300-15-2.5	32.4	3.75	0.13
B-450-15-2.5	42.9	3.75	0.18
B-300-5-2.5	829.4	3.76	0.19
B-300-14-2.5	630.1	3.73	0.17
B-300-15-2.10	547.5	3.75	0.19

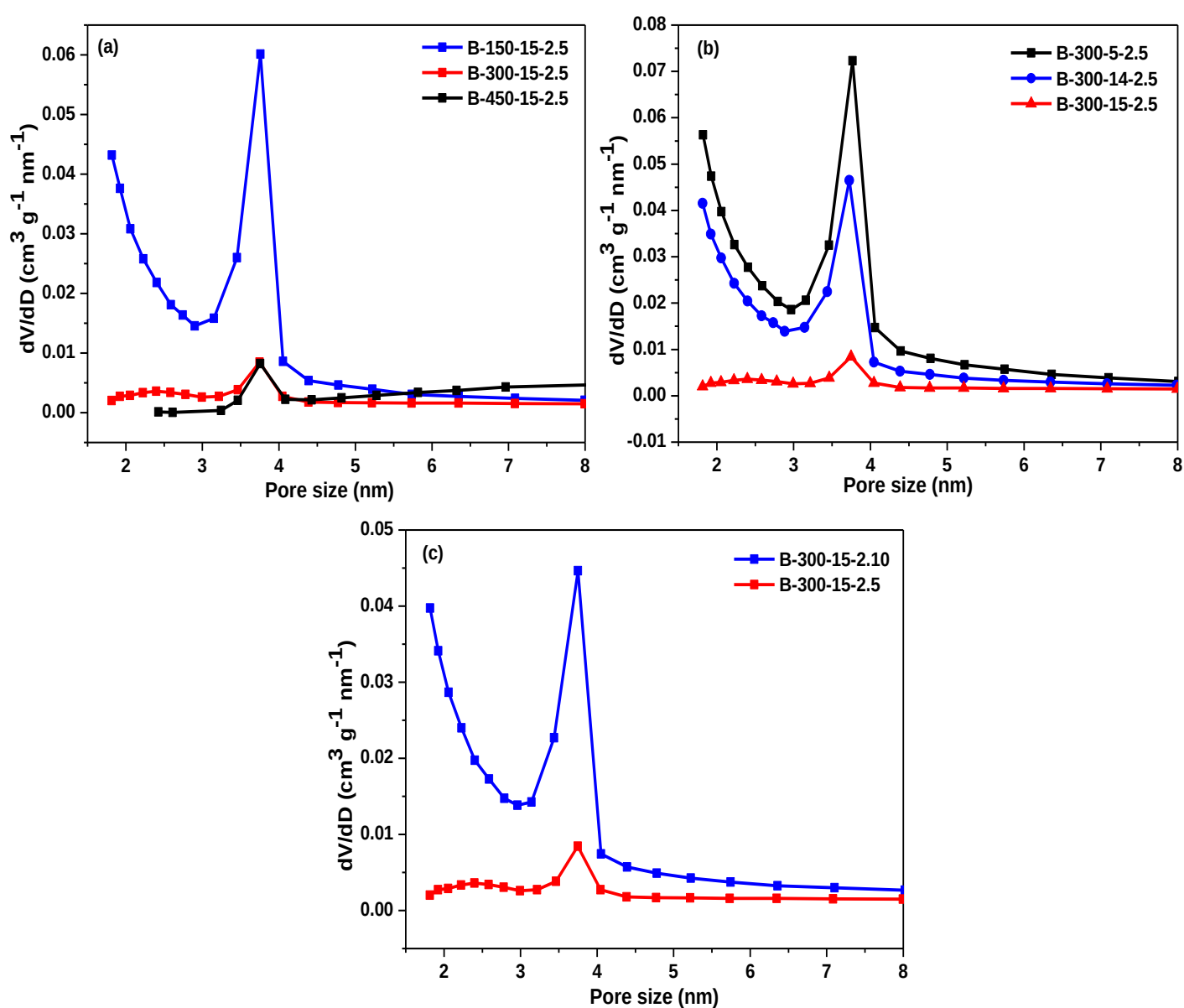


Figure 4.63: Pore size distribution curves of the desorption branch of samples obtained with variation in (a) RPM (b) milling time and (c) amount of Mg.

The pore size distribution (PSD) obtained from the desorption isotherm using Barrett-Joyner-Halenda (BJH) method is shown in fig. 4.63. The pore size distribution in all the samples shows narrowly distributed mesopores with mean pore size of ~ 3.7 nm. Another peak at less than 2 nm shows the presence of micropores in the sample milled at lower milling parameters. The specific surface area, pore diameter and total pore volume of the synthesized samples are shown in table 4.24. The decrement in the pore volume at higher milling parameters is related to the increase in graphitization during excessive milling which decreases the micropore and mesopores in the sample that results in the lower surface area and pore volume [54]. These results are in good agreement with the XRD results. Similarly, increasing the amount of reducing agent leads to enhancement in the crystallinity in the milled product, displaying lower surface area and pore volume. These results are in well agreement with the DTA and Raman analysis.

The samples synthesized in the present work were further used as grain growth inhibitor in WC-Co composite which are discussed in the next chapter.

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CHAPTER 5

RESULTS AND DISCUSSION-II

(Preparation of WC-Co-VC Nanocomposite)

Overview

This chapter deals with the discussion on the results related to the applicability of the synthesized vanadium carbide nanopowder (VC) as grain growth inhibitor used in WC-Co composite during sintering. The sintering behaviour of these nanocomposites (WC-Co-VC) by varying the amount of VC at different temperatures in argon atmosphere is discussed in detail. Microstructural examination of the obtained nanocomposite was done. The effect of VC on the hardness of WC-Co composite has been studied.

5.1 Effect of VC on sintering behaviour of WC-Co composite

In order to study the effect of VC on mechanical and structural properties of WC-Co composite, the as-milled nano VC synthesized in the present work was further used for making WC-Co-VC composite. The details about it have been given in the experimental section. The details of the prepared composition alongwith sintering conditions are given in table 5.1.

Table 5.1: Sample composition with sintering parameters.

Sample	WC/Co (wt.%)	Sintering Temperature (°C)	VC (wt.%)	Microhardness (HV)	Relative Density (%)
S-1	90/10	1250	0	100	55
S-2	90/10		0.5	104	58
S-3	90/10		0.7	133	60
S-4	90/10		1	200	61
S-5	90/10		5	578	79
S-6	80/20		5	256	70
S-7	90/10	1350	0	201	62
S-8	90/10		0.5	501	71
S-9	90/10		0.7	1124	75
S-10	90/10		1	1560	77
S-11	90/10		5	2216	81
S-12	80/20		5	1897	72
S-13	90/10	1400	0	904	88
S-14	90/10		0.5	1484	90
S-15	90/10		0.7	1587	92
S-16	90/10		1	1933	94
S-17	90/10		5	2366	97
S-18	80/20		5	1862	90

5.1.1 XRD analysis

Figure 5.1 shows the XRD pattern of starting powder (C-WC) and the samples sintered at 1400 °C with and without adding VC. The peaks corresponding to W_2C and W also appeared

in the XRD pattern of starting powder (C-WC). The amount of different phase(s) present in the respective XRD pattern has been calculated and given in table 5.2. Figure 5.1(b) shows the XRD pattern of consolidated WC-Co(10%)-VC(0%) composite.

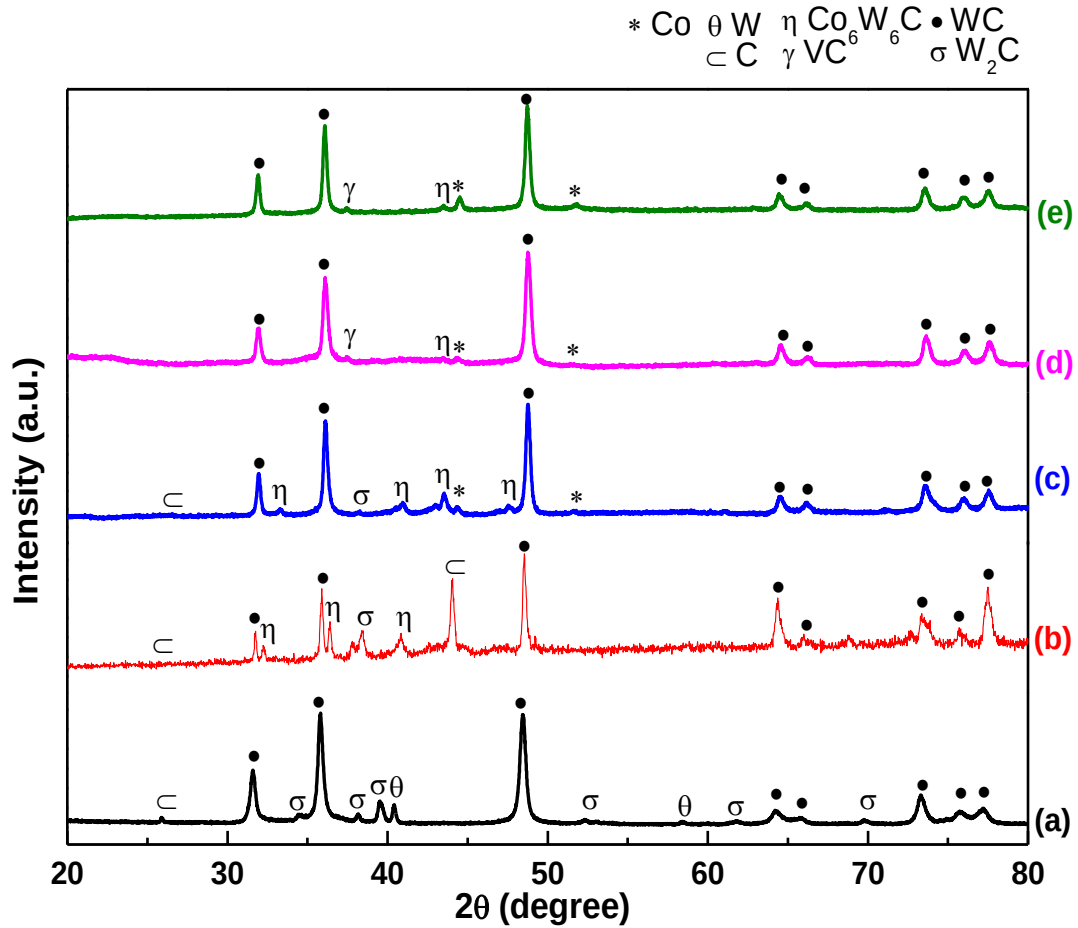


Figure 5.1: XRD patterns of samples (a) C-WC (b) S-13 (c) S-16 (d) S-17 and (e) S-18.

It shows the presence of different phases as WC, W_2C , Co_6W_6C (η) and C. However, inspite of the higher temperature, the diffraction peaks of W_2C with higher volume fraction (table 5.2) also appear in the XRD pattern which attributes to the decarburization process in sample S-13 during sintering. It occurs due to the surface oxidation of the fine WC powder. The process of decarburization in conventional liquid phase sintering (LPS) normally occurs due to the presence of either moisture or adsorbed air in the heating chamber irrespective of the fact that LPS is conducted in vacuum. [1]. The decarburization of WC during sintering has also been confirmed by many authors in the same WC-Co systems [2, 3]. However, the formation mechanism of η phase may also be explained by the interaction of W_2C with liquid Co at higher temperatures alongwith the presence of carbon (C) in the sample [4]. While on the other hand, the already present tungsten content in the raw material also reacts with Co at

lower temperature ($< 900\text{ }^{\circ}\text{C}$) and form Co_3W [4]. But, the absence of this phase in XRD pattern shows that by increasing sintering temperatures consistently upto $1400\text{ }^{\circ}\text{C}$, Co-containing phase (Co_3W) reacts with already present W_2C and free carbon in the sample and form η ($\text{Co}_6\text{W}_6\text{C}$) phase [4]. The well-defined reflections of η phase in WC-Co(10%)-VC(0%) composite in fig. 5.1(b) supports this fact. Hence, it is clear that metal binder (Co) migrate in the liquid form towards carbon deficient phase (W_2C and W) and results to the formation of η phase [1, 5]. These phases ($\text{Co}_6\text{W}_6\text{C}$, W_2C) are considered as unwanted phases which deteriorate the mechanical properties of the material considerably [3, 4, 6]. The higher volume fraction of η and W_2C phases in sample S-13 decreased with the addition of VC (S-16). With further increase in the VC content (S-17), it becomes negligible (table 5.2). This effect of decrement is due to the decomposition of $\text{Co}_6\text{W}_6\text{C}$ into WC and Co via reaction ($\text{Co}_6\text{W}_6\text{C} + 5\text{C} \rightarrow 6\text{WC} + 6\text{Co}$) that occurred at higher temperature ($> 1100\text{ }^{\circ}\text{C}$) which is also reported by many authors [6, 7].

Table 5.2: Volume fraction of the phases obtained after heating at $1400\text{ }^{\circ}\text{C}$.

Sample	grain size (nm)	Strain (* 10^{-3})	Volume fraction of phases (%)						
			WC	W_2C	W	VC	$\text{Co}_6\text{W}_6\text{C}$	C	Co
C-WC	18	3.02	71	14	12	-----	-----	3	-----
S-13	32	2.69	58	17	-----	-----	17	8	-----
S-16	25	2.18	80	2	-----	-----	13	2	3
S-17	19	2.10	90	-----	-----	3	2	-----	5
S-18	25	2.38	83	-----	-----	3	4	-----	10

Hence, the decomposition of η phase increases the content of WC and Co in composites which is clear from the table 5.2. The effect of VC in decreasing the volume fraction of η phase was also observed by Dai et al. [8]. One of the aspects of decreasing the presence of η phase is the solubility of VC in liquid Co which restricts its interaction with carbon deficient phase. It results in conversion of W_2C into WC because of the concentration gradient of carbon, which is already present in the raw material as well as associated with added VC content [2]. These results confirmed that the addition of VC with extra free carbon not only homogenise the carburization throughout the system but also acts as a catalyst to restrict the formation of unwanted phases. However, with 5% addition of VC in WC-Co(10%), the dominant phase is WC with minor peaks of VC and Co. No peak of subcarbides (W_2C and η

phase) and extra carbon could be found in XRD pattern and maximum volume fraction of WC was obtained in this case.

However, in order to observe the effect of higher amount of Co binder on the mechanical properties of WC-Co composite, the content of Co has been increased in sample S-18 by 20% in WC-Co(20%)-VC(5%). It shows the increment in the fraction of η phase with increased crystallite size which is observed from table 5.2. This is related to the fact that increasing Co content increases the availability of more Co atoms to migrate which increases the dissolution of WC into Co matrix and also increases the η phase [9-11]. The crystallite size and strain produced in sintered samples was calculated using Scherrer formula. It shows the decreasing trend as the content of VC is increased in WC-Co(10%) sintered at 1400 °C. While, on the other hand, it increases with increase in the Co content for sample S-18. The positive value of strain in all the samples shows the tensile strain in the system which decreases with the increasing VC amount. Moreover, the XRD results attribute the increase in the peak broadening of WC-Co composite with the addition of VC which is indicative of the grain refinement [4].

These results are based on the fact that after the addition of higher surface energy VC nanoparticles in WC-Co composite, a homogeneous layer of VC is obtained at the interface of WC and Co because of the dissolution of VC into Co. This will restrict the migration of Co binder into WC and thus suppresses the solubility of WC in Co phase. Consequently, the process of grain growth is inhibited resulting into finer, homogeneous structure with high hardness.

Therefore, high VC content appears to be more effective in controlling the η phase formation and grain growth.

5.1.2 Microstructure analysis

In order to investigate the role of VC as GGI in WC-Co composite, microstructure of the sintered samples was taken with the variable content of VC. The effect of temperature and content of inhibitor (VC) on the WC-Co was clearly observed in the micrographs of the sintered composites. Figure 5.2(a) shows the optical micrograph of WC-Co composite sintered at 1250 °C containing 10% Co. When the addition of 5% VC is done, the grain growth is restricted as is evident from fig. 5.2(b). However, with the increase of binder content to 20% in WC-Co(20%) having 5% VC, a slight enhancement in the grain growth was observed because of excess Co (fig. 5.2(c)).

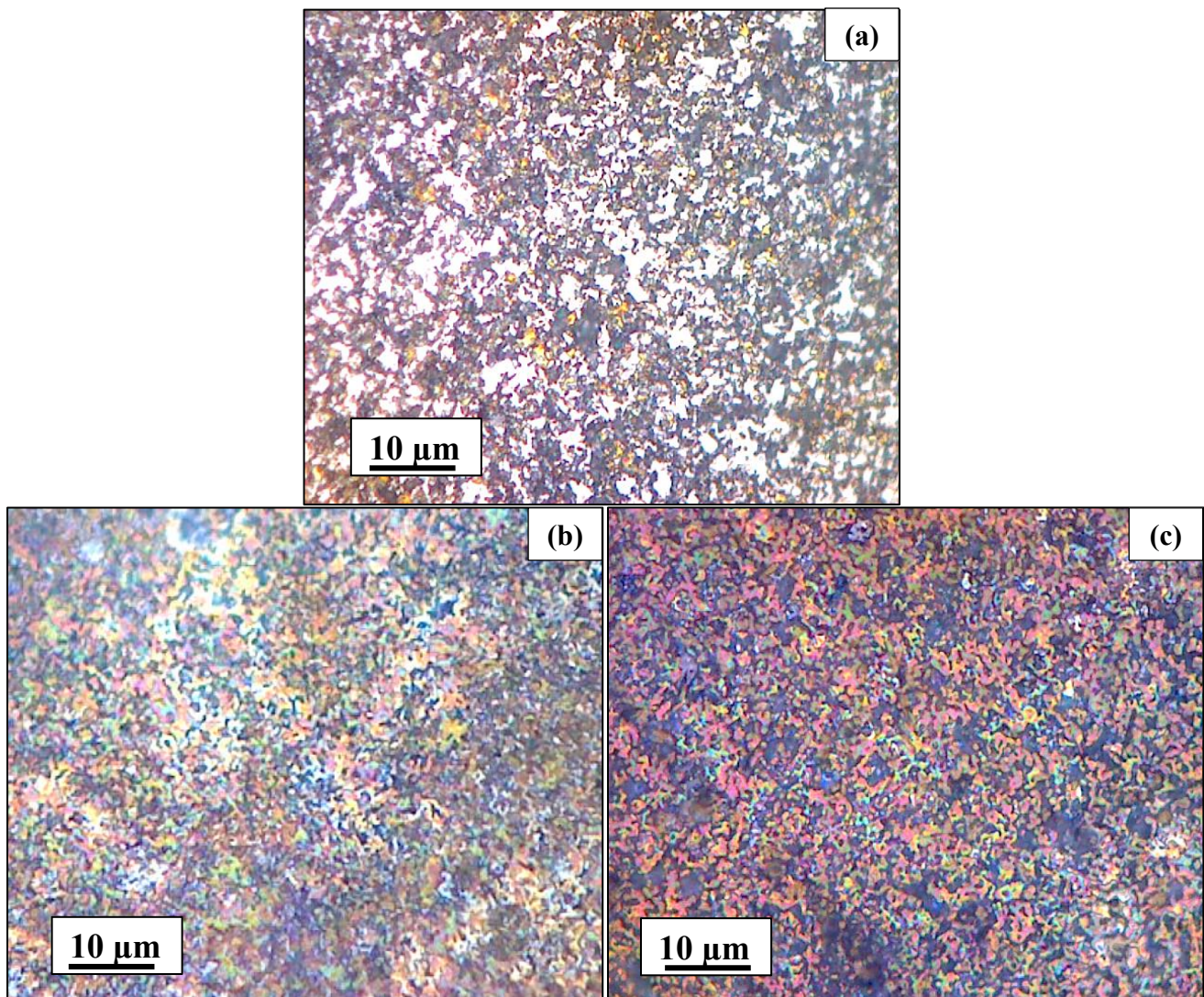


Figure 5.2: Optical micrographs of WC-Co composite sintered at 1250 °C with **(a)** 10% Co and 0% VC **(b)** 10% Co and 5% VC and **(c)** 20% Co with 5% VC at 1000x.

With the increase of the sintering temperature to 1350 °C, better microstructure has been observed (fig. 5.3). No significant change was observed in the shape of WC particles. A refinement was clearly observed in the WC particles with 5% VC addition (fig. 5.3(b, d)) as compared with 0.5% (fig. 5.3(a, c)). At certain places, small pores are visible between WC grains. The dark field image at high magnification clearly shows the role of VC as GGI having different VC contents (fig. 5.4). Very fine grains of WC particles were observed in case of 5% VC addition. However, some growth was also seen in some areas but it is negligible as compared to that of 0.5% VC. Interestingly, the coalescence of grains was not observed in these micrographs which is the main process responsible for grain growth in WC-Co composite during sintering.

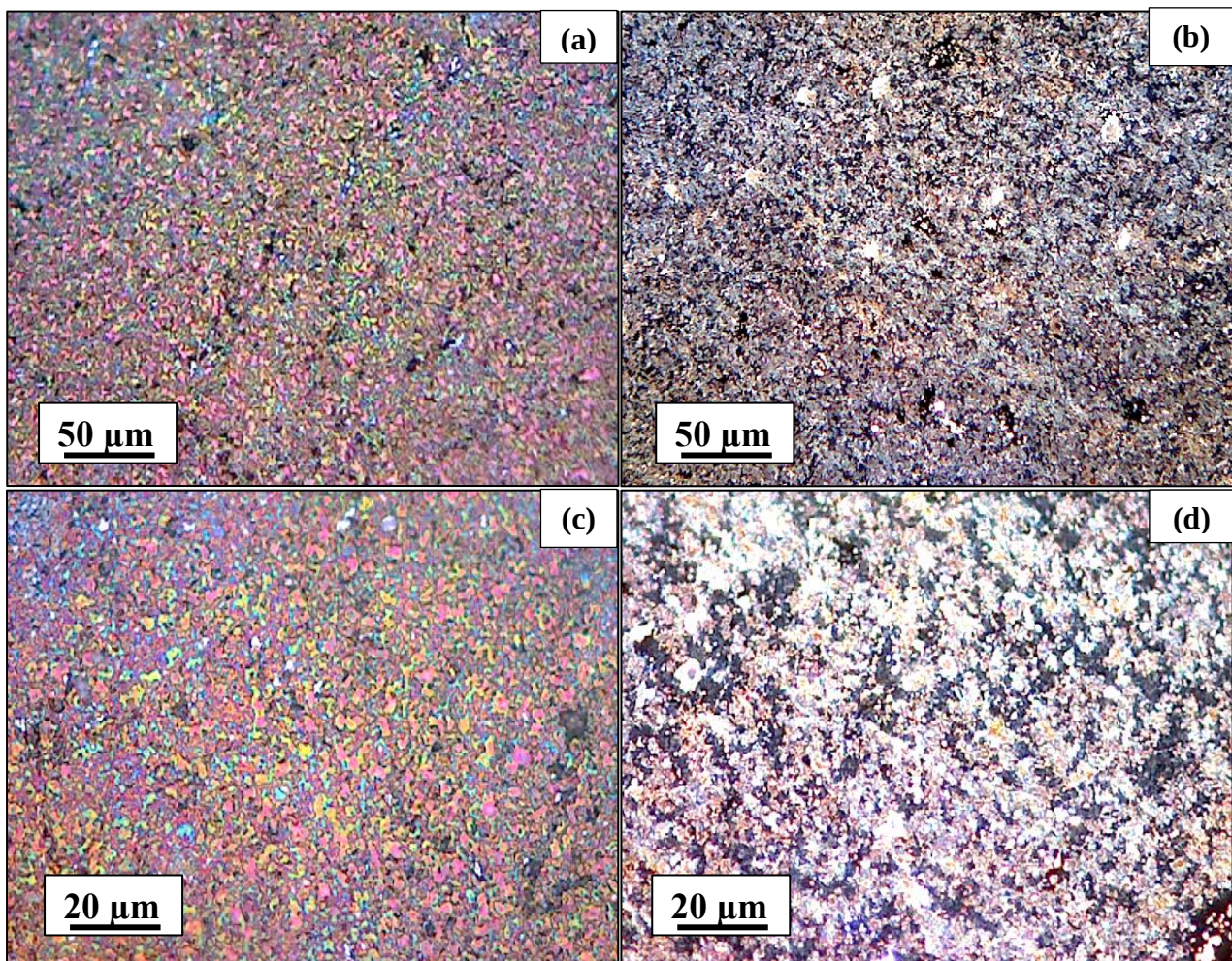


Figure 5.3: Optical micrographs of WC-Co(10%) composite sintered at 1350 °C with VC content of (a & b) 0.5% & 5% at 200x and (c & d) 0.5% & 5% at 500x.

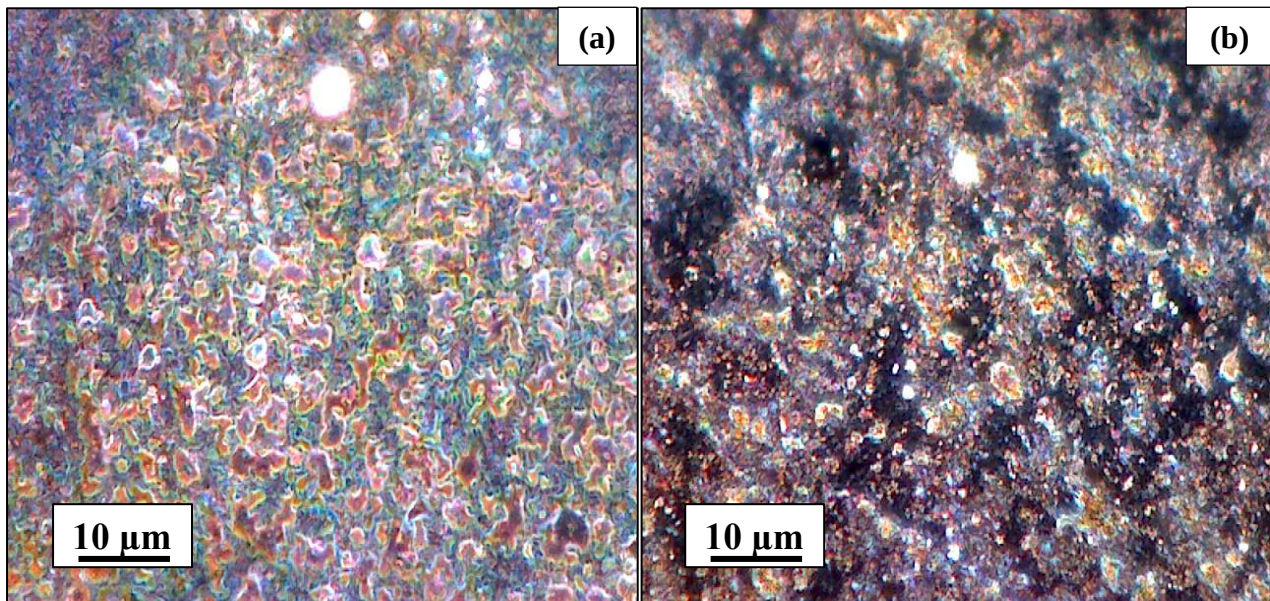


Figure 5.4: Dark field micrographs of WC-Co(10%) composite sintered at 1350 °C with VC content of **(a)** 0.5% and **(b)** 5% at 1000x.

Figure 5.5(a) shows the SEM micrographs of WC-Co(10%) containing 5% VC. The structure depicts the LPS process having uniform morphology of grains. The corresponding EDS analysis (fig. 5.5(b)) depicts the presence of different elements in it. The presence of around 3 wt% V in EDS indicates that nearly 4% VC is present in the system. Considering the fact that our synthesized VC contains some carbon also, it indicates fair distribution in the synthesized product.

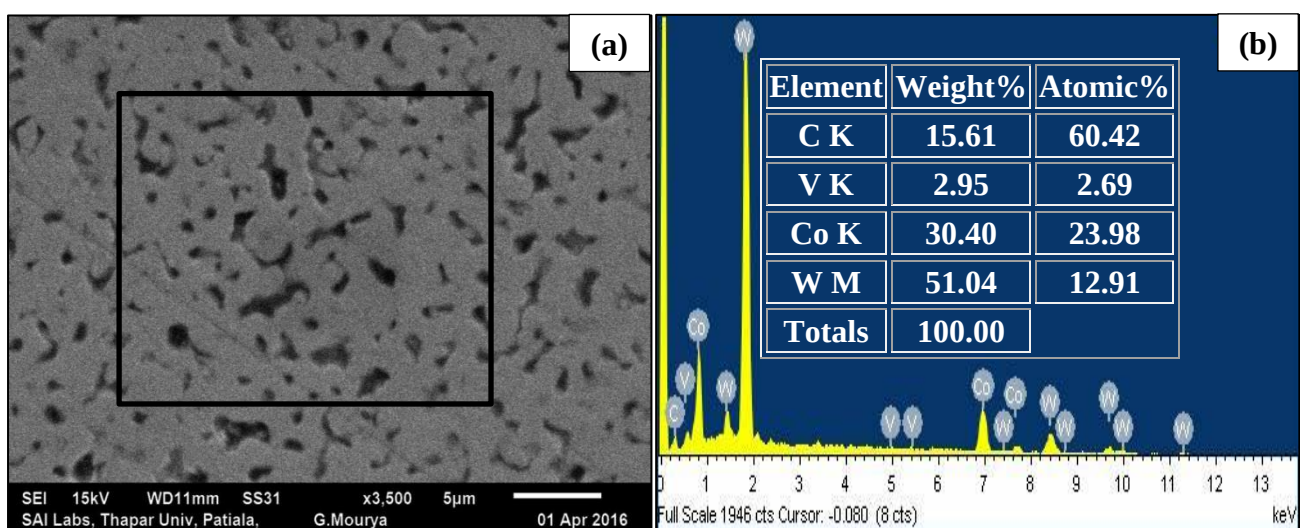


Figure 5.5: SEM images of WC-Co(10%) composite sintered at 1350 °C with 5% VC addition.

At higher sintering temperature (1400 °C), more refined and homogeneous structure is observed as shown in fig. 5.6. In fig. 5.6(a), WC-Co(10%) without VC shows the formation of η phase with large voids as also discussed in the XRD analysis. Eso et al. [6] have reported that the formation of η phase depends on the carbon level and temperature. The irregular growth of η phase can be seen at several places in fig. 5.6(c). η phase nucleates during LPS at the grain boundaries of WC-Co composite, which can be easily seen in the dark field image of fig. 5.6(c) shown in fig. 5.6(d). Because of the formation of η phase, crack at the grain boundaries develops which deteriorate the mechanical properties of sintered samples [6].

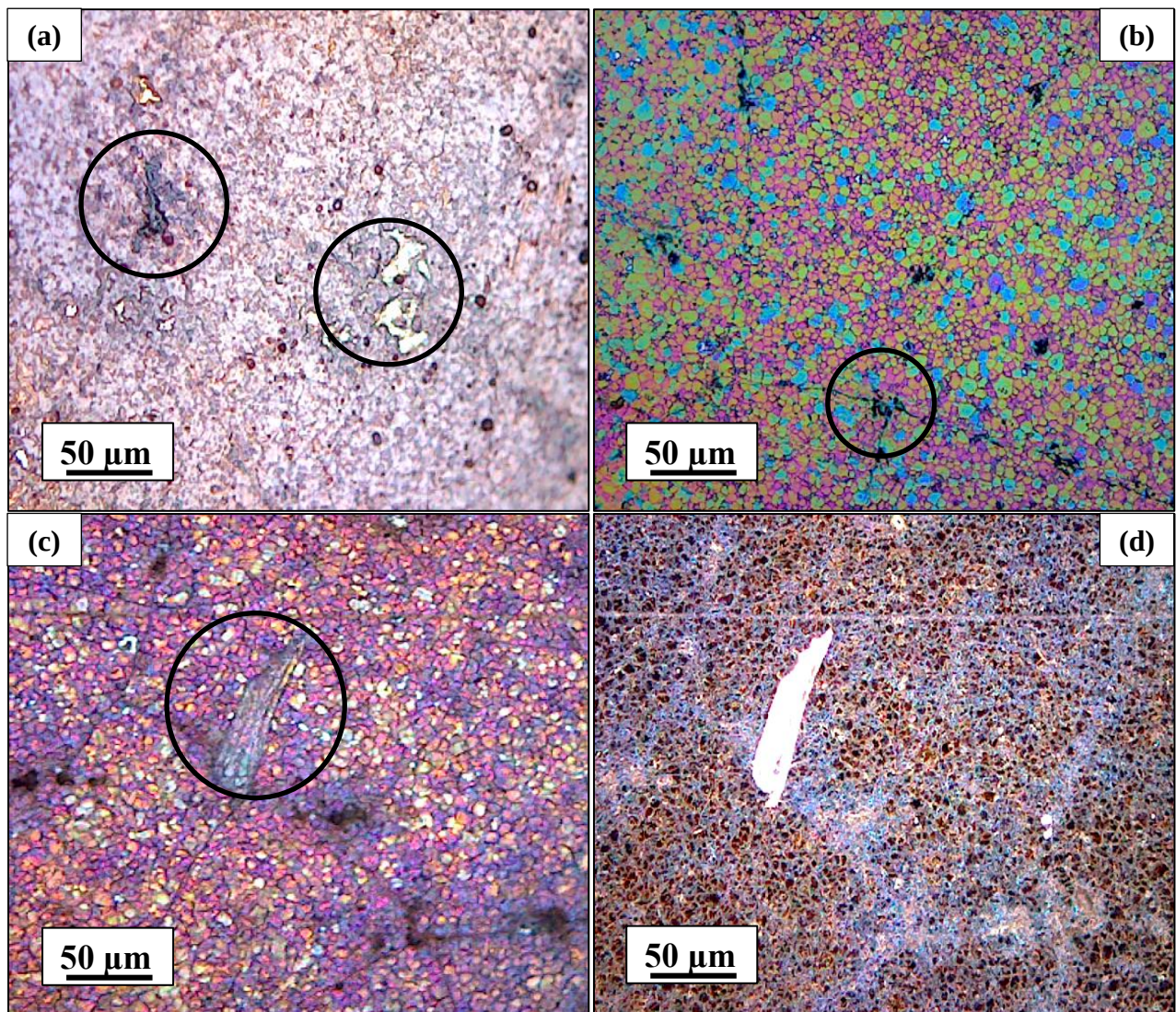


Figure 5.6: Optical micrographs of WC-Co(10%) composite sintered at 1400 °C with VC content of (a) 0% (b) 0.5% (c) 1% and (d) dark field image of (c) at 200x.

The crack initiation with the increase of GGI was also reported by Sun et al. [12]. With the addition of VC, it forms a thin layer over the WC grains that results in the crack initiation at the grain boundaries which deteriorate its mechanical properties [6].

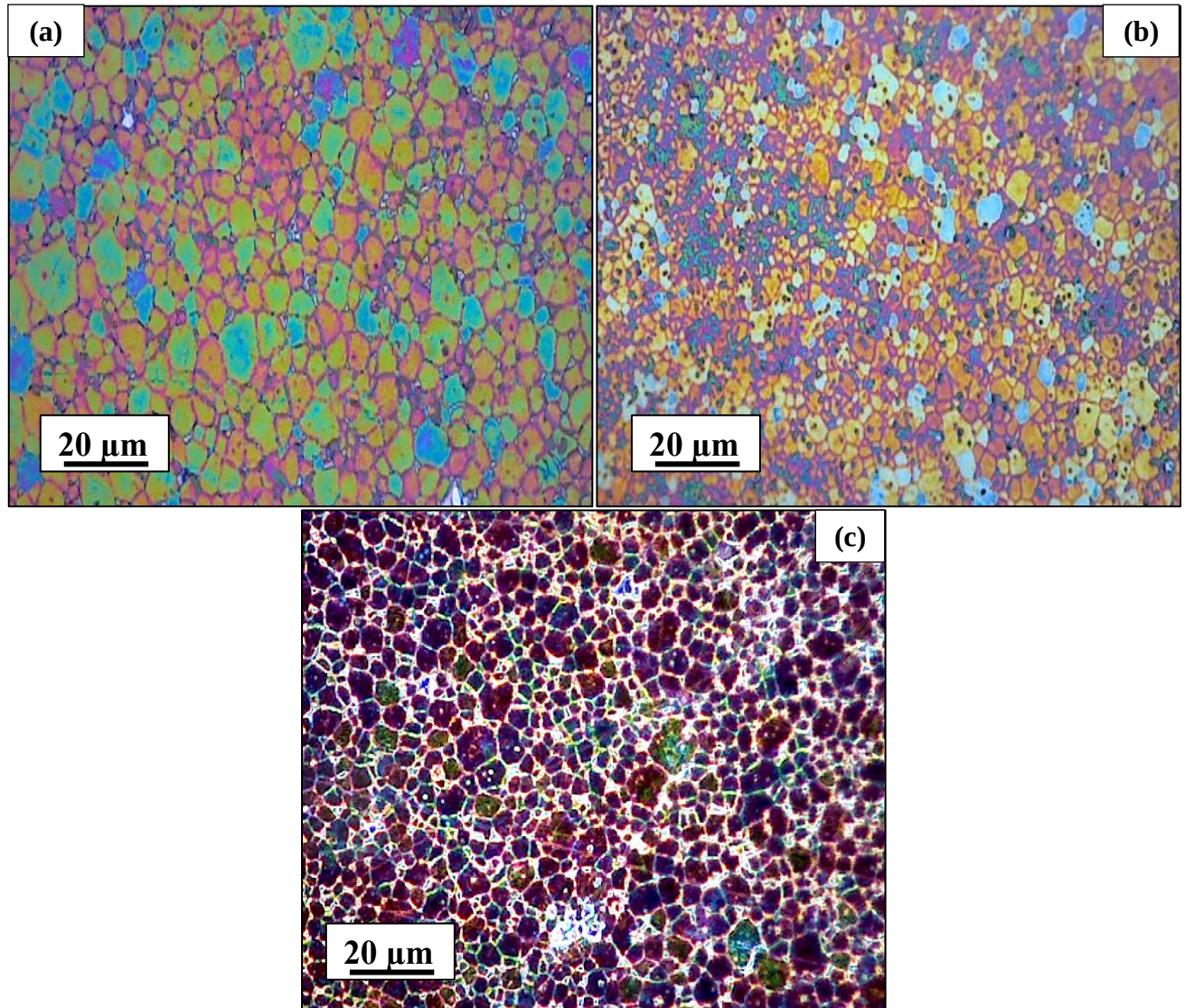


Figure 5.7: Optical micrographs of WC-Co(10%) composite sintered at 1400 °C with VC content of **(a)** 0.5% **(b)** 5% and **(c)** dark field image of **(a)** at 500x.

Faceted morphology of WC particles can be seen in fig. 5.7(a) with the addition of VC(0.5%) sintered at 1400 °C. With the increase in the VC content to 5%, well refined grains were observed as compared to less VC content (0.5%) which is clearly seen in fig. 5.7(b). The structure is fully dense with cuboid type of WC particles. The small black regions with circular shape on the WC particles correspond to the pores or may be the residual carbon which increases with the increased amount of VC addition in sample (fig. 5.7(b) and 5.8(b)). Moreover, adding VC as GGI in WC-Co restricts the atomic diffusion and Co migration that

results in the low densification and formation of voids/microporosity [10, 13]. The structure shown in fig. 5.8 is at higher magnification. It shows circular type of morphology. The dark field images shown in fig. 5.7(c) and 5.8(c) clearly shows the formation of structure having uniform grain size.

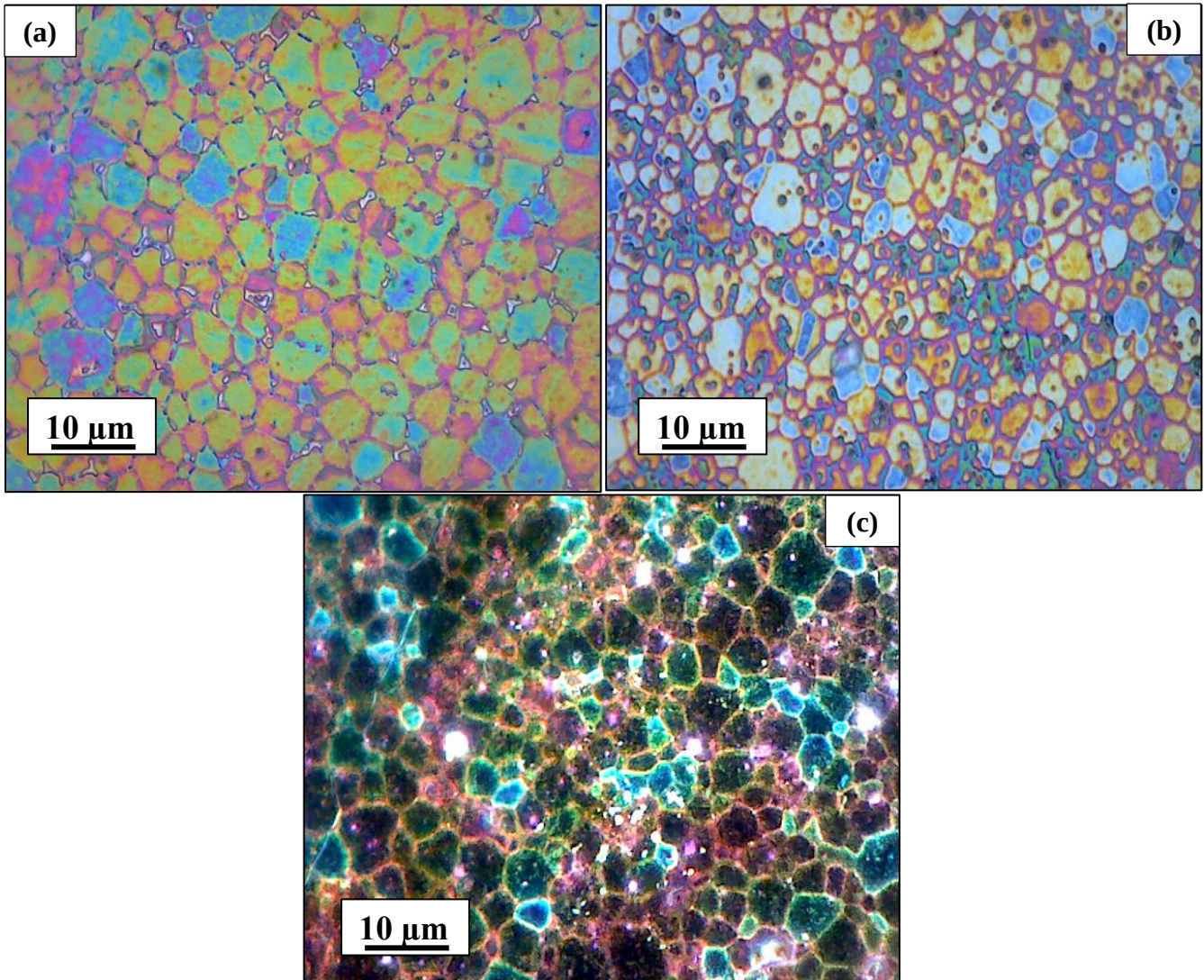


Figure 5.8: Optical micrographs of WC-Co(10%) composite sintered at 1400 °C with VC content of **(a)** 0.5% **(b)** 5% and **(c)** dark field image of **(b)** at 1000x.

The microstructural examinations of the WC-Co(20%) synthesized with higher binder content (20%) and 5% VC sintered at 1400 °C shows the mixed morphology of faceted and rod shape (fig. 5.9). Such type of features is developed because of the non-uniform temperature throughout the sample. Such structures are not desired. It indicates that Co content upto 10% is optimum for achieving better microstructure.

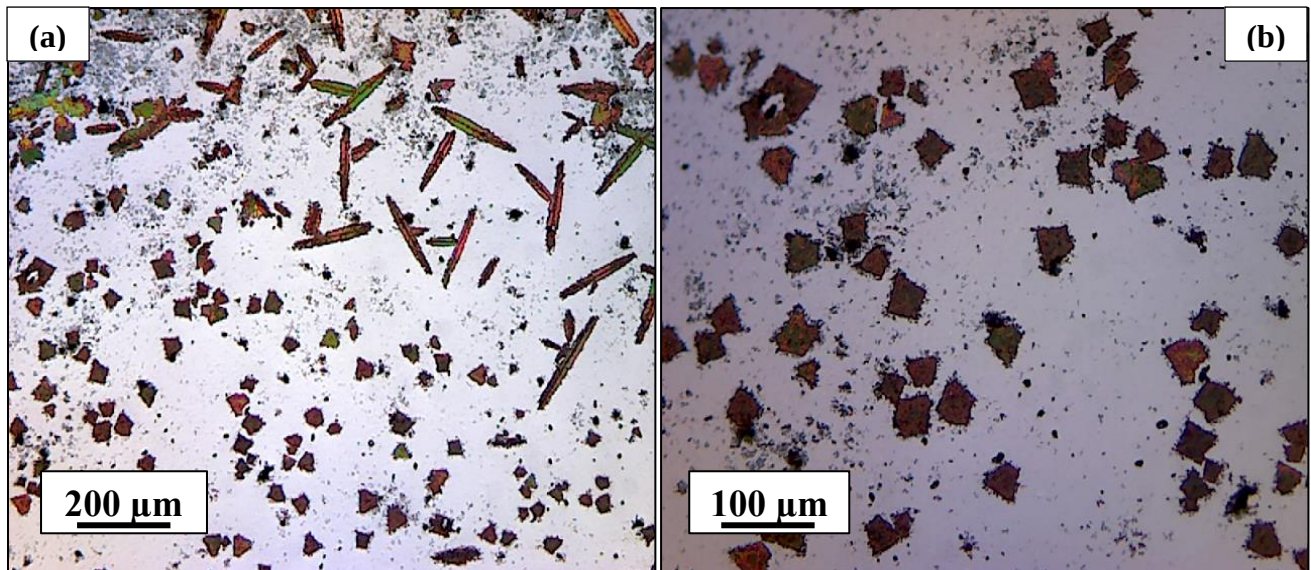


Figure 5.9: Optical micrographs of WC-Co(20%) composite sintered at 1400 °C with 5% VC at (a) 50x and (b) 100x.

Higher Co content leads to rod-shaped morphology of WC by coalescence during LPS alongwith faceted shape (fig. 5.9(a)). These rods thicken with time and ultimately grow as elongated rectangular shape as shown in fig 5.9(b). These types of structural features occur as a result of agglomeration of individual platelet crystals along certain preferred orientation.

5.1.3 Hardness analysis of the composites

In order to study the effect of VC on the mechanical properties of WC-Co/VC composite, microhardness of the prepared samples were measured. Hardness of all the sintered samples along with calculated density with different compositions and processing parameters is given in table 5.1. The microhardness values of the sintered composites containing VC are higher than the base WC-Co alloy in all cases. The fineness of the grains can also be estimated from the hardness values as finer structure gives rise to maximum hardness according to Hall-Patch relation [2, 8]. Lower hardness observed in WC-Co samples is because of coarse structure.

With the addition of lower content of VC (0-1%) at 1250 °C, no significant improvement in the hardness values was observed. According to Kurlov et al. [4] the most intense densification of the hard metals occurred at the sintering temperature of > 1330 °C because Co binder becomes liquid at this temperature. However, density of WC-Co(10%) composite sintered at 1250 °C was improved with the addition of higher content of VC(5%) which is

also reflected in increment in the microhardness of the composite. The reason for the low microhardness and density of the samples sintered at 1250 °C is because of the viscous nature of Co binder at low temperature. As a result, Co pools are created in some areas of the material during sintering. Because of this it is unable to flow into the nanopores of WC grains. Hence, absence of Co binder between WC grains, which acts as a diffusion barrier, results in abnormal grain growth, low hardness and low density [10]. Hence, in order to observe the effect of temperature on the density and microhardness of WC-Co(10%) composite, analysis has been done at higher sintering temperature with the addition of VC content. At higher sintering temperature (> 1330 °C), mechanical properties of WC-Co composites are related to the completely molten state of Co binder. The improvement was observed with the increase of sintering temperature to 1350 °C. The variation of microhardness and relative density of the sintered samples as a function of VC content and sintering temperature is shown in fig. 5.10. The increased value of hardness in the present study than the reported ones [10, 14, 15] with the addition of VC might be because of the nano size VC powder produced by mechano-chemical route with uniform distribution. Therefore, with the addition of the VC, grain coarsening was inhibited which increases the hardness and could be proved as a better GGI as compared to the conventional VC powder.

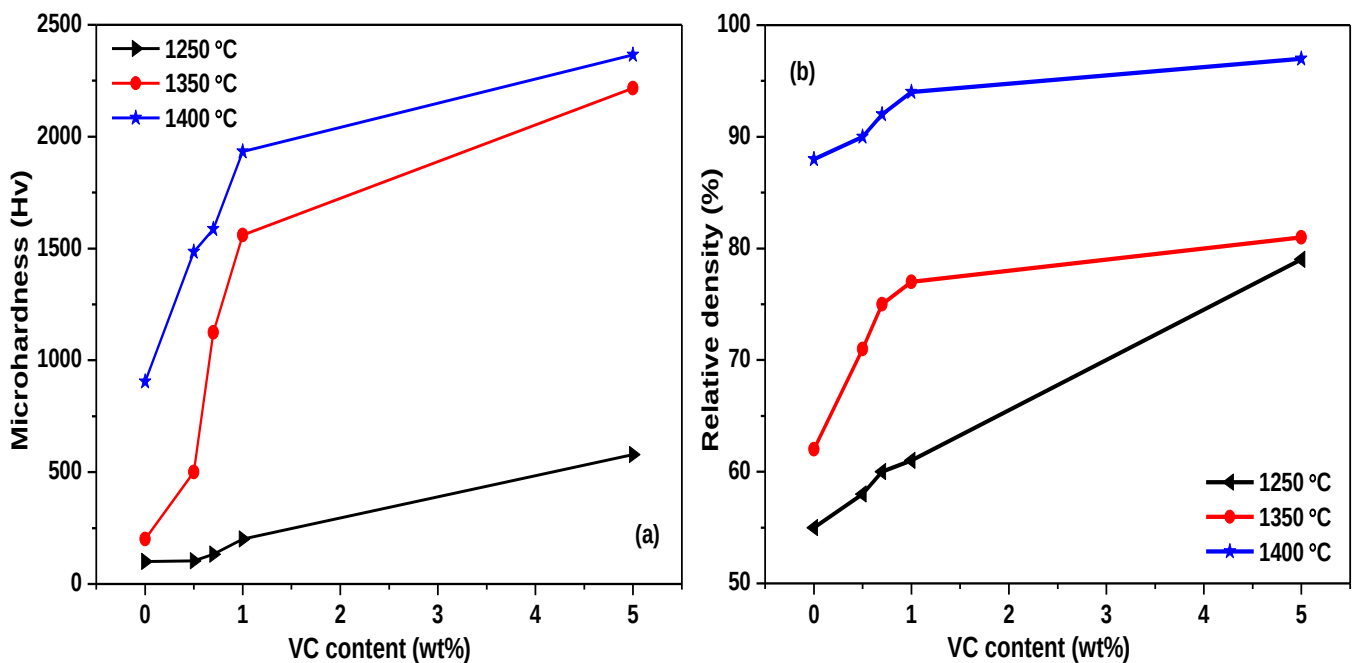


Figure 5.10: Effect of VC content on **(a)** Microhardness and **(b)** Relative density of WC-Co(10%) composite at different sintering temperatures.

Irrespective of the sintering temperature, the value of microhardness and density of the WC-Co(10%) composites was observed to increase consistently with the increase in VC content and attained higher value with 5% VC addition. Therefore, after considering the best result obtained at this composition of VC, the effect of Co content was also analysed by increasing the Co amount to 20% in WC-Co(20%) composite.

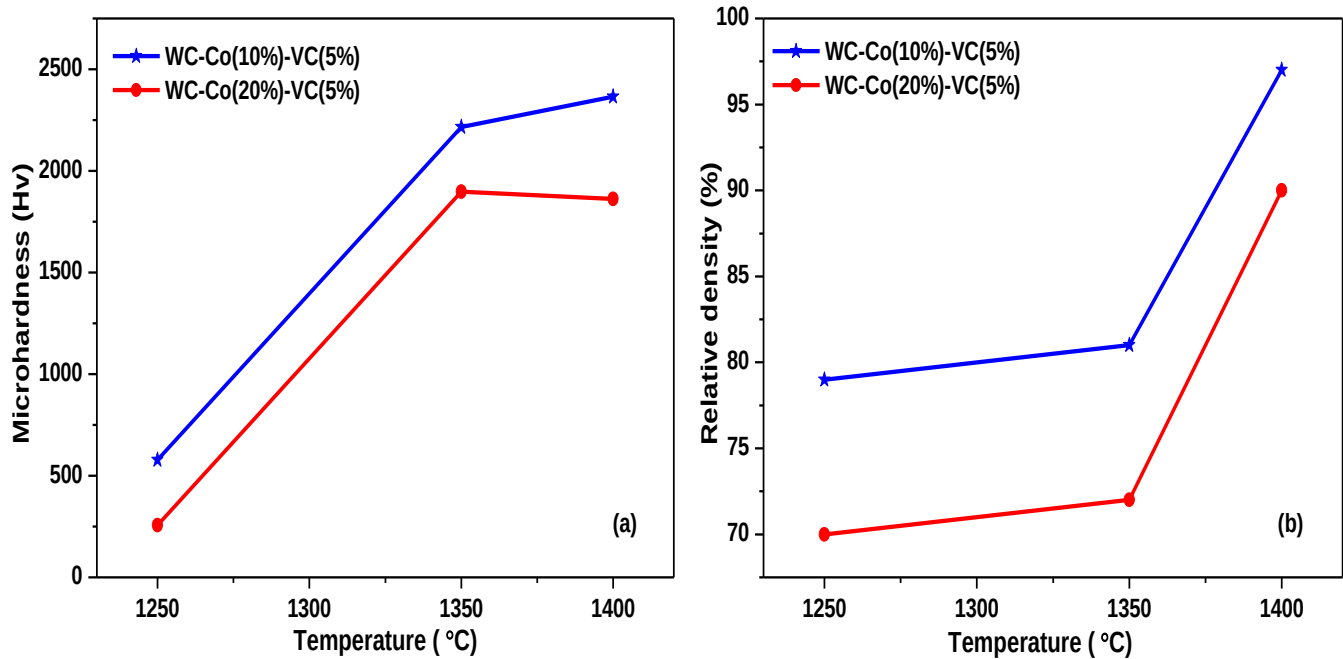


Figure 5.11: Effect of Co content on (a) Microhardness and (b) Relative density of WC-Co composite with 5% VC addition at different sintering temperatures.

However, the results obtained with the increase in Co content displays the decrease in microhardness and density in WC-Co(20%) composite for the same VC content (5%) (fig. 5.11). It arises due to the availability of higher content of binder elements in WC-Co system in the form of liquid phase [11] which results in increase in the dissolution of WC into Co matrix and increases the grain growth. The abnormal grain growth with high Co content was also observed by Pellán et al. [16]. The decrement in the hardness with increase in the concentration of ductile matrix (Co) is also observed by many authors [9, 10].

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CHAPTER 6

CONCLUSIONS AND FUTURE SCOPE

Overview

In this chapter, entire work of the present study is summarized. The suitable techniques which can facilitate the synthesis of nano VC was used. The nano VC was synthesized by thermo-chemical and mechano-chemical route. During synthesis, the optimization of various processing parameters for obtaining high purity vanadium carbide(s) nanoparticles has been done and concluded in this chapter. The role of as-synthesized product as grain growth inhibitor in WC-Co composite was also studied and concluded here. At the end, suggestions for future work in this field are given.

6.1 Conclusions

The aim of the present work was to develop single-step and low temperature route for the synthesis of VC nanoparticles from V_2O_5 which might be cost-effective. Thermo-chemical (solvothermal) method was used for the reduction of V_2O_5 with acetone and Mg as the reactants. The effect of carbon content, temperature and time was studied for the synthesis of single phase VC. Results show that increasing the amount of carbon increases the pressure inside the system which is sufficient for the formation of carbon-coated structure of VC nanoparticles (VC@C) of 40-50 nm in size. Moreover, pressure inside the system also increases with the increase in temperature which helps to get high purity product with nano range. Single phase of VC@C was obtained at reaction temperature of 800 °C. Reaction time plays a very important role in the reduction/carburization process. Increasing the reaction time, the reduction/carburization process increases and complete transformation of V_2O_5 to VC has been observed. After the optimized time, further increase in time leads to the formation of mixed phase of VC along with its lower oxides. On the basis of experimental results, the possible mechanism for the reduction/carburization of the final product has been discussed. TEM results showed that the VC nanoparticles of faceted morphology were covered by 20-22 layers of graphitic carbon (VC@C). Thermal analysis of the obtained samples showed that the coating of carbon onto VC surface protects it from oxidation and maintains its thermal stability at higher temperatures.

In order to study the morphology of carbon which facilitates the formation of the VC phase, decomposition of acetone was studied at 600 °C. Results indicated that the carbon generated during the decomposition of acetone was in the form of interconnected spheres. The possible mechanism for the formation of carbon nanospheres (CNS) was also documented. These CNS was further used for various catalytic applications and results shows that the catalytic applications of CNS was better than the other reported carbon spheres because of the small size and interconnected structure which is clear from their TEM micrographs.

It is possible to synthesize VC nanoparticles without heating via a mechano-chemical reaction route. As compared to the thermo-chemical route for the synthesis of VC nanoparticles at high temperature, the mechano-chemical route was considered as the better route where synthesis was done at room temperature. Using this route, single phase VC nanoparticles having uniform morphology was obtained. With the variation of the milling parameters viz. rotation speed, milling time and amount of reducing agent, the suitability of

the product at best milling parameters are confirmed. With increasing the rotation speed, the amount of excess carbon was decreased and diffusion of carbon occurs into V_2O_5 , leading to the reduction/carburization of the oxide precursor. The optimization of milling parameters for the synthesis of nano VC was done. It was observed that beyond the optimum milling parameters of the high energy milling, adverse effect was created and a low temperature phase vanadium hexacarbonyl ($V(CO)_6$) started to form. The volume fraction of this phase was further increased with simultaneous decrease in the volume fraction of VC phase at higher milling parameters. It shows that the performance and efficiency of the milling decreases after a critical milling parameter. The thermal analysis of the milled samples has confirmed the purity of phase formation by observing its weight gain at lower temperature. Moreover, the shifting of DSC peak towards higher temperature also attributes the thermal stability in the respective milled product. Microstructure analysis of the milled samples shows the presence of uniform distribution of VC particles having faceted morphology with minimum carbon coating over the VC nanoparticles.

In the reduction process during milling, Mg plays an important role. In the absence of Mg, complete reduction of V_2O_5 was not observed whereas complete transformation of V_2O_5 to VC was observed in the presence of Mg. In order to get high purity and good yield of VC nanopowder, the optimized amount of Mg was 2.5 g for 15 h at 300 RPM.

The as-milled VC powder was further used as GGI in WC-Co composite. The WC-Co(10%)-VC nanocomposite was prepared using different contents of VC at different sintering temperatures with 10 wt% of cobalt binder. Results showed that VC addition is effective in controlling the eta (η) phase formation and grain growth. The presence of these unwanted phases deteriorates the mechanical properties of the material. However, with the addition of VC, formation of the η phase is decreased, whereas the volume fraction of WC is increased. The effect of VC is more pronounced with higher contents at higher sintering temperatures (1350 and 1400 °C). The hardness and relative density of the WC-Co(10%)-VC nanocomposite increases with the addition of 5 wt% of VC content at 1400 °C. However, for comparison, WC-Co(20%)-VC nanocomposite was also prepared and the decrease in mechanical properties (microhardness) and relative density of the material were observed.

6.2 Scope for future work

Different forms of vanadium carbide(s) as V_8C_7 , VC, V_4C_3 and V_2C have different metallurgical and catalytic applications because of their different properties. The processing parameters can be optimized to get these synthesized as single phase materials. The carbon deficient compounds have higher hardness but V_5C_3 (newly discovered compound) has been found abnormally harder than all other forms of vanadium carbide. Due to its exceptionally energetic and mechanical stability, the synthesis of this novel compound of vanadium carbide along with its other compounds should be done by these studied techniques.

Further, the role of carbon deficient vanadium carbide(s) as GGI can be studied in WC-Co composite which can facilitate the high hardness also. Because of the high purity and homogeneity of the material obtained by present routes, the present material can also be investigated as catalyst in oxygen reduction reactions and other electronic devices.