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$_2$O$_5$ 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$_2$O$_3$ 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$_2$C, V$_8$C$_7$, V$_6$C$_5$ and V$_4$C$_3$. Among the different forms of vanadium carbides, V$_6$C$_5$ and V$_8$C$_7$ 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$_2$C$_y$) 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 □) are distributed in the MC$_y$□$_{1-y}$ 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].
In $\text{VC}_y$ carbide, ordered $\text{V}_8\text{C}_7$ possess a cubic structure in the range of $\text{VC}_{0.86} - \text{VC}_{0.88}$ with the double lattice spacing than that of the disordered carbide with space group $\text{P}4_3\text{3}2$ (or $\text{P}4_1\text{3}2$) [18, 21, 22]. The other ordered phase $\text{V}_6\text{C}_5$ possesses trigonal or monoclinic structure with space group $\text{P}3_1$ or $\text{C}2$ or $\text{C}2/\text{m}$ in $\text{VC}_y$ carbide in the range of $0.76 \leq y \leq 0.86$ [18, 23, 25]. Another carbide phase $\text{V}_2\text{C}_y$ 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 $\text{V}_4\text{C}_3$ having cubic crystal structure with space group $\text{Fm}3\text{m}$ [28]. Inspite of different space groups and lattice parameters, the structure of VC, $\text{V}_4\text{C}_3$ and $\text{V}_8\text{C}_7$ is same if position of carbon atoms is neglected [29]. $\text{V}_8\text{C}_7$ crystal belongs to the space group $\text{P}4_3\text{3}2$ 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].

Figure 1.1: Applications of vanadium carbide in various fields.
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 $V_8C_7$, P4₃m) 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 \( \Delta E_f \) (eV atom\(^{-1} \)) and cohesive energy \( E_{coh} \) (eV atom\(^{-1} \)) of VC, \( V_4C_3 \) and \( V_8C_7 \) phases [28].

<table>
<thead>
<tr>
<th>Phases</th>
<th>Total Energy (keV)</th>
<th>( \Delta E_f ) (eV atom(^{-1} ))</th>
<th>( E_{coh} ) (eV atom(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC</td>
<td>-8.5</td>
<td>-0.494</td>
<td>-9.138</td>
</tr>
<tr>
<td>( V_4C_3 )</td>
<td>-8.4</td>
<td>-0.413</td>
<td>-8.988</td>
</tr>
<tr>
<td>( V_8C_7 )</td>
<td>-67.6</td>
<td>-0.607</td>
<td>-9.219</td>
</tr>
</tbody>
</table>
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).
References


