Overview

In this chapter the details of the transition metal carbides (TMCs) with their crystal structure and properties are given. Among all the TMCs, the importance of tungsten carbide(s) has been presented. The history on the development of tungsten carbide is also mentioned. The phase diagram of tungsten–carbon along with the crystal structures of different allotropes (WC/W₂C/WC₁₋ₓ) of tungsten carbide(s) is also discussed. The applications of the WC in the form of cemented carbide (WC-Co) for mechanical and platinum deposited active catalyst (Pt/WC) for energy production applications are discussed. At last a brief idea about the different synthesis techniques for the preparation of tungsten carbide(s) nano powder with their limitations has been described.
1.1 Transition metal carbides (TMCs)

The term carbides are only applied to those compounds which are formed by carbon and other elements of lower or equal electronegativity. Metal carbides because of higher strength and durability constitute a diverse class of materials and traditionally have been used in extreme conditions of temperature and pressure; for example, in rocket nozzles and drill bits. The higher hardness property increases its usage in cutting tools, golf shoe spikes and in ferrous alloys to enhance the toughness of steels. Moreover, due to the higher melting point (>1800 °C) these carbides are also called refractory carbides [1].

Among all types of carbides, the interstitial carbide known as transition metal carbides (TMCs) from group IV-VI is only carbide, which meets the criteria of refractory and its structure leads to combinations of metallic, covalent and ionic bonds. Although in carbides, the C-atoms are situated in the interstitial voids of the metallic sublattice to form a nonmetallic sublattice [2] but these interstitial C-atoms have greater influence on the crystal structure and certain properties of the parental metal lattice. Moreover, due to the stability of interstitial carbides over a broad range of composition, it can be considered essentially as non-stoichiometric materials [3]. In other words, there exist vacancies in terms of missing C-atoms within the lattice of carbides which are called structural vacancies. However, the presence of these vacancies is a characteristic feature of carbides that are related to the group of non-stoichiometric compounds. The concentration of vacancies as well as their ordered or disordered distribution in a crystal lattice has a strong effect on the properties of such carbides. Because of such a kind of nature, TMCs have highest melting point, high thermal and chemical stability and could be considered as potential low cost substitutes for now-a-days industrial refractory materials.

1.2 Crystal structure of interstitial metal carbides/TMCs

Since, in carbides the metallic sub lattice symmetry differs from that of transition metallic lattices, hence, the crystal structure of metals get modified with the formation of carbides e.g. metals with the body centered cubic (bcc) structure (W, Nb, Mo, Ta, V, Cr) form carbides having cubic or hexagonal metallic sublattices. Moreover, both the experimental and theoretical studies also confirm that with introducing C-atom into the lattice of the early transition metals an expansion of the lattice constant occurs [4]. The changes within the crystal structure of metals after the formation of carbides attribute strong metal-carbon
interactions while direct interactions between carbon atoms are negligibly small [5]. Such kind of variation has been explained by Hagg’s rule. According to Hagg’s rule the formed structure depends on the ratio \( r = r_X/r_M \); where \( r_X \) and \( r_M \) corresponds to the radii of the nonmetal (C atom) and metal atoms, respectively. When \( r \) is less than 0.59, the common structures will be simple like face-centered cubic (fcc), hexagonal closed packed (hcp) or simple hexagonal (hex), with the C atoms placed in the large interstitial sites of octahedral. However, with the increase in value of \( r \) greater than 0.59, the metallic arrangement distorts and forms complicated structure. When \( r \) is less than 0.59, the light elements are accommodated in the large interstitial sites of the relatively simple host metal structure. The interstitial site must be smaller than the interstitial atom to avoid insufficient bonding between C-atoms and metal atoms, which makes the structure unstable. On the other hand, the interstitial site should not be too much smaller than the interstitial atom otherwise the interstitial atom will expand the host metal lattice. It leads to weak the metal-metal interactions, and the structure will lose its stability.

It has been shown that the TMCs shows the range of performances depending on the nature of the metal centers, the carbon (C)/metal (M) ratio, and orientation of the carbide surfaces [6-8]. The increase in M/C ratio in moving towards the right in the periodic table represents the rejection of C by the metal and reflects the decreasing stability of the carbides.

1.3 Properties of carbides

- The bonding in carbides arises due to the interaction of carbon 2s and 2p orbital with d orbital of metal. Moreover, due to the comparable electronic properties of carbides with noble metal, tungsten carbide (WC) has an electrocatalytic property similar to platinum (Pt).

- The physical and mechanical properties of carbides resemble to ceramic materials but not to metals. Carbides are well known materials for high melting point, higher hardness and strength. These properties are even highest as compared to ceramic materials.

- The electric and magnetic properties of carbides are similar to metals. The carbides have higher resistivity than pure metals, but the region of resistivity still exists within the range of metals. Moreover, the carbides also show paramagnetism with lower magnetic susceptibility within the range of magnitude of parent metal.
As shown in figure 1.1, transition metal carbides (TMCs) become the backbone of several components and utilized for different applications like metal cutting, mining, rock drilling, wear parts, corrosion resistance parts, coating materials, catalyst, thermal protection systems, superconductor, hypersonic vehicles [4, 9-14]. However, in most of the high-performance applications, the material of choice among TMCs is ultimately based upon tungsten carbide(s) (WC/W₂C) either as cemented carbide WC-Co for mechanical tools [15-18] or electrocatalyst used in fuel cell applications [19-21].

![Figure 1.1: Applications of transition metal carbides.](image)

### 1.4 Properties of tungsten carbide (WC)

Tungsten carbide (WC) was first synthesized by H. Moissan in 1893. Moissan had also produced fused tungsten metal by the electro-thermal way (earlier tungsten metal produced which is only in the form of a powder) in 1897. Since, in metal carbide (MC), the C-atoms modify the chemical reactivity through ensemble and ligand effects to moderate level [22-24], so due to the presence of the C-atoms the number of metal atoms will be limited that can be exposed to metal carbide surface. Moreover, the formation of metal-carbon (M-C) bonding changes the electronic properties of the metal [25]. Hence, the specific features of formed compound are the combinations of main attributes of parental metal (thermal and electrical conductivity) and compound (hardness). So, the metal carbides can exhibit clear advantages over their parent metals in terms of activity, selectivity, and durability [22]. Moreover,
partially filled $5d$ subshell of W extends outward to the periphery of the atom and is strongly influenced by carbon atom. Since, the change of symmetry and a slight expansion of the metallic lattice in carbide ensure stability in the structure. So, the practical interest in WC determines the active elementary investigations of its concentrations through phase diagram and crystal structure.

1.5 Crystal structure and phase diagram of tungsten carbide(s)

![Phase diagram of W-C system](image)

**Figure 1.2:** Phase diagram of W-C system [26].

The phases of tungsten carbide(s) formed in the W–C systems belong to the group of non-stoichiometric interstitial compounds. The W–C system has mainly three phases, WC$_{1-x}$, W$_2$C and WC, having several structural modifications. These phases are stable in certain temperature and concentration ranges (figure 1.2). The major phase in the W–C system is the higher tungsten carbide $\delta$-WC (WC), which has no homogeneity region, while lower carbide W$_2$C has relatively wide homogeneity regions. In $\delta$-WC (figure 1.3(a)) system, both the W and C atoms form simple hexagonal sub-lattices (space group $P-6m2$) with lattice parameters $a = 0.2906$ nm and $c = 0.28375$ nm.
The host-metal atom (tungsten) is arranged in a close-packed structure, and the C-atom occupies specific interstitial sites in that structure as shown in **Figure 1.3(a)**. Moreover, the lower tungsten carbide $W_2C$ is designated by three modifications viz low-temperature $\beta''$-$W_2C$, intermediate $\beta'$-$W_2C$ and high-temperature $\beta$-$W_2C$, which are also represented as $\alpha$, $\beta$- and $\gamma$-$W_2C$, respectively [26]. In all $W_2C$ types, the W-atoms form hcp structure (space group $P6_3/mmc$), in which one-half of octahedral interstitials are occupied by C-atoms (**Figure 1.3(b)**). Depending on the distribution of C-atoms, the lower carbide $W_2C$ can be disordered at a high temperature or ordered at a low temperature. Hence, due to the different types of C-atom distribution, the possibility of the formation of several structural modifications of $W_2C$ exists. In the composition range between the lower tungsten carbide $\beta$-$W_2C$ and the higher carbide $\delta$-$WC$, there exists the cubic phase (space group $Fm\overline{3}m$) $WC_{1-x}$ (**Figure 3(c)**) [26].

### 1.6 Applications of tungsten carbide(s)

Tungsten carbide (WC) has the potential to improve the mechanical properties of cutting tools. Moreover, among hard alloys and refractory carbides specifically in group VI, tungsten carbide (WC) is one of the carbide which has high melting point (2800 °C), high hardness ($H_v = 22$ GPa), low coefficient of thermal expansion ($5.2 \times 10^{-6}$ /K), high thermal conductivity, good wear resistance over as wide range of temperature [26, 27-29]. In industries, tungsten carbide (WC) in the form of cemented carbide with nanocrystalline grain.
structure after sintering has been well known for its exceptional hardness and wear/erosion resistance.

![Graph showing densification percentage vs. temperature for WC-Co with various initial particle sizes.](image)

**Figure 1.4:** The percent of densification of WC–Co as a function of the temperature during continuous heating for various initial particle sizes [30].

Basically cemented carbide is a metal matrix composite which is formed by hard ceramic particles, like WC, into a cobalt metallic (Co) matrix [31]. Cemented carbides have a unique combination of good toughness and high hardness within a wide range and used in the most versatile hard materials group for engineering and tool applications. The proportion of carbide phase is normally 70 % to 97 % of the total weight of the composite having grain between 0.2 µm and 20 µm. The hardness which is indirectly depended on the densification of the materials is significantly higher especially from consolidation of nanosized powders as could be expected from conventional powders (figure 1.4).

### 1.6.1 Importance of WC/W$_2$C in catalysis

Moreover, in recent years, all fuel cells used in electric vehicles require hydrogen (H$_2$) as a fuel [32] which can be generated directly by reforming the methanol, ethanol, butane, or biomass-derived materials. It converts chemical energy of fuel into electrical energy through an electrochemical reaction [33] by using a material (Pt) which effectively catalyzes the electrochemical reactions on each electrode surface of fuel cells [34]. However, Pt as a catalyst suffers from several drawbacks, including slow kinetics, low efficiency, high cost, and limited lifetime [35, 36]. So, in order to commercialize the usage of energy conversion
technologies one of the most important challenges is to either replace or support the high-cost metal catalyst with a high surface area substrate. But due to the continuous advancing development of energy storage and production, the carbon supported Pt catalysts (Pt/C) have been used extensively [36, 37]. However, due to the higher operating temperature conditions and cycling conditions of fuel cells carbon support catalysts corrode rapidly [38, 39]. Furthermore, due to the carbon oxidation/corrosion Pt catalyst agglomeration occur which tends to degrade the performance significantly [40]. Thus, current research is focused upon the development of new non carbon-based support catalyst materials, which have low cost, high performance, stability, and durability.

Among the non-carbon supports candidates; metal carbide (MC) appears to be an important material that shows good electronic conductivity, chemically inert, low cost, tolerance to CO poisoning and are widely used in cutting tools [15, 41, 42]. Moreover, the experimental results showed that at ambient conditions MC has been oxidized at around 600 °C [43, 44], which is much higher than the required temperature for operating the low temperature operated fuel cells. In addition, the Pt like catalytic behavior of MC could result in a cooperative way with the metal catalyst, leading to enhancement in the catalyst activity [45].

Moreover, an early study of Levy and Boudart [45] on an isoelectronic structure of WC and platinum has focused a considerable amount of attention on the new scope of WC in the research field. The continuous extensive study on WC has made it a good candidate as a catalyst for substitute materials like noble metals (Pt, Pd, Au etc.). For the application of tungsten carbide(s) (WC, W₂C) as a catalyst, it has been observed that it shows high catalytic activity in fuel cells because of its noble metal-like activity, high stability, and CO poisoning tolerance [46, 47]. Some research has also revealed that WC can act as excellent anodic and cathodic materials [46]. Furthermore, many experiments and calculations indicate that WC/W₂C is utilized as an excellent candidate for fabrication of a high-efficient and stable catalyst system in which small-sized metal nano particles (Pt, Pd, etc.) are deposited onto the surface of WC/W₂C [14, 46-48]. Moreover, the synthesis of materials in nano range increased the exposed active sites and improved contact areas with reactants [49-51] which results in improvement of the performance. So, WC/W₂C in nano sized can be considered as a promising candidate for next-generation as an electrocatalyst support due to its synergistic effect when combined with platinum nanoparticles (figure 1.5). It could lead to Pt/WC electrocatalysts with a higher intrinsic activity [52].
Figure 1.5: Schematic process of platinum nano particles deposition on WC nano particles.

1.7 Synthesis of nano crystalline tungsten carbide(s)

In the era of nanotechnology, when we discuss about nano particles then we usually emphasize on particles with dimensions less than 100 nm on an atomic and molecular scale. However, the significant contributions of nanotechnology have been revealed in the fields of materials science. Many recent important technological breakthroughs can be attributed to the ongoing developments in nanotechnology. There are many ways to synthesize nano materials by suitable processing techniques such as top-down and bottom-up approaches. In the top-down approach the nano structured material has been prepared by breaking up the bulk shaped material into the lower size until the microstructure exhibit nanostructure. While in bottom-up approach, involve the synthesis of nanocrystalline materials from nanocrystalline particle even at atom, ions or molecules orderly assembled into the desired structure. While several techniques to produce WC nanopowders have been developed, but only a few of them have been proven at the industrial level. Production challenges include economic considerations, properties of powder and its process-ability. The preparation techniques cover a diverse array of processes as is evident from the discussion below:

1.7.1 Mechano-chemical synthesis

In mechanical ball milling process a powder mixture has been placed in the ball mill to produce homogeneous material via high-energy collision from the balls. It was found that this process, named as mechanical alloying could successfully produce fine, uniform dispersions of particles. Hence, their advancement in synthesis techniques has changed the conventional methods to obtain the material which is carried out by high-temperature synthesis. The high-energy ball milling method not only synthesized the materials but also modified the conditions of reactivity of as-milled solids (higher reaction rates, lowering reaction
temperature of milled powders) or inducing the chemical reactions during milling process (mechano-chemistry) [53]. Many ceramic powders, alloys as well as composites have been prepared by this method.

Furthermore, high-energy milling is one of the simplest methods to produce WC nano powder by mechanical activated chemistry occurred between tungsten sources and carbon sources during milling process [54-56]. The mechanical activation is responsible to enlarge the surface area or to accelerate the reactions by correct mixing of the reagents for enhancing the reactivity of solids. However, the biggest problem associated with this process is to produce nanosized particles which require long processing times, contamination, and high energy expenditures [53, 57].

1.7.2 Spray conversion process

Spray conversion process is a continuous and scalable process dedicated for converting liquid streams (slurries, pastes or even melts, suspensions, emulsions, solutions) into dry free-flowing powders. It further enables to produce the particles with controlled size and morphological aspects, which subsequently scaled up to the production at an industrial level. Moreover, the advantages of processing the materials from chemical precursors seem to be a reduction in the production cost of novel materials having homogeneous ultrafine microstructures (nanostructures) and improved properties [58]. Furthermore, due to controlling of the processing parameters, the chemical and microstructural uniformity at the nanoscale has been maintained [59]. So, the spray conversion process allows the mixing of precursors at the molecular level which yield nano sized materials. However, the problem with this process is that it consists of three-step, which involve the formation of aqueous solution, spray drying to form an amorphous powder, and carburization with carbon containing gases to form pure WC phase [60].

1.7.3 Chemical vapor phase reaction synthesis

In this method, the vapor phase precursors are brought into a hot-wall chamber under the conditions in which instead of the deposition of a film on the wall, nucleation of particles in the vapor phase occur. It is called chemical vapor synthesis or chemical vapor condensation in similar to the chemical vapor deposition (CVD) technique which is used to obtain thin solid films on surfaces. In current approach the nanoparticles has been synthesized by creating conditions where the vapor phase mixture is thermodynamically less stable as
compared to solid material prepared in the nano form [61]. Furthermore, in this process a chemical supersaturation stage is included, which is thermodynamically favorable for the vapor phase molecules to react chemically and form a condensed phase [61]. Moreover, the reactions at vapor phase offer the advantages of getting highly pure nanopowders which have good control over the size, shape, and crystal structure as well as easy control of reaction rate. The precursors can be solid or liquid in nature but are introduced into the reactor as a gas. Normally in case of chemical vapor phase reaction synthesis, metal chloride precursors are used due to their lower volatilization temperature [62]. But in case of WC nano powder synthesis, different precursors like tungsten hexacarbonyl (W(CO₆)) [63], tungsten hexafluoride [64], have also been used. In the next chapter the advancement in the synthesis and electrochemical studies of tungsten carbide(s) has been given.
References: