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Chapter 3

Tungsten Carbide as an Addition to High Speed Steel Based Composites

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1. Introduction

Design criteria for high strength tool materials have to include wear resistance of the abrasive particle, high hardness and adequate toughness. Cold compaction and vacuum sintering of PM high speed steels (HSSs) to full density is now a well established technique [1-3]. In recent years, work has been undertaken to sinter metal matrix composites that contain ceramic particles in HSSs by the same route. Most studies have focused on sintering with additions of hard ceramics such as Al₂O₃, VC, NbC, TiC, WC and TiN with the aim of producing a more wear resistant HSS type material [4-18]. These composite materials have been developed for wear resistance applications as attractive alternative to the more expensive cemented carbides. Compared with high strength steels, these composite materials have higher hardness, wear resistance and elastic modulus. However, depending on size and distribution, the addition of brittle ceramic particles may cause degradation of bend strength and toughness owing to the initiation of cracks at or near the reinforcing particles. In order to ensure good bonding at the ceramic/matrix interfaces, the ceramic particles must exhibit some reactivity with the matrix. In contrast to Al₂O₃, which presents no interface reactions with the iron matrix, the diffusion of iron from the matrix into the MC carbide particles establishes a good cohesion across the ceramic/matrix interface. Besides, these carbides are stable in contact with iron during sintering and do not dissolve extensively. Therefore, MC particles were chosen as the reinforcement. A cheap and easy route to develop high speed steels reinforced with MC carbides consists of mixing powders of commercial high speed steel powders with the carbides.

There are two methods by which tungsten carbide powders are produced from the tungsten-bearing ores. Traditionally, tungsten ore is chemically processed to ammonium paratungstate and tungsten oxides. These compounds are then hydrogen-reduced to tungsten metal powder. The fine tungsten powders are blended with carbon and heated in a
hydrogen atmosphere between 1400 and 1500 °C (2500 and 2700 °F) to produce tungsten carbide particles with sizes varying from 0.5 to 30 µm. Each particle is composed of numerous tungsten carbide crystals. Small amounts of vanadium, chromium, or tantalum are sometimes added to tungsten and carbon powders before carburization to produce very fine (<1 µm) WC powders. In a more recently developed and patented process, tungsten carbide is produced in the form of single crystals through the direct reduction of tungsten ore (sheelite). The melting point of hexagonal tungsten carbide WC is equal to ~2780°C which is less than melting point of nonstoichiometric TiC, ZrC, HfC, NbC, and TaC carbides [1,2]. Hardness of tungsten carbide WC is equal to 18-22 GPa at room temperature which is less than that of nonstoichiometric TiCy, ZrCy, HfCy, VCy, NbCy and TaCy carbides [1, 2]. However, the hardness of WC is sufficiently stable in a wide temperature interval. For example, the microhardness HV of hexagonal WC carbide decreased from ~18 to ~12GPa at heating from room temperature to 1000°C whereas the HV of nonstoichiometric transition metal carbides decreased under the same conditions from their maximum values to 3-8GPa. A thermal expansion coefficient of WC is equal to ~5.5·10⁻⁶ K⁻¹ [4-10] and is half as much as that of other transition metal carbides.

Metal matrix composites MMC have appeared as a bright option for wear applications. These materials combine a soft metallic matrix with hard ceramic particles that withstand wear. Different matrixes were studied, and aluminum, stainless steel and high speed steel HSS. Matrix composites showing outstanding wear behaviour. High hardness, mechanical strength, heat resistance and wear resistance of high speed steel (HSS) make it an attractive material for manufacture MMC. High speed steels comprise a family of alloys mainly used for cutting tools. Their name – high speed steel – is a synthesis of the following two features [11]:

a. the alloys belong to the Fe–C–X multicomponent system, where X represents a group of alloying elements in which Cr, W or Mo, V, and Co are the principal ones;
b. the alloys are characterized by their capacity to retain a high level of hardness even when submitted to elevated temperatures resulting from cutting metals at high speed.

The carbides are predominantly formed from the strong carbide formers V, W, Mo and Cr. Depending on the composition and on the thermal parameters (sintering temperature and cooling rate) several types of carbides can be formed. The main types are M6C, M2C, MC and M23C6. Their formation is a result of cooling rate and alloy composition. The carbides can be formed directly from the melt during solidification, by eutectic reaction or by decomposition of other types of carbide. The latter case can be seen from the decomposition of M6C carbide into MC and MC carbides when HSS is annealed at temperatures above 1000°C. The importance of the alloying elements in HSS is the effect they have on the type of carbide formed and the temperature of formation, and also the effect they have on the tempering of martensite. The types of carbides are different in crystal structure and composition. The carbides MC, M6C and M23C6 have a fcc crystal structure, while the metastable M2C has a hcp structure. The carbides are also different in composition with higher V and Ti levels and
lower Fe and Cr levels in MC compared with M6C and M23C, which are rich in Mo and W. The carbide M23C6 is Cr rich, with high solubility for Fe and low solubility for W and Mo. Iron can substitute Cr when W and Mo are dissolved in this carbide. Annealed HSS generally contains M23C6. Considering HSS grades such as M3/2 it is clear that primary M6C formation and growth along cell boundaries is a key problem. If the M6C formation can be limited, while sintering to near full density is maintained, an acceptable final microstructure can result. The alloy composition of HSS may favour the formation of a certain type of carbide. For a given amount of V, increasing the amount of W favours the formation of M6C at the expense of MC. A high amount of Mo has the opposite effect. The carbides that form by eutectic reaction increase in volume fraction with increasing C content, higher W/Mo ratio in the case of eutectic M6C, the V content9, and decreasing cooling rate. Many studies demonstrate how the as sintered microstructure of HSS can be tailored by means of addition of elemental powder to gas atomised M3/2 powder. The experiments include the addition of elemental Si to repel C from the melt when sintering, the addition of elemental Ni to avoid the formation of pearlite and stabilize austenite, and finally the addition of elemental V to form MC on the expense of cementite. Additions of carbides to high speed steels have been studied by a number of authors [9-19]. Thermodynamically less stable carbides (SiC, Cr3C2) easily dissolve in the high speed steel matrix during sintering or annealing and are not retained as discrete hard particles. Intermediate carbides such as WC, VC, Mo2C and NbC, which include elements that are alloyed to high speed steel react with the steel matrix to produce new carbide phases with compositions similar to those of the normal primary carbides present in high speed steel, e.g M6C (FeW3C or FeMo5C) and niobium or vanadium rich MC type carbides. Thermodynamically stable carbides such as TiC are retained more less in their original form but also encourage MC carbides to form within the steel matrix and the steel/TiC interface because of some slight dissolution of the TiC particles. The TiC additions decreases sinterability by raising the sintering temperature required to achieve full density in a number of grades high speed steels, including M3/2. Most authors report also that the TiC addition reduces bend strength of the HSS and causes some slight increase in hardness.

The use of powder metallurgy PM techniques for manufacturing HSS is on the increase. In addition to the typical advantages of PM raw material savings, low energy costs. PM HSS present better microstructural features than conventional wrought steels homogeneity of carbide distribution in the matrix and smaller grain and carbide sizes, among others. These advantages mean an improvement of properties. PM techniques allow a higher content of alloying elements and the addition of the ceramic particles previously mentioned. If conventional compacting or CIP is used as the powder forming technique, a sintering process is then necessary. Sintering is usually carried out under vacuum conditions at temperatures below solidus temperature, although nitrogen-based atmospheres can sometimes be used, but this process does not completely eliminate porosity. A technique that provides densities as high as HIP but at a lower cost is liquid phase sintering. Liquid phase can be obtained in three ways:
1. by addition of a compound with a lower melting point than the material to be sintered, or that forms a eutectic,
2. by supersolidus sintering, which consists of heating to temperatures above the solidus temperature of the material to be sintered,
3. by infiltration technique [20, 21].

Infiltration is basically defined as "a process of filling the pores of a sintered or unsintered compact with a metal or alloy of a lower melting point." In the particular case of copper infiltrated iron and steel compacts, the base steel matrix, or skeleton, is heated in contact with the copper alloy to a temperature above the melting point of the copper, normally within the range of 1095° to 1150°C [22, 23]. Through capillary action, the molten copper alloy is drawn into the interconnected pores of the skeleton and ideally fills the entire pore volume. Filling of the pores with higher density copper can result in final densities in excess of 95% of the composite theoretical value. Completely filled skeletons also allow for secondary operation such as pickling and plating without damaging the structure through internal corrosion. Pressure tight infiltrated components are also possible for specific applications that demand the absence of interconnected porosity. The infiltration process is generally subdivided into two fundamental methods: single step or double step. The single step or single pass is presently the preferred infiltration method that consists of one run or passes through the furnace. In this process, the unsintered (green) steel and copper alloy compacts are placed in contact prior to furnace entry. The typical arrangement is to place the copper alloy infiltrant compact on the top surface of the steel compact. In some cases, it is preferred to place the steel compact on top of the infiltrant compact, or, infiltrate from top and bottom simultaneously. During the full furnace cycle, the steel base compact is ideally partially sintered prior to attaining the melting points of the infiltrant composition. Preferably, multi-independent zone furnaces are employed allowing for preheat, or lubricant burn-off, followed by pre-sintering (graphite solution) and finally infiltration. The double step or double pass infiltration method consists of pre-sintering or full sintering of only the steel compact in one pass through the furnace. After the first sintering pass, the unsintered (green) infiltrant compact is placed in contact with the sintered steel part, and the full furnace cycle is repeated. The infiltrating powders available may be used for both the single and double step processes. Most, if not all, infiltrating powders are prepared as a pre-blended and/or a pre-lubricated lot or batch and are designed for typical compacting operations. Shapes of infiltrant compact forms vary substantially depending upon the amount required and the configuration of the steel skeleton. Usually, simple infiltrant shapes, such as bars, cylindrical slugs, or annuli are compacted to a specific weight and are placed on the iron components in single or multiple contact arrangements.

The M3/2 high speed steel reinforced with tungsten carbide and infiltrated with copper was chosen for this investigation. The present paper describes and discusses the microstructural characteristics and mechanical behaviour of the composite system M3/2-WC-Cu.
2. Experimental procedure

2.1. The powders

Water atomised M3 grade 2 powder of -160µm were obtained from POWDREX SA in the annealed condition. This powder was chosen, in preference to the more commonly used M2, for its better compressibility and sinterability. Chemical composition of this powder is given in the Table 1. As reinforcement’s commercial tungsten carbides of -3µm were used. The powder properties, including electrolytic copper are given in Table 2.

<table>
<thead>
<tr>
<th>compound</th>
<th>C</th>
<th>Cr</th>
<th>Co</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>Si</th>
<th>V</th>
<th>W</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>composition</td>
<td>1.23</td>
<td>4.27</td>
<td>0.39</td>
<td>0.21</td>
<td>5.12</td>
<td>0.32</td>
<td>0.18</td>
<td>3.1</td>
<td>6.22</td>
<td>rest</td>
<td>626ppm</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of M3/2 HSS powders, wt-%

<table>
<thead>
<tr>
<th>Powder properties</th>
<th>M3/2</th>
<th>WC</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density, g/cm³</td>
<td>2.26</td>
<td>2.70</td>
<td>1.60</td>
</tr>
<tr>
<td>Flow time, s/50g</td>
<td>38.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Densification at 600MPa, g/cm³</td>
<td>6.08</td>
<td>6.71</td>
<td>6.90</td>
</tr>
<tr>
<td>Particle size, µm</td>
<td>0±160</td>
<td>0±3</td>
<td>0±40</td>
</tr>
</tbody>
</table>

Table 2. Properties of the used powders

The powders morphology is shown in fig 1.

Figure 1. Scanning electron microscopy (SEM) morphology of powder particles:

a) high speed steel M3/2 class, b) tungsten carbides WC

It can be seen that the microstructure of the M3/2 grade HSS powders consists of a thin carbides in a martensitic-bainitic matrix. MC carbides being the white ones, Chile M C carbides are grey. Typical microhardness values for a powder is μHV₀.₅₈₅ = 284 ± 17.
2.2. Experimental technique

The compositions of powder mixtures are:

1. 100% M3/2,
2. M3/2 + 10% WC,
3. M3/2 + 30% WC.

Composite mixtures were blended in a Turbula® T2F blender for 30 min. The M3/2 powder and composite powders were uniaxially cold compacted in a cylindrical die at 800 MPa.

The infiltration process is subdivided into two fundamental methods: single step or double step. In the single step the unsintered (green) high speed steels or composite mixtures and copper alloy compacts were placed in contact prior to vacuum furnace entry. The copper alloy infiltrant compacts were placed on the top surface of the green compacts. The double step infiltration method consists of pre-sintering of only the green compacts. After the first sintering process, the infiltrant compacts (specify weight copper green compacts) were placed on the top surface of the sintered composites and were placed to vacuum furnace entry.

Half of green compacts were sintered in vacuum at 1150°C for 60 minutes. Sintered specimens and green compacts were analysed before infiltration. Density measurements via the Archimedes method were used to define the level of porosity.

Thereby obtained skeletons were subsequently infiltrated with copper, by gravity method, in vacuum furnace at 1150°C for 15 minutes. The infiltrated composites were cooled as fast as vacuum furnace.

The sintering and infiltration process was carried out in vacuum better than 10⁻² Pa.

Densities of sintered materials were evaluated by a method based on the Archimedes principle, according to MPIF standard 42. Measured values were compared with theoretical
values to obtain relative densities ($\rho_t$). The theoretical densities for the composites were calculated according to the expression (1):

$$\rho_t = (\rho_a \times X_a + \rho_b \times X_b)$$  \hspace{1cm} (1)

where $\rho_a$ is carbide density, $X_a$ the volumetric fraction of WC carbide, $\rho_b$ the density of high speed steel M3/2, and $X_b$ the volumetric fraction of the HSS.

The MMC composites materials were characterized using various techniques. The infiltrated specimens were subsequently tested for mechanical properties. Therefore, mechanical properties were characterized by Brinell hardness, wear resistance test and three points bend tests in order to determine the influence of tungsten carbide. The microstructure of the composites was examined by means of both light microscopy (LM) and scanning electron microscopy (SEM). Characterization of microstructures and the identification of phases present were performed by both optical and scanning electron microscopy, assisted by the use of X-ray energy dispersive analysis (EDX), backscattered electron image contrast, and some X-ray diffraction data. Reaction temperatures were determined by dilatometric study.

The wear tests were carried out using the block-on-ring tester (Figure 3).

![Figure 3. Tribosystem T05 - wear test principle](image)

During the test a rectangular wear sample (1) was mounted in a sample holder (4) equipped with a hemispherical insert (3) ensuring proper contact between the test sample and a steel ring (2) rotating at a constant speed. The wear surface of the sample was perpendicular to the loading direction. Double lever system was used to force the sample towards the ring with the load accuracy of $\pm 1\%$.

The wear test conditions were:

- test sample dimensions: 20 x 4 x 4 mm,
- rotating ring: heat treated steel 100Cr6, 55 HRC, $\phi 49.5$ x 8 mm,
- rotational speed: 500 rpm,
- load: 165 N,
- sliding distance: 1000 m.

The measured parameters were:

- loss of sample mass,
- friction force $F$ (used to calculate the coefficient of friction).
The friction coefficient was measured continuously during the test, and the wear coefficient was calculated by means of the following expression (2):

\[ F = \frac{\text{friction force}[N]}{\text{load}[N]} \]  

(2)

Wear tracks were analyzed by LM to clarify wear mechanisms.

3. Results and discussion

3.1. Characterization of porous skeletons

The combined effects of tungsten carbide content and powder processing route on the relative density and shrinkage of the porous skeleton are shown in Figure 4 and 5.

Figure 4 shows the effect of WC content on compressibility and shrinkage of high speed steel powders. It is evident that green density of compact decreases with increasing WC content. This attributes to hard and non-deforming nature of the tungsten carbide WC reinforcements, which constricts HSS-particle deformation, sliding and rearrangement during compaction. Additions of 30% tungsten carbide increase the as-sintered density.

Figure 4 shows that the M3/2 grade HSS cannot be fully densified at 1150°C, and that the as-sintered density is approximately equal to the green density. Additions of 30% tungsten carbide increase the as-sintered density presumably due to the occurrence of a liquid phase
resulting from a chemical reaction occurring between the HSS matrix and tungsten carbide particles. As exemplified in Fig. 6, marked specimen expansion followed by its rapid contraction has indicated that the chemical reaction takes place at temperatures between 1080 and 1110°C.

Figure 5. Shrinkage of compacts during sintering as a function of tungsten carbide WC content

Figure 6. Dilatometric curves recorded on heating the M3/2 and HSS M3/2 + 30% WC material to the sintering temperature