Microstructure and Hardness of Fe-TiCN Cermets Fabricated by Powder blending and Powder Coating Routes Followed by Powder Metallurgy Process

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ABSTRACT

Cermets composed of titanium carbonitride with iron have been prepared by conventional powder blending in comparison with powder coating method followed by conventional powder metallurgy process (pressing and vacuum sintering). The target composite of this study is made by 50 vol. % of titanium carbonitride reinforcing an iron base matrix (pure iron, stainless steel and high speed steel). Electroless coating of titanium carbonitride particles with iron metal was performed using sodium borohydride as a reducing agent of iron salts. A proper characterization of powders is necessary and it was carried out by different means: scanning electron microscopy (SEM with EDAX analysis to study the particle morphology, and composition) and X-ray diffraction (XRD) to find possible transformations during the sintering process. A study of pressing and sintering processes has also been done to find out the possibility of further processing. Vickers micro-hardness test of sintered samples was preformed to evaluate and compare between the samples prepared by mixing process and by the coating process.

Keywords: Cutting Tools, Iron Base Composite, Titanium Carbonitride, Electroless deposition, Powder Metallurgy.

1. Introduction

Nowadays, there are many classes of cutting tools. Examples of these tools include the following: high speed steel; alloys of iron and carbon that contain Cr, W, Mo, Ti and other refractory metals [1]; ceramics such as Al$_2$O$_3$, Al$_2$O$_3$/TiC, Si$_3$N$_4$, and Al$_2$O$_3$/SiC [2]; super-hard materials, such as polycrystalline diamond and polycrystalline cubic boron nitride [3]; cemented carbides[4]; and cermets based on TiC and TiN with a multi-component alloy binder consisting of Co, Ni, Mo and W [5].

Cermets can be classified as metal matrix composites with high content of ceramic phase [6]. They are developed to combine the high hardness and wear resistance, provided by ceramic particles, with toughness and thermal shock.
resistance, provided by the metallic matrix. Among them, titanium carbonitride-based cermets are gaining increasing technical importance [7–9] due to the high hardness of this compound, and the lower density than other types of reinforcement usually employed, like carbides of refractory metals.

Titanium carbonitride cermets are mainly used as cutting tool materials. Compared to cemented carbides, TiCN-based cermets exhibit an excellent combination of high temperature hardness, strength, wear resistance, thermal conductivity, chemical stability also used as a promising material for applications at high temperature or highly corrosive environments, and is being used for semi-finishing and finishing work. Being the performance of those cermets to machine steels as good as or even better than that of coated hard-metals [10]. However, they present some disadvantages such as low toughness, and low sintering behavior. Additions of some elements or compounds can improve the sintering performance by improving the wettability between the ceramic and the liquid phase, enhance density and decrease particle growth rate such as Mo, Mo₂C, or WC [11,12].

The use of iron as the matrix of cermets has been studied because of its advantages over Co or Ni. These include non-toxicity, abundance of resources leading to lower cost, and the ability to be hardened by heat treatment, which could lead to high hardness with lower quantity of ceramic phase. Fe-based cermets also present low sintering performance due to poor wettability of the liquid phase, the risk of producing reaction products with the reinforcement that lead to embitterment, and the risk of agglomeration of the ceramic particles that do not permit a homogeneous dispersion of hard phase into the matrix [13]. The addition of Cr to Fe can improve the wettability, as it lowers the contact angle close to 0°, thus wetting the surface of TiCN with the alloy. As elements like W, Mo and their carbides have also been reported to improve sintering behavior of TiCN cermets; high-speed steel (grade M2) has been chosen as matrix of a new Fe-based composite reinforced with TiCN particles. The M2 is one of the most widely employed high-speed steels, whose sintering behavior and heat treatment response are well known, but changes are expected when ceramic particles are added [14]. Following the idea of producing an iron-based cermet, and trying to obtain a good sintering response, it was proposed to use 1) a high-speed steel for the matrix, as it contains Cr, Mo and W, elements reported to improve sintering as previously mentioned, 2) stainless steel (430 L) for matrix which contain C, Mn, Cr, Ni, and 3) iron coated TiCN particles. These elements are also carbide formers, increasing the volume fraction of hard phase in the final cermet [10].

Composite coatings improved properties of composites heavily depend on the nature and content of reinforcements in the coatings. The most important point is to obtain continuous, uniformly distributed and dense coated metal layer. Otherwise, the layer with voids or gaps may weaken; even destroy the integration between the ceramic reinforcement and the metal matrix, lowering the expected advantages of metal–matrix reinforced by ceramics. Electroless metal coating technique has been widely used to prepare the composite coatings. As the advancement of electroless powder coatings, in which particles are used as reinforcing phase and the coated metal as a matrix. Electroless plating with catalytic metals was an effective way for necessary surface treatments [15], after which the coated layers can serve as medium for adhesion and transferring loads. Previous studies proceeded with coating ceramic particles (such as SiC and Si₃N₄) by metals with sensitization by stannous chloride followed by activations with palladium chloride and after that coating of the activated particles surfaces with metal layer followed by mixing these composite powders with
metal power and underwent powder metallurgy processing of these composites [16, 17].

To produce TiCN ceramets in an applicable form as cutting tools, we used high-energy milling and Electroless powder coating methods to obtain a TiCN/Fe base composite powder and cold compaction and vacuum sintering to produce the sintered compacts. All of them were reinforced with 50vol.% of TiCN particles, and were prepared by the conventional powder metallurgy (PM) route: mixing of starting powders or Coating of TiCN with iron by electroless deposition and then pressing and vacuum sintering. The densification and properties of the prepared TiCN ceramets were characterized by microstructure investigations based on measurements of physical properties, such as density, porosity and mechanical properties such as hardness.

2. Experimental

Three composite materials were studied (1) TiCN/M2, constituted by a high-speed steel matrix (M2 grade, containing 6%W, 5%Mo, 4%Cr, 2%V, 0.85%C), (2) TiCN/stainless steel (430 L grade) which mixed with TiCN, stainless steel contain Cr 16.2%wt; Si 0.75 %wt; Mn 0.71 %wt; and C 0.026 %wt. and (3) TiCN/Fe prepared by electroless powder coating technique and was prepared by the conventional powder metallurgy (PM) route of mixing of starting powders, pressing and sintering. The M2 and 430 L powders were selected for the particle size ranged from 2-10µm, which is bigger than the TiCN particles 2-4µm. The same powders were used for manufacturing M2 and 430 L reference samples. Powders of the two series M2, 430 L and TiCN were dry milled for 24 hours in a high strain home made rod mill machine of 180 rpm and 3:1 rod: powder ratio.

On the other hand TiCN particles were coated by electroless deposition technique. The known weight of TiCN powder was cleaned by stirring in concentrated HCl for 30 min. to dissolve any inorganic contaminates and to etch its surface followed by washing with distilled water, filtration and drying. The dried TiCN powder surfaces were metalized using two step activation processes. Sensitization for 30 min by 10 gm/l of stannous chloride solution at pH ≈ 3 followed by decantation, washing and filtration. The sensitized TiCN powder was chemically treated by 0.2gm/l palladium chloride solution for 2hrs at pH ≈ 3. The produced TiCN powder was coated by electroless iron coating technique. Ferrous sulphate (30gm), 50gm of potassium sodium tartarate was dissolved in one liter of distilled water by continuous stirring. The pH of the solution was adjusted to be ~9 by using NaOH. The palladium metalized TiCN powder was added and stirred in the to the electroless iron bath for 30mins. The sodium borohydride was added to deduce the ferrous ions to metallic iron on the surface of the metalized TiCN particles. By controlling the concentration, the pH value and the temperature of the solution, the coating process started spontaneously and finished within 30 minutes. The coated powders were washed with distilled water, dried and weight. The TiCN powder was selected with the composition 50Vol.%.

The blended powders and the coated powders were cold uniaxially pressed at 200 MPa to obtain cylindrical samples of 20 mm diameter and 10 mm height and rectangular samples of 25 mm length, 8 width and 5 mm height. The characteristics of the starting and the prepared powders are given in Table 1. The green compacts were
sintered in vacuum ($10^{-3}$ mbar) at 1400°C for 60 min. Figure 1 shows the heating cycle of the compacts under vacuum.

The microstructures and the composition of the polished samples were investigated by optical microscopy and Cr 16.2%wt; Si 0.75 %wt; Mn 0.71 %wt; and C 0.026 %wt scanning electron microscopy (SEM) conducted with EDS. The samples were also analysed by XRD to identify the main phases. The hardness was measured by applying a 30 kg load using the Vickers tester (HV30).

**Table 1** The apparent and tap densities of the investigated powders.

<table>
<thead>
<tr>
<th>Material</th>
<th>Apparent density, gm/cm³</th>
<th>Tap density, gm/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCN</td>
<td>1.07</td>
<td>1.52</td>
</tr>
<tr>
<td>stainless steel</td>
<td>2.67</td>
<td>3.55</td>
</tr>
<tr>
<td>High Speed Steel</td>
<td>3.04</td>
<td>4.40</td>
</tr>
<tr>
<td>(50Vol% TiCN) / Stainless Steel</td>
<td>1.76</td>
<td>2.44</td>
</tr>
<tr>
<td>(50Vol% TiCN) / High speed steel</td>
<td>1.68</td>
<td>2.24</td>
</tr>
<tr>
<td>(50Vol% TiCN) / Fe</td>
<td>1.60</td>
<td>2.20</td>
</tr>
</tbody>
</table>

**Figure 1** Sintering cycle for the composite materials under study.
3. Results and Discussion

3.1 Powder blending, milling and coating

Figures 2 (a-d) show SEM images of starting powders: the high speed steel (M2 grade), stainless steel (430 L), (50Vol.% TiCN) / Stainless Steel mixture and (50Vol.% TiCN) / High speed steel mixture respectively. It was observed that the TiCN particles were homogeneously distributed in the mixtures. Figures 2(e, f) show EDS semi-quantitative analysis of each mixture of (50Vol.% TiCN) / Stainless Steel mixture and (50Vol.% TiCN) / High speed steel mixture respectively. Several kinds of peaks were detected due to the presence of the TiCN particles in the prepared mixtures. Figure 3 shows the XRD patterns of the as received TiCN powder and the (50Vol.% TiCN) / Stainless Steel mixture and (50Vol.% TiCN) / High speed steel mixture respectively blended and milled powders. It can be seen that the XRD patterns of powders milled have identical patterns of its constituents, and neither transformations nor new compounds appear after the time of milling used.

On the other hand the electroless Fe bath was used for preparing the coated TiCN/Fe composite powder. The TiCN surfaces were etched by acid treatment with stirring to cleanup the surface of the particles. The acid-treated TiCN underwent sensitizations by stannous chloride. The sensitized TiCN were activated and metallized by palladium chloride solution according to the following reaction:

\[
\text{Sn}^{2+}_{\text{(adsorbed)}} + \text{Pd}^{2+}_{\text{(in solution)}} \rightarrow \text{Sn}^{4+}_{\text{(in solution)}} + \text{Pd}^0_{\text{(adsorbed)}} \tag{1}
\]

The palladium activated TiCN particles were stirred in the iron bath followed by electroless Fe deposition on the activated surface of TiCN. The electroless Fe deposition reaction was finished within about 30min. after all the iron salt content in the solution was reduced to metallic iron and all the green color of the ferrous salt in the solution was disappeared. The most important feature of the process is the coating of TiCN with Fe metal. Figures 4(a, b) show SEM images with different magnifications of the iron coated TiCN particles which prepared by electroless deposition technique. It was observed that the prepared composite powder TiCN/Fe was coated with iron as implanted type and the iron metal covers the surface of the particles by a homogeneous layer. The EDAX analysis in Figure 4c shows an intensive peak due to the deposited iron metal on the TiCN particles.
Figure 2 SEM micrographs with EDS analysis of the investigated powders. a) high speed steel, b) stainless steel, c) 50Vol.%TiCN/high speed steel blend, d) 50Vol.%TiCN/stainless steel blend,
Figure 3 The XRD pattern of a) the received TiCN raw material, b) the prepared (50vol.% TiCN)/Stainless steel, c) (50vol.% TiCN)/High speed steel blended powders.

Figure 4 SEM micrographs for the iron coated TiCN particles; where a) and b) SEM image with different magnifications but c) an EDS semi-quantitative analysis of the 50Vol.%TiCN/Fe coated powder.
3.2 Microstructure of the Sintered Compacts

The density of the sintered samples was calculated by the Archimedes method using water as a floating liquid. Table 2 shows the green density (calculated from dimensions and mass of the green compacts) and the sintered densities of the samples. It was observed that the sintered materials prepared by the iron coating method has higher relative density than the sintered materials prepared by the conventional bending and milling technique. This is due to the encapsulation of the reinforcement phase of TiCN by the iron layer which increases the homogenity distribution of the TiCN particles in the matrix and decreases the TiCN particle particle interaction and grain growth.

**Table 2** The green, sintered and relative density values of materials under study.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Green density, gm/cm³</th>
<th>Relative Green density, gm/cm³</th>
<th>Theoretical density, gm/cm³</th>
<th>Sintered density, gm/cm³</th>
<th>Relative Sintered density, gm/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCN</td>
<td>-----</td>
<td>-----</td>
<td>5.08</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>5.85</td>
<td>75.50</td>
<td>7.75</td>
<td>7.50</td>
<td>96.77</td>
</tr>
<tr>
<td>High speed steel</td>
<td>6.22</td>
<td>72.50</td>
<td>8.58</td>
<td>8.46</td>
<td>98.60</td>
</tr>
<tr>
<td>(50Vol.% TiCN) / Stainless Steel</td>
<td>4.45</td>
<td>69.42</td>
<td>6.41</td>
<td>6.26</td>
<td>97.66</td>
</tr>
<tr>
<td>(50Vol.% TiCN) / High speed steel</td>
<td>4.76</td>
<td>72.56</td>
<td>6.56</td>
<td>6.40</td>
<td>97.56</td>
</tr>
<tr>
<td>(50Vol.% TiCN) / Fe</td>
<td>4.50</td>
<td>69.23</td>
<td>6.5</td>
<td>6.42</td>
<td>98.7</td>
</tr>
</tbody>
</table>

Figures 5(a-f) shows SEM images taken in BSE mode at different magnifications of the as-sintered samples. Figures 5(a, b) Cr 16.2%wt; Si 0.75 %wt; Mn 0.71 %wt; and C 0.026 %wt are a typical example of the microstructures found in the (50vol.% TiCN)/Stainless steel materials, where two phases can be distinguished the steel matrix (bright contrast) and the TiCN particles (black contrast). The (50vol.% TiCN)/High speed steel can be seen in Figure 5c; being constituted by a ferritic steel matrix (grey contrast), TiCN particles (black contrast) and carbides from the alloying elements of the M2 steel (bright contrast). These phases can be seen in more detail in Figure 6d, where it is clearer that bright carbides were surrounding the TiCN particles, acting as an interphase. There was no any other type of reaction between matrix and reinforcement, as it is usual for other cermets. On the other hand Figures 5(e, f) show (50Vol.%TiCN)/Fe sintered samples. The Fe matrix samples prepared by the electroless powder coating show a homogenous microstructure constituted by two phases, the Fe matrix and the TiCN reinforcement phase. In addition the coated TiCN by Fe layers inhibit the coarsening and the grain growth TiCN in the Fe matrix and improve the physical and the mechanical properties.
3.3 Hardness of the Sintered Compacts

Hardness was measured for all the compositions. Table 3 gives the average values of the sintered materials. The results show the hardness of the base materials is, in general, lower than the TiCN composites. Also the highest values are achieved for the (50vol.% TiCN)/High speed steel, followed by (50vol.% TiCN)/Stainless steel and (50vol.%TiCN)/Fe sintered samples. The higher hardness of the high speed steel base composite is due to the high content of alloying elements that form carbides. These carbides create a good bonding between matrix and reinforcement and also increase the content of the hard phase. Additionally, part of the alloying elements remains dissolved into the matrix increasing the hardness. On the other hand, the hardness of the stainless steel base composite is higher than the Fe-base one due to the solid solution hardening of the alloying elements of the steel matrix. The hardness of the Fe-TiCN composite is the lowest, despite its density is the highest, and due to the matrix is unalloyed.
Nevertheless, the hardness of this composite is much higher than other composites with the same composition obtained by blending or milling [10]. The reason is related to the homogeneous distribution of the hard particles, and the smaller particle size. It could be related to the coating of TiCN particles by Fe, which impedes the grain growth (in Figure 5f, the size of TiCN seems to be smaller than in Figure 5b and d).

Table 3 Hardness (HV30) of the investigated sintered materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness, HV$_{30}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCN</td>
<td>3000 ± 200</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>590 ± 20</td>
</tr>
<tr>
<td>High Speed Steel</td>
<td>620 ± 30</td>
</tr>
<tr>
<td>(50Vol.% TiCN) / Stainless Steel</td>
<td>1270 ± 10</td>
</tr>
<tr>
<td>(50Vol.% TiCN) / High speed steel</td>
<td>1300 ± 20</td>
</tr>
<tr>
<td>(50Vol.% TiCN) / Fe</td>
<td>1160 ± 20</td>
</tr>
</tbody>
</table>

4. Conclusions
In the present work the effect of the matrix composition on the sinterability and properties of Fe-based cermets reinforced with TiCN have been investigated. A comparative study Cr 16.2%wt; Si 0.75 %wt; Mn 0.71 %wt; and C 0.026 %wt Cr 16.2%wt; Si 0.75 %wt; Mn 0.71 %wt; and C 0.026 %wt between the conventional blending of the powder constituents and the powders prepared by electroless powder coating technique is present. The electroless powder coating process achieve a great encapsulation of the TiCN by Fe layer which increase the homogenity and the distribution of the reinforcement TiCN phase in the Fe matrix, and seems to reduce the coalescence of hard particles that occur in the other cases. The highest hardness values have been found for high-speed steel based composites, due to the higher level of alloying and the formation of carbides from these elements. However, the hardness value of unalloyed Fe based composite obtained from coated powders is higher than expected, due to the microstructural characteristics mentioned.
REFERENCES