EFFECT OF CARBON CONTENT ON SINTERABILITY AND PROPERTIES OF ZrO₂ DOPED WC-CERMETS

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Abstract: The control of carbon amount has an important role in controlling the mechanical properties of cemented carbides. In this study an integral effect of adding different carbon amounts in combination with three different sintering techniques was investigated. Graphite was used as carbon source and was added to the WC - 8 wt.% Ni - 6 wt.% ZrO₂ mixture in 0 wt.% C, 0.2 wt.% C, 0.4 wt.% C, 0.7 wt.% C and 1 wt.% C in order to reveal influence of carbon amount on the mechanical properties and microstructure of the composites. The composite with 0.2 wt. % C showed the highest density and hardness, ~ 100 % T.D. and 1700-1800 HV20 respectively, for all sintering techniques. Increasing the amount of carbon further caused clear grain growth during hot isostatic pressing and vacuum sintering. In spark plasma sintering the grain growth was suppressed regardless of carbon addition.

Keywords: Cermets, Sintering, Carbon, Microstructure, Zirconia

1. INTRODUCTION

Cermets are heterogeneous combination of metals or alloys with one or more ceramic phase with a relatively low solubility between metallic and ceramic components [1]. The largest category of cermets is called hardmetals and they are mostly referred to cemented tungsten carbides which are extensively used in cutting tools and wear parts. Nickel is one of the metallic binders used in liquid phase sintering of WC and offer better stability over other binders in presence of oxide additives, e.g. ZrO₂ [2]. Doping by yttria stabilized zirconium dioxide is used as a grain growth inhibitor and improves the fracture toughness of cemented tungsten carbides [3-5]. Zirconia is well known for its high toughness owing to stress-activated tetragonal to monoclinic transformation which started a new class of ceramics combining ceramics properties with improved toughness [6].

Carbon content in cemented carbides has a significant influence on the physical and mechanical properties of the materials. Carbon deficiency in the microstructure yields to formation of lower carbides which are brittle, such as the η-phase in tungsten carbide. On the other hand carbon precipitates when it is excessive in amount [7,8]. Since the carbon content can be changed substantially during sintering by reactions with oxygen-containing phases and by carbon exchange reactions with the metallic content in the initial material, control of the composition of the starting powder as well as the furnace atmosphere is essential to produce high-quality P/M parts. If an excessive amount of carbon is present in the material the free carbon will appear along the grain boundaries as a separate phase. This carbon rich pocket like structures will disrupt the WC-Ni matrix and affect the properties of the material. Excessive carbon content is also determined by ASTM as C type porosity [9].

In this study effect of carbon content on the densification, mechanical properties and microstructure of WC-Ni containing partially stabilized ZrO₂ (PZT) as a toughening agent was investigated. The composites were sintered by applying Vacuum Pressureless Sintering (VPS), Hot
Isostatic Pressing (HIP) and Spark Plasma Sintering (SPS) techniques and their effect on the material properties is also evaluated.

2. EXPERIMENTAL PROCEDURE

WC - 8 wt.% Ni - 6 wt.% (ZrO₂/3mol.%Y₂O₃) composite powders (referred as WC/Ni/PZT later in the text) were prepared by rotary ball milling of the commercial powders in ethanol for 72 h. The prepared compositions and milling parameters are given in Table 1. The particle sizes of WC (Wolfram GmbH, Austria), 3 mol. % yttria partially stabilized zirconia (TOSOH, Japan) and nickel (Russia) powders were 0.9-1.1 μm, 25 nm and 5-7 μm respectively and measured by Fritsch Particle Size Analyzer. Throughout the experiments the same powder composition was used for WC/Ni/PZT and in one of the composites, 0.4 wt.% of Cr₃C₂ (2-3 μm, Tokyo Tungsten Co.) was added as a grain growth inhibitor. KS6 grade graphite (TIMCAL) with a particle size of 5.5 μm was used as the carbon source and it was added in amount of 0.2, 0.4, 0.7 and 1 wt.%. After the milling the powder mixtures were dried at 60 °C in air and granulated by a 1 mm sieve. A pre-compaction was made before VPS and HIP by uniaxial pressing with a pressure of approximately 10 MPa.

Prior to the sintering processes removal of the organic binders in the precompacts (powder in case of SPS) was carried out at 700 °C for 1h under hydrogen. Compacted green bodies and as milled powders were consolidated by VPS, HIP and SPS respectively. Parameters of sintering are described in Table 2.

After the sintering the densities of the sintered composites were measured using Archimedes method. The Vickers hardness was measured by Indentec 5030 SKV with a load of 20 kg or 200N according to ISO 6507. Fracture toughness was measured using IFT (indentation fracture toughness) technique from the Vickers indent imprint. Toughness evaluation was made for both Palmquist and median crack systems on the base of equations given elsewhere [12-14]. The microstructure of the sintered compacts was investigated by SEM (Zeiss EVO MA-15. Phase identification was carried out using X-ray diffraction (XRD) with Cu-Kα radiation (Bruker AXS D5005).

3. RESULTS AND DISCUSSION

3.1 Physical and Mechanical Properties

When no carbon was added to the material presence of so called η-phase was observed for HIPed material. Ni₂W₄C was detected in XRD studies up to 20 wt.% in materials HIPed without any graphite (Fig. 1a). High hardness of this carbide phase was reported in various sources [15,16] which is known for XₙWyC type of structures (X: Ni, Co, Fe, B etc.). Despite its relatively high hardness the formation of this phase is not favorable since it promotes brittleness and unpredictable behavior during wear. The formation of η-phase was prevented by adding different amounts of graphite and in XRD studies ternary carbide phases were not observed in presence of additional carbon.

<table>
<thead>
<tr>
<th>C content, %</th>
<th>Technique</th>
<th>T, °C</th>
<th>Pressure, MPa</th>
<th>Heating rate, °C/min</th>
<th>Cooling rate, °C/min</th>
<th>Dwell time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1.0</td>
<td>HIP</td>
<td>1450</td>
<td>200</td>
<td>12</td>
<td>8</td>
<td>60</td>
</tr>
<tr>
<td>0.2-1.0</td>
<td>VPS</td>
<td>1450</td>
<td>2x10⁻⁵</td>
<td>10</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>0.2-1.0</td>
<td>SPS</td>
<td>1200</td>
<td>50</td>
<td>~150</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Sintering parameters for the applied techniques.

<table>
<thead>
<tr>
<th>Composition</th>
<th>86WC-8Ni-6ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C wt.%</td>
<td>0 0.2 0.4 0.7 1</td>
</tr>
<tr>
<td>Ball to powder Ratio</td>
<td>6:1 10:1 6:1 6:1 7:1</td>
</tr>
<tr>
<td>Milling balls</td>
<td>ZrO₂ WC-Co ZrO₂ ZrO₂ ZrO₂</td>
</tr>
<tr>
<td>Ball dia., mm</td>
<td>10 12 10 10 10</td>
</tr>
<tr>
<td>Milling t, h</td>
<td>72</td>
</tr>
<tr>
<td>PCA, plasticizer</td>
<td>3g PEG &amp; 100ml ethanol</td>
</tr>
</tbody>
</table>

*Contains Cr₃C₂

Table 1 Powder compositions and milling parameters.
A comparison of XRD measurements of the powder and the compacts with 0.2 wt.% C for different sintering methods are given in Fig. 1b. The densities of the carbon containing composites are given in Fig. 2a. The upper curve represents the theoretical densities of the studied compositions and the curves below it represents the densities of the compacts consolidated with different techniques. In presence of 0.2 wt.% graphite the measured density of the material is very close to its theoretical density, which indicates almost full densification. In other compositions with or without additional carbon the densities are slightly lower than the theoretical density values. Even though there is no evidence of \( \eta \)-phase in the XRD results of 0.2 wt.% C grades, the amount of this phase can be below the detection limits of XRD, which will also yield a lower relative density. The measured density of the HIPed material was 13.40 g/cm\(^3\) and it increased slightly in presence of 0.2 wt.% C to 13.43 g/cm\(^3\). When the carbon amount was 0.4 wt.% densities of all the compositions regardless of the production technique were dropped significantly, to 12.77, 13.10 and 12.54 g/cm\(^3\) for HIPed, VPSed and SPSed samples respectively. The major cause for this drop is the effect of additional carbon on composition and the formation of \( \eta \)-phase which has a much higher density. When the carbon content was further increased the densities of the materials showed some variation depending on the sintering method. Measured densities of SPSed materials were increased first to 12.64 g/cm\(^3\) and then to 12.78 g/cm\(^3\) for additions of 0.7 and 1.0 wt.% C. Density of HIPed samples showed a continuous drop with the increasing C content while the density of VPSed sample was slightly increased with 1.0 wt.% C addition.

Hardness of the tested cermets was lowered to some extent by the increasing amount of graphite additive (Fig. 2b) Materials with 0.2 and 0.4 wt.% C addition had higher hardness when they were sintered by VPS. Similar behavior was observed with the density change, the hardness of SPSed samples first dropped from 1722 HV20 to 1382 HV20 when the C content went up from 0.2 to 0.4 wt.% and it increased first to 1386 HV20 and
then to 1507 HV20 for 0.7 and 1.0 wt.% C, respectively. SPS technique has the unique advantage of suppressed grain growth over other sintering methods. This is probably the main reason for the increase in hardness with higher C content along with better densification compared to HIPed and VPSed samples.

Fracture toughness of the materials showed evident variation (Fig. 3). Fracture toughness of HIPed materials was in a declining regime when the carbon amount was increased. VPSed materials on the other hand had an increase in their fracture toughness up to 0.7 wt.% C which was dropped when C amount was 1 wt.%.

SPSed materials showed a more unique behavior and almost no difference was observed for 0.2 and 1.0 wt.% C addition. Fracture toughness had a small increase at 4 wt.% and remained almost the same for 0.7 wt.%.

SPSed materials had an inverse relation between their hardness and fracture toughness. Presence of additional carbon not only hindered η-phase formation but also made some improvement on the densification overall. In the grades produced by HIP IFT was very high especially for low carbon content grades. In general higher fracture toughness is assumed to be a result of synergistic influence of microstructure and zirconia transformation toughening effect. However behavior of HIPed specimens was not very clear.

3.2 Microstructure

Difference in the microstructure development and morphology with increase in carbon content and effect of different sintering techniques were observed by SEM studies. The images in Fig. 4 represent the microstructures of the materials with various carbon contents and sintered with different techniques. The carbon content in Fig. 4 a-d is 0.2-1.0 wt.% of C and the materials were sintered by VPS. In Fig. 4 e-g is for the same carbon content but obtained using SPS. The HIPed materials had almost the same microstructures with those consolidated by VPS. A significant difference in the microstructure was the grain growth in the materials sintered by VPS and HIP compared to SPS as a result of much shorter sintering cycle for the latter. The change in the carbon content had a clear influence on the grain size evolution, where 0.2 wt.% C grade had a finer microstructure and the change was in an increasing manner for 0.4, 0.7 and 1.0 wt.% C grades. The increase was observed both for WC and ZrO₂.

The specimens with 0.2 wt.% C were doped by Cr₃C₂ and as a result the grain growth was less compared to other grades when they were sintered by VPS and HIP. Coarser grain structure for 1 wt.% C grade samples compared to 0.4 and 0.7 wt.% grades indicates the enhanced discontinuous grain growth namely the effect of carbon addition on the microstructure. The microstructure of SPSed materials showed almost none or very little grain growth and seemed to be unaffected by the graphite addition. WC grains were in submicron range and ZrO₂ particles were in the range of ultrafine to nanoscale.

The microstructure of Cr₃C₂ containing grade was more preferable for both VPS and HIPed samples as it had more homogeneous distribution of the submicron size grains. WC demonstrated a tendency of grain elongation and having a rectangular shape with the increasing carbon content (Fig. 4 c-d). This type of
Fig. 4. SEM images of a) VPS, (0.2 wt.% C) b) VPS, (0.4 wt.% C), c) VPS, (0.7 wt.% C), d) VPS, E (1 wt.% C) e) SPS, (0.2 wt.% C) f) SPS, (0.4 wt.% C) g) SPS, (0.7 wt.% C) h) SPS, (1 wt.% C) morphology was reported for WC - 30 wt.% Co composites when the carbon content was increased from 0.1 to 1.0 wt.% [17].
4. CONCLUSION

Effect of carbon content in combination with various sintering techniques on the microstructure and mechanical properties of the WC-Ni hardmetals with 6 wt.% of PZT was investigated. The microstructure of the VPSed and HIPed materials was changed significantly by the addition of extra carbon. There was almost no grain growth in SPSed materials due to shorter process duration. The hardness of the composites were decreased in presence of extra carbon up to 0.7 wt.% for VPS and HIP and 0.4 wt.% for SPS. Fracture toughness of the materials was consistent with their hardness with some deviation.

5. REFERENCES


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