SINTERING ROUTES FOR ZIRCONIA DOPED HARDMETALS.

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Abstract: Three sintering routes (hot isostatic pressing; vacuum pressureless sintering; and spark plasma sintering) were used for fabrication of zirconia doped hardmetals to reveal the optimum conditions for manufacturing of the final product with improved mechanical properties. The effect of fabrication parameters on the microstructure development and properties of WC-Ni and yttria-stabilized zirconia doped hardmetals was studied. Each sintering technique has its own impact on the formation of the chemical compounds and mechanical properties of the material. The SPSed specimens had ultra-fine grained microstructure in combination with high hardness and density close to theoretical. HIPed and vacuum sintered materials although have low porosity suffer from the abnormal grain growth that influences their mechanical properties.

Key words: Hardmetals, Sintering, Zirconia, Hot Isostatic Pressing, Spark Plasma Sintering, Vacuum Pressureless Sintering

1. INTRODUCTION

Production of cemented carbides has been rapidly developed over the past six decades and hardmetals are found in different applications for example, wear resistant parts, automotive components, can tooling, metal forming tools and etc. The most representative member of this group of materials is a well known cobalt-bonded tungsten carbide (WC-Co cermets) that is widely used in situations where high wear resistance is needed [1,2,3].

Zirconium dioxide is one of the most studied ceramics and one of the most versatile materials commercially available today [4]. It resists high temperatures, corrosion, wear and impact, is chemically inert in the presence of most substances and one of the most intriguing oxide ceramics for investigation due to stress-induced tetragonal-to-monoclinic (martensitic) phase transformation, which is characterized by a large volume change (3 - 5%) and shear deformation (1 - 7%) [5]. Addition of zirconia to the cemented carbides matrix (or using zirconia as matrix) has been intensively studied [6-9]. Nevertheless development and optimization of such kind of materials is far away from its final point.

There is a great influence of the processing conditions on the formation of microstructure and mechanical performance of sintered materials [10-12].

Cemented carbides can be produced either by conventional sintering methods with or without isostatic pressure or by spark plasma sintering (SPS), which is one of the best ways to densify ultra-refractory compounds [13].

In this work vacuum pressureless sintering (VPS), hot isostatic pressing (HIP) and spark plasma sintering (SPS) routes were employed to produce WC-8wt.% Ni-6wt.% ZrO₂ bulk bodies for their further investigation and optimization. Usually SPS technology is compared to hot pressing (HP) technology because of the similarity of the furnaces construction and difficulty of producing near-net shape complex details. The aim of the present study was to reveal features of microstructure development during
different routes of processing and their influence on mechanical properties of the composites.

2. EXPERIMENTAL

2.1 Materials

The raw materials used in the production of WC/Ni/ZrO$_2$ multiphase cermets were fine grained WC (Wolfram GmbH, Austria), micro-scale Ni powders as binder materials and 3 mol. % yttria partially stabilized zirconia (PSZ-ZrO$_2$) nanopowders (TOSOH, Japan). Because of possible η-phase formation during sintering of these mixtures revealed in the previous study [10] 1 wt.% C was added to eliminate the formation of unfavorable phases. Table 1 lists the characteristics of the raw powders to be mixed based on the data from the suppliers and analyzes conducted in the laboratory of Tallinn University of Technology using Fritsch Particle Sizer analysette 22.

2.1 Mixing and compaction

Mixing of the below mentioned powders was carried out in a rotary ball mill device of a vertical rotation direction. Process duration was 72 hours. Grinding was made using WC-Co balls with a diameter of 12mm. Ball to powder ratio was 7:1 and 100ml of ethanol together with 3g of PEG (Polyethylene-glycol) were added as a PCA (process control agent). PEG also serves as a plasticizer during compaction. After milling powders were dried in air. Then powders were compacted in a single ended press under pressure of 8.5MPa with a die having dimensions of 15mmx10mmx5mm. Green bodies were then held at 700°C in hydrogen for 30 min to burn plasticizers off. SPS procedure does not require the green bodies.

2.2 Sintering

The green bodies were sintered in HIP furnace at a pressure of 200 MPa using capsule free method and vacuum furnace under medium vacuum conditions, which varied slightly during heating from 20 Pa to 5 Pa. Maximum temperature for both processes was 1450°C and in both cases specimens were held at a maximum temperature for one hour.

The conditions of SPS sintering for the present materials are of special consideration and need to be optimized. Review of the literature [10,13-15] has shown the theoretical temperature parameters to be chosen and the first trial sintering was held under the specified parameters; then the process was re-considered and specified parameters were applied to the sintering process. A schematic of the sintering cycles are illustrated in Figure 1. Maximum temperature of the SPS cycle was 250°C lower than in the case of HIP and VPS and was 1200°C. Dwell time at maximum temperature during SPS cycle was 1 minute and the pressure applied to punches was 50 MPa.

2.3 Characterization

The microstructure was investigated by SEM (Zeiss EVO MA-15). The bulk Vickers hardness was measured using Indentec 5030 SKV at the load of HV20 or 200N according to ISO 6507. The density was measured using Archimedes method. 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 some researches and equations [17-19].

<table>
<thead>
<tr>
<th>Powder</th>
<th>WC</th>
<th>Ni</th>
<th>ZrO$_2$</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>0.9$\mu$m</td>
<td>5-7$\mu$m$^3$</td>
<td>25 nm$^3$</td>
<td>6.5$\mu$m$^3$</td>
</tr>
<tr>
<td>Purity %</td>
<td>≥99.0</td>
<td>99.7</td>
<td>98.2</td>
<td>-</td>
</tr>
<tr>
<td>Grade</td>
<td>WC</td>
<td>Ni</td>
<td>PSZ</td>
<td>KS6</td>
</tr>
<tr>
<td>Supplier</td>
<td>Wolfram</td>
<td>-</td>
<td>TOSOH</td>
<td>TIMCAL GmbH</td>
</tr>
</tbody>
</table>

a-suppliers data, b-measured data

Table 1 The characteristics of the starting powders
3.RESULTS AND DISCUSSION

3.1 Microstructure

SEM analysis revealed a great difference in the microstructures of the SPSed specimens and specimens sintered under pressure and pressureless conditions. SPS process is unique because the most significant parameters influencing grain grows (i.e. sintering temperature and time) are reduced to minimum. Main three phases are indicated with arrows on the Figure 3a. Tungsten carbide grains are bright white grains, zirconia particles are rounded black clusters and nickel phase is in a view of grey shapeless spots. Grain coarsening of the HIPed and VPSed specimens can be clearly seen from Figures 3 b and c. However, reducing dwell time during HIP and VPS as microstructure optimization parameter does not perceptibly result in grain refinement while it could influence unfavorably the densification process and porosity level. The temperature was also chosen to prevent simultaneous zirconia particles transformation from tetragonal to monoclinic crystal lattice state during cooling after sintering. Some grain growth inhibitors can be used to prevent the WC grain growth (e.g. Cr\textsubscript{17}C\textsubscript{2}, VC), though they were not added deliberately in order to compare the effect of different techniques on the behavior of WC grains under different conditions. Nevertheless, the composites produced are of low porosity as it can be proved by SEM analysis. SPSed microstructure is ultra-fine grained with submicron WC grains of different shapes and sizes. The boundaries of the WC grains cannot be clearly determined from the images made of SPS specimens, but the compact grain structure is indisputable. The refinement of the WC grains after ball milling should also be mentioned here. Although the initial particle size of WC is 0.9 μm in average, after SPS sintering there are many grains, which are smaller in size, which means that grain growth was minimal. Zirconia grains can be also determined as ultra-fine in the range of 0.2-0.5μm. Usually it is difficult to get zirconia particles of this size because their tendency to agglomerate due to a great surface area of the initial nanoparticles.
3.2 Density, hardness and fracture toughness

Densities of the sintered compacts were compared to theoretical densities calculated with the rule of mixtures on the basis of the starting nominal compositions assuming no impurities and no reactions and transformations during processing.

Two graphs representing hardness and density values of the sintered bulk bodies are shown in Figure 4. Hardness of the specimens produced by HIP and pressureless sintering are lower than that of the sample produced by SPS route. The main reason for the lowered hardness is most probably grain coarsening of the HIP and VPS grades. It is a known fact that hardness is inversely dependent on the grain size.

The specimen sintered by SPS has also the highest density. Higher densification degree of the grade sintered with SPS is also likely to contribute to higher hardness shown in Figure 4.

Fracture toughness of the specimens sintered in pressureless conditions is higher than sintered in SPS. It is a common rule that if a material has high hardness it is more brittle and less fracture resistant than a similar material having a lower hardness. Lower fracture toughness can most likely be attributed to higher hardness and smaller porosity of the SPS processed samples, because in some cases fracture toughness can be enhanced by the presence of microcracks.
of pores in the microstructure of the material.

4. CONCLUSIONS

Tungsten carbide based ZrO₂ doped cemented carbide was sintered using vacuum pressureless sintering, hot isostatic pressing and spark plasma sintering techniques. The production process has shown that temperature needed for the densification of material during SPS sintering cycle can be 200°C lower than for comparable technologies. The microstructure generated by the SPS technique can be defined as submicron and ultrafine grade, while HIP and vacuum sintered microstructures refer to submicron and micronized grains. As a consequence of fine and preferable microstructural parameters the materials produced by SPS had higher hardness in the range of 1500 HV20 units. As a result of high hardness the fracture toughness of the SPS grade was lower than grades sintered by HIP and VPS furnaces.

Although the results obtained by SPS are impressive a more detailed comparison and investigation on the effects of sintering technologies on the properties of cemented carbides are needed. In the near future further studies on the SPS sintering of different cemented carbides will be carried out.

5. ACKNOWLEDGMENTS

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6. REFERENCES


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