Pressureless Sintering of TaC-HFC-VC

H.R.Rasouliasiabi*1, B.shahbahrami*2

*1Faculty of Materials Science and Engineering, Semnan University, Semnan, Iran
*2Department of material science and engineering, Saveh Branch, Islamic Azad University, Saveh, Iran
E-mail: Hr.rasooli@gmail.com

Abstract - Tantalum carbide (TaC) matrix composite was produced by the pressureless sintering at temperatures of 2200 °C for 1 & 2 hours and 2300 °C for 1 hr. Various combinations of TaC, HFC and VC were used. The amount of VC was constant as 2 vol%, and the HFC content was 0-15 vol% variable. Vanadium carbide particles diffused in the structure of TaC and formed solid solution in both temperatures, but the amount of HFC had a different influence on the sinterability and mechanical properties of the TaC. The HFC particles located on the grain boundaries and inhibited from grain growth through the sintering at temperature 2200 °C. The relative density was decreased from 94.2% to 85% for 1 hr, and from 94.8% to 88% for 2 hrs, when the amount of HFC was increased from 0 to 15 vol%. By increasing the temperature to 2300 °C, solid solution of TaC-HFC-VC was formed. The relative density increased from 96.1% to 98.2% when the amount of HFC was increased to 10 vol%.

Keywords: Tantalum Carbide; Hafnium Carbide; Vanadium Carbide; Pressureless sintering; Composite

1. Introduction

The physical and chemical properties of group IV and v transition metal carbides (TMC) are of interest for basic research and several technological applications [1]. Industrial applications such as cutting tools and hard coating because of their great strength and high hardness have been applied [1-5]. Furthermore, optical, electronic and magnetic properties of TMC have attracted much attention for coatings, electrical contacts and diffusion barriers [1]. Applications of TaC, however are rather limited, because of the difficulties that exist in obtaining fully dense bodies. Monolithic TaC is difficult to densify even by hot pressing at high temperature because of its highly covalent bonding, low self-diffusion coefficient and rapid grain growth at high temperatures [6-8].

Pressureless sintering of TaC without use of additives was investigated by Xuan Liu et al.[9]. They obtained a relative density of 97.5% at sintering temperature of 2300 °C. Silvestroni and Sciti [10] consolidated TaC by pressureless sintering with the addition of MoSi2. They have reported that 10 vol% MoSi2 is enough to achieve the full density at 1950 °C. Patterson et al. [8] used TiC, ZrC, HFC, VC and NbC as the additives to produce TaC matrix composites. All of these samples were produced by hot press under the similar conditions, which is an effective technique to densify TaC.

In the previous works, different sintering aids have been used for tantalum carbide separately, but have not been yet used two additives as sintering aid for TaC. In this study, the effect of the HFC on the pressureless sintering of TaC was investigated when vanadium carbide additive presence in the system with a constant content. Also, although hot press is an effective technique to densify, but it can only produce ceramics with simple shapes. For preparation ceramics with complex shapes, pressure-less sintering is a cost effective method. The mechanical properties such as hardness were measured and correlated to the microstructure evolution and densification behavior.

2. Experimental procedures

The starting powders were TaC (purity>99.9 wt%, average particle size=500nm), HFC (purity>99.9 wt%, average particle size=260nm) and VC (purity > 99.99 wt%, average particle size=240nm).

Various amount of hafnium carbide powders (0, 5, 10 and 15 vol%) was added to TaC-VC composites. The amount of vanadium carbide was 2 vol% in the entire samples. The powders were wet blended in hexane by a planetary ball mill (Fritsch company-model pulverisette 5), which it's balls and container are made from ZrC. After mixing for 2 hours, the slurry was dried at 80 °C in an oven for 24 hours.

The powder mixtures were pressed into pellets using a 12 mm diameter die by uniaxial press at a pressure of 10 MPa. They were also isostatically pressed at a pressure of 400 MPa. The sample pellets were then sintered for 1 & 2 hrs at 2200°C and 2300°C, using a heating rate of 5°C/min, under a high-purity atmosphere (<5 ppm of oxygen gas) in a graphite furnace. The relative densities of the ceramics were measured by the Archimedes method based on ASTM B311. The phase analysis of the pellets was carried out on the solid samples by X-ray diffraction.
using CuKα radiation (Model 3003-IT - Seifert Company). The Vickers hardness was determined according to ASTM C1327. The microstructure of the samples was studied using SEM (Philips, model XL30), that was equipped with energy-dispersive X-ray spectroscopy (EDAX). For the microstructure evaluation, the surface of the specimens was polished by 1, 6 and 30µm diamond abrasive paste, and then etched for 30 in 3:1 HNO3 to HF solution.

3. Results and discussion

The effect of HfC addition amount and sintering temperature on the relative density of the samples are given in table 1. As it is shown, the density of all compositions at 2200°C was decreased with increasing hafnium carbide (fig.1). The relative density of the pellets sintered at 1 hr, were decreased from 94.2% to 85% when the amount of HfC increases from 0 vol% to 15 vol%. Similar behavior was observed for samples sintered for 2 hrs. At this holding time, the relative density was decreased from 94.8% to 88% as the level of hafnium carbide increases from 0 vol% to 15 vol%. It is concluded hafnium carbide can not dissolve in TaC at this temperature. Although base on literature [3] hafnium carbide and tantalum carbide have completely solubility behavior, but it seems temperature is low for solubility even by increasing time of sintering. Of course increasing of time has more effect on sintering process.

The relative density at sintering temperature 2300 °C, had however a different behavior. In this temperature, relative density increased from 96.1 to 98.2% as the level of hafnium carbide increased from 0 to 10 vol% respectively, then decreased to 96% when the amount of HfC increased to 15 vol%. The increasing temperature causes mass transport and increases diffusion process as equation $D=D_0 \exp(-Q/RT)$ [11]. Then, the solubility of hafnium carbide happens in tantalum carbide as it confirmed by XRD analysis (fig.2). The formation of solid solution causes the grain growth and increasing density [12] as it can be seen from the micrograph analysis (fig.3). It is seen from figures 3(a)-(c), by increasing hafnium carbide up to 10 vol%, grain growth decreases the porosities and increases the density, so after that causes the lock of porosities and decrease of density. Also, by comparison of figure 3(c) to figure 3(e), the effect of sintering temperature on the microstructure can be seen. At sintering temperature 2200 °C for 2 hr, the main constituents exist separately (fig.3e), but there is only one type particle in the microstructure for the sample sintered at 2300 °C for 2 hours (fig.3c). This behavior related to formation of solid solution.

Table 2 is given the hardness of sintered samples. Also, the hardness of the specimens as a function of the hafnium carbide content is shown in figure 4. Experimental results show that the density and microstructure may have significant influence on the hardness of the specimens. The hardness was increased with increasing holding time and specially sintering temperature. Increasing sintering temperature enhances the density, and reduces the amount of the porosities. Therefore, the hardness was increased with increasing sintering temperature. Since the hardness of hafnium carbide(26.1 GPa) is higher than the hardness of TaC(16.7 GPa), the hardness of the specimens sintered at 2200 °C for 1 & 2 hours, also was improved by increasing the level of HfC, while the density was decreased. Similar behavior was seen for the samples sintered at 2300 °C, except of the HfC content 10 and 15 vol% which is equal.

4. Conclusions

4.1. Due to low energy activation at sintering temperature 2200°C, HfC is insoluble in TaC.

4.2. The relative density of the composites sintered at 2200°C for 1 hour, was decreased from 94.2% to 85% when the amount of HfC increases from 0 vol% to 15 vol%. It also was decreased from 94.8% to 88% for holding time 2 hours.

4.3. The relative density of the composites sintered at 2300°C for 1 hour, was increased from 96.1% to 98.2% by increasing the level of HfC up to 10 vol%. However at 15 vol% of HfC, the density was reduced to 96%.

4.4. The significant grain growth was occurred during densification at sintering temperature 2300 °C due to solid solution.

4.4. The hardness was improved with increasing the amount of hafnium carbide and specially sintering temperature.

5. References


Table 1 - The effect of HFC content on the relative densities of the samples sintered at 2200 °C (1 & 2 hours) and 2300 °C (1h)

<table>
<thead>
<tr>
<th>HfC content (Vol%)</th>
<th>Relative density (2200°C-1 hr)</th>
<th>Relative density (2200°C-2 hr)</th>
<th>Relative density (2300°C-1 hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>94.2</td>
<td>94.8</td>
<td>96.1</td>
</tr>
<tr>
<td>5</td>
<td>88.5</td>
<td>94</td>
<td>97.1</td>
</tr>
<tr>
<td>10</td>
<td>87.1</td>
<td>93</td>
<td>98.2</td>
</tr>
<tr>
<td>15</td>
<td>85</td>
<td>88</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 2 - The effect of HFC content on the hardness of the samples sintered at 2200 °C (1 & 2 hours) and 2300 °C (1h)

<table>
<thead>
<tr>
<th>HfC content (Vol%)</th>
<th>Hardness(GPa) (2200°C-1 hr)</th>
<th>Hardness(GPa) (2200°C-2 hr)</th>
<th>Hardness(GPa) (2300°C-1 hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.1</td>
<td>14.7</td>
<td>15.5</td>
</tr>
<tr>
<td>5</td>
<td>14.5</td>
<td>15.1</td>
<td>18.3</td>
</tr>
<tr>
<td>10</td>
<td>14.8</td>
<td>15.1</td>
<td>21</td>
</tr>
<tr>
<td>15</td>
<td>15.2</td>
<td>16</td>
<td>21</td>
</tr>
</tbody>
</table>
Figure 1 - The relative density as a function of HfC addition to TaC-2 vol% VC compositions sintered at 2200 °C for 1 & 2 hours and 2300°C for 1hr.

Figure 2 - X-ray diffraction patterns TaC-10 vol% HfC-2 vol% VC composite sintered at 2300°C for 1hr.
Figure 3 - Microstructures of TaC-2 vol% VC-HfC composite sintered at 2300°C for 1 hr as a function of HfC additive; (a) 0 vol%, (b) 5 vol%, (c) 10 vol%, (d) 15 vol%; and composite sintered at 2200°C for 2 hr, with HfC additive 10 vol%.
Figure 4 - The hardness as a function of HfC addition to TaC-2 vol% VC compositions sintered at 2200 and 2300°C for 1 hr.