Comparison between a conventional sintering process and by SPS (Spark Plasma Sintering) consolidation of WC-6Co (%wt).

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Abstract. This work aims to compare cemented carbide (WC-6%wtCo) obtained by a conventional sintering process and the SPS (Spark Plasma Sintering) process. The blended material was compacted in a closed die hence a preformed cylinder was obtained. A heat treatment at 1120°C for 30 min was carried out to assist the handling of the samples. Subsequently, the consolidation was carried out at 1280°C for 60 min following a conventional route. The material was also consolidated by Spark Plasma Sintering (SPS) at 1100°C for 1 min. Archimedes’ method was used to evaluate the relative density of the materials after consolidation. Optical and scanning electron microscopy were carried out to characterize the microstructural features of the samples and mechanical properties was obtained by Vickers hardness. The SPS samples showed the best results regarding the density (93%) and Vickers hardness as well.

Introduction.

Hard materials have been used as tools in several applications and among them; one can highlight the cemented carbide, which is usually manufactured by powder metallurgy. Cemented carbide is made of WC and Co, with Co (wt%) ranging between 4 and 30%, since the Co content depends on the application. The cobalt works as a binder and it decreases significantly the sintering temperature due to the liquid formation between the particles of WC [1]. The sintering temperature usually ranges from 1350 to 1600 °C, depending on the amount of the Co [2].

Regarding the sintering process, it can be performed at different conditions depending on the equipment and the facilities. The sintering process, namely conventional in this study, usually consists of heating a preformed powder (raw or blended materials) at high temperatures, although slightly lower than the melting point, during minutes to hours [2]. Whilst the SPS can be considered as a non-conventional sintering process, in which the material is heated by Joule effect and, a load applied on the material throughout the consolidation. It is worth noting that, the SPS process usually takes only a few minutes and, does not need a preformed material, since the sintering is carried out inside a high-density graphite die, which is an additional feature of the SPS process. Therefore, lower sintering temperatures, holding times and, finer grain size are usually obtained by means of SPS [3]. This process was developed in 1990s [4] and many works have been carried out showing the prospective applications of SPS as shown in the reviewed literature [5].

This work aims to compare the WC-6wt%Co preformed sample sintered at 1280°C for 60 min by a conventional process and by SPS at 1100°C for 1 min. The use of preformed and the previous heat-treated material in the SPS process was carried out to keep the initial step up for both analyses.
Materials and Methods.

Materials. The material evaluated was a WC-6wt%Co powder, with a particle size of about 1 µm. This blended material was supplied by Sandvik S.A.

Methods. First of all the blended powder was placed inside a closed die and, a cylinder with 17.5 mm diameter and, 5.7 mm length was obtained by applying a pressure of 200 MPa (22kN load) at room temperature. Subsequently, a heat treatment was carried out at 1120°C for 30 min to increase the green mechanical properties of the preformed material and make easier the handling.

The preformed material was consolidated in two different conditions: (i) in the SPS process, the preformed sample was not a prerequisite. However, to maintain the conditions established in the conventional sintering process, the preformed samples were placed inside the graphite die. The SPS allows applying a load throughout the process. Therefore, a pressure of 60 MPa (18.8kN load) was applied after the temperature has reached 900°C, so that cracks can be avoided in the preformed material. It was considered the blended material be plastic above 900°C. The parameters of sintering were: the heating rate of 100°C/min up to 1100°C and the holding time was 1 min. (ii) It follows that in the conventional process the sample was heat treated at 1280°C for 60 min (vacuum atmosphere). The heating rate to reach 1280°C was 8.5°C/min following a conventional route. It’s worth mentioning, to compare the results the sintering SPS temperature is usually lower than that used in conventional processes. Therefore, the temperature selected for the conventional consolidation was about 15% higher than SPS as well as a longer holding time. The Table 1 summarizes the process parameters.

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature (°C)</th>
<th>Heating Rate (°C / min)</th>
<th>Holding Time (min)</th>
<th>Load (kN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Sintering</td>
<td>1280</td>
<td>8.5</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>SPS</td>
<td>1100</td>
<td>100</td>
<td>1</td>
<td>18.8</td>
</tr>
</tbody>
</table>

After the consolidation, the density of the samples was evaluated by the Archimedes’ method, in which the mass of the sample and its apparent mass immersed in water is related with the amount the volume of the liquid that it displaces [2].

The microstructural characterization was carried out by optical and scanning electron microscopy. The traverse section of the samples was observed after metallography grinding and polishing with diamond suspension, using an automated procedure.

The mechanical properties were also measured by Vickers hardness, in which 5 and 30kgf load were applied to evaluate the different conditions and crack formation.

Results.

Relative Density. Table 2 displays the results of the mass of solid (m1), the mass of a pycnometer (m2), the mass of a pycnometer with the solid immersed (m3); m1, m2 e m3 were the average obtained from 5 measurements. Density (\(D_{WC6Co}\)) were calculated based on m1 averaged and the volume (V) displaced by water. The relative density was calculated between density obtained (\(D_{WC6Co}\)) and expected. Eq. (1) and Eq. (2) were used to calculate the volume displaced and the density of the WC6wt%Co.

\[ V = \frac{(m1+m2-m3)}{d} \]  \hspace{1cm} (1)

\[ D_{WC6Co} = \frac{m1}{V} \]  \hspace{1cm} (2)
Although the SPS process was conducted at lower temperatures than conventional process, the results show the consolidation of the material was obtained as well as much shorter holding times can be applied. The relative density was much higher than in the conventional process.

Table 2. Parameters to determine relative density of consolidated materials by means of Archimedes’ method for the material consolidated conventionally and by SPS. The uncertainty in measurement of mass is 1.0x10^{-5}.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conventional process</th>
<th>SPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average mass of solid -m1- (g)</td>
<td>0.91311_0</td>
<td>1.8968 _0</td>
</tr>
<tr>
<td>Average mass of a pycnometer -m2- (g)</td>
<td>46.6993_6</td>
<td>46.7005 _9</td>
</tr>
<tr>
<td>Average mass of a pycnometer with the solid immersed -m3- (g)</td>
<td>47.5313_2</td>
<td>48.4601_0</td>
</tr>
<tr>
<td>H$_2$O temperature (ºC)</td>
<td>23.0</td>
<td>23.0</td>
</tr>
<tr>
<td>H$_2$O density at room temperature -d- (g/cm$^3$)</td>
<td>0.9973</td>
<td>0.9973</td>
</tr>
<tr>
<td>Calculated density WC-6%Co -D$_{WC6Co}$ (g/cm$^3$)</td>
<td>11.2</td>
<td>13.8</td>
</tr>
<tr>
<td>Density of WC-6%Co expected (g/cm$^3$)</td>
<td>14.8</td>
<td>14.8</td>
</tr>
<tr>
<td>Relative density</td>
<td><strong>76.0%</strong></td>
<td><strong>93.1%</strong></td>
</tr>
</tbody>
</table>

**Microstructural characterization.** The microstructural characterization of the samples is displayed in Fig. 1 and Fig. 2. It is worth mentioning, the highest density can be observed and the grain size of the SPS sample is also lower than in the sample obtained from the conventional method. The literature has reported the benefits of the SPS consolidation [3-5]. The composition maps are also shown regarding the distribution of Co and W, which can be considered almost homogeneous, mainly in the SPS sample.

![Conventional process](a) ![SPS](b)

Fig. 1 (a) sample conventionally consolidated and (b), manufactured by SPS. Backscattered electrons SEM.
Fig. 2 (a) and (c) sample conventionally consolidated; (b) and (d) manufactured by SPS. Backscattered electrons SEM and map of composition. The Co distribution can be observed and, in the SPS sample it is more homogeneous.

**Vickers hardness.** The hardness obtained has been an average of 5 measurements carried out. The results are displayed in Table 3. The highest values of hardness of the SPS sample are in agreement with the relative density obtained (Table 1). The hardness of the conventionally sintered sample was of about a quarter of SPS sample, which is very low and indicates no consolidation occurred.

Table 3. Vickers hardness of the material consolidated conventionally and by SPS.

<table>
<thead>
<tr>
<th>Conventional process</th>
<th>SPS</th>
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<tbody>
<tr>
<td>472 ± 19 (HV5)</td>
<td>1786 ± 42 (HV5)</td>
</tr>
<tr>
<td>536 ± 27 (HV30)</td>
<td>1796 ± 44 (HV30)</td>
</tr>
</tbody>
</table>

Fig. 3 and Fig 4 show Vickers hardness indentations characterized by optical (OM) and scanning electron microscopy (SEM), where cracks were observed in the SPS sample. The absence of cracks and low hardness in the conventionally sintered sample can be related to the weak consolidation (low density) of this sample. On the other hand, the hardness obtained in the SPS sample is comparable to that found in other cemented carbides [1]. Therefore, these results corroborate to the use of SPS. Some stains can be observed, mainly in the optical micrographs, which are related to the low density of the materials, mainly the conventionally sintered. Porosity can store water/alcohol throughout metallographic preparation leading to the stains observed.
Fig. 3 Vickers hardness indentations (HV5) were carried out. (a) and (b) optical microscopy, (c) and (d), indentation marks are indicated in the SEM micrographs (secondary electrons).

Fig. 4 Vickers hardness (HV30) was carried out. Indentation mark and cracks formed due to the indentations in the SPS sample can be observed. (a) and (b) optical microscopy, (c) and (d), indentation marks are indicated in the SEM micrographs (secondary electrons).
Final remarks.

This work aimed to compare two different consolidation process: a namely conventional and the SPS (Spark Plasma Sintering). Although the temperature of the consolidation and the holding time was greater in the conventional process than in the SPS, the best results were obtained by SPS. Higher density results of SPS sample were confirmed by microstructural analyses and Vickers hardness.

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References