Complete Thermal Properties of the Composite WC/Co (15% wt)

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ABSTRACT

Hardmetal is usually processed by the conventional powder technology techniques: mix of WC + Co powders, compacting, and liquid phase sintering. A new method to process hardmetal parts is hereby described. Parts of WC-15%wt Co were processed by using high pressure – high temperature sintering (HPHT). It was used the pressure of 5GPa, temperature of 1350°C, and time of 2 minutes of sintering. Results are shown as a function of micro-structure, densification, and hardness measurements. The open photoacoustic cell technique (OPC) was carried out in order to measure the thermal diffusivity of the hardmetal. In addition, heat capacity was considered and the thermal conductivity calculated. Results matched with the values of the literature where other photoacoustic techniques have been employed.

Keywords: HPHT Sintering, Hardmetal, Thermal Characterization, Photoacoustic technique.
INTRODUCTION

Hardmetals are liquid-phase sintered powder metallurgical composites that consist of very hard refractory carbides embedded in a tough metal binder. They are used extensively in applications demanding wear resistance (e.g., metal cutting or forming tools, drilling and mining equipment, wire-drawing or metal-forming dies). The excellent wear resistance exhibited by the hardmetals is due to their unique combination of high hardness and moderate levels of fracture toughness [1,2]. The most common hardmetals, WC/cobalt (Co), are called straight grades. Co is widely used as the binder metal because of its good wetting behavior, favorable solubility for WC, and good mechanical properties [3]. The amount of Co can vary depending on the application area for the cemented carbide, but it is usually less than 15 vol% [4].

As seen, hardmetal processing is by a powder metallurgy/ceramics type route in which comminuted powder blends are granulated, shaped, debinded, and sintered. Sintering is usually carried out in a vacuum or a low pressure gas environment, but in recent years there has been increased the use of either hot isostatic pressing (HIP) following vacuum sintering, or a single pressure sintering cycle. By applying pressure at high temperature, these processes assist in the removal or shrinkage of pores in the microstructure. Usually, hardmetal is used in applications that require good thermal properties, such as metal cutting tool, although its thermal properties are scarcely studied. In this sense this paper presents the thermal characterization of the hardmetal alloy WC-15%wtCo by the photoacoustic techniques, which enables the determination of some interesting properties such as thermal conductivity, diffusivity, and capacity. This is of great importance because when hardmetal is used as cutting tools thermal damage takes place, due to the tool flank wear – abrasion and friction. Therefore, the thermal characterization may be used to predict the tool behavior during metalworking. In this paper the alloy WC-15%wtCo were processed through an alternative route, called high pressure-high temperature (HPHT), employing a pressure of 5GPa, temperature by 1350°C, during 2 minutes.
METHODOLOGY

Commercial powders of WC and Co, mean particle size of 5µm both, were purchased from Derivata Ind.Com. These powders were manually mixed to perform the stoichiometry WC-15%wtCo. The theoretical density of this hardmetal is 14.7g/cm³. Mixture was divided in samples of about 1g each. Samples was put into a graphite cylinder that acts as a heater (current flux during pressing) and then assembled into a calcite capsule – responsible for the gasket formation, that ensures a good high pressure distribution into the material. Sintering treatments were carried out using a special hot press (by Ryazantyashpressmash - O138B type – 2500tons) at a pressure of 5GPa, temperature by 1350°C, during 2 minutes. Aiming at to determine the sintered samples’ densities, it was used the standard water displacement (Archimedes) method, measuring the mass (balance by Scaltec SBC 31 – 0.0001g resolution). Vickers Hardness (Hv) was determined using a hardness device – PANTEC RBS, by applying a load (C) of 10kgf. This procedure was performed 10 times for 7 samples. To verify if dissolution of graphite from the mold has occurred, or further phase transition/formation, it was conducted an analysis via XRD (diffractometer Seifert URD 65, CuKα radiation). Scanning electron microscopy (Zeiss DSM 962) was used for the study of the micro-structural aspect of the hardmetal's samples. In this sense, samples were cold resin embedded, SiC paper ground and diamond paste polished.

The OPC technique uses the heat transmission configuration. In this case, the sample was mounted directly onto the front sound inlet of a commercial electret microphone and fixed with vacuum grease. The sound inlet was a circular hole of 3mm diameter, and the front microphone chamber adjacent to the metallized face of the diaphragm was a cylinder of 7mm diameter and 1mm long. The photoacoustic (PA) signal is generated by illuminating the samples (5mm diameter and 300µm thick) with a modulated light beam. It was used a 25 mW He-Ne laser (Unilaser mod.025) modulated with an optical chopper (Stanford Research Systems SR540) and uniformly focused on the sample. The signal from the microphone was sent, via a pre-amplifier, to a Lock-in amplifier (Stanford Research Systems SR830). The signal amplitude and phase was both recorded as a function of the modulation
frequency. The PA signal depends not only on the amount of heat generated in the sample, but also on how this heat diffuses through the sample. The quantity that measures the rate of heat diffusion in the sample is the thermal diffusivity \( \alpha \), defined by equation A:

\[
\alpha = \frac{k}{\rho c},
\]

(A)

where: \( k \) is the thermal conductivity, \( \rho \) is the density, and \( C \) is the heat capacity of the sample at a constant pressure.

The meaning of \( \alpha \) as a thermo-physical parameter to be monitored is due to the fact that the optical absorption coefficient is individualized for each material. Thus, it is dependent upon the effects of composition and micro-structural variables, as well as processing conditions. Here, the hardmetal samples were thermally thick and obeyed the OPC equation (B):

\[
S_{PA} = \frac{A}{f} e^{-b/\sqrt{f}},
\]

(B)

Where: \( S_{PA} \) is the PA signal, \( A \) is a constant that take into account the microphone characteristics and response time, room temperature, incident radiation intensity, and thermal properties of the material and the air, \( f \) is the modulation frequency of the incident light, and \( b = l(\pi/\alpha)^{1/2} \), where \( l \) is the sample thickness and \( b \) the linear adjusting parameter.

On the other side, to measure the heat capacity, it was adopted a continuous incident light method, where the laser beam reached the hanging sample in the top of a dewar. A thermocouple was in contact with the sample and the data was collected in a computer. It was provided two measurements: one with the increasing temperature of the samples and another with the cooling down to room temperature. The temperature gradient is compared with the time, following equation C:

\[
\rho c = \frac{(l/\theta t)(1-\theta \Delta T/l l_0)}{.}
\]

(C)
Here, \( l \) is the sample thickness, \( t \) is the light exposure time on the sample, \( I_0 \) is the incident radiation, \( \Delta T \) is the temperature variation on the sample, and \( \theta = 8\sigma T_o^3 \) is a constant, where \( T_o \) is the environment (room) temperature and \( \sigma \) is the Stefan-Boltzman constant.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction pattern for the HPHT sintered hardmetal. It shows that under 5GPa of pressure, the used temperature and sintering time promoted no new compound formation, such as \( \text{Co}_2\text{C} \), \( \text{Co}_3\text{C} \) and several other tungsten carbides. Other aspect of relevant importance is the absence of carbon peaks - indicating its maintenance as carbide.

![X-Ray diffraction pattern](image)

**Figure 1.** X-Ray diffraction pattern of the HPHT sintered hardmetal.

Table I shows a comparison of density and hardness for several WC hardmetals. When comparing the hardness of the WC-15%wtCo hardmetal of various cited references, for same WC mean particle size (5\( \mu \text{m} \)) of this present work, it is observed the same level of magnitude, despite of the small difference in the sintered densities – less than 2%. It is also noted that increase in hardness is observed for hardmetals with finer WC size, and with use of a grain growth inhibitor.
Table I. Nominal composition, sintered density, and Vickers hardness of several WC/Co hardmetals.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>REF.</th>
<th>DENSITY</th>
<th>HARDNESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC 1µm</td>
<td>[5]</td>
<td>94%</td>
<td>HV 30</td>
</tr>
<tr>
<td>WC 5µm</td>
<td>[5]</td>
<td>93%</td>
<td>HV 30</td>
</tr>
<tr>
<td>WC 10µm</td>
<td>[5]</td>
<td>92%</td>
<td>HV 30</td>
</tr>
<tr>
<td>WC – 15%wtCo</td>
<td>[6-8]</td>
<td>--</td>
<td>HV 30</td>
</tr>
<tr>
<td>WC – 15%wtCo</td>
<td>[9]</td>
<td>95%</td>
<td>HV 30</td>
</tr>
<tr>
<td>WC nanopowder</td>
<td>[10]</td>
<td>--</td>
<td>HV 30</td>
</tr>
<tr>
<td>WC 1.4µm</td>
<td>[11]</td>
<td>96%</td>
<td>HV 30</td>
</tr>
<tr>
<td>WC 1.4µm</td>
<td>[11]</td>
<td>98%</td>
<td>HV 30</td>
</tr>
<tr>
<td>WC 0.82µm</td>
<td>[11]</td>
<td>95%</td>
<td>HV 30</td>
</tr>
<tr>
<td>WC – 14%wtCo</td>
<td>[12]</td>
<td>--</td>
<td>HV 10</td>
</tr>
<tr>
<td>WC fine 1-2µm</td>
<td>[12]</td>
<td>--</td>
<td>HV 10</td>
</tr>
<tr>
<td>WC medium 3-4µm</td>
<td>[12]</td>
<td>--</td>
<td>HV 10</td>
</tr>
<tr>
<td>WC coarse 6-10µm</td>
<td>[12]</td>
<td>--</td>
<td>HV 10</td>
</tr>
<tr>
<td>WC very coarse</td>
<td>[12]</td>
<td>--</td>
<td>HV 10</td>
</tr>
<tr>
<td>WC – 15%wtCo</td>
<td>WC 5µm</td>
<td>This work</td>
<td>92.25%</td>
</tr>
<tr>
<td>WC 5µm</td>
<td>This work</td>
<td>92.25%</td>
<td>HV 10</td>
</tr>
</tbody>
</table>

One can observe from the figure 2 the evidence of a strong densification at the center of the figure (see circle), where complete sintering took place – small and spheroid porosity, necks formation. It is also seen the presence of a large pore (≈5µm – see arrow), and a beginning of grain growth process (left top side).

Figure 3 shows the thermal diffusivity for the hardmetal samples. The samples were thermally thick, that is, show \( f^1 \) phase behavior. The thermal diffusivity measured was \( \alpha = 0.35 \text{ cm}^2/\text{s} \).
The thermal capacity was $\rho c = 3.34 \text{ J/cm}^3\text{K}$, as demonstrated in figure 4, in which red points refers to measurements under heating, and the blue ones to cooling down to room temperature.
Figure 4. Thermal capacity of the WC-15%wtCo HPHT sintered hardmetal.

Thus, it is possible to find the thermal conductivity, here, $k = 116.9 \text{ W/mK}$. It was observed that this value is compatible with the values found by Miranzo et al [13], when using the laser flash method [14] reached values of $\alpha=0.32 cm^2/s$ and $k = 105.6 \text{ W/mK}$ for the WC-6%wtCo hardmetal.

As expected, the thermal conductivity for WC-15%wtCo is greater than for the thermal conductivity for hardmetal with less cobalt. Zhang Li and Sun Baoqi [15] measured a value of $\alpha=0.205 cm^2/s$ for the hardmetal WC-8%wt(Co-75%wtNi), thus indicating that the addition of Ni to the binder metal phase negatively influences the thermal properties, thus the type of binder matrix is also a matter of great interest for hardmetals.

It is also worth to comment that ceramic materials are thermal insulators, as a rule. Its mechanism of thermal conduction is said to be by phonons. Metals conducts heat by means of electrons, and are the best thermal conductors. In the point of view of a cutting tool, it is necessary to combine the hardness of a ceramic to the high thermal conduction of a metal. Cermets such as hardmetals possess both characteristics, what makes this class of material so promising in metalworking.
CONCLUSIONS

The objective was reached. The open photoacoustic cell method is very satisfactory and readily provides thermal diffusivity measurements for hardmetals. The values present results greater than the reference ones, due to a higher amount of Co, which gives the metal aspect to the sample. It is possible to continue the route to process hardmetal, called HPHT, which is a promising technique to sinter cermets bodies. As a first attempt, it was conceived a new technology where a mix of powders of WC and Co were pressed (high pressure) and sintered in very short times, and a binder/lubricant was avoided. The main conclusions are that good densification of 92.25% was achieved, compatible with the reference values; It was reached a satisfactory value of hardness, HV30=11.24GPa, in the same order of magnitude cited in literature for the WC-15%wtCo hardmetal; and It was achieved a thermal capacity of 3.34J/cm$^3$K, thermal diffusivity of 0.35cm$^2$/s, and thermal conductivity of 116.9W/mK. It reveals that the HPHT processed WC-15%wtCo hardmetal is able to work as a cutting tool, in the thermal point of view.

Acknowledgements:

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REFERENCES


