MICROSTRUCTURAL CHARACTERIZATION OF THE POWDER AND THE CEMENTED CARBIDE WC-8NI- 2MO$_2$C

Nádia Alves Nery Balbino
Edmilson Otoni Corrêa
Lívio de Carvalho Valeriano
Júlio Navarro Santos

Federal University of Itajuba - Unifei. 1303 BPS avenue, Pinheirinho, Zip Code: 37500-903., Itajubá-MG, Brasil. Institution and address
nadiaanery@gmail.com
ecotoni@unifei.edu.br
liviovaleriano@yahoo.com.br
Navarro@unifei.edu.br

Abstract. *The cemented carbides are a high performance tool material having high hot hardness at room temperature, low coefficient of thermal expansion, excellent corrosion resistance and wear resistance. Cemented carbides are conventionally obtained by compacting and liquid phase sintering process. The aim of this work was to characterize microstructurally 90%WC-8%Ni-2%Mo$_2$C cemented carbides obtained by powder metallurgy. The powders were mixed for 80 hours and sintered at 1460ºC. The microstructural characterization of powders was done by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The sintered sample was microstructurally characterized through the analysis in optical microscopy. The density was measured by the Archimedes' method. In the Microstructural analysis, were identified the hard phase (WC) and metal binder phase (Ni). However it was not indentified molybdenum carbide, indicating a good sintering league for contents of Mo$_2$C adopted. With optical microscopy was possible to verify the presence of porosity in the sintered samples, which implies that the samples are not fully dense. However, the relative density, 94,9%, it is in agreement with the literature.*
Keywords: *90% WC-8%Ni-2%Mo$_2$C, cemented carbides, XRD, SEM*

1. INTRODUCTION

Cemented carbide is used to designate a composite constituted of hard ceramic particles, normally WC, into a metallic matrix. Conventional tungsten carbide hard metal alloys consist of tungsten carbide and a ductile binder phase. A simple variation of these phases can easily change the cemented carbide properties and adjust as the desired application. The cemented carbide is produced by liquid phase sintering of powders of tungsten carbide and of the binder, in which, during the sintering the binder is diffused by the structure. (Chang and Chen, 2013; Santos, *et al*, 2010; Santos and Filgueira, 2012).

Cemented carbides are widely used in diverse engineering applications, such as metal cutting, molds, mineral and petroleum industries and, more recently, as catalyst electrodes in fuel cells and coatings for aerospace components, due to their excellent properties like the high hardness, high hot-hardness, wear/corrosion resistance, and low thermal expansion coefficient (Lin, *et al*., 2011; Santos, *et al*. 2010; Correa, *et al*., 2010;).

Cobalt currently dominates the market as a binder of cemented carbide because of its excellent mechanical properties and wear resistance. However, due to short supply, market price fluctuations, low corrosion resistance, toxicity of the cobalt and the increasing demand for special materials with defined and optimized properties, the possibility of complete or partial replacement of cobalt by other metals have been investigated (Guo, *et al*, 2008; Lin, *et al*, 2011; Guo, *et al*, 2009; FERNADES and Senos, 2011).

Since nickel belongs to the same group as cobalt, it is considered to be an ideal alternative binder. Furthermore, nickel has relatively low price and nearly unlimited resources. However, nickel dissolves smaller amounts of tungsten and carbon in the sintering stage than the cobalt during cooling. Thus, the Ni-WC alloy has the properties of hardness and strength lower than those observed in carbide WC-Co. So, to improve these properties is proposed in this paper, basically add the molybdenum carbide to nickel, which added to W and C, to produce the desired hardening effect by the solid solution. (Guo, *et al*, 2009; Santos, *et al*, 2010).

Therefore, this work presents the microstructural characterization of a hard metal developed with nickel as binder phase and strengthened by solid solution with molybdenum.

2. EXPERIMENTAL PROCEDURE

The composition of the samples is *90%WC+8%Ni+2%*Mo_2C, by weight, produced from the following powders:

- Tungsten carbide powder (WC), with an average particle size of 2.5 µm;
- Nickel oxide powder (NiO), with nickel content of approximately 50% and an average particle size of 2.5 µm;
- Carbon powder, with an average particle size of 2 µm to 3 µm;
- Molybdenum carbide powder (Mo_2C), with a purity of 99% and an average particle size of 2 µm to 3 µm.

After being weighed in the desired fractions, the powders were mixed for 80 hours under the atmosphere of heptane in a ball mill, coated by cemented carbide. After milling, due to the presence of nickel oxide in the mixtures, an oxygen reducing treatment in flowing dry hydrogen was carried out at 750 °C for 1 hour. After that, it was added in the mixture 1.75% of paraffin dissolved in heptane to improve its compaction.

The compression of the mixture was made in a steel matrix floating type. After that, the sintering cycle started. Firstly, the removal of the paraffin was carried out using a slow heating (10 ° C / min - 20 ° C / min) to about 500 °C in hydrogen flow. After 1 hour at 500 ° C, the temperature was raised to 750 ° C, which was maintained for 30 minutes for pre-sintering happen. With the samples in the desired geometry, the sintering finally was carried out in 1.460 ºC for 1hour in a vacuum oven (2 Pa to 6 Pa).

For the microstructural characterization, the samples were polished with sandpaper of SiC 320/600 to 1200, the polishing was carried out in cloth MD mol with OPU.

The Microstructural characterization of the powders was performed with the aid of scanning electron microscope (SEM) of the ZEISS brand and model EVO MA 15 and a X-ray diffractometer from PANalytical brand.

The sintered sample was microstructurally characterized through the analysis in optical microscopy of the ZEISS brand. The apparent density of the sintered sample was measured by Archimedes' method with the aid of the analytical balance Shimadzy brand and model AY220. The theoretical density, ρ_T, was calculated by the Eq. (1):

$$\rho_T = \frac{m_A + m_B + m_C}{\frac{m_A}{\rho_{TA}} + \frac{m_B}{\rho_{TB}} + \frac{m_C}{\rho_{TC}}} \quad (1)$$

Where:
m_A: Mass of WC;
m_B: Mass of Ni;
m_C: Mass of Mo_2C;
ρ_{TA}: Theoretical density of WC;
ρ_{TB}: Theoretical density of Ni;
ρ_{TC}: Theoretical density of Mo_2C.
The theoretical densities of WC, Ni and Mo are 15.7 g/cm^3 8.5 g/cm^3 and 9,18 g/cm^3, respectively. The relative density was defined as the percentage of the apparent density to their corresponding theoretical density (Savi, 2011; Martins, 2010; Torres, 2009).

3. RESULTS AND DISCUSSION

The Figure 1 shows the SEM images of *90%WC-8%Ni-2%*Mo_2C powders. It can be seen from the Fig. 1 a certain homogeneity in the particles, also can be noted a rounded morphology and agglomeration of the particles.

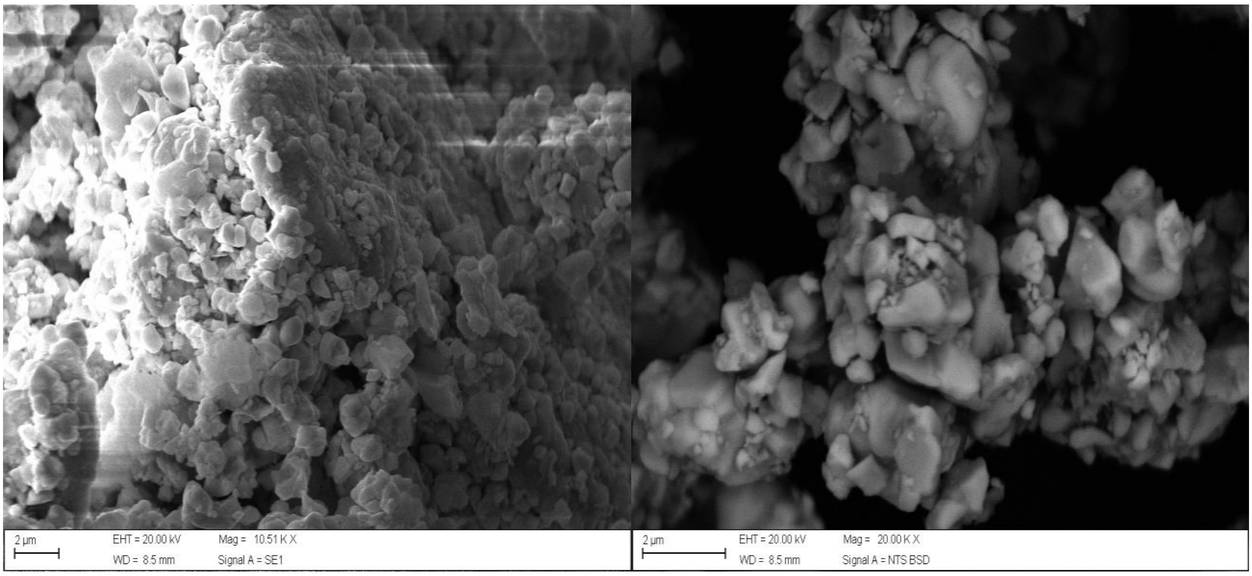

Figure 1. SEM Images of *90%WC-8%Ni-2%Mo_2C* powders

The Figure 2 shows the XRD of the *90%WC-8%Ni-2%Mo_2C* powders. Only Ni and WC peaks were detected and the intensity of the peaks of Ni is lower than that of WC peaks, which was expected, because these are predominant phases and WC powder is the major component. Due to the small addition amounts of Mo_2C (2%), the phase was not detected by XRD. These results are in agreement with the studies of Kim, et al.,(2006), Ren, et al., (2013) and Kai, et al., (2013). Moreover, there was no carbon phase detected in the samples, which would be helpful to improve the hardness and strength of the samples for the absence of low strength carbon–carbon interface (Rong, et al., 2012).

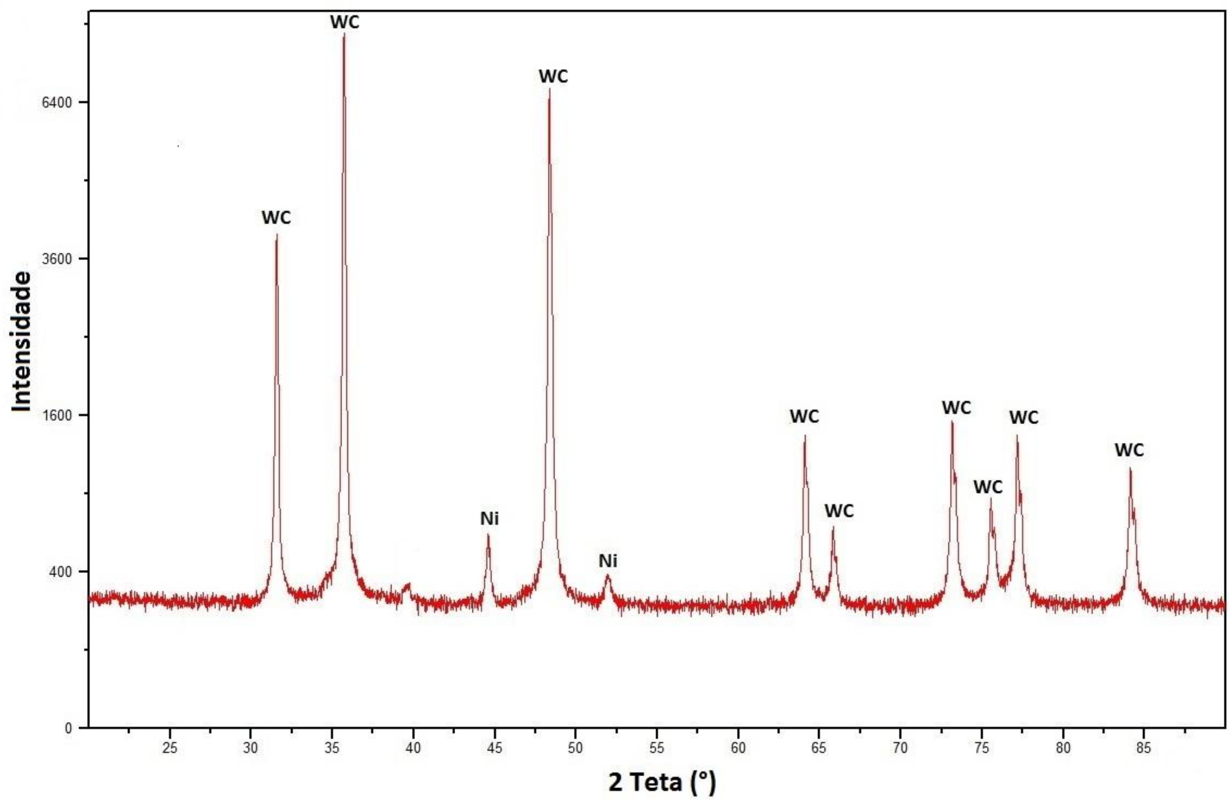

Figure 2. XRD of *90%WC-8%Ni-2%Mo_2C* powders

The Figure 3 shows the polished surface of the *90%WC-8%Ni-2%Mo_2C* cemented carbide, before etching. Microstructures quite similar to that one are also observed in cemented carbides with cobalt as the binder alloy. It was not detected the presence of undissolved *Mo_2C* particles as well as the presence of small free graphite nodules in the microstructure. The absence of these phases in the microstructure indicates that there was a satisfactory sinterability of the cemented carbide for the Mo and C contents and sintering parameters adopted.

It can be seen from the Fig. 3 the presence of islands of binder metal in the microstructure showing an accumulation of the binder phase in some regions. This indicates a lower uniformity of the binder distribution in the microstructure in comparison with that observed in the corresponding cobalt cemented carbide. It may be attributed to the lower wetting and WC dissolution rate of the Ni binder when compared with Co binder; which leads to a deficient spreading of the Ni liquid phase between the grains as it dissolves WC. In addition, the lower chemical homogeneity in the prepared compacts, as a result of insufficient mixing conditions also may contribute significantly for this uneven distribution of the binder metal. However, was expected a better wet ability of the Ni, due de adition of Mo. The wettability of WC by the liquid phase is defined by the contact angle (θ). Densification requires a low contact angle to ensure that grains are pulled together. The good wetting of WC by Co is due to the contact angle of 0°, while the poor wetting of WC by Ni is due to a large contact angle. The contact angle is altered by factors that change the solubility or surface chemistry. The addition of Mo has been appointed as a way to reduces the contact angle and hence, improve the solubility (Correa, et al., 2010; Genga, et al., 2013).

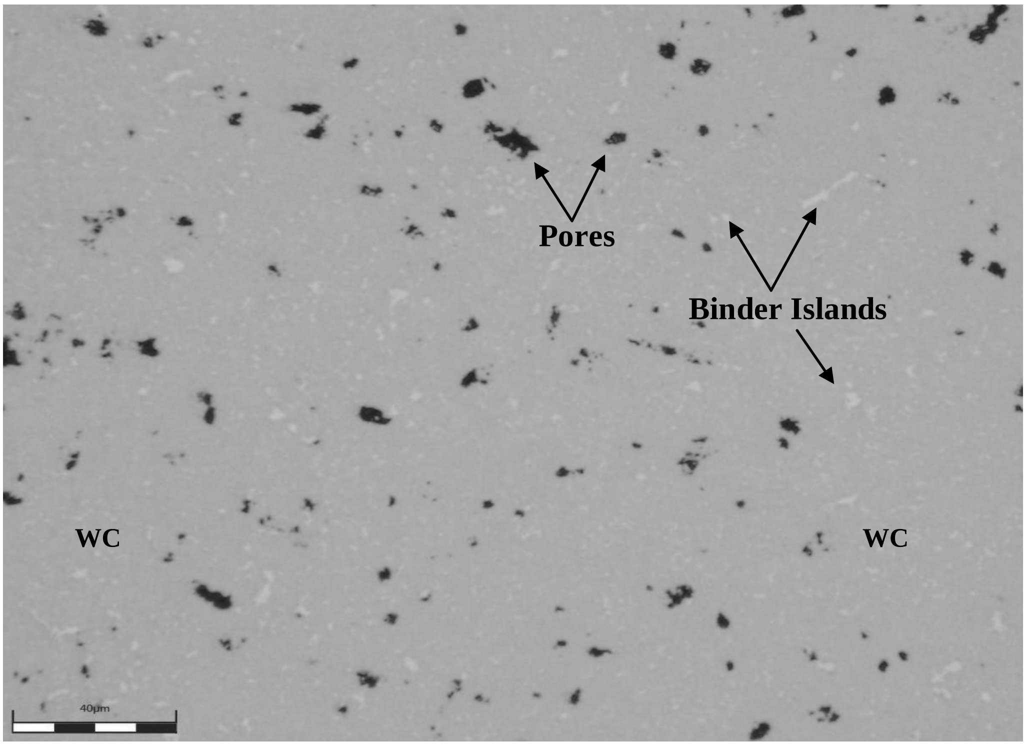

Figure 3. The optical micrograph of the *90%WC-8%Ni-2%Mo_2C* cemented carbide, before etching.

Also in Fig. 3, it can be seen that there were uniformly distributed pores in the samples. These pores can be explained by a number of factors. Firstly, the adopted binder metal, Ni, has a relatively low wet ability during sintering in comparison with Co, which would be harmful for the spread of the binder phase during the sintering. Secondly, although Ni was mixed and milled, particle deformation and agglomeration still happened, which could promoted the formation of pores during the sintering. Thirdly, since the cemented carbides were fabricated by powder metallurgy, liquid phase was formed during heating and the bond of particles depends on the formation of this liquid. Thus, the formation and flow of the liquid phase are key factors which influence the microstructure of the cemented carbides. However, if the formed liquid was not sufficient and the flow of liquid was not enough during the sintering, pores would inevitably be formed (Rong, et al., 2011).

This porosity means that samples are not fully dense, which is consistent with the measurement of the relative density of the sample. The Table 1 shows the apparent density, theoretical density and relative density of the sample. As expected the relative density, 94,9%, of the sample is lower than those of WC–10Co cemented carbides, normally around 99% or more, so the addition of molybdenum does not promote the densification desired. However it is in agreement with the literature and this value is slightly higher than those of the WC-10%Ni (91,90%) and the WC-6%Co-1%Mo (93,60%) cemented carbides reported in “Rong, et al., (2011)" and “Savi, et al., (2010)” respectively.

Table 1. Apparent density, theoretical density and relative density of the cemented carbide 90%WC-8%Ni-2%Mo_2C

Apparent density (g/cm^3)	Theoretical density (g/cm^3)	Relative density (%)
13,7721	14,51	94,9

4. CONCLUSIONS

During the sintering there was no formation of harmful phases to the properties of the cemented carbide.

Pores and islands of binder metal were identified in the microstructure. These indicate a lower density and a lower uniformity of the binder distribution in the microstructure in comparison with that observed in the corresponding cobalt cemented carbide.

The relative density of the obtained WC–8%Ni-2%Mo_2C cemented carbides was approximately 94,9%, which was somewhat lower than that of WC–Co cemented carbides with the same binder fraction in the literature, due to the existence of pores. However, it is slightly higher than those of the WC-10% Ni cemented carbides reported in literature, which shows that with the alteration of the chemical composition via the addition of Mo_2C to WC–Ni cemented carbide, the wetting of WC by Ni was improved.

5. ACKNOWLEDGEMENTS

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