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Contents:

(continued on inside back cover)

Praise Worthy Prize

(continued from inside back cover)

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Results Produced by Adding Nb, Mo, Cr and Ti in Microstructure on the WC-6Co

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Abstract – *The hard metals constitute a group of materials known as composite sintered hard phases that associate (carbides) with a metallic phase being widely used in applications where it is desired hardness and wear resistance coupled with high toughness. In this paper we present the results of adding 1% by weight of the elements Nb, Ti, Cr and Mo in the microstructure of cemented carbide from a commercial composite WC-6% Co. To this composite was added 1.5% (by weight) of zinc stearate as a lubricant and sintered at a temperature of 1450 °C in an atmosphere of argon. Aiming to analyze the efficiency of the product were characterized by micro structural testing of green density, shrinkage, density sintering, microstructure and microhardness.* ***Copyright © 2012 Praise Worthy Prize S.r.l. - All rights reserved.***

***Keywords**: Balancing Mass, Powder Metallurgy, Carbide, Sintering*

I. Introduction

Produced by powder metallurgy, the carbide is a composite material that has found many applications in engineering fields, especially in the manufacture of cutting tools, forming dies, drills and mining wear resistant components. The high hot hardness and temperature, good resistance to corrosion, abrasion, coupled with low coefficient of thermal expansion are the main reasons for the increasing use of carbide [1], [2]. The composite WC-Co is a material consisting of hard particles enclosed in a metal binder produced by powder metallurgy by sintering technique [6]. The particles of high hardness are formed of carbides of transition metals of groups IV and VI of the periodic table and used primarily in applications of technological importance. Among these materials the most important is the tungsten carbide (WC) [4]. The metals most commonly used linkers for the production of hard metal are of iron group, among which stands out cobalt, due to wettability of the tungsten carbide by the same liquid phase at sintering temperature [3]. Cobalt is an expensive metal, sparse and when used as a powder or vapor becomes detrimental to human health. So there is a concern to restrict its use to purposes in which their presence is extremely essential [2]. This paper aims to present the main effects of adding 1% Nb, Ti, Cr and Mo on microstructure and mechanical properties of cemented carbide WC-6% Co processed via sintering [5].

II. Materials and Methods

For this study, we started with the WC-powder 6Co, 99% composition given in Table I, supplied by Alfa Aesar, -325 Mesch, which served as a raw material base.

TABLE I
CHEMICAL COMPOSITION OF COMPOSITE POWDER WC-6CO

Element	WC	Co
% By weight	94	6

The desired composites were obtained by mixing conventional WC-6CO with 1 wt% of Nb, Mo, Cr and Ti

To this composite was added zinc stearate (1.5 wt%) as a lubricant. The components of each alloy were mixed for the time of 15 min. in a blender type "Y" at 24 rpm, as shown in Fig. 1.

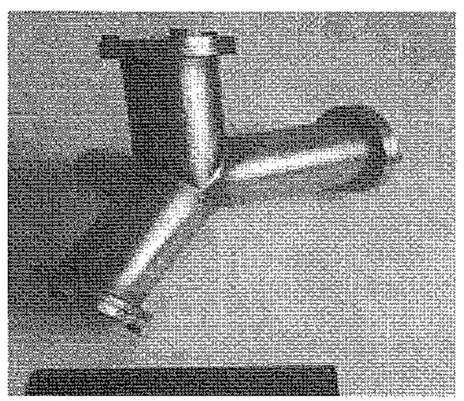

Fig. 1. Details mixer type Y used in this step of the process

The samples were compressed in size, geometry and composition of the required material, having sufficient integrity to be handled. It was found by curve compressibility of the material, which from 400 MPa to a green density pressure became constant. It was determined the compaction pressure, obtained through the compressibility curve of the alloy, drawn based on ASTM B331. We chose to use a 200 MPa pressure and therefore the average green density around 8.31 g/cm3 for samples with the addition of elemental powders of Nb, Mo, Cr and Ti.

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III. Results and Discussion

At this stage of the study, and based on the objectives, will be presented the following results: a micrograph of the powders, the green density, sintered density, shrinkage, hardness and microstructure of the composites studied for sintering cycle. We used scanning electron microscopy to submit microscopy of the powders used in this work. Fig. 2 shows the dust particles of WC-6Co with magnification of 3000x and Fig. 3 shows the dust particles of WC-6Co with magnification of 5000x. These two figures show that particle sizes ranging between 1 and 5 μm and are bonded with sizes 10-20 μm.

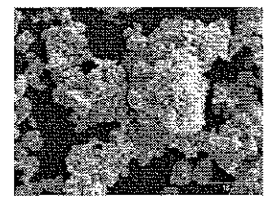

Fig. 2. Powder particles WC-6Co (3000x)

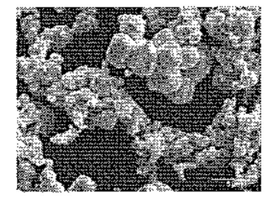

Fig. 3. Powder particles WC-6Co (5000x)

The Fig. 4 shows the powder particles of niobium (Nb) with magnification of 1500x and Fig. 5 shows the powder particles of molybdenum (Mo) with magnification of 2000x.

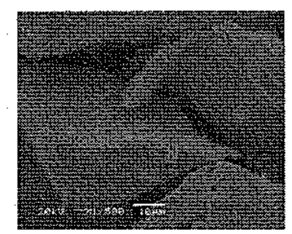

Fig. 4. Powder particles Nb (1500x)

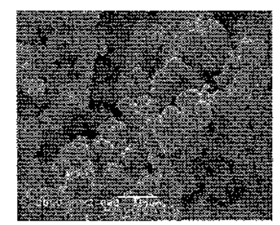

Fig. 5. Powder particles Mo (2000x)

The particles of niobium is very coarse, with size greater than 50 μm, unlike molybdenum particles, which have a size less than 5 μm, and the same are agglomerated into large particles. The Fig. 6 shows particle size of powder of chromium between 1 and 2 μm, agglomerated particles 10 and 20 μm, with magnification of 1000x. The Fig. 7 shows particle size of titanium powder between 2 and 5 μm, agglomerated particles of 5 and 10 μm , with magnification of 1000x.

The Fig. 8 shows the powder particles of WC-6CO with 1% Nb, with magnification of 5000x, with size of 1 to 5 μm and Fig. 9 shows the powder particles of WC-6CO with 1% Mo, with magnification 5000x and size of 5 μm. Both images show that the particle sizes range from 1 to 5 μm and are bonded with size 10-20 μm.

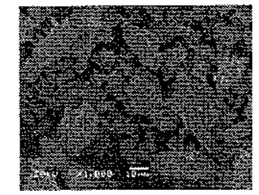

Fig. 6. Powder particles Cr (1000x)

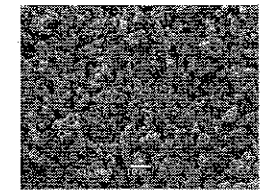

Fig. 7. Powder particles Ti (1000x)

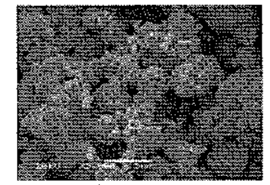

Fig. 8. Particles of the mixture WC-6Co-Nb (5000x)

Fig. 9. Particles of the mixture WC-6Co-Mo (5000x)

The Fig. 10 shows the dust particles of WC-6CO with 1% chromium, with magnification of 5000x and Fig. 11 shows the dust particles of WC-6CO with 1% titanium, with a magnification of 5000x. These two illustrations show that the particle sizes range from 1 to 5 μm and are bonded with size 10-20 μm, not being possible to distinguish the particles of the composite carbide and particles of elemental powders.

Fig. 10. Particles of the mixture WC-6Co-Cr (5000x)

Fig. 11. Particles of the mixture WC-6Co-Ti (5000x)

The Table II shows the values obtained from the green density for a compaction pressure of 200 MPa. In this stage was reached pieces with the green density, used in industrial manufacturing process.

TABLE II
DENSITY VALUES FOR THE GREEN CARBIDE COMPOSITES

Sample	Volume part to green (cm^3)	Mass (g)	Density of green (g/cm)
WC-6Co	1,21	9,57	7,91
WC-6Co-Nb	1,23	10,04	8,16
WC-6Co-Mo	1,14	9,43	8,27
WC-6Co-Cr	1,17	9,96	8,51
WC-6Co-Ti	1,18	9,88	8,37

The sintering was performed in argon atmosphere due to the fact that an inert gas. From a scientific viewpoint, the vacuum is considered the best atmosphere because they enable the sintering of metals whose oxides are hardly reduced, such as aluminum and niobium, among others. However, vacuum sintering is very costly due to the low production rate and high cost of equipment.

After sintering were measured densities of the samples, using the Archimedes principle as standard MPIF-95. The Fig. 12 shows two samples of WC-6Co-Cr, and the compressed left and right sintered at 1450 °C. Note the large shrinkage and low distortion of the sample with respect to its initial geometry.

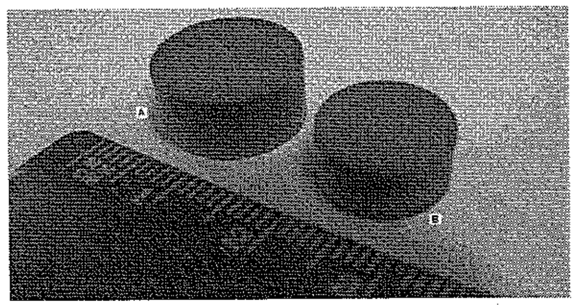

Fig. 12. (A) sample to green
(B) sample WC-6Co-Cr sintered at 1450°C.

The Fig. 13 shows the relative density of the composites WC-6Co, WC-6Co-Nb, WC-6Co-Mo, WC-6Co-Cr, WC-6Co-Ti amples sintered at 1450°C.

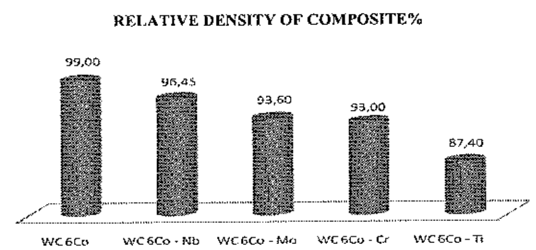

Fig. 13. Relative density for composites sintered at 1450°C

The Table III shows the results of hardness, depending on the sintering temperature, 1450 °C, for composite carbide proposed.

TABLE III
DENSITY AND HARDNESS IN g/cm³ OF THE SINTERED SAMPLES

Composite	Sintered density, (g/cm³)	Microhardness, (HV, 500g)
WC-6Co	14,75	1685 ± 20
WC-6Co-Nb	14,30	1603 ± 105
WC-6Co-Mo	13,90	1226 ± 148
WC-6Co-Cr	13,78	1602 ± 180
WC-6Co-Ti	12,93	1504 ± 104

The Table III shows that the composite WC-6Co has the highest density and the highest hardness with less variation. This last feature matches your type of processing in manufacturing and obtaining carbide. The hard metal of WC-6Co-Nb showed the second highest density and hardness, indicating a better wettability of niobium compared to commercial composite WC-6Co during sintering with the indicated temperature.

The composite WC-6Co-Mo showed the third highest density of the sintered and worst microhardness of composites studied, this can mean a good wettability with respect to molybdenum tungsten, causing the grain growth in the composite, but the sintering temperature is relatively correct. The composite commercial chromium showed the third hardness in relation to carbide compounds studied with the second worst density. The carbide WC-6Co-Ti had the second lowest hardness and low density, the latter being directly influenced the density of titanium. The Table IV shows a relationship between sintering temperature, density and volumetric shrinkage for samples WC-6Co.

TABLE IV
SHRINKAGE AND DENSITY OF SITERED IN g/cm³

Composite	Sintered density, (g/cm³)	Shrinkage, (%)
WC-6Co	14,75	45,90
WC-6Co-Nb	14,30	43,08
WC-6Co-Mo	13,90	40,60
WC-6Co-Cr	13,78	38,46
WC-6Co-Ti	12,93	34,74

The Table IV lists the density of sintered composites with shrinkage, indicating the possibility of a greater need for deeper study of sintering temperature of the compositions. The shrinkage may indicate that the sintering temperature used was below the necessary temperature for satisfactory contraction, as indicated in literature range from 40 to 50%. Assays of potentiodynamic polarization curves were performed in aerated 0.5 M in H_2SO_4, using the sweep rate of 30 mV / min to make possible an overview of the electrochemical behavior of sintered carbides compared curves as a function of content of binders.

The cathodic curves for WC-6Co-Mo and WC-6Co-Cr exhibit similar behavior. A sample of WC-6Co-Ti showed a large reduction of anodic current when compared with the other samples. The potentiodynamic curve of the sample apparently no titanium oxide film had its destroyed, ie, the material is undergoing slower corrosion, this means it is more resistant. The Fig. 14 shows potentiodynamic polarization curves with different additions of 1% of elemental metal powders. It is noted that the potential of the samples refers to the saturated calomel electrode (SCE).

The sample WC-6Co-Cr may have undergone intergranular corrosion due to chromium sensitization upon sintering. The titanium and chrome are the most reactive what causes the low shrinkage.

From the graphs were obtained the values of corrosion potential (E_{corr}) and corrosion current density (J_{corr}) by Tafel extrapolation method, as shown in Table V.

From these data we conclude that there is a difference in the values of E_{corr}.

The more positive value (nobler) is observed in the sample WC-6CO-Ti, and the lower density of corrosion current J_{corr}. A sample of WC-6Co showed more negative value of E_{corr} and greater J_{corr}.

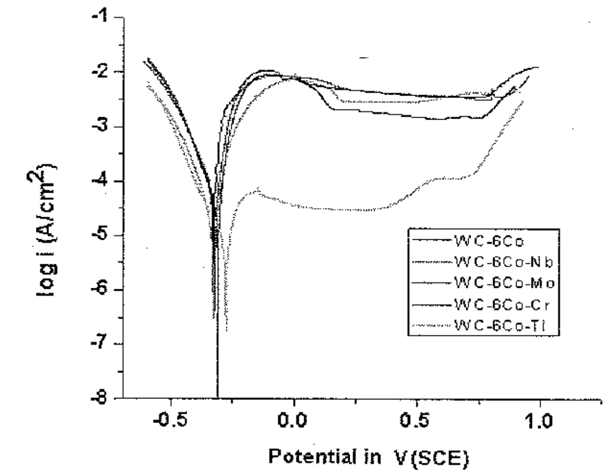

Fig. 14. Potentiodynamic polarization curve

TABLE V
AMOUNTS OF THE CORROSION POTENTIAL AND CURRENT DENSITY

Composite	E_{corr}(V)	J_{corr}(A/cm²)
WC-6Co	-0,33	$1{,}32x10^{-4}$
WC-6Co-Nb	-0,32	$1{,}56x10^{-5}$
WC-6Co-Mo	-0,32	$5{,}67x10^{-5}$
WC-6Co-Cr	-0,31	$2{,}96x10^{-5}$
WC-6Co-Ti	-0,28	$8{,}31x10^{-6}$

IV. Conclusion

This study consisted of the determination of the production and properties of green density, relative density, hardness, volumetric shrinkage of a composite material of WC 6% Co added with 1% of Nb, Mo, Cr and Ti. The parameters of the experiment show that the sintering curve corresponded satisfactorily results due to shrinkage and sintered density.

The compressibility curve determined the correct pressure for compaction around 200 MPa, which does not require much of the tooling and parts are obtained with the green resistance in handling.

The percentage of metal added in composite trading carbide WC-6CO is down to the metal identification in the MEV micrograph of the post. The green density behaved according to the results found in literature, ranging from 7.5 to 8.5 g / cm ³.

The relative density shows that the percentage of higher densification occurred in the composite WC-6Co, followed by WC-6Co-Nb, WC-6Co-Mo, WC-6Co-Cr e WC-6Co-Ti, presenting this trend due wettability of the metal powder matrix with tungsten carbide. The shrinkage may indicate that the sintering temperature used was below the necessary temperature for satisfactory contraction, according to literature within the range of 40 to 50%. This information offers a more detailed study of the last two composites in relation to temperature and time effective sintering.

The microhardness of the compositions showed similar to the literature validating again the mass balancing process for obtaining the compositions. In microstructures presented was not possible to identify the alloying elements that have been added due to its solubility in WC6Co.

In the dynamic test potentiometric polarization in sulfuric acid, the composition WC-6Co-Ti showed a value more positive than E_{corr} and lower corrosion current density (J_{corr}). For the sample of WC-6Co, showed more negative value of E_{corr} and current density greater J_{corr}.

The greatest corrosion resistance of the sample of WC-6Co-Ti relative to the other samples can be assigned due to presence of the ligand titanium.

A better understanding of the behavior of some materials, for different processing routes, facilitates the synthesis of new materials.

The proper characterization of the properties of the compositions is important in the manufacture of tooling for obtaining rings of mechanical seals, and the design and fabrication been successfully executed.

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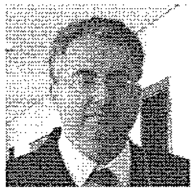

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