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SYNTHESIS OF WC-12wt%Co NANOCOMPOSITES BY HIGH ENERGY BALL MILLING AND THEIR MORPHOLOGICAL CHARACTERIZATION

Waleska Campos Guaglianoni [1]
Antonio Takimi [1]
Juliane Vicenzi [1]
Carlos Pérez Bergmann [1]

Abstract

In this work micrometric particles of WC and Co were processed by high energy ball milling in a planetary ball mill. We evaluated the phase formation and changes in microstructure of WC-12wt%Co as a result of the following milling parameters: ball-to-powder weight ratio, milling time and speed. The material was characterized by X-ray diffraction (crystalline phases and crystallite size), particle size analysis (average grain diameter), the BET method (surface area), and scanning electron microscopy (powder morphology). The average particle size (D50) and crystallite size were respectively 1.63μm and 13.8nm, for a surface area of 4.709 m^2/g, using a ball-to-powder weight ratio of 1:20, a milling time of 5h and a milling speed of 500 rpm.
Keywords: High energy ball milling; WC-12wt%Co; Nanocomposites; Microstructure.

SÍNTESE DE NANOCOMPÓSITOS DE WC-12wt%Co POR MOAGEM DE ALTA ENERGIA E SUA CARACTERIZAÇÃO MORFOLÓGICA

Resumo

Neste trabalho, partículas micrométricas de WC e Co foram processadas por moagem de alta energia em um moinho planetário. Avaliamos a formação de fases e mudanças na microestrutura do WC-12wt%Co como resultado dos seguintes parâmetros de moagem: razão mássica bolas/pó, tempo e velocidade de moagem. O material foi caracterizado por difração de Raios-X (fases cristalinas e tamanho de cristalito), análise granulométrica (diâmetro médio), método BET (área superficial) e microscopia eletrônica de varredura (morfologia do pó). O tamanho médio de partícula e o tamanho de cristalito foram 1.63μm e 13.8nm, respectivamente, para uma área superficial de 4.709m^2/g, usando razão mássica bolas/pó de 1:20, tempo de moagem de 5h e velocidade de moagem de 500rpm.
Palavras-chave: Moagem de alta energia; WC-12wt%Co; Nanocompósitos; Microestrutura.

1 INTRODUCTION

Because of their high hardness, resistance to abrasion and erosion, tungsten carbide cobalt composites (WC-Co) are widely used as coatings of metal cutting tools and parts that are subject to wear. The technological properties of these composites depend on their microstructure, especially the size and degree of dispersion of the high hardness phase (WC). The need to improve such properties as wear resistance and strength has advanced the development of nanostructured materials. Many studies have been conducted about WC-Co nanocomposites obtained by high energy ball milling [1-7].

High energy ball milling is a technique to manufacture nanostructured materials, in which conventional materials are transformed into nanostructured powders through plastic deformation. The characteristics of the processed materials are influenced by such process variables as type of mill, milling energy/speed, milling time and ball-to-powder weight ratio (BPR) [8]. As such, the objective of this work is to evaluate the phase formation and changes in the microstructure of WC-12wt%Co as a result of the following milling parameters: ball-to-powder weight ratio, milling time and milling speed.

2 MATERIAL AND METHODS

The high energy ball milling was carried out in a Pulverisette 6 planetary mill manufactured by Fritsch. A tempered steel grinding bowl and AISI 52100 steel balls with 10 mm diameter were used. Ethanol was the employed

[1] *Federal University of Rio Grande do Sul - UFRGS, Porto Alegre, RS, Brazil. E-mail: waleskaguaglianoni@yahoo.com.br*

milling medium, which according to [5] is better for WC grain size reduction when compared with distilled water and acetone. A commercial carbide powder (WC-727) was used as the raw powder material. Table 1 shows the chemical composition of the starting powder, produced by Praxair Surface Technologies.

The milling parameters (Table 2) were determined based on the studies by Mahmoodan et al. [2], Enayati et al. [3] and Zhang et al. [5]. Two ball-to-powder ratios – BPR (1:5 and 1:20), three milling times (1, 5 and 10h) and two milling speeds (250 and 500 rpm) were used.

Powders were characterized by X-ray diffraction (XRD), particle size analysis (D50), surface area (SA), and scanning electron microscopy (SEM). The crystalline phases and crystallite sizes were determined using X-ray powder diffraction (Phillips diffractometer, X'Pert MPD model). The diffractometer has a graphite monochromator, Cu-Kα radiation (λ= 1,5406), and a fixed anode operated at 40 kV and 40 mA. Table 3 shows the selected parameters for the phase analysis and determination of the crystallite size.

The crystallite size was calculated with the WinFit software (version 1.2). The experimental peaks were fitted using asymmetric Pearson VII functions. These can be corrected for instrumental broadening and decomposed into two components: Gaussian and Lorentzian functions. The Gaussian contribution characterizes the effect on the crystallites size and the Lorentzian contribution characterizes the effect of the microstrain on the breadth of diffraction peaks. Therefore, determining Pearson VII specific functions for each diffraction maximum, enables us to calculate the average size of crystallites [9].

The particle median size (D50) of the composite particle was measured with a CILAS 1180 particle size analyzer (CILAS). The surface area was determined using an AutosorbQuantachrome (model NOVA 1000) apparatus. The microstructure of the ball milled WC-12wt%Co powders were observed with a scanning electron microscope (SEM, JEOL-JSM 6060).

Table 1. Chemical composition of WC-12wt%Co commercial powder (Praxair Surface Technologies)

Element	W	Co	C
Composition (%)	82.6	12	5.4

Table 2. Parameters of high energy milling of WC-12wt%Co

Sample number	Ball to powder weight ratio (BPR)	Milling time (h)	Milling speed (rpm)
1	1:5	1	250
2			500
3		5	250
4			500
5		10	250
6			500
7	1:20	1	250
8			500
9		5	250
10			500
11		10	250
12			500

Table 3. XRD analysis parameters

Parameter	Phase analysis	Crystallite size
$\Delta 2\theta$	25° - 80°	25° - 43°
Step	0.05	0.02
Time per step (s)	1	4
Cracks	¼	¼

3 RESULTS AND DISCUSSION

Figure 1 shows the XRD diffractograms of the raw material and the ball-milled powders. The presence of the WC phase can be identified (JCPDS file 00-051-0939). No traces of Co were observed on XRD patterns as the X-ray scattering intensity of Co is much lower than that for WC. Other phases were not identified. After ball milling, the diffraction peaks broaden and decrease, as a result of reduction in crystallite size and increase of internal strain. The broadening of the diffraction peaks increased on continued milling. A higher peak broadening can be observed for BPR of 1:20 and milling speed of 500rpm.

Table 4 presents the values for crystallite size, D50 and SA of the WC-12wt%Co particles after high energy milling as a function of milling time, milling rotation speeds, and ball-to-powder weight ratio.

The lowest crystallite size values were obtained with a BPR of 1:20, milling speed of 500 rpm and milling time of 5 h (sample 10) and 10 h (sample 12). A reduction in

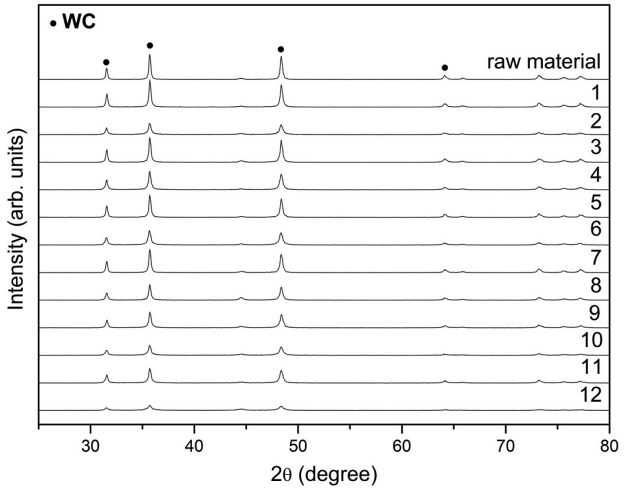

Figure 1. X-ray patterns of WC-12wt%Co powders prepared by ball milling under different condition designed in Table 2.

Table 4. Crystallite size, D50, and surface area (SA) response of WC-12wt%Co particles as a function of the milling parameters

Sample number	Parameters of milling			Results		
	Ball-to-powder weight ratio – BPR	Milling time (h)	Milling speed (rpm)	Crystallite size (nm)	D50 (μm)	SA (m^2/g)
1	1:5	1	250	53.6	6.93	5.100
2			500	42.2	2.33	4.837
3		5	250	41.7	2.03	5.546
4			500	24.1	2.43	5.950
5		10	250	34.2	2.99	6.020
6			500	16.9	2.53	8.176
7	1:20	1	250	48.3	2.03	5.020
8			500	27.8	2.61	5.150
9		5	250	23.5	1.37	5.293
10			500	13.8	1.63	4.709
11		10	250	25.3	2.65	5.186
12			500	13.7	2.38	5.880

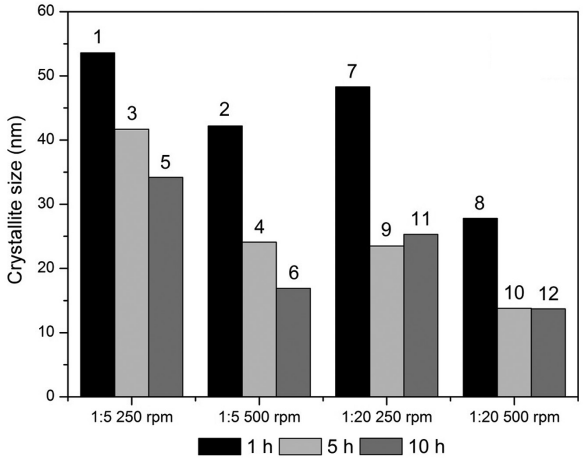

Figure 2. Crystallite size of WC-12wt%Co particles as a function of the milling parameters (1-12 see Table 2).

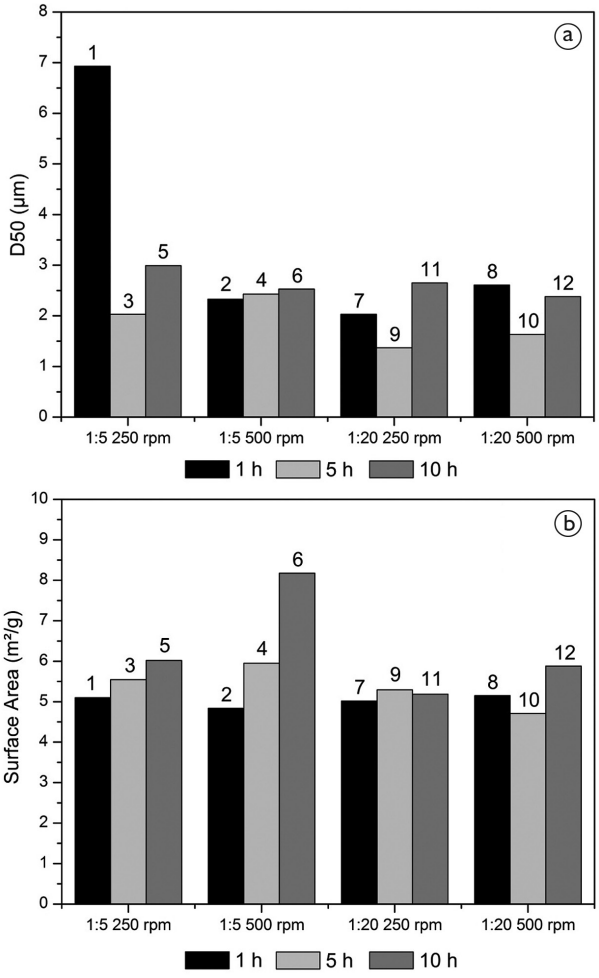

Figure 3. (a) D50 and (b) surface area of WC-12wt%Co particles as a function of the milling parameters (1-12 see Table 2).

crystallite size could be observed as time, rotation speeds and BPR increased (Figure 2). One can also see that shorter times are needed to obtain similar crystallite size values when a BPR of 1:20 and milling speed of 500rpm are used. According to Suryanarayana [10], this behavior is explained by the higher energy and frequency of impacts of the milling balls as a result of their higher speed.

Figure 3a shows the D50 variation as a function of the milling parameters. The particle median size of the raw material is 31.44 μm. A significant reduction of the particle size after the milling can therefore be observed. Samples with larger BPRs (1:20) presented smaller particle sizes. D50 increases for the milling time of 10 h, probably due to overlap and the cold welding of small fragments [10]. The surface areas of the ball milled powders are shown in Figure 3b. All samples had a small change in surface area in relation to the material without milling (with SA=5,751m^2/g).

The SEM images in Figure 4 reveal that the WC-12wt%Co particles lost their starting morphology and had their size significantly reduced. Commercial material (Figure 4a and 4b) particles were nearly spherical, typical of production process used (agglomeration and sintering). After ball milling the particles were fragmented into fine powder. In Figure 4c the particle agglomeration can be seen.

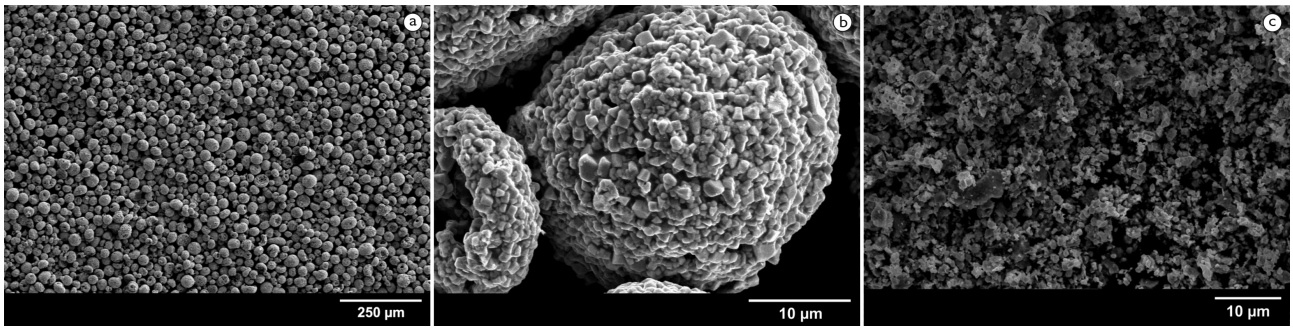

Figure 4. SEM images of WC-12wt%Co powder before (a) and (b), and after 5 h milling (c) (sample 10).

4 CONCLUSION

This study has investigated the phase formation and changes in microstructure of WC-12wt%Co as a function of the milling parameters like milling time, milling speed and ball-to-powder weight ratio. According to the results presented, it can be concluded that:

- High energy ball milling was effective to refine the microstructure of WC-12wt%Co powders to a nanometer scale size.
- Significant lower crystallite size values were obtained as time, rotation speed and BPR increased.
- The microstructural changes observed in the WC-12wt%Co powders were in accordance with the surface area and D50 variation.
- The best results were achieved using 5h of milling, a ball-to-powder weight ratio of 1:20 and a milling speed of 500 rpm. The crystallite size of the WC-12wt%Co powder diminished to 14 nm, with a particle size of 1.63 μm and a surface area of 4.709 m^2/g.

Acknowledgements

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REFERENCES

1 Hewitt SA, Kibble KA. Effects of ball milling time on the synthesis and consolidation of nanostructured WC–Co composites. International Journal of Refractory Metals & Hard Materials. 2009;27(6):937-948. http://dx.doi.org/10.1016/j.ijrmhm.2009.05.006.

2 Mahmoodan M, Aliakbarzadeh H, Gholamipour R. Microstructural and mechanical characterization of high energy ball milled and sintered WC–10 wt%Co–xTaCnano powders. International Journal of Refractory Metals & Hard Materials. 2009;27(4):801-805. http://dx.doi.org/10.1016/j.ijrmhm.2009.02.001.

3 Enayati MH, Aryanpour GR, Ebnonnasir A. Production of nanostructured WC–Co powder by ball milling. International Journal of Refractory Metals & Hard Materials. 2009;27(1):159-163. http://dx.doi.org/10.1016/j.ijrmhm.2008.06.005.

4 El-Eskandaranya MS, Mahdaya AA, Ahmedb HA, Amera AH. Synthesis and characterizations of ball-milled nanocrystalline WC and nanocomposite WC–Co powders and subsequent consolidations. Journal of Alloys and Compounds. 2000;312(1-2):315-325. http://dx.doi.org/10.1016/S0925-8388(00)01155-5.

5 Zhang FL, Zhu M, Wang CY. Parameters optimization in the planetary ball milling of nanostructured tungsten carbide/cobalt powder. International Journal of Refractory Metals & Hard Materials. 2008;26(4):329-333. http://dx.doi.org/10.1016/j.ijrmhm.2007.08.005.

6 Raihanuzzaman RM, Jeong TS, Ghomashchi R, Xie Z, Hong SJ. Characterization of short-duration high-energy ball milled WC–Co powders and subsequent consolidations. Journal of Alloys and Compounds. 2014;615:564-568. http://dx.doi.org/10.1016/j.jallcom.2013.12.104.

7 Mandel K, Krüger L, Schimpf C. Particle properties of submicron-sized WC–12Co processed by planetary ball milling. International Journal of Refractory Metals & Hard Materials. 2014;42:200-204. http://dx.doi.org/10.1016/j.ijrmhm.2013.09.006.

8 Suryanarayana C. Mechanical alloying and milling. Boca Raton: CRC Press; 2004. 488 p.

9 Onisei S, Badilita V, Stoiciu F, Velea T, Predica V, Lupu C, et al. Mechanochemical Activation of Copper Concentrate and the Effect on Oxidation of Metal Sulphides. Revista de Chimie. 2012;63:591-597.

10 Suryanarayana C. Mechanical Alloying and Milling. Progress in Materials Science. 2001;46(1-2):1-184. http://dx.doi.org/10.1016/S0079-6425(99)00010-9.

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