Comparative analysis of niobium and vanadium carbide efficiency in the high energy mechanical milling of aluminum bronze alloy

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Abstract

This study aims to analyze the efficiency of niobium and vanadium carbides in the high energy mechanical milling of aluminum bronze alloy. Two series of experiments were made following the same steps for both niobium carbide (NbC) and vanadium carbide (VC) additions: 30 g of chips were weighed and placed in a stainless steel jar with 3 % of carbide and 1 % of stearic acid for a mass/sphere relationship of 1:10. The milling was realized using a planetary ball mill for 10, 30 and 50 hours in an inert argon atmosphere at 300 rpm. Results shown in laser diffraction indicate a great reduction in the particle sizes of powders when VC is used. For 30 hours milling, D50 values ranged from 1580 µm with NbC to 182.3 µm with VC addition. The D50 values ranged from 251.5 µm with NbC to 52.26 µm with VC addition, for 50 hours milling. The scanning electron microscopy showed that in 10 hours of milling, the energy was not sufficient to achieve the shear of chips in both cases. For 30 hours, it's possible to observe particles with sizes between 100 µm and 800 µm with NbC addition while for the same milling time, with VC it's possible to see particles with different sizes, but with many shapes of fine particulates. For 50 hours milling, particles achieved the smaller sizes between 50 and 200 µm with NbC and ranging from 5 until 50 µm with VC addition.

Keywords: aluminum bronze; niobium carbide; vanadium carbide; high energy ball milling; powder metallurgy.

1. Introduction

The aluminum bronze alloy is a highly reliable material due to high corrosion resistance, currently being applied in the aerospace and shipbuilding industry for the production of forgings, sheet, extruded rods, gears, bearings, dies, valves and propellers. This alloy is still compared to high strength low alloy steels due to its high mechanical strength, wear, cavitation and impact, thus being required for some specific industrial sectors. It is machined to produce parts and discarded. However, this process is not correct for environmental reasons, which justifies reuse through the powder metallurgy route (CENOZ, 2010; BARABASH, POKROVSKY, FABRITSIEV, 2007; KEAR, 2007; PISAREK, 2007).

It can contain 4-11 wt. % aluminum, which increases the mechanical properties of the alloy establishing a face-centered cubic phase (FCC that improves the casting properties. The chemical composition of this alloy showed the elements: 73.6 % Cu; 12.7% Al; 7.2 % Fe; 4.9 % Ni and 0.9 % Mn, similar to the alloy classified by the Standard Specification UNS C63020, according to ASTM B150/B150M-12 (ASTM B150/B150M-12, 2012; DONATUS, OMOTOYINBO, MOMOH, 2012; DEREK & WILLIAM, 1990).

Powder metallurgy (PM) is a technique for manufacturing composites and processing, commonly used for the fabrication of engineering components. The PM technology route involves two different terms commonly used in literature to denote the processing of powder particles in high-energy ball mills: mixing of powder elements milled (mechanical alloying). In this situation, material transfer is involved in the process to obtain a homogeneous alloy. When there occurs milling of metal scraps or milling of uniform (often stoichiometric) composition powders, such as pure metals, intermetallics, or pre-alloyed powders, where material transfer is not required for homogenization, it has been termed Mechanical Milling (MM). Then pure metals or intermetallics are compacted in a die at room temperature and for the sintering of the consolidated powders for densification, a furnace is used (NAWATHE *et. al,* 2009; ANKLEKAR *et. al,* 2005; SURYANARAYANA, 2001).

In PM, the level of porosity, densification and mechanical resistance of final product can be controlled by manufacturing variables such as: compaction pressure, sintering time and temperature, as well as by variation of powder properties such as particle shape, particle size, size distribution and surface texture (JABUR, 2013; WANG & JIANG, 2007).

In recent years, extensive work has been undertaken for sinter metal matrix composites which contain ceramic particles embedded in their own matrix. This class of ceramic material is termed carbide and has drawn great interest due to exceptional profile of mechanical, physical and chemical properties. In addition, with metal powders from mechanical milling and alloying, the final sintered product has a greater hardness, elastic modulus and resistance to wear than high strength steels. Niobium and vanadium carbides (NbC/VC) are refractory metals having a bulk compound that exhibits a substantial hardness beyond 20 GPa, good chemical properties, elevated Young's modulus and a high melting point above 3000°C (GUBERNAT & ZYCH, 2014; MADEJ, 2013; Handbook of Advanced Ceramics, 2003; SHATYNSKI, 1979).

2. Materials and methods

Initially, the cast aluminum bronze was submitted to quantitative and quantitative chemical analysis to determine its elemental chemical composition. Then, the raw material in form of chips to realize the milling process was obtained through the step of machining of cast aluminum bronze alloy at slow speed and no use of lubricants to avoid oxygen and oil-soluble contamination.

After this process, larger chips were broken into small pieces of approximately 10 mm. For milling, 30 g of chips were weighed for both millings with NbC and VC and placed separately in stainless steel jars where upon 3% of carbide and 1% of stearic acid was added, as shown in Table 1 for milling with NbC. Milling with 300 g of spheres of three different diameters with the same proportion: large with 21 mm, medium with 13 mm and small with 8 mm was then performed. The milling was realized using a planetary ball mill for 100 hours in inert argon atmosphere to avoid oxidation of the powders at a milling speed of 300 rpm and a mass/sphere relationship of 1:10. The milling was realized using a planetary ball mill for 10, 30 and 50 hours in an inert argon atmosphere at 300 rpm.

Samples	Milling time (h)	Aluminum Bronze weight (g)	NbC weight (g)	Stearic acid weight (g)
1	10	30.012	0.901	0.301
2	30	30.039	0.908	0.309
3	50	30.007	0.904	0.305

Table 1
Mixtures composition for milling process.

The characterization of the aluminum bronze milled powder was realized using a scanning electron microscope (SEM) Carl Zeiss EVO® MA15. In the secondary electron (SE) mode, the particle size variation and morphology of powder were analyzed. Using the back scatter electron (BSD) and energy dispersive x-ray (EDS and Mapping) modes, the distribution of VC and NbC produced by Hermann C. Starck Company in matrix was evaluated. Particle size distribution was performed in Microtrac Bluewave S3500 equipment using the laser diffraction method to analyze powder size with increasing milling time.

3. Results and discussion

The chemical spectrometry of cast aluminum bronze alloy to determine its composition can be verified in Table 2.

Table 2
Chemical composition
of cast aluminum bronze (wt.%).

Elements	Cu	Al	Fe	Ni	Mn	Au	Sb	C
	73.6	12.69	7.2	4.87	0.940	0.120	0.107	0.072
Elements	Pb	Si	Co	Bi	As	Sn	Cr	S
	0.058	0.038	0.026	0.021	0.017	0.014	0.012	0.006

The initial characterization in Fig. 1 shows the micrographs of niobium and vanadium carbides. It is possible to note that there are agglomerates with an average size between 20 and 40 µm composed of small particles upon larger particles and smaller particles with near nanometer sizes.

It is reasonable to conclude from Fig. 2 that 10 hours of milling chips from the machining process were not sufficient for the formation of particles or material powder for both carbide additions. Chips still have a size larger than 1000 µm. The energy of 10 hours of milling was not sufficient to achieve the shear of chips. As the aluminum bronze has a face-centered cubic (FCC) crystalline structure, due to the greater number of crystal planes in its structure, there is a higher chance of slipping these planes, reducing strain hardening of material.

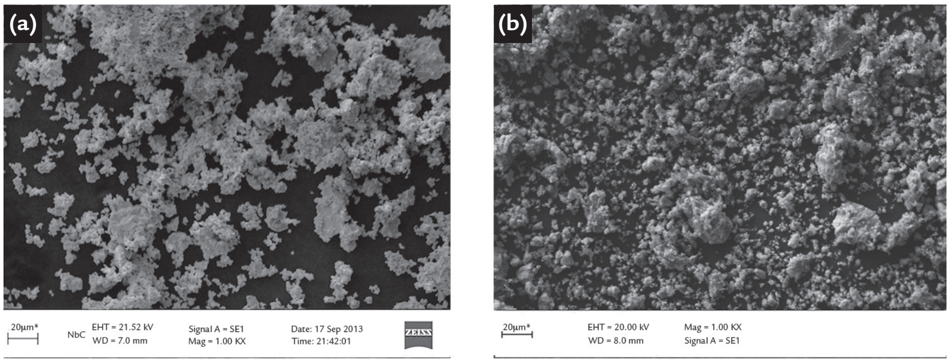

Figure 1
SEM of niobium
(a) and vanadium (b) carbides.

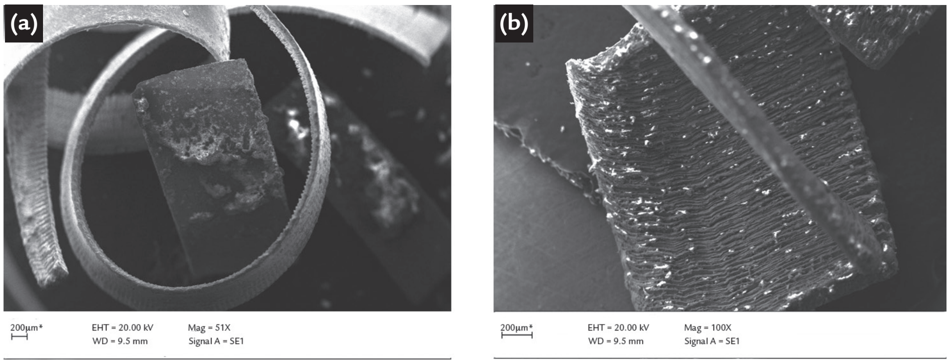

Figure 2
Aluminum bronze alloy milled for
10 hours with NbC (a) and VC (b) additions.

It can be observed in Fig. 3 that, after 30 hours of milling, the aluminum bronze chips modified their morphology and dimension in comparison with the chips milled for 10 hours both for NbC and VC. With an increase of the milling time to 30 hours, the chips of the aluminum bronze alloy with NbC addition were transformed into particles with irregular morphology tending towards a rod shape and size between 100 and 800 µm. However, for milling with VC addition, in addition to becoming particles with rod shaped morphology and different sizes, there was the formation of a considerable amount of particulate of very small dimensions on larger particles of the order of few microns, which indicates the beginning of the micro shear process on the surface of the material, which indicates the beginning of the micro shear process on the surface of the material with the increase in the milling time and percentage of VC.

Finally, there was observed a significant reduction in the particles size of the aluminum bronze milled with 30 hours in comparison to the milling process of 50 hours, in Fig. 4, for both NbC and VC addition. It can be seen that the particles from milling with NbC are beginning to get spherical shape with few microns, although there are still large and irregular particles with sizes between 100 and 300 µm. However, the milling with VC shows great efficiency with presence of spherical shape powders containing dimensions of few microns between 10 and until 80 µm. The increasing of the shear surface of the particles is caused by deformation, and the consequent displacement of crystal planes during collisions between particles in the milling process is improved due the high VC efficiency in the high energy mechanical milling.

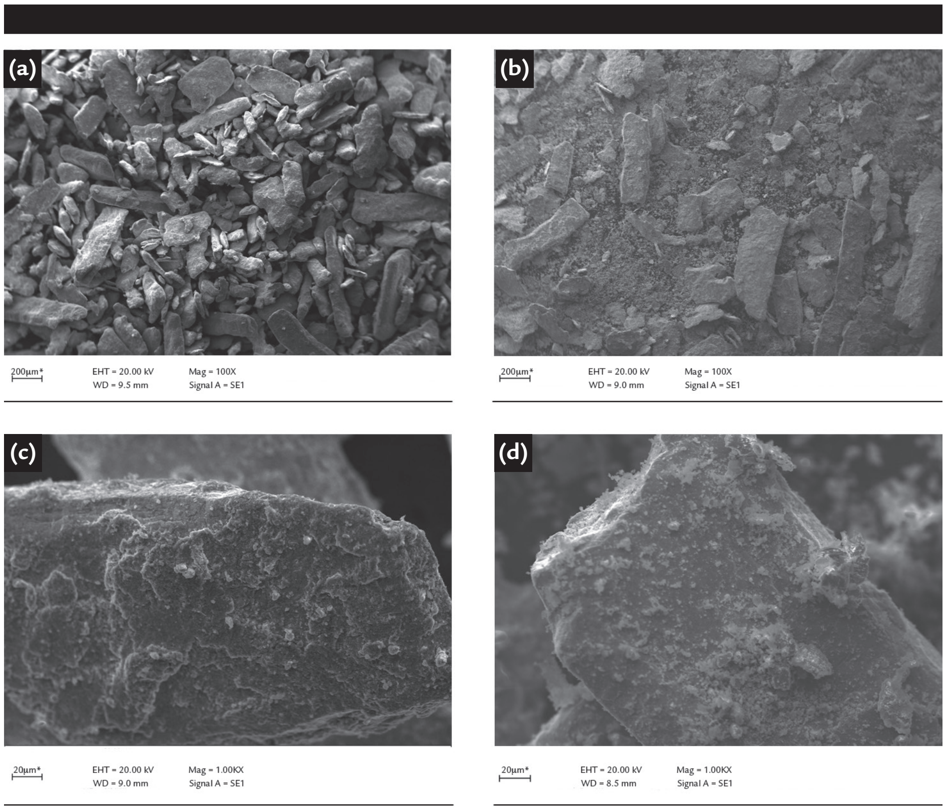

Figure 3
Aluminum bronze alloy milled for 30 hours with NbC (a,c) and VC (b,d) additions.

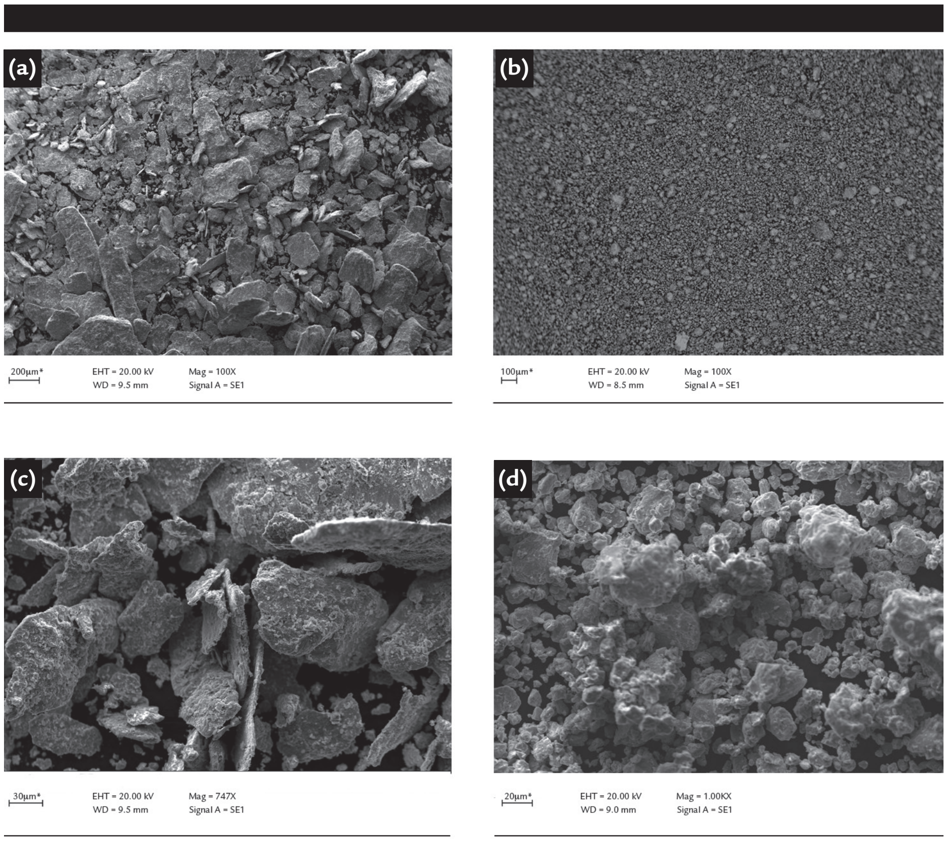

Figure 4
Aluminum bronze alloy milled for 50 hours with NbC (a,c) and VC (b,d) additions.

The distributions of NbC and VC on the particles of powders milled were evaluated under the SEM using the energy dispersive x-ray (EDS) mode and mapping analysis. It was detected in both cases that carbide particles were located homogeneously on the surface of the aluminum bronze solid particles milled for 50 hours.

The NbC particles were identified by their chemical elements carbon and niobium. Fig.5 (a) presents the alloy analyzed using the backscattered electrons (BSD) mode where the brighter spots represent the niobium because of the higher atomic weight of niobium. The Fig. 5 (b) represents the distribution of Nb and C in the matrix, where the green stains represent the C element and red stains represent the Nb element. The spectrum shown in Fig. 5 (c) confirms the presence of Nb in the bright particles analyzed.

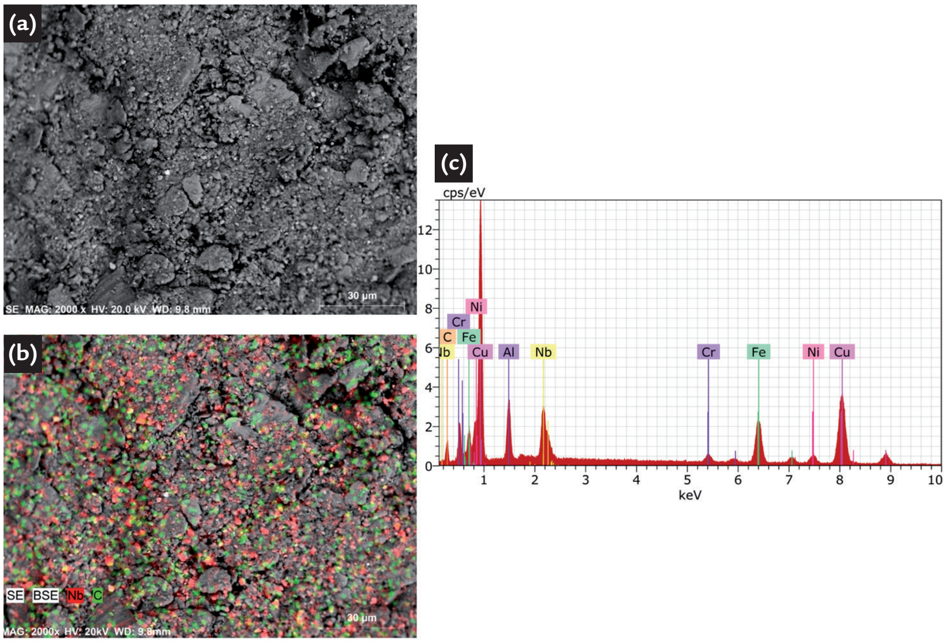

Figure 5
Chemical composition of aluminum bronze powders with NbC and 50 hours milling.

The VC particles were identified by the chemical elements of carbon and vanadium. In the Fig.6 (a), there was encountered a certain difficulty in locating VC particles because their size was reduced due to the effects of milling time. The Fig. 6 (b) represents the distribution of vanadium in the matrix where the red stains represent the few elements identified by detector. The spectrum shown in Fig. 6 (c) verifies the presence of vanadium in the matrix of material, despite its small dimensions and confirms the high efficiency of this carbide in the grinding process.

However, the presence of Fe and Cr in both cases shown is plausibly due to the contamination of the milling jars made of stainless steel.

In addition, the presence of the Fe element is also justified in considerable quantity because it forms part of the alloy composition. The Cr element, found in low quantity, is possibly deposited in the matrix of the material, since there is no solid solution formation between Cu and Cr due to their different crystalline structures. However, the presence of a compound formed by Fe and Cr can contribute to increase the corrosion and mechanical resistance of the alloy studied.

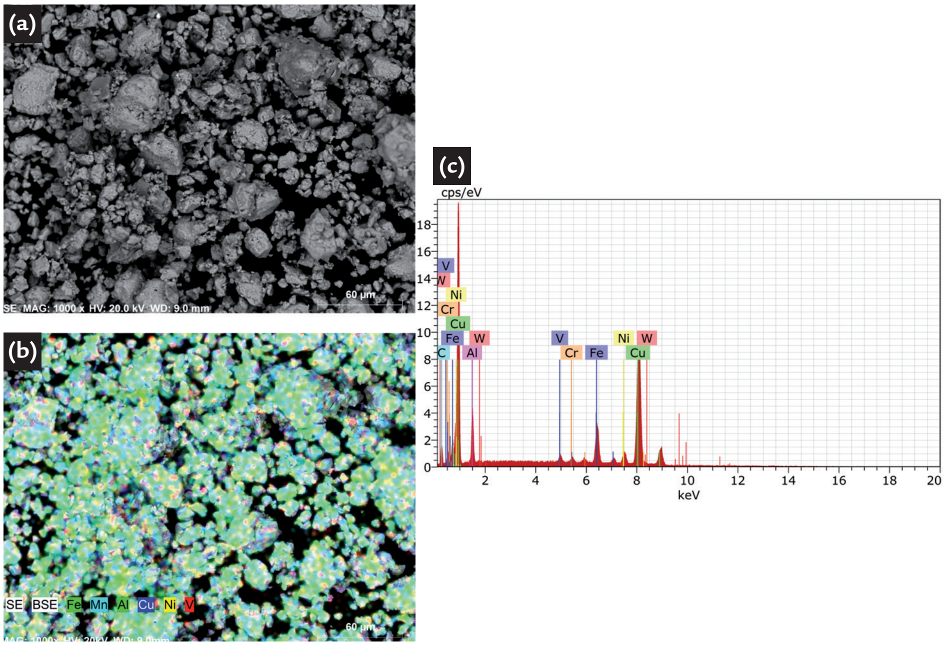

Figure 6
Chemical composition of aluminum bronze powders with VC and 50 hours milling.

The evolution of milling process in the particle size reduction can be seen in Fig.7. For the same milling time, the VC additions exert great influence in the breaking of chips and subsequent size reduction of the aluminum bronze particles, if compared with NbC addition. For both cases, the particle size distribution analyses were performed after 10 hours milling, since with 10 hours the material was presented in chips form. With 30 hours, the material mixed with NbC still has large particles around 1200 µm while for the same milling time, powders with VC are around 400 µm. Finally in 50 hours milling, powders with NbC show a mean particle size of 250 µm, while with VC addition displays a significant reduction, around 50 µm, due to high energy collisions, the milling factors such as time and carbide addition, besides the formation of a ductile-fragile particle system.

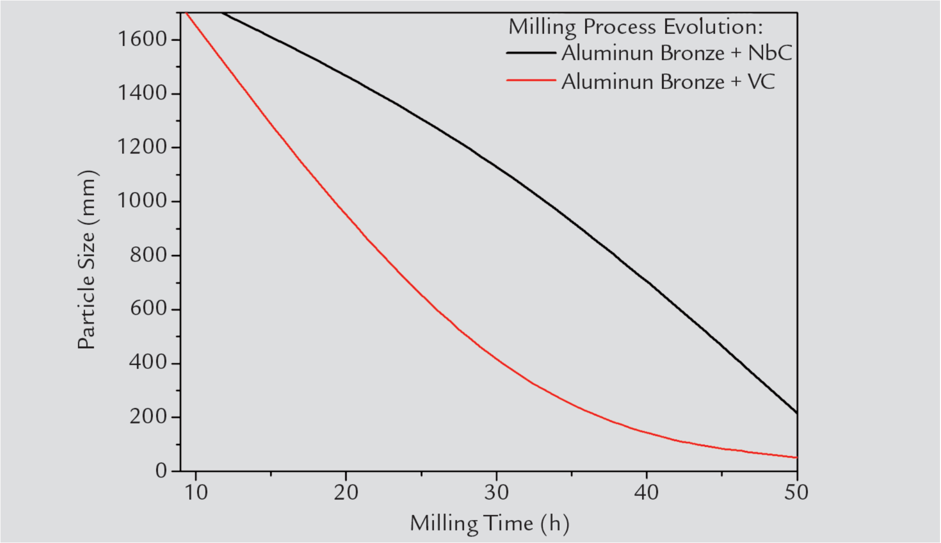

Figure 7
Progress of high energy milling process in the particle size reduction with NbC and VC.

The results of the particle size distribution are shown in Fig.8. Graphs can be evaluated by cumulative particle size analysis where the limits D10, D50, and D90 are used as the acceptance criteria for the laser diffraction method. According of values provided by the equipment, it can be noted in the graph that for 50 hours milling with VC addition, the D50 value is 52.26 μm, and that 50% of particle sizes are below this value (median diameter). Similarly D10 and D90 are 9.85 μm and 167.9 μm, indicating that 10% of particles are below 9.85 μm and 90% of particles are below 167.9 μm respectively. For the same milling time with NbC addition, the D50 value is 252.5 μm while D10 and D90 values have measures of 90.47 μm and 866.2 μm respectively.

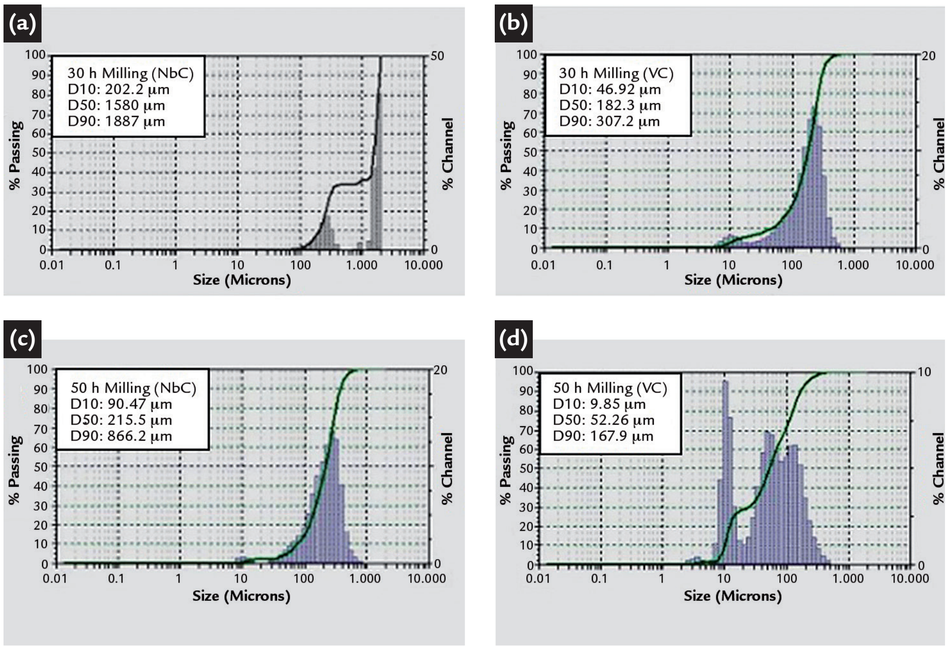

Figure 8
Aluminum bronze powder particle size distribution: 30 h milling with NbC (a) and VC (b) addition; 50 h milling with NbC (c) and VC (d) addition.

4. Conclusions

From the use of a high energy ball milling process, it was possible to obtain powders of the aluminum bronze alloy machined using the discarded chips of material under various milling times. Two parameters, carbide addition and milling time, were crucial to reducing the size of the initial material, from sizes of millimeters to powders of a few microns, as seen in 50 h milling time where the D50 values begin at 182.3 and go up to 52.26 μm for VC addition and for NbC addition ranging from 1580 μm to 251.5 μm. The evolution of the milling process efficiency producing ever smaller particles can be observed both in the SEM images as in particle size analysis. An additional observation with VC additions is that there was a significant increment in the milling efficiency, which enables the obtainment of powders in the sub-micrometric scale. The presence of carbide particles in the aluminum bronze subjected to 50 hours milling can improve some properties of powders after the sintering process, such as density and porosity that increase mechanical resistant.

Acknowledgements

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References

ALDINGER, F., UCHINO, K., KOUMOTO, K., KANENO, M., SPRIGGS, R. M., SOMIYA, S. Handbook of advanced ceramics: materials, applications, processing and properties. Academic press, , Elsevier Science & Technology Books, 2003. 1320 p.

ANKLEKAR, R. M., BAUER, K., AGRAWAL, D. K., ROY, R. Improved mechanical properties and microstructural development of microwave sintered copper and nickel steel PM parts. ***Powder Metallurgy,*** v. 48, n. 1, 2005.

ASTM B150/B150M-12, Standard Specification for Aluminum Bronze Rod, Bar, and Shapes. ASTM International, West Conshohocken, PA, 2012, www.astm.org.

BARABASH, V., POKROVSKY, A., FABRITSIEV, S. The effect of low-dose neutron irradiation on mechanical properties, electrical resistivity and fracture of NiAl bronze for ITER. ***Journal of Nuclear Materials,*** 367/370, p. 1305-1311, 2007.

CENOZ, I. Metallography of aluminum bronze alloy as cast in permanent iron die. ***Association of Metallurgical Engineers of Serbia (AMES),*** (UDC:620:186:699:715), v. 16, n. 52, p. 115-122, 2010. (Scientific paper).

DEREK, E. T., WILLIAM, T. B. Specific metal and alloys: introduction to copper and copper alloys. (10th. ed.). ***ASM Handbook,*** v.2, 1990. 2521 p.

DONATUS, U., OMOTOYINBO, J. A., MOMOH, I. M. Mechanical properties and microstructure of locally produced aluminum bronze alloy. ***Journal on Mineral and Material Characterization and Engineering,*** v. 11, p. 1020-1026, 2012.

GUBERNAT, A., ZYCH, L. The isothermal sintering of the single-phase non-stoichiometric niobium carbide (NbC1–x) and tantalum carbide (TaC1–x). ***Journal of the European Ceramic Society,*** v. 34, p. 2885-2894, 2014.

JABUR, A. S. Effect of powder metallurgy conditions on the properties of porous bronze. ***Powder Technology,*** 237, p. 477–483, 2013.

KEAR, G. et al. Electrochemistry of non-age 90-10 copper-nickel alloy (UNSC70610) as a function of fluid flow. ***Electrochemical Acta,*** v. 52, p. 2343-2351, 2007. (Issue 7).

MADEJ, M. Phase reactions during sintering of M3/2 based composites with WC additions. ***Archives of Metallurgy and Materials,*** 2013.

NAWATHE S., WONG W. L. E., GUPTA M. Using microwaves to synthesize pure aluminum and metastable Al/Cu nanocomposites with superior properties. ***Journal of Materials Processing Technology,*** 209, p. 4890-4895, 2009.

PISAREK, B. P. The crystallization of the aluminum bronze with additions of Si, Cr, Mo and/or W. ***Archives of Materials Science and Engineering,*** 2007.

SHATYNSKI, S. R. The thermochemistry of transition metal carbides. ***Oxidation of Metals,*** v. 13, n. 2, 1979.

SURYANARAYANA, C. Mechanical alloying and milling. ***Progress in Materials Science,*** v. 46, n. 1-2, p. 1-184, 2001.

WANG, L. L., JIANG, J. S. Preparation of a-Fe2O3 nanoparticles by high-energy ball milling. ***Physica B***, v. 390, n. 1-2, p. 23-27, 2007.

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