

## Analysis of the densification of a composite obtained by sintering process of aluminum bronze powders with different carbides

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Alexandre Nogueira Ottoboni Dias<sup>1,3</sup>

<https://orcid.org/0000-0003-0989-9350>

Geovani Rodrigues<sup>2,4</sup>

<https://orcid.org/0000-0003-1906-2407>

Claudiney Sales de Pereira Mendonça<sup>1,5</sup>

<https://orcid.org/0000-0002-2271-9900>

Gilbert Silva<sup>2,6</sup>

<https://orcid.org/0000-0002-3923-3982>

<sup>1</sup>Universidade Federal de Itajubá – UNIFEI,  
Instituto de Física e Química – IFQ,  
Itajubá – Minas Gerais - Brasil.

<sup>2</sup>Universidade Federal de Itajubá – UNIFEI,  
Instituto de Engenharia Mecânica,  
Itajubá – Minas Gerais - Brasil.

E-mails: <sup>3</sup>[aottoboni@unifei.edu.br](mailto:aottoboni@unifei.edu.br),  
[aottoboni@yahoo.com.br](mailto:aottoboni@yahoo.com.br), <sup>4</sup>[grodrigues@unifei.edu.br](mailto:grodrigues@unifei.edu.br),  
<sup>5</sup>[sales.claudiney21@gmail.com](mailto:sales.claudiney21@gmail.com), <sup>6</sup>[gilbert@unifei.edu.br](mailto:gilbert@unifei.edu.br)

### Abstract

Aluminum bronze alloy is applied in environments that require materials of high mechanical resistance and wear, such as marine, oil & gas and aerospace ones. This study analyzes the densification of composites based on aluminum bronze with additions of the vanadium (VC) and niobium (NbC) carbides, and the influence of these carbides in the milling efficiency and improvement of the diffusion process between particles to obtain better results for density and porosity. The composites were produced by powder metallurgy from aluminum bronze powders obtained from the mechanical milling process of discarded scraps. The efficiency of the sintering process depends on parameters, such as the time and temperature of sintering, together with the size of the particles obtained from the milling process. This study aimed to obtain and characterize the composites produced by the powder metallurgy route, with NbC and VC addition and to analyze physical properties, such as density and porosity. The powder morphologies, particle sizes and samples sintered were performed by scanning electron microscopy (SEM), X ray diffraction (XRD), laser diffraction analysis and optical microscopy (OM). The results indicate that addition of VC improves the milling efficiency, when compared to NbC addition, since it promotes a greater reduction of the particle size, directly favoring the sintering process. In this case, to achieve similar particle size, twice the milling time was required when NbC was used. The density values achieve ~ 73% of reference material for VC addition and ~ 68% for NbC and porosities varying between 27% and 38%.

**Keywords:** aluminum bronze; sintering process; powder metallurgy; densification; composites.

### 1. Introduction

Aluminum bronze has been investigated (Dias *et al.*, 2017, 2018; Wang *et al.*, 2018), due to its wide range of applications, making them preferable to other engineering materials, notwithstanding its high strength, abrasion, wear, cavitation and impact resistance. Aluminum is the principal alloying metal added to copper, which improves its mechanical and corrosion properties, in addition to other elements such as iron, nickel and manganese in varying proportions (Makhlouf *et al.*, 2016; Nwambu *et al.*, 2017).

As was reported by various authors, its characteristic microstructure is constituted by  $\alpha$  and  $\beta$  phases, along with the “retained  $\beta$ ” or martensitic  $\beta'$  and forms of the intermetallic kappa phases obtained

from heat treatments. This fact enables its use in the aerospace industry, such as for landing gear bushings and bearings; in the marine industry for propeller hubs and wear rings; and in the oil and gas industries for vertical pump columns and seawater lift pumps (Pisarek, 2007; Lv *et al.*, 2015; Thapliyal and Dwivedi, 2016).

In traditional processes to manufacture parts and components, after this metal is machined, no more than 54% of scraps are recovered in opposition to alternative processes as powder metallurgy (PM), which reutilizes 95% of these discarded metals, providing economy of energy and preservation of the environment. The PM involves two processes: mechanical alloying by mixing of pow-

dered elements, and mechanical milling of scraps for subsequent compaction in a die, at room temperature; and the sintering of the consolidated powders for densification using a furnace (Gronostajski, Chmura, Gronostajski, 2006; Nawathe, Wong, Gupta, 2009; ASTM B925-15, 2015).

In addition, powders obtained from mechanical milling and alloying can be reinforced with refractory compounds to aid in the reduction of particle sizes. Carbides are based on metals which have good properties, such as great hardness, temperature stability and thermal conductivity (Suryanarayana, 2001; Hossein-Zadeh *et al.*, 2016).

When compared with the conventional forging mechanical processing, PM

technology can optimize the production process and reduce working hours, and the raw material can be reused, while maintaining at the same time, the mechanical properties of the materials, such as high mechanical strength and wear resistance (German, 2005; Hai-Dong, Hao-Wei, Liang, 2013; Jabur, 2013).

Sintering is an important step in the PM process, which influences final density of the sintered material, achieving densities between 25% and 85% of the reference material. The most important parameters of the sintering cycle are sintering time and temperature, besides the sintering atmosphere, which has great influence on corrosion behavior and mechanical properties. Hydrogen, argon, and vacuum atmospheres are the correct conditions for

sintering (Mariappan *et al.*, 2011; Jabur, 2013; Ertugrul *et al.*, 2014).

Usually, the temperature specified for the sintering process is in the order of 2/3 to 3/4 of the alloy melting temperature considered. In systems of various constituents, such as aluminum bronze, the sintering is performed at a temperature exceeding the lower melting point metal, in this case being the formation of a liquid phase which promotes the sintering conditions (German, 2005; Klar and Samal, 2007).

The level of porosity and size distribution of pores that influence the final density, can be controlled by manipulation of these cited parameters to obtain powders with good particle sizes, shapes and surface texture. Furthermore, the

reduction of porosity can be achieved by increasing the sintering temperature, which results in a diffusion increasing due to temperature rise (Suryanarayana, 2001; Upadhyaya, 2002).

This study aims to analyze the influence of different carbides on the microstructure and densification of aluminum bronze sintered specimens obtained from scraps of a machining process. In addition, the level of porosity under these conditions was evaluated and compared to the reference material (cast). Smaller particle sizes imply a more efficient sintering process, since the diffusion between the atoms of neighboring particles is more effective to obtain good properties for a composite suitable for engineering applications.

## 2. Materials and methods

### 2.1 Powder Preparation

The starting powders were obtained by the mechanical milling process of aluminum bronze scraps with the addition of NbC and VC produced by Hermann C. Starck Company. The alloy has the nominal composition of 73.60% Cu,

12.69% Al, 7.20% Fe, 4.87% Ni and 0.94% Mn (wt. %).

The mixture of powders was performed in a planetary ball mill (NQM 0.2L/ Noah-Nuoya Corp.) under air protection to avoid oxidation by 30 h

milling time with addition of 3% VC, and 60h, for the addition of 3%NbC, (all in weight percent), where the parameter milling speed and ball to powder weight ratio were fixed at 350 rpm and 1:20, respectively.

### 2.2 Compacting and Sintering

Powder mixtures with 1.0 gram of material for each carbide addition were compacted in a cylindrical die with 1% of

the zinc stearate binder. Then it was pressed in a uniaxial press at 400 MPa for 30 seconds (3 times) at room temperature and

transformed into pellets, whereby its diameter and height were measured to determine the green density, according Equation 1:

$$\rho_g = m/v = \frac{m}{(\pi \cdot d^2/4) \cdot h} \text{ [g/cm}^3\text{]} \quad (1)$$

Where:  $\rho_g$  is the green density, m is the mass, v the volume, d the diameter and h is the height.

The green samples were sub-

sequently sintered in a furnace with vacuum atmosphere, where they remained for 20 min. at the temperature of 400°C for binder evaporating and

more 60 min. for complete sintering at 900°C. Lastly the samples were cooled inside the furnace.

### 2.3 Microestructural characterization & analysis

The samples were characterized through metallography and their microstructure and porosity were analyzed by an optical microscope Carl Zeiss Jenavert® coupled to a digital camera and the image analyzer Image Pro-Plus®.

The microstructure and morphology of the aluminum bronze powders, besides the distribution of carbides the matrix sur-

face, was performed by Carl Zeiss EVO® MA15 SEM using secondary electron (SE) and back scatter electron (BSD) modes and also coupled with an X-ray energy dispersive spectrometer (EDS).

All conditions of the aluminum bronze were characterized by X-ray Diffraction (XRD) in an X-ray Panalytical X'pert PRO® diffractometer with CoK $\alpha$  radiation

at a scanning speed of 0.02°/ second.

Particle size analysis was performed in a Microtrac Bluewave S3500 system by the laser diffraction method. The apparent densification and porosity of all sintered samples were evaluated using the Archimedes' Principle (ASTM B962-17, 2017) with samples immersing in distilled water at the ~ 25°C air temperature.

## 3. Results and discussion

### 3.1 Influence of milling process on particle size and morphology

The characterizations of aluminum bronze resultant powders with addition of different carbides are

shown in Fig. 1, where it is possible to observe a significant difference between particles in each case, with

respect to sizes and shapes, due to presence of each carbide in particular.

The Fig. 1a shows the mixture

of aluminum bronze powders with VC addition, milling for 30 h. It is observed that, in this condition, the powder presents very heterogeneous particles, with shapes varying from very small diameters to elongated particles with approximately 550  $\mu\text{m}$ . The smaller particles have a rounded morphology and the larger ones have an elongated morphology. Fig. 1b shows the aluminum bronze powder, milled for 60 h, with NbC addition. It

is observed that, similar to the samples milled with VC, the powder has a very irregular granulometry, with particles varying from very small diameters to elongated particles with approximately 700  $\mu\text{m}$ . However, aluminum bronze powder, milling with VC addition, has a much larger volumetric fraction of small particles than when milling with NbC, indicating a greater increasing in the milling efficiency with the VC addition.

Obtaining a higher volumetric fraction of small particles, even at shorter milling times, indicates that VC is a high hardness material and therefore has a higher efficiency for hardening the material being milled, making it more brittle and easier to mill. The NbC, most ductile carbide, is first cold-welded to the surface of the material, slowing the hardening process and embrittlement of the material being ground.

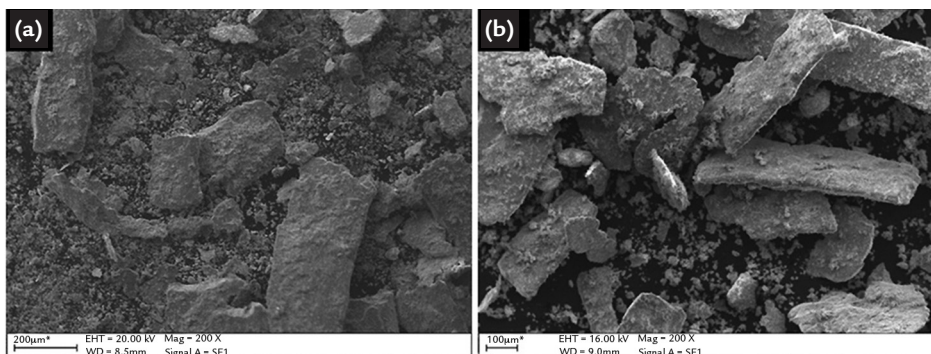


Figure 1  
Particles morphology  
of aluminum bronze alloy  
submitted to mechanical milling  
(a) 30 h milling time with VC addition and  
(b) 60 h milling time with NbC addition.

Fig. 2 shows the curves of volumetric and cumulative particle size distribution with the D10, D50 and D90 values, for the aluminum bronze milled by 60 h, with NbC addition and ground for 30 h, with VC addition, obtained by the laser diffraction method. It can be observed that the granulometric distribution was much similar for the two milling times (30 and 60 h).

The mean particle volume diameter of the powders with NbC addition was 194.2  $\mu\text{m}$ , whereas for the

powders with addition of VC, it was 182.2  $\mu\text{m}$ . By means of the D50 values, it was possible to determine that 50% of the powder particles of the aluminum bronze, milled for 60 h and with NbC addition, are less than 193.8  $\mu\text{m}$ . Likewise, the values verified for D10 and D90 were 12.71  $\mu\text{m}$  and 369.3  $\mu\text{m}$ , respectively, indicating that 10% and 90% of the particle sizes are lower than these values.

The results show that the same milling efficiency, in other words,

powders with very similar granulometry, was achieved with 30 h of milling time with the addition of VC. The results showed that the particles with a size for the D50 value was 182.3  $\mu\text{m}$ , D10 value was 46.92  $\mu\text{m}$  and the D90 value was 307.2  $\mu\text{m}$ . However, it was observed that the small particle volume fraction was significantly larger when the aluminum bronze was milled with the VC addition. These results were observed in the regions highlighted in the Fig. 2.

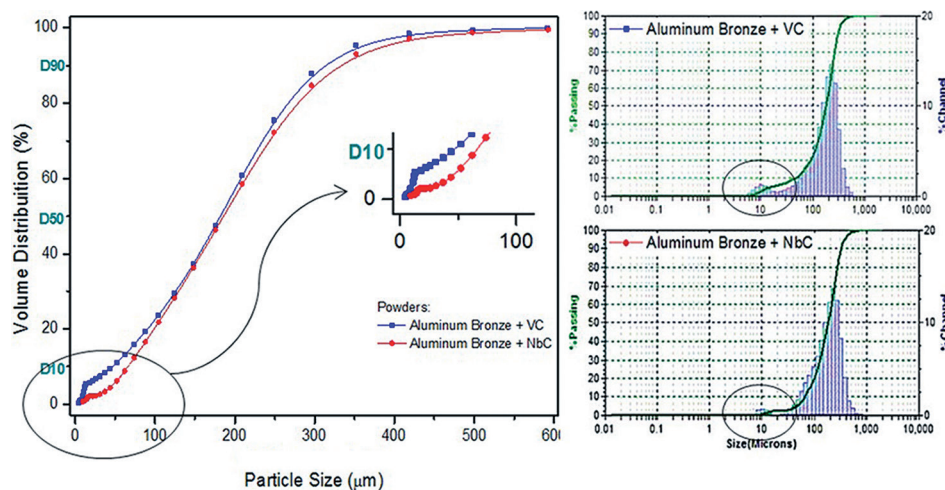


Figure 2  
Volumetric and cumulative  
particle size distributions as a  
function of the particle size of aluminum  
bronze powders with different carbides.

### 3.2 Microstructural analysis of sintered pellets

#### 3.2.1 Carbides Distribution

Fig. 3 shows the distribution of the carbides on the surface of sintered samples, obtained by the mapping of chemical elements in Scanning Electron

Microscopy (SEM). The results show the presence of the chemical elements Cu, Al, Fe, Ni and Mn that make up the aluminum bronze alloy and the elements

Nb and V that identify the NbC and the VC respectively. It is observed that the carbides are homogeneously distributed in the sample.

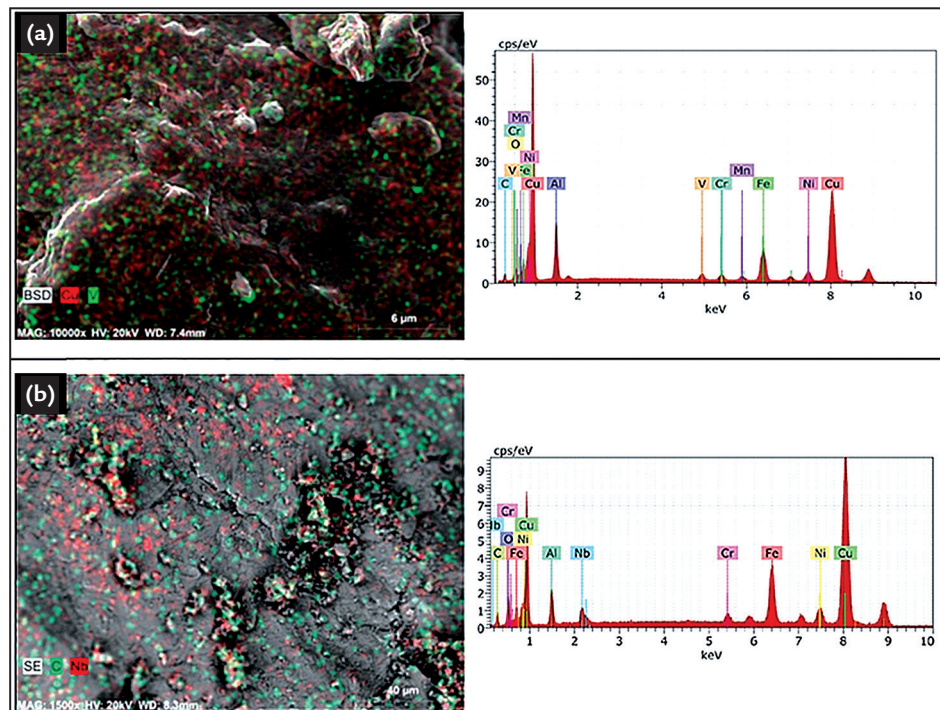


Figure 3 SEM images for Mapping and EDS analysis of aluminum bronze sintered for identification of VC (a) and NbC (b) and its main chemical elements.

### 3.3 Analysis of sintered pellets

Figure 4 shows the X ray diffractogram of the aluminum bronze produced by the melting process (starting material), milling for 30 h with the VC addition, milling for 60 h with the NbC addition, and these powders sintered at 900°C. It is observed that the high energy milling process caused distortions in the crystalline lattice of the material, identified by the enlargement and decrease in the peak intensities of the  $\alpha$ ,  $\beta$  and  $\kappa$  phases, that

make up the aluminum bronze structure. It is observed that this enlargement and decrease of the peak intensities was more significant in the sample milled for 60 hours. The diffractograms also show that much of this distortion of the crystalline lattice was reversed, due to the rearrangement of the atomic positions during the sintering process, which can be verified by the narrowing of the peaks of the sintered samples. The narrowing of the peaks was

more significant in the sample milled for 60 h, which may be related to the higher energy stored in the milling process.

In addition, it can be observed that the sintering process did not cause any change in the structure of the aluminum bronze; that is, the sintered materials have the same phases of the starting material, in this case,  $\alpha$ ,  $\beta$  and  $\kappa$  phases.

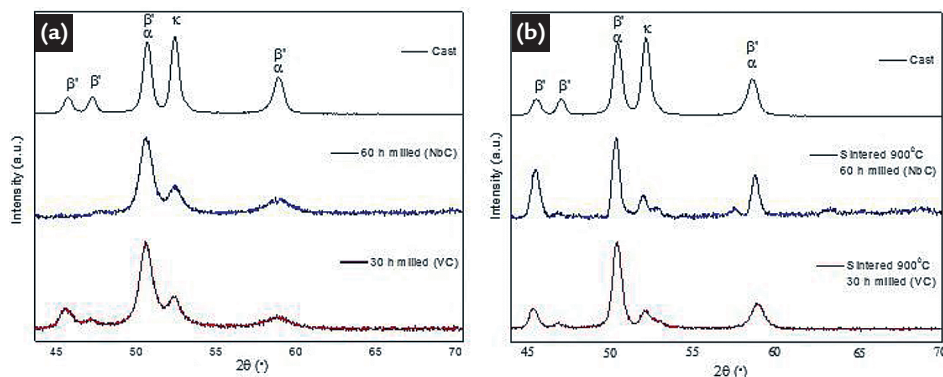


Figure 4 X ray diffraction plots of cast aluminum bronze and pellets sintered with addition of VC and NbC at 900°C.

### 3.4 Analysis of densification and porosity of sintered pellets

The densification of powdered materials is a process of pore elimination whereby the porosity of these sintered alloys decreases with the increase of the time and correct sintering temperature (German, 2005; Jabur, 2013).

The results show that sintering of aluminum bronze powders presented an increase in the apparent density values and a decrease in the apparent porosity values, for both conditions. However,

these results were significant in the sintering of the aluminum bronze powder, milling with the VC addition. This better densification and lower porosity were possible because the samples milling with VC presented a higher small particle volumetric fraction, when compared to the powder milling with NbC addition.

With respect to green density, obtained by Equation 1, and apparent density, from Archimedes' principle, it

is possible to verify that the density of the reference material (cast) achieves an average value of 7.32 g/cm<sup>3</sup>, while values of the green densities of the samples of both carbides obtained an average value of 4.82 g/cm<sup>3</sup> and the sintered samples had average values of 5.35 g/cm<sup>3</sup> with the addition of VC and 4.96 g/cm<sup>3</sup> with addition of NbC.

It is observed that the green density of the powders compacted was ~ 65%

of the reference material value, while that apparent density measurement for the samples with addition of VC was  $\sim 73\%$  and for the samples with addition of NbC was  $\sim 68\%$ .

When comparing the values of the green density of the compacts with the apparent density obtained for the sintered material, it can be noted that samples with NbC had an increase of

only 3% of their density and samples with VC an elevation of 10%, after the sintering process. Fig. 5 shows all densities obtained from compacts and sintered samples with its variations.

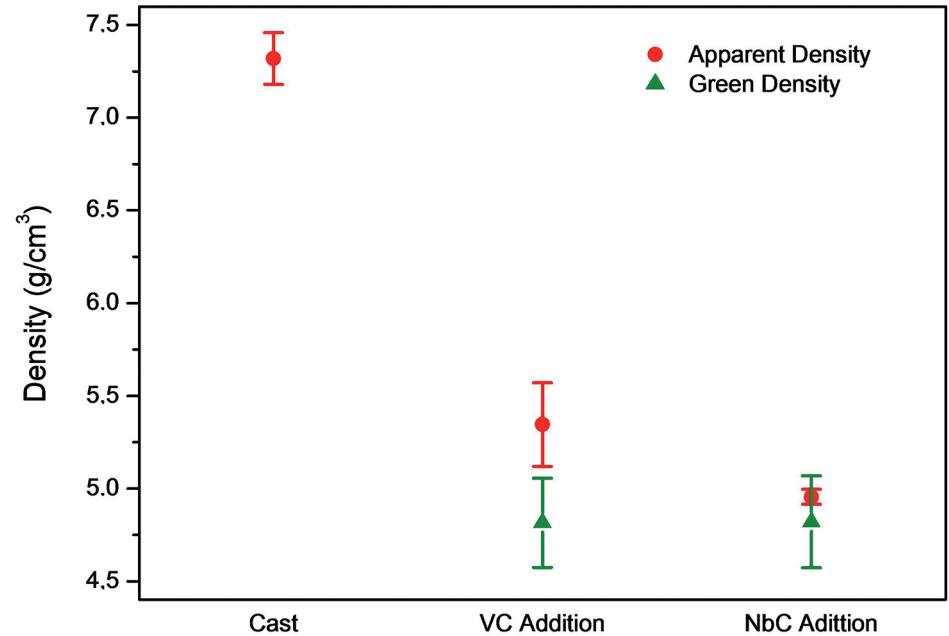


Figure 5  
Comparison of densifications between cast, compacted and sintered aluminum bronzes.

The apparent porosity was determined by two methods for comparison, since there is a considerable variability of method performed by imaging software in OM in relation to the apparent porosity of the material determined by the Archimedes' principle.

From the results, it is possible to observe that there is a variation  $\sim 15\%$  in the values of the apparent porosity and

those obtained through imaging software of sintered aluminum bronze samples with NbC. In samples with the addition of VC, it is observed that this variation reaches  $\sim 20\%$ .

The lower porosity, in both techniques, is seen with the presence of VC in the sintered aluminum bronze, due to the production of reduced particulate in the milling process favoring the diffu-

sion between neighboring atoms. When comparing the sintered powders milled with different carbides, it was noted that the difference of apparent porosities of samples sintered with the addition of VC and NbC is  $\sim 17\%$ . For the porosities obtained from imaging software this value achieves  $\sim 13\%$ . In Fig. 6, all the porosity values for the samples of aluminum bronze sintered are presented.

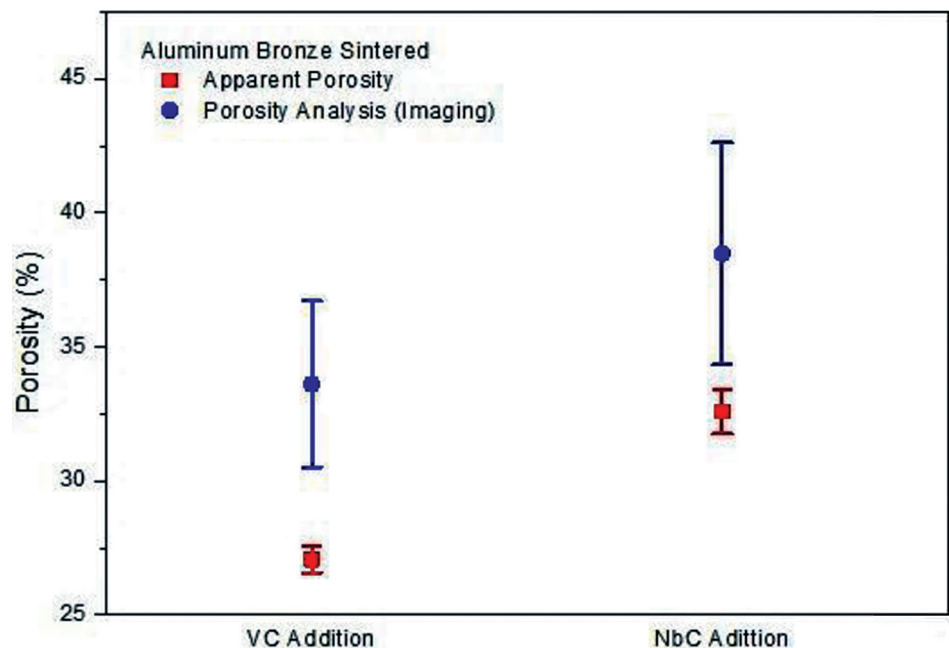


Figure 6  
Comparison of porosities between sintered aluminum bronzes.

The Fig. 7 shows the porosity behavior of the samples sintered with additions

of VC and NbC. It is possible to observe a more pronounced porosity in the sample

with NbC, whose particles assumed more irregular and elongated shapes, resembling

rods. The sample with VC addition presents a more regular size, circular forms of particles and also better pore distribution.

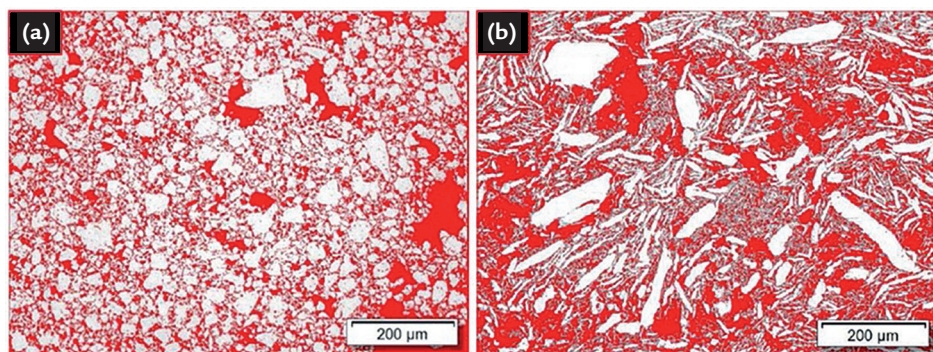


Figure 7  
Software images of the pellets with addition of VC (a) by 30h milling and NbC (b) with 60h.

In addition, this study shows the results obtained from the sintering process of aluminum bronze powders with the addition of VC and NbC. Powders

sintered with VC present an increase of 8% in the apparent densification and a decrease of 17% in the apparent porosity when compared to pellets with

NbC, which can be attributed to the particle size reduction achieved in the milling process.

#### 4. Conclusion

This study applied the powder metallurgy route to obtain aluminum bronze composites from the sintering process of powders with reduced particle sizes and addition of different carbides to evaluate their physical properties, such as density and porosity and its microstructure.

The results showed that addition of carbides in the milling mixture contributed to accentuate the particle

size reduction of material which have shown sub-micrometer sizes.

The results showed that the apparent density of the sintered samples in relation to the reference material was ~ 73% for addition of VC and ~ 68% for NbC. In general, the apparent porosities and that obtained from imaging software presented values between 27% and 38% for all sintered samples, especially the lower porosity reached in

the sintered samples with VC addition.

Moreover, it can be concluded that the presence of micrometric carbides can improve the milling efficiency, to obtain sub-micrometric powders, and also the diffusional efficiency in the sintering process, resulting in composites with interesting values of density and porosity for soft applications that allow some variability of these parameters.

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