Sintering of a metal matrix composite Cu-Ti-TiC assisted by abnormal glow discharge

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Abstract. A metal matrix composite based copper with ceramic reinforcement at 1% w/w of titanium carbide had been studied under variable titanium at 10%, 15% and 20%, in order to evaluate the microstructure and tribological properties (coefficient of friction and wear rate) in the composite material after abnormal glow discharge sintering. The metal matrix composite was manufactured by powder metallurgy process that included: mechanical and ultrasonic mixing in a suspension of 2-propanol, compaction at 200 MPa and sintering by abnormal glow discharge in an atmosphere of 10% nitrogen and 90% argon. As a result, a differentiation in the morphology and properties had been found due to the temperature, this effect was related with diffusion phenomena and energy provide by the plasma process. The final porosity of the samples at 750 °C decreases with titanium increments, reach to 2.6% with 20%. Additionally, in the grain limits of the titanium particles were detected CuTi and CuTi₂ phases. On the other hand, at 850 °C the porosity increased with concentration of titanium, a value of 16.8% was shown at 20%. Furthermore, intermetallic phases as Cu₃Ti, Cu₅Ti, CuTi₂ had been identified in the sintered at 850°C. Tribological properties had evidenced that the samples at 750 °C with Ti contents of 20% presented a wear rate value of 7.2x10⁻⁸ mm³.N⁻¹.m⁻¹, despite the porous morphology of the compound at 850 °C was estimated in 2.0x10⁻⁸ mm³.N⁻¹.m⁻¹ with concentration of 20%.

1. Introduction
Interest in the use of novel plasma-based sintering techniques applied to the powder metallurgy has led to the investigation in this field. For instance, abnormal glow discharge (AGD) has proved useful in sintering composite materials and metals compared to conventional routes, particularly ferrous alloys but their field of study in non-ferrous remains in development [1–3]. Copper is one of the metals with extensive use in modern life, however, its use has been limited due to its low mechanical and tribological resistance. The development of copper-based materials with the purpose of improving their final properties has been researched through the incorporation of secondary phases (ceramic and metals). As a result, in this field has been observed improvement of the final properties against wear with the incorporation of TiB₂ [4], Al₂O₃ [5], AlN [6], TiC [7,8] and graphite [9], but in reason of the low compatibility between the matrix and the reinforcing aggregates have not been achieved satisfactory results. It has been established an adequate mechanical response with Cu-TiC combination in a metal matrix composite (MMC), especially in concentrations of 1% TiC [10]. In spite of this, this combination exhibits some compatibility problems between the matrix and the reinforcement, promoting a poor
response to wear and stress. Integration of a third phase within the MMC is foreseen as a solution to these problems. Titanium could be a suitable component in order to decrease the surface energy between the copper matrix and the ceramic reinforcement components [11], by virtue of its low density, compatibility with copper and wettability with TiC [12].

The sintering by abnormal glow discharge consolidate the particles as cathodic discharge points. This is able to promote the relationship between the particle aggregates through the interfacial reactions. The behavior of the Cu-Ti-TiC system such as abnormal glow discharge has not been extensively studied. It has been evidenced that the use of reactive atmospheres in the Cu-Ti system promotes the appearance of intermetallic species of interest as CuTi, CuTi₂, Cu₃Ti, Cu₄Ti, Cu₅Ti₃ [13–15], which due to their high hardness, could offer an excellent advantage against wear. The possibilities offered by the low intermetallic density in the Cu-Ti system in combination with the mechanical properties will provide an adequate alternative to conventional applications. Besides this type of material has proved to be an appropriate candidate in reason to its compatibility with the tissues and tribological properties [16,17]. The aim of this work is to study the interactions in a Cu-Ti-1%TiC MMC with titanium concentrations of 10%, 15% and 20% sintered by AGD at 750 °C and 850 °C. In order to characterize their final morphology and tribological properties under different synthesis conditions to provide knowledge that expands the range of applications, especially, in the aeronautical, automotive and biomedical fields in which these kinds of materials for applications such as electrical and thermal conduction, mechanical or structural applications.

2. Methodology

There were selected copper, titanium, and titanium carbide powders with particle sizes of 75 μm, 60 μm and 4 μm, respectively. The sintered samples were observed by scanning electron microscopy (SEM) on a LEO 430 microscope operated at 30 kV. The compositional characterization of the sintered was performed in dots mode by Energy-dispersive X-ray spectroscopy (EDS) with a device Oxford instruments model 7059.

Three mixtures with different concentrations in titanium mass 10%, 15% and 20% were elaborated, maintained as reinforcement in each one of them 1% of titanium carbide. The mixing of the powders was carried out in suspensions of 2-propanol, which were submitted to ultrasonic bath (40 W) during 10 minutes and magnetic stir at 1250 rpm for 30 minutes with subsequent drying at 50 °C. In addition, a target without titanium particles was manufactured retaining 1% titanium carbide.

The mixtures were subjected to compaction at 200 MPa in order to obtain cylindrical specimens with a diameter of 10 mm and thickness of 5 mm. The green preforms were sintered by abnormal glow discharge, with operating parameters: direct current, pressure 2 Torr, protective atmosphere of Ar-N₂ with a constant flow of 90 ml.min⁻¹ of argon and 10 ml.min⁻¹ of nitrogen, operating voltage and current variable according to the temperature 750°C (468 V-135 mA) and 850°C (592 V-197 mA), with heating rate of 100 °C.min⁻¹ and sintering time 30 minutes. The porosity was determined through scanning electron microscopy, using image analysis with the software Image J version 1.51, according to ASTM E1382 standard [18]. X-ray diffraction (XRD) was used to determine the type of phases in sintered. XRD was evaluated in Pertpro PANalytical X-ray equipment with cobalt anode. The diffractograms were taken using Bragg-Brentano geometry by sweeping the angle 2θ between 20° and 90°, with a pitch of 0.013. The sintered samples were subjected to wear test in a tribometer pin on disk MicroTest MT/60/NI, with a hardened steel pin as contramaterial. The conditions of the test were: normal load of 10 N, sliding distance of 300 m, speed of 0.1 m.s⁻¹ and environmental atmosphere with average relative humidity of 62% and temperature 20 °C. The coefficient of friction was registered continuously during the test and wear rate (k) was estimated through Equation 1:

\[ k = \frac{\text{loss of material volume [mm}^3\text{]}}{\text{applied load [N]}*\text{sliding distance [m]}} \]  \hspace{1cm} (1)
3. Results and discussion

3.1. Microstructural and morphological details
In the Figure 1 is presented the microstructure of the compound sintered at 750 °C and EDS results with table of possible phases, according to the stoichiometry of these compounds. The morphology was characterized by definite form of titanium grains. It was distinguished contrast changes in the grain borders of Ti particles, this was related to the presence of phases formed between the copper and titanium during the sintering process. A possible cause of the presence of these formations (CuTi$_3$, CuTi$_2$ and Cu(Ti)) had been reported in the literature [19–21], showing that in this range of temperature these intermetallics are the most stable to appear in the diffusive scenario and the growing of layers require time greater than 3600 s.

![Microstructure and EDS results of sintered samples at 750 °C with titanium concentrations of (a) 10%, (b) 15%, and (c) 20%.

Figure 1. Microstructure and EDS results of sintered samples at 750 °C with titanium concentrations of (a) 10%, (b) 15%, and (c) 20%.

The results of samples sintered at 850 °C are depicted in Figure 2, there was a marked differentiation in morphology with porosity in the material and defined intermetallic formations in the matrix. The
presence Cu₄Ti, Cu₃Ti, CuTi₂, CuTi, Cu₂Ti₃ stands out that titanium increments the consolidation and tendency to form this kind of specimens in this composite. Similar cases by cause of diffusion had been observed in the Ti-Ni system [22,23] on account of stabilization of the β phase of titanium in this range of temperature by virtue of the reaction with beta-establishing cubic components of titanium (Body-centered cubic structure) such as copper and nickel (Face-centered cubic structures) [24,25].

![Microstructure and EDS results of sintered samples at 850 °C with titanium concentrations of (a) 10%, (b) 15%, and (c) 20%.
](image)

**Figure 2.** Microstructure and EDS results of sintered samples at 850 °C with titanium concentrations of (a) 10%, (b) 15%, and (c) 20%.

Table 1 are shown the porosity results for the different synthesis conditions. It was presented in the sintered samples at 750 °C porosity values lower than those found in the samples at 850 °C. At 750 °C there was a decrease in porosity with titanium increases reaching 2.6% porosity in concentrations of 20% Ti. In this case the porosity showed a strong tendency to be associated with low deformation of copper around the titanium particles and short sintering time. This did not promote the rapid sealing of pores, indicating that energy needed in the mass transport process was consumed in the nucleation and growth of the intermetallic layers around the particle borders.
Table 1. Porosity results for different synthesis conditions.

| Sample  | Porosity (%) |
|---------|--------------|
| 750 °C  | 850 °C       |
| Target  | 4.90 1.80    |
| 10% Ti  | 4.80 11.4    |
| 15% Ti  | 3.20 15.8    |
| 20% Ti  | 2.60 16.8    |

On the other hand, in the samples at 850 °C had an increase in porosity with the concentration of titanium, reaching 16.8% porosity with 20% Ti. This was related to the phenomena of stabilization of titanium with copper in this temperature and the diffusion of the Cu-Ti system. The diffusive process at 850 °C compared to 750 °C had shown more sensitivity to the effects of sintering, resulting in the appearance of greater porosity due to the differences in the interdiffusion of the elements. This caused the differentiated migration of titanium to copper, forming intermetallics that consumed in their growth the energy necessary to generate the transport of mass to the voids left by the diffused titanium particles. Other factor that made this possible was the high difference between the thermal conductivity of titanium and copper (Ti: 21.9 W.K⁻¹.m⁻¹ [26], Cu: 400 W.K⁻¹.m⁻¹ [27]), promoting the formation of heat concentrations located inside the titanium grains produced by a less heat dissipation. This concentration of heat due to the Joule effect inside the grains of the particles acted as cathodic emitters of the discharge, providing energy for intermetallic formation but not enough to seal the pores. In the border areas of the titanium particles in contact with the matrix had a greater possibility of dissipating heat in the first stages of the sintering through the interface with copper, promoting the strong interaction with the matrix. The areas with heat concentrations suffered greater diffusion to the outside, thus over time increases the pore size.

The diffractograms are shown in Figure 3, the majority phases are detected in the sintered at 750 °C and 850 °C. It was observed in low temperature of sintering a strong indexation of the elemental phases (Cu-Ti) due that intermetallic phases of borders the titanium particles had low volumetric presence in the material. On the other hand, at 850 °C, the marked appearance of intermetallics were detected with titanium increments. It was noted that in the low titanium contents the intermetallic formation process was less in comparison to other concentrations. It had been reported in the literature that at 850 °C owing to the decrease in energy associated with nucleation, phases such as CuTi, CuTi₂, Cu₃Ti and Cu₄Ti₃ increase their stability [14,28].

![Diffractograms of samples sintered at (a) 750 °C and (b) 850 °C.](image-url)
3.2. Tribological properties

The titanium concentration had effect in the depletion of the coefficient of friction (CoF) as it is shown in Figure 4. For sintered composites at 750 °C was observed a linear decrease behavior with the increment of titanium with values of CoF from 0.82 to 0.18. This was attributed to the formation of mixed oxide layers of copper, titanium and iron on the wear track. That promoted self-lubricating layers, providing reduction of the friction and mechanical losses of energy. In contrast, in the sintered at 850 °C was presented a decreasing behavior with slight variations around values closed to 0.5. This effect could be attributed to the macroporosities of the MMC, originating that porosity serves as debris deposit which by compressive phenomena increases the friction between the components and inhibit the diminution of frictional energy.

The wear rates of the Figure 4 had a similar behavior between the sintered at 750 °C and 850 °C. In 10% had a high degradation with a value of 2.9x10^-6 mm^3.N^-1.m^-1 at 750 °C and 3.6x10^-6 mm^3.N^-1.m^-1 at 850 °C compared to the compounds with concentrations to 20% with a wear rate of 7.2x10^-6 mm^3.N^-1.m^-1 at 750 °C and 2.0x10^-6 mm^3.N^-1.m^-1 at 850 °C. Intermediate levels of wear were found in concentration of 15% with 1.9x10^-7 mm^3.N^-1.m^-1 at 750 °C and 1.2x10^-7 mm^3.N^-1.m^-1.

The wear rate on MMC at 750 °C was explained by the increase of hard zones towards the interior of the material in particular in the limits of the titanium grains. The high modulus of the phases in that zone [29,30] verify the origin of the reduced wear with the incorporation of titanium. By other side, in sintered at 850 °C was explained by the appearance of intermetallics as a consequence of the homogeneity towards the material that implies an increase in resistance to wear. At concentration of 10% the degradation was greater than the other conditions due to the strong influence of the copper phase. In contents above 15% phases Cu_3Ti, CuTi_2, Cu_4Ti_3 could have favored the tribological properties as had been reported in similar tribological pairs [31]. This results are associated to the behavior of porosity in the system and distribution of pores around phases with high hardness due to the strong covalent bonds of this phases [29,30], stimulating redeposit of free-material in low deformation regions. This phenomenon associated with reducing of wear is not fully clear in many metallic systems [32–34] in view of that each system the improvement and benefit of tribological properties is strongly related to pore size and distribution, hardness, and the nature of the released materials.

4. Conclusions

A Cu-Ti-TiC MMC had been observed under different synthesis conditions. It had been determined two types of morphologies due to the synthesis temperatures: at 750 °C a demarcation of the grains in the absence of extensive pores formation and at 850 °C different intermetallics compounds with presence of porosity in values reach to 16.8%. Phases such as CuTi, CuTi_2 had been detected in the grain limits of titanium at 750 °C and intermetallics Cu_3Ti, CuTi_2, CuTi_3, and Cu_4Ti_3 had been found in the interior.
of the MMC at 850 °C. The microstructural and tribological results suggest that a Cu-Ti-1%TiC MMC with titanium proportions higher than 15% have an adequate wear resistance in both process temperatures, despite the porosity the highest degree of wear resistance was obtained in sintering at 850 °C. Further studies are therefore necessary to determine the effects of heat and thermomechanical treatments in the configuration of the intermetallic layers, sealing of the porosity and degradation in this system under the same manufactured features to contribute in the interest and broadening of knowledge about this type of materials to enhance their applications in the industries.

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