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Additional Information

Synthesis and processing of improved graphite-molybdenum-titanium composites by colloidal route and spark plasma sintering

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Abstract

Graphite-molybdenum-titanium composites might attract significant interest as heat sinks for different sector applications due to their excellent thermal, electrical and mechanical properties. This type of composites was already studied but following the powder metallurgy and spark plasma sintering (SPS) route. The aim of the present investigation is to study a new route of fabrication of these composites to improve their properties: colloidal synthesis and SPS process. The results obtained for graphite-10 vol.% Mo-1 vol.% Ti composites prepared by both routes are compared. It has been proved that the properties of the composites are significantly improved by the colloidal route compared with the powder metallurgy route, i. e. electrical conductivity by a factor of 3, thermal properties by a factor of 8 and bending strength by a factor of 4.

1. Introduction

Graphite-molybdenum composites have been subject of research for many years due to the excellent thermal-mechanical properties conferred by the graphite and molybdenum carbides, which are formed when sintered together. Graphite itself exhibits good thermal and electrical conductivities, which explains some of its potential applications in electrodes, batteries, heat sinks, etc. However, it is an isotropic material, and when it is pressed, planes of atoms in the basal

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plane tend to orientate in the direction perpendicular to the pressing, which gives better thermal-mechanical properties in this direction.

The addition of reactive metals allows strengthening the carbons and, specially, the graphite. In the case of graphite and molybdenum, several researchers investigated the addition of molybdenum (carbides) to strengthen graphite. White and Pontelandolfo appreciated an improvement of thermal, electrical and mechanical properties of graphite-molybdenum carbide composites prepared at temperatures that involved liquid phase [1], [2], [3]. Harada and Rubin [4] investigated different mixtures of graphite-metals and graphite-metal carbides, including molybdenum, for which they studied the temperature when carbides appear and analyzed their electrical and mechanical properties. Graphite-molybdenum composites are used for extreme conditions applications (rocket nozzles [5]; collimators [6] or particle accelerators [7] that are used in the Large Hadron Collider at CERN [8]) due to the extraordinary thermal and electrical properties conferred by the molybdenum added to the graphite.

As opposed to the above-mentioned research articles, which are focused on graphite-molybdenum composites to be used in extreme conditions applications, the aim of the present work is to study the influence of using a colloidal route instead of the powder metallurgy one in the final properties of graphite-molybdenum-titanium composites after sintering them by spark plasma sintering.

2. Processing and characterization of the nanocomposites

2.1. Synthesis of powders

Graphite/molybdenum/titanium nanocomposites, containing 10 vol.% Mo and 1 vol.% Ti, were prepared following two different synthesis routes:

(1) Colloidal route: Graphite powder (grade 93004, Asbury Carbons Company), consisting of crystalline natural graphite with spheroidal-flake morphology with an average particle size in volume of $d_{50} = 6.007$ μm and a BET (Brunauer, Emmett and Teller) specific surface area of 16.84 m^2/g, was dispersed in absolute ethanol. A solution of molybdenum (V) chloride (Sigma-Aldrich, Spain) and a solution of titanium isopropoxide (ABCR, Spain) were added dropwise into the graphite dispersion. The slurry was first heated under magnetic stirring at 70 ºC and subsequently in air at 120 ºC for 24 hours to start the nucleation of molybdenum and titanium and eliminate any traces of alcohol. Dried powder was grounded and sieved through <180 μm. A thermal treatment at 450 ºC for 2 hours in air was made in order to eliminate chloride traces.

(2) Powder mixing by attrition milling: Graphite from Asbury Carbons Company, molybdenum (purity of 99.5%) from H. C. Starck, spherical particles with a mean particle size (d_{50}) of 5.5 μm (mode: 3.5-5.5 μm)) and titanium (titanium (purity of 99.5%) from Abcr GMbh, powder with

irregular morphology and a particle size < 45 μm) were mixed in propanol liquid medium using an attrition mill for 1 hour. Later, the slurry was first heated under magnetic stirring at 70 ºC and subsequently in air at 120 ºC for 24 hours to eliminate any traces of alcohol. Dried powder was grounded and sieved through <180 μm.

2.2. Spark Plasma Sintering (SPS)

Spark plasma sintering was chosen as sintering technique. Cylindrical samples with 40 mm were uniaxially pressed in a metallic mould at 15 MPa. Samples were inserted in the graphite mould and sintered at a heating rate of 25 ºC·min^{-1} up to 1500 ºC and 10 ºC·min^{-1} to the final temperature in a spark plasma sintering apparatus (FCT-HP D25/1) under an applied pressure of 30 MPa during all sintering process and in a vacuum condition (10^{-1} mbar). The final temperature achieved was 2000 ºC and holding time of 15 min.

2.3. Characterization techniques

High-resolution transmission electron microscopy (HRTEM) was employed using a JEOL JEM 2100F with an acceleration voltage of 200 kV with a field emission gun. This technique was used to check that molybdenum and titanium are chemically adhered to the surface of the graphite particles. Doped graphite by colloidal route was prepared for HRTEM by dispersing the final powder in ethanol. One drop of the dispersion was then dropped on the carbon-copper grid.

Powder and sintered samples were characterized by X-ray diffraction (XRD) on a Philips X' Pert Pro X-ray diffractometer by using Cu-Kα radiation (λ= 0.15406 nm) in the range from 5° to 70°. The step size was 0.03º and the step time 0.5 s. The identification of the crystalline phases was made by using diffraction pattern files provided by JCPDS (International Centre for Diffraction Data).

The microstructural characterization of graphite/molybdenum/titanium nanocomposites synthetized by colloidal route and attrition milling was performed by field emission scanning electron microscopy (FESEM) on a Quanta FEG 650 in the backscattered electron mode.

Relative density of the sintered samples was determined by geometric model using Eq. (1).

$$\rho \ (\%) = {^d}/_{d_{th}} \cdot 100 \qquad \text{Eq. 1}$$

where d is the measured-apparent density and d_{th} is the theoretical density obtained by helium pycnometer using AccuPyc 1330 V2.04N.

Young's modulus has been estimated from measurements of the resonance frequency (Grindosonic MK7, Belgium). The flexural strength values of the tested samples were obtained from three-point bending tests with 3 mm x 4 mm x 40 mm polished surface bars using a universal mechanical testing machine (Shimadzu-series AGS-IX, Japan) with a 10 kN load cell at a crosshead speed of 0.5 mm·min^{-1}. Those properties were measured on perpendicular and parallel face of the samples. The flexure strength (σ) was evaluated using the equation 2. Three samples (n = 3) were used, and data were presented as mean ± standard deviation (SD).

$$\sigma = {3FL}/{2bd^2} \qquad \qquad \text{Eq. 2}$$

where F is the load (force) at the fracture point, L is the length of the support spam, b and d are the width and the thickness of the sample, respectively.

Electrical conductivity was determined on the sample by four-point probe measurement, using the equipment PSM1735 - NumetriQ - Newtons 4th on parallel and perpendicular face to the uniaxial pressure. The average value of 10 measurements was considered as representative value of electrical conductivity of the sample.

The thermal diffusivity was measured according to the flash method using commercial equipment (LFA 457 MicroFlash, Netzsch). Samples with 10 mm x10 mm x 3 mm dimensions were prepared and the thermal diffusivity was measured in the parallel face to the uniaxial pressure. Specific heat was determined to calculate the thermal conductivity using a C80 (Setaram Instrumentation) calorimeter equipped with stainless steel cells (S60/1413). Specific heat determination is carried out in continuous mode, using a heating ramp of 0.1 °C·min^{-1} from 20 to 40 °C, with 2 hours of stabilization at the start and end temperatures. The data processing was carried out using the Calisto Software. Thermal conductivity values in the perpendicular face to the uniaxial pressure were calculated using the electrical conductivity following the equation 3 corresponding to Wiedemann-Franz law.

$$k/\sigma = L\,T \qquad \qquad \text{Eq. 3}$$

where k is the thermal conductivity, σ is the electrical conductivity, L is the Lorenz number and T is the temperature.

3. Results and discussion

3.1. Phase identification

Figure 1 shows the XRD pattern of samples of doped graphite powders by colloidal route and sintered by SPS. Graphite and MoO_3 are detected when the powders are heated in air at 450 ºC for 2 hours. After sintering in SPS at 2000 ºC, graphite and molybdenum carbide, MoC, are the mineralogical phases present in the samples prepared by colloidal route and powder mixing. MoC presents a cubic structure (a = 4.27 Å) and graphite peaks corresponding to very high levels of graphitization, matching the positions close to an ideal graphite structure (a = 2.46400 Å and c = 6.71100 Å) [9]. Carbon donates electron to metal atoms changing the coordination of metal atoms to conform the carbide structures. The metal-carbon bond is essentially of a metallic nature and contributes to stability of the carbide structure. At low temperatures Mo and graphite react to form hexagonal Mo_2C and this reaction continues by the diffusion of carbon inside Mo_2C to obtain MoC.
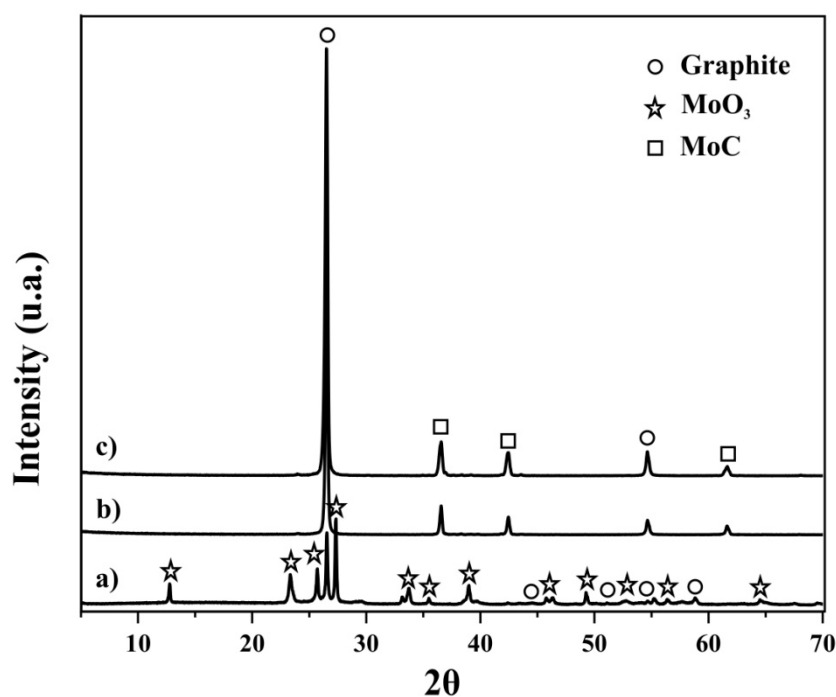

Figure 1. X-ray diffraction patterns of doped graphite powder obtained by colloidal route and calcined at 450 ºC for 2 hours (a), doped graphite powder obtained by colloidal route and sintered by SPS (b) and doped graphite powder obtained by attrition milling and sintered by SPS (c).

3.2. Microstructural characterization

High-resolution transmission electron microscopy (HRTEM) images at different magnification were taken to further investigate the configuration of reduced graphite-10 vol.% Mo-1 vol.% Ti synthesized by colloidal route at 850 ºC in H_2/Ar atmosphere. Images are shown in **Figure 2** where molybdenum carbide nanoparticles with a globular shape and with sizes ranging from 3 nm to 50 nm appear pinned to the layers of graphite.
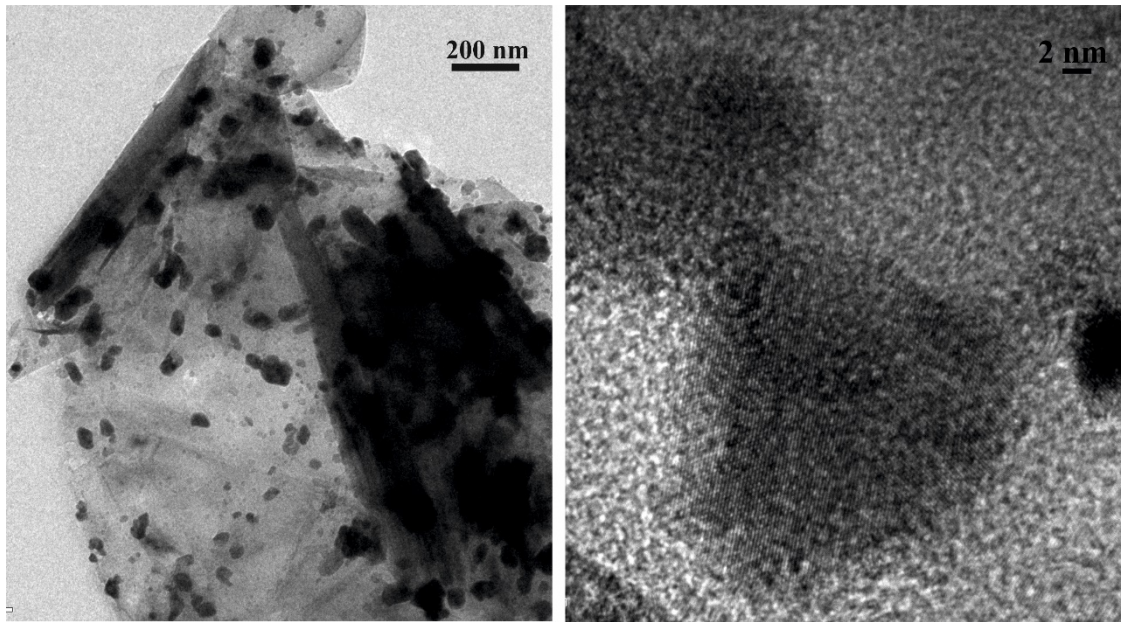

Figure 2. HRTEM images of reduced modified graphite at 850 ºC for 2 hours and synthetized by colloidal route.

Figure 3 shows FESEM micrographs of polished doped graphite samples prepared by both attrition milling (**Figure 3a**) and colloidal processing route (**Figure 3b**) and sintered by SPS. Both samples show a homogeneous distribution of second phase (white phase, molybdenum carbide) on the graphite matrix (black phase). The main difference between both samples is related to the particle size, 6 μm in case of the sample prepared by attrition milling and 4 μm for sample obtained by colloidal route, due to the presence of MoC agglomerates in the first case. Doping process has a great influence on the microstructure and is reflected on the final properties of the sintered samples.
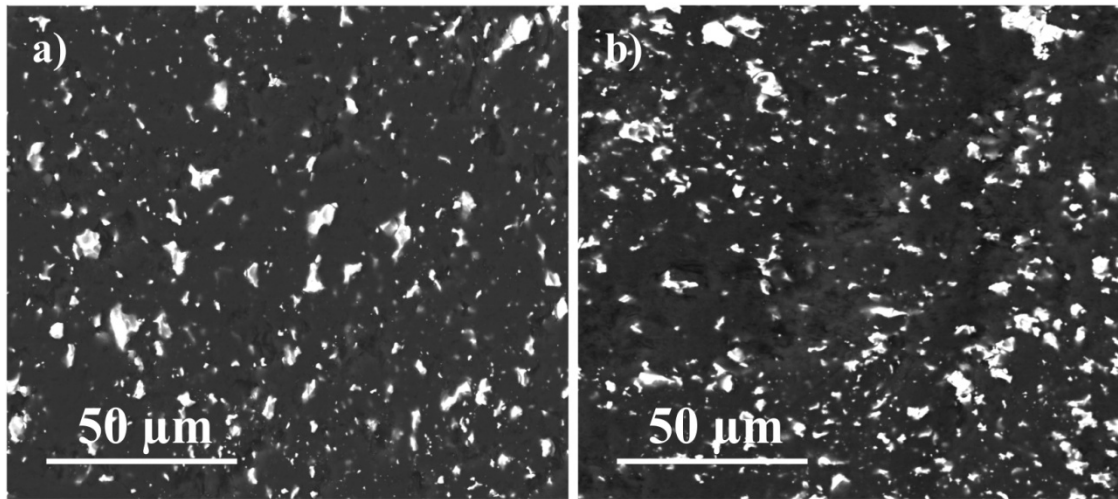
Figure 3. FESEM polished surface of dopped graphite by attrition milling (a) and colloidal route (b) and sintered by SPS.

3.3. Density

Natural graphite powders compact into high density samples with very little applied pressures. This behaviour is caused by its self-lubricating properties that allow intimate packing. However, when metal powders are cold compacted together with the graphite, the presence of these metallic particles reduces the graphite lubricating properties and therefore the packing of the composite.

Green density of the sample has been measured for both processing routes (attrition milling and colloidal route). Results are collected in **Table 1**. Higher green density value has been obtained in case of the samples sintered by colloidal route. Deformation temperature of the composite depends on the amount of disperse constituent. In case of samples processed by attrition milling, MoC nanoparticles are more agglomerated (they are less homogeneously distributed in the graphite matrix) increasing the particle size and the distance between the particles. A homogeneous distribution of the MoC in the graphite matrix for the sample obtained by colloidal route allows obtaining higher density values of the sintered samples.

Table 1. Density of SPS sintered samples.

Reference	Green density (g/cc)	SPS sample density (%)
Attrition milling	1.54	92.1
Colloidal route	1.59	95.2

3.4. Mechanical characterization

Strength and elastic properties have been evaluated and the obtained results are presented in **Table 2**. The properties of molybdenum-doped graphite show a clear anisotropic behaviour since the properties depend on the orientation of the graphite flakes due to the stronger interatomic bond in the perpendicular direction to the applied pressure. The presence of MoC nanoparticles and the strong carbide-graphite bond in samples obtained by colloidal route allows obtaining better mechanical properties: in the bending strength test, samples improve up to 65% and 80% when the orientation is perpendicular and parallel, respectively to attrition milling.

Table 2. Mechanical properties of doped graphite samples obtained by attrition milling and colloidal route after sintered by SPS.

Direction	Attrition milling		Colloidal route	
	⊥	∥	⊥	∥
Bending strength (MPa)	48.09	29.90	135.54	129.68
Elastic modulus (GPa)	79.57	54.25	134.68	60.48

3.5. Electrical conductivity

Superficial electrical conductivity measurements on sintered samples obtained by attrition milling and colloidal route are shown in **Table 3**. The electrical conductivity in the perpendicular direction to the applied pressure is higher than in the parallel direction in both types of samples.

Table 3. Electrical properties of doped graphite samples obtained by attrition milling and colloidal route after sintered by SPS.

	Attrition milling		Colloidal route	
Direction	⊥	∥	⊥	∥
Electrical conductivity (MS·m^{-1})	0.32	0.26	0.99	0.16

3.6. Thermal conductivity

Thermal conductivity in graphite is dominated by phonon conduction and the values obtained follow the trend of the electrical conductivity being this value higher in the perpendicular direction to the pressure in both samples. Diffusivity in the perpendicular direction to the applied pressure cannot be determined by means of the equipment model LFA 457 MicroFlash, Netzsch

because of the thickness of the samples. Therefore, we use the Wiedemann-Franz law to indirectly determine the thermal conductivity by means of the electrical conductivity in this direction. The Lorenz Number is calculated by the thermal and electrical conductivities obtained in the perpendicular direction for each sample, and it is assumed that the Lorenz Number is the same in both directions.

Results are collected in **Table 4**. As in the case of other properties, better results are obtained in the case of samples synthesized by colloidal route.

Table 4. Thermal properties of SPSed doped graphite samples obtained by attrition milling and colloidal route.

	Powder metallurgy + SPS		Colloidal route + SPS	
Direction	⊥	∥	⊥	∥
Thermal conductivity (W·m^{-1}·K^{-1})	17.54	14.25	136.68	22.09

3.7. Discussion

Graphite reinforced with metallic materials is attracting significant interest for applications in the thermal domain (heat sinks for electronic devices or for high speed trains) due to the excellent properties. In the case of the graphite-molybdenum, there is no significant research, and most of it is mainly focused on applications for extreme conditions as different parts for rockets [**¡Error! Marcador no definido.**] or, most recently, for collimators to be used in the Large Hadron Collider at CERN [**¡Error! Marcador no definido.**]. However, graphite-molybdenum composites might find application in more common fields as those above indicated.

A main relevant conclusion is that the sintered material exhibits directional properties, with better properties in the direction perpendicular to the applied pressure, and discs sintered from powders obtained by the colloidal route have better properties than those sintered from powders obtained by simple mixing of powders, i. e. bending strength increases by a factor of 4. The first question can be explained because graphite particles orient themselves perpendicular to the pressing direction by SPS, where the best properties are exhibited. Additionally, molybdenum carbides when finely dispersed as nanoparticles (see **Figure 2**) inhibit basal planes slip through a pinning effect according to scheme shown in **Figure 4** and, therefore, enhance mechanical properties. The second question can be explained by the more homogeneous distribution of the molybdenum in the graphite matrix. This way, the improvement conferred by the molybdenum carbides is not deteriorated. And the third and significant question is that the sintering does not involve liquid

phase, as in other research work with graphite-molybdenum composites, since temperature did not exceed 2000 ºC.
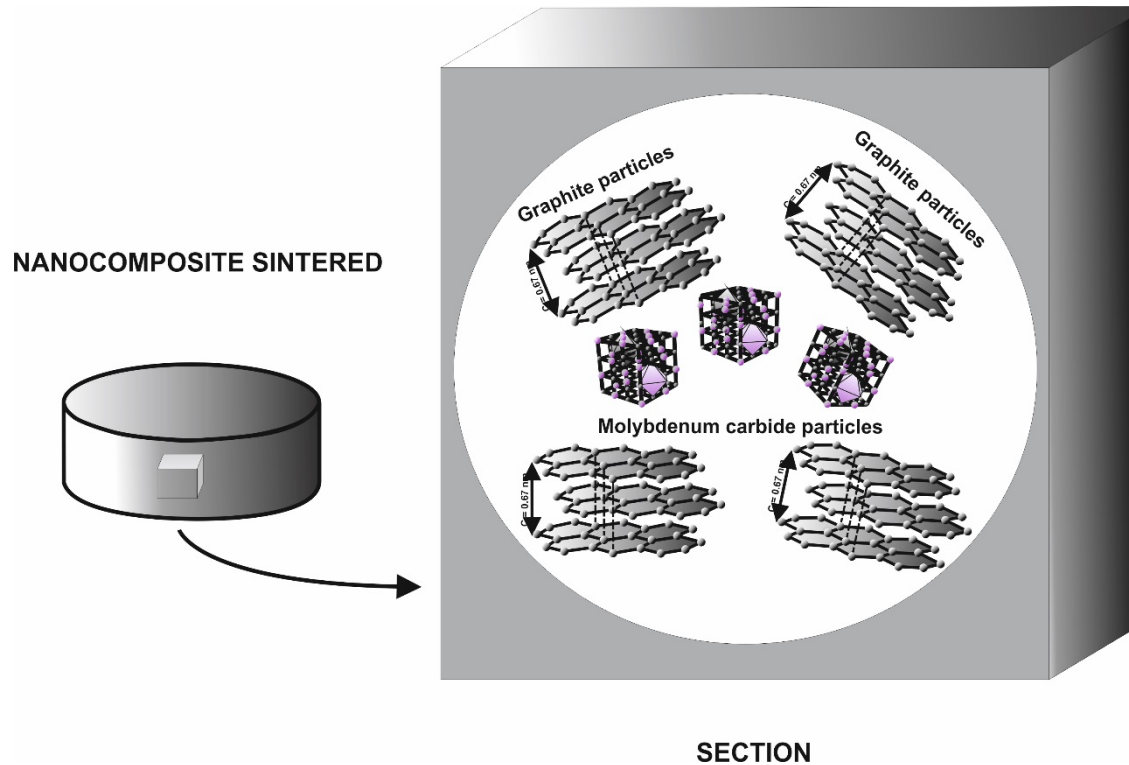

SECTION

Figure 4. Distribution of molybdenum carbide on the graphite matrix in SPS samples.

The dependence of the properties on the direction was observed by J. L White and J. M. Pontelandolfo [2] in 1966. There is a strong interatomic bond in the perpendicular direction to the applied pressure of the molybdenum-doped graphite composite. Properties also depend on the doping method followed for preparing the materials. According to the results shown in **Table 2**, the bending strength, and the elastic modulus in the perpendicular direction to the applied pressure (136 MPa and 135 GPa, respectively) are three and two times greater, respectively, in samples obtained by colloidal route than by attrition milling. These values are significantly greater if compared with those found in the literature for this kind of materials [¡**Error! Marcador no definido.**]. Three reasons would explain the increase of the strength: 1) increasing amounts of metal additions, 2) increasing pressing temperature and 3) decreasing carbide particle size.

Samples prepared by colloidal route have in perpendicular direction an electrical conductivity about three times higher than samples obtained by attrition milling. This value is like that of sintered molybdenum-graphite composites prepared at temperatures as high as 2600 ºC [¡**Error! Marcador no definido.**]. Colloidal route technique allows obtaining composites with high electrical conductivity at a temperature as low as 2000 ºC (versus the 2600 ºC usually used) since

the good contact and homogeneous distribution between graphite carbon layers and MoC nanoparticles enhances the electrical conductivity of the composites in one direction [10].

4. Conclusions

Graphite-molybdenum-titanium composites were prepared by spark plasma sintering from powders prepared by either colloidal route or powder mixing by attrition milling. Specimens were characterized by different techniques and mechanical, thermal, and electrical properties are significantly better (electrical conductivity by a factor of 3, thermal properties by a factor of 8 and bending strength by a factor of 4) in the case of the composites prepared by means of the colloidal synthesis. Therefore, graphite-molybdenum-titanium composites could be prepared by the colloidal route and spark plasma sintering at temperature <2000 ºC in solid state, which is 600 ºC lower than in other researches, with adequate properties for heat sink in different sector applications.

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