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Electron microscopy characterization of mechanically alloyed and hot consolidates $Cu\text{-}Cr_3C_2$ particles(•)

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Abstract

Mechanically alloyed copper-ceramic composites have been obtained with the purpose of studying their use as copper-based material for electrical equipment. For high-temperature applications, dispersion-strengthened copper alloys are attractive due to their excellent combination of thermal and electrical conductivity, mechanical strength retention and microstructural stability. In this work, powder mixtures of pure copper with 2 vol % Cr_3C_2, milled during 4, 6, 10, 12 and 15 h in a high-energy planetary balls mill under argon atmosphere, were consolidated by hot isostatic pressing, applying a pressure of 100 MPa at 1073 K for two hours, to obtain materials with a fine microstructure. The $Cu\text{-}Cr_3C_2$ alloys were studied by scanning electron microscopy (SEM), electron microprobe (EPMA) and transmission electron microscopy (TEM). Mechanical properties and electrical conductivity were also studied. The average tensile strength and electrical conductivity were found to be 500 MPa and 50 % IACS, respectively. The Cr_3C_2 ceramics show good stability during hot consolidation. Contributing to a further strengthening of the alloy during the hot consolidation, uniformly-distributed Fe-carbide particles of nanometric size precipitated in the copper matrix. Fe-Cr oxycarbides formed in the interphase between Cr_3C_2 particles and the copper matrix cause the low ductility of $Cu\text{-}Cr_3C_2$ alloys. Said particles are attributed to impurities/contamination generated from the milling process.

Keywords Mechanical alloying. Copper-ceramics. Composites. Properties.

Caracterización por microscopía electrónica de partículas $Cu\text{-}Cr_3C_2$ aleadas mecánicamente y consolidadas en caliente

Resumen

Se obtuvieron aleaciones compuestas de $Cu\text{-}Cr_3C_2$, aleadas mecánicamente, para estudiar futuras aplicaciones en componentes eléctricos. A altas temperaturas, las aleaciones de base cobre reforzadas por dispersión, son atractivas por su excelente conductividad térmica y eléctrica, propiedades mecánicas y estabilidad microstructural. En este estudio, mezclas de polvo de cobre puro con un 2 % en vol. de Cr_3C_2, obtenidas mediante molienda en un molino de bolas planetario de alta energía, durante 4, 6, 10, 12 y 15 h, se compactaron isostáticamente en caliente a 1.073 K durante 2 h con una presión de 100 MPa en argón, para obtener un material con una microestructura fina. Las aleaciones de $Cu\text{-}Cr_3C_2$ se estudiaron mediante microscopía electrónica de barrido MEB y de transmisión MET, además de microsonda electrónica. También, se caracterizaron las propiedades mecánicas y la conductividad eléctrica, obteniéndose valores de 500 MPa y 50 % IACS, respectivamente. Las cerámicas de Cr_3C_2 presentan una buena estabilidad durante la compactación en caliente. Se observó la precipitación de partículas de tamaño nanométrico en la matriz de cobre, consistentes en carburos de hierro precipitados en ella, lo que contribuye al reforzamiento adicional de estas aleaciones. Los oxicarburos de Fe-Cr, formados en la interfase entre partículas de Cr_3C_2 y la matriz de cobre provocan la baja ductilidad de estas aleaciones. Estas partículas son atribuibles a impurezas y contaminación generada durante el proceso de molienda.

Palabras clave Cobre-cerámicas. Compuestos. Aleado mecánico. Propiedades.

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1. INTRODUCTION

Copper and copper alloys are extensively used for a wide range of applications requiring high electrical and thermal conductivities and good mechanical properties such as electric switches and contactors, brushes and electrodes for welding and electro discharge machining. However, above 530 K, wrought copper has only moderate tensile and yield strength, and a low hardness. To overcome this problem, any inhomogeneity interacting with dislocations can be used as a strengthener. The most effective are: grain boundary pinning and precipitation, or dispersion of submicron particles. For the latter, there are three main methods to produce fine particles of secondary phases in materials: fine precipitation particles from a supersaturated solid solution, mechanical alloying (MA), and internal oxidation[1]. These methods have been used for the development of several strengthened copper alloys during the last years, trying to find a good combination of electrical conductivity and relatively high mechanical strength and hardness, at moderate temperature[2-5]. The MA process, developed initially for the production of oxide-dispersion-strengthened superalloys, has been reported as a method for producing composite metal ceramics powders, refining the microstructure to the nanometer range and obtaining alloys with extended solubilities. One of the important determinants of this process is the large amount of energy transmitted to the powders during high-energy ball milling. This energy is used to deform heavily and repeatedly the starting materials, producing an alloy or a composite material of metal and ceramic particles, both with a fine microstructure. Dispersion-strengthened copper alloys have also been obtained by mechanical alloying or milling with different kind of ceramics and intermetallic dispersoids[3-7]. Ceramics are required to have a very low solubility in copper, high melting points and low interphase energy in order to guarantee the stability of the microstructure during the consolidation process. In this work, dispersion-strengthened copper materials have been developed by mechanical alloying with Cr_3C_2 compounds. The main purpose was to test the feasibility of their use as base material for usual applications: electrical contactors, switches, contact tips for welding, electrode caps and others. As residual porosity has a detrimental effect on the mechanical and electrical properties, consolidation was performed by hot isostatic pressing (HIP). This technique and other hot consolidation processes such as extrusion, forging and rolling are conventionally used to produce powder metallurgy (PM) components without porosity[7 and 8].

2. MATERIALS AND EXPERIMENTAL PROCEDURE

MA process was carried out using a planetary ball mill made of stainless steel with a ball/powder ratio of 5:1 and 10:1 under argon atmosphere. The starting materials were spherical copper powders under 150 mesh and 2 vol % of chromium carbide particles with a size smaller than 325 mesh. Ethylene glycol was added as a process control agent (PCA) to minimize powder sticking and agglomeration. As results of preliminary evaluation, it was determined that a milling time of 12 hours was required to ensure a homogeneous dispersion of carbide particles lower than 20 µm in size[6]. Milled powders were characterized by X-ray diffraction, scanning electron microscope and a Vickers microhardness tester. Powders mechanically alloyed for 12 h were consolidated by hot isostatic pressing (HIP) under argon atmosphere at 1073 K and 100 MPa for 2 h to obtain a fully dense composite material. After consolidation, microstructural characterization was performed using a JEOL transmission electron microscope equipped with an energy dispersive X-ray analyzer (EDAX) and a JEOL-WDX microprobe. Electrical conductivity was measured by a Kelvin Bridge.

3. RESULTS AND DISCUSSION

Table I shows the variation in microhardness of the mechanically alloyed powders as a function of milling time for each of the two ball-to-powder charge ratios used. Upon incrementing the milling time, the hardness increases up to a maximum value of 461 HV after 12 h. The saturation hardness is reached after 12 h. For longer milling times, the HV varies scarcely, indicating that a steady state, in which hardening and softening processes are balanced, is achieved[3]. The microhardness of the Cu-Cr_3C_2 samples with a 10:1 ball/powder ratio was ≅ 9 % higher than that of 5:1 ratio samples. This behavior is associated with the increase of cold work applied to the powder.

The X-ray diffraction patterns of the MA powder for the five milling times selected, show that the spectra becomes broader and peak

Table I. Microhardness (HV) variation of MA powders

Tabla I. Variación de la microdureza Vickers en polvos AM

Alloy	Milling time (h)				
	2	4	6	12	15
Cu-Cr_3C_2 (5:1)	103.0	99.5	355.5	423.3	384.6
Cu-Cr_3C_2 (10:1)	91.8	356.4	438.3	461.1	430.9

intensities decrease, but positions stay at the same diffraction angles with milling time, indicating a change in the crystal parameters of copper due to its lattice deformation, excluding any formation of solid solution. Since the milling process involves massive plastic deformation, the broadening of the peaks was attributed to an increase of residual strength and a decrease of the grain size.

The mechanical and physical characteristics of the consolidated alloys by hot isostatic pressing as a function of the ball-to-powder charge ratio, are shown in table II.

The use of the steel vial and balls and the required PCA, inevitably introduces Fe, Cr, C and oxygen into the milled powder. The increase in tensile stress compared with the reported data for pure Cu was related with the presence of Fe-Cr and oxide dispersoids. Two strengthening effects can be attributed to the presence of these dispersoids: blocking of dislocation slip produced by Fe-Cr particles finer than 5 nm included within the grain, and control of the grain size induced by the bigger Fe-Cr and copper oxide particles during powder consolidation by HIPing. The sum of both strengthening mechanisms leads to an increase of tensile strength from 220 MPa for pure copper to 516 MPa for theCu-Cr_3C_2 reinforced material. The low ductility of Cu -Cr_3C_2 alloys, less than 5 %, is also to be attributed to contamination. These impurities could produce precipitation of Fe-Cr-C-O rich phases or new fine particles of second phase during HIPing. The composite materials developed herein present higher strength and mechanical properties than pure copper a decrease in electrical conductivity to 52 IACS (IACS: International Annealed Copper Standard; 100 % IACS equals 58.0 m/ Ω mm^2) was found. Although this value does not fulfill the requirements for electrical conductors, these materials could be still be successfully used in other fields of electrotechnology. Copper alloys used for household power outlets, contact tips for submerged welding, and electrodes for electrical spot welding, to name a few, must provide high mechanical strength in addition to high values of electrical conductivity. Copper alloys used at present show similar electrical conductivity and tensile strength or hardness to those of the Cu-Cr_3C_2 alloy developed for this investigation. Dispersion-strengthened PM Cu-Al-Ti-C-O alloy manufactured for contact tips used in submerged welding and resistant welding exhibit 95HRb and 48%IACS[9]. Furthermore, the decrease in electrical conductivity of both Cu-Cr_3C_2 alloys herein seems to be related to the impurity content rather than the degree of deformation and the grain size refinement.

Table II. Electrical and mechanical properties

Tabla II. Propiedades eléctricas y mecánicas

Alloy/ Material	Resistivity mΩ	Conductivity % IACS	Hardness HRb	Tensile strength MPa
Cu 99,99% wrought	1.724	101	28	216
Cu-Cr_3C_2 5:1	3.32	52	96	516
Cu-Cr_3C_2 10:1	3.85	44	92	436
Cu- 99,99% (5:1)(*)	2.43	71	68HRT	208

(*)hot-pressed powder

3.1. Microstructure of consolidated alloys

As showed in figure 1, the hot-consolidated Cu-Cr_3C_2 (10:1) material shows, after etching, a bimodal microstructure composed of coarse copper grains of about 10 µm in size and irregular fine-grained areas. Figure 2 shows the distribution of Cr_3C_2 dispersoids (black particles), of different sizes, near the hole boundary on the TEM sample. Second-phase precipitates are not visible in this SEM image. A maximum of 0,84 % Fe and 0,15 % Cr was detected in the coarse copper grains of figure1 and observed as residual free copper particles. EDX spectrum showed in figure 4, revealed the presence of some amount of Fe, Cr, C and O in the grained regions. EPMA microprobe measured the average contents of these elements on different points of the samples, where a content of iron and chromium of 1.8 and 1.73 wt %, respectively, was determined after 12 hours milling. Oxygen content of 0.69 wt % was measured by LECO analyzer. An examination of these zones at high magnification performed by TEM analysis revealed the presence of very small dispersed particles with irregular morphology, as observed in figure 3.

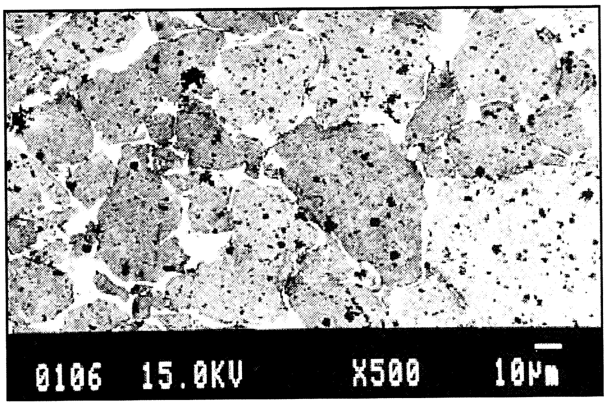

Figure 1. EPMA BEI image of HIPed powders, showing an heterogeneous structure with two phases. White phase are pure copper regions and grey phase is a copper alloy with fine dispersoids of chromium carbides.

Figura 1. Imagen BEI de microsonda, muestra la microestructura heterogénea de dos fases. Fase blanca es región de cobre puro y fase gris corresponde a mezcla aleada de Cu con Cr_3C_2 finamente dispersos.

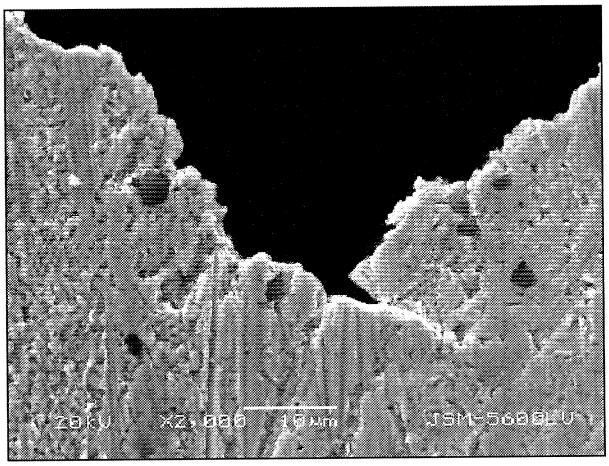

Figure 2. SEM image of fine-sized Cr3C2 ceramics near hole boundary on TEM sample.

Figura 2. Imagen MEB de cerámicas de Cr_3C_2 de tamaño fino en borde de la perforación de muestra MET.

The heterogeneous two-phase structure consisted of carbides dispersed in a copper matrix (predominant gray regions) joined by practically pure copper regions. Pure copper regions appear as the welding diffusion interphase between the particles of the alloy, suggesting that those regions were never in contact with the surface of the ball. The non-uniform microstructure suggests an incomplete MA process or milling time.

Residual pure copper regions present neither Fe-Cr nor oxide particles, all of which block dislocation slip. Thus, grain growth during hipping at 850 °C

Figure 3. TEM micrograph, shows bright field image.

Figura 3. Imagen TEM en campo claro.

could take place in these regions. The heterogeneity of the structure and the excess of impurities precipitated as small oxide particles during hot consolidation by the reaction of Fe, C and O with the Cr_3C_2 added in their interface with copper matrix, are probably the main causes of the low ductility, showed by the whole alloy. Similar precipitation was found in other dispersion-strengthened PM copper alloys[10]. The effect of HIP on the mechanical alloying studied by TEM observations confirmed the precipitation of Fe,Cr-rich phases, as shown in figure 3. TEM examination reveals refined nanometric Cr_3C_2 particles and precipitates corresponding to other phases within the copper grain. The size of most of the precipitates is quite small for EDAX analysis, so it is not clear whether the precipitates are (Fe,Cr,Cu) oxycarbides, (Fe,Cr) phase or other second-phase compound. EDAX microanalisys of coarse precipitates, around 50 nm in size, shows mainly Cr and Fe peaks. On the other hand, TEM examination of milled and hot-pressed pure copper reveals only deformation lines in copper without precipitated base (Fe,Cr)-rich particles as shown in

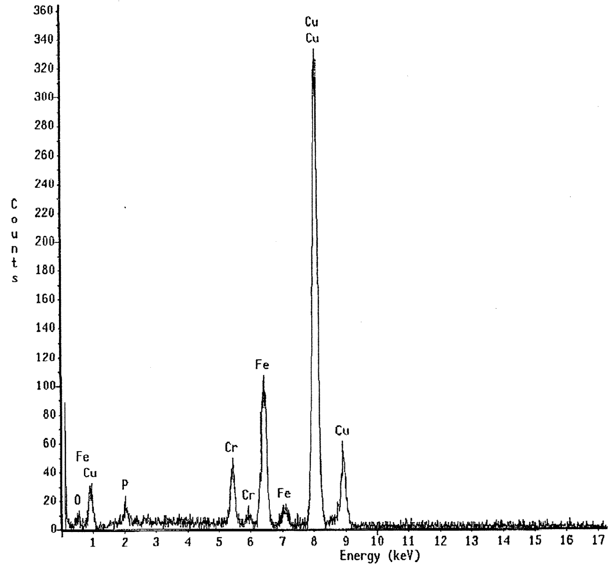

Figure 4. EDAX spectra of precipitate in Cu-Cr_3C_2 alloy.

Figura 4. Espectro de EDAX en el precipitado de la aleación Cu-Cr_3C_2.

figure 5. This suggests that the nucleation mechanism of (Fe,Cr) precipitates is similar to the precipitate nucleation mechanism in many age-hardened alloys, where a minimum content of them in solid solution state is required.

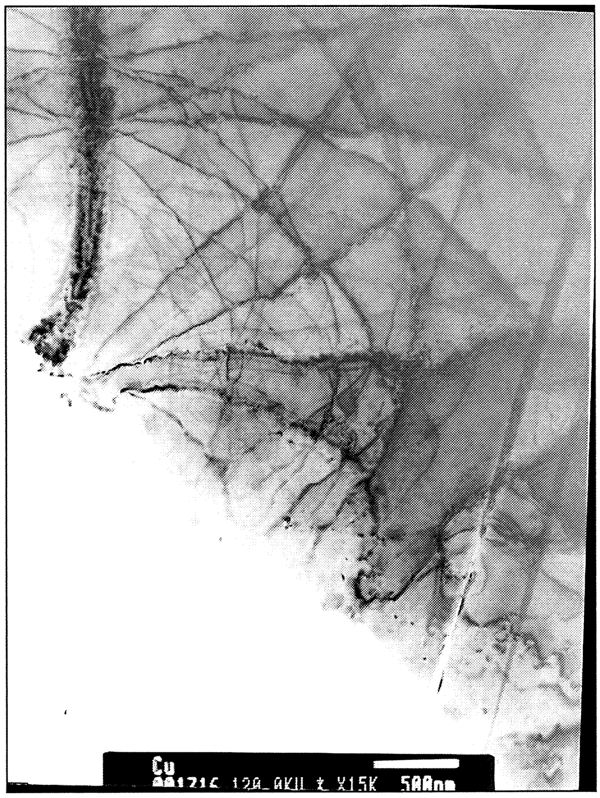

Figure 5. TEM bright field image of pure milled and hot-consolidated Cu.

Figura 5. Imagen TEM en campo claro de cobre puro molido y compactado.

4. CONCLUSIONS

- Cu-Cr_3C_2 alloys were successfully produced by a combination of mechanical milling and hot isostatic pressing without porosity. Cr_3C_2 carbides dispersed by mechanical alloying substantially increase the mechanical strength and hardness of copper. Contributing to a further strengthening of the alloy during the hot consolidation, uniformly-distributed Fe-carbide particles of nanometric size precipitate in the copper matrix. Fe-Cr oxycarbides formed in the interphase between Cr_3C_2 particles and the copper matrix excite the low ductility of Cu-Cr_3C_2 alloys. Said particles are attributed to impurities/contamination generated from the milling process.
- The combination of electrical and mechanical properties obtained provide excellent grounds to decide on the suitability for a certain application of this alloy as base material for some special electrical contactors.

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FE DE ERRATAS

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En la segunda línea de la cabecera de cada una de las páginas, dice:

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