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Liquid phase sintering of mechanically alloyed Mo-Cu powders

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ABSTRACT

In the Mo-Cu system, Mo has very low solubility in liquid Cu. To reach high densities after liquid phase sintering it is required the solution-reprecipitation step, which induces shape change. One technique that allows to form solids solutions out of equilibrium is the mechanical alloying. In the present work, the effect of the mechanical alloying of the elemental Mo and Cu (10, 20 and 30 vol%) powders and the sintering atmosphere (Ar vs Ar + 10 vol% H_2) on the densification, microstructure and hardness of sintered samples in liquid phase at 1150 °C for 1 h, was studied. It is hypothesized that the sintering can be facilitated by the generation of a solid solution of Mo in Cu out of equilibrium which, allows the Mo to enter solution in the Cu liquid and re-precipitate on the solid Mo particles during the process.

The results show that mechanically alloyed Mo-Cu and sintered powders in the reducing atmosphere of Ar + 10 vol% H_2, have the highest densities and densification of all studied alloys. This is explained by the formation of solid solution of Mo in Cu during the mechanical alloying, evidenced by the EDS analysis. It is suggested that these milled and sintered powders reach the highest hardness due to their microstructural refinement, high density of Mo dislocations and low porosity.

1. Introduction

Mo-Cu alloys have been investigated for many years because of their relatively low and constant coefficient of thermal expansion (of up to 1073 K) and their high thermal and electrical conductivity, which make them suitable for contact materials in cooling and electronic packages [1]. The significant difference between the melting points of both metals and their insolubility make traditional metallurgical processes inappropriate to obtain these alloys due to their the high-energy consumption. The infiltration method by which a pre-sintered porous Mo skeleton infiltrates with Cu, high density obtained, but this method is a complex process due to Cu exudation and grain growth in the microstructure [2]. Liquid phase sintering (LPS) of mixed microcrystalline powders usually does not reach high density since the solution-reprecipitation (SR) step requires solid constitutes (Mo) to enter in liquid phase (Cu) leading to the change of shape and thus increasing density will not occur. Due the mutual insolubility of the solid and liquid state of Mo and Cu [3–5].

The Mechanical Alloying (MA) is a method developed over the past decades (since the 1970s), which allows an increase in the solubility of the insoluble elemental powders outside of the equilibrium [2,5,6]. In this method, the powders are subjected to repetitive impacts at high speed, which cause plastic deformation and hardening and cold welding. At the same time, together with the hardening, the fracture of the powders occurs. All the processes are continuously repeated to achieve the desired results of mechanical alloying [6,7].

The use of the MA method to incorporate Mo in Cu has been studied by Martínez et. al. [7]. It showed an increase of Mo in solid solution in the Cu with the milling time of up to 100 h. The increase in the solubility of Mo in Cu was explained by a thermodynamic analysis. At 21 h, crystallite sizes of approximately 15–40 nm were obtained whereas higher molybdenum powders showed a lower decrease of grain size. After 21 h of grinding, recrystallization and agglomeration processes were observed.

In another work [8], the mechanical alloying of Cu-Mo under a controlled atmosphere of Ar was carried out. The evolution of grain size as a function of milling time was studied and it was determined that, for 50 h of milling time, a minimum crystallite size of 20 nm was reached for the compound powders of Cu-8 at% in Mo.

Xi and others [9] analyzed the AM of binary and ternary systems based on the Cu-Mo alloys. They found the possibility of dissolving Mo up to 10 wt% in copper by MA.

Jinglian and others [10] were able to obtain pre-alloyed Mo-18, 30, and 40 wt% Cu using the sol-spray-drying process in which Mo and Cu

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Table 1
Description of the samples and their characteristics.

Samples	Process Conditions	Sintering atmosphere
Simple mix: (Mo + Cu)m	Elemental powder Mo and Cu mixed Mo − 10 vol%Cu Mo − 20 vol%Cu Mo − 30 vol%Cu	Ar + 10 vol% H_2
MA powders	Elemental powder Mo and Cu Mo − 10 vol%Cu Mo − 20 vol%Cu Mo − 30 vol%Cu	Ar + 10 vol% H_2
Mix: Mo + (Mo + Cu)m-Ar	MA powders + Mo elemental mixed (Mo + (Simple mix) 10 vol%Cu) (Mo + (Simple mix) 20 vol%Cu) (Mo + (Simple mix) 30 vol%Cu)	Ar
Mix: Mo + (Mo + Cu)m-(Ar + 10 vol%H_2)	MA powders + Mo elementary mixed (Mo + (Simple mix) 10 vol%Cu) (Mo + (Simple mix) 20 vol%Cu) (Mo + (Simple mix) 30 vol%Cu)	Ar + 10 vol% H_2.

salts were heated and reduced to a size of 30 nm and 28 nm for the Mo and Cu, respectively. The powders were compacted and sintered in the liquid phase with a controlled atmosphere of H_2. After sintering, high densities (99%) were obtained in the samples with 30 wt% Cu. It was also found that a maximum amount of liquid phase was achieved for 30 wt% Cu; for higher amounts of Cu, the density decreased. This phenomenon was attributed to the high temperature and the volatilization of the copper rich phase.

Song et al. [11] studied the effect of liquid phase sintering of prealloyed Mo-15 wt% Cu powders, which were made through the chemical gelling-reduction process. Powders having sizes in the ranges from 100 to 200 nm were obtained. These powders were subjected to three sintering temperatures (1050, 1100, and 1150 °C) under a controlled atmosphere of H_2, reaching a final relative density of 99.59% for the sample sintered at 1150 °C.

Based on the literature review, it can be concluded that to achieve high density of Mo-Cu alloys in the LPS, it is necessary to produce nanometric powders of Mo and Cu using chemical methods. It should be noted that the LPS of mechanically alloyed Mo-Cu powders was not investigated.

In the present study, it is proposed that the SR mechanism can be proceed in three stages to overcome the mutual insolubility of Mo and Cu that prevents the occurrence of SR. In the first stage, during MA occurs the incorporation of Mo in solid solution in the Cu, out of equilibrium. In the second stage, during the LPS and when the Cu-rich phase is transformed from solid to liquid, the Mo atoms of this phase entered into the liquid solution of Cu. In the final stage, the atoms of Mo in the liquid phase would re-precipitate on the particles of solid Mo, leading to the change of form and them, densification. The stages mentioned could occur, since milled powder of Mo must contain Cu in solid solution beyond equilibrium, is a situation similar to what happens in transient liquid phases, in which one of the initial components, the low melting point (Cu in this case) melts and homogenizes the composition until it reaches equilibrium. Then, in this case, liquid Cu would initially be formed in greater quantity than the equilibrium and the amount of liquid would be reduced by homogenization, reaching equilibrium.

During this process, the influence of the mechanical alloying on the density, microstructure, and hardness for elemental Mo-Cu powders was analyzed. Also, the influence of adding Mo elemental powders to the mechanically alloyed Mo-Cu powders was investigated with the aim of increasing the green density of the compact and allowing a higher sintering density to be obtained as compared to the process with only mechanically alloyed powders, which have the difficulties that requires high pressures for compaction to achieve high green density.

Finally, the effect of the atmosphere on densification was investigated by comparing Ar to Ar + 10 vol% H_2. It was expected that H_2 would act to reduce surface oxides of Mo and Cu powders and thus would facilitate the LPS [5].

2. Materials and methods

2.1. Powders

Cu elemental powders with a purity of 99.99% and 90% and the size less than 45 µm of dendritic morphology were purchased from ACU Powder International. Mo powders with 99.95% purity and an average size of 5.1 µm were supplied by Molymet S.A. (Chile).

2.2. Mechanical alloying

(1-x)%Mo-xCu (x = 10, 20 and 30 vol%) powders were milled using a home-made Szegvari Attritor Grinding Mill with 1500 cc capacity stainless steel container at 500 rpm under a controlled atmosphere of Ar with a flow of 1 l/min and Hexane as the controlling agent. The mass ratio of 4.8 mm stainless steel balls to the powder was 10:1. The milling times were 10, 20 and 30 h for each of Mo-Cu alloys. Once the process was completed, the recovered powders were dried for one hour under halogen lamp, and compacted at 450 MPa to fabricate 1.5 g bars with 12 mm diameter which were sintered at 1150 °C for 1 h in a mixture of Ar + 10 vol% H_2 or only Ar and cooled down in the furnace.

Table 1 shows the process conditions for the four series of manufactured alloys and their designation.

2.3. Materials characterization

The elemental powders of Mo and Cu were characterized by scanning electron microscopy (SEM; JEOL, JSM-IT300) and EDS to determine their shape, distribution, size and composition. Structural characteristics of samples were analyzed through X-Ray Diffraction (XRD; Bruker D8), using Cu° Kα1 radiation (λ = 1.5405 Å) with an increase of 0.02° and a passage time of 56.7 s. The sweep angle range varies from $2° < 2\theta < 80°$. The green density of the samples was obtained by geometrical method. After sintering, the Archimedes Method was used to obtain the density. Porosity was measured from the density by the following Eq. (1):

$$\varepsilon = 1 - \frac{\rho_{final}}{\rho_{theoric}} \quad (1)$$

where ε is the porosity and ρ is the density.

The microstructural features such as type and distribution of present phases were characterized by optical microscope. The Vickers