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Effect of processing parameters on the mechano-chemical synthesis of nano crystalline Mo-Cu/Al_2O_3 composite

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ABSTRACT

In this study, molybdenum-copper/alumina nano composite was synthesized with mechano-chemical method using high energy planetary ball milling. The molybdenum oxide, copper oxide and aluminum powder were used as starting materials and reaction appeared to occur through a rapid combustion reaction process. The evaluation of powder particles after different milling times was studied by X-ray diffraction (XRD), differential thermal analysis/thermogravimetric (DTA/TG) and scanning electron microscopy (SEM). XRD results show that with increasing milling time at ambient temperature the peak intensities of powders decreases and significant peak broadening due to decrease in the size of crystallites observed. As a result, after 100 h milling time a molybdenum-copper/alumina metal matrix nanocomposite was formed which matrix had a crystallite size of about 42 nm for cu, calculated from Williamson-Hall equation. In fact by increasing the milling time after reduction of metal oxides, molybdenum dissolves in copper matrix and supersaturated Cu(Mo) solid solution with a homogenous distribution of nano-sized Al_2O_3 as reinforcement materials was formed. The thermal analysis curves of 10 minutes milled sample shows some peaks related to reduction of copper and molybdenum oxide with aluminum. In addition the small endothermic peak at 650 °C observed from DTA curve is due to the melting of remaining Al.

Keywords: *Ball milling; Mo-Cu/Al_2O_3; Nano-composite.*

1. Introduction

Mechanical activation of chemical reactant could be caused chemical and microstructural changes with the help of mechanical energy [1, 2]. Unstable phases, nano-crystalline, amorphous and disordered to ordered intermetallic compounds were synthesized via mechanical milling as advanced material production method. Mechanical milling is a simple and versatile method due to its ability to increase solid solubility at ambient temperature and expected that this process could achieve a larger solid solubility extension [3-6]. During milling powder mixtures plastic deformation, fracture and cold welding of the particles are taken intermittently, leading to the synthesis of nanoparticles [7-11]. Copper and copper alloys has excellent properties such as thermal and electrical conductivity, corrosion resistance, but the main problem of this alloy is low strength and wear resistance at high temperatures. This problem could be resolved by blending and the use of reinforcement oxide particles such as Al_2O_3. In some of the researches stated that the dissolution of the solid Cu(Mo) produced by mechanical alloying. Nano-crystalline alloy of Cu(Mo) could be reinforced with the homogeneous distribution of the Al_2O_3 to achieve better mechanical properties of nanocomposites [4, 6]. Alumina in the Cu(Mo) network is not only conducive to improving the hardness of the material but also reduces the rate of grain growth occurs even at temperatures close to the melting point of copper. The amount, number

and distribution of reinforcement particles play an important role in the enhancing or limiting the overall properties of the composite. This particle has the least impact on the thermal and electrical conductivity of matrix [8, 9]. Mo-Cu alloys is immiscible in both solid and liquid states and do not form any alloy using conventional equilibrium methods such as casting or liquid metallurgy and non-equilibrium methods such as mechanical milling preferred for alloy production. Since molybdenum has lower density than tungsten, so it can be a better alternative for heat sink materials and alumina also improve the mechanical properties of composite such as hardness. This study focused on the production of Mo-Cu/Al_2O_3 nano-composite via mechanical alloying method using a ball milling technique. This composite would be a good candidate for heat sinks in many applications due to low thermal expansion coefficient and high thermal conductivity.

2. Materials and methods

Mixtures of commercial aluminum (99.7%, 30-60 μm), MoO_2 (99.9%, ~100 μm) and CuO (99.9%, 80 μm) powders were used as starting materials. Ball milling was performed in the planetary ball mill using hardened chromium steel vial and balls under argon atmosphere. The ball to powder weight ratio and rotational speed were 20:1 and 120 rpm respectively. The milling times were up to 100 h. For preventing excess agglomeration stearic acid ($C_{17}H_{35}COOH$) amount of 1 mole% was used as PCA. Reactive milling has also been carried out with 20%, 60% and 100% mole of excess reductant (Al) than stoichiometric amount.

The structural changes of powders during milling was investigated by XRD (Bruker-D8-Advance) using Cu-K_α (λ=1.5405 Å) and the mean crystallite size for produced samples was calculated using the Williamson-Hall formula:

$$D=(0.9\boldsymbol{\lambda}/\boldsymbol{\beta}\cos\boldsymbol{\theta})+\boldsymbol{\eta}\tan\boldsymbol{\theta} \quad \text{(eq. 1)}$$

Where D is the crystallite size, λ is the X-ray wavelength, β is the line width at one-half the maximum intensity, η is internal strain and θ is the Bragg angle (in degrees). The XRD patterns were recorded in the 2θ range of 20-80 degree. A Linseis DTA/TG unit was used to investigate the thermal behavior of the 10 minutes milled sample under the protection of Ar from room temperature up to 1000 °C with a heating rate of 5 °C/min. Isothermal annealing was also carried out to study the thermal behavior of milled powders. Powder samples were milled for 1 h and then annealed in a conventional tube furnace with the argon atmosphere at 350, 550, 700 and 1000 °C for 1 h.

3. Results and discussion

Mo-Cu/Al_2O_3 nano-composite can be synthesized by a displacement reaction between Al and mixture of MoO_2/CuO according to the following reaction:

$$MoO_2 + CuO + 2Al = Mo\text{-}Cu + Al_2O_3,\ \Delta G^\circ_{298} = -916\ kJ/mol.,\ \Delta H^\circ_{298} = -926\ kJ/mol.$$

ΔG°_{298} and ΔH°_{298} calculated theoretically with using data in literature [12]. ΔH°_{298} value indicates that the reaction between Al and MoO_2/CuO is highly exothermic, as ΔG°_{298} value indicate that this reaction can thermodynamically take place at room temperatures. Also mechanical alloying can enhance kinetics of reaction by creating high diffusivity path, providing extensive interface area between reactants and by the dynamic removal of reaction product from interfaces due to repeated fracturing and cold welding of powder particles which enhance kinetics of reaction [1]. If the value of adiabatic temperature (T_{ad}) is above 1800 K, it yields self-propagating combustion reaction in thermally ignited system [13]. Thus the value of T_{ad} can be used as a suitable criterion to anticipate the occurrence of self-propagating combustion reaction in ball milling process [14]. The T_{ad} calculated using the heat reaction and thermodynamic data was found to be about 7385 K which is higher than critical value of 1800 K, so thermodynamic analysis predicts that above reaction should take place in a combustion mode.

Fig. 1 shows XRD patterns of the milled powder obtained from different milling times with 20% mole of excess Al. The diffraction peaks of initial powders (CuO, MoO_2 and Al) are clearly visible at the mixed powder. Oxide peaks tend to broaden and their intensities decrease because of the crystallite refinement and buildup of the lattice strain in the milled powder particles. In 2 h milled sample no CuO peaks observed which indicate complete reduction of CuO after 2 h milling. This means that all CuO is reduced to copper, but molybdenum oxide is still present which means that the reaction is not completely carried out and requires more milling times. With the rise of the time to 10 h, MoO_2 peaks

dropped and Mo peaks could be observed which indicate partial reduction of MoO_2. In 10 h milled sample, the intensity of copper and molybdenum peak has increased but at times of more than 10 h, the intensity of molybdenum peak decreases so that in 70 h milled sample disappeared completely that can be for two reasons: first amorphous formation of molybdenum and second the dissolution of molybdenum in copper matrix. By increasing the milling time up to 70 h, the position of Cu peaks shifted slightly left side. This suggests that the lattice parameter of Cu matrix is increased as a result of dissolution of a larger Mo atom into a Cu lattice. Figure 1 shows that with increasing milling time to 100 h, a large amount of MoO_2 could be reduced to Mo and the intensity of MoO_2 decreased. Also, the alumina phase is not visible due to amorphous phase in the XRD analysis. The crystallite size of Cu matrix during ball milling can be determined from broadening of XRD peaks by Williamson-Hall equation. By increasing the milling time to 2 h crystallite refinement occurs and Cu had a crystallite size of about 48 nm. With further milling time crystallite size reduced again and reached to about 42 nm at 100 h milled sample. Table 1 show the dependence of milling time on crystallite size and internal strain of Cu which was calculated from peak broadening of Fig. 1. As shown in the figure 1

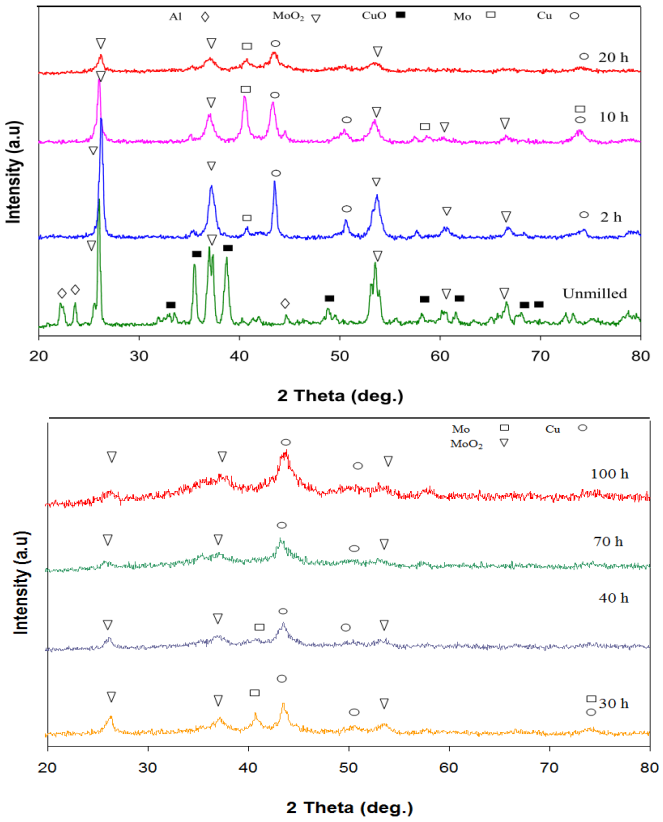

Fig. 1- XRD patterns of Al-CuO–MoO_2 mixture milled for different times with 20% mole of excess Al.

Table 1- Effect of milling time on crystallite size and internal strain of synthesized Cu

Milling time (h)	Crystallite size (nm)	Internal strain (%)
2	48	1.1
10	52	1.4
20	51	1.6
30	43	1.6
70	44	1.7
100	42	1.9

there are a little unreacted oxide in the composite mixture. In order to complete reduction of metal oxides the content of extra Al increased to 60 and 100% mole.

Figure 2 shows the XRD results of mixture with 60 % mole extra Al milled for 60, 80 and 100 h. This figure show small MoO_2 oxide after milling for 100 h. Finally milling with 100 % mole extra Al as shown in figure 3, reduction of oxides take place completely. According to figure 3, since alumina is amorphous, its peaks are not visible at XRD investigation that this subject proved with other researcher [4]. In order to show Al_2O_3 peaks this sample annealed at 1000 °C for 1 h and all peaks of Al_2O_3 are visible due to crystallization.

As shown in the figure 1, high milling time are needed to complete molybdenum and copper oxides reduction at room temperature. The effect of thermal activation of mixed milled powders was also investigated. Fig. 4 shows thermal analysis results of 10 min milled powder mixture with 20% mole of excess Al at argon atmosphere from room temperature to 900 °C. The DTA curve exhibited one exothermic and one endothermic peak at 500 and 650 °C, respectively. The exothermic peak at about 500 °C represents the reduction of oxides by

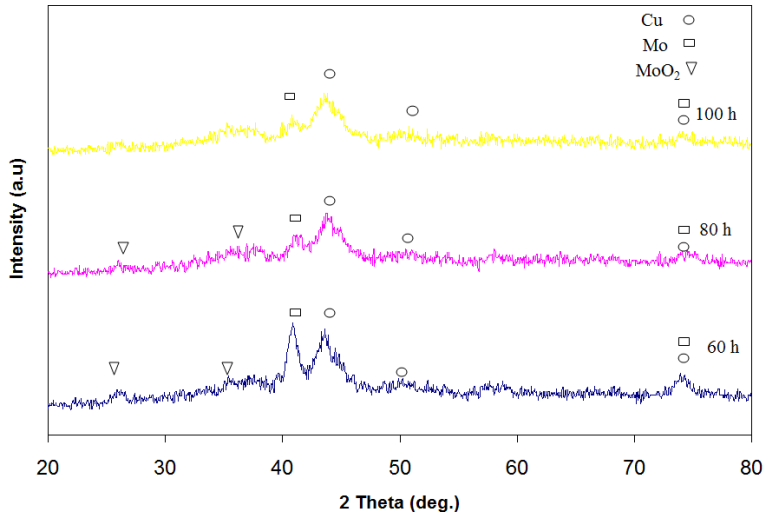

Fig. 2- XRD patterns of Al-CuO–MoO_2 mixture milled for different times with 60% mole of excess Aluminum.

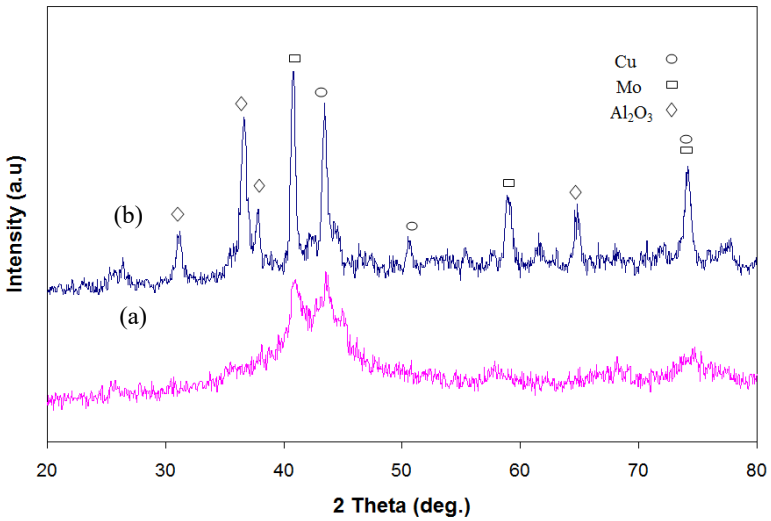

Fig. 3- XRD patterns of synthesized Cu-Mo/Al_2O_3 composite with 100% mole extra Al after (a) 100 milling and (b) 100 h milling followed by heat-treatment at 1000 °C for 1 h.

Al. The endothermic peak at 650 °C is due to the melting of remaining Al. The total weight loss of the sample after treatment is 3.5% that is because of the evaporation of absorbed moisture on the surface of particle and gas production during heating. To clarify the phase transition underlying each peak, the milled samples were heat treated to the selected temperatures and then followed by XRD examinations.

Fig. 5 shows XRD patterns taken from the 1 h milled sample after heat treatment at 350, 550, 700 and 1000 °C at an argon atmosphere. As it is clear from the XRD patterns, from 350 to 1000 °C, the MoO_2 phase is still visible, indicating that the reaction is not complete. The results show with annealing at 350 °C the $Cu_6Mo_5O_{18}$ complex phase formed and with increasing that heat treatment temperature to 500 °C copper reflections started to appear. This figure shows $Cu_6Mo_5O_{18}$ peaks got decreased when the temperature reached at 1000 °C and most of MoO_2 has transferred to Mo. Eventually when the temperature reached to 1000 °C the nano-crystalline Mo and Cu produced and the intensities of the Cu(111), Cu(200), Cu(220),

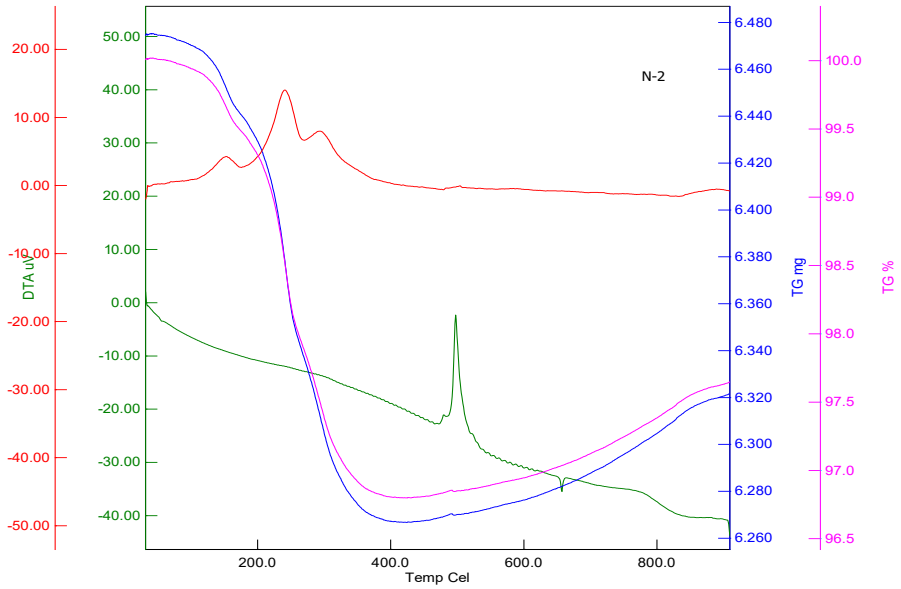

Fig. 4- Thermal analysis curves of a powder mixture of Al-CuO–MoO_2 after 10 min milling with 20% mole of excess Al.

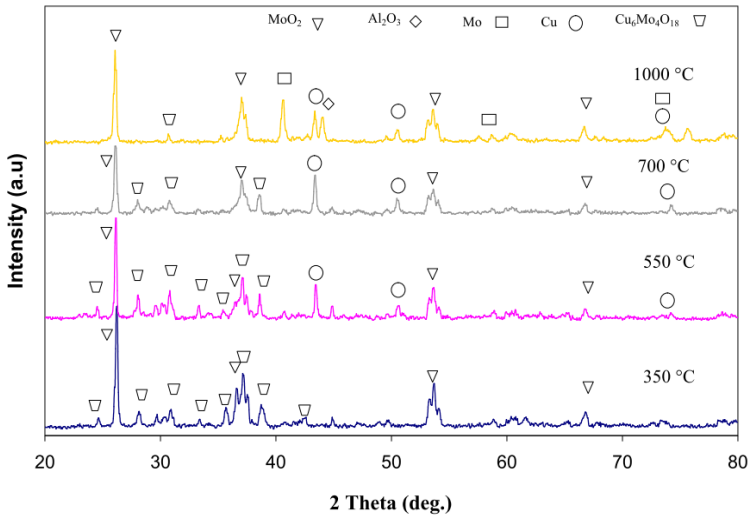

Fig. 5- XRD patterns taken from the 1h milled mixture after reduction at different temperature for 1 h.

Mo(110), Mo(200), and Mo(211) peaks are observed.

To further gain insight into the effect of mechanical activation and subsequent reduction of the powders, we study the evolution of the microstructures of milled and heat treated powders with different heat treatment temperature. Fig. 6 shows FESEM images of 10, 40 and 100 h milled mixture. It can be seen that the powders consists of agglomerated particles after 10 h milling and with increasing milling time agglomerated particles fractured and superfine spherical nanoparticles with particle size below 100 nm has been synthesized. These spherical particles exhibit high specific surfaces area, regular shape and uniform size distribution. Plastic deformation of powder

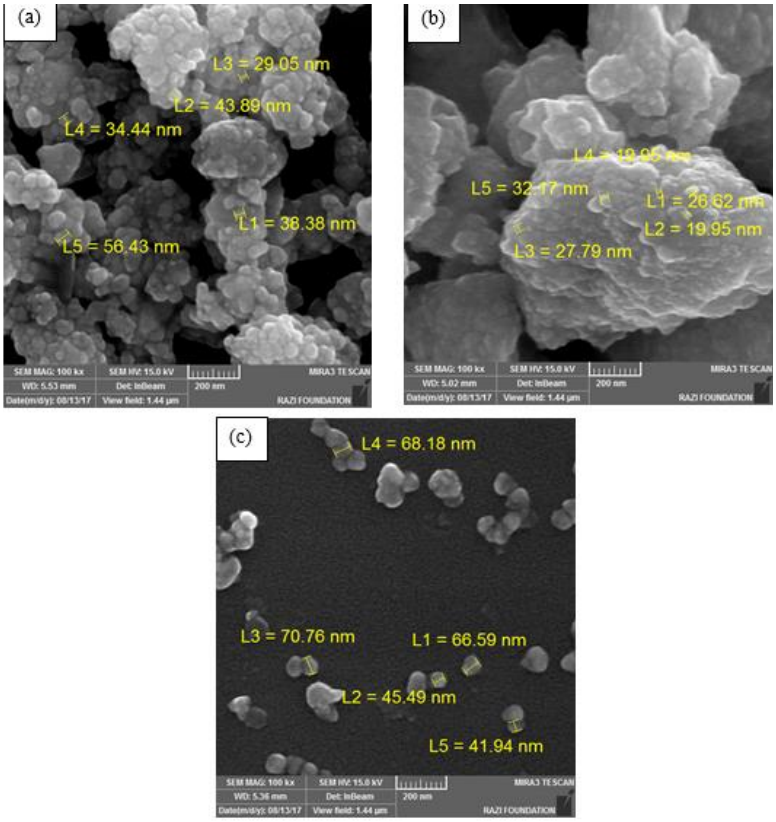

Fig. 6- FESEM images of (a) 10, (b) 40 and (c) 100 h milled samples.

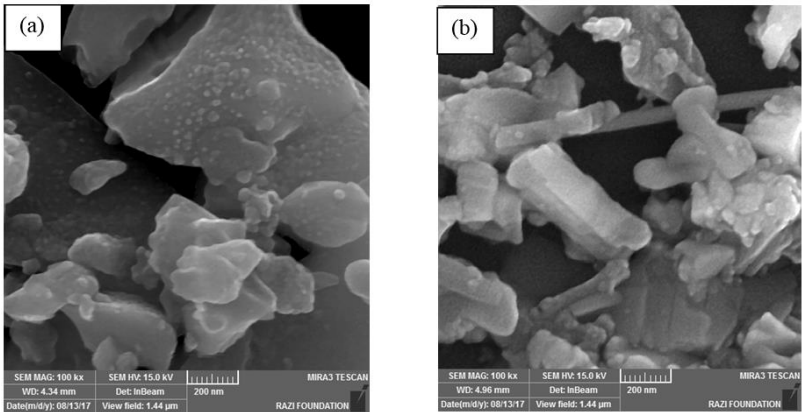

Fig. 7- FESEM images of 10 h milled mixture after reduction at a) 350 and b) 1000 °C for 1 h.

particles during MA, caused to a microstructure refinement of particles and increasing specific surface area. Stacking faults and vacancy inside the crystallites increased during the process of milling of the powder. Another advantages of mechanical milling is increasing the solid solubility of elements during milling which could shorter the diffusion pathway in the mixture. Fig. 6 shows FESEM images of 10 h milled mixture after reduction at 350 and 1000 °C. Nonetheless, we can still observe the appearance of large particles, which may be formed by the agglomeration of small compact particles. Because of high heat treatment temperature to synthesis Mo-Cu/Al_2O_3 composite, the particle size is somewhat bigger than that in the milled sample and grain growth is observed.

Conclusions

Cu(Mo)/Al_2O_3 nanocomposite has been successfully synthesized by ball milling of CuO, MoO_2 and Al powders. The mechano-chemical reaction between MoO_2-CuO and Al takes place at the 100 h of milling. After 100 h of milling with 100% mole of excess Al, the formed nanocomposite contains supersaturated Cu(Mo) matrix containing Al_2O_3 as reinforcing materials. The effect of thermal activation of mixed milled powders was also investigated and shown that with reduction at 1000 °C of mixture, metal oxides could be reduced.

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