Structural Evolution Properties of Cu-25 wt %Sn Alloy During Ball Milling

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Abstract: In the present study, Cu-25 wt %Sn alloy samples were prepared by the mechanical alloying process using planetary high-energy ball mill. The alloy formation and different physical properties associated with their formations were investigated as a function of milling times of 0, 10, 20, 70, 80, 100, 120, 150 and 200 h by means of the x-ray diffraction (XRD) technique, scanning electron microscopy (SEM) and differential scanning calorimeter (DSC). After milling time of 80 h, the complete formation of martensite transformation is observed. When milling time increases from 70 to 120 h, the grain size decreases from 20.8 to 8.6 nm, while the strain increases from 4.73 % to 7.59 %. It is inferred that the martensite volume fraction increases from 30 to 55 % when milling time increases from 20 to 200 h. Moreover, by using SEM the grain morphologies at different formation stages during ball milling are observed.

Keywords: Mechanical alloying, phase transitions, martensitic transformation, ball milling, Cu-Sn alloys.

1. INTRODUCTION

The genesis of nanostructure is the key feature inherent in the preparation of nano crystalline materials using powder methods. The structure of particles originates from synthesis conditions. The density of defects such as twins, domains, stacking faults, core-and-shells as well as particle aggregates and agglomerates, strongly depends on the process parameters. These features of particles define behavior of powder during consolidation and effect on the structure of the monolithic sample. Such heredity has been revealed in the past in coarse particles and micron size-grained bulk materials [1]. The most important achievement of today’s techniques of synthesis and consolidation of nano particles is flexible control over properties [2]. There are some investigations dealing with ball-milling procedure [3-7].

Ball milling is a materials synthesis technique that is a key process in many applications under the shield of mechanical alloying. Ball milling has become an innovative technique in the fields of materials synthesis and mechano chemistry.

Mechanical alloying (MA) was developed around 1966 by John Benjamin *et al*. at the Paul D. Merica Research Laboratory of the International Nickel Company (INCO) to produce a material combining oxide dispersion strengthening with gamma prime precipitation hardening in a nickel-based super alloy for gas turbine applications [8-10]. Ball milling is an efficient and simple method for the fabrication of sub-micron or nano structured powder materials, especially for manufacturing of some composite powders [11]. There are different types of ball milling methods based on the movement of milling balls and vial, such as vibration mill and planetary mill. In the case of planetary ball milling, main factors that affect the particle size reduction include rotation speed, size of balls, weight ratio of balls to powder, medium of milling, milling time etc.

It is known that the mechanical alloying through the ball milling is an important route to obtain amorphous or nano crystalline alloys. Mechanical alloying is a processing technique that allows alloys production starting from mixtures of elemental and /or compounds powders. During MA, a lamellar structure arises in the powders due to the cold welding and fracture of the particles [10].

Among the copper based alloys the Cu-Sn system is the least investigated experimentally and theoretically one. The Cu-Sn alloys, although, are quite ancient, their microstructure has been just studied in the last few years [12].

Due to the variety of powder materials, the selection of parameters also varies substantially [13-15]. The present study was carried out to report the preparing of nano structured Cu-25 wt % Sn alloy by ball milling method and studying the effect of milling time on the micro structural and mechanical properties of the prepared alloys. Several methods have been used to investigate the changes in the ball milled powders. The formation of those resultant alloys was identified by X-

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ray diffraction (XRD). Moreover, the thermal stability of the alloys was also studied using differential scanning calorimeter (DSC). In addition, their metallographic structure was investigated by a scanning electron microscope (SEM).

2. EXPERIMENTAL PROCEDURE

Elemental Cu (99.99 %) and Sn (99.999 %) powders were mixed in appropriate proportions to obtain the compositions of Cu-25 wt % Sn alloy and average particle sizes less than 40 µm were used as the starting materials and mixed at the desired composition. In order to avoid oxidation, the mixture and a number of stainless steel balls with different diameter were sealed in a cylindrical stainless steel vial under dry argon inside a glove box. The typical weight ratio of the balls to powders was 10 to 1. Mechanical alloying was performed at room temperature using planetary miller (Fritsch Pulverisette-5) with a rotation speed about 300 r /min. All the samples were milled for 0-200 h.

X-ray diffraction (XRD) was carried out on a Philips X Pert PRO X-ray diffract meter using $Cu\ K_a$ radiation (wave length = 0.15405 nm) and the excitation voltage and current were 40 kV and 30 mA, respectively. Differential scanning calorimeter (DSC) was conducted with a Perkin-Elmer Pyris DTA-TG Thermal System.

3. RESULTS AND DISCUSSION

Figure **1** shows a sequence of the x-ray diffraction (XRD) patterns recorded for the nanocrystalline Cu-25 wt % Sn samples subjected to milling for increasing time. There exist sharp XRD peaks of Sn and Cu in the initial powders. It can be seen at milling time of 10 h that, all the x-ray patterns characterized by five mean peaks which refer to austenite phase. Ball milling of powders results in very fast partial transformation of austenite into martensite structure, observed already after 70 h of processing. During martensite transformation the austenite peaks intensities decreases, their positions shift to a lower angle with increasing milling time and considerable peak broadening can also be observed. Further milling only changes the proportions between both phases. The significant broadening of the diffraction peaks belonging to both phases testifies their nano crystalline nature with an enhanced lattice parameter. This gradual shift in peaks location may be attributed to the solid state dissolution of Sn in Cu. Similar observation was also reported in the previous work by researchers in ref. [16] during mechanical alloying in a Cu–Sn system. It is worth noting that the reverse transformation of martensite into austenite occurs with further milling since the x-ray diffraction patterns of the powders milled for 70 – 200 h display clearly the coexistence of martensite (M) and austenite (A). The phase transformation sequence during mechanical alloying of the powders is as follows: Cu-25 wt %Sn: β-Cu (cubic) + Sn (tetragonal) → orthorhombic structure (martensite).

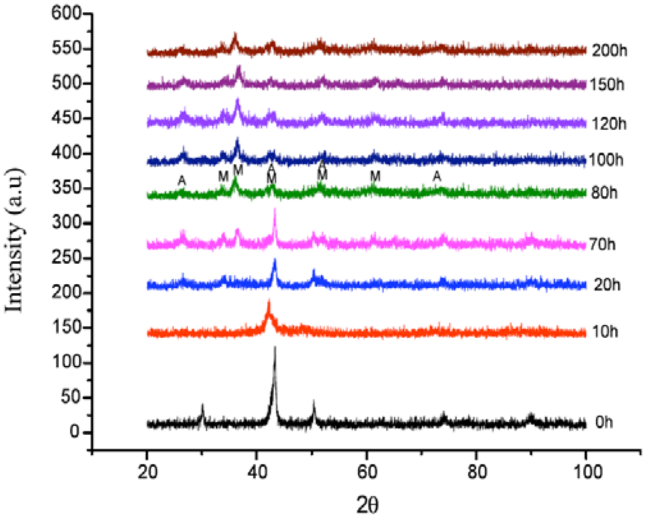
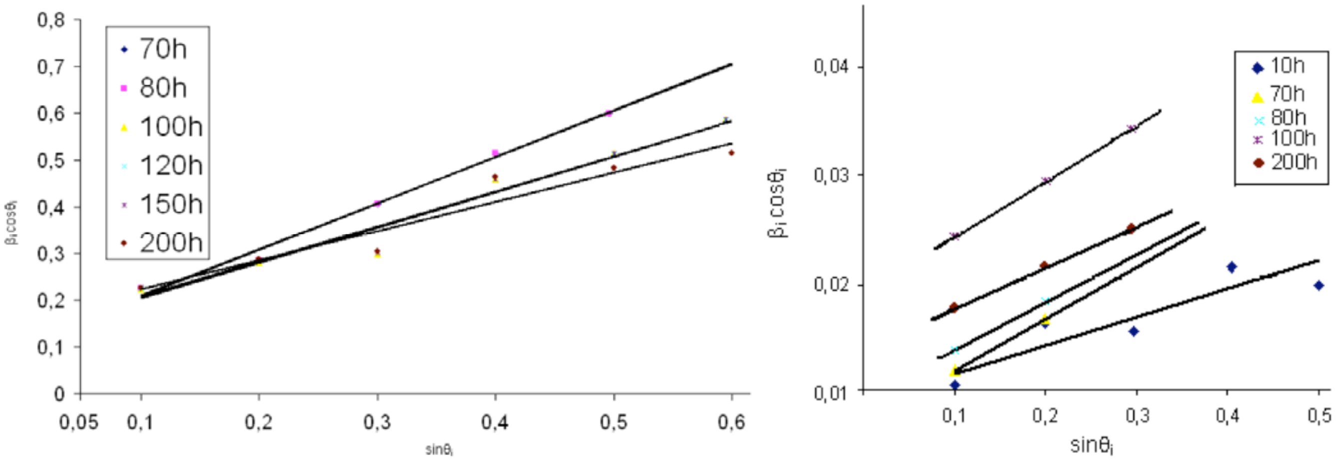


Figure 1: XRD patterns of powders milled with increasing time. A and M denote austenite martensite phases, respectively.

The plotting of $\beta_i\cos\theta_i$ versus $\sin\theta_i$ for martensite (a) and austenite phase (b) is shown in Figure **2** by using Williamson-Hall method. The goodness of fitting (R^2) for the linear regression are determined in these plots for martensite phase as: $\beta_i\cos\theta_i = 0.9923 \sin\theta_i + 0.11$ ($R^2 = 0.98$) for 70h, $\beta_i\cos\theta_i = 0.9879 \sin\theta_i + 0.1113$ ($R^2 = 0.98$) for 80h, $\beta_i\cos\theta_i = 0.7606 \sin\theta_i + 0.1272$ ($R^2 = 0.92$) for 100h, $\beta_i\cos\theta_i = 0.7525 \sin\theta_i + 0.1315$ ($R^2 = 0.93$) for 120h, $\beta_i\cos\theta_i = 0.7521 \sin\theta_i + 0.11324$ ($R^2 = 0.93$) for 150h, $\beta_i\cos\theta_i = 0.6259 \sin\theta_i + 0.1608$ ($R^2 = 0.93$) for 200h. Similar expressions for austenite phase can also be written as: $\beta_i\cos\theta_i = 0.0258 \sin\theta_i + 0.0093$ ($R^2 = 0.63$) for 10h, $\beta_i\cos\theta_i = 0.0473 \sin\theta_i + 0.0074$ ($R^2 = 1$) for 70h, $\beta_i\cos\theta_i = 0.0436 \sin\theta_i + 0.0098$ ($R^2 = 1$) for 80h, $\beta_i\cos\theta_i = 0.0759 \sin\theta_i + 0.0177$ ($R^2 = 1$) for 100h, $\beta_i\cos\theta_i = 0.0375\sin\theta_i + 0.0179$ ($R^2 = 0.98$) for 200h.

Figure **3** shows that 10 and 80 h of milling time for austenite leads to the grain size enlargement, while 100 and 120 of millings lead to the grain size refinement quickly and 150 and 200 h of millings slowly. The average grain size increases until the



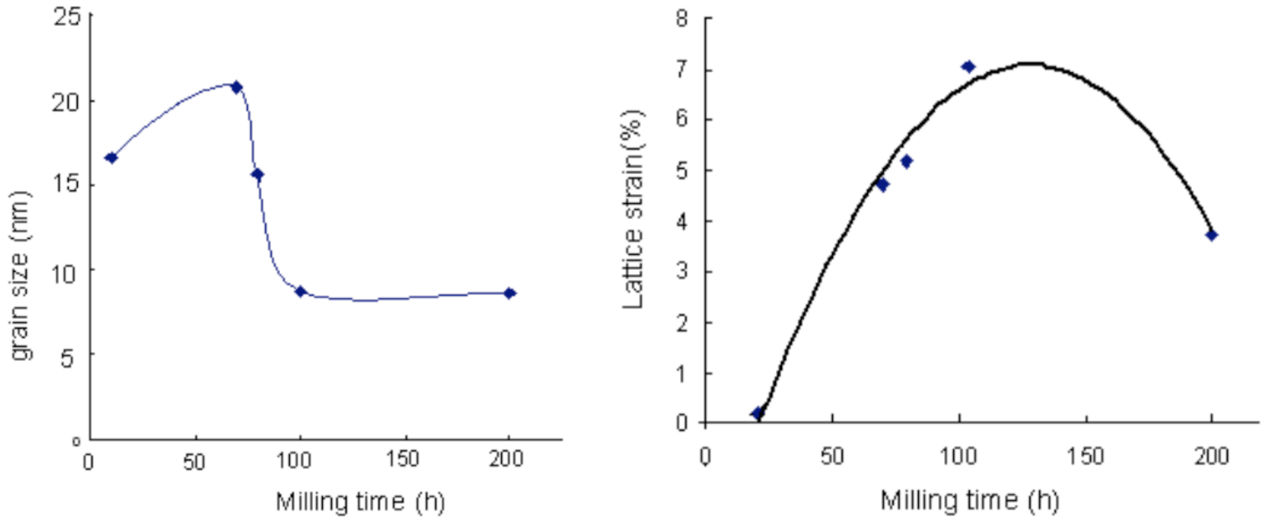
(**a**) (**b**)

Figure 2: Plotting of $\beta_i \cos\theta_i$ versus $\sin\theta_i$ for martensite (**a**) and austenite phase (**b**).

welding process dominates the milling process and oppositely it decreases after fracture process becomes dominant. The mean grain size of the powder particles for austenite phase is about 5 nm according to the XRD profile analysis; it is indicating that the grain reaches to nanometer scale after ball milling [16, 17].

The martensite structure (orthorhombic) was observed in the product of short time milled powders. On the other hand, the lattice parameters of the two phases were calculated from the XRD peaks using the $Cu\ K_\alpha$ wave length of 0.15405 nm. The microstructure of mechanical alloying after 100 h milling is nano crystalline, a Cu solid solution with a lattice parameter of a_0 = 2.983 A^0 for austenite and a= 2.686 A^0, b = 4.487 A^0 and c = 4.813 A^0 for martensite phases, respectively. This result is in a good agreement with those obtained from study made by Kennon and Bowles for Cu-Sn alloy [18].

The changes of martensite fraction in the structure of Cu-25 wt % Sn alloy with milling time, determined by XRD technique are shown in Figure **4**. The maximum content of martensite (approximately 46 %) is observed after relatively short milling time such as 20 h, as determined from XRD measurements. For longer milling times an increase of martensite fraction down to 49 % is observed, followed by an increase up to 57 % after 100 h of processing. It was not possible to obtain 100% martensite in powders. This case is suggested to be related to the presence of the probably the stabilization of the austenite by the small crystallite size and by the residual stresses generated during milling.



(**a**) (**b**)

Figure 3: Dependence of grain size and the lattice internal strain associated with the austenite phase on milling time.

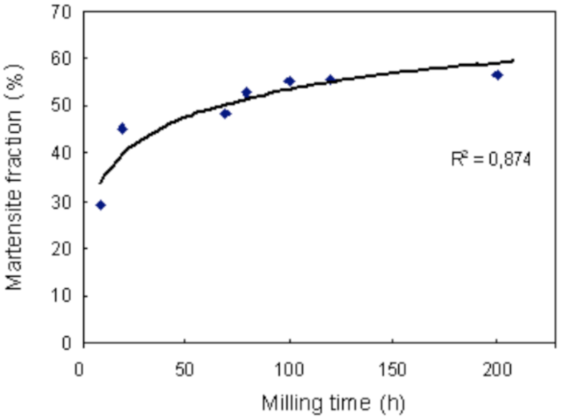
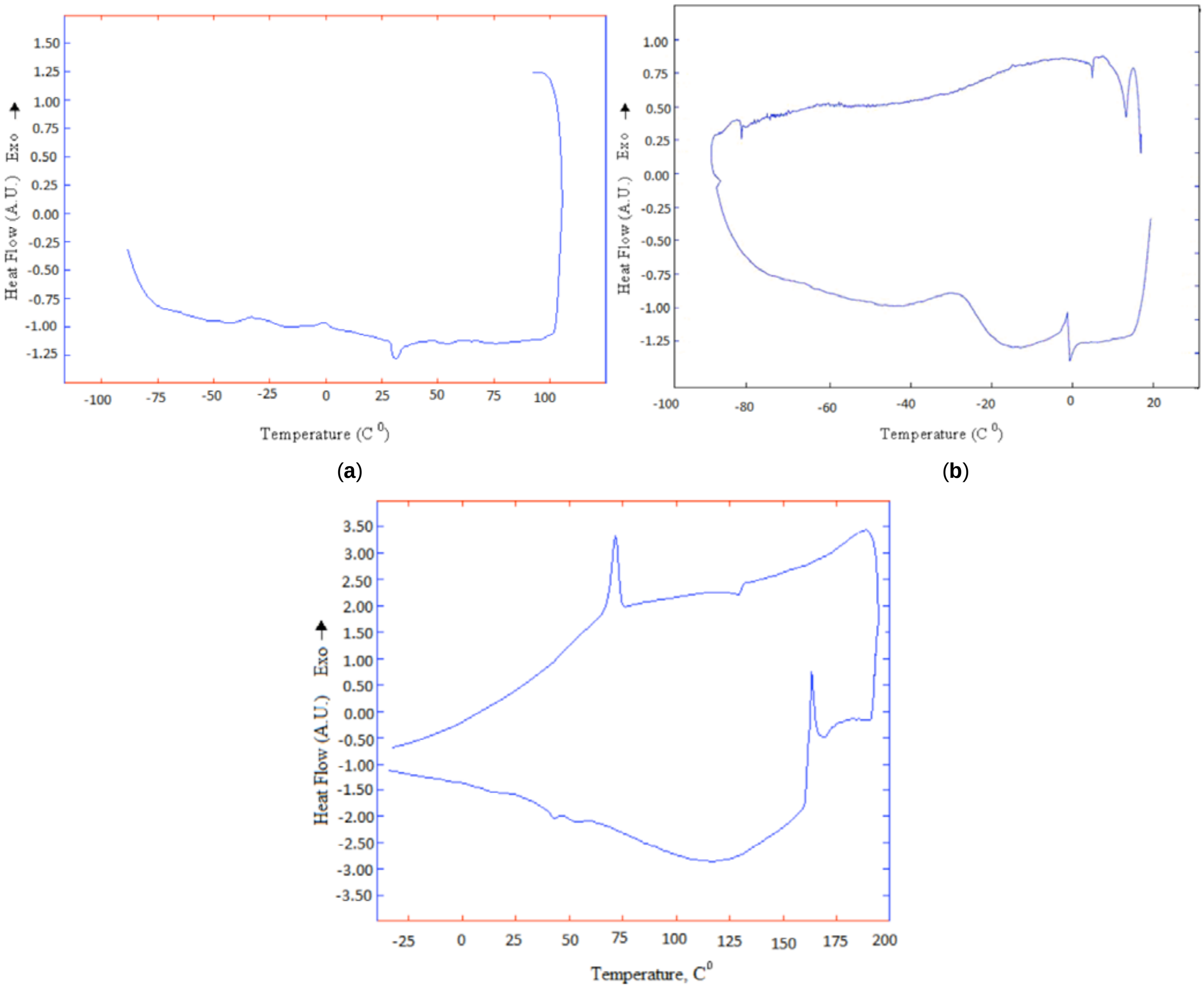


Figure 4: Dependence of martensite fraction in the structure of the alloy Cu-25 wt % Sn on milling time, determined by XRD technique. Dependence of martensite fraction on the milling time is a function in the following form: Martensite fraction (%) = 8.613 ln [milling time (nm)] + 13.8.

Using the DSC experiments for 100 h milling time, an endothermic reaction due to martensitic transformation was found in the Cu-25 wt % Sn sample. The austenite start temperature, A_s, was nearly-10 ^{0}C. This temperature observed in the alloy just mentioned above is close to that obtained from the previous study where the grain sizes of Cu–Sn alloy are of the order of nanometers [19]. An also typical shape memory alloy, such as Cu-25 wt % Sn alloy experiencing one martensitic forward and reverse transformation can be detected by DSC measurement. The results of DSC measurements in Figure **5** show that there exist broad two endothermic peaks in all the milled samples of 10, 120 and 200 h. The causes for the disappearance of exothermic transformation peaks on cooling can be described as follows: it is known from Figure **5**, that the heat entropy of the reverse



(**a**) (**b**)

(**c**)

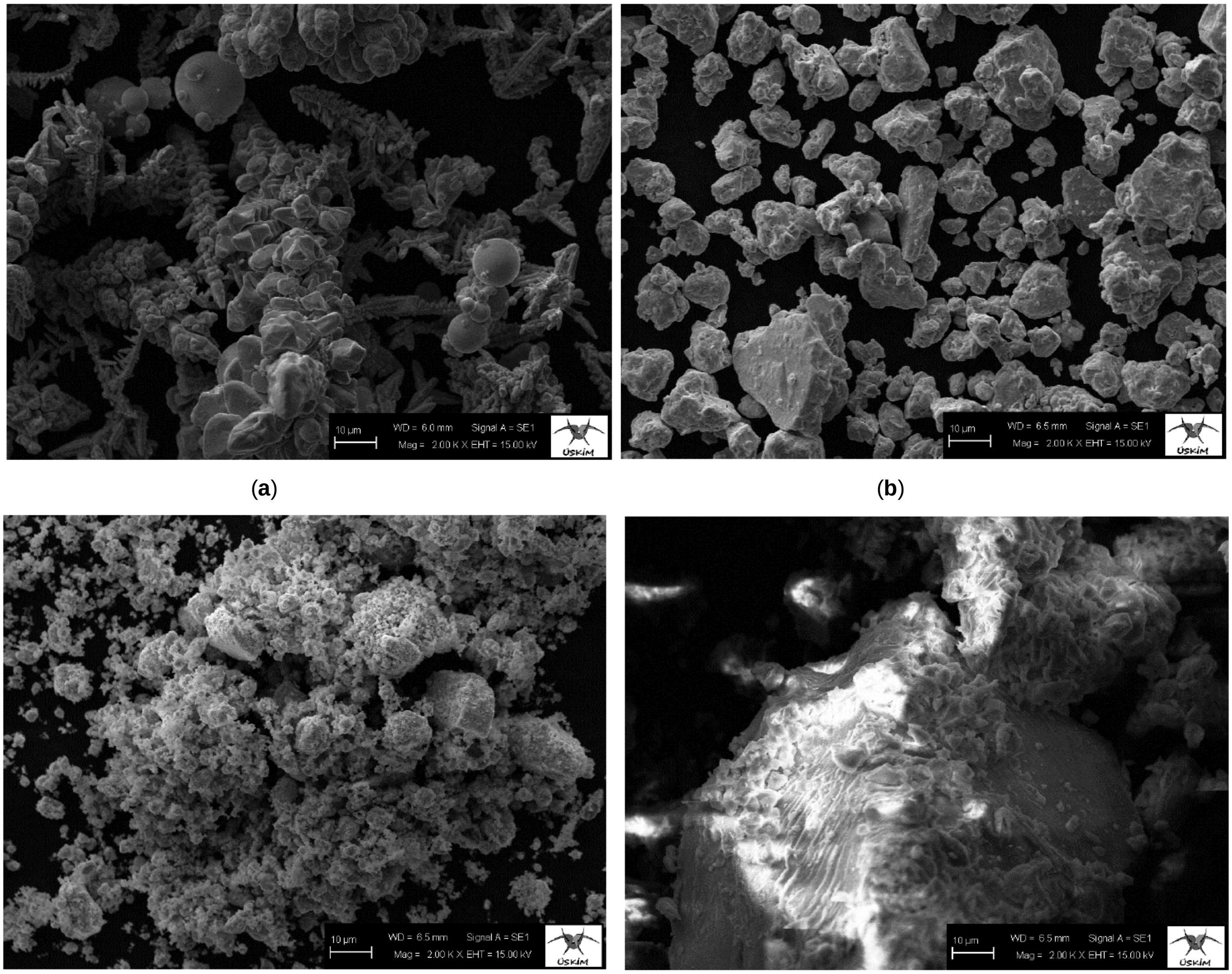
Figure 5: DSC curves registered for selected ball milled samples of (**a**) 10 h, (**b**) 120 h and (**c**) 200 h.

transformation is very little. Such small heat entropy indicates that it is very difficult to detect the transformation on cooling. The authors in references [20, 21] also report the formation enthalpy of some Cu–Sn binary intermetallic phases. For 200 h milling time, it is inferred that the largest exothermic and endothermic peaks seen in 75 ^{0}C and 125 ^{0}C in this figure are associated with some phase transitions.

Figure **6** depicts SEM microstructure of Cu-25 wt % Sn alloy specimens at a magnification of 200, for various stages of milling times: (a) as received (0 h), (b) 20 h, (c) 70 h, (d) 200 h. From measurements with a lot of grains, the grain sizes are 150–300 nm for the Cu–Sn alloy. The un milled powders have rounded shapes and their grain sizes range between 1 and 10 nm and are very fine.

It is reported that the peak broadening and the reduction in intensity of the diffraction peaks of ball-milled powders are associated with the refinement in crystallite size, lattice internal strain, and the instrumental effects [22, 23]. In the sample with 10 h ball-milling or less, little solid solution took place between the powder particles, as evidenced by the presence of the diffraction peaks of Sn. As is shown in SEM micrograph in Figure **6b**, the presence of Sn diffraction peaks at this stage is in agreement with the in homogeneity of powder microstructure.

On the other hand, although the grain size is not drastically reduced, the powders tend to becoming elongated and platelet shapes are developed Figure **6b** as the milling time increases. Moreover, the rounded shapes of the grains remain roughly unchanged after milling for large hours. Moreover, SEM observations



(**a**) (**b**)

(**c**) (**d**)

Figure 6: SEM micrograph observed in Cu-25 wt % Sn sample for various milling times of (**a**) as received (0 h), (**b**) 20 h, (**c**) 70 h, (**d**) 200 h.

reveal that after milling for 20 h, these rounded shapes are often found to be composed of a large number of grains, which form aggregates of a few micrometers. Mechanical alloying is a solid-state powder processing involving repeated welding, fracturing and re-welding of particles in a high-energy ball milling [24]. The agglomerated particles are obviously observed at the milling time of 70 h, with the particle size of 16.7 µm (Figure **6c**). Therefore, serious welding occurred at this time interval.

It is known that the martensite phase is formed subsequently by cooling below the martensite start temperature. The reaction proceeds while the temperature is falling. Taking into considering this situation, a variation of martensite volume fraction as a function of the grain size had been plotted in Figure **7**. In prolonged milling, it is seen that the volume fraction of stress-induced martensite during ball milling decreased from 57 % for the sample with the smallest grain size of 8.6 nm down to 53% for the one with largest grain size of 20.8 nm, *i.e.,* the larger the grain size is, the lower the volume fraction of stress-induced martensite is. It is reported in ref. [25] that the martensitic transformation temperature, M_S, decreases with a decrease in grain size, because the grain boundaries serve as barrier of nucleation of the transformation, while it is reported in ref. [26] the martensitic transformation temperature increases as the grain size decreases because the interaction between martensite plates and grain boundaries increases the elastic strain energy which facilitates the nucleation of new plates. Moreover, it is reported by Suzuki *et al.* in an another ref. [27] that a significant lowering of the transformation temperatures in nanometer crystals compared to those in micrometer crystals since the difference in transformation behavior between the nanometer crystals and the micrometer crystals may be originated from the transformation mechanisms of nucleation. Based on the above results, it can be inferred, even though unverified, that the martensitic transformation temperature should increase as the grain size decreases. Whereas, in DSC plot, small heat entropy associated with the martensitic transformation indicates that it is very difficult to detect the transformation temperature on cooling. The results just mentioned above are rather opposite to the well-known effect of M_S temperature increase as the grain size increase [28].

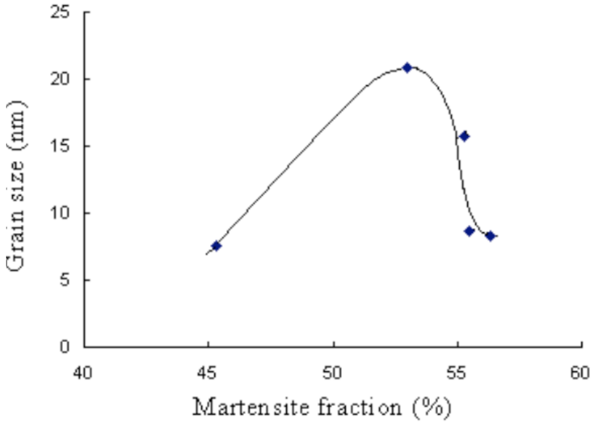


Figure 7: Grain size vs. martensite fraction.

4. CONCLUSION

From this study, the following main conclusions can be drawn:

The effect of different ball-milling times on the structural characteristics of the powders alloy Cu-25 wt % Sn was investigated for various periods of milling time from 0 to 200 h. Ball-milling for 200 h led to the formation of a relatively equiaxed shape and smaller size powder particles with more asymmetrical particle-size distribution than the powders ball-milled for 10 and 20 h. Considering the flattened particle morphology shown in Figure **5** it seems that a balance was not achieved after 20 h milling time.

In Figure **3** the crystallite size and lattice strain were estimated from Williamson-Hall plot. It can be seen that the crystallite size increased at very beginning of the milling process, decreased rapidly at the 70 h of the milling process, and then continued to decrease slowly with the prolonged milling. Therefore, the most intensive refinement occurs in the stages of milling, nearly 70-100 h, when the crystallite size abruptly decreases from approximately 22 nm to 9 nm.

With the increase of milling time, the martensitic volume fraction increases generally and then decreases during mechanical alloying of Cu-25 wt % Sn because the whole energy occurred in ball milling process initiates the phase transition and more energy can be provided for the reverse transformation.

The optimum ball milling time for fabricating Cu-25 wt % Sn alloy powders is determined as 70 h, while Cu-25 wt % Sn alloy powders are fabricated successfully by the optimum milling conditions deduced from Cu and Sn powders.

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