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# Unraveling the Effects of Process Control Agents on Mechanical Alloying of Nanostructured Cu-Fe Alloy

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**ABSTRACT**

Nanostructured Cu-20Fe alloy was synthesized by mechanical alloying process and the effects of process control agents (PCA) on the phase formation, crystallite refinement and morphology of powder particles were studied. The dissolution of Fe into Cu matrix and the morphology of powder particles were analyzed by X-ray diffraction (XRD) technique and scanning electron microscopy (SEM), respectively. The mean crystallite size was approximated by the method developed by Williamson and Hall. It was found that in the absence of PCA (Toluene in the present work), the iron peaks vanish after 5 h of mechanical alloying process and the mean crystallite size of the matrix decreases to 35 nm and large agglomerated particles are formed during milling. In this regard, it was found that the addition of PCA decreases the rate of crystallite refinement and formation of solid solution but does not affect the final mean crystallite size. It was also found that the addition of PCA during milling decreases the powder particle size considerably and by preventing agglomeration can lead to a finer powder particle size compared with the initial unmilled powders. It was also revealed that the effect of PCA on particle size is much greater than the effect of milling time.

***Keywords:*** *Crystallite Refinement; Mechanical Alloying; Nanomaterials; Process Control Agent.*

## 1. Introduction

Mechanical alloying is one of the most promising and rapidly developing methods for synthesizing nanomaterials [1,2], in which the limits of solubility can also be enhanced significantly even for immiscible elements [3,4]. Repeated fracturing and welding of particles during mechanical alloying can result in appropriate mixing of constituents, which can lead to a change in solubility limits and formation of metastable solid solutions [1]. Excessive cold welding and formation of agglomerated particle might be a problem during milling, especially for ductile metals [5,6,7]. This can results to the formation of large agglomerates [5,6] or low powder yield [7]. Therefore, process control agents (PCA) are usually added to the powder mixture during milling to control the effect of excessive cold welding [8]. On the other hand, PCAs could affect the final phase formation [1], change the solid solubility levels [9], the formation rate of solid solutions [8,9], the rate of crystallite refinement [9,10], alter the contamination levels [1], and the resultant mechanical properties [11]. Moreover, the effect of PCA has been successfully modeled by Canakci et al. [12,13]. Therefore, it can be deduced that the effect of PCA is important in optimization of mechanical alloying process for each given system.

In the present work, a Cu–Fe solid solution was synthesized by mechanical alloying process with and without PCA addition to investigate the effect of PCA on the rate of crystallite size refinement, the final crystallite size, the rate of formation of solid solution, and the evolution of the size and morphology of powder particles. It should be noted that the mechanically alloyed Cu-Fe supersaturated solid solutions have received a great deal of attention due to their high strength and high conductivity. However, the effect of PCA on this system has not been systematically studied.

## 2. Experimental procedure

Commercially pure Fe powder (<150μm, 99.5% purity, Germany) and electrolytic copper powder (<150μm, 99.5% purity, China) were used as starting materials. Fig. 1 shows the SEM micrographs of the initial powders as performed by S360 Mv2300 scanning electron microscope. Mechanical alloying of the powders was carried out in a planetary ball mill with hardened steel vial and balls under argon atmosphere. The mixture of Cu-20wt% Fe was milled up to 10 h. In the beginning of milling, 3wt% of toluene was added for investigation of PCA effects. The ball-to-powder weight ratio (BPR) and milling speed were adjusted as 20:1 and 300 rpm, respectively. The details of the specimens are summarized in Table 1. Phase identification or dissolution of Fe into Cu matrix was studied by X-ray Diffraction (XRD) using a Philips PW-3710 diffractometer with Cu-Kα radiation. The crystallite size of matrix was determined from the X-ray peak broadening technique based on the Williamson-Hall method. Finally, the morphology of mechanically alloyed products was studied by field-emission scanning electron microscopy using a HITACHI S-4160 SEM.

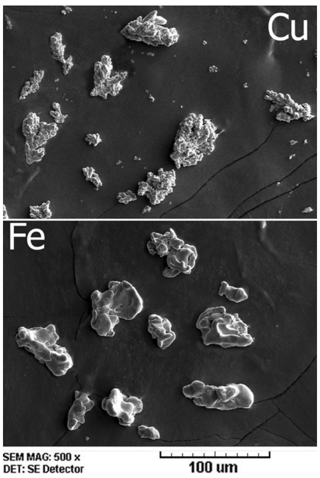


Fig.1- The SEM images of the initial powders.

Table 1- The details of the specimens

| Specimen name | composition | Milling time (h) | PCA content |
|---|---|---|---|
| Cu-20Fe-5h | Cu-20wt%Fe | 5 | 0 |
| Cu-20Fe-5h-PCA | Cu-20wt%Fe | 5 | 3 wt% Toluene |
| Cu-20Fe-10h | Cu-20wt%Fe | 10 | 0 |
| Cu-20Fe-10h-PCA | Cu-20wt%Fe | 10 | 3 wt% Toluene |

## 3. Results and Discussion

### 3.1. Phase identification

The XRD patterns of Cu-20wt% Fe along with those synthesized with the addition of PCA are shown in Fig. 2. For the samples synthesized without PCA, the Fe peaks vanish after 5 h milling probably due to the dissolution of Fe in the Cu lattice. While Fe has negligible solubility in Cu lattice at room temperature, Eckert [14] et al. have reported the formation of fcc (Cu) solid solution with 60 at% of Fe. Moreover, in comparison with initial powder's pattern, by continued milling the peaks become broad due to the crystallite refinement and introduction of lattice strain. These results are in a good agreement with previous reports on mechanical alloying of Cu-based alloys [15,16].

As can be seen in Fig. 2, the high intensity peak of Cu-Fe alloy milled for 5h with addition of PCA shows some branches which could be related to the undissolved Fe. On the other hand, by additional 5 h milling, these branches vanish for the Cu-20Fe-10h-PCA due to the dissolution of Fe in the Cu lattice after 10 h milling. Therefore, it can be concluded that the addition of PCA postpones the dissolution of Fe. It can be imagined that toluene is adsorbed on the surface of powder particles and inhibits alloying. Shaw et al. [9] claimed that the effects of stearic acid and methanol as PCA materials on the prevention of excessive cold welding, the grain-size refinement, the lattice-strain increment, and the formation of Al-based solid solutions are most likely achieved via the adsorption on the metal surface and the lubricating function provided by these molecules. The former prevents the clean metal- to-metal contact necessary for cold welding, whereas the latter reduces the degree of plastic deformation of powder particles during each impact, which, in turn, slows down the grain-size refinement and the formation of solid solutions [9]. It should be noted that for other mechanically alloyed systems, it has been also reported that the addition of PCA could change the solid solubility level and lead to a decrease in the rate of the formation of solid solution [1,8,9,17].

### 3.2. The effect of PCA on the crystallite size refinement

The mean crystallite size as a function of milling time for the Cu-20Fe system is shown in Fig. 3. As can be seen, in the case of milling without PCA, after 5 h milling, the mean crystallite size decreased suddenly and there is no pronounced refinement by continued milling. However, the mean crystallite size of the Cu-20Fe milled for 5h in the presence of PCA differs considerably from that processed without PCA. This difference could be related to the amount of dissolved Fe for Cu-20Fe-5h and Cu-20Fe-5-PCA.

The above statement needs more explanation based on the melting points of the alloys [18,19]. Fig. 4 shows the minimum obtainable crystallite size of different elements based on their melting point [18]. As can be seen in this figure, by increasing the melting point, the minimum crystallite size decreases. Now, based on the phase diagram of Cu-Fe, the melting point of Cu solid solutions increase with the addition of Fe. As discussed earlier, in the presence of PCA, Fe does not dissolve completely in Cu lattice after 5 h and hence the melting point of the resultant solid solution is lower, and as a result, the corresponding crystallite size is coarser. Finally, after milling for 10 h, Fe dissolves in the Cu lattice, and hence, the addition of PCA has no pronounced effect on the final mean crystallite size as shown in Fig. 3.

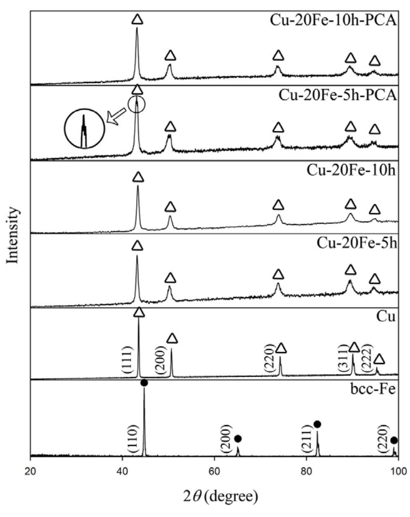


Fig. 2- The obtained XRD patterns.

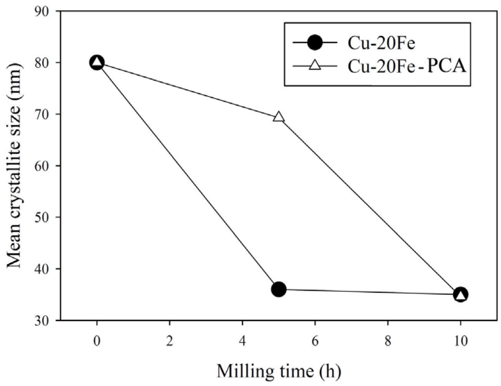


Fig. 3- Mean crystallite size versus milling time.

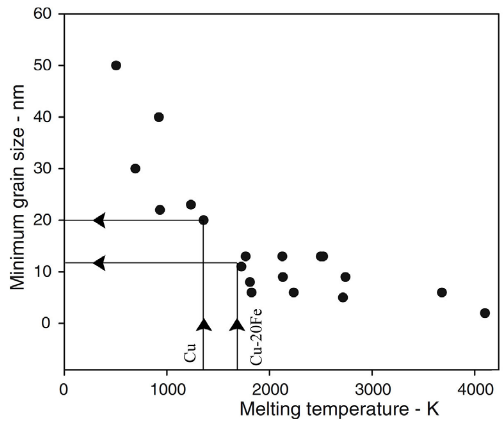


Fig. 4- The minimum grain size as a function of melting point of ball milled elements [18].

### 3.3. The effect of PCA on the morphology of powder particles

Fig. 5 (a) and (b) show the SEM images of mechanically alloyed powder particles without PCA. Compared with the initial powders (Fig. 1), it is obvious that milling for 5 h results in an increase in the mean particle size, which means that excessive cold welding has occurred during milling. The formation of large particles in the Cu-20Fe-5h sample may be attributed to the presence of fcc crystal structure in which particles are easily deformed and cold welded to each other to form large agglomerates [5,8]. Fig. 5 (C) and (d) show the powder which mechanically alloyed with PCA for 5 and 10 h. In contrast to Fig. 5 (a), Fig. 5 (c) shows that the particle size of the sample milled for 5 h with PCA is much finer. By analyzing the image, it can be seen that, by addition of PCA during milling, the mean particle size of Cu-20Fe-5h decreases from almost 540 μm to 15 μm. In fact, PCA adsorb on the surface of the powder particles and minimize cold welding among powder particles, thereby inhibiting agglomeration [1,9]. Therefore, it can be concluded that addition of PCA during mechanical alloying is beneficial for producing Cu-Fe supersaturated solid solution with desirable particle attributes if enough milling time is applied to grant alloying and crystallite refinement. The figure also shows that the additional 5 h milling time leads to finer powder particles and the obtained powders after milling for 10 h in the presence of PCA are finer compared with the initial unmilled powder particles. To better evaluating the effect of milling time, the milling process was continued without addition of PCA. Fig. 6 (a) and (b) shows the SEM images of Cu-20Fe-20h and compared with Cu-20Fe-10h-PCA in Fig. 6 (c). Fig.6 reveals that additional 10 h milling without PCA can significantly reduce particle size toward particle size of Cu-20Fe-10h-PCA, which was achieved by particle fracturing. However, the particle size after 20 h is still larger. This proves that the effect of PCA on particle size is much greater than the effect of milling time. Fig. 6 (b) also shows that each powder particle is agglomerated of nanometer particles.

## 4. Conclusions

The Cu-20Fe supersaturated solid solutions were synthesized by mechanical alloying up to 10 h milling in the presence and absence of Toluene as the PCA material. The effect of Toluene on the phase formation, crystallite refinement and morphology of powder particles was studied and the following conclusion can be drawn from this work:

1. During mechanical alloying of Cu-Fe without PCA, Fe dissolved into Cu lattice after 5 h milling and the mean crystallite size of Cu decreased to 35 nm. Also, large agglomerated formed by 5 h milling due to excessive cold welding and by additional milling, finer particles were formed.

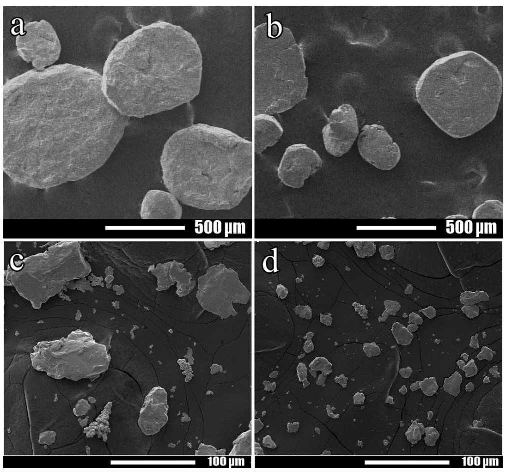


Fig. 5- SEM images of mechanically alloyed powder particles, (a) Cu-20Fe-5h, (b) Cu-20Fe-10h, (c) Cu-20Fe-5h-PCA, and (d) Cu-20Fe-10h-PCA.

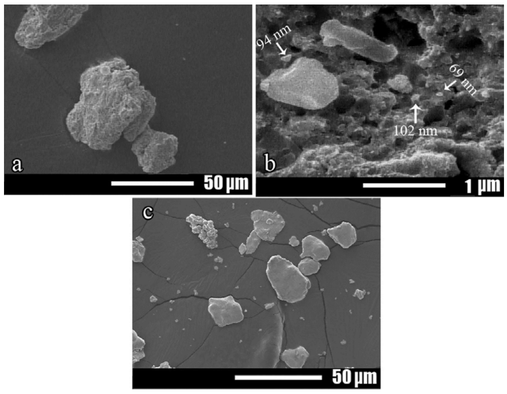


Fig. 6- SEM images of mechanically alloyed powder particles to investigate the effect of additional milling time: (a,b) Cu-20Fe-20h and (c) Cu-20Fe-10h-PCA.

2. The presence of Toluene during milling postponed the dissolution of Fe into Cu lattice and led to a decrease in the rate of solid solution formation and crystallite refinement. However, the addition of PCA did not change the final mean crystallite size of Cu due to the dissolution of Fe by continued milling.

3. The powder particle size decreased considerably with addition of Toluene during milling and led to finer powder particle compared with the initial unmilled powder. It was also revealed that the effect of PCA (Toluene in this case) on particle size is much greater than the effect of milling time.

## Acknowledgement

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