

MECHANICAL ALLOYING OF CUFE IMMISCIBLE ALLOY USING DIFFERENT MILLING CONDITIONS

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Abstract

In the last years, immiscible alloys have gained significant attention, mainly due to the use of their immiscible nature for the preparation of new advanced multiphase alloys. Most of these alloys are based on the Cu-Fe system. The advantages of Cu and Fe elements are their easy availability and low price, good mechanical properties, and medium melting temperature. Currently, most bulk Cu-Fe-based immiscible alloys are produced by casting. However, this method requires several additional steps to obtain appropriate microstructure. An interesting alternative is powder metallurgy, which provides an easy way to produce immiscible alloys with very fine heterogeneous microstructure. An essential requirement is to prepare a milled powder with a sufficiently small particle size, which consists of a metastable solid solution of all elements. The small particle size allows achieving full density during sintering, in which supersaturated solid solution decomposes into a fine dual-phase microstructure.

In this work, two sets of milling conditions ("soft" and "hard") for the preparation of CuFe powders were tested. They differed in the milling speed and the size of milling balls. The milled powders were analyzed after several milling times and the evolution of powder particle size, morphology, and microstructure were evaluated. Based on the results, optimal milling times were selected for both sets of milling conditions and these parameters were verified by the preparation of new CuFe milled powders. Surprisingly, different results were obtained as the resulting powder particle sizes were significantly larger.

Keywords: Immiscible alloys, mechanical alloying, high energy ball milling

1. INTRODUCTION

Cu-Fe alloys are one of the most studied immiscible systems. They gained their original interest mainly due to their great combination of high electrical conductivity and good mechanical strength [1,2]. Recently, much attention has been paid to these alloys since the Cu-Fe system is used as a basis for new advanced multiphase alloys that have excellent mechanical properties [3–5]. The advantages of Cu and Fe elements are their easy availability and low price, good mechanical properties, and medium melting temperature. At room temperature, the microstructure of the Cu-Fe alloys consists of the BCC-Fe phase and FCC-Cu phase, which is the result of the positive enthalpy of mixing of these elements [6]. By a suitable selection of alloying elements, it is possible to control the microstructure and properties of both phases and thus tailor the mechanical properties of the resulting alloy [4,7,8].

The most common method of producing Cu-Fe and Cu-Fe-based alloys is casting. An interesting alternative is powder metallurgy (PM), which consists of mechanical alloying (MA) of elemental powders using high-energy ball milling and subsequent sintering of the milled powder using Spark Plasma Sintering (SPS). The advantage of PM compared to casting is the ability to create finer and more uniform microstructure [9]. Moreover, there is no risk of melt separation due to metastable liquid miscibility gap when using PM. The aim of MA is to prepare a milled powder with a sufficiently small particle size to allow full density to be achieved

during sintering. The microstructure of the milled powder should consist of a metastable supersaturated solid solution, which decomposes at elevated temperature into a fine dual-phase microstructure [10,11]. To achieve this aim, it is necessary to choose a suitable MA condition.

In this work, two sets of MA conditions (“soft” and “hard”) for the preparation of CuFe milled powders were tested. The conditions varied in milling speed, milling balls size, and milling time scheme. The particle size, morphology, and microstructure of milled powders were evaluated depending on the milling time. Based on the results, optimal milling times were selected for both sets of MA conditions, and these parameters were verified by the preparation of new CuFe milled powders.

2. MATERIALS AND METHODS

Commercially pure Cu (purity > 99.7 wt.%, particle size < 45 μm) and Fe (purity > 99.5 wt.%, particle size < 10 μm) were used as a starting material. The powder mixture with the equimolar chemical composition of CuFe was milled together with hardened bearing stainless steel balls in chromium-molybdenum-vanadium tool steel. The ball-to-powder weight ratio (BPR) was chosen to be 10:1. Mechanical alloying was conducted in an argon atmosphere in a planetary ball mill Fritsch Pulverisette 6. These parameters were common to both sets of MA conditions. The remaining parameters are listed in **Table 1**.

For microstructural observation, the powders were prepared by hot mounting in a polymeric resin and grinding with SiC papers up to 4000 grit size, followed by polishing with 3 μm and 1 μm diamond paste. Scanning electron microscope (SEM) characterization was performed by ZEISS Ultra Plus. Secondary electrons (SE) were used for observing loose particles of milled powders and back-scattered electrons (BSE) were used for identifying different phases in the microstructure. Chemical composition was measured by energy-dispersive X-ray spectroscopy (EDS, X-max, Oxford Instruments). The presented values of powder particle sizes were calculated as an average from at least 20 values.

Table 1 The remaining parameters of both MA conditions

| MA conditions | Milling speed (rpm) | Diameter of balls (mm) | Milling time scheme | Milling time (h) |
|---------------|---------------------|------------------------|-------------------------------|------------------|
| Soft | 240 | 10 and 15 | 30 min milling + 30 min pause | 5, 15, 30, 50 |
| Hard | 300 | 17 and 20 | 5 min milling + 10 min pause | 8, 15, 20, 25 |

3. RESULTS AND DISCUSSION

3.1. “Soft” MA conditions

After 5 hours of milling, the powder particle size was 31.2 μm . All particles had a flake shape with a thickness in the order of microns. The particle size and shape were relatively the same for the whole milled powder. In the microstructure, it was possible to observe that the Cu and Fe powders were mixed. However, the mixing was not complete since the lamellar microstructure was observed. This is characteristic of the MA initial stage for the ductile-ductile component system [12]. In addition, it was possible to find unmixed original Fe particles embedded in the matrix.

After 15 hours of milling, it was apparent that the powder fragmentation had occurred as the powder particle size decreased to 24.8 μm . Most of the powder particles had a flake shape, however, several coarser particles were also present (**Figure 1 (a)**). It is not possible to unambiguously determine whether these particles had not yet been fragmented or formed because of the beginning of particle coarsening. In the microstructure (**Figure 1 (b)**), it was possible to observe relatively good mixing and the matrix consisted of a metastable supersaturated solid solution of both immiscible elements. Nevertheless, it was still possible to detect small

inhomogeneous areas where complete mixing had not yet occurred. Unmixed original Fe particles were still present in the matrix. In addition, there were also particles that, according to EDS, contained the elements Fe, Cr, Si, Mo, V, and C. Their chemical composition corresponded to the chemical compositions of the steels from which the milling bowl and milling balls were made. Therefore, the cause of the presence of these particles was the wear of milling equipment [12,13].

After 30 hours of milling, there was a significant increase in the powder particle size. The average particle size increased approximately 10 times to 226.8 μm . The shape could be described more like platelet due to its greater thickness. It was obvious that in this case the cold-welding effect was already more pronounced than the fragmentation. In the microstructure, the inhomogeneous areas observed in the previous powders were dissolved. However, it was still possible to find several unmixed original Fe particles that still maintained the same round shape, regardless of the relatively long milling time. Due to longer milling time, the amount of powder contamination increased.

After 50 hours of milling, further coarsening occurred. The powder particle size was 409.8 μm . The shape and microstructure were comparable to a milling time of 30 hours, only the level of contamination was slightly higher.

Based on the results obtained from the performed optimization, 15 hours was chosen as a suitable milling time for the preparation of CuFe powder using "soft" MA conditions. The particle size of the newly milled powder was 621.8 μm , which was approximately 25 times higher than the size achieved in the optimization (after 15 hours of milling the size was 24.8 μm). Some powder particles had a platelet shape with great thickness, however, most particles had a relatively spherical shape (**Figure 1 (c)**). The microstructure showed very good mixing and the matrix consisted of a metastable supersaturated solid solution of Cu and Fe. Similar to optimization, it was possible to observe several unmixed original Fe particles as well as a low level of contamination (**Figure 1 (d)**).

3.2. "Hard" MA conditions

After 8 hours of milling, the powder particle size was 329.9 μm . Most of the particles had platelet shape, but almost spherical particles were also present. In the microstructure, it was observed that the Cu and Fe powders were mixed, although a very fine lamellar microstructure still appeared. Nevertheless, considering the low contrast of the lamellae, it could be assumed that these were no longer separated metals, but only very small differences in the chemical composition of metastable supersaturated solid solution. The microstructure also contained several unmixed original Fe particles. In addition, particles rich in Cr, Si, Mo, V, and C had already appeared, which were caused by the wear of milling equipment.

After 15 hours of milling, considerable powder fragmentation occurred, and the powder particle size decreased to 152.2 μm . Compared to previous powder, there was a significant flattening of the particles that had a flake shape. In the microstructure, it was possible to observe very good mixing as the fine lamellar microstructure disappeared and the matrix was thus composed of a metastable supersaturated solid solution. However, several unmixed original Fe particles were embedded in the matrix. The level of contamination was comparable to previous powder.

After 20 hours of milling, there was still a slight powder fragmentation, and the powder particle size decreased to 141.3 μm . The shape and microstructure were the same as described for 15 hours of milling (**Figure 1 (e,f)**).

After 25 hours of milling, the powder particle size increased significantly to 423.4 μm . Most of the particles had platelet shape, but some of them were almost spherical in shape. No changes were observed in the microstructure except for a higher level of contamination, which was caused by the wear of milling equipment.

Based on the results obtained from the performed optimization, 20 hours was chosen as a suitable milling time for the preparation of CuFe powder using "hard" MA conditions. Moreover, a powder with a milling time of 15

hours was prepared, which according to the optimization should also have very good properties and can be compared with a powder prepared using the same milling time and “soft” MA conditions. The resulting particle sizes of the powders milled for 15 hours, and 20 hours were 1761.1 μm , and 2126.4 μm , respectively. This was more than 10 times the size achieved in the optimization. Particles of both powders had plate shape with a great thickness. However, it was also possible to observe the small number of particles with a perfectly spherical shape. The shape of the powders was completely different compared to the shape of the powders obtained in the optimization (**Figure 1 (g)**). The microstructure of the two newly prepared powders was identical. Good mixing has taken a place and the matrix consisted of a metastable supersaturated solid solution. Nevertheless, it was possible to observe small areas of unmixed iron as well as powder contamination in the microstructure (**Figure 1 (h)**).

To test the effect of possible overheating of the powder during milling, the third powder with a milling time of 20 hours and milling time scheme of 5 min milling + 30 min pause was prepared (milling time scheme of other powders was 5 min milling + 10 min pause). The resulting powder particle size was 1550.7 μm . The shape of the powder particles and their microstructure were the same as the other two newly milled powders.

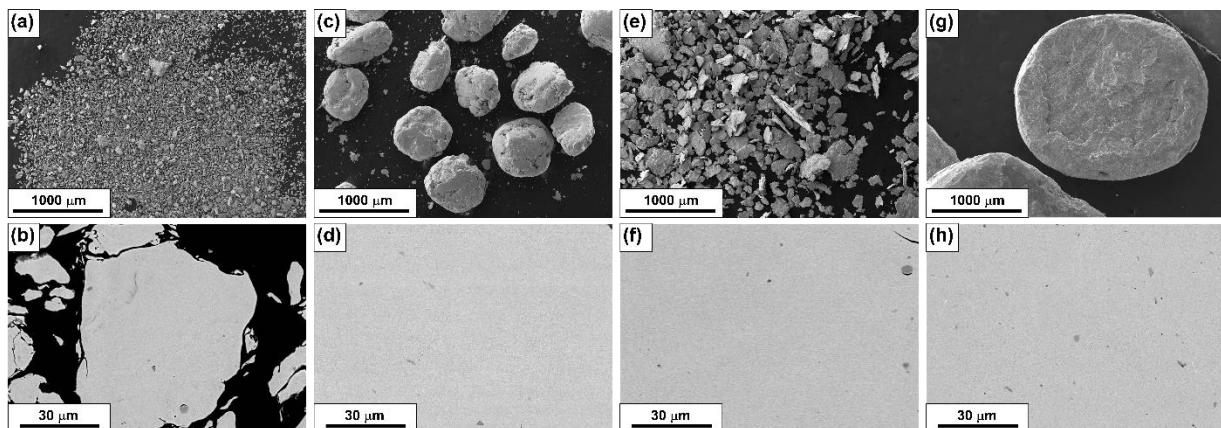


Figure 1 Morphology and microstructure of milled powders prepared by “soft” MA conditions (a-d) and “hard” MA conditions (e-h). (a,b) optimization, 15 hours of milling; (c,d) newly milled, 15 hours of milling. (e,f) optimization, 20 hours of milling; (g,h) newly milled, 20 hours of milling.

3.3. Summary

In terms of the resulting powder particle size, the optimization results showed that the “soft” MA conditions were better than “hard” MA conditions (**Figure 2**). “Hard” MA conditions possessed higher milling energy which in combination with very plastic Cu led to an enhanced cold-welding effect and thus resulted in larger powder particle size. However, both MA conditions showed the same trend when at first, the powder particle size had decreased, and from the milling time longer than 15 – 20 hours, there was a significant coarsening. The coarsening of milled powders continued even after 50 hours of milling. This result did not correspond to the general idea of the principle of MA [12,14] when in the initial stage of milling, the powder particles should increase their size, subsequently, the plasticity of milled powders is depleted, and their size decreases back to the original value. In this last stage, the true alloying begins to occur. The reason why the powder still coarsened even at long milling time was not obvious, the probable reason could be the very high plasticity of Cu.

In terms of the resulting microstructure, the optimization results showed that the “hard” MA conditions were better. After 15 hours of milling, the microstructure of the milled powder showed a very good mixing of the elements and consisted of the metastable supersaturated solid solution of Cu and Fe. In the case of “soft” MA conditions after 15 hours of milling, inhomogeneous areas were still present in the microstructure and their

dissolution required a longer milling time (at which the powder particles had already coarsened). This result was again related to the milling energy since higher milling energy ensured faster alloying of the elements.

The newly milled powders prepared by chosen parameters showed significantly higher values of powder particle sizes compared to the results of the optimizations (**Figure 2**). In accordance with the optimizations, “hard” MA conditions produced larger powder particles. In addition, when comparing the particle sizes of the newly milled powders for 15 and 20 hours (“hard” MA conditions), the opposite trend was evident than in the case of optimizations. This result suggested that the stage of particle size reduction did not occur in the newly prepared powders and the cold-welding effect was more pronounced than fragmentation throughout the milling. One of the possible causes of such significant coarsening could be overheating of the powder during milling. Within the optimization, the milling bowl was opened after a certain milling time, a small amount of powder was taken out, then the bowl was resealed and filled with argon. After that, the milling continued. This provided more time to cool the powder and the whole milling equipment. As the results of the newly milled powder with a prolonged pause between milling cycles showed, a longer time for cooling led to a smaller powder particle size. However, the effect was not so significant as to be the main cause. As the main cause was considered the oxidation of the powder surface. Within the optimization, the milling bowl was opened in the air atmosphere. Although the time between opening the bowl and refilling it with argon was very short (a few minutes), it can be assumed that the surface of the powders was at least partially oxidized. This slightly strengthened the powder particles, which could lead to enhanced fragmentation at the expense of the cold-welding effect. In contrast, newly milled powders were sealed in an argon atmosphere throughout the milling and thus the oxidation of the powder was prevented. This allowed the milled powders to retain high plasticity (mainly due to Cu). In terms of microstructure, the optimization results were comparable to the newly milled powders.

Preparation of advanced immiscible alloys requires a small particle size of a milled powder with a homogeneous microstructure composed of metastable supersaturated solid solution. Based on the results, “soft” MA conditions seemed to be more appropriate. Nevertheless, with regard to the resulting powder particle size, chosen parameters were probably not completely ideal and further optimization is necessary, including other parameters such as e.g., ball-to-powder weight ratio.

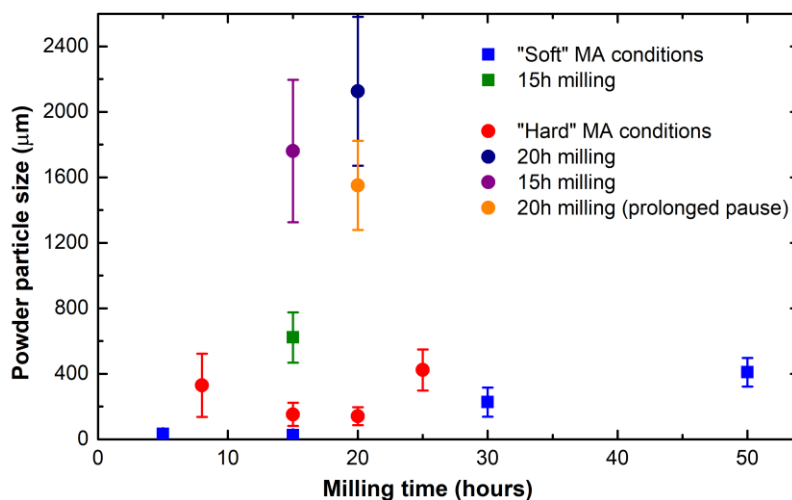


Figure 2 Particle size comparison of all powders

4. CONCLUSIONS

In this work, two sets of MA conditions (“soft” and “hard”) for the preparation of CuFe powders were tested. Based on the results, the following conclusions can be drawn:

- “hard” MA conditions led to a larger powder particles
- the microstructure of the milled powders contained particles rich in Cr, Si, Mo, V, and C, which were the result of the wear of the milling bowl and milling balls
- for both sets of MA conditions, regarding the optimization, the optimal milling time appeared to be 15 – 20 hours
- the newly milled powders prepared by chosen parameters showed significantly higher values of powder particle sizes compared to the results of the optimizations; the estimated reason was the oxidation of the powder surface during optimization

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