

Mechanical Alloying of Fe-Cu Alloys from As-received and Premilled Elemental Powder Mixtures

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Keywords: FeCu, Mechanical alloying, Mössbauer spectroscopy

Abstract

We have investigated the effect of premilling elemental powders of Fe and Cu on the mixture mechanism of a Fe₅₀Cu₅₀ alloy. The alloying process was compared and studied using electron probe microanalysis, X-ray diffraction, scanning electron microscopy and Mössbauer spectroscopy. In both processing routes (with and without premilling), a broad distribution of different local environments of the iron atoms was observed in the Mössbauer spectra of the fcc-FeCu phase. Mössbauer spectra show further that a fcc non magnetic Fe-rich phase is formed transiently besides the bcc-Fe phase. The reactions are slowed down when premilled powders are used as starting powders but similar fcc solid solutions are formed after 16 h and 32h in our milling conditions when as-received and premilled powders are used respectively as starting powders.

Introduction

Alloying of Fe and Cu is known to be feasible by high-energy ball-milling [1-3]. We have investigated the preparation of fcc-Fe₅₀Cu₅₀ alloys by mechanical alloying using two different methods in order to characterise the influence of the mixing mode on the final steady state in our milling conditions. Firstly, the classical method of mechanically alloying of as-received elemental Fe and Cu powder blends was used. Later on, as-received powders of Fe and Cu were milled separately and then mixed in the required proportions and milled again. Premilling, which modifies the mechanical properties of the initial powders and thus the transfer of energy [4], might change the way Fe and Cu are mixed at a nanometric scale. The highest solubility of magnesium in titanium was for instance achieved when both elemental powders were premilled before mechanical alloying [5]. Mechanical mixing by shearing during plastic deformation of powder particles is expected to occur when mixtures of as-received elemental powders are ground while mixing due to welding of the particles should occur predominantly when the powders are premilled separately and then mechanically alloyed together.

Experimental Details

Fe₅₀Cu₅₀ alloys were synthesised by mechanical alloying from Fe and Cu powders with a nominal purity of 99% and an average particle size of 60 and 150µm, respectively. Milling was performed in a planetary ball mill using hardened steel vial (250 ml) and balls (15 balls with 20 mm diameter each). A ball-to-powder weight ratio of 20:1 was used. The disc rotation speed was 300 rpm. Milling was performed in an argon atmosphere to avoid air contamination. The powders were mechanically alloyed in the as-received condition (hereafter “straight condition”) and after premilling the elements separately. Thereby, two different batches were obtained. The as-mechanically alloyed powders were characterized by means of electron probe microanalysis

(EPMA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Mössbauer spectroscopy (MS). The X-ray diffractograms were obtained using Co K_{α} radiation ($\lambda=0.17889$ nm). Mössbauer spectra were recorded at room temperature in transmission geometry with a spectrometer operating in conventional constant acceleration mode. A ^{57}Co source in Rh matrix with a strength of ≈ 10 mCi was used. The spectra were analysed by the method of Le Caër [6], which extracts a hyperfine magnetic field distribution, $P(B)$, from an experimental spectrum. Lorentzian line-shapes were employed in this procedure.

Results and discussion

The X-ray diffractograms of the two $\text{Fe}_{50}\text{Cu}_{50}$ samples batches as a function of milling time are presented in fig. 1. In both cases, a broadening of the diffraction peaks of both Cu and Fe occurs gradually with increasing milling time. The diffraction intensity of Fe decreases more rapidly compared with that of Cu. The diffraction peaks of Cu are no longer observed after different periods of time depending on the milling process. In the straight process, Fig. 1(a), the X-ray reflections of Fe are no longer visible for milling times longer than 8h. In the second process (premilled powders), Fig. 1(b), vanishing of the Fe diffraction lines occurs for longer milling times, i.e longer than 16h. In both processes, iron is incorporated in the fcc-Cu structure, giving rise to a fcc-Cu(Fe) solid solution whose diffraction peaks shift to higher angles with milling time as a consequence of a steadily increasing solubility of iron in copper. In equilibrium, the elements Fe and Cu are immiscible and the equilibrium Fe-Cu phase diagram does not exhibit intermediate phases. The lattice parameters of the fcc-Cu(Fe) solid solutions obtained after the two milling processes (straight and premilled powders) are equal to 0.3636 and 0.3635 nm, respectively, which correspond to expanded fcc-Cu lattices (0.3615 nm). In spite of the larger atomic size of copper when compared to iron, the fcc Cu lattice is expanded by the incorporation of iron atoms in agreement with previous works [1-3]. Harris *et al* [7] propose a model in which the strong interaction between like atom pairs (Fe-Fe, Cu-Cu) provides Coulombic forces which establish geometrical limitations prohibiting the unlike Fe-Cu pairs from coming any closer than the measured distances. In fact, the dilated bonds measured between Cu and Fe indicate that either a very weak interaction or a repulsion exists between unlike neighbours as a result of a positive heat of mixing in this system [9].

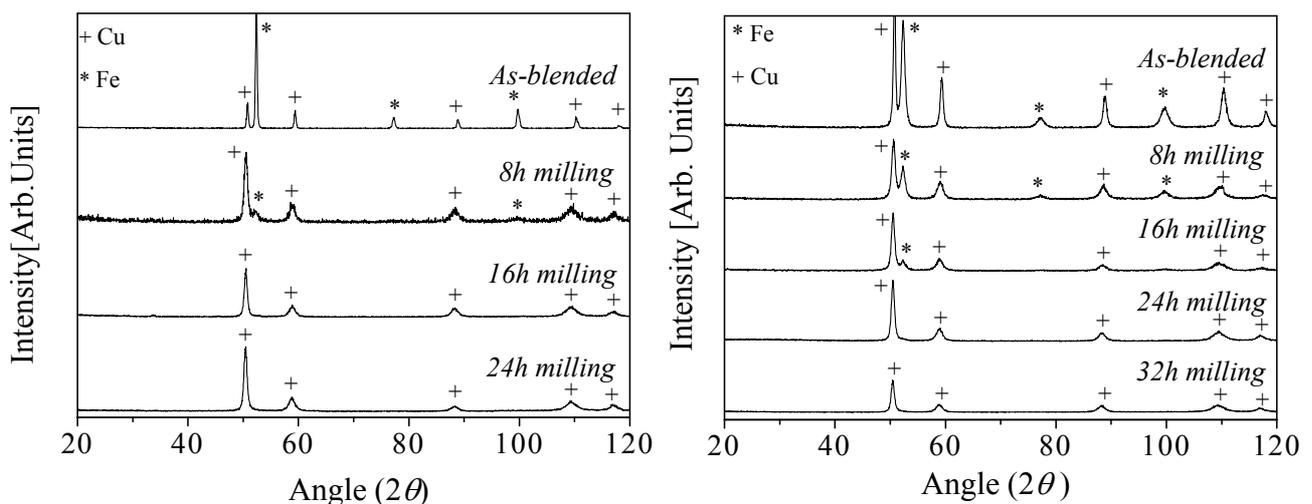


Figure 1 - X-ray diffractograms of the two $\text{Fe}_{50}\text{Cu}_{50}$ samples batches as a function of milling time. (a) straight condition, (b) premilled powders.

The crystallite size and microstrains of the final state of the milled powders, determined from the width of X-ray diffraction peaks using the Williamson-Hall method [10], are 23 nm and 1.5% (straight process) and 13 nm and 1% (premilled powders), respectively.

Figure 2 shows the Mössbauer spectra of the two sample batches, i.e. (a) straight and (b) premilled, for different times of milling. Three different components can be distinguished. The first is a broadened sextet caused by the occurrence of a hyperfine magnetic field distribution, which is attributed to the fcc-FeCu phase. This indicates that a broad distribution of environments of iron atoms exists in the fcc-FeCu phase and demonstrates that Fe and Cu were alloyed at an atomic level. The second is a sextet with a hyperfine field of 33 T characteristic of the bcc-Fe phase. The bcc-Fe phase was not detected by XRD for milling periods equal or longer than 16h (straight process) or than 24h (premilled powders). This can be explained by the very small amount and the small crystallite size of this residual phase which may at least partly come from a contamination by milling tools. The third contribution is a single line with an $IS = -0.09$ mm/s characteristic of the fcc-Fe phase [11]. This phase was not detected by XRD, likely for similar reasons.

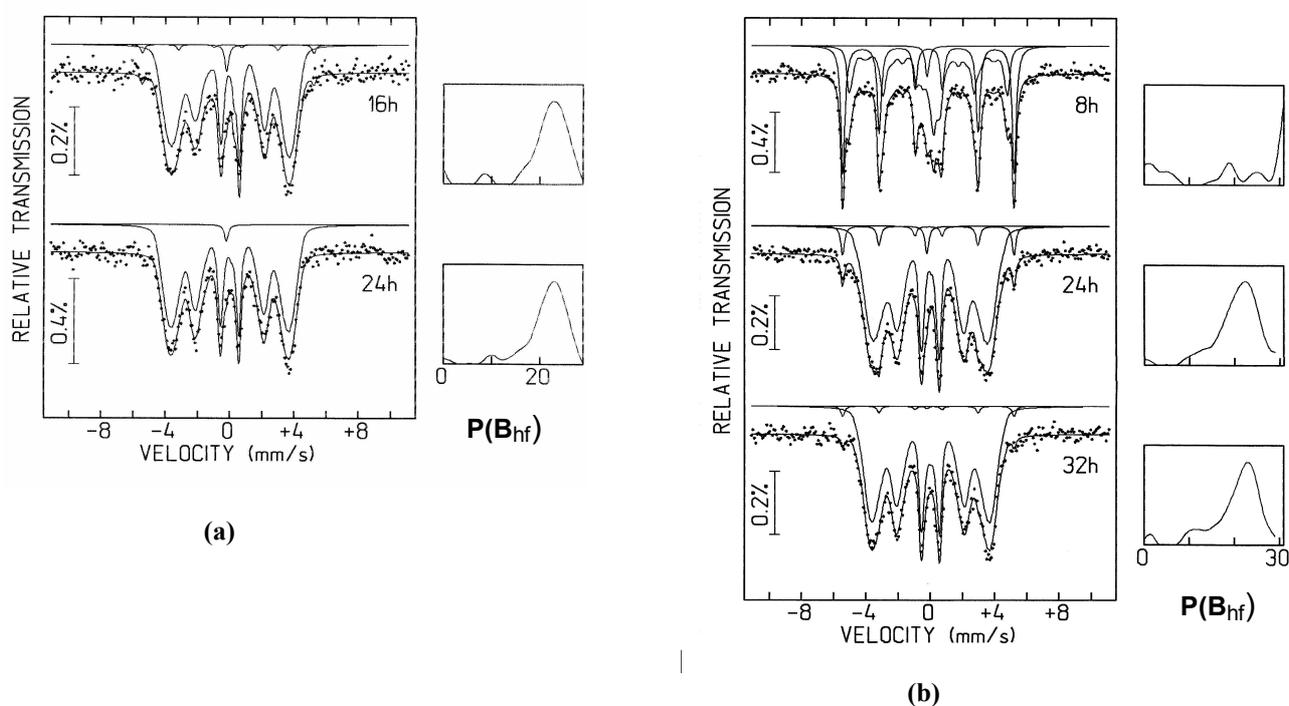


Figure 2 – Room temperature ^{57}Fe Mössbauer spectra and the corresponding hyperfine magnetic field distributions for $\text{Fe}_{50}\text{Cu}_{50}$ samples after different milling times. (a) Powders mechanically alloyed in the as-received condition, (b) Fe and Cu premilled separately.

Figures 3 and 4 shows some SEM micrographs of the particle morphologies as a function of milling time. As can be seen, in the final state the samples have a pellet shape of about 0.7 mm in diameter and about 0.3 mm in thick, independently of the milling process (Fig. 3 (a) and (b)). This shape is obtained earlier in the straight milling process. Fig. 4 compares the morphologies of the particles milled for 1h using the two milling processes. In the case of inverted back-scattered (BE) images, black and white zones correspond to copper and iron respectively. In the straight milling process, mixing is faster than in the second process, in which plates of iron and copper can be easily differentiated. Quantitative electron microprobe analysis confirms these observations. No significant compositional variations were observed in particles obtained from the straight process after 1h of milling. By contrast, there are some compositional fluctuations in particles alloyed from premilled powders for 1h (Fe- and Cu-rich zones). Some iron particles were detected in the latter

powders. The Cu-rich particles are actually Cu(Fe) solid solutions with a significant iron amount. This means that, contrarily to the bcc-Fe structure, there is an incorporation of iron in the fcc-Cu structure from the beginning of the milling process.

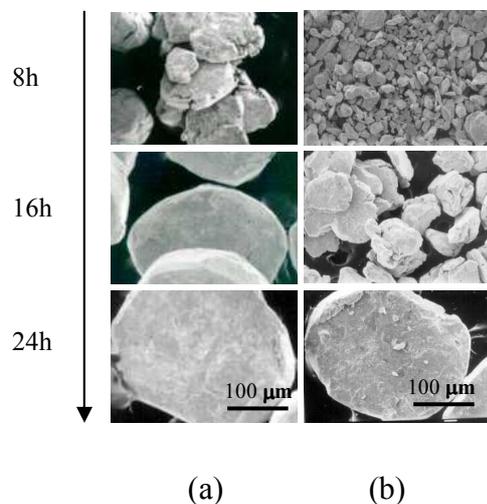


Figure 3 – SEM particle morphologies (70x) as a function of milling time. (a) straight condition, (b) with premilling.

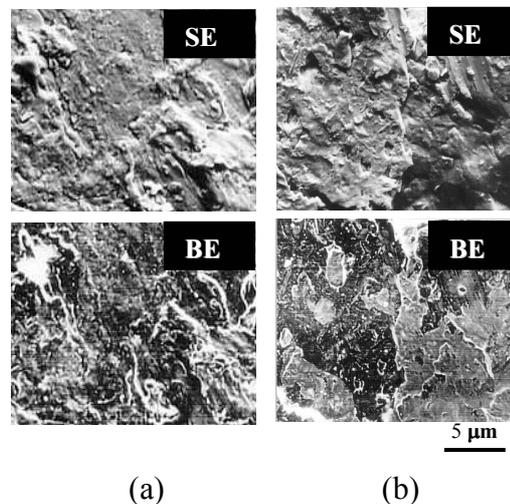


Figure 4 – SEM images (1500x) of the particles milled for 1h. (a) straight condition, (b) with premilling. SE = secondary electrons, BE = back-scattered electrons.

Conclusions

The XRD and MS results show that it is possible to incorporate iron in the fcc-Cu matrix by the two milling processes used in this work. In both procedures, a broad distribution of different local environments of iron atoms was observed in the Mössbauer spectra of the fcc-FeCu phase. This indicates that Fe and Cu are mixed at an atomic level. Mössbauer spectra show further that a fcc non magnetic Fe-rich phase is formed transiently besides the bcc-Fe phase. The reactions are slowed down when premilled powders are used as starting materials. In our milling conditions, similar fcc solid solutions are formed for 24 h (straight condition) and 32h (premilled powders).

Acknowledgements

This work was partly funded by the Portugese-French ICCT-Ambassade de France à Lisbonne cooperation. The authors also thank Pierre Delcroix (LSG2M) for useful suggestions.

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