Microstructure evolution of Cu-Fe-based immiscible alloys prepared by powder metallurgy

O Adam[1], V Jan[1]

Institute of Materials Science and Engineering, Brno University of Technology, Technicka 2896/2, Brno 616 69, Czech Republic

E-mail: Ondrej.Adam@vutbr.cz

Abstract. The work is focused on the preparation of bulk immiscible Cu-Fe-based alloys by powder metallurgy. Three samples with chemical composition $Cu_{70}Fe_{30}$, $Cu_{70}Fe_{15}Co_{15}$, and $Cu_{50}Fe_{25}Co_{25}$ were prepared by mechanical alloying and spark plasma sintering (SPS). Microstructure evolution during sintering and the effect of Co on the resulting microstructure and hardness of the bulk samples were evaluated. Despite the immiscibility of Cu with Fe and Co, the FCC supersaturated solid solution was formed upon mechanical alloying. This supersaturated solid solution was decomposed during SPS and fine microstructure, consisting of separated BCC and FCC phases, was formed. The results showed that cobalt influenced the particle size of milled powders as the particle size of $Cu_{70}Fe_{30}$ alloy was about an order of magnitude higher compared to other alloys. Cobalt also affected the resulting microstructure of bulk samples, however, its effect on the hardness was negligible. It has been shown that powder metallurgy can be used for the preparation of bulk immiscible alloys with the fine microstructure consists of separate phases, which can be individually alloyed by the selected elements, and therefore, powder metallurgy can be considered as a suitable alternative to the more used casting.

1   Introduction

In the last years, much attention has been paid to heterogeneous materials due to their ability to overcome strength-ductility trade-off [1–4]. The good combination of strength and ductility is achieved by hetero-deformation induced strengthening (HDI). It is the result of the heterogeneous microstructure composed of two domains with different mechanical properties (typically hard and soft domains) that can be caused by microstructural, crystal structure, or/and compositional heterogeneities [5,6]. Soft domains are easily plastically deformed than hard domains, which creates gradients of plastic deformation in soft domains. These plastic gradients need to be accommodated by geometrically necessary dislocations (GNU) that contribute to the overall strengthening of the material.

Immiscible alloys can be noted as heterogeneous materials due to their crystal structure heterogeneity. These alloys are characterized by the positive enthalpy of mixing that significantly limited mutual solubility of present elements and the microstructure at room temperature is composed of separated phases of nearly pure elements [7]. Creating domains with different properties is an inherent feature of the immiscible alloys, therefore, these alloys seem to be a promising group of materials for creating advanced heterogeneous materials with a superior combination of strength and ductility. Cu-Fe system is one of the most studied immiscible alloys because it is assumed to be suitable material for electronic components [8,9] and recently has been used as a base for new advanced alloys [3,10]. At room temperature, the microstructure consists of two domains, BCC-Fe phase and FCC-Cu phase [7]. Each domain can be alloyed individually which allows controlling of

its microstructure and properties that leads to the tailoring of mechanical properties. Currently, most bulk Cu-Fe-based alloys are produced by casting although in order to achieve fine and uniform microstructure (thus better mechanical properties) by this method, it is often necessary to subsequently perform homogenization, followed by mechanical and thermal treatment [3,11,12]. On the other hand, powder metallurgy (PM) provides a relatively easy way how to produce material with comparable mechanical properties, in some cases PM can even outperform cast materials [13]. Moreover, PM enables better control of microstructure during processing by setting various parameters during milling and sintering. It has been proven that it is possible to prepare a metastable homogeneous solid solution of Cu-Fe alloy by mechanical alloying (MA) [7,14]. However, there is a lack of studies focusing on sintering such a prepared powder and on the evolution of microstructure during sintering.

This study deals with the microstructural evolution of Cu-Fe alloys prepared by PM and with the effect of cobalt on the resulting microstructure and hardness. For this purpose, three alloys $Cu_{70}Fe_{30}$, $Cu_{70}Fe_{15}Co_{15}$, and $Cu_{50}Fe_{25}Co_{25}$ (at. %) were prepared using the same parameters of MA and sintering. Cobalt was chosen due to its immiscibility with copper, which should lead to alloying only BCC-Fe phase and therefore to increasing heterogeneity between Fe and Cu phases.

2   Materials and method

Immiscible alloy powders with the chemical composition of $Cu_{70}Fe_{30}$, $Cu_{70}Fe_{15}Co_{15}$, and $Cu_{50}Fe_{25}Co_{25}$ were prepared by a high-energy ball milling process. Commercially pure Cu, Co, Fe (purity 99.5 wt. %) elemental powders with particle size corresponds to 325 mesh were used as starting materials. The powder mixtures were milled together with hardened bearing steel balls of 10 mm and 15 mm in diameter, at a ball-to-powder weight ratio of 10:1. Mechanical alloying was performed in an argon atmosphere at the milling speed of 240 RPM for 16 hours using planetary ball mill Fritsch Pulverisette 6. The time scheme of MA was set to 60 min of milling and 30 min of idle to prevent overheating. Additionally, wet milling in ethanol for 15 min was done to fully remove the powder stuck to the milling equipment.

The milled powders were sintered by SPS (Dr. Sinter SPS625) in a 20 mm diameter graphite die in a vacuum atmosphere. Graphite foil was placed between the powder and die to ensure proper electrical contact. Sintering was performed from room temperature with a heating rate of 100 °C/min to the final temperature of 800 °C with 5 min dwell time and uniaxial pressure of 50 MPa. After sintering, the setup was left to spontaneous cool down, until the chamber was opened at ~ 200 °C. The amount of used powder was calculated to obtain 6 mm thick cylindrical samples.

The phase composition of powder and bulk samples was measured by X-ray diffraction (XRD). Philips X'Pert Pro diffractometer was used with Cu-Kα radiation (λ = 1.5418 Å), operated at 40 kV with a current of 30 mA. A continuous scanning was performed for 2θ from 20° to 105° by a speed of 0.011°/min and a step size of 0.0167°. The microstructural analysis of bulk samples was performed by field-emission scanning electron microscope (SEM; ZEISS Ultra Plus) using back-scattered electrons (BSE) for identifying present phases. Secondary electrons (SE) were used for observing milled powders. Chemical composition was measured by Energy-dispersive X-ray spectroscopy (EDS; Aztec, Oxford Instruments). Microhardness measurement was carried out by Qness Q10A hardness tester with a load of 200 g and 10 s dwell time. The presented values are an average of at least six measurements.

3   Results and discussion

3.1   Mechanically alloyed powders

XRD analysis showed that despite the positive enthalpy of mixing, at least partially dissolution of Fe and Co into Cu occurred in all samples, resulting in the formation of FCC supersaturated solid solution (SSS). $Cu_{70}Fe_{30}$ and $Cu_{70}Fe_{15}Co_{15}$ powders showed complete dissolution and their microstructure consisted of only FCC SSS. The microstructure of $Cu_{50}Fe_{25}Co_{25}$ powder contained approximately

14% of BCC phase, which was caused by a higher amount of Fe and Co that had to be dissolved during mechanical alloying. To achieve fully alloyed powder, prolongation of milling time is required. Regardless of the chemical composition, the powder particles flattened to platelet shape during milling (Figure 1). The particle size of powders containing Co was very similar, the average value was in the order of tens micrometers (Figure 1 b), c)). The average particle size of $Cu_{70}Fe_{30}$ powder was one order of magnitude higher, suggesting its low hardness that leads to a reduction of powder fragmentation and an excessive cold-welding effect. On the other hand, greater platelet thickness of $Cu_{50}Fe_{25}Co_{25}$ powder indicates that it had the highest value of hardness.
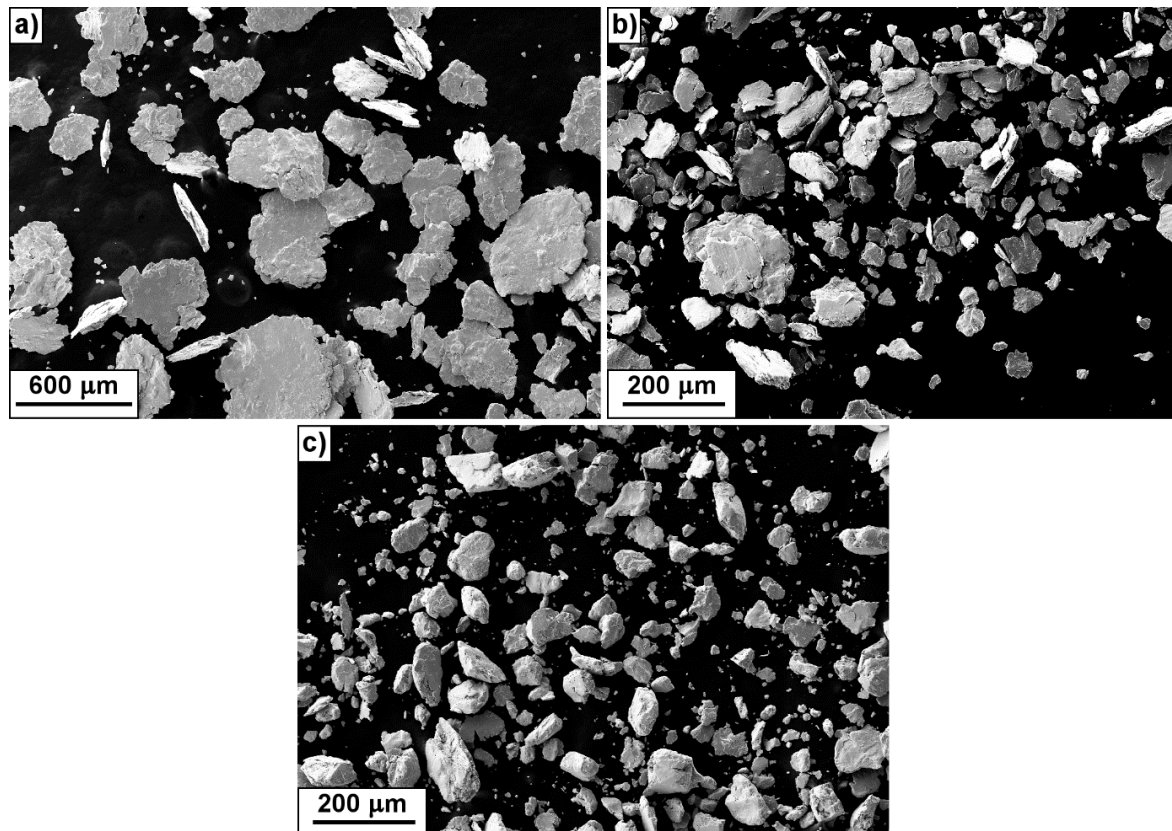
Figure 1. Mechanically alloyed powders: a) $Cu_{70}Fe_{30}$; b) $Cu_{70}Fe_{15}Co_{15}$; c) $Cu_{50}Fe_{25}Co_{25}$. Note that the image of $Cu_{70}Fe_{30}$ was taken at a lower magnification due to the powder size.
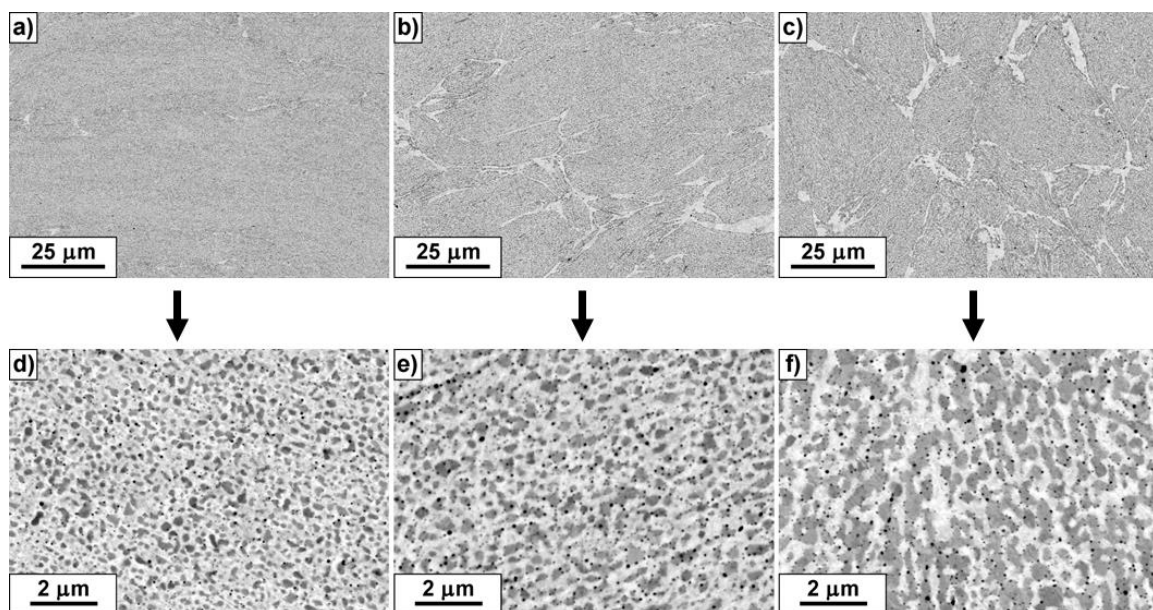
3.2   Bulk samples
XRD analysis revealed that FCC SSS decomposed during SPS and the microstructure of bulk samples was composed of BCC and FCC phase. FCC phase corresponds to Cu and BCC phase corresponds to Fe, in the case of $Cu_{70}Fe_{30}$ alloy [7] or to (Fe, Co) solid solution, in the case of $Cu_{70}Fe_{15}Co_{15}$ and $Cu_{50}Fe_{25}Co_{25}$ alloys [15]. The BCC (Fe, Co) solid solution should be ordered under 730°C (B2 structure), however XRD patterns of samples containing Co were similar to the pattern of $Cu_{70}Fe_{30}$ alloy and no superlattice peak was observed. Therefore it was assumed that the structure of BCC (Fe, Co) solid solution was disordered (A2 structure). The amount of BCC phase of all samples is presented in Table 1. It can be seen that amount of BCC phase of $Cu_{70}Fe_{30}$ and $Cu_{70}Fe_{15}Co_{15}$ alloys was equal to the equilibrium amount, which means that full decomposition of FCC SSS occurred. The equilibrium amount of BCC phase for $Cu_{50}Fe_{25}Co_{25}$ alloy is 48 wt. % indicating the decomposition of FCC SSS during SPS was incomplete and Fe and Co are still partially dissolved in the FCC phase. The separated phases formed a very fine mixture in the microstructures of bulk samples (Figure 2), but relatively large single-phase areas with the chemical composition of pure Cu were also observed. The shape of these areas indicates that they were formed on the surfaces of the milled powder particles, but

the origin of their formation is not clear. However, it is evident that the presence of these areas was more pronounced in the samples containing Co, which forms a solid solution with Fe and is immiscible with Cu. It is therefore assumed that Co increased the driving force of phase separation that leads to the formation of large pure Cu areas. The effect of Co on the resulting microstructure can be also seen on the micrographs of the fine mixture of separated phases that are shown in Figure 2 d)–f). Microstructures of $Cu_{70}Fe_{30}$ and $Cu_{70}Fe_{15}Co_{15}$ alloys were very similar, composed of the submicron BCC phase embedded in the continuous FCC phase. However, $Cu_{70}Fe_{15}Co_{15}$ alloy contained coarser BCC phase suggesting that phase separation was more pronounced in this case, and thus that Co promotes phase separation. The microstructure of $Cu_{50}Fe_{25}Co_{25}$ alloy was relatively coarse with an obvious gradual merging of BCC phases. It has to be noted, that in this case, the phase separation was not completed and the continuous FCC phase was still formed by the SSS as was evaluated by XRD. The microstructures of all alloys contained also homogeneously dispersed round nano-sized particles, which were determined as oxides and carbides by EDS. The presence of carbides and oxides is common in materials prepared by PM. Moravcik et al. [16] have shown that the main oxides source is the oxidation of elemental powder surfaces and carbides are formed due to the carbon contamination during milling (wear of milling bowl and balls) and SPS (carbon-rich environment inside graphite die).

Table 1 also presents the average hardness of all samples. By comparing the results of $Cu_{70}Fe_{30}$ and $Cu_{70}Fe_{15}Co_{15}$ alloys it is clear that Co has no effect on the hardness of bulk samples. In this study, $Cu_{70}Fe_{30}$ alloy achieved even slightly higher average value of hardness (234 ± 2 HV0.2) than $Cu_{70}Fe_{15}Co_{15}$ alloy (228 ± 4 HV0.2), although, with respect to data scattering, the values can be considered as equal. $Cu_{50}Fe_{25}Co_{25}$ alloy showed the highest hardness (282 ± 12 HV0.2). Since the amount of BCC phase is comparable to other samples, this increase in hardness is attributed to the solid solution strengthening of present FCC SSS.

Table 1. Amount of phases measured by XRD and average Vickers hardness.

Alloy	Amount of phases [wt. %]		Hardness [HV0.2]
	FCC	BCC	
$Cu_{70}Fe_{30}$	72	28	234 ± 2
$Cu_{70}Fe_{15}Co_{15}$	72	28	228 ± 4
$Cu_{50}Fe_{25}Co_{25}$	76	24	282 ± 12

Figure 2. Microstructures of bulk samples. The bottom row of images shows a close-up view of a fine mixture of separated phases. a), d) $Cu_{70}Fe_{30}$; b), e) $Cu_{70}Fe_{15}Co_{15}$; c), f) $Cu_{50}Fe_{25}Co_{25}$. FCC phase is bright, BCC phase is dark. Black dots in the images in the bottom row are oxides and carbides.

3   Conclusion

In this paper, three immiscible alloys with the chemical composition of $Cu_{70}Fe_{30}$, $Cu_{70}Fe_{15}Co_{15}$, and $Cu_{50}Fe_{25}Co_{25}$ were prepared by powder metallurgy. Based on the results, the following conclusions can be drawn:

- combination of mechanical alloying and SPS provides a suitable method for the preparation of immiscible alloys with fine microstructure
- Co reduced excessive cold-welding effect during MA that led to the smaller particle size of milled powder
- the microstructure of bulk samples was composed of pure Cu areas, a mixture of separated BCC and FCC phases, and round nano-sized oxides and carbides
- it is assumed that Co promoted phase separation leading to the more pronounced formation of pure Cu areas and a coarser BCC phase
- Co had a negligible effect on hardness of bulk samples

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