

## **EFFECT OF Cr AND Ni ELEMENTS ON THE MICROSTRUCTURE AND PROPERTIES OF Cu-Fe-BASED IMMISCIBLE ALLOYS**

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### **Abstract**

The immiscible Cu-Fe system is often used as a base for advanced heterogeneous alloys. With a suitable selection of alloying elements, it is possible to alloy individual phases and therefore tailor microstructure and final properties of a material as needed. To prepare the mentioned multicomponent alloys, it is necessary to understand the effect of individual alloying elements on the microstructure and properties of the Cu-Fe system. Although mostly used method in production of such materials is casting, mechanical alloying appears to be a suitable alternative, enabling a very fine microstructure to be created.

The following study is focused on the characterization of  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  and  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  alloys and the effect of the alloying elements on their microstructure. Cr and Ni were selected as a BCC and FCC phase enhancing elements, respectively. The alloys were prepared by mechanical alloying using high-energy ball mill, with subsequent densification using spark plasma sintering. The microstructure of milled powders, as well as bulk samples, was examined, and the evolution of the microstructure during sintering evaluated with respect to the alloying elements. In addition, the hardness of bulk samples was measured. During the mechanical alloying a complete mixing was not achieved, as the milled powders were not single phase. However, a metastable FCC supersaturated solid solution was formed at least partially in both alloys, further decomposing into a multiphase microstructure after sintering

**Keywords:** Immiscible alloys, mechanical alloying, spark plasma sintering, heterogeneous materials

### **1. INTRODUCTION**

The elements of the Cu-Fe system are characterized by a positive enthalpy of mixing which prevents them from forming solid solutions neither intermetallic compounds at room temperature. The peritectic Cu-Fe binary diagram exhibits a metastable miscibility gap in the liquid state, suggesting that a liquid-liquid phase separation is inevitable to occur when an ordinary solidification method is used [1]. However, the advantages of such a material combining the properties of iron and copper could outweigh the difficulties connected with their preparation. With a suitable choice of alloying elements, a range of tailor-made microstructures could be developed according to various specific needs [2].

Although casting ranks as the most used material production method, in these circumstances it seems to be problematic to overcome the phase separation as the solidification proceeds on a large scale [3], as a sufficiently high cooling rates are necessary [4]. So far, immiscible Cu-Fe alloys were prepared utilizing for instance casting [5] high pressure torsion [6], gas atomization [7] or mechanical alloying [8]. Particularly mechanical alloying seems to be a convenient alternative, due to its ability to increase the mutual solubility of iron and copper, as well as create generally very fine microstructure [9, 10]. In ideal case this could be done by firstly creating a homogenous supersaturated solid solution during mechanical alloying, which would then decompose into heterogeneous microstructure consisting of harder and softer domains with high interface density, enhancing both strength and ductility [11].

Moreover, by adding alloying elements further adjustments to the microstructure can be made according to different preferences, therefore this study is focused on two extra alloying elements to the Cu-Fe system and their effect on the microstructure and phase distribution. Particularly nickel which is soluble with both iron and copper, and chromium soluble with iron only. Such a choice of alloying elements is interesting regarding different lattice, keeping in mind the Fe and Cr have both BCC lattice, whereas Cu and Ni possesses FCC lattice, and altering the mechanical properties by changing the percentage of original phases present. The use of powder metallurgy in preparation of such alloys brings extra advantages connected with the possibility to examine the materials during the preparation process, after mechanical alloying and after sintering, and therefore, obtain a better overall understanding of the material's microstructure and properties.

## 2. MATERIALS AND METHODS

The chemical compositions of the studied immiscible alloys were  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  and  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$ , both prepared by the same process, using powder metallurgy. The purity of used elemental powders was >99.5 % for all the elements, with particle size <45  $\mu\text{m}$ . Hardened bearing stainless steel balls of 10 mm and 15 mm diameter were used as milling medium, in a 1:10 balls-to-powder weight ratio (BPR). The milling was performed using Fritsch Pulverisette 6 planetary ball mills at the speed of 240 rpm for 15 h under argon atmosphere, followed by a 15 min of wet milling in ethanol, in order to minimize the residual powder situated on the surfaces of milling balls, bowl and lid. The scheme of milling cycles was set to 30 min of milling and 30 min of pause time, in order to prevent undesirable temperature increase.

Consolidation of the milled powder was performed by spark plasma sintering (SPS) using Dr. Sinter SPS 625 machine. The process was carried out in a vacuum atmosphere and a graphite die with a 10 mm inner diameter was used, with a graphite paper placed between the die and the powder to provide sufficient electrical contact. Starting from the room temperature, the sintering scheme was set to 800 °C at a heating rate of 100 °C/min with a 5 min dwell time at final temperature, and the pressure was set to 50 MPa. The sample was left to cool down to room temperature in vacuum. The resulting bulk sample obtained is of cylindrical shape, with a 10mm diameter and 7 mm in thickness.

Both powder and bulk samples were hot mounted in a polymeric resin and grinded with SiC papers up to 4000 grit size, followed by polishing with 3  $\mu\text{m}$  and 1  $\mu\text{m}$  diamond paste and mechano-chemical polishing by Struers OP-U suspension, to prepare them for microstructural observations.

Measurements of phase composition were performed by X-ray diffraction (XRD), Philips X'Pert Pro diffractometer was used Cu-K $\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ), operated at 40 kV with a current of 30 mA. A continuous scanning was performed for  $2\theta$  from 20° to 100 ° by a speed of 0.011 °/min and a step size of 0.02°. The amount of present phases was determined by the Rietveld method.

Scanning electron microscope (SEM) characterization was performed utilizing ZEISS Ultra Plus FEG microscope and energy dispersive X-ray spectroscopy (EDS), Aztec, Oxford Instruments was used to measure the chemical composition.

The thermal stability behavior of the milled powder was examined by differential scanning calorimetry (DSC), Setaram Setsys Evolution. The measurement was performed with an amount of 30 mg of loose powder inserted into an alumina crucible with a lid. An identical crucible used as a reference. The heating scheme was set to 1400 °C, starting from 100 °C, at a heating rate of 20 K/min in an argon atmosphere, in two subsequent cycles.

The Vickers microhardness was measured using Qness Q10A tester with a load of 200 g and 10 s dwell time. The values of hardness presented are an average of 10 measurements.

In addition, the equilibrium phase fraction of the phases was calculated by CALPHAD calculation using ThermoCalc software (version 2020b) with thermodynamic database TCHEA v4.1.

### 3. RESULTS AND DISCUSSION

#### 3.1. Powder samples

The XRD analysis suggested that despite the positive enthalpy of mixing, at least a partial dissolution of the alloying elements occurred. The phase composition consisted of FCC and BCC phase. In case of  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$ , the amount of FCC phase was 70.6%, whereas in case of  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  it was 97.1% (**Table 1**). The reason of the inferior intermixing of  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  may be the phase strength difference of used elemental powders [12], which is more pronounced in  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$ , with combination of the immiscibility of Cr with Cu.

According to EDS, the chemical composition of both mechanically alloyed powders corresponded to the intended one, and therefore, no extensive contamination during alloying occurred. The microstructure of  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  powder contained a notable amount of inhomogeneity composed of unmixed Cr and Fe. The chemical composition of the powder matrix contained slightly higher percentage of Cu and Fe, than was originally intended, whereas the amount of Cr was lower. The results suggested that Cr, rather than intermixing with Fe, stayed separated and embedded within the matrix of the solid solution, despite of their mutual solubility.

The microstructure of  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  was more homogenous, when compared to  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$ . Only small amount of separated Fe-rich areas was present in the matrix. As well as  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  powder, the chemical composition of matrix contained all three elements. According to XRD and EDS results, it could be suggested that the matrix of both powders consisted of metastable supersaturated solid solution.

The difference in degree of homogeneity in both samples indicated, that adding Cr as ternary alloying element presumably slowed down the process of forming a homogenous metastable supersaturated solid solution, due to the mutual immiscibility of Cr with Cu. Addition of Ni did not seem to decelerate this formation, when compared to times necessary for creating a single-phase metastable supersaturated solid solution of Cu-Fe system [13, 14].

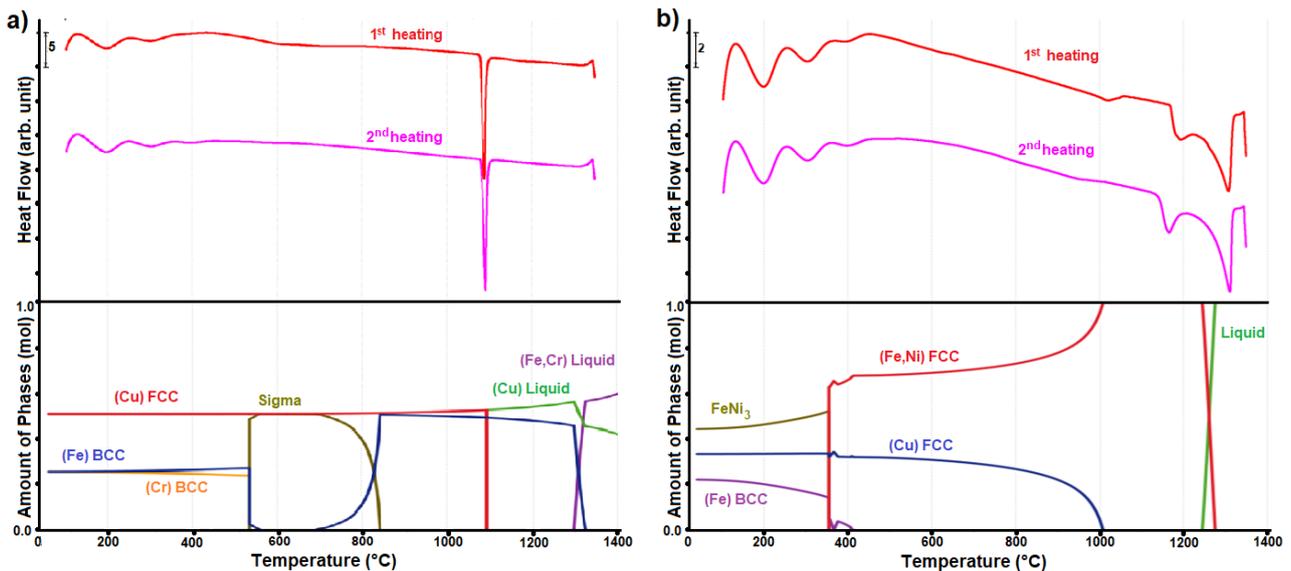
**Table 1** Amount of phases determined by XRD

| Sample        | Amount of phases (wt%) |        |        |
|---------------|------------------------|--------|--------|
|               | FCC                    | BCC #1 | BCC #2 |
| CuFeCr powder | 70.6                   | 29.4   | -      |
| CuFeCr bulk   | 52.9                   | 25.6   | 21.5   |
| CuFeNi powder | 97.1                   | 2.9    | -      |
| CuFeNi bulk   | 83.7                   | 16.3   | -      |

Yet it was interesting that in case of  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  the unmixed segments either contained nearly pure Cr or Fe with only traces of Cr (< 5 at%), whereas in case of  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  the unmixed Fe-rich segments contained a noticeable amount of Ni and Cu (up to 10 and 20 at%, respectively). This could indicate that whereas in  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$ , Fe and Cr were alloying individually into Cu, the co-deformation induced by mechanical alloying took place more thoroughly through the  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  sample, primarily by alloying Fe and Ni into Cu, secondarily by alloying Cu and Ni into Fe. This suggested another difference in the effect of ternary alloying element.

The DSC curves in **Figure 1** further confirmed at least partial existence of a metastability in both samples. The exothermic peak around approximately 400 °C in both  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  and  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  corresponded to the decomposition of metastable FCC supersaturated solid solution. The endothermic peak in  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  sample at 1100 °C represented the melting of Cu and was in accordance with the calculated equilibrium diagram. Despite of more phase transformations being predicted to take place by the course of the equilibrium

diagram, none of them were noticeable on DSC curve (**Figure 1a**). The probable reason was that the powders prepared by mechanical alloying were generally far from equilibrium state, and therefore undergo transformations other than those predicted by the equilibrium phase diagram. The DSC curve of  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  (**Figure 1b**) seemed to be more in accordance with the equilibrium diagram. The small exothermic plateau occurring shortly after the sample was heated over 1000 °C corresponded to the crossing of solvus line and the two subsequent peaks indicated a ternary peritectic reaction [15].



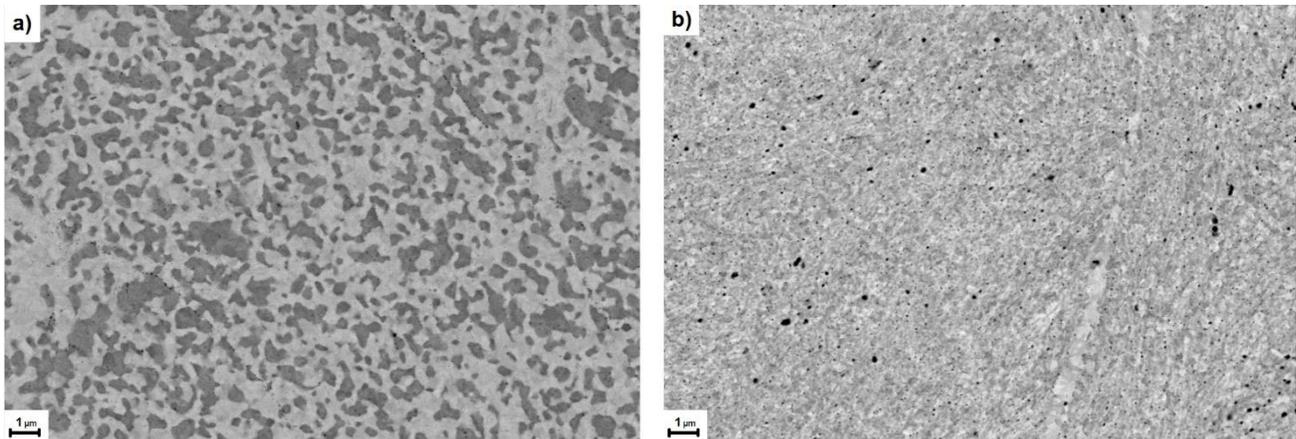
**Figure 1** DSC curves of milled powder and equilibrium phase diagrams: a)  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$ ; b)  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$

### 3.2. Bulk samples

The phase composition of the consolidated samples changed, according to XRD. The amount of FCC phase dropped, suggesting that the original supersaturated solid solution decomposed during SPS.  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  contained one FCC and two BCC phases (for detailed values see **Table 1**). This was in accordance with the calculated equilibrium phase diagram. The FCC phase should correspond to Cu-rich phase and the BCC phases to Fe-rich and Cr-rich phases. The chemical composition of the sample stayed roughly the same, according to EDS, although noticeable carbon peaks were detected, indicating that a slight contamination by C occurred during the sintering, as the process took place in a graphite die [16]. Despite XRD results, only two phases were observed in the microstructure, namely Cu-rich phase and a phase containing Fe and Cr in an equimolar proportion. The second BCC phase, identified by XRD, was not observed (**Figure 2a**). The reason for this inconsistency between the XRD analysis and bulk microstructure could not be defined based on the results and will be the subject of further research. A considerable quantity of very fine dark particles appeared mainly in (Fe, Cr)-rich phases. Although the size of the particles was below the EDS detection limit, it could be assumed that carbides and oxides might have been present as a result of contamination during mechanical alloying and sintering. This phenomenon is common in alloys prepared by powder metallurgy [17].

$\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  contained FCC and BCC phases (**Table 1**), according to XRD, which was not in agreement with the equilibrium phase diagram, as FCC Cu-rich, ordered FCC ( $L_{12}$ )  $\text{FeNi}_3$  and BCC Fe-rich phase should be present. A very fine mixture was formed in the microstructure (**Figure 2b**). According to the difference in contrast, it could be possible that three phases were present in the microstructure, which would then correspond with the equilibrium phase diagram. It is therefore possible, that an overlapping of peaks occurred during XRD analysis, due to their suchlike position in the examined range [18,19]. Nevertheless, with respect to the very small size of the phases, it was not possible to verify this theory using EDS. Another explanation

could be that a full decomposition of the FCC supersaturated solid solution did not occur during SPS process, and equilibrium was not reached. Therefore, the microstructure contained BCC Fe-rich phase and a metastable FCC phase, consisted of Cu and Ni. The different phase contrast would be then caused by a different grains orientation. To solve this problem, a TEM analysis is necessary.



**Figure 2** Microstructures of bulk samples: a)  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$ ; b)  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$

The Vickers hardness was evaluated to  $279.3 \pm 5.3 \text{ HV0.2}$  in  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  sample and the hardness of  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  was  $268.2 \pm 2.9 \text{ HV0.2}$ . Cr, which should induce higher hardness of alloy in comparison with Ni, did not cause a significant difference in hardness. This was probably a consequence of microstructure.  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  has a coarser microstructure, where (Fe, Cr)-rich phases were embedded in Cu-rich matrix. On the contrary  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  had significantly finer microstructure, increasing its hardness.

#### 4. CONCLUSION

In this paper, immiscible  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  and  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$  immiscible alloys were prepared by means of powder metallurgy. Based on the results, the following conclusions can be drawn:

- Alloying of Cr as a ternary element slowed down the process of mechanical alloying
- In both samples a supersaturated solid solution was formed at least partially
- After sintering,  $\text{Cu}_{50}\text{Fe}_{25}\text{Cr}_{25}$  microstructure was coarser in comparison with  $\text{Cu}_{50}\text{Fe}_{25}\text{Ni}_{25}$
- The hardness of both samples did not differ significantly and was approximately 270 HV0.2

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