An assessment of the homogeneity of nano-crystalline Fe–Cu powders as studied by means of APT

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ABSTRACT

In this contribution the homogeneity of mechanically alloyed Fe–Cu powders for two different compositions (Fe-10 and Fe-2.5 at%Cu) has been systematically characterised by atom probe tomography. Since Fe–Cu exhibits the Invar effect, it is among the most attractive systems for technical application. Furthermore, this system is immiscible and characterised by a large positive heat of mixing. In combination with the widespread application and accessibility, this predestines Fe–Cu as a binary model alloy to elaborate the enforced nonequilibrium enhanced solubility for immiscible systems. Depending on the parameters composition and milling time, results on the extension of the solubility limit and on the homogeneity of the alloy are presented, discussed and compared to earlier works. Only for the alloy with lower Cu content and for the prolonged milling time of 50 h, chemical homogeneity of the sample as measured by the atom probe was fully reached on the nano-scale. For all other parameter combinations homogeneity could not be achieved, even for long milling times and for those samples that appear to be homogeneous via X-ray analysis. Moreover, impurities were determined, mostly stemming from the fabrication procedure. The arrangement and homogeneity of the most common impurity, oxygen, was evaluated from atom probe data for different samples.

Thus, the local concentration, segregation effects and the distribution of impurities could be quantified on the nano-scale, depending on the different nominal compositions and processing parameters.

Additionally, structural information could be gained employing transmission electron microscopy and diffraction measurements.

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1. Introduction

The process of mechanical alloying (MA) has been in industrial application for decades. It presents a simple and cheap preparation route, which can easily be scaled up from laboratory to industrial performance. Thus, MA allows for the mass production of metastable material such as supersaturated solid solutions, chemically disordered intermetallics, nano-crystalline and amorphous materials [1]. These metastable states can be reached via ball milling due to the severe plastic deformation processes, repeated fracture and cold-welding processes exerted on the powder particles in the form of collisions with the balls in a vial. These massive impacts result in repeated fracture and cold-welding processes.

Nano-crystalline materials due to their nonequilibrium state often outclass their polycrystalline counterparts regarding macroscopic properties especially concerning hardness and wear resistance. Thus, they constitute favoured materials for coatings and other powder metallurgical processing routes, e.g. as feedstock for consolidation to bulk materials. But for the time being the process of MA has to be adapted to every new material via trial and error as there is no commonly accepted model for the mixing of miscible elements during this process.

Benjamin and Violin [2] were the first to describe the alloying of two ductile elements A and B with negative heat of mixing, observing a lamellar structure of A and B upon ball milling. The interdiffusion process is regarded to be enhanced due to a reduced diffusion length, an increased defect density and a drastically enhanced temperature at the sites of impact. This enhanced temperature will promote the alloying in miscible systems, but impede or even prevent this process in immiscible systems.

Hence, it is not surprising that the comprehension of the fundamental alloying mechanisms is still lacking for systems with a positive heat of mixing, even though MA has been observed for

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several alloys [3–6]. As mentioned above, a diffusion-controlled mechanism as suggested for miscible alloys cannot hold in immiscible systems. Currently, several models are subject of great controversy. The main topic to be addressed within these models is the mode of energy storage, when the solid solution is formed.

The enormous amount of grain boundary energy provided by the nano-crystalline structure is held responsible for the formation of supersaturated solution in the context of the theory of Veltl et al. [7]. An increased dislocation density is suggested by Eckert et al. [8] as the driving force for mixing. Yavari and Desree [9] suspected the large amount of oxygen in their samples, which was introduced by the ball milling process itself, to lower the enthalpy of mixing of the ternary system substantially, resulting in a negative value. An additional process was subsequently proposed by Yavari et al. [10] based on the finding of crystallite fragments of particularly small tip radii within the milled composite powders. For such small tip radii the capillary pressure forces are dramatically increased, leading to the dissolution of the fragments and further on to the formation of a homogeneous solid solution. Yavari et al. [10] estimated the chemical interfacial energy in dependence of the crystallite diameter for the Fe–Cu system. The calculations yielded a critical diameter of 2 nm for the transition from composite structure to solid solution. While Yavari et al. [10] assumed the formation of incoherent interfaces, Gente et al. [3] suggested a different model by assuming coherent interfaces for the Cu–Co system.

Evidently, the distinction between these models can only be drawn on the nano-scale. Owing to its exceptional capability of spatially resolved, quantitative chemical analysis, atom probe tomography (APT) offers a unique possibility to elucidate these questions [11].

Recently, the major difficulty of preparing the fine needle-shaped specimen, required for APT analysis, directly from powder materials was overcome. The application of the focused ion-beam (FIB) milling to powders constitutes a recent breakthrough in the preparation [12–14]. Due to this achievement, APT could be successfully applied to the native ball milled powders to elucidate the underlying alloying process of the Fe–Cu system.

2. Experimental procedure

A high-energy planetary ball mill (AGO-2) was used to prepare nano-crystalline Fe–Cu powders by MA. Elemental powders with purities $\geqslant 99.7\%$ were processed under a protective argon atmosphere using milling tools made of hardened steel and at a rotation speed of 400 rpm at the Research Center for Machine Parts and Materials Processing (University of Ulsan, Korea). Milling times were varied systematically from 2 to 50 h to produce powders of nominal Cu-concentrations of 2.5 at% and 10 at%, respectively. The overall temperature of the grinding vessel was kept constant at room temperature by a continuous high flow of cooling water during the entire milling process.

To gain insight into the physical mechanisms of the alloying process itself, they had to be separated from other mechanisms occurring during further mechanical treatment, like encapsulation or consolidation. Thus, the unaltered powder was used directly, employing an alternative processing route for the fabrication of samples for APT and transmission electron microscopy (TEM). The powders were dusted onto double-stick carbon tape and mounted onto conventional sample holders used for scanning electron microscopy (SEM). By means of a dual-beam FIB (FEI Nova Nanolab 600) with Ga-ions of 10–30 kV accelerating voltage, specimens suitable for APT and TEM investigations were produced. In addition to ion milling, this instrument allows for

micro-manipulation via a needle probe and for Pt deposition via ion-beam-assisted chemical vapour deposition.

As scanning electron micrographs confirmed powder particle sizes in the range of 10–100 μm, the in-situ lift-out technique described by Miller et al. [12] and Choi et al. [13,14] could be applied to the samples. This adopted process is described in detail in [15]. The tomographic atom probe, its operation principle and the experimental setup have been described in detail by Blavette et al. [16]. In this study a specimen temperature of 30 K, a pulse voltage to base voltage ratio of 25% and a pulse frequency of 1000 Hz were found to be the most adequate acquisition parameters. These enabled mechanically stable samples during APT analysis and an optimum agreement of the detected concentrations with the nominal compositions.

The X-ray diffraction (XRD) was conducted in a Siemens D500 apparatus using a Co source with a K-alpha wavelength of 0.17902 nm.

3. Results and discussion

XRD patterns of Fe-10 at%Cu for various milling times are shown in Fig. 1. The Fe-2.5 at%Cu was not considered for X-ray analysis due to the detection limit inherent in this method. At least 2 vol% of a constituent phase is needed to reliably produce a peak. Thus, it is much more likely to identify Cu peaks in Fe-10 at%Cu than in Fe-2.5 at%Cu.

Nevertheless, even for Fe-10 at%Cu the shortest milling time of 2 h suffices to distribute enough Cu within the Fe-matrix to extinguish the fcc Cu peaks. Only peaks of bcc Fe can be identified when compared with the tabulated powder standards. Regarding the detection limit mentioned above, it can be assumed that the fraction of remaining pure Cu is less than about 2 vol% of the whole sample. But it has the exception that the XRD pattern of the material scarped from the vial walls (after 2 h of milling) shows distinct peaks of fcc Cu.

TEM was successfully applied to confirm the nanocrystallinity of the material. The overall aspect was dominated by manifold and numerous lattice defects. Furthermore, two morphologically different regions could be distinguished within the individual powder particle. For Fe-10 at%Cu after 10 h, the region of the TEM
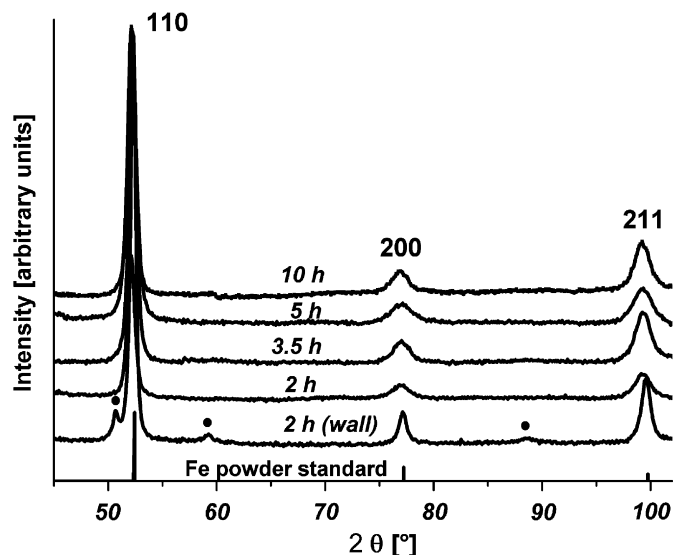

Fig. 1. No peaks of pure fcc Cu can be found in the diffraction patterns of Fe-10 at%Cu. Only the material scraped from the vial walls exhibits peaks of unalloyed Cu (see dots).