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The effect of impact energy on the formation of nanocrystalline powders in Cu–50% Fe immiscible alloy systems

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The study of mechanical alloying in the Cu–Fe system, as a model system for those with positive heats of mixing, has been investigated. The effects of impact force which pertains to ball-to-powder ratio, rotation speed and milling time, on the strain and grain size of final powders have been studied. The aim of this research was to find the optimum condition for mechanical alloying of Cu–Fe system by the automatic design and analysis of Taguchi experiments. X-ray diffraction (XRD) was used to analyze the effect of incoming energy on the diffusion rate.

Key words: *mechanical alloying; nanocrystalline; immiscible systems; diffusion; Taguchi design*

1. Introduction

Over the last three decades, powder processing by ball milling has attracted wide practical interest as it offers a simple but powerful way to synthesize non-equilibrium phases and microstructures from nanograin materials to extended solid solutions, amorphous phases [1–3], chemically disordered compounds [4–7], and nanocomposites [8, 9]. Mechanical alloying (MA) can be comparable with those methods accompanied by cold working (dislocation density about 10^{11} cm^{-2}). In MA, powders are entrapped between ball–ball and ball–wall and the impact force of the collision transfers to them. Therefore, powders undergo a severe plastic deformation, which causes a strain rate of 10 s^{-1} and, therefore, significantly enhances dislocation density. If two different kinds of powder particles are joined together and then flattened because of the impact force, they become like a lamellar composite (thickness ca. 0.1–0.5 μ), and

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the diffusion distance decreases. Another significant parameter which promotes diffusion during MA is the presence of new surfaces. Fracturing powders results in appearance of new surfaces which are clean, i.e. without oxide layers, and prepare good sites for atomic motion and diffusion. Mechanically alloyed powders also exhibit extension of equilibrium solid solubility limits, which is important in miscible systems [10, 11]. It becomes more significant in systems such as Cr–Cu [12], Ag–Cu, Cu–Fe [13], Cu–W [14, 15] and Al–Pb [16] which are immiscible at room temperature by using other methods and are partially or even fully soluble by using MA.

The Cu–Fe system does not form any intermetallic compounds and has negligible mutual solid solubility in equilibrium at temperatures below 700 °C because of the large positive enthalpy of mixing [17]. During MA, the energy of balls transfers to the entrapped powders and causes severe plastic deformation, thus enhancing density of dislocations and promotes the formation of excess vacancies [18]. On the other hand, pipe diffusion needs low temperature and high strain rate or stress which are provided by MA [19, 20]. These conditions together increase atomic diffusion and consequently lead to the formation of solid solutions of Cu(Fe). Although there exist lots of research work on the formation [21–23] and characterization [24–27] of the Cu–Fe immiscible system, there is no analytical viewpoint on the effect of milling parameters and mixed fraction of its mechanical alloying. Note that according to Jiang et. al. [25], mechanical alloying leads to the formation of single-phase solid solutions of up to 60 at. % Fe in Cu, and 20 at. % Cu in Fe but according to our research, based on XRD peak position and width changes, no detectable dissolution of Cu in Fe is observed. This research work addresses the optimum parameters to diffuse Fe in Cu, and also the effects of impact force on the strain and grain size of final powders in Cu–Fe systems have been studied. The Taguchi method is a scientifically rigorous mechanism for evaluating and implementing improvements in processes, materials, equipment, and facilities. These improvements are aimed at improving the desired characteristics and simultaneously reducing the number of defects by studying the key variables controlling the process and optimizing the procedures or design to yield the best results. In other word, Taguchi helps to design samples to find these optima and reduces the number of required samples and consequent tests.

2. Experimental

Mechanical alloying was performed in a high-energy ball milling Fritsch P-5 planetary mill using stainless steel containers and balls (15 mm in diameter). The 50% Cu–50% Fe alloy powders were produced by milling 3.2 g of copper powder (99.7% pure, <100 μm) and 2.8 g of iron powder (> 99% pure), both purchased from Merck. Stearic acid (1 wt. %) was added to the initial powders in order to prevent agglomeration. After milling, the powders were removed from the container. The milled samples were analyzed by X-ray diffraction (XRD) in a Siemens (D-500) diffractometer using CuK$_\alpha$ radiation (λ = 0.1540510 nm).We used an automatic design and the analysis of Taguchi experiments to find the optimum parameter values. Three most significant factors including ball-to-powder ratio (BPR), time and speed were chosen. We assumed that arranging two levels for each of these factors can help to realize the values of most significant parameters. Therefore, the BPR values 10 and 20 have been chosen. For time and speed, levels of 10–20 h and 200–400 rpm realized to be the finest amounts. Based on 2-level control factors Taguchi offers L-4 design which is listed in Table 1. CF0 represents a mixture of unmilled elemental powders.

Table 1. Conditions and parameters of the experiment

Sample	BPR	Time [h]	Speed [rpm]
CF1	10	10	200
CF2	10	20	400
CF3	20	10	400
CF4	20	20	200

3. Results and discussion

XRD spectra of the milled samples are shown in Fig. 1. The diffraction Bragg peaks are broadened, shifted and reduced in intensity. Several factors such as decrease in crystalline size, internal strain and broadening, due to the X-ray machine itself, can be related to the peak broadening. We omit the third factor and investigate on the first two. Each sample has its own conditions (different BPR, speed and milling time) which cause the changes in peaks. Note that each of the selected parameters affects changes in peaks by its own power which can be analyzed employing Taguchi procedure. This power is a combination of impact factor (which pertains to BPR and speed) and milling time. On the other hand, it is clear that diffusion of Fe atoms in Cu lattice results in broadening of peaks. Diffusion of Fe atoms in Cu lattice leads to increase in the lattice constant. It means that the lattice parameter of Cu increases which leads to the reduction in degree of peaks. Although Fe and Cu have similar atomic radii, and mechanical alloying can promote the formation of both Fe(Cu) and Cu(Fe), based on XRD results (changes in width and position of (110) peak) and even considering atomic radius and melting temperature prove that atomic diffusion of Fe into Cu matrix and consequently formation of Cu(Fe) is more likely than Cu atoms to diffuse into Fe matrix.

Table 2 lists peak position, broadening values, relative crystallite sizes and lattice parameters of Cu. The crystallite size evolution for milled powders was determined by the Williamson–Hall method. The method is based on the broadening of the diffraction lines due to the strain and crystallite size. The Williamson–Hall equation is expressed as [28]:

$$\sqrt{(B_i^2 - B_0^2)}\cos\theta = \frac{0.89\lambda}{d} + S\sin\theta \tag{1}$$

where B_i is the full width at a half-maximum (FWHM) of the peaks of mechanically alloyed powders, B_0 the width at a half-maximum of peaks of unmilled powders, θ – the Bragg angle, λ the wavelength of X-ray, S the internal microstrain and d – crystallite size.

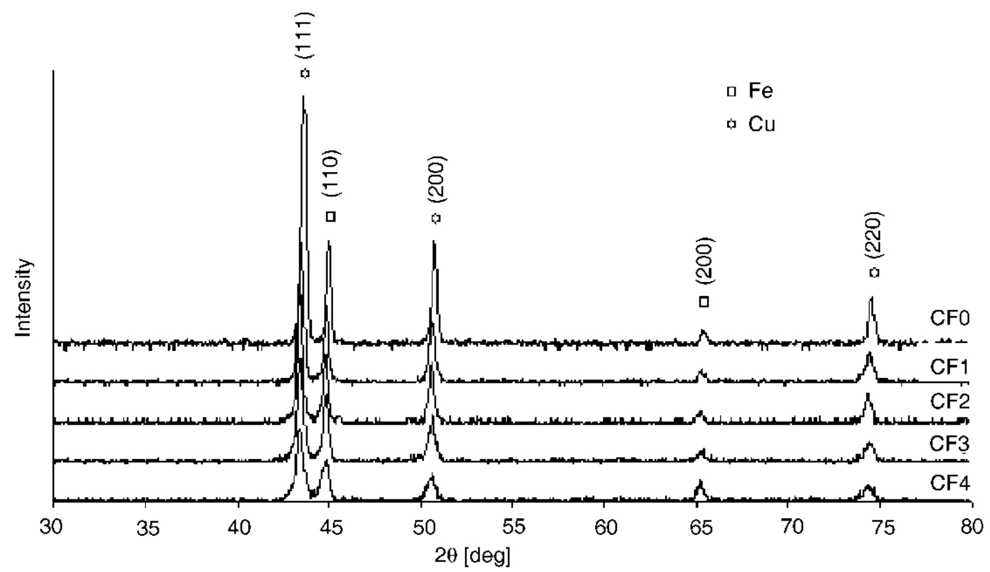

Fig. 1. XRD spectra of milled samples at various milling conditions

Table 2. Peak positions, width of (111) peak, microstrain and crystallite size of samples

Sample	2θ (111) [deg]	FWHM	Microstrain S	Crystallite size d [nm]	Lattice parameter [nm]
CF0	43.64	0.27	–	-	0.3588
CF1	43.50	0.32	–0.0017	42	0.3594
CF2	43.46	0.29	–0.0011	65	0.3592
CF3	43.50	0.36	–0.0024	30	0.3597
CF4	43.44	0.41	–0.0031	23	0.3599

A comparison of these values with each other shows that the shift of (111) peak is more significant in CF4, which means that its operating condition is the most significant. From Taguchi design and its analysis, it is clear that the important factors are BPR, speed and time, respectively.

According to Eq. (1), the crystallite size of samples can be calculated from the intercept of the straight line, whereas the values of microstrain can be obtained from the slope of this line. Figure 2 illustrates the effect of milling condition on the microstrain and the crystallite size of samples. As shown in Fig. 2, the value of $\sqrt{(B_i^2 - B_0^2)}\cos\theta$ decreases linearly with sinθ. It is obvious that negative slope of these lines correlates to the compressive induced stress caused by ball collisions. The impact energy of balls has a direct relationship with their collision speed and their numbers (which create the PBR factor). These factors, i.e. impact energy and milling time can explain the arrangement of the straight lines. The greater the impact energy, the higher is the induced strain. Another noticeable parameter is lattice parameter of Cu matrix. As listed in Table 2, and considering dissolution of Fe atoms in Cu lattice, substituting Fe atoms into Cu lattice result in increasing of the distance of Cu planes. Difference between Cu and Fe atomic radii causes this change. So as a result of Fe dissolution into Cu lattice, in addition to the effect of induced microstrain, lattice parameters change (Table 2). Taguchi design can estimate the optimum condition to achieve the least crystalline size which was the last sample. One can estimate that using BPR of 20, time of 20 h and speed of 200 rpm are the optimum parameters just like sample CF4. Although it might seem that increasing the speed could enhance the impact energy, it should be kept in mind that an increase above the criyical value leads to adhesion of balls to the wall of vials. Incidentally, at speeds higher than the critical value, there is no effective impact and collision, therefore energy of balls is not transferred to the powders. This fact can be seen in sample CF2. This sample was treated at a speed of 400 rpm, which is estimated to be over the critical value. As is explained about the impact energy, this sample has the least effective incoming energy. Another point which can be inferred about milling condition is that although mechanical alloying is a time-dependent process, optimizing other factors could help to improve the milling process and consequently decrease milling time dramatically. For example, although sample CF2 is milled for about 20 h due to deviation of other milling parameters from their optimum values, it has the least induced strain.

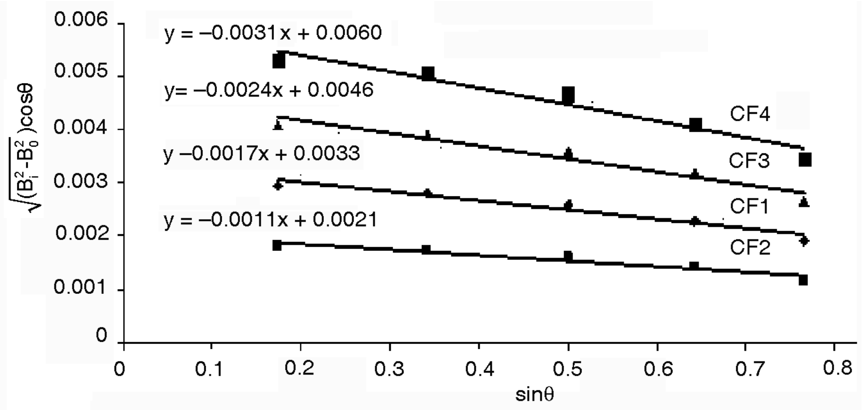

Fig. 2. Williamson-Hall plot: effect of milling parameters on microstrain and crystallite size

Each sample was milled at different milling times to investigate on the effect of these conditions on Fe fraction which diffused into Cu lattice. Kinetic of Fe dissolution into Cu lattice can be followed by the evolution of the (110) X-ray peak intensity of the unmixed Fe as a function of milling time. The obtained curves of the mixed fraction of Fe which are considered as the fraction transformed (Fig. 3) can be well described by the Johnson–Mehl–Avrami kinetics formalism in which the fraction transformed exhibits a time dependence of the following form [29, 30]:

$$X = 1 - \exp\left(-(kt)^n\right) \tag{2}$$

where n is the order of reaction or the Avrami parameter, X is the volume fraction transformed, t is the milling time and K is the rate constant.

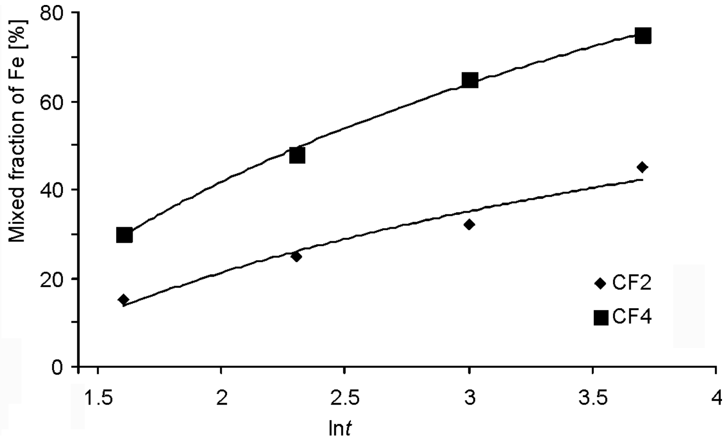

Fig. 3. Mixed fraction of Fe in function of ln$t$

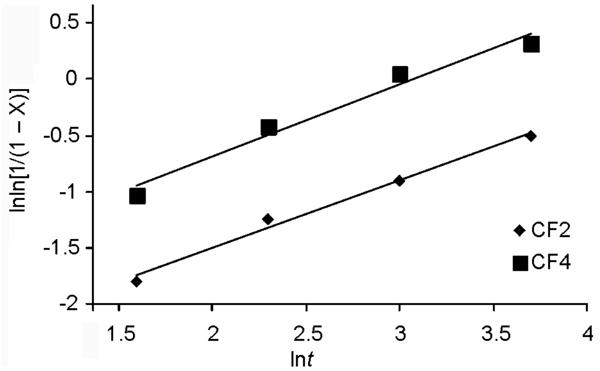

Fig. 4. Johnson–Mehl–Avrami plot in function of milling time

The kinetic parameters, n and k, can be deduced from the double logarithmic plot $\ln\ln(1/(1-X))$ vs. ln$t$. These curves represent the amount of mixed fraction for the least intensive and most intensive condition across milling time. As expected, milling with the most effective condition results in diffusion of more Fe atoms into Cu lattice for the same milling time. For instance, while less than 10% of Fe can diffuse into Cu lattice during the first 5 h of milling for CF2, up to 30% of Fe atoms diffuse into Cu lattice for CF4. Another point, the rate of solubility is higher for CF4 in comparison with other samples, which can be seen in Fig. 4. The obtained Avrami parameters $n_2 = 0.60$ and $n_4 = 0.64$ are quite small ($n < 1$) and differ significantly from those usually obtained for the nucleation and growth during the crystallization process.

These values are comparable to those obtained for transformation controlled by the diffusion at the interface and by the dislocation segregation. This might be correlated to the existence of a high density of dislocations and various types of defects induced by severe plastic deformations during milling [31, 32].

4. Conclusion

Ball-milled Cu–50 % Fe powdered mixture has been studied by X-ray diffraction. Using Taguchi design L-4 introduces 4 different samples which can estimate significant values of three most significant factors: BPR, time and speed among 2 levels. It predicts that using PBR of 20 and time of 20 hrs together with a speed of 200 rpm can reduce the crystalline size to the minimum achievable value, and increase microstrain to the highest available. One of the samples which was produced at these data shows a crystalline size of 23 nm and microstrain of 0.0031. Calculating the Avrami parameter proved how it is possible to enhance atomic diffusion by finding the best combination of milling conditions.

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