The crystallization process of amorphous Al\textsubscript{80}Fe\textsubscript{20} alloy powders prepared by ball milling

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Abstract

The amorphous-to-crystalline transition during thermal annealing of amorphous Al\textsubscript{80}Fe\textsubscript{20} alloy powders prepared by ball milling was investigated by means of magnetothermal analysis and X-ray diffraction. Following structural relaxation and stress relief processes, a metastable phase precipitates during primary crystallization, and a mixture of intermetallic compound (θ-Al\textsubscript{13}Fe\textsubscript{4}) and fcc Al is developed further. On heating at constant rate annealing the first and succeeding reactions overlap to some extent in temperature. The apparent activation energy for primary crystallization amounts to 1.99 ± 0.10 eV by using the Kissinger method. In addition, the structure of the metastable phase, which has not been identified yet, is briefly discussed.

1. Introduction

Al-based amorphous and/or nanocrystalline alloys have received appreciable attention during the last decade owing to their potential application as high strength materials \cite{1,2}. It has been shown that these types of alloys can be prepared by using either melt spinning or mechanical alloying techniques. Among these alloys, the Al–Fe system is attractive due to the two practically used metals. Several previous investigations revealed the ball milling feasibility in producing amorphous Al–Fe samples containing about 80 at.% Al \cite{3–6}. As further materials-processing strategies, such as hot consolidation, must be employed to compact the powder amorphous materials into bulk shapes for a range of engineering applications, it is important to have knowledge of the thermal instability and phase transformations of these metastable alloys. This paper reports preliminary results on the transition from amorphous to crystalline state during thermal annealing of an amorphous Al\textsubscript{80}Fe\textsubscript{20} alloy synthesized by ball milling.

2. Experimental procedures

Commercial elemental powder blends of Al and Fe (with a purity at least 99.9% and a particle size of about 50 μm) were mixed with an overall composition of Al\textsubscript{80}Fe\textsubscript{20} (at.%) and then sealed together with wear-resistant chrome steel balls (ball-to-powder weight ratio of 20:1) in a hardened steel vial under argon atmosphere (99.99% purity). Powder amorphous samples were obtained after milling in a planetary mill for 240 h based on X-ray diffraction (XRD) evidence. The crystallization of the amorphous alloy during subsequent thermal annealing was investigated by XRD and
magnetothermal analysis (MTA). The XRD experiments were performed on a X-ray diffractometer (Rigaku D/max-8 A, 12kW) with Cu Kα radiation and a graphite monochromating crystal. MTA, i.e., the measurement of magnetic susceptibility during thermal annealing, was conducted in a magnetic balance of the Faraday type under an argon (99.999% of purity) atmosphere [7]. For each measurement a sample of about 20 mg of powder was used. Our previous studies have proved that MTA is a useful complimentary tool for investigating the kinetics of solid state reactions [8].

3. Results

Fig. 1 shows the susceptibility, $\chi$, at room temperature (20°C) of the samples after 8 h annealing at various temperatures ($T_a$). $\chi$ reduces slightly at $T_a < 150°C$. With increasing $T_a$ to 400°C, $\chi$ decreases significantly, reaching half of the value for the as-milled state at about 275°C. Further increase of $T_a$ beyond 400°C causes only a much smaller decrease of $\chi$.

Microstructural changes in these isothermally annealed samples can be seen from XRD results as given in Fig. 2. At $T_a \leq 200°C$, no evidence of crystallization is detectable. For $T_a = 250°C$, splitting of the broad peak indicative of initial crystallization begins. As annealing at 350–400°C, a double-peak located in the amorphous broad background is the main feature in the diffraction spectra. On annealing at 450°C, the double-peak turns into a single-peak, together with a shift of other Bragg peaks with smaller intensities at lower reflection degrees. We note that, both the single- and double-peak may be composed of several unresolved peaks in each case, as indicated by the feature of the two peaks. The overlapping peaks, which result in the difficulty to identify the formed phases, may be caused by peak broadening due to nanometer-sized crystals precipitated in the samples.

Meanwhile, the entire course of crystallization upon isochronal annealing was followed by MTA heating traces, a typical example of which is shown in Fig. 3. Upon heating to 800°C at 10 K/min, $\chi$ decreases monotonically: it falls rapidly to about 20% of the $\chi$ of the as-milled state at about 400°C and then much less rapidly above that temperature to $\chi \approx 0$ at 800°C (see Fig. 3(a)). From the $\chi^{-1}$ vs. $T$ curve in Fig. 3(b), we see a distinct slope change around 400°C and other changes of slope at higher temperatures. To determine the transition temperatures, $dT^{-1}/dT$ (the first derivative of $\chi^{-1}$ with $T$) was calculated and is plotted versus $T$ in Fig. 3(c). Here, it should be pointed out that the local maxima and corresponding areas of this plot are not necessarily related to energy changes of phase transformation. From the plot, we note three stages beyond 300°C, among which the second stage exhibits a shoulder between the first
peak (at 422.3°C) and third peak (at 610.6°C). These results agree qualitatively with those obtained by use of differential scanning calorimetry.

To examine microstructural changes in the three stages observed, XRD measurements on corresponding samples were conducted. Fig. 4 shows the XRD spectra for samples A, B, and C (heated to 450, 550, and 720°C, respectively at a rate of 10 K/min). Consisting with isothermal annealing, the transition from the double-peak to the single-peak, which is respectively the main feature of strong Bragg peaks for samples A and B, also occurs during continuous heating. For sample C, an intermetallic compound with monoclinic structure, $\theta$-Al$_{13}$Fe$_4$ [9,10], was identified and fcc Al may also exist as a result of composition of the sample.

4. Discussion

From the above MTA and XRD experimental results, the entire crystallization process can be established. Primary crystallization of the amorphous phase produces a metastable phase with still unidentified structure and a residual amorphous phase. These phases transform further at higher temperatures. A comparison between the two upper XRD patterns in Fig. 4 shows evident difference in the maximum intensities but similar positions for these Bragg peaks, implying sample B contains the same phases as sample C, i.e. mainly $\theta$-Al$_{13}$Fe$_4$. Based on this point, we deduce that the second stage observed in MTA curve is the formation of nanometer sized crystallites of $\theta$-phase and a few Al, which are the equilibrium phases according to the Al–Fe binary diagram [11], and the third stage is a subsequent grain growth process. We note that the first and the succeeding transformation stages are not isolated, rather connected together, during continuous heating of the amorphous sample.

Our experimental results also show structural relaxation and stress relief of the sample before onset of the crystallization. As indicated by the XRD results in Fig. 2, in spite of substantial decrease of $\chi$, crystallization is essentially not detected at $T_a \leqslant 200°C$ for isothermal annealing of 8 h. For annealing at a constant heating rate, the
variation of $\chi$ or $\chi^{-1}$ with $T$ deviates from linearity in a range of about 120–300°C (see Fig. 3), which may be regarded as an indication of relaxation. In fact, we found that the $\chi$ vs. $T$ curve of the as-milled sample is reversible as the annealing temperature is cycled from room temperature to about 120°C, while it is irreversible on annealing at higher temperatures. The irreversible manner may suggest topological short-range order of the amorphous structure [12]. In our case, measured $\chi$ in effect reflects any changes of atomic distance between nearest neighbour Fe–Fe. On the other hand, the decrease of $\chi$ could be also be attributed to internal stress relief introduced during ball milling process.

The apparent activation energy, $E$, for the primary crystallization is obtained by varying the heating rate in the MTA experiments (1, 2, 5, 10 and 20 K/min) and applying the Kissinger method [13] to the measured peak values of crystallization temperature. Fig. 5 is the Kissinger plot and $E$ amounts to 1.99 ± 0.10 eV. This value might suggest a diffusion-controlled process during the primary reaction.

The structure of the metastable phase precipitated in primary crystallization has not been clarified yet. Many investigations revealed the existence of quasi-crystalline structures, namely the icosahedral and decagonal, in quenched Al-rich Al–Fe and Al–Mn alloys (for example Ref. [14]). In our case, however, there is no indication that the metastable phase is quasicrystalline, since the main strong reflection peaks are apparently different from those of icosahedral or decagonal quasicrystal structures [14,15]. The XRD data obtained for the metastable phase do not coincide with those for other metastable phases reported so far, including Al$_m$Fe [16,17], Al$_b$Fe$_2$, and Al$_6$Fe. Actually we found the metastable phase Al$_b$Fe during the crystallization of amorphous phase in an Al-rich metastable alloy (Al$_{90}$Fe$_{10}$). Further investigation on this issue by use of transmission electron microscopy is in progress.

5. Conclusion

For an annealing time of 8 h, a metastable phase, the structure of which has not been identified yet, crystallizes at temperatures ranging from 250°C to 400°C; later, equilibrium phases of intermetallic compound $\theta$-Al$_{13}$Fe$_4$ and fcc Al are formed in crystallization at temperatures >450°C and subsequent grain growth processes. On annealing at constant heating rates the first and succeeding reactions overlap to some extent in temperature. Before crystallization, relaxation of amorphous structure and stress relief decrease substantially magnetic susceptibility.

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References