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Preparation of 6.5 wt % Si–Fe by mechanical alloying

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A mechanical alloying process was studied by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and magnetic measurements for 6.5 wt% Si–Fe powders. The alloying process was divided into three stages. In the first stage (< 11 ks of the milling time), the Curie temperature, T_C, was the same as that of pure Fe, which indicated that the particles were not yet alloyed. At a milling time of 22 ks, the second stage, a large calorific value and a large coercive force, H_c, were observed and T_C was not clearly observed, which indicated that the particles had a precise lamellar structure and had a large internal stress. In the third stage (> 90 ks), the calorific value and H_c decreased. At the same time, a unique, and smaller T_C was observed, which indicated that the uniformity of the powders increased.

1. Introduction

Transition-metal–metalloid amorphous alloys prepared by melt-quenching are known to have a low coercive force [1]. Recently, a new method of mechanical alloying (MA) which produces amorphous alloy powders has been developed. The major interest in this MA has concentrated on amorphization. Since the alloys made by MA have large internal stresses, they are supposed to have a large coercive force. So far, very few studies have reported the soft-magnetic properties of both amorphous and crystalline Fe-based alloy powders made by MA [2–5].

In an Fe–Si system, the solid solubility of Si in α-Fe decreases to 14 wt % at 1523 K and to 5 wt % at room temperature; while the region of the superlattice Fe_3Si expands. Fe–Si alloys are useful materials; crystalline Fe–Si alloys containing low Si have been used for soft-magnetic materials. Furthermore, 6.5 wt % Si–Fe is known to have a low magnetostriction. However, studies of mechanical alloying have been reported only for $Fe_{75}Si_{25}$ [2].

In this paper, we investigated a 6.5 % Si–Fe powders made by MA in order to study the alloying process in a solid-solution system and to obtain Fe-based soft-magnetic powders.

2. Experimental procedure

MA was carried out in a planetary high-energy ball mill (Fritsch Pulverisette P-5) starting from pure-element powders (Fe of 99.8% purity, with a particle size under 100 μm; Si of 99.9% purity, with a mean particle size of 20 μm). All the alloys studied were prepared from a mixture of Fe and Si powders with a nominal composition of 6.5 wt % Si–Fe. Each of the powder samples was loaded into a cylindrical stainless-steel vial together with balls of the same material in an argon atmosphere. The ball-to-powder ratio was 120:15. The milling process was performed at a speed of 200 r.p.m. (revolutions per minute) for 360 ks. The alloys obtained were annealed in a vacuum. The sample characterization was carried out by X-ray diffraction (XRD) using CuK$_\alpha$ radiation, by thermal analysis with differential scanning calorimetry (DSC) under an argon atmosphere at a heating rate of $0.33\ \mathrm{K\,s^{-1}}$, and by magnetic measurements obtained with a vibrating-sample magnetometer (VSM). Also, measurements were made of the mean particle size. The Si contents in the milled alloys were measured by chemical analysis and the alloys were confirmed to have a Si content of 6.5 ± 0.4 wt %.

3. Results

The Si solution in the metal Fe powder was observed by XRD. Although the Si content was as small as 6.5%, many reflections of (2 1 1), (2 2 0), (3 1 1), (4 0 0), (3 3 1) and (4 2 2) were observed for the mixed powder. With milling, the reflection angles, 2θ, of α-Fe shifted to slightly higher angles, indicating that the Fe alloyed with the Si. For example, the reflection angle for α-Fe (2 1 1) at high angles had shifted from 82.4° to 82.8° by a milling time of 360 ks. Also, the metal–Si peaks disappeared. Fig. 1 shows the decrease in the relative intensity of the metal–Si reflection. The Si (1 1 1) peak decreased rapidly with time, and it disappeared at a milling time of 22 ks. Since line broadening for the Si (1 1 1) peak was observed , the ratio $I_{Si(1\,1\,1)}/I_{Fe(1\,1\,0)}$ was not necessarily proportional to the alloying rate. The precise shift angle of the reflection could not be

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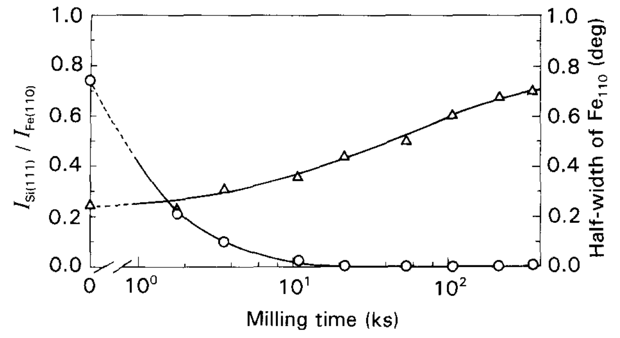

Figure 1 Changes in (○) the X-ray-reflection-intensity ratio of Si (1 1 1) to Fe (1 1 0), $I_{Si(1\,1\,1)}/I_{Fe(1\,1\,0)}$, and in (△) the half-width of Fe (1 1 0).

determined using a conventional X-ray diffractometer. By this milling time (22 ks), the half-width of the α-Fe (1 1 0) reflection increased gradually, indicating that the grain size had decreased and that the internal stress had increased. At a milling time of 360 ks, the half-width reached 0.7°, and using the Scherrer expression this gave a grain size of 15 nm.

Fig. 2 shows the decrease in the mean particle size with milling time. The mean particle size decreased from 70 to 20 μm at a milling time of 360 ks.

Fig. 3a shows changes in the saturation magnetization, σ_s, measured under a field of 800 kA m^{-1}. The value of σ_s decreased slightly with the milling time. At a time of 360 ks, σ_s was 232×10^{-4} Wb m kg^{-1}. This value is close to the value reported in [6] of a saturation magnetization of 241×10^{-4} Wb m kg^{-1} for the same composition. The difference is due to insufficient applied magnetic fields in the measurements and to the oxidization of the powders after 360 ks (3600 p.p.m.) (parts per million). Before 220 ks, however, the oxygen content was kept below 2800 p.p.m. Fig. 3b shows the changes in the coercive force, H_c. H_c increased with milling time, reaching a maximum of 4.5 kA m^{-1}, and then it decreased. At 360 ks, H_c was 1.43 kA m^{-1}, which is higher than the value for pure Fe (~ 0.64 kA m^{-1}). By annealing, the values decreased rapidly; an annealing temperature of 673 K was sufficient to decrease H_c for powders milled for 360 ks. The value 0.4 kA m^{-1} is smaller than that for the original pure Fe particles. Although the alloy had a small magnetostriction ($\lambda_s \simeq 0 \times 10^{-6}$) [7], H_c was severely influenced by the internal stress.

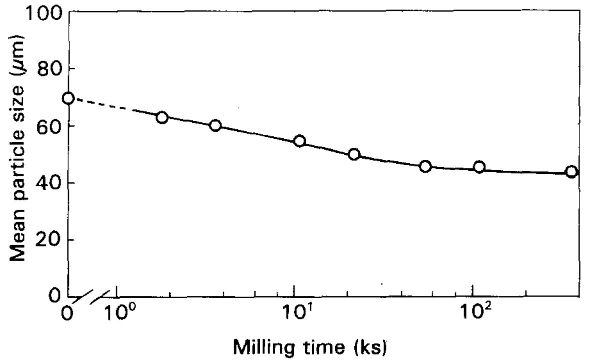

Figure 2 The change in the mean particle size with the milling time.

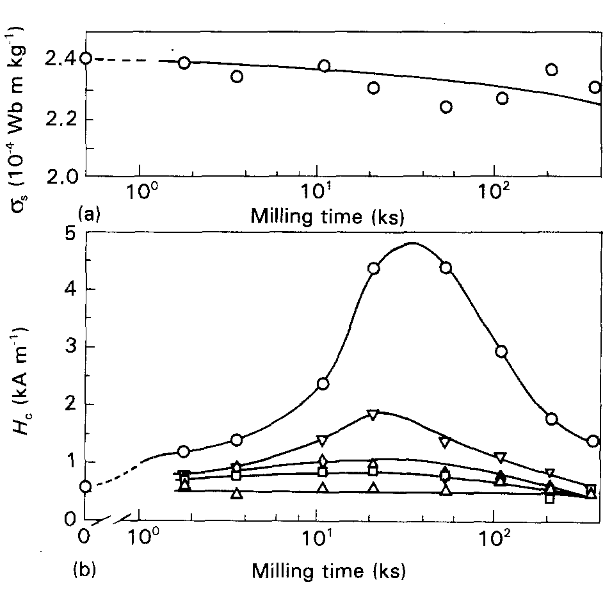

Figure 3 The dependence of (a) the saturation magnetization, σ_s, and (b) the coercive force, H_c, on the milling time: (○) as-milled samples and samples annealed at (▽) 673 K, (◇) 873 K, (□) 1073 K, and (△) 1273 K.

The thermal characteristics were studied by DSC. Fig. 4 shows thermograms of samples at 1.8, 22 and 360 ks. The sample at 1.8 ks had an absorption at 1043 K, which corresponds to the Curie temperature, T_C, of pure iron. The change in T_C is shown in Fig. 5. Until 11 ks, T_C remained equal to 1043 K. Between 11 and 72 ks, a unique T_C was not observed, shown in Fig. 4b, for powder milled for 22 ks. After 72 ks, the homogeneity increased and only one peak of T_C was clearly observed (see Fig. 4c). At 360 ks, T_C was observed at 953 K, which is nearly the same as the value reported in [8] of 6.5% Si–Fe.

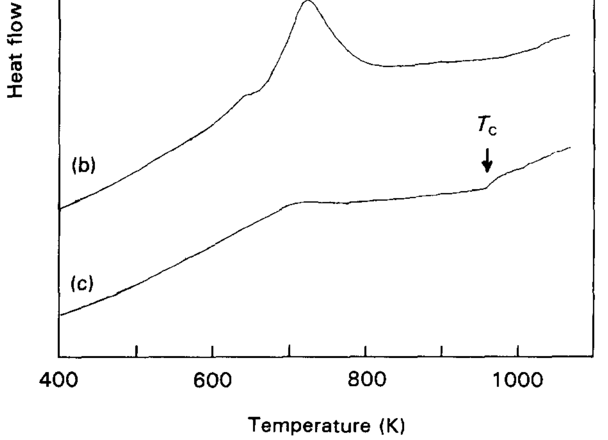

Figure 4 DSC thermograms of powders after: (a) 1.8 ks, (b) 22 ks, and (c) 360 ks.

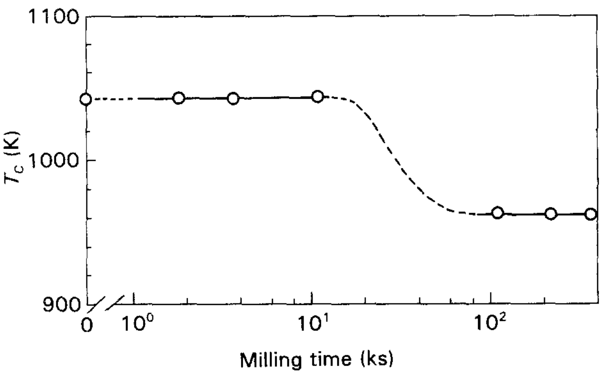

Figure 5 Changes in the Curie temperature, T_C, with time.

In Fig. 4, another outstanding feature is the strong exothermic peaks observed at a temperature of around 723 K for all the powders. The calorific value peaked at 22 ks, as shown in Fig. 6. The energy was due to mixing from a lamellar structure to a homogeneous structure and due to the internal stress. The change in calorific value is shown in Fig. 6. The value was quite small at a time of 1.8 ks, and it increased reaching a maximum at a milling time of 22 ks, and then it decreased rapidly. With increases in the homogeneity, the calorific value decreased.

4. Discussion

The alloying process was divided into three stages. In the first stage (< 11 ks), the ductile Fe particles were deformed as a flake shape and the brittle Si particles fractured. Si layers formed on the surface of the iron flakes. With deformation, the internal stress increased and consequently the exothermic peak at 723 K appeared. The value of H_c increased from 0.64 to 2.4 kA m^{-1}. The alloyed surface layer might be thin, because T_C is uniquely determined as the value of pure Fe. After the powders were annealed at 873 K, XRD showed three phases: metal Si, Fe_3Si-like and α-Fe(Si). The Fe_3Si peak was the strongest and metal–Si was observed. These results support that there is a prealloying stage. However, precise studies on the powers annealed at lower temperatures are required.

The second stage (11 ~ 90 ks) was the intense cold welding period. The Si reflection peaks disappeared and the particles might have had a lamellar structure, each layer having different Si contents because T_C was not clear in the DSC results. Both the calorific value, which was due to the change from the lamellar to the homogeneous structure, and H_c reached a maximum. Although cold rolling is known to be difficult for the Fe–Si alloys with Si contents (> 4%), alloying is possible by MA, as in this study.

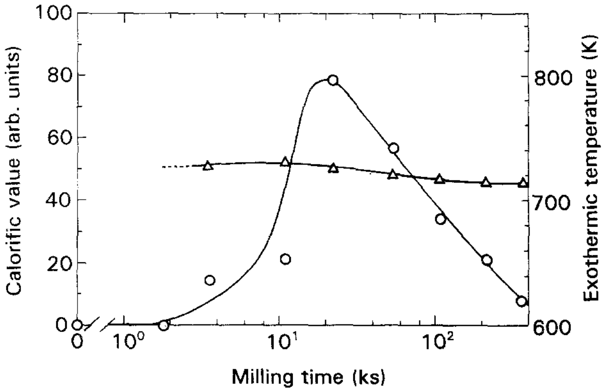

Figure 6 Changes in (○) the calorific value and (△) the exothermic temperature with time.

In the final stage (> 72 ks) the lamellar structure disappeared and the internal homogeneity increased. The evidence is that both the calorific value and the H_c decreased. Alloying of Fe to Si was confirmed by the decrease in T_C. At 360 ks, the grain size became as small as 15 nm. Although the alloy had a small magnetostriction, its H_c was severely influenced by the internal stress; however, an annealing temperature of 873 K was sufficient to decrease the value of H_c. Since the value of H_c at 360 ks was not a minimum, a lower H_c value might be obtained by a longer milling time.

5. Conclusion

An alloying process in 6.5% Si–Fe was studied by XRD, DSC and magnetic measurements. Until 11 ks, T_C had the same value as pure Fe, which indicated that the particles were not yet alloyed. At a milling time of 22 ks, both a large calorific value and a large H_c were observed; this indicated that the particles had a precise lamellar structure and contained large internal stresses. At a milling time of 360 ks, the calorific value decreased and H_c decreased. At the same time, the value of T_C for the alloyed Fe–Si was observed again but it showed a smaller constant value, indicating that the homogeneity was increasing. Soft-magnetic powders with $H_c = 1.4$ kA m^{-1} were obtained after milling for 360 ks; H_c was improved by annealing at temperatures as low as 673 K.

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