JOURNAL OF MATERIALS SCIENCE 28 (1993) 6571–6574

Solid-state reaction between crystalline nickel and amorphous $Fe_{78}Si_{12}B_{10}$ powders during mechanical milling

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The solid-state reaction between crystalline nickel and pulverized melt-spun amorphous $Fe_{78}Si_{12}B_{10}$ powders during mechanical milling has been investigated. For the powder mixtures with low nickel content ($\leq$ 30 at%), the reaction results in the production of a new amorphous phase. For the powder mixture with a high nickel content (up to 50 at%), crystalline γ(Fe, Ni) and new amorphous phases are obtained. During the milling process, nickel atoms can dissolve in the amorphous matrix by diffusion due to severe deformation. The existence of "free volume" in the melt-spun amorphous phase may favour the diffusion of nickel atoms. At the same time, the elemental atoms (such as iron) in the amorphous phase may also dissolve into the nickel matrix. The amorphization between the amorphous and crystalline phases is attributed to the asymmetry of interdiffusion of the atoms in different matrices.

1. Introduction

Metallic amorphous alloys have usually been prepared by rapid quenching from the melt or by vapour quenching. It has now been shown that amorphous alloys can also be prepared by the mechanical alloying (MA) of elemental crystalline powders [1, 2] or by the mechanical grinding (MG) of crystalline intermetallic compounds [2, 3]. In general, solid-state reaction of elemental powders during MA is considered to occur by interdiffusion [2]. The structure of amorphous phase prepared by MA is similar to that prepared by melt-spinning [4].

Iron–nickel-based metalloid amorphous alloys have been most widely used because of their good soft magnetic properties. These materials can also be prepared by mechanical alloying or mechanical grinding [5, 6]. However, amorphous powders of such metal–metalloid systems are more difficult to prepare by mechanical alloying or mechanical grinding [5, 6]. Recently, Trudeau *et al.* [7] reported that mechanical milling of nickel powder with Metglas 2605S-2 ($Fe_{78}Si_9B_{13}$) ribbon resulted in stability of the amorphous phase. More recently, the present authors [8] reported that mechanical milling of nickel powders with partially amorphous $Fe_{78}Si_{12}B_{10}$ ribbon resulted in crystallization of amorphous matrix and production of γ(Fe, Ni) phase. The purpose of the present work was to investigate the solid-state reactions between different contents of crystalline nickel and pulverized melt-spun amorphous $Fe_{78}Si_{12}B_{10}$ powders during mechanical milling (MM).

2. Experimental procedure

Metallic glass $Fe_{78}Si_{12}B_{10}$ ribbons were prepared by the melt-spinning method in an argon atmosphere. The milling process was performed in a planetary ball mill with an argon atmosphere, in order to avoid oxidation of the powders. At first, the ribbon cut into small pieces, was milled at a high weight ratio of balls to sample in order to pulverize it into fine powder. The powder sizes ranged from 100–300 μm. The powders were also confirmed to be fully amorphous by X-ray diffractometry. The pulverized melt-spun amorphous powders were mixed with crystalline nickel powder (99.9 at % purity, size less than 20 μm) in different compositions. The three mixtures are as follows: 17 at % Ni + 83 at % $Fe_{78}Si_{12}B_{10}$ (final composition $Fe_{65}Ni_{17}Si_{10}B_8$, Sample A), 30 at % Ni + 70 at % $Fe_{78}Si_{12}B_{10}$ (final composition $Fe_{55}Ni_{30}Si_8B_7$, Sample B) and 50 at % Ni + 50 at % $Fe_{78}Si_{12}B_{10}$ (final composition $Fe_{39}Ni_{50}Si_6B_5$, Sample C). These three mixtures were loaded into the above mill. The weight ratio of balls to sample was 60:1, and the rotation rate was 720 r.p.m. The powders were characterized by X-ray diffraction (XRD) with CuK_α radiation ($\lambda = 0.154$ nm). Differential scanning calorimetric (DSC) measurements were made using a Perkin–Elmer DSC 2 system. The heating was done in a sealed gold pan at 20 °C min^{-1} under a flow of purified argon.

3. Results

Fig. 1a shows the XRD pattern of Sample A in an

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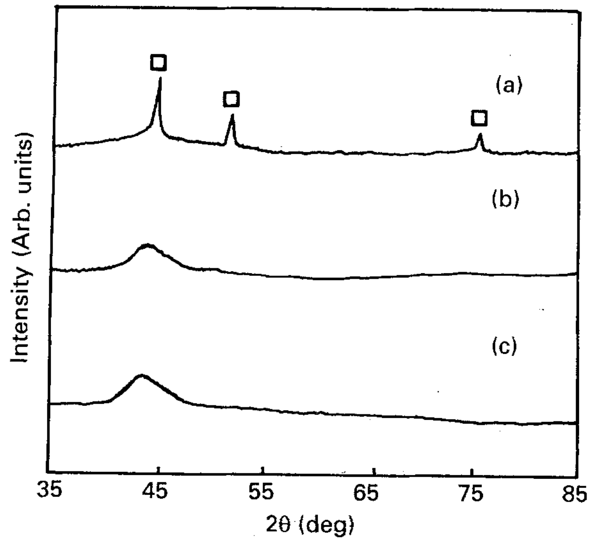

Figure 1 X-ray diffraction patterns of powder mixtures (Sample A) (a) unmilled, (b) milled for 12 h, and (c) milled for 24 h. (□) Ni.

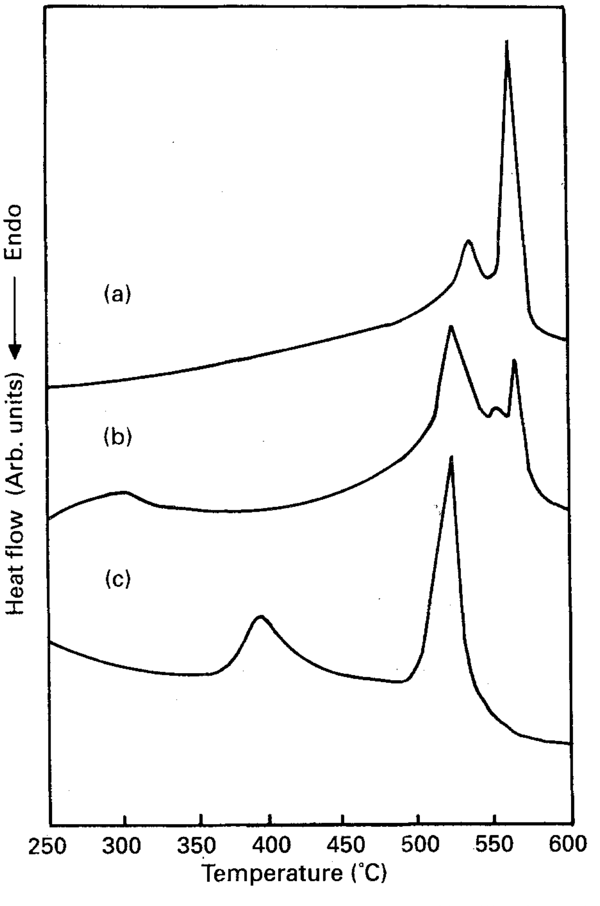

Figure 2 DSC curves of Sample A (a) unmilled, (b) milled for 12 h, and (c) milled for 24 h.

unmilled state. The crystalline nickel diffraction peaks are clearly seen in this pattern. After milling for 12 and 24 h, there were no distinct diffraction peaks of crystalline nickel, and the typical broad maximum (around 2θ = 44.5°) of the amorphous phase appeared in the XRD pattern (see Fig. 1b and c). The powder mixtures unmilled and milled for 12 and 24 h were characterized by the thermal analysis, as shown in Fig. 2a–c. The DSC curves of the three samples are completely different, although the XRD patterns show similar results for the powder mixtures milled for 12 and 24 h. The XRD patterns of those products after heating to 620 °C at 20 K min^{-1} are shown in Fig. 3a–c. For the unmilled powder mixture, the products after DSC scanning were α-(Fe, Si), Fe_2B and nickel (see Fig. 3a), which indicates that the exothermic peaks in Fig. 2a are due to the crystallization of amorphous $Fe_{78}Si_{12}B_{10}$ phase, but no interdiffusion of nickel and amorphous phase. For the powder mixtures milled for 12 and 24 h, the products after DSC scanning were the same: α-Fe(Si), Fe_2B, Fe_3B and γ(Fe, Ni) phases (see Fig. 3b and c), respectively. The reason for different exothermic peaks may be attributed to the inhomogeneity of composition during the first milling stage. This result shows that the nickel atoms had dissolved into the amorphous matrix. In other words, the amorphization reaction between crystalline nickel and the amorphous $Fe_{78}Si_{12}B_{10}$ phase occurred after severe deformation. The crystallization of as-milled powders was also similar to crystallization of melt-spun $Fe_{50}Ni_{30}Si_{10}B_{10}$ alloy, as reported by Zaluska and Mityia [9].

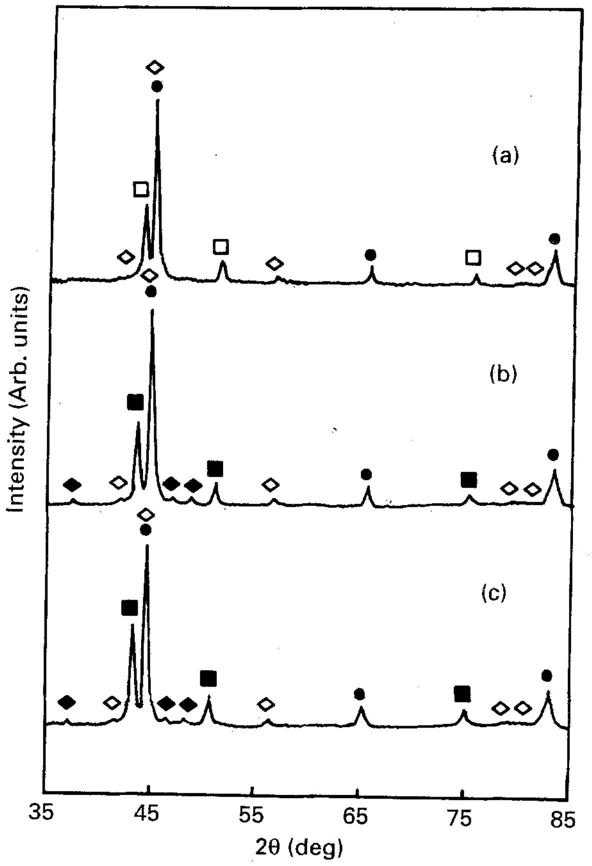

Figure 3 X-ray diffraction patterns of products in Fig. 2, after DSC scanning: (a) unmilled, (b) milled for 12 h, and (c) milled for 24 h. (□) Ni, (●) α-Fe(Si), (■) γ(Fe, Ni), (◇) Fe_2B, (◆) Fe_3B.

For Sample B after 24 h milling, the typical broad maximum (around 2θ = 44.5°) of the amorphous phase appeared, and no distinct diffraction peaks of a crystalline nickel peaks were found in the X-ray diffraction pattern (see Fig. 4a). The DSC curve of the as-milled powder of Sample B showed the typical exothermal peaks (see Fig. 4c), which is completely different from Fig. 2a. This indicates that the amorphization reaction between the amorphous $Fe_{78}Si_{12}B_{10}$ powders and crystalline nickel powders (additional to 30 at % Ni) is accomplished after 24 h

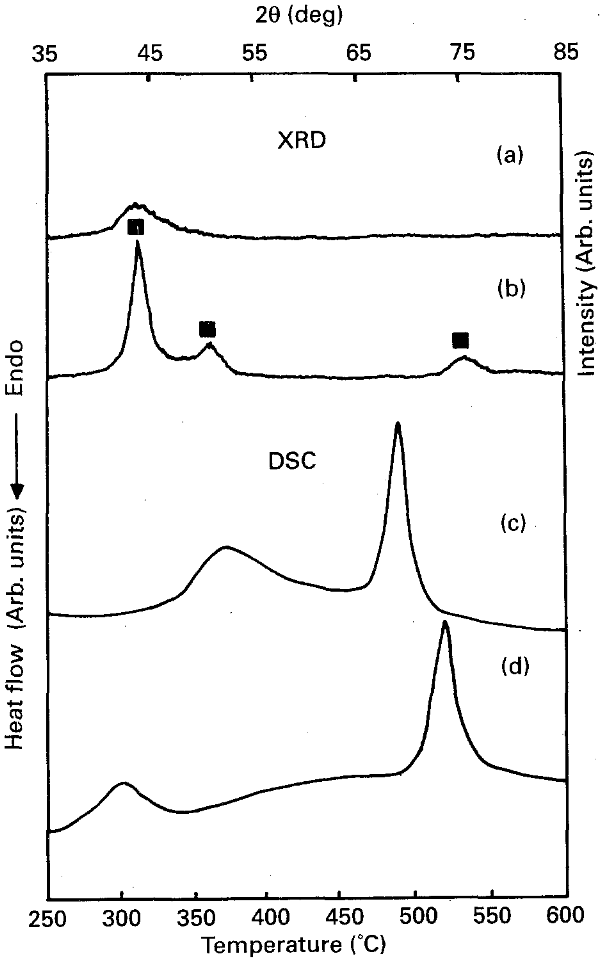

Figure 4 X-ray diffraction patterns of powder mixtures: (a) Sample B after milling for 24 h, and (b) Sample C after milling for 50 h. DSC curves of powders mixtures: (c) Sample B after milling for 24 h, and (d) Sample C after milling for 50 h. (■) γ(Fe, Ni).

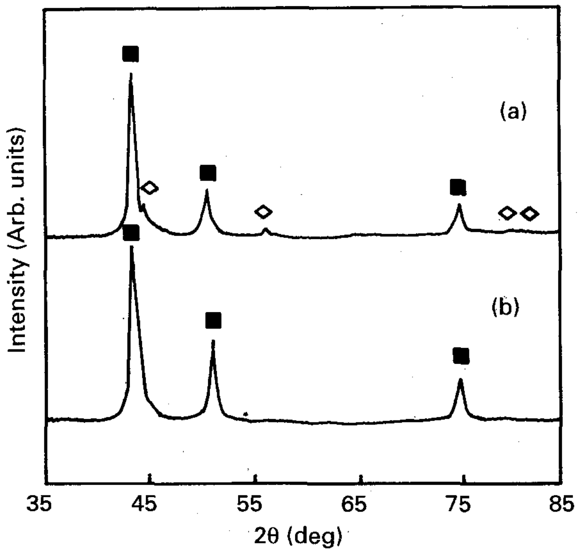

Figure 5 X-ray diffraction patterns of products in Fig. 4, after DSC scanning: (a) Sample B after milling for 24 h, and (b) Sample C after milling for 50 h. (■) γ(Fe, Ni) and (◇) Fe_2B.

milling. For Sample C after 50 h milling, one can see that the broadened crystalline γ(Fe, Ni) peaks occur in the diffraction pattern (see Fig. 4b). The DSC curve of the as-milled powder of Sample C also showed typical exothermal peaks (see Fig. 4d), which are attributed to the crystallization of amorphous phases containing a high nickel content. This obviously indicates that the amorphization and solid-state reaction between the amorphous $Fe_{78}Si_{12}B_{10}$ powders and crystalline nickel powders (additional to 50 at % Ni) occur after severe deformation.

The XRD patterns of the products after heating to 620 °C at 20 K min^{-1} for Sample B milled for 24 h and Sample C milled for 50 h, are shown in Fig. 5. Fig. 5a shows the crystallized products of Sample B milled for 24 h: γ(Fe, Ni) and Fe_2B phases. Fig. 5b, shows that the crystallized product of Sample C milled for 50 h is only the γ(Fe, Ni) phase. The results show that the crystallized products are completely different for Sample A, B and C after mechanical milling. This also indicates that the solid-state reactions may be different for the different nickel contents in the powder mixtures.

4. Discussion

It can be seen that the mechanical milling of the crystalline nickel powder with amorphous $Fe_{78}Si_{12}B_{10}$ powder results in amorphization and solid-state reaction in this experiment. The amorphization reaction during this process is different from that of mechanical alloying (MA) and mechanical grinding (MG). Schwarz *et al.* [4] and Hellstern and Schultz [10] have argued that the process of amorphization by MA of elemental powders leads to an ultrafine composite in which a solid-state amorphizing reaction takes place. In the process of mechanical grinding of intermetallic compounds, the defects introduced by severe plastic deformation during milling must raise the free energy of the crystalline phase such that at a critical increase in energy it may destabilize and transform to the amorphous structure. In the present case, the heavy deformation results in the diffusion of nickel atoms into the amorphous matrix. The crystallization products of amorphous $Fe_{78}Si_{12}B_{10}$ are α-(Fe, Si) and Fe_2B in sequence (see Fig. 3a). The first crystallization product α-(Fe, Si) is expelled from the nickel element according to the phase diagram [11]. The nickel atoms dissolving in the amorphous matrix will stabilize the amorphous structure [7]. Therefore, the iron–nickel metalloid amorphous powders can be prepared over a rather wide composition range by mechanical milling of iron-based amorphous phase and crystalline nickel. The iron–nickel metalloid amorphous alloy (Fe–Ni–P–B and Fe–Ni–Si–B) obtained by mechanical alloying required over 200 h milling time [6]. In this work, we obtained amorphous Fe–Ni–Si–B powder at a much shorter milling time.

The "free volume" model can describe the structure of the melt-spun amorphous alloy [12, 13]. When some nickel atoms diffuse into $Fe_{78}Si_{12}B_{10}$ amorphous alloy by heavy deformation, the "free volume" will play an important role in the short-circuit diffusion paths. It appears that continuous ball milling, i.e. fracturing and cold welding, leads to a refinement of crystalline nickel during the initial stage. Consequently, heavy deformation during the mechanical milling process results in interdiffusion of nickel atoms and atoms in the amorphous phase. Because of the fast anomalous diffusivity of nickel atoms in the amorphous iron-based alloy [14], the asymmetry of the diffusion of nickel atoms results in the production of an amorphous alloy which contains nickel. When the nickel content is low, nickel atoms dissolve into the amorphous matrix. No sign of amorphous matrix atoms dissolving in the nickel matrix occurs. On increasing the content of nickel in the powder mixtures during the mechanical milling process, the metalloid content in the powder mixtures decreases. In general, with a metalloid content less than 12 at % in rapid-quenching iron-based metallic glass, it is difficult to obtain a completely amorphous alloy [15]. In the present case, when the nickel content is $\leqslant 50$ at %, the corresponding metalloid content is < 12 at % in Sample C. It can be seen that completely amorphous powder cannot be obtained even by milling up to 50 h. In a previous paper [16], we have reported the amorphization reaction during mechanical milling of aluminium and amorphous $Fe_{78}Si_{12}B_{10}$ powders as 75 at % Al + 25 at % $Fe_{78}Si_{12}B_{10}$. Further increasing the aluminium content in the powder mixture of aluminium and amorphous $Fe_{78}Si_{12}B_{10}$ powders, the result shows that new amorphous phase and nanocrystalline aluminium phase are obtained during mechanical milling of aluminium and amorphous $Fe_{78}Si_{12}B_{10}$ powders as 90 at % Al + 10 at % $Fe_{78}Si_{12}B_{10}$ [17]. From the phase diagram [11], one can see that the solubility of iron in aluminium is very low (< 0.01 at % at 300 °C) but the solubility of iron in nickel may be $\leqslant 5$ at % at 300 °C. Therefore, owing to the interdiffusion of the nickel atoms and atoms in the amorphous $Fe_{78}Si_{12}B_{10}$ phase, the iron atoms in the amorphous phase may also dissolve in the nickel matrix with the addition of 50 at % Ni into the amorphous phase. This results in the production of γ(Fe, Ni) phase.

5. Conclusion

From the above results, we conclude that the preparation of the iron–nickel metalloid amorphous phase can be achieved by mechanically milling the crystalline nickel powder with the amorphous $Fe_{78}Si_{12}B_{10}$ powder. The amorphization and solid-state reaction between the crystalline metal and the rapid-quenching amorphous metal differs from either the mechanical alloying of crystalline elements or the mechanical grinding of the intermetallic compounds. The reaction mechanism may also be the interdiffusion mechanism.

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Received 2 June 1992
and accepted 7 May 1993