Soft Magnetic Properties of Nanocrystalline Fe–Si–B–Nb–Cu Rod Alloys Obtained by Crystallization of Cast Amorphous Phase

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An amorphous alloy rod of 0.5 mm in diameter was produced for an Fe_{72.5}Si₁₀B_{12.5}Nb₄Cu₁ alloy by copper mold casting, though the maximum diameter of 1.5 mm for (Fe_{0.75}Si_{0.1}B_{0.15})₉₆Nb₄ alloy decreased by the addition of 1 at% Cu and the decrease in B content. The amorphous alloy rod crystallizes through multi-stage exothermic reactions. The first exothermic peak is due to the precipitation of nanoscale bcc-Fe phase and the following exothermic peaks result from the transition of bcc-Fe + amorphous → bcc-Fe + Fe₂₃B₆ + Fe₂B + Fe₃Si + Fe₂Nb. The bcc-Fe phase has a particle size of about 10 nm and its volume fraction is approximately 70% after annealing for 300 s at 883 K. The alloy rod consisting of bcc-Fe and amorphous phases exhibits good soft magnetic properties, *i.e.*, high saturated magnetic flux density of 1.21 T, low coercive force of 1.8 A/m and high initial permeability of 32000. The good soft magnetic properties for the nanocrystalline Fe_{72.5}Si₁₀B_{12.5}Nb₄Cu₁ alloy in a rod form of 0.5 mm in diameter are encouraging for future development as a new type of nanocrystalline soft magnetic bulk material.

(Received June 12, 2002; Accepted August 8, 2002)

Keywords: iron-based alloy, cast amorphous alloy, nanocrystalline alloy rod, nanocrystallization, soft magnetic property

1. Introduction

It is known that bulk glassy alloys with diameters above 1 mm are formed in a number of multi-component alloy systems which can be divided into nonferrous and ferrous alloy groups.^{1–4)} The development of bulk glassy alloys was performed by nonferrous alloy systems, followed by ferrous alloy systems. When we focus on Fe-based bulk glassy alloys, one can list the following alloy systems, *i.e.*, Fe–(Al, Ga)–(P, C, B),⁵⁾ Fe–(Al, Ga)–(P, C, B)–(Cr, Mo, Co),⁶⁾ Fe–Ga–(P, C, B),⁷⁾ Fe–Ga–(P, C, B)–(Cr, Mo, Co),^{8–10)} Fe–(Zr, Hf, Nb, Ta)–B,¹¹⁾ Fe–(Zr, Hf, Nb)–(Cr, Mo, W)–B,¹²⁾ Fe–Co–Ln (lanthanide metal)–B,¹³⁾ Fe–(Nb, Cr, Mo)–(P, C, B),¹⁴⁾ Fe–(Cr, Mo)–(B, C),¹⁵⁾ Fe–Ni–(P, B),¹⁶⁾ Fe–Si–B–Nb¹⁷⁾ and Fe–Si–B–Zr¹⁸⁾ *etc.* All these Fe-based bulk glassy alloys exhibit a supercooled liquid region of 35 to 90 K before crystallization and the largest diameter is about 5 to 6 mm for Fe–(Zr, Nb, Ta)–(Mo, W)–B system.¹⁹⁾ In addition, almost all Fe-based bulk glassy alloys exhibit ferromagnetism at room temperature and the saturated magnetic flux density (B_s) is in the range from 1.2 to 1.4 T for Fe–Ga–(P, C, B),⁵⁾ Fe–Co–Ln–B²⁰⁾ and Fe–Ga–(P, C, B, Si)²¹⁾ alloys. It has subsequently been found that the B_s exceeds 1.5 T for Fe–Si–B–Nb¹⁷⁾ and Fe–Si–B–Zr¹⁸⁾ alloys. The bulk glassy alloys in Fe–Si–B–Nb and Fe–Si–B–Zr systems are very attractive as a new type of soft magnetic bulk alloy. Thus the bulk glassy alloys with good soft magnetic properties were developed in a number of Fe-based multi-component systems. However, there have been no data on the synthesis of a nanocrystalline Fe-based bulk alloy with good soft magnetic properties. Very recently, we have found that a cast amorphous alloy rod with a diameter of 0.5 mm is also formed in Fe–Si–B–Nb–Cu system and the subsequent annealing causes the formation of a nanostructure consisting of nanoscale bcc-Fe particles surrounded by the remaining amorphous phase, accompanying the appearance of good soft magnetic proper-

ties. This paper intends to present the alloy composition at which an amorphous alloy rod is formed in Fe–Si–B–Nb–Cu system by copper mold casting as well as the relation between partially crystallized structure and magnetic properties for the bulk amorphous alloys.

2. Experimental Procedure

Multi-component Fe-based alloy ingots with composition of Fe_{95–x–y}Si_xB_yNb₄Cu₁ were prepared by arc melting the mixtures of pure Fe, Nb and Cu metals, pure silicon and crystal boron in an argon atmosphere. The alloy compositions represent the nominal atomic percentages. From the alloy ingots, alloy rods with different diameters up to 2 mm were produced at an ejection pressure of 0.2 MPa by the copper mold casting method. Alloy ribbons were also produced for comparison by the melt spinning method. The crystallization process of the amorphous alloys was determined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The as-quenched and annealed samples were examined with an X-ray diffractometer with Cu K α and Cr K α radiation (XRD), respectively. The nanocrystalline structure of the ribbon and bulk samples after annealing was observed by a transmission electron microscope (TEM) operating at 400 keV linked with selected area electron diffraction. The composition of the bcc phase for the ribbon and bulk samples annealed under optimal conditions was examined by high-resolution transmission electron microscopy (HRTEM) combined with energy-dispersive spectroscopy (EDS) analyses. Liquidus and solidus temperatures were determined by differential thermal analysis (DTA). Magnetic properties of saturated magnetic flux density (B_s) and coercive force (H_c) were measured with a vibrating sample magnetometer (VSM) under a maximum applied magnetic field of 400 kA/m and with an DC B–H loop tracer under a magnetic field up to 800 A/m, respectively. The permeability (μ_i) at 1 kHz under 0.8 A/m

was measured with an AC B-H loop analyzer.

3. Results

Figure 1 shows the X-ray diffraction pattern of the cast $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ alloy rod of 0.5 mm in diameter and about 30 mm in length obtained by XRD with $\text{Cu K}\alpha$ radiation, together with the data of the corresponding melt-spun alloy ribbon. In addition, the data of the cast $(\text{Fe}_{0.75}\text{Si}_{0.1}\text{B}_{0.15})_{96}\text{Nb}_4$ alloy rod of 1.5 mm in diameter and 50 mm in length are also shown for comparison. Only broad peaks are seen for all the samples, indicating the formation of an amorphous phase in the rod diameter range up to 0.5 mm for the $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ alloy and 1.5 mm for the $(\text{Fe}_{0.75}\text{Si}_{0.1}\text{B}_{0.15})_{96}\text{Nb}_4$ alloy. The glass-forming ability is significantly reduced by the addition of 1 at% Cu as well as by the decrease of B content. Such a modification of alloy composition is attributed to the synthesis of Fe–Si–B–Nb base alloy with multi-stage crystallization mode. Figure 2 shows the DSC curves of the $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ alloy in ribbon and rod (0.5 mm in diameter) forms together with the data of the $(\text{Fe}_{0.75}\text{Si}_{0.1}\text{B}_{0.15})_{96}\text{Nb}_4$ alloy rod of 1.5 mm in diameter. The latter 0% Cu alloy rod exhibits a sequent change in glass transition, supercooled liquid and then crystallization. On the other hand, the former 1% Cu-containing alloy exhibits distinctly separated exothermic peaks, indicating that the crystallization proceeds through at least two stages in the absence of the supercooled liquid state. The temperature interval between the main two exothermic peaks is as large as 105 K. The multi-stage crystallization mode is in agreement with that for the $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ (FINEMET) alloy²² with differ-

Fig. 1 X-ray diffraction pattern of a cast $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ alloy rod with a diameter of 0.5 mm. The data of the corresponding melt-spun amorphous alloy ribbon and a cast $(\text{Fe}_{0.75}\text{Si}_{0.1}\text{B}_{0.15})_{96}\text{Nb}_4$ glassy alloy rod with a diameter of 1.5 mm are also shown for comparison.

Fig. 2 DSC curves of the $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ amorphous alloys in a ribbon and rod (0.5 mm in diameter) forms. The data of the $(\text{Fe}_{0.75}\text{Si}_{0.1}\text{B}_{0.15})_{96}\text{Nb}_4$ glassy alloy rod with a diameter of 1.5 mm are also shown for comparison.

Fig. 3 X-ray diffraction patterns of the $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ amorphous alloy rod with a diameter of 0.5 mm annealed for 300 s at 883 K and 600 s at 1073 K.

ent metalloid and Nb contents. Here, it is important to point out that the use of the FINEMET alloy does not produce any amorphous phase by the copper mold casting method, being consistent with the previous data.²²⁾

The crystalline phases during the two-stage exothermic reactions were examined by XRD with Cr $K\alpha$ radiation and TEM. The reason for the use of Cr $K\alpha$ radiation here is because of large absorption ability of Cu $K\alpha$ radiation for Fe. Figure 3 shows the X-ray diffraction patterns of the 1%Cu-containing alloy rod annealed for 300 s at 883 K and 600 s at 1073 K corresponding to the peak temperatures of the first- and third-exothermic peaks, respectively. The X-ray diffraction patterns are identified as bcc-Fe + amorphous phases for the former sample and bcc-Fe + Fe₂₃B₆ + Fe₂B + Fe₃Si + Fe₂Nb phases for the latter sample, indicating that the crystallization reaction proceeds in the multi-stage process including the primary precipitation phase of bcc-Fe even for the rod sample. Figure 4 shows bright- and dark-field TEM images and selected-area electron diffraction pattern of the mixed bcc-Fe and amorphous phases in the rod sample. It is seen that bcc-Fe grains with a particle size of about 10 nm disperse homoge-

neously in a surrounded state by the remaining amorphous phase. The nanobeam EDX data were taken from ten particles of the bcc-Fe phase. The average analytical compositions except B were 82.3 at%Fe, 13.7 at%Si, 2.7 at%Nb and 1.3 at%Cu. It is clearly confirmed that Si element is enriched into the bcc-Fe phase while Nb element is rejected. The similar tendency is also obtained in the Fe_{73.5}Si_{13.5}B₉Nb₃Cu₁ ribbon alloy.^{23,24)} The decrease in Si content and the increase in Nb content in the remaining amorphous phase cause an increase in the thermal stability of the remaining amorphous phase, in conjunction with the nanoscale bcc-Fe particles.

Table 1 summarizes thermal stability and soft magnetic properties of the nanocrystalline Fe_{72.5}Si₁₀B_{12.5}Nb₄Cu₁ alloy rod consisting of the mixed bcc-Fe and amorphous phases obtained by annealing the cast amorphous alloy rod for 300 s at 883 K. The data of the nanocrystalline Fe–Si–B–Nb–Cu alloy ribbon obtained by the same annealing treatment are also presented for comparison. It is noticed that the nanocrystalline alloy rod exhibits good soft magnetic properties, *i.e.*, a high saturated magnetic flux density (B_s) of 1.21 T, a low coercive force (H_c) of 1.8 A/m and a high initial permeability (μ_i) of

Fig. 4 Bright- and dark-field TEM images (a and b) and selected-area electron diffraction pattern of the Fe_{72.5}Si₁₀B_{12.5}Nb₄Cu₁ amorphous alloy rod with a diameter of 0.5 mm annealed for 300 s at 883 K.

Table 1 Thermal stability and soft magnetic properties of the Fe_{72.5}Si₁₀B_{12.5}Nb₄Cu₁ alloy rod with a diameter of 0.5 mm annealed for 300 s at 883 K. The data of the as-cast glassy (Fe_{0.75}Si_{0.1}B_{0.15})₉₆Nb₄ alloy rod with a diameter of 1.5 mm and nanocrystalline Fe_{73.5}Si_{13.5}B₉Nb₃Cu₁ (FINEMET) and Fe₈₆Zr₇B₆Cu₁ (NANOPERM) alloy ribbons are also shown for comparison.

Alloy	t (μm)	Structure	T_a (K)	T_{x1} (K)	B_s (T)	μ_e (1 kHz)	H_c (A/m)
Fe _{72.5} Si ₁₀ B _{12.5} Nb ₄ Cu ₁ (ribbon)	40	bcc	883	841	1.23	80000	0.71
Fe _{72.5} Si ₁₀ B _{12.5} Nb ₄ Cu ₁ (bulk)	500	bcc	883	841	1.21	32000	1.8
(Fe _{0.75} Si _{0.1} B _{0.15}) ₉₆ Nb ₄ (bulk)*	1500	amorphous	782	885	1.47	17000	2.9
Fe _{73.5} Si _{13.5} B ₉ Nb ₃ Cu ₁ (ribbon)**	18	bcc	823	775	1.24	100000	0.53
Fe ₈₆ Zr ₇ B ₆ Cu ₁ (ribbon)***	21	bcc	873	792	1.52	41000	3.2

*Ref. 17), **Ref. 22), ***Ref. 25)

32000. One can notice clearly the achievement of good soft magnetic properties in the nanocrystalline structure state even for the bulk alloy rod form. The B_s and H_c are nearly the same as those for the corresponding nanocrystalline alloy ribbon. However, the initial permeability of the nanocrystalline alloy rod is considerably smaller than that (80000) for the ribbon sample. The difference is presumably because of the influence of reversed magnetic field resulting from the rod shape. That is, as mentioned above, the shape of the rod sample is about 30 mm in length and 0.5 mm in diameter. In comparison with the ribbon sample with much larger length and much smaller thickness, the demagnetizing factor of the rod sample is much larger than that of the ribbon sample, resulting in the decrease of the initial permeability of the nanocrystalline alloy rod. It is further noticed that the B_s and H_c of the present nanocrystalline alloy are nearly the same as those for commercial nanocrystalline Fe–Si–B–Nb–Cu alloy ribbon (FINEMET) in spite of the significant change in alloy composition leading to the increase of the glass-forming ability.

4. Discussion

It has previously been described that the increase in the glass-forming ability of the $\text{Fe}_{75}\text{Si}_{10}\text{B}_{15}$ alloy by the addition of 2 to 4 at%Nb is due to the enhancement of the thermal stability of supercooled liquid against crystallization and the increase in the reduced glass transition temperature (T_g/T_l) by the increase in T_g and the decrease in T_l .¹⁷⁾ The increase in the thermal stability of supercooled liquid has been demonstrated by the appearance of the glass transition phenomenon for the $(\text{Fe}_{75}\text{Si}_{10}\text{B}_{15})_{100-x}\text{Nb}_x$ alloys containing more than 2 at%Nb.¹⁷⁾ However, as shown in Fig. 2, no glass transition was observed for the $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ alloy, accompanying the decrease in the maximum amorphous rod diameter from 1.5 to 0.5 mm. It is concluded that the addition of Cu with a positive heat of mixing against Fe²⁶⁾ is harmful for stabilization of supercooled liquid against crystallization, in agreement with the previous concept on the stabilization of supercooled liquid.^{1–3)} In addition, another reason for the disappearance of the glass transition seems to result from the decrease in B content leading to the decrease in the numbers of the Nb–B and Fe–B atomic pairs with large negative values²⁶⁾ which have a dominant effect on the glass-forming ability of Fe–B based alloys. However, it is noticed that despite the harmful influence of Cu and the decrease in B content, the amorphous alloy rod of 0.5 mm in diameter was produced for the $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ alloy.

We further discuss the reason for the formation of the amorphous alloy rod in the Fe–Si–B–Nb–Cu system. Figure 5 shows the DTA curves of the $\text{Fe}_{75}\text{Si}_{10}\text{B}_{15}$, $(\text{Fe}_{0.75}\text{Si}_{0.1}\text{B}_{0.15})_{96}\text{Nb}_4$ and $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ alloys. The liquidus temperature (T_l) is determined as 1450 K for the Fe–Si–B alloy, 1374 K for the Fe–Si–B–Nb alloy and 1365 K for the Fe–Si–B–Nb–Cu alloy. Although no glass transition is observed for the Fe–Si–B–Nb–Cu alloy, it is noticed that the T_l of the Cu-containing alloy is the lowest and no primary precipitation reaction is seen. The lowest T_l which is comparable to that for the Fe–Si–B–Nb alloy as well as the nearly single solidification reaction is presumed to have enabled us to form the amorphous alloy rod for the Fe–Si–B–Nb–Cu al-

Fig. 5 DTA curves of $\text{Fe}_{75}\text{Si}_{10}\text{B}_{15}$, $(\text{Fe}_{0.75}\text{Si}_{0.1}\text{B}_{0.15})_{96}\text{Nb}_4$ and $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ alloys.

loy, though the rod diameter is limited to less than 0.5 mm. Considering the significant decrease in T_l and the appearance of glass transition for the Fe–Si–B–Nb alloys, the rather high glass-forming ability for the Fe–Si–B–Nb–Cu alloys seems to reflect the enhancement effect of Nb addition exceeding the harmful influence by the addition of Cu and the decrease in B content.

5. Summary

We examined the possibility of forming a nanocrystalline Fe-based bulk alloy exhibiting good soft magnetic properties. The results obtained are summarized as follows.

(1) An amorphous alloy rod of 0.5 mm in diameter was obtained in the $\text{Fe}_{72.5}\text{Si}_{10}\text{B}_{12.5}\text{Nb}_4\text{Cu}_1$ alloy by copper mold casting.

(2) The amorphous alloy rod exhibits multi-stage crystallization process in which the first stage is due to the precipitation of bcc-Fe phase and the following stages are attributed to the transition of bcc-Fe + amorphous to bcc-Fe + Fe_{23}B_6 + Fe_2B + Fe_3Si + Fe_2Nb phases. The bcc-Fe phase has a very fine grain size of 10 nm and its volume fraction is about 70% after the completion of the first-stage precipitation reaction.

(3) The nanoscale mixed phase alloy consisting of bcc-Fe and remaining amorphous phases exhibited good soft magnetic properties, i.e., high B_s of 1.21 T, low H_c of 1.8 A/m and high μ_i of 32000.

The first synthesis of the nanocrystalline Fe-based alloy rod exhibiting good soft magnetic properties is expected to extend significantly the future application field as soft magnetic ma-

terials.

REFERENCES

- 1) A. Inoue: Bulk Amorphous Alloys, (Trans Tech Publications, Zurich, 1999) pp. 1–148.
- 2) A. Inoue: Acta Mater. **48** (2000) 279–306.
- 3) A. Inoue: Mater. Sci. Eng. **A304-306** (2001) 1–10.
- 4) A. Inoue, A. Takeuchi and B. L. Shen: Mater. Trans. **42** (2001) 970–978.
- 5) A. Inoue, Y. Shinohara and J. S. Gook: Mater. Trans., JIM **36** (1995) 1427–1433.
- 6) A. Inoue and J. S. Gook: Mater. Trans., JIM **37** (1996) 32–38.
- 7) B. L. Shen, H. Koshiba, T. Mizushima and A. Inoue: Mater. Trans., JIM **41** (2000) 873–876.
- 8) T. D. Shen and R. B. Schwarz: Appl. Phys. Lett. **75** (1999) 49–51.
- 9) B. L. Shen, H. Koshiba, H. Kimura and A. Inoue: Mater. Trans., JIM **41** (2000) 1478–1481.
- 10) B. L. Shen, H. M. Kimura, A. Inoue and T. Mizushima: Mater. Trans., JIM **41** (2000) 1675–1678.
- 11) H. Koshiba, A. Inoue and A. Makino: J. Appl. Phys. **85** (1999) 5136–5138.
- 12) A. Inoue, T. Zhang, H. Koshiba and A. Makino: J. Appl. Phys. **83** (1998) 6326–6328.
- 13) W. Zhang and A. Inoue: Mater. Trans. **41** (2000) 1679–1682.
- 14) S. J. Pang, T. Zhang, K. Asami and A. Inoue: Acta Mater. **50** (2002) 489–497.
- 15) S. J. Pang, T. Zhang, K. Asami and A. Inoue: Mater. Trans. **42** (2001) 376–379.
- 16) T. D. Shen and R. B. Schwarz: Acta Mater. **49** (2001) 837–847.
- 17) A. Inoue and B. L. Shen: Mater. Trans. **43** (2002) 766–769.
- 18) A. Inoue and B. L. Shen: Mater. Trans. (to be submitted).
- 19) A. Inoue, T. Zhang and A. Takeuchi: Appl. Phys. Lett. **71** (1997) 464–466.
- 20) W. Zhang and A. Inoue: Mater. Trans. **42** (2001) 1835–1838.
- 21) B. L. Shen and A. Inoue: Mater. Trans. **43** (2002) 1235–1239.
- 22) Y. Yoshizawa, S. Oguma and K. Yamauchi: J. Appl. Phys. **64** (1988) 6044–6046.
- 23) K. Hono, A. Inoue and T. Sakurai: Appl. Phys. Lett. **58** (1991) 2180–2182.
- 24) K. Hono, K. Hiraga, A. Inoue and T. Sakurai: Acta Mater. **40** (1992) 2137–2147.
- 25) A. Makino, K. Suzuki, A. Inoue and T. Masumoto: Mater. Trans., JIM **32** (1991) 551–556.
- 26) F. R. Niessen: *Cohesion in Metals*, (Elsevier Science Publishers, B.V., Amsterdam, 1988) pp. 224–391.