EPJ Web of Conferences **15**, 01008 (2011)
DOI: 10.1051/epjconf/20111501008
© Owned by the authors, published by EDP Sciences, 2011

Crystallization of $Fe_{82}Si_2B_{16}$ and $Fe_{82}Si_4B_{14}$ metallic glasses upon isothermal and non-isothermal annealing

A.P. Shpak[1], A.G. Il'inskii[1], A.V. Marunyak[1], O.I. Slukhovskyy[1], Yu.V. Lepeeva[1], A. Dekhtyar[1], I. Kaban[2,a], N. Mattern[2], and J. Eckert[2,3]

[1]G.V. Kurdymov Institute for Metal Physics, National Academy of Sciences of Ukraine, 36 Vernadsky Str., 03142 Kyiv, Ukraine
[2]IFW Dresden, Institute for Complex Materials, P.O.B. 270116, D-01171 Dresden, Germany
[3]TU Dresden, Institute of Materials Science, D-01062 Dresden, Germany

Abstract. Crystallization of $Fe_{82}Si_2B_{16}$ and $Fe_{82}Si_4B_{14}$ metallic glasses upon heat treatment has been studied. The amorphous ribbons have been isothermally annealed at different temperatures (673, 693, 733 and 743 K) and for various times (from 15 min to 78 hours). Phase compositions and the sequence of their appearance in dependence on the annealing temperature and time have been established.

1 Introduction

Metallic glasses and nanocrystalline materials based on Fe-Si-B ternary alloys are soft magnetic materials characterized by high permeability and low energy loss. They have successfully substituted crystalline ferromagnetic materials in magnetic cores of transformers, chokes and other inductive devices [1,2]. Their magnetic properties are mainly determined by the nanocrystalline structure obtained by controlled heat treatment via crystallization of amorphous ribbons. Therefore, knowledge of the crystallization sequence and the ranges of thermal stability is extremely important for practical application of these alloys.

Crystallization of Fe-Si-B metallic glasses upon annealing has been extensively studied already [3-12]. In recent works [10-12] three amorphous alloys within a narrow composition range were investigated ($Fe_{82}Si_2B_{16}$, $Fe_{80}Si_6B_{14}$, and $Fe_{77}Si_8B_{15}$). The $Fe_{82}Si_2B_{16}$ metallic glass was found to crystallize in two stages. It was suggested that at first, b.c.c. phases of α-Fe and probably Fe_3Si appear together with the metastable Fe_3B phase; then, the metastable Fe-boride transforms into the stable Fe_2B and α-Fe phases. On the other hand, glasses with lower boron content ($Fe_{80}Si_6B_{14}$ and $Fe_{77}Si_8B_{15}$) crystallized without formation of the metastable Fe_3B phase whatever thermal treatment was applied. Taking into account that the metastable Fe-boride was found over the whole concentration range of binary Fe-B metallic glasses upon crystallization [12], it is reasonable to suppose that the observed phenomena are related to the Si content in the Fe-Si-B ternary alloys. In [3] the crystallization kinetics of $Fe_{90-x}Si_xB_{10}$ amorphous alloys was studied. It has been shown that the hypoeutectic glasses ($x < 14$) and hypereutectic glasses ($x > 14$) crystallize differently.

In the present work, a detailed investigation of the thermal-time treatment of two metallic glasses with constant Fe content and different Si-B ratio – $Fe_{82}Si_2B_{16}$ and $Fe_{82}Si_4B_{14}$ – has been carried out.

2 Experimental

$Fe_{82}Si_2B_{16}$ and $Fe_{82}Si_4B_{14}$ amorphous ribbons were prepared from the precursor alloys by melt spinning, as described elsewhere [2, 12]. Isothermal annealing of the amorphous ribbons has been carried under vacuum (~10^{-5} mbar) in a furnace enabling fast heating to the desired temperatures.

X-ray diffraction experiments were performed with a standard DRON-3M diffractometer in θ - 2θ geometry using monochromatic Mo K_α irradiation. The X-ray scattering intensity has been measured between 7° and 90° of 2θ in steps of 0.1°. The statistical error at the tail of the scattering curves did not exceed 1%.

Thermal properties were investigated with a Perkin Elmer DSC-7 differential scanning calorimeter. The DSC measurements were carried out from room temperature up to 953 K. The temperature and energy calibration of the device was performed using high purity metals supplied as standards. The temperature of the samples studied was measured with an accuracy of ±0.1 K.

[a] e-mail: i.kaban@ifw-dresden.de

This is an Open Access article distributed under the terms of the Creative Commons Attribution-Noncommercial License 3.0, which permits unrestricted use, distribution, and reproduction in any noncommercial medium, provided the original work is properly cited.
Article available at http://www.epj-conferences.org or http://dx.doi.org/10.1051/epjconf/20111501008

3 Results and discussion

Figure 1 shows the DSC curves obtained for $Fe_{82}Si_2B_{16}$ and $Fe_{82}Si_4B_{14}$ metallic glasses at a heating rate of 20 K/min. Substitution of 2 at.% Si for B at the constant Fe content in the ternary Fe-Si-B alloys results in a remarkably different crystallization behaviour upon constant-rate heating. There is one exothermal signal with a peak at about 767 K in the DSC curve of the $Fe_{82}Si_2B_{16}$ amorphous alloy, while the DSC curve of the $Fe_{82}Si_4B_{14}$ metallic glass reflects two exothermal events with peaks at 756 K and 813 K (Fig. 1).

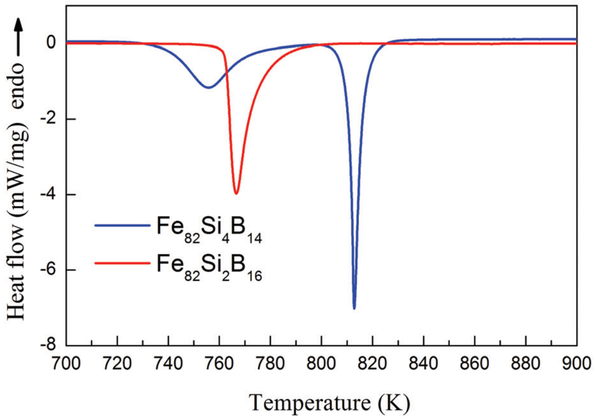

Fig. 1. DSC curves for the $Fe_{82}Si_2B_{16}$ [10] and $Fe_{80}Si_6B_{14}$ metallic glasses measured at a heating rate of 20 K/min.

Upon heating, the $Fe_{82}Si_2B_{16}$ alloy crystallizes with formation of the metastable Fe_3B phase. At first, crystals with b.c.c. structure (either α-(Fe,Si) solid solution or α-Fe and Fe_3Si) and Fe_3B phase appear; then, the metastable Fe_3B transforms into the stable Fe_2B and α-Fe phases [10,11]. It has been shown that the $Fe_{82}Si_2B_{16}$ glass can also crystallize upon isothermal annealing at a temperature remarkably lower than the onset of non-isothermal crystallization: at 693 K against 733 K [10,11]. However, only reflexes of the b.c.c. crystalline phase [α-(Fe,Si)] have been detected in the XRD patterns after 24 hours annealing in those works. One of the aims of the present study was to elucidate whether or not crystalline Fe-borides (Fe_3B, Fe_2B) can precipitate at 693 K if the annealing is further prolonged.

In the present work, the $Fe_{82}Si_2B_{16}$ glass was annealed at 693 K for 24 hours. Then, the same sample was additionally heat-treated at 693 K for 11 hours. It is noteworthy that after the additional annealing, crystallites of a boride phase appeared indeed. However, this was already the stable Fe_2B phase. Distinct crystalline (110) and (202) reflexes characteristic of the stable Fe_2B phase are seen at about 11° and 25° in the XRD curve obtained after a total of 35 hours heat treatment (Fig. 2). Moreover, a weak increase of the intensity at the position of the reflexes of the Fe_2B phase has already been observed after annealing for 24 hours in our study.

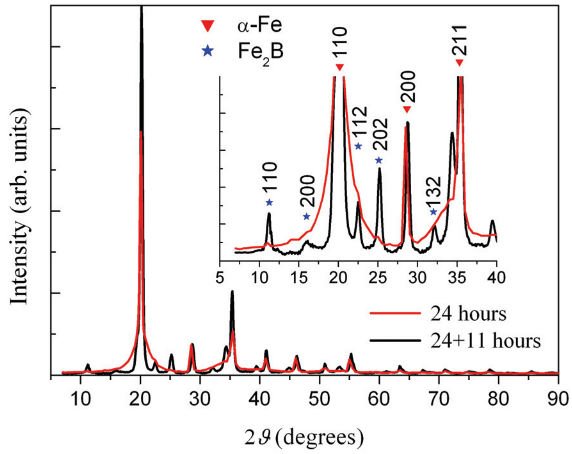

Fig. 2. XRD patterns for the $Fe_{82}Si_2B_{16}$ amorphous ribbon annealed at 693 K for 24 hours and after additional annealing for 11 hours.

Therefore, more detailed investigations of the $Fe_{82}Si_2B_{16}$ amorphous ribbons annealed from 15 min to 24 hours have been performed. The reflexes of b.c.c. α-Fe crystallites are observed in the diffraction pattern after 3 hours of annealing (Fig. 3). The lines corresponding to borides start to appear after 15 hours of annealing. Mainly, these are reflexes of the stable boride Fe_2B. Even if there are reflexes of the metastable Fe_3B phase visible, their intensity is very weak, obviously due to a small volume fraction of this phase.

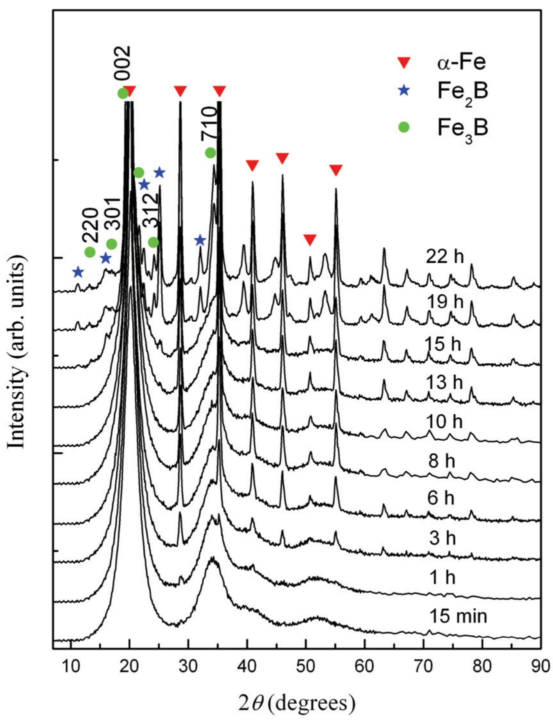

Fig. 3. XRD patterns of $Fe_{82}Si_2B_{16}$ amorphous ribbons annealed at 693 K for different time.

Hence, our results confirm precipitation of the stable Fe_2B crystals upon annealing of the $Fe_{82}Si_2B_{16}$ metallic glass at a rather low temperature (693 K) if the annealing time is long enough. Considering this finding, one can suppose that the metastable boride Fe_3B formed in a $Fe_{82}Si_2B_{16}$ amorphous sample annealed at a higher temperature for a short time (i.e. after the first stage of crystallization) might transform into the stable Fe_2B phase by increasing the annealing time. Therefore, X-ray diffraction measurements of the $Fe_{82}Si_2B_{16}$ metallic glass annealed at 743 K for 1 to 24 hours have been performed.

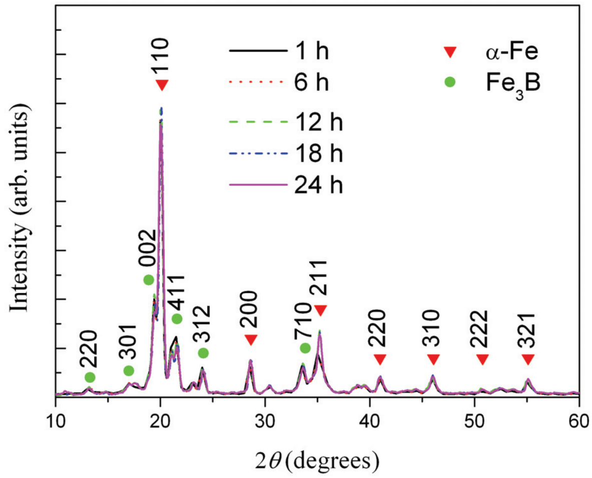

Fig. 4. XRD patterns for $Fe_{82}Si_2B_{16}$ metallic glass annealed at 743 K for different times.

However, despite the rather high annealing temperature (just 20 K below the position of the exothermic peak in the DSC curve, Fig. 1) and a long annealing time, the stable Fe_2B boride was not obtained. Only reflexes of the b.c.c. phase and reflexes of metastable Fe_3B are observed in the XRD patterns corresponding to different annealing times at 743 K (Fig. 4).

At a heating rate of 20 K/min, the $Fe_{82}Si_4B_{14}$ amorphous alloy starts to crystallize at about 723 K (Fig. 1). Therefore, similar to the $Fe_{82}Si_2B_{16}$ alloy, the $Fe_{82}Si_4B_{14}$ amorphous ribbons have been at first isothermally annealed at 693 K (Fig. 5). However, such annealing temperature turned out to be high for this composition. Already after 15 min, the volume fraction of the b.c.c. crystalline phase was remarkable, and it was not possible to determine when this phase starts to precipitate. On the other hand, it was established that the stable Fe_2B phase appears already in the first stage of crystallization, i.e. without formation of the metastable boride Fe_3B. In Fig. 5, (110) and (202) reflexes of the Fe_2B crystals are clearly visible in the XRD pattern recorded after 12 hours of isothermal annealing at 693 K). It should be noted that the metastable Fe_3B phase has not been found for the $Fe_{82}Si_4B_{14}$ amorphous alloy whatever heat treatment was applied.

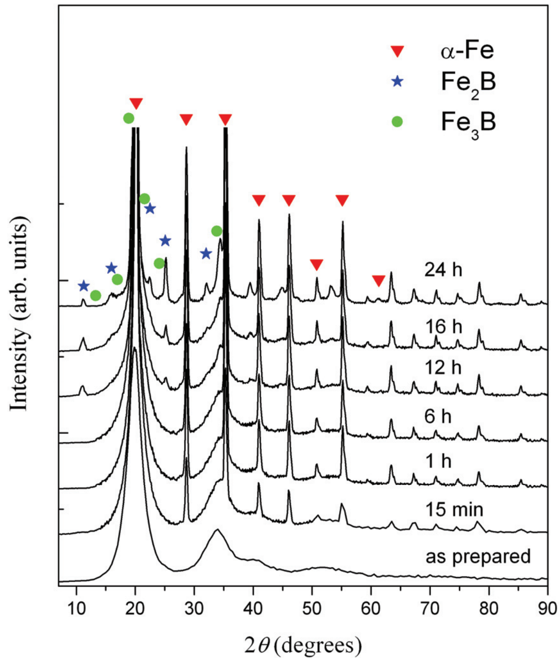

Fig. 5. XRD patterns for $Fe_{82}Si_4B_{14}$ metallic glass annealed at 693 K for different time.

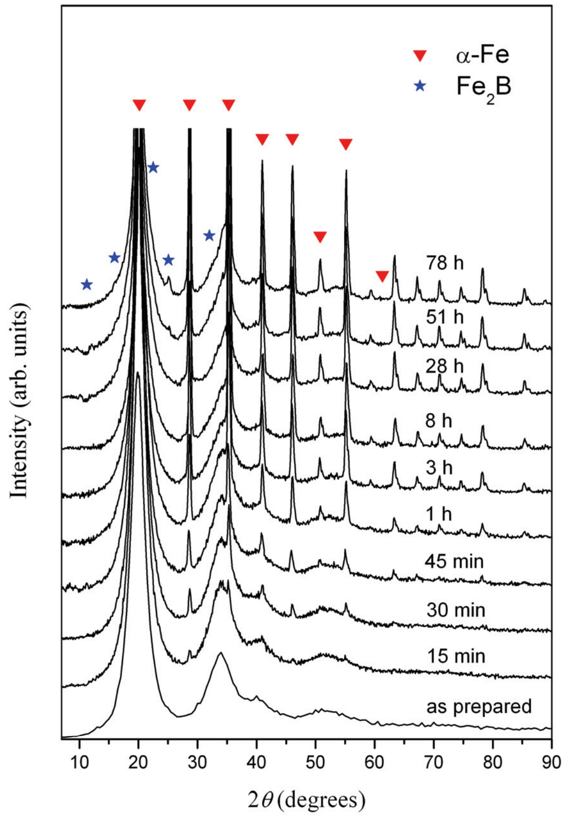

Fig. 6. XRD patterns for $Fe_{82}Si_4B_{14}$ metallic glass annealed at 673 K for different time.

As we were not able to determine the start of the α-(Fe,Si) precipitation at 693 K, the annealing temperature was decreased to 673 K. The XRD curves measured for the $Fe_{82}Si_4B_{14}$ amorphous ribbons after different annealing times at 673 K are plotted in Fig. 6. Also in this case, crystals of the b.c.c. phase started to appear after 15 min of heat treatment. However, their volume fraction was small. It is interesting that the decrease of the annealing temperature by 20 K slowed the nucleation rate of the Fe-boride significantly down. The reflexes corresponding to the Fe_2B phase have been observed in the XRD curves only after 51 hours of annealing, and even after an annealing time of 78 hours the volume fraction of the Fe_2B phase was rather small.

Both $Fe_{82}Si_2B_{16}$ and $Fe_{82}Si_4B_{14}$ amorphous alloys were also isothermally annealed at other temperatures between 673 K and 743 K. No principal differences in the crystallization process from that described above have been found, only the crystallization rate was different. As an example, Fig. 7 shows two X-ray diffraction patterns for the $Fe_{82}Si_4B_{14}$ amorphous ribbons measured after isothermal annealing at 693 K for 6 hours and at 733 K for 1 hour. The coincidence of the XRD intensities demonstrates how the same final result (in this case, b.c.c. α-(Fe,Si)) can be obtained by controlling the annealing time and temperature.

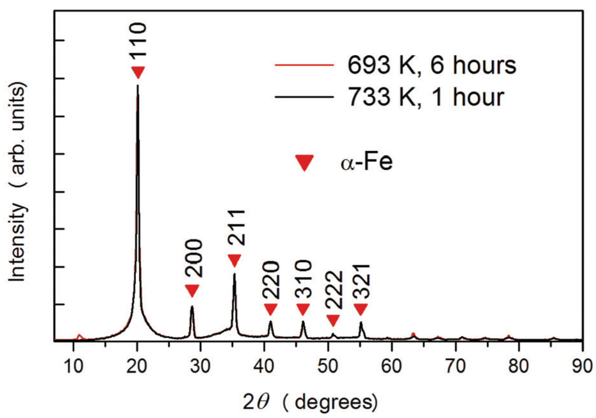

Fig. 7. XRD patterns for $Fe_{82}Si_4B_{14}$ metallic glass annealed at different temperatures and for different times.

4 Conclusions

In spite of rather close compositions, the $Fe_{82}Si_2B_{16}$ and $Fe_{82}Si_4B_{14}$ amorphous alloys crystallize in a different way. The DSC curve for $Fe_{82}Si_2B_{16}$ metallic glass exhibits only one exothermic maximum, while there are two exothermic peaks in the DSC curve for amorphous $Fe_{82}Si_4B_{14}$.

It is shown that the stable Fe_2B phase can be obtained already in the first stage of crystallization upon annealing $Fe_{82}Si_2B_{16}$ amorphous ribbons at 693 K if the annealing time is long enough.

If the metastable Fe_3B phase appeared after a short time heat treatment of amorphous $Fe_{82}Si_2B_{16}$, subsequent prolonged annealing at the same temperature did not result in a transformation from the metastable Fe_3B to the stable Fe_2B phase.

Upon annealing of the $Fe_{82}Si_4B_{14}$ amorphous alloy, the metastable Fe_3B phase was not found whatever heat treatment was applied.

Acknowledgments

O. Slukhovskyy acknowledges the Saxonian Ministry of Science and Art (SMWK) for the financial support of his stay at the IFW Dresden.

References

1. Y. Yoshizawa, S. Oguma, K. Yamauchi, J. Appl. Phys. **64**, 6044 (1988)
2. V.K. Nosenko, V.V. Maslov, V.V. Kirilchuk, A.P Kochkubey, J. Phys.: Conf. Ser. **98**, 072016 (2008)
3. W. Minor, B. Schönfeld, B. Lebech, B. Buras, W. Dmowski, J. Mater. Sci. **22**, 4144 (1986)
4. S.G. Kim, N.E. Lee, H.Y. Ra, J. Cryst. Growth **92**, 629 (1988)
5. A.R. Bhatti, B. Cantor, J. Mater. Sci. **29**, 816 (1994)
6. J. Kohlbrecher, A. Wiedemann, H. Wollenberger, N. Mattern, G. Goerigk, Nanostr. Mater. **6**, 449 (1995)
7. E. Illekova, Thermochim. Acta **280-281**, 289 (1996)
8. E. Illekova, F. Malizia, F. Ronconi. Thermochim. Acta **282-283**, 91 (1996)
9. Y.R. Zhang, R.V. Ramanujan, Mater. Scie. Eng. A **416**, 161 (2006)
10. A.G. Il'inskii, G.M. Zelins'kaya, V.V. Maslov, V.K. Nosenko, Yu.V. Lepeeva, Metallofizika I Noveishie Technologii **26**, 1501 (2004)
11. A.P. Shpak, A.G. Il'inskii, G.M. Zelinskaya, Yu.V. Lepeeva, A.I. Dehktyar, Li Chengdong, Metallofizika I Noveishie Technologii **28**, 1 (2006)
12. A.G. Il'inskii, V.V. Maslov, V.K. Nosenko, G.M. Zelinskaya, T.M. Khristenko, Li Chengdong, Metallofizika I Noveishie Technologii **28**, 1369 (2006)