

Crystallization of Fe-Based Metallic Glasses by Mossbauer Spectroscopy

著者	Hanada R.
journal or publication title	CYRIC annual report
volume	1996
page range	40-43
year	1996
URL	http://hdl.handle.net/10097/49962

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Introduction

Metallic glasses (or amorphous alloys) have been one of the recent subjects in materials science because of their novel physical properties and of their technological applications. In the present, their crystallization processes have been studied by a Mössbauer spectroscopy.

The purposes of the experiments are three fold. Namely, to examine (1) how the non crystalline metallic glass state is reflected in the Mössbauer spectrum. (2) how the spectrum changes into that of the crystalline state upon annealing. (3) how the alloying elements distribute among several phases formed after the crystallization.

Experimental

5 different metallic glasses were obtained from NILACO, of which compositions are given as in Table 1 by the supplier. They are Fe based alloys with Si and B as the alloying elements (2605S2 and 2605S3A) with some modification with Ni and Mo (2826MB) or Co (2605CO) or C (2605SC). $2 \times 2 \text{ cm}^2$ foils with $25 \mu \text{ m}$ thickness were cut from the original sheets and Mössbauer spectra were measured in the as received state as well as after the isochronal annealing (30min) in a vacuum (10^{-7} Torr) at temperatures between 400C and 1000C. The spectroscopy was in a transmission mode with $^{57}\text{Co}/\text{Rh}$ source. The spectra were analyzed by a program from Wissel GmbH to obtain the hyperfine field distribution.

Results and Discussion

Fig. 1 shows an example of the present spectroscopy for 2605S2($\text{Fe}_{78}\text{B}_{13}\text{Si}_9$), one of the simplest alloys studied in the present. In the as received state, the spectrum is a magnetic sextet with a smaller hyperfine field magnitude than that of the crystalline pure Fe and also with a broad distribution of the hyperfine field. This shows Fe atoms in the metallic glass are in a ferromagnetic environment though Fe atoms experience a broad and continuous internal field distribution. This is a typical result for a metallic glass and proves that the obtained specimens are really in a metallic glass in the as received state. The specimen stays to be a

metallic glass state up to 670K (400C), though several new components start to develop at 770K (500C) and they tends to grow up to 1073K (800C). This trend is observed more clearly in Fig.2 where the hyperfine field distributions are shown. In the as received state or after 670K annealing, the hyperfine field shows a distorted Gaussian distribution with the center at H_{MG} with a half width $+\Delta H_f$ or $-\Delta H_f$. Here $+\Delta H_f$ and $-\Delta H_f$ are distinguished since the distribution is usually asymmetric for the alloys investigated. Namely, the field distributes more widely in the lower side than the higher. ($-\Delta H_f > +\Delta H_f$). After the annealing at 770K, part of the continuous hyperfine field distribution changes into a discrete one. Here a part of metallic glass transforms to a crystal state. After the annealing at 770K and above, the field distribution develops into 4 well defined peaks at 33, 31, 28 and 24T. Here we label them as H_0 , H_1 , H_2 and H_{PPT} respectively, as shown in Fig. 2 after the 1270K annealing. Since each H_n has a unique magnitude with the width comparable with that of pure Fe in the crystalline state, we may conclude that they correspond to Fe atoms in different crystalline states. Namely, the metallic glass starts to transform into crystalline states at 770K and the crystallization is completed at 880K. Further annealing at higher temperatures causes redistribution of alloying elements among several phases as suggested by the relative magnitude change in H_n 's population above 880K, which will be discussed later.

The trend described above was found to be in common for all 5 different metallic glasses investigated in the present and summarized in Table I. The alloy containing Co (2605CO) shows a lower crystallization temperature (670K) than others.

Next, we discuss the nature of H_n 's in Fig. 2. The magnitude of H_0 is almost the same with that of pure Fe. So we may conclude H_0 corresponds to Fe in a crystalline state with no impurities around it. The magnitude of H_1 is comparable with that of the 1st satellite in Fe-Si alloys (30.7T) and H_2 is for the 2nd satellite(27.8T) and these have been interpreted as due to Fe atoms with 1 and 2 Si atoms in the 1st neighbor site (8 for bcc Fe lattice) respectively¹⁾. So we may conclude that the alloy crystallizes into an Fe-Si alloy as the host with precipitates to give H_{PPT} , corresponding to a metallic compound of Fe, B and Si.

This interpretation is reasonable since Si is quite soluble in Fe host while B is insoluble and so the alloy tends to achieve the thermodynamical equilibrium state for B and a part of Si to form a compound once the alloy is relieved from the metallic glass state.

The relative change among H_0, H_1 and H_2 population above 880K is due to the Si concentration decrease in the Fe host with the compound growth. As well known in Fe-Si alloys studies, the H_1 or H_2 populations decrease with the Si concentration decrease in the host according to a binomial distribution.

This picture of the phase separation observed in the Fe-B-Si alloys can be extended to other alloys containing Ni, Mo and Co studied in the present. First, these elements are all soluble in Fe as in the case of Si. So upon the crystallization they form a complete solid solution as the host. Ferromagnetic elements Ni and Co have been known to give satellites at

higher positions than H_0 and a paramagnetic element Mo at the lower side. The examination of the spectrum after the crystallization indeed reveals this trend. Namely, 2826 MB (Mo and Ni) shows a broad H_0 due to Mo (a lower field side) and Ni (a higher field side). 2605 CO (Co) shows a higher H_0 than that of pure Fe due to Co in the host. The H_{PPT} 's show almost the same value for all alloys showing it is determined mainly by Si and B and additional elements (Ni, Co, Mo) contribution is only minor if they are incorporated in the precipitates.

Since the hyperfine distribution has been determined in the present Mössbauer study, it is interesting to examine how it will be reflected in the PAC spectroscopy for the metallic glass. The result of the experiment will be reported in a separate paper in this volume.

Adding to this spectroscopic observation, all metallic glasses were found to become extremely brittle after the crystallization and easily be powdered upon handling. So care must be taken in cases they are activated by particles irradiations or by activity implantation and then crystallized.

Acknowledgement

This work is supported by a Grant-in-Aid for Scientific Research in Priority Area from the Ministry of Education, Science and Culture of Japan.

Reference

- 1) Kobayashi M.: A Masters Thesis, Dept. Materials Science, Tohoku Univ.(1989).

Table 1. Summary of the Mössbauer Spectroscopy on Metallic Glasses.

No. Alloys	Composition/at%	H_{MC}/T	$+\Delta H_f/T$	$-\Delta H_f/T$	Cryst.Temp./K
0 2826MB	$\text{Fe}_{40}\text{Ni}_{32}\text{Mo}_4\text{B}_{18}$	23	3	6	6
1 2605S2	$\text{Fe}_{72}\text{B}_{13}\text{Si}_9$	26	4	6	6
2 2605S3A	$\text{Fe}_{72}\text{B}_{16}\text{Si}_6$	23	4	8	8
3 2605CO	$\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_1$	28	4	4	4
4 2605SC	$\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$	25	4	4	4

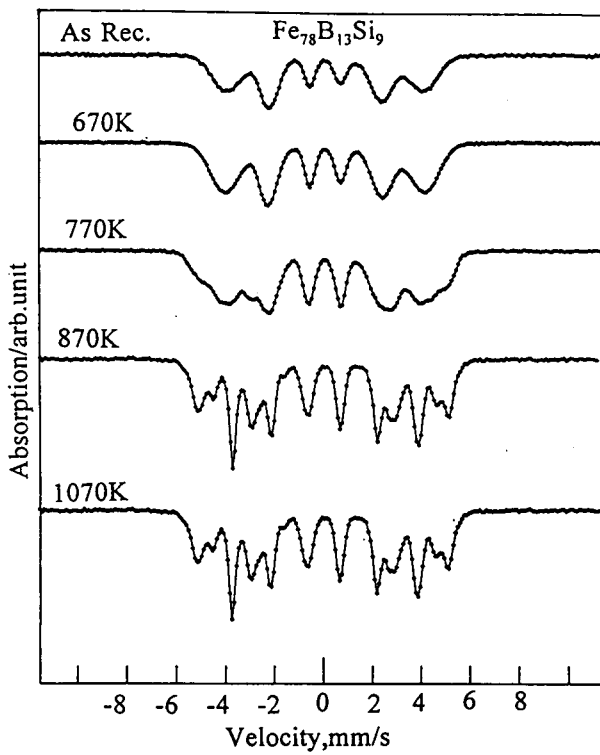


Fig.1 Transmission Mössbauer spectra for a metallic glass $\text{Fe}_{78}\text{B}_{13}\text{Si}_9$, during annealing between RT and 1000C.

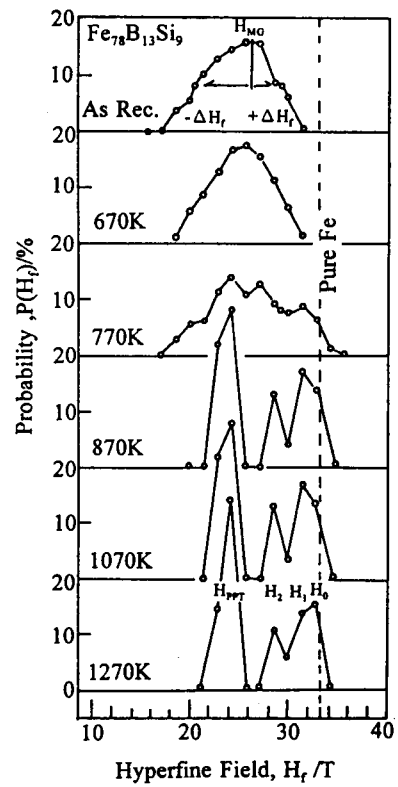


Fig.2 Hyperfine field distributions obtained from Fig.1.