JOURNAL OF MATERIALS SCIENCE 14 (1979) 1245–1248

Microhardness characterization of stability of Fe-Ni-base metallic glasses

M. STUBIČAR
Institute of Physics, University of Zagreb, 41001 Zagreb, P.O. Box 304, Yugoslavia

The stability of Fe–Ni-base metallic glasses on annealing in the range 30 to 1000° C was investigated by microhardness measurements. The results (i.e. two maxima in all recorded curves, for annealing temperatures below and above ~400° C) were correlated with other recent experimental evidence for structural relaxation and structural changes in the same metallic glasses.

1. Introduction

The fundamentally interesting and technically attractive properties of metallic glasses are determined by their amorphous structure. To date, numerous papers have been devoted to investigations on Fe–Ni-base metallic glasses [1, 3–6, 11–17]. In addition to examination of the structure and properties of glasses in the as-quenched state, their changes during annealing have also been investigated because, like all glasses, these phases are metastable and on heating the alloys revert to the crystalline state.

This work has been stimulated not only by recent developments in techniques of rapid quenching from the melt [10], by which production of metallic glasses in ribbons of practically unlimited length is now possible, but also by the exciting properties of Fe–Ni-base glasses which have been revealed in these studies.

In two previous papers the results of investigations on the decomposition of $Fe_{40}Ni_{40}B_{20}$ metallic glass during annealing [12] and on the observed correlation between microhardness and magnetic properties for two series of amorphous alloys: $Fe_xNi_{80-x}B_{20}$ and $Fe_xNi_{80-x}P_{14}B_6$ [5] were described. In this paper the results of a microhardness study of the stability for a number of samples belonging to the same series of glasses subjected to isochronal annealing in the temperature range 30 to 1000° C will be reported.

2. Experimental details

The samples of Fe–Ni-base metallic glasses were obtained in the form of long ribbons prepared from master alloys of predetermined concentrations by the use of a melt-spinning device [10]. For the purpose of microhardness measurements, samples were cut from ribbons (which varied from about 0.3 to 1.5 mm in width and 20 to 50 μm in thickness) into pieces about 1.5 cm long.

The samples of the following nominal compositions (in at. %) were studied: $Fe_{20}Ni_{60}P_1B_{19}$, $Fe_{40}Ni_{40}B_{20}$, $Fe_{60}Ni_{20}B_{20}$, $Fe_{80}B_{20}$, $Fe_{80}Si_2B_{18}$, $Fe_{10}Ni_{70}P_{14}B_6$, $Fe_{20}Ni_{60}P_{14}B_6$, $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{60}Ni_{20}P_{14}B_6$ and $Fe_{80}P_{14}B_6$, in order to gain an overall picture of the reactions which can occur during the annealing treatment of amorphous alloys. In this study the Ni-rich side of the same glasses was omitted because some traces of crystallinity were observed by X-ray diffraction.

The heat-treatment consisted of isochronal annealing in vacuum in the temperature range 50 to 1000° C. This temperature range was covered in 20 equal steps and the samples were successively annealed at each chosen temperature for 30 min. After each annealing step, samples were air-cooled to room temperature in order to follow microhardness changes during heat-treatment. For the purpose of microhardness measurements they were glued on to a glass slide with the shiny face up. The microhardness data were obtained using Zeiss (Jena) equipment with a 136° diamond pyramid indenter and a 100 ponds* load. At least 20 indentations were made for each mean micro-

---

*1 pond = 1 g wt = 9.81×10^{-3} N.

hardness value reported in this paper and the standard deviation was near to 7% of the mean value.

On continuing the heat-treatment a thin layer was formed on the surface of samples [14, 16], and changed not only the colour but also the quality of surfaces for the hardness tests. Several attempts to measure the influence of the surface layer on the microhardness did not succeed, apparently it caused too small a change. In order to follow microhardness changes more precisely, particularly at higher annealing temperatures, the surface layers were repeatedly removed by means of mechanical polishing using alumina powder of 0.05 μm diameter. During heat-treatment the samples became very brittle [14] and microhardness measurements were performed carefully.

3. Results and discussion

For the results described in this paper the problem of the choice of indenter load was carefully considered. This was done not only because of the experimental fact that measured microhardness depends on the load applied to the indenter during measurements, but also because the measured value for samples of the same composition may possibly be influenced by the sample thickness because of the anvil effect [2]. Indeed different investigators have reported several hardness values for the same metallic glasses. In order to shed light on both effects and to resolve these questions, two sets of experiments were performed. The results of the first are shown in Fig. 1a, where plots of recorded hardness values, H_V, versus load, F, for two samples ($Fe_{40}Ni_{40}B_{20}$ and $Fe_{80}Si_2B_{18}$) of metallic glasses are given. From Fig. 1a one can conclude that H_V decreases with F, but for F exceeding roughly 100 ponds this dependence is hardly observable and H_V is independent of F within experimental error.

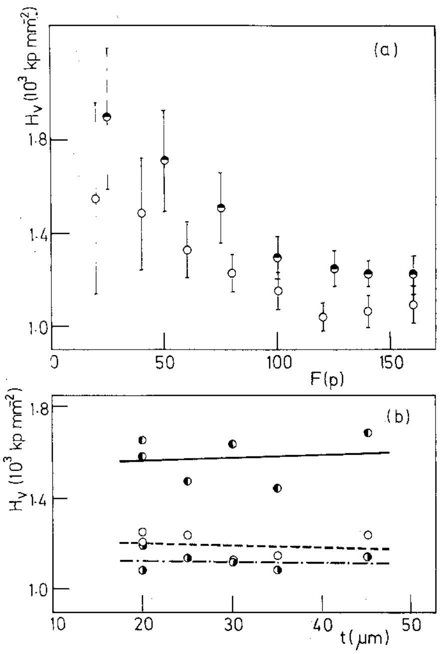

Figure 1 (a) Variation in microhardness and in experimental error with the indenter load for ○, $Fe_{40}Ni_{40}B_{20}$ and ◒, $Fe_{80}Si_2B_{18}$ metallic glasses. (b) Variation in microhardness with the sample thickness of $Fe_{40}Ni_{40}B_{20}$ metallic glass and the indenter load: ◐, 50 p; ○, 100 p; ◑ 160 p. The lines drawn in the figure are obtained by the use of the linear least square fits to the experimental data.

The results of the second experiment, in which the influence of the sample thickness, t, on H_V were investigated, are shown in Fig. 1b, again for $Fe_{40}Ni_{40}B_{20}$ amorphous alloy and for three different values of applied load. From Fig. 1b one can conclude that, fortunately, in the explored thickness range (20 to 50 μm) the sample thickness did not seriously influence the hardness values. Thus, we conclude that the different reported H_V values have not been caused by the anvil effect but they might be due to the load effect. So, on the basis of the result shown in Fig. 1 (i.e. the constancy of H_V on F and H_V on t, and also the decrease of the standard deviation, s, with F), higher loads are preferable to some extent. For measurements of microhardness carried out in annealing experiments, the load of 100 ponds was selected and in this case the values of s were somewhere near 7% of the mean hardness values. This value did not vary too much during annealing in the temperature range up to 350° C, but at higher temperatures it increased for the reasons mentioned above.

Before making systematic investigations of the stability of metallic glasses, and in order to form some idea of the difference between hardness values belonging to metallic glasses and to some known crystalline states, a sample containing equiatomic proportions of Fe and Ni and having the austenite type structure was prepared in the form of a strip about 50 μm thick. Two microhardness values were obtained for two different states of the sample; 290 ± 20 kp mm^{-2} for the plastically deformed state (as-received strip) and 130 ± 10 kp mm^{-2} for the annealed state (as-received strip subjected to an another annealing treatment for 2 h at 1000° C).

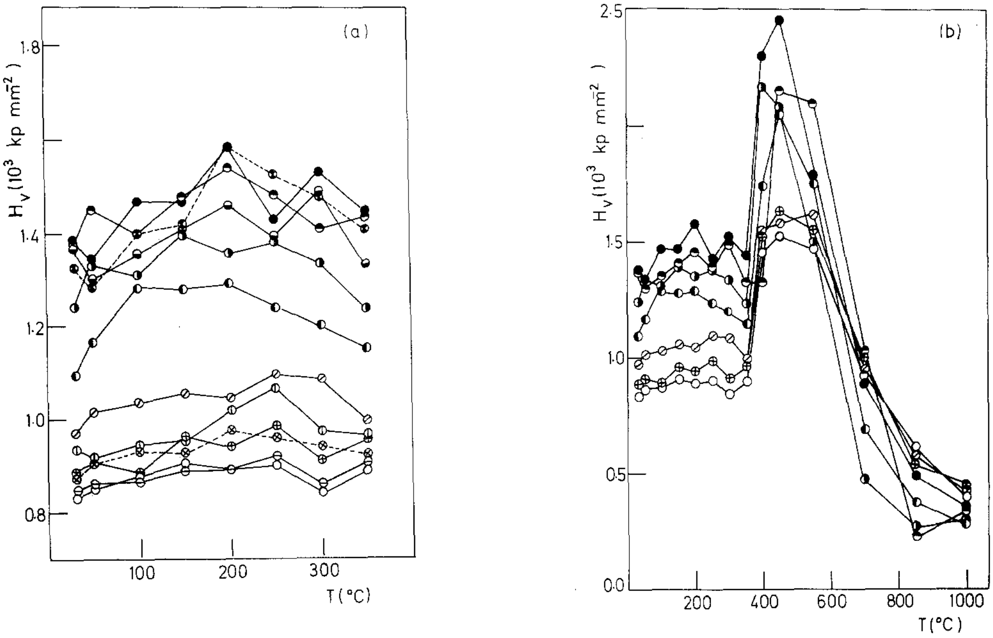

Figure 2 (a) Microhardness changes of metallic glasses during isochronal annealing for 30 min. Alloy compositions: ○, $Fe_{10}Ni_{70}P_{14}B_6$; ⊖, $Fe_{20}Ni_{60}P_{14}B_6$; ⊗ and ⊕, $Fe_{40}Ni_{40}P_{14}B_6$; ⦶, $Fe_{60}Ni_{20}P_{14}B_6$; ⊘, $Fe_{80}P_{14}B_6$; ◐, $Fe_{20}Ni_{60}P_1B_{19}$; ◑, $Fe_{40}Ni_{40}B_{20}$; ◓, $Fe_{60}Ni_{20}B_{20}$, ⊛ and ●, $Fe_{80}B_{20}$; ◒, $Fe_{80}Si_2B_{18}$. (b) Microhardness changes of metallic glasses during isochronal annealing for 30 min. Alloy compositions: ○, $Fe_{10}Ni_{70}P_{14}B_6$; ⊕, $Fe_{40}Ni_{40}P_{14}B_6$; ⊘, $Fe_{80}P_{14}B_6$; ◐, $Fe_{20}Ni_{60}P_1B_{19}$; ◑, $Fe_{40}Ni_{40}B_{20}$; ●, $Fe_{80}B_{20}$; ◒ $Fe_{80}Si_2B_{18}$.

The results for metallic glasses studied in this work and obtained in the course of annealing are shown in Fig. 2a for samples belonging to all alloy compositions and for the temperature range 30 to 350° C and for samples of only some characteristic compositions and the temperature range up to 1000° C in Fig. 2b. Fig. 2a shows that for the as-quenched glasses, microhardness values are approximately 900 and 1300 kp mm^{-2}, for the $Fe_xNi_{80-x}P_{14}B_6$ and the $Fe_xNi_{80-x}B_{20}$ series, respectively. Furthermore, all the curves in Fig. 2b show maxima below and above the crystallization temperature, T_c (we note that for all the amorphous alloys investigated here T_c is near to 400° C [1, 6, 11, 12]). The heights of both hardness maxima are about 100 and 600 kp mm^{-2} for BP containing samples, and about 200 and 800 kp mm^{-2} for those containing only B metalloid. The lowest hardness values for both series of glasses (about 350 kp mm^{-2}) are obtained for samples exposed to the highest annealing temperature chosen in experiments, i.e. 1000° C.

It has been demonstrated many times that valuable empirical information can be obtained by means of microhardness measurements, but for their proper explanation one has to turn to other techniques by which the changes in structure can be revealed. The appearance of the higher hardness maxima in the temperature range above 400° C can be correlated with the recently published data on structural changes, because these amorphous alloys begin to crystallize in this temperature range [1, 6, 11, 12]. The crystallization process for metallic glasses may be complicated by a series of decomposition reactions in which a multiphase aggregate can be produced. However, in spite of all the possible differences in the actual crystallization process, during crystallization of the various metallic glasses investigated in this work, two common features were observed: (i) the appearance of metastable, in some cases complex, crystalline phases of the A_3B type isomorphous with Fe_3P [1, 4, 6, 13, 15, 17] or Fe_3C [4, 12, 13] crystal structures, according to the alloy composition, and (ii) the subsequent decomposition of these phases [1, 4, 6, 12, 13], which again may proceed by several reactions, into more stable phases, according to the equilibrium phase diagrams of the system considered. Both the appearance of metastable phases and their consequent disappearance on annealing cause the higher maxima observed on all recorded curves.

However, in contrast, the marked changes in hardness and the smaller hardness maxima observed on curves in the range below 400° C are as yet unexplained. There is some experimental evidence [2, 3, 6, 13, 14, 16] indicating that they might be due to the occurrence of local ordering and/or microsegregation in the amorphous state, but in these directions further investigations are needed.

Furthermore, it is interesting to note that the behaviour of the microhardness during isochronal annealing for Fe–Ni-base metallic glasses resembles that of other supersaturated solid solutions, e.g. Al-base Ag alloys. In both cases the equilibrium phases evolve via the metastable phases and two maxima are observed [7, 8, 12]. In contrast, for Al-base Sn solutions the equilibrium products emerge directly from the unstable solutions and consequently only one maximum was observed in the hardness curves [9].

4. Conclusions

The following features of the microhardness of Fe–Ni-base metallic glasses emerge from the results described above:

(1) the microhardness increases with increasing Fe as well as B content in metallic glasses;

(2) similar microhardness behaviour was observed for all samples investigated although they covered a wide range of composition. This indicates the possible similarity of the structural changes on heating all amorphous Fe–Ni-base alloys;

(3) two maxima appeared on each hardness curve, indicating possible structure changes in the amorphous as well as in crystalline states, and thus characterizing their stability on heating.

Acknowledgements

The author expresses his sincere thanks to Dr H.H. Liebermann and Dr F.E. Luborsky for donating the amorphous ribbons, to Dr E. Babić for the continuous support and discussions in the course of this work and to Dr J.R. Cooper for reading the manuscript.

References

1. H. CHANG and S. SASTRI, *Met. Trans. A,* 8A (1977) 1063.
2. H. S. CHEN and C. C. LO, in "Proceedings of the 2nd International Conference on Rapidly Quenched Metals", Section I, edited by N.J. Grant and B.C. Giessen (M.I.T., Cambridge Mass., 1976) p. 413.
3. T. EGAMI and T. ICHIKAWA, *Mat. Sci. Eng.* 32 (1978) 293.
4. U. HEROLD and U. KÖSTER, *Z. Metalk.* 69 (1978) 326, and Paper presented at 3rd International Conference on Rapidly Quenched Metals, 3–7 July 1978, Brighton, England, to be published.
5. T. IVEZIĆ, M. OČKO, E. BABIĆ, M. STUBIČAR and Ž. MAROHNIĆ, *ibid.*
6. T. KEMÉNY I. VINCZE, B. FOGARASSY and S. ARAJS, *ibid.*
7. W. KÖSTER and F. BRAUMANN, *Z. Metalk.* 43 (1952) 193.
8. K. KRANJC and M. STUBIČAR, *Fizika 2 Suppl.* 2 (1970) 31. 1; *Met. Trans.* 4 (1973) 2631.
9. D. KUNSTELJ, D. PIVAC, D. ROČAK, M. STUBIČAR and A. BONEFAČIĆ, *Phil. Mag.* 34 (1976) 67.
10. H. H. LIEBERMANN and C. D. GRAHAM JUN., *IEEE Trans. Mag.* Mag–12 (1976) 921.
11. F. E. LUBORSKY *Mat. Sci. Eng.* 28 (1977) 139.
12. M. STUBIČAR, E. BABIĆ, D. SUBAŠIĆ, D. PAVUNA and Ž. MAROHNIĆ, *Phys. Stat. Sol. (a)* 44 (1977) 339.
13. M. STUBIČAR, to be published.
14. J. L. WALTER, F. BACON and F. E. LUBORSKY, *Mat. Sci. Eng.* 24 (1976) 239.
15. J. L. WALTER, S. F. BARTRAM and R. R. RUSSELL, *Met. Trans. A.* 9A (1978) 803.
16. J. L. WALTER, D. G. LEGRAND and F. E. LUBORSKY, *Mat. Sci. Eng.* 29 (1977) 161.
17. J. L. WALTER, P. RAO, E. F. KOCH and S. F. BARTRAM, *Met. Trans. A* 8A (1977) 1141.

Received 31 August and accepted 6 October 1978.