Journal of Alloys and Compounds 495 (2010) 327–329

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

The supercooled liquid region span of Fe-based bulk metallic glasses

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ARTICLE INFO

Article history:
Received 4 July 2008
Received in revised form 13 June 2009
Accepted 11 October 2009
Available online 20 October 2009

Keywords:
Metallic glasses
Rapid-solidification
Quenching
Thermal analysis

ABSTRACT

This work presents the results of the study of the magnetically soft, iron-based bulk metallic glasses, from the viewpoint of their ability to deform in the supercooled liquid region and to resist the tendency to crystallise. The calorimetric measurements of glass transition and crystallisation temperatures (T_g and T_{x1} respectively) were employed, accompanied by the measurements of magnetic properties as the monitor of structural changes after heat treatment. It was found that the widest supercooled liquid region was obtained when zirconium was selected as one of the alloying elements, yielding the T_{x1}–T_g span of about 70 °C. Also, it was observed that the values of T_g and T_x may be controlled by the proportions of the main elements (Fe, Co, Ni), and the glass forming elements (such as B, Nb, Zr). As a guideline, it is suggested that the glassy Fe-based alloys may be maintained in the supercooled liquid state without crystallisation for several minutes, if T_{x1}–T_g is wider than 50 °C. Basing on this estimation, calorimetric measurements may be a good indicator of the ability of bulk metallic glasses to be suitable for superplastic compaction into larger shapes.

1. Introduction

The iron-based bulk metallic glasses (BMGs) are the novel materials exhibiting a combination of attractive properties, such as magnetic softness (low losses, low coercivity), mechanical resistance (high strength, high wear resistance), good corrosion resistance, etc. [1]. Compared to other BMGs, they are also cheaper, as they contain relatively inexpensive elements as main components. Their disadvantages are mainly poor glass forming ability and brittleness at room temperature (plastic strain does not exceed 2%). It is rather difficult to manufacture a toroid of, say, 10 mm in diameter, which would serve well as the core for an inductive component of electronic devices in practical applications. It is therefore necessary to develop the technique to create a large element from the available small-section pieces of BMG. This is possible using the high temperature deformation, i.e. when the material is in the supercooled liquid state [2]. Alternatively, BMGs may be used for micromechanical systems parts, which are also produced by superplastic forming at elevated temperature [3]. However, the bulk metallic glasses have the tendency to crystallise when temperature increases. This limits the parameters of heat treatment during the process (whatever the method is: friction welding, hot pressing, etc.) [4]. This work was devoted to the assessment of stability of an amorphous structure of several BMGs in the conditions of elevated temperature imitating the process of e.g. hot pressing. The results will suggest which alloys will be suitable for the superplastic forming without crystallisation.

2. Experimental

The $(Fe_{0.5}Co_{0.5})_{65}Si_5Nb_5B_{25}$, $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Zr_6Nb_6B_{18}$, $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Zr_5Nb_5B_{20}$, $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Si_6Nb_6B_{18}$, $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Si_5Nb_5B_{20}$ and $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{68}Si_6Nb_6B_{20}$ alloys were prepared from pure elements and the Fe–B prealloy by arc melting in argon atmosphere. The alloys' composition was selected to see the impact of several alloying elements on the width of the supercooled liquid thermal range. The alloys were amorphised by injection casting into the copper mould. The amorphous rods had 1 mm in diameter and 50 mm in length, and their amorphousness was verified with X-rays diffractometry and quasistatic magnetic hysteresis loop recording. The thermal stability was studied with the use of a DSC-7 calorimeter, either with continuous heating mode (scanning rate of 40 °C/min), and with isothermal mode. From continuous heating mode, glass transition temperature (T_g, defined as the convex-to-concave point) and crystallisation onset temperature, T_{x1}, were read to establish the width of supercooled liquid region, ΔT_x, and the range of possible isothermal annealing tests.

3. Results

The studied alloys were subjected to continuous heating to evaluate their glass transition temperature and crystallisation temperature. The calorimetric curves are shown in Fig. 1. The values of T_g and T_{x1} are given in the text with the results of isothermal experiment.

For the selected alloys, isothermal annealing was performed to estimate the stability of an amorphous phase at temperature below crystallisation temperature in static conditions. As the dynamic heating is much different from isothermal treatment and crystalli-

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doi:10.1016/j.jallcom.2009.10.059

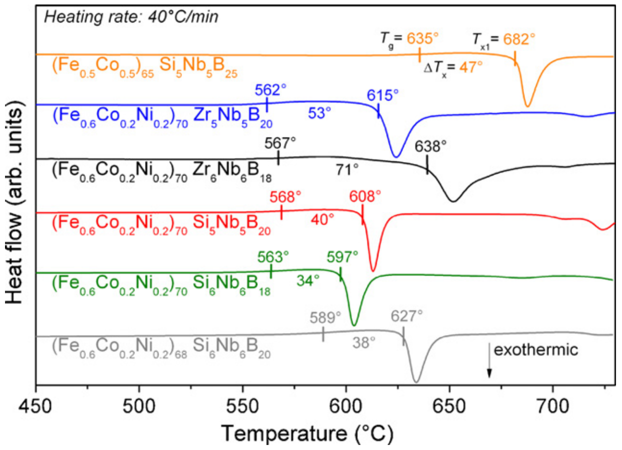

Fig. 1. Calorimetric curves of as-cast (Fe–Co)–(Ni)–(Zr,Si)–B alloys. Continuous heating, 40 °C/min.

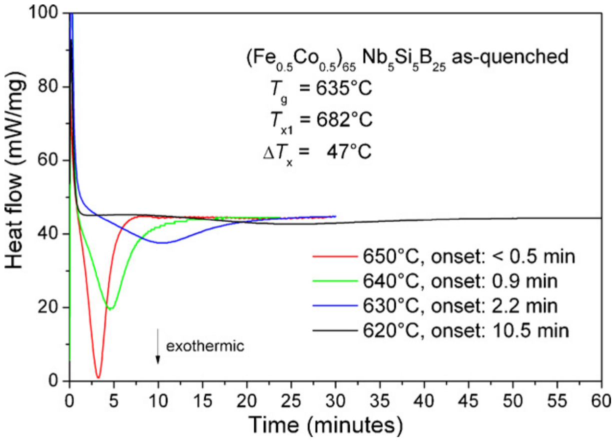

Fig. 3. Calorimetric curves of as-quenched $(Fe_{0.5}Co_{0.5})_{65}Si_5Nb_5B_{25}$ alloy. Isothermal annealing.

sation temperature is shifted up by 40 °C/min heating rate, it was expected that just below T_{x1}, crystallisation would be immediate in isothermal conditions, so the temperatures closer to T_g were preferred for isothermal annealing experiments.

It was observed that for the isothermal annealing at the lowest selected temperature (not expected to provoke crystallisation) there were little exothermic effects at the beginning of isothermal stage (see Fig. 2, line “as-quenched”). This could be the result of the nature of the calorimeter and of the thermal cycle applied. In order to verify whether this was an artefact, a fully crystalline sample was measured in identical conditions. This sample did not show this effect (Fig. 2, “crystalline”), meaning that for the as-quenched samples the observed exothermal effect is the result of some structural changes in the studied material. An assumption was made that this could be the effect of structural relaxation of the as-quenched amorphous phase. If this was true, a sample after first isothermal annealing at 550 °C for 15 min (relaxed, with no crystallisation effect) should not exhibit this behaviour if resubjected to the same thermal cycle. Indeed, the sample after heat treatment does not exhibit the exothermal effect (Fig. 2, “relaxed”), and its calorimetric curve is similar to the one of the crystalline reference. It may be therefore concluded that this small effect (several J/g) should be neglected in the analysis of the crystallisation events that may occur.

As the starting composition, $(Fe_{0.5}Co_{0.5})_{65}Si_5Nb_5B_{25}$ was selected. The T_g and T_{x1} temperatures are 635 and 682 °C. The ΔT_x span is of 47 °C. For this alloy, the series of isothermal annealing at 650–620 °C was carried out, and the results are presented in Fig. 3. As expected, with the decrease of annealing temperature, the crystallisation event starts later, and the heat flow recorded is lower. Although at 620 °C the crystallisation starts as late as 10.5 min after the final temperature is reached, for 630 °C (close to T_g estimated with 40 °C/min) crystallisation starts after only 3.1 min. For this composition, superplastic deformation without crystallisation will be rather difficult to carry out in industrial practice, but in laboratory conditions it seems to be feasible. Hence, the T_{x1}–T_g span of about 50 °C may be a bookmark for the minimum ΔT_x that allows superplastic forming.

For the next experiments, $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Zr_6Nb_6B_{18}$ was selected, for which T_g and T_{x1} are 567 °C and 638 °C (ΔT_x = 71 °C). Isothermal annealing between 570 °C (close to T_g) and 590 °C causes no crystallisation within 30 min, and the only crystallisation event is observed at 610 °C, but the onset of crystallisation is of 2.3 min in the latter case (see Fig. 4). This means that this alloy should be easily deformed for about 30 min, if the process is conducted at relatively low temperature, and any accidental increase of temperature may result in deterioration of desired properties. However, the difference between T_{x1} and T_g of 71 °C indicates that the superplastic forming may be safely accomplished.

To compare the impact of Nb and Zr on the crystallisation behaviour, the $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Zr_5Nb_5B_{20}$ alloy was examined similarly. The T_g and T_{x1} temperatures are 562 and 615 °C respectively (ΔT_x = 53 °C). Isothermal annealing at temperature of 560 °C (close to T_g) and 570 °C revealed that crystallisation may be

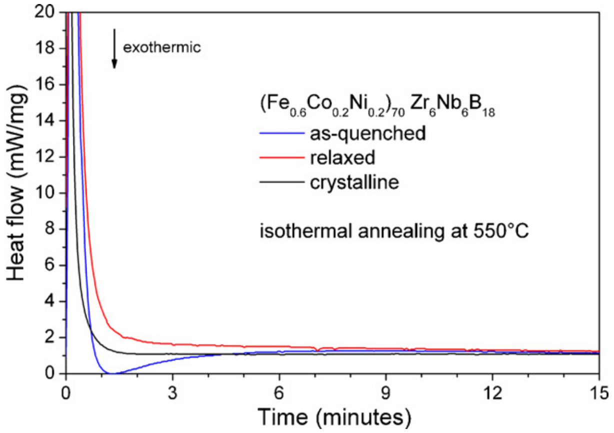

Fig. 2. Calorimetric curves of an as-quenched glass, relaxed glass and crystalline $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Zr_6Nb_6B_{18}$ alloy. Isothermal annealing at 550 °C.

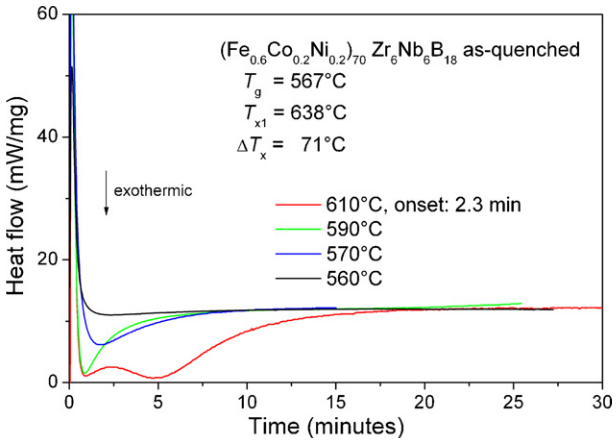

Fig. 4. Calorimetric curves of as-quenched $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Zr_6Nb_6B_{18}$ alloy. Isothermal annealing.

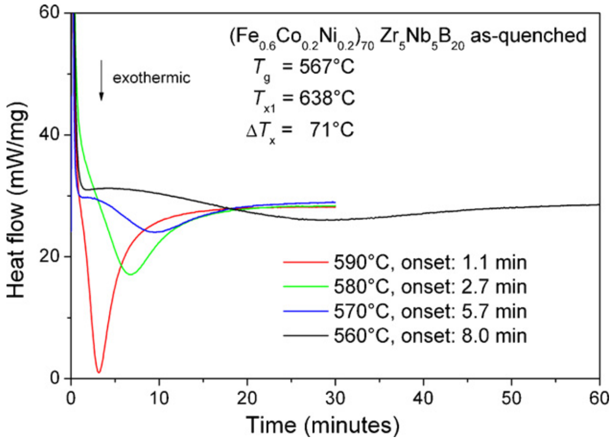

Fig. 5. Calorimetric curves of as-quenched $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Zr_5Nb_5B_{20}$ alloy. Isothermal annealing.

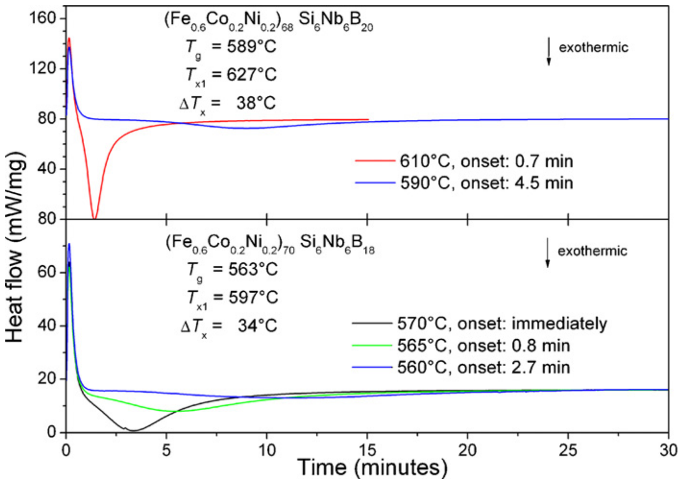

Fig. 6. Calorimetric curves of as-quenched $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{68}Si_6Nb_6B_{20}$ and $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Si_6Nb_6B_{18}$ alloy. Isothermal annealing.

retarded by about 8 and 5.7 min, respectively, from the moment of reaching the ultimate temperature (see Fig. 5). So, the limit value of ΔT_x observed for the Fe–Co–Nb–Si–B alloy (around 50 °C) is confirmed. Heat treatment at higher temperature shortens this incubation time to 1.1 min in the case of 590 °C. The comparison on the two Zr-containing alloys suggests that for the alloy with the larger content of Nb and Zr, which exhibits ΔT_x of 71 °C, deformation of the supercooled liquid may be carried out easily with only little threat of crystallisation, while for the alloy with lower Nb and Zr content (ΔT_x = 53 °C), heating up to the supercooled liquid state causes the commencement of crystallisation considerably faster. It is then evident that the wide supercooled liquid region span has an enormous impact on the possibility of superplastic deformation. Also, a larger content of Zr and Nb helps to extend this region, mainly due to the increase of crystallisation temperature.

From the above results it may be anticipated that if the difference between isothermal annealing temperature and crystallisation temperature evaluated from constant heating experiment is larger than, approximately, 50 °C, crystallisation will not occur within about 15 min, which is a reasonable time for carrying out the superplastic deformation process. These numbers are indicative, and may apply to the alloys of similar composition, because they depend on the activation energy of crystallisation of the alloys. However, evaluation and discussion of kinetics of crystallisation are beyond the scope of this work.

Silicon was also used, instead of zirconium, to produce magnetically soft, bulk glassy alloys. Similar experiment was carried out on $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Si_6Nb_6B_{18}$, $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Si_5Nb_5B_{20}$ and $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{68}Si_6Nb_6B_{20}$ alloys. First of all, T_g and T_{x1} temperatures are: 563 and 597 °C (ΔT_x = 34 °C), 568 and 608 °C (ΔT_x = 40 °C) as well as 589 and 627 °C (ΔT_x = 38 °C), respectively. The addition of 1% of Si and Nb, each, and the reduction of B content shrinks the ΔT_x span by 6 °C. However, the addition of Si and Nb without the decrease of B percentage (on the cost of Fe, Co and Ni) does not change the ΔT_x much, although significantly increases the absolute values of T_g and T_{x1}. This suggests that boron is also important in the control of thermal properties of the studied alloys. The important issue is that the simple replacement of Zr with Si in the case of $(Fe–Co–Ni)_{70}Zr_6Nb_6B_{18}$ and $(Fe–Co–Ni)_{70}Si_6Nb_6B_{18}$ alloys reduces ΔT_x from 71 to 40 °C. This indicates how useful zirconium is in the extension of the supercooled liquid range. The $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{70}Si_6Nb_6B_{18}$ and $(Fe_{0.6}Co_{0.2}Ni_{0.2})_{68}Si_6Nb_6B_{20}$ alloys were subjected to the isothermal experiment, and the calorimetric curves of the alloys are presented in Fig. 6. Clearly, if isothermal annealing is carried out at, or close to, T_g, for $(Fe–Co–Ni)_{70}Si_6Nb_6B_{18}$ alloy crystallisation starts within 1 min, or, for $(Fe–Co–Ni)_{68}Si_6Nb_6B_{20}$ alloy, 4.5 min past the ultimate temperature is reached. These results indicate that for both alloys, T_g is too close to T_{x1} and superplastic deformation will be practically difficult.

From the above results it may be anticipated that if the difference between isothermal annealing temperature and crystallisation temperature evaluated from constant heating experiment is larger than, approximately, 50 °C, crystallisation will not occur within about 15 min, which is a reasonable time for carrying out the superplastic deformation process. If ΔT_x is not larger than about 40 °C, chances for practical superplastic forming without deterioration of magnetic properties due to crystallisation are minimal. These numbers are indicative, and may apply to the alloys of similar composition, because they depend on the activation energy of crystallisation of the alloys. However, evaluation and discussion of kinetics of crystallisation are beyond the scope of this paper.

4. Conclusions

The width of supercooled liquid state region, ΔT_x, depends on chemical composition of the glass. Addition of zirconium increases the width in comparison to silicon. In this study, the widest supercooled liquid state span equals 71 °C, which is remarkably much for the iron-based metallic glasses. For the selection of alloys for superplastic forming, the width of supercooled liquid state region obtained from the constant heating experiment is a good indicator of suitability. As a ballpark figure, it may be assumed that ΔT_x = 50 °C is the minimum for an alloy that is to avoid crystallisation during high temperature compaction.

Acknowledgements

The authors gratefully acknowledge the financial support of this study from the Polish Ministry of Science and Higher Education through the grants No. 3 T08A 069 29 and PBZ-MNiSW-3/3/2006.

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