Archives of Materials Science and Engineering

Volume 31
Issue 1
May 2008
Pages 33-36

International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Structural changes of Ni-base metallic glasses during thermal activation

T. Poloczek [a,*], S. Griner [b], R. Nowosielski [b]

[a] Rostfrei-Stahl Geisweid GmbH, 57250 Netphen-Deuz, Weiherdamm 1, Germany

[b] Division of Nanocrystalline and Functional Materials and Sustainable Pro-ecological Technologies, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

* Corresponding author: E-mail address: poloczek@rostfrei-stahl.de

Received 26.02.2008; published in revised form 01.05.2008

ABSTRACT

Purpose: The paper presents a crystallization process of $Ni_{68.7}Cr_{6.6}Fe_{2.65}Si_{7.8}B_{14}C_{0.25}$ metallic glasses. The $Ni_{68.7}Cr_{6.6}Fe_{2.65}Si_{7.8}B_{14}C_{0.25}$ metallic glasses was produced by the CBMS method with cooling rate corresponding for amorphous structure manufacturing.

Design/methodology/approach: The crystallization of $Ni_{68.7}Cr_{6.6}Fe_{2.65}Si_{7.8}B_{14}C_{0.25}$ metallic glasses by method internal friction (IF) differential thermal analysis (DTA), X-ray and transmission electron microscopy (TEM) were studied.

Findings: The investigation showed, that metallic glasses during thermal activation go through from metastable amorphous state by few medial states to the stable crystalline state (relaxation and crystallization process).

Research limitations/implications: During thermal activation of metallic glasses two processes can be distinguished: structural relaxation of amorphous structure and complex crystallization process of alloy.

Practical implications: Perception of structural relaxation and crystallization processes of metallic glasses can used for analysis of thermal stability of metallic glasses.

Originality/value: The paper presents, that the thermal activation of metallic glasses conduct to the structural changes, which the final stage is crystalline state.

Keywords: Amorphous materials; Crystallization of metallic glasses; Internal frictions

MATERIALS

1. Introduction

Thermal activation of metallic glasses leads to the structural changes, for which the final stage is crystalline state. It is therefore, that the metallic glasses, obtained by speed cooling from the liquid state, show thermodynamic unbalance. Thermal activation of metallic glasses leads to the changes of the internal structure of the metallic glass and leads to its crystallization eventually. With the change of the structure of metallic glasses, the change of their physical properties is connected in the turn. The susceptibility of material to the changes of the structure and the changes the property of metallic glasses during their thermal activation is connected with the definite thermal stability of the material. The term "thermal stability" of metallic glasses hugs processes setting in glassy phase called structural relaxation (SR) [1-6] as well crystallization [7-13] this means, the passage from metastable glassy phase through the row of indirect states in the final equilibrium's crystalline state.

The thermal stability investigations of metallic glasses led by suitable research methods allow to the perception of subtle alternatively setting in glassy phase - structural relaxation, the nucleation and crystallization mechanisms of as also in the more far order of changes occurring in already crystalline phase. The changes of physical properties occurring during thermal activated process, the changes in amorphous structure and in the crystallization process of alloy accompany.

© Copyright by International OCSCO World Press. All rights reserved. 2008

In present work, the thermal activation of metallic glasses conduct to the course of structural changes and crystallization processes of $Ni_{68.7}Cr_{6.6}Fe_{2.65}Si_{7.8}B_{14}C_{0.25}$ metallic glass was introduced. By method of differential thermal analysis (DTA), the internal friction (IF) and transmission electron microscopy (TEM method) as well X-ray method was studied the structural changes of metallic glass.

In result of metallic glass investigations after thermal activation, two stages of metallic glass changes, proceeds from relaxation and crystallization processes, clear were observed.

2. Experimental procedure

Material for investigations was $Ni_{68.7}Cr_{6.6}Fe_{2.65}Si_{7.8}B_{14}C_{0.25}$ alloy appointed according to American Welding Society as BNi_2. Material was cast as metallic glass in form of tapes with dimensions: thickness 0.030 mm, width 5 mm on surface of turning chromic copper drum. The casting of the tapes was conducted in Institute of Engineering and Biomedical Materials of Silesian Technical University and was performed at pressure of gas stuffing 70 kPa and at circumferential cooling rates drum 24 m/s. The tapes were produced by method of „chill - block - melt- spinning" - it is method of continuous casting of the liquid alloy. In the works [14-16] the exact data concern production of studied alloy were presented. Manufactured metallic glasses in form of tapes, showed after casting large plasticity ($\varepsilon = 1$; and amorphous structure) what was confirmed by X-ray and electron diffraction.

The measurement of method differential thermal analysis (DTA) was applied MICRON ATD-M5 of Setaram firm, at heating rates v_g = 1.75 K/min). For internal frictions measurements inverse torsion pendulum of type Kê was applied. The measurements of internal friction $Q^{-1}(T)$ were conducted in the temperatures range to 950 K at constant heating speed carrying out 2 K/min. The curves of temperature dependences of relative elasticity module were presented in standardized form $f^2/f_0^2(T)$.The investigations of structure were performed on thin foils by the method of transmission electron microscopy and X-ray method by Philips diffractometer. The X-ray investigations were conducted for samples heated for selected temperatures 690, 740, 790 and 920 K and cooled to room temperature.

3. Results

The investigation by the method of transmission electron microscopy $Ni_{68.7}Cr_{6.6}Fe_{2.65}Si_{7.8}B_{14}C_{0.25}$ alloy as a cast showed amorphous structure characterize uniform scattered contrast and lack of coherent scattering on the electron pictures. The amorphous state of samples acknowledges both, the structure observations and investigation by method of selective electron diffraction. Generally there are typical pictures for amorphous structure. The broad diffraction rings formed as a result of electron beam dissipation, characteristic for amorphous state, showed electron diffraction pictures (Fig. 1).

The internal friction (IF) $Q^{-1}(T)$ and the relative elasticity module $f^2/f_0^2(T)$ as a function of temperature are presented on Fig. 2.

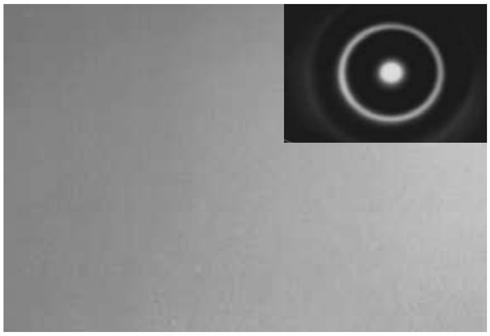

Fig. 1. Amorphous structure of samples in quenched state, TEM: magn. 80 000 x, with electron diffraction

On the internal friction (IF) $Q^{-1}(T)$ curve two peaks at temperature A-729 K and B-769 K and also plateau C at 850-890 K were observed. On the curve of relative elasticity module $f^2/f_0^2(T)$ minimum at 550 K and local maximum at 680 K were observed. For temperatures of A and B peaks on the internal friction curve, on the curve of elasticity module $f^2/f_0^2(T)$ answer two clear minimum. At higher temperatures up to 800 K the value of $f^2/f_0^2(T)$ speedy increase. for C plateau at temperatures range 850-890 K on the curve of the elasticity module $f^2/f_0^2(T)$ decrease and next minimum are observed. Above 890 K the increase of internal friction and decrease of elasticity module were observed.

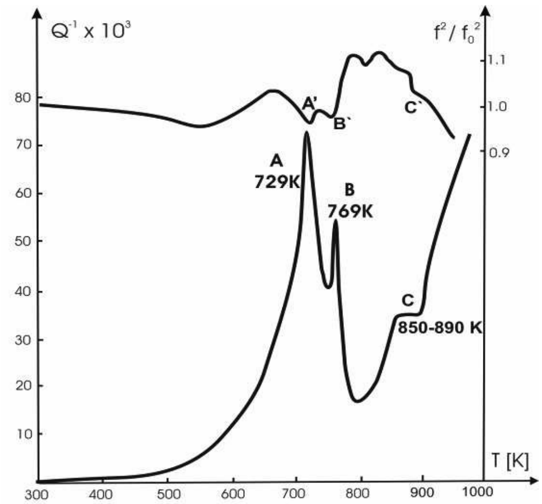

Fig. 2. Temperature relation of internal friction $Q^{-1}(T)$ and normalized elasticity modulus f^2/f_0^2 (T), $f \approx 0,5$ Hz, $v_g = 2$ K/min

On DTA curve the three sharp peaks were observed, which were described as A, B, C and small exothermal effect as D. This curve has character of widespread exothermal background with distinguish very high exothermal peaks.

The thermal analyzes (DTA) curves for sample determined for heating rates v_g = 1.75 K/min was presented on Fig. 3. The study of thin foils from samples after heating to 650 K in transmission electron microscopy (TEM) showed small changes of contrast for amorphous structure image (Fig. 5). The X-ray diffractions prepared for samples heated at 690 K and for as quenched state showed lack of changes (Fig. 4).

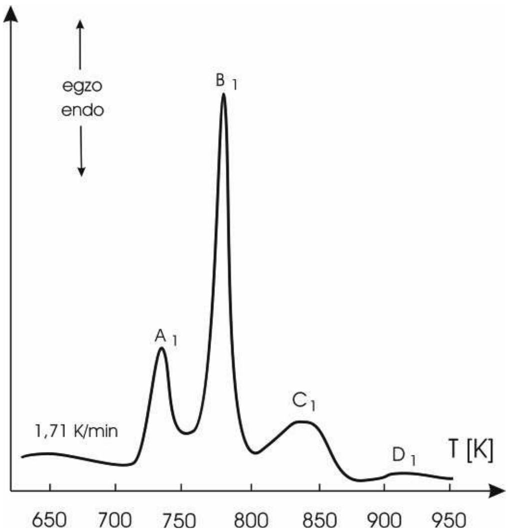

Fig. 3. Selected DTA curves determined for heating rates v_g = 1.71 K/min

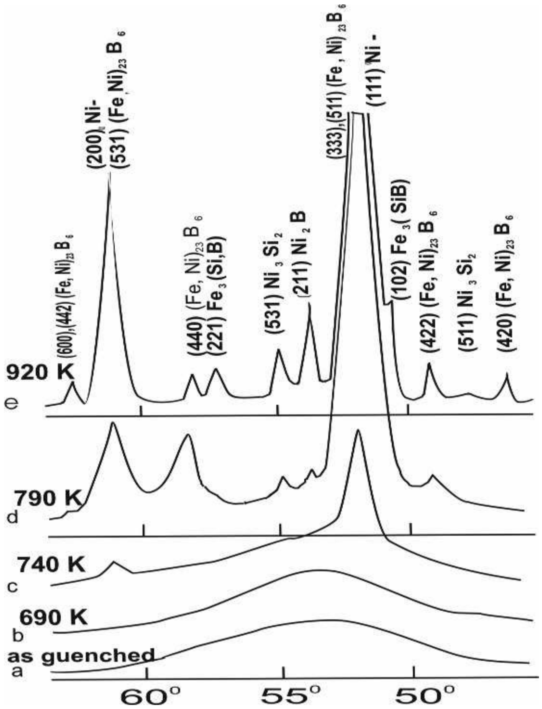

Fig. 4. X-ray curves of Ni-base alloy in as quenched state and after annealing at 690, 740, 790 and 920 K

The samples answering the occurrence of the first crystallization. The samples peak A showed in microscopic picture (TEM), has the result in the amorphous structure with numerous crystallites with diverse size of the Ni solution, what is testifying about similarity nucleation process and the crystals growth of nickel solution Fig. 6. Simultaneously in this temperature (729 K) the part of crystallites in amorphous structure is able clearly smaller for samples. On X-ray diffraction line for sample heated at 740 K, it is

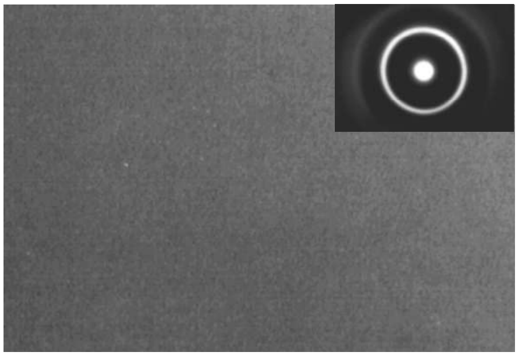

Fig. 5. Amorphous structure of samples after heating in temperature, 650 K magn. 100 000 x

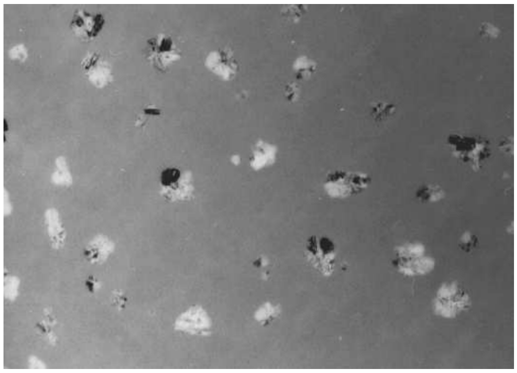

Fig. 6. Large quantity of small crystallites of nickel solution in amorphous matrix after heating in temperature 729 K, magn. 35 000 x

Fig. 7. Large quantity of crystallites of nickel solution and Borides Ni_2B in amorphous matrix after heating in temperature 743 K, magn. 90 000 x

for temperature a little higher then occurrence of A pick on IF curve and DTA peak, except background from amorphous structure, two clear maximum as diffraction reflexes from lattice planes (111)Ni and (200)Ni have been determined.

Above the temperature of the first crystallization peak for studied samples in more far order leads to more far growth of crystals mainly, clear their defected, and in more far order for precipitation of borides mainly Ni_2B inside the Ni crystallites as well as on their inter-phase boundaries with amorphous phase.

The beginning of precipitation of borides was affirmed, and the largest intensification of this process steps out in temperature of the second crystallization peak B Fig. 7.

In the branch temperature about the plateau C the transition to equilibrium crystalline state take place. This phenomenon is associated with peak D on the DTA curve. But for the internal friction curves this phenomenon is associated with high temperatures back ground.

4. Conclusions

The result of investigations shown, that thermal activation of metallic glasses $Ni_{68.7}Cr_{6.6}Fe_{2.65}Si_{7.8}B_{14}C_{0.25}$ conduct to the change of its internal structure. Firstly, structural changes occurring in amorphous phase. Indicate for it variation on the curve of temperature dependences of relative elasticity module $f^2/f_0^2(T)$. On this curve at 550 K the clear minimum proceed from relaxation process was observed. In this range temperature existing of amorphous phase the results from transmission electron microscopy and X-ray method has been confirmed. In this temperature range passing the structural changes in studied metallic glass should be connected with the structural relaxation, which can divide for two stages: to 550 K - topological structural relaxation (TRSO), depending on change in amorphous structure the relative positions of atoms what influence for moving and the atrophy of the excessive volume and above 550 K - chemical relaxation (CSRO) consisting in the relation change of the of close range and atoms arrangement of the given kind of the component.

The result from transmission electron microscopy and X-ray method showed, that observed on IF and DTA curve peaks A are connected with elementary crystallization process of mention above metallic glasses, starts from creation in amorphous matrix crystallites of Ni solution with A1 structure. Next stages of crystallization peaks B on the curve IF and DTA are connected with precipitation of borides Ni_2B, $(Fe,Ni)_{23}B_6$ mainly, and small quantity Ni_3Si_2 phases. The peak C on DTA curve and plateau C on IF curve, should interpret as peak on high temperature background of IF, connected with precipitation of $Fe_3(Si,B)$ phase. Father course of crystallization process relies on further borides precipitation and achieves equilibrium crystalline state. This process is represented by peak D on the DTA curve.

References

[1] H.S. Chen, Dynamic viscosity of a simple glass-forming liquid, Journal of Noncrystalline Solids 27 (1978) 257-262.

[2] H.S. Chen, Glasses Metals Report on Progress in Physics 43 (1980) 355-428.

[3] A. Van Den Beukel, Structural relaxation in FeCrPMnC amorphous alloy, Journal of Noncrystalline Solids 83 (1986) 134-140.

[4] G.P. Tiwari, R.V. Ramanujan, M.R. Gonal, R. Prasad, P. Raj, B.P. Badguzar, G.L. Goswami, Structural relaxation in metallic glasses, Materials Science and Engineering A304-306 (2001) 499-504.

[5] R. Nowosielski S. Griner, T. Poloczek, Influence of amorphous structure's different stages on structural relaxation and the elementary stage of metallic glasses crystallization, Proceedings of the 11th Scientific Conference "Contemporary Achievements in Mechanics, Manufacturing and Materials Science" CAM3S'2005, Gliwice – Zakopane, 2005, 720-727, (CD-ROM).

[6] J.W. Graydon, S.J. Thorpe, D.W. Kirk, Effect of coposition on the formation and thermal stability of $Ni_{72}(Mo,Co)_8B_{20}$ metallic glass, Acta Metalurgica Materiala 43/4 (1995) 1363-1373.

[7] Y.J. Liu, I.T.H. Chang, Compositional dependence of crystallization behavior of mechanically alloyed amorphous Fe-Ni-Zr-B alloys, Materials Science Engineering A325 (2002) 25-30.

[8] T. Ohkubo, H. Kai, A. Makino, Y. Hirotsu, Structural change of amorphous $Fe_{90}Zr_7B_3$ alloy in the primary crystallization process studied by modern electron microscope techniques, Materials Science Engineering A312 (2001) 274-283.

[9] E. Matsubara, S. Sato, M. Imafuku, T. Nakamura, H. Koshiba, A. Inoue, Y. Waseda, Structural study of amorphous $Fe_{70}M_{10}B_{20}$ (M=Zr, Nb and Cr) alloys by X-ray diffraction, Materials Science Engineering A312 (2001) 136-144.

[10] H. Chiriac, F. Vinai, M. Tomut, A. Stantero, E. Ferrara, On the crystallization of amorphous $Fe_{85}B_{15}$ ribbons produced with different heat treatments of the liquid alloy before ejection, Journal of Noncrystalline Solids 250-252 (1999) 709-713.

[11] W.J. Botta F.D. Negri, A.R. Yavari, Crystallization of Fe-based amorphous alloys, Journal of Noncrystalline Solids 247 (1999) 19-25.

[12] T. Poloczek, S. Griner, R. Nowosielski, Crystallisation process of Ni-base metallic glasses, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 133-136.

[13] T. Poloczek, S. Griner, R. Nowosielski, Crystallization process of Ni-base metallic glasses by electrical resistance measurements, Archives of Materials Science and Engineering 28/6 (2007) 353-356.

[14] Ł. Cieślak, J. Tyrlik - Held, D. Szewieczek: Casting the tapes with the technique of very quick cooling from liquid state for the chosen of metals and alloys, Scientific Book PAN of No. 3, Casting Committee, Katowice, 1980 (in Polish).

[15] Ł. Cieślak, D. Szewieczek, J. Tyrlik - Held, A. Waszczuk, Infuse gland - surveyor's of continuous casting parameters he the and quality of metallic ribbons of non - crystalline structure, Solidification of Metals and Alloys, Report 6, Ossolineum, Wrocław, 1983, 109, (in Polish).

[16] T. Poloczek, Crystallization of $Ni_{68,7}Cr_{6,6}Fe_{2,65}Si_{7,8}B_{14}C_{0,25}$ amorphous alloy, Doctoral dissertation, Silesian University of Technology, Gliwice, 2004.