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Crystallisation process of Ni-base metallic glasses by electrical resistance measurements

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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 were produced by the CBMS method for two different conditions of the casting, with different cooling rate.

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 methods of electrical resistance measurements (ERM), differential thermal analysis (DTA), and transmission electron microscopy (TEM) was studied.

Findings: The investigation has shown, that the conditions of vitrification (different, but higher than critical cooling rate) influence different course elementary crystallization processes during thermal activation.

Research limitations/implications: The differences in temperature of beginning of elementary crystallization processes of alloy, as a function of thickness of strip was disclosed.

Practical implications: The electrical resistance measurements method (ERM) can be used for analysis of thermal stability of metallic glasses.

Originality/value: The paper presents, that the conditions of vitrification influence different course elementary crystallization processes during thermal activation.

Keywords: Amorphous materials; Crystallization of metallic glasses; Electrical resistance measurements; Internal frictions

MATERIALS

1. Introduction

The metallic glasses, obtained by speed cooling from the liquid state, show thermodynamic unbalance. Thermal activation of metallic glasses conduct to the structural changes, which the final stage is crystalline state. Condition of metallic glasses production can influence course of structural relaxation [1-5] and crystallization [6-12] during thermal activation.

The conditions of metallic glasses production have essential influence on their amorphous structure – on different degree of ordering or disordering. of amorphous structure. Therefore condition of liquid alloy solidification, decide about phenomena which proceed during thermal activation of metastable metallic glasses and its structure and properties. Is possibility of occurrence of different states of metallic glasses, produced by the quick cooling of liquid alloy, with different speeds of cooling.

In present work, the course of processes of crystallization metallic glass of type $Ni_{68,7}Cr_{6,6}Fe_{2,65}Si_{7,8}B_{14}C_{0,25}$ for two strips with same chemical composition, but with different transverse sections – and this way, probably with different vitrification state, was introduced. By method of electrical resistance measurements method (ERM), and differential thermal analysis (DTA) as well as method transmission electron microscopy (TEM) the processes crystallization was studied. In result of investigating metallic glass after thermal activation it was shown that crystallization processes run in dependence from initial amorphous structure state differently (the state of vitrification) produced in result application of the different cooling rates of liquid alloy assuring vitrification conditions of the alloy.

It is know that electrical resistivity is sensitive to the microstructure development in solid state[13,14]. The ERM is, in principle, more sensitive in the phase transformation and any recover defects. The electrical resistance measurements method (ERM) has been widely utilized in studying the crystallization kinetics from amorphous alloys and gives detailed information in the very early stage of crystallization. The electrical resistivity variation during the crystal nucleation process might be substantially different from that for the crystal growth process.

Resistivity measurement method used in this work is based on the Matthienssen's rule. According to this rule, the total resistivity ρ_C for given temperature is the sum .

$$\rho_C = \rho_T + \rho_r \qquad (1)$$

where:
ρ_T – resistivity connected with electrons conductivity dispersion related to the crystal lattice vibrations (depend from temperature).
ρ_r – remainder resistivity connected with conductivity electrons dispersion related to stationary crystal defects (very weak depend from temperature)

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 BNi2 Material which was cast as metallic glass in form of tapes with dimensions:

- thickness 0,045 mm, width 3 mm - appointed as a_F,
- thickness 0,030 mm, width 5 mm - appointed as a_T

on a 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 conducted at pressure of gas stuffing 70 kPa and at two circumferential cooling rates drum 20 and 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 work [15] the exact data concerning the production of the studied alloy was presented. Manufactured metallic glasses in form of tapes, appointed as a_T and a_F after casting shown large plasticity ($\varepsilon = 1$; and amorphous structure) what was confirmed by x-ray and electron diffraction.

The resistivity measurement was performed after samples heating with rate 2,4 K/min, with application of constant electric current compensator – type Diesselhorsta of Tettex firm, and double-point sond method. The sample was fixed in the handle equipped in two electric current supple electrodes and two prismatic electrodes for differences potentials measurement.

The measurement of differential thermal analysis method (DTA) was applied using MICRON ATD-M5 of Setaram firm, at fourteen heating rates.

The investigations of structure were performed on thin foil by the method of transmission electron microscopy.

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).

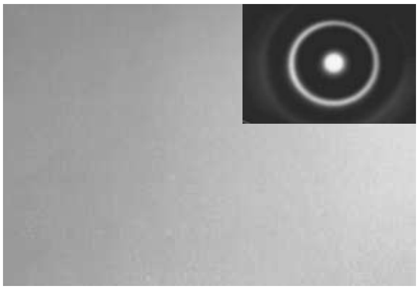

Fig. 1. Amorphous structure of samples as quenched state, TEM: magn. 80 000 x, with electron diffraction

The temperature relations of resistivity showed for both types of samples a_F i a_T , that with the temperature changes large changes of resistivity occur(Fig. 2 i 3).

The curve of temperature relation of resistivity performed for samples a_F showed weak, uniform resistivity decrease in the range from room temperature up to 620 K. Demonstrated resistivity changes run in one step, at keeping the amorphous state, because in this temperature range in samples changes of amorphous structure by TEM method were not found.

Presented investigation results are evidence that finding structural changes in this temperature range should be connected with topological structural relaxation of amorphous phase and atrophy of excess volume.

In the temperature 620K, resistivity curve $\rho(T)$ achieve minimum, and after resistivity increase up to achieving of maximum at temperature 740 K. After that maximum, with further growth of temperature large resistivity change is observed, and curve achieves minimum at 768 K. For higher temperatures again jump of resistivity value is observed to achieve next maximum at 785 K. After achieving this maximum resistivity curve falls down constantly up to 950 K. On the falling down slope of resistivity curve at about 850 K, one can see weak and explicit inflection. After achievement about 850 K resistivity reduction is a little smaller, and after achievement about 1000 K during futher temperature growth resistivity practically not change (Fig. 2).

The curve of temperature to resistivity relation performed for samples a_T proved to be similar for samples a_F regarding weak uniform resistivity decrease in the range from room temperature to 670 K

In this case, for the temperature range two explicit stages of small resistivity changes are observed. In the stage there is first weak decrease of resistivity and then resistivity achieves steady value up to about 550 K.

This stage one can connect, similar as for sample a_F, with topological structural relaxation of amorphous phase and atrophy of excess volume.

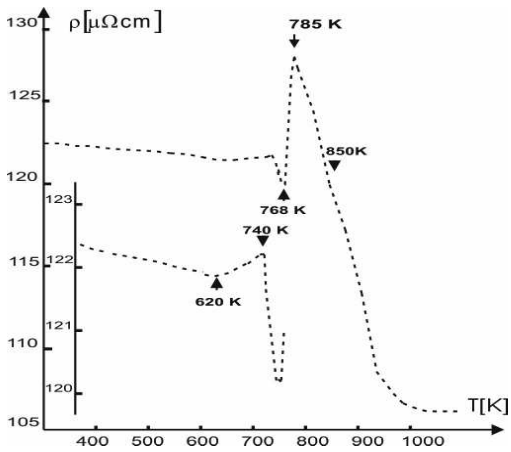

Fig. 2. Temperature relaxation of electrical resistance for samples a_F, determined for heating rates 2,4 K/min.

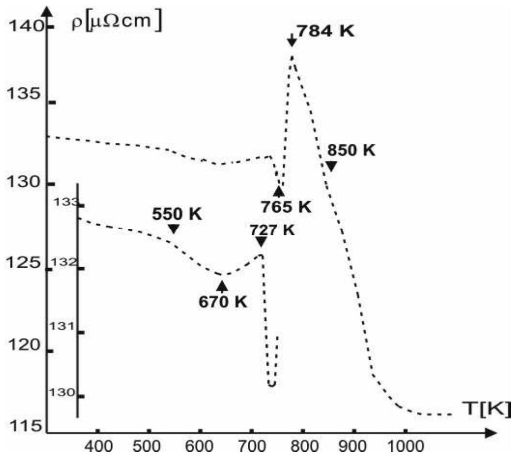

Fig. 3. Temperature relation of electrical resistance for samples a_T, determined for heating rates 2,4 K/min.

In range temperature above 550 K exist second stage, about higher intensity of changes resistivity up to minimum on the curve ERM at 670 K (sanples a_T)). The second stage can be connected with chemical structural relaxation relying on change relation of close range find among different chemical components of alloy and ordering of given groups of atoms. After achievement of minimum at 670 K, together with growth of temperature, increase of resistivity take place up to achievement of local maximum at 727 K. After overrun this temperature, take place strong decrease of resistivity at minimum for 765 K. Futher temperature growth conduct to obtain of maximal resistivity at 784 K. Heating of samples to higher temperature lead to large resistivity decrease, and above about 1000 K the resistivity practically not change and achieve steady value.

On DTA curves obtained for both samples a_F and a_T for 14 heating rates, the three sharp peaks were observed, which were described as A,B,C and small exothermal effect as D. This curves have character of widespread exothermal background with distinguish very high exothermal peaks. The peaks temperatures shift to higher temperature with growth of heating rates. The character of DTA curves is basically same for all curves, but differences at peaks region are observed.

The typical thermal analyzes (DTA) curves for sample a_F determined for two extreme heating rates v_g = 1,75 and 45 K/min were presented on fig.4.

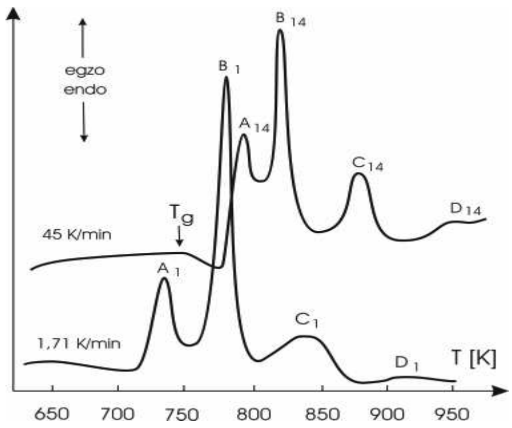

Fig. 4. Selected DTA curves for samples a_F determined for extreme heating rates v_g = 1.71 and 45 K/min

Peak A on the DTA curve (740 and 727K) and resistivity maximum on the ERM curve answering occurrence of primary crystallization of amorphous structure. The TEM microscopic pictures showed amorphous structure with different size crystallites of Ni solid solution (Fig.5 and 6, sample at), what confirm of crystallites nucleation at temperature answering of peak A. Next process, occurring at higher temperature is connected with borides precipitation (Fig.6).

Above the temperature of the first crystallization peak A 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.

The study of think foils in transmission electron microscopy (TEM) were shown, that in the peak C (DTA) and inflection on the curve (ERM) temperature, stepped for both samples a_F and a_T in the temperature about 850 K, precipitation of $Fe_3(Si,B)$ takes place.

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.

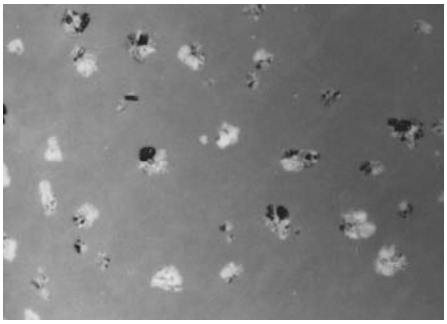

Fig. 5. Large quantity of small crystallites of nickel solution in amorphous matrix in the samples a_T after heating in temperature 729 K, magn. 35 000 x

Fig. 6. Large quantity of crystallites of nickel solution end borides Ni_2B in amorphous matrix in the samples a_T after heating in temperature 743 K, magn. 90 000 x

4. Conclusions

The conducted investigations shown, that the production conditions of metallic glasses influencing on the geometry of got metallic tapes and what it for this goes differentiating the speed of cooling of metallic liquid, they are the cause of changes in course of structural relaxation and crystallization process during thermal activation of got metallic glasses.

Analyze of temperature dependence of resistivity showed difference run of structural relaxation of amorphous phase for two strips with same chemical composition of metallic glass $Ni_{68,7}Cr_{6,6}Fe_{2,65}Si_{7,8}B_{14}C_{0,25}$, but with different transverse sections – and this way, with different vitrification state.

Elementary crystallization process of mention above metallic glasses start from creation in amorphous matrix crystallits of Ni solution with A1 structure and its course depend from vitrification condition of strip. Next stages of crystallization rely on precipitation of borides Ni_2B, $(Fe,Ni)_{23}B_6$, and phases Ni_3Si_2 and $Fe_3(Si,B)$. Futher course of crystallization process relies on further borides precipitation and achieves equilibrium crystalline state independently from vitrification conditions.

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