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Crystallization process of Ni-base metallic glasses

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Materials

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 method differential thermal analysis (DTA), internal friction (IF), X-ray diffraction and transmission electron microscopy (TEM) were studied. For calculation of activation energy of crystallization processes was used modified Kissingers formula.
Findings: The investigation showed, that the conditions of vitrification (different, but higher than critical cooling rate) influence for different course elementary crystallization processes during thermal activation.
Research limitations/implications: The differences in temperature of beginning of elementary crystallization processes of alloy, the activation energy of crystallization process as a function of thickness of strip were disclosed.
Practical implications: The calculation values of activation energy of crystallization processes can used for analysis of thermal stability of metallic glasses.
Originality/value: The paper presents, that the conditions of vitrification influence for different course elementary crystallization processes during thermal activation.
Keywords: Amorphous materials; Crystallization of metallic glasses; Internal frictions; Activation energy

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 producing can influence for course of structural relaxation [1-5] and crystallization [6-11] 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 differential thermal analysis (DTA), and the internal friction (IT) as well as method transmission electron microscopy (TEM) was studied the

processes crystallization. In result of investigations metallic glass after thermal activation, 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.

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 - Material 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 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 works [12,13] the exact data concern production of studied alloy were presented. Manufactured metallic glasses in form of tapes, appointed as a_T and a_F 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 fourteen heating rates. For internal frictions measurements inverse torsion pendulum of type

Kê was applied. The measurements of internal friction were conducted in the temperatures range to 950 K at constant heating speed carrying out 2 K/min. In aim of determination the activation energy of crystallization processes additionally the heating speeds 1; 1,5; 2,5; and 3 K/min were applied. For both studied ribbons, 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.

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).

On DTA curves obtained 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 grow 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.2.

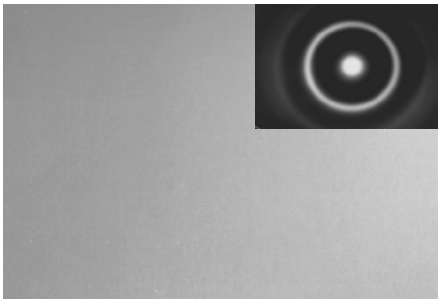

Fig. 1. Amorphous structure of samples as quenched state, TEM: magn. 80 000 x, + electron diffraction

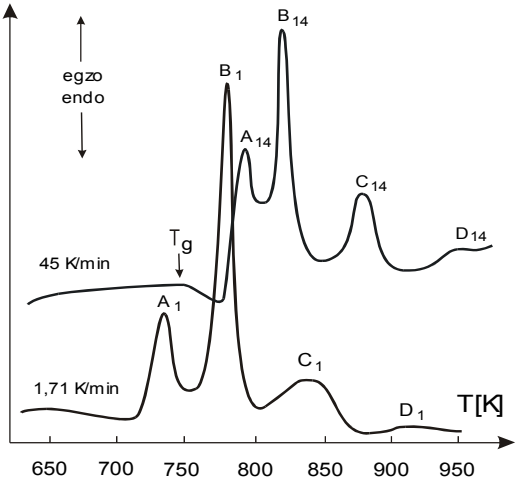

Fig.2. Selected DTA curves for samles a_3 determined for extreme heating rates v_g = 1.71 and 45 K/min

The internal friction (IF) curve for sample a_T is presented on fig.3. On this curve two peaks and plato C were observed. The character of IF curves obtained for a_F i a_T samples is similar. Similar as for DTA curves, for the case of IF curves, the relation of peaks location from heating rates was observed. Relation of peaks temperatures from heating rates is presented in table 1.

Change peaks temperature effect on DTA and IF curves was used for calculation of activation energy of crystallization process.

The samples answering the occurrence of the first crystallization 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 of nucleation process and the crystals growth of nickel solution (Fig. 4 for sample a_T).

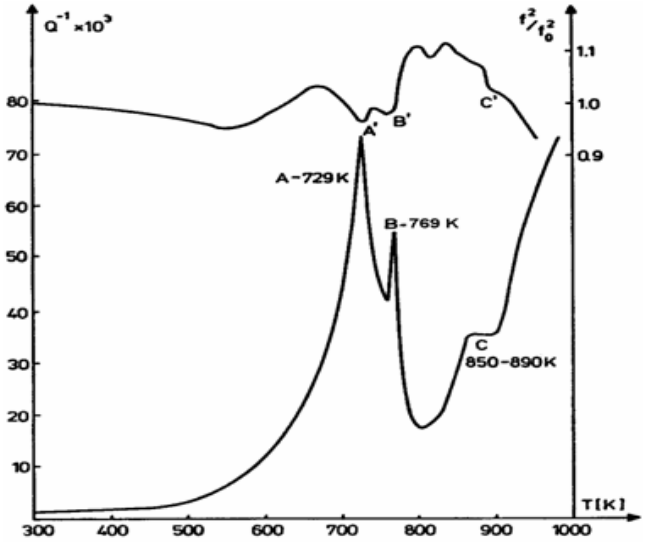

Fig. 3. Temperature relation of internal friction $Q^{-1}(T)$ and normalized elasticity modulus $f^2/f_0^2(T)$, for samples a_T, f ≈ 0,5 Hz, v_g = 2 K/min.

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.

The values of activation energy set up in the table 1,2. For calculation of activation energy of crystallization (table 3,4) processes was used formula (1) applied by Kissinger [14] and modified in the work [15] in the form:

$$\ln\frac{T_p' - T_0}{v_g} = \frac{E}{k_B}\cdot\frac{1}{T_p'} - \ln K_0 \qquad (1)$$

where:
E - activation energy,
k_B - Boltzmann's constant,
v_g - heating speed ,
T_p - temperature peak.
T_o - initial temperature of process. For initial temperature of process admitted the room temperature - 300 K, it is beginning of experiment

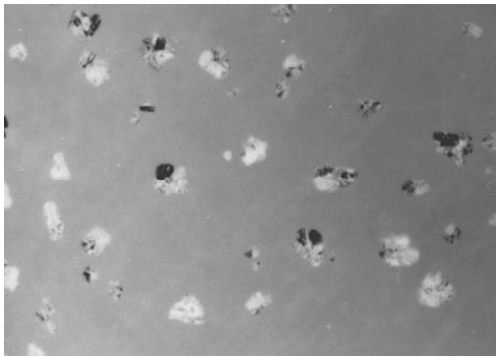

Fig.4. Large quantity of small crystallites of nickel solution in amorphous matrix in the samples a_T after heating in temperature 729 K, magn. 35 000 x

Table 1.
The peaks temperature and vitrification temperature T_g determined from DTA curves at different heating rates for samples a_F.

V_g [K/min]	1,71	2,8	4,18	5,85	7,25	8,9	10,17	15,75	19,2	19,33	22,58	28,33	34,5	45
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Tg	–	–	694	–	705	712	–	719	724	727	729	731	737	742
Peak A	743	751	756	761	763	766	768	772	776	776	778	781	783	786
Peak B	777	782	785	788	792	796	798	803	808	809	810	811	813	816
Peak C	838	844	850	855	857	858	864	869	877	878	882	885	888	893
Peak D	–	902	906	913	922	926	936	939	948	950	957	961	968	972

Table 2.
Temperatures of occurrence of peaks A and B determined from IF for the samples a_F and a_T appointed at different heating speeds.

Sample	v_g (K/min)	1	1,5	2	2,5	3
a_F	Temperature of peak A [K]	735	739	743	746	748
	Temperature of peak B [K]	764	767	769	771	773
a_T	Temperature of peak A [K]	721	726	729	732	735
	Temperature of peak B [K]	764	767	769	771	773

Table 3.
Energy activation values for crystallization process from peaks A,B,C,D determined by DTA method.

Peaks DTA	Samples a_F		Samples a_T	
	Activation energy [eV]	Correlation coefficient	Activation energy [eV]	Correlation coefficient
Peak A	3,7 ± 0,1	0,997	3,6 ± 0,1	0,996
Peak B for V_g = 1,71 – 5,8 K/min	5,8 ± 0,1	0,998	5,9 ± 0,1	0998
Peak B for V_g = 4,18 – 45 K/min	3,9 ± 0,1	0,991	3,8 ± 0,1	0,995
Peak C	3,5 ± 0,1	0,986	3,5 ± 0,1	0,994
Peak D	2,6 ± 0,1	0,980	2,6 ± 0,1	0,991

Table 4.
Activation energy of crystallization processes setting for temperatures of occurrence of internal friction peaks A and B.

Internal friction peak	Samples a_F		Samples a_T	
	Activation energy [eV]	Correlation coefficient	Activation energy eV]	Correlation coefficient
Peak A	3,9 ± 0,2	0,998	3,6 ± 0,2	0,998
Peak B	6,2 ± 0,3	0,997	6,2 ± 0,3	0,997

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 crystallization process during thermal activation of got metallic glasses. The appointed activation energy value of the first crystallization process for the both structural states of alloy is different. The smaller value of activation energy was marked for crystallization processes stepping out for tapes with smaller thickness, got at larger cooling rates from liquid state.

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