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EFFECT OF THE STORING TIME ON THE THERMAL STABILITY AND CRYSTALLIZATION KINETICS OF METALLIC GLASSES $Ni_{78}Si_xB_{22-x}$

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Temperature dependencies of the intensity of photostimulated exoelectron emission (EEE) and differential thermal analysis (DTA) signal from metallic glasses $Ni_{78}Si_xB_{22-x}$ (x = 6, 9 and 12) have been measured: a – about half a year after production, and b – for samples stored for many years at the room temperature. It has been found that the long term storage decreases the thermal stability of investigated materials and changes their crystallization kinetics. The usability of the parallel measurements of the temperature dependencies of the EEE intensity and DTA signal in investigations of the crystallization kinetics of amorphous materials has been demonstrated.

Key words: metallic glasses, crystallization kinetics, exoelectron emission, activation energy.

For over forty years the amorphous alloys (metallic glasses) are the subject of permanent research activity spurred by both the science and technology, and especially by a wide range of their potential applications. The applications are, however, limited by the difficulties resulting from their thermodynamical instability. Being thermodynamically metastable metallic glasses unavoidably tend to crystallize at a proper combination of time and temperature, what in turn causes a drastic deterioration of their unusual combination of properties. After crystallization amorphous materials become practically useless [1–2].

Crystallization of amorphous materials is a thermally activated process and in order to evaluate the thermal stability of metallic glasses one has to determine the activation energy for crystallization process and the crystallization temperature determined at a well defined heating rate. There is an additional complication arising from the fact that the values of the parameters determining the thermal stability of the volume and that of the surface layer of metallic glasses are, as a rule, different. In the mid-eighties of the XX century we developed a method enabling the determination of the activation energies and crystallization temperatures for both the volume and the surface layer of amorphous materials by parallel differential thermal analysis, DTA (or differential scanning calorimetry, DSC) and the measurements of the intensity of photostimulated exoelectron emission, EEE. The results obtained using this procedure for various amorphous materials were already published in many papers (see e.g. [3, 4]).

Physical properties of metallic glasses are very sensitive even to a small content of crystalline phases. Although the crystallization temperatures of Ni - and Fe – based metallic glasses are about 700 K, the long-term exploitation (e.g. in transformer cores – about 20 years) temperature should not exceed 420 K. The long lasting exploitation at higher temperature causes a drastic deterioration of physical (electrical and magnetic) and mechanical properties and unavoidably leads to the failure of the working element [1].

The hitherto performed investigations of the effect of long term storage of metallic glasses were carried, as a rule, in the temperature close to the glass transition point T_g ($T = T_g \pm 100K$). In the existing literature there is a lack of reports on investigations of the effect of long term storage at temperature distinctly lower than T_g on the thermal stability and crystallization kinetics of metallic glasses. The aim of this work is to fulfill, at least partly this gap.

For this purpose we measured the temperature dependencies of the photostimulated exoelectron emission (EEE) and of the differential thermal analysis signal (DTA) from metallic glasses of the composition $Ni_{78}Si_xB_{22-x}$ with x = 6, 9 and 12, obtained by a continuous casting on the surface of rapidly rotating massive metallic wheel. The 20 μm thick and 10 mm broad tapes of investigated materials were produced in the Institute of Materials Engineering of the Warsaw Technical University. The EEE and DTA investigations were performed about half a year after casting (a – type samples) and in the case of alloys with x = 6 and 12 after 7 years storing at the ambient temperature (~290 K) (b – type samples). For b – type samples of the alloy with x = 9 the storing time was much larger – 17 years.

Measurements of the temperature dependencies of photostimulated exoelectron emission (EEE) intensity were carried out by means of the arrangement described in [5]. An open point counter with saturated ethanol quenching vapor was used for detecting the exoelectrons. The sample temperature, controlled using an Pt-PtRh thermocouple with an accuracy of about 5 K, was changed at five constant heating rates (5, 10, 20, 40 and 70 K/min). The sample surface was irradiated during the measurements by unfiltered radiation from a quartz lamp with a Q-400 burner. All the EEE measurements were performed in an air atmosphere under ambient pressure.

The calorimetric investigations of the volume crystallization were performed at ten different heating rates (0,5, 1, 2, 5, 10, 12, 14, 20, 31 and 50 K/min) using the NETZSCH DSC 404/3/F differential calorimeter with Pt-PtRh DSC measuring head and platinum sample pans. An empty platinum crucible was used as the reference. All the DTA measurements were performed in air.

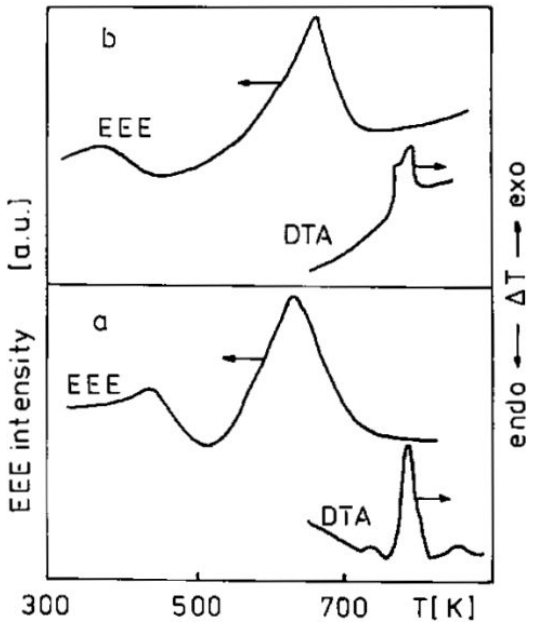

Fig. 1. DTA curves and the temperature dependencies of exoelectron emission (EEE) for the *a* – and *b* – type samples of metallic glass $Ni_{78}Si_9B_{13}$, registered at a heating rate of 20 K/min (first heating run)

The results obtained for samples *a* have been already published in [3], and the results for *b* – type samples of glasses containing 6 and 12% (x = 6, 12) were preliminary presented in [6]. The temperature dependencies of the intensity of photostimulated exoemission and DTA signal for the *a* – and *b* – type samples of metallic glass $Ni_{78}Si_9B_{13}$, all registered in the first heating run at the heating rate of 20 K/min, are presented in Fig. 1. The temperature dependencies of DTA signal for the a-type samples displays three exothermal maxima at temperatures of about 740, 785 and 855 K, the exotherms occurring at 740 and 855 K being much weaker than the central exothermal effect peaking at 785 K. A detailed discussion of the effects occurring during the continuous heating of the a-type samples, observed by both the EEE and DTA techniques can be found in [3, 7].

DTA curve for the b-type samples displays two mutually overlapping exothermal effects at about 765 K, similar to the temperature of the strongest central exotherm observed for the a-type samples. In contrast to the a-type samples, the DTA traces for the b-type samples do not exhibit the two weak exotherms at temperatures of about 740 and 855 K. This suggests that the processes responsible for occurrence of these exotherms on the DTA curves for the a-type samples do not occur in the long stored b-type samples, or their intensity is so strongly suppressed by the long lasting storage, that their detection by the DTA technique becomes impossible.

The shapes of the temperature dependencies of the intensity of photostimulated EEE for the a-type and b-type samples are distinctly different. For a-type samples two maxima of EEE intensity, located at temperatures of about 440 and 630 K, were

registered, whereas the temperature dependencies of the intensity of photostimulated EEE for the b-type samples displays one distinct maximum at about 660 K and a weak increase ("shoulder") of the EEE intensity at about 375 K.

Exoelectron emission is a surface effect connected with structural transformations in the surface layer, whereas the DTA measurements give information on the processes occurring in the volume of the sample. Structural transformations in the surface layers of metallic glasses occur at lower temperatures and with activation energies smaller than those in the volume. Thus, the effect of long lasting storing on the structure and properties of the surface layers of amorphous alloys is much stronger than that on the volume of investigated material.

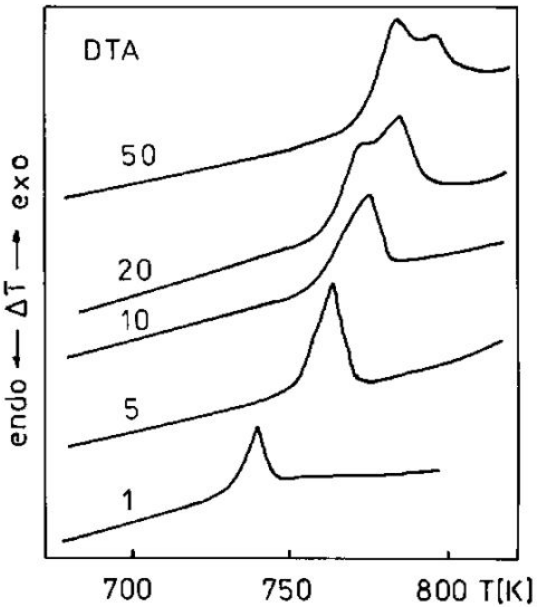

Fig. 2. DTA traces for the b-type samples registered at different heating rates. Parameter – heating rate in K/min

The DTA traces for the b-type samples for metallic glass $Ni_{78}Si_9B_{13}$, registered at different heating rates in the first heating run are presented in Fig. 2. As it follows from the results shown in Fig. 2, at small heating rates ($V \leq 10$ K/min) the volume crystallization occurs at one stage (one maximum on the DTA curves). At higher heating rates crystallization occurs in two stages, evidenced by two mutually overlapping exothermal peak on the DTA curves. Therefore, it may be concluded that the crystallization kinetics of investigated materials changes with changing the heating rate. The results presented in Fig. 3 strongly support the last statement.

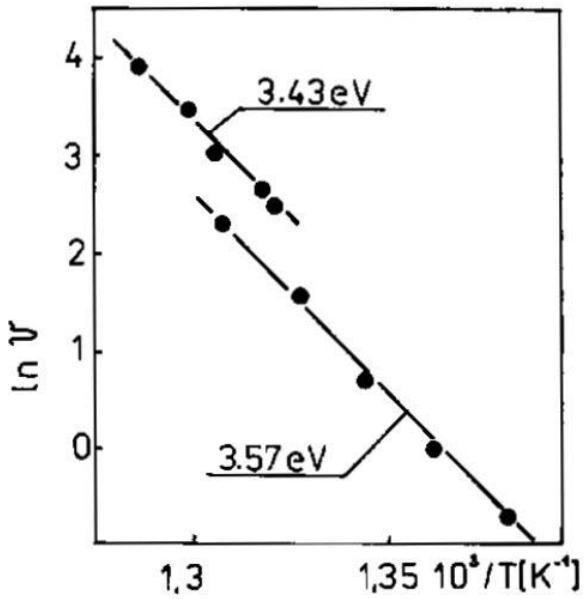

Fig. 3. The effect of the heating rates V on the temperature T of volume crystallization of the b-type samples of metallic glass $Ni_{78}Si_9B_{13}$, presented in the Ozawa's coordinates lnV = f(1/T)

Fig. 3 represents the dependence of the crystallization temperature T of investigated material on the heating rate V in the Ozawa's coordinates lnV = f(1/T). The crystallization temperature T has been determined from the position of the deflection point of the exotherm from the base line of the registered DTA traces. The "Ozawa plots" shown in Fig. 3 display a discontinuity at a heating rate of 10 K/min. This discontinuity results from the change in the mechanism of the crystallization process which is turn induces the changes in the activation energy and crystallization temperatures, observed in the experiments.

Table 1

Activation energies for two stages of the volume crystallization of investigated metallic glasses $Ni_{78}Si_xB_{22-x}$ (x = 6, 9, 12)

Sample type	Si content x	Activation energy in eV	
		I stage	II stage
a	6	3,36	3,40
	9	4,11	3.68
	12	4,27	4,89
b	6	2,82	3,16
	9	3,57	3,43
	12	3,29	3,61

The value of the activation energy is an important parameter characterizing adequately the thermal stability of amorphous materials. It can be easily determined from the shift of the crystallization temperature with changing the heating rate, presented in the Ozawa coordinates – the slope of the Ozawa's plot is simply the activation energy divided by the Boltzmann's constant k (see Fig. 3).

Activation energies for the volume crystallization of all the materials investigated in the present work, determined by the Ozawa method on the basis of DTA traces registered at different heating rates, are collected in Table 1.

The results of the present study, depicted in Fig. 1–3 and summarized in Table 1 indicate that:

- activation energy (and thus the thermal stability, too) for the volume crystallization of metallic glasses long time (several years) stored at temperature well below the glass point T_g is distinctly lower than that for the freshly produced material;
- in contrast to the DTA method, the exoelectron emission technique can be very useful for controlling the changes in the structure of the surface layer of metallic glasses.

Parallel applications of both the DTA and EEE techniques enables to follow the structural transformations in both the surface and in the volume of amorphous materials. It is very important because the lowering of the thermal stability of the surface layer, with respect to that for the volume of material, can seriously restrict the potential applications of metallic glasses.

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ВПЛИВ ТРИВАЛОСТІ ЗБЕРІГАННЯ НА ТЕРМІЧНУ СТАБІЛЬНІСТЬ І КІНЕТИКУ КРИСТАЛІЗАЦІЇ МЕТАЛІЧНОГО СКЛА $Ni_{78}Si_xB_{22-x}$

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Досліджено температурну залежність фото-стимульованої екзоелектронної емісії (ЕЕЕ) та сигналу диференціального термічного аналізу (ДТА) для металічного скла $Ni_{78}Si_xB_{22-x}$ (x = 6, 9 і 12): *а* – півроку після синтезу, *б* – після багатьох років зберігання за кімнатної температури. З'ясовано, що довготермінове старіння знижує термічну стабільність досліджуваних матеріалів і змінює кінетику їхньої кристалізації. Зазначено переваги одночасного дослідження температурних залежностей інтенсивності ЕЕЕ та сигналу ДТА під час вивчення кінетики кристалізації аморфних матеріалів.

Ключові слова: металічні стекла, кінетика кристалізації, екзоелектронна емісія, енергія активації.

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