

PACS number(s): 79.75.+g; 71.23.Cq

**EFFECT OF ELECTROLYTICAL HYDROGENATION ON THE
THERMAL STABILITY AND CRYSTALLIZATION KINETICS
OF METALLIC GLASS $\text{Ni}_{78}\text{Si}_{12}\text{B}_{10}$**

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The effect of electrolytical hydrogenation on both the surface and volume crystallization kinetics and thermal stability of amorphous alloy $\text{Ni}_{78}\text{Si}_{12}\text{B}_{10}$ has been investigated. The surface crystallization has been investigated by the exoelectron emission (EEE) technique, whereas the volume crystallization has been followed by differential thermal analysis (DTA). It has been found that both the surface and volume crystallization of investigated material occur in three stages. The surface crystallization of investigated material occurs at temperature lower and with activation energy smaller than the volume crystallization. Hydrogenation of the investigated metallic glass reduces its thermal stability which is manifested by an decrease in the activation energies for both the surface and volume crystallization.

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

For over forty years the amorphous alloys (metallic glasses) remain to be subject of intensive research activity, spurred by both the science and technology. The main reason for this permanent interest is the broad variety of potential applications of metallic glasses. Among others, the application for hydrogen storage are very intensively investigated [1, 2]. Applications of metallic glasses are, however, limited by the difficulties resulting from their thermodynamic instability. Being thermodynamically unstable, metallic glasses always tend to crystallize at proper combination of temperature and time. After crystallization they change drastically their properties and as a rule become useless..

The crystallization of amorphous materials is a thermally activated process and in order to assess the thermal/temporal stability of metallic glasses one has to determine the activation energy and the crystallization temperature determined at well defined heating rate. There is an additional complication caused by the fact that the parameters describing the thermal stability of the volume and that of the surface layer of amorphous materials are, as a rule, different. In the mid-eighties of XX century we developed a

method for determination of the thermal stability for both the surface and the volume crystallization of amorphous materials by parallel differential thermal analysis (DTA) or differential scanning calorimetry (DSC) and measurements of the temperature dependencies of the intensity of photostimulated exoelectron emission (EEE). The results of such investigations for a variety of amorphous materials have been reported in a series of papers [3–7].

Considering the potential application of metallic glasses as the hydrogen storage materials, one has to take into account the possible effect of hydrogen charging on their thermal stability. The purpose of the present study is to report the results of investigation of the effect of electrolytic hydrogenation on the thermal stability and crystallization kinetics of amorphous alloy $\text{Ni}_{78}\text{Si}_{12}\text{B}_{10}$, as determined by the parallel DTA and EEE measurements.

The investigated amorphous ribbon $\text{Ni}_{78}\text{Si}_{12}\text{B}_{10}$, prepared from high-purity metals was produced in the Institute of Materials Science of the Warsaw Technical University.

Prior to the measurements some of the samples were by 3 hours cathodically charged with hydrogen in a 0,1 N aqueous solution of H_2SO_4 with 2 g thiourea per litre. The current density was 0,5 A/dm².

Measurements of the temperature dependencies of photostimulated exoelectron emission (EEE) intensity were carried out by means of the arrangement described in [8]. An open air point counter with saturated ethanol quenching vapour was used for detecting the exoelectrons. The sample temperature, controlled using an Ni-CrNi 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.

DTA measurements of investigated samples were performed at eight (0,5, 1, 2, 3,2, 5, 10, 20 and 50 K/min) heating rates using the NETZSCH DSC 404/3F microcalorimeter, with Pt-PtRh measuring head and high-density Al_2O_3 sample pans. An empty high density Al_2O_3 crucible was used as the reference. All the EEE and DTA measurements were performed in air under normal pressure.

Two sets of samples of amorphous alloy $\text{Ni}_{78}\text{Si}_{12}\text{B}_{10}$ were investigated: a – as delivered (uncharged) and b – type samples electrolytically charged with hydrogen.

The experimentally determined temperature dependence of the EEE intensity and DTA curves for a- and b-type samples, all measured in the first heating run at the same heating rate of 20 K/min, are shown on fig. 1. As may be seen, the DTA curves display two exothermal peaks at about 760 and 820 K. The temperature dependencies of the intensity of photostimulated EEE display three, distinctly broader, maxima located at temperatures of about 450, 630 and 780 K. The high temperature maximum of EEE intensity coincides well with the exotherm on the DTA curve, corresponding to the volume crystallization of investigated metallic glass.

The two remaining peaks of EEE intensity have no counterparts on the DTA curve. They are, most probably, connected with the surface crystallization occurring in the investigated material [4–7]. There are at least two reasons for supposing that the peaks occurring on the temperature dependencies of EEE intensity are connected with irreversible, thermally activated surface crystallization in the investigated material.

Firstly, the positions of the EEE maxima depend on the heating rate (fig. 2), in a manner similar to that of the DTA peaks connected with the volume crystallization (fig. 3).

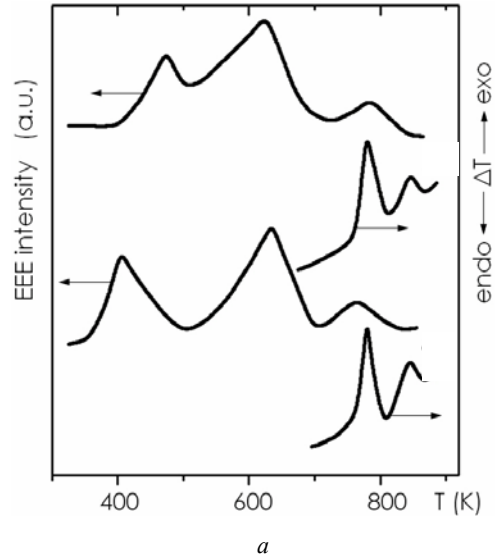


Fig. 1. Comparison of the temperature dependencies of the EEE intensity and DTA curves for the uncharged (*a*) and charged with hydrogen (*b*) samples of metallic glass $\text{Ni}_{78}\text{Si}_{12}\text{B}_{10}$, registered at a heating rate of 20 K/min. (first heating run)

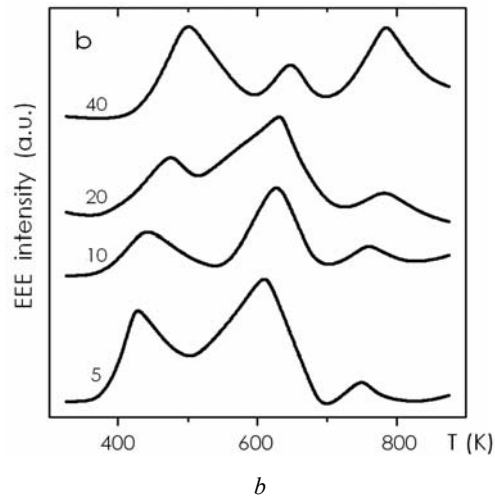


Fig. 2. Temperature dependencies of the intensity of EEE emission from $\text{Ni}_{78}\text{Si}_{12}\text{B}_{10}$ metallic glass charged with hydrogen. Parameter – heating rate in K/min

Secondly, similar to the DTA case, there are no anomalies on the EEE curves measured in the second and further heating runs.

The measurements of the temperature dependencies of EEE intensity performed at five different heating rates ranging from 5 to 70 K/min together with the registration of the DTA curves performed at eight heating rates ranging from 0,5 to 50 K/min, enabled the determination of the activation energies for both the surface and the volume crystallization processes governing the appearance of the maxima on the temperature dependencies of EEE intensity and on the DTA curves. To exemplify the results

obtained in this series of measurements, the EEE curves for b-type samples, registered at four different heating rates have been presented on fig. 2. At it is seen on fig. 2, with increasing the heating rate the peaks on the EEE curves systematically shift towards higher temperatures. This behaviour is typical of thermally activated phenomena.

The DTA traces for the b-type samples, registered at five different heating rates, are presented in fig. 3. As it follows from the results shown in figs. 3 and 4 at small heating rates ($v \leq 2$ 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 – $v = 3,2$ and 5 K/min) exothermal peaks on the DTA curves. Therefore, it may be concluded that the crystallization kinetics of investigated metallic glass changes with changing the heating rate.

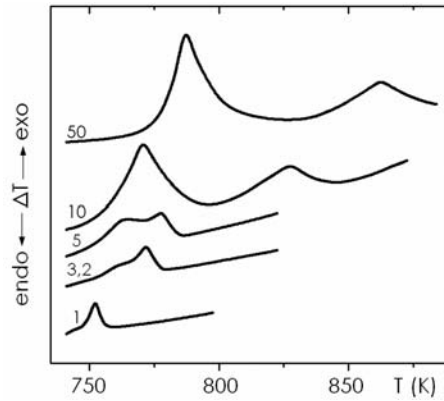


Fig. 3. DTA traces for the b-type samples registered at different heating rates. Parameter – heating rate in K/min

From the shifts of the DTA and EEE peaks the activation energies for the volume and surface crystallization of both the a- and b-type samples were determined using the well-known Ozawa relation [9]:

$$\ln v = A - \frac{E}{kT}$$

where v is the heating rate, A – constant, E – activation energy, k – Boltzmann's constant and T – crystallization temperature.

The crystallization temperature T has been determined from the position of the maximum on the EEE curves [8], and as the deflection point (from the base line) on the DTA curves [10].

The dependencies of the crystallization temperatures T , determined from temperature dependencies of the DTA signal, on the heating rate v , represented in the Ozawa coordinates $\ln v = f(1/T)$ (so called Ozawa plots) for a- and b- type samples are shown on Fig. 4. For both the uncharged (*a*) and charged with hydrogen (*b*) samples the Ozawa's plot in the Fig. 4 displays a distinct discontinuity [12] at a heating rate of 3,2 K/min. This suggests a change in the crystallization mechanism with changing the heating rate, leading to an abrupt change in the crystallization temperature and in the activation energy.

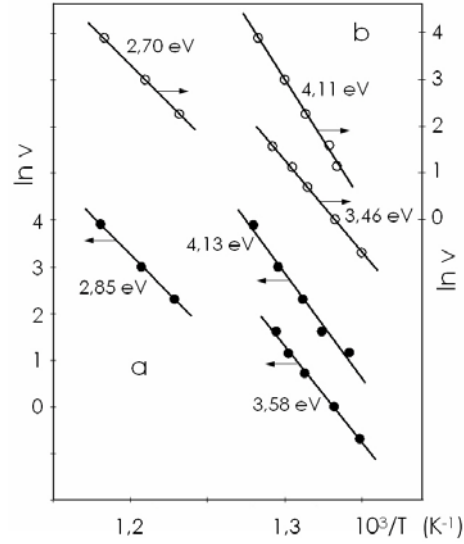


Fig. 4. Ozawa's plots for volume crystallization in uncharged (a) and charged with hydrogen (b) samples

The value of the activation energy is an important parameter characterizing adequately the thermal stability of amorphous materials. The values of the activation energies for all stages of the surface and volume crystallization of both the a- and b-type samples, determined by Ozawa's method, are collected in Table 1.

Table 1

Experimentally determined values of the activation energies for the all stages of the volume (DTA) and surface (EEE) of the $\text{Ni}_{78}\text{Si}_{12}\text{B}_{10}$ metallic glass samples uncharged (a – type) and charged with hydrogen (b – type)

Sample	Activation energy in eV		
	1-th stage	2-nd stage	3-th stage
a-type	3,58 DTA 0,46 EEE	4,13 DTA 2,35 EEE	2,85 DTA 2,68 EEE
b-type	3,46 DTA 0,50 EEE	4,11 DTA 2,14 EEE	2,70 DTA 2,64 EEE

The data presented in Table 1 indicate, that surface crystallization of investigated material occurs at temperature much lower and with activation energy smaller than the volume crystallization. The hydrogenation causes a slight decrease in the activation energies for all stages of the surface as well as of the volume crystallization. So, the hydrogenation does not deteriorate the thermal / temporal stability of investigated amorphous alloy [11], only slightly reduces it. It seems very interesting to check if this statement holds also for other metallic glasses.

Parallel applications of both the DTA and EEE techniques enable to follow the structural transformations in both the surface and in the volume of amorphous materials. The difference between the activation energies for the volume and surface crystallization may result from the existence of crystal nuclei [13] formed in the surface layer already during the fabrication process. 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 ЕЛЕКТРОЛІТИЧНОЇ ГІДРОГЕНЕРАЦІЇ
НА ТЕРМОСТАБІЛЬНІСТЬ І КІНЕТИКУ КРИСТАЛІЗАЦІЇ
МЕТАЛІЧНОГО СКЛА $Ni_{78}Si_{12}B_{10}$**

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Досліджено вплив електролітичного гідрогенерування та величину кінетики кристалізації для аморфного скла $Ni_{78}Si_{12}B_{10}$. Поверхневу кристалізацію досліджували за допомогою техніки екзоелектронної емісії, а величину кристалізації – технікою диференційно-термічного аналізу. З'ясовано, що кристалізація досліджуваного матеріалу відбувається у три етапи. Гідрування досліджуваного металевих скла зменшує його термостабільність, що виявляється у зниженні енергії активації для обох поверхонь і обсягів кристалізації.

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

**ВЛИЯНИЕ ЭЛЕКТРОЛИТИЧЕСКОЙ ГИДРОГЕНЕРАЦИИ
НА ТЕРМОСТАБИЛЬНОСТЬ И КИНЕТИКУ КРИСТАЛЛИЗАЦИИ
МЕТАЛЛИЧЕСКОГО СТЕКЛА $Ni_{78}Si_{12}B_{10}$**

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Исследовано влияние электролитического гидрогенерирования и значение кинетики кристаллизации для аморфного стекла $Ni_{78}Si_{12}B_{10}$. Поверхностную кристаллизацию исследовали с помощью техники экзоэлектронной эмиссии, а величину кристаллизации – техникой дифференциально-термического анализа. Установлено, что кристаллизация исследуемого материала происходит в три этапа. Гидрирование исследуемого металлического стекла уменьшает его термостабильность, что проявляется в снижении энергии активации для обеих поверхностей и объемов кристаллизации.

Ключевые слова: металлические стекла, кинетика кристаллизации, экзоэлектронная эмиссия, энергия активации.

Стаття надійшла до редколегії 04.06.2008

Прийнята до друку 25.03.2009