Effect of electrolytical hydrogenation on the thermal stability and crystallization kinetics of metallic glass Fe\textsubscript{79}Si\textsubscript{9}B\textsubscript{12}

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Abstract. The effect of electrolytical hydrogenation on both the surface and volume crystallization kinetics and thermal stability of amorphous alloy Fe\textsubscript{79}Si\textsubscript{9}B\textsubscript{12} has been investigated. The parameters of the surface and volume crystallization (temperature, activation energy) have been determined applying the exoelectron emission (EEE) and differential thermal analysis (DTA) methods, respectively.

It has been found that the surface crystallization of investigated material occurs at temperature much lower and with activation energy smaller than the volume crystallization. The determination of the activation energies for the volume and surface crystallization by the combination of DTA and EEE techniques enables the determination of activation energies for both the nucleation and growth of the crystalline phase in metallic glasses and other amorphous materials. Hydrogenation of the investigated metallic glass reduces its thermal stability, what is manifested by a decrease in the activation energies for both the surface and volume crystallization.

1. Introduction

For many years amorphous metallic alloys (metallic glasses) remain to be subject of intensive research activity [1-3], 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].

The applications of metallic glasses are, however, limited by the difficulties arising from their thermodynamical instability. Amorphous alloys tend to crystallize at a proper combination of temperature and time. After crystallization they change drastically their properties and as a rule become useless [1-3].

The crystallization is a thermally activated process and in order to know the thermal stability of metallic glasses one has to determine the activation energy for this process and the crystallization temperature determined at well defined heating rates. There is an additional complication caused by the fact that the parameters describing the thermal stability (activation energies, crystallization temperature) 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 elaborated 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 [4-9].

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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 aim of the present communication is to report the results of investigation of the effect of electrolytic hydrogenation on the thermal stability and surface and volume crystallization kinetics of metallic glass $\text{Fe}_{79}\text{Si}_{9}\text{B}_{12}$, as determined by the parallel DTA and EEE measurements.

2. Experimental conditions

The investigated amorphous ribbon $\text{Fe}_{79}\text{Si}_{9}\text{B}_{12}$, prepared from high purity metals by liquid quenching on a rotating wheel, was produced in the Institute of Materials Science of the Warsaw Technical University.

The samples were by 2 and 5 hours cathodically charged with hydrogen in a 1 N aqueous solution of $\text{H}_2\text{SO}_4$ with 2 g of thiourea per litre. The current density was 0.5 A/dm$^2$.

Measurements of the temperature dependencies of photostimulated EEE intensity were carried out by means of the arrangement described in [10]. 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 seven (0.5, 1, 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 $\text{Al}_2\text{O}_3$ sample pans. An empty high density $\text{Al}_2\text{O}_3$ crucible was used as the reference. All the EEE and DTA measurements were performed in air under normal pressure.

3. Results and discussion

Three sets of samples of metallic glass were investigated: 0h - as delivered (uncharged), 2h – samples electrolytically charged with hydrogen by 2 hours and 5h – samples electrolytically charged with hydrogen by 5 hours.

The experimentally determined temperature dependencies of the EEE intensity and DTA curves for 0h and 2h type samples, all measured in the first heating run at the same heating rate of 10 K/min, are shown on Fig. 1. As it is seen, the DTA curves display two exothermal peaks at about 740 K and 790 K. This means that the volume crystallization of investigated material occurs in two stages.

![Figure 1](image-url)
The temperature dependencies of the intensity of photostimulated exoelectron emission display a maximum located at a temperature of about 670 K. There are at least two reasons for supposing that the peak of EEE intensity is caused by irreversible surface crystallization. First, the positions of EEE maximum depend on the heating rate (Fig. 3) in a manner similar to that of the DTA peaks connected with the volume crystallization (Fig. 2). This permits to explain the occurrence of the EEE maximum as the effect connected with some thermally activated process. Secondly, similarly as in the case of DTA, there are no peaks on the EEE curves registered in the second and further heating runs.

**Figure 2.** DTA traces for the 0h-type samples registered at different heating rates. Parameter – heating rate in K/min.

The measurements of the temperature dependencies of the DTA curves performed at seven heating rates ranging from 0.5 to 50 K/min together with the registration of the temperature dependencies of EEE intensity performed at five different heating rates ranging from 5 to 70 K/min, enabled the determination of the activation energies for both the volume and the surface crystallization processes governing the appearance of the maxima on the temperature dependencies of the DTA curves and of EEE intensity. Exemplary DTA traces for the 0h-type samples, registered at four different heating rates, are presented in Fig. 2. As it follows from the results shown in Figs. 3 and 4 the volume crystallization occurs in two stages (two peaks on the DTA curves).

**Figure 3.** Temperature dependencies of the intensity of EEE from 0h-type samples.. Parameter – heating rate in K/min.
The experimentally determined temperature dependencies of the EEE intensity for 0h-type samples, registered at four heating rates, are presented in Fig. 3. As it is seen on Figs. 2 and 3, with increasing the heating rate the peaks on the DTA and EEE curves systematically shift towards higher temperatures. This behaviour is typical of thermally activated phenomena.

From the shifts of the DTA and EEE peaks the activation energies for the volume and surface crystallization of investigated samples were determined using the Ozawa relation [11]:

\[
\ln V = A - \frac{E}{kT}
\]

where \(V\) is the heating rate, \(A\) – constant, \(E\) – activation energy, \(k\) – Boltzman’s constant and \(T\) – crystallization temperature. The crystallization temperature \(T\) has been determined from the position on the maximum on the EEE curves [10] and as the deflection point (from the base line) on the DTA curves [11].

The dependencies of the crystallization temperatures \(T\), determined from both temperature dependencies of the DTA signal and of the EEE intensity, on the heating rate \(V\), represented in the Ozawa coordinates \(\ln V = f(1/T)\) - so called Ozawa plots for 0h-type samples are shown on Fig. 4. The accuracy of the determination of the activation energies was better than 0,2 eV. The same procedure was applied for determining the activation energies of all the three types of investigated samples.

![Figure 4. Ozawa’s plots for the surface (EEE) and the volume (DTA) crystallization processes in 0h-type samples.](image)

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 the surface and the volume crystallization of all types of investigated samples in the present work, determined by the Ozawa method on the basis of DTA and EEE measurements, are collected in Table 1.

The data presented in Table 1 indicate that hydrogenation causes an increase in the activation energies for both stages of the volume as well as of the surface crystallization. So, the hydrogenation not only does not deteriorate the thermal / temporal stability of investigated amorphous alloy Fe\(_{79}\)Si\(_{9}\)B\(_{12}\), [13] but slightly enhances it. It seems very interesting to check if this statement holds also for other metallic glasses.

Parallel applications of both the EEE and DTA methods enable to follow the structural transformations in both the surface and in the volume of metallic glass. The surface crystallization of investigated metallic glass occurs at temperature much lower and with activation energy smaller than the volume crystallization. The difference between the activation energies for the volume and surface crystallization may result from the existence of crystal nuclei [12] formed in the surface layer already
during the fabrication process. The bulk of the investigated material crystallizes by usual nucleation and growth mechanism, thus the difference between the activation energy for the first stage of the volume crystallization and the activation energy for the surface crystallization could be treated as a measure for the nucleation energy. 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.

Table 1. Effect of the hydrogenation time on the activation energies for volume (DTA) and surface (EEE) crystallization of Fe$_{79}$Si$_{9}$B$_{12}$ metallic glass.

| Hydrogenation time [h] | Activation energy in eV |
|------------------------|------------------------|
|                        | Volume crystallization - DTA | Surface crystallization - EEE |
|                        |                          |                          |
| 0                      | 4.33                    | 1.21                     |
|                        | 4.61                    |                          |
| 2                      | 3.74                    | 0.80                     |
|                        | 4.37                    |                          |
| 5                      | 3.85                    | 0.84                     |
|                        | 4.03                    |                          |

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