Effect of electrolytical hydrogenation on the thermal stability and crystallization kinetics of METGLASS MBF-50

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Abstract. The effect of electrolytical hydrogenation on both the surface and volume crystallization kinetics and thermal stability of amorphous alloy METGLASS MBF-50 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 two stages. The surface crystallization occurs at temperature lower and with activation energy distinctly smaller than the volume crystallization. Hydrogenation of the investigated metallic glass enhances its thermal stability by increasing the activation energies for both the surface and volume crystallization. The results of DTA measurements indicate that hydrogenation causes an increase in the enthalpy of both stages of volume crystallization.

1. Introduction

Almost 50 years after their discovery by Duvez, the amorphous alloys 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 arising 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 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] and a comprehensive review has been presented during the 10th International Symposium on Exoelectron Emission and Applications (Ekaterinburg, 1992) [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 METGLASS MBF-50, as determined by the parallel DTA and EEE measurements.

2. Experimental conditions

The investigated amorphous alloy METGLASS MBF-50, prepared from high purity metals by liquid quenching on a rotating wheel, has been produced by Allied Signal Corporation.

The samples were by 5 hours cathodically charged with hydrogen in a 1 N aqueous solution of H₂SO₄ with 2 g of thiourea per litre. The current density was 0.5 A/dm².

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 Al₂O₃ sample pans. An empty high density Al₂O₃ crucible was used as the reference.

Measurements of the temperature dependencies of photostimulated 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 six constant heating rates (2, 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 and DTA measurements were performed in air under normal pressure.

3. Results and discussion

Two sets of samples of amorphous alloy METGLASS MBF-50 were investigated: a - as delivered (uncharged) and b – type samples electrolytically charged with hydrogen.

The experimentally determined DTA curves and dependencies of the EEE intensity 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 it is seen, the DTA curves display two exothermal peaks at about 735 K and 800 K. This means that the volume crystallization of investigated material occurs in two stages. The temperature dependencies of the EEE intensity also display two, distinctly broader, maxima located at temperatures of about 690 K and 815 K. There are at least two reasons for supposing that the peaks of EEE intensity are caused by irreversible surface crystallization. First, the positions of EEE maxima

![Figure 1](image.png)

Figure 1. Comparison of the temperature dependencies of the EEE intensity and DTA curves for MBF-50 samples uncharged (a) and charged with hydrogen (b). Heating rate – 20 K/min.
depend on the heating rate (Fig. 2) in a manner similar to that of the DTA peaks connected with the

![Figure 2](image)

**Figure 2.** Temperature dependencies of the intensity of EEE emission from MBF-50 not charged with hydrogen. Parameter – heating rate in K/min.

volume crystallization. Secondly, similarly as in case of DTA, there are no peaks on the EEE curves registered in the second and further heating runs.

In order to determine the activation energies for the two stages of both the volume and surface crystallization, the EEE curves and DTA traces for the a– and b-type samples were registered at different heating rates. To exemplify the results obtained in this series of measurements, the DTA curves for the a– and b-type samples, registered at three different heating rates (1, 5 and 20 K/min) have been presented on Fig. 3. The EEE curves for a-type samples, registered at four different heating

![Figure 3](image)

**Figure 3.** Comparison of DTA traces for uncharged (a) and charged (b) with hydrogen MBF-50 samples. Parameter – heating rate in K/min.

rates have been already presented on Fig. 2. As it is seen on Figs. 2 and 3, with increasing the heating rate the peaks on the EEE and DTA 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 both the a– and b-type samples were determined by the Ozawa’s method, i.e. from the plots of the \( \ln v = f(1/T) \) dependence, where \( v \) denotes the heating rate and \( T \) – the crystallization temperature determined from the positions of the EEE peaks (surface crystallization) and DTA exotherms (volume crystallization). The slope of the Ozawa’s plot multiplied by Boltzmann’s constant gives the activation energy value. Ozawa’s plots for the positions of the EEE and DTA peaks for the a-type samples are presented on Fig. 4. Similar plots were constructed for the b-type samples. The values of the activation energies for the two stages of the surface and volume crystallization of both the a– and b-type samples, determined from these plots, are collected in Table 1.

**Table 1.** Experimentally determined values of the activation energies for the two stages of the volume (DTA) and surface (EEE) crystallization of MBF-50 samples uncharged (a – type) and charged with hydrogen (b – type).

| Sample | Activation energy in eV |
|--------|-------------------------|
|        | 1-th stage   | 2-nd stage   |
| a – type | 3.73 – DTA  | 3.56 – DTA   |
|          | 0.90 – EEE   | 3.56 - EEE   |
| b – type | 3.96 – DTA   | 3.80 – DTA   |
|          | 0.97 – EEE   | 3.80 - EEE   |

The data presented in Table 1 indicate, that hydrogenation causes a slight increase in the activation energies for both stages of the surface as well as of the volume crystallization. So, the hydrogenation not only does not deteriorate the thermal / temporal stability of investigated amorphous alloy METGLASS MBF-50, but slightly enhances it. It seems very interesting to check if this statement holds also for other metallic glasses.

**Figure 4.** Ozawa’s plots for the two stages of volume (DTA) and surface (EEE) crystallization of MBF-50 samples not charged with hydrogen.
A more detailed comparison of the DTA traces for a– and b-type samples indicate, that the areas under both the exotherms for the hydrogenated (b-type sample) are systematically (by about 10 %) larger than those for their counterparts for not hydrogenated samples. As the peak area is proportional to the heat effect of phase transition observed, it can be concluded that the latent heat of volume crystallization of hydrogenated samples is greater than that for unhydrogenated samples. This is another indication of the positive effect of hydrogenation on the thermal stability of investigated material. This observation also deserves further studies, which are in progress.

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