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# Thermal stability of the $Fe_{80-x}V_xB_{20}$ metallic glasses as studied by the EEE and DTA methods*

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The surface and volume crystallization of $Fe_{80-x}V_xB_{20}$ ($x = 6, 10, 20$) metallic glasses, produced by the melt spinning method, have been investigated by means of exoelectron emission (EEE) and differential thermal analysis (DTA). A comparison of the results of the EEE and DTA measurements shows clearly that surface crystallization occurs at temperatures ~200 K lower than volume crystallization. The activation energy for the surface crystallization is also distinctly lower than that for crystallization in the bulk.

## 1. Introduction

Amorphous alloys, and especially those obtained by rapid quenching from the melt (metallic glasses), are the subject of increasing research activity spurred by both science and technology. Being metastable, metallic glasses tend, however, to crystallize at an appropriate combination of temperature and time, which in turn causes a drastic deterioration of their unusual combination of properties, which is important for their use in various practical applications. This restricts the broad use of metallic glasses and therefore the investigation of their crystallization behaviour is of great importance from both the purely scientific and the technological viewpoint.

One of the factors limiting the stability and potential applications of metallic glasses is the surface crystallization, which in many non-crystalline materials precedes that in the bulk [1–3]. The premature surface crystallization of metallic glasses occurs, as a rule, at temperatures much lower and with a smaller activation energy than the volume crystallization [4].

In a series of papers [3–5] it has been shown that the exoelectron emission (EEE) technique could be used for studying the tendency of amorphous alloys to undergo premature surface crystallization. The purpose of the present paper is to present the results of our recent investigation of the temperature dependence of the intensity of photostimulated EEE from metallic glasses with chemical composition given by the formula $Fe_{80-x}V_xB_{20}$ ($x = 6, 10, 20$).

## 2. Experimental conditions

The investigated metallic glasses $Fe_{80-x}V_xB_{20}$, prepared from high purity metals by the single-roll melt-spinning method, were produced in the Institute of Materials Science of the Warsaw Technical University.

Measurements of the temperature dependence of EEE intensity were carried out by means of the arrangement described in details in [6]. An open air point counter with saturated quenching vapour of ethanol was used for detecting the (exo)-electrons. The sample surface was irradiated during the measurements by unfiltered radiation from a quartz lamp with a Q-400 burner.

The differential thermal analysis (DTA) measurements were performed in air using a Linseis L62/30/80 thermoanalyser. Crystallized metallic glass of the same composition and weight was used as the reference. Both the investigated and reference samples were encapsulated in platinum crucibles.

## 3. Results and discussion

The temperature dependences of the intensity of photostimulated EEE and of the DTA signal for investigated metallic glasses, both measured at the heating rate of $20\,K\,min^{-1}$, are shown in Fig. 1. As may be seen, all the DTA curves display an exotherm above 800 K, the maximum temperature being higher for higher vanadium content. This implies that the volume crystallization occurs in one stage and the crystallization temperature, determined by the heating rate used, increases with increasing vanadium content. The temperature dependences of EEE intensity for alloys containing 6 and 10% of vanadium display one peak at temperature of about 600 K, whereas the EEE curve for alloy containing 20% of vanadium exhibits two maxima occuring at ~550 and ~750 K. The single maxima of the intensity of photostimulated EEE of alloys with low vanadium content ($x = 6, 10$) as well as the low-temperature EEE maximum for $x = 20$ could be ascribed to the surface crystallization of investigated materials. The possible origin of the second maximum on the EEE curve for the alloy with the highest vanadium content will be discussed later.

The results presented in Fig. 1 suggest that, as for $Fe_{40-x}Ni_{40}Cr_xB_{20}$ [7], the surface crystallization of the metallic alloys investigated markedly precedes the volume crystallization.

Because of its dependence on the heating rate, and

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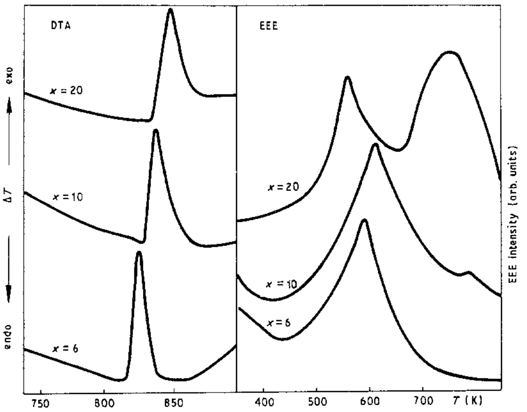

*Figure 1* DTA curves and the temperature dependences of the intensity of photostimulated EEE from metallic glasses $Fe_{80-x}V_xB_{20}$ as measured at the heating rate of $20\,K\,min^{-1}$.

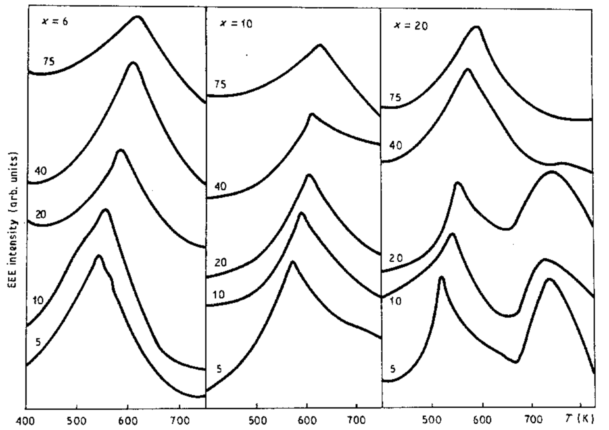

*Figure 2* Effect of the heating rate on the shape of the temperature dependence of EEE intensity for investigated metallic glasses. The heating rate is given on the graphs in Kelvin per minute.

on the thermal history of the sample in general, the crystallization temperature is not the best characteristic of the thermal stability of amorphous materials. Much better characterization of the thermal stability could be achieved by determining the activation energy of the crystallization process.

The values of the activation energy for both the volume and surface crystallization were determined by the Ozawa's method [8], i.e. from the shifts of the DTA and EEE peaks, respectively, upon changing the heating rate. In the DTA measurements seven different heating rates (0.5, 1, 2, 5, 10, 20 and $50\,K\,min^{-1}$) were used and the activation energy for volume crystallization was determined with an accuracy better than ±0.1 eV. In the EEE experiments the activation energy for surface crystallization was determined with an accuracy of about 0.3 eV, based on the EEE curves registered at the heating rates of 5, 10, 20, 40 and $70\,K\,min^{-1}$ (Fig. 2). The values obtained of the activation energy for the volume and surface crystallization of alloys investigated, together with the crystallization temperatures measured at the heating rate of $20\,K\,min^{-1}$, are collected in Table I. As can be seen from these data, the most stable against both volume and surface crystallization is the ribbon containing 10% vanadium.

TABLE I Temperatures and activation energies for the volume and surface crystallization of investigated $Fe_{80-x}V_xB_{20}$ metallic glasses as determined from the DTA and EEE measurements, respectively

| Parameter | Vanadium content, $x$ | | |
|---|---|---|---|
| | 6 | 10 | 20 |
| Temperature of volume crystallization, $T_v$ [K] (heating rate $20\,K\,min^{-1}$) | 815 | 830 | 835 |
| Activation energy for volume crystallization, $E_v$ [eV] | 4.4 | 4.7 | 3.85 |
| Temperature of surface crystallization, $T_s$ [K] (heating rate $20\,K\,min^{-1}$) | 585 | 610 | 555*<br>750 |
| Activation energy for surface crystallization, $E_s$ [eV] | 1.25 | 1.40 | 1.15* |

*Indication of the EEE maximum for which the activation energy has been determined

The results presented in Fig. 2 also shed some light on the possible origin of the high-temperature peak in the intensity of EEE from alloy containing 20% of vanadium. As can be seen, the position of this peak does not depend on the heating rate, but its intensity decreases with increasing heating rate up to its complete disappearance at a heating rate greater than $40\,K\,min^{-1}$. This suggests that the occurrence of this peak could be ascribed to the oxidation of the crystallization product.

Concerning the observed difference between the activation energies for the volume and surface crystallization, it can be assumed that the surface crystallization occurs by growth of the crystal nuclei formed in the surface layer during the fabrication process. The bulk of the investigated alloys crystallizes by a usual nucleation and growth mechanism, thus the difference between the activation energy for the volume and surface crystallization could be treated as a measure for the energy of nucleation. This opens a new possibility for the determination of both the nucleation and growth energies.

Further studies are in progress.

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