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Structural transformations in surface layers of amorphous ribbons $Ni_{78}Si_xB_{22-x}$

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The thermal stability of $Ni_{78}Si_xB_{22-x}$ (x = 6, 9, 12, 15) metallic glasses, produced by the single-roll melt spinning method, has been investigated by differential thermal analysis (DTA) and by measuring the temperature dependences of the exoelectron emission (EEE) and contact potential difference (CPD) relative to platinum. It has been found that both CPD and EEE show anomalies at temperatures corresponding to the structural transformations in the surface layer of investigated materials. The surface crystallization occurs at temperature of ~150 K lower than the volume crystallization. The activation energy for the surface crystallization is also distinctly lower than that for crystallization in bulk.

1. Introduction

Metallic glasses are the subject of an increasing research effort, spurred by both science and technology. The research in this field helps our understanding of condensed matter in general. Being metastable, amorphous alloys tend to crystallize at proper combination of temperature and time. However, the most promising properties of metallic glasses deteriorate drastically during crystallization, thus the stability against crystallization determines the effective working limits of amorphous alloys [1, 2]. The methods most commonly applied for monitoring the crystallization are differential thermal analysis (DTA) and differential scanning calorimetry (DSC), both used to obtain information about enthalpy, activation energy and temperature of crystallization. Recently, the systematic studies on the applicability of exoelectron emission (EEE) technique for monitoring the structural transformations in metallic glasses has been started [3–5]. The measurements of the temperature dependence of the intensity of photostimulated EEE show clearly that the shapes of the temperature dependences of the EEE intensity and DTA curves measured at the same heating rate are always very similar and in most cases the peaks occurring on both curves lie at the same temperature. There are, however, compositions for which the positions of the peaks of EEE intensity are shifted towards lower temperatures with respect to the exothermal crystallization peaks on the DTA curve [3–5]. The last effect could be ascribed to the premature surface crystallization which in many non-crystalline materials precedes the bulk crystallization [6, 7], and the fact that the EEE phenomenon is the surface phenomenon (the average emergence depth of exo electrons is of the order of 10 nm) whereas the sensitivity of the conventional DTA technique permits one only to follow the heat evolution in the volume of the sample.

The determination of the surface work function is an important part of the overall characterization of a surface. Any change in the chemical or physical state of the surface, such as adsorption or geometric reconstruction, can be observed through a work function modification.

The Kelvin–Zisman vibrating capacitor method is one of the most sensitive techniques for measuring the contact potential difference (CPD) between two surfaces. It has been proven to be particularly useful for the study of changes in work function (WF) due to temperature or the adsorption of gases on surfaces. The method itself does not use high temperatures, strong electric fields or beams of electrons and photons. This makes the Kelvin method very useful in studies of real surfaces of materials, especially in air under atmospheric pressure [8, 9].

Recently we have started systematical investigations of the changes in CPD due to the structural transformations in metallic materials [10–12]. The results of measurements performed in atmospheric air correlate well with those of parallel investigations of the temperature dependence of the intensity of photostimulated exoelectron emission [12]. The purpose of the present paper is to represent the results of investigations of the surface and volume crystallization of some transition metal–metalloid glasses by parallel measurements of the temperature dependences of EEE intensity and contact potential difference relative to platinum as well as by the thermal analysis method.

2. Experimental conditions

The temperature dependence of CPD was measured by means of an automatic Kelvin probe described in detail in [10, 11]. The reference electrode (Pt plate) of an electrodynamically driven Kelvin probe, vibrated at frequency of 390 Hz. The induced signal current was amplified and phase-sensitively detected by a multiplying system. The specimen was attached to a holder made of nickel acting simultaneously as a heater. The vibration amplitude of the platinum electrode and its average (equilibrium) distance from the

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specimen were kept constant during all the measurements by a feedback loop operating at the frequency of 120 kHz.

CPD was measured in the process of continuous heating of the sample at a constant heating rate of $20\,\mathrm{K\,min^{-1}}$. No correction was made for the thermoelectromotive force because of the lack of appropriate data.

Measurements of the temperature dependences of EEE intensity were carried out by means of the arrangement described in detail in [13]. An open air point counter with saturated quenching vapour of ethanol above the free surface of liquid was used for detecting the exoelectrons. The sample surface was irradiated during the measurement by unfiltered radiation from a quartz lamp with a Q-400 burner. Prior the measurements the samples were not submitted to any form of excitation (irradiation, deformation, etc.). Both the CPD and EEE measurements were performed in air under atmospheric pressure.

DTA measurements were performed in atmospheric air using a Linseis L62/30/80 thermoanalyser. The samples were encapsulated in platinum crucibles. As reference, a crystallized ribbon of the same chemical composition and weight was used.

The investigated metallic glasses $Ni_{78}Si_xB_{22-x}$ and $Fe_{80-x}Cr_xB_{20}$, 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. The amorphous structure of the continuous ribbons of 10 mm width and 30 μm thickness was checked by X-ray diffraction technique.

3. Results and discussion

The experimentally determined temperature dependences of the contact potential difference and exoelectron emission intensity for $Ni_{78}Si_xB_{22-x}$ metallic glasses, both measured at the same heating rate of $20\,\mathrm{K\,min^{-1}}$, are represented in Figs 1 and 2. As it may be seen from Fig. 1, the temperature dependences of the intensity of photostimulated EEE from $Ni_{78}Si_6B_{16}$ and $Ni_{78}Si_9B_{13}$ display maximum at temperatures of 540 K and 610 K, respectively. For the glass containing 9 at % Si the EEE peak displays a distinct shoulder on its high-temperature side. This suggests that there are two mutually overlapping EEE maxima. The shape of the CPD curves for both the alloys is very similar, they exhibit a broad maximum at about 500 K, a minimum at ~675 K and a small narrow peak at 710 K.

The results of parallel measurements of the temperature dependence of the contact potential difference and the intensity of photostimulated EEE for glasses containing 12 and 15 at % Si are shown in Fig. 2. As it may be seen, the temperature dependences of the EEE intensity for both the alloys display two maxima at temperatures of 470 and 615 K.

Conversely to the situation observed for $Ni_{78}Si_{15}B_7$ alloy, the high-temperature peak of EEE intensity for glass containing 12 at % Si is much lower than that occurring at 470 K. The temperature dependences of the CPD for alloys containing 12 and 15 at % Si differ much more among themselves than those for $Ni_{78}Si_6B_{16}$ and $Ni_{78}Si_9B_{13}$ metallic glasses. The CPD curves for both the $Ni_{78}Si_{12}B_{10}$ and $Ni_{78}Si_{15}B_7$ glasses exhibit, however, some anomalies (broad peak or shoulder) at 425 to 450 K and at 550 to 600 K, i.e. in the temperature intervals close to the temperatures at which the peaks of the EEE intensity are observed.

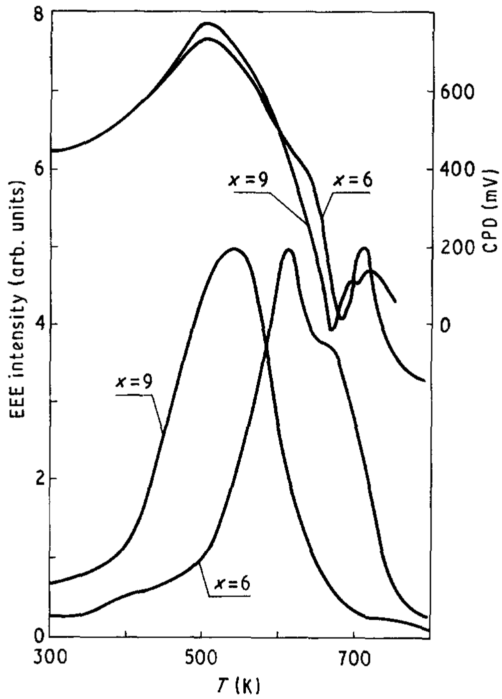

Figure 1 Temperature dependences of the EEE intensity and CPD relative to platinum for $Ni_{78}Si_xB_{22-x}$ (x = 6, 9) amorphous alloys.

It can be concluded that for all the materials investigated the positions of the peaks of EEE intensity agree fairly well with the temperature intervals in which the anomalies on the CPD curves are observed. As a rule, the EEE maxima occur at a temperature slightly higher than their CPD counterparts. It must be noted, however, that the CPD peak observed for $x = 6$, 9 and 12 at 700 K has no counterpart on the EEE curve.

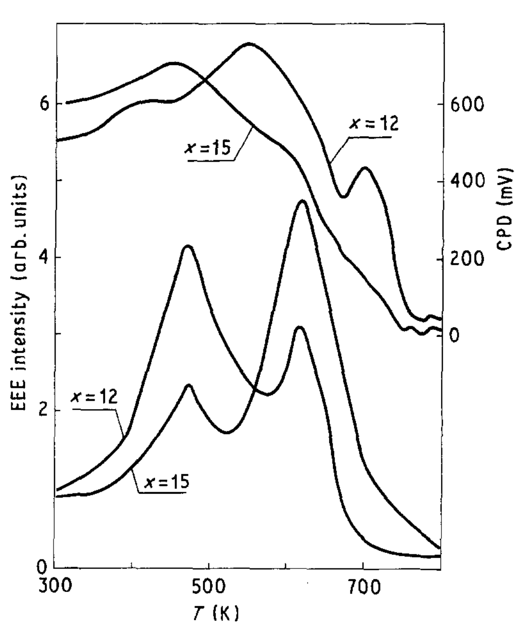

Figure 2 Temperature dependences of the EEE intensity and CPD relative to platinum for $Ni_{78}Si_xB_{22-x}$ ($x = 12$ and 15) amorphous alloys.

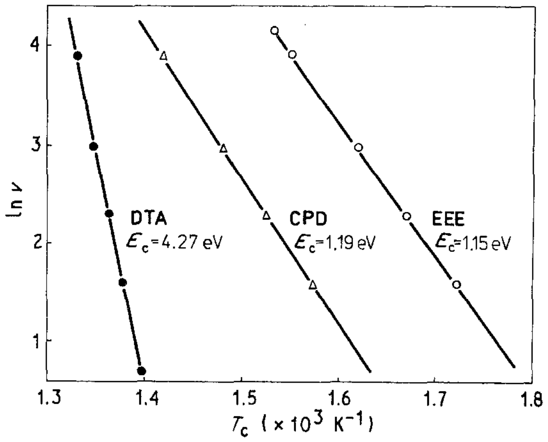

Figure 3 Ozawa's plots of the dependence of the position of the first DTA peak, the second EEE maximum and the minimum of temperature dependence of CPD for $Ni_{78}Si_{12}B_{10}$ on the heating rate.

In the case of our CPD measurements an increase of the contact potential difference corresponds to a decrease in the work function of the investigated sample. The qualitative coincidence of the anomalies observed on the EEE and CPD curves permits us to suggest that the processes of structural transformations, reflected by the EEE peaks [3–5], are also revealed by the contact potential difference measurements. There are at least two reasons for supposing that the observed EEE and CPD effects are associated with irreversible surface crystallization. First, the position of the anomalies on the EEE and CPD curves depends on the heating rate in a manner similar to that observed for the DTA peaks connected with the normal bulk crystallization. Second, similarly as in the case of DTA measurements, there are no anomalies on the EEE and CPD curves measured in the second and further heating runs, no matter how long was the time lapse between the succeeding heating runs. This permits us to exclude the surface effects connected with the thermal desorption of polar molecules.

Systematic CPD, EEE and DTA investigations were performed using different heating rates ranging from 2 to 70 K min^{-1}. The results enabled the determination of the activation energies for the processes governing the appearance of the observed anomalies on the temperature dependences of CPD and EEE intensity as well as for the volume crystallization. The well-known Ozawa's [14] relation

$$\ln v = A - E_c/kT_c$$

was applied, in which v denotes the heating rate, E_c the activation energy, T_c the crystallization temperature, k the Boltzmann's constant and A is a constant.

We have identified T_c with the position of a peak on the EEE and DTA curves, and with the position of a minimum on the CPD curve. The resulting Ozawa's plots of the crystallization temperature on the rate of heating of the $Fe_{78}Si_{12}B_{10}$ metallic glass are shown in Fig. 3. As it may be seen, the results of all the CPD, EEE and DTA measurements give straight lines, the slope of the EEE and CPD curves (and consequently, the activation energies) being nearly the same. This confirms our supposition that the temperature dependences of CPD and EEE reflect the same thermally activated process. The obtained values of the activation energy for the volume and surface crystallization of investigated $Fe_{78}Si_xB_{22-x}$ alloys, together with the crystallization temperatures measured at the heating rate of 20 K min^{-1}, are collected in Table I. The activation energy for volume crystallization was determined with an accuracy better than ± 0.1 eV. In the EEE and CPD experiments the activation energy for surface crystallization was determined with an accuracy of about 0.3 eV. The values of the activation energy for the surface crystallization collected in Table I represent the results obtained from EEE measurements. The difference between the results obtained from EEE and CPD investigations was always smaller than the sum of experimental errors involved in both sets of measurements.

Concerning the shift between the positions of the anomalies on the CPD and EEE curves, one should remember that all the electron emission phenomena favour the patches of lowest work function, whereas the Kelvin method gives the mean of the work function patches.

Another reason for the shift between the CPD and EEE anomalies may be a possible change of the roughness of the sample surface [9], due to the relaxation processes as well as the surface crystallization. Additionally, for exact determination of the temperature dependence of CPD the results of measurements should be corrected for the possible changes in the thermal e.m.f., which also may change during the structural transformations occurring on heating the sample.

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 already in 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 of determination of both the nucleation and growth energies.

TABLE I Temperatures and activation energies for the volume and surface crystallization of investigated metallic glasses as determined from DTA and EEE measurements

Parameter	Chemical composition, x			
	6	9	12	15
Temperature of volume crystallization, T_V (K) (heating rate 20 K min^{-1})	750 755	740 785 855	740 785 850	 785 810
Activation energy for volume crystallization, E_V (eV)	3.36 3.40	4.11 3.68 3.98	4.27 4.89 3.50	 3.02 2.91
Temperature of surface crystallization, T_s (K) (heating rate 20 K min^{-1})	540	610	470 615*	470 615
Activation energy for surface crystallization, E_s (eV)		1.15	1.15*	

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