Investigation of partially crystalline metallic glass

Fe$_{38}$Ni$_{36}$B$_{18}$Si$_{8}$

K Hrvat$^1$, M Lozančić$^1$, S Sulejmanović$^1$, I Gazdić$^2$, N Bajrović$^3$ and A Salčinović Petić$^1$

$^1$ Faculty of Science, University of Sarajevo, Zmaja od Bosne 33, 71000 Sarajevo, Bosnia and Herzegovina
$^2$ Faculty of Natural Sciences and Mathematics, Univerzitetska 4, 75000 Tuzla, Bosnia and Herzegovina
$^3$ The Federal Ministry of the War Veterans Sarajevo, Hamdije Čemerića 2, 71000 Sarajevo, Bosnia and Herzegovina

E-mail: kerim.hrvat@gmail.com

Abstract. Partially crystalline metallic glass Fe$_{38}$Ni$_{36}$B$_{18}$Si$_{8}$ was produced by rapidly solidifying in the form of ribbon. Chemical composition and homogeneity of the sample were determined using Scanning Electron Microscopy, equipped with energy-dispersive X-ray spectroscopy. The diffractogram exhibits a characteristic diffuse halo pattern superimposed with crystalline peaks, indicating existence of crystalline phases. The crystallization kinetics in non-isothermal conditions was studied by Differential Scanning Calorimetry. The electrical resistivity and the dimensions of samples Fe$_{38}$Ni$_{36}$B$_{18}$Si$_{8}$ were measured at room temperature. The temperature dependence of electrical resistivity was studied from 80 to 273 K. The measurements have shown a positive coefficient of electrical resistivity.

1. Introduction

The first metallic glass was obtained exactly 60 years ago as an exclusively man-made solid material. Glass is defined as a uniform solid, prepared by continuous cooling of a glass forming liquid, fast enough to avoid crystallization. If the cooling of melt is rapid enough to avoid nucleation and crystal growth, the melt is in metastable equilibrium, and its viscosity increases. When the viscosity becomes high enough that any rearrangement of atoms is no longer possible, a glassy state is formed. The glass transition temperature depends on the cooling rate. For conventional metallic glasses, the cooling rate would be between $10^4$ and $10^6$ K/s.

However, the glass transition is not fully explained, and according to Anderson, the theory of glass and the nature of the glass transition is the most interesting unsolved problem in Solid State Physics [1]. These materials are characterized by the absence of long range arrangement, but exhibit short range order. Being in a metastable state, the metallic glass crystallizes when heated above glass transition temperature. Hereby a lot of the physical properties, such as the electrical resistivity, the modulus of elasticity, the magnetic coercivity and the saturation magnetization, are significantly changed [2]. Metallic glasses can be fully amorphous or partially crystalline. The electrical resistivity of metallic glasses significantly differs from their crystalline counterparts.
Whereas crystalline metallic systems exhibit a positive temperature coefficient of resistance (TCR), metallic glasses have very small TCR values which could be positive, negative, or even zero within the temperature range up to crystallization [3]. In 1973 Mook [4] established an interesting correlation between the magnitude of the resistivity (at around room temperature) and the sign of TCR. If the metallic glass has resistivity greater than 150 $\mu\Omega\text{cm}$, its TCR is negative. Metallic glasses with resistivity below 150 $\mu\Omega\text{cm}$ have positive values of TCR [5].

Temperature dependence of electrical resistivity is extremely sensitive to the number of quenched-in crystallites within the glassy matrix.

2. Experimental
The master alloy and the metallic glass $\text{Fe}_{38}\text{Ni}_{36}\text{B}_{18}\text{Si}_{8}$ were obtained in the Laboratory of Metal Physics at Physics Department, Faculty of Science, Sarajevo. Metallic glass was obtained through the chill-block melt spin (CBMS) technique, whereby the molten alloy was ejected onto a rotating drum.

The ribbon was viewed under a MIM 7 vertical metallographic microscope, its thickness was gauged using a ULM length measuring instrument ULM 01-600C and its width was measured by a universal two-coordinate measuring microscope ZKM 01 - 250 C. The sample's chemical composition and homogeneity were determined by the Scanning Electron Microscope (SEM) TESCAN VEGA, equipped with BRUKER energy-dispersive spectrometer (EDS) at the Faculty of Metallurgy Sisak, University of Zagreb.

X-ray diffraction (XRD) pattern was obtained at the Department of Chemistry, Faculty of Science, University of Zagreb. Diffractograms of the sample were taken on the Philips PW 1840, using the software package Philips X Pert Data Collector.

In the investigation of phase transitions Differential Scanning Calorimetry (DSC) is commonly used. Monitoring of the crystallization process was performed by Diamond DSC, using the power compensation approach.

The electrical resistance measurements in temperature range from 80 K to 273 K were performed by the standard four-point probe method [6].

3. Results and discussion
The sample was observed as flat edged and non-porous through examination using the MIM 7 vertical metallographic microscope. In Figure 1 the difference between two surfaces is presented, one having been in contact with the copper drum – dark side of the ribbon (DSR), the other surface having been in contact with inert atmosphere – the shiny side of the ribbon (SSR).

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Figure 1. Metallographic examination of dark (a) and shiny (b) side of $\text{Fe}_{38}\text{Ni}_{36}\text{B}_{18}\text{Si}_{8}$ alloy.
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The chemical composition of partially crystalline metallic glass Fe$_{38}$Ni$_{36}$B$_{18}$Si$_8$ was confirmed by EDS (Figure 2).

Figure 2. EDS analysis of Fe$_{38}$Ni$_{36}$B$_{18}$Si$_8$ alloy.

XRD experiments showed that the examined sample is partially crystalline: the resulting diffractogram containing a set of crystalline peaks superimposed on a broad maximum corresponding to an amorphous phase. XRD patterns are presented for SSR in Figure 3 (a) and for DSR in Figure 3 (b).

Figure 3. XRD of (a) shiny and dark (b) side Fe$_{38}$Ni$_{36}$B$_{18}$Si$_8$ alloy.
The crystallization process of the metallic glass was studied by means of DSC. In temperature range 200-550 °C DSC curves of the metallic glass Fe$_{38}$Ni$_{36}$B$_{18}$Si$_8$ show two exothermic peaks. Values of heat flow versus temperature, at different heating rates, are presented in Figure 4.

![DSC curves](image)

**Figure 4.** DSC curves recorded at different heating rates.

Peak temperature for applied heating rates are presented in Table 1.

| Heating rate s (K/s) | $T_{c1}$ (K) | $T_{c2}$ (K) |
|----------------------|-------------|-------------|
| 5                    | 698.5       | 766.8       |
| 10                   | 706.2       | 777.7       |
| 20                   | 714.7       | 787.8       |
| 30                   | 719.8       | 792.8       |
| 40                   | 723.9       | 796.9       |

For study of crystallization kinetics Kissinger’s model [7] was used. According to this model, the heating rate $s$ is related to the peak crystallization temperature $T_c$ through the following equation:

$$\ln \left( \frac{s}{T_c^2} \right) = \frac{-E_a}{k_B T_c} + \ln \left( \frac{A k_B T_c}{E_a} \right) , \quad (1)$$

where $A$ is a constant value, $E_a$ is the activation energy and $k_B$ is the Boltzmann constant.

The activation energy can be calculated from the slope of the approximately straight line $\ln \left( \frac{s}{T_c^2} \right)$ vs. $\frac{1000}{T_c}$ and the plot for the second peak of crystallization is shown in Figure 5.

Overall activation energy calculated by Kissinger’s method is 332 kJ/mol and 341 kJ/mol for the first and the second peak, respectively.
Figure 5. Kissinger plot for Fe$_{38}$Ni$_{36}$B$_{18}$Si$_8$.

Electrical resistance of the partially crystalline metallic glass Fe$_{38}$Ni$_{36}$B$_{18}$Si$_8$ was estimated at room temperature. The value of the calculated electrical resistivity equals $(249 \pm 5)$ $\mu\Omega$cm. Changes in electrical resistivity occurring within temperatures ranging from 80 to 273 K are shown for two samples (Figure 6) which have been successively cut from the ribbon. It should be noted that the changes in dimensions of samples have not been taken into account. In accordance to the Mooij correlation a negative TCR is expected.

Figure 6. Electrical resistivity of Fe$_{38}$Ni$_{36}$B$_{18}$Si$_8$ alloy.

On the contrary, metallic glass Fe$_{38}$Ni$_{36}$B$_{18}$Si$_8$ exhibits a positive temperature coefficient of resistivity. It could be a consequence of structural disorder in partially crystalline glass [8].
4. Conclusion
Partially crystalline metallic glass Fe$_{38}$Ni$_{36}$B$_{18}$Si$_{8}$ was obtained by melt-spinning method in the form of a ribbon. It was shown that it was stable under non-isothermal conditions up to 674 K, when two-step structural transformation started. Values of overall activation energy of crystallization, calculated by Kissinger model are 332 kJ/mol for the first peak and 341 kJ/mol for the second peak. Although the value of the electrical resistivity is greater than 150 $\mu\Omega$cm, the temperature coefficient of the electrical resistivity is positive. Electrical resistance is primarily determined by the disorder scattering so the positive temperature coefficient can be the consequence of crystals present in an amorphous matrix.

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