Investigation of Partially Crystalline $Zr_{77}Ni_{23}$ Metallic Glass

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***Abstract* – This paper presents the results of an extensive research of partially crystalline $Zr_{77}Ni_{23}$ metallic glass (indicated numbers refer to atomic percentages). The partially crystalline $Zr_{77}Ni_{23}$ samples were prepared by melt-spinning using a device constructed in the Metal Physics Laboratory, Faculty of Science in Sarajevo. XRD pattern shows crystalline peaks which correspond to an orthorhombic structure of Zr_3Ni superimposed on an amorphous pattern. Homogeneity and chemical composition were investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Crystallization was studied by differential scanning calorimetry (DSC). DSC analysis indicated a simple thermally activated process. Overall activation energy of the crystallization was calculated using Kissinger's model for nonisothermal process and compared with those given by the Augis-Bennett model. By monitoring of the electrical resistance in the temperature range 80 – 270 K a small and negative thermal coefficient of electrical resistance was observed. This means that electrical resistance varies slightly with temperature and it makes this metallic glass suitable for application in electronic circuits for which this property is an important requirement.**

***Keywords* – metallic glass, crystallization, activation energy, electrical resistance**

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1. Introduction

By varying the quenching rate during the melt-spinning it is possible to produce either amorphous or partially crystalline ribbons [1]. In principle, the pre-existing crystals within the glassy matrix might be potential nucleation sites and destabilize the amorphous matrix. Our interest in the partially crystalline systems stems mainly from the fact that the presence of quenched-in crystals within the glassy matrix can increase stability against crystallization [2].

The crystallization process can be investigated thermally (i.e. DSC) and by monitoring the change in other physical properties such as electrical resistivity, saturation of magnetization, etc. [3]. Many desirable properties which determine the level of application of metallic glasses are lost as an effect of crystallization.

The value of electrical resistivity of metallic glasses is higher than those of their crystalline counterparts. It is primarily determined by the disorder scattering. In accordance with very small temperature dependence of the electrical resistivity, the temperature coefficient of resistivity is small, very often negative or even zero.

2. Experiment

The alloy $Zr_{77}Ni_{23}$ was prepared by arc melting under argon atmosphere. The initial materials were Zr (99.85 %) and Ni (99.995 %). Metallic glass ribbon approximately 2.5 m long, (1.315±0.030) mm wide and (36.2±0.9) mm thick was produced by melt-spinning in argon atmosphere. Tangential speed on the surface was 27 m/s and the ejection pressure 0.5 bars.

The chemical composition and homogeneity of the ribbon were examined by scanning electron microscopy, using TESCAN VEGA SEM, equipped with BRUKER device for dispersive X-ray spectroscopy. Phase identification in as-quenched samples was performed by X-ray powder diffraction experiment (XRD), on PHILIPS PW 1840 X-ray diffractometer.

Thermal stability and the crystallization processes of the partially crystalline $Zr_{77}Ni_{23}$ metallic glass were investigated by means of differential scanning calorimetry. Non-isothermal measurements were performed at different heating rates by calorimeter Phoenix DSC 204.

The electrical resistance measurements from 80 K to 270 K were carried out by AC four-point probe method [4]. AC signal from lock-in of 1mA was applied on a 40 mm long sample and voltage was registered by software specially made for this purpose.

3. Results

XRD pattern shows a set of well-defined crystalline peaks superimposed on a broad maximum corresponding to an amorphous phase. The broad maximum position is 2θ=36,4° (Figure 1).

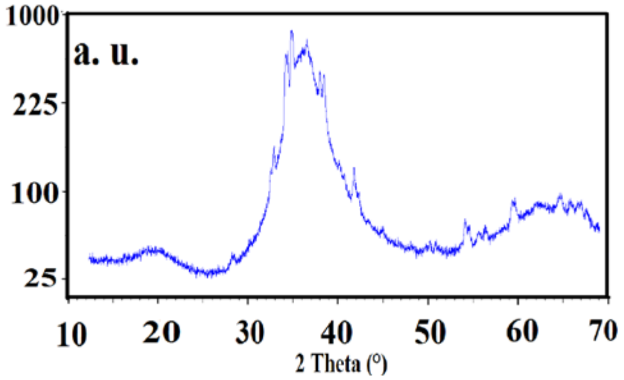

Figure 1. XRD intensity as a function of scattering angle for partially crystalline $Zr_{77}Ni_{23}$

We have fitted the crystalline peaks to an orthorhombic structure Zr_3Ni, with lattice parameters a=(1.086± 0.001) nm, b=(0.912 ± 0.002) nm and c=(0.334 ± 0.002) nm.

The DSC measurements show $Zr_{77}Ni_{23}$ crystallizes by one-stage process. Values of heat flow (mW/mg) at heating rates 10, 20, 30, 40 and 50 K/min are shown in Figure 2. According to figure 2 the crystallization peak shifts to higher temperatures with increasing heating rates.

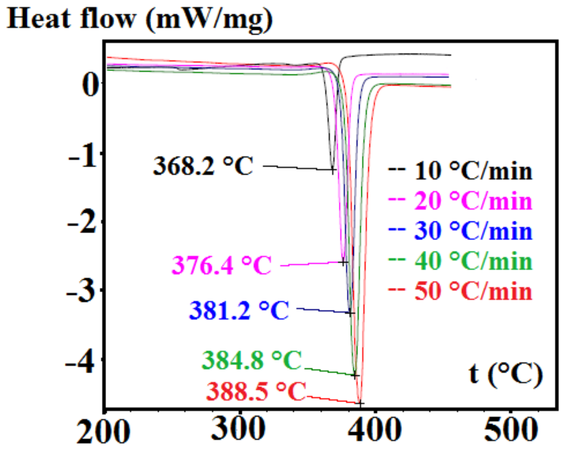

Figure 2. DSC traces obtained at heating rates 10, 20, 30, 40, 50 K/min

The crystallization kinetics of metallic glasses has been usually studied using Johnson-Mehl-Avrami (JMA) phenomenological theory of isothermal kinetics in which the crystallization fraction x can be described as a function of time. JMA equation is usually written as:

$$x(t) = 1 - \exp\left\{-(Kt)^n\right\} \quad (1)$$

where n is the Avrami exponent and K is the rate constant which is given by:

$$K = K_0 \exp\left(-\frac{E_a}{k_B T}\right). \quad (2)$$

In equation (2) E_a is the activation energy for the overall crystallization process, k_B is the Boltzmann constant and T is the isothermal temperature. Based on the JMA model, different methods have been developed for the study of non-isothermal crystallization.

Kissinger's model [5], [6] suggests that the heating rates s in terms of the peak crystallization temperature T_c can be expressed using the equation:

$$s = AT_c^2 \exp\left(-\frac{E_a}{k_B T_c}\right), \quad (3)$$

where A is constant. The equation (3) can be rewritten as:

$$\ln\left(\frac{s}{T_c^2}\right) = -\frac{E_a}{k_B T_c} + \ln A. \quad (4)$$

In accordance with equation (4) value of the activation energy can be obtained by plotting $\ln(s/T_c^2)$ versus $1/T_c$. The plot of $\ln(s/T_c^2)$ versus $1/T_c$ for partially crystalline $Zr_{77}Ni_{23}$ is a straight line which confirms a one-step crystallization process that is shown in Fig. 3.

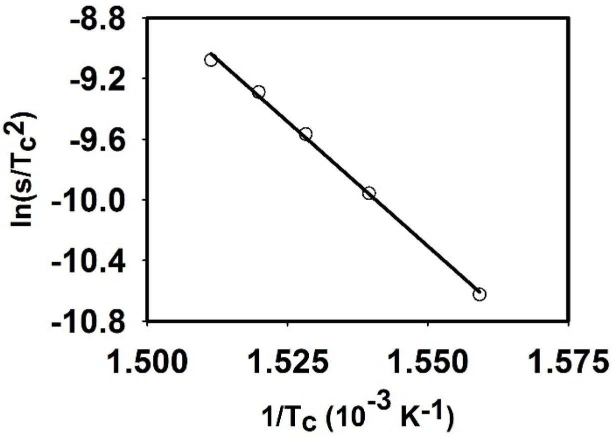

Figure 3. Kissinger plot for the partially crystalline $Zr_{77}Ni_{23}$

From the slope of Kissinger plot the calculated value for the activation energy $E_a = 2.83$ eV/atom.

Augis and Bennett [7], [8] proposed the following relation to be valid:

$$\ln\left(\frac{s}{T_c - T_0}\right) = -\frac{E_a}{kT_c} + \text{const}, \qquad (5)$$

where T_0 is the initial temperature of DSC thermal curves.

Value of activation energy deduced from Augis-Bennett plot (Figure 4) is E_a=2.82 eV/atom.

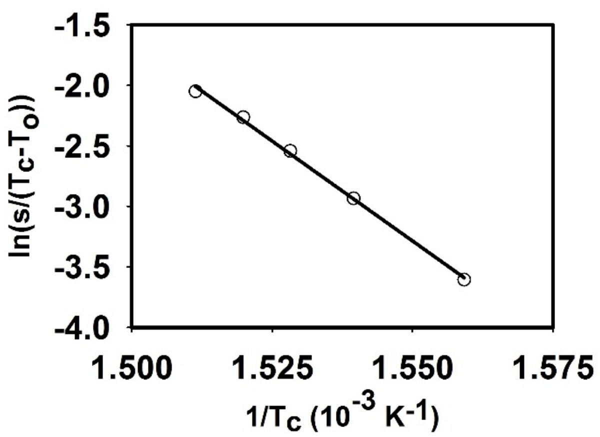

Figure 4. Augis-Bennett plot for the partially crystalline $Zr_{77}Ni_{23}$

Total heat of crystallization was determined from the area of the crystallization exotherm and its value is 71,3 J/g.

Mean value of the electrical resistivity is estimated on 168 μΩcm. The temperature dependence of normalized electrical resistance for partially crystalline $Zr_{77}Ni_{23}$ is shown in Figure 5. Above the temperature range from 80 K to 270 K the electrical resistance decreases very slightly.

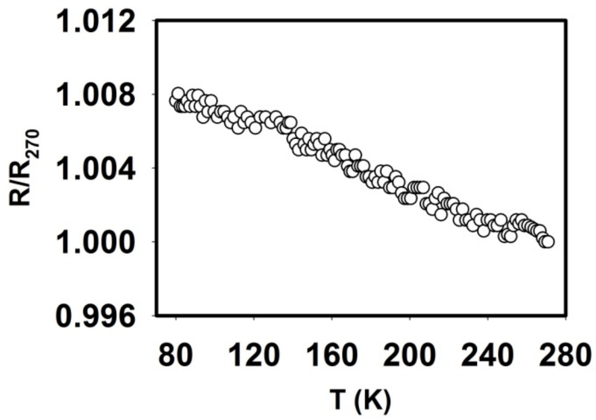

Figure 5. Temperature dependence of normalized electrical resistance partially crystalline $Zr_{77}Ni_{23}$

Fitted to a linear function, the slope of temperature dependence of normalized electrical resistance in investigated range is -4,2 $*10^{-5}$ K^{-1}.

4. Conclusions

The partially crystalline metallic glass $Zr_{77}Ni_{23}$ in the form of ribbon was prepared by melt-spinning. Its electrical resistivity and therefore also electrical resistance shows low sensitivity on temperature variations. Small changes in electrical resistance due to temperature variations make this metallic glass suitable for use in various electronic circuits, where this feature is a necessary condition.

It is therefore very important to evaluate the thermal stability of the glass and determine the limits of application. The value of the dynamic crystallization temperature and activation energy of the overall crystallization process indicates a significant thermal stability of partially crystalline $Zr_{77}Ni_{23}$. Results for the activation energy of crystallization obtained by Kissinger and Augis-Bennett models, for investigated glass, are in good agreement.

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