18th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2014, Budapest, Hungary 10-12 September, 2014

KINETICS OF CRYSTALLIZATION IN PARTIALLY CRYSTALLINE METALLIC GLASS $Zr_{53}Cu_{40}Al_7$

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ABSTRACT
Metallic glass $Zr_{53}Cu_{40}Al_7$ was prepared in the form of ribbon by melt-spinning the master alloy in a purified argon atmosphere at a lower quenching rate. Its thickness of 0.1 mm is near limit of bulk glasses. Presence of crystallites in the amorphous matrix was confirmed by X-ray diffraction (XRD). Homogeneity and chemical composition were investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Metallic glasses are metastable and it is of great importance to investigate their stability. The crystallization process was studied by means of differential scanning calorimetry (DSC). Overall activation energies of the crystallization were calculated using various models for non-isothermal process and their values are close to 2.97 eV.
Keywords: partially crystalline metallic glass, thermal stability, differential scanning calorimetry, activation energy, non-isothermal process.

1. INTRODUCTION
Metallic glasses do not possess a long range order, but short range order can exist. From a thermodynamics standpoint, a crystal is more favorable than glass. Upon cooling from the melt, the metallic glass exhibits a glass transition. Values of the glass transition temperature will be lower at slower cooling rates. At the glass transition temperature the first derivatives of the Gibbs free energy such as volume, entropy, and enthalpy are continuous but exhibit a change in slope. There is a discontinuity in derivatives of these thermodynamic variables such as heat capacity and the abrupt change in heat capacity indicates the glass transition [1]. Depending on the cooling rate, the obtained ribbons can be fully amorphous or partially crystalline.
Metallic glasses are metastable structures and tend to undergo a transition to a more stable state, which is followed by changes in desirable physical properties. This fact imposes a strong limit for their applications at elevated temperatures. Thermal stability examination and determination of glass transition temperature is typically performed by DSC. The crystallization kinetics can be studied in two processes, isothermal and non-isothermal, and the experimental results can be interpreted in terms of several theoretical models.
The crystallization kinetics of metallic glasses has usually been studied using the Johnson-Mehl-Avrami (JMA) phenomenological theory of isothermal kinetics in which the crystallization fraction x can be described as a function of time. The JMA equation is usually written as:

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

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

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

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 method [2,3] assumes that the reaction rate has a maximum at the peak temperature T_c and also implies a constant degree of conversion at T_c. It suggests that the heating rates s in terms of the peak crystallization temperature T_c can be expressed using the equation:

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

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

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

The value of activation energy can be calculated from the slope of the approximately straight line $\ln\left(s/T_c^2\right)$ versus $1/T_c$.
Ozawa proposed that the activation energy at peak temperature can be determined according to:

$$\ln s = -1.0516\frac{E_a}{k_B T_c} + const\,. \tag{5}$$

Kissinger-Akahira-Sunose (KAS) [4,5] method uses the temperatures T_x which correspond to fixed values of the crystallized volume fraction x at different heating rates:

$$\ln\left(\frac{s}{T_x^2}\right) = -\frac{E_{ax}}{k_B T_x} + \ln\left(\frac{K_0 k_B}{E_{ax}} F(x)\right). \tag{6}$$

The activation energy can be calculated from the slope of the straight line given by (6).

2. EXPERIMENTAL PROCEDURES

Master alloy was prepared using an argon arc furnace from Zr (99.98 %), Cu (99.999 %) and Al (99.999 %). Metallic glass was obtained by melt-spinning in argon atmosphere [6,7]. The process parameters were selected as follows: wheel velocity of 15 m/s, ejection argon pressure of 0.8 bar and the crucible orifice diameter of 0.5 mm. The final product was the ribbon 1.5 mm wide and 0.1 mm thick. Homogeneity and the chemical composition of the ribbon were examined by scanning electron microscopy (SEM), using TESCAN VEGA SEM, equipped with BRUKER device for dispersive X-ray spectroscopy (EDX). The XRD experiment was performed on a Philips PW-1840 diffractometer using the software package Philips X´Pert Data Collector.
Thermal stability of the metallic glass was studied by differential scanning calorimetry. Measurements were performed using Diamond DSC.

3. RESULTS AND DISCUSSION

Results of EDX analysis show that the sample is homogeneous. Distribution of the constituents in the sample is shown in Figure 1.

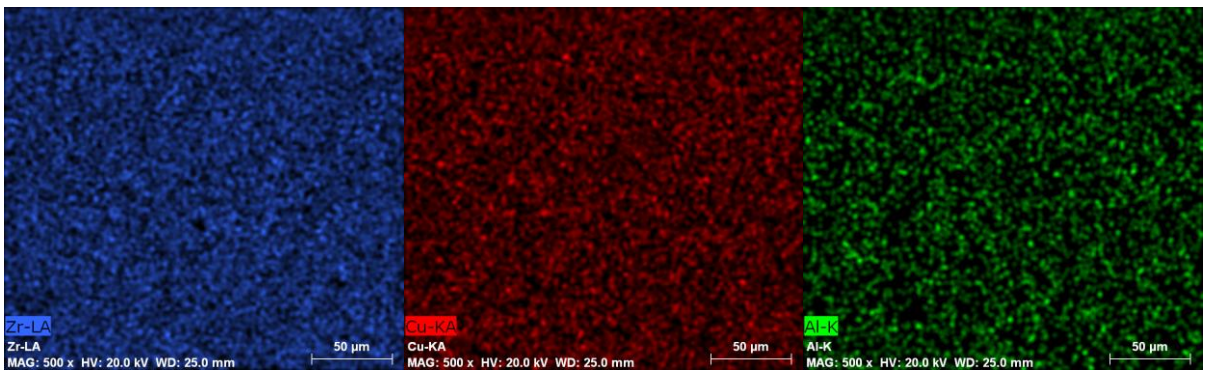

Figure 1. Distribution of Zr, Cu and Al in metallic glass $Zr_{53}Cu_{40}Al_7$

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 $2\theta = 38^{\circ}$ as shown in Figure 2.

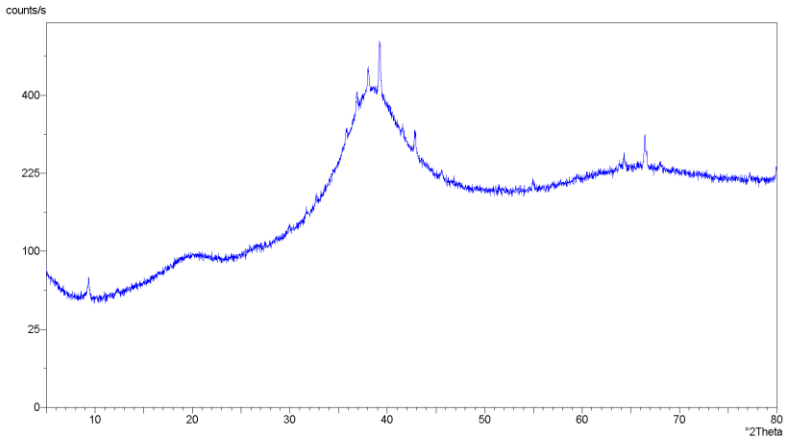

Figure 2. XRD intensity as a function of scattering angle for the partially crystalline $Zr_{53}Cu_{40}Al_7$

Well defined endothermic and exothermic peaks are observed at glass transition temperature (T_g) and crystallization temperature (T_c). The glass transition temperature is not a constant of the material, but rather a function of experimental conditions. Values of heat flow (mW/mg) at 30 and 50 K/min heating rates are shown in Figure 3.

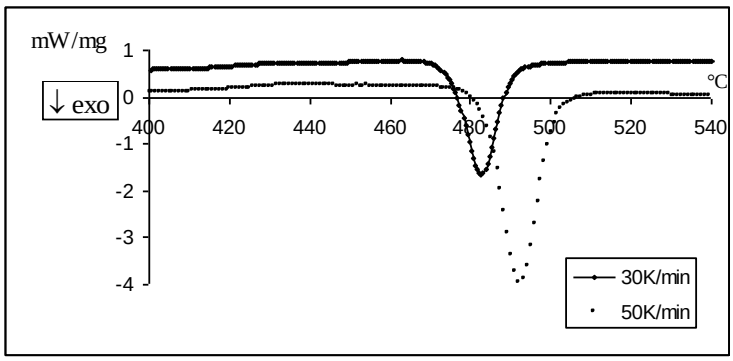

Figure 3. DSC scans recorded at different heating rates

The crystallization peak shifts to higher temperatures with increasing heating rates. The temperature of glass transition has been found less dependent on the heating rate than the peak temperature.
The activation energy for the overall crystallization process was calculated using Kissinger's and Ozawa's method. The plot corresponding to Ozawa's method is presented in Figure 4.

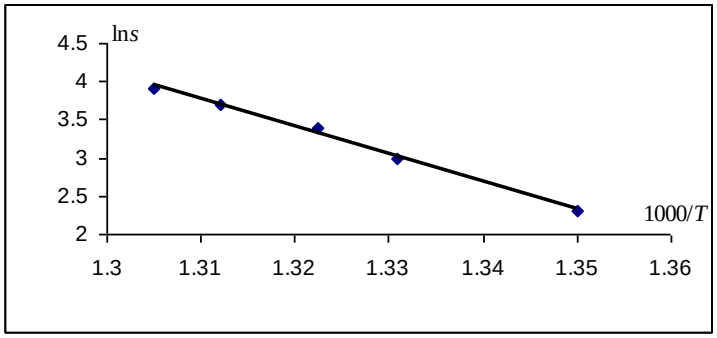

Figure 4. Ozawa's plot for partially crystalline metallic glass $Zr_{53}Cu_{40}Al_7$

The plot is approximately a straight line. The value of the activation energy obtained by Ozawa's method is 2.96 eV. The activation energy obtained by Kissinger's method is 2.98 eV. The fractions of crystalline phase, e.g. degrees of conversion, at peak temperatures have also been calculated at different heating rates and the results are between 50.15 % and 53.28 %. These degrees of conversion are calculated as the quotient of the area above DSC curve between the onset temperature of crystallization and the actual temperature and the area above the DSC curve between the onset and offset temperatures. The activation energies at different degrees of crystallization were calculated using KAS method and are presented in Table 1. Maximum difference between E_{ax} is 1.44%.

Table 1. Activation energies at corresponding degrees of conversion

x (%)	E_{ax} (eV)
10	2.994
20	2.985
30	2.983
40	2.988
50	2.990
60	2.992
70	2.999
80	3.007
90	3.026

4. CONCLUSIONS

The process of obtaining metallic glass and its crystallization kinetics can be presented as follows:

1. Metallic glass ribbon is obtained by melt-spinning with carefully selected process parameters.
2. It is homogeneous considering the composition, but is not fully amorphous. XRD analysis shows a set of sharp crystalline peaks.
3. Process of crystallization has been studied using three methods. The glass transition temperature is very noticeable in the thermogram.
4. Comparison of the activation energies for different degrees of conversion indicates a single-stage process of crystallization.

Further research will be aimed at identification of crystalline phases in the amorphous matrix of the as-quenched samples as well as change of structure during crystallization.

5. REFERENCES

[1] Butterworths monographs in materials, ed. by F. E. Luborsky, Butterworth & Co (Publishers) Ltd, London, 1983.

[2] H. E. Kissinger: Reaction Kinetics in Differential Thermal Analysis, Analytical Chemistry, Vol. 29, No. 11, (1957), 1702 – 1706.

[3] H. Kumar, K Singh and N. Mehta: Thermal Characterization of $Se_{78-x}Te_{20}Sn_2Pb_x$ $(0 \le x \le 6)$ glassies for phase change optical recording technique, Glass Physics and Chemistry, Vol.39, No.5 490-498, 2013.

[4] D. M. Minić, B. Adnađević: Mechanisms and kinetics of crystallization of α-Fe in amorphous $Fe_{81}B_{13}Si_4C_2$ alloy, Thermochimica Acta 474 (2008), 41-46.

[5] B. Anđević, B. Janković, D. Minić: Kinetics of the apparent isothermal and non-isothermal crystallization of the α-Fe phase within the amorphous $Fe_{81}B_{13}Si_4C_2$ alloy, Journal of Physics and Chemistry of Solids 71, (2010) 927-934.

[6] S. Sulejmanović; T. Mihać, S. Bikić and N. Bajrović: Relaxation in Metallic Glass $Ni_{36,5}Zr_{63,5,}$ Acta Physica Polonica, Vol.117, No 5, (2010) , 817 – 819.

[7] S. Sulejmanović, T. Mihać, S. Bikić, N. Bajrović, I. Gazdić: Crystallization of the partially crystalline Cu-Zr metallic glasses, 13th international research/expert conference "Trends in the development of machinery and associated technology", TMT 2009 Proceedings

Acknowledgements

We would like to thank Mr. Andrija Franković for his technical support.

This investigation is supported by Federal Ministry of Education and Science (Contract Nr. 05-14-4564-1/12).