19h International Research/Expert Conference
”Trends in the Development of Machinery and Associated Technology”
TMT 2015, Barcelona, Spain 22-23 July 2015

# THE ELECTRICAL RESISTIVITY OF PARTIALLY CRYSTALLINE ZrCuAl METALLIC GLASSES

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## ABSTRACT
*Partially crystalline metallic glasses $Zr_{53}Cu_{40}Al_7$, $Zr_{43,5}Cu_{47,5}Al_9$ and $Zr_{40}Cu_{53}Al_7$ in the form of ribbons were obtained by melt-spinning. The diffractogram (XRD) confirmed the existence of crystalline peaks superimposed on an amorphous matrix. Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy was performed to examine the homogeneity and chemical composition of the material. The crystallization process was observed using differential scanning calorimetry (DSC). The electrical resistivity of partially crystalline ZrCuAl metallic glasses has been studied as a function of temperature between 80 and 273 K. The temperature dependence of the resistivity was monitored by standard four-point probe method for compositions with less than 10% Al. Despite the fact that the samples were partially crystalline, a low negative temperature coefficient of resistivity (TCR) similar to that of an amorphous metallic glass is observed.*
**Keywords**: partially crystalline metallic glass, resistivity, four-point probe method, amorphous metallic glasses

## 1. INTRODUCTION
The Zr-Cu-Al ternary alloys have a good combination of strength, ductility, corrosion resistance and low production cost. This system is suitable for the production of bulk metallic glasses, e.g. glassy alloys obtained with significantly lower cooling rates than required for traditional glassy alloys.
Ternary Zr-Cu-Al alloy vitrified in single amorphous phase in a wide composition range of 20-75 at.% Zr and 20-70 at.% Cu, when the Al content is limited to 8-15 at%. The Al content is the crucial factor in the formation of the Zr-Cu-Al glassy alloys. A ternary eutectic point is located around $Zr_{50}Cu_{40}Al_{10}$. [1]. It is found that the precipitation of nanocrystals in the amorphous alloys can improve their properties [2]. Therefore, research of partially crystalline metallic glasses is important. The partially crystalline metallic glass can be produced by annealing of amorphous ones or using a lower quenching rate during the melt-spinning. The electrical resistivity can be regarded as one of the most sensitive properties related to the structure. It is higher in metallic glasses than in their crystalline counterparts. Of course, it corresponds to a disordered system. Temperature dependence of

the electrical resistivity of metallic glasses is usually discussed in terms of the TCR value. This value is usually small, can be positive and negative or even zero. This is in contrast to crystalline metals, which have large and positive TCR values [3].

## 2. EXPERIMENTAL PROCEDURES

Specimens of $Zr_{53}Cu_{40}Al_7$, $Zr_{43,5}Cu_{47,5}Al_9$ and $Zr_{40}Cu_{53}Al_7$ (numbers indicate at%) alloys were prepared by arc melting in an argon arc furnace from Zr (99,98 %), Cu (99,999 %) and Al (99,999 % purity).

The final products, ribbons of metallic glasses, were obtained by melt-spinning in an argon atmosphere. Homogeneity and the chemical composition of the ribbons were examined by SEM, using TESCAN VEGA SEM, equipped with BRUKER device for energy dispersive X-ray spectroscopy (EDX). The glassy phase was identified by XRD. These experiments were performed on Philips PW-1840 diffractometer using the software package Philips X´Pert Data Collector. Thermal stability of the metallic glasses was studied by DSC. Measurements were performed using Diamond DSC.

Four-point probe measurements of electrical resistance were made using a Lock-in amplifier. The monitoring of electrical resistance temperature dependence is performed in the 80 – 273 K temperature interval.

## 3. RESULTS AND DISCUSSION

The diffractogram patterns of samples show a broad halo peak, representing a typical characteristic of the amorphous structure and a set of crystalline peaks related to crystalline phases (Figure 1. a).

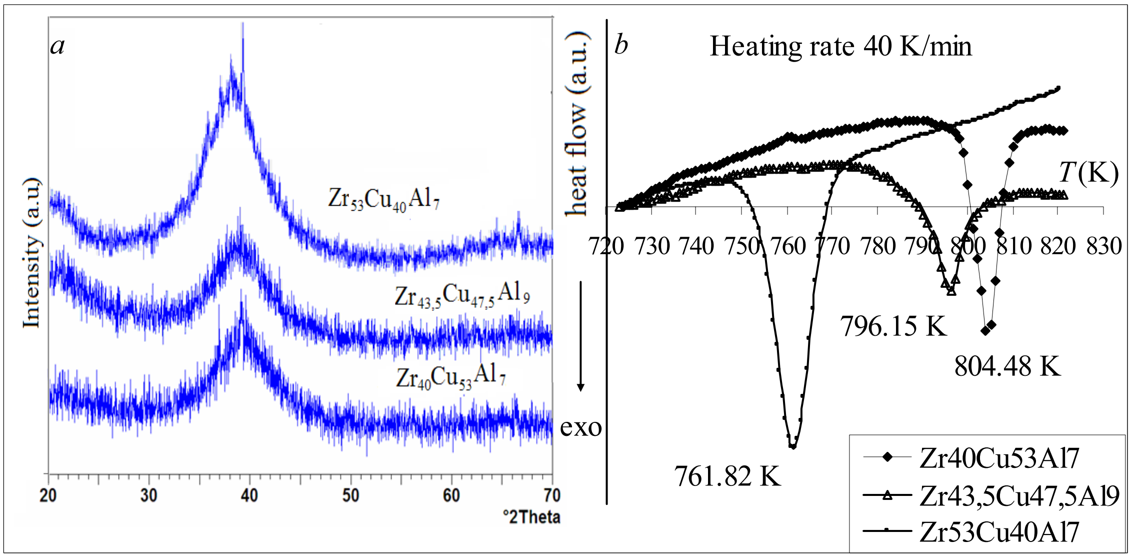


*Figure 1. a) The XRD intensity as a function of scattering angle for tested samples. b) DCS curves of the samples at a 40K/min. heating rate.*

Monitoring of the crystallization was obtained in a continuous heating mode by DSC. In the DSC heating curves an exothermic peak which is ascribed to the crystallization is observed. Characteristic peak temperatures of crystallization for heating rate of 40 K/min are presented in Figure 1. b. It is in good agreement with the peak temperature of fully amorphous metallic ribbons of similar compositions and the bulk metallic glasses ZrCuAl with high glass forming ability [4], [5]. The fractions of crystalline phase at peak temperatures for presented measurements are near 50 % [6].

For the measurement of electrical resistance the metallic glass ribbons were cut in parts 25 mm in length. More than three measurements on succesive parts cut from a single specimen were performed for all compositions. The value of the AC electric current was small enough not to heat the specimen. Good contacts for the four-point probe measurements were secured.

The electrical resistance of samples increases as the temperature is lowered from 273 to 80 K. It is also characteristic of ZrCu and ZrNi binary metallic glasses. Figure 2. shows a plot of the normalized resistance variations ($R/R_{273}$) with temperature for the two as-quenched samples $Zr_{43,5}Cu_{47,5}Al_9$. It should be noted that the changes in dimensions of samples have not been taken into account.

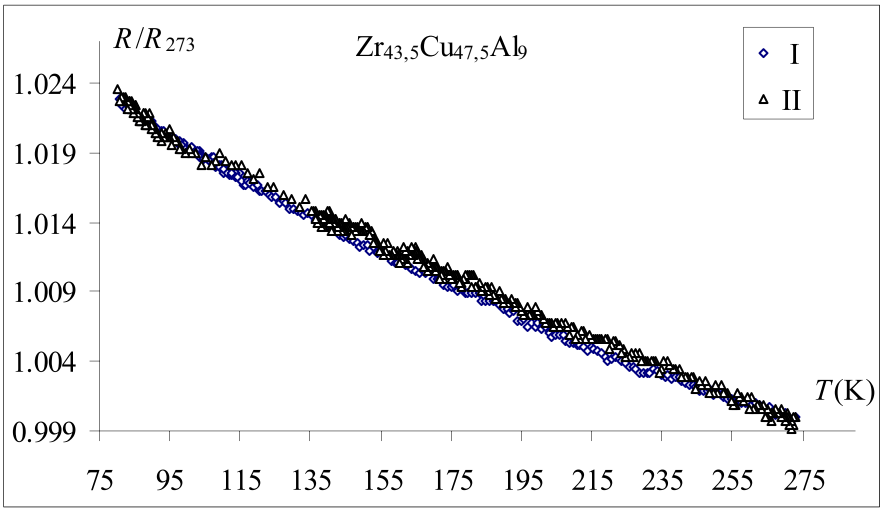


*Figure 2. The normalized resistance versus temperature for two $Zr_{43,5}Cu_{47,5}Al_9$ samples*

A plot of the normalized electrical resistance for three examined specimens is presented in Figure 3. From 273 to 80 K, the increases in the resistance are about 2,3 % ($Zr_{43,5}Cu_{47,5}Al_9$), 1,8% ($Zr_{40}Cu_{53}Al_7$) and 1,5 % ($Zr_{53}Cu_{40}Al_7$).

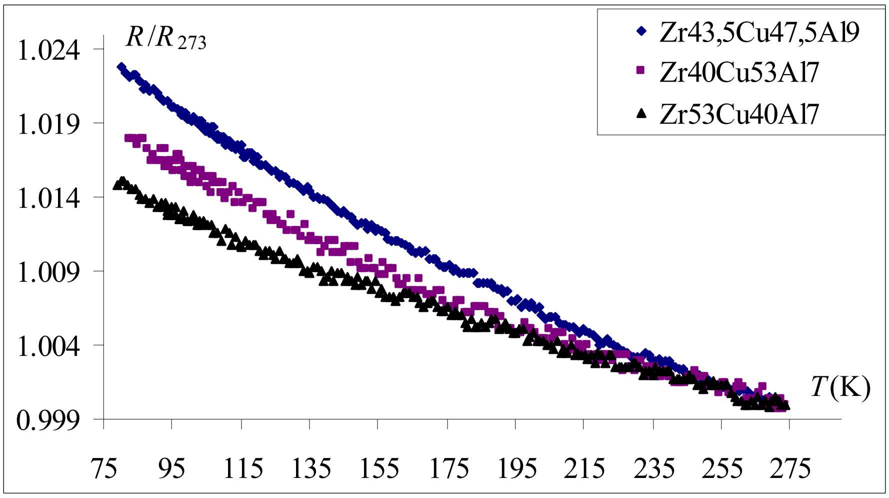


*Figure 3. The normalized resistance versus temperature for examined samples*

It is important to note that the temperature dependence of electrical resistance is linear in the higher temperature range, but departs from linearity below about 160 K for test samples. Such behaviour is in accordance with Ziman's nearly-free electron model. The overall temperature behaviour of the resistance is similar to that found in the amorphous ZrCuAl metallic glasses [7], [8].

## 4. CONCLUSIONS

The results obtained in a great series of experiments can be summarized as follows:

1. Specimens of three different compositions Zr-Cu-Al metallic glasses in form of ribbon are obtained by melt-spinning.
2. They are homogeneous considering the composition, but are not fully amorphous. XRD analysis shows an amorphous matrix but also a set of sharp crystalline peaks indicating the existence of crystalline phases, which makes this material a partially crystalline metallic glass.

3. DSC analysis for examined specimens points out to one step crystallization processes. The data is in good agreement with those for amorphous ribbons and bulk metallic glasses with similar compositions.
4. The measurements of the electrical resistance were carried out in 80 – 273 K temperature interval. Despite the fact that the samples were partially crystalline, a low negative temperature coefficient of electrical resistance and also electrical resistivity, similar to those of amorphous metallic glasses are observed for all test samples.

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**Acknowledgements**

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

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