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CRYSTALLIZATION OF THE PARTIALLY CRYSTALLINE Cu-Zr METALLIC GLASSES

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ABSTRACT
The partially crystalline Cu-Zr metallic glasses of different compositions were prepared by melt spinning. As they were obtained by lower quenching rates they are always thicker in comparison with the amorphous metallic ribbons, but as well as the amorphous ones these samples have desirable mechanical properties. The crystallization process was monitored by measurement of electrical resistance in temperature interval from 300 K to 673 K. We have noticed significant differences in their behaviour during the cooling process after crystallization, when for copper rich alloys the function R(T) turned out to have a maximum.
Keywords: amorphous metallic glass, partially crystalline metallic glass, electrical resistance, relaxation, crystallization.

1. INTRODUCTION
The nature of glass transition is not completely explained and is one of the questions left to be explained in the 21st century. The investigation of glassy materials is therefore still very important.
Our special interest was to produce and investigate glassy systems with an ability to vitrify in a wide range of compositions. One of those systems is a combination of noble-transition metals and therefore we choose Cu-Zr.
By varying the quenching rate during melt-spinning it is possible to produce either amorphous or partially crystalline ribbons. At lower rotation speeds of the wheel the quenching of the ribbons is not enough rapid and so the produced samples are not amorphous but partially crystalline. They possess elasticity and are also some thicker than the amorphous ones. Metallic glasses differ from other glassy systems by their relative instability against crystallization. Pre-existing crystals within amorphous matrix might be potential nucleation sites [1]. In description of the conductivity of Cu-Zr glasses one should introduce two separate mean free paths for s-and d-electrons and write the total electrical conductivity as a sum of the both contributions. According to the two-band model in copper rich alloys the s-states that have been scattered into the d-states are dominant in conductivity and in zirconium rich alloys the conduction due to d-band electrons becomes an important mechanism [2]. The two bands are in parallel and the total electrical resistivity is given by:

$$\frac{1}{\rho} = \frac{1}{\rho_s} + \frac{1}{\rho_d} \qquad (1)$$

The hybridization between the s-and d-states in a simplified model can be neglected. The measurement of electrical resistivity is a very sensitive and therefore perhaps the best method to detect the beginning of the crystallization.

2. EXPERIMENTAL

The Cu-Zr master-alloys of different compositions were made by melting in argon arc furnace. The partially crystalline Cu-Zr metallic glasses were produced by melt-spinning at fast rotating copper drum; the surface velocity of the drum was 15 m/s and the ejection pressure 0.5 bar and these are the proper conditions for obtaining the desired samples.

The partially crystalline samples used for electrical resistivity measurements were about 50μm thick, 20 mm long and 1 mm wide, they were placed in a mica holder and provided with good contacts based on four wire pressures [3]. Measurements were carried out by dc method and the experimental setup is shown in Fig.1. The samples were heated in vacuum of 10^{-3}Pa and the heating rates were controlled by Process controller ESM-4450. Experimental data were recorded by use of TEST POINT software.

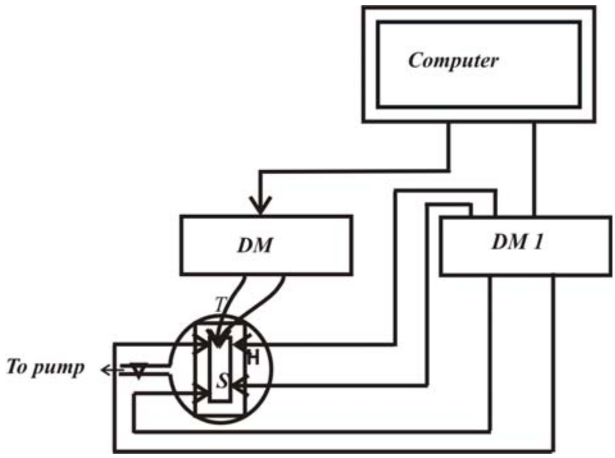

Figure 1. Scheme- system for measuring of resistance: DM-Keithley multimeter 2002; DM1-Keithley multimeter 2000; T-termocouple, S-sample, H- heater.

3. RESULTS

We have investigated the electrical resistance of partially crystalline Cu-Zr samples from room temperature to 673K and the results for three alloys of different compositions $Cu_{38}Zr_{62}$, $Cu_{51}Zr_{49}$ and $Cu_{60}Zr_{40}$ at heating rate of 3K/min are shown in Fig.2-Fig.4. First that one can conclude is that the partially crystalline metallic glasses expose a very small temperature dependence of the electrical resistance until the crystallization process occurred. Crystallization is accompanied by reduction in electrical resistance which is caused by ordering of the system. Stability of metallic glasses is characterized by the crystallization temperature. Some authors define it as the temperature of the onset crystallization T_x and some others as the temperature of the crystallization peak T_p [4].

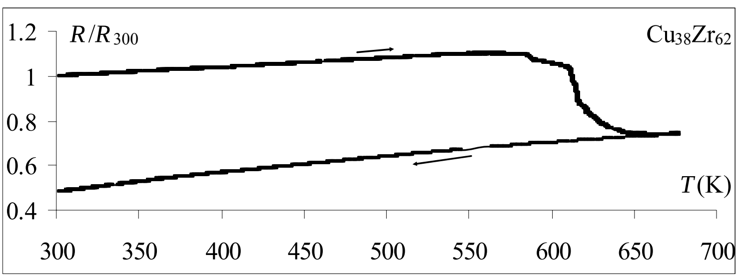

Figure 2. Normalized electrical resistance for Zr-rich partially crystalline glass versus temperature

We have detected both of them as seen in Fig.2. When the sample reaches T_x an abrupt fall in electrical resistance occurs and when the sample reaches T_p this process is finished. In Fig.3 and Fig.4 we could detect only the onset temperature T_x. We have annealed and than cooled the samples in the same temperature interval and in the same manner.
During the cooling after the crystallization the values of the electrical resistance Zr-rich samples decreased as in ordinary metals. But we also observed that during the cooling of the glasses with more than 50% content of Cu the electrical resistance turned out to have a maximum.

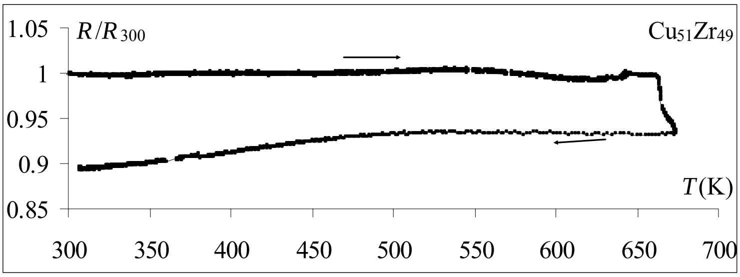

Figure 3. Temperature dependences of normalized electrical resistance for partially crystalline metallic glass with smaller contents of Zr

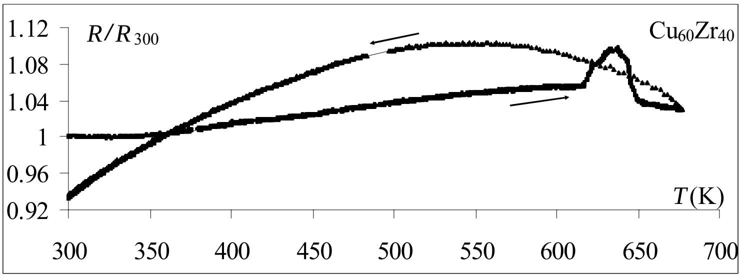

Figure 4. Temperature dependences of normalized electrical fo Cu-rich partially crystalline metallic glass

It should be noticed that the effects of thermal expansion were not taken into account.
From the obtained results we could see significant differences in resistance behaviour after crystallization. The reason for this different behaviour of the partially crystalline metallic glasses Cu-Zr might be due to the mechanism of conduction rather than due to the mechanism of crystallization.
It will be useful to make in future a comparison between amorphous and partially crystalline samples.

4. CONCLUSIONS

The results obtained in a great series of experiments can be summarized as follows:
1. The most important influence on the crystallization process is due to the initial composition of the constituents of the alloy.
2. There are two different mechanisms that govern the process of the conducting influencing the behaviour of the electrical resistance.
3. The Cu-rich glasses exhibit a maximum of the resistance during the cooling after the crystallization and this can be noticed even for alloys with 51% content of Cu.
4. The process of the devitrification is obviously a very complex process and some interesting results could be obtained by comparison of amorphous and partially crystalline samples.

5. ACKNOWLEDGMENT

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