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Relaxation in Metallic Glass $Ni_{36.5}Zr_{63.5}$

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The metallic glass ribbons of $Ni_{36.5}Zr_{63.5}$ were prepared by melt spinning. The samples have a large frozen-in structural disorder and in comparison with their crystalline state, a very high electrical resistivity. They are metastable and they relax structurally towards more stable state whenever atoms attain noticeable mobility. As the most structurally sensitive property the electrical resistivity of these samples was used to follow the relaxation process from room temperature to 673 K. To complete the investigation of structural relaxation the electrical resistance of as-quenched, annealed and about twenty years aged $Ni_{36.5}Zr_{63.5}$ samples was measured in the temperature range from 77 K to 275 K. The obtained results were presented graphically.

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1. Introduction

Amorphous TE-TL alloys (TL is the late and TE the early transition metal in the Periodic System) have been extensively studied in the recent decades and interest in these alloys increased after discovery of Zr-base bulk metallic glasses [1]. Wide glass forming range in these alloys enables the study of the changes in physical properties on compositions. Metallic glass possesses a frozen-in structural disorder. An amorphous sample is metastable in two ways, in respect to the so-called ideal amorphous state and also to its crystalline state [2]. During annealing it relaxes structurally. This relaxation process at low temperatures causes some local ordering, but for longer time and at higher temperature crystallization can be noticed. Crystallization is always accompanied by changes in physical properties such as heat capacity, electrical resistivity, volume and magnetic properties [3]. Crystallization is the final stage of annealing and it causes the abrupt falling of electrical resistance. In this paper we have investigated the relaxation of as quenched and about twenty years aged metallic glass $Ni_{36.5}Zr_{63.5}$ by monitoring of electrical resistance.

2. Experimental

The $Ni_{36.5}Zr_{63.5}$ (at %) alloy was made by melting the required amounts of 99.995% Zr and Ni in an argon arc furnace. The ribbons of metallic glass about 35 μm thick and 1 mm wide were formed by fast cooling on rapidly rotating copper drum (melt-spinning method). The measurement of electrical resistance from 77 K to 275 K was made by ac four-point probe method and the scheme of the setup is presented in Fig. 1a. In order to provide a gradual and continuous temperature change from liquid nitrogen temperature to 275 K, quartz granules, earlier cooled in liquid nitrogen, were carefully thrown into the Dewar with liquid nitrogen, the sample holder immersed into it and heated by evaporation of liquid nitrogen. The equipment with sample holder is shown in Fig. 1b. The ac referent signal from lock-in amplifier passes through the sample and current contacts are labeled as C1. Signal has a constant intensity of 1 mA and from contacts C2 voltage was measured by lock-in amplifier and registered by software specially made for this occasion.

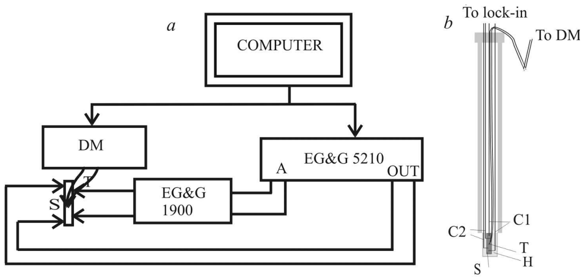

Fig. 1. (a) Scheme of experimental setup for electrical resistance measurement by ac method: EG&G 5210 — the phase sensitive detector (lock-in amplifier); DM-Keithley multimeter for temperature measurement; T-thermocouple; EG&G1900-transformer; S-sample. (b) The sample holder-H.

Monitoring of electrical resistance during the annealing from room temperature to 673 K was obtained by dc four-point probe method. Setup for dc measurement of electrical resistance is shown in Fig. 2. Sample, set in a mica holder and supplied with good contacts of four wire pressure was heated by an alumina heater. The

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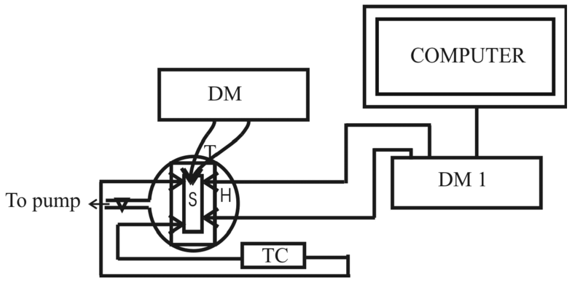

Fig. 2. Scheme of experimental setup for electrical resistance measurement by dc method: DM-Keithley multimeter 2002; DM1-Keithley multimeter 2000 with installed Scan card; T-thermocouple; TC-thermostatic chamber with voltage regulation; S-sample; H-heater.

heating rate was controlled in a wide range by Process controller ESM-4450. The experimental data were continually recorded by use of TEST POINT software.

3. Results

The ac four-probe method was used to measure the electrical resistances of as-quenched and about twenty years aged samples from 77 to 275 K. Furthermore, we have annealed these two samples at the temperatures in the range from room temperature to 673 K. Upon heating from room temperature to 673 K at heating rate 60 K/min (Fig. 3), the electrical resistance of both samples increased for approximately same amounts about

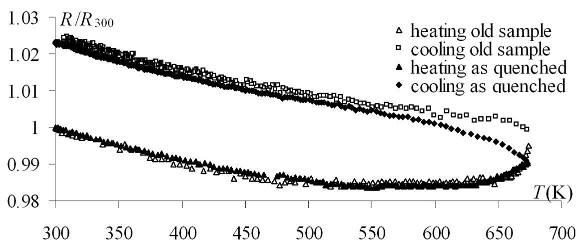

Fig. 3. Normalized electrical resistance for as quenched and about twenty years aged samples during annealing versus temperature. Heating rate was 60 K/min.

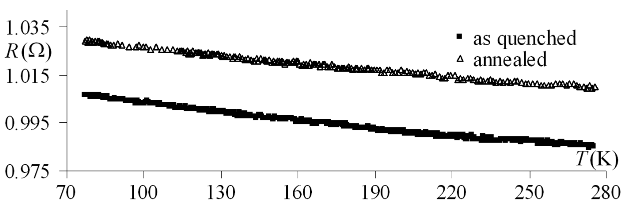

Fig. 4. Electrical resistance of as quenched and annealed sample versus temperature.

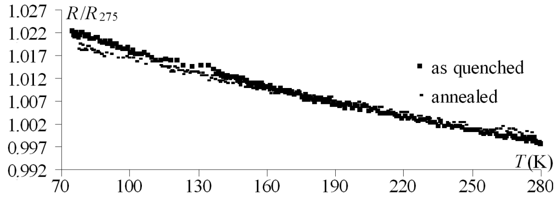

Fig. 5. Normalized electrical resistance of as quenched and annealed sample versus temperature.

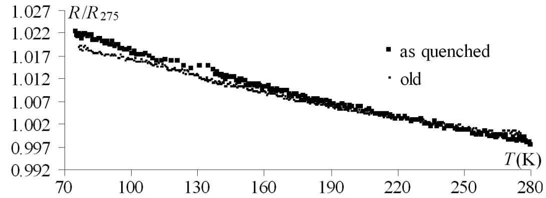

Fig. 6. Normalized electrical resistance of as quenched and about twenty years aged sample versus temperature.

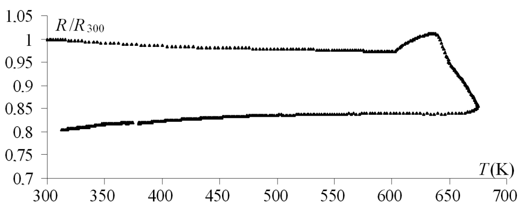

Fig. 7. Normalized electrical resistance for as quenched sample during annealing with crystallization versus temperature. Heating rate was 60 K/min to 550 K and then 3 K/min. Crystallization is accompanied by the falling of electrical resistance. Lower part of curve represents the cooling process.

2.5% in the temperature interval from 600 to 673 K and retained that increasing in the whole temperature interval during the cooling. It has to be pointed out that we have not noticed any significant difference in the behaviours of the as-quenched and about twenty years aged samples. After annealing of the as-quenched sample we have also measured the electrical resistance of annealed sample from 77 K to 275 K (Fig. 4). For the as-quenched sample and the old sample, the calculated values for the temperature coefficients of resistance $\mathrm{d}R/R\mathrm{d}T$ at room temperature are approximately equal i.e., -1.20×10^{-4} K^{-1} and for the annealed sample -1.18×10^{-4} K^{-1}. The comparisons of the temperature dependence of normalized resistance for as-quenched, annealed and old samples are presented in Fig. 5 and Fig. 6. The annealed samples have exposed elasticity up to the crystallization.

The final stage of annealing is crystallization in samples and this is accompanied by an abrupt falling of electrical resistance. For comparison, the annealing to crystallization of as-quenched sample $Ni_{36.5}Zr_{63.5}$ is presented in Fig. 7. This process is irreversible and the temperature of crystallization depends on heating rate [4]. After the crystallization all the samples became fragile.

4. Conclusions

We investigated and compared the relaxation in as--quenched and twenty years aged metallic $Ni_{36.5}Zr_{63.5}$ glass. By analyzing the graphically obtained results of temperature dependence of electrical resistance of the both samples, we noticed no difference in their behaviour. For the amorphous $Ni_{36.5}Zr_{63.5}$ sample being held at room temperature for almost twenty years the properties have not been changed. That could be taken as a reliable sign that the structure did not changed. But, perhaps twenty years are insufficient time for ageing of amorphous $Ni_{36.5}Zr_{63.5}$. From this we can conclude that the amorphous $Ni_{36.5}Zr_{63.5}$ alloy is a very stable system.

The crystallization temperature for the investigated amorphous alloy is relatively high and depends on heating rate, which was in our experiment 60 K/min to 550 K and then 3 K/min.

The calculated temperature coefficients of resistance at room temperature for amorphous $Ni_{36.5}Zr_{63.5}$ samples are negative, the obtained values for as-quenched and aged samples at room temperature are approximately equal i.e., -1.20×10^{-4} K^{-1} and for the annealed sample -1.18×10^{-4} K^{-1}.

After annealing upon to the crystallization temperature samples preserved their elasticity, which disappeared after crystallization and all the samples, became fragile.

Acknowledgments

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