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Electrical and thermal conductivities of rapidly crystallized Cu-Zr alloys: The effect of anharmonicity

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ABSTRACT

We present a comprehensive study of electrical and thermal conductivities, specific heat and magnetic susceptibility of rapidly crystallized $Cu_{100-x}Zr_x$ (x = 20–90) alloys. X-ray diffraction analysis has revealed that all the prepared compositions had strongly textured and distorted crystal structures. Different monoclinic and other non-equilibrium phases were detected in the case of glass-forming samples, whereas the alloys without a tendency to form glassy state show almost equilibrium phase content. Metallic type of electrical conductivity and the Kondo anomaly were observed for all the examined samples. It was found that the electrical resistance data cannot be adequately described within the standard Bloch–Grüneisen theory. We use the Debye characteristic temperature as a linear function to fit the electrical conductivity accurately. The composition dependence of the electron density of states at the Fermi level (DOS) has been extracted from room temperature magnetic susceptibility. We found that the glass-forming alloys are characterized by abnormally large values of DOS, which are comparable to those of glassy analogues. Noticeable anharmonic contribution in total specific heat has been revealed for all the studied compositions. In order to estimate the effect of anharmonicity in the system under consideration, we analyzed composition and temperature dependencies of the studied thermal characteristics related to the Grüneisen coefficient. Basing on the results obtained in this study we propose a phenomenological concept to explain abnormal behavior of physical properties of glass-forming Cu-Zr alloys within the standard solid state theory taking into account anharmonic effects.

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1. Introduction

Cu-Zr is one of the best glass-forming systems among binary metal-metal type alloys. The most important feature of these alloys is ability to form bulk amorphous ingots at reduced cooling rates [1–7]. It is well known that the glass thin films of Cu-Zr can be produced over the wide composition range of 30 – 70 at % Zr using standard spinning technique. Whereas the bulk amorphous ingots can be prepared only at narrow concentration intervals called as “pinpoint” compositions [1,4–8]. There are a lot of works devoted to synthesis of these metallic glasses, investigations of their different properties and crystallization kinetics. A number of thermodynamic criteria have been discovered to estimate glass-forming ability of the system [7–11]. Nevertheless, some questions on mechanisms of glass formation in these materials remain to be answered. As rule, the alloys in amorphous state are considered to resolve these issues. We believe that study of the Cu-Zr alloys in crystalline state may also give new insights into understanding of the nature of their glass-forming ability. As far as we know, there are only few reports devoted to the subject [12–15]. Moreover, physical properties of crystalline Cu-Zr alloys have not been systematically investigated yet.

The main purpose of this work is to provide a comprehensive characterization of rapidly crystallized Cu-Zr alloys comparing them to the corresponding amorphous materials in order to determine new aspects regarding glass formation in this metallic system. To achieve this purpose, we studied electrical and thermal conductivities, heat capacities and magnetic susceptibilities of arc-melted $Cu_{100-x}Zr_x$ (x=20–90) alloys. Analyzing the experimental data sets, we have revealed correlation between non trivial behavior of these properties and glass-forming ability of the alloys.

2. Experiment

A series of the Cu-Zr alloys containing 20–90 at.% of zirconium was prepared by arc-melting the appropriate amounts of pure

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metals (> 99.98 wt.%) under helium atmosphere. The samples with the nominal compositions of $Cu_{100-x}Zr_x$ (x= 20, 21.5, 25, 32, 34, 36, 36.5, 37, 39, 41.2, 44, 46, 48, 50, 52, 54, 60, 64, 66.6, 70, 72.5, 75, 80, 90, 95, 100) were synthesized. The ingots were re-melted at least five times to ensure homogeneity. In order to prepare the rapid crystallized polycrystalline samples, the melts were cooled down on the arc-furnace copper mold at a cooling rate of about 100 K/sec.

The crystal structure and phase content of the samples were studied using X-ray diffraction analysis (XRD) with a Shimadzu XRD-7000 diffractometer. The XRD patterns were obtained using CuK_α - radiation, graphite monochromator, the 2Θ range of 25–100 deg, step size of 0.04° and a count time of 3 seconds / step. The unit cell parameters were calculated using the RTP software [16].

The alloy compositions as well as the concentrations of iron, cobalt and nickel impurities were controlled by atomic-emission method using a SpectroFlame Modula S analyzer.

Electrical resistance and magnetic susceptibility of the samples were measured using a Cryogenic VSM CFS-9T-CVTI equipment. Standard four-probe method and vibrating sample magnetometry were applied to determine the electrical and magnetic characteristics of the alloys, respectively. To perform the resistance measurements we used a Keithley K2400 multimeter as a source of direct current (DC), and a Keithley K2182 nanovoltmeter for recording the voltage data. The magnitude of DC was chosen to be 100 mA. The samples for the resistivity investigations were cut into rectangular bars with sizes of length × width × height, 8 mm × 3 mm × 3 mm, respectively. Soldering by pure indium was used to achieve the electrical contacts between the samples and the resistivity probe holder. The electrical resistivity data as a function of temperature were collected during continuous cooling at the rate of 0.7 K/min in the temperature range of T=4–300 K. The relative error for the conductivity measurements was estimated to be about 0.2%.

The magnetic studies were performed at room temperature. We obtained the isothermal magnetizations applying external magnetic fields in the range of ± 5 T. In order to calculate the static magnetic susceptibility of the samples, we fitted the isotherms with linear functions using the least squares method. The relative error for the magnetic measurements was less than 15%. The noticeable uncertainty was caused by weak magnetization of the alloys.

Temperature dependencies of thermal conductivity λ(T) of the samples were calculated as the product of thermal diffusivity a(T), specific heat C_p(T) and density d(T). The thermal characteristics (thermal diffusivity, specific heat) were determined by laser flash method (LFA) using a Netzsch LFA 457 device in the temperature interval of T=300–500 K under vacuum with the residual pressure of 0.1 mPa. The measurements were carried out in stepwise manner with the step of 25 K and the isothermal exposition of 15 minutes at each temperature. The specific heat capacity of the alloys at constant pressure (C_p) was calculated using standard comparison method [17]. The hydrostatic weighing was used to measure density of the alloys. The changes of densities of the samples with temperature were taken into account using volume thermal expansion coefficient. The last was estimated from the linear thermal expansion data measured with a Netzsch 402CD dilatometer. The temperature dependence of the density d(T) was estimated with the expression: $d(T)=d_o/(1+3\alpha T)$, where d_o is the density at room temperature and α is the coefficient of linear expansion. The uncertainties for the thermal diffusivity, specific heat and thermal conductivity values of the alloys were ± 1%, ± 3% and ± 5%, respectively.

3. Results and discussion

3.1. Structural analysis

According to XRD analysis, exclusively crystalline structures were revealed in the prepared alloys (Fig.1). As seen in the Fig. 1, Bragg reflections in XRD patterns of the alloys are relatively broad. It can be explained by strong structure disorder due to high density of lattice imperfections. Such structure is expectable for the rapidly cooled alloys with competition of different structures, especially for the glass-forming compositions. The results of structural analysis of all the examined compositions (phases detected and lattice parameters) are collected in Table 1. All the investigated compositions can be divided into several groups: first – the Zr-rich samples characterized by two phases of α-Zr and tetragonal intermetallic compound $CuZr_2$, second – the alloys whose phase content consists of the $CuZr_2$ and different monoclinic CuZr phases, third – the alloys group characterized by the presence of the orthorhombic $Cu_{10}Zr_7$ phase and various non-equilibrium intermetallic compounds, and four – the Cu-rich compositions ($Cu_{75}Zr_{25}$, $Cu_{78.5}Zr_{21.5}$, $Cu_{80}Zr_{20}$), where only the intermetallic $Cu_{51}Zr_{14}$ with a hexagonal structure was identified. It is obvious that this phase not only exists as a stoichiometric compound, but may also form a solid solution. The similar single-phase structure was found in $Cu_{56}Zr_{44}$ and $Cu_{58.8}Zr_{41.2}$ compositions. Since there is no impurity phases peaks in the diffraction patterns of $Cu_{56}Zr_{44}$, $Cu_{75}Zr_{25}$ and $Cu_{80}Zr_{20}$, we can assume that a solid solution is probably formed in these compositions.

It was found that the $CuZr_2$, $Cu_{10}Zr_7$ and $Cu_{51}Zr_{14}$ phases revealed in the alloys are strongly textured. In contrast, there is no preferred orientation of crystalline grains in the observed monoclinic structures. It is interesting to note that only monoclinic phases [18] were identified in equimolar sample of $Cu_{50}Zr_{50}$. Besides, unusual primitive monoclinic structure we have found in $Cu_{40}Zr_{60}$ composition. This phase has previously been recognized by the authors [19] as the second martensitic phase in rapidly cooled CuZr compound. Instead of the equilibrium $Cu_{51}Zr_{14}$ phase, Cu_8Zr_3 intermetallic compound [20] has been detected in some Cu-rich samples, see Table 1. Moreover, in some specimens we see the number of phases more than that predicted by the Gibbs' phase rule. Such non-equilibrium structure state is expectable for the glass-forming alloys. Whereas the samples without a tendency to form glassy state show almost equilibrium phase content expected in the phase diagram of Cu-Zr system [21]. In order to verify the phases detected by XRD, some Cu-Zr compositions were examined with an electronic microscope Carl Zeiss EVO 40. Scanning electron microscopy (SEM) and Energy-dispersive X-ray analysis (EDX) have shown that the observed crystalline phases correspond to those found by XRD. No unusual features in the alloys we observed by SEM. The SEM images and some comments for it are provided in Supplementary material.

3.2. Electrical resistance

Let us consider the resistivity data first. As seen in Figs. 2 and 3, the $\rho(T)$ dependencies have a non-linear behavior with a positive slope in the temperature range of 20–300 K. At temperatures lower than 20 K, Kondo-like anomaly is observed for all the samples. According to the results of chemical analysis, the initial zirconium and copper metals as well as prepared samples contain uncontrollable impurities of iron (up to 200 ppmw), cobalt (up to 20 ppmw), nickel (up to 450 ppmw) and manganese (up to 20 ppmw). Since the samples under investigation actually have these magnetic impurities into the host non-magnetic matrix,

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