

ELECTRON TRANSPORT PROPERTIES OF AMORPHOUS ALLOYS $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{M}_5$ (M = Nb, Si)

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Abstract. The amorphous alloys $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{M}_5$ (M = Nb, Si) are precursors for bulk amorphous materials with broad supercooled region. Temperature dependence of electrical resistivity and thermoelectric power in a broad temperature range are analyzed in a framework of the Boltzmann and localization models. The low temperature variation of electrical resistivity reveals a strong quantum interference effect observable even above the Debye temperature. Additional influence of the phonon assisted electron tunneling and hopping processes on electrical resistivity and thermoelectric power at high temperatures are discussed. The stronger localization effects are observed in Nb than in the Si containing alloy, which is related to the electronic structure of these elements. An influence of electron structure on thermal stability of alloys is also observed.

1. INTRODUCTION

The ternary alloys Ni-Ti-Zr are materials which satisfy an empirical rule to have high glass forming ability (GFA) [1-3]. Yi *et al.* [4] show that Si atoms improve this effect. The authors related the higher GFA of these alloys with large heat mixing Si with Ni, Ti and Zr.

We investigate the influence of Nb and Si atoms on electron transport phenomena since the electrical resistivity and thermoelectric power are known to be sensitive to the atomic arrangement and electronic structure of amorphous metallic alloys [5,6]. In particularity we correlate the electron structure of Ni-Ti-Zr-M alloys with GFA.

2. EXPERIMENTAL

Amorphous alloys $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{M}_5$ (M = Nb, Si) were prepared by copper roller melt spinning method in argon atmosphere. The amorphicity of the samples was checked by means of X-ray diffraction. The

electrical resistivity was measured in a range 20 - 1000K by DC four-probe method with accuracy of 0.1%. The thermoelectric power was measured by differential method [7]. The measurements were made in vacuum of 10^{-6} hPa. These techniques were supplemented by DSC measurements. The heating rate during all the measurements was 20 K/min.

3. RESULTS AND DISCUSSION

3.1. Electrical resistivity

At room temperature the amorphous $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{M}_5$ alloys exhibit a high resistivity of 255 and 245 $\mu\Omega\text{cm}$ for alloys with Nb and Si, respectively. The electrical resistivity is a decreasing function of temperature in a whole broad temperature range studied (Fig. 1). Such a temperature variation is in contrast to majority of metallic alloys [8]. The detailed resistivity analysis presented below, enables to distinguish three temperature intervals with different

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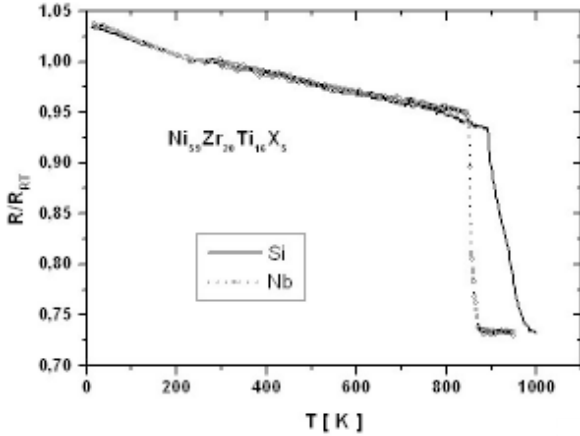


Fig. 1. Temperature dependence of electrical resistivity normalized to the room temperature value.

temperature dependencies. Above room temperature the $\rho(T)$ dependence may be approximated by the linear function with negative temperature coefficient of resistivity (TCR) equal to -0.93 to $-1.12 \cdot 10^{-4} \text{ K}^{-1}$ for Nb and Si, respectively (Fig. 1). Below room temperature a deeper inspection of low temperature resistivity data reveals two temperature intervals with different temperature dependencies, which are discussed first.

A correlation between the high electrical resistivity and the negative temperature coefficient of resistivity was first reported by Mooij [9]. Such a correlation was initially interpreted within a framework of extended Ziman theory assuming that it occurs in alloys when the $2k_F$ vector is close to the maximum of structural factor k_p [8]. However, it was found that the experimentally determined resistivity decrease is often much stronger than that one predicted for Debye Waller factor for the main peak in the structural factor. Then the more plausible explanation of Mooij rule, based on incipient localization of electrons, was proposed by Girvin and Jonson for highly disordered metals [10]. In this picture, the interference of elastically backscattered electronic wave functions causes the resistivity increase at low temperature. Since the inelastic scattering increases at higher temperatures, the quantum interference is suppressed.

Thus, the electrical conductivity $\sigma = 1/\rho$ of high resistivity alloys can be written as [11]:

$$\sigma = \sigma_B - \Delta\sigma_{el} + \Delta\sigma_{in}, \quad (1)$$

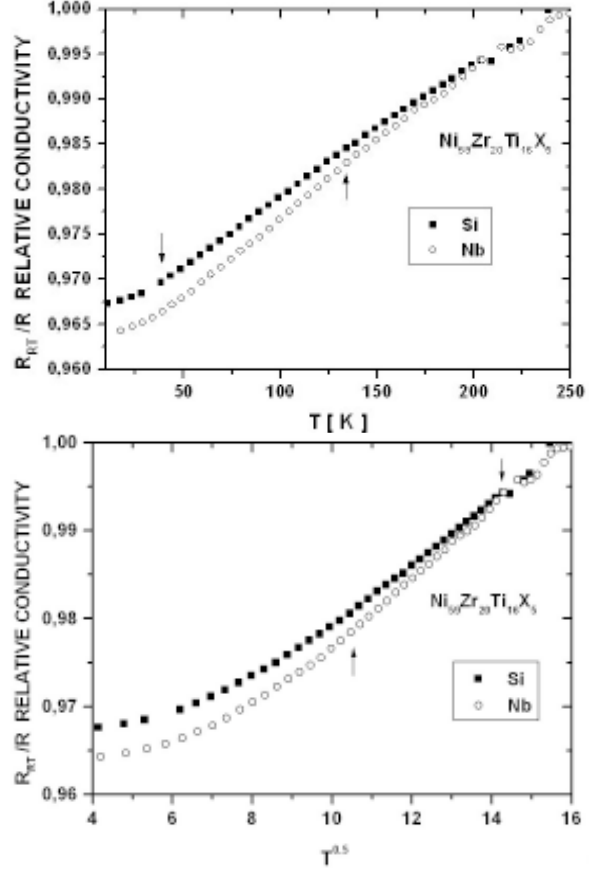


Fig. 2. Electrical conductivity normalized to room temperature value as a function of temperature (a) and of square root of temperature (b). Arrows indicate the fitting intervals.

where σ_B is the Boltzmann conductivity and $\Delta\sigma_{el}$ describes a reduction in conductivity due to a constructive interference of backscattered wave functions. The $\Delta\sigma_{in}$ term describes the decay of the interference at enhanced temperatures. A sum of the last two terms is equal to:

$$\Delta\sigma(T) = \frac{Ce^2}{3\pi^2\hbar} \left[\frac{1}{l(T)} - \frac{1}{\left(\frac{l_{in}(T)l(T)}{3}\right)^{0.5}} \right], \quad (2)$$

where l and l_{in} are elastic and inelastic mean free paths, respectively.

The low resistivity amorphous alloys exhibit usually a resistivity ρ_B of the order of $100 \mu\Omega\text{cm}$ and are described by the Boltzmann model. Thus, we expect that the high resistivity $\rho(T)$ of the alloys

studied is due to the additional $\Delta\rho_{el}$ term, which is responsible for the enhancement of electrical resistivity, when inelastic scattering at very low temperature is negligible. In high resistivity alloys elastic mean free path $l(T)$ is very small and comparable with atomic spacing. Then the first term in Eq. (2) corresponding to weak localization becomes relatively large and plays a role even at high temperatures. When the temperature raises, the competitive inelastic scattering grows up and destroys the quantum interference effect. As the elastic mean free path $l(T)$ in amorphous alloys weakly depends on temperature, the temperature dependence of $\Delta\rho(T)$ is determined mainly by the $l_{in}(T)$ term.

The temperature dependence of inelastic mean free path for electron-phonon scattering in disordered metals is given by [12]

$$l_{in} \propto T^{-2} \text{ for } T \leq \Theta/3, \quad (3a)$$

$$l_{in} \propto T^{-1} \text{ for } T \geq \Theta/3, \quad (3b)$$

Thus, one arrives to the temperature dependence of conductivity as follows:

$$\Delta\sigma \propto T \text{ for } T \leq \Theta_D/3, \quad (4a)$$

$$\Delta\sigma(T) \propto T^{0.5} \text{ for } T \geq \Theta_D/3, \quad (4b)$$

Our experimental conductivity results are presented in Figs. 2a and 2b as a function of T and $T^{0.5}$, respectively. These plots confirm that the dependencies 4a and 4b are well obeyed in ranges 40 to 130K and 130 to 200K, respectively. Taking into account that a switch off between the 4a and 4b dependencies occurs at $\Theta_D/3$ one finds that Θ_D is about 390K, which is a reasonable value.

Above the room temperature the electrical resistivity data $\rho(T)$ plotted in Fig. 1, may be best fitted to the linear relation between resistivity and temperature with the negative temperature coefficient of resistivity. The correlation factor 0.995 is found for the interval from 300 up to 830K. At elevated temperatures besides the scattering mechanisms described above some other ones may also come into a play. For the phonon assisted tunneling of d electrons [13] the rate of tunneling increases both with the increasing structural disorder as well as with the raising temperature. This mechanism leads to the electrical resistivity suppression at elevated temperatures. The second plausible mechanism may be the electron hopping. Since hopping is a thermally activated process, in this case we can predict exponential dependence on T . Unfortunately

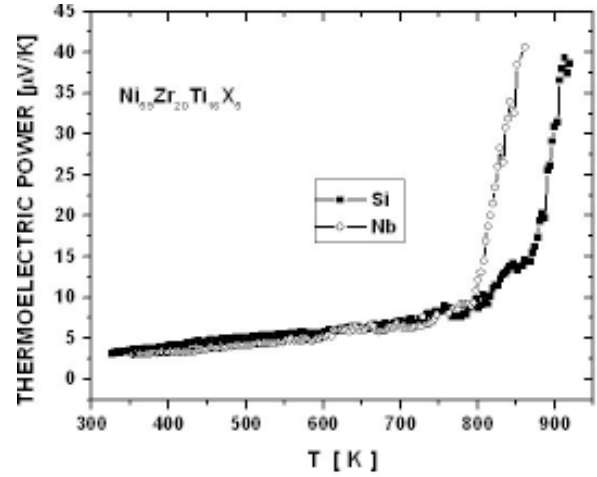


Fig. 3. Temperature dependence of thermoelectric power.

the conduction mechanisms are not elaborated enough for the high electrical resistivity alloys. Thus, one may expect that further theoretical studies will elucidate, how the interplay of the above listed scenarios (inelastic scattering, localization, tunneling and hopping) may result in the linear decrease of electrical resistivity at elevated temperatures.

The abrupt drop in resistivity (Fig. 1) above 846 and 889K for Nb and Si, respectively, is due to crystallization process and precipitation of crystalline phases: $Ni_{10}(Zr, Ti)_7$ and $Ni(Ti, Zr)$ [4]. The threshold temperatures obtained from $R(T)$ dependence agree well with our DSC data and those reported by Yi [4].

3.2. Thermoelectric power

The thermoelectric power (TEP) of investigated alloys (Fig. 3) is positive and increases in amorphous phase almost proportionally with temperature for both the alloys. The room temperature values of TEP increase from 2.9 to 3.3 $\mu\text{V/K}$ when passing from Nb to Si. The abrupt increase of TEP above 800K is due to crystallization processes and has been observed in a variety of alloys [5].

By analogy to Eq. (1), the value of TEP for high resistivity alloys can be written as [11]:

$$S = S_B + \Delta S_{el} - \Delta S_{in}, \quad (5)$$

where ΔS_{el} and ΔS_{in} terms correspond to elastic and inelastic scattering, respectively. The S_B term corresponds to the Boltzmann thermopower.

For temperature above Debye temperature, when electron phonon mass enhancement effect is negligible, these terms become:

$$S_B = (\pi^2 k^2 T / 3e) (\partial \ln \sigma_B / \partial E), \quad (6)$$

$$\Delta S_{el} = (\Delta \sigma_{el} / \sigma) (S_B + A \partial \ln l / \partial E), \quad (7)$$

$$\Delta S_{in} = (\Delta \sigma_{in} / \sigma) [S_B + 1/2A(\partial \ln l / \partial E + \partial \ln l_{in} / \partial E)], \quad (8)$$

Thermoelectric power in low resistivity amorphous alloys ($\rho < 150 \mu\Omega\text{cm}$) is frequently found to be negative, usually from about -1 to -8 $\mu\text{V/K}$ [8]. On the other hand, thermoelectric power in high resistivity alloys is found to be positive, as observed for the alloys studied and reported for other alloys [8]. A difference in TEP variation of the low and high resistivity alloys may be explained when analyzing the contributions to Eq. (5). As it is well known that $\Delta \sigma_{el} > \Delta \sigma_{in}$, then $\Delta S_{el} > \Delta S_{in}$, and the thermoelectric power is affected by the incipient localization mainly via the term ΔS_{el} , which adds to the bare S_B value. In analogy to the Mooij correlation Kaiser [11] proposed that localization contribution to thermoelectric power $\Delta S \propto \rho^2$.

Therefore, the TEP value shifts from the bare S_B by ΔS_{el} towards positive S . Taking into account the temperature dependencies in Eqs. (6) and (7), one arrives to the proportionality between S and temperature. The nonlinearities of S may be caused by the last term in Eq. (8) ($(\partial \ln l_{in} / \partial E)$) since l_{in} varies with temperature. Deviations from $S(T)$ linearity do not exceed a few percent and are hardly observed in experiment. If the incipient localization is accompanied by hopping, then TEP becomes even more positive due to the additional term $\Delta S_h \propto \rho^{0.5}$ [14].

The experimental data of $S(T)$ for amorphous alloys (Fig. 3) were fitted using the T and $T^{0.5}$ contributions. Despite of the relatively high correlation coefficients (0.99 for Si and 0.95 for Nb containing alloys) it is hard to conclude, if the localization or hopping mechanism dominates. The relatively lower correlation factor for the Nb containing alloy reveals a stronger nonlinearity than for the Si case. Moreover, the higher values of resistivity prove a larger localization for this alloy. This may be related to the electronic $4d^4 5s^1$ configuration of Nb transition atom, whereas Si is a metalloid with $3s^2 3p^2$ structure. The sp electrons are known to enhance conductivity being weakly bonded to ions. These electrons fill the d states of transition met-

als and stabilize the amorphous structure [15]. Such a tendency is confirmed by the broader supercooled region and by the threshold crystallization temperature, which is 40K higher for the Si than for the Nb containing alloy.

4. CONCLUSIONS

The multi-element amorphous alloys Ni-Ti-Zr-Nb and Ni-Ti-Zr-Si are the high resistivity solids with the negative temperature coefficient of resistivity. The absolute values and temperature variation of electrical resistivity prove that the incipient localization quantum interference effect occurs even above the Debye temperature. At elevated temperatures the additional localization effects, like the phonon assisted tunneling and hopping processes can be seen. Localization is stronger for Nb than for Si containing alloy, what is due to electron structure of these atoms. The weaker electron localization in the Si containing alloy enables the stronger interatomic bonding, which stabilizes the amorphous structure and broadens the supercooled region.

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