Formation of the temperature dependence of the electrical resistance of the Ti$_{67}$Al$_{33}$ intermetallic

D K Palchaev$^1$, Zh Kh Murlieva$^{1,2}$, M Kh, Rabadanov$^1$, M E Iskhakov$^1$, R M Emirov$^1$, S Kh Gadzhimagomedov$^1$, Z M Omarov$^3$

$^1$Dagestan State University, Makhachkala, Russia
$^2$Dagestan State University of National Economy, Makhachkala, Russia
$^3$Institute of Physics of Dagestan Federal Research Center RAS, Makhachkala, Russia

E-mail: dairpalchaev@mail.ru

Abstract. On the basis of experimental studies (in situ) of the electrical resistance and thermal expansion of the Ti$_{67}$Al$_{33}$ intermetallic compound in a metastable and stabilized state, the relationship between the temperature coefficients of athermal electrical resistance (TCAR) and thermal expansion (TCE) is shown. This relationship is universal because it is preserved under transitions from one state to another. The anomalies associated with the competition between the metallic and semiconducting types of conductivity observed in the TCAR, TEC and heat capacity curves coincide in temperature.

1. Introduction

It is generally accepted that the finiteness of electronic conductivity due to scattering by thermal vibrations of lattice atoms is mainly associated with an increase in the amplitude of their vibrations. In this case, the effect of vibration anharmonicity, which leads to a change in the equilibrium interatomic distance, is neglected. The decisive role of thermal expansion in the processes associated with the formation of the temperature dependence of the electrical resistance $\rho$ in condensed media was pointed out in [1-5]. Based on the analysis of experimental data on $\rho(T)$ and the coefficient of thermal expansion $\beta(T)$ of metals, [1-5], the linear relationship between $\rho(T)$ and the thermodynamic complex $\beta(T)T$ was shown:

$$\rho(T) = \rho_0 + \rho^* \beta(T)T, \quad (1)$$

where $\rho_0$ is the contribution to the electrical resistance at $T = 0$K; $\rho^* \beta(T)T$ is the contribution due to thermal excitation of various subsystems (atomic, magnetic) of pure metals and alloys; $\rho^*$ — the characteristic value of the electrical resistance for each phase of the conductor within the phase existence. Note that $\beta(T)$ of metals in the solid state from ~ 0K to the melting temperature $T_m$ changes by four or more orders of magnitude, while the temperature changes by no more than three orders of magnitude. According to (1), with changes in $T$ and $V(T)$ for pure metals (at $\rho_0 = 0$), the contribution due to elementary excitations of the electronic and phonon subsystems is represented as:

$$\rho(T,V) = \rho^* \beta(T)T. \quad (2)$$

The athermal part of the resistance, according to (2), is determined by $\beta(T)$:
\[ \rho(T,V)/T = \rho^* \beta(T). \]  

(3)

For conductors with a mixed type of bond, for example, the Ti\textsubscript{67}Al\textsubscript{33} intermetallic compound, as was shown in [5], the temperature coefficient of the resistance correlates with the athermal coefficient of thermal expansion \((\beta(T)/T)\). This is due to the fact that both metallic and semiconducting types of conductivity are observed [1] in this intermetallic compound. Detailed analysis showed that for Ti\textsubscript{67}Al\textsubscript{33} a closer relationship exists between the temperature coefficient of athermal resistance and the coefficient of thermal expansion. For intermetallides with a mixed type of bond, one should not expect a linear correlation, such as in (1). However, one should expect the manifestation of features on the temperature dependences of the coefficient \((\alpha_R = dR/RdT)\) of athermal resistance \((R = \rho/T)\) and \(\beta(T)\), associated with competition between the types of conductivity.

Figure 1a shows the temperature dependences of the specific heat and CTE for titanium and aluminum, which are determined by the peculiarities of the excitations of the electronic and phonon subsystems. They are of the same character. According to Grüneisen, the ratio of these parameters can be considered constant if the volume change is neglected. In practice, this ratio is highly temperature dependent. However, according to the theory, it is believed that thermal expansion is proportional to the heat capacity in each equilibrium state in a quasi-static process. Figure 1b shows the temperature dependences of the athermal components of the heat capacity \(C(T)/T\) and CTE. As seen, for pure Ti and Al at the same temperatures of 90 K and 100 K, respectively, extrema are observed in the temperature dependences \(C(T)/T\) and \(\beta(T)/T\). The similar coincidences of temperatures at the extrema of the dependences \(C(T)/T\) and \(\beta(T)/T\) on temperature take place for all pure metals. Based on this, one can assume these temperatures as an characteristic parameters for each metal. They seem to divide the temperature range into high and low temperatures. According to the theory, this role belongs to the Debye temperature \(T_D\), which is selected so that the interpolation expressions of Debye and Grüneisen describe well the temperature dependences of heat capacity and resistance, respectively. Note that the \(T_D\) values obtained as a result of the fitting procedures are typically different.

![Figure 1](image-url)

**Figure. 1.** Temperature dependences of heat capacity and CTE [6] (a) and athermal components of heat capacity and CTE (b).
The temperature dependences of the athermal values of the heat capacity and CTE, as in (3), indicate a significant role of $V(T)$, which, along with the change in temperature, characterizes the state of the condensed system. A change in the volume by fractions of a percent significantly rearranges the electronic subsystem of interacting polarized [7] atoms, as a result of a change in the energy spectrum specified by the reciprocal lattice parameter.

2. Experimental details
The polycrystalline intermetallic compound Ti 67 at.% – Al 33 at. % was made of grade titanium (99.8%) and aluminum (99.995%) in a water-cooled copper crucible using argon-arc smelting of a consumable electrode. As the result, the sample contained traces of copper. Combined $\rho(T)$ and linear CTE measurements of Ti$_{67}$Al$_{33}$ were carried out in situ in the range from 300 to ~ 1000 K on the same sample under the same conditions by respectively the four-probe and the quartz dilatometer methods.

3. Results and discussion
In works [8-10] it is shown that in the high-temperature region for single-crystal intermetallic compounds based on Ti and Al with the Ti$_3$Al structure the values $\rho > 2 \times 10^{-6} \text{Ohm}\cdot\text{m}$, and of the temperature coefficient of resistance (TCR) has a semiconducting character. In the same temperature range the microcrystalline Ti$_67$Al$_{33}$ has $\rho < 2 \times 10^{-6} \text{Ohm}\cdot\text{m}$ and demonstrates a competition between metallic and semiconducting types of conductivity [1,11]. This is caused by [1,11] diffusion phase transitions in Ti$_{67}$Al$_{33}$ taking place because of the large area of crystallite boundaries and the presence of Ti vacancies in crystallites occurring due to violation of the stoichiometry of the Ti$_3$Al phase.

Figure 2 shows the dependences of the temperature coefficients of athermal resistance $\alpha_R$ and TEC for the Ti$_{67}$Al$_{33}$ intermetallic compound in the high temperature range, where $\rho(T)$ increases linearly for ordinary metals. Before the measurements the investigated sample was in a metastable (tempered) state. In the course of measurements, it was passed into a stabilized state, as evidenced by the disappearance of hysteresis on the $\rho(T)$ and $\beta(T)$ dependences upon heating and cooling [1,11] already in the fourth cycle.

![Figure 2](image_url)

**Figure. 2.** Temperature dependences of coefficients of athermal resistance and CTE for tempered (a) and stabilized (b) sample.

Figure 2a shows data on $\alpha_R$ and TEC during the first heating of the sample in the initial metastable state. Figure 2b shows the $\alpha_R$ and CTE data on cooling in the fourth time, when the sample has passed into a stabilized state. Attention is drawn to the changes in the temperature dependences of $\alpha_R$ and CTE before and after ~750K, due to the competition between the metallic and semiconducting types of conductivity. The inset in Fig. 2a shows the presence of the same irregularity on the temperature de-
pendence of the heat capacity as on $\alpha_R$ and CTE in the initial metastable state. This irregularity in the temperature dependences of $\alpha_R$, CTE, and heat capacity decreases when the sample passes into a stabilized state.

4. Conclusion
Data presented in Figures 1 and 2 indicate an importance of the role of $\beta(T)$, and therefore $V(T)$ in the formation of equilibrium (heat capacity) and nonequilibrium (resistivity) properties, both at high and low temperatures. This brings us closer to the possibility of obtaining a simple, like (1), universal expression for establishing the mechanism for the formation of the temperature dependence of the electrical resistance of materials with a mixed type of conductivity.

Acknowledgments
This work was supported by state assignment FZNZ–2020–0002

References
[1] Murlieva Zh Kh, Palchaev DK, Iskhakov M E, et al. 2019. J. High Temp. 57(2) 182–185
[2] Murlieva Zh Kh, Iskhakov M E, Palchaev D K, et al. 2012. J. High Temp. 50(5) 602–610
[3] Kazbekov K K, Murlieva Zh Kh and Palchayev D K 2003 J. Tech. Phys. Letters 29(13) 19–25
[4] Palchayev D K, Murlieva Zh Kh and Kazbekov K 2007 J. High Temperature 45(5) 17
[5] Palchayev D K, Murlieva Zh Kh, Rabadanov M Kh, et al. 2020 J Phys.: Conf. Ser. 1686 012051
[6] Larikov L N, Yurchenko Yu F Structure and properties of metals and alloys (Handbook) Thermal properties of metals and alloys 1985 (Kiev, Naukova Dumka) 437
[7] Slater J C Insulators, semi-conductors and metals 1967 (New York: McGraw-Hill book comp., INC) 647
[8] Veeraraghavan D, Vijay and Vasudevan K 1995 J. Materials Science and Engineering A 192-193(2) 950-956
[9] Li J G, Wei B C, Pan M X, Zhao D Q, Zhang Y G and Chen C Q 1999 J. Materials Science and Engineering A 268 193196
[10] Mooij J H 1973 Phys. Stat. Sol. (a) 17 521
[11] Murlieva Zh Kh, Palchayev D K, Iskhakov M E, et al. 2019 J Phys.: Conf. Ser. 1385 012017