Correlation between the electrical resistivity and thermal expansion of intermetallide Ti₃Al

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Abstract. The results of in situ studies of the electrical resistivity (ρ) and the thermal expansion coefficient (α) of the polycrystalline Ti₆₇Al₃₃ intermetallide in the 300–1000 K range are presented. It has been established that the temperature dependence of the electrical resistance of single-crystal and polycrystalline samples differs significantly, and the corresponding heat treatment of this alloy makes it possible to control the values of the resistivity. It is shown that there is a correlation between the dependences ρ = f(T) and α = f(T) in the indicated temperature range.

Due to the relatively low density, as well as high values of mechanical strength and heat resistance, the operating temperatures of Ti–Al alloys used in aircraft building, rocket building, shipbuilding, etc., reach 650–700 °C. The structure and properties of alloys based on titanium and aluminum, including the α₂–Ti₃Al phase, under various external influences were investigated in [1–9]. The phase α₂–Ti₃Al is characterized by the appearance of an additional directed interatomic bond leading to superstructural ordering, which is destroyed under weak external influences. The lability of this crystal structure leads to diffusion phase transitions associated with the redistribution of atoms along the nodes with an unchanged structure.

As shown in [6, 8], for the single-crystals Ti₇₁.₃Al₂₈.₇, Ti₆₈.₁Al₃₁.₉ and Ti₆₇Al₃₃ with the α₂–Ti₃Al structure [6], as well as the mechanical mixture Ti₆₀Al₄₀ (α₂ + γ) [5] inherent high values of the resistivity. The authors [6] assume that the stoichiometric intermetallic compound Ti₇₅Al₂₅ has the greatest value of electrical resistivity ρ > 2.₅ · 1₀⁻⁶ Om-m. The temperature coefficient of resistance (TCR) is decreased for all these alloys at temperature increasing [5,6,8]. According to Mooij’s rule [8], conductors with values ρ < 2 · 1₀⁻⁶ Om-m have predominantly positive TCR, and with ρ > 2 · 1₀⁻⁶ Om-m – negative. It is noted [5, 6, 8] that there is still no unambiguous understanding of the causes of the anomalous behavior of TCR for single-crystal (ρₛ₋ₐ) and polycrystalline (ρₚₒˡ) intermetallides. Note that in practice it is preferable to use polycrystalline conductors, since their production is less labor-consuming and energy-intensive. For intermetallic compounds, the rule: ρₛ₋ₐ = ρ∥ + 2ρ⊥ = ρₚₒˡ, where ρ∥ and 2ρ⊥ are values of the parallel and perpendicular to the direction of the main axis of the crystal lattice respectively, is violated because of the possibility of the existence of a two-phase state (as a result of diffusion phase transitions), whereas for ordinary metals it is fulfilled, because the grain boundaries do not affect the resistance value. According to the results of our investigations and the data of other

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authors, which we give in [10–14], it is established that the electrical resistivity $\rho(T)$ of classical metallic conductors (with positive TCR) is related linearly to the product of the volumetric coefficient of thermal expansion ($\beta$) by the temperature ($\beta(T)T$)

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

where $\beta = 3\alpha$ (for polycrystalline samples), $\rho_0$ and $\rho^*$ are the residual (at 0 K) and the characteristic phonon electrical resistivity – the maximum possible electrical resistance value for a given metal (or a given phase), determined by the interatomic distance. The linear relation (1) is satisfied for twenty six normal metals and 3d–metals (in ferro– and para– phases) [10, 11], as well as alloys that undergo second–order phase transitions of the “atomic order–disorder” type [12]. The same relationship is established for stainless steels [13] with relatively low static disorder. According to the virial theorem and the second law of thermodynamics, the thermodynamic complex $\beta(T)T$ represents the ratio of the energy dissipated by the excited system to the total energy of the system acquired in the presence of an external field. In fact, it can be regarded as an attenuation coefficient [14] and it actually reflects the effect of an increase in the anharmonicity of vibrations of lattice atoms with temperature. The justification of the regularity (1) within the framework of recognized theories is given in [10, 11, 14]. In this paper, an attempt has been made to establish mechanisms that lead to an anomalous behavior of the electrical resistivity of titanium–aluminum intermetallics with the Ti$_3$Al structure on the basis of in situ studies of the electrical resistivity and the thermal expansion of polycrystalline Ti$_{67}$Al$_{33}$, as well as the correlation between $\rho(T)$ and $\beta(T)T$ for this intermetallic compound.

### 1. Experimental details

A polycrystalline sample of Ti$_{67}$Al$_{33}$ was obtained by induction melting at $\sim$ 1800°C from pure titanium of grade BT1–0 (99.8%) and aluminum of ABP grade (99.995%) with subsequent machining. The sample sizes are $\sim$ 5×5×80 mm, the working section for measuring the potential difference $\sim$ 70 mm. The resistance measurements (4–probe method) and TEC (the quartz dilatometer method) in situ in the range from 300K to $\sim$ 1000 K were performed simultaneously on the same sample, under the same conditions. The limiting error in estimating $\rho$ and $\alpha$ was (0.5–1)% and (5–10)%, respectively. We carried out three series of studies on a sample of Ti$_{67}$Al$_{33}$: the original sample (after melting and cooling in the furnace); a sample, hardened from 1100°C after the first four heating cycles – cooling the original sample; sample after annealing from 1100°C for 40 hours after three cycles of heating and cooling.

### 2. Results and discussion

The results of four cycles of precision measurements of the $\rho(T)$ Ti$_{67}$Al$_{33}$ dependences in the initial state are shown in figure 1. As can be seen, for this (metastable) sample in the first cycle “heating–cooling” hysteresis is clearly manifested, which decreases significantly already in the 2nd and practically disappears in the 4th cycle, which indicates that the sample reaches a stabilized state. The maximum value of the resistance ($\sim$ 2 $\cdot$ 10$^{-6}$ Ohm·m) of our sample is lower than for single-crystal samples of Ti$_{71.3}$Al$_{28.7}$, Ti$_{68.1}$Al$_{31.9}$, and Ti$_{67}$Al$_{33}$ from [5, 6], for which the TCR is negative in the range 200–1000 K. For our sample up to $\sim$ 525 K, the character $\rho(T)$ is metallic, which is replaced by a semiconductor (up to $\sim$ 950 K), and then again – by a metallic one. From figure 1 one can see, that as the proportion of Ti decreases, the values of $\rho$ alloys with Ti$_3$Al structure decrease. This trend is maintained for the mechanical mixture Ti$_{60}$Al$_{40}$ [5], in which the Ti$_3$Al phase predominates. Moreover, for this polycrystalline mixture, a weak negative TCR is observed, as for Ti$_{71.3}$Al$_{28.7}$ and Ti$_{68.1}$Al$_{31.9}$ single crystals from [6]. Such a course of dependence in Ti$_{60}$Al$_{40}$ appears [5] as a result of cooling at a rate of 100°C/s from temperatures above the eutectic temperature. This indicates the ability to control the resistance values in such systems. The lability of the structure of the Ti$_3$Al crystal lattice can
Figure 1. Dependence $\rho = f(T)$: our sample on heating and cooling (in parentheses are the numbers of cycles) and of the samples from [6, 8]. On the bottom insert is a unit cell of stoichiometric Ti$_3$Al (white balls – Al) [9].

be understood from the fragment of its unit cell, which is shown in the inset of figure 1. When Ti atoms are substituted by Al atoms in structures close to Ti$_3$Al, the $c/a$ ratio in the hexagonal structure of $\alpha$–Ti significantly changes with the formation of the Yum–Rosery phases, when the number of electrons per atom is close to 3.75. Stabilization of structures similar to Ti$_3$Al ($a = 0.579$ nm, $c = 0.465$ nm, $c/a = 0.803$) is associated not only with the dimensional but also with the electronic factor, since there is a weak superstructural contraction (on the average in the lattice) [9].

Figure 2 shows the temperature dependences of $\rho(T)$ upon heating in a “metastable” state and upon cooling in a “stabilized” state when $\rho(T)$ does not change, when heated and cooled, for each series of sample measurements: initial, after harding and after annealing. After quenching at 1100°C, of the sample (figure 2), the values of decreased, and, as in the first cycle “heating–cooling” of the initial sample, a hysteresis with an even larger amplitude appeared, which disappeared already in the third cycle. After annealing at 1100°C, the resistance of the sample at room temperature turned out to be the same as after harding. During heating from 300 K to 1000 K, $\rho$ increases to the value for the initial sample in the stabilized state at 1000 K. Further, upon cooling, a hysteresis is observed with increasing electrical resistivity, in contrast to the previous series. In this case, the absolute values of $\rho$ and its temperature dependence are close to the values of the resistance of the initial sample in the stabilized state $\rho(T)_{init, stab}$. Perhaps, the fact that the dependence $\rho(T)$ of the annealed sample returns to the initial stabilized state, appears to be a manifestation of the effect of the electrical resistivity memory. Figure 3 shows the results of detailed studies of the dependences $\rho(T) = f(T)$ and $\alpha(T) = f(T)$ during the first heating of a metastable sample, which are well described by two polynomials fourth and second
Figure 2. Dependences $\rho = f(T)$ of Ti$_{67}$Al$_{33}$ upon heating and cooling: the initial sample, after its hardening and annealing (in brackets, the cycle numbers).

Figure 3. Temperature dependences of the electrical resistivity and TEC in the first heating cycle.

degree respectively. As can be seen, a direct correlation exists between them. The inflection points on both curves are near $\sim 765$ K. A larger spread of the experimental TEC values is due to the error in determining this parameter. The peculiarities on the sections, marked with
vertical lines, are clearly visible on each of the dependencies. This is most clearly manifested on the curve $\rho = f(T)$. These peculiarities are associated with competition and the dominance of metallic and semiconductor conductivity characters at each of the temperature intervals. In the 300–400 K range the metallic behavior dominates, after that the semiconductor character is switched on and growing, which leads to saturation of the dependence $\rho = f(T)$, which passes through a maximum at 525 K. According to our data, at this temperature the contributions from these mechanisms are compared, and then the semiconductor conduction mechanism begins to dominate up to $\sim 835$ K.

The corresponding number of electrons per atom results in the overlap of the wave functions of the socialized electrons and the formation of additional weak covalent bonds [15] due to the dispersion forces. In [6] it is noted that with increasing temperature the degree of covalence and atomic ordering decrease. This is accompanied by an increase in the concentration of elementary electronic excitations, which should lead to a decrease in $\rho$, but this does not occur because of thermal chaos, since the mean free path also decreases. Due to the presence of vacancies in alloys of non–stoichiometric composition, including Ti$_{67}$Al$_{33}$, additional disordering is observed. Polycrystalline samples have less favorable factors for the formation of covalent bonds, so the effect of negative TCR is manifested in a small temperature range, where the resistance reaches the highest values (figures 1–3). On the same range starting from 628 K, an anomaly occurs in the form of a dip in an annealed sample, the cause of which requires additional studies.

To interpret the competition between the metallic and semiconductor behavior of the $\rho = f(T)$ dependence, it is necessary to understand the scenario of formation and relaxation of charge excitations under different external influences. The decoding of this scenario can be performed on the basis of the correlation analysis of the values of obtained as a result of in situ measurements $\rho$, reflecting the formation and relaxation of charge excitations and $\beta$, characterizing the deformation potential, which determines the matrix scattering element in each equilibrium state.

A preliminary correlation analysis between $\rho(T)$ and $\beta(T)T$ in the temperature range of dominance of one of the two conduction mechanisms indicates the presence of a linear relationship between these parameters like for classical metals [10,11]. This will make it possible to establish the nature of the formation and relaxation of charge excitations in intermetallic compounds, which are characterized by diffusion phase transitions. The results of a detailed analysis of such correlation for Ti$_{67}$Al$_{33}$ after different heat treatments will be given in another paper.

3. Conclusion

Local disordering of atoms in the unit cell Ti$_{67}$Al$_{33}$ after the appropriate heat treatment makes it possible to control the values of $\rho$ and TCR of this intermetallide, which is important for the development of innovative materials based on it with specified properties, for example, with the effect of resistive memory.

It is established that in the Ti$_{67}$Al$_{33}$ intermetallide a direct correlation of the anomalies of the dependencies $\rho = f(T)$ and $\alpha = f(T)$ is observed. The change in the interatomic distances is due to the anharmonicity of the vibrations of the lattice atoms, which indicates the decisive role of anharmonicity not only in the formation of the scattering potential of elementary excitations, but also in the formation of charge excitations as a result of the weakening of dispersion forces and changes in ion polarization.

Unlike single crystals with a Ti$_3$Al structure, in a polycrystalline Ti$_{67}$Al$_{33}$ sample, the extrapolated to 0 K (residual) electrical resistivity depends on temperature and it can change sign. Despite the competition of various mechanisms forming the dependence $\rho(T)$ in a polycrystalline sample, relation (1) is fulfilled in the region of dominance of each of mechanisms of electrical conductivity.
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