N. V. GRUM-GRZHIMAILO, I. I. KORNILOV, E. N. PYLAEVA

and M. A. VOLKOVA

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N. V. GRUM-GRZHIMAILO, I. I. KORNILOV, E. N. PYLAEVA and M. A. VOLKOVA

METALLIC COMPOUNDS IN THE REGION OF α-SOLID SOLUTIONS OF THE TITANIUM—ALUMINUM SYSTEM

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As a result of investigations by many authors ([1–5]), the phase diagram of the binary titanium—aluminum system is characterized by an extensive region of solid solutions based on the α- and β-modifications of titanium. According to microstructural and X-ray studies, the region of the α-solid solution of aluminum in titanium extends from 0 to 25 wt.% aluminum; with increasing aluminum content, the temperature of the polymorphic transformation of the phase $\alpha \rightarrow \beta$ rises. Alloys from the region of α-solid solutions are characterized by a hexagonal close-packed lattice.

Concurrently with the study of the phase diagram of titanium alloys with aluminum, we carried out determination of their properties. In studying the creep of alloys by bending deformation using the centrifugal-force method ([6]), it was established that, within the limits of aluminum concentration from 7.5 to 20 wt.%, their creep resistance increases sharply, with a simultaneous decrease in plasticity.

Such changes in properties in the solid-solution region of alloys of the binary titanium—aluminum system could not be explained by the usual methods of metallographic analysis.

The aim of the present work was to study the region of the α-solid solution in the titanium—aluminum system and to establish the nature of the existing phases by the method of measuring the Hall effect ([7,8]), as a function of alloy composition.

Previously obtained data ([9,10]) showed that galvanomagnetic effects are related to the composition of various alloys in such a way that, on composition—Hall-effect diagrams, points of inflection and discontinuities are observed. The points of inflection correspond to the stoichiometric compositions of chemical compounds. This phenomenon is explained by the fact that, upon application of a magnetic field, a change occurs in the electronic states of the outer shells of atoms, which affects the behavior of conduction electrons, causing a change in the value of the Hall constant.

Galvanomagnetic effects are directly connected with the behavior of the electronic constituents of the peripheral shells of atoms; therefore, with their aid it is possible, in a very sensitive manner, to investigate the state of the periphery of atoms and thus to reveal the character of the chemical bond between different atoms of metallic alloys.

Experimental Part

From pure metals, titanium and aluminum, a series of alloys was prepared with different contents of components (from 0 to 40 wt.% aluminum). The alloys were prepared by two methods: 1) by the powder-metallurgy method, by pressing shaped specimens, followed by their sintering in vacuum according to the schedule 1000°–100 hr, 800°–50 hr, 600°–100 hr; 2) by the method

melting in an arc furnace with a nonconsumable tungsten electrode, with subsequent preparation of specimens for determining the Hall constant in the form of plates 10 × 30 × 1.5 mm and of current pickups in the form of triangles. At the point of contact with the specimen, the current pickups had a knife-like shape and, by means of micrometer screws, slid along the lateral polished surfaces of the specimen.

The testing procedure and the setup of the apparatus are described in the literature (11). The obtained average values of measurements of the Hall constant for sintered, cast alloys and after annealing are presented in Table 1.

Table 1

Data on the Hall constants of sintered, cast, and annealed alloys of the Ti–Al system

Al content, %	Hall constant $\times 10^{-12}$ for sintered alloys	Hall constant $\times 10^{-12}$ for cast alloys	Hall constant $\times 10^{-12}$ for cast annealed alloys
0	0	0	0
4,36 a 2,5	0, 062035 ± 0, 026	0	
8,52 a 5,0	0, 223999 ± 0, 015	0	
10,16 a 6,0	0, 268054±0, 6141	0, 15434 ± 0, 0150	0, 193491±0, 0141
12,60 a 7,5	–	0, 1170503±0, 045	0, 293334±0, 0178
13,45 a 8,0	–	0, 2474267±0, 185	0, 1865846 ± 0, 0106
14,14 a	–	0, 6823133 ± 0, 0120	0, 51303 ± 0, 120

Al content, %	Hall constant ×10^{-12} for sintered alloys	Hall constant ×10^{-12} for cast alloys	Hall constant ×10^{-12} for cast annealed alloys
9,0			
16,51 a			
10,0	0,562180	0,731783±0,0215	0,7808003±0,170
17,25 a			
11,0	–	0,5795207 ± 0,0492	1,228103±0,0714
19,57 a			
12,0	–	–	0,92553
20,0 a			
12,5	4,45879 ± 0,173	–	
20,91 a			
13,0	–	2,10010 ± 0,0180	2,080289 ± 0,161
22,41 a			
14,0	3,43710 ± 0,170	2,33797 ± 0,157	2,17404 ± 0,0512
23,95 a			
15,0	4,115600 ± 0,187	4,40590 ± 0,1345	4,387189 ± 0,200
25,10 a			
16,0	3,887287 ± 0,228	2,70210 ± 0,172 2,79959 ± 0,132 2,554097	2,756826 ± 0,080
26,62 a	–		
17,0			
28,07 a			
17,5	2,8075 ± 0,0871		2,86689 ± 0,178
30,83 a			
20,0	2,63763 ± 0,0162	2,755197±0,0244	
33,39 a			
22,0	2,4460 ± 0,0266	–	2,218308±0,0836
34,05 a			
22,5	2,102906 ± 0,043	2,1344980±0,310	2,161103±0,0153
34,68 a			
23,0	2,391420 ± 0,220		
35,95 a			
24,0	2,27879 ± 0,0719		
38,72 a			
26,0	2,71220 ± 0,208		
39,68 a			
27,5	1,506357±0,0261		
21,11 a			
30,0	0,745089±0,0264		
46,16 a			
33,0	–	0,3479517±0,103	

Fig. 1

Figure 1: Fig. 1

Al content, %	Hall constant ×10^{-12} for sintered alloys	Hall constant ×10^{-12} for cast alloys	Hall constant ×10^{-12} for cast annealed alloys
50,00 a 36,0	–	$0,3035150 \pm 0,151$	
51,53 a 38,00	–	$1,172150 \pm 0,0518$	
53,85 a 40,0	–	$1,183276 \pm 0,167$	

Note. a –atomic percent, –weight percent.

In Fig. 1, from the data of Table 1, a plot has been constructed of the dependence of the Hall constant on composition for alloys prepared from powdered titanium; in the figure one can see two abrupt transitions from one linear variation of the Hall constant to another. These transitions correspond to: the first –to the compound Ti_6Al with 14.3 at.% (9 wt.%) aluminum; the second–to the compound Ti_3Al with 25 at.% (16 wt.%) aluminum. The results of measuring the Hall constant for cast alloys, presented in Table 1 and in Fig. 1, do not differ in any essential way from the results of the investigation of sintered alloys (Fig. 1).

The compounds Ti_6Al and Ti_3Al, detected in sintered alloys, are confirmed by investigation of the change in the Hall constant with composition in cast alloys. After measurement of the Hall effect, the cast alloys, in order to attain equilibrium, were subjected to homogenizing annealing at 900° for 200 h, 800° for 300 h, and 600° for 350 h.

Fig. 1

The results of measuring the Hall constant of the annealed alloys are given in Table 1 and in Fig. 1. The changes in the Hall constant with composition for annealed alloys of the titanium–aluminum system have a character analogous to that for sintered and cast alloys. Breaks are observed at the same stoichiometric compositions of the compounds for both the sintered and the cast alloys.

The limited region of α-solid solutions, with two metallic compounds present in it, presents great difficulties for determining the sequence of changes in the Hall constant, since this determination requires increased accuracy of measurement. On the available apparatus the required accuracy was attained.

To verify the results, three series of alloys prepared by different methods were investigated. Their overall results are in complete agreement with one another, despite some discrepancies in the magnitudes of the Hall effect for alloys close in composition but prepared by different methods.

Solid solutions of aluminum in α-titanium are distinguished by a complex character of interaction, at the basis of which lies the existence of two compounds, Ti_6Al and Ti_3Al. These compounds apparently have a hexagonal

lattice, are formed from solid solutions and correspond to compounds of the Kurnakov type [12].

We also determined the values of the Hall constant for alloys of the titanium—aluminum system from the γ-phase region. Alloy compositions from the γ-phase region were studied that corresponded to 46.16 at.% (33 wt.%), 50.0 at.% (36.02 wt.%), 51.53 at.% (38.0 wt.%), and 53.85 at.% (40.0 wt.%) aluminum.

A sharp break in the Hall-effect—composition curve is observed for the alloy composition with 50.0 at.% (36.02 wt.%) aluminum, which corresponds to the compound TiAl, established by other methods of physicochemical analysis.

The equilibrium state of these compounds and the regions of their distribution in the phase diagram of the titanium—aluminum system depend on the conditions and kinetics of their formation. These questions require further investigation. The appearance of the compounds Ti_6Al, Ti_3Al, and TiAl in this system is the reason for the increase in heat resistance and the sharp decrease in the plastic properties of titanium alloys when the Al content exceeds 7-8 wt.%.

A. A. Baikov Institute of Metallurgy
Academy of Sciences of the USSR

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