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Continuous Solid Solutions of the Metallides Ti_3Al–Ti_3Sn in the Ti–Al–Sn System

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The study of chemical interaction between metallic compounds is of considerable interest. Solid solutions based on these compounds have been called metallide solutions. In work ([1]), the principal considerations determining the formation of continuous solid solutions between compounds with metallic bonding were examined theoretically. These investigations were developed in ([1]–[7]). In the literature ([8]–[12]) there are indications of the possibility of formation, in the Ti–Al system, from α-solid solutions of titanium, of the compounds Ti_3Al and Ti_6Al. These assumptions are based on data obtained in studying various properties of the binary Ti–Al system. According to work ([10]), an x-ray investigation of alloys established the presence of an ordered phase of composition Ti_3Al. In work ([12]), in a study of alloys by the galvanomagnetic method, the compositions of the compounds Ti_6Al and Ti_3Al were established from the inflection points on the composition—Hall-effect diagram. Thus it may be considered that one of these compounds, Ti_3Al, is formed in the Ti–Al system from α-solid solutions of titanium with an ordered structure. The lattice of this compound is hexagonal and is isomorphous with the structure of the compound Ti_3Sn (45.24 wt. % Sn) (see ([13])). It melts with an open maximum; its melting temperature is 1663° ([14]), and it has a hexagonal close-packed lattice. In an investigation of the equilibrium diagram of the ternary titanium–aluminum–tin system ([15]), carried out by microstructural and x-ray methods, the formation of a considerable region of ternary solid solutions based on α-titanium and the compound Ti_3Sn, having a hexagonal lattice, was established.

In the present work, the phase diagram and properties of alloys of the ternary Ti–Al–Sn system corresponding to compositions of alloys located on the Ti_3Al–Ti_3Sn section were studied. The alloys were investigated by methods of thermal, microstructural, and x-ray analyses and by measurements of electrical resistivity and hardness.

For preparation of the alloys, ductile titanium of grade TG-00 (with a tensile strength of ~38 kg/mm^2), aluminum, and tin of high purity were used. The alloys were prepared by melting in an arc furnace with a nonconsumable tungsten electrode in an argon atmosphere. To study crystallization and phase transformations in the solid state of alloys of the Ti_3Al–Ti_3Sn section, the method of

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contactless thermal analysis on the apparatus of N. A. Nedumov ([16]) was used, by recording heating and cooling curves. The thermographing rate was 23-25°/min. The investigation was carried out on specimens annealed according to the regime given below.

Analysis of the thermograms made it possible to construct the liquidus and solidus lines of alloys of the Ti_3Al-Ti_3Sn section, and also to indicate the transformation points in the solid state for alloys having polymorphic or other types of transformation. According to thermal-analysis data, the constructed melting diagram shows that the alloys crystallize according to the eutectic type with mutually limited solid solutions. The liquidus and solidus temperatures decrease both from the side of crystallization of the β-solid solution of the Ti-Al system and from the side of Ti_3Sn. In the interval 1590-1615°, alloys containing 40-80% Ti_3Sn (~16-36% Sn) crystallize as eutectic mixtures consisting of two phases: a β-solid solution based on

of the Ti—Al system and a ternary δ-solid solution based on the compound Ti_3Sn. The eutectic point corresponds to 45% Ti_3Sn ($\sim$ 20 wt.% Sn).

Most of the alloys studied undergo a transformation in the solid state caused by the polymorphism of titanium. For an alloy of composition Ti_3Al, the onset of the transition from the $\alpha(\delta)$ region to the $\beta + \alpha(\delta)$ region corresponds to a temperature of 1120°. Addition of Ti_3Sn to Ti_3Al initially causes a certain decrease in the temperature of the $\alpha \rightleftarrows \beta$ transformation, down to a minimum of 990° at 60% Ti_3Sn, followed by a slight increase to 1035° (see Fig. 1).

Fig. 1. Phase diagram of the Ti_3Al—Ti_3Sn section

In the thermograms of alloys of the Ti_3Al—Ti_3Sn section adjacent to the Ti_3Al composition, at temperatures below 960° additional thermal effects appear, denoted in Fig. 1 by crosses. The presence of these effects is associated with the formation of the compound Ti_3Al from $\alpha(\delta)$ solid solutions. According to thermal-analysis data, the temperature of formation of this compound in the binary Ti—Al system is 960°. This temperature gradually decreases as Ti_3Sn is added, as shown by the dotted line.

The microstructure of the alloys of this section was studied in the cast state and after the following heat-treatment regimes: 1) homogenizing and step annealing at temperatures of 1200, 1100, 1000, 800, and 600° for, respectively, 100, 50, 200, 300, and 500 h, followed by cooling with the furnace; 2) quenching in water from temperatures of 1500, 1200, and 1000°, with holding at each temperature for 3, 50, and 100 h. Quenching from 1500° was carried out in a vacuum quenching furnace, and from 1200 and 1000° in evacuated quartz ampoules. To accelerate the attainment of equilibrium, almost all alloy compositions were deformed by

Figure 2

Figure 2: Figure 2

Figure 1

Figure 3: Figure 1

upsetting in a press with a small degree of deformation, 10–15%.

Etching of the alloy specimens was carried out with a mixture of acids: hydrofluoric and concentrated nitric acid with glycerin (1 : 1 : 2).

Microexamination of the cast alloys confirms the eutectic character of alloy crystallization. In this state, alloys with a content of up to 30% Ti_3Sn (13.5 wt.% Sn) are solid solutions based on β-titanium. In alloys with a content of more than 30% Ti_3Sn, precipitation of a second phase–δ–takes place. The two-phase $\beta + \delta(\alpha)$ region of this section has a considerable extent. With a further increase in the Ti_3Sn content in the alloys, the amount of eutectic decreases and the amount of the excess phase (based on the compound Ti_3Sn) increases. Alloys containing more than 80% Ti_3Sn are solid solutions based on the compound Ti_3Sn. Study of the microstructure of quenched alloys shows a certain increase in the solubility limit of the compound Ti_3Sn in the β-solid solution of titanium as the quenching temperature is raised.

Study of the microstructure of annealed and slowly cooled alloys showed that all alloys have a single-phase structure, which indicates the formation of a continuous series of solid solutions based on the α-solid solution of the Ti–Al system and the compound Ti_3Sn. As an example, Fig. 2 shows the change in the microstructure of an alloy containing 50% Ti_3Sn, 50% Ti_3Al during annealing. The structure of the cast alloy consists of excess precipitates of δ-phase crystals, etched white, and a $\beta + \delta(\alpha)$ eutectic (Fig. 2a). The same alloy after annealing has a single-phase structure–polyhedra of the $\alpha(\delta)$ solid solution are visible (Fig. 2b).

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Fig. 2. Microstructures of alloys.
a –50% Ti_3Al, 50% Ti_3Sn, as-cast;
b –50% Ti_3Al, 50% Ti_3Sn, annealed.
200×

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Fig. 1. 1-3, 5-7 –*Nummulites prestwichianus* Jones; 4, 8, 9 –*N.* ex gr. *variolarius* (Lamarck); 10, 11 –*Operculina* sp.; 12 –*Nummulites tchavannesi* de la Harpe; 13 –*N. orbignyi* Galeotti; 14 –*Discocyclina* sp. 10×

Prolongedly annealed alloys were subjected to X-ray structural analysis. X-ray photographs of the powders were taken with copper radiation. The X-ray

Fig. 3. Specific electrical resistance and hardness of alloys of the Ti_3Al—Ti_3Sn section

Figure 4: Fig. 3. Specific electrical resistance and hardness of alloys of the Ti_3Al—Ti_3Sn section

photographs of the annealed alloys of this section are identical for all the alloy compositions studied and have only one system of lines, corresponding either to α-titanium or to the compound Ti_3Sn. Superstructure lines on the X-ray photographs of the ternary alloys, as well as of the binary alloy of composition Ti_3Al, have not yet been detected. This question requires further investigation.

Fig. 3. Specific electrical resistance and hardness of alloys of the Ti_3Al—Ti_3Sn section

The continuous series of solid solutions of the annealed alloys of the section studied, Ti_3Al—Ti_3Sn, is confirmed by the hardness and electrical-resistance curves presented in Fig. 3. Both these curves have a sympathetic character and, on the composition—property diagram, pass through a broad maximum, characteristic of systems with continuous solid solutions.

Thus, on the basis of the data of thermal, microstructural, and X-ray structural analyses, a phase diagram was constructed for the section of the ternary system Ti—Al—Sn passing through the compositions of the metallides Ti_3Al—Ti_3Sn (Fig. 1). The alloys of the indicated section crystallize as mutually limited solid solutions based on the β-solid solution of the Ti—Al system and on the compound Ti_3Sn, with formation of a eutectic mixture. Upon slow cooling, owing to phase transformations, these mixtures pass into a continuous series of $\alpha(\delta)$-solid solutions. At 960°, during prolonged annealing, the compound Ti_3Al is formed from the α-solid solution of the Ti—Al system; this compound, in turn, gives solid solutions with the compound Ti_3Sn. In this state the alloys of the Ti_3Al—Ti_3Sn section represent continuous solid solutions with a hexagonal crystal lattice.

The alloys investigated in this section of the Ti—Al—Sn system are an example of a complex phase equilibrium that changes considerably depending on temperature and on transformations in the solid state.

Metallide continuous solid solutions in alloys of the Ti_3Al—Ti_3Sn section exist in prolongedly annealed alloys. The formation of such solid solutions should be regarded as the continuous substitution in the Ti_3Sn lattice of tin atoms by aluminum atoms without a change in the type of crystal lattice.

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Note: Figure translations are in progress. See original paper for figures.