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Abstract

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INTERACTION BETWEEN THE METALLIC COMPOUNDS Ni_3Al AND Ni_3Nb

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The study of various metallic phases and their interaction is of great interest, since the behavior of modern complexly alloyed alloys under service conditions depends to a considerable extent on the nature of the phases formed in them, on the kinetics of the processes of precipitation and coagulation of these phases, and on their interaction. At present the structures of a large number of metallic compounds have been determined, and the melting temperatures of many compounds have been established. As for the properties of these compounds, however, the data are still very limited, while the interaction between different metallic compounds constitutes an even less studied field.

In continuation of earlier work (1,2), the present paper considers the interaction between the compounds Ni_3Al and Ni_3Nb. In view of the absence of conditions for unlimited solubility (1), in contrast to the Ni_3Ta—Ni_3Nb system (2), the interaction of Ni_3Al with Ni_3Nb was expected to yield a phase diagram of a more complex type. The existence of a phase based on the compound Ni_3Al (86.72 wt.% Ni) was first established in (3), and was later also confirmed by a number of other studies (4–9). According to the compiled phase diagram of the Ni—Al system (10), the phase based on the compound Ni_3Al (the γ' phase) is formed by a peritectic reaction between a melt based on the compound NiAl (β phase) at 1395° and by a eutectic reaction at 1385°. In the binary Ni—Al system the compound Ni_3Al has a narrow homogeneity range: at 600° it lies between 72.5 and 77.0 at.% (85.1-87.6 wt.%) Ni. The data obtained in various works (5,6,8) concerning the boundaries of the single-phase region based on the compound Ni_3Al and the adjacent two-phase regions differ considerably from one another. According to (11), the region of single-phase alloys based on Ni_3Al at room temperature lies between 85.6 and 87.4 wt.% Ni. The compound Ni_3Al has a face-centered cubic structure of the Cu_3Au type (4,5,12,13), with lattice parameter $a = 3.589$ Å at 75 at.% Ni (4). According to (14,15), in a series of alloys of the Ni—Al system the compound Ni_3Al corresponds to a singular minimum on the curves composition—electrical resistivity, composition—hardness, and composition—coefficient of linear expansion, and to a singular maximum on the curve composition—temperature coefficient of electrical resistivity. After 24 hr annealing at 1200°, an alloy of stoichiometric composition has a specific electrical resistivity of $37.4 \cdot 10^{-6}$ ohm • cm; a temperature coefficient of electrical resistivity of $25.7 \cdot 10^{-4}$; hardness 137 H_B; and a temperature coefficient of linear expansion $\alpha_{300} = 8.5 \cdot 10^{-6}$. A number of works (^{14,16}) note the high ductility of the compound Ni_3Al. As shown in (^{17}), the compound Ni_3Al exhibits a temperature dependence of hardness different from that of all other compounds and alloys studied so far: with increasing temperature up to 700–750° the hardness of Ni_3Al increases somewhat; at 800° the hardness of this compound is only 10 H_B units lower than at room temperature.

In the earliest work on the study of the Ni—Nb system (^{18}), it was established that the compound Ni_3Nb is formed by a peritectic reaction, whereas according to the data of (^{19}) this compound corresponds to an open maximum at 1403°. The data of the latter work should be considered more reliable. According to (^{19}), the compound Ni_3Nb has a narrow region of solid-

solid solutions, terminating at 900° between 23.3 and 26.2 at.% (32.5-36.0 wt.%) Nb. The existence of the compound Ni_3Nb was confirmed in studies (^{20},^{21}) by microscopic and X-ray structural analysis methods. In work (^{22}) it was established that the compound Ni_3Nb has a deformed close-packed hexagonal structure with an ordered arrangement of atoms, while in works (^{23},^{24}) it was found to be rhombic, with parameters: according to (^{23}), $a = 5.106$ kX, $b = 4.55$ kX, $C = 4.25$ kX, and, according to (^{24}), $a = 5.10$ kX, $b = 4.53$ kX, $c = 4.24$ kX. According to (^{25}), the specific electrical resistivity of the compound Ni_3Nb is $6.0 \cdot 10^{-6}$ ohm • cm.

In the present work, the interaction between the compounds Ni_3Al and Ni_3Nb was studied by methods of thermal, metallographic, and X-ray structural analysis, as well as by methods for studying hardness and electrical resistivity; the phase diagram and the diagrams composition—hardness and composition—electrical resistivity were constructed. As charge materials in preparing alloys of the Ni_3Al—Ni_3Nb system, electrolytic nickel, niobium in rods (99.15), and a Ni—Al master alloy (30.7 wt.% Al), obtained by fusing grade N—O electrolytic nickel and aluminum (99.999% Al) in a corundum crucible in a high-frequency furnace, were used. The alloys were prepared in an arc furnace with a nonconsumable tungsten electrode, in an argon atmosphere. The ingots obtained were used for thermal analysis: after melting them in corundum crucibles in a high-frequency inductor, cooling curves were recorded with a Kurnakov pyrometer. After thermal analysis the alloys were remelted: samples in the form of rods, 4 mm in diameter and about 100 mm long, were prepared from the melt by the Stepanov method. The microstructure was studied on samples in the cast state, and also after quenching from various temperatures with stepwise treatment according to the regime: 1200°—5 h, 1000°—100 h, 800°—300 h, and at 600°—750 h, or after slow cooling. The microstructure was revealed by electrolytic etching in a 10% solution of oxalic acid. Electrical resistivity was measured by a potentiometric circuit; hardness, on a Vickers-type instrument under a load of 10 kg. X-ray phase investigation was carried out on filtered cobalt K_α-radiation from powder samples in a standard Debye-type camera (diameter 57.3 mm). At the same time, at the Kiev Institute of Civil Air Fleet, V. G. Chuprina, under the direction of Prof. M. P. Arbuzov, performed an X-ray structural investigation of the alloys of the Ni_3Al—Ni_3Nb system prepared by us. In the present article some data from the work of M. P. Arbuzov and V. G. Chuprina are presented; a detailed description of the results of the X-ray structural investigation was published by the authors ([26]).

The melting diagram of the Ni_3Al—Ni_3Nb system, constructed from thermal-analysis data, contains two lines of primary crystallization intersecting at one point, corresponding to a composition of 70.0 wt.% Ni_3Nb and 30.0 wt.% Ni_3Al and a temperature of 1285°. The microstructure of alloys containing 10–40% Ni_3Nb is a homogeneous solid solution, like pure Ni_3Al. The alloy of the stoichiometric composition Ni_3Al crystallizes in the interval 1400–1390° by a peritectic reaction; apparently, alloys containing up to 30 wt.% Ni_3Nb also crystallize by a peritectic reaction. In alloys with a Ni_3Nb content of more than 30 wt.% the γ'-phase crystallizes directly from the melt; with an increase in the concentration of nickel and niobium in the solid solution based on Ni_3Al, the crystallization interval of the alloys narrows somewhat. All alloys with a Ni_3Nb content up to 50 wt.% are single-phase in the solid state; however, under rapid cooling and insufficient homogenization of the alloys during subsequent heat treatment, remnants of a second phase (β) were sometimes observed in alloys containing up to 30% Ni_3Nb.

In alloys containing more than 50% Ni_3Nb, in addition to the excess γ'-phase, a eutectic constituent was observed in the microstructure (Fig. 1a). The amount of eutectic increased up to the alloy with 70% Ni_3Nb, which

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Fig. 1. Microstructure of alloys after thermal analysis and annealing of ingots:
a —alloy with 50% Ni_3Nb (γ_1+ eut.);
b —alloy with 70% Ni_3Nb (eut.);
c —alloy with 80% Ni_3Nb (δ+ eut.).
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can be regarded as purely eutectic (Fig. 1); when the alloy contains more than 70% Ni_3Nb (Fig. 1), the amount of eutectic decreases, and the excess phase is Ni_3Nb (the δ-phase).

The constitution diagram of the Ni_3Al—Ni_3Nb system, constructed from thermal-analysis and microstructural data (Fig. 2a), is a diagram with a eutectic. On the Ni_3Al side there is a broad region of solid solutions which, forming by a peritectic reaction, at

Table 1

Compositions and properties of alloys of the Ni_3Al—Ni_3Nb system

No.	Composition, wt. % Ni_3Al	Composition, wt. % Ni_3Nb	Crystallization temp., °C: beginning	Crystallization temp., °C: end	Microstructure 1200°	Microstructure 1000°	Microstructure 800°	Microstructure 20°	Electrical resistivity $\rho\, 10^6$ ohm·cm: quench from 1100°	Electrical resistivity $\rho\, 10^6$ ohm·cm: anneal	Hardness H_{v10}: quench from 1100°	Hardness H_{v10}: anneal	X-ray
1	100	0	1410	1360	γ'	γ'	γ'	γ'	40	36	210	140	fcc $a = 3.562$
2	90	10	1375	1340	γ'	γ'	γ'	γ'	79	78	214	271	fcc $a = 3.572$
3	85	15	1370	–	γ'	γ'	γ'	γ'	90	89	–	–	–
4	80	20	1365	1330	γ'	γ'	γ'	γ'	103	102	318	310	fcc $a = 3.576$
5	75	25	1365	–	γ'	γ'	γ'	γ'	120	106	301	–	–
6	70	30	1375	1330	γ'	γ'	γ'	γ'	128	116	333	372	fcc $a = 3.585$
7	65	35	–	–	γ'	γ'	γ'	γ'	130	130	362	–	–
8	60	40	1350	1310	γ'	γ'	γ'	γ'	128	128	401	396	fcc $a = 3.592$
9	55	45	–	–	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	130	130	405	–	–
10	50	50	1320	1290	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	115	122	418	444	1) fcc $a = 3.596$ 2) rhomb. $a = 5.110$ $b = 4.238$ $c = 4.538$

No.	Composition: wt. % Ni_3Al	Composition: wt. % Ni_3Nb	Crystallization temp., °C: beginning	Crystallization temp., °C: end	Microstructure 1200°	Microstructure 1000°	Microstructure 800°	Microstructure 20°	Electrical resistivity $\rho\,10^6$ ohm · cm: quench from 1100°	Electrical resistivity $\rho\,10^6$ ohm · cm: anneal	Hardness H_{v10}: quench from 1100°	Hardness H_{v10}: anneal	X-ray
11	40	60	1285	1260	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	116	101	341	385	1) fcc $a = 3.592$ 2) rhomb. $a = 5.096$ $b = 4.233$ $c = 4.531$
12	30	70	1280	–	eutectic	eutectic	eutectic	eutectic	102	90	383	402	1) fcc $a = 3.593$ 2) rhomb. $a = 5.098$ $b = 4.236$ $c = 4.532$
13	20	80	1340	1275	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	84	82	383	371	1) fcc $a = 3.592$ 2) rhomb. $a = 5.100$ $b = 4.235$ $c = 4.535$

No.	Composition: wt. % Ni_3Al	Composition: wt. % Ni_3Nb	Crystallization temp., °C: beginning	Crystallization temp., °C: end	Microstructure: 1200°	Microstructure: 1000°	Microstructure: 800°	Microstructure: 20°	Electrical resistivity $\rho\,10^6$ ohm·cm: quench from 1100°	Electrical resistivity $\rho\,10^6$ ohm·cm: anneal	Hardness H_{v10}: quench from 1100°	Hardness H_{v10}: anneal	X-ray
14	10	90	1370	1270	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	$\gamma' + \delta$	71	65	326	326	1) fcc $a = 3.593$ 2) rhomb. $a = 5.111$ $b = 4.237$ $c = 4.533$
15	0	100	1408	–	δ	δ	δ	δ	50	50	–	320	rhomb. $a = 5.090$ $b = 4.234$ $c = 4.524$

lower temperatures are completely single-phase up to approximately 40 wt. % Ni_3Nb. On the Ni_3Nb side it was not possible to establish the boundary of the single-phase region by the microstructural method, because, with the alloy-preparation procedure adopted in the present work, it was impossible to obtain an alloy with an exactly specified Ni_3Al content if the content of the latter was less than approximately 10%.*

The results of the microstructural study were confirmed by phase X-ray analysis: in alloys containing 0–40 wt. % Ni_3Nb, only one phase with the Ni_3Al lattice was found. All the remaining alloys (with the exception of pure Ni_3Nb) contained lines of two phases: Ni_3Al and Ni_3Nb. Moreover, with increasing Ni_3Nb content in the two-phase alloys, the intensity of the Ni_3Nb lines increased markedly, while the intensity of the Ni_3Al lines decreased. According to M. P. Arbuzov and V. G. Chuprina (Table 1), the period of the face-centered lattice of the solid solution based on Ni_3Al increases when Ni_3Nb dissolves in it from 3.562 Å to 3.592 Å. On the X-ray diffraction patterns of the two-phase alloys there are two systems of lines: the lines of a face-centered lattice (the solid solution of Ni_3Nb in Ni_3Al) and the lines of the rhombic lattice of Ni_3Nb, whose parameters are somewhat larger than the parameters of pure Ni_3Nb, which indicates the

Fig. 2

Figure 1: Fig. 2

presence of some solubility of Ni_3Al in Ni_3Nb.

* Preparation of alloys of any exactly specified composition is possible by the amalgam method or by the method of co-reduction of a mixture of oxides or salts.

According to the data of microstructural analysis, the solubility of Ni_3Nb in Ni_3Al in the solid state at temperatures below 1200° does not change as the temperature is lowered.

Fig. 2. Phase diagrams of the Ni_3Al—Ni_3Nb system (*a*), composition—hardness (*b*), composition—electrical resistivity (*c*).
1 —single-phase, 2 —two-phase structures, 3 —quenched state, 4 —annealed state

Despite some scatter of the experimental points, the general character of the change in hardness as a function of composition (Table 1, Fig. 2) has a definite regularity, namely: the pure compounds Ni_3Al and Ni_3Nb have the lowest hardness. In the single-phase region based on Ni_3Al, with increasing Ni_3Nb content the hardness increases, reaching its greatest value near the solubility boundary. On the side of pure Ni_3Nb the hardness curve also rises. The hardness curves for alloys in the annealed and quenched states (allowing for the scatter of points) practically coincide.

In the alloy system Ni_3Al—Ni_3Nb, the lowest value of electrical resistivity (Table 1, Fig. 2*c*) is found for the pure compounds. In the region of solid solutions based on Ni_3Al, a curvilinear increase in electrical resistivity is observed with increasing Ni_3Nb content in Ni_3Al; the highest value of electrical resistivity corresponds to a single-phase alloy of limiting concentration (approximately 35% Ni_3Nb). In the two-phase region, the electrical resistivity does not change additively. As is seen from Fig. 2*c*, the maxima on the composition—electrical resistivity and composition—hardness curves are somewhat displaced relative to one another. Both maxima lie near the solubility boundary, but the maximum of electrical resistivity corresponds to a single-phase alloy of limiting concentration, while the maximum of hardness corresponds to a two-phase alloy.

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