SELECTIVE ISOLATION OF THE METALLIC COMPOUNDS Ni$_3$Al AND Ni$_3$Ti FROM MULTICOMPONENT NICKEL ALLOYS

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Abstract

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SELECTIVE ISOLATION OF THE METALLIC COMPOUNDS Ni_3Al AND Ni_3Ti FROM MULTICOMPONENT NICKEL ALLOYS

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The properties of many heat-resistant nickel alloys are associated with the formation in them of an intermetallic phase based on the metallic compound Ni_3Al (γ'-phase), which is a phase of variable composition. The following elements dissolve in it to varying degrees: titanium, chromium, tungsten, molybdenum, silicon, manganese, vanadium, etc. The lattice parameter of the γ'-phase isolated from Ni—Cr—Ti—Al alloys can vary primarily depending on the content of aluminum, titanium, and chromium in the phase, within the limits from 3.56 (the parameter of the pure Ni_3Al phase) to 3.59 Å. It has been established that titanium has a great influence on the properties of the Ni_3Al phase; it can replace $^3/_5$ of the aluminum atoms in the phase ([1]), and therefore the Ni_3Al phase may be represented in the form $Ni_3(Al_x, Ti_{1-x})$. In various nickel alloys containing aluminum and titanium, the following phases may be present: Ni_3Ti, Ni_3Al, and $Ni_3(Al_x, Ti_{1-x})$ ([1,2]). The structure of the last two phases is close to that of the solid γ-nickel solution and is isomorphous with it. The parameters of their crystal lattices differ very little, which makes detection of these phases by the X-ray method difficult.

The literature describes methods for the electrolytic isolation of the intermetallic phases Ni_3Ti and Ni_3Al from complex alloys ([3–8]).

The present investigation was carried out on a two-phase ternary alloy,* containing 75 wt.% Ni_3Ti and 25 wt.% Ni_3Al (the composition of this alloy according to chemical analysis (in wt.%): Ni 80.63, Ti 16.10, Al 3.32), and on a multicomponent nickel alloy having a three-phase structure and the following composition (in wt.%): Ni_3Ti 52.5, Ni_3Al 17.5, γ^4 30 (γ^4—nickel solid solution, containing: Cr 10, W 6, Mo 3%). The composition of this alloy according to chemical analysis (in wt.%): Ti 11.6, Al 2.21, Cr 2.74, W 1.77, Mo 0.90, Ni balance.

Electrolytic selective isolation of the intermetallic phases Ni_3Ti and Ni_3Al when they are present together in an alloy is very difficult, because the values of their electrode potentials ([9]) in different electrolytes are close. The literature describes aqueous electrolytes for anodic isolation of the Ni_3Al phase from chromium-nickel alloys ([3,10]). However, in the indicated electrolytes the anodic precipitate of the alloys investigated by us is not separated. This circumstance evidently indicates the special anodic behavior of an alloy containing two metallic compounds: Ni_3Ti and Ni_3Al.

To select electrolytes for the selective separation of phases, we studied the electrochemical behavior of the alloys investigated in various electrolytes by recording anodic polarization curves (Figs. 1 and 2) by the compensation circuit, relative to a standard calomel electrode, using a high-resistance P-300 potentiometer. Potential–time curves were also recorded (Fig. 3).

* The alloys were prepared and provided for the investigation by L. I. Pryakhina ([11]).

Table 1

Microchemical analysis of anodic precipitates isolated from a binary alloy
(75 wt. % Ni_3Ti and 25 wt. % Ni_3Al) at a current density of 0.1 A/cm^2.
Duration of the experiment: 3 hours

Weight of anodic powder, g	Ni, wt. %	Ti, wt. %	Al, wt. %	Sum, wt. %	Ni_3Al, wt. %	Ni_3Ti, wt. %	$Ni_3(Al,Ti)$, wt. %	Ni, at. %	Ti, at. %	Al, at. %	Sum, at. %	Ni_3Al, at. %	Ni_3Ti, at. %	$Ni_3(Al,Ti)$, at. %	X-ray analysis data* for anodic powders
Electrolyte No. 1: 20 ml $HClO_4$ (57%), 50 ml HNO_3 (sp. gr. 1.40), 1000 ml CH_3OH															
0,0067	79,84	18,22	1,94	100,00	$\frac{12,65}{1,94}$ 6,52	$\frac{67,19}{18,22}$ 3,68	$\frac{-}{-}$ —	75,04	20,99	3,97	100,00	$\frac{12,07}{3,97}$ 3,04	$\frac{62,97}{20,99}$ 3	$\frac{-}{-}$ —	2 phases: Ni_3Ti, Ni_3Al

Weight of anodic powder, g	Ni, wt. %	Ti, wt. %	Al, wt. %	Sum, wt. %	Ni_3Al, wt. %	Ni_3Ti, wt. %	Ni_3(Al, Ti), wt. %	Ni, at. %	Ti, at. %	Al, at. %	Sum, at. %	Ni_3Al, at. %	Ni_3Ti, at. %	Ni_3(Al, Ti), at. %	X-ray analysis data* for anodic powders
Electrolyte No. 3: 35 g citric acid, 5 g $(NH_4)_2SO_4$, 15 ml HNO_3 (sp. gr. 1.40), 1000 ml CH_3OH															
0,0318	83,81	12,34	3,53	99,69	–	–	$\frac{83,81}{3,53 + 12,34}$ 5,28	78,56	14,18	7,20	99,94	–	–	$\frac{78,56}{14,18 + 7,20}$ 3,67	Phase Ni_3(Al, Ti)0,7 0,3

* Analysis performed by K. P. Myasnikova.

Table 2

Microchemical analysis of an anodic precipitate isolated from a multicomponent alloy.
Electrolyte: 50 ml HNO_3 (1.40), 20 ml $HClO_4$ (57%), 1000 ml CH_3OH,
at a current density of 0.1 A/cm^2.

Duration of the experiment: 3 hours

Weight of collected powder, g	Ni, wt. %	Ti, wt. %	Al, wt. %	Cr, wt. %	W, wt. %	Mo, wt. %	Sum, wt. %	Ni_3Ti, wt. %	Ni, Cr / Al, Mo, W, wt. %	Ni, at. %	Ti, at. %	Al, at. %	Cr, at. %	W, at. %	Mo, at. %	Sum, at. %	Ni_3Ti, at. %	Ni, Cr / Al, Mo, W, at. %
0,1217	77,25	14,99	2,56	2,30	2,14	0,76	100,00	$\frac{55,02}{14,99} = 3,67$	$\frac{24,55}{5,46} = 4,50$	73,58	17,51	5,31	2,47	0,65	0,44	99,96	$\frac{52,53}{17,51} = 3,00$	$\frac{23,52}{6,40} = 3,66$

X-ray analysis data* for anodic powders. 2 phases: Ni_3Ti with a hexagonal lattice, $c = 8,19$, $a = 5,07$, $c/a = 1,615$, and a Ni_3Al phase with a face-centered cubic lattice, $a = 3,595$ kX.

* Analysis performed by K. P. Myasnikova.

Table 3

Microchemical analysis of an anodic precipitate isolated from a multicomponent alloy.
Electrolyte: 35 g citric acid, 5 g ammonium sulfate, 15 ml HNO_3 (1.40),
1000 ml CH_3OH, at a current density of 0.1 A/cm^2.
Duration of the experiment: 3 hours

Weight of dry powder, g	Ni	Ti	Al	Cr	W	Mo	Sum	Ni, Cr/Ti, Al, W, Mo	X-ray analysis data* for anodic powders
Experiment with cooling									

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Weight of dry powder, g	Ni	Ti	Al	Cr	W	Mo	Sum	Ni, Cr/Ti, Al, W, Mo	X-ray analysis data* for anodic powders
0,9	$\frac{78,38}{72,36}$	$\frac{10,89}{12,25}$	$\frac{6,46}{12,90}$	$\frac{1,53}{1,58}$	$\frac{2,34}{0,70}$	$\frac{0,40}{0,21}$	$\frac{100,00}{100,00}$	$\frac{3,97}{2,85}$	Ni_3Al phase, cubic face-centered lattice
Experiment without cooling									
0,9	$\frac{77,36}{71,64}$	$\frac{11,0}{12,48}$	$\frac{6,26}{11,35}$	$\frac{3,50}{3,60}$	$\frac{2,06}{0,61}$	$\frac{0,45}{0,26}$	$\frac{100,00}{100,00}$	$\frac{4,08}{3,04}$	$a = 3,5972$ kX

* Analysis performed by K. P. Myasnikova.
Note. The numbers above the line are weight percent; those below the line are atomic percent.

During anodic dissolution of a two-phase alloy (75 wt.% Ni_3Ti and 25 wt.% Ni_3Al) in electrolyte No. 1, two phases—Ni_3Ti and Ni_3Al—are released simultaneously in the anodic residue, whereas in electrolyte No. 3 one phase is released —Ni_2Al, in which part of the aluminum atoms is replaced by titanium atoms and, consequently, its composition should be: $Ni_3(Al, Ti)$. A study of the effect of current density showed that the optimum current density is 0.1 A/cm^2. The results of microchemical analysis of the anodic residues of the alloy are presented in Table 1.

Fig. 1. Curves of anodic polarization: **A**—of a two-phase ternary alloy (charge composition: 75 wt.% Ni_3Ti, 25 wt.% Ni_3Al), **B**—of a multicomponent alloy (charge composition: 52 wt.% Ni_3Ti, 17.5 wt.% Ni_3Al, 30 wt.% γ^4). Electrolytes:
1—20 ml $HClO_4$ (57%), 50 ml HNO_3 (1.40), 1000 ml CH_3OH;
2—20 ml $HClO_4$ (57%), 50 ml HNO_3 (1.40), 1000 ml C_2H_5OH;
3—35 g citric acid, 5 g $(NH_4)_2SO_4$, 15 ml HNO_3 (1.40), 1000 ml CH_3OH;
6—50 ml $HClO_4$ (57%), 50 ml HNO_3 (1.40), 1000 ml CH_3OH;
7—50 ml $HClO_4$ (57%), 50 ml HNO_3 (1.40), 1000 ml C_2H_5OH;
10—20 ml $HClO_4$ (57%), 50 ml HNO_3 (1.40), 1000 ml H_2O.

Fig. 2. Potential-time curves of the alloy (Ni_3Ti—Ni_3Al—solid solution). Electrolytes:
2—20 ml $HClO_4$ (57%), 50 ml HNO_3 (1.40), 1000 ml C_2H_5OH;
3—35 g citric acid, 5 g $(NH_4)_2SO_4$, 15 ml HNO_3 (1.40), 1000 ml CH_3OH;
6—50 ml $HClO_4$ (57%), 50 ml HNO_3 (1.40), 1000 ml CH_3OH;
7—50 ml $HClO_4$ (57%), 50 ml HNO_3 (1.40), 1000 ml C_2H_5OH;
10—20 ml $HClO_4$ (57%), 50 ml HNO_3 (1.40), 1000 ml CH_3OH.

The results of microchemical analysis of the anodic residues of the multicomponent alloy having a three-phase structure indicate that, when it is dissolved in electrolyte No. 1, two phases are released in the anodic powder: Ni_3Ti and Ni_3Al (Table 2). Table 3 presents the results of microchemical analysis of the anodic residue selectively isolated in electrolyte No. 3 and consisting of the intermetallic γ'-phase based on the compound Ni_3Al, in which part of the aluminum atoms is replaced by other elements. The composition of this phase is as follows: $(Ni, Cr)_3(Al, Ti, W, Mo)$, where $Ni, Cr/Al, Ti, W, Mo = 4.50$.

Thus, selective isolation of the two metallic compounds Ni_3Ti and Ni_3Al can be carried out in the selected electrolytes.

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