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Figure 2

Figure 1: Figure 2

Abstract

Full Text

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INVESTIGATION OF METALLIC COMPOUNDS IN MULTICOMPONENT NICKEL ALLOYS CONTAINING NIOBIUM

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The investigation of phase equilibrium in the seven-component system (Ni–Cr–W–Mo–Nb–Ti–Al), carried out by I. I. Kornilov and L. I. Pryakhina for the construction of the state diagram, made it necessary to study in detail the excess phases forming in alloys located in individual regions of this system.

Fig. 2. Electrode potentials of the compound Ni_3Nb *(a)* and of the γ-solid solution in various electrolytes: **1**–50 ml $HClO_4$ (57%), 35 g citric acid, 1000 ml CH_3OH; **2**–5 g NH_4Cl, 7.5 ml HCl (1.19), 20 g citric acid, 1000 ml CH_3OH; **3**–50 ml $HClO_4$ (57%), 10 ml HCl (1.19), 35 g citric acid, 1000 ml CH_3OH; **4**–50 ml HCl (1.19), 35 g citric acid, 1000 ml CH_3OH

In the present work we give the results of a study, by the method of intermetallic analysis, of the isolation and determination of the composition and structure of the metallic compound formed in alloys containing different amounts of niobium. As our experiments have shown, in these multicomponent alloys solid solutions based on the metallic compound Ni_3Nb are formed.

We studied cast alloys prepared by L. I. Pryakhina, after heat treatment according to the following regime: heating to 1200°, holding for 200 hours, and cooling in air. The microstructure of several of the alloys studied is seen from Fig. 1 *(a, b, c)*.

Preliminary experiments showed that isolation of the intermetallic phase containing niobium (Ni_3Nb) is favored by an inert medium, owing to the strong oxidizability of the anodic precipitate during electrolysis in aqueous electrolytes. In order to choose correctly the optimal composition of the electrolyte, we measured the electrode potentials of the chemical compound Ni_3Nb and of the γ-solid solution in various electrolytes (Fig. 2), according to the method described in ([1], [2]).

Figure 3

Figure 2: Figure 3

Fig. 3. Anodic polarization curve for an electrolyte: 50 ml $HClO_4$ (57%), 10 ml HCl (1.19), 35 g citric acid, 1000 ml CH_3OH

Comparative data at room temperature on the isolation of the Ni_3Nb phase in various electrolytes are presented in Table 1. Microchemical analysis of anodic precipitates isolated in various electrolytes showed that in all cases the composition of the compound is the same, close to stoichiometric.

For the article by R. B. Golubtsova and L. A. Nuda, p. 318

Figure labels in the micrographs: , , .

Fig. 1. Microstructure of the alloys studied: a—alloy 3, b—alloy 8, c—alloy 21a. 200×

Fig. 4. X-ray diffraction patterns of the Ni_3Nb phase isolated from alloy 8

For the article by A. V. Topchiev, E. A. Mukhina, A. I. Perelman, and B. A. Krentsel, p. 344

Fig. 1. X-ray diffraction patterns of crystalline polyvinylcyclohexane obtained on catalysts: chromium oxide (a), chromium oxide with addition of $(u = C_4H_9)_3Al$ (b), and $(u = C_4H_9)_3Al + TiCl_4$ (c).

The results of studying the influence of current density on the yield and composition of the Ni_3Nb phase are presented in Table 4. These results show that, at a current density in the process of anodic dissolution from 0.01 to 0.2 A/cm^2, the phase yield was 16.30%, while at a current density above 0.2 A/cm^2 there is a sharp decrease in the percentage yield of the phase; however, current density has no influence on the composition of the phase. It may be assumed that the decrease in the percentage yield of the phase at elevated current density occurs because of heating of the electrolyte near the specimen during electrolysis.

No oxidative reactions associated with the discharge of anions occur; dissolution of the anode at different current densities (0.05; 0.1; 0.2; 0.3 A/cm^2) proceeds with a very slight change in the anodic potential. The nature of the polarization curve (Fig. 3) indicates that the process proceeds without jumps in the value of the potential.

Data from the study of the influence of temperature during electrolysis on the yield and composition of the phase are given in Table 5. These data indicate that at temperatures of +18 and 0° a metallic compound based on Ni_3Nb is deposited (phase yield 16.30%). On cooling to −8°, along with the Ni_3Nb phase, a solid solution is passivated, which somewhat increases the percentage yield of the phase. Passivation of the solid solution evidently occurs because of a decrease in the activating action of Cl′ ions under strong cooling.

On the basis of all the above, the optimum regime for isolating the Ni_3Nb phase was established. The data of intermetallic and X-ray structural analysis of the alloys studied are given in Table 2 and in Fig. 4. X-ray diffraction was carried out by the powder method in iron radiation in a GFTI-1 camera.

In all alloys the phase that is liberated is a solid solution based on the metallic compound Ni_3Nb, which has a rhombic crystal lattice.

On the basis of the closeness of the atomic radii, it may be assumed that Cr atoms (1.28 Å) can substitute for atoms

Table 4

Isolation of the Ni_3Nb phase in various electrolytes (comparative data)

Electrolyte composition	Specific electrical conductivity, $\mu\Omega^{-1}$ cm^{-1} at 20°C	Current density, A/cm^2	Duration, min	Electrolyte temperature, °C — initial	Electrolyte temperature, °C — final	Weight of dissolved anode, g	Phase yield, wt.%	Phase composition, wt.% — Ni	Phase composition, wt.% — Nb	Phase composition, wt.% — Cr	Phase composition, wt.% — W	Phase composition, wt.% — Mo	Phase composition, wt.% — total	Ni/Nb	Cr, Nb, W, Mo	X-ray structural analysis data
5 g NH_4Cl, 7.5 ml HCl (1.19), 20 g citric acid, 1000 ml CH_3OH	$0.658 \cdot 10^{-2}$	0.01	180	18	18	0.3430	6.35	59.85	29.80	2.66	5.20	2.22	99.73	2.01	1.68	Ni_3Nb

Electrolyte composition	Specific electrical conductivity, $\mu\Omega^{-1}\cdot cm^{-1}$ at 20°C	Current density, A/cm^2	Duration, min	Electrolyte temperature, °C — initial	Electrolyte temperature, °C — final	Weight of dissolved anode, g	Phase yield, wt.%	Phase composition, wt.% — Ni	Phase composition, wt.% — Nb	Phase composition, wt.% — Cr	Phase composition, wt.% — W	Phase composition, wt.% — Mo	Phase composition, wt.% — total	Ni/Nb	Cr, Nb, W, Mo	X-ray structural analysis data
5 g NH_4Cl, 7.5 ml HCl (1.19), 20 g citric acid, 1000 ml CH_3OH	$0.658\cdot10^{-2}$	0.1	18	18	28	0.3007	72.82	59.85	29.75	2.66	5.20	2.20	99.66	2.01	1.68	Ni_3Nb
50 ml $HClO_4$ (57%), 10 ml HCl (1.19), 50 ml CH_3OH, acids, 1000 ml [[unclear: solvent]]	$2.86\cdot10^{-2}$	0.1	18	18	21											Ni, Ni_3Nb

Electrolyte composition	Specific electrical conductivity, $\mu\Omega^{-1}\cdot cm^{-1}$ at 20°C	Current density, A/cm^2	Duration, min	Electrolyte temperature, °C — initial	Electrolyte temperature, °C — final	Weight of dissolved anode, g	Phase yield, wt.%	Phase composition, wt.% — Ni	Phase composition, wt.% — Nb	Phase composition, wt.% — Cr	Phase composition, wt.% — W	Phase composition, wt.% — Mo	Phase composition, wt.% — total	Ni, Cr, Nb, W, Mo	X-ray structural analysis data
50 ml HCl (1.19), 35 g citric acid, 1000 ml CH_3OH	$3.01\cdot10^{-2}$	0.1	18	18	20	0.3716	16.30	59.92	29.87	2.65	5.20	2.20	99.84	2.00	1.68	Ni_3Nb
50 ml HCl (1.19), 35 g citric acid, 1000 ml CH_3OH	$3.01\cdot10^{-2}$	0.1	18	18	20	1.4002	16.30	59.90	29.80	2.66	5.20	2.20	99.76	2.01	1.68	Ni_3Nb

Table 2

Microchemical analysis of anodic powders isolated from the alloys under study

Alloy No.	Ni, wt. %	Nb, wt. %	Cr, wt. %	W, wt. %	Mo, wt. %	Al, wt. %	Sum, wt. %	Ni/Nb	Ni, Cr / Nb, W, Mo	Ni, at. %	Nb, at. %	Cr, at. %	W, at. %	Mo, at. %	Sum, at. %	Ni/Nb	Ni, Cr / Nb, W, Mo	X-ray structural-analysis data*
1a	—	—	—	—	—	—	—	—	—	Anodic powder is not isolated	Anodic powder is not isolated	Anodic powder is not isolated	Anodic powder is not isolated	Anodic powder is not isolated	Anodic powder is not isolated	—	—	—
3	—	—	—	—	—	—	—	—	—	Anodic powder is not isolated	Anodic powder is not isolated	Anodic powder is not isolated	Anodic powder is not isolated	Anodic powder is not isolated	Anodic powder is not isolated	—	—	—
8	59.92	29.87	2.65	5.20	2.20	—	99.84	2.00	1.68	70.64	22.36	3.53	1.94	1.59	100	3.17	2.87	Ni_3Nb; a = 5.09 Å; b = 4.24 Å; c = 4.47 Å

Alloy No.	Ni, wt. %	Nb, wt. %	Cr, wt. %	W, wt. %	Mo, wt. %	Al, wt. %	Sum, wt. %	Ni/(Nb + W + Mo)	Ni, Cr / Nb, W, Mo	Ni, at. %	Nb, at. %	Cr, at. %	W, at. %	Mo, at. %	Sum, at. %	Ni/(Nb + W + Mo)	Ni, Cr / Nb, W, Mo	X-ray structural-analysis data*
21a	59.60	29.76	3.15	5.20	2.20	—	99.91	2.00	1.69	70.04	22.19	4.23	1.94	1.60	100	3.15	2.88	Ni_3Nb; a = 5.06 Å; b = 4.24 Å; c = 4.49 Å
21	59.80	29.85	2.80	5.20	2.20	—	99.85	2.00	1.68	70.49	22.13	3.80	1.93	1.59	100	3.18	2.89	Ni_3Nb
21	60.64	30.43	3.93	3.40	1.50	—	99.91	1.99	1.83	70.22	22.36	5.18	1.22	1.02	100	3.14	3.06	Ni_3Nb; a = 5.07 Å; b = 4.21 Å; c = 4.46 Å

* X-ray structural analysis was carried out in the X-ray laboratory of the Central Scientific Research Institute of Technology and Machine Building by S. A. Yuganova, M. D. Nesterova, and R. N. Rogova.

Table 3

Distribution of alloying elements between the γ-solid solution and the Ni_3Nb phase

Alloy No.	Product of electrolysis	Phase	Ni, %	Nb, %	Cr, %	W, %	Mo, %	Al, %	Sum, %	Ni, wt. %	Nb, wt. %	Cr, wt. %	W, wt. %	Mo, wt. %	Al, wt. %
1a	Electrolyte	γ-solid solution	82.00	—	8.95	6.00	2.98	—	99.93	100	—	100	100	100	—
1a	Anodic precipitate	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent
3	Electrolyte	γ-solid solution	77.26	6.73	6.96	5.95	3.00	—	99.90	100	100	100	100	100	—
3	Anodic precipitate	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent	Anodic precipitate absent
8	Electrolyte	γ-solid solution	60.27	8.25	6.57	5.13	2.64	0.9	83.76	86.05	2.88	93.86	85.88	0.00	100
8	Anodic precipitate	Ni_3Nb	9.77	4.87	0.43	0.85	0.36	—	16.28	13.95	37.12	6.14	14.20	12.00	—
8	Sum	—	70.04	13.12	7.00	5.98	3.00	0.9	100.04	100	100	100.01	100	100	100

Alloy No.	Product of electrolysis	Phase	Ni, %	Nb, %	Cr, %	W, %	Mo, %	Al, %	Sum, %	Ni, wt. %	Nb, wt. %	Cr, wt. %	W, wt. %	Mo, wt. %	Al, wt. %
21a	Electrolyte	γ-solid solution	49.39	8.32	8.12	4.55	2.38	—	72.76	75.18	50.55	90.42	76.22	79.87	—
21a	Anodic precipitate	Ni_3Nb	16.31	8.14	0.86	1.42	0.60	—	27.33	24.82	49.45	9.58	23.78	20.13	—
21a	Sum	—	65.70	16.46	8.98	5.97	2.98	—	100.09	100	100	100	100	100	—

Ni (1.24 Å), while W (1.41 Å) and Mo (1.40 Å) atoms can replace Nb atoms (1.47 Å).

Therefore the formula of the compound formed in the alloy may be represented as follows: $(Ni, Cr)_3(Nb, W, Mo)$.

Table 4

Effect of current density on the yield and composition of the Ni_3Nb phase
(electrolyte: 50 ml $HClO_4$ (57%), 10 ml HCl (1.19), 35 g citric acid, 1000 ml CH_3OH)

Current density, A/cm²	Electrolysis duration, min	Electrolyte temperature, °C, initial	Electrolyte temperature, °C, final	Weight of dissolved anode, g	Phase yield, wt. %	Phase composition, wt. % Ni	Phase composition, wt. % Nb	Phase composition, wt. % Cr	Phase composition, wt. % W	Phase composition, wt. % Mo	Phase composition, wt. % total	X-ray structural analysis data
0.01	180	18	18	0.3802	16.28	59.98	29.92	2.65	5.20	2.22	99.97	Ni_3Nb
0.05	36	18	19	0.3700	16.27	59.98	29.92	2.65	5.20	2.22	99.97	Ni_3Nb
0.1	18	18	20	0.3716	16.30	59.92	29.87	2.65	5.20	2.20	99.84	Ni_3Nb
0.2	9	18	22	0.3740	16.27	59.98	29.92	2.65	5.20	2.22	99.97	Ni_3Nb
0.25	7.5	18	25	0.3750	9.92	59.98	29.92	2.65	5.20	2.20	99.95	Ni_3Nb

Current density, A/cm^2	Electrolysis duration, min	Electrolyte temperature, °C, initial	Electrolyte temperature, °C, final	Weight of dissolved anode, g	Phase yield, wt. %	Phase composition, wt. % Ni	Phase composition, wt. % Nb	Phase composition, wt. % Cr	Phase composition, wt. % W	Phase composition, wt. % Mo	Phase composition, wt. % total	X-ray structural analysis data
0.3	6	18	28	0.3784	7.07	59.98	29.92	2.65	5.20	2.22	99.97	Ni_3Nb

The analysis carried out on the electrolysis products (analysis of the anodic precipitate and the electrolyte) made it possible to establish the distribution of the alloying elements between the γ-solid solution and the Ni_3Nb phase (Table 5).

Table 5

Effect of temperature on the yield and composition of the phase
(electrolyte: 1000 ml methanol, 35 g citric acid, 50 ml hydrochloric acid (57%), 10 ml HCl (1.19))

Electrolyte temperature, °C, initial	Electrolyte temperature, °C, final	Current density, A/cm^2	Electrolysis duration, min	Weight of dissolved anode, g	Phase yield, wt. %	Composition of anodic powder, wt. % Ni	Composition of anodic powder, wt. % Nb	Composition of anodic powder, wt. % Cr	Composition of anodic powder, wt. % W	Composition of anodic powder, wt. % Mo	Composition of anodic powder, wt. % total	X-ray structural analysis data
18	20	0.1	18	0.3716	16.30	59.92	29.87	2.65	5.20	2.20	99.84	Ni_3Nb
0	+2.5	0.1	18	0.3642	16.33	60.00	29.88	2.66	5.25	2.20	99.99	Ni_3Nb
−8	−7	0.1	18	0.3554	17.20	60.11	29.40	2.65	5.52	2.27	99.95	Ni_3Nb, Ni (Ni cubic) a = 3.59 Å

The investigation carried out made it possible to establish the amount and composition of the Ni_3Nb phase and the γ-solid solution in individual alloys of the system studied.

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REFERENCES CITED

1. R. B. Golubtsova, L. A. Mashkovich, *DAN*, **111**, No. 4 (1956); **106**, No. 6 (1956).

2. R. B. Golubtsova, *DAN*, **118**, No. 1 (1958); **124**, No. 1 (1959).

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