R. B. Golubtsova

1965

SovietRxiv

Abstract

Full Text

R. B. Golubtsova

SELECTIVE ISOLATION OF METALLIC COMPOUNDS FROM AN ALLOY OF THE SYSTEM Ni_3Al–Ni_3Nb

(Presented by Academician I. I. Chernyaev, 15 VI 1964)

Metallic compounds (metallides) are characterized by special physical properties (^{1}); they constitute new substances sharply different from other known simple substances and from the elements that form them (^{2}).

In the development of phase analysis, methods of differentiated separation of metallic compounds–phases based on the use of their chemical properties (^{3}) –should now be applied in combination with differentiated methods of electrochemical phase analysis.

The literature describes methods for the chemical separation of multiphase anodic precipitates into individual phases ($^{3-5}$), based on selective chemical dissolution, by means of which the desired phase is left in the precipitate and the remaining phases are transferred into the filtrate. X-ray structural analysis of the precipitate must confirm the purity of the phase separation. These methods have become widespread mainly in carbide analysis.

The present work is devoted to a study of the conditions for selective electrolytic isolation of the metallic compounds Ni_3Al and Ni_3Nb, present together in a two-phase alloy* with subsequent microchemical analysis of the anodic precipitates. The phase diagram of the Ni_3Al–Ni_3Nb system was studied in (^{2}).

To choose the optimum electrolyte composition for the selective electrochemical isolation of the metallic compounds Ni_3Al and Ni_3Nb contained in the alloy Ni_3Al–Ni_3Nb, the electrochemical behavior of this alloy in various electrolytes was investigated. Anodic-polarization curves at various current densities were recorded by the compensation method against a calomel electrode, using a high-resistance P-300 potentiometer.** The best electrolytes (Fig. 1) for isolating the Ni_3Nb phase are electrolytes No. 8 (^{6}) and No. 7 (^{7}), which confirms the regular relation between the electrochemical behavior of an alloy containing the metallic compound Ni_3Nb and the data on its solubility in various chemical media that we had studied earlier. The character of the anodic-polarization curve in electrolyte No. 8 depends on the nature of the electrolyte and especially on the nature of the anions in the electrolyte solution, and also, evidently, on the nature of the phase. Electrolyte No. 4 differs from electrolyte No. 8 by the absence of HCl, which strongly shifts the potential.

The anodic-polarization curves recorded in electrolytes VII and IV, tested for isolating the Ni_3Al phase, lie in the region of high electrode-potential values. Anodic dissolution of the alloy in these electrolytes occurs with considerable polarization, the magnitude of which indicates passivation of the alloy surface. The best electrolyte for isolating the Ni_3Al phase is electrolyte VII.

* The alloy was prepared by L. I. Pryakhina in connection with the study of its quasi-ternary system γ'-Ni_3Al—Ni_3Nb—Ni_3Ti ([13]) and was provided to us.
** The curves were recorded by S. M. Savvateeva.

The potential of electrolyte IV lies in the region of high values. It should be noted that the alloy studied by us does not dissolve anodically and no anodic powder is precipitated in this electrolyte, which fully confirms the conclusion of the authors of this electrolyte[^8], who established that in the indicated electrolyte the Ni_3Al phase can be anodically precipitated only in the presence of chromium in the alloy.

The best electrolyte for the electrolytic isolation of the compound Ni_3Nb is electrolyte No. 8, which contains hydrochloric acid; this evidently gives the smallest polarization value in comparison with electrolyte No. 4, which differs by the absence of hydrochloric acid.

Fig. 1

Fig. 1. Curves of anodic polarization of a two-phase Ni—Al—Nb alloy (50% Ni_3Nb and 50% Ni_3Al) in various electrolytes

	Electrolytes	Electrolytes	Electrolytes	Electrolytes	Electrolytes	Electrolytes		Electrolytes	Electrolytes	Electrolytes	Electrolytes	Electrolytes	Electrolytes
	No. 4	No. 5	No. 7	No. 8	IV	VII		No. 4	No. 5	No. 7	No. 8	IV	VII
$HClO_4$ (57% aq.), ml	50	50	–	50	–	20	CH_3OH, ml	–	–	1000	1000	–	–
CH_3OH, ml	1000	1000	–	–	–	1000	$(NH_4)_2SO_4$, g	–	–	–	–	10	–
NH_4Cl, g	–	–	5	–	–	–	H_2O, ml	–	–	–	–	1200	–
HCl (1.19), ml	–	–	7.5	10	–	–	Citric acid, g	35	–	20	35	10	–
HNO_3 (1.40), ml	–	–	–	–	–	50	Oxalic acid, g	–	5	–	–	–	–

Fig. 2

Fig. 2. Curves of anodic polarization of the metallic compound Ni_3Nb and of a nickel solid solution (with 2.5% Nb No. 6) in electrolytes Nos. 8 and 7 (see caption to Fig. 1)

Separation of the two phases Ni_3Nb and Ni_3Al is based on the large difference in the potentials of the alloy (Fig. 1), observed in electrolytes No. 8 and VII, which creates conditions for the selective isolation of the indicated phases. This was confirmed experimentally during anodic dissolution of the alloy in the selected electrolytes.

A study of the electrochemical behavior of phases synthetically melted for methodological purposes—Ni_3Nb and a solid solution containing 2.5% Nb—in various electrolytes showed that the greatest difference between the potentials of the phase and the solid solution is observed in electrolyte No. 8 (Fig. 2). In electrolyte No. 7[^9] this difference is considerably smaller. In the investigated binary alloy containing two metallic compounds, Ni_3Nb and Ni_3Al, in electrolyte No. 7 the magnitude of anodic polarization is insignificant; however, this electrolyte has low electrical conductivity[^10], which limits the increase in current density necessary for shortening the duration of anodic dissolution.

The dependence of the potential on time at a current density of 0.1 A/cm^2 in electrolyte VII (Fig. 3) and in electrolytes No. 8 and No. 7 (Fig. 4) shows that these potentials are established rapidly.

The light-absorption curves, recorded on an SF-4 spectrophotometer, in electrolytes VII and No. 8 lie in different regions, which, obviously, also indicates the possibility of selective separation of the two metallic compounds Ni_3Nb and Ni_3Al in the indicated electrolytes.

Fig. 3. Electrode potential of the alloy (50% Ni_3Nb and 50% Ni_3Al) as a function of time in electrolyte VII (see caption to Fig. 1)

Fig. 4. Change in the anodic potential of the Ni—Nb—Al alloy (50% Ni_3Al and 50% Ni_3Nb) with time at a current density of 0.1/cm^2 in electrolyte VII (see caption to Fig. 1)

The dispersed powder released in the course of anodic dissolution on the specimen—the anode—was scraped off with a razor blade or scalpel into alcohol and washed by centrifuging five times with ethyl alcohol, then five times with ether. Drying of the anodic precipitate to constant weight was carried out in a centrifuge tube according to the following regime: in a desiccator with P_2O_5 for 24 hours, then in a drying oven at 30° with a further gradual increase of the temperature to 65°.

In the dried anodic powder (sample weight 0.01 g), the niobium content was determined by the method proposed by the author (^{11}), and aluminum by the method of E. A. Kashkovskaya and I. S. Mustafina (^{12}).

The results of the microchemical analysis of the anodic precipitate are presented in Table 1.

According to X-ray structural analysis, the anodic powder isolated in electrolyte No. 1 is single-phase. The reflections on the X-ray pattern corresponded to the reflections of the face-centered cubic lattice of Ni_3Al with a period of 3.6035 kX. At the same time, the lattice period of the pure compound Ni_3Al is $a = 3.562$ kX ([2]). Thus, the anodic powder is a solid solution based on Ni_3Al. Calculated from the data of the microchemical analysis (Table 1), the anodic powder contains (in wt. %): Ni_3Al 62.57, Ni_3Nb 37.43. According to the phase diagram, this composition corresponds to the composition of the limiting solid solution released during the anodic dissolution of the initial alloy.

Table 1

Results of microchemical determination of the composition of the anodic precipitate isolated at a current density of 0.10 A/cm^2. Alloy composition: Ni_3Al 50%, Ni_3Nb 50%. Electrolyte No. 1. 20 ml $HClO_4$ (57%), 50 ml HNO_3 (sp. gr. 1.40), 1000 ml CH_3OH. Duration of experiment 1.5 hours.

Dry weight of anodic powder, g	Phase yield, %	Found in anodic precipitate, wt. %	Found in anodic precipitate, wt. %	Found in anodic precipitate, wt. %	Found in anodic precipitate, wt. %	Found in anodic precipitate, wt. %	Found in anodic precipitate, wt. %	Found in anodic precipitate, atomic %	Found in anodic precipitate, atomic %	Found in anodic precipitate, atomic %	Found in anodic precipitate, atomic %	Found in anodic precipitate, atomic %	Found in anodic precipitate, atomic %	Result of X-ray structural analysis*
		Ni	Nb	Al	Sum	Ni/Al	Ni/Nb	Ni	Nb	Al	Sum	Ni/Al	Ni/Nb	
0.0555	7.54	78.83	12.93	8.24	100.00	$\frac{54.33}{8.24} = 6.59$	$\frac{24.50}{12.93} = 1.896$	75.18	7.77	17.05	100.0	$\frac{51.87}{17.05} = 3$	$\frac{23.31}{7.77} = 3$	Ni_3Al; $a = 3.6035$ kX

* X-ray structural analysis in all experiments was carried out by K. N. Myasnikova.

Theoretically, in the compound Ni_3Al, Ni/Al = 6.52, and in Ni_3Nb, Ni/Nb = 1.895. The results obtained (Table 1) are in agreement with the theoretical values. Thus, 37.43% of the Ni_3Nb phase is dissolved in 62.57% of the Ni_3Al phase. These data fully correspond to the phase diagram ([2]).

Table 2

Microchemical determination of the composition of the anodic precipitate. Alloy composition: Ni_3Al 50%, Ni_3Nb 50%; electrolyte No. 2. 50 ml $HClO_4$ (57%), 10 ml HCl (sp. gr. 1.19%), 35 g citric acid, 1000 ml CH_3OH

Dry weight of anodic precipitate, g	Phase yield, %	Found in anodic precipitate, wt. %: Ni	Found in anodic precipitate, wt. %: Nb	Found in anodic precipitate, wt. %: Al	Found in anodic precipitate, wt. %: Sum	Found in anodic precipitate, wt. %: Ni/Nb	Found in anodic precipitate, wt. %: Ni/Al	Found in anodic precipitate, at. %: Ni	Found in anodic precipitate, at. %: Nb	Found in anodic precipitate, at. %: Al	Found in anodic precipitate, at. %: Sum	Found in anodic precipitate, at. %: Ni/Nb	Found in anodic precipitate, at. %: Ni/Al	X-ray structural analysis result
Precipitate isolated at a current density of 0.1 A/cm^2. Experiment duration 1.5 hours														
0.0413	5.39	66.84	32.83	0.44	100.11	$\frac{63.97}{32.83} = 1.94$	$\frac{2.87}{0.44} = 6.52$	75.36	23.54	1.08	99.98	$\frac{72.12}{23.54} = 3$	$\frac{3.24}{1.08} = 3$	Ni_3Nb phase

Dry weight of anodic precipitate, g	Phase yield, %	Found in anodic precipitate, wt. %: Ni	Found in anodic precipitate, wt. %: Nb	Found in anodic precipitate, wt. %: Al	Found in anodic precipitate, wt. %: Sum	Found in anodic precipitate, wt. %: Ni/Nb	Found in anodic precipitate, wt. %: Ni/Al	Found in anodic precipitate, at. %: Ni	Found in anodic precipitate, at. %: Nb	Found in anodic precipitate, at. %: Al	Found in anodic precipitate, at. %: Sum	Found in anodic precipitate, at. %: Ni/Nb	Found in anodic precipitate, at. %: Ni/Al	X-ray structural analysis result
Precipitate isolated at a current density of 0.15 A/cm^2. Experiment duration 3 hours														
0.0382	2.12	66.09	33.77	0.15	100.01	$\frac{65.11}{33.77} = 1.92$	$\frac{0.98}{0.15} = 6.52$	75.32	24.37	0.37	100.06	$\frac{74.21}{24.37} = 3$	$\frac{1.11}{0.37} = 3$	Ni_3Nb phase

For the selective isolation from the alloy of the Ni_3Nb phase, electrolyte No. 2 was used. The experiments were carried out at various current densities. The results of the microchemical analysis are presented in Table 2.

According to the conclusion of the X-ray structural analysis, the anodic powder is also single-phase, consisting of the Ni_3Nb phase, in which the Ni_3Al phase is dissolved.

According to the microchemical analysis data (Table 2), the anodic precipitate contains 96.8 wt. % Ni_3Nb and 3.31 wt. % Ni_3Al, which corresponds to the composition of the limiting solid solution of Ni_3Al in Ni_3Nb and fully coincides with the data of the phase diagram ([2]), and also confirms the solubility limit tentatively established by Mintz et al. ([2]).

The investigation carried out showed the selective action of the chosen electrolytes, making it possible, in a differentiated manner, by electrochemical (anodic) dissolution in them, to isolate metallide phases from an alloy with a two-phase structure.

Institute of Metallurgy
named after A. A. Baikov

Received
23 III 1964

REFERENCES

[1] I. I. Kornilov, *Interaction between Metallic Compounds (Metallides)*, 1963.
[2] R. S. Mintz, G. F. Belyaeva, Yu. S. Malkov, ZhNKh, 7, issue 10, 6 (1962).
[3] Yu. A. Klyachko, *Collected Volume: Physicochemical Methods of Analysis of Alloys and Metals*, Seminar Materials, Moscow, 1962, p. 147.
[4] N. M. Popova, *Carbide Analysis of Steel*, 1956.
[5] E. F. Yakovleva, *Collected Volume: Physicochemical Methods of Analysis of Alloys and Metals*, Seminar Materials, Moscow, 1962, p. 128.
[6] R. B. Golubtsova, L. A. Nudd, DAN, 130, No. 2, 318 (1960).
[7] R. B. Golubtsova, L. A. Mashkovich, ZhNKh, 3, 3 (1958).
[8] N. I. Blok, A. I. Glazova et al., *Collected Volume: Phase Analysis, Structure and Properties of Heat-Resistant Steels and Alloys*, 1960, p. 6.
[9] I. I. Kornilov, E. N. Pylaeva, DAN, 91, No. 4, 841 (1953).
[10] R. B. Golubtsova, L. A. Nudd, *Proceedings of the Central Scientific Research Institute of Technology and Mechanical Engineering*, No. 11, 20 (1960).
[11] R. B. Golubtsova, ZhAKh, 6, issue 1 (1951).
[12] E. A. Kashkovskaya, I. S. Mustafin, *Zav. lab.*, 24, No. 10 (1958).
[13] L. I. Pryakhina, DAN, 139, No. 3 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.