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Abstract

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Yu. A. Bagaryatskii and L. E. Ivanovskaya

Form of the Phase Diagram of Ni–NiAl–Mo Alloys

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Nickel-based alloys are of great importance as alloys operating at high temperatures and loads ([1,2]). Heat-resistant alloys may be sought, in particular, in the ternary system Ni–Al–Mo ([3]); more complex heat-resistant alloys on a nickel-chromium base with additions of Al, Ti, Mo, and Co ("nimonic-100," "udimet-500," etc. ([2])) are also successfully used. Nevertheless, up to the present time not even a ternary phase diagram has been constructed for Ni–Al–Mo alloys, to say nothing of more multicomponent nickel alloys containing Al and Mo. In the bibliographic handbook on alloys ([4]), as well as in a later work ([14]), there is a reference to only one work in which the Ni–Al–Mo phase diagram was studied. However, the schematic arrangement of phase fields in the nickel corner of the diagram given in this single work ([5]) was obtained only on the basis of studying the microstructures of alloys (without identification of the phases), and moreover of alloys that had obviously not been brought to equilibrium (the specimens were annealed for 3-10 hours at 700°). In addition, at that time (1925) the phase diagrams of the binary systems Ni–Al and Ni–Mo were not yet accurately known. Therefore it is natural that the scheme of arrangement of phase fields presented in work ([5]), as shown by the data we obtained, does not correspond to reality. In the work mentioned above ([3]) only the heat-resistant properties of ternary Ni–Al–Mo alloys were studied, and no attempt was made to construct a phase diagram; however, it followed from that work that from the complete Ni–Al–Mo system a partial Ni–Al–NiMo system could be isolated. As will be seen below, this assumption is incorrect, and in reality the partial system is Ni–NiAl–Mo, similar to what occurs in the phase diagrams of the Ni–Al–Cr ([6–8]) and Ni–Al–W ([9]) systems.

The alloys in our work were melted from pure materials in a high-frequency furnace; alloys with a Mo content of more than 50 at.% could not be melted because of their high melting point. The melts were carried out in an argon atmosphere, in corundum crucibles, without casting. To avoid segregation of composition, the melted ingots were remelted again, but in an inverted position. Seven alloys of the binary Ni–Mo system were melted (designated by the letters a–zh in Table 1) and 30 alloys of the ternary system (designated by numbers). The compositions of the alloys (in at.%) are given from the charge, since chemical

analyses showed that deviations in the content of each element from the specified value in most cases do not exceed 1 at.%.

The alloys were homogenized at 1200° in a vacuum furnace for 100 hours; the alloys richest in Al (containing large amounts of NiAl) were homogenized again at 1500° (2 hours), since after the first homogenization the dendritic structure was still clearly visible on the polished sections.

It was intended to study the alloys along three isothermal sections: at 1200, 1000, and 800°; accordingly, three batches of specimens underwent the following heat treatments:

Table 1

Number of phases according to microstructural data and phase identification (by means of X-ray diffraction data) in the alloys studied after quenching from 1200°

Alloy	Content, at. % Mo	Content, at. % Al	Number of phases	Phases	Alloy	Content, at. % Mo	Content, at. % Al	Number of phases	Phases
	7	–	1	γ	12	18	2 1/2	1	γ
	16	–	1	γ	13	21	2 1/2	1	γ
	20	–	1	γ	14	20	5	1	γ
	25	–	1	γ	15	17 1/2	10	2	$\alpha + \gamma$
	28	–	2	$\gamma + (\delta)$	16	15	20	2	$\alpha + \gamma'$
	38	–	2	$\gamma + \delta$	17	5	47 1/2	2	$\alpha +$ [[unclear: phase symbol]]
	48	–	2	$(\gamma) + \delta$	18	10	45	2	$\alpha +$ [[unclear: phase symbol]]
1	10	20	2	$\alpha + \gamma'$	19	20	40	2	$\alpha +$ [[unclear: phase symbol]]

Alloy	Content, at. % Mo	Content, at. % Al	Number of phases	Phases	Alloy	Content, at. % Mo	Content, at. % Al	Number of phases	Phases
2	10	15	3	$(\alpha)+\gamma+$ [[unclear: phase symbol]]	20	30	35	2	$\alpha +$ [[unclear: phase symbol]]
3	10	5	1	γ	21	25	30	2	$\alpha +$ [[unclear: phase symbol]]
4	5	25	3	$(\alpha)+\beta+$ [[unclear: phase symbol]]	22	20	25	3	$\alpha +$ (β) $+ \gamma'$
5	5	10	1	γ	23	40	20	?	$\alpha +$ γ'
6	2 1/2	10	1	γ	24	45	10	?	$\alpha +$ $\gamma(\gamma')$
7	2 1/2	22 1/2	2	$\gamma +$ γ'	25	30	5	2	$\alpha +$ γ
8	2 1/2	25	1	γ'	26	5	2 1/2	2	$\alpha +$ γ'
9	7 1/2	10	1	γ	27	2 1/2	40	2	(α) $+$ [[unclear: phase symbol]]
10	12 1/2	5	1	γ	28	2 1/2	48	2	$\alpha +$ [[unclear: phase symbol]]
11	15	5	1	γ	29	50	2 1/2	2	$\alpha +$ [[unclear: phase symbol]]

Alloy	Content, at. % Mo	Content, at. % Al	Number of phases	Phases	Alloy	Content, at. % Mo	Content, at. % Al	Number of phases	Phases
					30	10	12 1/2	1	γ

Note. Parentheses denote the non-observation of the lines of the given phase on the X-ray diffraction patterns.

1) 1200°—100 h → quenching;

2) 1200°—100 h + 1000°—100 h → quenching;

3) 1200°—100 h + 1000°—100 h + 800°—100 h → quenching.

The study of the alloys obtained was carried out in parallel by microstructural and X-ray diffraction methods, since each of these methods separately either does not provide reliable phase identification (microstructural *), or does not reveal small amounts of the second and third phases (X-ray diffraction **). For temperatures of 1000° and 800°, insufficiently reliable results were obtained (except for the γ-region), apparently owing to the inadequacy of the 100-hour duration of annealing at these temperatures; the results obtained for 1200° are given in Table 1. The isothermal section corresponding to these data is shown in Fig. 1; the boundaries of the γ-region at 800° and 1000° are also shown there. In constructing it, data for the binary systems Ni—Al (7, 10) and Ni—Mo (11) were used. (The latter agree well with the results we obtained

Table 2

Angles of reflections and intensities of the lines of the δ-phase (NiMo) on X-ray diffraction patterns obtained with Cu K_α radiation

θ°	Intensity	θ°	Intensity	θ°	Intensity	θ°	Intensity
27.2	weak	38.7	medium	52.8	weak	66.1	weak
28.6	medium	39.6	weak	55.4	very weak	68.0	weak
30.6	strong	40.6	weak	57.2	very weak	69.0	weak
31.2	very weak	41.3	weak	57.6	very weak	69.8	weak
21.8	very weak	43.6	very weak	58.8	weak	70.4	weak
32.1	strong	45.0	medium	59.8	very weak	71.6	weak
3.0	medium	46.1	medium	60.8	very weak	72.8	weak

Figure 2

Figure 1: Figure 2

Figure 3

Figure 2: Figure 3

$\theta°$	Intensity	$\theta°$	Intensity	$\theta°$	Intensity	$\theta°$	Intensity
3.7	medium	47.1	medium	61.8	very weak	75.6	very weak
34.7	weak	48.8	weak	62.6	very weak	76.8	very weak
23.9	medium	49.8	very weak	63.4	very weak	78.0	very weak
5.3	medium	50.8	very weak	64.2	very weak	80.4	very weak
7.4	medium	51.6	very weak	65.3	medium	81.6	weak
8.2	medium						

* For example, in work (3), the α-phase based on Mo was apparently taken in micrographs to be the compound NiMo.

** In the present case, in addition, γ (solid solution based on Ni) and γ' phases (solid solution based on the compound Ni_3Al) are not always distinguishable by X-ray diffraction.

Fig. 2. X-ray diffraction patterns of Ni–Al–Mo alloys quenched from 1200°.
a –binary alloy *zh*: Ni + 48 at. % Mo (δ-phase);
b –alloy 29: Ni + 50 at. % Mo + 2.5 at. % Al ($\alpha + \gamma$);
c –alloy 21: Ni + 25 at. % Mo + 30 at. % Al ($\alpha + \beta$);
d –alloy 16: Ni + 15 at. % Mo + 20 at. % Al ($\alpha + \gamma'$).
Filtered Cu $K\alpha$ radiation.

Fig. 3. Microstructure of Ni–Al–Mo alloys quenched from 1200°.
a –alloy 22: Ni + 20 at. % Mo + 25 at. % Al ($\alpha + \beta + \gamma'$);
b –alloy 29: Ni + 50 at. % Mo + 2.5 at. % Al ($\alpha + \gamma$);
c –alloy 21: Ni + 25 at. % Mo + 30 at. % Al ($\alpha + \beta$);
d –alloy 16: Ni + 15 at. % Mo + 20 at. % Al ($\alpha + \gamma'$).
Marble' s etchant, 300×.

for binary alloys *a*–*g* at 1200°.) The compounds Ni_4Mo (β_1-phase) and Ni_3Mo (γ_1-phase) could not be detected in the binary system, although at 800° they should have formed in alloys with 20 and 25 at.% Mo, respectively ([11]). The δ phase (NiMo) is the predominant phase in alloy *g* at all three temperatures;

Fig. 1. Isothermal section of part of the phase diagram of Ni—Al—Mo alloys at 1200°, constructed from the experimental data obtained. The numbers beside the circles are alloy numbers.

Figure 3: Fig. 1. Isothermal section of part of the phase diagram of Ni—Al—Mo alloys at 1200°, constructed from the experimental data obtained. The numbers beside the circles are alloy numbers.

this is clearly revealed by x-ray diffraction (Fig. 2a). Judging from the data in Pearson' s handbook ([12]), the compound NiMo has a complex tetragonal structure ($a = 9.108$, $c = 8.852$ Å) with 56 atoms in the elementary cell. Since detailed data on this structure were given by the authors (Shoemaker, Brink, and Fox) only in a report ([13]) and

Fig. 1. Isothermal section of part of the phase diagram of Ni—Al—Mo alloys at 1200°, constructed from the experimental data obtained. The numbers beside the circles are alloy numbers.

have not yet been published, in Table 2 we give the reflection angles found by us for the δ-phase (with K_α Cu radiation), indicating the relative line intensities*. These data may be useful in identifying the δ-phase in other cases. It is interesting that the δ-phase almost does not dissolve Al; indeed, alloy 29, containing only $2\frac{1}{2}$ at.% Al, already consists of the phases γ and α (solid solution based on Mo) (Fig. 2b). These same two systems of lines are also visible in the radiograph of alloy 15. It follows directly from this that the existence is impossible both of a two-phase region $Ni_3Al + NiMo$ ($\gamma' + \delta$) and of a three-phase region, i.e. $Ni + Ni_3Al + NiMo$ ($\gamma + \gamma' + \delta$), as was assumed in work ([3]). The data presented in the indicated work for two alloys: with 16 at.% Mo and 18 at.% Al (treatment temperature 1150°) and with 9 at.% Mo and 25 at.% Al (treatment temperature 1250°), agree well with our data for 1200° (Fig. 1), if one assumes that in work ([3]) the α-phase based on Mo was erroneously taken in microsections for the δ phase (NiMo). The position of the three-phase region $\gamma + \delta + \alpha$ in Fig. 1 is indicated by a dashed line because of the insufficiency of the experimental data.

As is evident from Table 1, the results of the x-ray diffraction investigation and of the microstructural investigation agree on the whole, provided only that the quantities of some phase are not too small to be detected by x-ray diffraction. The only exceptions are alloys 22 and 23, in which the β-phase (based on the compound NiAl) is not detected by x-ray diffraction,

* The lines cannot be reliably indexed with the structure assumed for the δ-phase, since the theoretical x-ray diffraction pattern, constructed only with knowledge of the dimensions of the elementary cell, contains an enormous number of lines whose intensity ratios are not known.

although alloy 22, for example, is clearly three-phase (Fig. 3, *a*): $\alpha + \beta + \gamma'$; however, also in alloys 17 and 18, where this phase is present in a mixture with

the α-phase in considerably larger amounts, and in alloys 19-21, the lines of the β-phase are poorly visible on the X-ray patterns (they are strongly broadened in comparison with the lines of the isomorphous α-phase, Fig. 2, *b*), despite the fact that the β-phase is well revealed in the micrographs (Fig. 3, *a*, *b*). For unknown reasons it was not possible to reveal the microstructure of alloys 23 and 24. The γ and γ' phases, on the contrary, can be distinguished only from micrographs (Fig. 3, *b* and 3, *g*), whereas on the X-ray patterns they give identical pictures (Fig. 2, *b* and 2, *g*). It should be noted that there is an appreciable solubility of Mo in the γ'-phase—not less than 2½-3 at. %, since alloy 8 is single-phase (γ'); in work (14) it is assumed that the solubility of Mo in the γ'-phase is much smaller (<1 at. %).

In conclusion, we note that the isothermal section of the Ni—NiAl—Mo system at 1200° is analogous to the isothermal sections of the Ni—NiAl—Cr system at temperatures below 1000°: according to the data of work (6), below this temperature in the Ni—NiAl—Cr system there exists an equilibrium of the γ' and α phases, as in the system studied. Above this temperature, in the Ni—NiAl—Cr system the γ and β phases coexist, analogously to what occurs also in the related Ni—NiAl—W system (9).

Institute of Metallurgy and Physics of Metals
of the Central Scientific Research Institute
of Ferrous Metallurgy

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