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The lattice parameters and microstructures of annealed, nickel-rich nickel–molybdenum alloys

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Metallographic and X-ray studies conducted at room temperature on annealed, nickel-rich nickel–molybdenum alloys indicate that ~10.5 at % Mo is soluble in the α (fcc) phase. The lattice parameter of this phase is given by a_0 (26.5 ± 1° C) = 0.000 409 × at% Mo + 0.352 48 nm. Grain- and twin-boundary nucleated volumes of the β (Ni_4Mo) phase were observed in samples with 15 to 20 at % Mo and co-existed with a discontinuous, nearly lamellar, precipitate in samples with 17.5 and 20 at % Mo.

1. Introduction

The primary purpose of this investigation was to determine the composition dependence of the lattice parameter of α-phase nickel–molybdenum alloys. The measurements were made at 26.5° C on slowly cooled powder samples that contained from 0 to 20% Mo (all concentrations given in at %). The portion of the nickel–molybdenum phase diagram of interest is shown in Fig. 1 [1, 2]. The α-phase is a face-centred cubic (fcc) solid solution composed of molybdenum atoms substitutionally dissolved in nickel. The dashed lines in Fig. 1 represent boundaries whose exact positions are uncertain at present. For example, although the solubility limit of molybdenum in α at 600° C shown here, 12.5%, appears to be the most reliable value, other diagrams indicate solubilities of 15.5% [3] and 16.5% Mo [4] near this same temperature.

Several previous investigations of the lattice parameters of α-phase alloys took advantage of the fact that this phase can be quenched-in for molybdenum concentrations up to at least 27%. Casselton and Hume-Rothery [5] examined quenched samples containing 17.1% to 27.0% Mo. Guthrie and Stansbury [6] worked with samples containing 11.8% to 22.4% Mo. Nosova and Polyakova [7] determined the lattice parameters of quenched single crystals containing 5.8% to 24% Mo. Brooks *et al.* [1] concluded that the data from these investigations were fit by the relation

$$a_0\,(\text{nm}) = 0.000\,405 \times \text{at\% Mo} + 0.352\,42 \quad (1)$$

However, an examination of the input data reveals that (a) the Casselton and Hume-Rothery results show unacceptable scatter, and (b) the Nasova and Polyakova data were obtained by a comparison technique the accuracy of which is an order of magnitude less than that of precision X-ray determinations. The present investigation was undertaken to provide improved lattice parameter data including results for alloys in the 0% to 10% Mo region.

The samples prepared for the present investigation were slowly cooled, therefore some were expected to be dual phase, $\alpha + \beta$. This presented the possibility of determining the maximum concentration of molybdenum remaining in solid solution in slowly cooled samples. Some of the problems that occur in this determination, and factors that condition the significance of the result, are

(a) given the reaction temperatures and the sluggishness of the reaction [1, 2, 8], equilibrium may be impossible to achieve at temperatures much below 550° C;

(b) because the β-phase is a superlattice of the α, it can be difficult to distinguish one from the other by powder diffraction techniques [1]. Fig. 2 illustrates the close correspondence of their diffraction patterns [9]. This problem is compounded if line broadening occurs as a result of a small β particle size, appreciable transformation strains, and/or the existence of concentration gradients in the parent and product phases;

(c) in addition to a homogeneously nucleated ordering reaction, Gust *et al.* [2] have shown that β is heterogeneously nucleated at, for example, α grain boundaries. The reaction product in this case can take the form of discrete β particles (continuous precipitation) or a nearly lamellar arrangement of α and β (discontinuous precipitation). Both forms have been observed in an alloy containing 17.5% Mo [2].

2. Experimental procedure

2.1. Preparation of wrought alloys

Nine alloys were prepared with the intended compositions 0, 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5, and 20.0% Mo. Fingers of each (~2 cm long and 1 cm diameter) were obtained by arc-melting quantities of 99.94% pure nickel and 99.82% pure molybdenum that had been weighed to the nearest 0.1 mg. Each alloy was melted six times while under a partial pressure of argon. The results of chemical analyses carried

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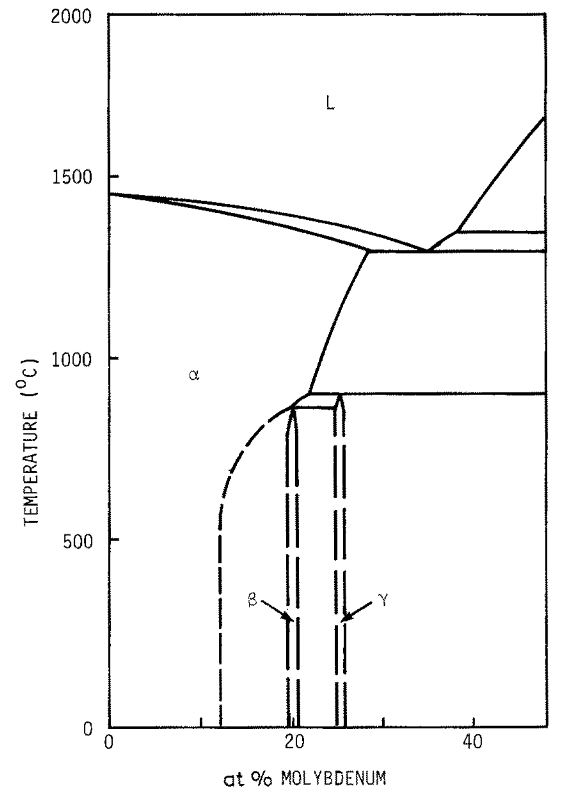

Figure 1 The nickel-rich side of the nickel–molybdenum phase diagram.

out on three of the alloys are given in Table I. Because the intended and directly determined compositions of these three were essentially identical, it was assumed that all alloys had their intended compositions.

The arc-melted fingers were sealed in individual, evacuated quartz capsules. These were heated to 1300° C for 5 d then step-cooled to room temperature in increments of $100^\circ \mathrm{C\,d^{-1}}$. In order to be certain that the alloys were chemically homogeneous, the fingers were heated under vacuum to 900° C then hot rolled (in the atmosphere) to a thickness of ~ 3.6 mm. After removing the oxidized surface layers, the rolled samples were re-encapsulated in quartz, heated to 1300° C for 3 d, then step-cooled to room temperature in increments of $100^\circ \mathrm{C\,d^{-1}}$. Coupons (14 mm × 10 mm × 3.15 mm) were machined from the central portion of each sample. It was at this point that portions were diamond-saw cut for the chemical analyses referred to earlier.

TABLE I Lattice parameters ($T = 26.5 \pm 1^\circ$ C) and compositions of slowly cooled nickel–molybdenum alloys

Composition (at % Mo)		a_0 (nm)
Intended	Analytical*	
0.0	–	0.352 47 ± 0.000 02
2.5	2.51	0.353 52 ± 0.000 02
5.0	5.00	0.354 52 ± 0.000 02
7.5	7.49	0.355 57 ± 0.000 02
10.0	–	0.356 55 ± 0.000 02
12.5	–	0.357 45 ± 0.000 04
15.0	–	0.358 37 ± 0.000 08
17.5	–	0.359 37 ± 0.000 08
20.0	–	0.360 40 ± 0.000 10

*Average of five wet-chemical determinations.

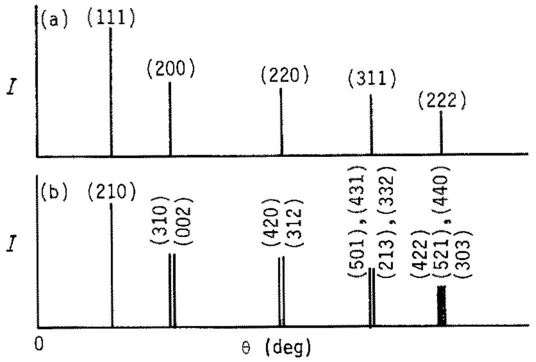

Figure 2 Schematic diffraction patterns for (a) the α and (b) the β phases in nickel–molybdenum alloys (only the strongest lines have been shown for the β).

Metallographic samples prepared after the above treatment revealed that

(a) the 0% to 10% Mo samples were single phase, free of impurity-phase particles (inclusions), and had grain- and twin-boundary morphologies typical of high-purity, annealed, f c c nickel-rich alloys. A micrograph of the 2.5% Mo alloy is shown in Fig. 3;

(b) the 15% Mo sample contained a small number of isolated precipitate particles at the α grain boundaries. These were similar in appearance to the continuous β phase precipitate particles seen by Gust *et al.* [2]. A few such particles may also have been present in the 12.5% Mo sample but their apparent size, combined with etching effects at the grain boundaries, precluded positive identification by light microscopy;

(c) both continuous and discontinuous reaction products were visible at the grain and twin boundaries of the 17.5% and 20% Mo samples. Light micrographs of these are shown in Fig. 4. Although the volume fraction of precipitates was greater in the 20% than in the 17.5% Mo sample, in neither case did it exceed more than about 1% of the total sample volume. Whereas it seemed probable that some β has also nucleated homogeneously, the etchant used in this work (Gerard's no. 2: 5 g $FeCl_3$ + 10 ml HCl + 100 ml H_2O) failed to develop metallographic features others have ascribed to its presence [1].

In view of the above observations, the powder X-ray

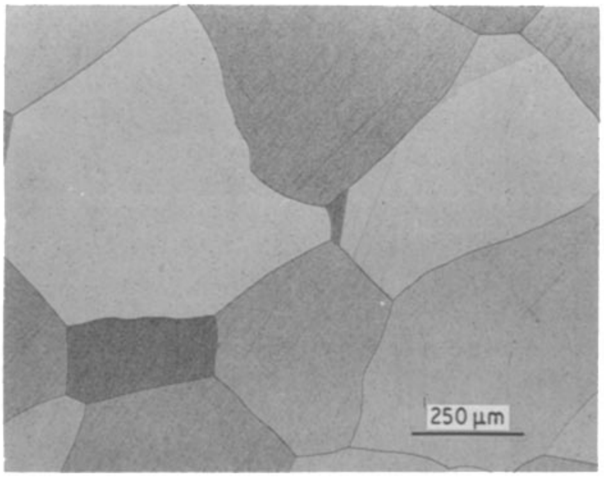

Figure 3 Light micrographs of nickel + 2.5%Mo alloy. Etchant: Gerard's no. 2 (5 g $FeCl_3$, 10 ml HCl, 100 ml H_2O). Some scratches and etch pits may be visible.

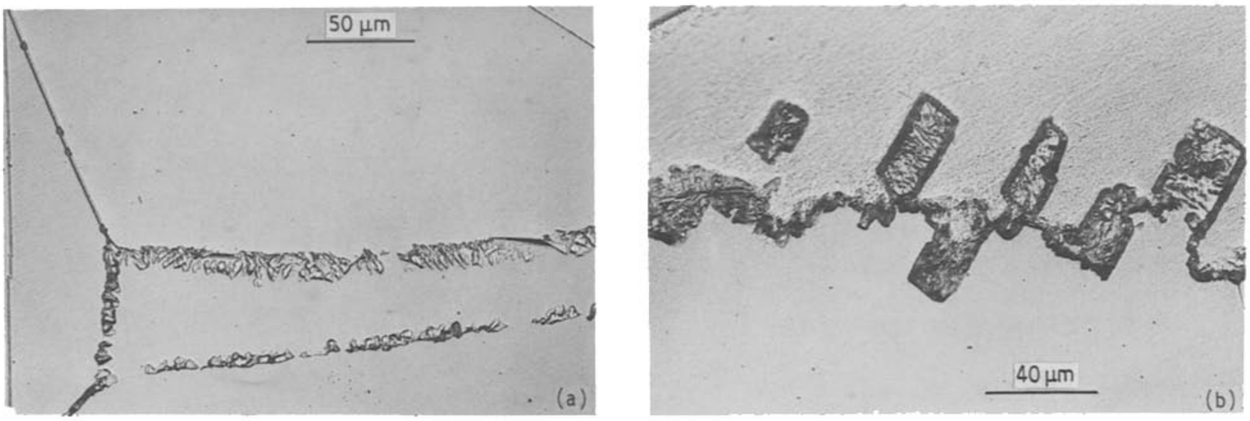

Figure 4 Light micrographs of (a) Ni + 17.5% Mo alloy showing β precipitate particles along grain and twin boundaries and (b) Ni + 20% Mo alloy showing blocky, discontinuous precipitation at grain boundaries. Etchant: Gerard's no. 2.

samples (prepared as described below) were step-cooled at a much slower rate (20° C d^{-1}) than the metallographic samples (100° C d^{-1}).

2.2. Powder X-ray samples

Filings were obtained from each coupon using separate, hardened steel, files. The filings were heat treated (under an ion-pumped vacuum of $\sim 10^{-8}$ torr) as follows: heat to 600° C for 8 h then step-cool to room temperature in increments of 20° C d^{-1}. X-ray powder samples were prepared using 0.2 mm diameter glass capillaries and the -270 mesh portion of the heat-treated filings.

2.3. Diffraction patterns and data reduction

Diffraction patterns were obtained using an 11.4 cm diameter Debye–Scherrer camera. One series was obtained with unfiltered Cu$K\alpha$ radiation and a second series using nickel-filtered Cu$K\alpha$ radiation. Line positions on the films were measured with a Norelco film reader. Lattice parameters were determined using the Taylor–Sinclair/Nelson–Riley expression for the systematic error function and a least-squares fit of the a_0 (observed) against error function line for extrapolation to $\theta = 90^\circ$. The correction for film shrinkage assumed uniform shrinkage over the length of the film. Input data were as follows: (a) for the 0 to 12.5% Mo samples: the six measured line positions to the (4 0 0), (3 3 1), and the (4 2 0) α_1 and α_2 lines, and (b) for the 15 to 20% Mo samples: the line positions for the (3 1 1), (2 2 2), (4 0 0), (3 3 1), and (4 2 0) $K\alpha$ reflections. A^* wavelengths were used in analysing the data: $K\alpha = 0.154184$ nm, $K\alpha_1 = 0.154056$ nm, $K\alpha_2 = 0.154439$ nm. The a_0 values reported here have not been corrected for refraction. Most of the exposures were completed in 4 h at an average camera temperature of $26.5 \pm 1^\circ$ C.

3. Experimental results

A visual examination of the diffraction patterns revealed that

(a) for the 0 to 10% Mo samples, all diffraction lines were sharp with the (3 1 1), (2 2 2), (4 0 0), (3 3 1), and (4 2 0) appearing as well-resolved α_1/α_2 doublets;

(b) significant line broadening was evident in the pattern from the 12.5% Mo sample. Although it was still possible to read the five lines listed above as doublets, α_1/α_2 overlap reduced the accuracy of the readings;

(c) all lines were severely broadened in the patterns from the 15 to 20% Mo samples. No doublets were observed in these patterns;

(d) the only diffraction lines (sharp or broadened as indicated above) observed in this work occurred at angles near those shown in Fig. 2a. Thus it was possible to index all patterns on a face-centred cubic basis even though those for samples with greater than 10% Mo were clearly representative of inhomogeneous materials.

It was concluded from the metallographic and X-ray diffraction work that the 0 to 10% Mo samples were homogeneous, single-phase, α. Metallographic work had, as noted earlier, revealed the presence of small amounts of heterogeneously nucleated β in the 15 to 20% Mo samples from which the filings were prepared. The cold work associated with filing should have converted all (ordered) β volumes (whether homogeneously or heterogeneously nucleated) into disordered α. During the 8 h at 600° C the filings were expected to recrystallize then begin to precipitate (or in the case of the 20% Mo alloy, transform to) β. The line broadening observed in the patterns from samples with 12.5% Mo and greater probably resulted from small β particle sizes, transformation strains (and concentration gradients for samples with compositions in the $\alpha + \beta$ field).

The lattice parameters of the samples and their estimated accuracies are listed in Table I. These are averages for the two films taken per sample. (Values obtained from filtered and unfiltered exposures of the same sample never differed by more than 0.00002 nm.) The a_0 values for the 12.5 to 20% Mo samples represent some "averaged" result for these inhomogeneous materials.

4. Discussion

The lattice parameter data from Table I are plotted in Fig. 5. The points from the 0 to 10% Mo, α-phase, samples lie on a straight line the least squares fit for which was determined to be

$$a_0\,(26.5^\circ\,\mathrm{C}) = 0.000409 \times \mathrm{at\,\%\,Mo} + 0.35248\,\mathrm{nm} \qquad (2)$$

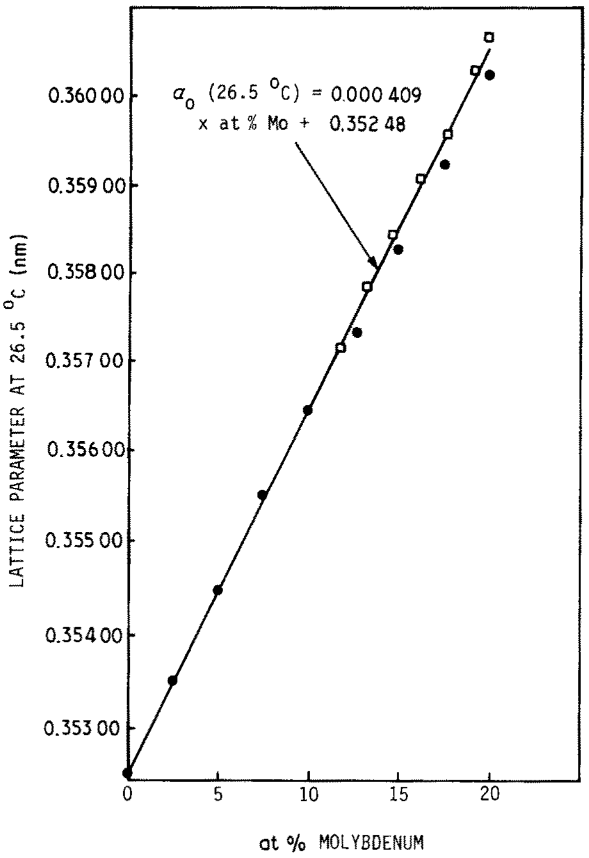

Figure 5 Lattice parameter – composition data (●) from the present investigation and (□) from Guthrie and Stansbury [6]. (——) The least-squares fit of the data from the 0 to 10% Mo alloys.

The correlation coefficient for the fit was 0.99978. If the data are corrected to a temperature of 21.5° C (using $13.4 \times 10^{-6}\,{}^\circ\mathrm{C}^{-1}$ for the thermal expansion coefficient [10]), the result is

$$a_0\,(21.5^\circ\mathrm{C}) = 0.000\,409 \times \text{at}\,\%\,\text{Mo} + 0.352\,54_5\ \text{nm} \qquad (3)$$

The intercept value in Equation 3 is in excellent agreement with an a_0 value determined earlier [11], 0.352 45 ± 0.000 02 nm (corrected to A^* wavelengths), for the same Johnson–Mathey nickel. Equation 3 is also in good agreement with the Brooks *et al.* equation (see Equation 1).

The Guthrie and Stansbury results from quenched samples are also plotted in Fig. 5. Their original values (see [12] for a listing) have been increased 0.000 035 nm to correct to A^* wavelengths and also to adjust their data to 26.5° C. They lie an average of 0.0001 nm above the extrapolation of the line given by Equation 2. This is good agreement considering differences in the two investigations in (a) sample processing methods (powder metallurgy compared to the methods described in this paper), and (b) purity of starting materials. This level of agreement does suggest that the atomic arrangements in quenched, higher solute concentration alloys are continuous with respect to lower concentration, slowly cooled, alloys of the present investigation.

Fig. 5 also shows that the lattice parameter values for samples from the present investigation with greater than 10% Mo fall below the line given by Equation 2. The point at which the divergence begins, ~ 10.5% Mo, marks the limit of solubility of molybdenum in the α-phase in this specimen set. This is considerably lower than the 12.5% Mo shown in Fig. 1. It is not clear whether the 10.5% limit applies to coherent or incoherent precipitates. In any event, the work of Gust *et al.* [2] combined with the results of the present investigation indicate a need to establish phase equilibria for this system for both coherent and incoherent precipitates.

Finally, the 0, 2.5 and 5% Mo samples were strongly magnetic at room temperature while the remaining samples were non-magnetic. This agrees with previous information on alloys in this system.

A paper by Vasudevan *et al.* [13] that appeared after this manuscript was originally completed is helpful in explaining one of the possible causes of line broadening observed in the patterns of the higher solute concentration alloys. Vasudevan *et al.* determined the average diameter of homogeneously nucleated, ordered, β-phase volumes in 20% Mo samples reacted for various times at temperatures from 600 to 850° C. Their results indicated that the particle size in the 20% Mo sample heat treated as in the present investigation would be of order of 4 nm or less.

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