

An Investigation of the Ti-Mo-N System at Low Nitrogen Activities

Walter Lengauer and Peter Ettmayer

(Institute for Chemical Technology of Inorganic Materials, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria)

The titanium-molybdenum-nitrogen system was investigated at low nitrogen activities with the intention to locate the position of the ζ -Ti₄N_{3-x} + β -Ti_xMo_{1-x}N_y phase field at the Ti-Mo boundary and to estimate the nitrogen solubility in β -Ti_xMo_{1-x} at 1420 K. The metallographic investigations were performed on arc-melted samples and on Ti-Mo alloys which had been equilibrated with the nitrogen partial pressure generated by TiN_{1-x} in silica tubes. It was found that ζ -Ti₄N_{3-x} coexists with β -Ti_xMo_{1-x} with $x = 0.64 \pm 0.01$ of the latter, in good agreement with X-ray investigations. The nitrogen solubility in the β phase decreased with increasing molybdenum content. Especially at Mo compositions just higher than 37 at.% a steep decrease of the nitrogen solubility in β -Ti_xMo_{1-x} could be observed, consistent with the position of the isothermal nonvariant point of the three phase field $\zeta + \beta + \delta$. An isothermal section of the equilibrium phase diagram Ti-Mo-N at 1420 K is presented.

Untersuchung des Systems Ti-Mo-N bei niedrigen Stickstoffaktivitäten

Das System Titan-Molybdän-Stickstoff wurde im Bereich niedriger Stickstoffaktivitäten untersucht, um den Fußpunkt des Zweiphasenfeldes ζ -Ti₄Ni_{3-x} + β -Ti_xMo_{1-x}N_y im Bereich des Randsystems Ti-Mo und die Löslichkeit von Stickstoff in β -Ti_xMo_{1-x} bei 1420 K zu ermitteln. Dazu wurden metallographische Untersuchungen an lichtbogengeschnittenen Proben und an Ti-Mo Legierungen, die mittels TiN_{1-x} mit Stickstoff in Silicaglasrohren beaufschlagt wurden, durchgeführt. Der Fußpunkt des ($\zeta + \beta$)-Phasenfeldes an der Kante Ti-Mo wurde bei 37 ± 1 At.-% Mo in guter Übereinstimmung mit Röntgenbeugungsuntersuchungen gefunden. Die Stickstofflöslichkeit in der β -Phase nimmt mit zunehmenden Molybdängehalt ab. Besonders im Bereich von Molybdängehalten größer als 37 At.-% wurde ein steiler Abfall des Stickstoffgehalts in β -Ti_xMo_{1-x}N_y beobachtet. Dies korrespondiert mit der Position des Fußpunktes des Dreiphasenfeldes $\zeta + \beta + \delta$. Ein isothermer Schnitt des Systems Ti-Mo-N bei 1420 K wird präsentiert.

1 Introduction

Titanium nitride (δ -TiN_{1-x}) is already used extensively for coatings on conventional tungsten carbide hard metals while (Ti, Mo) (C, N) is used as a hard component in cermets bonded by Ni alloys (Ni, Ni-Mo, Ni-Ti-Mo). For special applications the latter are superior to the conventional – even TiN coated – hard metals¹⁾. A general disadvantage of iron metal binders, however, is their only moderate hot strength, which is a limiting factor in applications requiring high cutting speeds. Refractory metals such as W and Mo show a significantly higher hot strength but – as the phase diagrams of the Ti-W-C and Ti-Mo-C systems²⁾ reveal – they react with TiC to form brittle mixed carbides. However, due to the instability of any molybdenum nitride, TiN and Mo do not form mixed nitrides³⁾. Thus, the combination TiN-Mo could be used as a basis for cermets with substantially increased hot strength.

General investigations in the quasibinary system TiN-Mo have been performed by several Soviet authors⁴⁾ to ⁶⁾. Detailed data, however, have been published by Ettmayer and Hörmanseder⁷⁾, who found a melting point minimum between TiN and Mo at 2500 K, with a eutectic composition of [TiN]/[Mo] = 1/3 and a nitrogen equilibrium pressure of 1 MPa. Further investigations⁸⁾⁹⁾ concentrated on the construction of isothermal sections of the entire Ti-Mo-N system. However, neither the exact location of the ζ -Ti₄N_{3-x} + β -Ti_xMo_{1-x}N_y phase field on the Ti-Mo boundary nor the extent of a possible solubility of nitrogen in β -Ti_xMo_{1-x} have been studied in detail (β -Ti_xMo_{1-x}N_y is a more appropriate notation for β -Ti_xMo_{1-x} carrying interstitially dissolved nitrogen).

The present paper reports the results of investigations undertaken to clarify these points.

2 Experimental

Under normal sintering conditions the preparation of fully dense TiN-Mo sintered bodies is difficult because of the unsatisfactory wetting properties of Mo and the high sintering temperatures necessary. Since the quality of metallographic investigations depends strongly on the porosity and since equilibrium conditions via solid-solid diffusion are reached much faster with dense samples, two other preparation techniques were used. One involved arc-melted Ti-Mo-N buttons and the other nitrogen treated Ti-Mo alloys. Since titanium nitride has a low stoichiometry-dependent nitrogen equilibrium pressure¹⁰⁾, the nitrogen pressure required for the precipitation of TiN in Ti-Mo alloys is, at least for Ti-rich Ti-Mo alloys, also very low. Substantial efforts were necessary if the low nitrogen pressures are to be maintained by means of a controlled dosage system. Since such a system was not readily available, TiN_{1-x} itself was used as a nitrogen source. This excludes also any error in the necessary nitrogen equilibrium pressure.

The Ti-Mo alloys were prepared by mixing and compacting Ti and Mo powders with low oxygen contents and arc-melting the compacts in a purified Ar atmosphere. For homogenization the samples were heat treated in Ar at 1670 K for 20 h. The buttons were cut into slices 0.5 mm thick.

For the preparation of the nitrogen source material, Ti and TiN powder were mixed, pressed into pellets and homogenized at 1770 K under Ar for 3 days. This yielded homogeneous single-phase δ -TiN_{1-x}. Before use as a nitrogen source the TiN_{1-x} pellets were crushed in a mortar.

The Ti-Mo alloys and the TiN_{1-x} grains were first wrapped separately in Mo foil and then both put in a Mo foil box. This

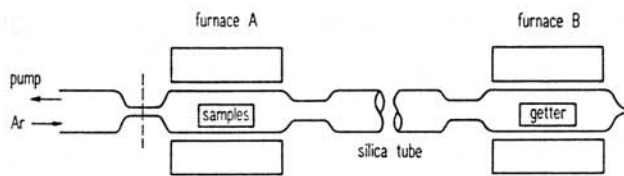


Fig. 1. Experimental set-up for the equilibration of Ti-Mo alloys with a TiN_{1-x} nitrogen source.

nitrogen partial pressure is sufficient for nitrogen saturation in Ti-Mo alloys from 0 to 45 at.% Mo at 1420 K.

Ternary Ti-Mo-N alloys with a nitrogen content of 2 to 5 at.% were prepared by arc-melting pellets of TiN-Ti-Mo mixtures. For equilibration they were heat treated in silica tubes for 14 days at 1420 K and subsequently quenched in water.

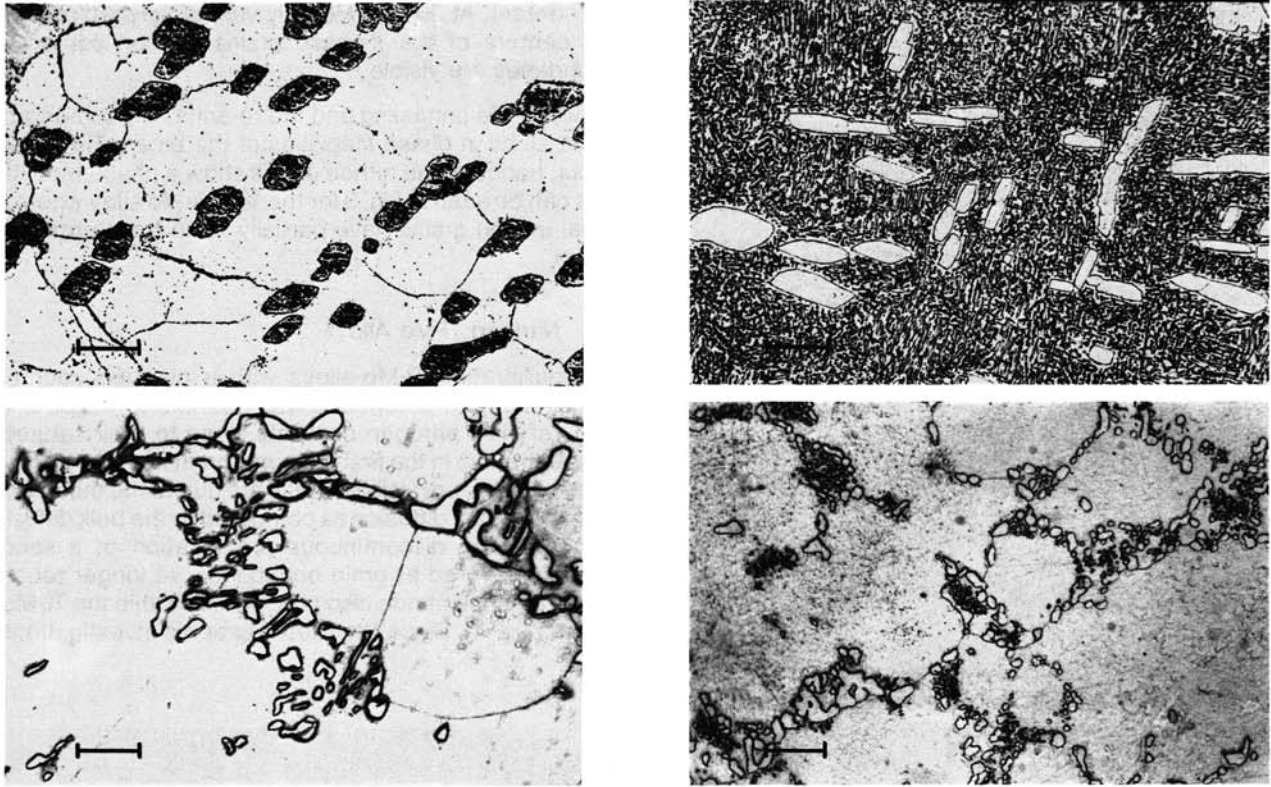


Fig. 2. Influence of the molybdenum content on the solubility of nitrogen in $\beta\text{-Ti}_x\text{Mo}_{1-x}$. Top: $\text{Ti}_{0.93}\text{Mo}_{0.07}\text{N}_y$ matrix, bottom: $\text{Ti}_{0.23}\text{Mo}_{0.77}\text{N}_y$ matrix before (left) and after (right) re-annealing. The sample with low Mo content shows a substantial increase in nitride precipitation upon annealing (top) whereas in the sample with high Mo content no secondary nitride precipitates can be observed (bottom). ---|--- = 30 μm , etched with HNO_3/HF .

box as well as a second Mo box containing a Zr getter foil were sealed in a silica tube at opposite ends (Fig. 1).

In order to remove surface impurities from the sample, the getter foil, the boxes and from the silica tubes they were heated to 720 K during an evacuation of several hours. Subsequently the silica tube was cooled to room temperature, flushed with Ar and sealed with a residual Ar pressure of 10 kPa. In the next step the Zr getter box was heated to 1120 K in order to remove any oxygen from the atmosphere. During that treatment the samples remained at room temperature. After this procedure the getter was cooled to room temperature and both the samples and the nitrogen source were heated to the reaction temperature of 1420 K. After 14 to 40 days the samples were quenched in water.

The nitrogen equilibrium pressure which develops in the silica tube during the last step depends on the stoichiometry of the nitrogen source. The nitrogen potential of the resulting Ti-Mo-N alloy cannot exceed that of the source material. In order to arrive at nitrogen compositions in the vicinity of the $\zeta\text{-Ti}_4\text{N}_{3-x} + \beta\text{-Ti}_x\text{Mo}_{1-x}\text{N}_y$ phase field the composition of the TiN_{1-x} nitrogen source was fixed at $[\text{N}]/[\text{Ti}] = 0.54$. According to our previous investigation of the tie lines in the $\beta\text{-Ti}_x\text{Mo}_{1-x}\text{N}_y + \delta\text{-TiN}_{1-x}$ phase field⁹⁾ the

The samples were investigated metallographically, by means of X-ray diffraction and by electron probe microanalysis.

For the direct measurement of dissolved nitrogen in the presence of titanium, physical methods of nitrogen analysis are unreliable because of the coincidence of the strongest element specific fluorescence lines. In the case of low nitrogen contents a quantitative analysis appears to be particularly difficult.

To arrive at a quantifiable estimate of the amount of nitrogen which had been dissolved at 1420 K in the β phase both series of samples were re-annealed at 1090 K for 40 h in silica tubes. The latter temperature is high enough to avoid the phase separation $\beta\text{-Ti}_x\text{Mo}_{1-x} \rightarrow \alpha\text{-Ti}(\text{Mo}) + \beta\text{-Ti}_y\text{Mo}_{1-y}$ ¹¹⁾ and should also be sufficiently low to precipitate most of the nitrogen in solid solution at 1420 K as TiN_{1-x} .

3 Results and Discussion

3.1 Arc-Melted Samples

The microstructures showed that the titanium content significantly influences the solubility of nitrogen in Ti-Mo

alloys. This is apparent in Fig. 2 where an alloy with a $Ti_{0.97}Mo_{0.03}N_y$ matrix (top) is compared to an alloy with a $Ti_{0.23}Mo_{0.77}N_y$ matrix (bottom). Primary titanium nitride grains as well as a generally unstructured β phase are visible (top left). Upon re-annealing a substantial increase in

secondary nitride precipitates is visible (top right). At a molybdenum content of 77 at.% the matrix remains essentially unchanged upon re-heating, indicating a very low nitrogen solubility at 1420 K.

This behavior was observed all along the Ti-Mo boundary. The microstructures given in Fig. 3 show the successive decrease of nitride precipitates with increasing Mo content. The clearly visible secondary nitride precipitates at a matrix composition of 7 at.% Mo (between large primary grains) become successively less frequent with increasing Mo content. At 30 at.% Mo only very small precipitates at the centers of the β -phase grains and on some grain boundaries are visible.

Between the annealing and the re-annealing temperature some shifts in phase stabilities of the binary Ti-N phases occur, hence some nitride grains show a phase transition. This can be seen in Fig. 3 for the 16 at.% Mo alloy where the initial α -Ti(N) grains have partially been transformed into ϵ -Ti₂N.

3.2 Nitrided Ti-Mo Alloys

By equilibrating Ti-Mo-alloys with a nitrogen source of known nitrogen potential it was possible to obtain alloys with very low nitrogen contents close to their saturation concentration. In the first step only grain boundary precipitates of TiN_{1-x} are visible. These are due to the much faster grain boundary diffusion as compared to the bulk diffusion. Generally the discontinuous precipitation of a second phase is favored at grain boundaries. At longer reaction times, titanium nitride also precipitates within the Ti_xMo_{1-x} grains (Fig. 4). Since the metallographic investigations in

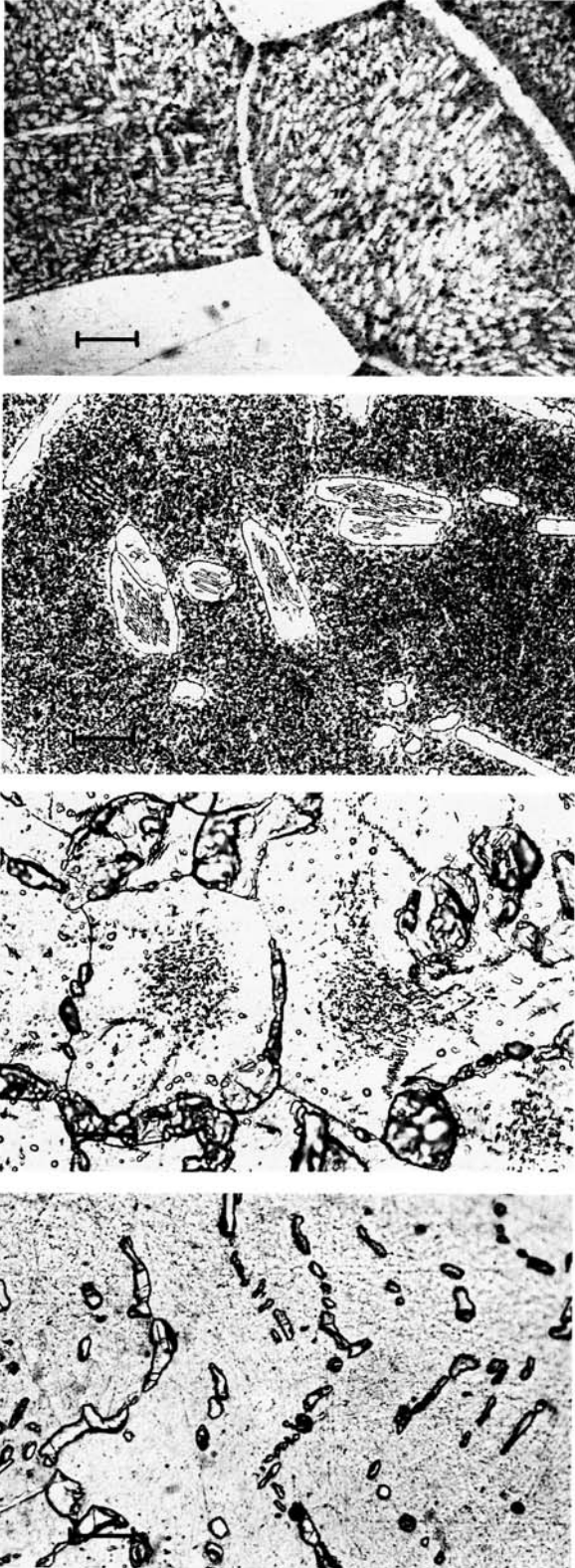


Fig. 3. Microstructures of samples re-annealed at 1090 K. The Mo content increases from top to bottom: 7, 16, 30, 77 at.% Mo in the matrix. With increasing Mo content the amount of nitride precipitates decreases. Note the substructure in the nitride grains of the alloy with 16 at.% Mo. --- = 10 μm , etched with HNO_3/HF .

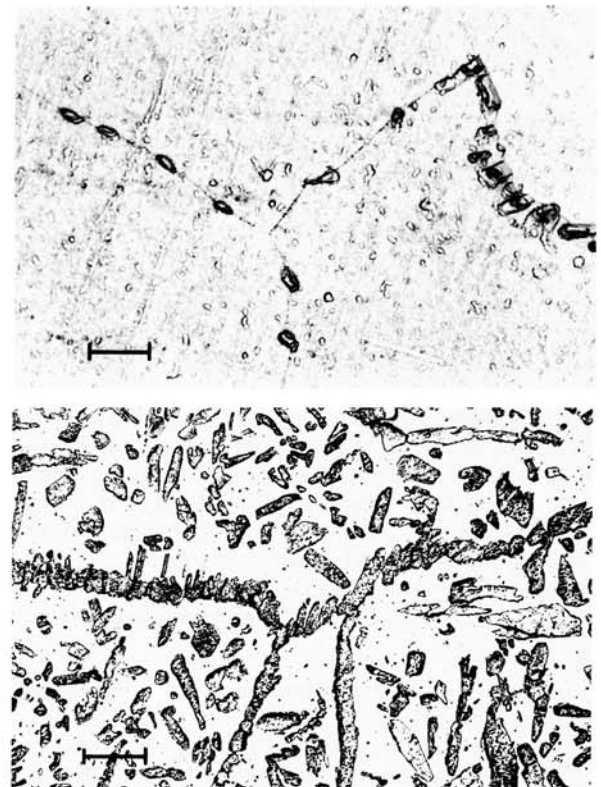


Fig. 4. Nitride precipitates obtained by nitriding Ti-Mo alloys with a titanium nitride nitrogen source. Top: grain boundary precipitates of titanium nitride, bottom: precipitates at grain boundaries and in the bulk at longer reaction times. --- = 10 μm , etched with HNO_3/HF .

the present study were made by means of a light optical microscope only, the submicroscopic pre-precipitates of titanium nitride as investigated by Yano et al.¹²⁾ could not be seen.

To establish more precisely the composition of β -Ti_xMo_{1-x}N_y which coexists with ζ -Ti₄N_{3-x} and which already was approximately known from previous investigations, several Ti-Mo alloys (30 to 42 at.% Mo in steps of 1 at.%) were reacted with nitrogen. Representative metallographic results are shown in Fig. 5. Numerous secondary nitride precipitates are visible, and some are located at secondarily formed grain boundaries of the matrix (top). At a Mo content of 34 at.% the amount of precipitates has even slightly increased (middle) but at 37 at.% Mo the amount of precipitates has dropped below the limit of detection (bottom). This change within a few at.% Mo is consistent with the general behaviour of phase boundaries near isothermal nonvariant points. In accordance with thermodynamic considerations the nitrogen solubility decreases

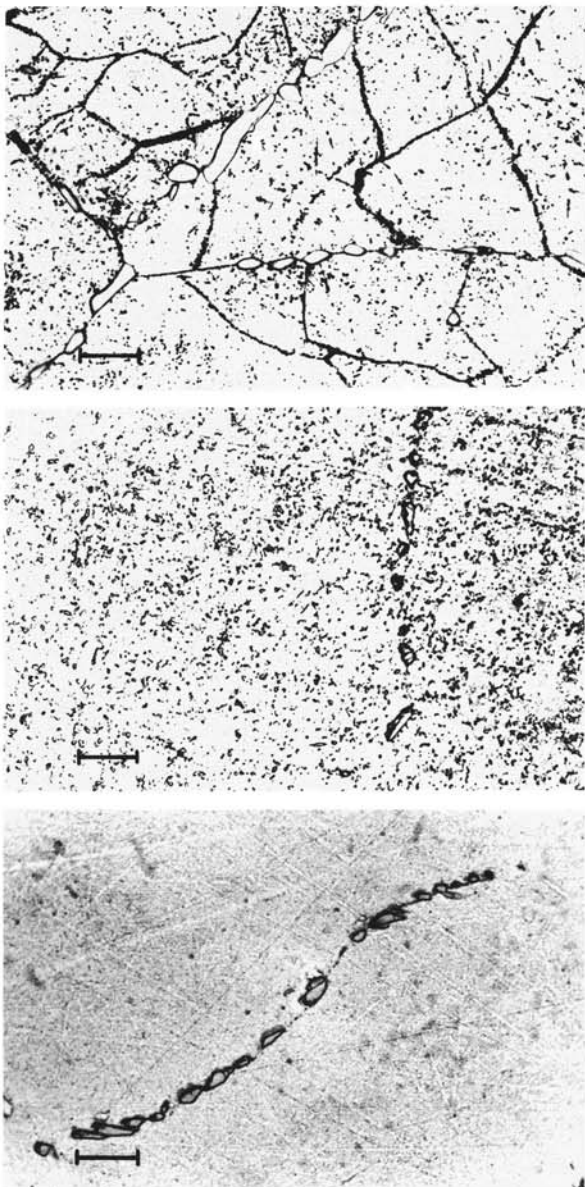


Fig. 5. Nitrided Ti-Mo alloys after re-annealing at 1090 K. Mo content from top to bottom: 30, 34, 37 at.%. Note the significant decrease of secondary precipitates between 34 and 37 at.% Mo. --- = 10 μm , etched with HNO₃/HF.

steeply with increasing Mo content in β -Ti_xMo_{1-x}N_y after having reached a relative maximum at the isothermal nonvariant point of the three phase field ζ -Ti₄N₃ + β -Ti_xMo_{1-x}N_y + δ -TiN_{1-x}.

3.3 Phase Diagram

Because of the limited resolution of the light-optical microscope and the very small size of the secondary nitride precipitates no quantitative results for the nitrogen solubility in β -Ti_xMo_{1-x} could be obtained. However, the microstructures of the arc-melted buttons reflect the general influence of the Mo content in the alloys. Obviously the solubility of nitrogen decreases rapidly with increasing Mo content. This qualitative observation is confirmed by the results from investigation of alloy samples nitrided via the equilibration technique with TiN_{1-x}. Metallographic investigations in the vicinity of the (ζ + β)-phase field show a steep decrease of nitrogen solid solubility for alloy compositions above 37 \pm 1 at.% Mo. Such a behaviour agrees well with expectations from previous results as well with phase theory. Based on X-ray diffraction investigations the isothermal nonvariant point of the three-phase field ζ -Ti₄N_{3-x} + δ -TiN_{1-x} + β -Ti_xMo_{1-x} is at 35 at.% Mo. No significant change in the lattice parameter of the β phase before and after re-annealing could be detected, although upon precipitation of titanium nitride a decrease would be expected. The amount of precipitated nitride is obviously too small to exert an observable influence on the lattice parameter.

The results are summarized in Fig. 6 in the form of a phase diagram. The results reported here are consistent with thermodynamic estimates (to be published) which predict

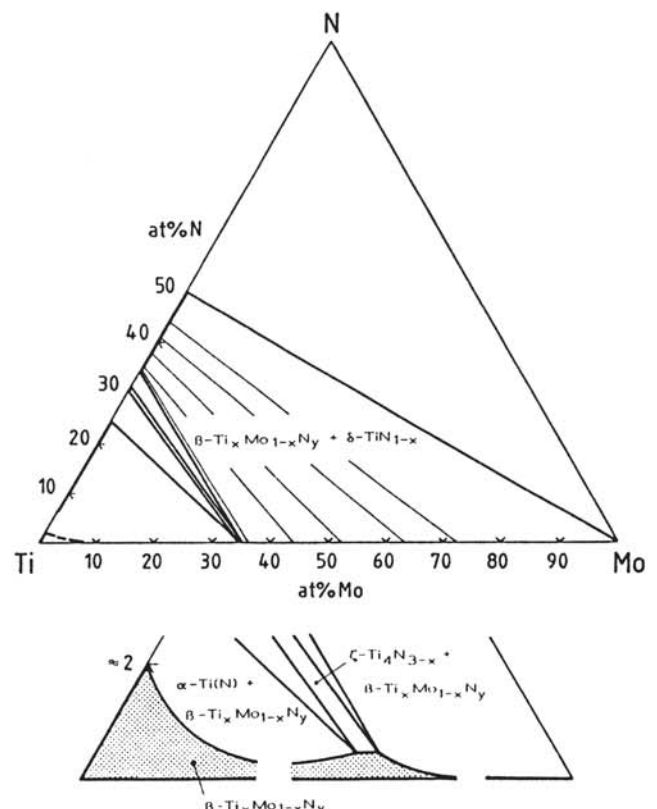


Fig. 6. Isothermal section at 1420 K of the Ti-Mo-N system as determined in this and a previous study⁹⁾. The qualitatively observed solvus line of nitrogen in β -Ti_xMo_{1-x}N_y is given in the detail figure.

a decrease in the solubility of nitrogen with increasing Mo content.

The authors would like to thank Mr. W. Prohaska for his efforts with the sealing of the silica tubes.

Literature

- 1) P. ETTMAYER and H. KOLASKA, Pulvermetallurgie in Wissenschaft und Technik **4** (1988)
- 2) E. RUDY, J. Less-Common Met. **33**, (1973) 245; E. RUDY, U.S. Air Force Techn. Doc. Report AFML-TR-69-117, Part I (1969); AFML-TR-65-2, Part II (1969).
- 3) H. JEHN and P. ETTMAYER, High Temp.-High Press **8** (1976) 93.
- 4) O. M. BARABASH and K. A. SHURIN, Izv. Akad. Nauk. SSSR, Met. **6** (1978) 234.
- 5) O. M. BARABASH, V. F. MOISEEV, E. P. PECHKOVSKII, Fiz. Khim. Mekh. Mater. **12** (1976) 109.
- 6) O. V. PSENICHNAYA and P. A. VERKHOVODOV, Porosk. Metall. **3** (1985) 26.
- 7) P. ETTMAYER and W. HÖRMANSEDER, High Temp.-High Press. **18** (1986) 161.
- 8) W. LENGAUER and P. ETTMAYER, Mater. Sci. Eng. **A105/106** (1988) 257.
- 9) W. LENGAUER, H.-J. ULLRICH, and P. ETTMAYER, Mikrochim. Acta I, **211** (1987).
- 10) P. GRIEVESON, Proc. Brit. Ceram. Soc. **8** (1967) 137.
- 11) J. L. MURRAY, Bull. Alloy Phase Diagr. **2** (1981) 185.
- 12) S. YANO, S. MOROZUMI, and S. KODA, Scripta Metall. **12** (1978) 467.

(Eingegangen am 1. Dezember 1988)