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The Ti–Mo–C–N system: stability of the (Ti, Mo)(C, N)$_{1-x}$ phase

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Abstract

The hard constituents in cermet cutting tools are based on titanium carbonitride, mostly with additions of molybdenum and tungsten carbides and usually other carbides such as TaC, NbC, ZrC, VC, etc. In order to gain insight into the typical cermet "core–rim" structure, the Ti–Mo–C–N system was investigated in the region of the (Ti,Mo)(C,N)$_{1-x}$ phase. Specific experiments were performed: (Ti,Mo)(C,N)$_{1-x}$ samples were annealed in nitrogen atmosphere and substoichiometric (Ti,Mo)C$_{1-x}$ as well as (Ti,W)C$_{1-x}$ were subjected to nitriding treatments. Although complete equilibrium may not have been reached in any of these experiments, they showed that the phase separation may occur at substoichiometric compositions but probably not at high nitrogen activities.

Keywords: Cermets; Hard metals; Titanium molybdenum carbonitride; Phase equilibria

1. Introduction

Certain aspects of the Ti–Mo–C–N system have been studied by Rudy [1] and Suzuki and Matsubara [2,3]. Rudy investigated the cubic carbonitride phase (Ti,Mo)(C,N) at 1450 and 1600–1650 °C as a model system for boundary phase stability predicted from thermochemical models. He found that this phase undergoes a (spinodal) phase separation featuring a miscibility gap between a N-rich, Mo-poor α' (Ti,Mo)(C,N) and a Mo-rich, C-rich (Ti,Mo)(C,N) α'' phase. Suzuki and Matsubara found that at 1700 °C in Mo-poor (Ti,Mo)(C$_{0.7}$N$_{0.3}$) and (Ti,Mo)(C$_{0.5}$N$_{0.5}$) are in thermodynamic equilibrium with Mo for nitrogen pressures lower than 1 mbar and 5–10 mbar respectively. At higher pressures N$_2$ tends to displace carbon from the carbonitride under formation of Mo$_2$C. The analogous system Ti–W–C–N was studied by Doi et al. [4], Rynemark [5] and Jonsson [6]. Doi et al. calculated the equilibrium nitrogen pressure of the B1 type (Ti$_x$W$_y$)(C$_u$N$_v$) solid solution in equilibrium with the WC phase at 1700 and 2100 K and found good agreement with his experimental results. These results were corroborated by the experimental work of Rynemark. In his work Jonsson modelled the Ti–W–C–N system on a two-sublattice thermodynamic model based mainly on the experimental data of Doi et al. He found that a miscibility gap within the cubic (Ti,W)(C,N) phase should be thermodynamically metastable at 1700 °C, with the exception of a very small zone with compositions near TiC. Otherwise WC is in equilibrium with W-poor (Ti,W)(C,N). After studying the aforementioned literature, it is apparent that much effort has been expended in producing thermodynamical models of these systems, but that few reliable experimental data are available. With regard to the work of Rudy, there are several points in his experiments which should be regarded with some reservations. There is little evidence that the samples he investigated were in thermodynamic equilibrium, and in order to be able to observe a spinodal phase separation, first a homogeneous one-phase (Ti,Mo)(C,N) should have been prepared by heating the samples above the critical temperature. Nickel was used as a diffusional aid. In recent investigations on the typical "core–rim" structure of Ti(C,N)-based cermets [7,8,9] it was found that nickel can actually lead to selective dissolution of the carbide components in the liquid metal, which results in the formation of nitrogen-rich precipitates. On cooling this leads to the precipitation of the carbides around undissolved nitride cores, featuring two phases in non-equilibrium with compositions close to those described by Rudy as α' and α''. While in the thermodynamic calculations a non-metal:metal ratio (stoichiometry factor $1-x$) of 1 was considered, the specimens investigated by Rudy

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were characterized by only partial occupation of the non-metal sublattice, in some cases with non-metal: metal ratios as low as 0.70–0.80. As a result of this, the influence of the stoichiometry on the phase equilibria was not taken into consideration. The influence of the non-metal:metal ratio could be inferred from the behavior of the Ti–Mo–N boundary system [10]. At nitrogen pressures of 30–300 bars, TiN_{1-x} in equilibrium with cubic γ-MoN_{1-x} can be observed. Forcing an increased occupation of the non-metal sublattice by increasing the nitrogen activity leads to total miscibility and formation of a cubic $(Ti,Mo)N_{1-x}$ phase. At any rate, the microstructures reported by Rudy above cannot be regarded as arising from a spinodal decomposition, the migration distances being much too large.

2. Experimental

The technical and analytical difficulties in proving a spinodal decomposition mechanism arise from the extremely small cluster size of the spinodally decomposed phases, which is usually only 1 to 2 orders of magnitude greater than the atomic radius. While the driving force of a spinodal decomposition is the energy gain by the development of clusters with divergent compositions, the growth of the clusters is a diffusion-dependent reaction and hence rather slow at lower temperatures. In order to be able to observe such a decomposition, long periods of sample heat treatments are usually needed. In the particular case of the Ti–Mo–C–N system the α' and α'' phases have similar lattice parameters and hence differentiation by means of classic X-ray diffractometry is nearly impossible. Therefore, a method using deconvolution of the diffraction patterns is being developed [11]. Because the driving force for a phase separation in a homogeneous (Ti,Mo)(C,N) phase is based on the very low chemical affinity between the Mo and N atoms, heat treatments of compact hot-pressed $(Ti_{0.72}Mo_{0.28})C_{0.86}$ and $(Ti,Mo)(C,N)_{1-x}$ samples in nitrogen atmospheres were expected to provide specimens to answer the question whether the formation of a nitrogen-enriched layer on the surface would lead to an enrichment of molybdenum in front of the nitrogen diffusion layer, as would be expected from the Rudy phase diagram. These samples were hot pressed at ~2000 °C with an axial pressure of 400 bar using pre-alloyed powders with grain sizes ranging from 1.6 to 3.5 μm. For comparison a $(Ti_{0.72}W_{0.28})C_{0.86}$ sample was hot pressed from TiC, WC and W powders. The $(Ti,Mo)(C,N)_{1-x}$ samples were designated LA, LB, GA and GB; their compositions after hot pressing were introduced in Rudy's diagram for (Ti,Mo)(C,N) at 1450 °C (see Fig. 1). The heat treatments were carried out in an autoclave and the temperature was measured with a thermocouple. The samples were wrapped in Ta foil and positioned in a crucible made of Mo foil with Zr foil acting as a getter for impurities in the gas atmosphere. The samples were investigated by means of SEM with an EDS detector, by optical microscopy and by X-ray diffraction. The C and N contents were determined by combustion analysis using gas chromatography [12]. This method yields results with an error ≤ ±1%. The Ti:Mo ratio was measured by means of EDS. This method is less accurate, with an error closer to ±4%.

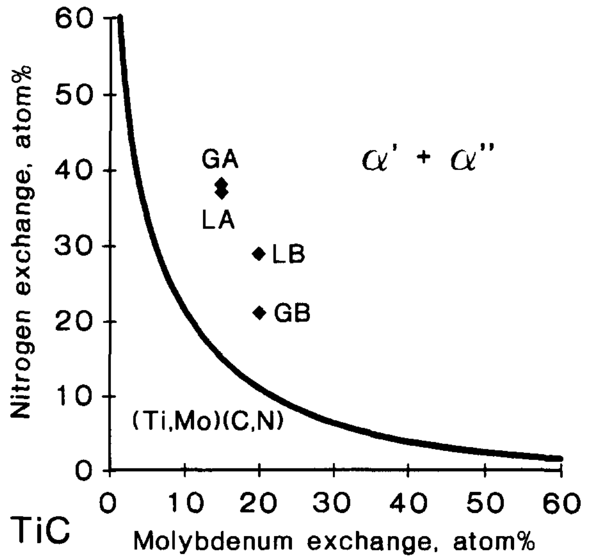

Fig. 1. Composition of the samples LA, LB, GA and GB in hot-pressed form.

3. Results

In the first experiment $(Ti_{0.72}Mo_{0.28})C_{0.86}$ was heat treated for 96 h at 1450 °C with a nitrogen pressure of 50 mbar. This pressure was calculated under the assumption that graphite formation from the reaction of nitrogen with Ti(C,N) could be avoided. Instead — according to Rudy — the α' phase $(Ti_{0.95}Mo_{0.05})(C_{0.63}N_{0.37})$ should form at the surface and just below the surface the α'' phase $(Ti_{0.63}Mo_{0.37})(C_{0.95}N_{0.05})$ should be formed. After the heat treatment, the samples showed a typical nitrided yellow surface. This nitrided layer was unexpectedly thick (>20 μm), and at the same time the carbon content in the neighborhood of this layer was found to be lower than the carbon content of the mixed carbide. An explanation of this phenomenon could be the removal of carbon via gaseous cyanogen [$(CN)_2$] at high temperatures by transport reactions to the surface of the water-cooled walls of the autoclave, where $(CN)_2$ decomposes, leading to soot formation. These transport reactions make a thermodynamic equilibration of the sample impossible. Owing to the carbon depletion, elementary molybdenum precipitated to some extent near the nitrided layer instead of diffusing into the bulk of the sample to form a molybdenum-rich α'' $(Ti,Mo)(C,N)_{1-x}$. The nitridation penetrated along the grain boundaries, leading to "uphill" diffusion of the Mo atoms towards the bulk of the sample. This displacement of the Mo atoms proceeded mainly along the grain boundaries, leading to a shift in the non-metal:metal ratio towards the bulk of the sample. The same was observed in the $(Ti_{0.72}W_{0.28})C_{0.86}$ sample. This behavior can be clearly seen in Fig. 2, which features a carbon-richer starting sample with the composition $(Ti_{0.8}Mo_{0.2})C_{0.94}$ in order to at least partially offset the carbon depletion due to the transport reaction.

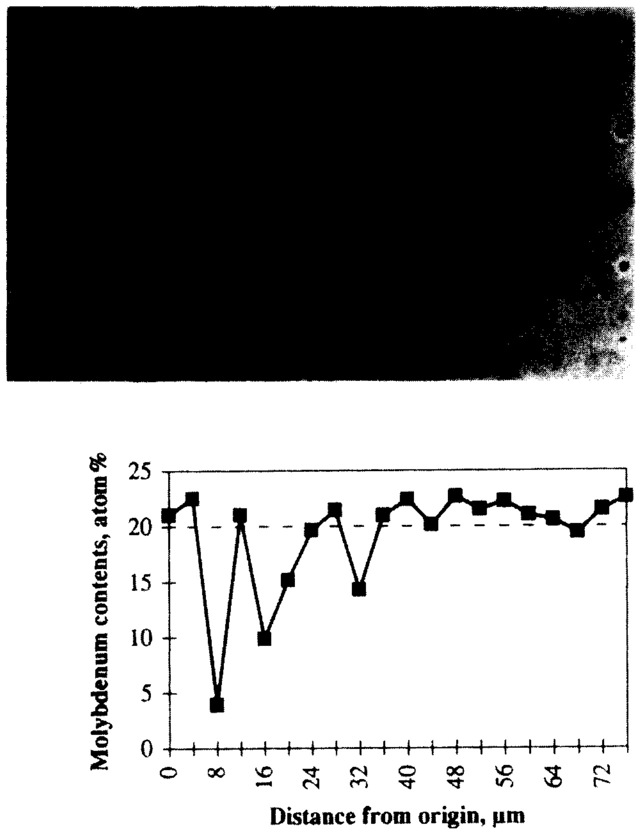

Fig. 2. Nitrided sample with the composition $(Ti_{0.8}Mo_{0.2})C_{0.94}$ (BSE, 850 ×). The diagram underneath shows the Mo composition at the marked points (y in the formula $(Ti_{1-y}Mo_y)(C,N)_{1-x}$) measured with EDS.

This long-range "uphill" diffusion of the Mo atoms under the action of nitrogen can be explained by the low chemical affinity between Mo and N atoms. Or, in other words, the activity of molybdenum in $(Ti,Mo)(C,N)_{1-x}$ is greater the higher the nitrogen content in the carbonitride is. These observations are consistent with Rudy's results. Furthermore, it must also be remembered that not only nitrogen but metal atoms as well are diffusing. This must proceed over a vacancy mechanism, which is why grain boundary diffusion is the generally preferred transport mechanism.

In another set of experiments the samples GA, GB, LA and LB were subjected to heat treatments under N_2 atmospheres of 0.1, 1 and 10 bar at 1500 °C for 9 days. The sample LB was additionally annealed in an Ar atmosphere of 0.4 bar. Table 1 gives the compositions of these samples in powder form and as hot pressed.

As in the first experiment, transport reactions were responsible for carbon depletion on the surface layer of the sample and hence thermodynamic equilibrium could not be achieved in the sample. Mo and Mo_2C precipitations were observed. The nitridation proceeded principally along the grain boundaries, displacing Mo atoms on its way. The higher the nitrogen pressure, the more pronounced was the Mo atom displacement towards the bulk of the sample. The extent of the carbon depletion was greater at lower nitrogen pressures, leading to precipitation of elementary Mo. The composition of the samples after heat treatment can be taken from Table 2. For this analysis, the surface layer of the sample was removed by grinding, making it possible to investigate the composition of the sample interiors. It was assumed that thermodynamical equilibrium had been reached in these regions.

It can be observed that — at higher nitrogen pressures — the non-metal:metal ratio is somewhat higher. In these samples Mo_2C precipitations near the surface layer were observed, consistent with the higher carbon contents. The sample GB treated with 10 bar N_2 showed evidence of a phase decomposition into a Mo-rich phase and a N-rich phase near the surface. The displaced molybdenum atoms had apparently not

Table 1
Samples subjected to heat treatments under N_2 and Ar at 1500 ° for 9 days

Sample	Powder composition	Composition as hot pressed	Pressures of heat treatments
GA	$(Ti_{0.85}Mo_{0.15})(C_{0.63}N_{0.37})_{1.02}$	$(Ti_{0.85}Mo_{0.15})(C_{0.62}N_{0.38})_{1.00}$	N_2: 0.1, 1, 10 bar
GB	$(Ti_{0.80}Mo_{0.20})(C_{.79}N_{0.21})_{0.96}$	$(Ti_{0.80}Mo_{0.20})(C_{.79}N_{0.21})_{0.99}$	N_2: 0.1, 1, 10 bar
LA	$(Ti_{0.85}Mo_{0.15})(C_{0.59}N_{0.41})_{0.98}$	$(Ti_{0.85}Mo_{0.15})(C_{0.63}N_{0.37})_{0.96}$	N_2: 0.1, 1, 10 bar
LB	$(Ti_{0.80}Mo_{0.20})(C_{0.70}N_{0.30})_{0.96}$	$(Ti_{0.80}Mo_{0.20})(C_{0.71}N_{0.29})_{0.97}$	Ar, N_2: 0.1, 1, 10 bar

Table 2
Composition of the samples after heat treatment under nitrogen

Sample	0.1 bar N_2	1 bar N_2	10 bar N_2
GA	$(Ti_{0.85}Mo_{0.15})(C_{0.61}N_{0.39})_{0.90}$	$(Ti_{0.84}Mo_{0.16})(C_{0.63}N_{0.37})_{0.94}$	$(Ti_{0.84}Mo_{0.16})(C_{0.63}N_{0.37})_{0.94}$
GB	$(Ti_{0.80}Mo_{0.20})(C_{0.77}N_{0.23})_{0.85}$	$(Ti_{0.78}Mo_{0.22})(C_{0.77}N_{0.23})_{0.88}$	$(Ti_{0.75}Mo_{0.25})(C_{0.77}N_{0.23})_{0.92}$
LA	$(Ti_{0.84}Mo_{0.16})(C_{0.60}N_{0.40})_{0.88}$	$(Ti_{0.83}Mo_{0.17})(C_{0.60}N_{0.40})_{0.90}$	$(Ti_{0.83}Mo_{0.17})(C_{0.60}N_{0.40})_{0.94}$
LB	$(Ti_{0.80}Mo_{0.20})(C_{0.68}N_{0.32})_{0.85}$	$(Ti_{0.79}Mo_{0.21})(C_{0.70}N_{0.30})_{0.86}$	$(Ti_{0.78}Mo_{0.22})(C_{0.70}N_{0.30})_{0.86}$

been able to diffuse toward the bulk of the sample because the nitridation had proceeded too fast. For this reason, the Mo atoms were compelled to diffuse into the bulk of the grains. Because the non-metal:metal ratio was not low enough for Mo_2C to precipitate, a phase decomposition through diffusion mechanisms may have taken place. This observation is in good agreement with the results reported by Rudy.

SEM micrographs of the samples GB after identical heat treatment periods but at different nitrogen pressures showed that an increase in the pressure of the nitrogen gas atmosphere, i.e. an increase of the nitrogen activity, led to a gradual homogenization of the microstructure. This can be clearly seen by comparing the microstructures in Fig. 3, which shows the effects of heat treatments on the GB samples whose microstructures had originally been the most inhomogeneous. The bright regions are molybdenum-rich particles and the dark ones are molybdenum-poor, probably nitrogen-rich particles. In Fig. 3(b) the homogenization has already led to diffusion zones around the originally dark as well as the bright particles. An increase of the nitrogen pressure apparently promoted this effect even if temperature and duration of the heat treatment remained constant. Fig. 4 shows the diffraction patterns of the samples in powder form, as hot pressed, and after the heat treatments. These measurements confirm the trend observed in the microstructures: a very inhomogeneous powder homogenizes somewhat during hot pressing and the diffraction lines become sharper with increasing pressure of the gas atmosphere, resulting at last in a clear separation of the α_1 and α_2 diffraction peaks. The same behavior was observed in the other samples, although — because of the higher original homogeneity — this effect was not as evident as in the GB series.

This homogenization cannot be attributed only to the diffusion of the non-metal atoms; an additional factor is the diffusion of the Mo atoms displaced from the periphery of the sample. In the carbon-depleted zone the gross non-metal:metal ratio is lower than in the bulk, whereas the nitrogen activity at the surface is probably higher than in the bulk because of incomplete thermodynamic equilibration. If the non-metal:metal ratio decreases below a value of about 0.8, Mo_2C will precipitate; at even lower ratios elementary Mo precipitates. Otherwise the Mo atoms diffuse towards the bulk of the sample, approaching a monophase state of $(Ti,Mo)(C,N)_{1-x}$ the higher the nitrogen activity becomes.

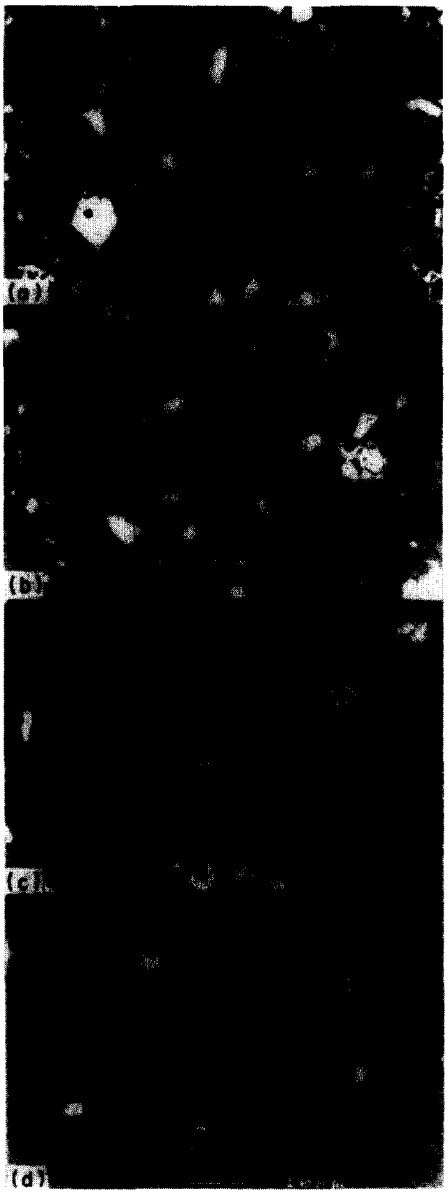

Fig. 3. (a)–(d), GB sample series (BSE, 850×): (a), hot-pressed; (b)–(d), heat treatments at 1500 °C with nitrogen at (b) 0.1, (c) 1 and (d) 10 bar. See compositions in Table 2.

In the sample LB, which had been annealed under Ar, no such homogenization could be observed, but the microstructure did show signs of metal atom

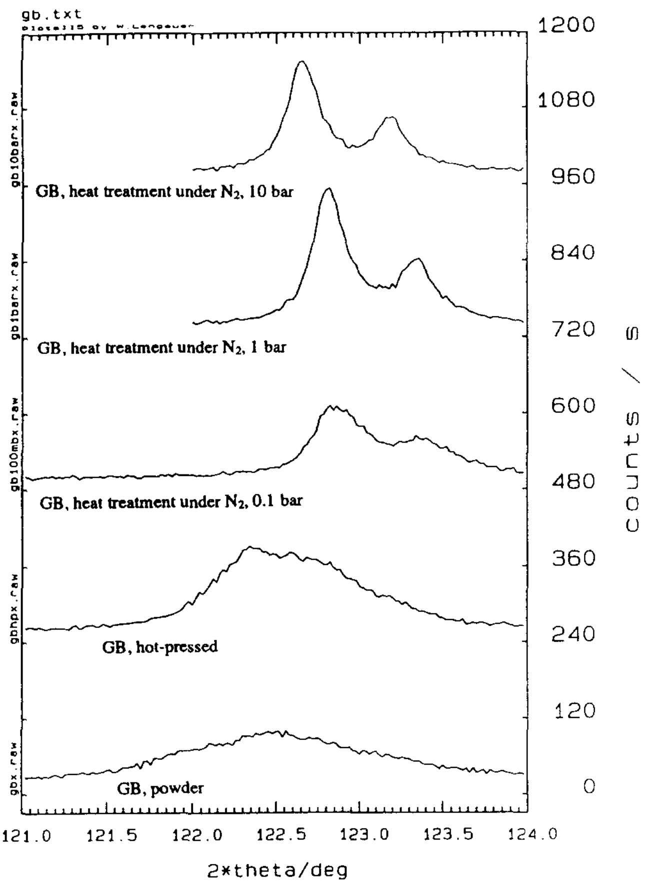

Fig. 4. Diffraction patterns of the GB samples in powder form, as hot-pressed and after the heat treatments.

diffusion. Probably the sample gradually gave off nitrogen during the heat treatment under these conditions, so that at the beginning of the heat treatment local phase equilibria played a major role, but with the removal of nitrogen the non-metal:metal ratio sank below a certain level and the homogenization ceased. Fig. 5 shows a qualitative representation of the phase equilibria in form of an isothermic section of the Ti–Mo–C–N system in a three-dimensional projection at a temperature of 1450 °C. The raster represents the boundary of the miscibility gap, beyond which a homogeneous $(Ti,Mo)(C,N)_{1-x}$ may be found. The binodals — determining the equilibrium between the α' and α'' phases for a certain nitrogen activity — are represented by bold lines. In an isothermal section of the system Ti–Mo–C–N and at high partial pressures of nitrogen, graphite will be in equilibrium with the $\alpha' + \alpha''$ phases (according to Rudy), whereby the nitrogen partial pressure will define the compositions of α' and α'' if Gibbs's phase rule is applied. If complete solid solutions exist within the phase field of the stoichiometric quaternary carbonitride $(Ti,Mo)(C,N)_{1-x}$, then the composition of the quaternary solid solution in equilibrium with graphite is determined by the nitrogen pressure and the Ti/Mo ratio in the carbonitride (in an isothermal section). If the nitrogen partial pressure is lower than that defined by the particular composition in the presence of graphite, then the stoichiometry factor $1-x$ decreases and a miscibility gap between α' and α'' will develop in such a way that its extension will increase with a decreasing stoichiometry factor $1-x$. This effect is graphically outlined as a curved binodal surface shown in Fig. 5. With a further decreasing stoichiometry factor $1-x$ and at molybdenum-rich compositions, the Mo_2C phase will eventually appear. The nitrogen partial pressure in equilibrium with α', α'' and Mo_2C is determined (at constant temperature) by the composition of α' and α''. At carbon-rich compositions of α' (and molybdenum-poor compositions of α'') metallic Mo will appear as the coexistent phase. The compositions of α' and α'' in equilibrium with both phases, Mo_2C and Mo, at a defined temperature are nonvariant. Due to the lack of experimental data and for the sake of clarity the insertion of these phase field boundary lines has been omitted in Fig. 5.

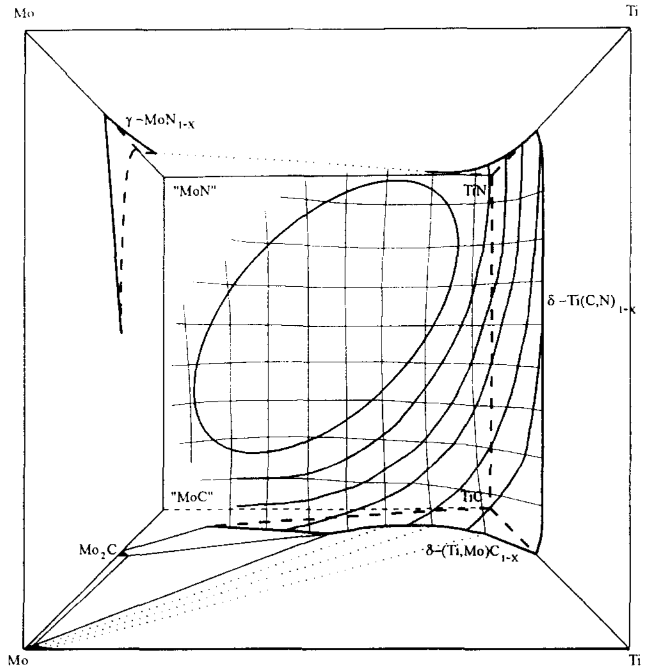

Fig. 5. Qualitative representation of the phase equilibria in the three-dimensional region Ti–Mo–C–N at a temperature of 1450 °C.

4. Conclusions

These results show that under thermodynamic equilibrium and with low nitrogen activities in the gas atmosphere, which result in a lower non-metal:metal ratio (stoichiometry factor $1-x$) in the composition of the hard materials, the existence of a miscibility gap within the $(Ti,Mo)(C,N)_{1-x}$ solid solution can be considered very likely. Considering the fact that technical cermets are as a rule sintered under vacuum, this could mean that the "core–rim" structure is actually thermodynamically stable in Ti(C,N)-based cermets, even if under normal production conditions the phase equilibrium cannot be reached. Providing that the nitrogen activity of the gas atmosphere is high enough to force an extensive occupation of the non-metal sublattice in the hard phase, the miscibility gap shrinks, which can lead to total miscibility within the cubic carbonitride phase $(Ti,Mo)(C,N)_{1-x}$. This phenomenon could be considered analogous to the increasing miscibility observed between TiN_{1-x} and cubic γ-MoN_{1-x} with increasing nitrogen activity within the boundary system Ti–Mo–N.

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