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A Constitutional Diagram of the System TiC—HfC—"MoC"

By

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With 5 Figures

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The system TiC—HfC—"MoC" was investigated by means of melting point, differentiothermoanalytical, X-ray diffraction and metallographic techniques on hotpressed as well as melted alloy specimens. A constitutional diagram from 1500 °C through the melting range was established.

Investigation of the (Hf, Mo)C system (isopleth: $HfC_{0.98}$—"$MoC_{1.0}$") showed a small miscibility gap within the cubic monocarbide solution (δ) [T_c = 1630 °C, $(HfC)_{0.45}(MoC)_{0.55}$]. The miscibility gap interacts with the solvus curve with a monotectoid-like decomposition reaction at 1575 °C, $(HfC)_{\approx 0.35}(MoC)_{\approx 0.65}$. At temperatures below 1630 °C, phase equilibria within TiC—HfC—"MoC" are characterized by a large miscibility gap connecting the TiC—HfC and HfC—MoC boundary systems. Additions of "MoC" to TiC—HfC alloys decrease the critical temperature (1780 °C); additions of TiC to HfC—"MoC" alloys raise the critical temperature (1630 °C). No maximum type ternary critical point or saddle point was found to occur.

Isothermal sections were prepared at 1500 °C and 1650 °C. At temperatures above 1960 °C (μ-MoC + C $\rightleftarrows$ δ-MoC) a complete solid solution (δ-B 1) is formed within TiC—HfC—"MoC". The melting behaviour (liquidus projection of TiC—HfC—"MoC") shows flat melting temperatures in the "MoC" corner but extremely heterogeneous melting near the TiC—HfC boundary.

Isothermal sections have been calculated assuming regular solutions.

I. Introduction and Summary of Previous Work

It was shown by *Rudy* that critical solution phenomena offer many interesting possibilities for microstructure and property control of alloys[1, 2].

A series of investigations of pseudoternary systems:

$$\mathrm{HfC—\{TiC, VC\}—\{WC, MoC\}}$$

was planned to study the phase behaviour with respect to the behaviour of miscibility gaps and recently complete constitutional diagrams of TiC—HfC—WC, VC—HfC—{MoC,WC} have been established[3]. In continuation of this work an investigation of the constitutional diagram TiC—HfC—"MoC" was carried out.

The phase relationship within TiC—HfC has been very well established and recently presented[3] (Fig. 1*a*).

A complete constitutional diagram of the ternary system Ti—Mo—C was given by *Rudy*[4], from which an isopleth TiC—"MoC" was constructed.

A similar investigation of the Ti—Mo—C system was recently presented by *Eremenko*[5]. His projection of the solidus temperatures indicates higher solidus temperatures than reported by *Rudy*, whereas the solubility of "MoC" in TiC at 1400 °C (83 Mole% MoC) reveals a lower value (90 Mole% MoC, 1500 °C; *Rudy*[4]).

Shulishova[6] presented a study of the HfC—"MoC" system and some of its physical properties. A maximum melting point was found near HfC (≈ 4000 °C) as well as a minimum melting point at 80% MoC (≈ 2000 °C). A more recent investigation of the ternary system Hf—Mo—C (1400 °C to melting) by *Eremenko*[7] showed a remarkable high solubility of MoC in HfC at low temperatures (85 Mole% MoC at 1400 °C, 88 Mole% 1700 °C), but his work does not support the maximum and minimum melting temperatures within the isopleth HfC—"MoC" as reported by *Shulishova*[6].

Some data on the melting behaviour along the join HfC—"MoC" were available from a preliminary investigation of the ternary system Hf—Mo—C by *Rudy*[8].

No previous data on the TiC—HfC—"MoC" system are known to exist in literature.

II. Experimental

Raw Materials

Carbide powders TiC—HfC and Mo_2C were used in preparing the experimental alloy specimens.

Titanium carbide powder (325 mesh particle size) was purchased from H. C. Starck, Berlin (Werk Goslar). The total carbon content was 19.2 wt% C (49.2 at%); 0.2% of which was free carbon. Major impurities included 0.065 wt% N, 0.1 wt% O. The measured lattice parameter was $a = 4.238$ Å.

Molybdenum carbide powder: Mo_2C was purchased from Wah Chang, Glen Cove, with an average particle size of 4 μ (total amount of iron metal impurities 0.01 wt%). The total carbon content was 5.99 wt% C (0.1 wt% of which was free carbon). The measured lattice parameters were $a = 3.008$ Å and $c = 4.732$ Å.

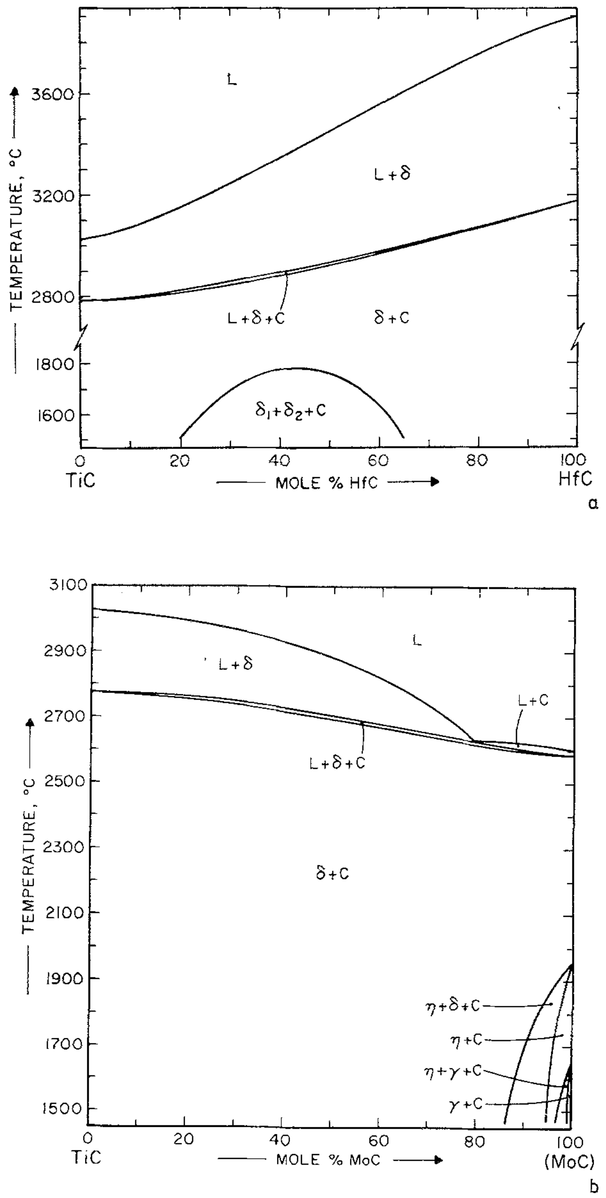

Fig. 1. *a* Isopleth TiC—HfC. *b* Isopleth TiC—"MoC"

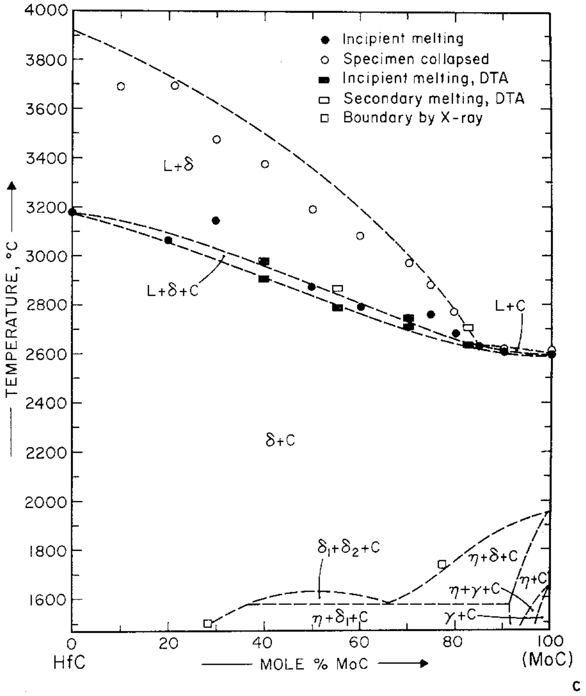

Fig. 1. *c* Experimental melting temperatures and phase distribution along the join HfC—"MoC"

Hafnium monocarbide powder was prepared in our laboratory by reduction of HfO_2 with lampblack carbon in a carbon furnace at ≈ 2000 °C. The total carbon content of the product was 49.5 at% C (0.2 wt% free C). Major impurities included 0.05 wt% N and O. The lattice parameter of the product was 4.640 Å.

Carbon was used as lampblack carbon (Wah Chang Company; major impurities in ppm: S $<$ 400, Si $<$ 238, iron metals $<$ 320) and in proper amounts added to the carbide powder mixtures in order to account for a hypothectical molybdenum monocarbide $MoC_{1.0}$.

Sample Preparation

A detailed description of the sample preparation was recently published in connection with the investigation of the pseudoternary system TiC—HfC—WC[3] and applies as well to the present investigation.

III. Graphical Representation

According to the carbon content of the powder materials used, as well as due to the substoichiometric carbon rich boundary of the monocarbide solid solutions (δ) the system TiC—HfC—"MoC" actually represents

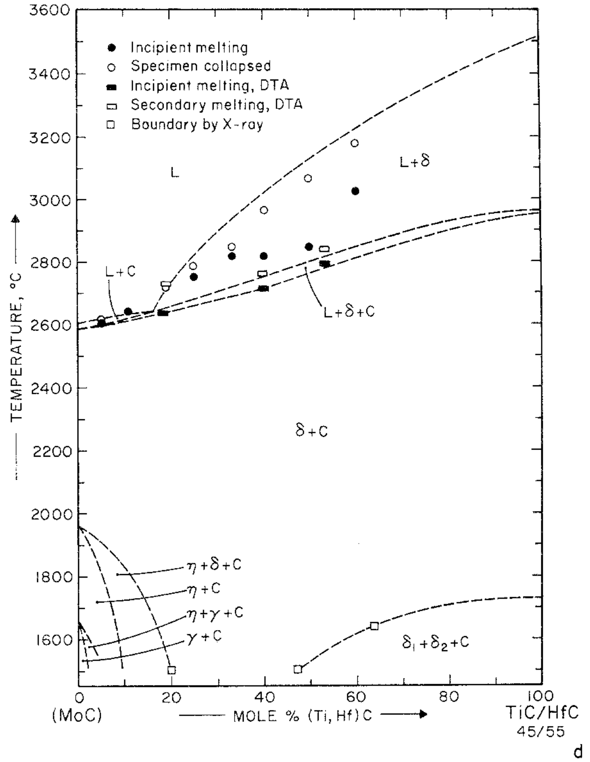

Fig. 1. *d* Experimental melting temperatures and phase distribution along the join $(Ti_{0.45}Hf_{0.55})C$—"MoC"

the section $TiC_{0.97}$—$HfC_{0.98}$—"$MoC_{1.0}$" of the quaternary system Ti—Hf—Mo—C. Due to the melting behaviour within the binary systems Ti—C, Hf—C, Mo—C at $TiC_{0.97}$, $HfC_{0.98}$ and "$MoC_{1.0}$" it should be emphasized, that the system $TiC_{0.97}$—$HfC_{0.98}$—"$MoC_{1.0}$" does not represent a pseudoternary system. As already discussed earlier[3], for a graphical representation the system was used as a pseudoternary system (section $TiC_{0.97}$—$HfC_{0.98}$—"$MoC_{1.0}$" as a basis and T as vertical axis).

But in this case the interpretation of phase behaviour is more complicated and different from that of a pseudoternary system. For instance the liquidus surface near the "MoC" corner (Fig. 4) does not represent the field of primary crystallization of "MoC" but of carbon (according to the melting behaviour within the Mo—C binary at $MoC_{1.0}$). Furthermore the $L + \delta + C$ fields do not degenerate when reaching the boundary isopleths TiC—HfC, TiC—MoC and HfC—MoC (Figs. 1*a*, *b*, *c*). In all cases if not specially denoted the symbols TiC, HfC, "MoC" are used for the carbon saturated carbides $TiC_{0.97}$, $HfC_{0.98}$ as well as for a hypothectical stoichiometric (cubic) molybdenum monocarbide $MoC_{1.0}$.

Because of the often misleading use of the different symbols for the various molybdenum carbides by different authors, Table 1 lists the carbide phases, their crystallographic discription as well as the symbols used throughout this work.

Table 1

Phase	Structure type	Space Group, Lattice Param.	Symbol used in this work
α-MoC_{1-x}[4] (also TiC, HfC)	NaCl	Fm3m $a = 4.280$ Å	δ
η-MoC_{1-x}[4]	Mo_3C_2	$P6_3/mmc$ $a = 3.010$ Å $c = 14.630$ Å	η
β- or γ-Mo_2C[4]	L′3	$P6_3/mmc$ $a = 3.011$ Å $c = 4.735$ Å	γ

For a more detailed description reference is made to a systematic work on the notation of transition metal carbides by *Parthé*[9].

IV. Results and Discussion

The Isopleth TiC—"MoC"

On samples along the join TiC—"MoC" incipient melting in the melting point furnace tends to be recorded consistently at higher temperatures as only very small amounts of liquid are formed during a melting run.

As the *DTA* equipment already[3] proved to be very sensitive to extremely small amounts of liquid involved in a melting process, *DTA* measurements were employed. The so obtained values showed good agreement to the investigation of the ternary system Ti—Mo—C by *Rudy*[4]; whereas the temperatures of incipient melting recorded in the melting point furnace proved be very close to those reported by *Eremenko*[5].

Investigation of the solid state equilibrium at 1500 °C showed slightly lower solubility of "MoC" in TiC (85 mole% MoC), more in favour of *Eremenko*'s[5] results (83% MoC at 1400 °C).

Fig. 2*a* gives the lattice parameter evaluation in comparison to the investigation by *Rudy*.

Fig. 1*b* shows the complete isopleth: TiC—"MoC" based on *Rudy*'s investigation and this work.

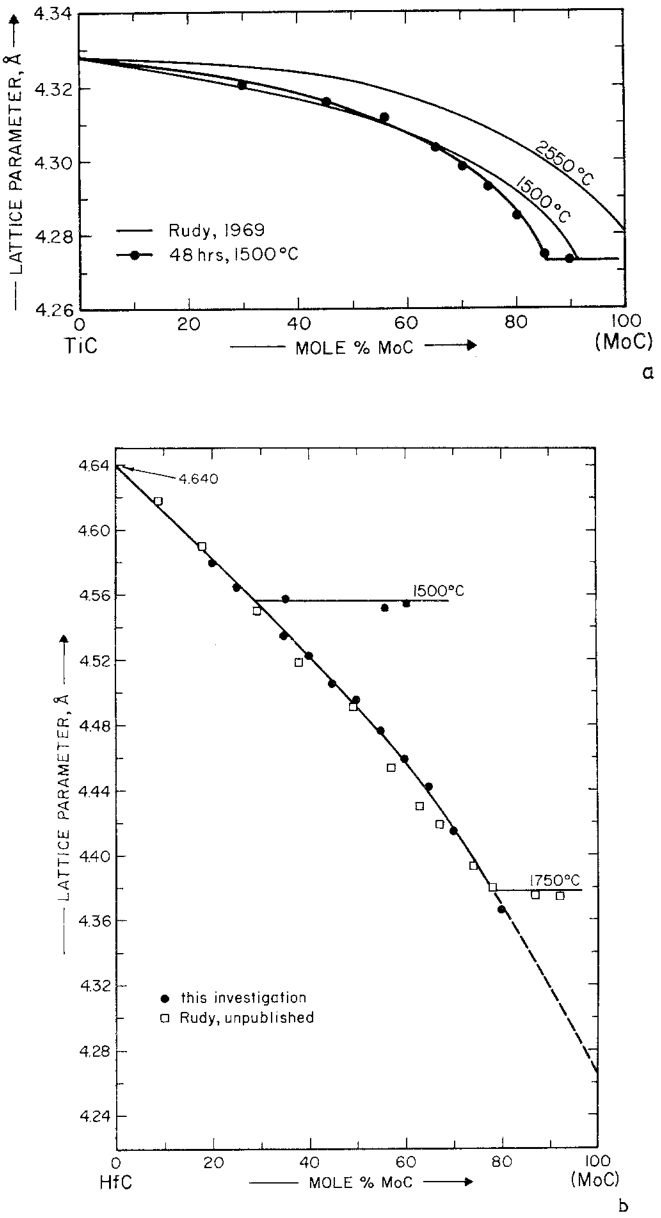

Fig. 2. *a* Location of the vertex of the three phase equilibrium: (Ti, Mo)C (δ) + MoC (η) + C at the cubic monocarbide solution by lattice parameter measurements. *b* Location of the vertex of the three phase equilibrium (Hf, Mo)C (δ) + MoC (η) + C at the cubic monocarbide solution by lattice parameter measurements

The Isopleth HfC—"MoC"

Solubility of "MoC" in HfC increases rapidly within the samll temperature range 1500—1750 °C (Fig. 2*b*). Lattice parameter evaluation showed that the cubic monocarbide solution δ exhibits a small and flat miscibility gap ($T_c = 1630$ °C, 55 mole% MoC). At lower temperatures the miscibility gap interacts with the solvus ($\approx$ 1575 °C) in a monotectoidlike reaction (Fig. 1 c). Evidence of the binary miscibility gap is also given by the phase relationship within the TiC—HfC—"MoC" system (see below). Melting behaviour within HfC—"MoC" is very similar to TiC—"MoC" and therefore melting points primarily have been determined by *DTA* measurements.

The intersection of the isopleth HfC—"MoC" with the eutectic trough across the Hf—Mo—C ternary at 84 mole% "MoC", is in very good agreement to the investigations by *Eremenko*[7] (82 mole% MoC) and *Rudy*[8] (83 mole%).

The remarkably high solubility (85 mole% HfC in "MoC", 1400 °C) as reported by *Eremenko*[7] seems to be due to nonequilibrium conditions, as arc melted samples were used which subsequently were heat-treated (2000 °C, 1700 °C, and finally at 1400 °C 300 hrs). But as already noted earlier[10] the reaction rates within the Hf—Mo—C system are very slow at even high temperatures (2000 °C) and do not always reveal equilibrium conditions.

Phase Equilibria in the Range From 1500—2000 °C

Phase equilibria at 1500 °C are characterized by a miscibility gap connecting the HfC—"MoC" with the TiC—HfC binary, already intersecting the solvus curve (boundary between the $\delta + C$ and $\eta + C$ phase fields, Fig. 3 *a*). Experimental analysis showed that η-MoC_{1-x} is stabilized by TiC as well as HfC to temperatures $\leqslant$ 1500 °C, as was already reported earlier[3, 4, 5]. However no detailed investigation of the ternary phase behaviour in the very MoC-rich corner was carried out during this study. An isothermal section was prepared at 1650 °C (Fig. 3 *b*) to study the behaviour of the critical curve of the miscibility gap. As indicated by Fig. 3 *b* the miscibility gap extends very far towards the HfC—"MoC" boundary, therefore a possible ternary saddle point on the critical curve would have to be located in the very vicinity of the HfC—"MoC" binary critical point.

But the extremely small temperature region in turn would not allow a sufficiently accurate experimental investigation. It is more likely from Fig. 3 *b* that the critical temperatures gradually decrease from $T_{c(\mathrm{HfC,TiC})}$ (1780 °C) towards $T_{c(\mathrm{HfC,MoC})}$ (1630 °C). This behaviour is also indicated by thermodynamic calculations (see section V).

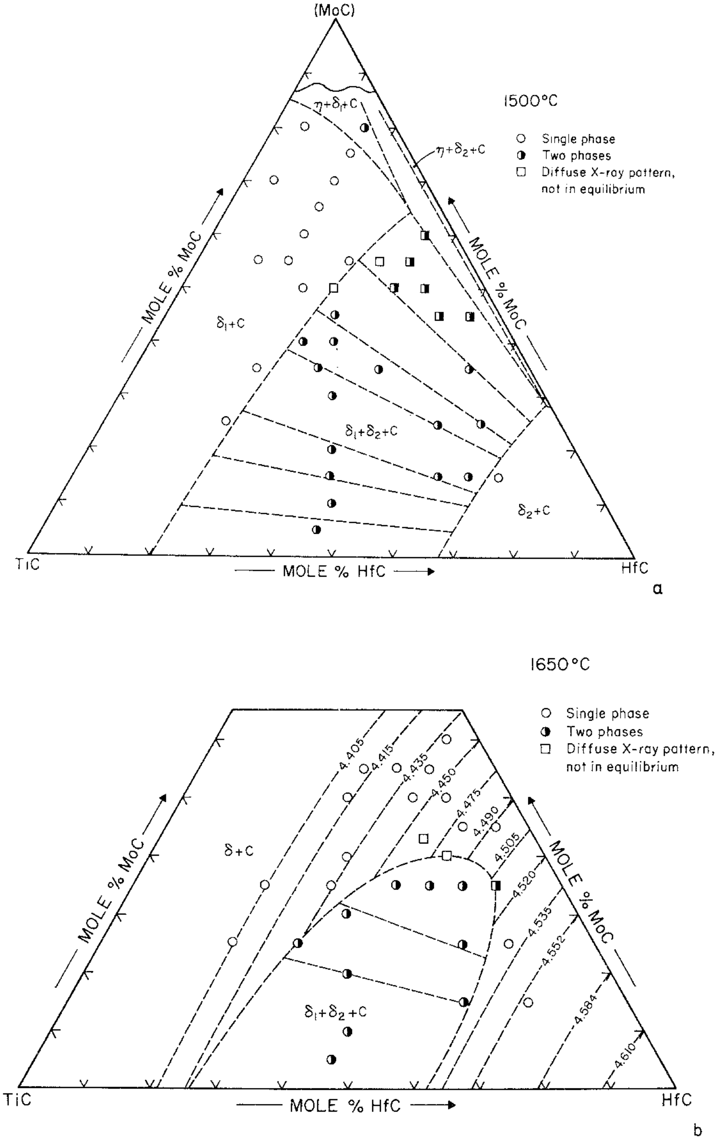

Fig. 3. Location and qualitative (X-ray) phase evaluation of alloy samples equilibrated at 1500 °C (*a*) and 1650 °C (*b*)

Investigation of alloy samples near the TiC—HfC binary at 1780, 1800 °C did not prove evidence of an isolated critical point similar to TiC—HfC—WC. This is in accordance to a thermodynamic calculation.

Above 1960 °C* a complete solid solution (cubic, B 1) is formed throughout the whole ternary: $TiC_{0.97}$—$HfC_{0.98}$—"MoC".

Phase Equilibria at Higher Temperatures

The Isopleth $(Ti_{0.45}Hf_{0.55})C$—"MoC"

Phase distribution and melting behaviour within the isopleth "MoC"—$(Ti_{0.45}Hf_{0.55})C$ is presented in Fig. 1 *d*. Melting near the join TiC—HfC is strongly heterogeneous.

Approximately 50 alloy specimens have been investigated by *DTA* and melting point techniques in order to determine the liquidus as well as solidus surface within the system TiC—HfC—"MoC" (Fig. 4). The dashed line in Fig. 4 represents the bottom line of a flat melting trough separating primary crystallization in $L + \delta$ and $L + C$ phase fields.

Assembly of the Phase Diagram

All experimental data available have been used to construct a constitutional diagram of the system TiC—HfC—"MoC". For a more detailed description a series of isothermal sections and isopleths is presented in Fig. 1*a*—3*b*.

V. Thermodynamic Calculations

In several recent papers the assumption of a regular solution (zeroth order approach) for monocarbide solutions in order to calculate isothermal sections within carbide systems revealed very satisfactory results especially in case of the VC—HfC—{MoC, WC} systems, according to an only slightly asymmetric binary (VC—HfC) as well as ternary miscibility gap[3].

Table 2

ε (cal/mole)	$\Delta F_{cub \rightarrow \eta}$ (cal/mole)
TiC—MoC = 0	TiC = 2000
HfC—MoC = 7563	HfC = 2300
TiC—HfC = 8166	(MoC) = 0.98 T—2184

In spite of the asymetric behaviour of the TiC—HfC miscibility gap calculation of isothermal sections proved to be very helpful in orienting the experimental work by precalculation of the phase equilibria. For the calculations a computer program was used as already described earlier[11] and Table 2 lists the values used in the calculations.

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* According to the transformation of η-MoC_{1-x}.

The values of the interaction parameters and transformation energies have been derived from consideration of the ternary M—M'—C phase equilibria as well as of the phase and solution behaviour in the isopleths (M,M')C.

Considering the influence of the third component on the critical temperature $\left(\frac{\partial T}{\partial x}\right)_c$ of each binary system (TiC—HfC, HfC—“MoC”), no ternary saddle point on the critical curve will occur as long as

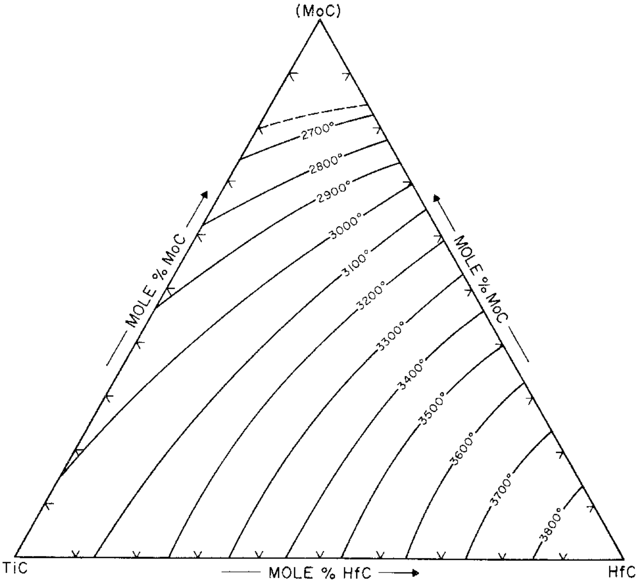

Fig. 4. Liquidus projection of the TiC—HfC—“MoC” system

$\varepsilon_{(\mathrm{Ti,Mo})\mathrm{C}} \leqslant [\varepsilon_{(\mathrm{Ti,Hf})\mathrm{C}} - \varepsilon_{(\mathrm{Hf,Mo})\mathrm{C}}]$[13] and in case of strictly regular solutions i.e. the critical curve gradually decreases from the TiC—HfC binary ($T_c = 1780$ °C) towards HfC—“MoC” ($T_c = 1630$ °C). Comparison between observed and calculated isothermal sections at 1500 °C and 1650 °C is presented in Fig. 5.

On the other hand, let us assume a higher interaction parameter of $\varepsilon_{\mathrm{TiC-MoC}} = 1000$ cal/mole. Now according to regular solution theory ($\varepsilon_{\mathrm{TiC-HfC}} < \varepsilon_{\mathrm{HfC-MoC}} + \varepsilon_{\mathrm{TiC-MoC}}$) the critical temperatures in all three binaries are lowered by additions of X, Y and Z respectively. Therefore a ternary saddle point would occur at 1620 °C on the critical curve, connecting the higher critical temperatures of TiC—HfC and HfC—“MoC”.

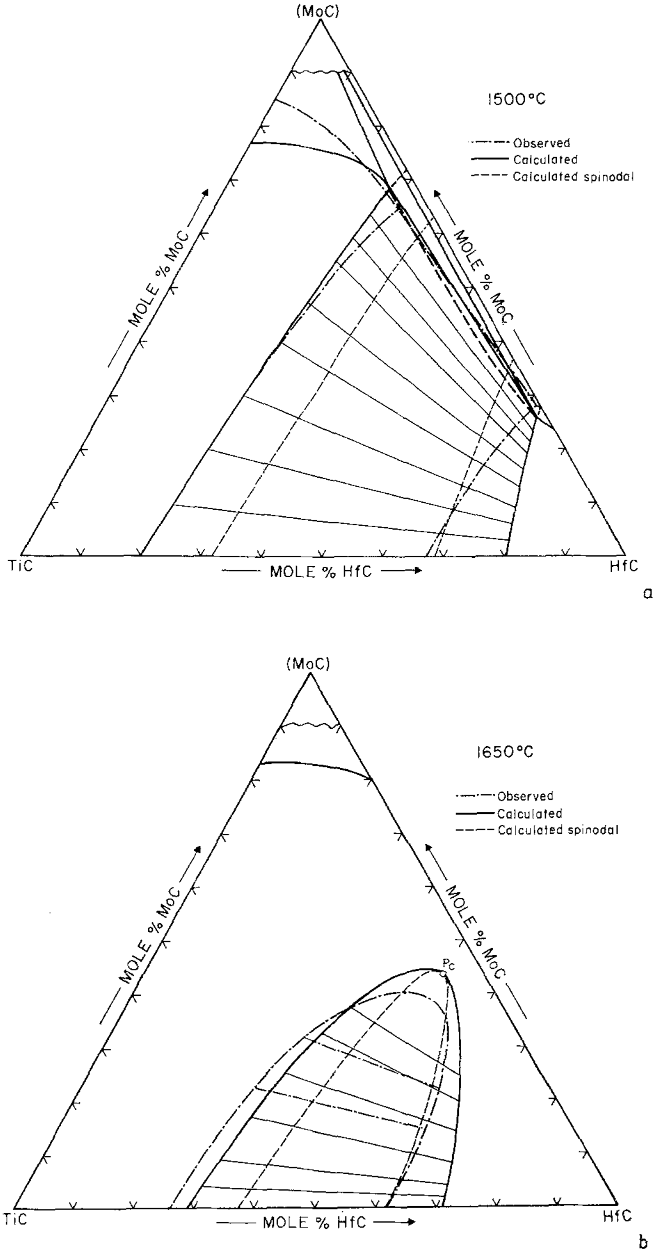

Fig. 5. Comparison between observed and calculated ternary miscibility gap of the TiC—HfC—"MoC" system at different temperatures: *a* 1500 °C, *b* 1650 °C

With this $\varepsilon_{\mathrm{TiC-MoC}} = 1000°\mathrm{C}$ a series of hypothetical isothermal sections have been calculated at 1610, 1620 and 1650 °C. Comparison of these calculated sections with the observed phase behaviour at 1650 °C shows far less accordance than calculations with $\varepsilon_{\mathrm{TiC,MoC}} = 0$. Therefore a gradually decreasing critical curve $[T_{c(\mathrm{Ti,Hf})\mathrm{C}} = 1780\ °\mathrm{C} \rightarrow \rightarrow T_{c(\mathrm{Hf,Mo})\mathrm{C}} = 1630\ °\mathrm{C}]$ seems to be much more likely than the occurrence of a ternary saddle point. No doubt exists about the nonexistence of an isolated critical point as $\varepsilon_{(\mathrm{Ti,Hf})\mathrm{C}} > \varepsilon_{(\mathrm{Hf,Mo})\mathrm{C}} - \varepsilon_{(\mathrm{Ti,Mo})\mathrm{C}}$.

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