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BORON NITRIDE AND SILICON NITRIDE SYSTEMS

•••••••••Final Technical Report•••••

by

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Abstract: (Approximately 75 words for Interim Report; 300 for Final)

A Compendium Of Boron Nitride and Silicon Nitride Phase Diagrams has been provided based on a critical assessment work of ternary systems: (Li,Na,K,Mg,Ca,Sr,Ba,Sc,Y,Tb,Ho,Dy,Er,Tm,Lu,U,Ti,Zr,Hf,V,Nb,Ta,Cr,Mo,W,Mn,Re,Fe,Co,Ni,Ru,Cu,Ag,Au,Zn,Cd,Al,In,Tl,Sn,Pb,Sb,Bi)-B-N and (Li,Be,Mg,Ca,Sr,Ba,Sc,Y,La,Ce,Sm,Ho,Ti,Zr,Hf,V,Nb,Ta,Cr,Mo,W,Mn,Re,Fe,Ru,Co,Rh,Ni,Cu,Ag,Au,Zn,Cd,Al,In,Tl,Sn,Pb,Sb,Bi)-Si-N including crystal data and thermodynamic data.

Key Words

Ternary systems: MetalBoronnitrides
MetalSiliconnitrides
Phase Equilibria
Crystal Data
Thermodynamics
Compatibility

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COMPENDIUM OF TERNARY PHASE DIAGRAMS OF METAL - BORON - NITROGEN and METAL - SILICON - NITROGEN SYSTEMS

PART A *TERNARY SYSTEMS M - B - N*

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PART A

Ternary Systems : Metal - Boron - Nitrogen

PART A *TERNARY SYSTEMS M - B - N*

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SYSTEM BORON - LITHIUM - NITROGEN (B-Li-N)

INTRODUCTION / EXPERIMENTAL

Information on phase equilibria and compound formation in the Li-B-N system is due to [59Gou, 60Wen, 61Wen, 66Kud, 69DeV, 72Dev, 86Yam] and [8 Yam], which all agree on the existence of a ternary compound Li_3BN_2 with several pressure modifications (see Table 1). Heating powder compacts of Li_3N + BN in a Mo-boat in a stream of nitrogen between 650 to 700°C was claimed as optimal conditions to obtain Li_3BN_2 [59Gou, 69DeV], the reaction being strongly exothermic [69DeV]. Melting of Li_3BN_2 was reported at 870∓5°C [59Gou].

Based on earlier preliminary data by [60Wen, 61Wen], the p-T diagram of Li_3BN_2 (Fig.1) was investigated over the pressure and temperature range from 1.0 to 6.5 GPa and 300 to 1900°C employing optical and X-ray powder diffraction analysis [69DeV, 72DeV]. All experiments were done in pyrophyllite/Ta cells in a belt apparatus where pressure was applied to a given value and then the temperature was raised at a rate of 400K/min; temperature and pressure were held at 10 to 15 min followed by quenching in ~ 30 sec with the pressure still applied.

BINARY SYSTEMS

No equilibrium diagram is available for the Li-B system; however, a series of lithium borides exist, which are listed in Table 1. For details see [84Mair, 89Oka, 90Mas]. At 1450°C Li_3B_{14} was found in equilibrium with β-boron [84Mai]; a result, which casts doubts on the existence of phases such as LiB_{12} or $LiB_{\sim 10}$ and rather suggests an extended solubility of Li in boron. There is practically no solubility of B in Li.

Phase equilibria in the Li-Li_3N subsystem are given in [90Mas] revealing Li_3N as the only stable phase; crystallographic data of Li_3N and of the azide LiN_3 are listed in Table 1. Interstitial solubility of N in Li is very low.

SOLID PHASES / ISOTHERMAL SECTIONS

Agreement exists on the structural modification of Li_3BN_2 obtained under 10^5Pa when quenched from the reaction temperature [59Gou, 69DeV, 86Yam]. Slow cooling of a mixture Li_3N + 1.0 to 1.2 BN, which was first heated to 900°C, kept at temperature for 7h and cooled to 700°C at a rate of 1.5 to 3 K/h in a stream of nitrogen, resulted, however, in a modification [86Yam] different from the one first reported by [59Gou] (see Table 1).

Fig.1 reveals the formation of two high pressure forms of Li_3BN_2 ; Li_3BN_2 (I) was recognized to be identical with the phase labelled "complex" by [60Wen, 61Wen]. Reversibility of the transition Li_3BN_2 - Li_3BN_2(I) was not established when held at 550°C, 5.5 GPa for 30 min, whereas partial conversion was seen when Li_3BN_2 (I) was heated at 700°C in 10^5 Pa of N_2 for 5h. As it proved unquenchable [69DeV], a layerlike structure was suggested for Li_3BN_2 (II) from optical, mechanical and thermal properties.

The section Li_3BN_2 - BN has been investigated by [72DeV] at 5.0 GPa and was reported to be pseudobinary revealing a eutectic l ==> Li_3BN_2 + cBN at 6 mol %BN at 1610∓25°C (Fig.2). As the upper limit of the l+cBN field was observed at 1450∓25°C, a possible crystal growth region for cBN is only 140°C, however, the corresponding liquidus is unfavourably steep. At 1550°C a ternary reaction involving cBN, Li_3BN_2(I), a boron containing phase plus liquid was observed; this temperature is lower than the first appearance of melt in the Li_3BN_2-BN section (1610°C) and corresponds to the lower limit of cBN formation from the reaction Li+BN [66Kud]. A comparision of the favourable pressure temperature conditions for the production of cBN using Li_3N, Mg_3N_2 or Ca_3N_2, is shown in Fig.3.

MISCELLANEOUS

Infrared spectra of the quenched form of Li_3BN_2 were interpreted in terms of $[N=B=N]^{3-}$ molecular ions; nearly linear $[N=B=N]^{3-}$ groups with B-N double bonds were observed for slowly cooled Li_3BN_2 [86Yam].

Li-ion conductivity of a polycristalline sample of slowly cooled Li_3BN_2 was 4.10^{-5} Sm^{-1} at 125°C with an activation energy of 64kJ/mol [85Yam].

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Table 1: Solid phases in the system B-Li-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Li 180.5– –193°	cI2 Im$\bar{3}$m W	a= 350.93	[90Mas]
α-Li <–193°	hP2 P6$_3$/mmc Mg	a= 311.1 c= 509.3	[90Mas]
β-rhB <2092°	hR111 R$\bar{3}$m β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
α-rhB <1200°	hR36 R$\bar{3}$m α-B	a= 490.9 c=1258.2	[85Vil]
LiB_{12}	tP* – LiB_{12}	a=1016 c=1428	[89Oka]
LiB_6	–		[89Oka]
Li_3B_{14}	tI136 I$\bar{4}$2d Li_3B_{14}	a=1076.4 c= 894.7	[84Mai] ρ_x=2.214 Mgm^{-3}
LiB_4	c** –	a= 720	[89Oka]
Li_6B_{19}	hP25 P6/mmm Li_6B_{19}	a= 823.3 c= 415.6	[84Mai] ρ_x=1.706 Mgm^{-3}
LiB_3	tP16 P4/mbm Li_2B_6 (CaB_6-deriv.)	a= 597.8 c= 418.8	[84Mai]
LiB_2	– –	–	[89Oka]

LiB	t** –	a=1391 c= 815	[89Oka]
Li_5B_6	hR10 R$\bar{3}$m or I$\bar{4}$3m Li_5B_6	a= 493	[89Oka] or Li_7B_6
Li_3B	c**		[89Oka]
Li_3N 815°	hP4 P6/mmm Li_3N	a= 364.8 c= 387.5	[85Vil]
LiN_3	mC8 C2/m	a= 562.7 b= 331.9 c= 497.9 β= 107.4°	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]
* Li_3BN_2 <870°	– Li_3AlN_2	–	[59Gou] at 10^5Pa,quench ρ_{exp}=1.755 Mgm^{-3}
* Li_3BN_2	mP24 $P2_1/c$ Li_3BN_2	a= 515.02 b= 708.24 c= 679.08 β= 112.956°	[86Yam] at 10^5Pa,slow c ρ_{exp}=1.74 Mgm^{-3}
* Li_3BN_2(I) >0.7 GPa	– –	–	[61Wen, 69DeV]
* Li_3BN_2(II) >2.5 GPa	–	–	[61Wen, 69DeV]

Fig.1: The P - T diagram for Li_3BN_2 (after [72DeV])

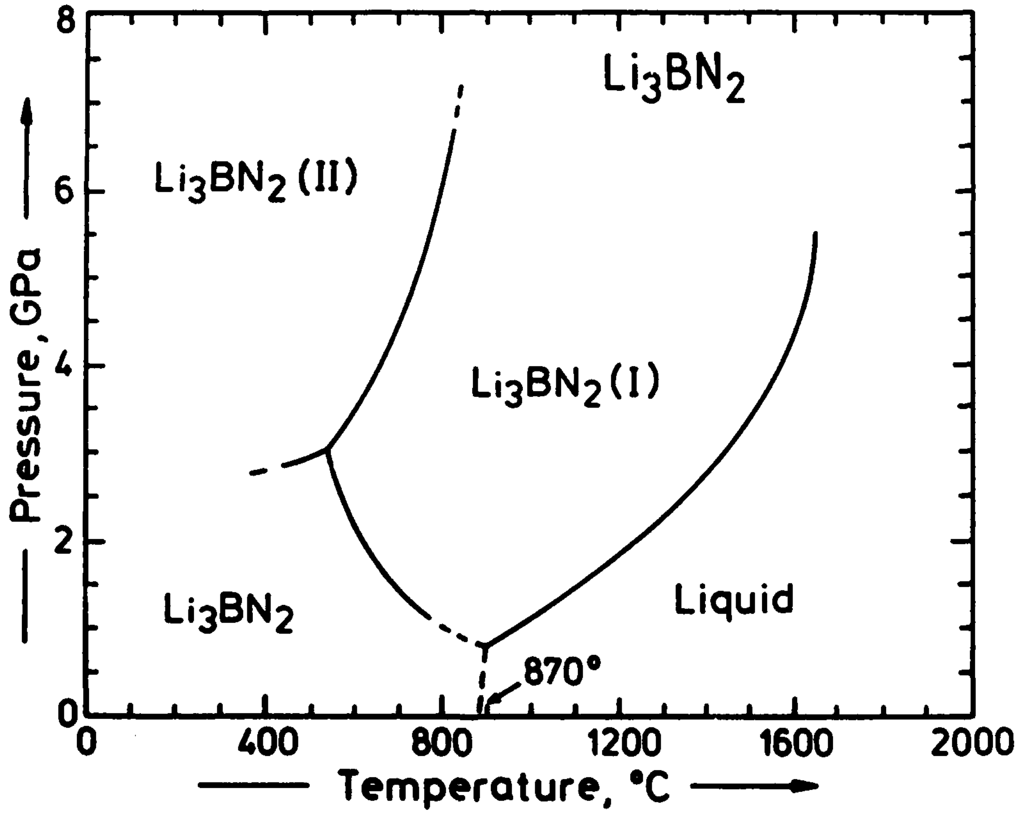


Fig.2. The pseudobinary section Li_3BN_2 - BN at 5 GPa (after [72DeV])

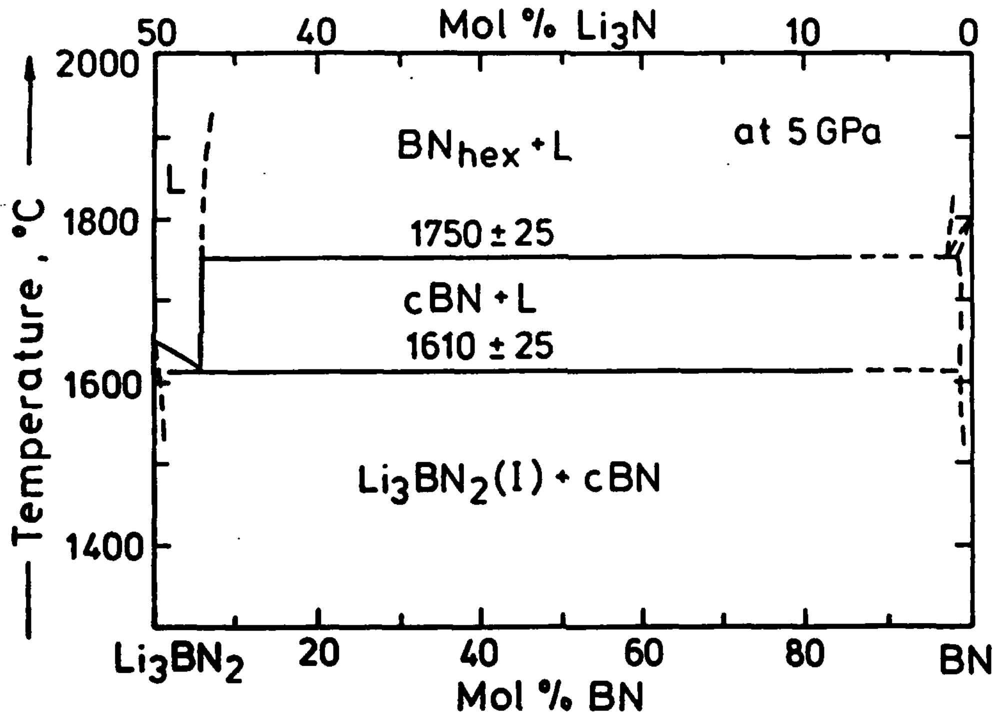
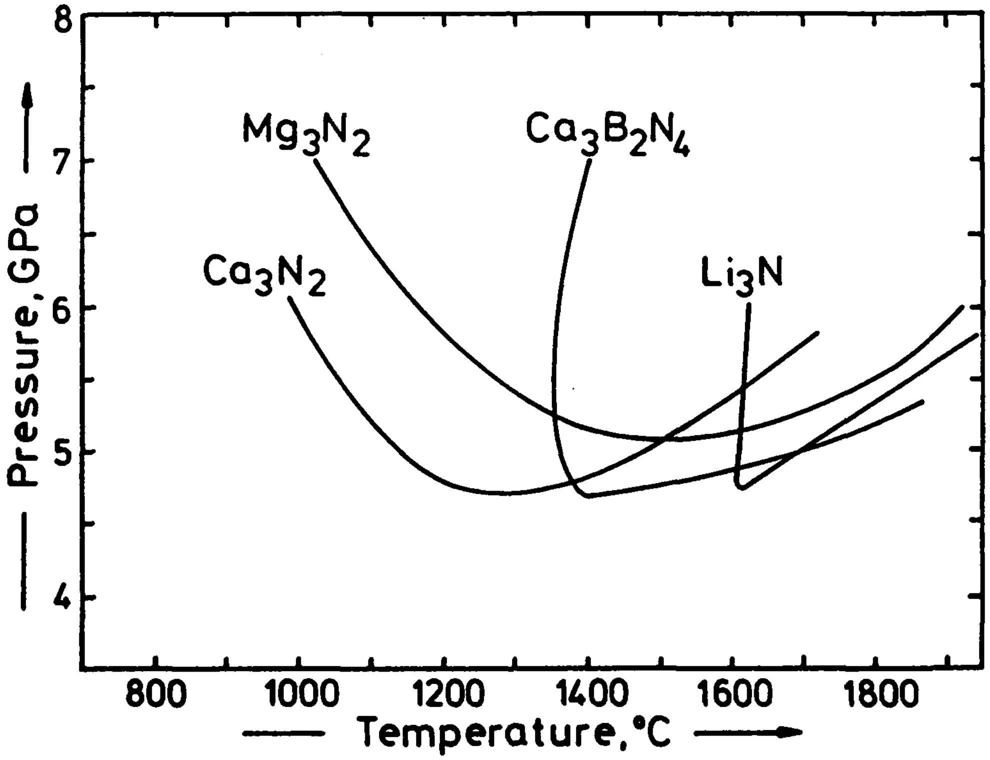


Fig.3. Comparision of the stability region for cBN using various catalysts.



SYSTEM BORON - SODIUM - NITROGEN (B-Na-N)

INTRODUCTION / EXPERIMENTAL

A black powder was obtained when sodium was heated with BN in sealed quartz capillaries at 400°C for 24h; after washing in ethanol the product was dark grey revealing new low angle X-ray peaks which were believed to correspond to intercalation; the formula $NaBN_{18}$ was obtained from chemical analysis [69Fre].

Hexagonal boron nitride was converted to cBN with sodium at 1750°C and 9.3 GPa [60Wen].

REFERENCES

[60Wen] R.H.Wentorf,Jr., "Abrasive Material and Preparation Thereof", US Patent 2947617 GEC, 2.Aug. (1960)

[69Fre] A.G.Freeman and J.P.Larkindale, "Evidence for the Formation of Boron Nitride-Alkali Metal Intercalation Compounds", Inorg. Nucl. Chem. Lett. 5 (1969) 937-939

Table 1: Solid phases in the system B-Na-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Na	cI2	a= 429.06	[90Mas]
97.86- -233°	Im$\bar{3}$m		
	W		
α-Na	hP2	a= 376.7	[90Mas]
<-233°C	P6$_3$/mmc	c= 615.4	
	Mg		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	R$\bar{3}$m	c=2381.43	[85Vil]
	β-B		
α-rhB	hR36	a= 490.9	[85Vil]
<1200°	R$\bar{3}$m	c=1258.2	
	α-B		
BN$_{hex}$	hP*	a= 250.4	[85Vil]
	P6$_3$/mmc	c= 666.1	
	BN$_{hex}$		
* NaBN$_{13}$	-	-	[69Fre]
	BN$_{hex}$-intercalation		

SYSTEM BORON - POTASSIUM - NITROGEN (B-K-N)

INTRODUCTION / EXPERIMENTAL

A black powder was obtained when potassium was heated with BN in sealed quartz capillaries at 300°C for 24h; after washing in ethanol the product was dark grey revealing new low angle X-ray peaks which were believed to correspond to intercalation; the formula KBN_{18} was obtained from chemical analysis [69Fre].

Hexagonal boron nitride was converted to cBN with potassium at 1700°C and 9.5 GPa [60Wen].

No reaction was observed when potassiumamide and Bn were heated in sealed iron containers up to 1200°C [61Gou].

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[60Wen] R.H.Wentorf,Jr., "Abrasive Material and Preparation Thereof", US Patent 2947617 GEC, 2.August (1960)

[69Fre] A.G.Freeman and J.P.Larkindale, "Evidence for the Formation of Boron Nitride-Alkali Metal Intercalation Compounds", Inorg. Nucl. Chem. Lett. 5 (1969) 937-939

Table 1: Solid phases in the system B-K-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
K	cI2	a= 532.1	[90Mas]
<63.71°C	$Im\bar{3}m$		
	W		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
α-rhB	hR36	a= 490.9	[85Vil]
<1200°	$R\bar{3}m$	c=1258.2	
	α-B		
BN_{hex}	hP*	a= 250.4	[85Vil]
	$P6_3/mmc$	c= 666.1	
	BN_{hex}		
* KBN_{18}	-	-	[69Fre]
	BN_{hex}-intercalation		

SYSTEM BORON - MAGNESIUM - NITROGEN (B-Mg-N)

INTRODUCTION / EXPERIMENTAL

Information on phase equilibria and compound formation in the Mg-B-N system is due to [66Kud, 72Dev, 79End1, 79End2, 81Sat, 81Ely, 89Pik, 89Shi] and [89Hoh], which all agree on the existence of a ternary compound Mg_3BN_4 for which two modifications have been observed [81Ely, 89Pik, 89Hoh](see Table 1).

Based on preliminary high pressure data by [60Wen, 66Kud, 67Fil] defining the minimum temperature for the formation of cBN at ~1700°C in the presence of magnesiumborides, phase relations along the join Mg - $Mg_3B_2N_4$ - BN have been investigated at 2.5 GPa in the temperature range from 800 to 1600°C employing DTA-, optical and X-ray powder diffraction analysis supported by conventional quenching techniques [79End1, 79End2, 81End] (see Fig.1). The experiments were done in pyrophyllite/Ta cells in a belt apparatus where pressure was applied to a given value and then the temperature was raised at a rate of 200 to 250K/min; temperature and pressure were held for 20 min followed by quenching in ~ 30 sec with the pressure still applied. No reaction was found between Mg and BN below 1100°C, whereas above 1150°C yellow lath-like plates of $Mg_3B_2N_4$ and magnesiumborides MgB_2,$MgB_{\sim 6}$, $MgB_{\sim 12}$ were formed [79End1]. The precipitation of hBN from the eutectic liquid was observed for temperatures higher than 1300°C.

BINARY SYSTEMS

A tentative equilibrium diagram for the Mg-B system is given in [90Mas], revealing the formation of three stable magnesium borides , which are listed in Table 1. There is practically no mutual solid solubility of B , Mg.

No phase diagram is available for the Mg-N system. For Mg_3N_2 only the α-modification has been reported [65Ell] (see Table 1). Interstitial solubility of N in Mg is very low.

SOLID PHASES / ISOTHERMAL SECTIONS

In a cursory p-T diagram of the system Mg_3N_2 - BN [81Ely] showed the ranges of existence of two modifications of α-$Mg_3B_2N_4$ (1000 to 1450°C, > 2GPa), β-$Mg_3B_2N_4$ (>1600°C, 3.5 to 6 GPa) with an intermediate two-phase region in between. The X-ray powder pattern as reported by [79End1] for $Mg_3B_2N_4$ was claimed to essentially correspond to this two-phase region α+β-$Mg_3B_2N_4$ [81Ely]. The existence of two modifications of $Mg_3B_2N_4$, however, is not confirmed by [89Hoh].

At 2.5 GPa $Mg_3B_2N_4$ was reported to melt at 1489∓5°C [79End1] and at 1685∓10°C at 6.5 GPa [89Hoh].

Fig.1 reveals the phase relations in two subsystems Mg - $Mg_3B_2N_4$ and $Mg_3B_2N_4$ - BN which at 2.5 GPa were shown to be of a simple eutectic type [79End1]. l == $Mg_3B_2N_4$ + hBN is at 1295∓7°C , 2.5 GPa [79End1] and at 1380∓10°C at 6.5 GPa [89Hoh].

The p-T regions of cBN in the systems Mg-BN and Mg_2N_3-BN were investigated up to 8 GPa and 2300°C [79End2, 81Sat]. In the Mg-BN system pressure and temperature necessary for the formation of cBN were found to decrease with increasing oxygen content of the starting hBN material [79End2]; the lower limit of the cBN region for hBN with 1.9 mass%O is ~1380°C at 6 to 8 GPa, but 1700°C at 6 GPa for hBN with 7.9 mass%O. In the Mg_3N_2 system oxygen had little effect on the lower limits of pressure and temperature, cBN-yields, however, deceased with oxygen contents [81Sat].

Coexistence of $Mg_3B_2N_4$ and Mg_3BN_3 was observed within the low-temperature cBN region [89Pik, 89Hoh].

A comparision of the favourable pressure temperature conditions for the production of cBN using Li_3N, Mg_3N_2 or Ca_3N_2, is shown in Fig.3 of the section Li-B-N.

MISCELLANEOUS

Infrared spectra of $Mg_3B_2N_4$ formed at 2.5 GPa were interpreted in terms of $[N{=}B{=}N]^{3-}$ molecular ions [79End1]. $Mg_3B_2N_4$ slowly decomposes in moist environment, at higher temperatures it easily oxidizes to $Mg_3(BO_3)_2$ [79End1].

The influence of P on the crystallization kinetics of cBN in the MgB_2-BN system has been studied by [89Shi] at 5 GPa and 1570 to 1800°C; 0.1 to 0.5 mass% P considerably increase the nucleation rate and reduce the nucleation energy.

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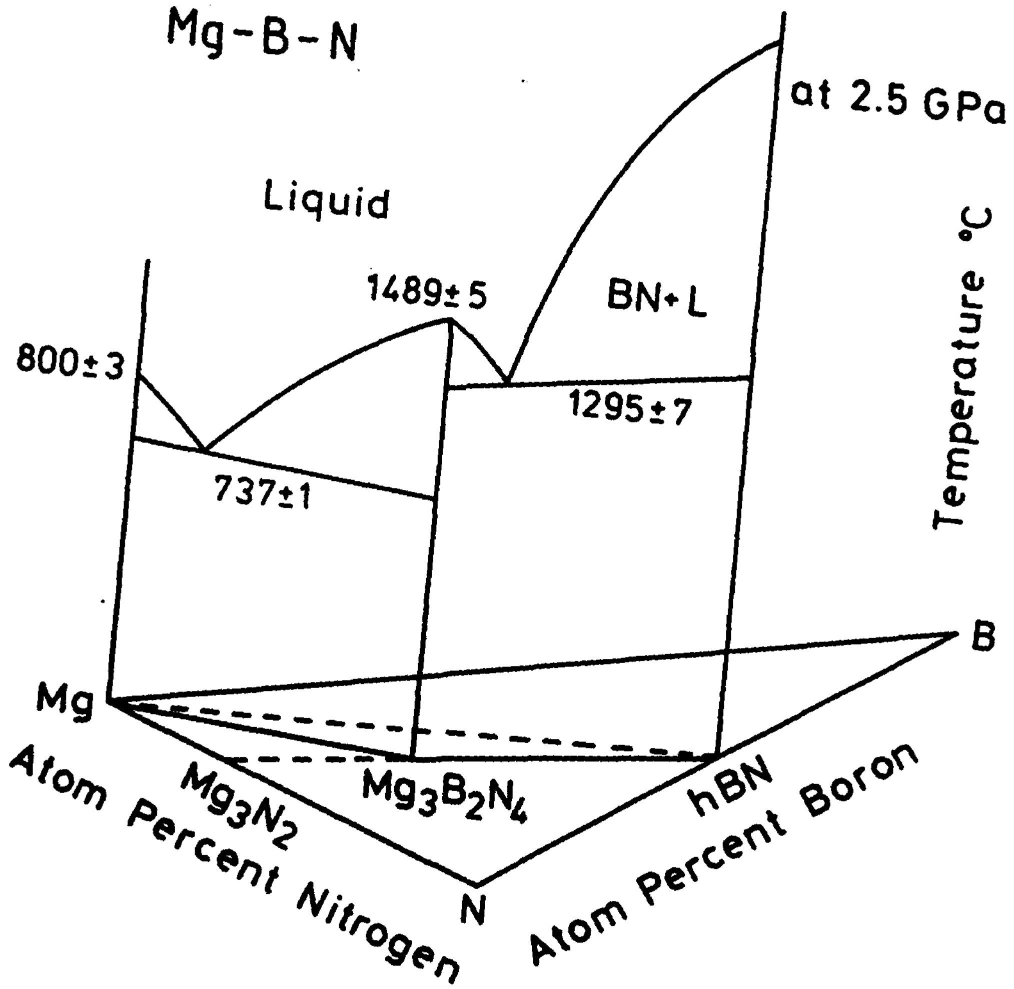
Table 1: Solid phases in the system B-Mg-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Mg 650°	hP2 $P6_3/mmc$ Mg	a= 320.94 c= 521.07	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
α-rhB <1200°	hR36 $R\bar{3}m$ α-B	a= 490.9 c=1258.2	[85Vil]
MgB_7 <2300°	oI64 Imma MgB_7	a= 597.0 b=1048.0 c= 812.5	[85Vil]
MgB_4 <1850°	oP20 Pnma MgB_4	a= 546.4 b= 442.8	[85Vil]
MgB_2 <1550°	hP3 P6/mmm AlB_2	a= 308.4 c= 352.2	[85Vil]
α-Mg_3N_2 <550°	cI80 $Ia\bar{3}$ Mn_2O_3	a= 996.4	[85Vil]

BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]	
* α-$Mg_3B_2N_4$ >2 GPa	-	-	[81Ely]	
* β-$Mg_3B_2N_4$ >3.5-6 GPa	-	-	[81Ely]	
* Mg_3BN_3	-	-	[89Hoh]	at 6.5 GPa

Fig.1: The partial system Mg-B-N (after [79End1])



SYSTEM BORON - CALCIUM - NITROGEN (B-Ca-N)

INTRODUCTION / EXPERIMENTAL

Information on phase equilibria and compound formation in the Ca-B-N system is due to [60Wen, 61Gou, 72Dev, 81End] and [83Sat], which all agree on the existence of a ternary compound $Ca_3B_2N_4$ (see Table 1).

Heating powder compacts of Ca_3N_2 + BN in a Mo-boat in a stream of nitrogen between 800 to 1150°C was claimed as optimal conditions to obtain $Ca_3B_3N_4$ [61Gou, 72DeV]. The reaction was said to be incomplete after 3h at 800°C. Melting of $Ca_3B_2N_4$ was reported at 1412∓3°C [81End

Based on preliminary high pressure data by [60Wen] defining the minimum temperature for the formation of cBN at ~1300°C and 6.9GPa, phase relations along the join Ca - $Ca_3B_2N_4$ - BN have been investigated at 2.5 GPa in the temperature range from 800 to 1600°C employing DTA-, optical and X-ray powder diffraction analysis supported by conventional quenching techniques [81End, 83Sat] (see Fig.1). The experiments were done in pyrophyllite/Ta cells in a belt apparatus where pressure was applied to a given value and then the temperature was raised at a rate of 200 to 250K/min; temperature and pressure were held for 20 min followed by quenching in ~ 30 sec with the pressure still applied. Above 1150°C , $Ca_3B_2N_4$ was formed together with small amounts of Ca_3N_2 and CaB_6 [81End]. The low temperature limit of the precipitation of cBN from the $Ca_3B_2N_4$-melt was found to be closely related to the $Ca_3B_2N_4$ + BN eutectic at 1316 ∓ 6°C [81End]. [83Sat] studied the nucleation and growth mechanism of cBN crystals.

BINARY SYSTEMS

A tentative equilibrium diagram for the Ca-B system is suggested in [90Mas], revealing the formation of only one stable calcium boride, CaB_6 despite there seem to be no doubts about the existence of CaB_4 [61Joh] , (see Table 1). There is practically no mutual solid solubility of B , Ca.

Informations on the Ca-N phase diagram are still unsatisfactory; a critical assessment is due to [90Itk]. Crystallographic data are listed in Table 1. Interstitial solubility of N in Ca is very low.

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 reveals the phase relations in two subsystems Ca - $Ca_3B_2N_4$ and $Ca_3B_2N_4$ - BN which at 2.5 GPa were shown to be of a simple eutectic type [81End]. ℓ == $Ca_3B_2N_4$ + hBN is at 1316∓6°C , 2.5 GPa and ℓ == Ca + $Ca_3B_2N_4$ is at 1032∓5°C at 2.5 GPa [81End] . At 2.5 GPa $Ca_3B_2N_4$ was reported to melt at 1412∓3°C [81End].

The p-T regions of cBN in the systems Ca-BN and $Ca_3B_2N_4$-BN were investigated up to 6.5 GPa and 1800°C [81End, 83Sat] and found to be practically identical. According to the composition -temperature diagam of the $Ca_3B_2N_4$-BN system at 5.4GPa (see Fig.2) , the growth of cBN was governed by the solubility difference of hBN and cBN in liquid $Ca_3B_2N_4$-flux [83Sat].

A comparision of the favourable pressure temperature conditions for the production of cBN using Li_3N, Mg_3N_2 or $Ca_3B_2N_4$, is shown in Fig.3 of the section Li-B-N.

MISCELLANEOUS

Infrared spectra of $Ca_3B_2N_4$ formed at 2.5 GPa were interpreted in terms of $[N=B=N]^{3-}$ molecular ions [61Gou]. $Ca_3B_2N_4$ slowly decomposes in moist environment, at higher temperatures it easily oxidizes to $Ca_3(BO_3)_2$.

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Table 1: Solid phases in the system B-Ca-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Ca 842-443°C	cI2 Im$\bar{3}$m W	a= 448.0	[90Mas]
α-Ca <443°C	cF4 Fm$\bar{3}$m Cu	a= 558.84	[90Mas]
β-rhB <2092°	hR111 R$\bar{3}$m β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
α-rhB <1200°	hR36 R$\bar{3}$m α-B	a= 490.9 c=1258.2	[85Vil]
CaB_4 <°	tP20 P4/mbm UB_4	a= 711 c= 411	[61Joh]
CaB_6 <2500°C	cP7 Pm$\bar{3}$m CaB_6	a= 414.5	[85Vil]
Ca_2N	hR3 R$\bar{3}$m Sm	a= 363.8 c=1878	[85Vil] stabil. by H_2?
	m**	a= 753.5 b= 363.8 c= 629.9 β= 123.85°	[68Lau]
α-Ca_3N_2	cI80 Ia$\bar{3}$ Mn_2O_3	a=1147.3	[85Vil]
γ-Ca_3N_2	o*40	a=1782 b=1156 c= 358	[85Vil] metastable?

Ca_3N_2 (I)	o**	a= 562.5 b=1114. c=1361.	[90Itk] at 4.6 GPa
$Ca_{11}N_8$	tP38 $P4_2/mnm$ $Ca_{11}N_8$	a=1445 c= 360	[85Vil]
CaN_6	oF56 Fddd	a=1132 b=1107 c= 595	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]
* $Ca_3B_2N_4$ <1412°C at 2.5 GPa	–	–	[61Gou] $\rho_{exp}=2.86 Mgm^{-3}$

Fig.1: The partial system Ca-B-N (after [81End])

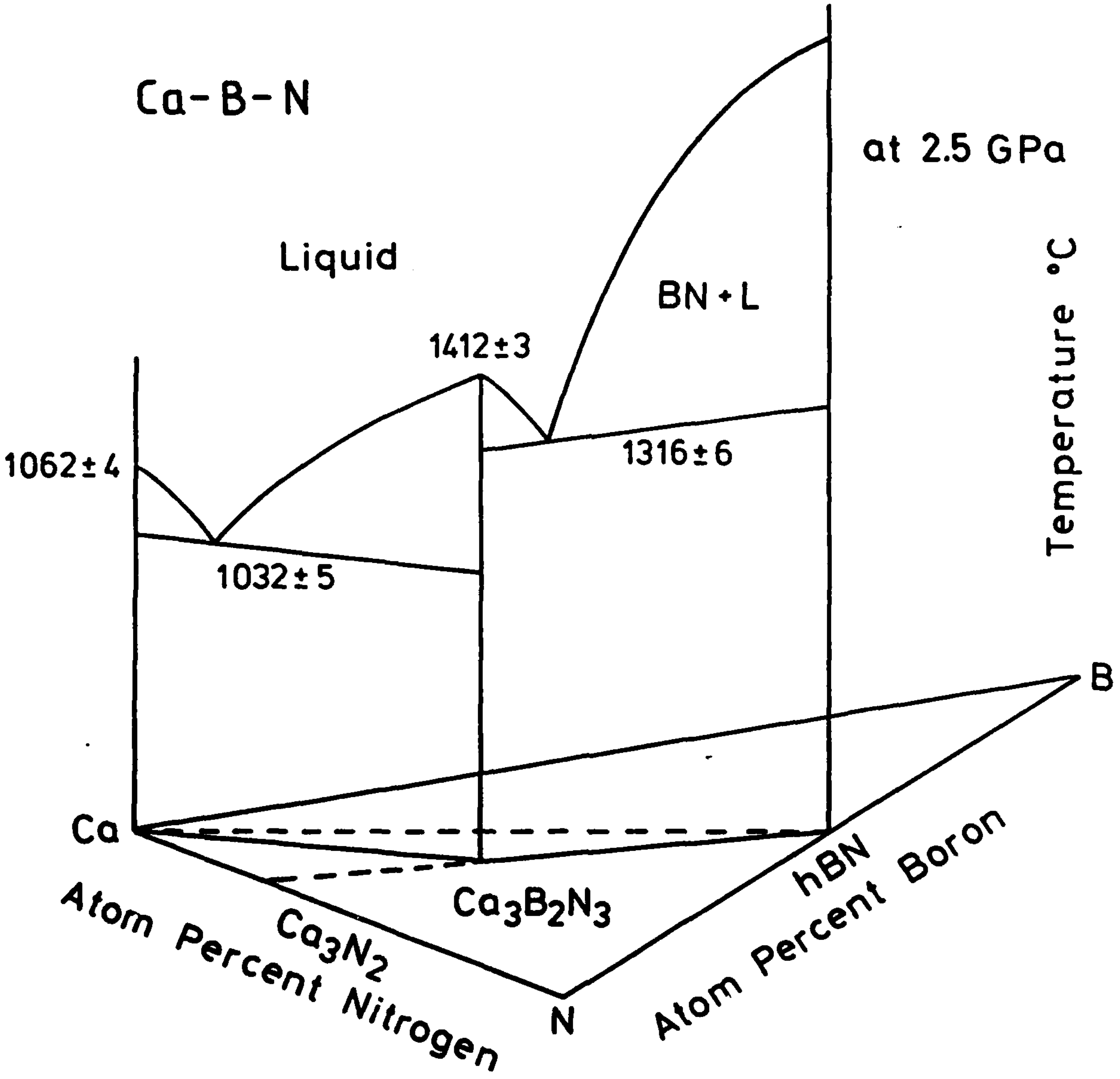
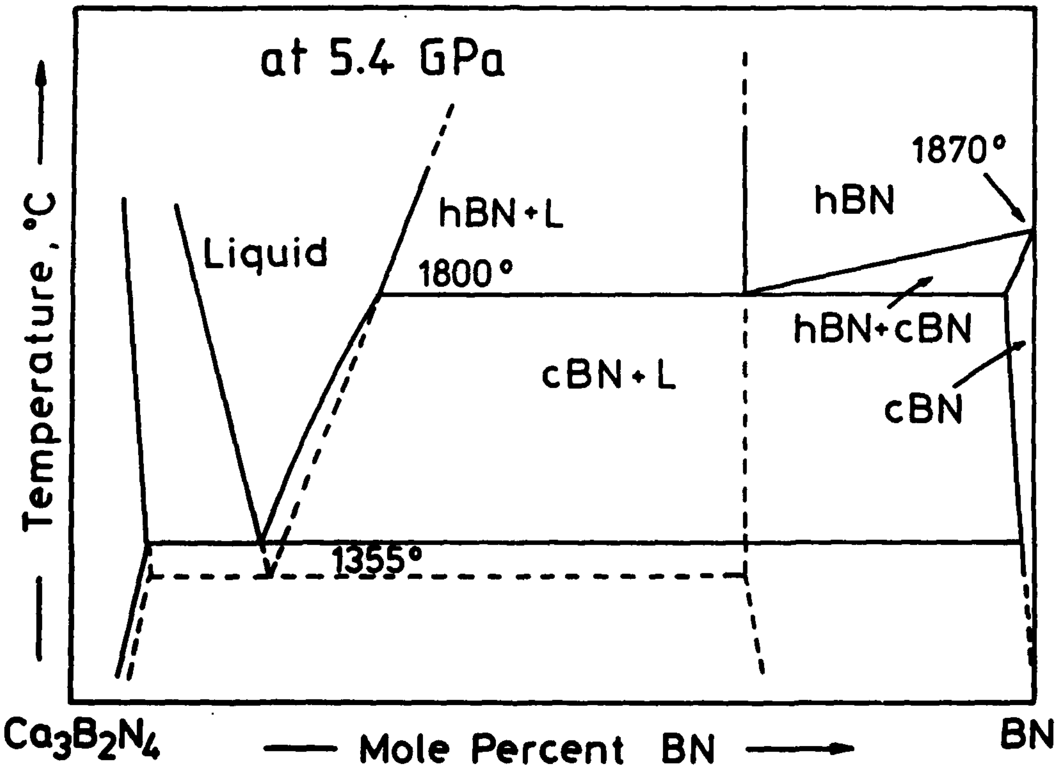


Fig.2: Phase equilibria in the section $Ca_3B_2N_3$ - BN at 5.4 GPa
(after [83Sat])



SYSTEM BORON - STRONTIUM - NITROGEN (B-Sr-N)

INTRODUCTION / EXPERIMENTAL

No phase diagram Sr-B-N exists; information on phase relations and compound formation is due to [74Gau] who reported on the existence of a ternary compound $Sr_3B_2N_4$ from X-ray analysis of samples reacted at 900°C for 30 h (see Table 1).

Preliminary high pressure experiments by [60Wen] reported the formation of cBN from hBN at 8.7 GPa and~1600°C using Sr-metal as a catalyst.

BINARY SYSTEMS

A tentative equilibrium diagram for the Sr-B system is given in [90Mas], revealing the formation of one stable strontium boride, SrB_6, (see Table 1). There is practically no mutual solid solubility of B, Sr.

No phase diagram is available for the Sr-N system. Crystallographic data are listed in Table 1. Interstitial solubility of N in Sr is very low.

SOLID PHASES / ISOTHERMAL SECTIONS

The X-ray powder pattern as reported by [74Gau] for $Sr_3B_2N_4$ was claimed to essentially correspond to the one of $Ca_3B_2N_4$ (isotypic?).

MISCELLANEOUS

Infrared spectra of $Sr_3B_2N_4$ were interpreted in terms of $[N{=}B{=}N]^{3-}$ molecular ions [74Gau]. $Sr_3B_2N_4$ slowly decomposes in moist environment, at higher temperatures it easily oxidizes to $Sr_3(BO_3)_2$ [74Gau].

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[90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2nd Ed., (Amer.Soc.Met.Intl., Metals Park,Oh, 1990)

Table 1: Solid phases in the system B-Sr-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Sr	cI2	a= 487	[90Mas]
769-547°	$Im\bar{3}m$		
	W		
α-Sr	cF4	a= 608.4	[90Mas]
<547°C	$Fm\bar{3}m$		
	Cu		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
α-rhB	hR36	a= 490.9	[85Vil]
<1200°	$R\bar{3}m$	c=1258.2	
	α-B		
SrB_6	cP7	a= 419.84	[85Vil]
<2500°C	$Pm\bar{3}m$		
	CaB_6		
Sr_2N	hR3	a= 724.6	[85Vil]
	$R\bar{3}m$	α= 30.8°	
	Sm		
	m**	a= 719	[70Gau]
		b= 385	
		c= 665	
		β= 108°	
Sr_3N_2	hP*		[85Vil]
<1030°	Ba_3N_2		
SrN_6	oF56	a=1180.88	[85Vil]
	Fddd	b=1153.43	
		c=611.62	
BN_{hex}	hP*	a= 250.4	[85Vil]
	$P6_3/mmc$	c= 666.1	
	BN_{hex}		
* $Sr_3B_2N_4$	-	-	[74Gau] ρ_{exp}=3.72Mgm^{-3}

SYSTEM BORON - BARIUM - NITROGEN (B-Ba-N)

INTRODUCTION / EXPERIMENTAL

No phase diagram Ba-B-N exists; information on phase relations and compound formation is due to [61Gou] who reported on the existence of a ternary compound $Ba_3B_2N_4$ from X-ray analysis of powder compacts of Ba_3N_2+BN which have been reacted in a sealed quartz capillary for 3 h at 700 to 900°C (see Table 1).

Preliminary high pressure experiments by [60Wen] reported the formation of cBN from hBN at 8.0 to 8.7 GPa and ~1600 to 1700°C using Ba-metal as a catalyst.

BINARY SYSTEMS

A tentative equilibrium diagram for the Ba-B system is given in [90Mas], revealing the formation of one stable barium boride, BaB_6, (see Table 1). There is practically no mutual solid solubility of B , Ba.

No phase diagram is available for the Ba-N system. Crystallographic data are listed in Table 1. Interstitial solubility of N in Ba is very low.

SOLID PHASES / ISOTHERMAL SECTIONS

The X-ray powder pattern as reported by [61Gou] for $Ba_3B_2N_4$ was claimed to essentially correspond to the one of $Ba_3B_2N_4$ (isotypic?).

MISCELLANEOUS

Infrared spectra of $Ba_3B_2N_4$ were interpreted in terms of $[N{=}B{=}N]^{3-}$ molecular ions [61Gou]. $Ba_3B_2N_4$ slowly decomposes in moist environment, at higher temperatures it easily oxidizes to $Ba_3(BO_3)_2$ [61Gou].

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Table 1: Solid phases in the system B-Ba-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Ba <727°	cI2 $Im\bar{3}m$ W	a= 501.3	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
α-rhB <1200°	hR36 $R\bar{3}m$ α-B	a= 490.9 c=1258.2	[85Vil]
BaB_6 <2500°C	cP7 $Pm\bar{3}m$ CaB_6	a= 426.8	[85Vil]
Ba_3N_2	hP* Ba_3N_2	a= 522 c= 550	[85Vil]
BaN_6	mP14 $P2_1/m$ BaN_6	a= 959 b= 439 c= 542 β=99.7°	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]
* $Ba_3B_2N_4$	-	-	[61Gou]

SYSTEM BORON - SCANDIUM - NITROGEN (B - Sc - N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Sc-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O_2 and $<$ 4 ppm H_2O. Starting materials were ingots of 3N-Sc,crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Sc system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. A critical assessment is due to [90Spe]. The solubility of B in Sc is negligible [90Spe]; the maximum solubility of Sc in β-B is close to ScB_{28} [78Cal].

No equilibrium diagram exists for the N-Sc system and solid solubility of N in Sc is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure ScN is the only stable nitride [72Kie] (Table 1).

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1400°C under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium ScN + ScB_2 + BN. Thus there is no compatibility between (Sc) and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Sc in BN at 1400°C, and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of N_2 at 1400°C (100h) and at 1800°C (20h) respectively : in both cases the limiting tie line reported was ScN + BN + N_2.

THERMODYNAMICS

A thermodynamic modelling of the binary system Sc-B is due to [90Spe]; see Table 2.

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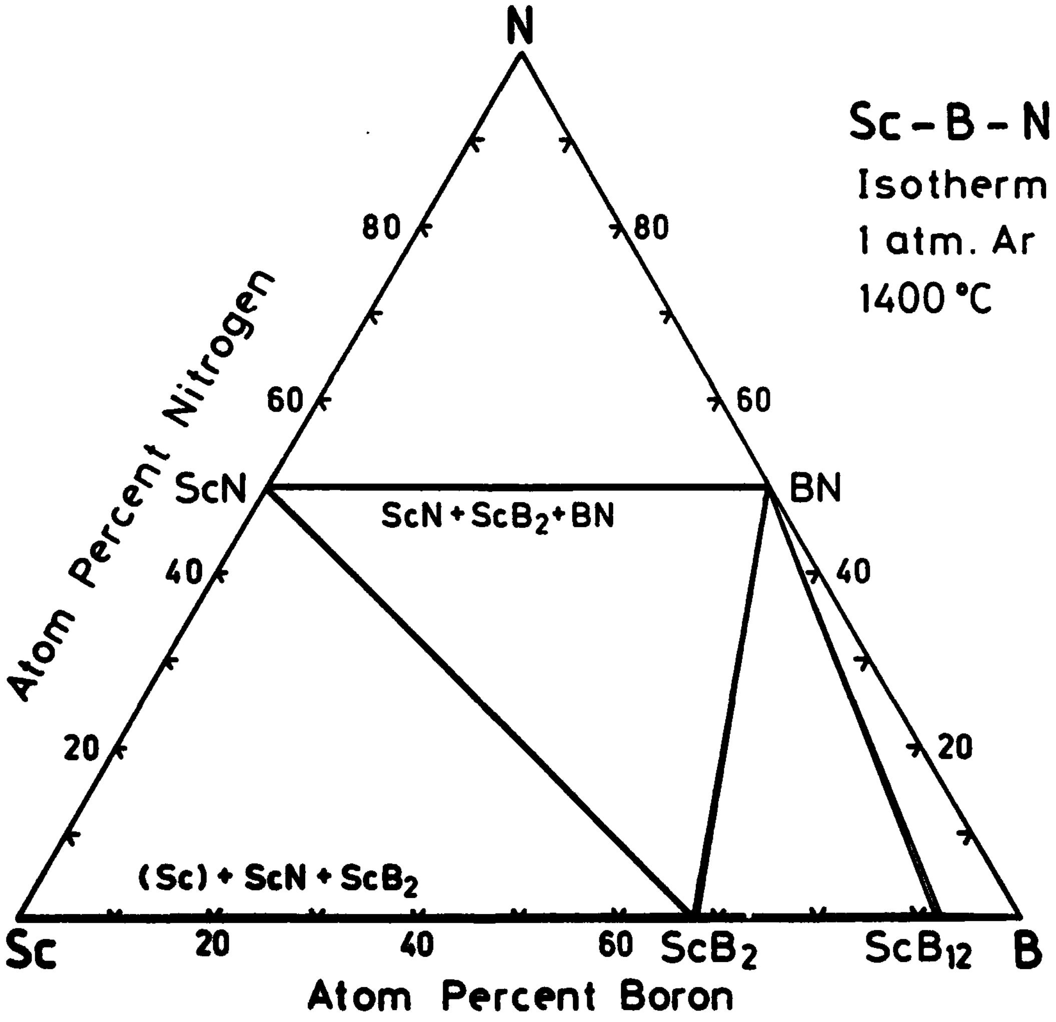
Table 1: Solid phases at 1400°C in the systems B - Sc - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Sc 1541-1337°	cI2 Im$\bar{3}$m W	a= 454.1	[90Mas]
α-Sc <1337°	hP2 P6$_3$/mmc Mg	a= 330.88 c= 526.80	[90Mas]
β-rhB <2092°	hR111 R$\bar{3}$m β-B	a=1092.51 c=2381.43	[78Cal]
		a=1096.58 c=2408.75	[78Cal] for ScB$_{28}$
ScB$_2$ <2250°	hP3 P6/mmm AlB$_2$	a= 314.8 c= 351.6	[85Vil]
ScB$_{12}$ <2040°	tI26 I4/mmm ScB$_{12}$	a= 523.47 c= 735.83	[78Cal]
ScN	cF8 Fm$\bar{3}$m NaCl	a= 450.5	[85Vil]
BN$_{hex}$	hP* P6$_3$/mmc BN$_{hex}$	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Sc-B (after [90Spe])

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 Sc	$\Delta_{fus} G(\mathrm{Sc}) = 18110-10.275\ T$	[90Spe]
1.0000 B	$\Delta_{fus} G(\mathrm{B}) = 50210-21.23\ T$	
1.0000 αSc	$\Delta_f G\ (\alpha\mathrm{Sc}) = 0$	
1.0000 βSc	$\Delta_f G\ (\beta\mathrm{Sc}) = 4010-2.495\ T$	
0.3333 ScB_2	$\Delta_f G(\mathrm{ScB_2}) = -102330+5.0\ T$	
0.0769 ScB_{12}	$\Delta_f G(\mathrm{ScB_{12}}) = -36980+2.0\ T$	
1.0000 βB	$\Delta_f G\ (\beta\mathrm{B}) = 0$	
Liquid	$\Delta\ G^{ex} = x(1-x)\{-177050-34.9\ T + (-3335+68.9\ T)(1-2x)\}$	

Fig.1: Isothermal section of the system B - Sc -N at 1400°C under 1 bar of argon (in the absense of external nitrogen).



SYSTEM BORON - YTTRIUM - NITROGEN (B-Y-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Y-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O_2 and < 4 ppm H_2O. Starting materials were ingots of 3N-Y, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Y system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1.

A tentative equilibrium diagram for the yttrium-rich region of the system N-Y is given by [74Car]; the solid solubility of N in Y was claimed to be 3 at% N at the temperature of the peritectoid formation of α-Y from β-Y + YN (1490°) [74Car]. A comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure YN is the only stable nitride (see Table 1); at higher nitrogen pressure Y_2N_{3-x} with the Mn_2O_3-type (cI80 - Ia$\bar{3}$)has been reported [72Kie].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1400°C under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium YN + YB_4 + BN. Thus there is no compatibility between (Y) and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Y in BN at 1400°C, and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of N_2 at 1400°C (100h) and at 1800°C (20h) respectively :in both cases the limiting tie line reported was YN + BN .

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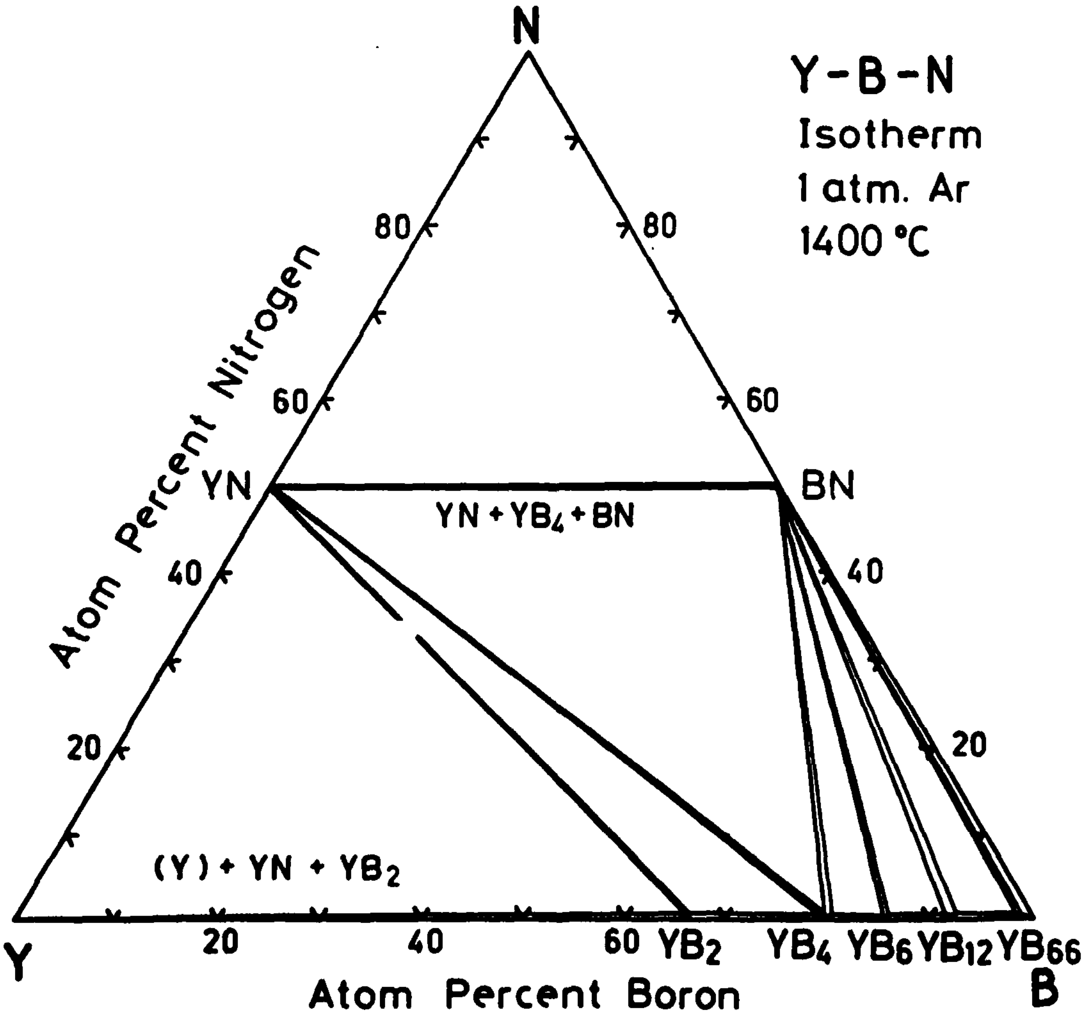
Table 1: Solid phases at 1400°C in the system B-Y-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
α-Y <1478°	hP2 $P6_3/mmc$ Mg	a= 364.82 c= 573.18	[86Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
YB_2 <2100°	hP3 $P6/mmm$ AlB_2	a= 328.9 c= 384.3	[85Vil]
YB_4 <2800°	tP20 $P4/mbm$ ThB_4	a= 711.1 c= 401.7	[85Vil]
YB_6 <2600°	cP7 $Pm\bar{3}m$ CaB_6	a= 412.8	[85Vil]
YB_{12} <2200°	cF52 $Fm\bar{3}m$ UB_{12}	a= 746	[85Vil]
YB_{66} <2100°	cF1608 $Fm\bar{3}c$ YB_{66}	a=2344	[85Vil]
YN	cF8 $Fm\bar{3}m$ NaCl	a= 487.8	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section of the system B – Y –N at 1400°C under 1 bar of argon (in the absense of external nitrogen).



SYSTEM BORON- TERBIUM- NITROGEN (B-Tb-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Tb-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O_2 and $<$ 4 ppm H_2O. Starting materials were ingots of 3N-Tb,crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [90Kle].

BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Tb system revealed consistency with the data available in [76Spe,90Lia] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Tb system and solid solubility of N in Tb is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure TbN is the only stable nitride (see Table 1); at higher nitrogen pressure Tb_2N_{3-x} with the Mn_2O_3-type (cI80 - $Ia\bar{3}$, a=1066 pm) has been reported [72Kie].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1400°C under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium TbN + TbB_4 + BN. Thus there is no compatibility between (Tb) and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Tb in BN at 1400°C, and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of N_2 at 1400°C (100h) and at 1800°C (20h) respectively : in both cases the limiting tie line reported was TbN + BN .

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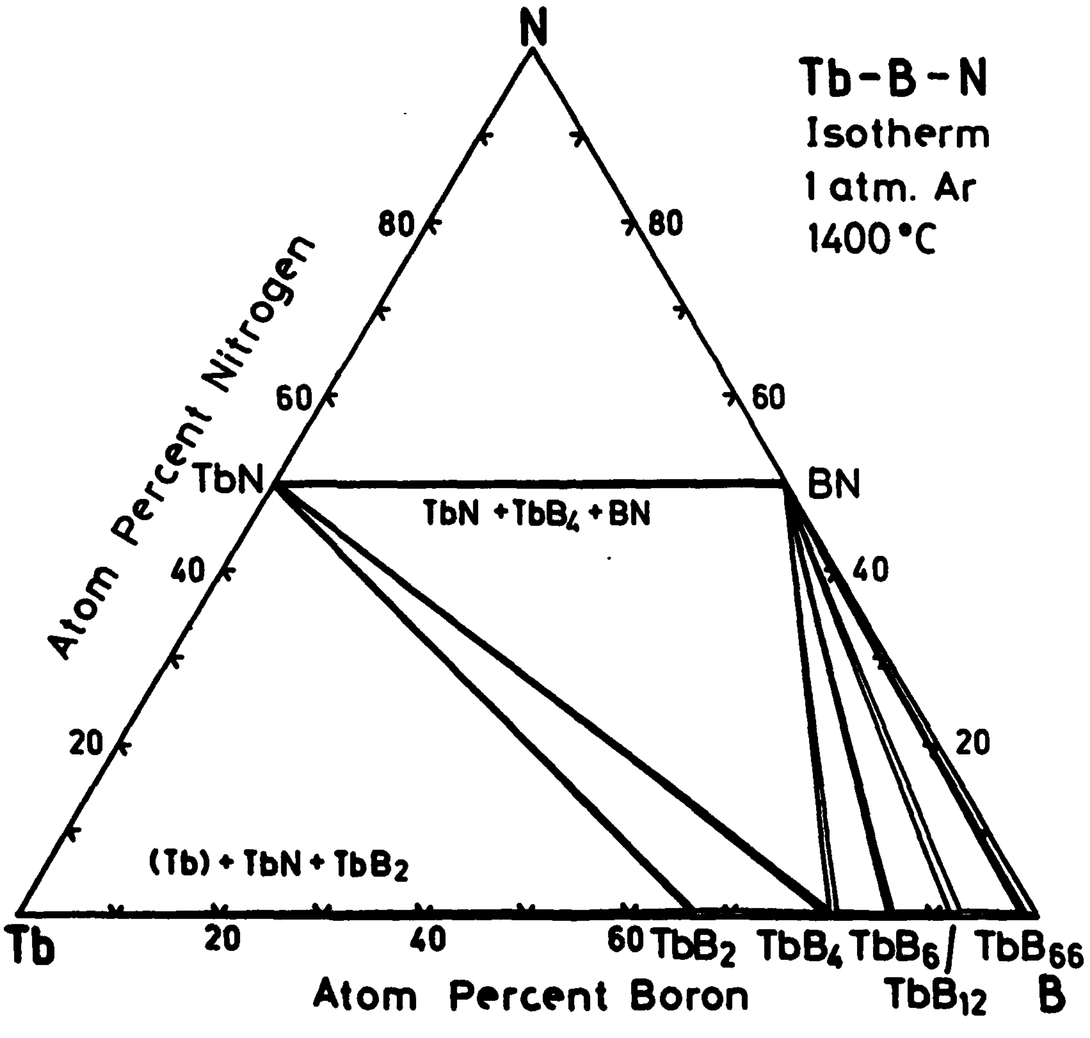
Table 1: Solid phases at 1400°C in the system B-Tb-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Tb 1356-1289°	cI2 $Im\bar{3}m$ W	a= 402	[86Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
TbB_2 <2100°	hP3 P6/mmm AlB_2	a= 329.0 c= 387.8	[85Vil]
TbB_4 <2600°	tP20 P4/mbm ThB_4	a= 712.0 c= 404.2	[85Vil]
TbB_6 <2340°	cP7 $Pm\bar{3}m$ CaB_6	a= 410.0	[85Vil]
TbB_{12} <2200°	cF52 $Fm\bar{3}m$ UB_{12}	a= 750.7	[85Vil]
TbB_{66} <2100°	cF1608 $Fm\bar{3}c$ YB_{66}	a=2345.7	[85Vil]
TbN	cF8 $Fm\bar{3}m$ NaCl	a= 493.6	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section of the system B - Tb -N at 1400°C under 1 bar of argon (in the absence of external nitrogen).



SYSTEM BORON- DYSPROSIUM- NITROGEN (B-Dy-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Dy-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20µm in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O_2 and $<$ 4 ppm H_2O. Starting materials were ingots of 3N-Dy,crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Dy system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Dy system and solid solubility of N in Dy is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure DyN is the only stable nitride (see Table 1); at higher nitrogen pressure Dy_2N_{3-x} with the Mn_2O_3-type (cI80 - $Ia\bar{3}$, a=1058 pm) has been reported [72Kie].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1400°C under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium DyN + DyB_4 + BN. Thus there is no compatibility between (Dy) and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Dy in BN at 1400°C, and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of N_2 at 1400°C (100h) and at 1800°C (20h) respectively : in both cases the limiting tie line reported was DyN + BN .

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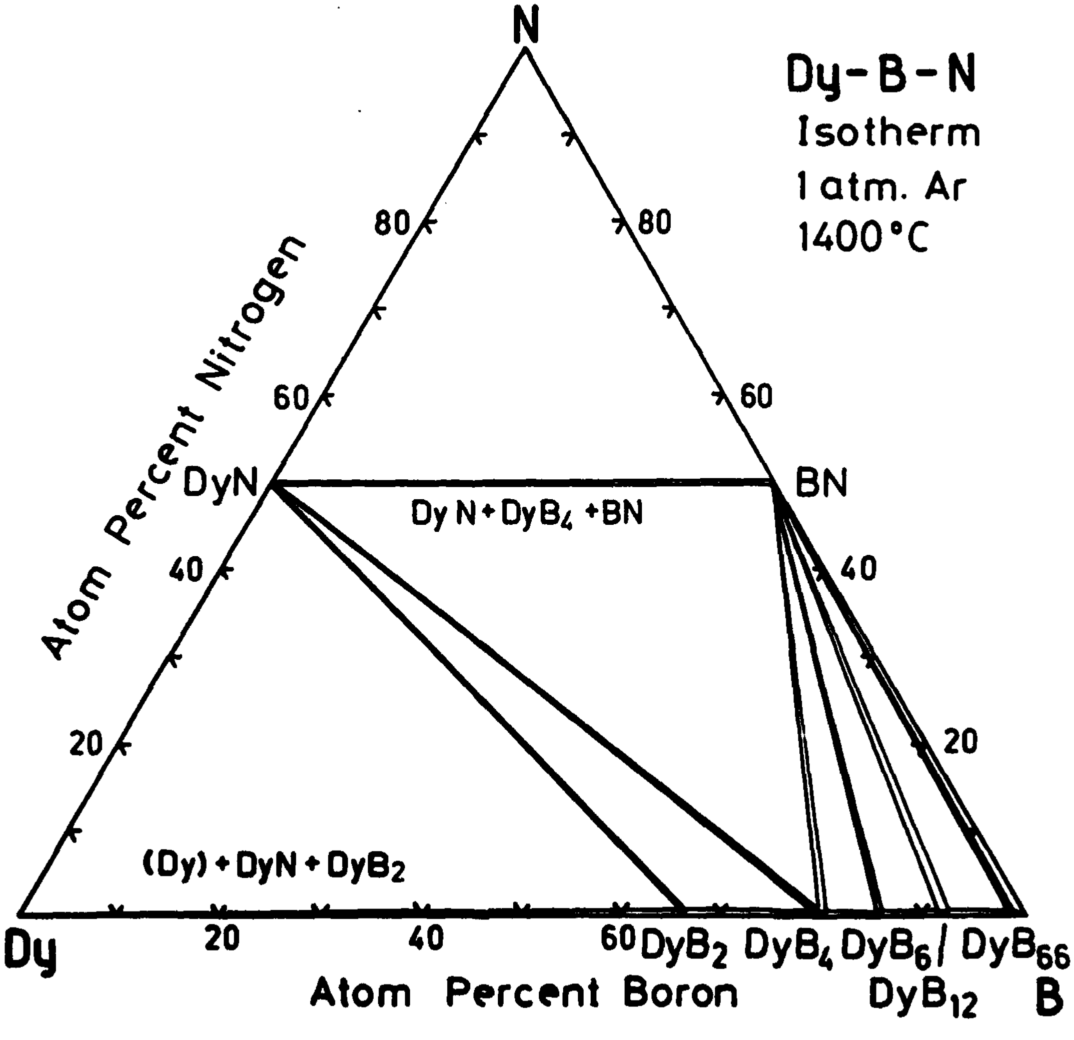
Table 1: Solid phases at 1400°C in the system B-Dy-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Dy 1409-1381°	cI2 Im$\bar{3}$m W	a= 398	[90Mas]
β-rhB <2092°	hR111 R$\bar{3}$m β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
DyB_2 <2100°	hP3 P6/mmm AlB_2	a= 328.7 c= 384.5	[85Vil]
DyB_4 <2500°	tP20 P4/mbm ThB_4	a= 702.1 c= 397.2	[85Vil]
DyB_6 <2200°	cP7 Pm$\bar{3}$m CaB_6	a= 409.8	[85Vil]
DyB_{12} <2100°	cF52 Fm$\bar{3}$m UB_{12}	a= 749.9	[85Vil]
DyB_{66} <2025°	cF1608 Fm$\bar{3}$c YB_{66}	a=2344.1	[85Vil]
DyN	cF8 Fm$\bar{3}$m NaCl	a= 493.6	[85Vil]
BN_{hex}	hP* $P6_3$/mmc BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section of the system B - Dy -N at 1400°C under 1 bar of argon (in the absence of external nitrogen).



SYSTEM BORON- HOLMIUM- NITROGEN (B-Ho-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Ho-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. ue to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O_2 and < 4 ppm H_2O. Starting materials were ingots of 3N-Y, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Ho system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible. HoB_6 has been found to be unstable below 1450°C [89Rem].

No equilibrium diagram exists for the N-Ho system and solid solubility of N in Ho is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure HoN is the only stable nitride (see Table 1), at higher nitrogen pressure Ho_2N_{3-x} with the Mn_2O_3-type (cI80 - Ia$\bar{3}$, a=1056 pm) has been reported [72Kie].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1400°C under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium HoN + HoB_4 + BN. Thus there is no compatibility between (Ho) and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Ho in BN at 1400°C, and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of N_2 at 1400°C (100h) and at 1800°C (20h) respectively : in both cases the limiting tie line reported was HoN + BN .

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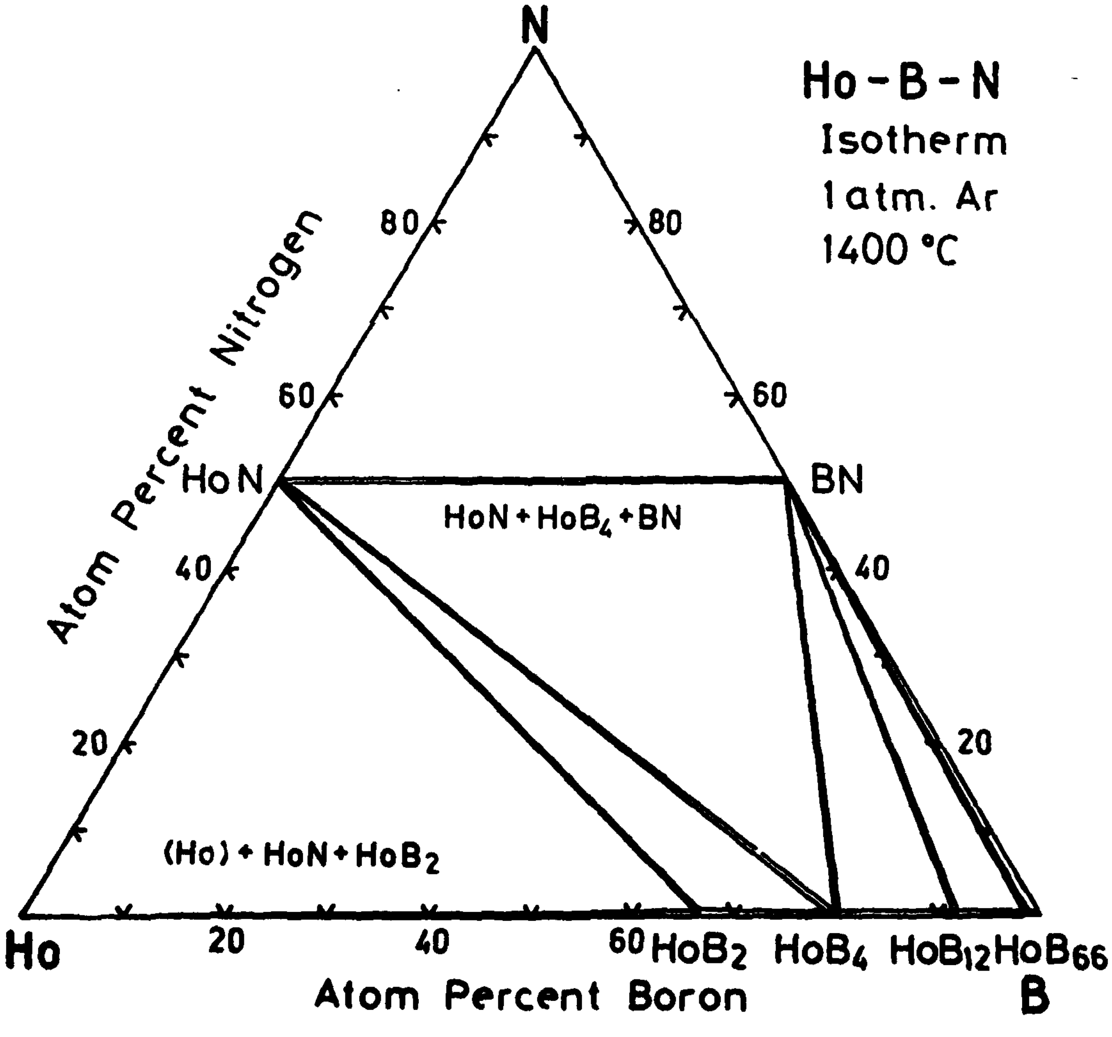
Table 1: Solid phases at 1400°C in the system B-Ho-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Ho <1470°	hP2 $P6_3/mmc$ Mg	a= 357.78 c= 561.78	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
HoB_2 <2200°	hP3 P6/mmm AlB_2	a= 327.3 c= 381.4	[85Vil]
HoB_4 <2500°	tP20 P4/mbm ThB_4	a= 708.7 c= 400.8	[85Vil]
HoB_{12} 2100°	cF52 $Fm\bar{3}m$ UB_{12}	a= 749.1	[85Vil]
HoB_{66} <2025°	cF1608 $Fm\bar{3}c$ YB_{66}	a=2344.1	[85Vil]
HoN	cF8 $Fm\bar{3}m$ NaCl	a= 487.7	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section of the system B - Ho -N at 1400°C under 1 bar of argon (in the absense of external nitrogen).



SYSTEM BORON- ERBIUM- NITROGEN (B-Er-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Er-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O_2 and $<$ 4 ppm H_2O. Starting materials were ingots of 3N-Er, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Er system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Er system and solid solubility of N in Er is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure ErN is the only stable nitride (see Table 1), at higher nitrogen pressure Er_2N_{3-x} with the Mn_2O_3-type (cI80 - Ia$\bar{3}$) has been reported [72Kie].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1400°C under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium ErN + ErB_4 + BN. Thus there is no compatibility between (Er) and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Er in BN at 1400°C, and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of N_2 at 1400°C (100h) and at 1800°C (20h) respectively :in both cases the limiting tie line reported was ErN + BN .

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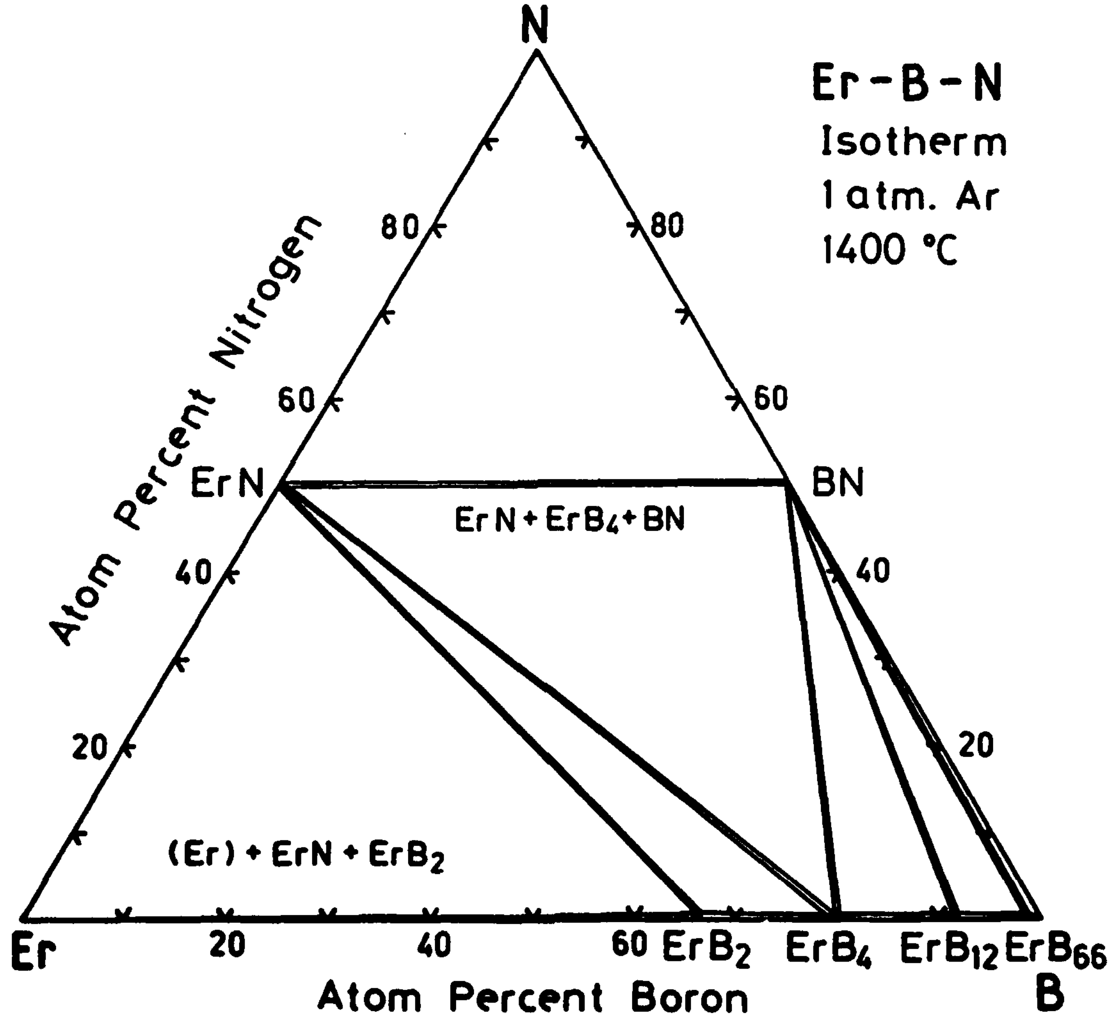
[91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE)-Boron-Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) in press

Table 1: Solid phases at 1400°C in the system B-Er-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Er <1522°	hP2 $P6_3/mmc$ Mg	a= 355.92 c= 558.50	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
ErB_2 <2185°	hP3 P6/mmm AlB_2	a= 326.5 c= 376.8	[85Vil]
ErB_4 <2500°	tP20 P4/mbm ThB_4	a= 707.05 c= 400.00	[85Vil]
ErB_{12} <2080°	cF52 $Fm\bar{3}m$ UB_{12}	a= 748.2	[85Vil]
ErB_{66} <2070°	cF1608 $Fm\bar{3}c$ YB_{66}	a=2344.0	[85Vil]
ErN	cF8 $Fm\bar{3}m$ NaCl	a= 483.6	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section of the system B - Er -N at 1400°C under 1 bar of argon (in the absence of external nitrogen).



SYSTEM BORON THULIUM – NITROGEN (B-Tm-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Tm-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O_2 and $<$ 4 ppm H_2O. Starting materials were ingots of 3N-Tm, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Tm system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Tm system and solid solubility of N in Tm is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure TmN is the only stable nitride (see Table 1); at higher nitrogen pressure Tm_2N_{3-x} with the Mn_2O_3-type (cI80 – Ia$\bar{3}$, a=1045 pm) has been reported [72Kie].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1400°C under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium TmN + TmB_4 + BN. Thus there is no compatibility between (Tm) and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Tm in BN at 1400°C, and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of N_2 at 1400°C (100h) and at 1800°C (20h) respectively :in both cases the limiting tie line reported was TmN + BN .

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[72Kie] R.Kieffer, P. Ettmayer and S. Pajakoff, "On The Mononitrides and on Nitrogen-rich Nitrides of the Rare Earths, 1st Commun.", (in German), Monatsh. Chemie 103 (1972) 1285-1298

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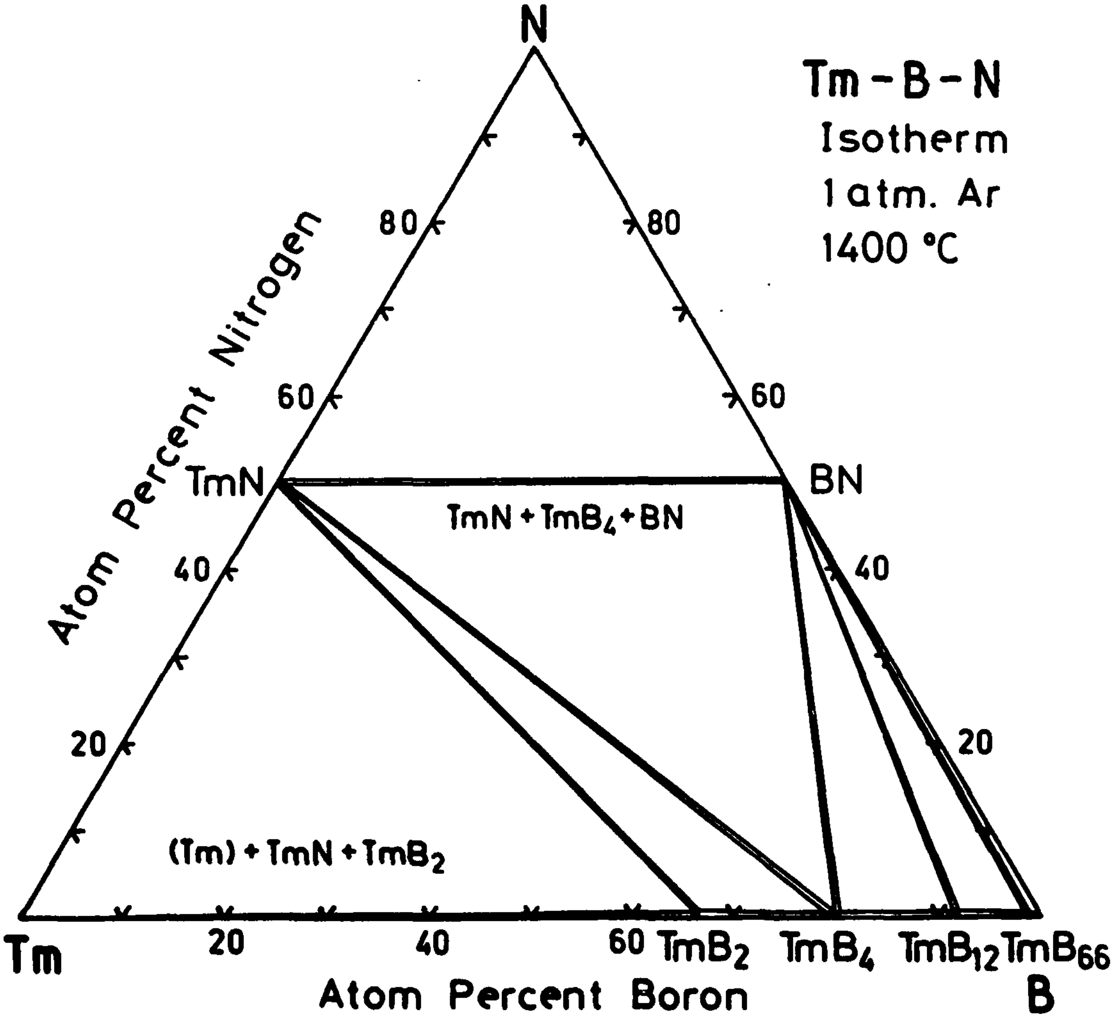
Table 1: Solid phases at 1400°C in the system B-Tm-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Tm <1545°	hP2 $P6_3/mmc$ Mg	a= 353.75 c= 555.40	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
TmB_2 2250°	hP3 $P6/mmm$ AlB_2	a= 326.1 c= 375.5	[85Vil]
TmB_4 <2550°	tP20 $P4/mbm$ ThB_4	a= 705.7 c= 398.7	[85Vil]
TmB_{12} <2180°	cF52 $Fm\bar{3}m$ UB_{12}	a= 747.4	[85Vil]
TmB_{66} <2100°	cF1608 $Fm\bar{3}c$ YB_{66}	a=2343.3	[85Vil]
TmN	cF8 $Fm\bar{3}m$ NaCl	a= 481	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section of the system B - Tm -N at 1400°C under 1 bar of argon (in the absence of external nitrogen).



SYSTEM BORON - LUTETIUM - NITROGEN (B - Lu -N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Lu-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O_2 and $<$ 4 ppm H_2O. Starting materials were ingots of 3N-Lu, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Lu system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Lu system and solid solubility of N in Lu is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure LuN is the only stable nitride (see Table 1), at higher nitrogen pressure Lu_2N_{3-x} with the Mn_2O_3-type (cI80 - $Ia\bar{3}$, a=1032 pm) has been reported [72Kie].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1400°C under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium LuN + LuB_4 + BN. Thus there is no compatibility between (Lu) and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Lu in BN at 1400°C, and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of N_2 at 1400°C (100h) and at 1800°C (20h) respectively :in both cases the limiting tie line reported was LuN + BN .

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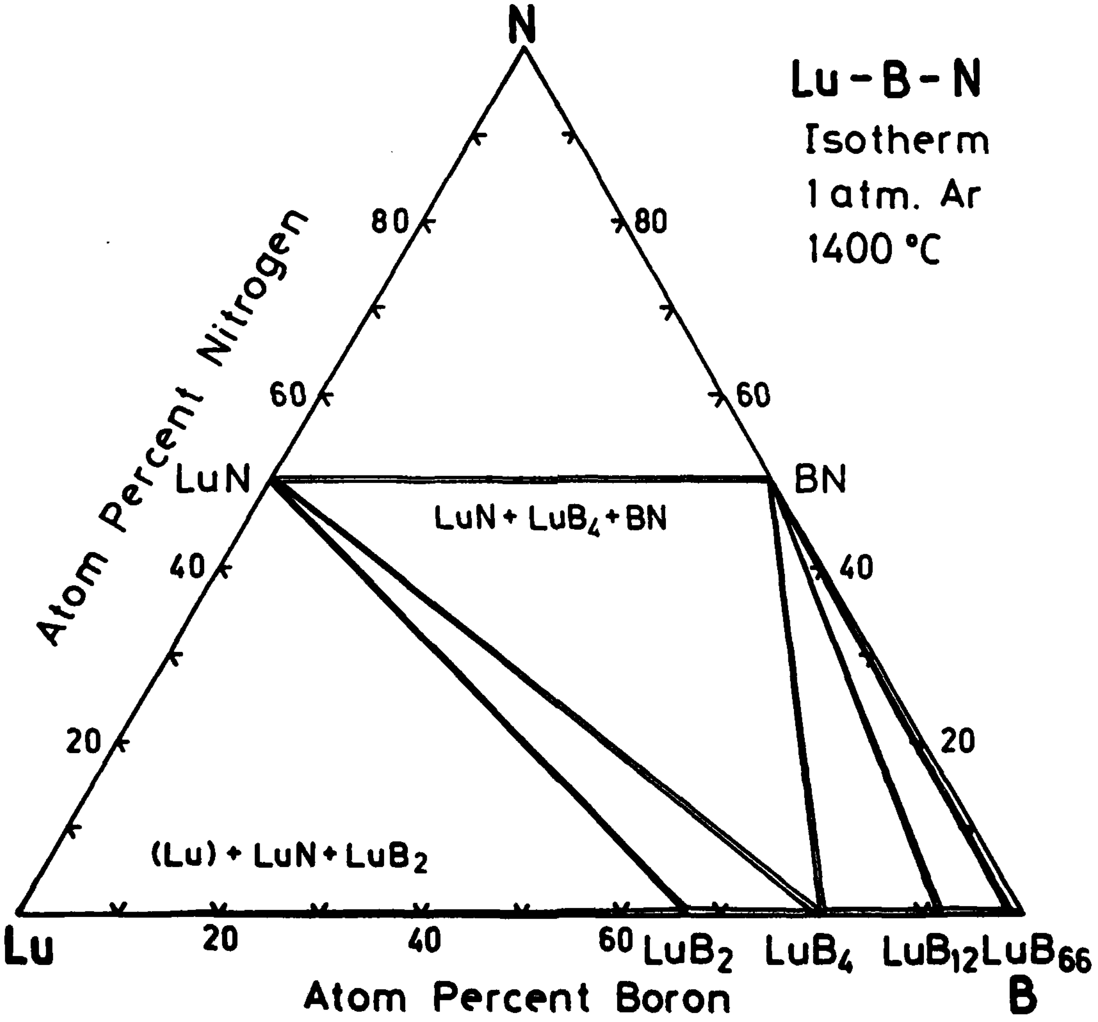
[91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE) - Boron - Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) in press

Table 1: Solid phases at 1400°C in the systems B – Lu – N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Lu	hP2	a= 350.52	[90Mas]
<1663°	$P6_3/mmc$	c= 554.94	
	Mg		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
LuB_2	hP3	a= 324.6	[85Vil]
<2250°	$P6/mmm$	c= 370.4	
	AlB_2		
LuB_4	tP20	a= 703.6	[85Vil]
<2550°	$P4/mbm$	c= 397.4	
	ThB_4		
LuB_{12}	cF52	a= 746.4	[85Vil]
<2170°	$Fm\bar{3}m$		
	UB_{12}		
LuB_{66}	cF1608	a=2341.2	[85Vil]
<2100°	$Fm\bar{3}c$		
	YB_{66}		
LuN	cF8	a= 476.6	[85Vil]
	$Fm\bar{3}m$		
	NaCl		
BN_{hex}	hP4	a= 250.4	[85Vil]
	$P6_3/mmc$	c= 666.1	
	BN_{hex}		

Fig.1: Isothermal section of the system B - Lu -N at 1400°C under 1 bar of argon (in the absence of external nitrogen).



SYSTEM BORON - URANIUM - NITROGEN (B-U-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-U-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [90Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O_2 and < 4 ppm H_2O. Starting materials were platelets of depleted uranium (E.Merck, FRG) which prior to use were surface cleaned in dilute HNO_3 , crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [90Kle].

BINARY SYSTEMS

A reinvestigation of the binary systems revealed consistency with the data available in [85Vil],and [90Mas] (see Table 1); for a recent critical assessment of the U - B binary see [91Pot].

The phase diagram N-U is given by [90Mas], see also Table 1; the maximal solid solubility of N in α,β- or γ-U was claimed to be less than 0.017at% N [78Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1400°C under 1 bar of argon (in the absence of external nitrogen pressure) [90Kle]. Phase equilibria are characterized by the existence of one of ternary compound UBN (isotypic with the structure type of UBC). Due to the formation of the stable three-phase equilibria: UB_2 + UBN + UN and UB_4 + UBN + BN , no compatibility was observed between (U) and BN nor between the uranium nitrides and boron. . From the close correspondance of the unit cell dimensions of the boundary phases in multiphase samples with the data for the binary compounds no significant solid solubility of N ($<$ 0.5at% N) in the uranium borides was concluded. Similarly solid solubility of U in BN at 1400°C was considered to be rather limited. No significant trends have been observed for the variation of the unit cell dimensions of the binary uranium nitrides as a function of the boron content [90Kle], thus the solid solubility of B is certainly smaller than originally suggested by [76Imo].

From heat treatments under 1 bar of N_2 at 1400°C (90h) the limiting tie line reported was between uranium nitride and boronnitride. Mutual solid solubilities remained restricted. Additional heat treatment for 60h at 1400°C in a high vacuum of 10^{-4}Pa was sufficient to entirely decompose the ternary compound UBN, and all nitrogen-rich samples were transferred to the tie lines UN + UB_2 and UB_4 + BN. X-ray Guinier photographs of UBN were completely indexed on the basis of an orthorhombic unit cell in close correcpondance with the UBC-type. Using the atom parameters derived from a single crystal study of stoichiometric UBC [91Rog], calculated and observed intensity data were said to be in excellent agreement for UBN [90Kle]. The variation of the unit cell dimensions of UBN, as observed from multiphase samples at 1400°C as well as under various N_2 partial pressures is rather small indicating only a small degree of boron/nitrogen substitution [90Kle].

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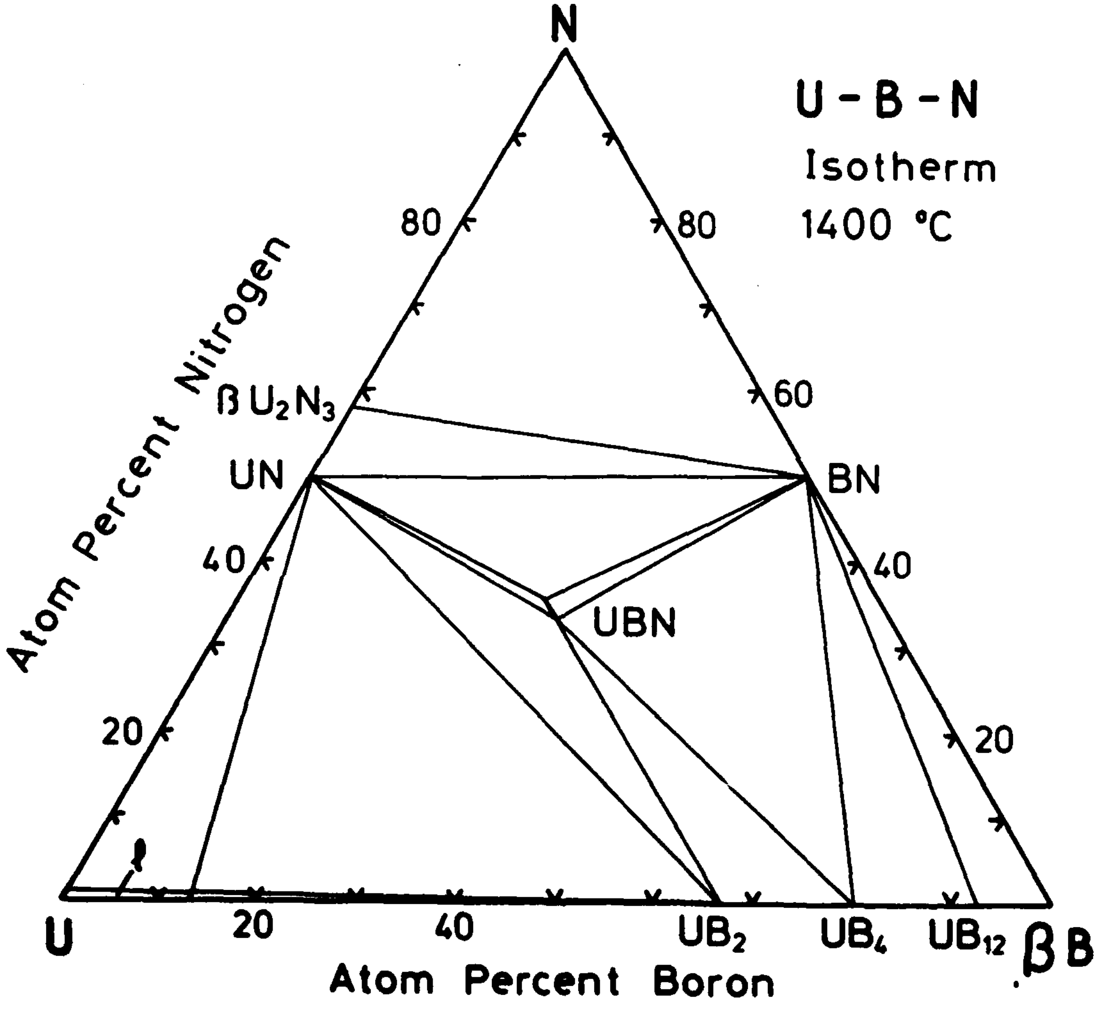
Table 1: Solid phases at 1400°C in the system B-U-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
γ-U	cI2	a= 352.4	[90Mas]
1135-776°	Im$\bar{3}$m		
	W		
β-U	tP30	a=1075.9	[90Mas]
776-668°	$P4_2/mnm$	c= 565.6	
	β-U		
α-U	oC4	a= 285.37	[90Mas]
<668°	Cmcm	b= 586.95	
	α-U	c= 495.48	
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	R$\bar{3}$m	c=2381.43	[85Vil]
	β-B		
UB_2	hP3	a= 312.93	[91Pot],U-rich
<2385°	P6/mmm	c= 398.53	
	AlB_2		
		a= 313.14	[91Pot],U-poor
		c= 398.57	
UB_4	tP20	a= 707.7	[91Pot]
<2495°	P4/mbm	c= 397.9	
	ThB_4		
UB_{12}	cF52	a= 747.0	[91Pot],U-rich
<2235°	Fm$\bar{3}$m		
	UB_{12}	a= 747.4	[91Pot],U-poor
UN	cF8	a= 488.94	[91Pot]
<2805°	Fm$\bar{3}$m		
	NaCl		
β-U_2N_3	cI80	a=1068	[85Vil]
1352-1000°	Ia$\bar{3}$		
	Mn_2O_3		

α-U_2N_3 <1132°	hP5 $P\bar{3}m1$ La_2O_3	a= 370 c= 582.5	[85Vil]
BN_{hex}	– BN	a=250.4 c=666.1	[85Vil]
* UBN	oC12 Cmcm UBC	a=358.51 b=1182.73 c=332.54	[90Kle]

Fig.1: Isothermal section of the system B – U – N at 1400°C under 1 bar of argon (in the absense of external nitrogen).



SYSTEM BORON - TITANIUM - NITROGEN (B-Ti-N)

INTRODUCTION / EXPERIMENTAL

Informations on the Ti-B-N ternary are due to [55Bre,61Now], [73Sam,80Yur,81Chu,83Tka,84Bor] and [87Šmi] with an early review by [72Med].

Based on an early thermodynamic estimation of the reaction TiN + 2 BN == $TiB_2 + \frac{3}{2} N_2$ under 0.5 10^5Pa of nitrogen, [55Bre] proposed stability of the mixture TiN + BN up to ca 1600°C. Accordingly phase equilibria at 1500°C under argon of 0.1% N_2 as derived by [61Now] are characterized by the absence of ternary boronnitride compounds and by a dominating three phase field TiB_2 + TiN_{1-x} + BN. Based on these data [80Yur] determined the heat of formation of TiB_2 via the experimentally monitored decomposition reaction of powder compacts TiN + 2 BN in the temperature range 1575 to 1850°C as a function of temperature. For equilibrium pressures of 100 Pa N_2 the decomposition was found to commence at ca 1350°C [80Yur]. These data are in essential agreement with a DTA study revealing the onset of decomposition at ca 1375 to 1440°C [84Bor].

[81Chu] claimed the existence of a quasibinary section of the eutectic type TiB_2+TiN revealing small mutual solid solubilities at the nitrogen-rich phase boundary $TiN_{0.96}$, whereas solubility of TiB_2 in $TiN_{0.58}$ was said to increase up to ca 12 mol% at 2300°C.

Phase equilibria in the B-Ti-N system have been furthermore investigated [87Šmi] at 1500° under high vacuum or 1 bar Ar or under 1 bar N_2 respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 10 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Ti, TiN ,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [87Šmi]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1500°C for 72h followed by a final reaction at 1500°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Ti, crystallized boron (99.8 % B), TiN_{1-x} (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [87Šmi].

BINARY SYSTEMS

The reinvestigation [87Šmi] of the B-Ti system in the range from 900 to 2400°C revealed consistency with the data available in [84Vil], and [90Mas]; a critical assessment is due to [86Mur]. The existence of Ti_3B_4 has been confirmed [87Šmi] The maximal solid solubility of boron in titanium was claimed to be less than 1 at%B at 1540°C [66Rud] and an interstitial type of B-solubility was suggested . The maximum solid solubility of Ti in β-B was reported to be less than 0.5 at% Ti at ~1800°C from X-ray powder data [70Car] (see Table 1).

The phase diagram for the system Ti-N as given in [90Mas] has to be modified according to [90Len] regarding the newly discovered phases Ti_3N_{2-x} and Ti_4N_{3-x} [86Len1,2].

Crystallographic information on the binary titanium compounds is found in Table 1.

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 summarizes the results on the phase relations Ti-B-N at 1500°C under 1 bar Ar as observed by [61Now] and confirmed by [87Šmi]. Phase equilibria are characterized by the absence of ternary compounds and by incompatibility of titanium metal and BN_{hex} due to the formation of a stable tie line TiB - TiN_{1-x} at temperatures below 1500°C. Heating binary as well as ternary alloys at 1500°C under 1 bar N_2 transfers all samples to the limiting tie line at the nitrogen rich boundary TiN + BN, equilibrium being reached after 75h of nitrogen exposure [87Šmi].

As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Ti in BN up to 1500°C, and mutual solubilities of the titanium borides, the titanium nitrides and BN up to 1500°C are rather restricted [87Šmi].

THERMODYNAMICS

A thermodynamic modelling of the binary system Ti-B is due to [86Mur]; see Table 2. The enthalpy of formation of TiB_2 as derived by [80Yur] from the decomposition reaction $TiN_{1-x} + 2BN = TiB_2 + \frac{3}{2} N_2$ was given as $\Delta_f H(298) = -104667$ kJ/gratom and is slightly lower than the optimized value obtained from the modelling of the Ti-B binary (Table 2).

MISCELLANEOUS

Fig.2 presents three isopleths TiB_2-TiN_{1-x} for x=0.04, 0.27 and 0.42 after [81Chu] revealing the eutectic nature of the quasibinary section TiB_2-TiN and the increasing solubility of TiB_2 in TiN_{1-x} with increasing x and temperature.

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Table 1: Solid phases in the system B-Ti-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Ti 1663-882°	cI2 $Im\bar{3}m$ W	a= 330.65	[80Mas]
α-Ti <882 °	hP2 $P6_3/mmc$ Mg	a= 295.06 c= 468.35	[80Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.53 c=2381.03	[70Car]
		a=1092.70 c=2388.65	[70Car] at TiB_x
TiB <2190°	oP8 Pbnm FeB	a= 456.01 b= 611.6 c= 305.65	[87Šmi]
Ti_3B_4 <2200°	oI14 Immm Ta_3B_4	a= 326.28 b=1373.5 c= 303.86	[87Šmi]
TiB_2 <3225°	hP3 P6/mmm AlB_2	a= 303.56 c= 322.78	[87Šmi]
ε-Ti_2N <1080°	tP6 $P4_2/mnm$ TiO_2	a= 494.28 c= 303.57	[85Vil] at 31 to 33 at% N [87Len]
η-Ti_3N_{2-x} 1103-1066°	hR6 $R\bar{3}m$ VTa_2C_2	a= 297.95 c=2896.5	[86Len1] at 29 at% N
ζ-Ti_4N_{3-x} 1291-1078°	hR8 $R\bar{3}m$ V_4C_3	a= 298.09 c=2166.42	[86Len2] at 31.5 at% N

δ'-TiN_{1-x} <800°	tI16 $I4_1/amd$ $ThSi_2$?	a= 414.0 c= 880.5	[87Len] metastable at 38 at% N
TiN_{1-x}	cF8 $Fm\bar{3}m$ NaCl	a= 423.9	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Ti-B-N

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 Ti	$\Delta_{fus}G(Ti) = 16234-8.368\ T$	[86Mur]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 αTi	$\Delta_f G\ (\alpha Ti) = 0$	
1.0000 βTi	$\Delta_f G\ (\beta Ti) = 4351-3.766\ T$	
0.5000 TiB	$\Delta_f G\ (TiB) = -109721+13.23\ T$	
0.1429 Ti_3B_4	$\Delta_f G(Ti_3B_4) = -114028+12.12\ T$	
0.3333 TiB_2	$\Delta_f G\ (TiB_2) = -108753+5.49\ T$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
Liquid	$\Delta G^{ex} = x(1-x)\{-272514-19.183\ T + (-67899)(1-2x)+$ $+(-68144)(1-2x)^2+(-38210)(1-2x)^3\}$	
0.5000 TiN	$\Delta_f G\ (TiN) = -167883+46.4424\ T\ (25° < T < 882°C)$ $-169138.2+47.4884\ T\ (882° < T < 1200°C)$	[76Fro]

Fig.1: Isothermal section at 1500°C in the system Ti - B - N under 1 bar Ar (in the absence of external nitrogen) [87Šmi].

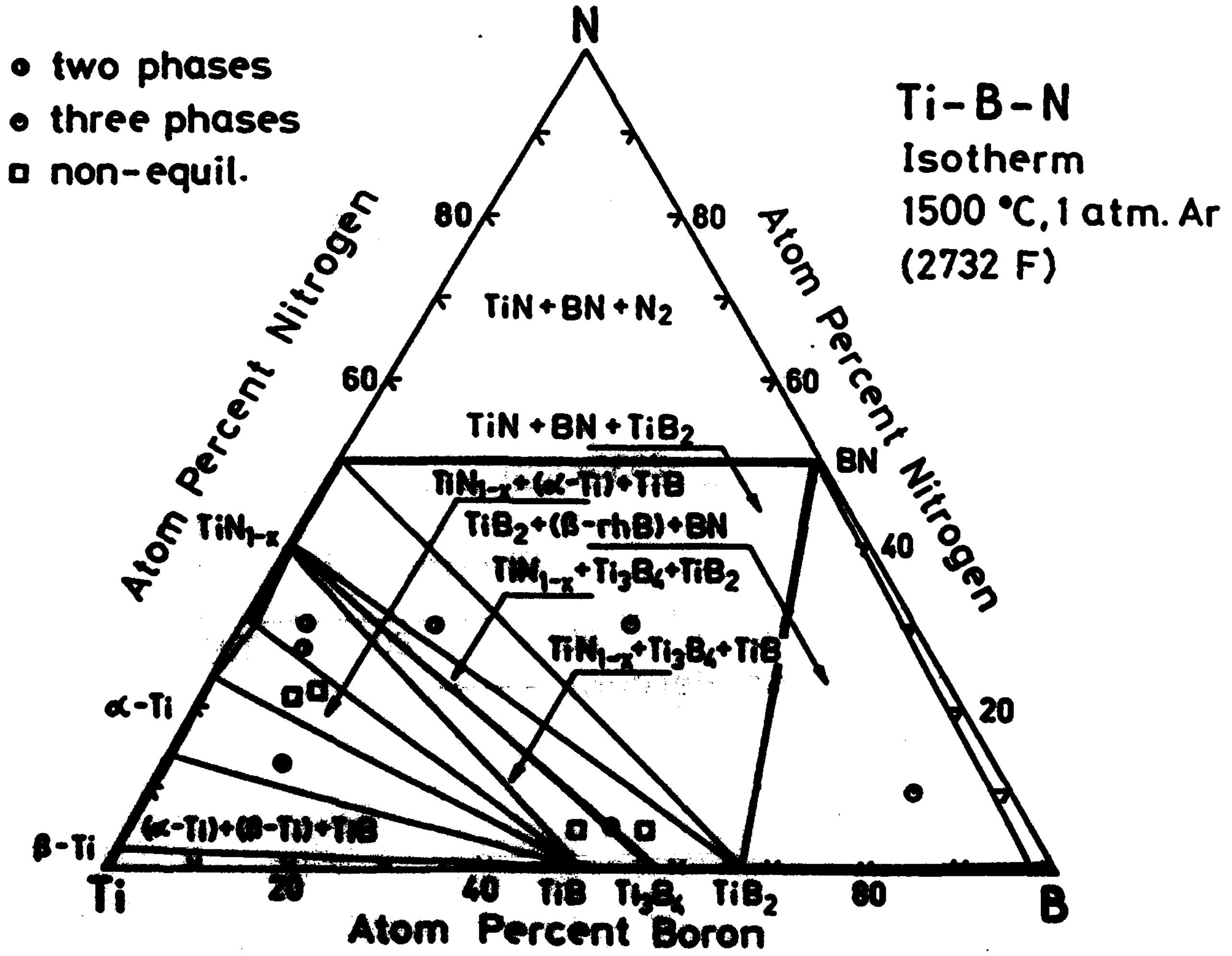
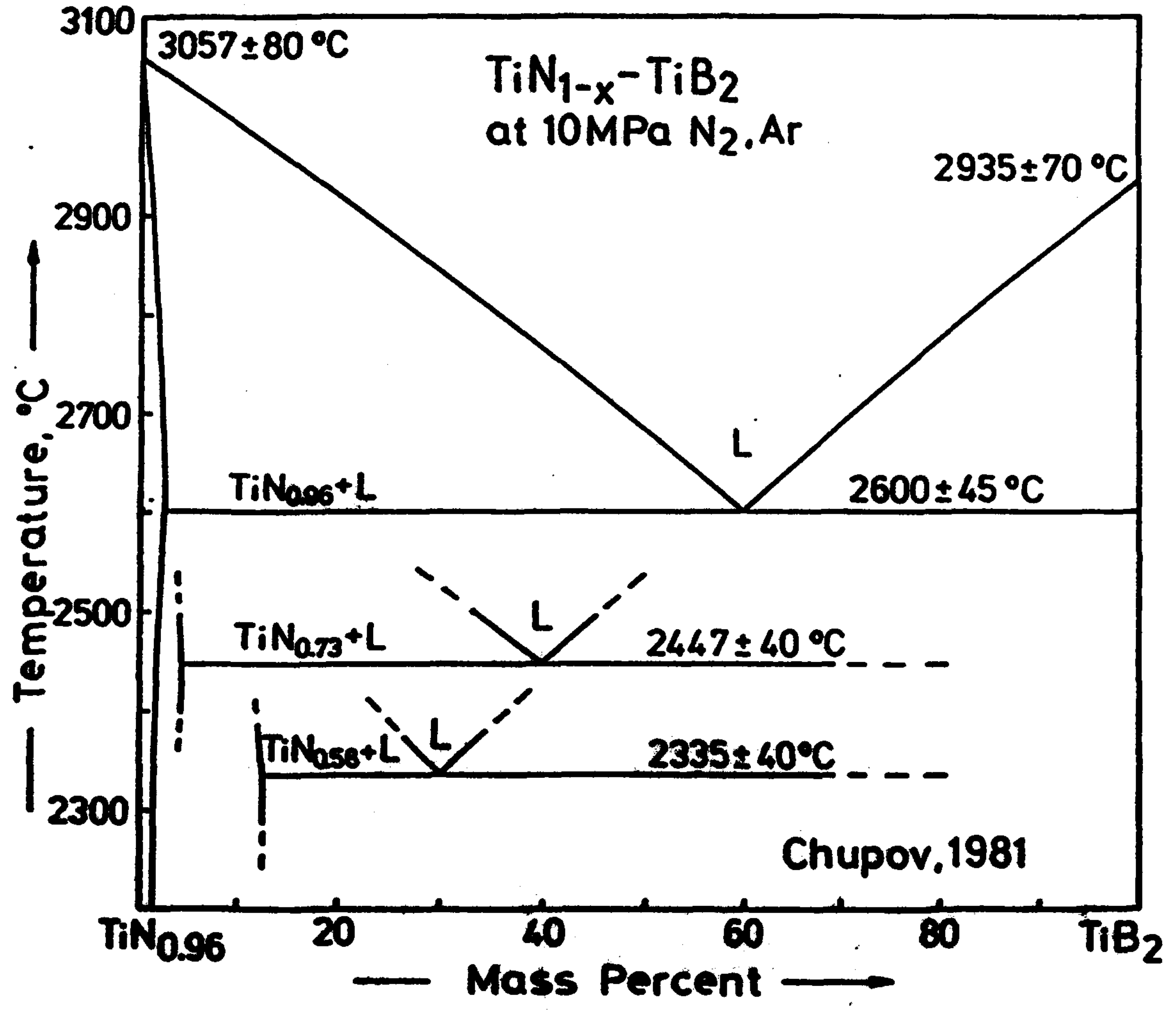


Fig.2: Comparision of the concentration sections TiB_2-TiN_{1-x} at $x = 0.04$, 0.27 and 0.42 (based on [81Chu]).



SYSTEM BORON - ZIRCONIUM - NITROGEN (B-Zr-N)

INTRODUCTION / EXPERIMENTAL

Informations on the Zr-B-N ternary are due to [55Bre, 61Rud, 73Sam, 74Spiv, 84Ord] and [87Šmi] with an early review by [72Med].

Based on an early thermodynamic estimation of the reaction ZrN + 2 BN == $ZrB_2 + \frac{3}{2} N_2$ under 0.5 10^5Pa of nitrogen, [55Bre] proposed stability of the mixture ZrN + BN up to ca 1550°C. Accordingly phase equilibria at 1500°C under argon of 0.1% N_2 as derived by [61Rud] are characterized by the absence of ternary boronnitride compounds and by a dominating three phase field $ZrB_2 + ZrN_{1-x} + BN$.

[84Ord] claimed the existence of a quasibinary section of the eutectic type ZrB_2+ ZrN revealing small mutual solid solubilities at the nitrogen-rich phase boundary $ZrN_{0.96}$ (~2 mol% ZrB_2 in $ZrN_{0.96}$).

Phase equilibria in the B-Zr-N system have been corroborated by [87Šmi] at 1500° under high vacuum or 1 bar Ar or under 1 bar N_2 respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 10 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Zr, ZrN ,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20µm in a steel mortar and/or a WC-Co mortar respectively [87Šmi]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1500°C for 72h followed by a final reaction at 1500°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Zr, crystallized boron (99.8 % B), ZrN_{1-x} (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [87Šmi].

BINARY SYSTEMS

The reinvestigation [87Šmi] of the B-Zr system in the range from 800 to 2400°C revealed consistency with the data available in [84Vil], and [90Mas]; a critical assessment is due to [88Rog]. The maximal solid solubility of boron in zirconium was claimed to be less than 1 at%B at 1660°C [66Rud] and an interstitial type of B-solubility was suggested . The maximum solid solubility of Zr in β-B was reported to be less than 0.5 at% Zr at ~1800°C from X-ray powder data [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Zr-B.

The phase diagram for the system Zr-N is in accordance with [90Mas]

Crystallographic information on the binary zirconium compounds is found in Table 1.

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 summarizes the results on the phase relations at 1500°C under 1 bar Ar as observed by [61Rud] and confirmed by [87Šmi]. Phase equilibria are characterized by the absence of ternary compounds and by incompatibility of zirconium metal and BN_{hex} due to the formation of a stable tie line ZrB - ZrN_{1-x} at temperatures below 1500°C. Heating binary as well as ternary alloys at 1500°C under 1 bar N_2 transfers all samples to the limiting tie line at the nitrogen rich boundary ZrN + BN, equilibrium being reached after 75h of nitrogen exposure.

As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Zr in BN up to 1500°C. There is furthermore no solubility of N in ZrB_2 whereas the solubility of zirconium boride in the zirconium nitride at 1500°C was observed to be rather extended [61Rud,87Šmi],see also Fig.2.

THERMODYNAMICS

A thermodynamic modelling of the binary system Zr-B is due to [88Rog]; see Table 2. For the calculation of the Zr-B-N phase equilibria see [55Bre].

MISCELLANEOUS

Fig.3 presents the isopleth ZrB_2-ZrN_{1-x} for $x=0.04$ after [84Ord] revealing the eutectic nature of the quasibinary. Microhardness and creep rate of ZrB_2-ZrN composits have been studied by [74Spi].

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Table 1: Solid phases in the system B-Zr-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Zr 1855-863°	cI2 $Im\bar{3}m$ W	a= 360.90	[90Mas]
α-Zr <863 °	hP2 $P6_3/mmc$ Mg	a= 323.16 c= 514.75	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.76 c=2381.41	[81Cre]
		a=1095.64 c=24.0201	[78Car] at ZrB_{51}
ZrB_2 <3245°	hP3 P6/mmm AlB_2	a= 316.94 c= 353.03	[62Lei] Zr-rich
		a= 316.92 c= 353.09	[62Lei] B- rich
ZrB_{12} 2250-1710°	cF52 $Fm\bar{3}m$ UB_{12}	a= 740.8	[85Vil]
ZrN_{1-x}	cF8 $Fm\bar{3}m$ NaCl	a= 458.5	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Zr-B-N

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 Zr	$\Delta_{fus}G(Zr) = 21000-9.868\ T$	[88Rog]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 αZr	$\Delta_f G\ (\alpha Zr) = 0$	
1.0000 βZr	$\Delta_f G\ (\beta Zr) = 4103.3-3.601\ T$	
0.3333 ZrB_2	$\Delta_f G\ (ZrB_2) = -108600+4.98\ T$	
0.0769 ZrB_{12}	$\Delta_f G(ZrB_{12}) = -20200-1.93\ T$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
Liquid(Zr,B)	$\Delta G^{ex} = x(1-x)\{-165408-16.03\ T + (66465)(1-2x) + (13412)(1-2x)^2\}$	
0.5000 ZrN	$\Delta_f G\ (ZrN) = -183230+48.325\ T$	[76Fro]

Fig.1: The binary system Zr - B; based on [90Mas] and [87Šmi].

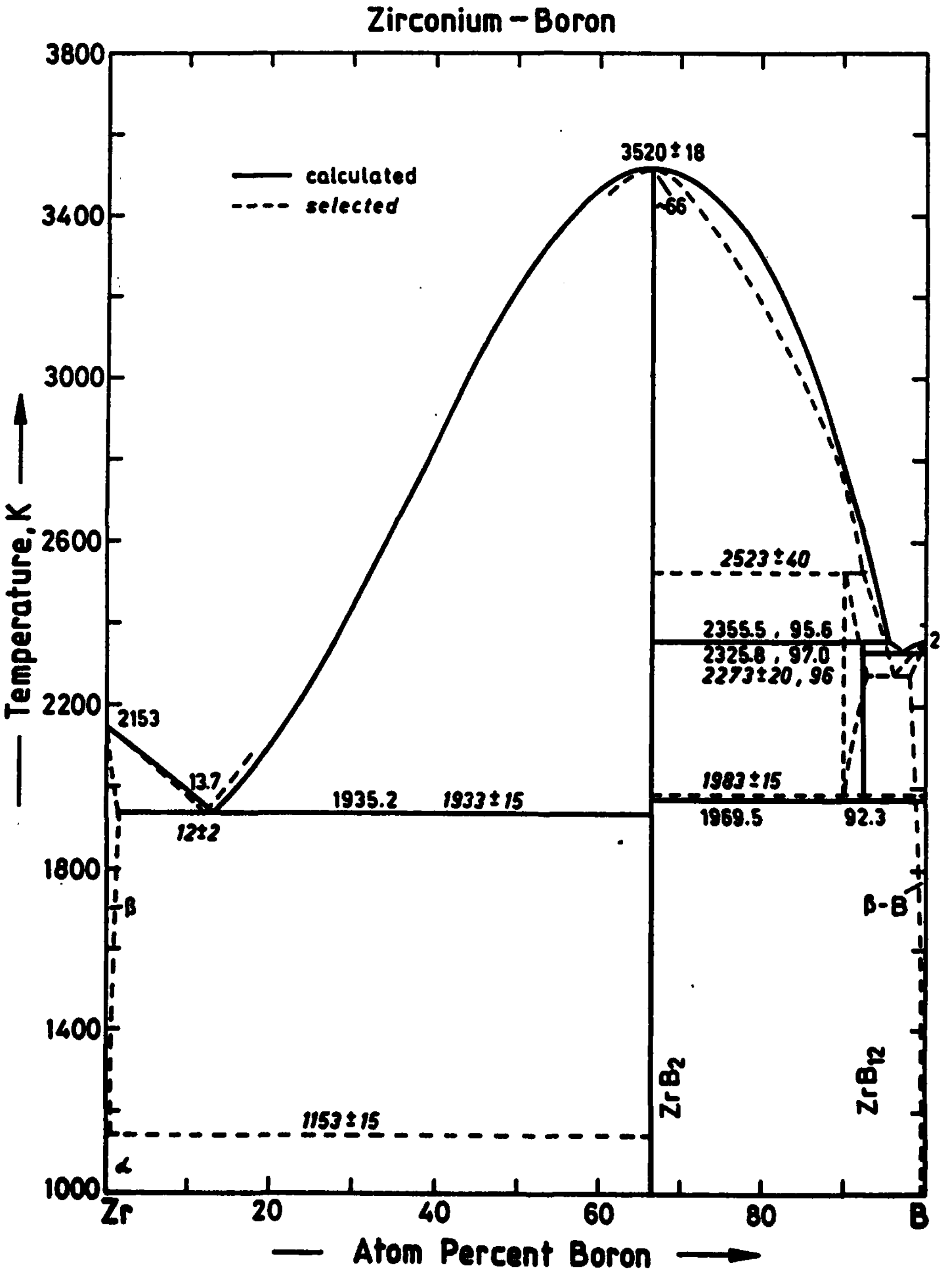


Fig.2: Isothermal section at 1500°C in the system Zr - B - N under 1 bar Ar (in the absence of external nitrogen) [87Šmi].

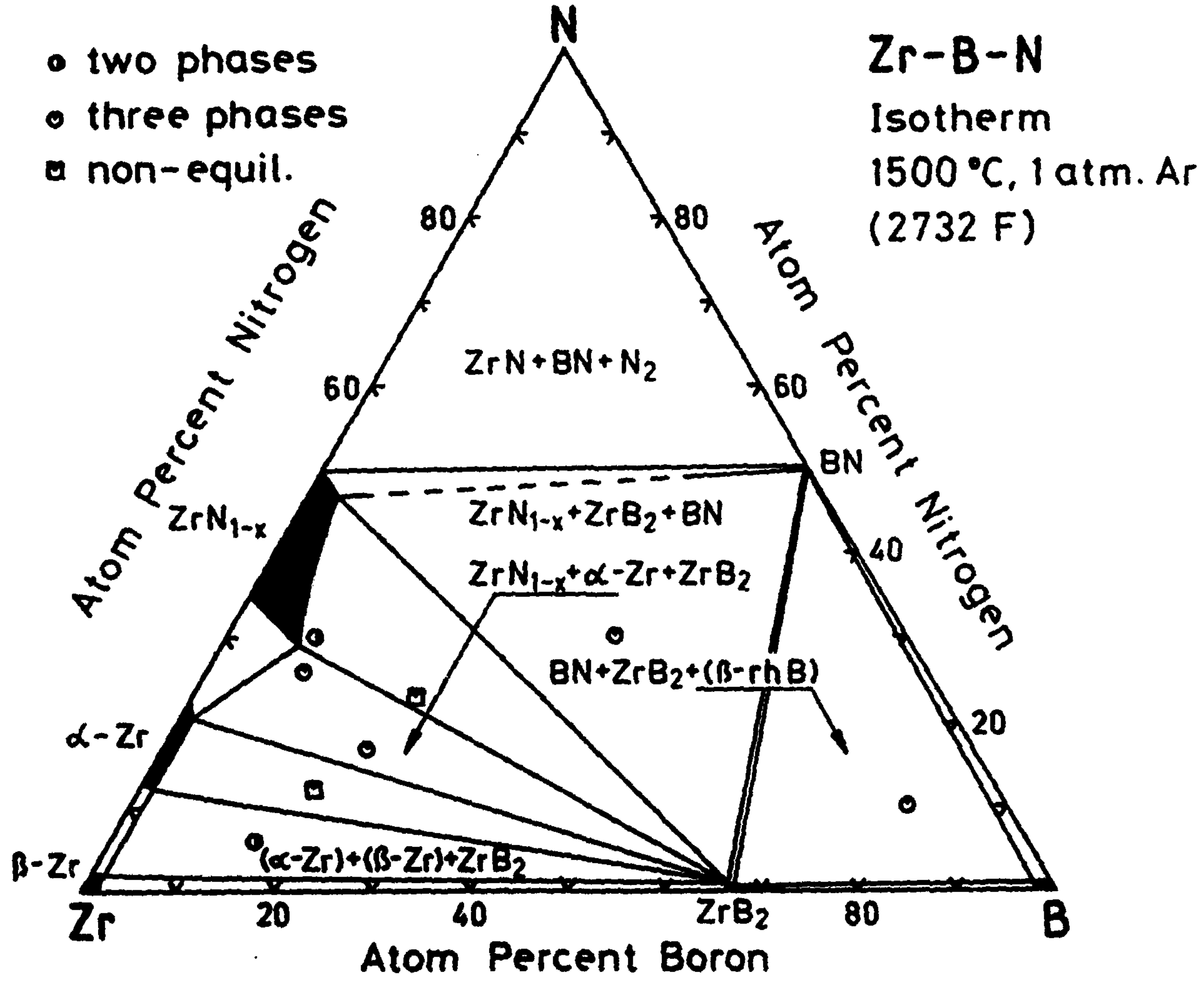
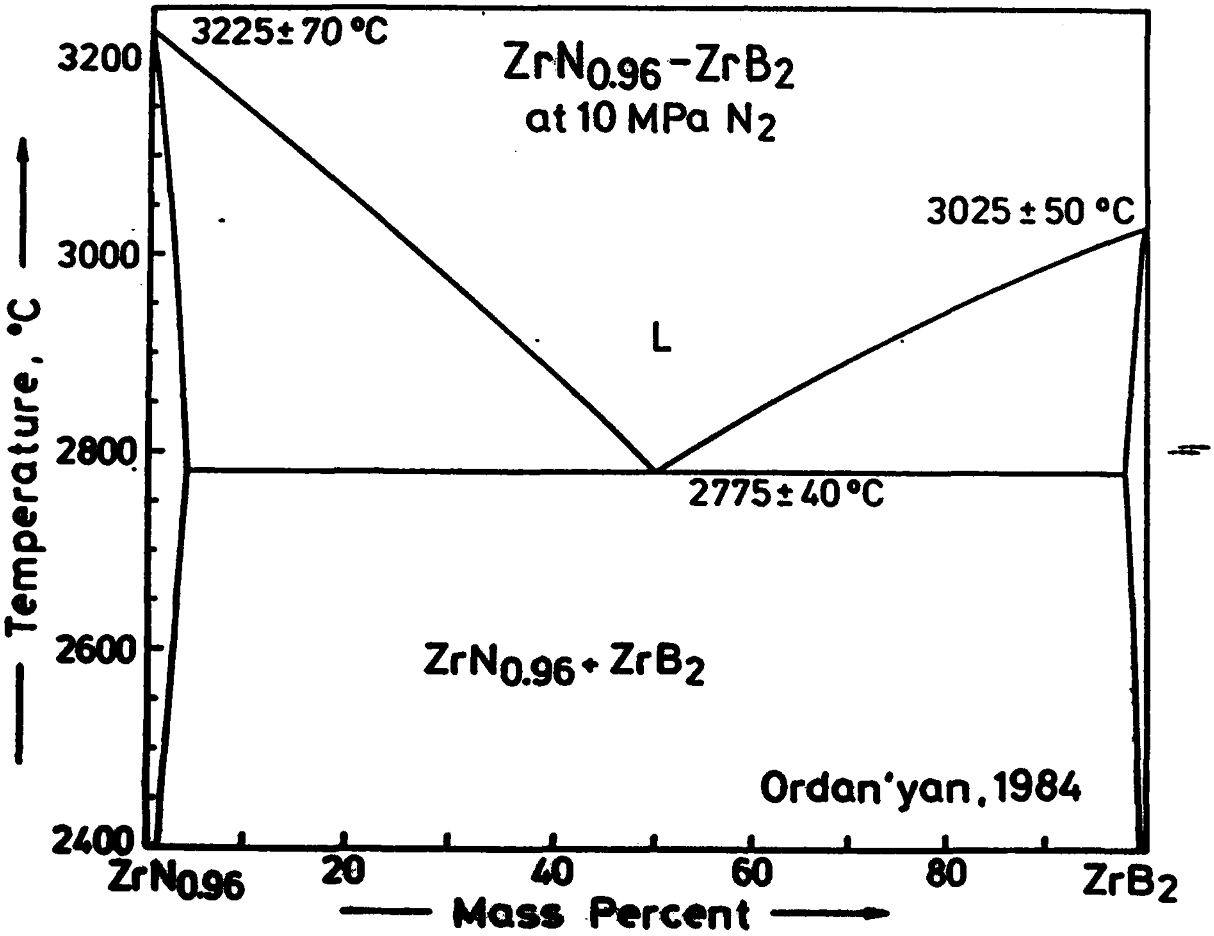


Fig.3: The concentration section ZrB_2-ZrN_{1-x} at x = 0.04 (based on [840rd]).



SYSTEM BORON - HAFNIUM - NITROGEN (B-Hf-N)

INTRODUCTION / EXPERIMENTAL

Informations on the Hf-B-N ternary are due to [61Rud, 73San, 84Ord] and [87Šmi] with an early review by [72Med].

Phase equilibria at 1500°C under argon of 0.1% N_2 as derived by [61Rud] are characterized by the absence of ternary boronnitride compounds and by a dominating three phase field HfB_2 + HfN_{1-x} + BN.

[84Ord] claimed the existence of a quasibinary section of the eutectic type HfB_2+ HfN revealing small mutual solid solubilities at the nitrogen-rich phase boundary $HfN_{0.97}$ (~2 mol% HfB_2 in $HfN_{0.97}$).

Phase equilibria in the B-Hf-N system have been corroborated by [87Šmi] at 1500° under high vacuum or 1 bar Ar or under 1 bar N_2 respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 10 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Hf, HfN ,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20µm in a steel mortar and/or a WC-Co mortar respectively [87Šmi]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1500°C for 72h followed by a final reaction at 1500°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Hf, crystallized boron (99.8 % B), HfN_{1-x} (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [87Šmi].

BINARY SYSTEMS

The reinvestigation [87Šmi] of the B-Hf system in the range from

900 to 2400°C revealed consistency with the data available in [84Vil], and [90Mas]; a critical assessment is due to [88Rog]. The maximal solid solubility of boron in hafnium was claimed to be less than 2 at%B at 1880°C [66Rud] and an interstitial type of B-solubility was suggested . The maximum solid solubility of Hf in β-B was reported to be less than 0.5 at% Hf at ~1800°C from X-ray powder data [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Hf-B.

A critical assessment of the phase diagram for the system Hf-N is due to [90Oka]

Crystallographic information on the binary hafnium compounds is found in Table 1.

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 summarizes the results on the phase relations at 1500°C under 1 bar Ar as observed by [61Rud] and confirmed by [87Šmi]. Phase equilibria are characterized by the absence of ternary compounds and by incompatibility of hafnium metal and BN_{hex} due to the formation of a stable tie line HfB - HfN_{1-x} at temperatures below 1500°C. Heating binary as well as ternary alloys at 1500°C under 1 bar N_2 transfers all samples to the limiting tie line at the nitrogen rich boundary HfN + BN, equilibrium being reached after 75h of nitrogen exposure.

As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Hf in BN up to 1500°C. There is furthermore no solubility of N in HfB_2 , whereas the solubility of hafniumboride in hafniumnitride at 1500°C was observed to be rather extended [61Rud,87Šmi], see also Fig.2.

THERMODYNAMICS

A thermodynamic modelling of the binary system Hf-B is due to [88Rog]; see Table 2. The thermodynamic data available are consistent with the ternary phase equilibria experimentally observed.

MISCELLANEOUS

Fig.3 represents the isopleth HfB_2-HfN_{1-x} for x=0.03 after [84Ord] revealing the eutectic nature of the quasibinary.

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Table 1: Solid phases in the system B-Hf-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Hf 2227-1743°	cI2 $Im\bar{3}m$ W	a= 361.0	[90Mas]
α-Hf <1743°	hP2 $P6_3/mmc$ Mg	a= 319.46 c= 505.10	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.76 c=2381.41	[81Cre]
		a=1095.57 c=24.0244	[81Cre] at HfB_{45}
HfB <2100°	oP8 Pbnm FeB	a= 492.38 b= 652.4 c= 322.35	[87Šmi]
HfB_2 <3380°	hP3 P6/mmm AlB_2	a= 314.28 c= 347.69	[87Šmi] Hf-rich
		a= 314.31 c= 347.80	[87Šmi] B- rich
Hf_3N_2 <1970°	hR6 $R\bar{3}m$ VTa_2C_2	a= 320.6 c=2326.	[85Vil]
Hf_4N_3 <2300°	hR8 $R\bar{3}m$ V_4C_3	a= 321.4 c=3112	[85Vil]
HfN_{1-x}	cF8 $Fm\bar{3}m$ NaCl	a= 451.18	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Hf-B-N

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 Hf	$\Delta_{fus}G(Hf) = 27196-10.861\ T$	[88Rog]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 αHf	$\Delta_f G\ (\alpha Hf) = 0$	
1.0000 βHf	$\Delta_f G\ (\beta Hf) = 5860.3-2.907\ T$	
0.5000 HfB	$\Delta_f G\ (HfB) = -98800-6.30\ T$	
0.3333 HfB_2	$\Delta_f G\ (HfB_2) = -109500+4.13\ T$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
Liquid(Hf,B)	$\Delta G^{ex} = x(1-x)\{-157123-17.19\ T + (38259+8.666\ T)(1-2x) + (2497)(1-2x)^2\}$	
0.5000 HfN	$\Delta_f G\ (HfN) = -1845105+42.48\ T$	[76Fro]

Fig.1: The binary system Hf - B; based on [90Oka] and [87Šmi].

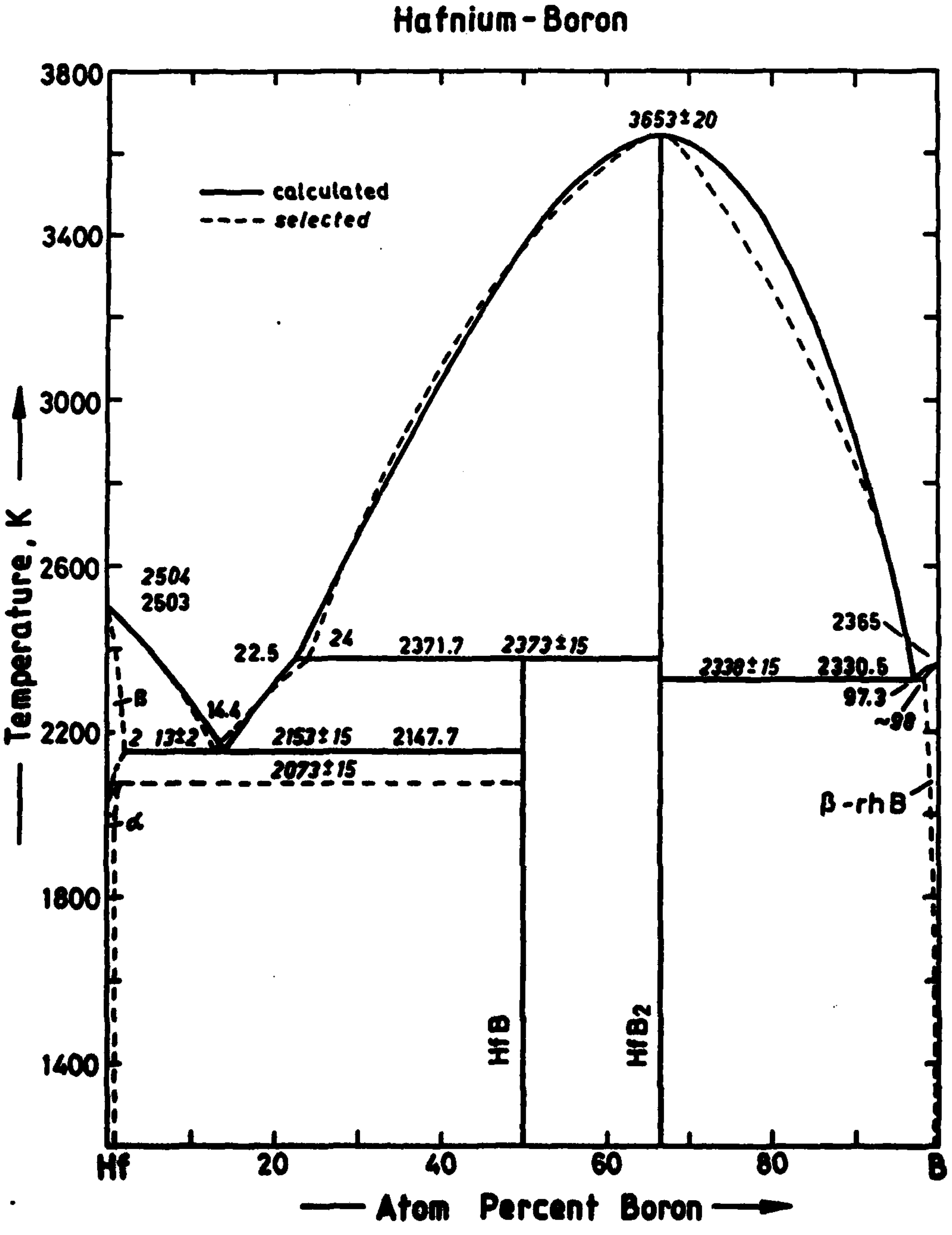


Fig.2: Isothermal section at 1500°C in the system Hf - B - N under 1 bar Ar (in the absence of external nitrogen) [87Šmi].

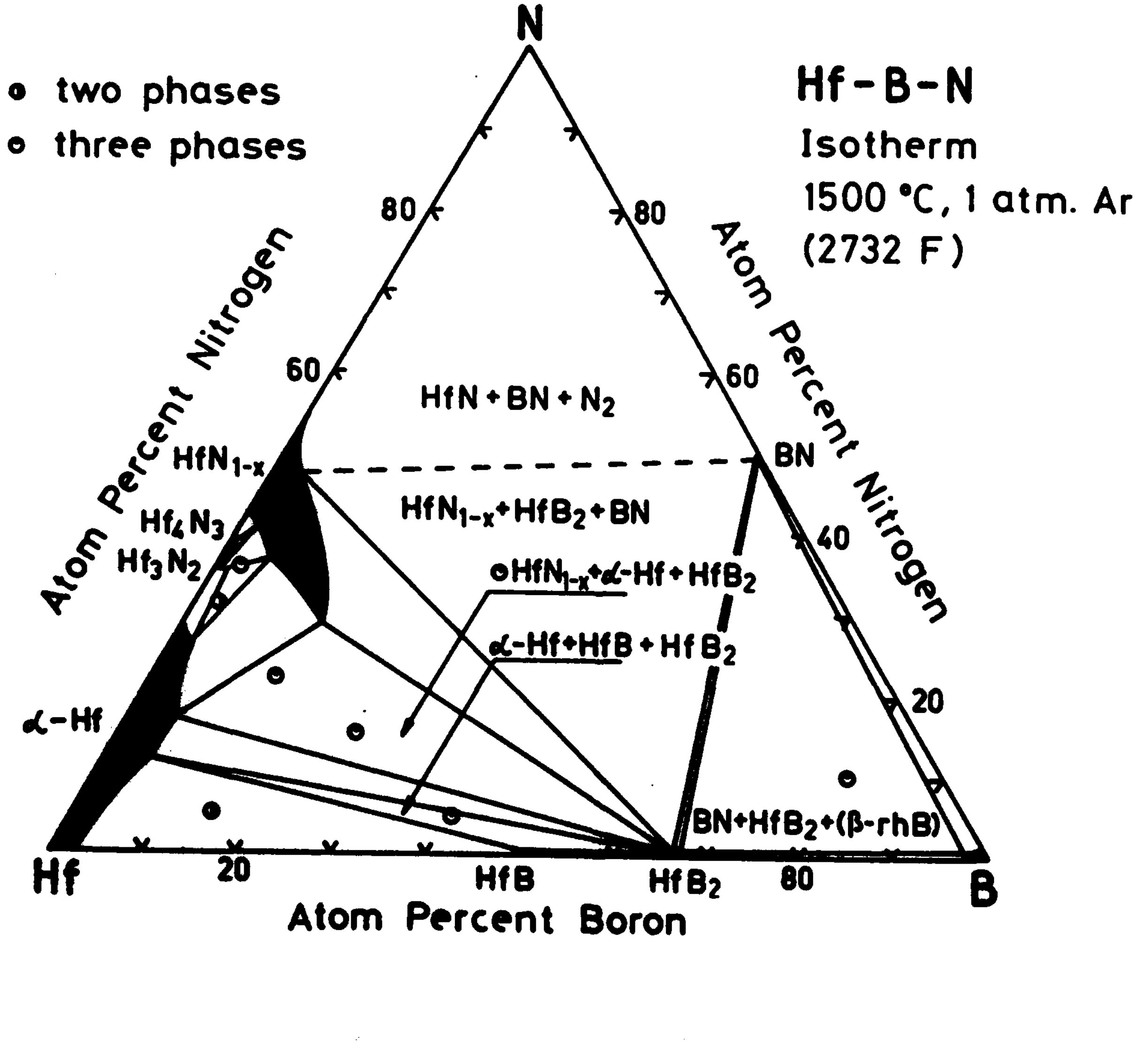
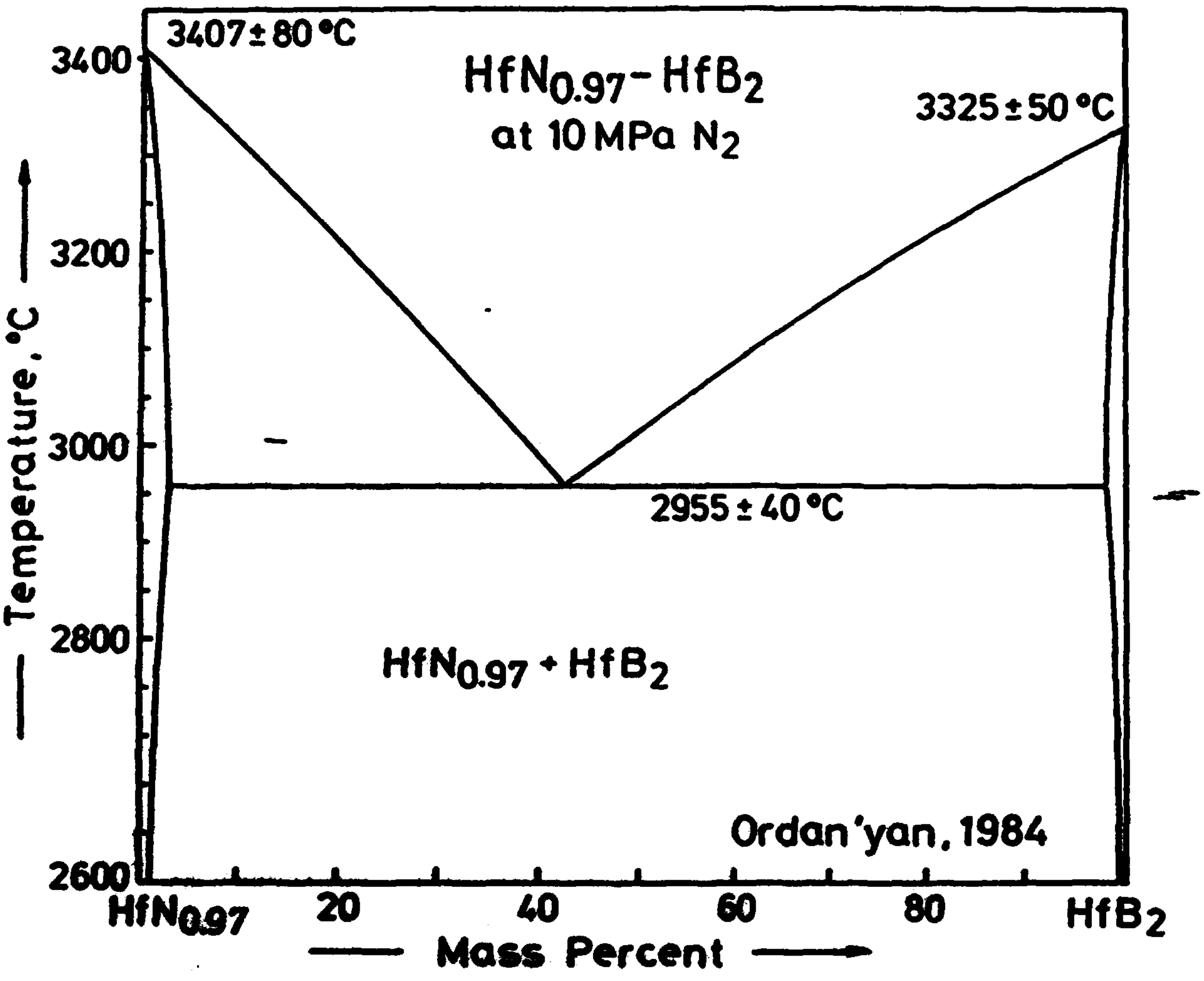


Fig.3: The concentration section HfB_2-HfN_{1-x} at x = 0.03 (based on [84Ord]).



SYSTEM BORON- VANADIUM - NITROGEN (B-V-N)

INTRODUCTION / EXPERIMENTAL

Informations on the V-B-N ternary are due to [68Spe] and [89Rem].

[68Spe] reported phase equilibria under 1 bar of nitrogen and listed the temperatures at which three solid phases are in equilibrium with the gas phase:

VN_{1-x} + VB + BN at 2010(20)K
VB + V_2B_3 + BN at 2180(25)K
V_3B_4 + V_2B_3 + BN at 2290(30)K
V_2B_3 + VB_2 + BN at 2290(30)K
VB_2 + B + BN at 2600(100)K

No details were given for the region V + VN_{1-x} + VB ,however, V_2B_3 was said to react with V_2N_{1-x} under 1 bar N_2 below ca 2010 K to VN_{1-x} + BN [68Spe] (see also Fig.1).

Phase equilibria in the B-V-N system have been furthermore investigated [89Rem] at 1200° under high vacuum or 1 bar Ar or under 1 bar N_2 respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 20 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, V, VN ,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [89Rem]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1200°C for 72h followed by a final reaction at 1200°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-V, crystallized boron (99.8 % B), VN_{1-x} (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [89Rem].

BINARY SYSTEMS

The reinvestigation [89Rem] of the B-V system in the range from 900 to 1600°C revealed consistency with the data available in [84Vil], and [90Mas]; a critical assessment is due to [87Spe]. The maximal solid solubility of boron in vanadium was claimed to be less than 1 at%B at 1737°C [66Rud] ; an interstitial type of B-solubility was suggested . The maximum solid solubility of V in β-B was reported to be less than 1 at% V at ~1800°C from X-ray single crystal data obtained on VB_{65} and VB_{165} by [86Gar] (see Table 1). Fig.1 is a representation of the constitutional diagram V-B.

The phase diagram for the system V-N is taken from [90Mas] modified according to [78Ono,82Ono] regarding the various ordered structures ocurring within the homogeneity range of β-V_2N_{1-x} (see Table 1) A detailed discussion of solubility data , physical properties and thermodynamic data is found in [76Fro].

Crystallographic information on the binary vanadium compounds is found in Table 1.

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 summarizes the results on the phase relations under 1 bar N_2 as observed by [88Spe].

Figs.3,4 represent the isothermal sections at 1200°C under 1 bar Ar and under 1 bar of N_2 respectively [89Rem]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher vanadium borides and BN. Vanadium metal is not compatible with BN_{hex} due to the formation of a stable tie line VB - VN_{1-x} at temperatures below 1750°C. Heating binary as well as ternary alloys at 1200°C under 1 bar N_2 transfers all samples to the limiting tie line at the nitrogen rich boundary VN + BN, equilibrium being reached after 75h of nitrogen exposure (Fig.3, [89Rem]).

As seen from a comparision of the unit cell dimensions there is no significant solid solubility of V in BN up to 1600°C, and mutual solubilities of the vanadium borides, the vanadium nitrides and BN up to 1200°C are rather restricted [89Rem].

THERMODYNAMICS

A thermodynamic modelling of the binary system V-B is due to [87Spe]; see Table 2.

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[90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2nd Ed., Amer.Soc.Met., Metals Park,Oh, 1990.

Table 1: Solid phases in the system B-V-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
V	cI2	a= 302.40	[90Mas]
<1910°	$Im\bar{3}m$		
	W		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
		a=1097.2	[86Gar] at VB_{65}
		c=2390.8	
		a=1094.9	[86Gar] at VB_{105}
		c=2384.0	
V_3B_2	tP10	a= 574.14	[89Rem]
<1900°	P4/mbm	c= 302.95	
	U_3Si_2		
VB	oC8	a= 306.03	[89Rem]
<2570°	Cmcm	b= 805.40	
	CrB	c= 297.20	
V_5B_6	oC22	a= 297.64	[89Rem]
<1750°	Cmmm	b=2130.8	
	V_5B_6	c= 305.85	
V_3B_4	oI14	a= 306.06	[89Rem]
<2610°	Immm	b=1322.0	
	Ta_3B_4	c= 298.10	
V_2B_3	oC20	a= 305.88	[89Rem]
<2670°	Cmcm	b=1842.2	
	V_2B_3	c= 298.46	
VB_2	hP3	a= 299.89	[89Rem]
<2747°	P6/mmm	c= 305.80	
	AlB_2		
V_9N_4	hP*	a= 491.0	[82Ono]
	$P6_322$	c= 455.	
	V_9N_4		

V_2N	hP9 $P6_322$ $Mn_2N_{0.86}$	a= 491.7 c= 456.8	[85Vil]
$V_{32}N_{26}$ <520°	tP58 $P4_2/nmc$ $V_{32}N_{26}$	a=2α(VN) c=2α(VN)	[78Ono]
VN_{1-x}	cF8 $Fm\bar{3}m$ NaCl	a= 413.6	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system V-B-N

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 V	$\Delta_{fus}G(V) = 20950-9.63\ T$	[87Spe]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 V	$\Delta_f G\ (V) = 0$	
0.4000 V_3B_2	$\Delta_f G\ (V_3B_2) = -56070+1.67\ T$	
0.5000 VB	$\Delta_f G\ (VB) = -69134+2.51\ T$	
0.5450 V_5B_6	$\Delta_f G(V_5B_6) = -70116+2.85\ T$	
0.5710 V_3B_4	$\Delta_f G(V_3B_4) = -70290+2.85\ T$	
0.6000 V_2B_3	$\Delta_f G(V_2B_3) = -69856+3.05\ T$	
0.3333 VB_2	$\Delta_f G(VB_2) = -67853+3.35\ T$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
Liquid(V,B)	$\Delta G^{ex} = x(1-x)\{-186352+12.55\ T + (107479-43.82\ T)(1-2x) + 57516(1-2x)^2\}$	
0.3431 $V_2N_{0.98}$	$\Delta_f G(V_2N_{0.98}) = -89591+30.55\ T$	[76Fro]
0.5000 VN_{1-x}	$\Delta_f G\ (VN_{1-x}) = -77404+46.024\ T$	[82Pom]

Fig.1: The binary system V - B; based on [65Rud, 86Mas] and [89Rem].

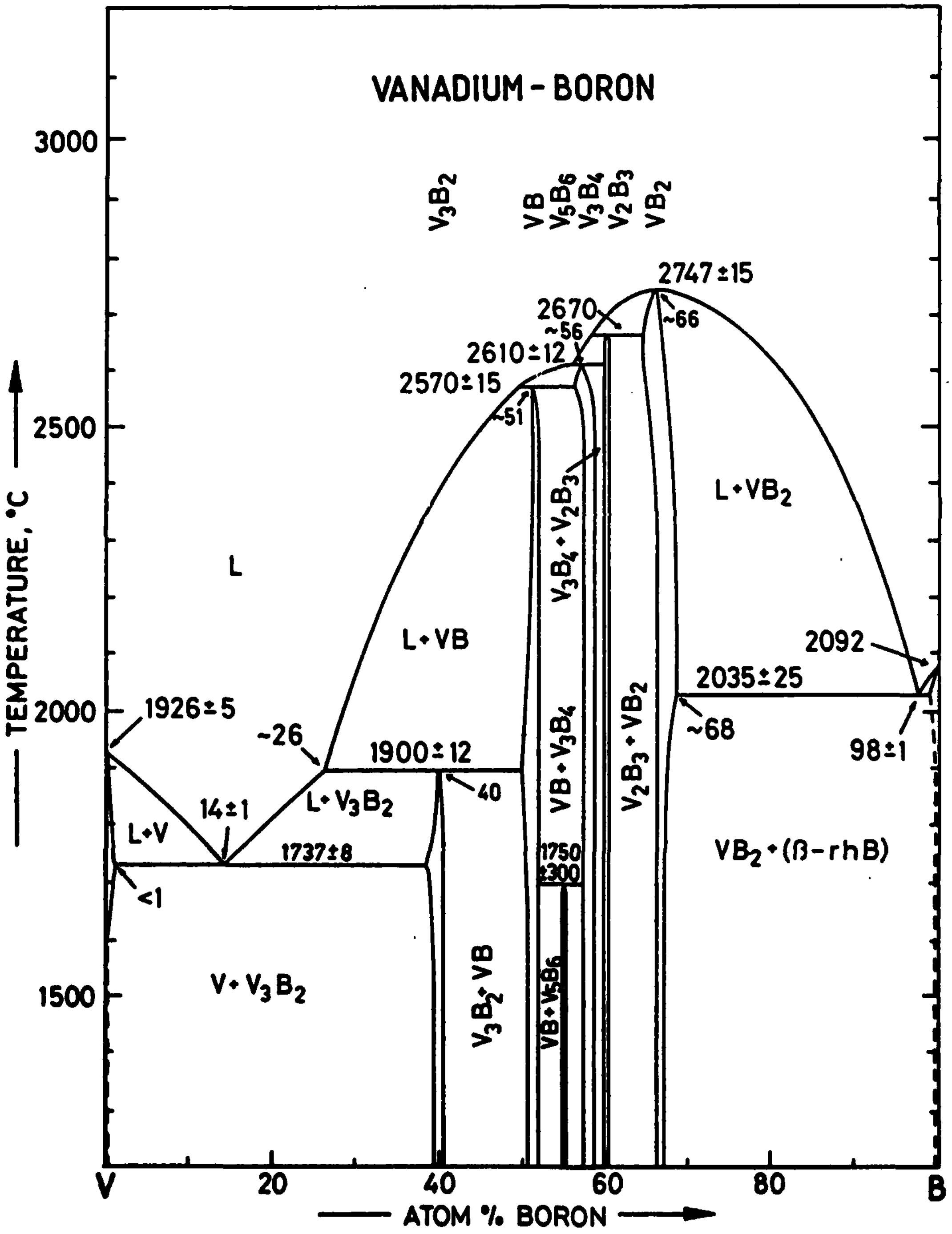


Fig.2: Phase relations in the system V - B - N under 1 bar N_2 (after [68Spe]), the temperatures listed refer to the maximal temperatures under which three solid phases are stable under 1 bar N_2.

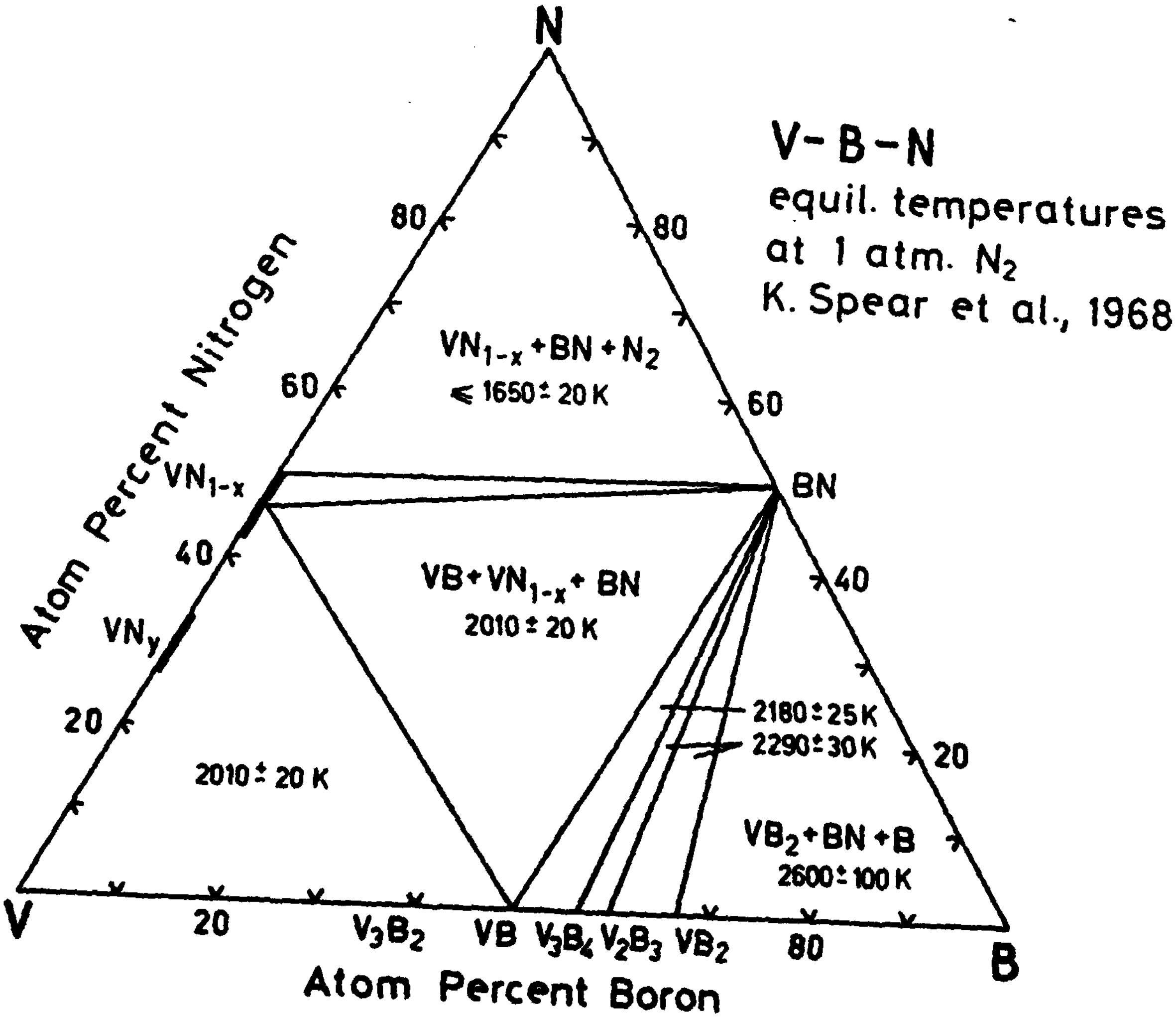


Fig.3: Isothermal section at 1200°C in the system V - B - N (in the absence of external nitrogen)

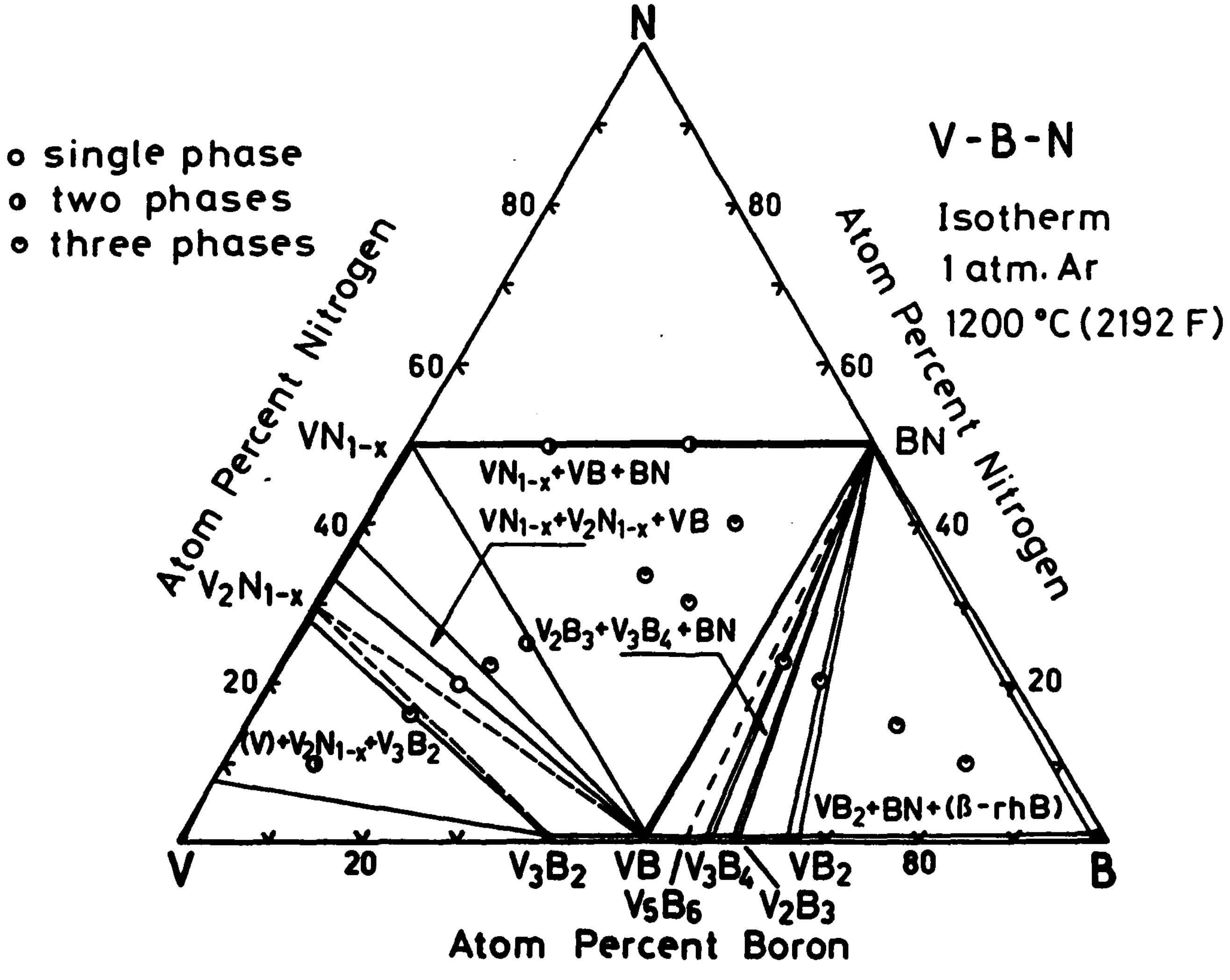
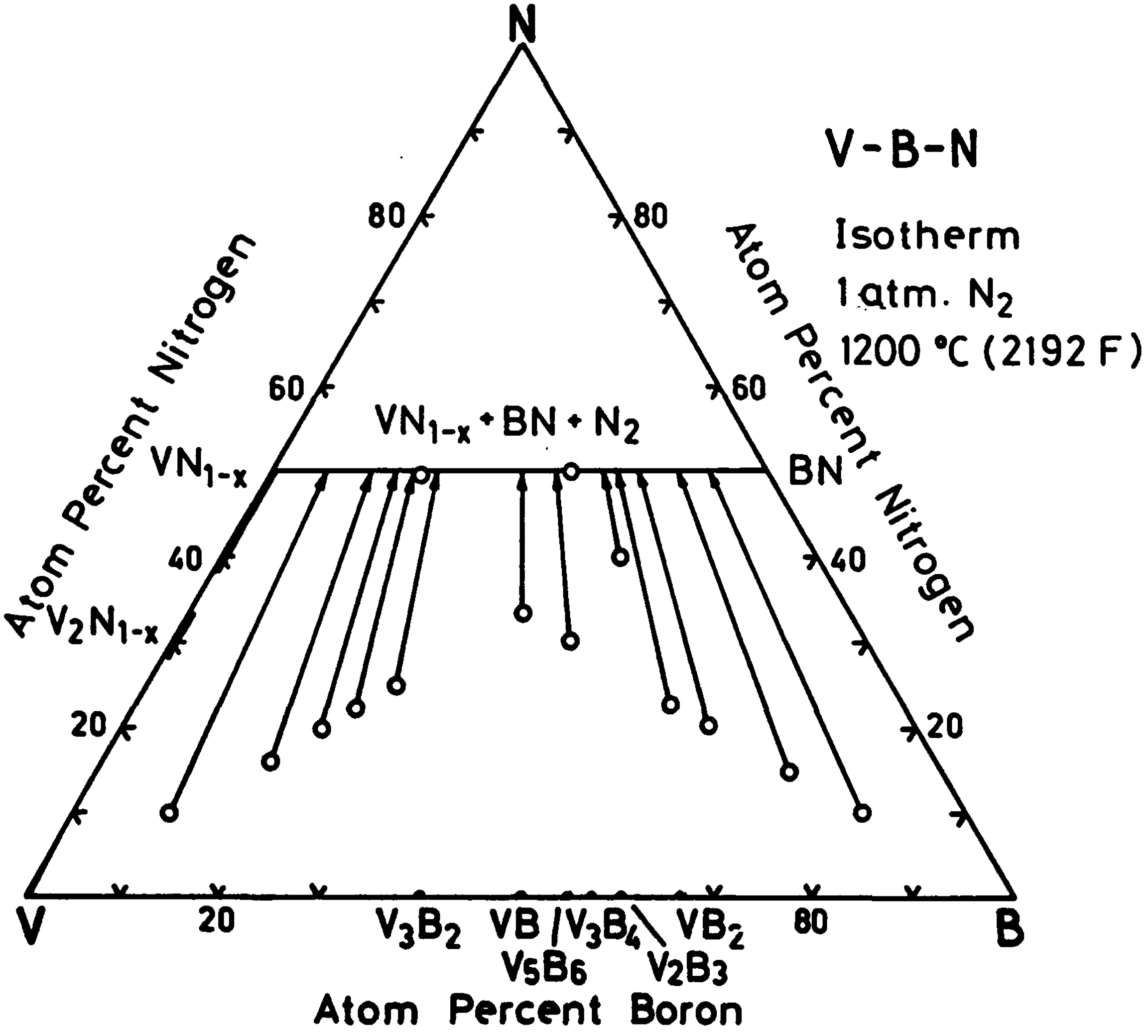


Fig.4: Isothermal section at 1200°C in the system V - B - N under 1 bar N_2.



SYSTEM BORON- NIOBIUM - NITROGEN (B-Nb-N)

INTRODUCTION / EXPERIMENTAL

Informations on the Nb-B-N ternary are due to a recent investigation by [88Rog,89Kle] at 1400° under high vacuum or at 1200°C under 1 bar of Ar respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 15 binary and 30 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Nb, NbN ,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [88Rog,89Kle]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1200°C for 70h followed by a final reaction at 1200°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. Treatments in vacuum (10^{-3}Pa) usually were 64h at 1400°C. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Nb, crystallized boron (99.8 % B), NbN (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Rog,89Kle].

BINARY SYSTEMS

The reinvestigation [89Kle] of the B-Nb system in the range from 900 to 1600°C revealed consistency with the data available in [84Vil], and [66Rud]; the data of [66Rud] , however, are modified with respect to the formation of Nb_5B_6 [88Rog, 89Kle]. The maximal solid solubility of boron in niobium was claimed to be less than 2 at%B at 2165°C [66Rud] ; an interstitial type of B-solubility was suggested . The maximum solid solubility of Nb in β-B was reported to be less than 0.5 at% Nb at ~1800°C from X-ray powder data [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Nb-B.

The phase diagram for the system Nb-N is essentially based on the critical assessment by [79Pol]. A detailed discussion of solubility data , physical properties and thermodynamic data is found in [76Fro].

Crystallographic information on the binary niobium compounds is found in Table 1.

SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2,3 represent the isothermal sections at 1200°C under 1 bar Ar and at 1400°C under a vacuum of 10^{-3}Pa respectively [88Rog,89Kle]. Phase equilibria are characterized by the formation of at least two ternary compounds Nb_2BN which is a superconductor (T_c=2.5K) and a phase Φ whose crystal structure has not been solved yet. Whereas compatibility exists between the higher niobium borides and BN, niobium metal is not compatible with BN_{hex} due to the formation of a stable tie line NbB - Nb_2N_{1-x} at temperatures below 1400°C. Heating binary as well as ternary alloys at 1200°C under 1 bar N_2 transfers all samples to the limiting tie line at the nitrogen rich boundary NbN + BN, equilibrium being reached after 75h of nitrogen exposure [89Kle]).

As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Nb in BN up to 1400°C, and mutual solubilities of the niobium borides ,the niobium nitrides and BN up to 1200°C are rather restricted [89Kle].

THERMODYNAMICS

A thermodynamic description of the binary system Nb-B is due to [84Kau]; see Table 2.

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Table 1: Solid phases in the system B-Nb-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Nb	cI2	a= 330.04	[90Mas]
<2469°	$Im\bar{3}m$		
	W		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
		a=1091.91	[81Cre] at 0.5at%Nb
		c=2382.24	
Nb_3B_2	tP10	a= 619.79	[89Kle]
<2080°	P4/mbm	c= 329.26	
	U_3Si_2		
NbB	oC8	a= 329.74	[89Kle]
<2917°	Cmcm	b= 872.38	
	CrB	c= 316.69	
Nb_5B_6	oC22	a= 315.30	[89Kle]
	Cmmm	b=2274.4	
	V_5B_6	c= 330.49	
Nb_3B_4	oI14	a= 330.19	[89Kle]
<2935°	Immm	b=1406.2	
	Ta_3B_4	c= 314.51	
NbB_2	hP3	a= 311.26	[89Kle] Nb-rich
<3036°	P6/mmm	c= 326.27	
	AlB_2	a= 308.61	[89Kle] B- rich
		c= 330.69	
Nb_2N (h2)	hP9	a= 526.7	[85Vil]
	$P\bar{3}1m$	c= 498.6	
	V_2N		
γ-Nb_4N_3	tI14	a= 438.2	[85Vil]
	I4/mmm	c= 863.2	
	Nb_4N_3		

δ-NbN_{1-x}	oF8	a= 439.4	[85Vil]
	Fm$\bar{3}$m		
	NaCl		
ε-NbN	hP8	a= 295.8	[85Vil]
	$P6_3/mmc$	c=1127.3	
	TiAs		
Nb_5N_6	hP22	a= 519.3	[85Vil]
	$P6_3/mmc$	c=1038.0	
	Nb_5B_6		
Nb_4N_5	tI18	a= 687.3	[85Vil]
	I4/m	c= 429.8	
	$RhLi_4N_4$		
BN_{hex}	hP*	a= 250.4	[85Vil]
	$P6_3/mmc$	c= 666.1	
	BN_{hex}		
* Nb_2BN	oC16	a= 317.12	[88Rog,89Kle]
	Cmcm	b=1785.04	
	Mo_2BC	c= 311.45	
* $Nb_{35}B_{45}N_{20}$	oP*		[89Kle]

Table 2: Thermodynamic data for the system Nb-B-N

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 Nb	$\Delta_{fus}G(Nb) = 18110-10.275\ T$	[84Kau]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 Nb	$\Delta_f G\ (Nb) = 0$	
0.2000 Nb_3B_2	$\Delta_f G(Nb_3B_2) = -51076+0.033\ T$	
0.5000 NbB	$\Delta_f G(NbB) = -82722-0.46\ T$	
0.1428 Nb_3B_4	$\Delta_f G(Nb_3B_4) = -70836+0.61\ T$	
0.3333 NbB_2	$\Delta_f G(NbB_2) = -85548+2.96\ T$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
Liquid(Nb,B)	$\Delta G^{ex} = x(1-x)\{-84336(1-x)-234990x+4.184\ T\}$	
0.3333 Nb_2N	$\Delta_f G\ (Nb_2N) = -90793+30.96\ T$	[76Fro]

Fig.1: The binary system Nb - B; based on [65Rud] and [89Kle].

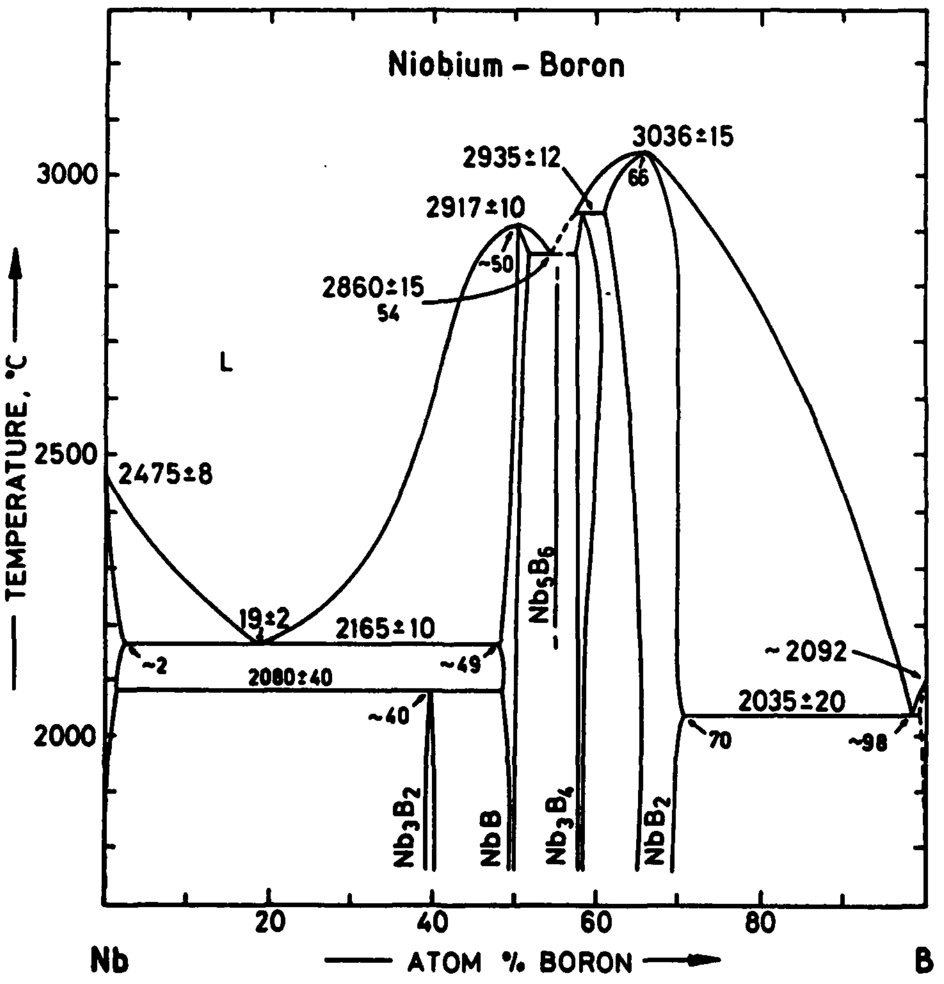


Fig.2: Isothermal section at 1200°C in the system Nb - B - N
(in the absence of external nitrogen)

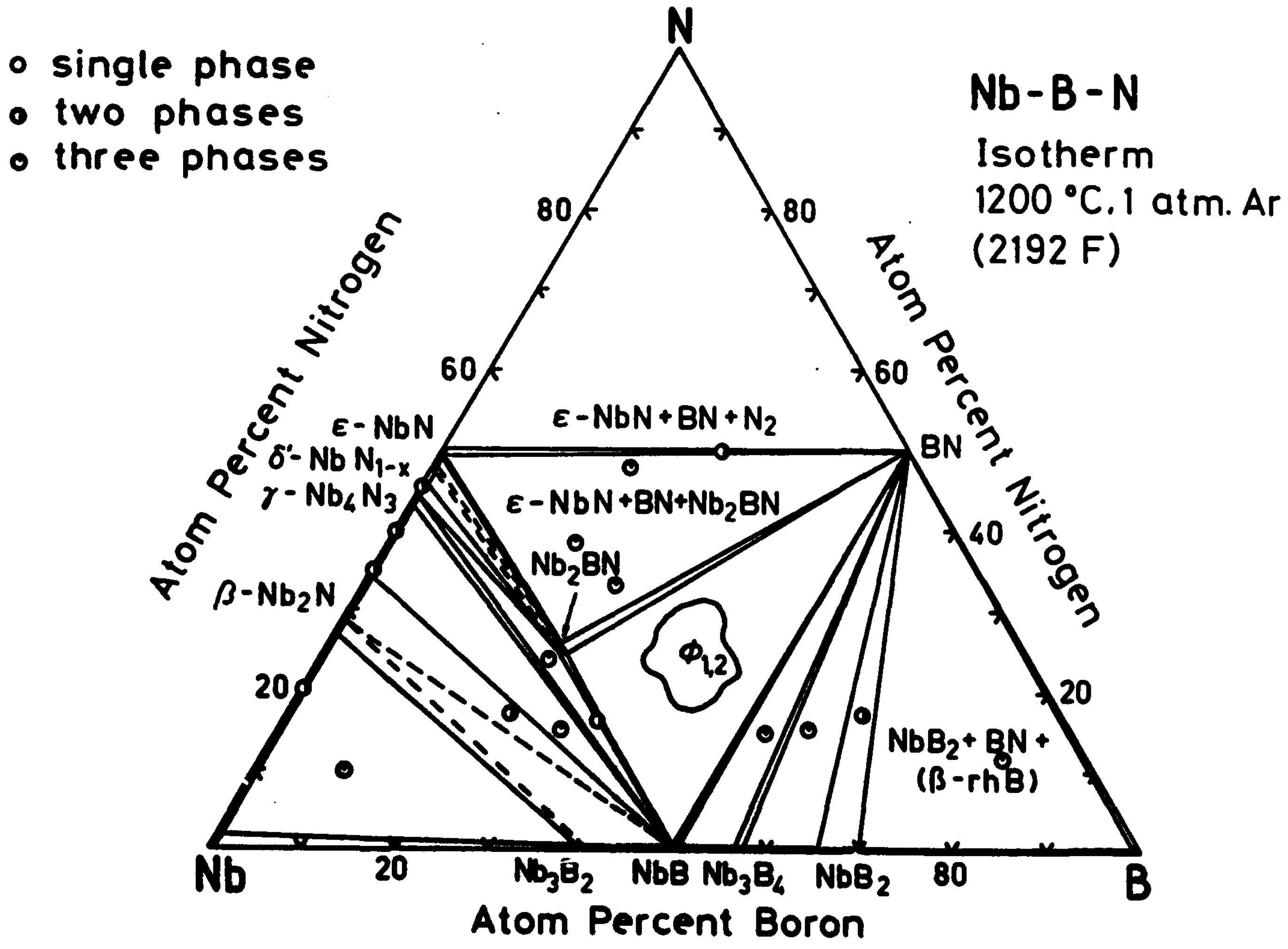
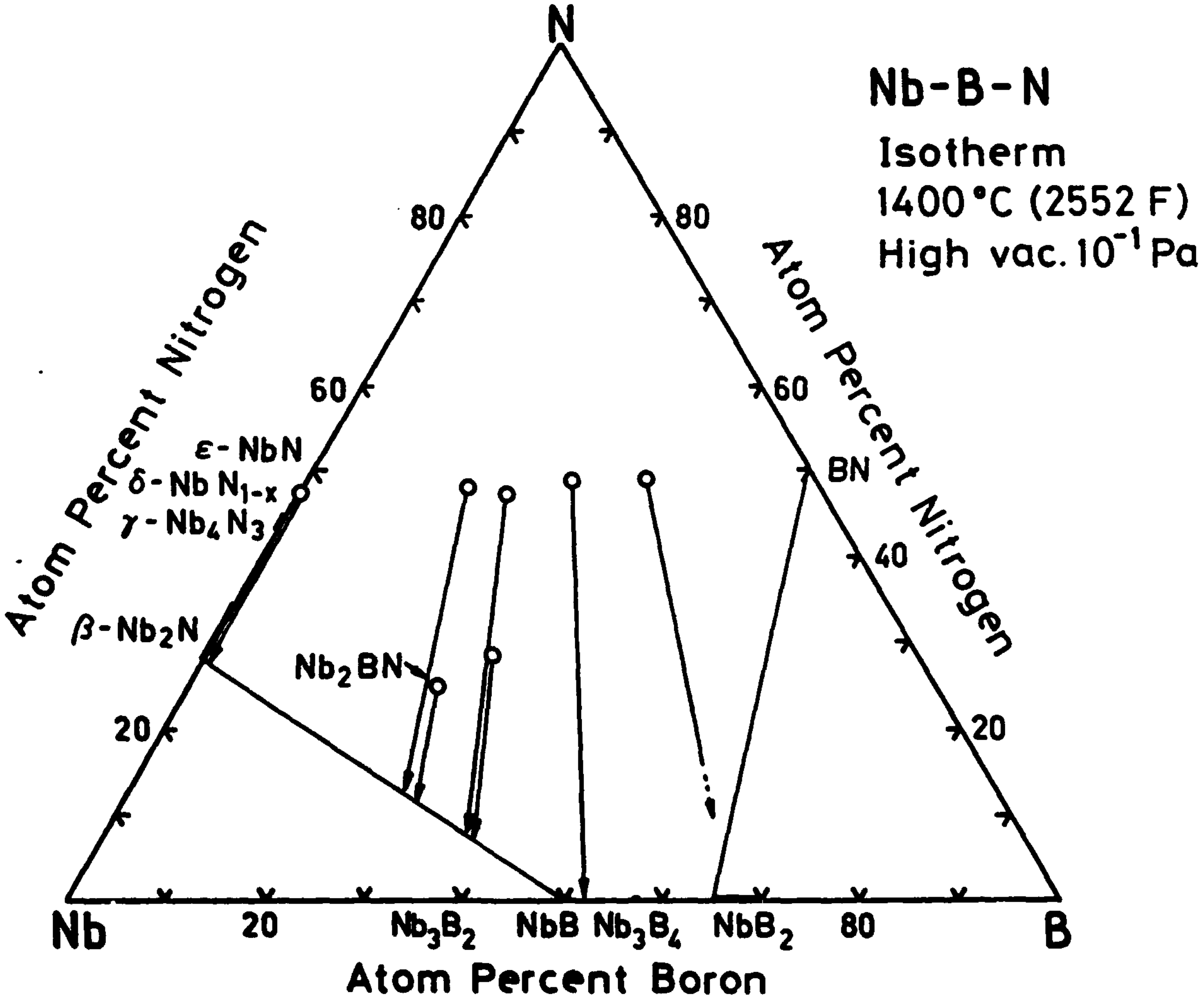


Fig.3: Isothermal section at 1400°C in the system Nb - B - N under a vacuum of 10^{-3}Pa.



SYSTEM BORON- TANTALUM - NITROGEN (B-Ta-N)

INTRODUCTION / EXPERIMENTAL

Informations on the Ta-B-N ternary are due to a recent investigation by [89Kle] at 1400° under high vacuum or at 1200°C under 1 bar of Ar respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 15 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Ta, TaN ,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [89Kle]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1200°C for 70h followed by a final reaction at 1200°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. Treatments in vacuum (10^{-3}Pa) usually were 64h at 1400°C. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Ta, crystallized boron (99.8 % B), TaN (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [89Kle].

BINARY SYSTEMS

The reinvestigation [89RKle] of the B-Ta system in the range from 900 to 1600°C revealed consistency with the data available in [84Vil], and [66Rud,71Por]; the data of [66Rud] are preferred, however, are modified with respect to recent reports on the existance of Ta_5B_6 [90Oka].The maximal solid solubility of boron in tantalum was claimed to be less than 2 at%B at 2385°C [66Rud] ; an interstitial type of B-solubility was suggested . The maximum solid solubility of Ta in β-B was reported to be less than 0.5 at% Ta at ~1800°C from X-ray powder data [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Ta-B.

The phase diagram for the system Ta-N is essentially based on the work of [83Ett] and [84Koy]. A detailed discussion of solubility data , physical properties and thermodynamic data is found in [76Fro].

Crystallographic information on the binary tantalum compounds is found in Table 1.

SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2,3 represent the isothermal sections at 1200°C under 1 bar Ar and at 1400°C under a vacuum of 10^{-3}Pa respectively [89Kle]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher tantalum borides and BN. Tantalum metal is not compatible with BN_{hex} due to the formation of a stable tie line TaB - Ta_2N_{1-x} at temperatures below 1400°C. Heating binary as well as ternary alloys at 1200°C under 1 bar N_2 transfers all samples to the limiting tie line at the nitrogen rich boundary TaN + BN, equilibrium being reached after 75h of nitrogen exposure [89Kle]). High pressure experiments (1000°C,6.0 GPa) proved the absence of hypothetical "Ta_2BN" isotypic with Nb_2BN [88Rog].

As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Ta in BN up to 1400°C, and mutual solubilities of the tantalum borides, the tantalum nitrides and BN up to 1200°C are rather restricted [89Kle].

THERMODYNAMICS

Only limited information on the thermodynamic data of the tantalum borides and nitrides is available; see Table 2.

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[90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2nd Ed., (Amer.Soc.Met., Metals Park,Oh, 1990.

[90Oka] T.Okada, Private commun. (1990)

Table 1: Solid phases in the system B-Ta-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Ta	cI2	a= 330.30	[90Mas]
<3020°	Im$\bar{3}$m		
	W		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	R$\bar{3}$m	c=2381.43	[85Vil]
	β-B		
		a=1092.05	[81Cre] at 0.5at%Ta
		c=2386.73	
Ta_2B	tI12	a= 577.93	[89Kle]
2417-2040°	I4/mcm	c= 486.38	
Ta_3B_2	tP10	a= 619.27	[89Kle]
<2180°	P4/mbm	c= 330.27	
	U_3Si_2		
TaB	oC8	a= 327.49	[89Kle]
<3090°	Cmcm	b= 868.16	
	CrB	c= 315.84	
Ta_5B_6	oC22	a=	[90Oka]
	Cmmm	b=	
	V_5B_6	c=	
Ta_3B_4	oI14	a= 328.84	[89Kle]
<3030°	Immm	b=1399.68	
	Ta_3B_4	c= 313.20	
TaB_2	hP3	a= 309.73	[89Kle] Ta-rich
<3037°	P6/mmm	c= 322.57	
	AlB_2	a= 305.86	[98Kle] B- rich
		c= 328.92	
Ta_9N_2	c**	a=1010.	[85Vil]
<790°			
Ta_2N (h1)	hP3	a= 304.76	[85Vil]
2950-1650°	$P6_3$/mmc	c= 491.87	
	Fe_2N		

Ta_2N (h2) <1850°	hP9 $P\bar{3}1m$ V_2N	a= 528.5 c= 491.9	[85Vil]
δ-TaN_{1-x} <1750°	cF8 $Fm\bar{3}m$ NaCl	a= 433.	[85Vil]
ε-TaN <1950°	hP6 $P\bar{6}2m$ TaN	a= 519.6 c= 291.1	[85Vil]
Ta_5N_6	hP22 $P6_3/mmc$ Nb_5N_6	a= 516. c=1027.	[85Vil]
Ta_4N_5	tI18 I4/m $RhLi_4N_4$	a= 683.1 c= 426.9	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Ta-B-N

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 Ta	$\Delta_{fus}G(Ta) = 36568.2-11.224\ T$	
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 Ta	$\Delta_f G\ (Ta) = 0$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
0.3333 Ta_2N	$\Delta_f G(Ta_2N) = -67920+17.015\ T$	[78Fro]

Fig.1: The binary system Ta - B; based on [65Rud] and [89Kle].

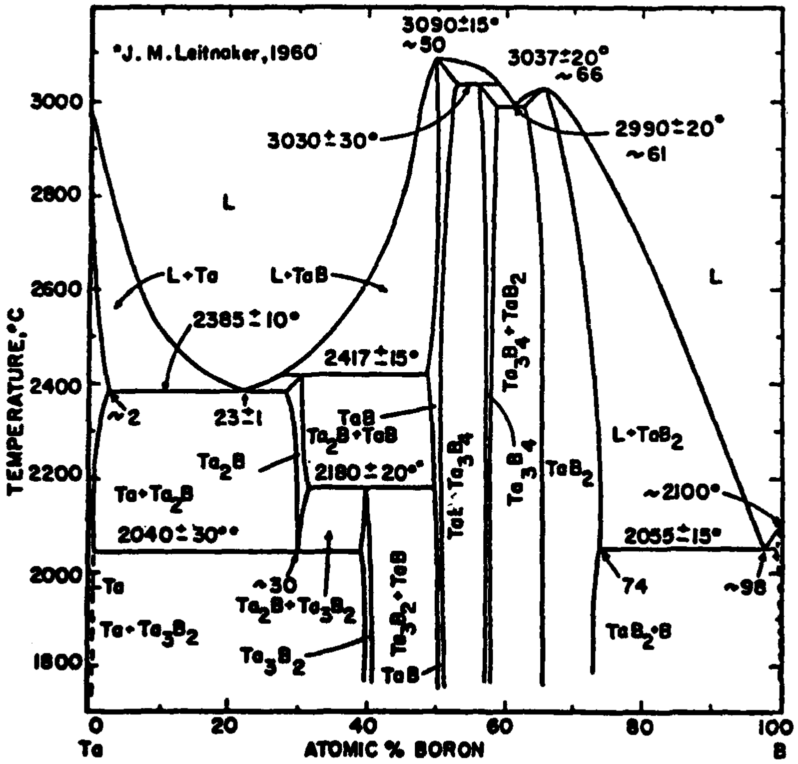


Fig.2: Isothermal section at 1200°C in the system Ta - B - N (in the absence of external nitrogen)

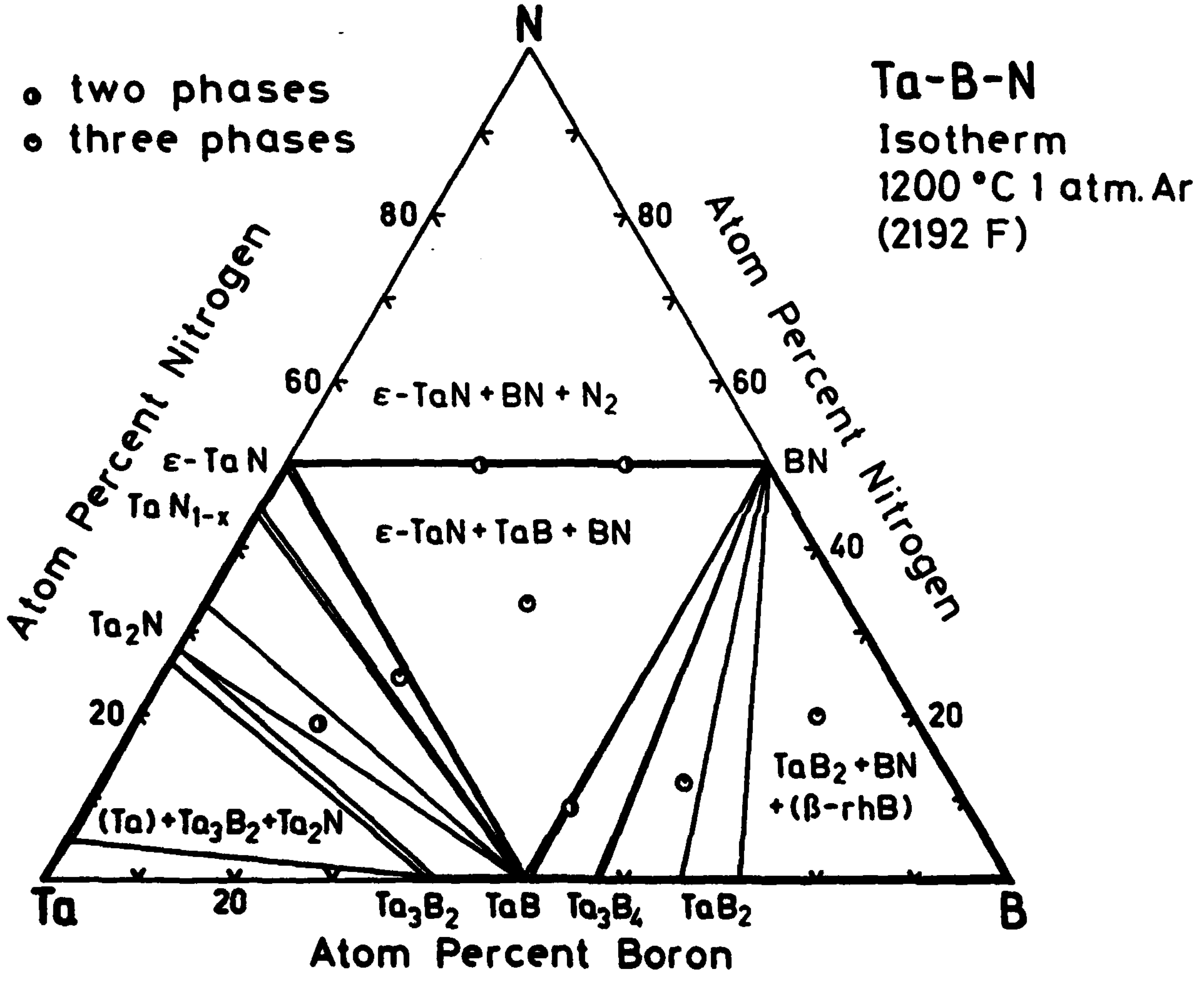
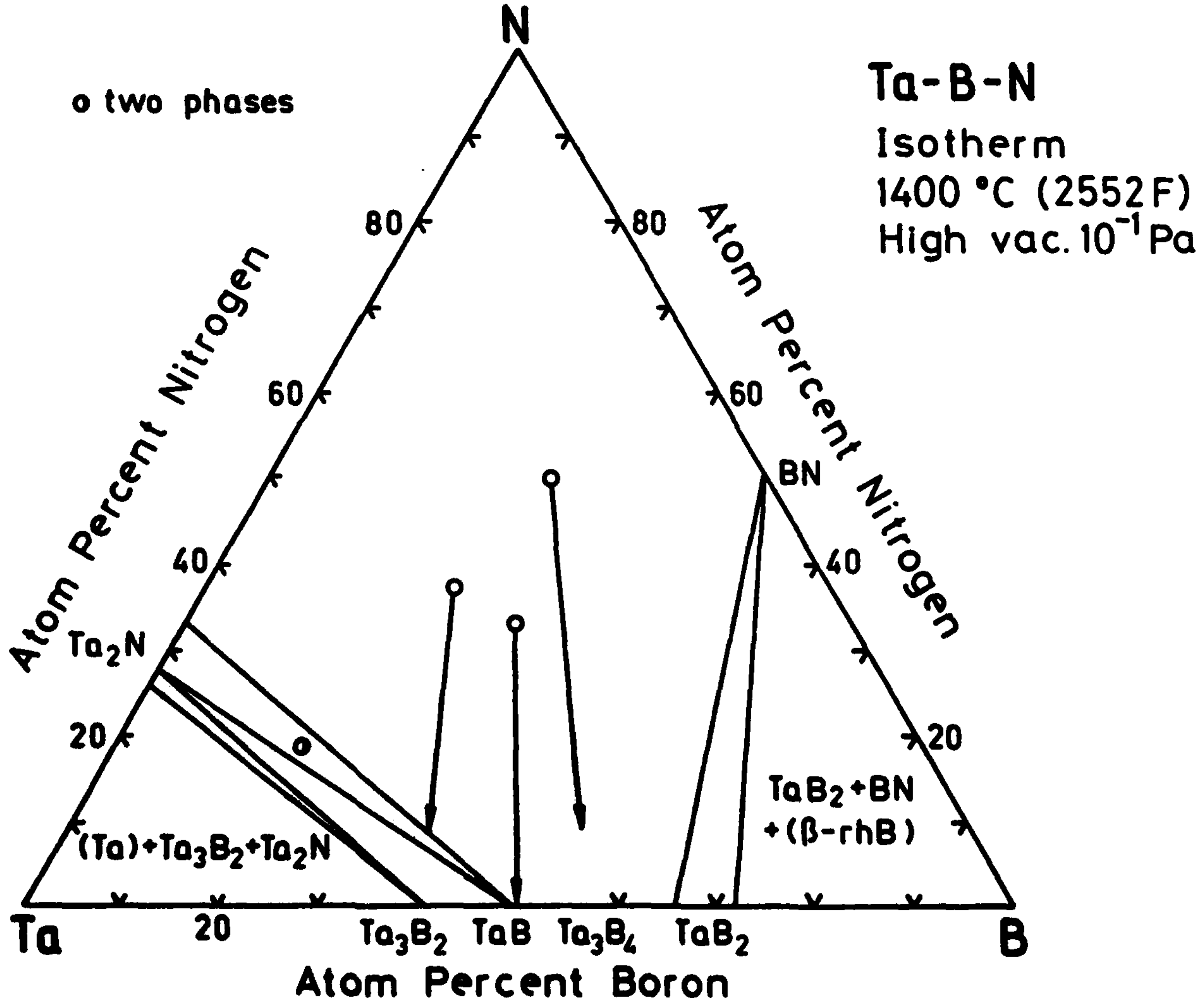


Fig.3: Isothermal section at 1400°C in the system Ta - B - N under a vacuum of 10^{-2} Pa.



SYSTEM BORON- CHROMIUM - NITROGEN (B-Cr-N)

INTRODUCTION / EXPERIMENTAL

Informations on the Cr-B-N ternary are due to [51Kis,55Bre,80Kat] and [87Šmi].

The thermal stability of binary chromium borides was investigated in a dry stream of ammonia at temperatures below 1180°C by [51Kis]. The resistance against attack by ammonia was found to increase with the boron content and no mutual solid solubilities were observed among borides and nitrides [51Kis]. Temperatures below 700°C were observed to be insufficient and chromium borides remained unchanged, whereas at temperatures 1100° and 1180°C the decomposition reaction was found to be complete for all chromium borides reaching the limiting tie line $Cr_2N + BN$ [51Kis].

From a preliminary study of the thermodynamic stability of chromium borides [55Bre] concluded instability of the tie line CrN + BN under 0.5 bar N_2 and temperatures above ca 1000°C; similarly the $Cr_2N + BN$ equilibrium was calculated to be unstable above ca 1000 to 1200°C, and in the temperature region 1200 to 1700°C the chromium borides were said to remain stable under a partial pressure of 0.5 bar N_2 [55Bre].

[80Kat] reinvestigated reactions and phase relations in the ternary system at 1600°C under 1 bar N_2 revealing the formation of three-phase equilibria among two solid phases and nitrogen i.e. $Cr_2N + Cr_2B + N$, $Cr_2B + Cr_5B_3 + N$ and $Cr_5B_3 + BN + N$. Accordingly chromium borides with a boron content higher than Cr_5B_3 were found to decompose into Cr_5B_3 + BN. For CrB_2 this decomposition process was demonstrated to follow a stepwise reaction path according to the following scheme being complete after 60 hrs:

$3\ CrB_2 + N_2 = Cr_3B_4 + 2\ BN$,

$Cr_3B_4 + 1/2\ N_2 = 3\ CrB + BN$ and

$5\ CrB + N_2 = Cr_5B_3 + 2\ BN$.

Phase equilibria in the B-Cr-N system have been furthermore investigated [87Šmi] at 1000° under high vacuum or 1 bar Ar respectively and at 1400° under 1 bar Ar or 1 bar N_2 respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 20 binary and 40 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Cr, Cr_2N or CrN ,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [87Šmi]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in vacuum sealed quartz capillaries usually consisted of a primary reaction at 1000°C for 170h followed by a final reaction at 1000°C (or 1400° respectively) for up to 400h with an intermediate step of crushing and recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Cr, crystallized boron (99.8 % B), CrN, Cr_2N (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [87Šmi].

BINARY SYSTEMS

The reinvestigation [87Smi] of the B-Cr system in the range from 900 to 1600°C revealed consistency with the data available in [84Vil], and [90Mas]. The maximal solid solubility of boron in chromium was claimed to be 0.72 at%B at 1100°C [84Sha] or 0.6 at%B at 1500°C [71Bor] ; an interstitial type of B-solubility was suggested . The maximum solid solubility of Cr in β-B was reported to be less than 2.4 at% Cr at ~1800°C from X-ray single crystal data by [70And] (see Table 1). "Cr_6B", Cr_3B_2" and tetragonal "t-Cr_2B" with the $CuAl_2$-type were shown to be impurity phases or metastable [87Šmi]. The existence of the CrB-type has been confirmed from samples annealed above 1000°C, whereas alloys prepared from sinter procedures at temperatures below 1000°C revealed an X-ray powder pattern essentially corresponding to the MoB-type [87Šmi]. It was shown that the X-ray pattern merely arises from rather statistically than regularly ocurring shifts by a vector of 1/2(*a+b*)CrB without long range order and with an overall average length of ca 80 Å for the undisturbed MoB-type units [87Smi]. Cr_3B_4 was never observed in alloys heat treated below 1200°C and thus was suspected to be a high temperature compound [87Šmi]. Fig.1 is a representation of the constitutional diagram Cr-B.

The phase diagram for the system Cr-N is taken from [86Mof] modified according to [76Fro]. The two chromium nitrides reported, Cr_2N and CrN, are unstable at 1000°C for $p(N_2)$ less than 70 Pa. A detailed discussion of solubility data , physical properties and thermodynamic data is found in [76Fro].

Crystallographic information on the binary chromium compounds is found in Table 1.

SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2-6 represent the isothermal sections at 1600°C under 1 bar N_2 after [80Kat], and at 1000°C under 1 bar Ar (from alloys sealed in quartz capillaries), at 1000°C under high vacuum and at 1400°C under 1 bar Ar (in the absence of external nitrogen pressure) and under 1 bar N_2 respectively [87Šmi]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher chromium borides and BN. Chromium metal is not compatible with BN_{hex} due to the formation of a stable tie line Cr_2B - Cr_2N at 1000°C. The limiting tie line CrN + BN and the formation of a three-phase equilibrium CrN + BN + N at 1000°C is due to nitrogen build-up within the sealed quartz capsules stabilizing CrN (Fig3). Application of a high vacuum (10^{-4}Pa) at 1000°C results in a rapid decomposition of CrN + BN into Cr_2N + BN followed by a subsequent but rather slow decomposition of Cr_2N (Fig.4,[87Šmi]) in perfect agreement with the decomposition pressure of the binary chromium nitrides (see [76Fro,70Mil]).

Phase equilibria at 1400°C and 1 bar Ar are characterized by the instability of CrN and Cr_2N and by an increased stability of the binary chromium borides against nitrogen (Fig.5). Heating binary as well as ternary alloys at 1400°C under 1 bar N_2 transfers all samples to the limiting tie line at the nitrogen rich boundary Cr_2N + BN, equilibrium being reached after 75h of nitrogen exposure (Fig.6, [87Šmi]).

As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Cr in BN up to 1600°C, and mutual solubilities of the chromium borides, the chromium nitrides and BN up to 1600°C are rather restricted [80Kat,87Šmi].

THERMODYNAMICS

A thermodynamic modelling of the binary system Cr-B is due to [86Lia]; see Table 2. Thermodynamic data of the chromium nitrides are due to [76Fro] and [70Mil].

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[90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2nd Ed., Amer.Soc.Met., Metals Park,Oh, 1990.

Table 1: Solid phases in the system B-Cr-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Cr <1863°	cI2 $Im\bar{3}m$ W	a= 388.48	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
		a=1096.66 c=2385.14	[81Cre] at 2.4at%Cr
Cr_2B <1870°	oF40 Fddd o-Mn_2B	a=1470.6 b= 741.33 c= 425.35	[87Šmi]
Cr_5B_3 <1900°C	tI32 I4/mcm Cr_5B_3	a= 546.40 c=1011.0	[87Šmi]
T-CrB <1000°	tI16 Transpos.Type α-MoB-rel.	a=294.93 b= 786.4 c= 294.32	[87Šmi]
β-CrB <2095°	oC8 Cmcm CrB	a= 296.89 b= 786.89 c= 293.33	[87Šmi]
Cr_3B_4 <2075°	oI14 Immm Ta_3B_4	a= 298.56 b=1302.2 c= 295.25	[87Šmi]

Cr_2B_3	oC20 Cmcm V_2B_3	a= 302.64 b=1811.5	[87Oka]
CrB_2 <2200°	hP3 P6/mmm AlB_2	a= 297.32 c= 307.25	[87Šmi]
CrB_4 <1450°	oI10 Immm CrB_4	a= 474.99 b= 547.89 c= 286.82	[87Šmi]
Cr_2N	hP9 $P6_322$ $Mn_2N_{0.86}$	a= 479.6 c= 447.0	[85Vil] [87Smi]
CrN	cF8 $Fm\bar{3}m$ NaCl	a= 414.8	[87Šmi]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Cr-B-N

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 Cr	$\Delta_{fus}G(Cr) = 21004-9.6349\ T$	[86Lia]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 Cr	$\Delta_f G\ (Cr) = 0$	
0.3333 Cr_2B	$\Delta_f G\ (Cr_2B) = -28285-0.330\ T$	
0.1250 Cr_5B_3	$\Delta_f G\ (Cr_5B_3) = -36700-2.300\ T$	
0.5000 CrB	$\Delta_f G\ (CrB) = -39920+0.395\ T$	
0.1429 Cr_3B_4	$\Delta_f G\ (Cr_3B_4) = -40768-0.584\ T$	
0.3333 CrB_2	$\Delta_f G(CrB_2) = -41432+0.818\ T$	
0.2000 CrB_4	$\Delta_f G(CrB_4) = -24723+0.400\ T$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
Liquid(Cr,B)	$\Delta G^{ex} = x(1-x)\{-181050+35.66\ T + 52800(1-2x)+18600(1-2x)^2-$ $-34200(1-2x)^3+13700(1-2x)^4\}$	
0.3632 $Cr_2N_{0.76}$	$\Delta_f G = -30663.4+15.22\ T$	[76Fro]

Fig.1: The binary system Cr - B; based on [71Pra,86Mas] and [87Šmi].

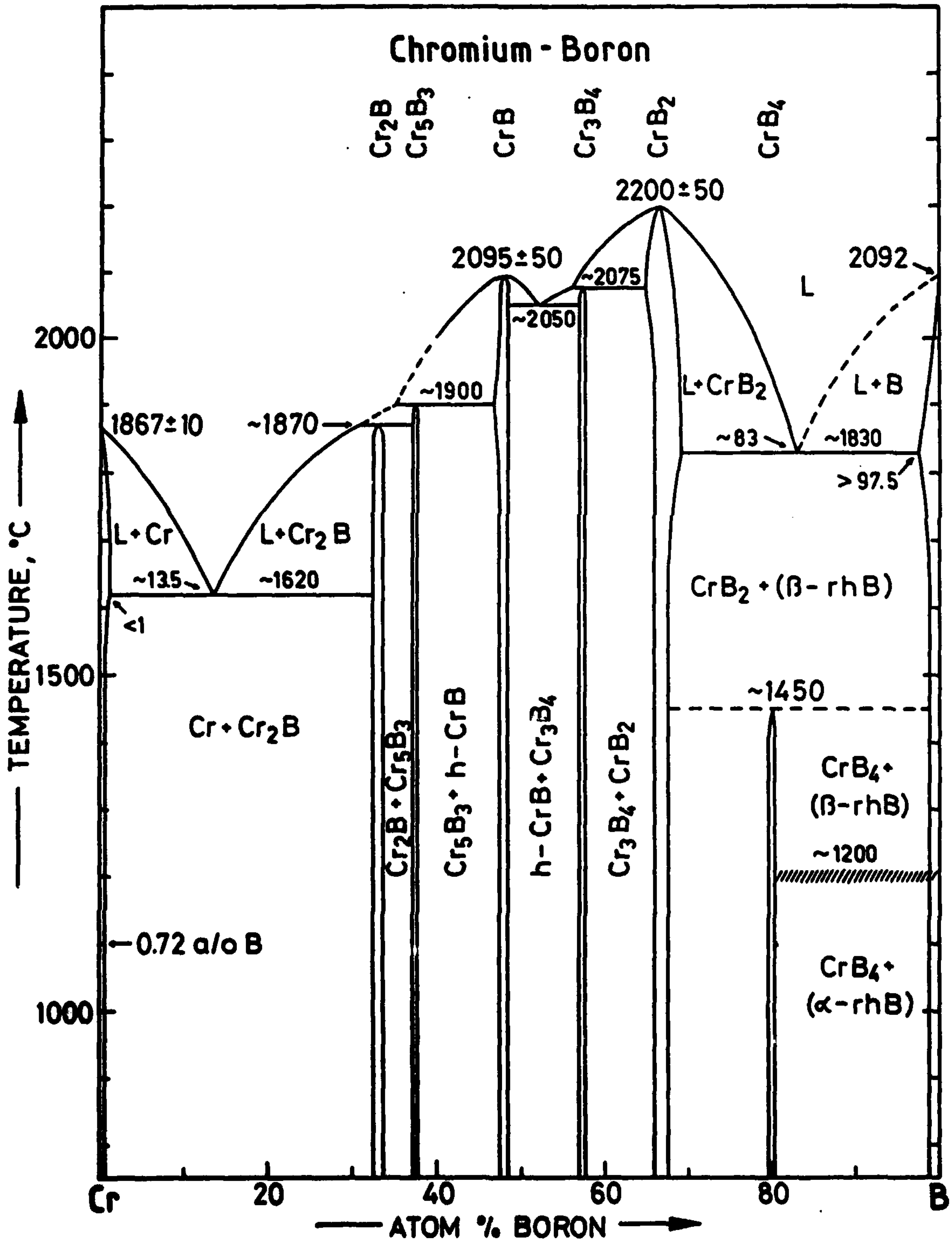


Fig.2: Isothermal section at 1600°C in the system Cr - B - N under 1 bar N_2 (after [80Kat])

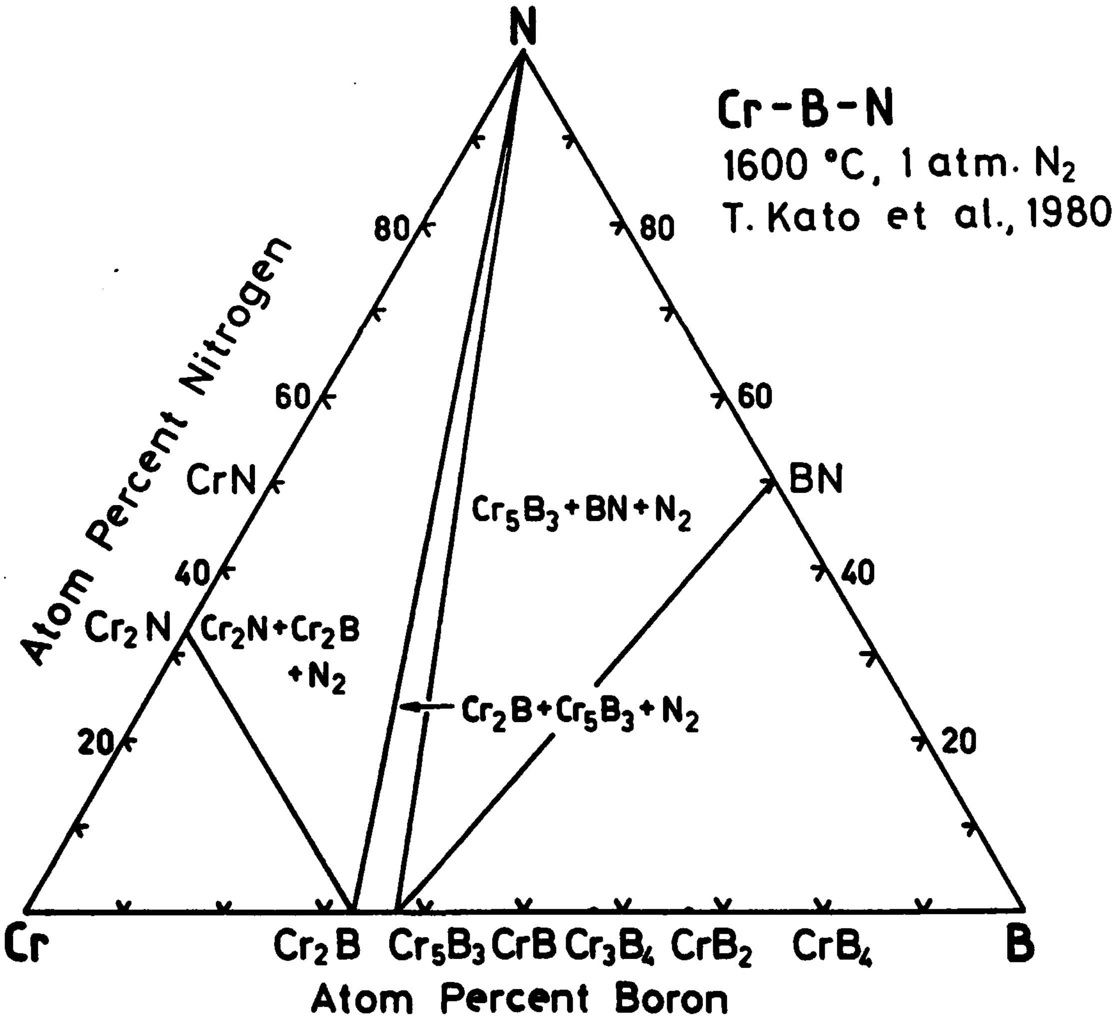


Fig.3: Isothermal section at 1000°C in the system Cr - B - N from samples sealed in quartz capillaries (in the absence of external nitrogen)

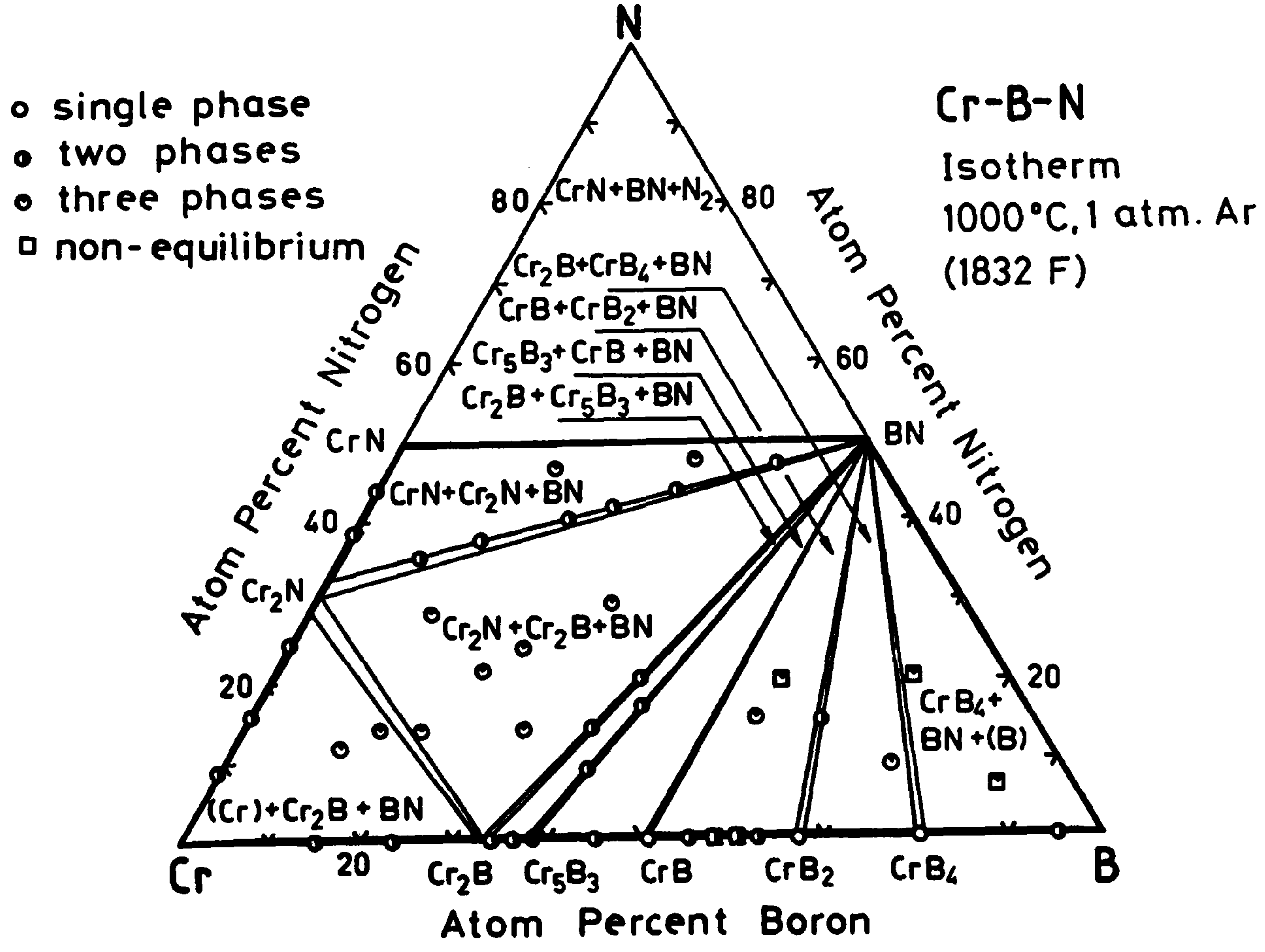


Fig.4: Isothermal section at 1000°C in the system Cr - B - N under a high vacuum (10^{-4}Pa)

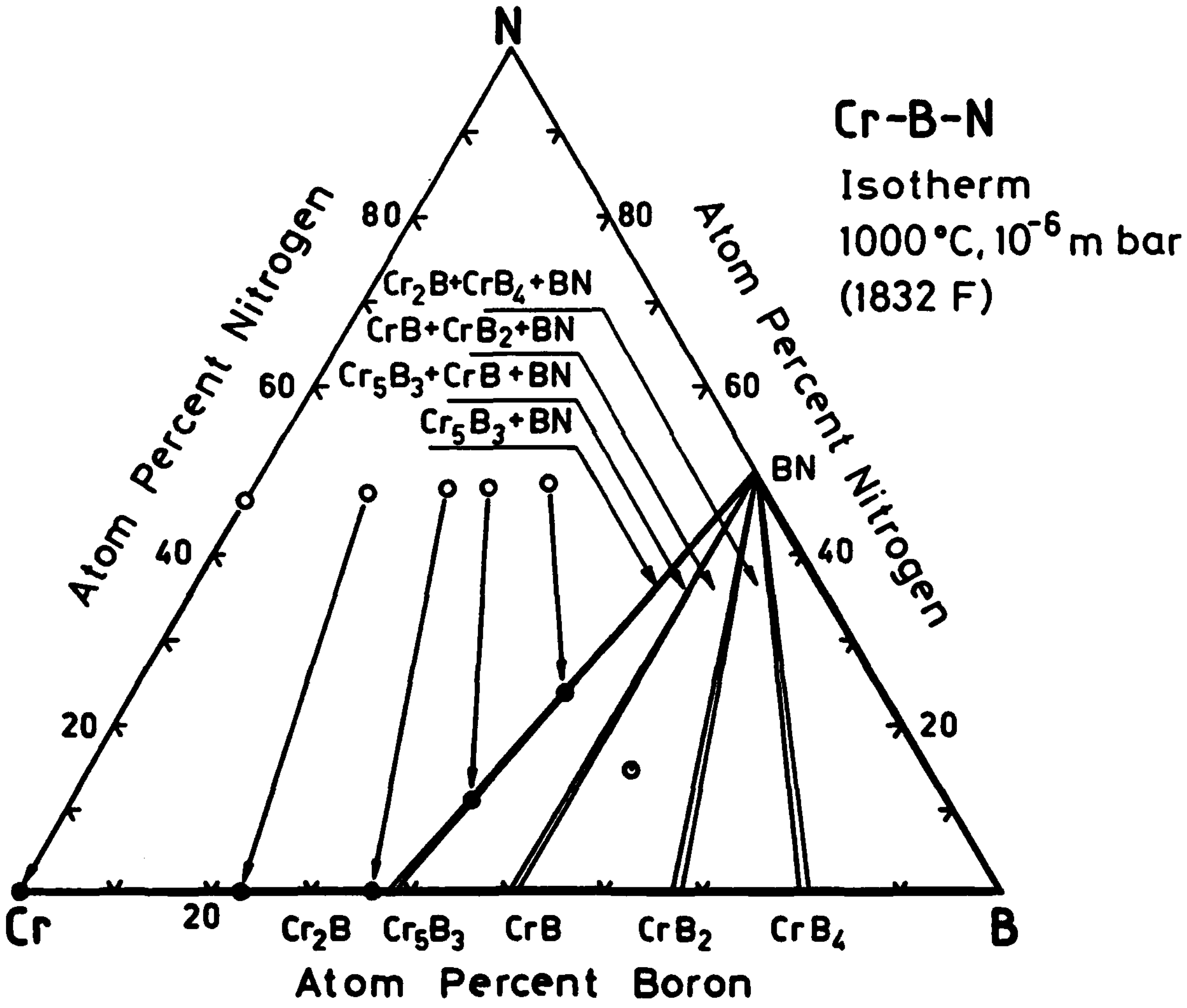


Fig.5: Isothermal section at 1400°C in the system Cr - B - N under 1 bar Ar (in the absence of external nitrogen pressure)

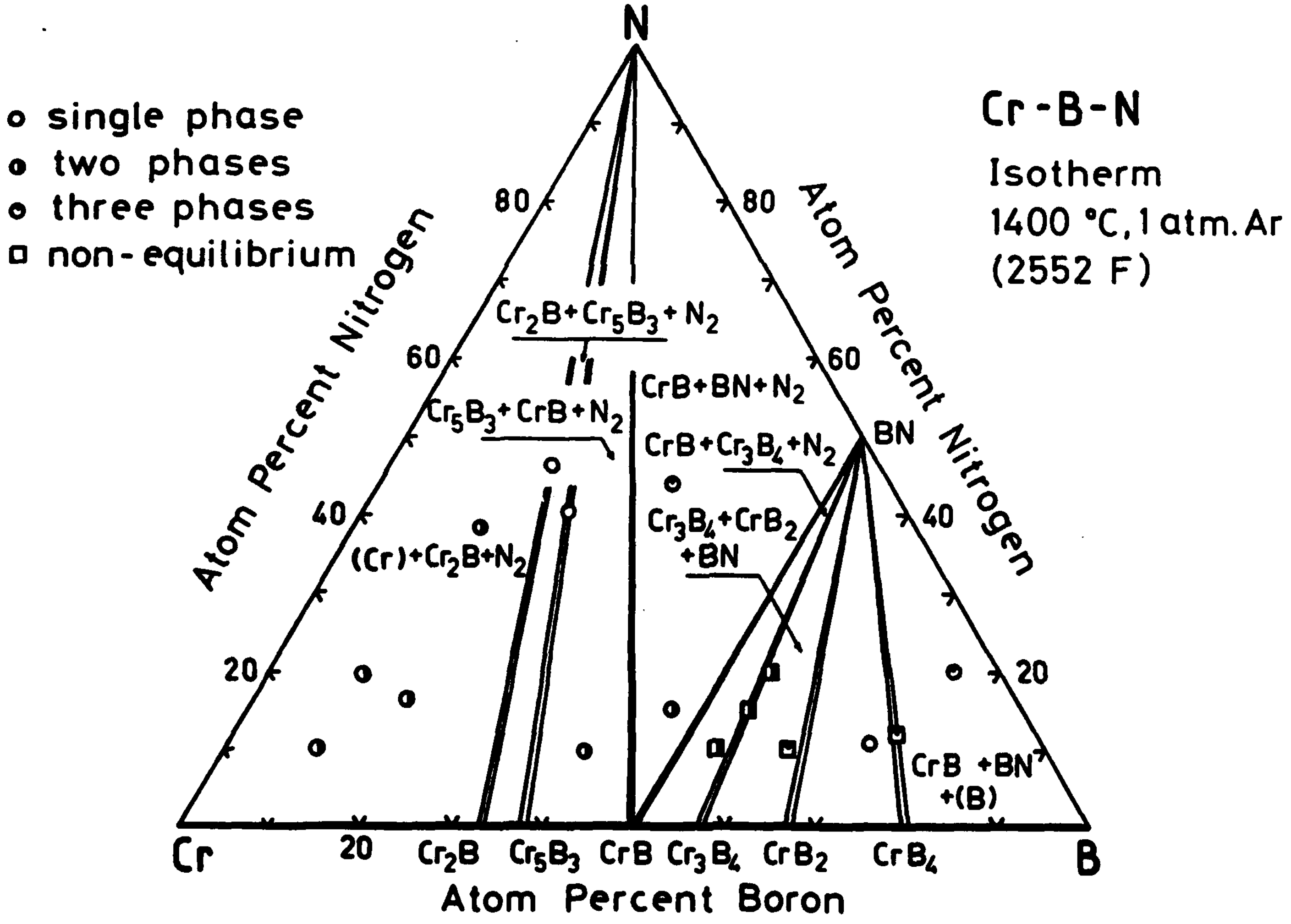
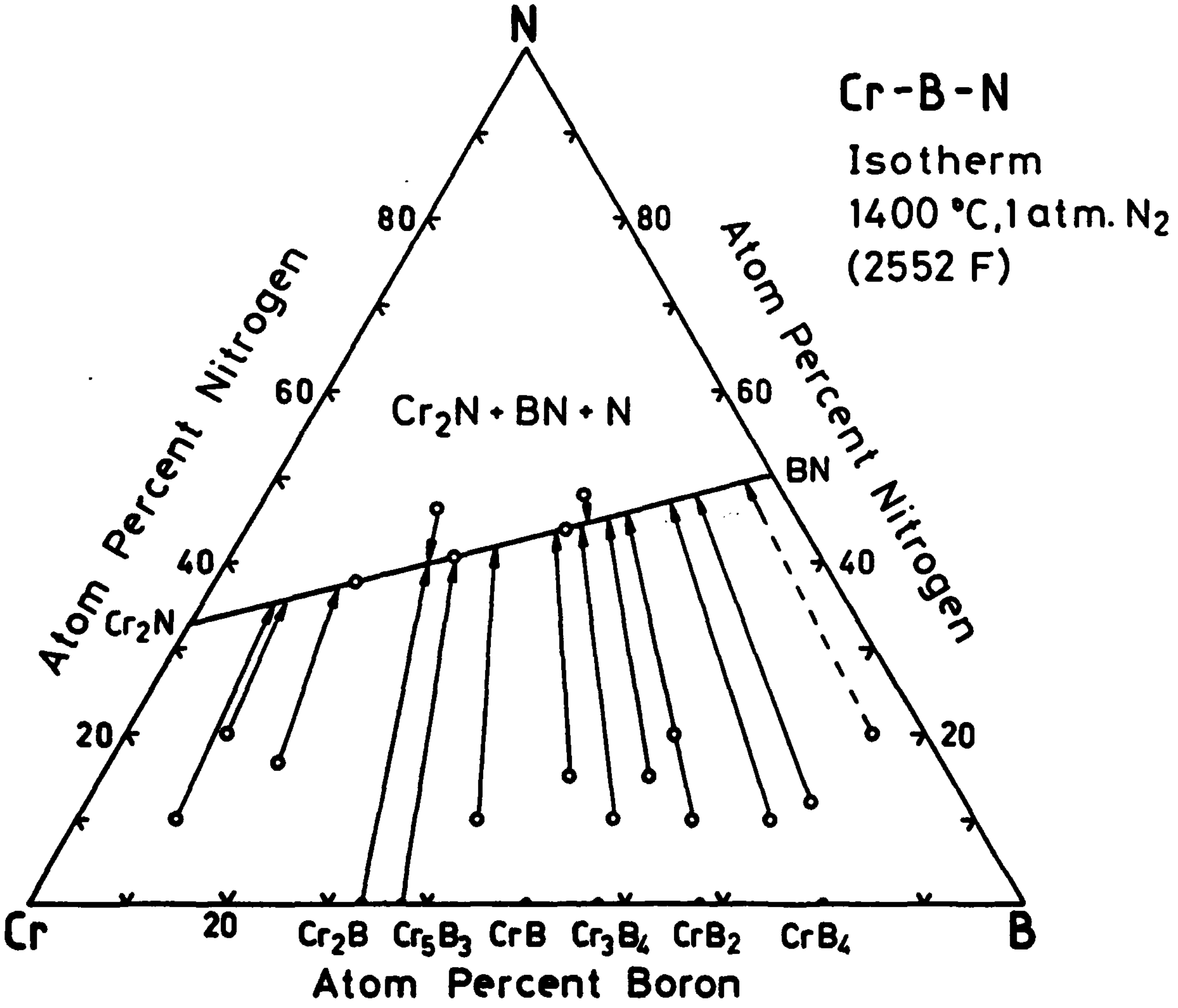


Fig.6: Isothermal section at 1400°C in the system Cr - B - N under 1 bar N_2



SYSTEM BORON- MOLYBDENUM - NITROGEN (B-Mo-N)

INTRODUCTION / EXPERIMENTAL

Informations on the Mo-B-N ternary are due to [89Bae1,2] (see section *Thermodynamics*)) and [88Kle].

Phase equilibria in the B-Mo-N system have been established at 1200°, 1400°, and 1600°C from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Mo,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [88Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 36h followed by a final reaction at 1200°C or 1400°, 1600°C respectively for up to 64h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled.Starting materials were powders of 3N-Mo, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Kle].

BINARY SYSTEMS

The reinvestigation of the B-Mo system in the range from 1200 to 1600°C revealed consistency with the data available in [84Vil], and [90Mas] amended by mass spectrometer data of [77Sto] determining the homogeneous ranges of the molybdenum borides. The solid solubility of boron in molybdenum was claimed to be less than 2 at%B at the Mo-Mo_2B eutectic temperature (2175°C); an interstitial type of B-solubility was suggested [65Rud]. The maximum solid solubility of Mo in β-B was reported to be less than 0.5 at% Mo at ~1800°C [65Rud] in agreement with X-ray data by [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Mo-B.

The phase diagram for the system Mo-N in [90Mas] is based on the original diagrams of [70Ett] and [78Jeh]; a critical assessment including the region below 1000°C is due to [80Bre]. The binary molybdenum nitrides are unstable at $T > 1000°C$ and $p(N_2) < 10^5$ Pa [78Jeh]. A detailed discussion of solubility data , physical properties and thermodynamic data is found in [78Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2-4 represent the isothermal sections at 1200°C, 1400°C and 1600°C under 1 bar of argon (in the absence of external nitrogen pressure) [88Kle]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher molybdenum borides and BN. Phase equilibria were found to be rather dependent on the nitrogen partial pressure. The stability of the (Mo + BN)- and the (Mo_2B+BN)-two phase equilibria as a function of T and $p(N_2)$ were investigated [88Kle] in good agreement to earlier data by [69Bae1,2] and confirm the observed phase equilibria (see also section *Thermodynamics*). Thus at 1200°C and under 1 bar Ar (Mo + BN) decomposes to $Mo_2B + N_2$, and similarly at higher temperatures (1400, 1600°C) the subboride Mo_2B becomes incompatible with BN and decomposes under formation of MoB + N_2 [88Kle]. Phase equilibria were furthermore checked at 1400°C applying a vacuum of 10^{-4}Pa for 100h revealing a rapid decomposition of (Mo+BN) starting compositions into Mo_2B, MoB, and MoB+BN [88Kle]. The kinetic of nitriding binary molybdenum borides was studied at 1200 and 1400°C under 1 bar of $6N$-N_2 and confirmed the phase equilibria in Figs.2-4 [88Kle].

As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Mo in BN up to 1000°C, and mutual solubilities of the molybdenum borides and BN up to 1600°C are rather restricted [88Kle].

THERMODYNAMICS

A thermodynamic modelling of the binary system Mo-B is due to [88Spe]; see Table 2.

[69Bae1,2] studied the reaction of Mo and BN using a Thermobalance. From these measurements the activation energies for the formation of the binary borides were derived. Furthermore the onset of the reaction 2Mo + BN ======= Mo_2B + $1/2N_2$ was measured as a function of the nitrogen partial pressure yielding free enthalpy data for the reaction and data for the free enthalpy of formation for Mo_2B.

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Table 1: Solid phases in the system B-Mo-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Mo <2623°	cI2 $Im\bar{3}m$ W	a= 314.70	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
		a=1093.03 c=2382.17	[81Cre] at 0.5at%Mo
Mo_2B <2280°	tI12 I4/mcm Al_2Cu	a= 554.80 c= 474.06	[88Kle]
α-MoB <2180°	tI16 $I4_1/amd$ α-MoB	a= 310.68 c=1696.18	[88Kle]
β-MoB <2600°	oC8 Cmcm CrB	a= 314.02 b= 848.90 c= 307.10	[88Kle]
MoB_2 2375-1517°	hP3 P6/mmm AlB_2	a= 303.78 c= 306.03	[88Kle]
Mo_2B_5 <2140°	hR7 $R\bar{3}m$ Mo_2B_5	a= 301.17 c=2094.9	[88Kle]
$Mo_{1-x}B_3$ <1807°	hP $P6_3/mmc$ $W_{1-x}B_3$	a= 520.36 c= 635.02	[88Kle]
β-Mo_2N <850°	tI12 $I4_1/amd$ Mo_2N	a= 420. c= 801.	[85Vil]

γ-Mo_2N <1950°	oF8 $Fm\bar{3}m$ NaCl-defect	a= 416.5	[85Vil]
δ-MoN	hP16 $P6_3/mmc$ MoN	a= 572.5 c= 560.8	[85Vil] >0.085 GPa
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Mo-B-N

Phase	$\Delta_f G$ (J/gramatom)		Ref.
1.0000 Mo	$\Delta_{fus}G(Mo)$	$= 37479.8-12.942\ T$	[88Spe
1.0000 B	$\Delta_{fus}G(B)$	$= 50210-21.23\ T$	
1.0000 Mo	$\Delta_f G\ (Mo)$	$= 0$	
0.3333 Mo_2B	$\Delta_f G\ (Mo_2B)$	$= -42860+2.43\ T$	
0.5000 MoB	$\Delta_f G(MoB)$	$= -53170+0.47\ T$	
0.3769 $MoB_{1.653}$	$\Delta_f G(MoB_{1.653})$	$= -45680-0.22\ T$	
0.3170 $MoB_{2.155}$	$\Delta_f G(MoB_{2.155})$	$= -50940+4.27\ T$	
0.2079 $MoB_{\sim 3.81}$	$\Delta_f G(MoB_{\sim 3.81})$	$= -34107+3.13\ T$	
1.0000 βB	$\Delta_f G\ (\beta B)$	$= 0$	
Liquid(Mo,B)	$\Delta G^{ex} = x(1-x)\{-148435+10.90\ T + 21000(1-2x)+25305(1-2x)^2\}$		
0.3333 Mo_2N	$\Delta_f G(Mo_2N)$	$= -19107.4+17.97\ T$	[76Fro]

Fig.1: The binary system Mo - B; based on [65Rud,77Sto] and [88Kle].

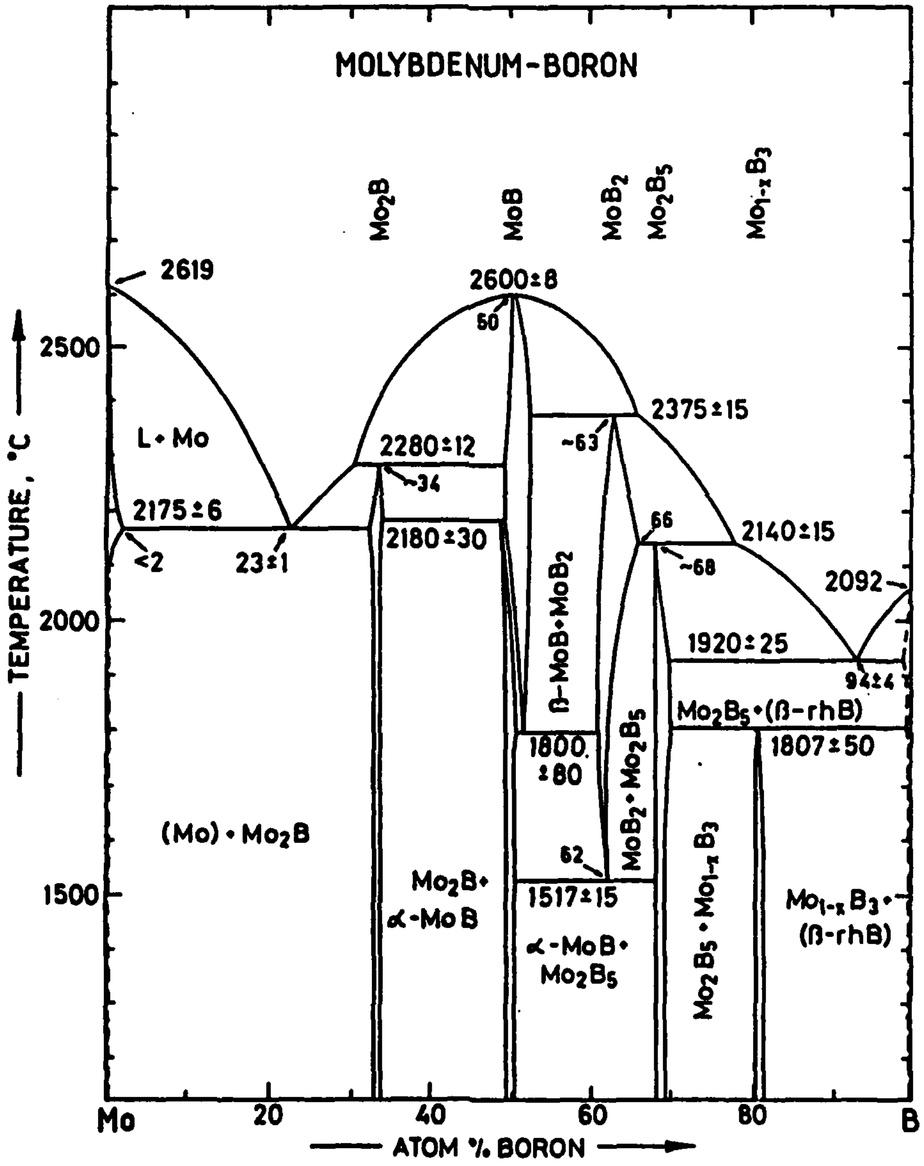


Fig.2: Isothermal section at 1200°C in the system Mo - B - N under Ar (in the absence of external nitrogen)

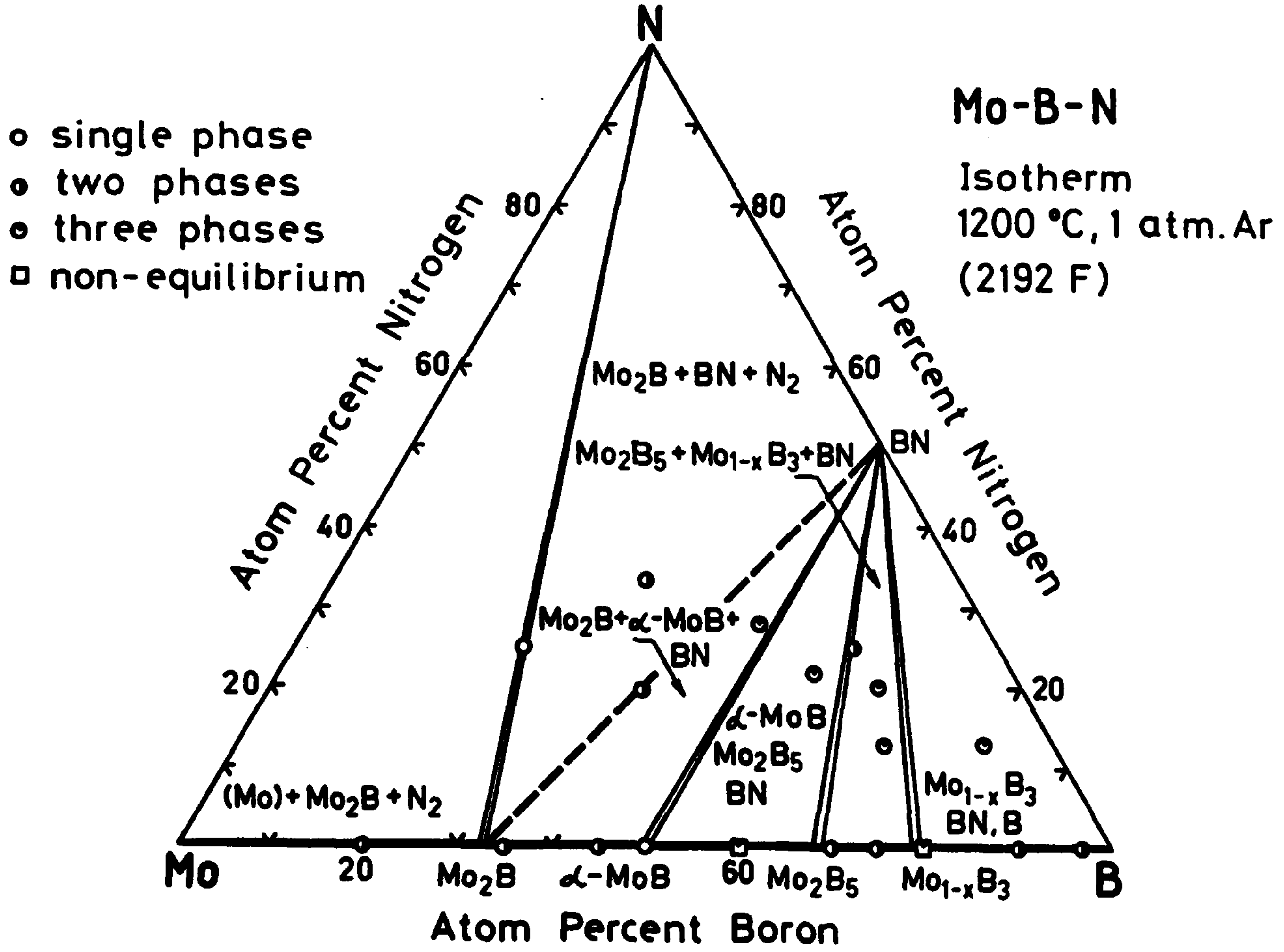


Fig.3: Isothermal section at 1400°C in the system Mo - B - N under Ar (in the absence of external nitrogen)

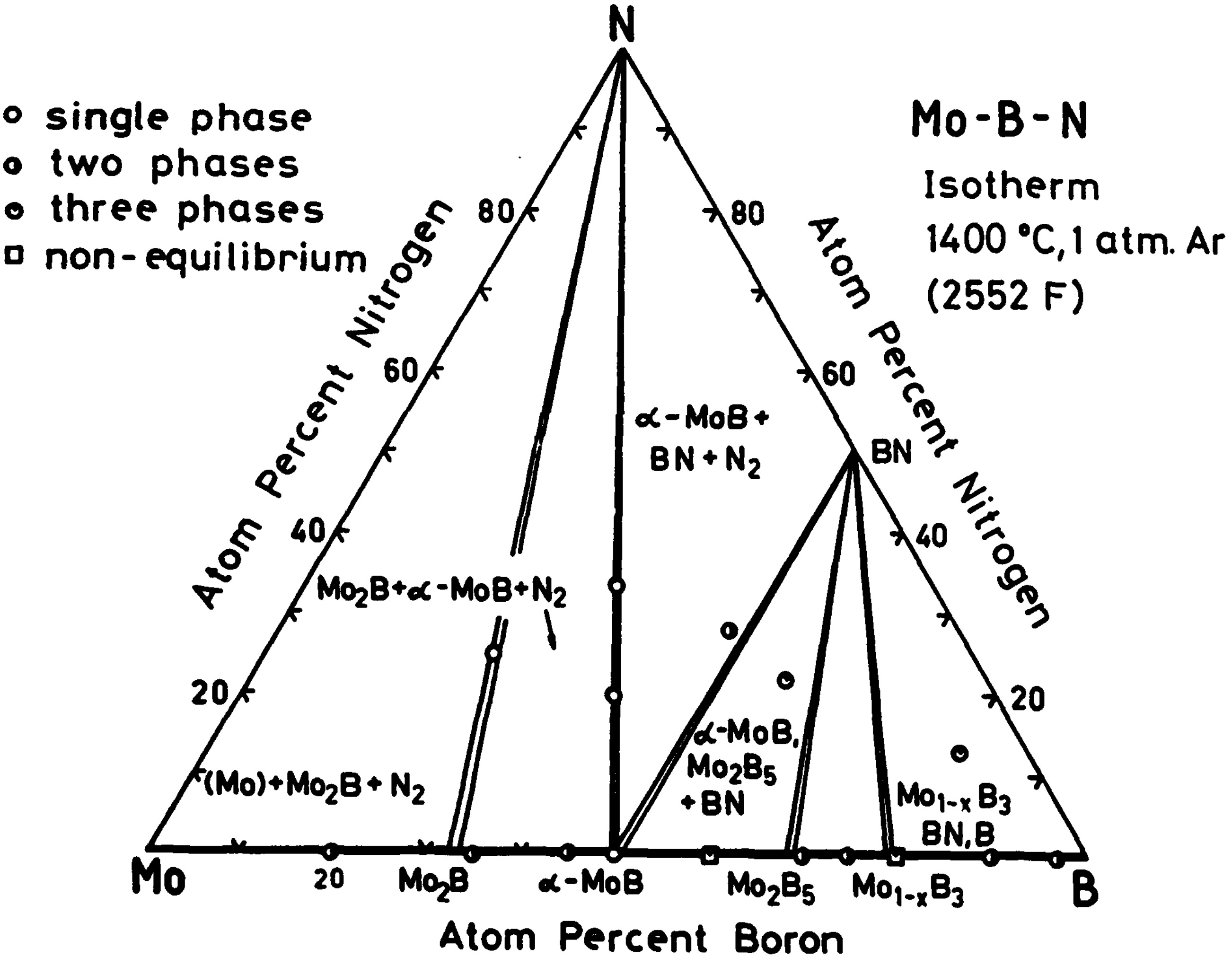
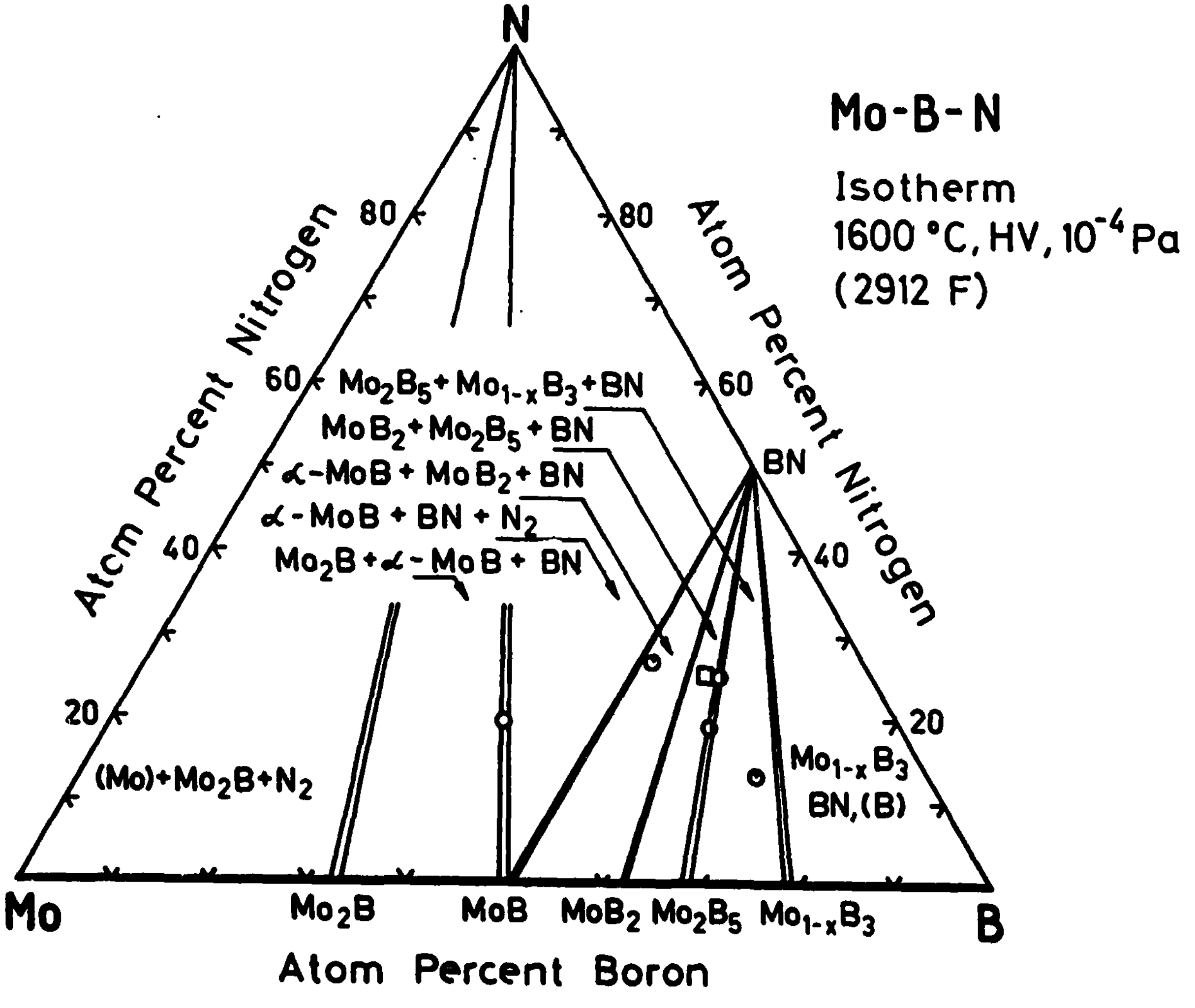


Fig.4: Isothermal section at 1600°C in the system Mo - B - N under Ar.(in the absence of external nitrogen)



SYSTEM BORON- TUNGSTEN - NITROGEN (B-W-N)

INTRODUCTION / EXPERIMENTAL

Informations on the W-B-N ternary are due to [51Kis], [69Bae1,2] (see section *Thermodynamics*)) and [88Kle].

The thermal stability of the binary tungsten borides was investigated in a dry stream of ammonia at temperatures below 1100°C by [51Kis]. The resistance against attack by ammonia was found to increase with the boron content and no mutual solid solubility was observed [51Kis].

Phase equilibria in the B-W-N system have been established at 1200°, 1400°, and 1600°C from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, W ,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [88Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 96h followed by a final reaction at 1200°C (or 1400°, 1600°C respectively)for up to 70h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled.Starting materials were powders of 3N-W, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Kle].

BINARY SYSTEMS

The reinvestigation of the B-W system in the range from 1200 to 1600°C revealed consistency with the data available in [84Vil], and [90Mas]. The maximal solid solubility of boron in tungsten was claimed to be less than 1 at%B at the W-W_2B eutectic temperature (2600°C); an interstitial type of B-solubility was suggested [65Rud]. The maximum solid solubility of W in β-B was reported to be less than 0.5 at% W at ~1800°C [85Rud] in agreement with X-ray data by [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram W-B.

No phase diagram is available for the system W-N ; a critical assessment is due to [89Wri]. The binary tungsten nitrides are unstable at T > 1000°C and $p(N_2) < 10^5$ Pa [89Wri]. A detailed discussion of solubility data , physical properties and thermodynamic data is found in [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2-4 represent the isothermal sections at 1200°C, 1400°C and 1600°C under 1 bar of argon (in the absence of external nitrogen pressure) [88Kle]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher tungsten borides and BN. Phase equilibria were found to be rather dependent on the nitrogen partial pressure. The stability of the (W + BN)- and the (W_2B + BN)-two phase equilibria as a function of T and $p(N_2)$ were investigated [88Kle] in good agreement to earlier data by [51Kis], [69Bae1,2] and confirm the observed phase equilibria (see also section *Thermodynamics*). Thus at 1200 and 1400°C and under 1 bar Ar (W + BN) decomposes to $W_2B + N_2$, and similarly at higher temperatures (1600°C) the subboride W_2B becomes incompatible with BN and decomposes under formation of WB + N_2 [88Kle]. Phase equilibria were furthermore checked at 1400°C applying a vacuum of 10^{-4}Pa for 100h revealing a rapid decomposition of (W+BN) starting compositions into W_2B, WB, and WB+BN [88Kle]. The kinetic of nitriding binary tungsten borides was studied at 1200 and 1400°C under 1 bar of $BN-N_2$ and confirmed the phase equilibria in Figs.2-4 [88Kle].

As seen from a comparision of the unit cell dimensions there is no significant solid solubility of W in BN up to 1000°C, and mutual solubilities of the tungsten borides and BN up to 1600°C are rather restricted [88Kle].

THERMODYNAMICS

A calculation of the W-B binary system was attempted by [84Kau]; see Table 2.

[68Bae1,2] studied the reaction of W and BN using a Thermobalance. From these measurements the activation energies for the formation of the binary borides were derived. Furthermore the onset of the reaction 2 W + BN ======= $W_2B + 1/2N_2$ was measured as a function of the nitrogen partial pressure yielding free enthalpy data for the reaction and data for the free enthalpy of formation for W_2B.

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[90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2nd Ed., Amer.Soc.Met., Metals Park,Oh, 1990.

Table 1: Solid phases in the system B-W-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
W	cI2	a= 316.52	[90Mas]
<3422°	$Im\bar{3}m$		
	W		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
		a=1093.82	[81Cre] at 0.5at%W
		c=2383.56	
W_2B	tI12	a= 556.50	[88Kle]
<2670°	I4/mcm	c= 474.32	
	Al_2Cu		
α-WB	tI16	a= 310.09	[88Kle]
<2170°	$I4_1/amd$	c=1695.6	
	α-MoB		
β-WB	oC8	a= 314.2	[65Rud]
<2665°	Cmcm	b= 850.6	
	CrB	c= 306.5	
W_2B_5	hP14	a= 298.45	[88Kle]
<2365°	$P6_3/mmc$	c=1387.3	
	W_2B_5		
$W_{1-x}B_3$	hP	a= 519.76	[88Kle]
<2020°	$P6_3/mmc$	c= 633.51	
	$W_{1-x}B_3$		
W_2N	cF8	a= 412.6	[85Vil]
	$Fm\bar{3}m$		
	NaCl		
δ-WN	hP2	a= 289.3	[85Vil]
	$P\bar{6}m2$	c= 282.6	
	WC		

BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system W-B-N

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 W	$\Delta_{fus}G(W) = 52313.69-14.158\ T$	[84Kau]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 W	$\Delta_f G\ (W) = 0$	
0.3333 W_2B	$\Delta_f G\ (W_2B) = -41783+1.406\ T$	
0.5000 WB	$\Delta_f G(WB) = -54392+1.125\ T$	
0.7140 W_2B_5	$\Delta_f G(W_2B_5) = -55229+2.564\ T$	
0.8000 $WB_{\sim 4}$	$\Delta_f G(WB_{\sim 4}) = -41840+2.075\ T$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
Liquid(W,B)	$\Delta\ G^{ex} = x(1-x)\{-75312-215058\ x\ -8.368\ T\}$	

Fig.1: The binary system W - B; based on [65Rud]

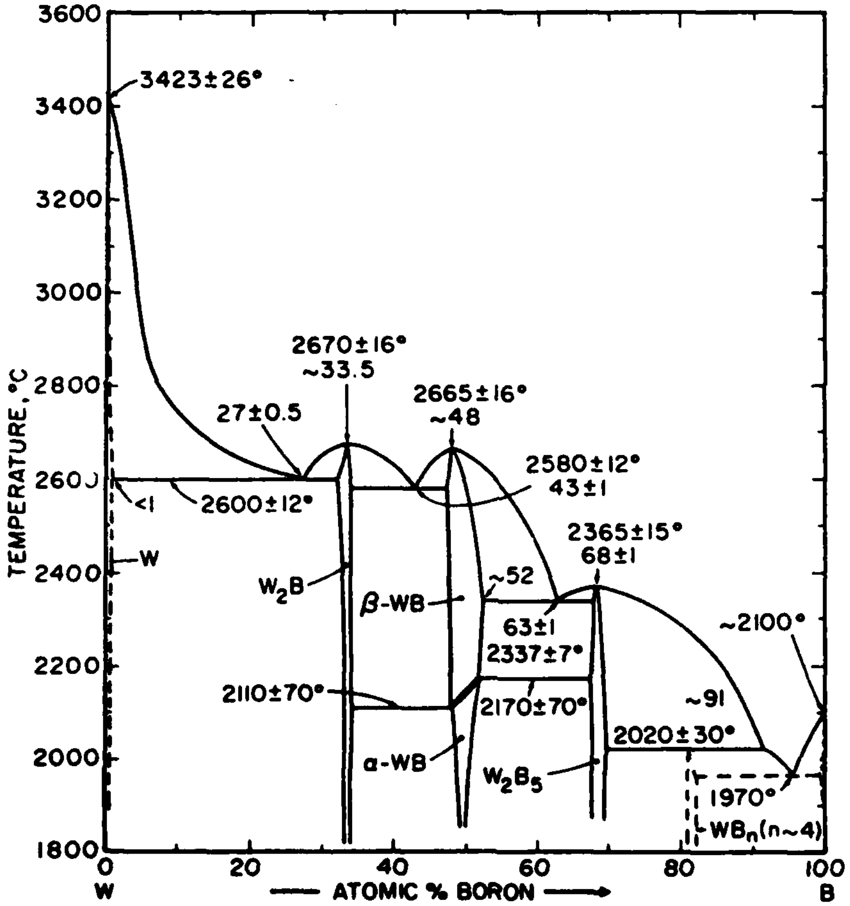


Fig.2: Isothermal section at 1200°C in the system W - B - N under Ar (in the absence of external nitrogen)

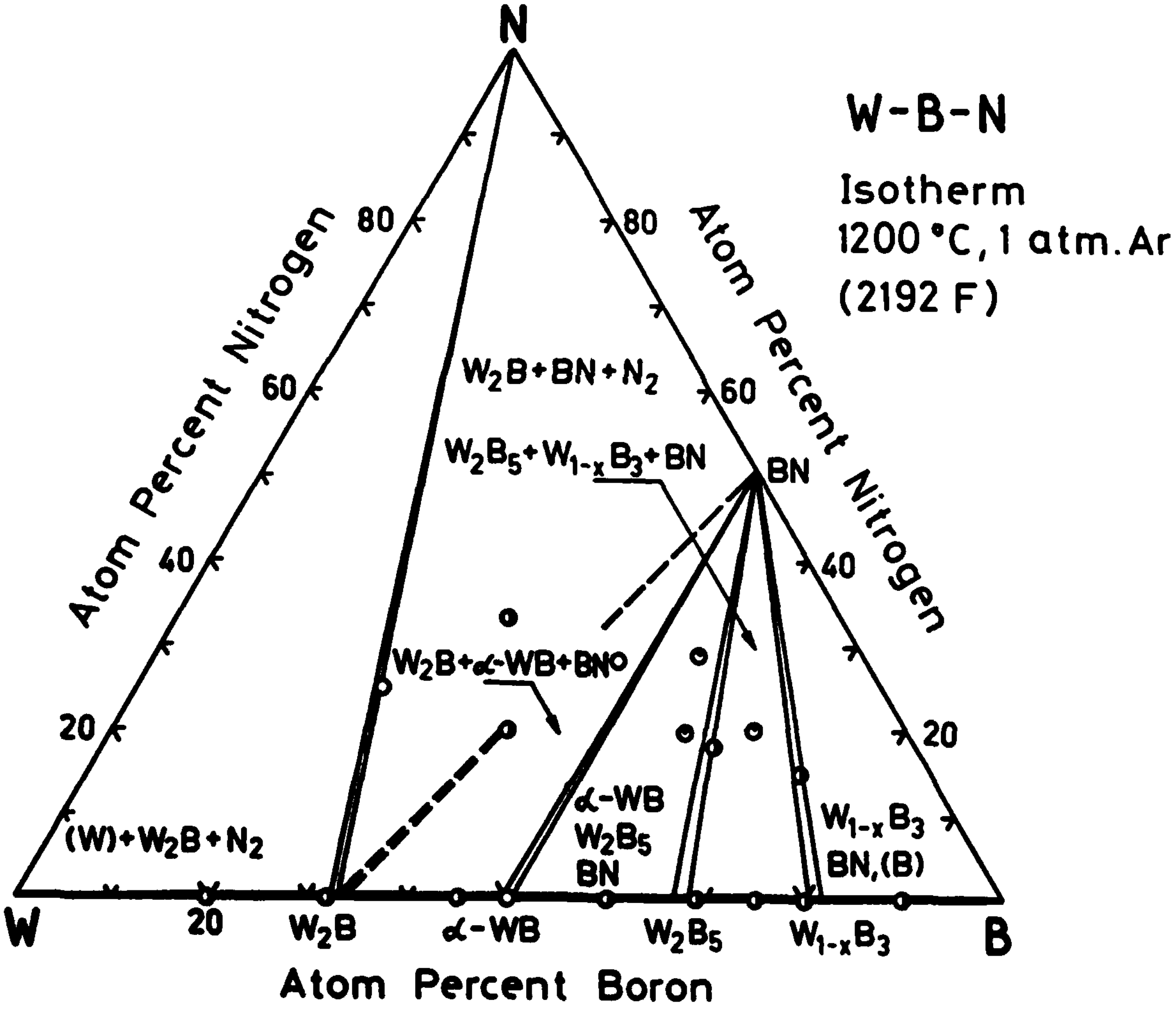


Fig.3: Isothermal section at 1400°C in the system W - B - N under Ar (in the absence of external nitrogen)

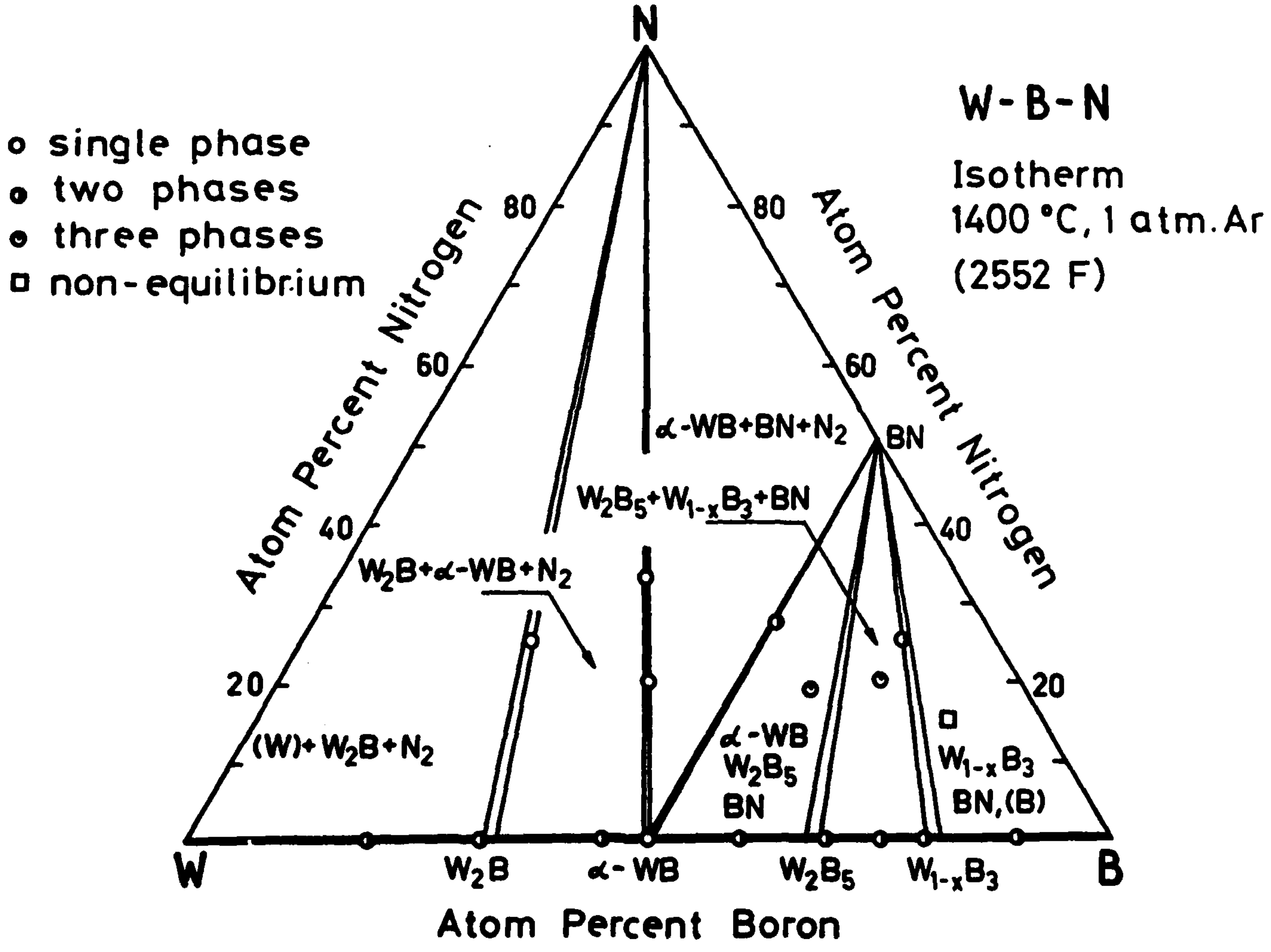
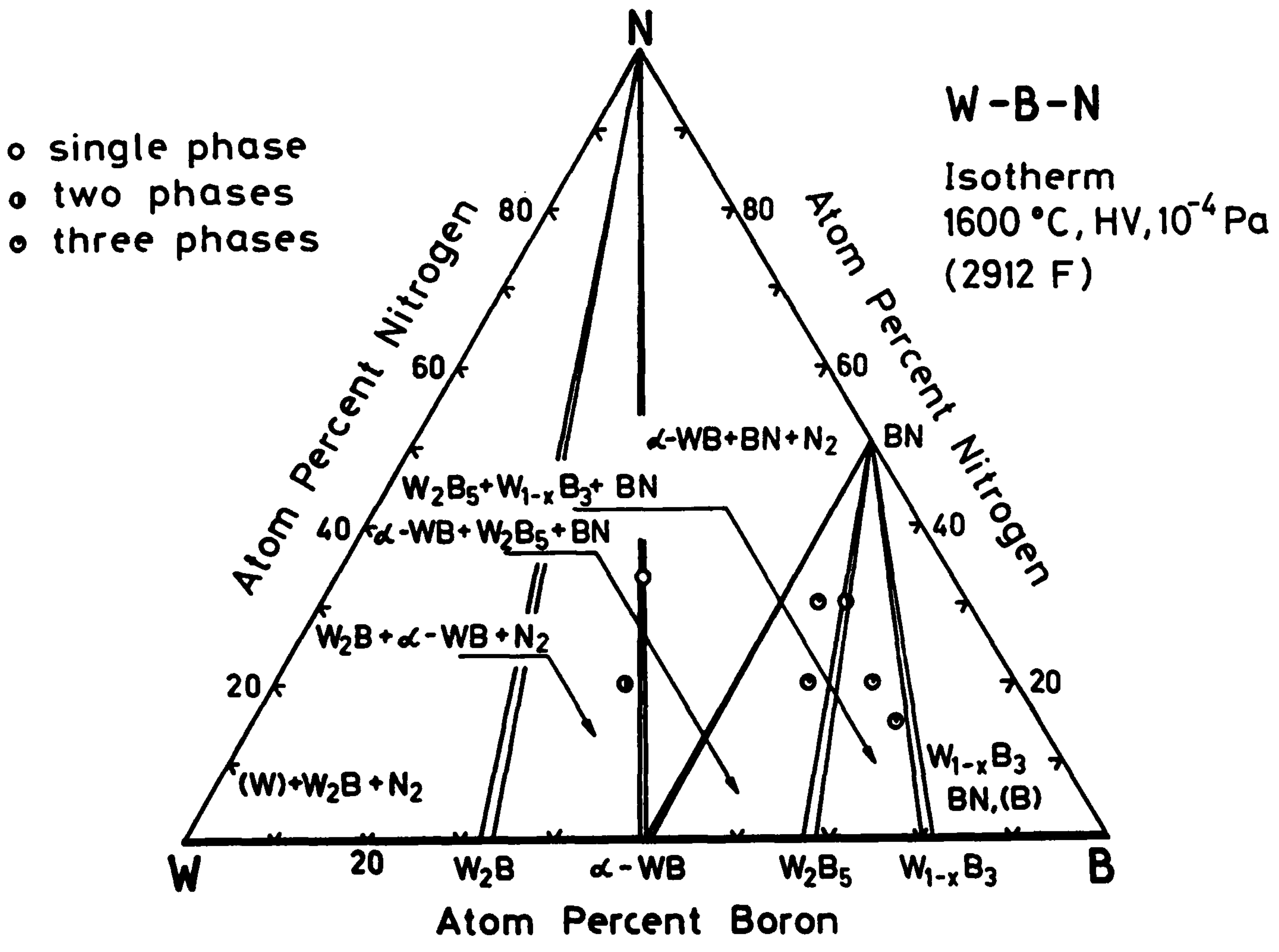


Fig.4: Isothermal section at 1600°C in the system W - B - N under Ar (in the absence of external nitrogen)



SYSTEM BORON- MANGANESE- NITROGEN (B-Mn-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Mn-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Mn, Mn_2N, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [89Šmi]. Annealing of the samples was either performed (a) in vacuum sealed silica tubes using a thin molybdenum foil to protect the sample from direct contact with the hot quartz wall or (b) in a 1 MHz-HF furnace under 1 bar of 5N-Ar or under various partial pressures of 5N-N_2 using hex-BN substrates in a tungsten or molybdenum susceptor crucible. Heat treatments usually consisted of a primary reaction at 900°C for 72 to 120h followed by a final reaction at 900°C up to 700h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were either monitored by calibrated microoptical pyrometry or by thermocouples; after heat treatment the samples were radiation cooled (HF-furnace) or quenched in water (silica capsules). Some of the samples were quenched in liquid nitrogen. In-situ high temperature X-ray data were recorded under Ti-gettered He using a W-sheet metal substrate and Au-powder as internal standard [89Šmi].

The starting materials were powders from 3N-Mn plates, surface cleaned in dilute HCl prior to use, powders of 99 % Mn_2N, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth or by direct sintering under argon; weight losses were checked to be within 1 wt% [89Šmi].

BINARY SYSTEMS

The reinvestigation of the B-Mn system from as-cast alloys and in the range from 800 to 1250°C confirmed the existence of six binary manganese borides [89Šmi]. In contrast to earlier data there is essential consistency with the data available from a recent compilation by [86Lia]. The low temperature modification of α-MnB was unambiguosly revealed to be CrB-type from X-ray diffactometry of single crystals grown by iodine vapour transport [89Šmi]. Homogeneous ranges of the binary borides at 900°C were found to be rather small except for MnB_2 indicating a typical "line-compound" type of character. The solid solubility of boron in the various allotropes of manganese (interstitial type) was claimed to be less than 0.5 to 1.0 at%B. From X-ray powder analysis the maximum solid solubility of Mn in β-B was concluded to be about 4.2 at%Mn at 1800°C. An extensive discussion of the Mn-B phase diagram has been recently published by [89Šmid]; for crystallographic data see Table 1.Fig.1 represents the critically assessed version of the Mn-B phase diagram, temperature versus concentration [89Šmi].

The reinvestigation of the phase relations in the Mn-rich part of the Mn-N diagram [89Šmi] revealed consistency with a critical assessment of the Mn-N diagram as presented by [90Gok]. It shall be mentioned, however, that the formation of the socalled δ′-phase (bct. martensitic transformation from the fcc-(Mn,N) γ-phase) was observed in all samples quenched from 900°C in water [89Šmi].

The maximum solid solubility of N in Mn was said to be smaller than 0.5 at% N for α-Mn, 2 at% N for β-Mn and 11 at% N for γ-Mn at 790°C [90Gok].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 represent the isothermal section at 900°C under 1 bar of argon (in the absence of external nitrogen pressure) [89Šmi]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between manganese and the binary manganese-borides and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Mn in BN at 900°C, and mutual solubilities of the manganese nitrides, the manganese borides and BN are rather restricted [89Šmi]. Due to insufficient quenching, the Mn_4N-phase is present in the 900°C section.

Phase equilibria in the Mn,N-rich region of the ternary system are rather dependent on the nitrogen partial pressure. According to the thermodynamic stability of the binary manganese nitrides , prolonged heating of ζ-Mn_2N at 900°C in a dynamic vacuum of 3.10^{-4}Pa resulted in a successive decomposition into lower nitrides (after 40 h) towards the nitrogen rich end of the (Mn) solid solution (after 80 h). In all ternary samples which had been reacted at 900°C under 10^5Pa N_2 prior to heat treatment in high vacuum, the (Mn) solid solution and all manganese borides revealed compatibility with respect to BN_{hex}. The reaction paths as well as the distribution of the phase fields at 900°C and under a high vacuum are presented in Fig.3.

X-ray analysis of alloys representing the (Mn + BN) twophase equilibrium which subsequently were held for 1 h at 1350°C under Ar, revealed instability with respect to decomposition into (Mn) + Mn_2B + N_2.

A detailed discussion of the phase relations in the Mn-B-N ternary is found in [89Šmi].

THERMODYNAMICS

A thermodynamic modelling of the binary system Mn-B is due to [86Lia] including a critical assessment of earlier attempts to calculate the phase diagram; see Table 2.

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Table 1: Solid phases at 900°C in the system B-Mn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments	
α-Mn <727°	cI58 I$\bar{4}$3m α-Mn	a= 891.39	[90Gok] [89Gok]	at RT
β-Mn 1100-727°	cP20 P$4_1$32 β-Mn	a= 631.51	[90Gok] [89Gok]	at RT
γ-Mn 1138-1100°	cF4 Fm$\bar{3}$m γ-Mn	a= 386.3	[90Gok] [89Gok]	at 1100°C
δ-Mn 1246-1138°	cI2 Im$\bar{3}$m W	a= 308.1	[90Gok] [89Gok]	at 1136°C
β-rhB	hR111 R$\bar{3}$m β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]	
		a=1099.07 c=2399.64	[85Vil]	at $MnB_{\sim 23}$
o-Mn_2B <~1285°	oF40 Fddd o-Mn_2B	a=1455.7 b= 728.7 c= 420.7	[89Šmi]	
t-Mn_2B <1580°	tI12 I4/mcm Al_2Cu	a= 514.8 c= 420.4	[89Šmi]	
α-MnB <1050°	oP8 Cmcm	a= 302.34 b= 767.59	[89Šmi]	

	CrB	c= 295.68		
β-MnB	oP8	a= 414.8	[89Šmi]	
1890-1050°	Pbnm	b= 555.6		
	FeB	c= 297.7		
Mn_3B_4	oI14	a= 303.4	[89Šmi]	
<1750°	Immm	b=1282.2		
	Ta_3B_4	c= 296.3		
MnB_2	hP3	a= 300.89	[86Lia]	
1990-1075°	P6/mmm	c= 303.84		
	AlB_2			
MnB_4	mC14	a= 548.5	[89Šmi]	
<1375°	C2/m	b= 537.5		
	MnB_4	c= 294.5		
		β=122.47°		
δ'-(Mn,N)	tI2	a= 267.2	[89Šmi]	
	I4/mmm	c= 355.0		
Mn_4N	cP5	a= 382.7	[89Šmi]	
<890°	$Fm\bar{3}m$			
	Fe_4N			
β-Mn_2N_{1-x}	hP3	a= 276.73	[89Šmi]	
	$P6_3/mmc$	c= 452.12		
	Fe_2N			
α-Mn_2N_{1-x}	hP12	a= 489.16	[89Šmi]	
	$P6_322$	c= 455.45		
	$Mn_2N_{0.86}$			
Mn_2N	oP12	a= 485.52	[89Šmi]	
	$C222_1$	b= 840.88		
	Mn_2N	c= 453.27		
Mn_2N	oP12	a= 566.8	[89Šmi]	
	Pbna	b= 490.9		
	Mo_2C	c= 453.7		
hP-Mn_3N_2	tI6	a= 297.4	[89Šmi]	at 0.6 GPa
	I4/mmm	c=1212.6		400°C
	ThH_2			
α-Mn_6N_5	tI4	a= 298.02	[89Šmi]	at 47.9at%N
<410°	I4/mmm	c= 414.8		
	NaCl-deriv.			

β-Mn$_6$N$_5$ >410°	cF8 $Fm\bar{3}m$ NaCl	a= 422.5	[89Šmi]
BN$_{hex}$	hP5 P6$_3$/mmc BN$_{hex}$	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Mn-B (after [86Lia])

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 Mn	$\Delta_{fus}G(\mathrm{Mn}) = 12908.94-8.4984\ T$	[86Lia]
1.0000 B	$\Delta_{fus}G(\mathrm{B}) = 50210-21.23\ T$	
1.0000 αMn	$\Delta_f G\ (\alpha\mathrm{Mn}) = 0$	
1.0000 βMn	$\Delta_f G\ (\gamma\mathrm{Mn}) = 1908.32-1.3525\ T$	
0.3333 Mn$_2$B	$\Delta_f G(\mathrm{Mn_2B}) = -31254+0.293\ T$	
0.5000 MnB	$\Delta_f G(\mathrm{MnB}) = -36225+0.439\ T$	
0.1429 Mn$_3$B$_4$	$\Delta_f G(\mathrm{Mn_3B_4}) = -27396-2.050\ T$	
0.3333 MnB$_2$	$\Delta_f G(\mathrm{MnB_2}) = -21902-2.040\ T$	
0.2000 MnB$_4$	$\Delta_f G(\mathrm{MnB_4}) = -26098+6.582\ T$	
1.0000 βB	$\Delta_f G\ (\beta\mathrm{B}) = 0$	
Liquid	$\Delta G^{ex} = x(1-x)\{-179800+41.73\ T - 29273(1-2x)+74194(1-2x)^2+$ $+66061(1-2x)^3-52134(1-2x)^4\}$	
0.2000 Mn$_4$N	$\Delta_f G(\ \mathrm{Mn_4N}) = -4534+3.266\ T$	[75Gme]
0.3333 Mn$_2$N	$\Delta_2 G\ (\mathrm{Mn_2N}) = -83667.7+5.807\ T$	[75Gme]
0.2000 Mn$_3$N$_2$	$\Delta_f G(\mathrm{Mn_3N_2}) = -6680+5.696\ T$	[75Gme]

Fig.1: Assessed diagram of the binary system Mn - B

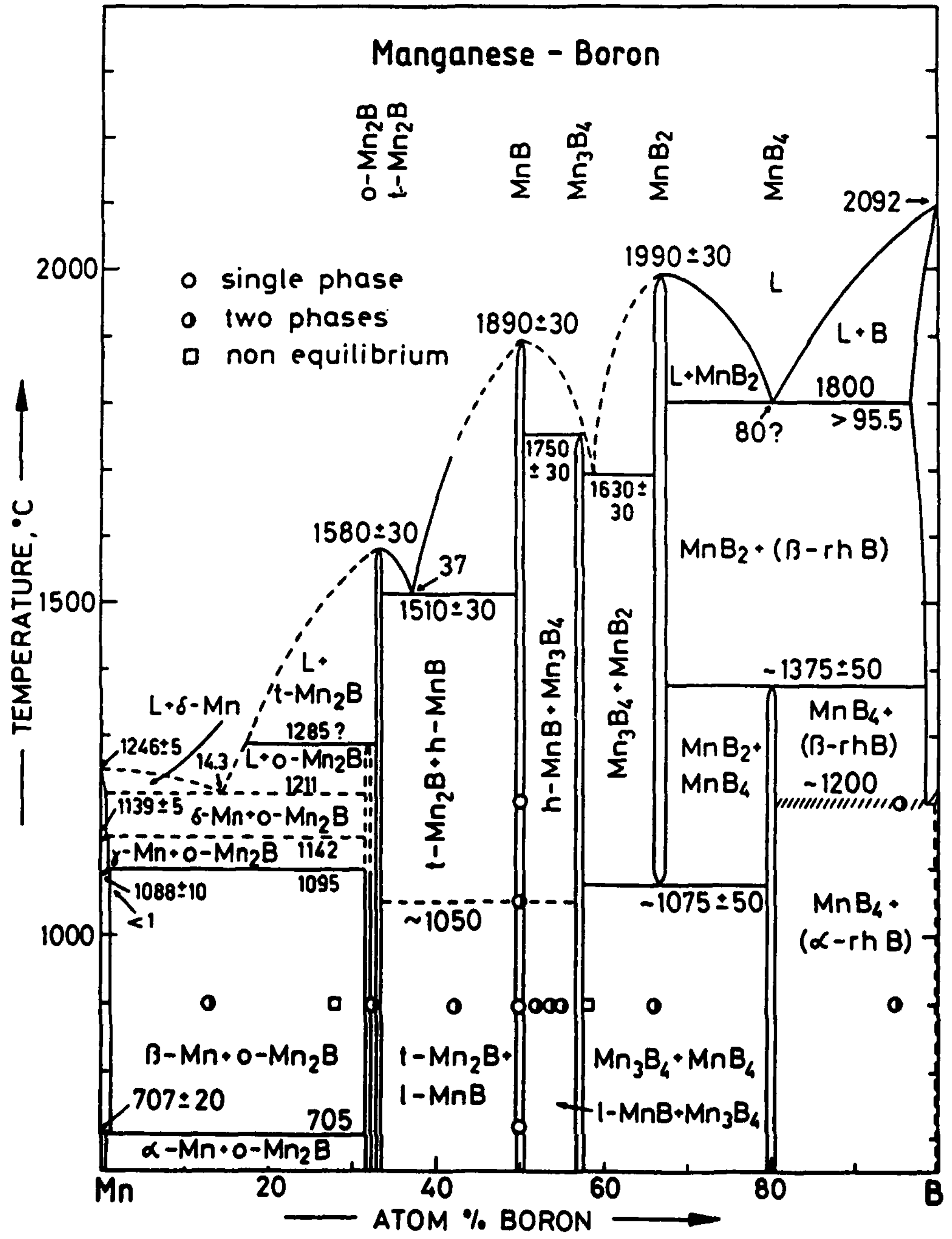


Fig.2: Isothermal section of the system B - Mn -N at 900°C under 1 bar of argon (in the absense of external nitrogen).

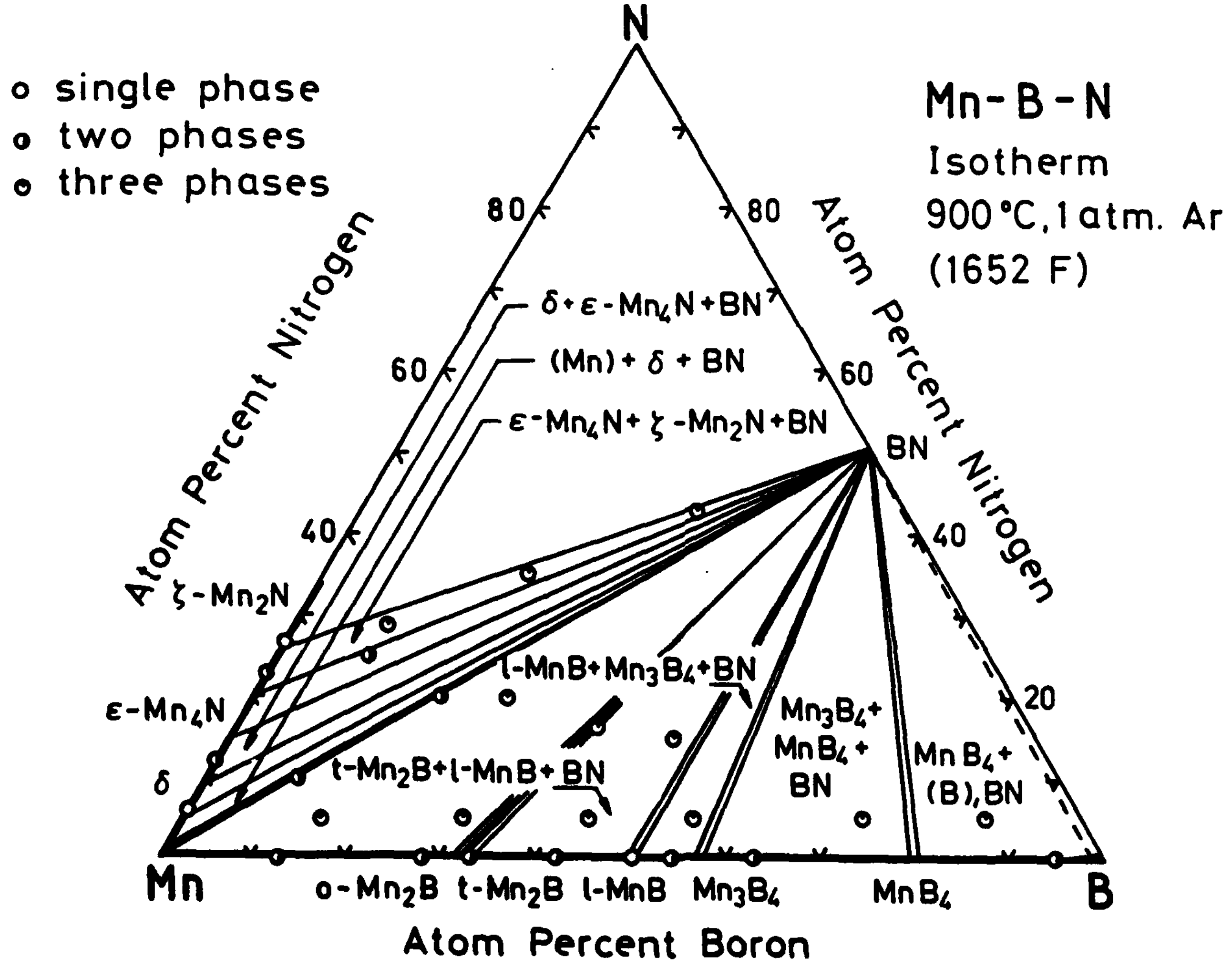
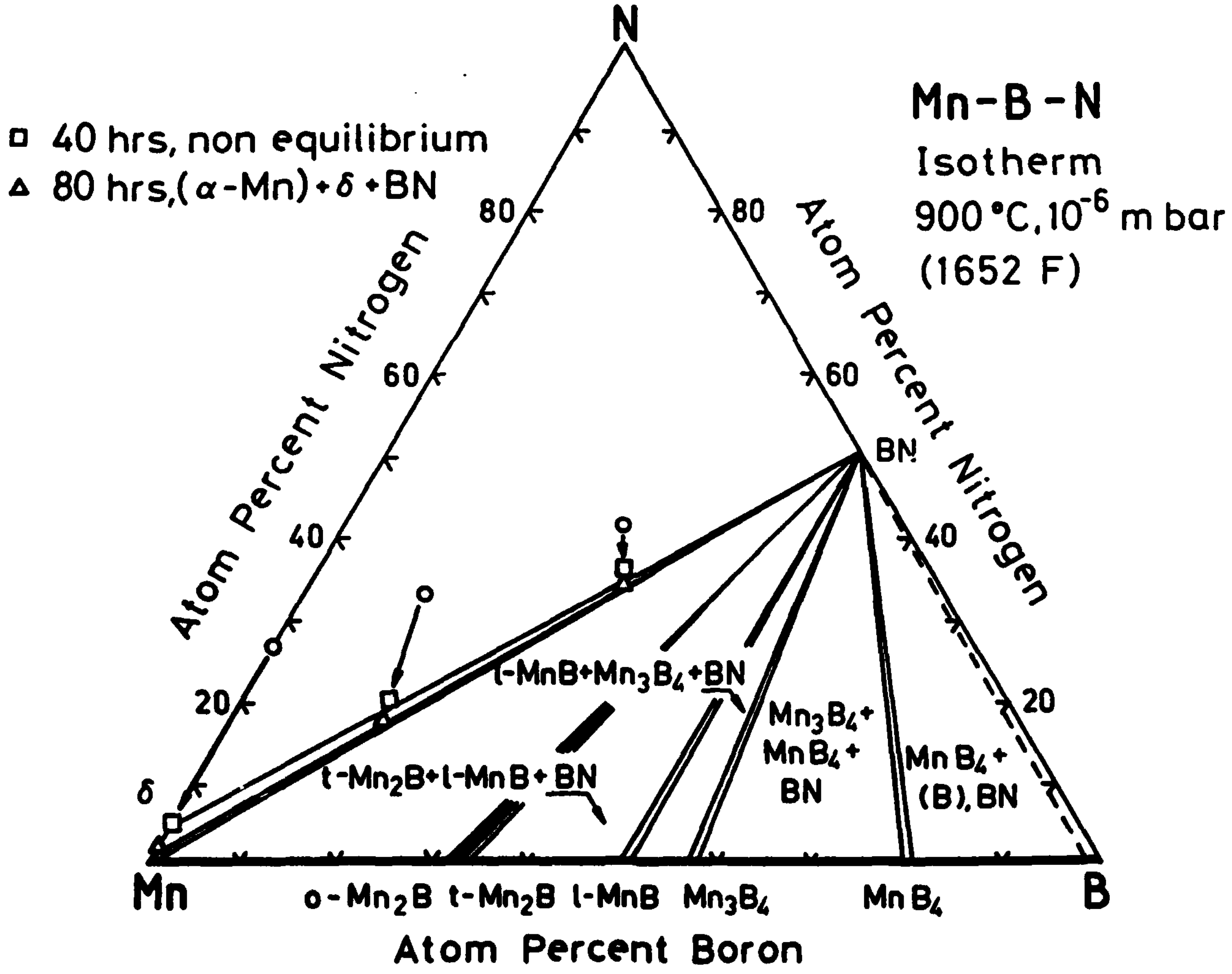


Fig.3 Isothermal section of the system B - Mn - N at 900°C under a vacuum of 10^{-4}Pa.



SYSTEM BORON- RHENIUM- NITROGEN (B-Re-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Re-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Re,and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [88Rog]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 24h followed by a final reaction at 1200°C for 84h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled.Starting materials were powders of 3N-Re, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Rog].

BINARY SYSTEMS

The reinvestigation of the B-Re system in the range from 1200 to 1500°C revealed consistency with the data available in [84Vil] and [90Mas]; see Table 1. Due to the rather sluggish diffusion reactions in the high melting B-Re system, thermodynamic equilibrium at 1200°C was not attained in those alloys which were arc melted prior to heat treatment at 1200°C. In correspondance to the observations by [88Por], a weak set of X-ray reflections was observed in the rhenium-rich alloys which was concluded to belong to a new Re-boride labelled as $Re_{8-x}B$, whose crystal structure is still unknown [88Rog]. Homogeneous ranges of the binary borides at 1200°C were found to be rather small indicating a typical "line-compound" type of character.

The solid solubility of boron in rhenium was claimed to be less than 2 at%B at the temperature of the peritectic formation of Re_3B (

ca 2150°C); an interstitial type of B-solubility was suggested [65Trz].The maximum solid solubility of Re in β-B was reported to be less than 1 at%Re at 1800°C [81Cre].

No equilibrium diagram exists for the N-Re system and solid solubility of N in Re is said to be small (10^{-3}at%N at 10^{5}Pa); only one binary nitride, ReN_{1-x} (cF8, Fm$\bar{3}$m, defect NaCl-type, a=0.393nm at 30at%N), exists, but decomposes in vacuum below 270°C;a comprehensive discussion of all reported information has been given by [78Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1200°C under 1 bar of argon (in the absence of external nitrogen pressure) [88Rog]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between rhenium metal and/or the binary rhenium-borides and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Re in BN at 1200°C, and mutual solubilities of the rhenium borides and BN are rather restricted [88Rog].

Phase equilibria in the Re-B-N system have been also checked by nitriding the binary rhenium boride powders under 1 bar of N_2. The results confirm the gradual decomposition of the higher borides via lower borides towards a limiting tie-line : (Re) + BN. No signs of compound formation at higher nitrogen contents were observed.

THERMODYNAMICS

[69Bae1,2] studied the reaction of Re and BN using a Thermobalance. From these measurements the activation energies for the formation of the binary borides were derived. Furthermore the onset of the reaction $3Re + BN ======= Re_3B + 1/2N_2$ was measured as a function of the nitrogen partial pressure yielding free enthalpy data for the reaction and data for the free enthalpy of formation for Re_3B.

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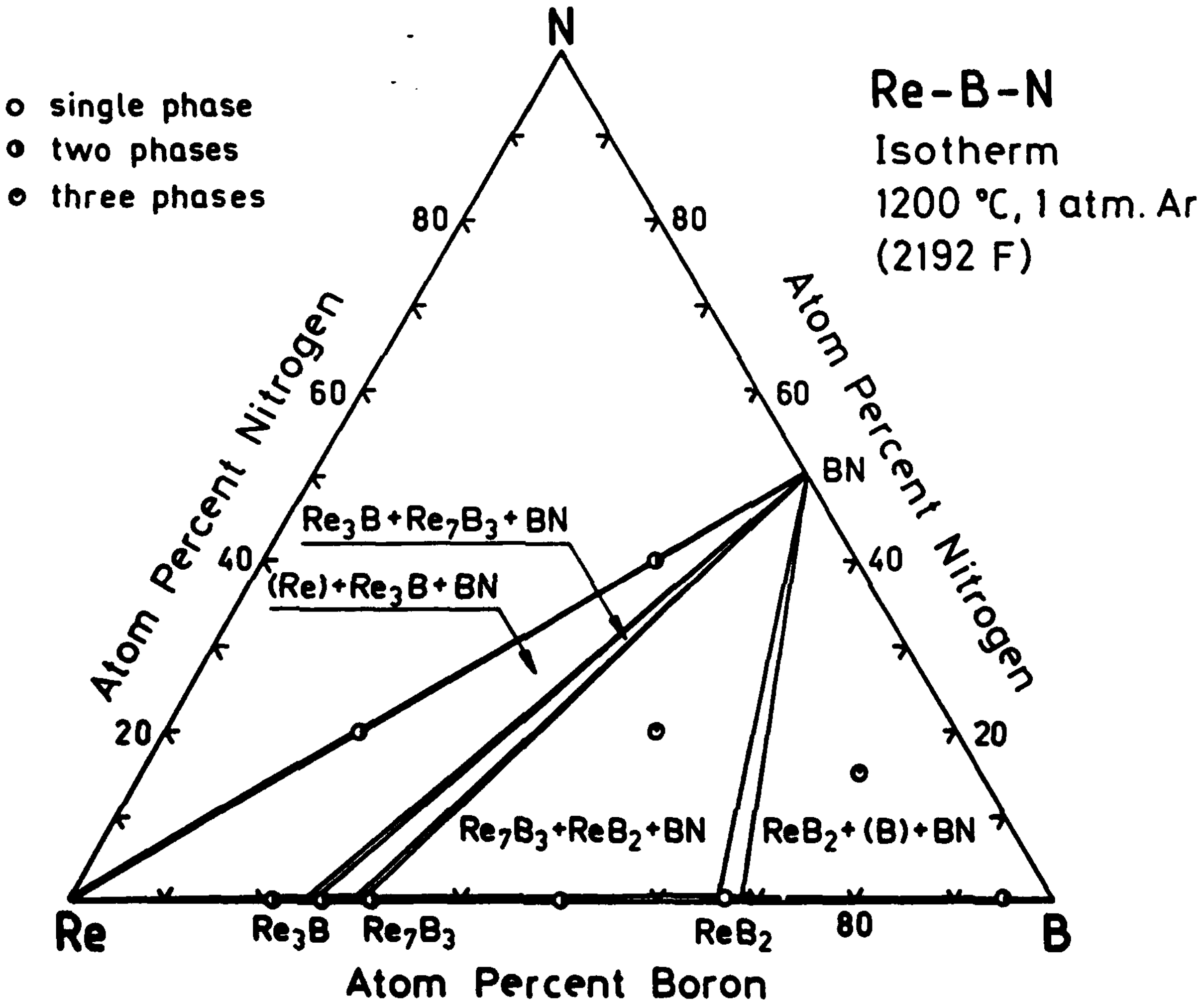
Table 1: Solid phases at 1200°C in the system B-Re-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Re <3186°	hP2 $P6_3/mmc$ Mg	a= 276.09 c= 445.8	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
Re_3B ~2150°	oC16 Cmcm Re_3B	a= 289.33 b= 932.08 c= 727.08	[88Rog]
Re_7B_3 <~2000°	hP20 $P6_3mc$ Th_7Fe_3	a= 750.48 c= 488.54	[88Rog]
ReB_2 <~2400°	hP6 P6/mmc ReB_2	a= 290.16 c= 747.99	[88Rog]
BN_{hex}	hP5 $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Re-B-N

Phase	$\Delta_f G$ (J/gramatom)		Ref.
1.0000 Re	$\Delta_{fus}G(Re)$	$= 60428-17.4698\ T$	
1.0000 B	$\Delta_{fus}G(B)$	$= 50210-21.23\ T$	
1.0000 Re	$\Delta_f G\ (Re)$	$= 0$	
0.2500 Re_3B	$\Delta_f G(Re_3B)$	$=-32320+7.32\ T$	[69Bae]
1.0000 βB	$\Delta_f G\ (\beta B)$	$= 0$	

Fig.1: Isothermal section of the system B - Re -N at 1200°C under 1 bar of argon (in the absense of external nitrogen).



SYSTEM BORON- IRON- NITROGEN (B-Fe-N)

INTRODUCTION / EXPERIMENTAL

Early information on the Fe-B-N system is due to [51Kis] who investigated the stability of binary iron borides in a stream of dry ammonia at temperatures between 352 and 768°C. The resistance against attack by ammonia was found to increase with the boron content; no mutual solid solubility was observed [51Kis] confirming earlier findings by [48Jac].

The solubility of nitrogen in iron-rich alloys (0.001 to 0.91 wt% B) has been studied by [62Fou] using Sievert's technique in the temperature range from 950 to 1150°C. Small amounts of desoxidising Si yielded a total of 0.5 wt% Si in the alloy whose effect on the N-solubility was determined from B-free samples. A TEM-study of extracted flakes of (BN_{hex}) revealed a lack of threedimensional perfection due to stacking faults and random displacement of the graphitic layers perpendicular to the *c*-axis, but with (hk0) reflections unaffected [62Fou]. At 1050°C the mutual solid solubilities of Fe - BN and Fe_2B - BN were said to be very small [62Fou].

The N-solubility limit in liquid Fe-B alloys was investigated by [64Eva] using (a) Sievert's technique and (b) equilibration of iron melts in BN crucibles under a constant partial pressure of N_2. Boron was found to decrease the N-solubility at a given partial pressure of N_2 and the first order interaction coefficient, determined between 1550 and 1750°C [64Eva], was expressed as a function of temperature by [74Sig] : $\varepsilon = 975/T - 0.4$ (T in K). Based on the results of [64Eva] and following a similar procedure the saturation phase boundaries L/(L + BN) have been calculated by [87Rag] for 1550, 1650, 1750°C and for 1, 5 and 10.10^5Pa N_2 .

Phase equilibria in the B-Fe-N system at 900°C have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Fe, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [85Šmi],[88Šmi]. Annealing of the samples was either performed (a) in vacuum sealed silica tubes using a thin molybdenum foil to protect the sample from direct contact with the hot quartz wall or (b) in a 1 MHz-HF furnace under 1 bar of 6N-Ar or under various partial pressures of 6N-N_2 using hex-BN substrates in a tungsten or molybdenum susceptor crucible. Heat treatments usually consisted of a primary reaction at 900°C for 48h followed by a final reaction at 900°C up to 72h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were either monitored by calibrated microoptical pyrometry or by thermocouples; after heat treatment the samples were radiation cooled (HF-furnace) or quenched in water (silica capsules). The starting materials were powders from 3N-Fe , crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements or by direct sintering under argon; weight losses were checked to be within 1 wt% [85Šmi, 86Šmi].

BINARY SYSTEMS

The reinvestigation of the B-Fe system from 400°C to the melting range employing X-ray powder, metallographic, DTA, and Pirani-melting point analyses confirmed the existence of only two binary iron borides [86Smi]. In contrast to earlier data there is essential consistency with the data available from a compilation by [82Kub]. In contradiction to a low temperature modification "α-FeB" as claimed earlier (for a review see [82Kan]), FeB-samples containing excess boron at temperatures below T~1000°C revealed a typical transposition type behavior (FeB-type ---- CrB-type) with an irregular arrangement of the FeB-type slabs in partly shifted positions but without long range order [85Šmi,86Šmi]. The maximal solid solubility of boron in α-Fe was said to be small, whereas detailed measurements of the electrical resistivity and the activity coefficients of B in α,γ-Fe reveal a solubility of B in γ-Fe, which is 2.7 times larger than that in α-Fe at the same temperature [83Bro]. While there seems to be no doubt about the interstitial type of B-solubility in γ-Fe, a substitutional mode was discussed for α-Fe by [84Hay]. From X-ray powder analysis the maximum solid solubility of Fe in β-B was concluded to be about 5 at% Fe at 1800°C. An extensive discussion of the Fe-B phase diagram can be found from [85Smid,86Smi] including a discussion on the metastable phases $Fe_{23}B_6$ and Fe_3B; for crystallographic data see Table 1. A thermodynamic modelling of the Fe-B system is due to [87Šmi].

Fig.1 represents the critically assessed version of the Fe-B phase diagram, temperature versus concentration [86Šmi].

The phase diagram Fe-N is due to critical assessments by [76Fro], [82Kub], [87Wri], [87Fri] and [86Kun].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 summarizes the results reported by [51Kis] in terms of an isothermal section at 400°C (in the absence of external nitrogen pressure). Fig.3 shows the phase equilibria in the iron rich corner of the Fe-B-N system at 950, 1050, and 1150°C as derived by [62Fou]. Fig.4 represents the phase relations in the Fe-B-N system at 900°C [85Šmi,86Šmi]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between iron and the binary iron-borides and BN. As seen from a comparision of the unit cell dimensions there is a small but significant solid solubility of Fe in BN at 900°C, whereas mutual solubilities of the iron nitrides, the iron borides and BN are rather restricted [85Šmi]. Alloys along the section Fe-BN with acomposition of about 20 mol % BN after heattreatment at 1350°C and 1 bar argon were reported to be molten and after quenching revealed the powder pattern of a cubic τ-phase $Fe_{23}(B,N)_6$. Technical conditions - using graphite susceptor crucibles and technical argon containing 0.01 % O_2, 0.02 % N_2 at 900°C and 48 h prompted the stabilization of aa $Fe_3(B,N,C)$ compound with the Fe_3C-type [86Šmi] (Fig.5).

The kinetic of nitriding was studied [86Šmi] from binary iron boride samples annealed at 900 and 1250°C under 1 bar of 6N-nitrogen and qualitatively confirmed the early observations by [51Kis].

THERMODYNAMICS

A thermodynamic modelling of the binary system Fe-B is due to [86Smi] of the Fe-N system due to [87Fri]; see Table 2.

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Table 1: Solid phases in the system B-Fe-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments	
α-Fe	cI2	a= 286.65	[87Wri]	at RT
<912°	$Im\bar{3}m$	a= 294.1	[87Wri]	at 1538°C
	W			
γ-Fe	cF4	a= 364.7	[87Wri]	at 912°C
<1394°	$Fm\bar{3}m$	a= 368.8	[87Wri]	at 1394°C
	Cu			
δ-Fe	cI2	a= 293.15	[85Vil]	
<1535°	$Im\bar{3}m$			
	W			
β-rhB	hR111	a=1092.51	[85Vil]	
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]	
	β-B			
		a=1095.14	[85Vil]	at $FeB_{\sim 49}$
		c=2386.1		
Fe_2B	tI12	a= 510.9	[85Vil]	
<1174°	I4/mcm	c= 424.9		
	Al_2Cu			
FeB	oP8	a= 406.1	[85Vil]	
<1588°	Pbnm	b= 550.6		
	FeB	c= 295.2		
$Fe_{23}B_6$	cF116	a=1067.	[85Vil]	metastable
	$Fm\bar{3}m$			
	$Cr_{23}C_6$			

Fe_3B	oP16	a= 443.9	[85Vil]	metastable
	Pbnm	b= 542.8		
	Fe_3C	c= 666.9		
Fe_3B	tI32	a= 865.5	[85Vil]	metastable
	$I\bar{4}$	c= 429.7		
	Fe_3P			
Fe_3B	tP32	a= 864.8	[85Vil]	metastable
	$P4_2/n$	c= 431.4		
	Ti_3P			
Fe_4N	cP5	a= 379.8	[87Wri]	at 20 at% N
<680°	$Pm\bar{3}m$			
	Fe_4N			
Fe_3N_{1-x}	hP9	a=435.3+1.337(at%N)		15.8-33.2at%N
	P31m	c=423.3+0.578(at%N)		[87Rag]
	Fe_3N			
Fe_2N	oP12	a= 551.2	[87Wri]	
<480°	Pbcn	b= 482.0		
	Fe_2N	c= 441.6		
Fe_8N	tI	a= 572.	[87Wri]	11.1at%N
	I4/mmn	c= 629.		metastable
	Fe_8N			
BN_{hex}	hP5	a= 250.4	[85Vil]	
	$P6_3/mmc$	c= 666.1		
	BN_{hex}			
*$Fe_{23}(B,N)_6$	cF116	a=1048.3	[85Šmi]	metastable
	$Fm\bar{3}m$			
	$Cr_{23}C_6$			
*$Fe_3(B,N,C)$	oP16	a= 445.9	[85Šmi]	C-stabil.
	Pbnm	b= 534.7		
	Fe_3C	c= 666.4		

Table 2: Thermodynamic data for the system Fe-B (after [86Šmi])

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 Fe	$\Delta_{fus}G(Fe) = 13806-7.6241\ T$	[86Šmi]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 αFe	$\Delta_f G\ (\alpha Fe) = 0$	
1.0000 γFe	$\Delta_f G\ (\gamma Fe) = 825.78-0.4953\ T$	
0.3333 Fe_2B	$\Delta_f G(Fe_2B) = -102330+5.0\ T$	
0.0769 FeB	$\Delta_f G(FeB) = -36980+2.0\ T$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
Liquid	$\Delta G^{ex} = x(1-x)\{-177050-34.9\ T + (-3335+68.9\ T)(1-2x)\}$	

Fig.1: Assessed diagram of the binary system Fe - B [85Šmi,88Šmi]

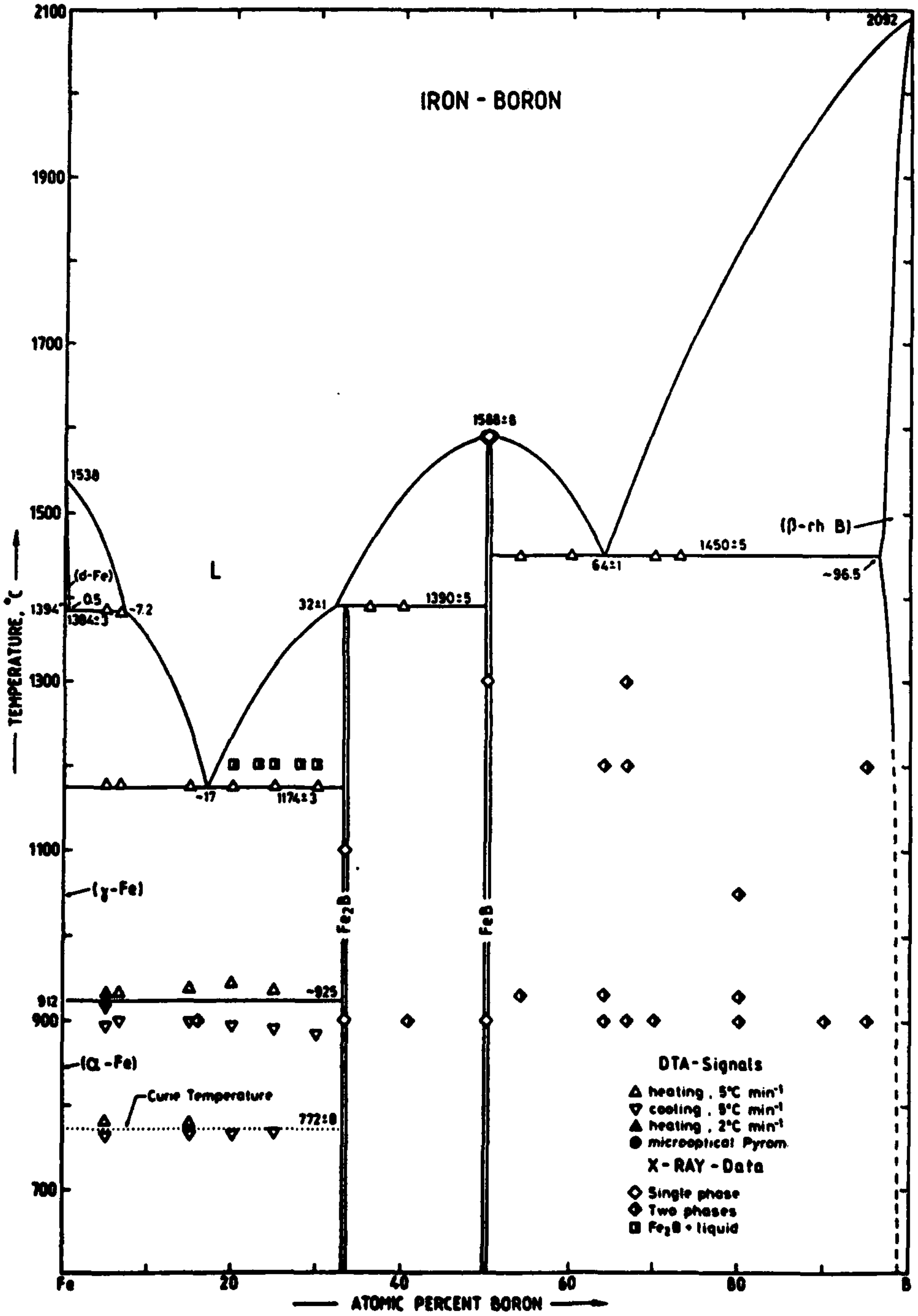


Fig.2: Isothermal section of the system B - Fe -N at 400°C (in the absense of external nitrogen) as based on data by [51Kis].

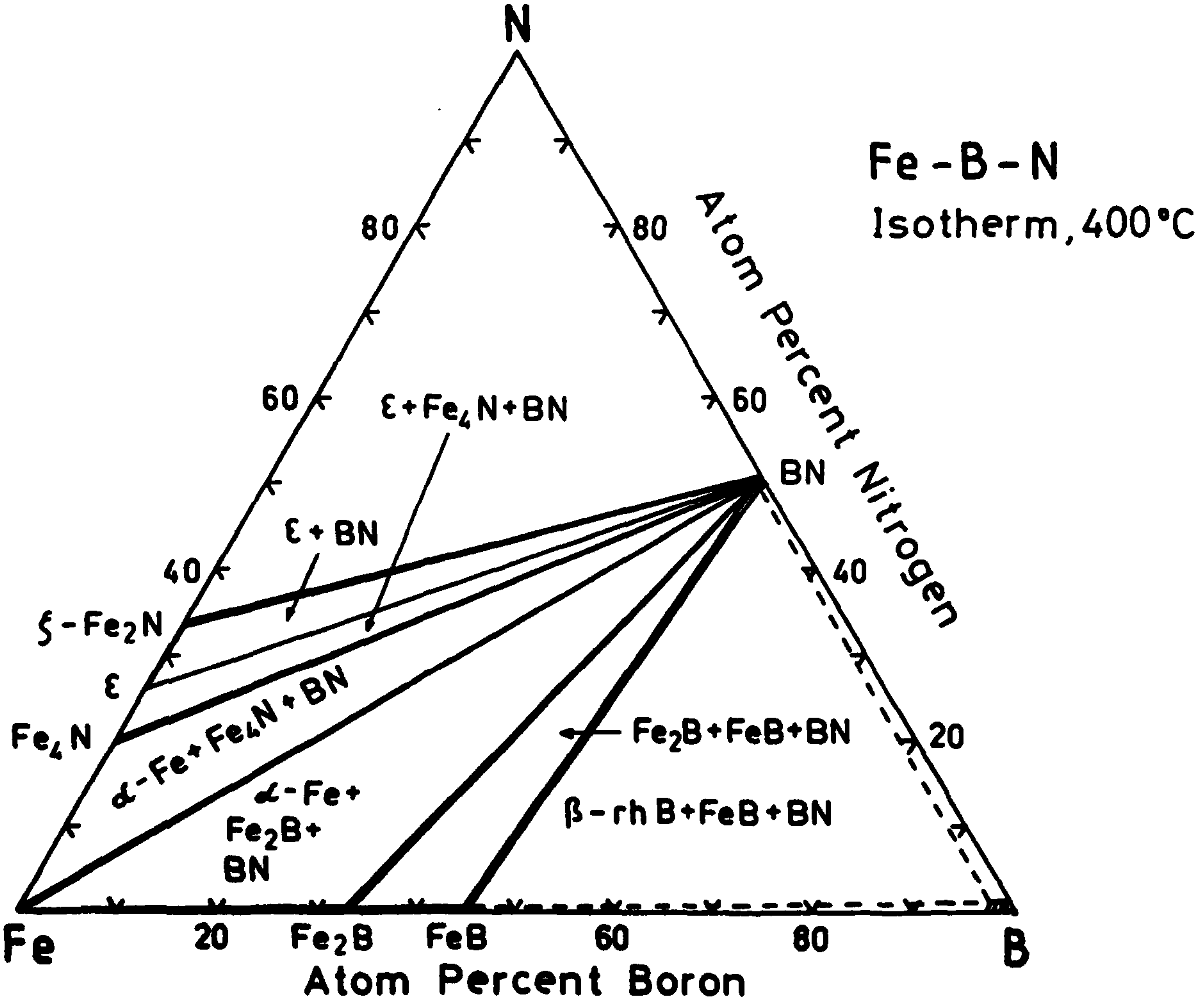


Fig.3 Phase equilibria in the iron rich corner of the system Fe - B - N at (a) 950°C, (b) 1050°C and (c) at 1150°C (after [62Fou], in mass percent).

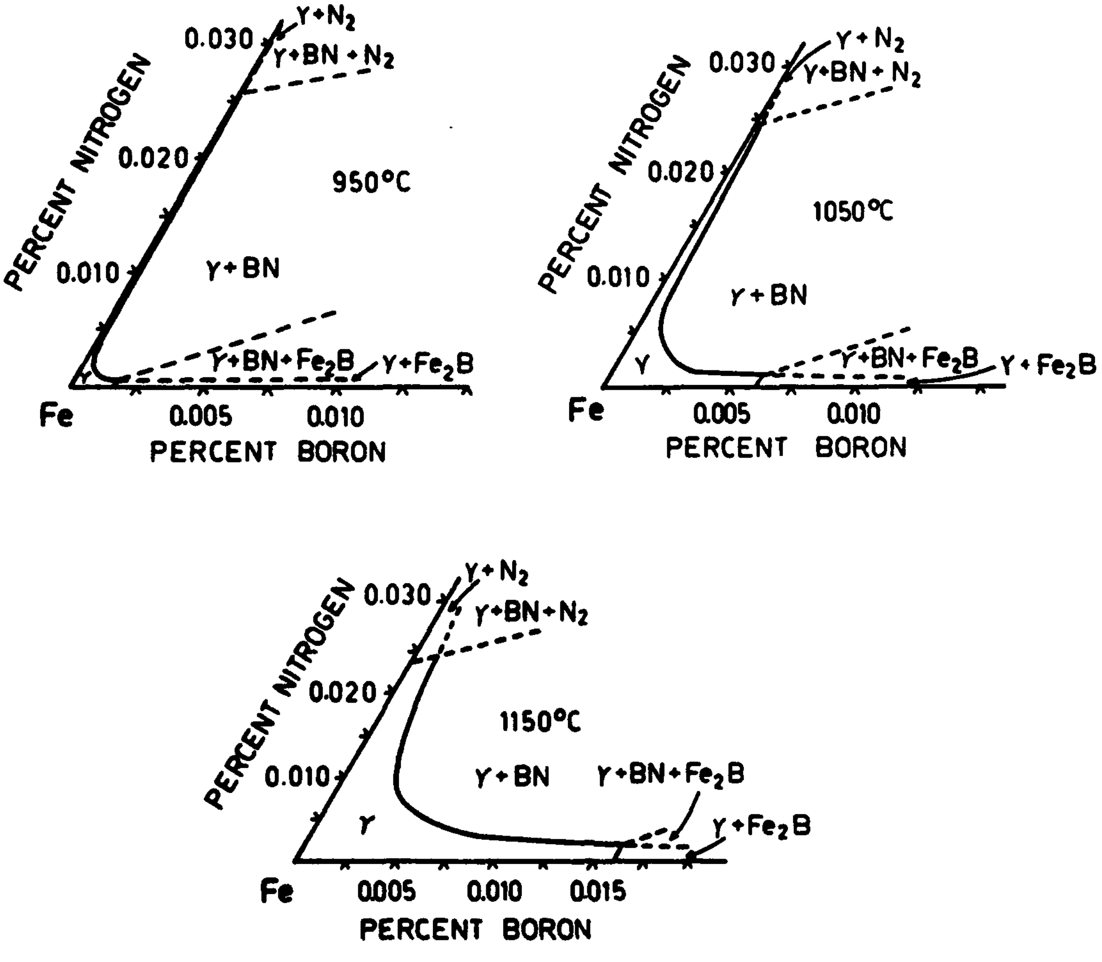


Fig.4 Isothermal section of the system B - Fe - N at 900°C under 1 bar of argon (in the absence of external nitrogen).

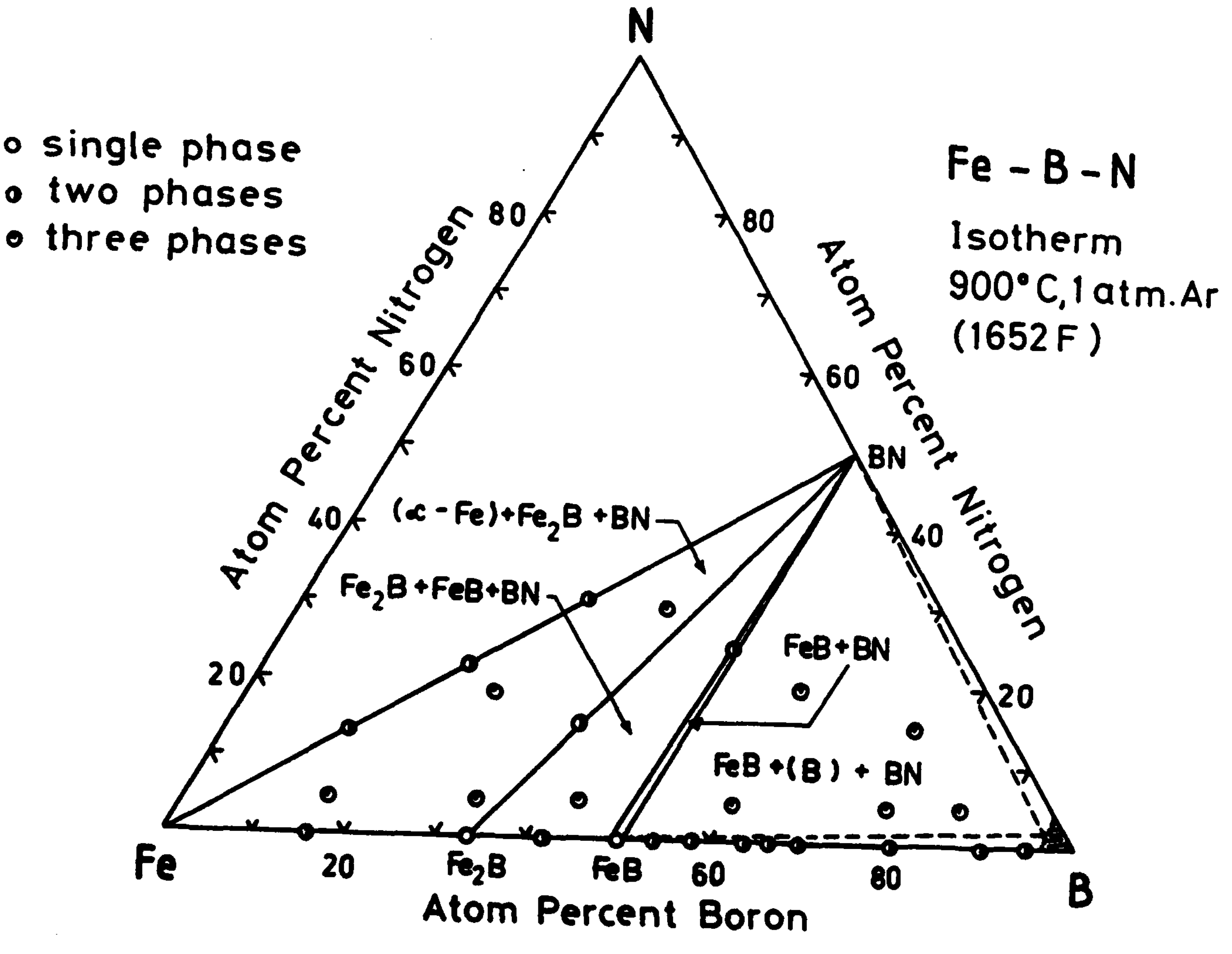
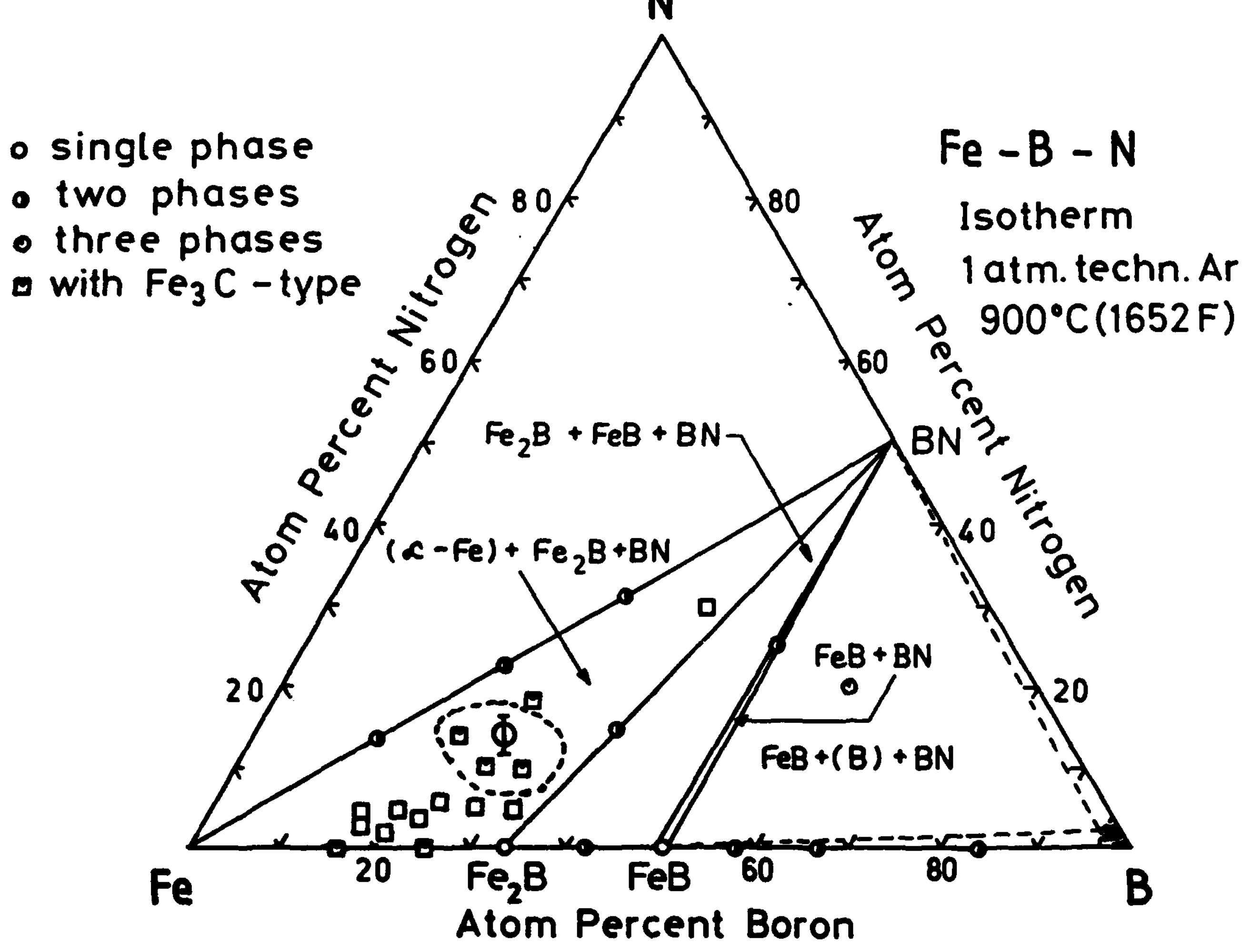


Fig.5 Isothermal section of the system Fe - B - N at 900°C under technical conditions (1 bar of technical argon, C-susceptor)



SYSTEM BORON- COBALT- NITROGEN (B-Co-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Co-N system at 900°C have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Co, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [85Šmi, 86Šmi]. Annealing of the samples was either performed (a) in vacuum sealed silica tubes using a thin molybdenum foil to protect the sample from direct contact with the hot quartz wall or (b) in a 1 MHz-HF furnace under 1 bar of 6N-Ar or under various partial pressures of 6N-N_2 using hex-BN substrates in a tungsten or molybdenum susceptor crucible. Heat treatments usually consisted of a primary reaction at 900°C for 48h followed by a final reaction at 900°C up to 72h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were either monitored by calibrated microoptical pyrometry or by thermocouples; after heat treatment the samples were radiation cooled (*HF-furnace*) or quenched in water (silica capsules). The starting materials were powders from 3N-Co , crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements or by direct sintering under argon; weight losses were checked to be within 1 wt% [85Šmi, 86Šmi].

BINARY SYSTEMS

The reinvestigation of the B-Co system at 900°C confirmed the existence of only three binary iron borides [86Šmi], in essential consistency with the phase diagram as given in [90Mas, 88Lia]. The maximal solid solubility of boron in α-Co was said to be 3 at% B at 1000°C [81Bas] and 5.2 at% B at 1100°C [38Koe]. From X-ray powder analysis the maximum solid solubility of Co in β-B was concluded to be about 3 to 5 at% Co at 1450°C [85Šmid, 86Šmi]; for crystallographic data see Table 1.

No phase diagram Co-N is available, however, the existence of a series of cobalt nitrides has been reported (see Table 1). All cobalt nitrides easily decompose on heating at 276°C in vacuum and none is stable at 900°C at 10^5Pa Ar [85Šmi, 86Šmi]. N was found to be practically insoluble in Co at $p < 10^5$Pa N_2 and up to 1200°C [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the phase relations in the Co-B-N system at 900°C [85Šmi, 86Šmi]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between cobalt and the binary cobalt-borides and BN. As seen from a comparision of the unit cell dimensions there is a small but significant solid solubility of Co in BN at 900°C, whereas mutual solubilities of the cobalt borides and BN are rather restricted [85Šmi]. Alloys along the section Co-BN with a composition of about 20 mol·% BN after heat treatment at 1350°C and 1 bar argon were reported to be molten and after quenching revealed the powder pattern of a cubic τ-phase $Co_{23}(B,N)_6$.

The kinetic of nitriding was studied [86Šmi] from binary cobalt boride samples annealed at 900 and 1250°C under 1 bar of 6N-nitrogen.

THERMODYNAMICS

A thermodynamic calculation/modelling of the binary system Co-B is due to [84Kau] and [88Lia]; see Table 2.

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Table 1: Solid phases in the system B-Co-N

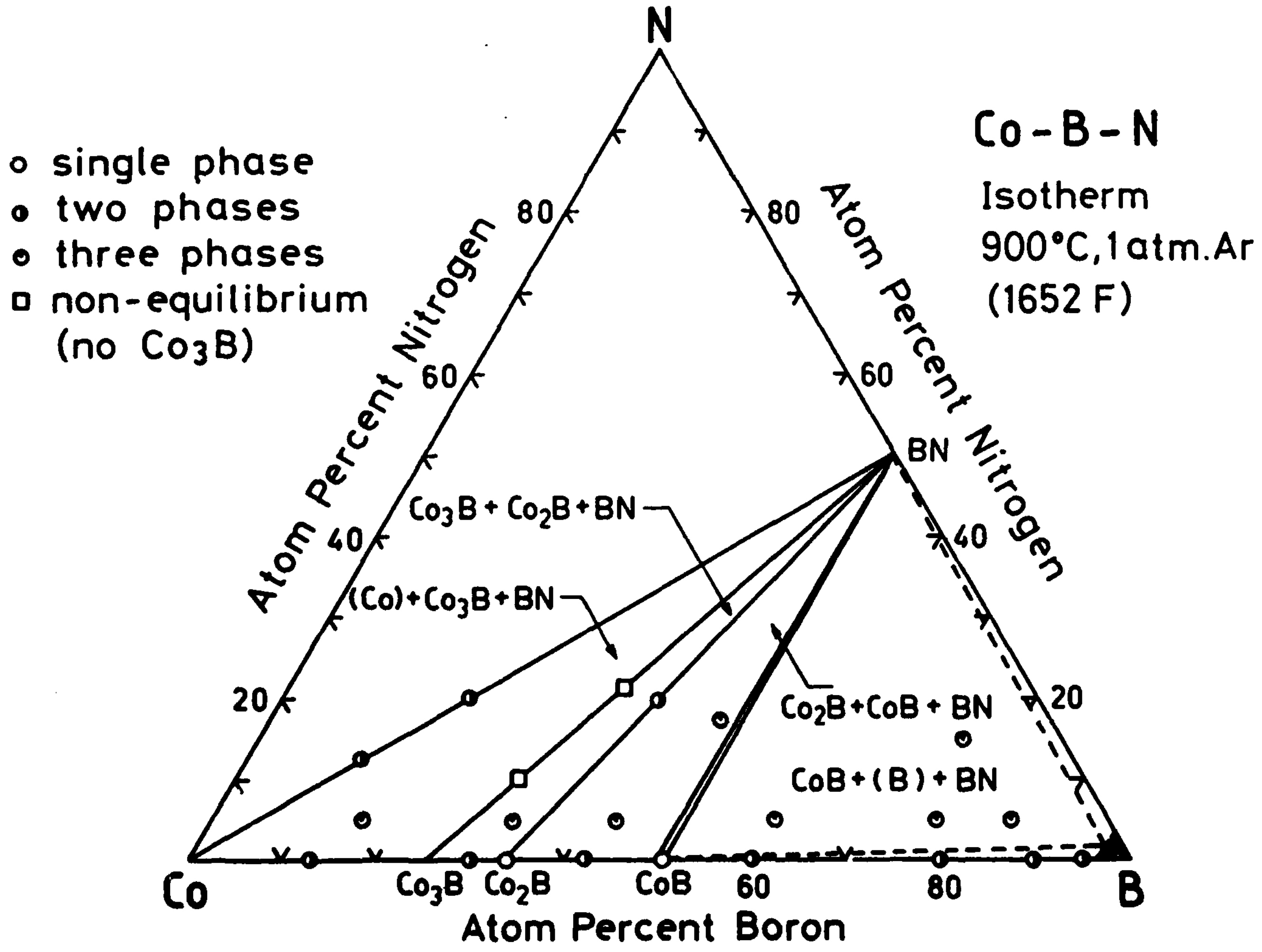
Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments	
ε-Co(r)	hP2	a= 250.71	[90Mas]	at RT
<422°	P6$_3$/mmc	c= 406.86		
α-Co(h)	cF4	a= 354.47	[90Mas]	
<1495°	Fm$\bar{3}$m			
	Cu			
β-rhB	hR111	a=1092.51	[85Vil]	
<2092°	R$\bar{3}$m	c=2381.43	[85Vil]	
	β-B			
		a=1094.59	[85Vil]	at CoB$_{\sim 25}$
		c=2383.97		
Co$_3$B	oP16	a= 440.8	[85Vil]	
<1125°	Pbnm	b= 525.5		
	Fe$_3$C	c= 662.9		
Co$_2$B	tI12	a= 501.6	[85Vil]	
<1280°	I4/mcm	c= 422.0		
	Al$_2$Cu			
CoB	oP8	a= 395.6	[85Vil]	
<1460°	Pbnm	b= 525.3		
	FeB	c= 304.3		
Co$_{23}$B$_6$	cF116	a=1106.	[85Vil]	metastable
	Fm$\bar{3}$m			
	Cr$_{23}$C$_6$			
Co$_4$N	cP5	a= 358.6	[87Kii]	
	Pm$\bar{3}$m	a= 373.8	[85Vil]	
	Fe$_4$N			
Co$_3$N	hP*	a= 274.6	[85Vil]	
		c= 432.2		
Co$_2$N	oP6	a= 460.56	[85Vil]	
	Pmnm	b= 434.43		
	Co$_2$N	c= 285.35		

BN_{hex}	hP5 $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]	
* $Co_{23}(B,N)_6$	cF116 $Fm\bar{3}m$ $Cr_{23}C_6$	a=1048.3	[85Šmi]	metastable

Table 2: Thermodynamic data for the system Co-B (after [88Lia])

Phase	$\Delta_f G$ (J/gramatom)	Ref.
1.0000 αCo	$\Delta_{fus}G(Co) = 16200-9.163\ T$	[88Lia]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 Co	$\Delta_f G\ (\alpha Co) = 0$	
0.2500 Co_3B	$\Delta_f G\ (Co_3B) = -25800+2.35\ T$	
0.3333 Co_2B	$\Delta_f G\ (Co_2B) = -26900-1.41\ T$	
0.5000 CoB	$\Delta_f G\ (CoB) = -34500+0.24\ T$	
1.0000 βB	$\Delta_f G\ (\beta B) = 0$	
Liquid	$\Delta G^{ex} = x(1-x)\{-110700\ -7.46\ T\ -24500(1-2x)+27100(1-2x)^2+ +21900(1-2x)^3\}$	

Fig.1 Isothermal section of the system B - Co - N at 900°C under 1 bar of argon (in the absence of external nitrogen).



SYSTEM BORON- NICKEL- NITROGEN (B-Ni-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Ni-N system at 900°C have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Ni, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [85Šmi, 86Šmi]. Annealing of the samples was either performed (a) in vacuum sealed silica tubes using a thin molybdenum foil to protect the sample from direct contact with the hot quartz wall or (b) in a 1 MHz-HF furnace under 1 bar of 6N-Ar or under various partial pressures of 6N-N_2 using hex-BN substrates in a tungsten or molybdenum susceptor crucible. Heat treatments usually consisted of a primary reaction at 900°C for 72h followed by a final reaction at 900°C up to 72h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were either monitored by calibrated microoptical pyrometry or by thermocouples; after heat treatment the samples were radiation cooled (HF-furnace) or quenched in water (silica capsules). The starting materials were powders from 3N-Ni , crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements or by direct sintering under argon; weight losses were checked to be within 1 wt% [85Šmi, 86Šmi].

BINARY SYSTEMS

The reinvestigation of the B-Ni system at 900°C confirmed the existence of five binary nickel borides [86Šmi], in essential consistency with the phase diagram as given in [90Mas]. The maximal solid solubility of boron in Ni was said to be 0.3 at% B at 1085°C [65Sch]. From X-ray powder analysis the maximum solid solubility of Ni in β-B was concluded to be about 3 at% Ni at 1035°C [85Šmid, 86Šmi]; for crystallographic data see Table 1.

No phase diagram Ni-N is available, however, the existence of a series of nickel nitrides has been reported; for details see [76Fro] and [83Dor]. All nickel nitrides easily decompose on heating at 480°C in vacuum and none is stable at 900°C at 10^5Pa Ar [85Šmi, 86Šmi]. The solubility of N in Ni at 445 was said to amount to less than 0.3 at% N; the solubility of N in liquid Ni is rather small; for details see [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the phase relations in the Ni-B-N system at 900°C [85Šmi, 86Šmi]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between nickel and the binary nickel-borides and BN. As seen from a comparision of the unit cell dimensions there is a small but significant solid solubility of Ni in BN at 900°C, whereas mutual solubilities of the nickel borides and BN are rather restricted [85Šmi]. Alloys along the section Ni-BN with a composition of about 20 mol % BN after heat treatment at 1350°C and 1 bar argon were reported to be molten and after quenching revealed the powder pattern of a cubic τ-phase $Ni_{23}(B,N)_6$.

The kinetic of nitriding was studied [86Šmi] from binary nickel boride samples annealed at 900 and 1250°C under 1 bar of 6N-nitrogen.

THERMODYNAMICS

A thermodynamic modelling of the Ni-B system is due to [84Kau] and [81Hac].

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Table 1: Solid phases in the system B-Ni-N

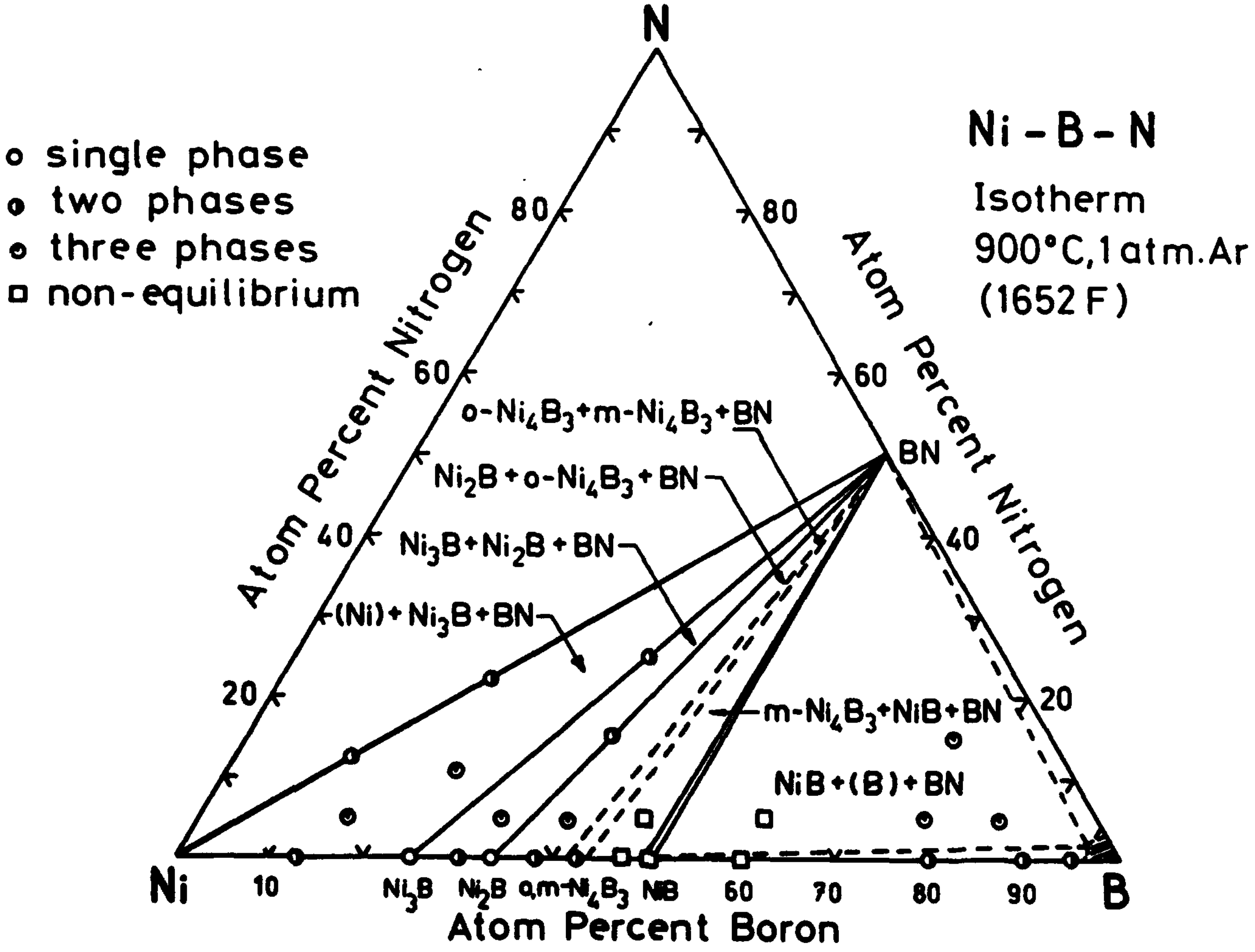
Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments	
Ni	cF4	a= 352.40	[90Mas]	at RT
<1455°	$Fm\bar{3}m$			
	Cu			
β-rhB	hR111	a=1092.51	[85Vil]	
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]	
	β-B			
		a=1095.84	[85Vil]	at $NiB_{\sim 20}$
		c=2385.46		
Ni_3B	oP16	a= 439.0	[85Vil]	
<1166°	Pbnm	b= 521.05		
	Fe_3C	c= 661.74		
Ni_2B	tI12	a= 499.1	[85Vil]	
<1125°	I4/mcm	c= 424.7		
	Al_2Cu			
o-Ni_4B_3	oP28	a=1195.40	[85Vil]	
<1025°	Pnma	b= 298.15		
	o-Ni_4B_3	c= 656.84		
m-Ni_4B_3	mC28	a= 642.82	[85Vil]	
<1031°	C2/c	b= 487.95		
	m-Ni_4B_3	c= 781.90		
		β=103.315°		
NiB	oP8	a= 292.8	[85Vil]	
<1035°	Cmcm	b= 739.1		
	CrB	c= 296.4		
$Ni_{23}B_6$	cF116	a=1048.	[85Vil]	metastable
	$Fm\bar{3}m$			
	$Cr_{23}C_6$			
Ni_4N	cP5	a= 374.	[87Wri]	
	Pm3m			
	Fe_4N			

Ni_4N	tP10	a= 372. c= 728.	[85Vil]	
Ni_3N <400°, N_2	hP* $P6_322$ or P312	a= 460.7 c= 430.4	[85Vil]	
BN_{hex}	hP5 $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]	
* $Ni_{23}(B,N)_6$	cF116 $Fm\bar{3}m$ $Cr_{23}C_6$	a=1044.8	[85Šmi]	metastable

Table 2: Thermodynamic data for the system Ni-B (after [81Hac])

Phase	Δ_fG (J/gramatom)	Ref.
1.0000 Ni	$\Delta_{fus}G(Ni) = 17479.82-10.1139\ T$	[81Hac]
1.0000 B	$\Delta_{fus}G(B) = 50210-21.23\ T$	
1.0000 Ni	$\Delta_fG\ (Ni) = 0$	
0.2500 Ni_3B	$\Delta_fG(Ni_3B) = -22240-1.908\ T$	
0.3333 Ni_2B	$\Delta_fG(Ni_2B) = -21240+0.234\ T$	
0.1465 Ni_4B	$\Delta_fG(Ni_4B_3) = -25600-3.850\ T$	
0.1410 Ni_4B_{3-x}	$\Delta_fG(Ni_4B_3) = -25650-4.179\ T$	
0.5000 NiB	$\Delta_fG(NiB) = -23220-3.665\ T$	
1.0000 βB	$\Delta_fG\ (\beta B) = 0$	
Liquid(Ni,B)	$\Delta G^{ex} = x(1-x)\{-150720-41.46\ T + (-51080-8.50\ T)(1-2x) + (54610+38.10\ T)(1-2x)^2 + (41030+4.34\ T)(1-2x)^3 + (-36280-25.68\ T)(1-2x)^4\}$	

Fig.1 Isothermal section of the system B - Ni - N at 900°C under 1 bar of argon (in the absence of external nitrogen).



SYSTEM BORON- RUTHENIUM- NITROGEN (B-Ru-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Ru-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Ru and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20μm in a steel mortar and/or a WC-Co mortar respectively [88Rog]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N_2) usually consisted of a primary reaction at 1200°C for 36h followed by a final reaction at 1200°C for 60h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Ru, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Rog].

BINARY SYSTEMS

The reinvestigation of the B-Ru system in the range from 800 to 1400°C revealed the existence of at least six binary ruthenium borides [88Rog]. Consistency with the data available in [84Vil] and [90Mas] is obtained for the formation and crystal structures of Ru_7B_3, $Ru_{11}B_8$, RuB, Ru_2B_3, and RuB_2, whereas near the composition of Ru_2B_3 two novel boride phases with a limited temperature region of existence were found labelled as Ru_2B_{3-x} and Ru_2B_{3-y}; see Table 1.. Ru_2B_{3-x} was reported to decompose peritectoidally at temperatures above 1275°C and eutectoidally below ca 1050°C into RuB + Ru_2B_3 [88Rog]. Due to the rather sluggish diffusion reactions in the high melting B-Ru system, thermodynamic equilibrium at 1000°C was not attained in those alloys which were arc melted prior to heat treatment at 1000°C.

Homogeneous ranges of the binary borides at 1200°C were found to be rather small indicating a typical "line-compound" type of character.

The solid solubility of boron in ruthenium (interstitial type) was claimed to be less than 1.5 at%B at the temperature of the peritectic formation of Ru_7B_8 (ca 1660°C) and was shown to rapidly decease with decreasing temperature [63Obr]. From X-ray powder analysis the maximum solid solubility of Ru in β-B was concluded to be less than 0.5 at%Ru at 1600°C [81Cre].

Fig.1 represents the critically assessed version of the Ru-B phase diagram, temperature versus concentration.

No equilibrium diagram exists for the N-Ru system and solid solubility of N in Ru is said to be very small [78Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2,3 represent the isothermal sections at 1200°C and 1400°C respectively under 1 bar of argon (in the absence of external nitrogen pressure) [88Rog]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the binary ruthenium-borides and BN. As seen from a comparision of the unit cell dimensions there is no significant solid solubility of Ru in BN at 1200°C and at 1400°C, and mutual solubilities of the ruthenium borides and BN are rather restricted [88Rog]. Whereas at 1200°C ruthenium metal is still compatible with BN, compatibility is lost at 1400°C owing to the reaction : $7Ru + 3BN ====== Ru_7B_3 + 3/2N_2$.

Phase equilibria in the Ru-B-N system have been also checked by nitriding the binary ruthenium boride powders under 1 bar of N_2. The results confirm the gradual decomposition of the higher borides via lower borides towards a limiting tie-line : (Ru) + BN. No signs of compound formation at higher nitrogen contents were observed.

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Table 1: Solid phases at 1200°C and 1400°C in the system B-Ru-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Ru	hP2	a= 270.58	[90Mas]
<2334°	$P6_3/mmc$	c= 428.18	
	Mg		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
Ru_7B_3	hP20	a= 746.96	[88Rog]
<1660°	$P6_3mc$	c= 471.55	
	Th_7Fe_3		
$Ru_{11}B_8$	oP38	a=1161.58	[88Rog]
<1457°	Pbam	b=1134.38	
	$Ru_{11}B_8$	c= 283.61	
RuB	hP2	a= 285.33	[88Rog]
<1520°	$P\bar{6}m2$	c= 285.57	
	WC (or def. AlB_2)		
Ru_2B_{3-y}	unknown		[88Rog]
<1200°			
Ru_2B_{3-x}	hP7	a= 500.42	[88Rog]
1275-1025°		c=1849.20	
	Ru_2B_{3-x}		
Ru_2B_3	hP10	a= 290.48	[88Rog]
<1600°	$P6_3/mmm$	c=1280.94	
	Ru_2B_3		
RuB_2	oP6	a= 464.48	[88Rog]
<1650°	Pmmn	b= 286.58	
	RuB_2	c= 404.62	
BN_{hex}	hP5	a= 250.4	[85Vil]
	$P6_3/mmc$	c= 666.1	
	BN_{hex}		

Fig.1: Assessed diagram of the binary system Ru - B

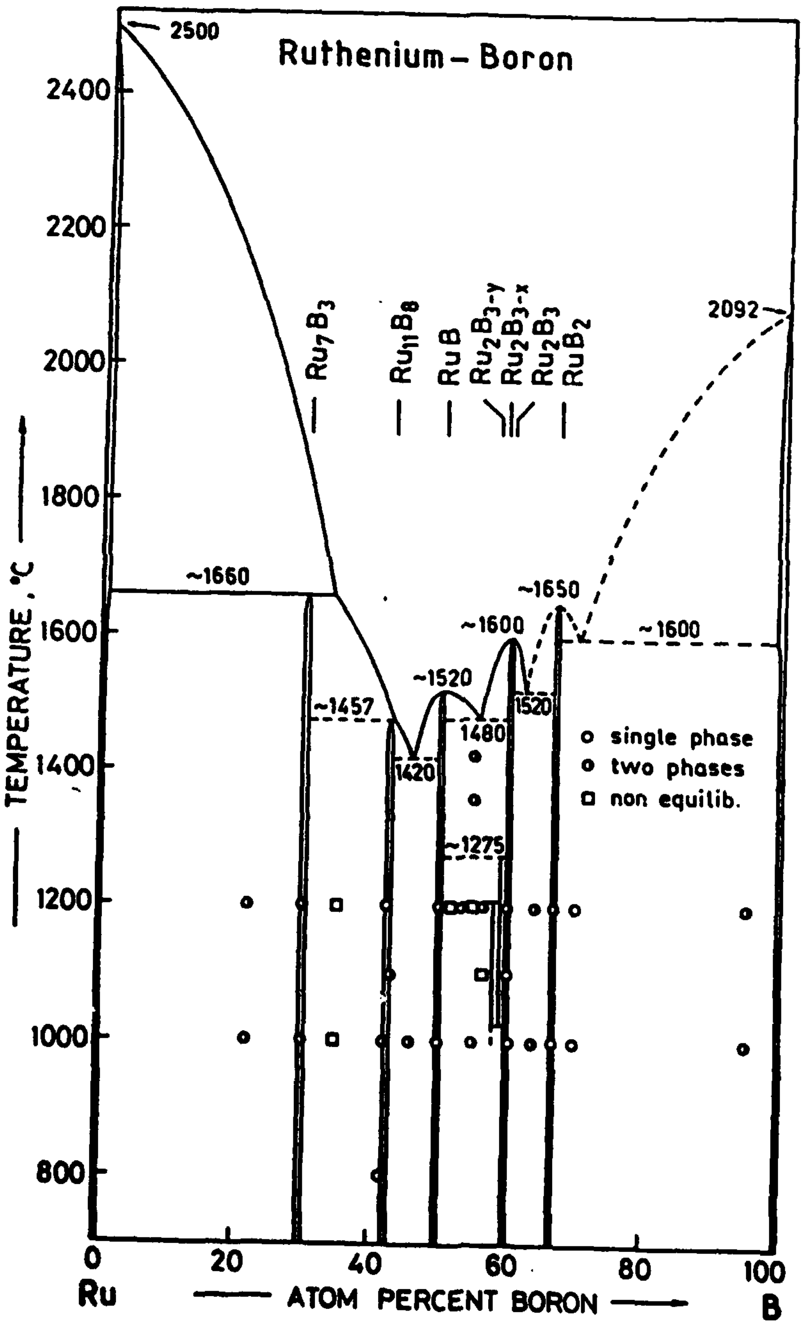


Fig.2: Isothermal section of the system B - Ru -N at 1200°C under 1 bar of argon (in the absense of external nitrogen).

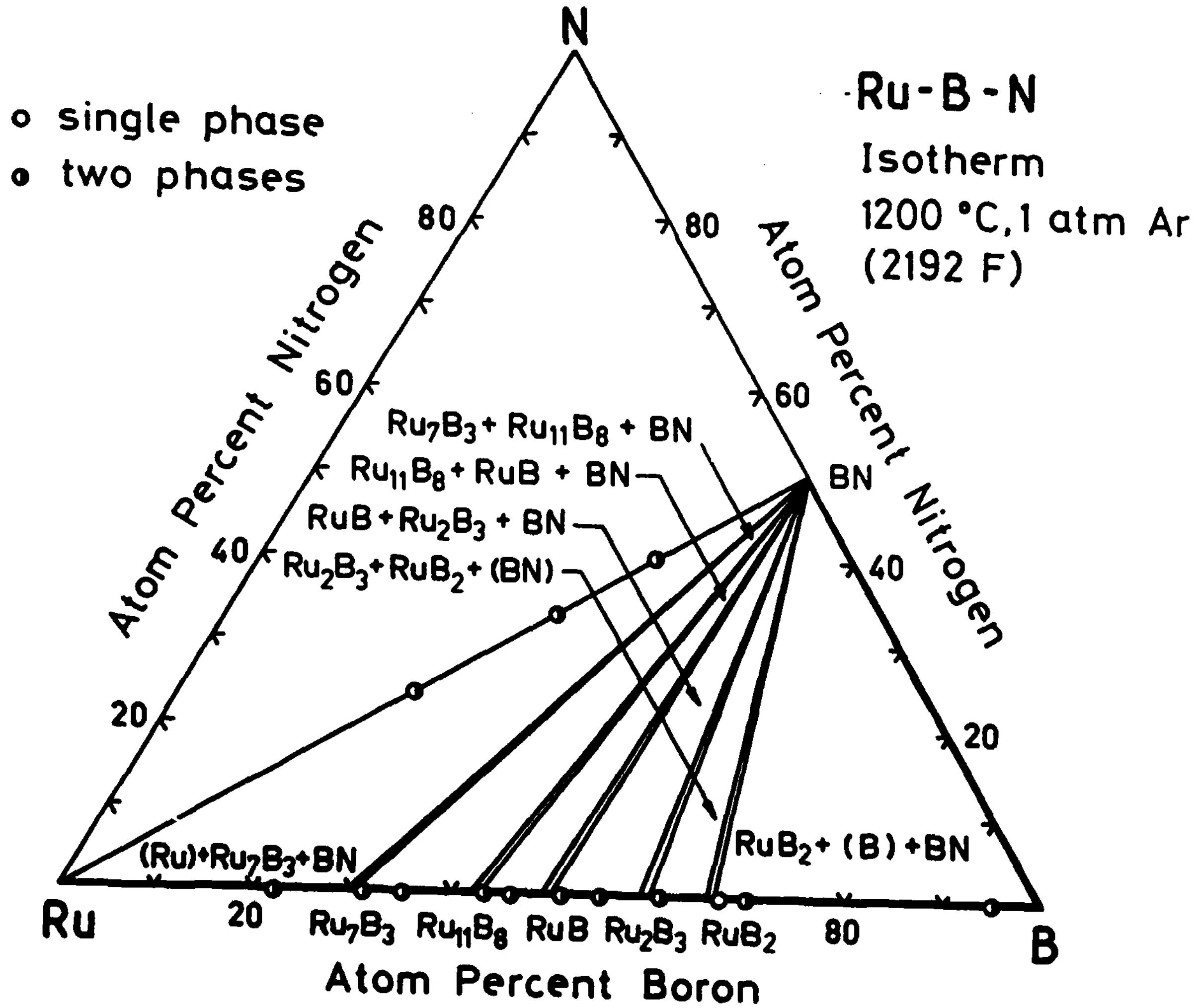
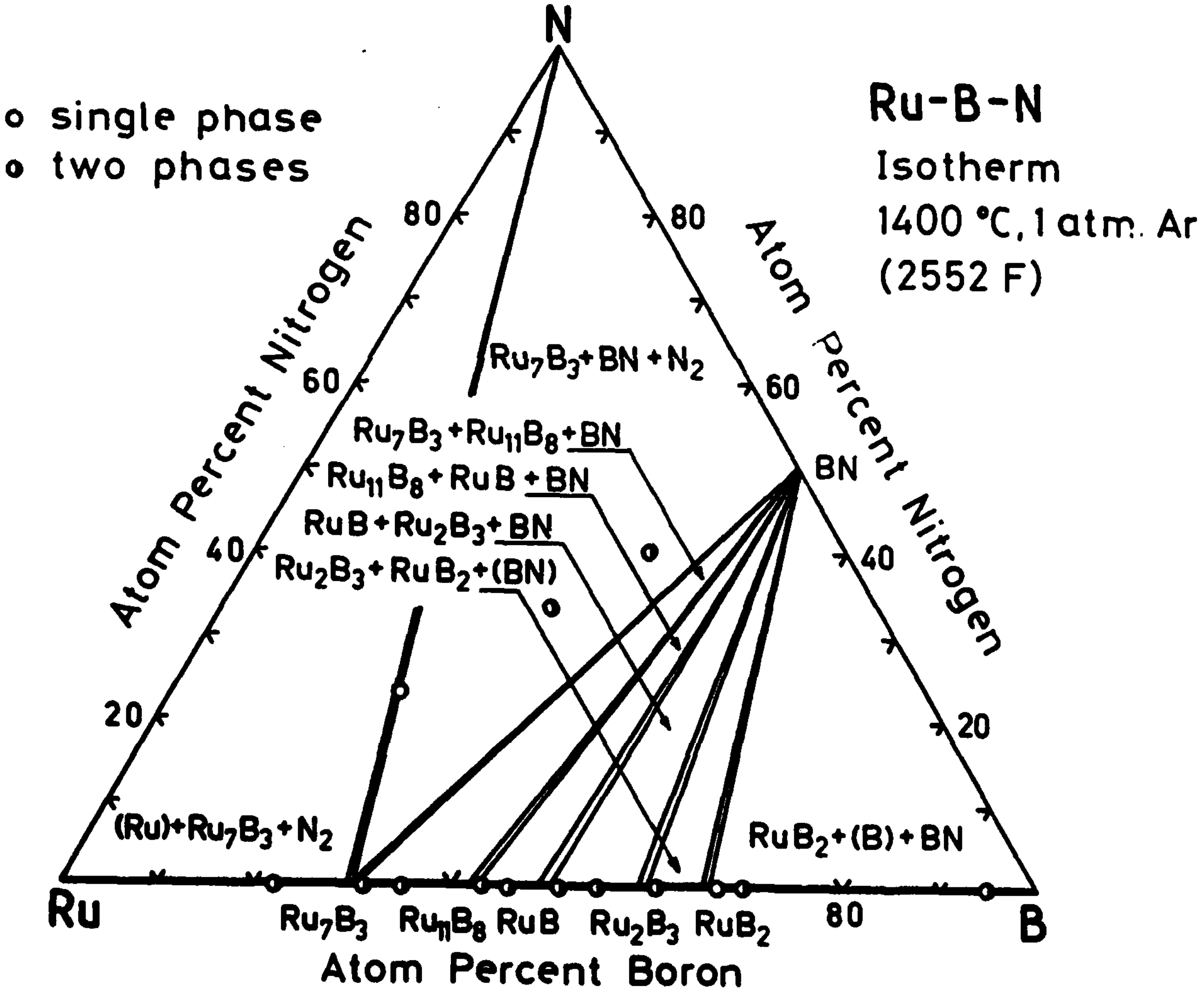


Fig.3 Isothermal section of the system B - Ru - N at 1400°C under 1 bar of argon (in the absence of external nitrogen).



SYSTEM BORON - COPPER - NITROGEN (B-Cu-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Cu-N system have been derived from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 900°C for a total of 800h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Cu, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C and GEC-cubic boron nitride of 99.8 % purity. After X-ray analysis the samples were exposed to 1 bar of nitrogen for an additional 400h at 900°C and examined.

BINARY SYSTEMS

A tentative equilibrium diagram for the system B-Cu is represented in [90Mas];for a detailed discussion see also [77Gur]. The equilibrium diagram is of a simple eutectic type (~1013°C, ~13.3 at%B) with a rather extended and retrograde solubility of Cu in β-rhombohedral boron [76Lun,91Lun] (~3 at%Cu at 1013°C, 3.17 at%Cu at 1300°C, 3.47 at%Cu at 1500°C and 3.65 at%Cu at 1700°C; see also Table 1). The solid solubility of B in Cu was said to be low (~0.29 at%Cu at 1013°C and 0.06 at%Cu at RT [86Mas]).

No phase diagram Cu-N is available yet, however, four binary compounds have been claimed to exist under various conditions : Cu_4N, prepared by d.c.-plasma ion nitriding of a Cu-sheet in a 260Pa - N_2/H_2- atmosphere at 450 to 530°C, probably is metastable [89Blu]; Cu_3N, was reported to be stable in hydrogen up to ca 310°C [84Bai] , whereas the azides CuN_3 and CuN_6 were synthesized at room temperature [48Wil,88Soe]; Table 1. The solubility of nitrogen in copper is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 900°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Cu) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (l-Cu) + BN at 1100°C [65Yas].

MISCELLANEOUS

The wetting angle of Cu on BN_{hex}, as measured by the sessile drop method, was given as $\Theta = 125^\circ$ [65Yas].

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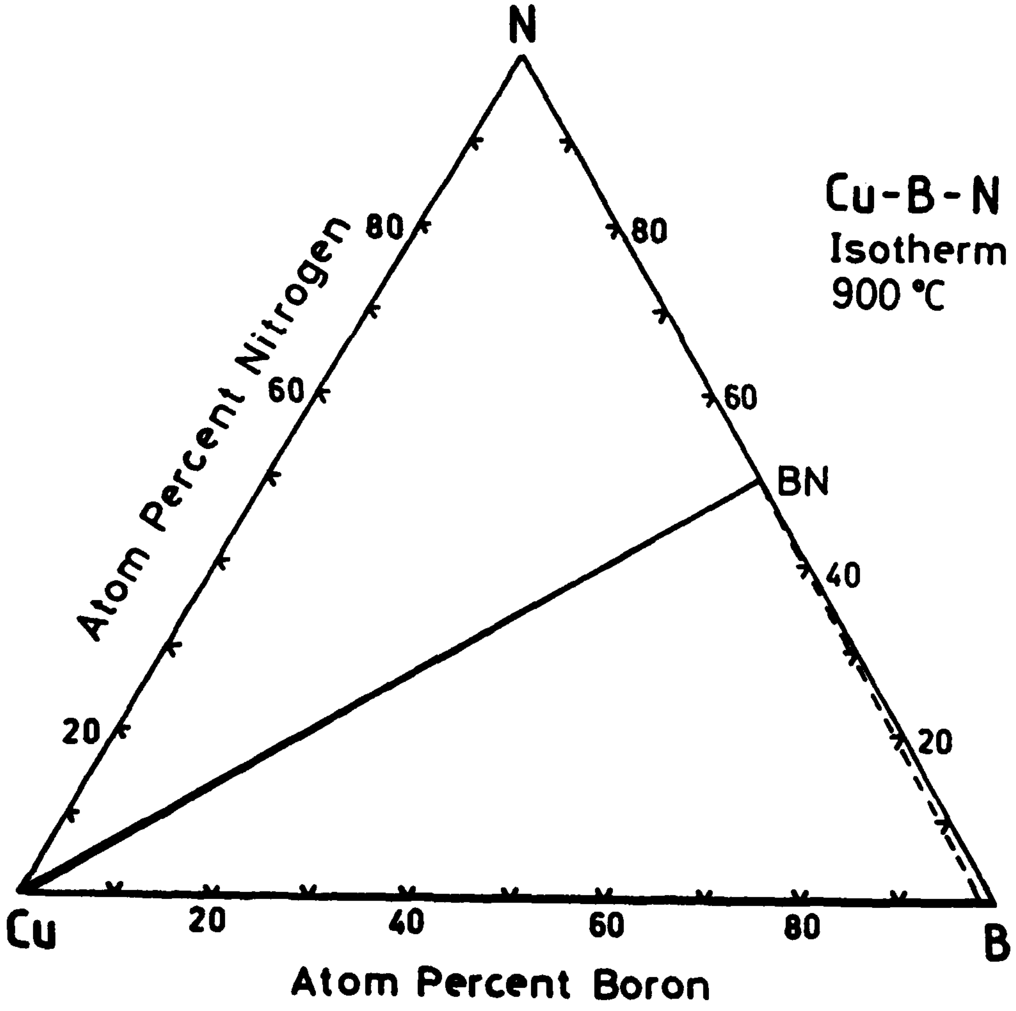
Table 1: Solid phases at 900°C in the system B - Cu - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Cu <1084.9°	cF4 $Fm\bar{3}m$ Cu	a= 361.49	[86Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1093.02 c=2381.66	[76Lun]
		a=1093.32 c=2382.92	[76Lun] for $CuB_{443.9}$
		a=1093.77 c=2384.27	[76Lun] for $CuB_{170.6}$
		a=1094.38 c=2386.28	[76Lun] for $CuB_{86.7}$
		a=1096.05 c=2387.93	[76Lun] for $CuB_{42.2}$
		a=1097.23 c=2388.94	[74And] for CuB_{28}
		a=1098.5 c=2392.5	[76Hig] for CuB_{28}
Cu_4N	cP5 $Pm\bar{3}m$ or $P\bar{4}3m$ Fe_4N	a= 319.3	[85Vil] metastable
Cu_3N	cP4 $Pm\bar{3}m$ ReO_3	a= 381.3	[85Vil]
CuN_3	tI32 $I4_1/a$	a= 865.3 c= 559.4	[85Vil]
CuN_6	oP28 Pnma	a=1348.1 b= 308.4 c= 907.6	[85Vil]

BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig 1: Isothermal section at 900°C in the system B - Cu - N



SYSTEM BORON - SILVER - NITROGEN (B-Ag-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Ag-N system have been derived from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 800°C for a total of 700h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of silver (Ögussa, "puriss"), crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C ,and GEC-cubic boron nitride of 99.8 % purity. After X-ray analysis the samples were exposed to 1 bar of nitrogen for an additional 400h at 800°C and examined.

BINARY SYSTEMS

A tentative equilibrium diagram for the system B-Ag which is supposed to be of a simple monotectic type with negligible solid solubility of B in Ag and without the existence of equilibrium compounds is presented in [Mof]; a detailed discussion is found in [77Gur]. The compound "AgB_2", claimed to crystallize with the AlB_2-type (C32, hP3 - P6/mmm, a=300.0, c= 324.0pm [61Obr]), is likely to be metastable, and has not been confirmed yet. A small solid solubility of Ag in β-rhombohedral boron is inferred from the X-ray data on an arc melted alloy [81Cre]; see Table 1.

No phase diagram exists for the system Ag-N, however, the existence of two compounds, which are unstable above 300°C, has been reported: Ag_3N and AgN_3 (see Table 1). The solubility of N in silver is very small [76Fro]. A critical assessment of the data available on the Ag-N system is due to [90Kar].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 800°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Ag) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed [90Wei].

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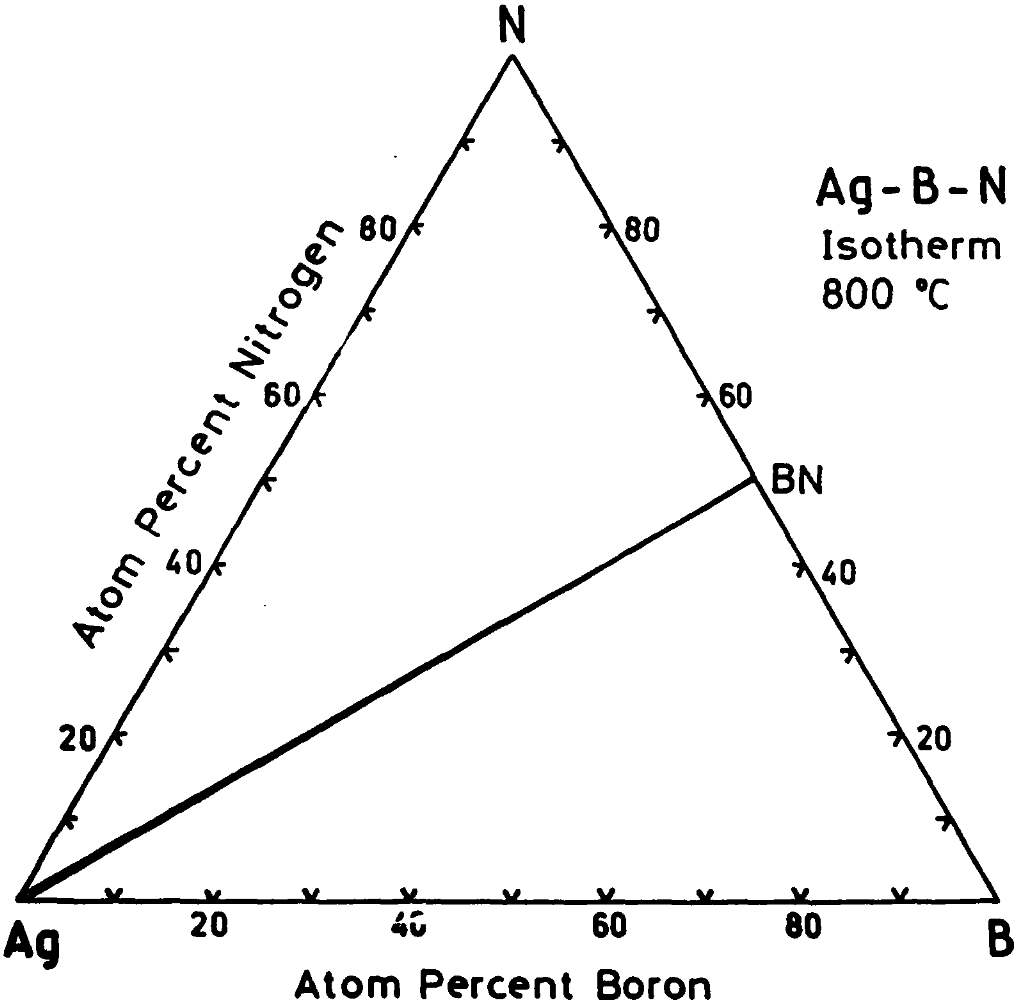
Table 1: Solid phases at 800°C in the system B - Ag - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Ag $<961.93^\circ$	cF4 $Fm\bar{3}m$ Cu	a= 408.61	[90Mas]
β-rhB $<2092^\circ$	hR111 $R\bar{3}m$ β-B	a=1092.65 c=2380.96	[81Cre]
		a=1093.55 c=2384.40	[81Cre] for AgB_x
Ag_3N	cF*	a= 437.8	[85Vil]
AgN_3	oI16 Ibam KN_3-deriv.	a= 561.70 b= 591.46 c= 600.57	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section at 800°C in the system B - Ag - N



SYSTEM BORON - GOLD - NITROGEN (B-Au-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Au-N system have been derived from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 800°C for a total of 1400h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Au, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C and GEC-cubic boron nitride of 99.8 % purity. After X-ray analysis the samples were exposed to 1 bar of nitrogen for an additional 400h at 800°C and examined.

BINARY SYSTEMS

A tentative equilibrium diagram for the system Au-B is shown in [90Mas]; a detailed discussion is also presented by [77Gur]. Without the existence of equilibrium compounds, the system Au-B is suggested to be of a simple monotectic type with negligible solid solubilities of Au, B. For the solubility of Au in β-B see [81Cre] and Table 1. The compound "AuB_2", claimed to crystallize with the AlB_2-type (C32, hP3 - P6/mmm, a=314, c= 352pm [61Obr]), is likely to be metastable, and has not been confirmed yet.

No phase diagram exists for the system Au-N, however, a critical assessment of the existing information is available by [84Oka]; the formation of two probably metastable compounds Au_3N_2 and AuN_3 both with unknown crystal structure is mentioned [84Oka]. The solubility of N in Au is negligible [84Oka,78Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 800°C in the absence of external nitrogen pressure. Phase equilibria are characterized by compatibility of (Au) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed.

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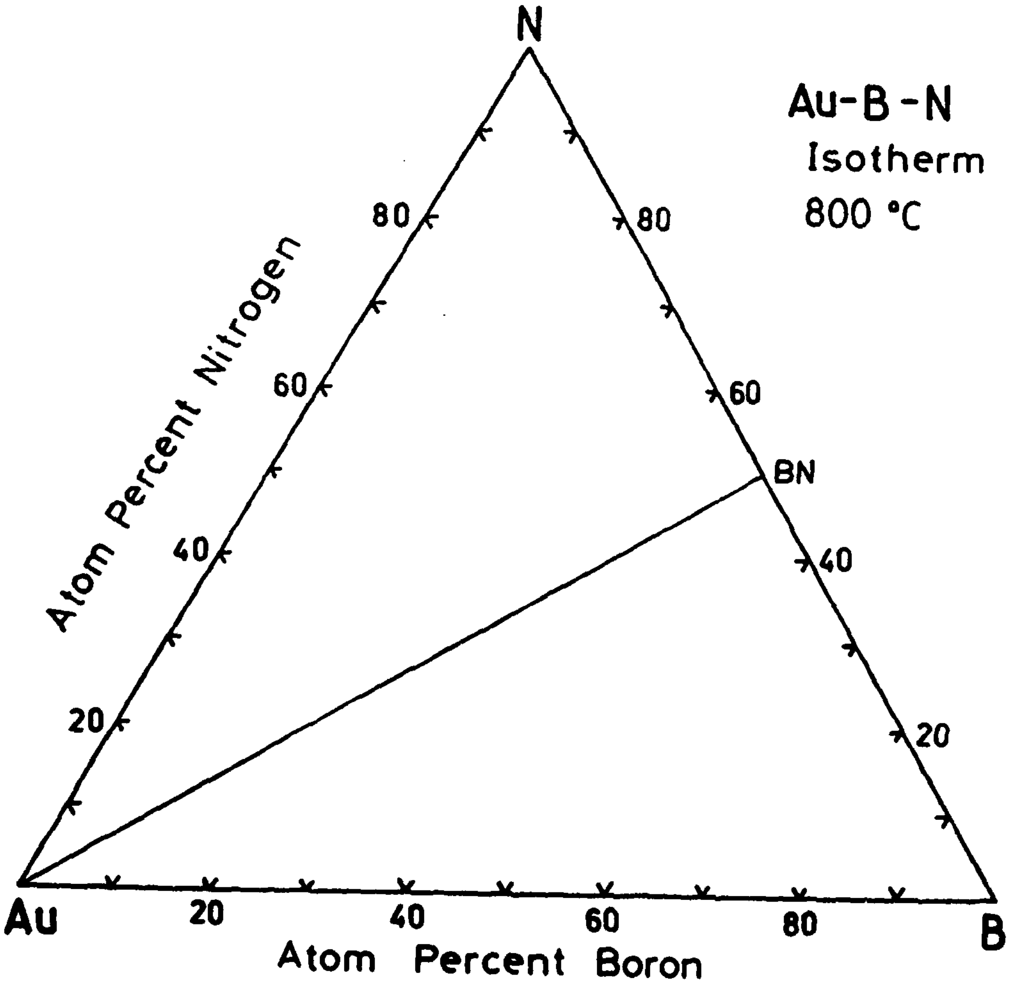
Table 1: Solid phases at 800°C in the system B - Au - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Au $<1064.4°$	cF4 $Fm\bar{3}m$ Cu	a= 407.84	[90Mas]
β-rhB $<2092°$	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil]
		a=1093.24 c=2382.38	[81Cre] for AuB_x
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section at 800°C in the system B - Au - N



SYSTEM BORON - ZINC - NITROGEN (B-Zn-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Zn-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 375°C for a total of 850h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Zn, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

BINARY SYSTEMS

A tentative equilibrium diagram for the system B-Zn is given in [Mof], however, does not account for the observed solid solubility of Zn in boron (see below); a comprehensive discussion of all reported information has been given by [77Gur]. There is no binary boride known and there is practically no solubility of B in Zn, whereas a rather extended solid solution $B_{100-x}Zn_x$ ($x < 5$) exists in β-rh boron (~ $B_{22}Zn$,[87Kuz]) as well as in α-rh boron (<1.3 at%Zn, [77Kor]); see Table 1. The interaction of Zn with the various modifications of boron at 500 to 900°C has been studied by [77Kor].

According to a recent critical assessment of the system N-Zn [88Wri] two binary compounds are known to exist: Zn_3N_2 (see Table 1), which was claimed to be stable up to 550°C under N_2, but decomposes in vacuum above 350°C [88Wri] and ZnN_6 which decomposes on heating around 300°C and for which two structural modifications have been reported (see Table 1) [88Wri]. Interstitial solubility of N in Zn is very low [88Wri].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 375°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Zn) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (ℓ-Zn) + BN at 940°C [65Yas].

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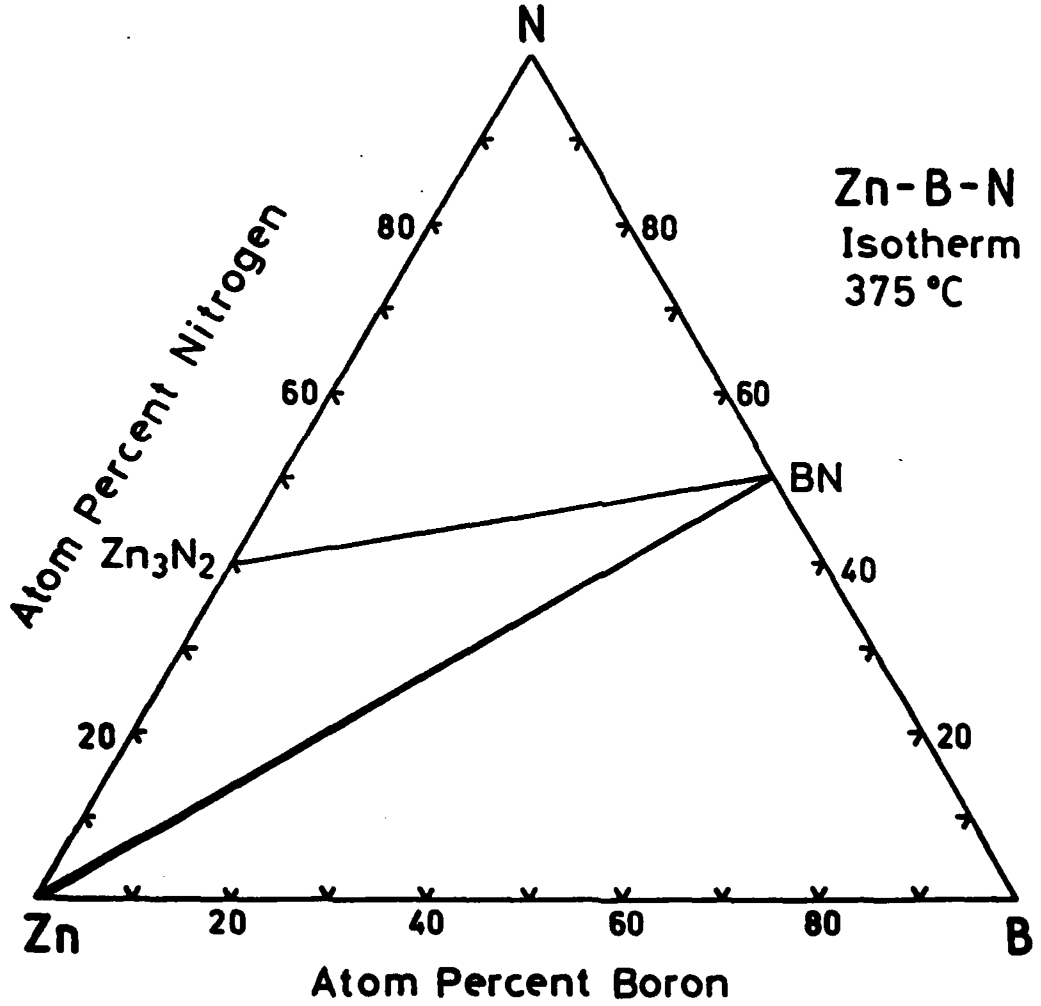
[90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)", J.Mater.Res. 5 (1990) 2152-2159

[90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams", 2nd Ed., (Amer.Soc.Met., Metals Park,Oh, 1990)

Table 1: Solid phases at 375°C in the system B-Zn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Zn	hP2	a= 266.44	[90Mas]
<419.6°	$P6_3/mmc$	c= 494.94	
	Mg		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
		a=1098.6	[87Kuz] for ZnB_{25}
		c=2401.6	
		a=1093	[77Kor]
		c=2374	
		a=1101	[77Kor] for ZnB_{218}
		c=2317	
		a=1100	[77Kor] for ZnB_{28}
		c=2404	
α-rhB	hR36	a= 490.9	[77Kor]
<1200°	$R\bar{3}m$	c=1258.2	
	α-B		
		a= 491.0	[77Kor] for ZnB_{80}
		c=1258.2	
BN_{hex}	hP*	a= 250.4	[85Vil]
	$P6_3/mmc$	c= 666.1	
	BN_{hex}		
Zn_3N_2	cI80	a= 976.3	[85Vil]
	$Ia\bar{3}$		
	Mn_2O_3		
α-ZnN_6	oP36	a=1098	[85Vil]
	$P222_1$	b= 692	[88Wri] gives Pcmn-oP84
		c=1633	
β-ZnN_6	o*28	a= 735	[88Wri]
		b= 437	
		c=1523	

Fig.1: Isothermal section at 375°C in the system B - Zn - N



SYSTEM BORON - CADMIUM - NITROGEN (B-Cd-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Cd-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 250°C for a total of 350h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Cd, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C and GEC-cubic boron nitride of 99.8 % purity.

BINARY SYSTEMS

A tentative equilibrium diagram for the system B-Cd is given in [Mof]. A binary compound "CdB_6" has been mentioned earlier but is supposed to be metastable or ill characterized; for a more detailed discussion see [77Gur]. B was said to be insoluble in Cd and whereas the solubility of Cd in β-B is said to be very low, ~5 mass% Cd was reported to dissolve in α-B at 800°C [77Gur].

According to a recent critical assessment of the system Cd-N [88Wri], the formation of two binary compounds has been reported: Cd_3N_2 and CdN_6; see Table 1. Whereas Cd_3N_2 was reported to decompose slowly at 180°C in an atmosphere of NH_3 (pressure not specified, [88Wri]), the azide CdN_6 decomposes nonexplosively when heated slightly above 100°C [88Wri]. The solubility of N in Cd is small [88Wri].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 250°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Cd) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (l-Cd) + BN at 550°C [65Yas].

MISCELLANEOUS

Nonwetting behavior ($\Theta > 90^{o}$) was claimed by [65Yas].

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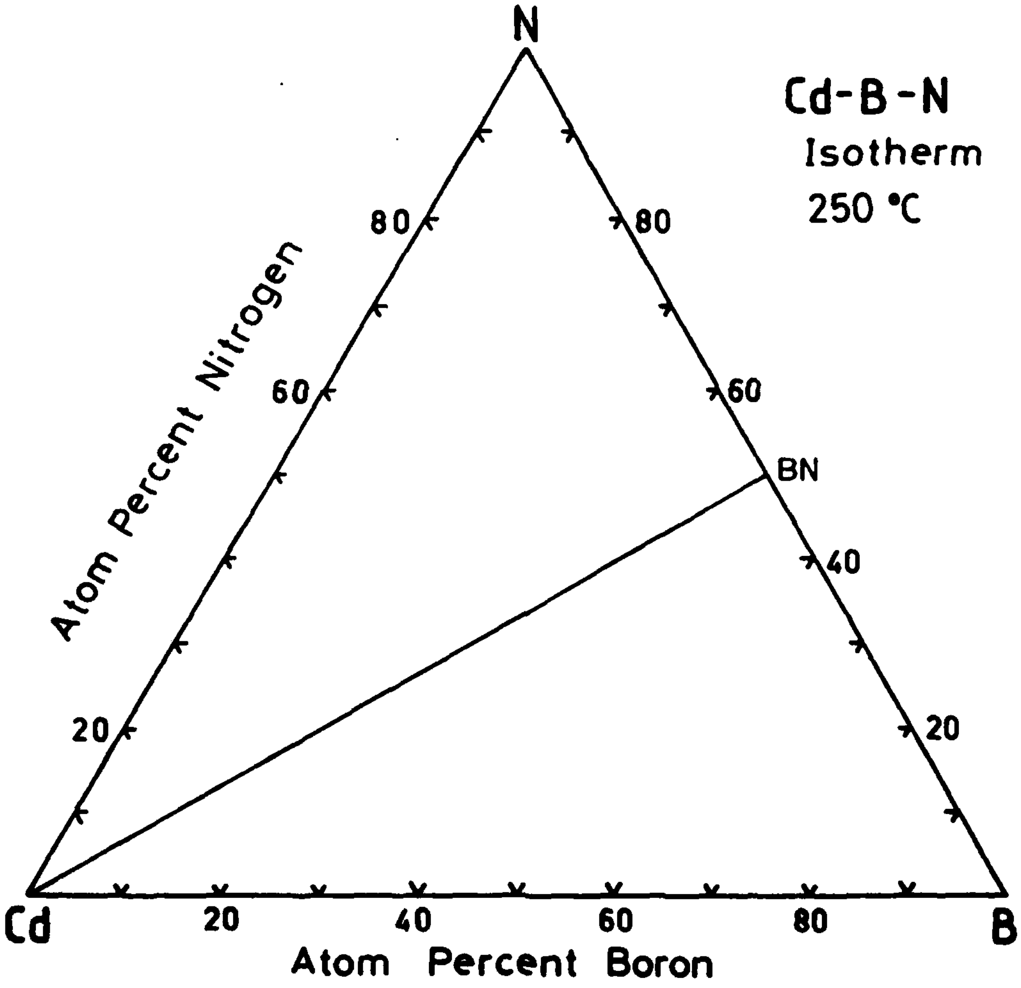
[90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams", 2nd Ed., (Amer.Soc. Met., Metals Park,Oh, 1990)

Table 1: Solid phases at 375°C in the system B - Cd - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Cd <321.11°	hP2 $P6_3/mmc$ Mg	a= 297.88 c= 561.67	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250 4 c= 666.1	[85Vil]
Cd_3N_2	cI80 $Ia\bar{3}$ Mn_2O_3	a=1081	[85Vil]
CdN_6	oP56 Pbca	a= 784 b= 647 c=1607	[88Wri]

Fig.1: Isothermal section at 250°C in the system B - Cd - N



SYSTEM BORON - ALUMINIUM - NITROGEN (B-Al-N)

INTRODUCTION / EXPERIMENTAL

Information on the phase relations in the Al-B-N system are due to several research groups [65Pri, 67Lue, 72Lyu, 73Lyu, 79Sir, 81Hir, 82And1, 82And2 and 91Rem]. A recent critical review has been provided by [90Jeh]. General agreement exists on the absence of ternary compounds. Various methods employed such as (a) nitriding of complex salts of Al and B or mixtures of metal and complex salts in NH_3 or (b) reaction sintering of polycrystalline samples Al+BN , resulted in the formation of extended solid solutions of the mononitrides $Al_{1-x}B_xN$ [65Pri, 72Lyu, 73Lyu, 79Sir, 82And1, 82And2, 91Rem]. AlN was found to act as a catalyst for the synthesis of cubic BN from hexagonal BN in lowering the temperature and pressure conditions to 1000°C and 7 GPa [81Hir]; sintering of BN+Al powder compacts in the range from 1500 to 3000°C and 5 to 9.5 GPa resulted in cubic BN with 2-3 mass% Al dissolved [79Sir]. The lattice parameter of BN was said to decrease from 361.5 to 361.0 pm on saturation with Al; higher Al contents yielded the formation of AlN, AlB_{12} and β-B [79Sir]. Two isothermal sections at 10^5Pa and 8GPa have been presented [73Lya, 79Sir, 82And1, 82And2].

Phase equilibria in the B-Al-N system at 900°C under 10^5Pa argon (in the absence of external nitrogen)have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20µm in a WC-Co mortar. For annealing the samples were kept on a Mo(or BN)-substrate within a wire resistance heated quartz recipient under argon. Heat treatments usually consisted of total of 1000h with repeated crushing and recompacting to ensure homogeneity [91Rem]. Starting materials were ingots of 3N-Al, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

BINARY SYSTEMS

A tentative phase diagram Al-B as presented in [E11] contains AlB_2 and AlB_{12} as the only binary phases (Table 1) and is in agreement with a reinvestigation at 900°C [91Rem]. The solid solubility of B in Al is less than 0.025 at%B at 659.7°C. No attempts have been made to establish the solubility of Al in boron. The assessed version of the Al-B diagram is shown in Fig.1.

The Al-N phase diagram, as suggested by [90Mas], is accepted; a detailed description is due to [86Wri]. AlN is the only binary phase (Table 1). The solid solubility of N in Al is low [86Wri].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig 2 shows the phase equilibria as determined by [82And2] at a pressure of 8 GPa.

Fig.3 represents the isothermal section at 900°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the formation of a stable equilibrium AlB_2+ (AlN) + (BN) with a small but significant mutual solubility of $Al_{1-x}B_xN$. No ternary compounds have been observed.

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Table 1: Solid phases at 900°C in the system B-Al-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Al <660.452°	cF4 $Fm\bar{3}m$ Cu	a= 404.96	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
AlB_2 <975°	hP3 P6/mmm AlB_2	a= 300.6 c= 352.2	[85Vil]
γ-AlB_{12}(r) <1450°	oP384 $P2_12_12_1$ γ-AlB_{12}	a=1657.3 b=1751.0 c=1018.0	[81Hig]
α-AlB_{12}(h) 1920-1450°	tP216 $P4_12_12$ α-AlB_{12}	a=1015.8 c=1427.0	[77Hig]
AlN	hP4 $P6_3mc$ ZnS	a= 311.14 c= 497.92	[86Wri]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: The binary system Al-B

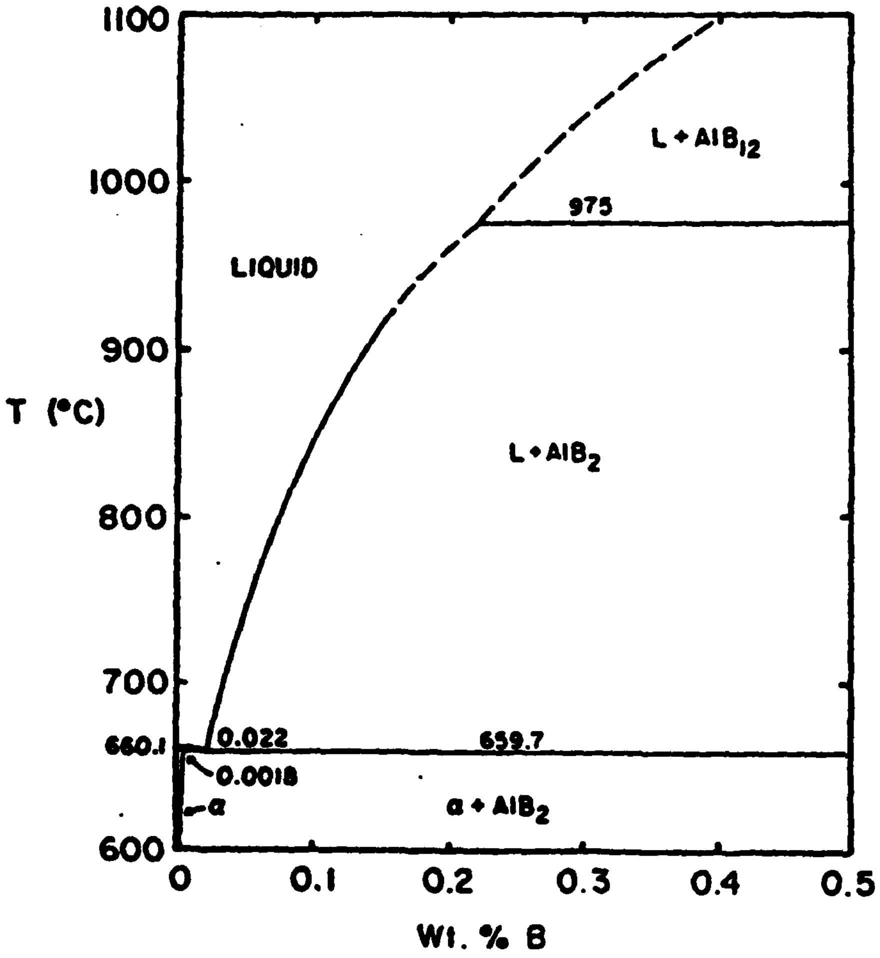


Fig.2: Isothermal section in the system B-Al-N under 8 GPa [82And2]

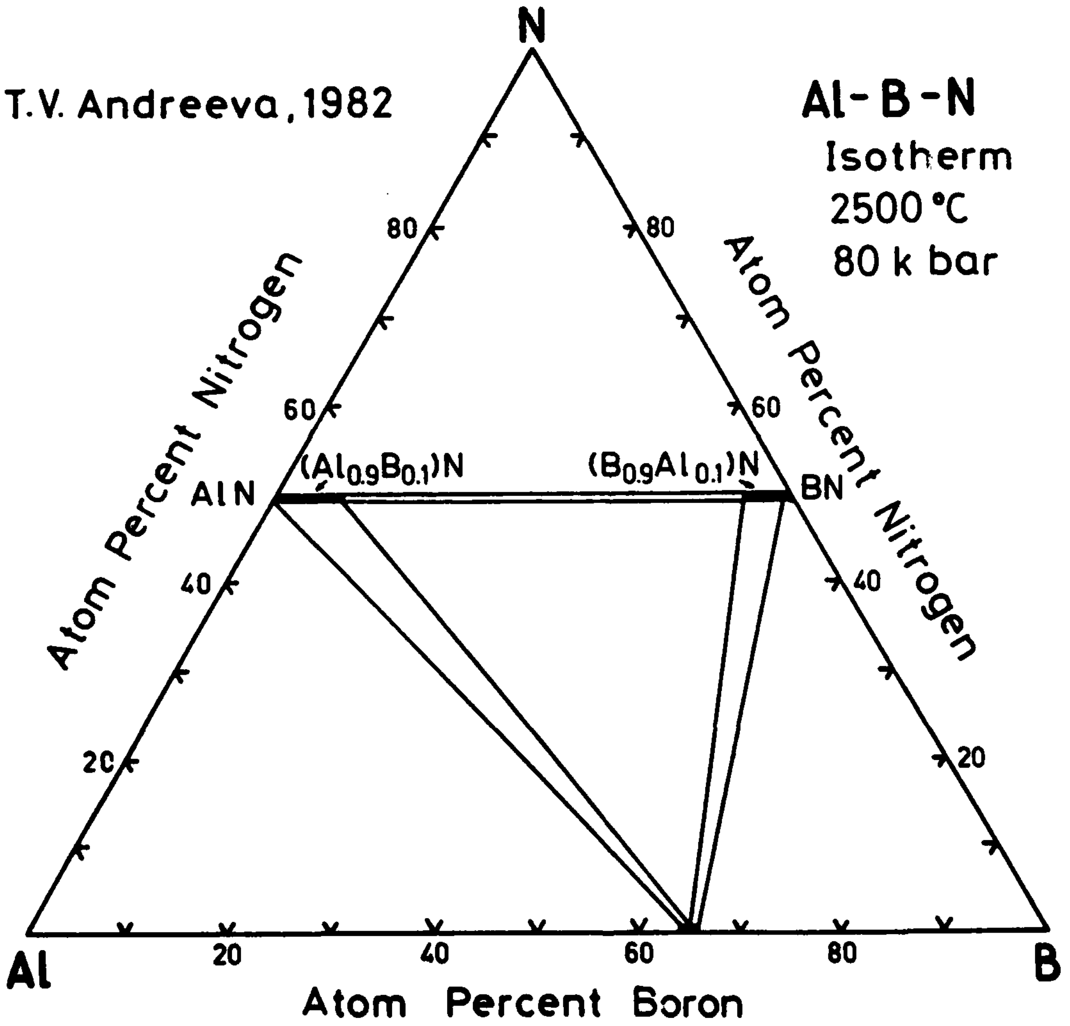
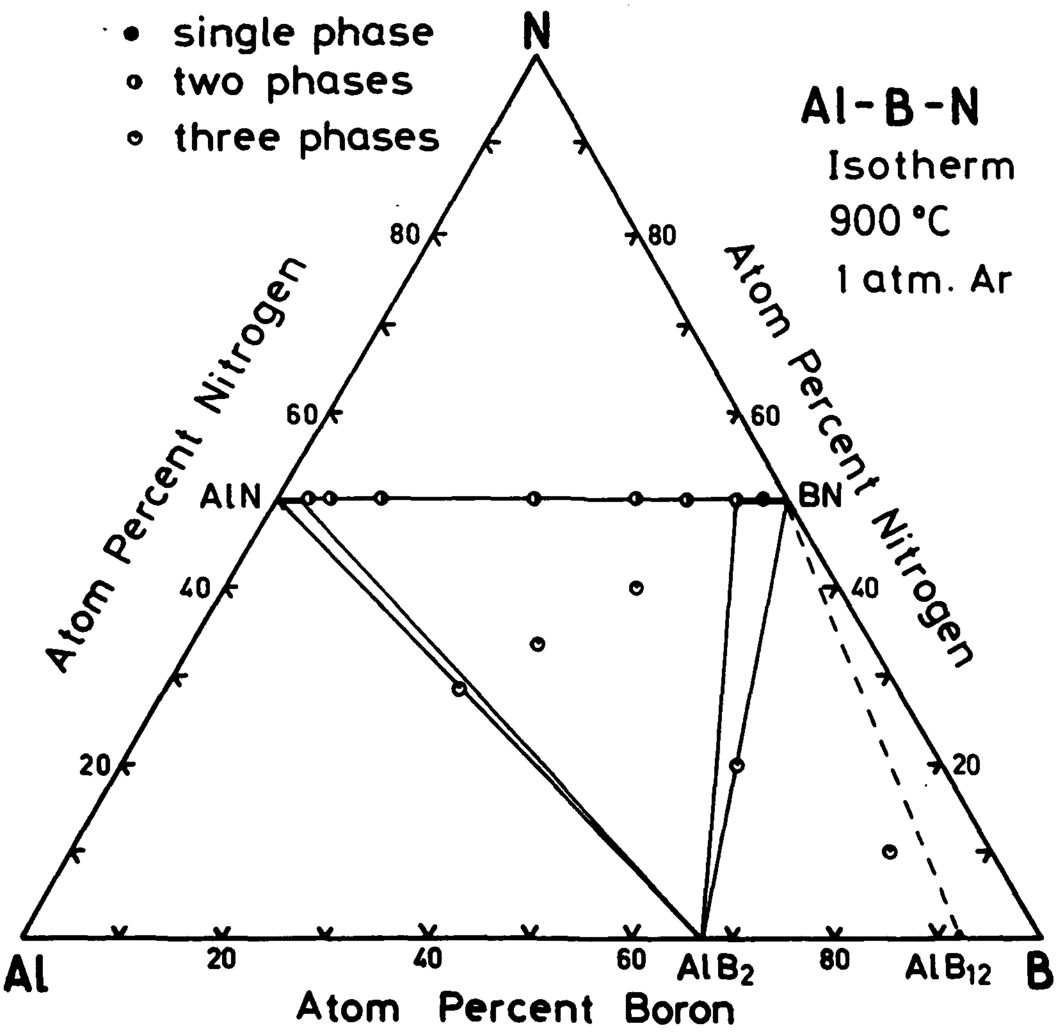


Fig.3: Isothermal section at 900°C in the system B - Al - N under 10^5Pa argon, in the absence of external nitrogen



SYSTEM BORON - INDIUM - NITROGEN (B-In-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-In-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 120°C for a total of 1800h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-In, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-In is given in [Mof,65Wal]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram In-N exists. According to a critical assessment by [89Oka] the only binary nitride InN was said to be rather unstable and to decompose at ca 680°C under 10^5Pa N_2 [38Juz], [87Jon]. The interstitial solubility of N in In is likely to be very low; no details are known so far [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 120°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (In) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed [90Wei].

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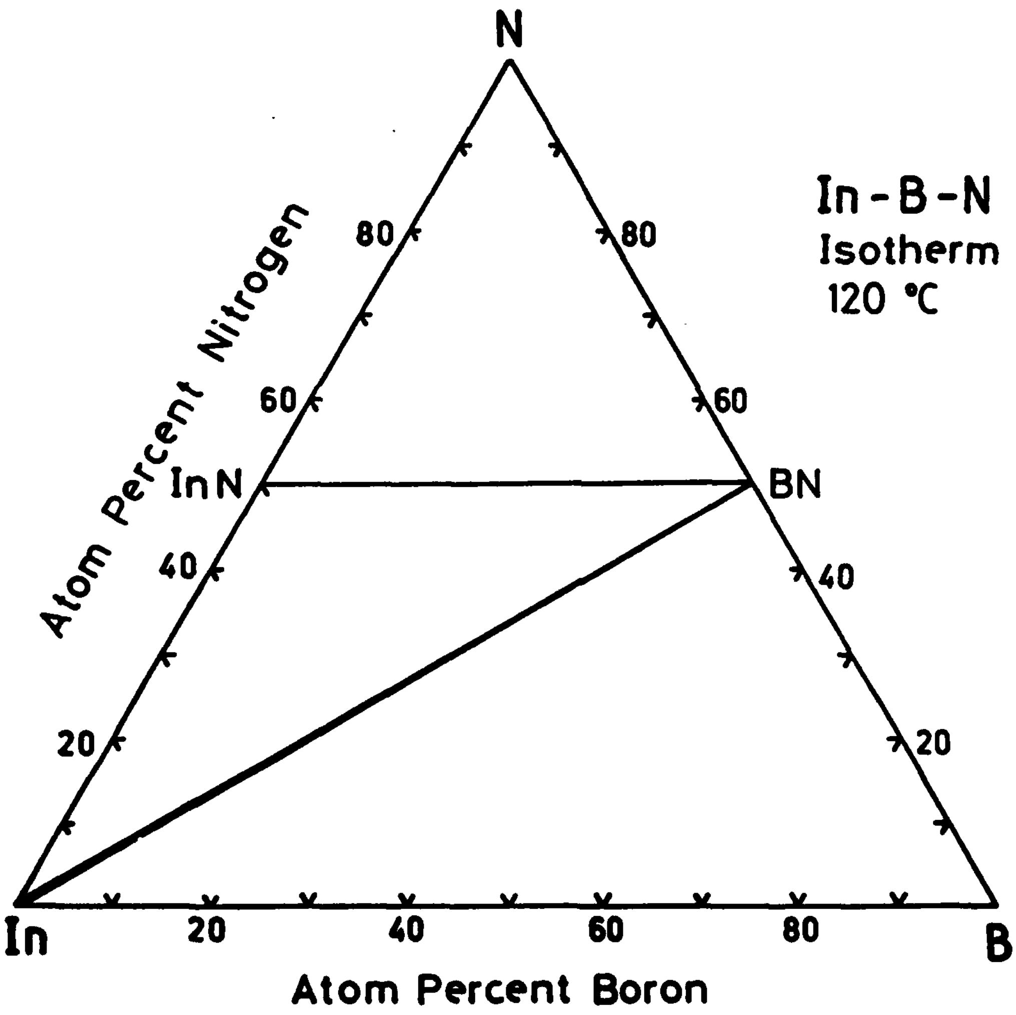
Table 1: Solid phases at 120°C in the system B-In-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
In <156.63°	tI2 I4/mmm In	a= 325.3 c= 494.70	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
InN	hP4 $P6_3mc$ ZnS	a= 354.0 c= 570.4	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section at 120°C in the system B - In - N



SYSTEM BORON - THALLIUM - NITROGEN (B-Tl-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Tl-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 200°C for a total of 1000h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were ingots of 3N-Tl, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Tl is given in [Mof,65Wal]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram is available for Tl-N.The binary nitrides TlN and TlN_3 were said to be rather unstable . TlN is obtained in the arc using Tl-electrodes under nitrogen [76Fro]. According to thermal expansion data in the range from 95 to 600 K, TlN_3 was observed with three modifications [73Mau]. TlN_3 at room temperature was reported to be isomorphic with KN_3 : β-TlN_3 (tI16 - I4/mcm, a=620.94, c=735.83pm [73Mau]) with a transition into an orthorhombic structure at temperatures below 248(5)K : α-TlN_3 (oP32, a=871.8, b=876.6, c=739.5pm [73Mau]); furthermore a cubic high temperature phase γ-TlN_3 ($Pm\bar{3}m$, structure unknown) has been discussed to be stable at 10^5Pa N_2 above 565.2 K ;see [73Mau]. No interstitial solubility of N in Tl was observed up to 600°C [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 200°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Tl) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed.

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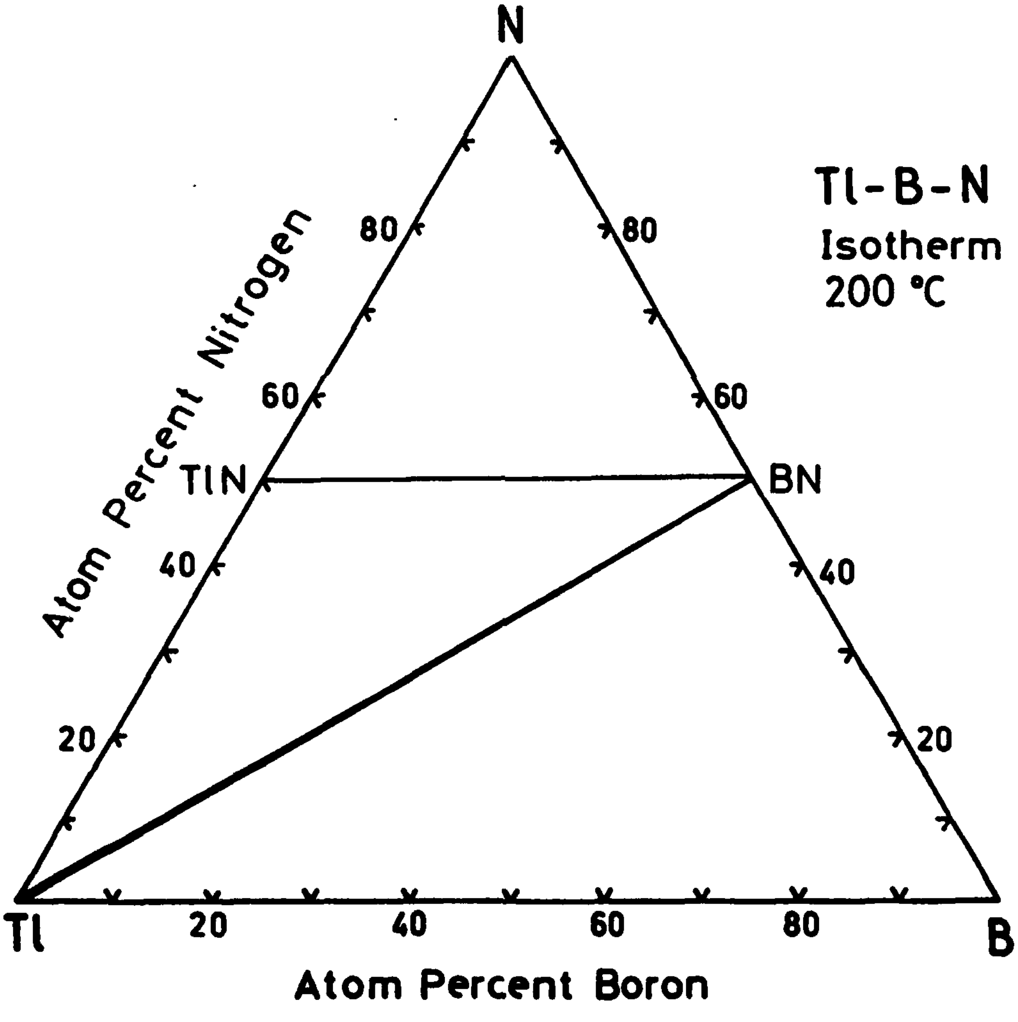
Table 1: Solid phases at 200°C in the system B-Tl-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
α-Tl <230°	hP2 $P6_3/mmc$ Mg	a= 345.66 c= 552.48	[90Mas]
β-Tl <303°	cI2 $Im\bar{3}m$ W	a= 387.1	[90Mas]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil]
TlN	hP4 $P6_3mc$ ZnS	a= 368 c= 601	[85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section at 200°C in the system B - Tl - N



SYSTEM BORON - TIN - NITROGEN (B-Sn-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Sn-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 200°C for a total of 1100h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Sn, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Sn is given in [Mof], for a more detailed discussion see [77Mak]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram exists for N-Sn. Binary nitrides Sn_3N_4 and Sn_3N_2 were said to be rather unstable and may be prepared by heating $Sn(NH_2)_3Cl$ or SnNH to 340°C in vacuum. In the temperature range 25° to 800°C the interstitial solubility of N in Sn is said to be negligible [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 200°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by compatibility of (Sn) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (ℓ-Sn) + BN at 800°C [65Yas].

MISCELLANEOUS

Nonwetting behavior ($\Theta > 90^\circ$) was claimed by [65Yas].

REFERENCES

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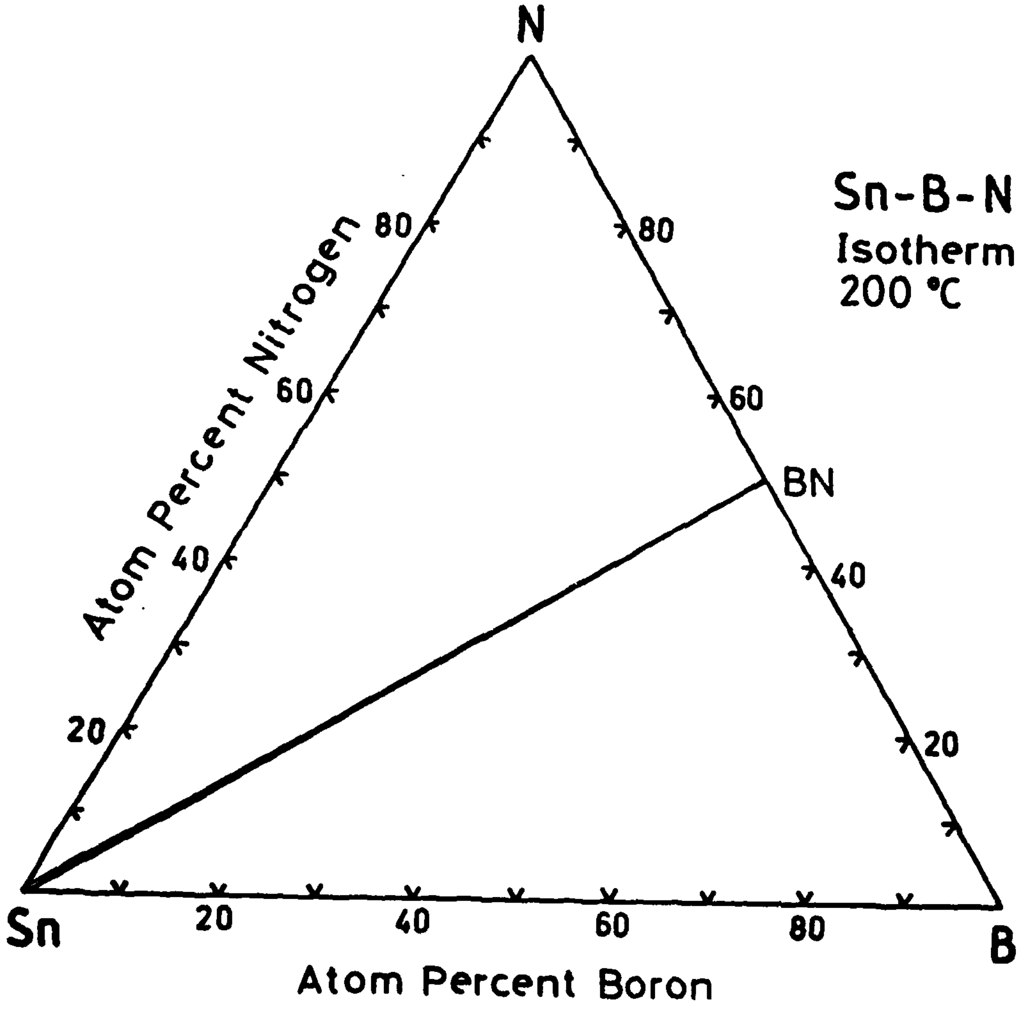
Table 1: Solid phases at 200°C in the system B-Sn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
β-Sn	tI4	a= 583.18	[90Mas]
<231.97°	$I4_1/amd$	c= 318.18	
	β-Sn		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
BN_{hex}	hP*	a= 250.4	[85Vil]
	$P6_3/mmc$	c= 666.1	
	BN_{hex}		

Fig.1: Isothermal section at 200°C in the system B - Sn - N



SYSTEM BORON - LEAD - NITROGEN (B-Pb-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Pb-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 200°C for a total of 1500h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were ingots of 3N-Pb, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Pb is given in [Mof]; a comprehensive discussion of all reported information has been given by [77Mak]. There is no binary boride known and there is practically no solid solubility of B in Pb. In the Pb-N system several rather unstable binary compounds have been claimed to exist: Pb_3N_2 and Pb_3N_4 , which have been prepared by cathodic sputtering [76Fro], and metastable PbN_6, for which two structural modifications have been reported (Table 1). There is practically no solubility of N in Pb up to 600°C [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 200°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Pb) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (ℓ-Pb) + BN at 800°C [65Yas].

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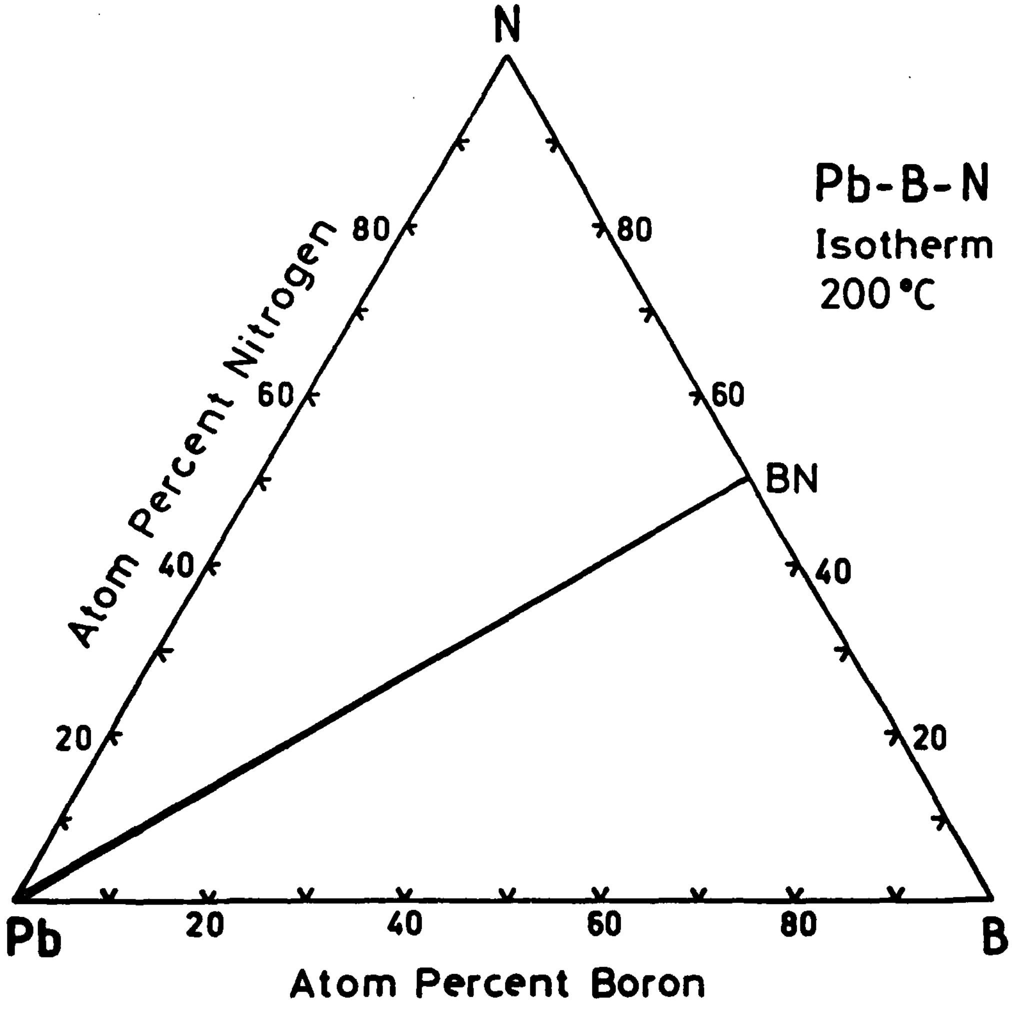
Table 1: Solid phases at 200°C in the system B-Pb-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Pb	cF4	a= 495.02	[90Mas]
<327.50°	$Fm\bar{3}m$		
	Cu		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	
	β-B		
BN_{hex}	hP*	a= 250.4	[85Vil]
	$P6_3/mmc$	c= 666.1	
	BN_{hex}		
α-PbN_6	oP84	a= 663	[85Vil]
	Pnma	b=1625	
		c=1131	
β-PbN_6	monoclinic	a= 509.0	[E11]
		b=8844	
		c=1750.8	
		β=90.016°	or
		a=1849	[E11]
		b= 884	
		c= 512	
		β=107.583°	

Fig.1: Isothermal section at 200°C in the system B - Pb - N



SYSTEM - BORON - ANTIMONY - NITROGEN (B-Sb-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Sb-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 575°C for a total of 900h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Sb, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Sb is given in [Mof,65Wal]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram is available for N-Sb and no binary nitrides of Sb have been reported. The solubility of N in Sb is likely to be very low.

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 575°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Sb) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed [90Wei].

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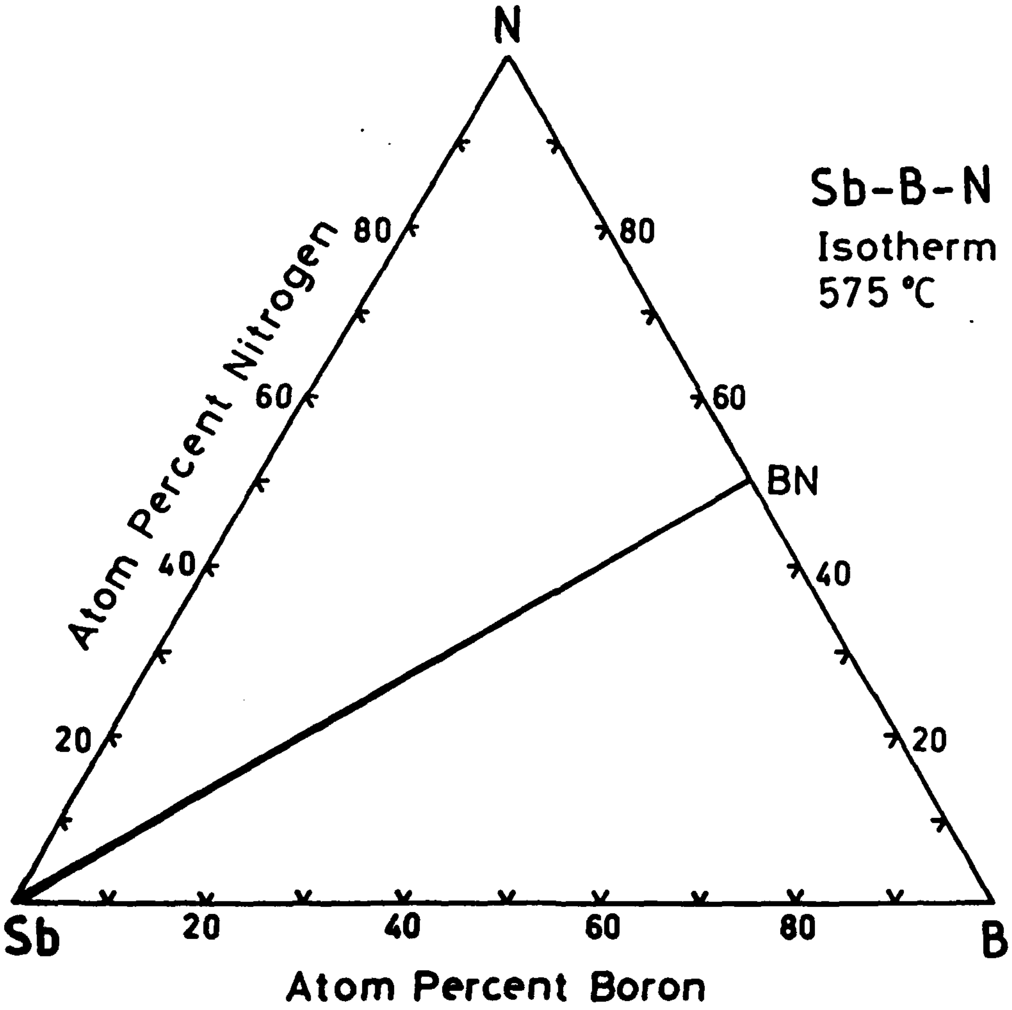
Table 1: Solid phases at 200°C in the system B-Sn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Sb	hR2	a= 430.84	[85Vil]
<630.78°	$R\bar{3}m$	c=1127.40	
	α-As		
β-rhB	hR111	a=1092.51	[85Vil]
<2092°	$R\bar{3}m$	c=2381.43	[85Vil]
	β-B		
BN_{hex}	hP*	a= 250.4	[85Vil]
	$P6_3/mmc$	c= 666.1	
	BN_{hex}		

Fig.1: Isothermal section at 575°C in the system B - Sb - N



SYSTEM BORON - BISMUTH - NITROGEN (B-Bi-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Bi-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 200°C for a total of 1500h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Bi, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Bi is given in [Mof,65Wal]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram Bi-N exists, however, the formation of a binary nitride BiN was claimed without further details [78Fro]. In the temperature range 25° to 800°C there is practically no solubility of N in Bi [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 200°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Bi) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (l-Bi) + BN at 800°C [65Yas].

MISCELLANEOUS

Nonwetting behavior ($\Theta > 90^\circ$) was claimed by [65Yas].

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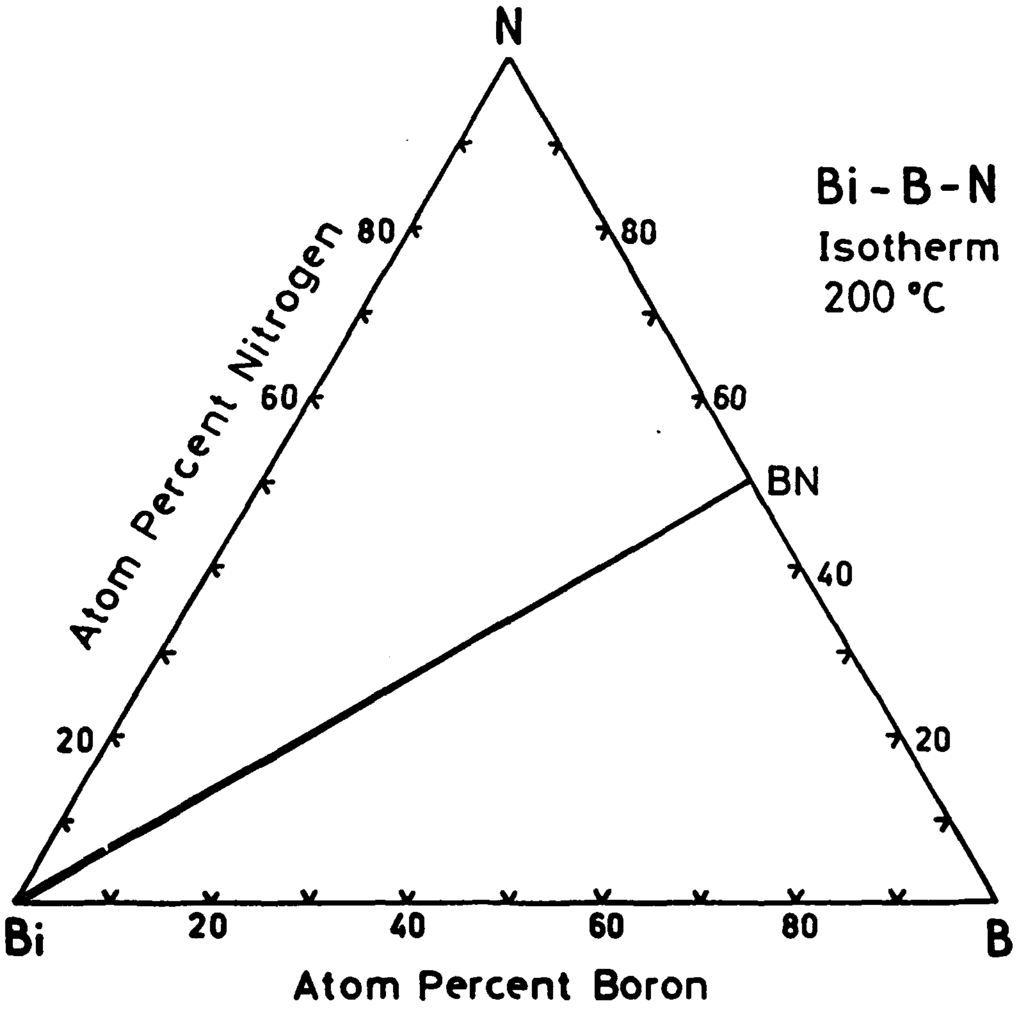
[90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)", J.Mater.Res. 5 (1990) 2152-2159

Table 1: Solid phases at 200°C in the system B-Sn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Bi <271.44°	hR2 $R\bar{3}m$ α-As	a= 454.60 c=1186.2	[85Vil]
β-rhB <2092°	hR111 $R\bar{3}m$ β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
BN_{hex}	hP* $P6_3/mmc$ BN_{hex}	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section at 200°C in the system B - Bi - N



Part B

Ternary Systems : Metal - Silicon - Nitrogen

PART B *TERNARY SYSTEMS M - Si - N*

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SYSTEM LITHIUM - SILICON - NITROGEN (Li-Si-N)

INTRODUCTION / EXPERIMENTAL

Six ternary phases are reported to exist in the system Li-Si-N [53Juz],[70Lan],[87Yam].In the latter work the phases were synthesized by heating mixtures of Li_3N (prepared from lithium (purity: 2N; from Wako Pure Chemical Ind.Ltd.,Japan) and nitrogen (purity: 5N)) and Si_3N_4 (UBE-SN-E 10 containing 2 wt% oxygen; from Ube Ind. Ltd.,Japan) under nitrogen at $T \geq 800°C$ for 24h and more.

BINARY SYSTEMS

The phase diagram for the system Li-Si due to [85Mar] is reported in [76Mof].Crystal structures of the intermediate phases are listed in tab.1.1.The diagram for Li-N is given in [86Mas].Li_3N is the only stable nitride (tab.1.1).In addition,the azide LiN_3 is structurally characterized.No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications:α-Si_3N_4 and β-Si_3N_4 (tab.1.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Only the section Li_3N-Si_3N_4 of the system Li-Si-N was investigated [53Juz],[70Lan][87Yam].At 800°C the sequence of coexisting phases is Si_3N_4 - Li_2SiN_2 - Li_5SiN_3 - $Li_{18}Si_3N_{10}$ - $Li_{21}Si_3N_{11}$ - Li_8SiN_4 - Li_3N [87Yam]. Crystal structure data of these phases are given in tab.1.1. It should be noted,that the phase labeled Li_5SiN_3 by [53Juz] was identified as $Li_{21}Si_3N_{11}$ by [87Yam] and the phase labeled Li_8SiN_4 by [70Lan] was identified as $Li_{18}Si_3N_{10}$ by [87Yam].A sixth ternary phase, $LiSi_2N_3$, was observed at 1200°C by [87Yam] and at above 750°C by [70Lan].

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Table 1.1: Solid phases in the system Li - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Li	cI2 $Im\bar{3}m$ W (A2)	a= 351.0	[85Vil];powder pattern: ASTM file card # 15-401
$Li_{22}Si_5$	cF432 F23 $Li_{22}Pb_5$	a= 1875	[85Vil];powder pattern: ASTM file card # 18-747
$Li_{13}Si_4$ (Li_7Si_2)	oP34 Pbam $Li_{13}Si_4$	a= 799 b= 1521 c= 443	[85Vil];powder pattern: ASTM file card # 29-830
Li_7Si_3	hR7 $R\bar{3}m$ Li_7Si_3	a= 443.5 c= 1813.5	[85Vil]
$Li_{12}Si_7$	oP152 Pnma $Li_{12}Si_7$	a= 861.0 b= 1973.8 c= 1434.1	[85Vil]

Tab.1.1 continued

Li_3N	hP4	a= 364.8	[85Vil];powder pattern:
	P6/mmm	c= 387.5	ASTM file card # 30-759
	Li_3N		
LiN_3	mC8	a= 562.7	[]85Vil];powder pattern
	C2/m	b= 331.9	ASTM file card # 22-680
	AuSe	c= 497.9	
		β= 107.4°	
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160
*$LiSi_2N_3$	oC24	a= 918.6	[85Vil];powder pattern:
	$Cmc2_1$	b= 530.2	ASTM file card # 26-1186
	Cu_2S_3Si	c= 477.6	
*Li_2SiN_2			[70Lan];powder pattern:
			ASTM file card # 23-365
*Li_5SiN_3	cI96	a= 472.40	[87Yam];
	$Ia\bar{3}$		gives powder pattern
	$AlLi_3N_2$ ($E9_d$)		
*$Li_{18}Si_3N_{10}$	t**	a= 1416.8	[87Yam];powder pattern:
		c= 1435.3	ASTM file card # 23-366
			and in [78Yam]
*$Li_{21}Si_3N_{11}$	t**	a= 947.0	[87Yam];powder pattern:
		c= 953.0	ASTM file card # 7-260
			and in [87Yam]
*Li_8SiN_4	t**	a= 1021.7	[70Lan];powder pattern:
		c= 953.6	given in [87Yam]

SYSTEM BERYLLIUM - SILICON - NITROGEN (Be-Si-N)

INTRODUCTION / EXPERIMENTAL

Seven ternary phases are reported to exist in the system Be-Si-N [60Rab],[67-1Eck],[67-2Eck],[75Hus],[77Tho],[80Sch].In the latter work the samples were prepared from beryllium nitride (reactor quality; from Serva Int.,FRG) and silicon nitride (HCST 3733 containing 1.2 wt% carbon, 2.1 wt% oxygen, 38.7 wt% nitrogen; from H.C.Starck Berlin,FRG) by hot pressing ($28 MN/m^2$) under nitrogen at 1760°C for 45'.

BINARY SYSTEMS

The phase diagram for the system Be-Si is given in [86Mas].No phase diagrams are reported for Be-N or Si-N. Be_3N_2 as well as Si_3N_4 exist in two modifications (tab.2.1).Under 10^5 Pa N_2 Be_3N_2 melts at 2200°C [87Wri].The solubility of nitrogen in silicon as well as in beryllium is very low [76Fro][87Wri].

SOLID PHASES / ISOTHERMAL SECTIONS

Only the section Be_3N_2-Si_3N_4 of the system Be-Si-N was investigated [60Rab],[67-1Eck],[67-2Eck],[75Hus],[76Tho],[77Tho],[80Sch].The ternary phases found can be described by the general formula $Be_{6+n}Si_nN_{4+n}$. At 1760°C the sequence of coexisting phases is Si_3N_4 - $BeSiN_2$ ($n=\infty$) - - $Be_6Si_3N_8$ (n=6) - $Be_{11}Si_5N_{14}$ (n=5) - $Be_5Si_2N_6$ (n=4) - $Be_9Si_3N_{10}$ (n=3) - - Be_4SiN_4 (n=2) - Be_7SiN_6 (n=1) - β-Be_3N_2 [80Sch].Crystal structure data of these phases are given in tab.2.1. β-Be_3N_2 dissolves 2.5 mol% Si_3N_4 [80Sch].

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[87Wri] H.A.Wriedt,"The Be-Si (Beryllium-Silicon) System",Bull.Alloy Phase Diagr.8 (1987) 136-139

Table 2.1: Solid phases in the system Be - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Be(r) T<1270	hP2 $P6_3/mmc$ Mg (A3)	a= 228.58 c= 358.43	[85Vil];powder pattern: ASTM file card # 22-111
β-Be(h) T>1270	cI2 $Im\bar{3}m$ W (A2)	a= 255.15	[85Vil]
α-Be_3N_2(r) T<1450	cI80 $Ia\bar{3}$ Mn_2O_3 ($D5_3$)	a= 815.0	[85Vil];powder pattern: ASTM file card # 4-786 33-192
β-Be_3N_2(h) T>1450	hP10 $P6_3/mmc$ Be_3N_2	a= 284.13 c= 969.3	[85Vil];powder pattern: ASTM file card # 12-649

Tab.2.1 continued

Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160
*$BeSiN_2$	oP16 $Pna2_1$ $MnSiN_2$	a= 497.7 b= 574.7 c= 467.4	[85Vil];powder pattern: ASTM file card # 20-167
*$BeSiN_2$	hP4 $P6_3mc$ ZnS (B4)	a= 286.9 c= 466.8	[85Vil];powder pattern: ASTM file card # 38-1430
*$Be_6Si_3N_8$	hR54	a= 286.2 c= 6511	[76Tho];powder pattern: ASTM file card # 32-103
*$Be_{11}Si_5N_{14}$	hR42	a= 286.0 c= 5098	[76Tho];powder pattern: ASTM file card # 32-104
*$Be_5Si_2N_6$	hP24	a= 286.0 c= 2910	[76Tho];powder pattern: ASTM file card # 32-102
*$Be_9Si_3N_{10}$	hR30	a= 285.7 c= 3632	[76Tho];powder pattern: ASTM file card # 32-106
*Be_4SiN_4	hP16	a= 286.2 c= 1922	[76Tho];powder pattern: ASTM file card # 32-105
*Be_7SiN_6	hR*	a= 286.1 c= 2152	[77Tho];powder pattern: ASTM file card # 33-196

SYSTEM MAGNESIUM - SILICON - NITROGEN (Mg-Si-N)

INTRODUCTION / EXPERIMENTAL

One ternary phase is reported to exist in the system Mg-Si-N [72Dav].The phase was synthesized from Mg_3N_2 (prepared using magnesium (purity: 2N8; from Th.Schuchardt,France) and desoxidized nitrogen) and Si_3N_4 (α+β Si_3N_4 containing 0.5 to 2 wt% free silicon; from Th.Schuchardt,France).

BINARY SYSTEMS

The phase diagram for Mg-Si is given in [86Mas].No phase diagrams are reported for Mg-N or Si-N. Mg_3N_2 reportedly exists in three modifications $\alpha \xrightarrow{550^\circ C} \beta \xrightarrow{788^\circ C} \gamma$ [65Ell].Only the crystal structure for α-Mg_3N_2 is reported (tab.3.1).The melting/dissoziation temperature is 1520°C [65Ell].Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.3.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Only the section Mg_3N_2-Si_3N_4 of the system Mg-Si-N was investigated. At 1200°C a ternary phase $MgSiN_2$ (tab.3.1) was observed [72Dav].At 1800°C Mg_3N_2 dissolves 5 mol% Si_3N_4 [85Uch].

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Table 3.1: Solid phases in the system Mg - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Mg	hP2 $P6_3/mmc$ Mg (A3)	a= 320.89 c= 521.01	[85Vil];powder pattern: ASTM file card # 35-821
Mg_2Si	cF12 $Fm\bar{3}m$ CaF_2 (C1)	a= 633.8	[85Vil];powder pattern: ASTM file card # 35-773
α-Mg_3N_2 T<550	cI80 $Ia\bar{3}$ Mn_2O_3 ($D5_3$)	a= 996.4	[85Vil];powder pattern: ASTM file card # 35-778
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160
*$MgSiN_2$	oP16 $Pna2_1$ $MnSiN_2$	a= 527.9 b= 647.6 c0 499.2	[85Vil];powder pattern: ASTM file card # 25-530

SYSTEM CALCIUM - SILICON - NITROGEN (Ca-Si-N)

INTRODUCTION / EXPERIMENTAL

Three ternary phases are reported to exist in the system Ca-Si-N [66-1Lau],[66-2Lau],[68Lau].The specimen were synthesized from Ca_3N_2 (prepared from calcium (from Planet,France) purified by vacuum desstillation and desoxidized nitrogen) and Si_3N_4 (α+β Si_3N_4;from Th.Schuchardt,France) by heat treatment under nitrogen at $T \leq$ 1180°C.

BINARY SYSTEMS

Phase diagrams for the systems Ca-Si and Ca-N are given in [86Mas]. Additional phases (tab.4.19) are reported for both systems.No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.4.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Only the section Ca_3N_2-Si_3N_4 of the system Ca-Si-N was investigated [66-1Lau],[66-2Lau],[68Lau].At 1180°C the sequence of coexisting phases is Si_3N_4 - $CaSiN_2$ - $Ca_5Si_2N_6$ - Ca_4SiN_4 - Ca_3N_2 [68Lau]. The crystal structures of these phases were not determined (tab.4.1). At 1050°C β-Ca_3N_2 dissolves 1 mol % Si_3N_4 [66-2Lau][68Lau].

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Table 4.1: Solid phases in the system Ca - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Ca(r)	cF4	a= 558.84	[85Vil];powder pattern:
T<443	$Fm\bar{3}m$		ASTM file card # 23-430
	Cu (A1)		
β-Ca(h)	cI2	a= 448.0	[85Vil];powder pattern:
T>443	$Im\bar{3}m$		ASTM file card # 10-348
	W (A2)		
Ca_2Si	oP12	a= 766.7	[85Vil];powder pattern:
	Pnma	b= 479.9	ASTM file card # 28-235
	Co_2Si (C23)	c= 900.2	
Ca_5Si_3	tI32	a= 764	[85Vil] note: not incl.
	I4/mcm	c= 1462	in the phase diagram
	Cr_5B_3 ($D8_l$)		
CaSi	oC8	a= 454.5	[85Vil];powder pattern:
	Cmcm	b= 1072.8	ASTM file card # 26-324
	CrB (B33)	c= 389.0	
$CaSi_2$	hR6	a= 385.5	[85Vil];powder pattern:
	$R\bar{3}m$	c= 3060	ASTM file card # 1-1276
	$CaSi_2$ (C12)		

Tab.4.1 continued

Ca_2N	hR3 $R\bar{3}m$ Sm (C19)	a= 363.8 c= 1878	[85Vil];powder pattern: ASTM file card # 21-837
or:	m**	a= 753.5 b= 363.8 c= 629.9 β= 123.85°	[68Lau]
$\alpha-Ca_3N_2$	cI80 $Ia\bar{3}$ Mn_2O_3 ($D5_3$)	a= 1147.3	[85Vil];powder pattern: ASTM file card # 22-152
$\gamma-Ca_3N_2$	o*40	a= 1782 b= 1156 c= 358	[85Vil];powder pattern: ASTM file card # 21-153
$Ca_{11}N_8$	tP38 $P4_2/mnm$ $Ca_{11}N_8$	a= 1445 c= 360	[85Vil];powder pattern: ASTM file card # 22-151
CaN_6	oF56 Fddd	a= 1132 b= 1107 c= 595	[85Vil];powder pattern: ASTM file card # 21-832
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
$\alpha-Si_3N_4$	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
$\beta-Si_3N_4$	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160
*$CaSiN_2$			[68Lau];powder pattern: ASTM file card # 20-230
*Ca_4SiN_4			[68Lau];powder pattern: ASTM file card # 21-162
*$Ca_5Si_2N_6$			[68Lau];powder pattern: ASTM file card # 21-160

SYSTEM STRONTIUM - SILICON - NITROGEN (Sr-Si-N)

INTRODUCTION / EXPERIMENTAL

Two ternary phases are reported to exist in the system Sr-Si-N [69Gau].The samples were synthesized from Sr_3N_2 (prepared from strontium purified by vacuum distillation and desoxidized nitrogen) and Si_3N_4 (α-β Si_3N_4, from Th.Schuchardt,France) by heat treatment under nitrogen at 960°C.

BINARY SYSTEMS

A phase diagram for the system Sr-Si is given in [86Mas].In addition the phases Sr_2Si and Sr_5Si_3 are reported (tab.5.1).
No phase diagrams are reported for Sr-N or Si-N.In the Sr-N system a phase ranging in composition fron $SrN_{0.5}$ to $SrN_{0.67}$ as well as the azide SrN_6 are structurally characterized (tab.5.1).Sr_3N_2 melts at 1030°C [65Ell].Si_3N_4 exists in two modifications:α-Si_3N_4 and β-Si_3N_4 (tab.5.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Only the section Sr_3N_2-Si_3N_4 of the system Sr-Si-N was investigated [69Gau].At 960°C the sequence of coexisting phases is Si_3N_4 - $SrSiN_2$ - - Sr_4SiN_4 - Sr_3N_2 [69Gau]. The crystal structures of these phases were not determined (tab.5.1).

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[86Mas] T.B.Massalski (ed.),"Binary Alloy Phase Diagrams" (Amer.Soc. Met.,Metals Park,OH.,1986)

Table 5.1: Solid phases in the system Sr - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Sr(r) T<547	cF4 $Fm\bar{3}m$ Cu (A1)	a= 608.4	[85Vil];powder pattern: ASTM file card # 15-305
β-Sr(h) T>547	cI2 $Im\bar{3}m$ W (A2)	a= 487	[86Mas];powder pattern: ASTM file card # 15-288
Sr_2Si	oP12 Pnma Co_2Si (C23)	a= 811 b= 515 c= 954	[85Vil] note: not. incl. in the phase diagram; powder pattern: ASTM file card # 30-1303
Sr_5Si_3	tI32 I4cm Sr_5Si_3	a= 805.5 c= 1568.8	[85Vil] note: not incl. in the phase diagram
SrSi	oC8 Cmcm CrB (B33)	a= 482.6 b= 1128.7 c= 404.2	[85Vil];powder pattern: ASTM file card # 16-8
$SrSi_2$	cP12 $P4_332$ $SrSi_2$	a= 654.0	[85Vil];powder pattern: ASTM file card # 38-1366
Sr_2N	hR3 $R\bar{3}m$ Sm (C19)	a= 724.6 α= 30.8°	[85Vil];powder pattern: ASTM file card # 27-855
or:	m**	a= 719 b= 385 c= 665 β= 108°	[70Gau]
Sr_3N_2	hP* Ba_3N_2		

Tab.5.1 continued

SrN_6	oF56 Fddd	a= 1180.88 b= 1153.43 c= 611.62	[85Vil];powder pattern: ASTM file card # 21-1466
Si	cF8 Fd$\bar{3}$m C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160
*$SrSiN_2$			[69Gau];powder pattern: ASTM file card # 22-1438
*Sr_4SiN_4			[69Gau];powder pattern: ASTM file card # 22-1439

SYSTEM BARIUM - SILICON - NITROGEN (Ba-Si-N)

INTRODUCTION / EXPERIMENTAL

One ternary phase is reported to exist in the system Ba-Si-N [72Gau],[84Mor].The samples were synthesized from Ba_3N_2 and Si_3N_4 by heat treating under nitrogen at 1000°C [72Gau] or 1500°C [84Mor].

BINARY SYSTEMS

For the system Ba-Si a phase diagram is given in [86Mas].Several additional phases are reported to exist (tab.6.1).No phase diagrams are reported for Ba-N or Si-N.The nitride Ba_3N_2 and the azide BaN_6 are structurally characterized (tab.6.1).Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.6.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

The section Ba_3N_2-Si_3N_4 of the system Ba-Si-N was investigated [72Gau][84Mor].The only ternary phase observed is $BaSiN_2$ (tab.6.1).

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Table 6.1: Solid phases in the system Ba - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ba	cI2 $Im\bar{3}m$ W (A2)	a= 501.3	[85Vil];powder pattern: ASTM file card # 6-235
Ba_2Si	oP12 Pnma Co_2Si (C23)	a= 843 b= 540 c= 988	[85Vil];powder pattern ASTM file card # 30-154 note: not included in the phase diagram
Ba_5Si_3	tP32 P4/ncc Ba_5Si_3	a= 843.6 c= 1653.5	[85Vil];powder pattern: ASTM file card # 27-187 note: not included in the phase diagram
BaSi	oC8 Cmcm CrB (B33)	a= 504.2 b= 1197 c= 414.2	[85Vil];powder pattern: ASTM file card # 19-135
Ba_3Si_4	tP28 $P4_2/mnm$ Ba_3Si_4	a= 852 c= 1184	[85Vil] note: not incl. in the phase diagram
$BaSi_2$	hP3 P6/mmm AlB_2 (C32)	a= 439 c= 483	[85Vil];
$BaSi_2$	oP24 Pnma $BaSi_2$	a= 892 b= 680 c= 1158	[85Vil];powder pattern: ASTM file card # 31-163
Ba_3N_2 (Ba_3N_4)	hP* Ba_3N_2	a= 522 c= 550	[85Vil];powder pattern: ASTM file card # 27-39
BaN_6	mP14 $P2_1/m$ BaN_6	a= 959 b= 439 c= 542 β= 99.7°	[85Vil];powder pattern: ASTM file card # 18-154

Tab.6.1 cont.

Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160
*$BaSiN_2$	o**	a= 559	[84Mor];powder pattern:
		b= 754.2	ASTM file card # 36-1257
		c= 1134.0	

SYSTEM SCANDUM - SILICON - NITROGEN (Sc-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Sc-Si-N at 800°C and 1000°C were determined by x-ray analysis [90Wei].The alloys were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si), silicon (purity: 3N) both from Alpha Div.,Ventron Corp., USA and scandium (purity 4N; from Rare Earth Products Ltd.,UK).Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil and heat treated for 340h at 800°C or 170h at 1000°C.

BINARY SYSTEMS

The phase diagram for Sc-Si due to [86Gok] is reproduced in [76Mof]. The intermediate phases are described in tab.7.1.The decomposition of the phase $ScSi_{2-x}$(Sc_3Si_5) into ScSi + Si is observed at temperatures below 1000°C [87Sch].No phase diagrams are reported for Sc-N or Si-N. At normal pressure ScN is the only stable scandium nitride [72Kie]. Si_3N_4 exists in two modifications:α-Si_3N_4 and β-Si_3N_4 (tab.7.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in the system Sc-Si-N (tab.7.1).ScN dominates the isothermal section at 800°C (fig.7.1 [90Wei]): It coexists with all phases stable at this temperature.At 1000°C (fig.7.2 [90Wei]) ScN coexists with all three binary scandium silicides but not with silicon.Thus, Si_3N_4 in contact with scandium is decomposed at elevated temperatures.

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Table 7.1: Solid phases in the system Sc - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Sc(r)	hP2	a= 330.8	[85Vil];powder pattern:
T<1337	$P6_3/mmc$	c= 526.7	ASTM file card # 17-714
	Mg (A3)		
β-Sc(h)	cI2	a= 454.1	[86Mas]
T>1337	$Im\bar{3}m$		
	W (A2)		
Sc_5Si_3	hP16	a= 786.1	[85Vil];powder pattern:
	$P6_3/mcm$	c= 581.2	ASTM file card #15-189
	Mn_5Si_3 ($D8_8$)		
ScSi	oC8	a= 398.8	[85Vil];powder pattern:
	Cmcm	b= 988.2	ASTM file card # 18-1161
	CrB (B33)	c= 365.9	
$ScSi_{2-x}$	hP3	a= 366	[85Vil];powder pattern:
(Sc_3Si_5)	P6/mmm	c= 387	ASTM file card # 17-93
T>800	AlB_2 (C32)		
ScN	cF8	a= 450.5	[85Vil];powder pattern:
	$Fm\bar{3}m$		ASTM file card # 3-951,
	NaCl (B1)		31-1493,35-753
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160

Fig.7.1: Isothermal section observed in the system Sc - Si - N at 800°C (in the absence of external nitrogen pressure)

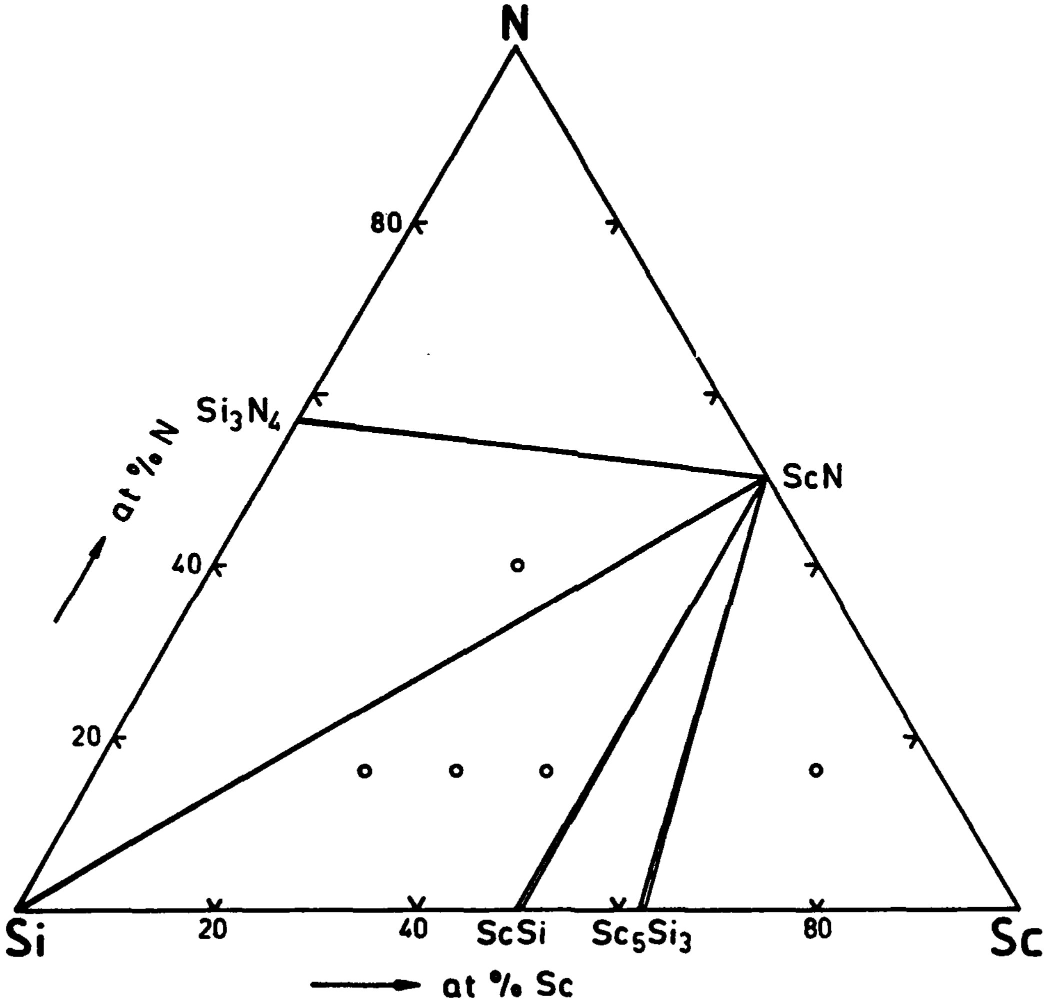
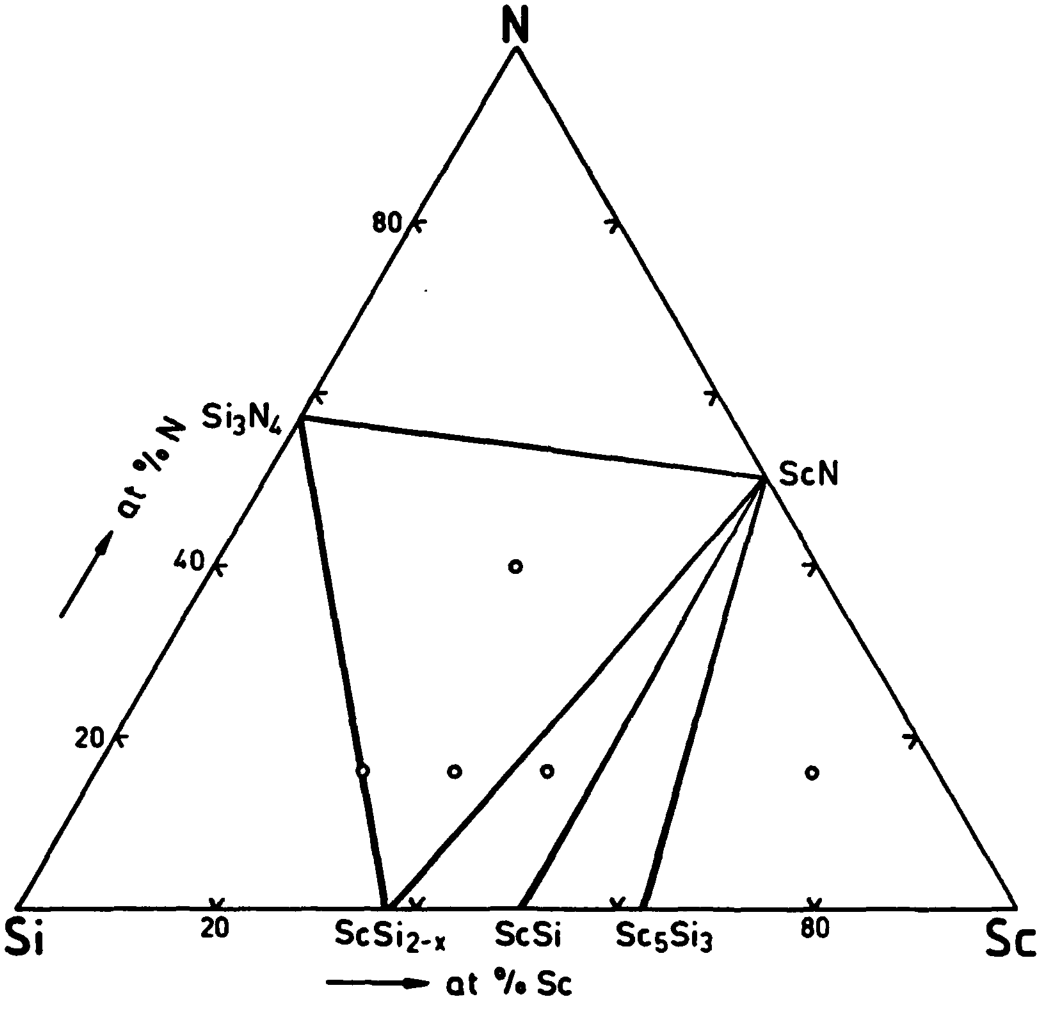


Fig.7.2: Isothermal section observed in the system Sc -Si - N at 1000°C (in the absence of external nitrogen pressure)



SYSTEM YTTRIUM - SILICON - NITROGEN (Y-Si-N)

INTRODUCTION / EXPERIMENTAL

Three ternary phases are reported to exist at 1700°C in the systen Y-Si-N [86Jac].No experimental details are given.

BINARY SYSTEMS

The phase diagram for Y-Si is given in [86Mas] and was thermodynamically modelled by [89Ran].The intermediate phases are described in tab.8.1. A tentative phase diagram for Y-N was proposed by [74Car] and is reproduced in [76Mof].No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications:α-Si_3N_4 and β-Si_3N_4 (tab.8.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

Only the section YN-Si_3N_4 of the system Y-Si-N was investigated [85Uch][86Jac].At 1700°C the sequence of coexisting phases is Si_3N_4 - - YSi_3N_5 - $Y_2Si_3N_6$ - $Y_6Si_3N_{10}$ - YN [86Jac].The crystal structures of these phases were not reported.Si_3N_4 dissolves 3 mol% YN at 1650°C and 5 mol% YN at 1800°C [85Uch].Using the thermochemical data given in tab.8.2 an isothermal section for 1000°C is calculated (fig.8.1) showing,that Si_3N_4 does not coexist with yttrium at high temperatures.

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Table 8.1: Solid phases in the system Y - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Y(r)	hP2	a= 365 09	[85Vil];powder pattern:
T<1478	$P6_3/mmc$	c= 573.88	ASTM file card # 33-1458
	Mg (A3)		
β-Y (h)	cI2	c= (407)	[86Mas]
T>1478	$Im\bar{3}m$		
	W (A2)		
Y_5Si_3	hP16	a= 840.3	[85Vil];powder pattern:
	$P6_3/mcm$	c= 630.3	ASTM file card # 24-1026
	Mn_5Si_3 ($D8_8$)		
Y_5Si_4	oP36	a= 739	[85Vil]
	Pnma	b= 1452	
	Sm_5Ge_4	c= 764	
YSi	oC8	a= 425.1	[85Vil];powder pattern:
	Cmcm	b= 1052.6	ASTM file card # 12-620
	CrB (B33)	c= 382.6	
YSi_{2-x}	hP3	a= 384.2	[85Vil];powder pattern:
(Y_3Si_5)	P6/mmm	c= 414.0	ASTM file card # 11-596
	AlB_2 (C32)		
YSi_2(r)	oI12	a= 405	[85Vil];powder pattern:
T<1250	Imma	b= 395	ASTM file card # 11-324
	$GdSi_2$	c= 1322	
YSi_2(h)	tI12	a= 404	[85Vil]
(Y_2Si_3)	$I4_1/amd$	c= 1342	
T>1250	$ThSi_2$ (C_c)		
YN	cF8	a= 488.9	[85Vil];powder pattern:
	$Fm\bar{3}m$		ASTM file card # 10-221
	NaCl (B1)		35-779
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		

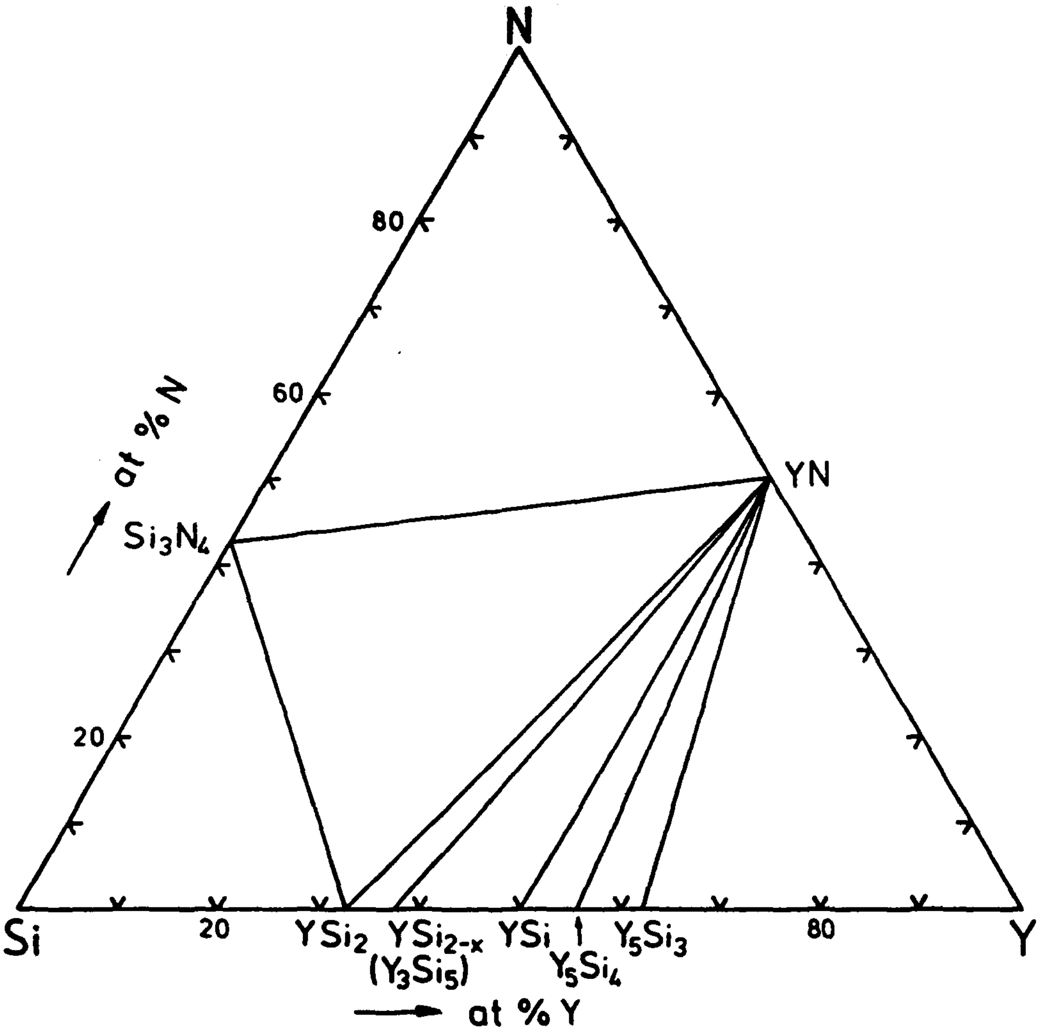
Tab.8.1 continued

α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160
*$Y_6Si_3N_{10}$			[86Jac]
*$Y_2Si_3N_6$			[86Jac]
*YSi_3N_5			[86Jac]

Tab.8.2:Thermodynamic data for the solid phases in Y - Si - N

phase	ΔG_f^o (J/gramatom)	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 YSi_2	-38921 + 2.500 T	[89Ran]
.1250 Y_3Si_5	-44430 + 4.0 T	[89Ran]
.5000 YSi	-61920 + 10.665 T	[89Ran]
.1111 Y_5Si_4	-65150 + 12.60 T	[89Ran]
.1250 Y_5Si_3	-60000 + 11.187 T	[89Ran]
.5000 YN	-149490 + 41.72 T	(289 1134K) [78Fro]
	-152415 + 44.32 T	(1134-1193K) [78Fro]
	-154515 + 46.105 T	(1193-2273K) [78Fro]

Fig.8.1: Isothermal section calculated for the system Y - Si - N at 1000°C (ignoring the possible existence of ternary phases)



SYSTEM LANTHANUM - SILICON - NITROGEN (La-Si-N)

INTRODUCTION / EXPERIMENTAL

One ternary phase is reported in the systen La-Si-N [80Ino][81Hol]. In the latter work samples were prepared by hot pressing from LaN and Si_3N_4 at 1800°C.

BINARY SYSTEMS

No phase diagrams are reported for any of the binary boundary systems.Six intermediate lanthanum silicides are known (tab.9.1). The phase LaN is under normal pressure the only stable lanthanum nitride [72Kie].Si_3N_4 exists in two modifications:α-Si_3N_4 and β-Si_3N_4 (tab.9.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

The ternary phase $LaSi_3N_5$ [80Ino][81hol]] is described in tab.9.1.

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Table 9.1: Solid phases in the system La - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-La(r) T<310	hP4 $P6_3/mmc$ La (A3′)	a= 377 c= 1215.9	[85Vil];powder pattern: ASTM file card # 2-618
β-La(h) 310<T<865	cF4 $Fm\bar{3}m$ Cu (A1)	a= 529.1	[85Vil];powder pattern: ASTM file card # 2-607
γ-La(h) T>865	cI2 $Im\bar{3}m$ W (A2)	a= 426	[85Vil]
La_5Si_3	tI32 I4/mcm Cr_5B_3 ($D8_l$)	a= 795.3 c= 1404	[85Vil];powder pattern: ASTM file card # 20-555
La_3Si_2	tP10 P4/mbm U_3Si_2 ($D5_a$)	a= 787 c= 450	[85Vil];powder pattern: ASTM file card # 19-660
La_5Si_4	tP36 $P4_12_12$ Zr_5Si_4	a= 804 b= 1543	[85Vil]
LaSi	oP8 Pnma FeB (B27)	a= 838 b= 399 c= 602	[85Vil];powder pattern: ASTM file card # 19-661
$LaSi_2$(r)	oI12 Imma $GdSi_2$	a= 427.0 b= 417.0 c= 1405	[85Vil];powder pattern: ASTM file card # 20-553
$LaSi_2$(h)	tI12 $I4_1/amd$ $ThSi_2$ (C_c)	a= 432.2 c= 1386	[85Vil];powder pattern: ASTM file card # 6-471
LaN	cF8 $Fm\bar{3}m$ NaCl (B1)	a= 530.5	[85Vil];powder pattern: ASTM file card # 15-892

Tab.9.1 continued

Si	cF8	a= 542.86	[85Vil];powder pattern:
	Fd$\bar{3}$m		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160
*$LaSi_3N_5$	oP36	a= 783.8	[85Vil];powder pattern:
	$P2_12_12_1$	b= 1123.6	given in [80Ino]
	$LaSi_3N_5$	c= 480.7	

SYSTEM CERIUM - SILICON - NITROGEN (Ce-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Ce-Si-N at 1000°C were determined by x-ray analysis [90Wei].The alloys were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si), silicon (purity: 3N) both from Alpha Div.,Ventron Corp., USA and cerium (purity 3N; from Rare Earth Products Ltd.,UK).Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil and heat treated for 240h at 1000°C.

BINARY SYSTEMS

The phase diagram for Ce-Si (fig.10.1) was assessed in [89Mun]. The intermediate phases are described in tab.10.1. A tentative phase diagram for Ce-N is given in [86Mas].No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications:α-Si_3N_4 and β-Si_3N_4 (tab.10.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in the system Ce-Si-N (tab.10.1).The isothermal section at 1000°C (fig.10.2 [90Wei]) shows CeN to coexist with all six binary cerium silicides as well as silicon nitride but not with silicon.Thus, Si_3N_4 in contact with cerium is decomposed at elevated temperatures.

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Table 10.1: Solid phases in the system Ce - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
β-Ce(r) T<61	hP4 $P6_3/mmc$ La (A3')	a= 368.10 c= 1185.7	[85Vil]
γ-Ce(h) 61<T<726	cF4 $Fm\bar{3}m$ Cu (A1)	a= 515.58	[85Vil];powder pattern: ASTM file card # 8-56
δ-Ce(h) T>726	cI2 $Im\bar{3}m$ W (A2)	a= 412.0	[86Mas]
Ce_5Si_3	tI32 I4/mcm Cr_5B_3 ($D8_l$)	a= 789 c= 1377	[85Vil];powder pattern: ASTM file card # 19-297
Ce_3Si_2	tP10 P4/mbm U_3Si_2 ($D5_a$)	a= 779 c= 436	[85Vil]
Ce_5Si_4	tP36 $P4_12_12$ Zr_5Si_4	a= 793 b= 1504	[85Vil]
CeSi	oP8 Pnma FeB (B27)	a= 830.2 b= 396.2 c= 596.4	[85Vil];powder pattern: ASTM file card # 18-320
$CeSi_{2-x}$ (Ce_3Si_5)	oI12 Imma $GdSi_2$	a= 416.8 b= 409.8 c= 1381.5	[82Yas]
$CeSi_2$	tI12 $I4_1/amd$ $ThSi_2$ (C_c)	a= 418.4 c= 1385.6	[85Vil];powder pattern: ASTM file card # 6-485
CeN	cF8 $Fm\bar{3}m$ NaCl (B1)	a= 502.45	[85Vil];powder pattern: ASTM file card # 15-882

Tab.10.1 continued

Si	cF8 Fd$\bar{3}$m C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.10.1: Phase diagram for the boundary system cerium - silicon

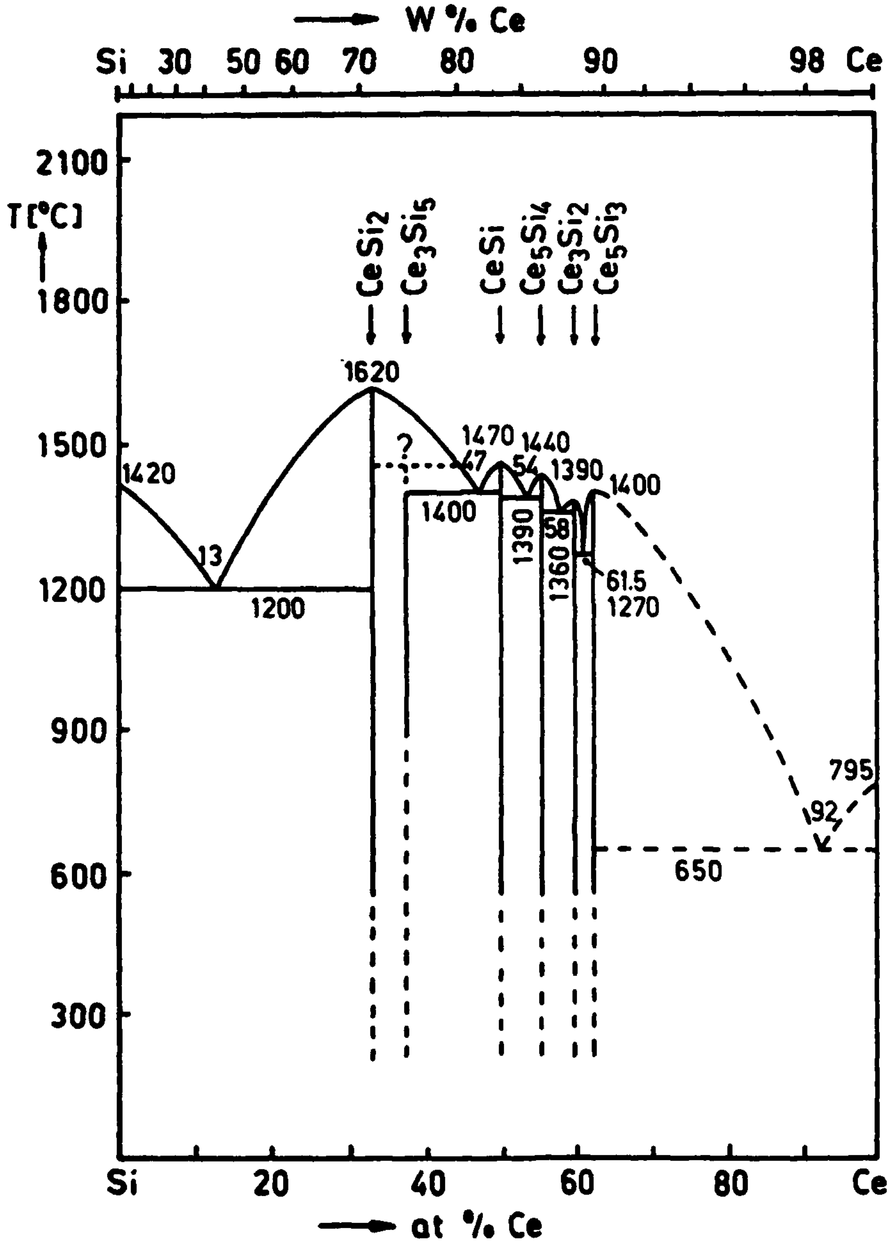
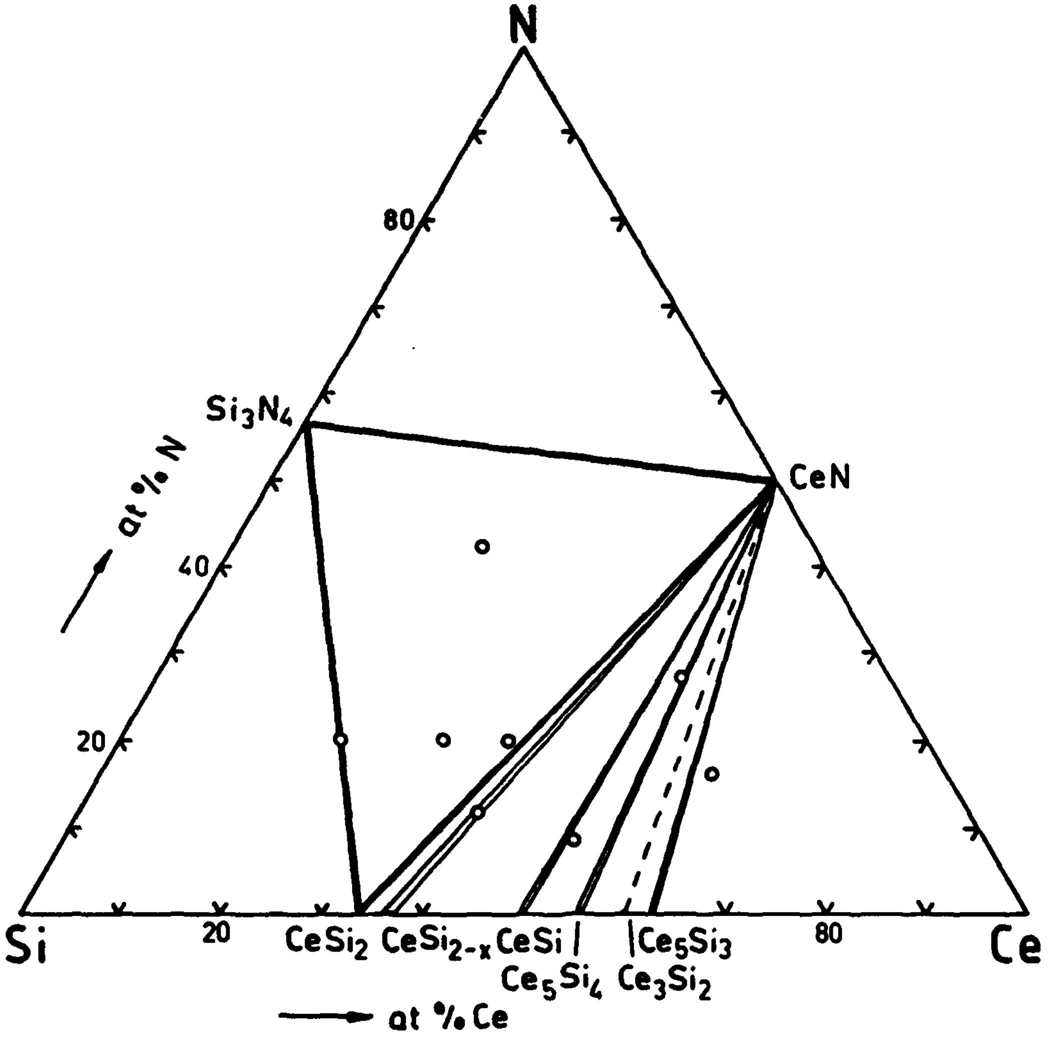


Fig.10.2: Isothermal section observed in the system Ce - Si - N at 1000°C (in the absence of external nitrogen pressure)



SYSTEM SAMARIUM - SILICON - NITROGEN (Sm-Si-N)

INTRODUCTION / EXPERIMENTAL

The ternary phase $Sm_3Si_6N_{11}$ is reported [83Gau].The sample was synthesized from SmN (prepared by reacting samarium with nitrogen) and Si_3N_4 (α+β Si_3N_4,from E.Merck,FRG) by heat treatment at 1200°C under nitrogen.

BINARY SYSTEMS

The phase diagram for the binary Sm-Si (fig.11.1) assessed by [88Gok].The intermediate phases are described in tab.11.1.No phase diagrams ares reported for Sm-N or Si-N. SmN is the only samarium nitride reported [72Kie].Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.11.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

The ternary phase $Sm_3Si_6N_{11}$ is described in tab.11.1.

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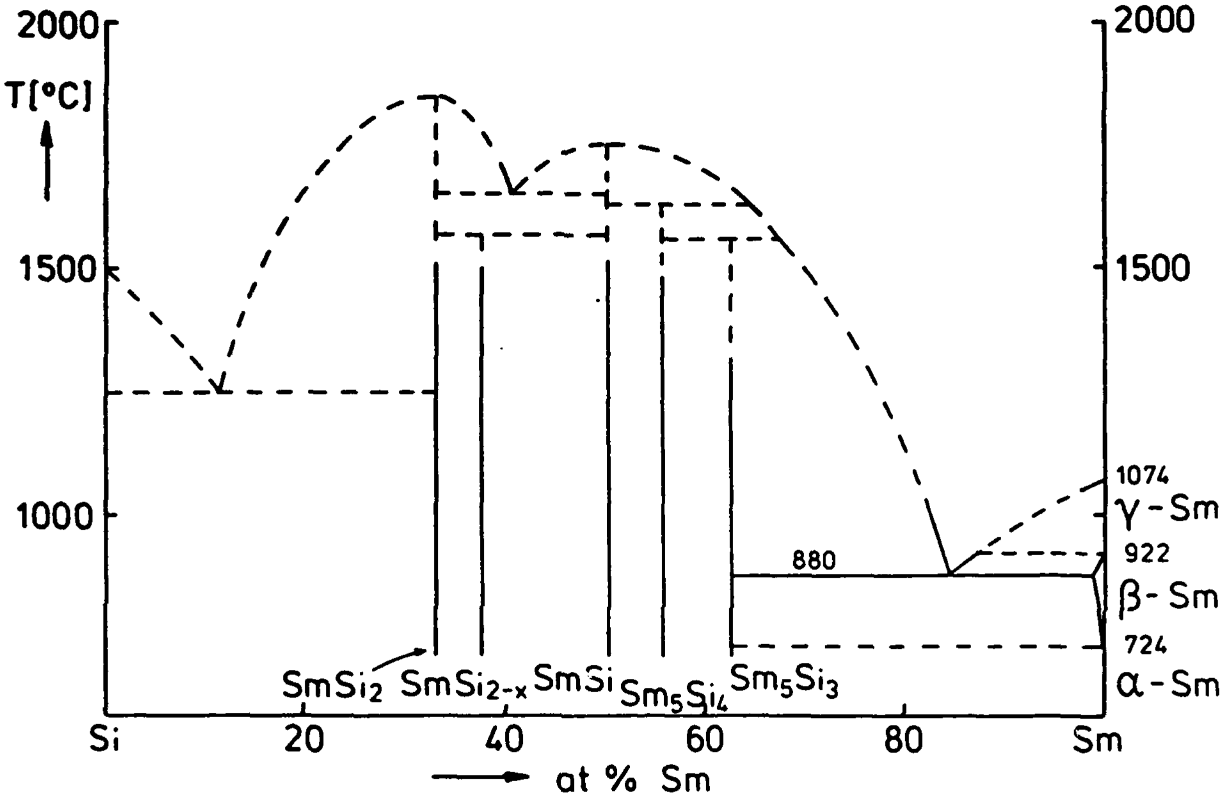
Table 11.1: Solid phases in the system Sm - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Sm(r) T<734	hR3 $R\bar{3}m$ Sm (C19)	a= 899.6 α = 23.22°	[85Vil];powder pattern: ASTM file card # 6-419
β-Sm(h) T>734	hP4 $P6_3/mmc$ La (A3')	a= 361.99 c= 1168.0	[86Mas];powder pattern ASTM file card # 37-1446
Sm_5Si_3	hP16 $P6_3/mcm$ Mn_5Si_3 ($D8_8$)	a= 856 c= 645	[85Vil]
Sm_5Si_4	oP36 Pnma Sm_5Ge_4	a= 757 b= 1488 c= 778	[85Vil]
SmSi	oP8 Pnma FeB (B27)	a= 805.5 b= 388.8 c= 580.4	[85Vil]
$SmSi_{2-x}$ (Sm_3Si_5)	hP3 P6/mmm AlB_2 (C32)	a= 390.3 c= 420.7	[85Vil]
$SmSi_2$ (Sm_2Si_3)	tI12 $I4_1/amd$ $ThSi_2$ (C_c)	a= 408 c= 1351	[85Vil]
SmN	cF8 $Fm\bar{3}m$ NaCl (B1)	a= 503.9	[85Vil];powder pattern: ASTM file card # 30-1104
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565

Tab.11.1 continued

α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160
*$Sm_3Si_6N_{11}$	t**	a= 999.31	[83Gau];powder pattern:
		c= 483.61	ASTM file card # 38-1291

Fig.11.1: Phase diagram for the boundary system samarium - silicon



SYSTEM HOLMIUM - SILICON - NITROGEN (Ho-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Ho-Si-N at 1000°C were determined by x-ray analysis [90Wei].The alloys were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si), silicon (purity: 3N) and holmium (purity 3N) all from Alpha Div.,Ventron Corp.,USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil and heat treated for 1000h at 1000°C.

BINARY SYSTEMS

A phase diagram for the system Ho-Si (fig.12.1) is presented in [90Wei].The intermediate phases are described in tab.12.1.No phase diagrams are reported for Ho-N or Si-N.Under normal pressure HoN is the only stable holmium nitride [72Kie].Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.12.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in the system Ho-Si-N (tab.12.1).The isothermal section at 1000°C (fig.12.2 [90Wei]) shows HoN to coexist with all binary cerium silicides exept $HoSi_2$.Si_3N_4 coexists with HoN,$HoSi_{2-x}$ and $HoSi_2$.Thus silicon nitride in contact with holmium is decomposed at elevated temperatures.The lattice parameters of Ho_5Si_3 in equilibrium with HoN increase relative to the value of the binary phase to a= 834.07pm and c= 645.35pm indicating extended solubility for nitrogen in this phase (fig.12.3).None of the other binary phases shows signs of solubiliy for the respective third component.

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Table 12.1: Solid phases in the system Ho - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ho	hP2	a= 357.73	[85Vil];powder pattern:
	$P6_3/mmc$	c= 561.58	ASTM file card # 2-910
	Mg (A3)		
Ho_5Si_3	hP16	a= 834	[85Vil];powder pattern:
	$P6_3/mcm$	c= 622	ASTM file card # 26-748
	Mn_5Si_3 ($D8_8$)		
Ho_5Si_4	oP36	a= 733.8	[85Vil]
	Pnma	b= 1444.9	
	Sm_5Ge_4	c= 762.5	
HoSi(r)	oC8	a= 422.8	[85Vil];powder pattern:
	Cmcm	b= 1042.9	ASTM file card # 19-561
	CrB (B33)	c= 380.1	
HoSi(h)	oP8	a= 780.8	[85Vil];powder pattern:
	Pnma	b= 380.1	ASTM file card # 19-562
	FeB (B27)	c= 563.3	

Tab.12.1 continued

$HoSi_{2-x}$	hP3	a= 381.6	[85Vil];powder pattern:
(Ho_3Si_5)	P6/mmm	c= 410.7	ASTM file card # 19-560
	AlB_2 (C32)		
$HoSi_2$	oI12	a= 399	[85Vil];powder pattern:
	Imma	b= 394	ASTM file card # 13-381
	$GdSi_2$	c= 1330	
HoN	cF8	a= 487.7	[85Vil];powder pattern:
	$Fm\bar{3}m$		ASTM file card # 15-889
	NaCl (B1)		
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160

Fig.12.1: Phase diagram for the boundary system holmium - silicon

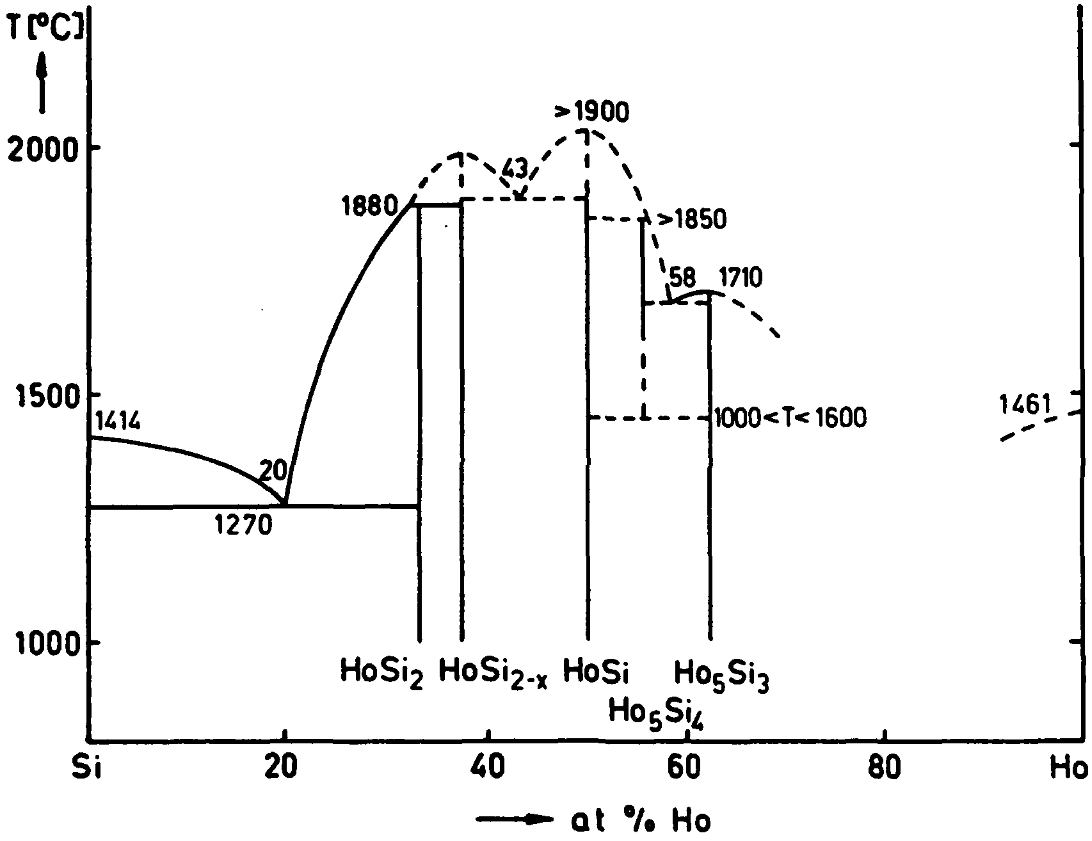


Fig.12.2: Isothermal section observed for the system Ho - Si - N at 1000°C (in the absence of external nitrogen pressure)

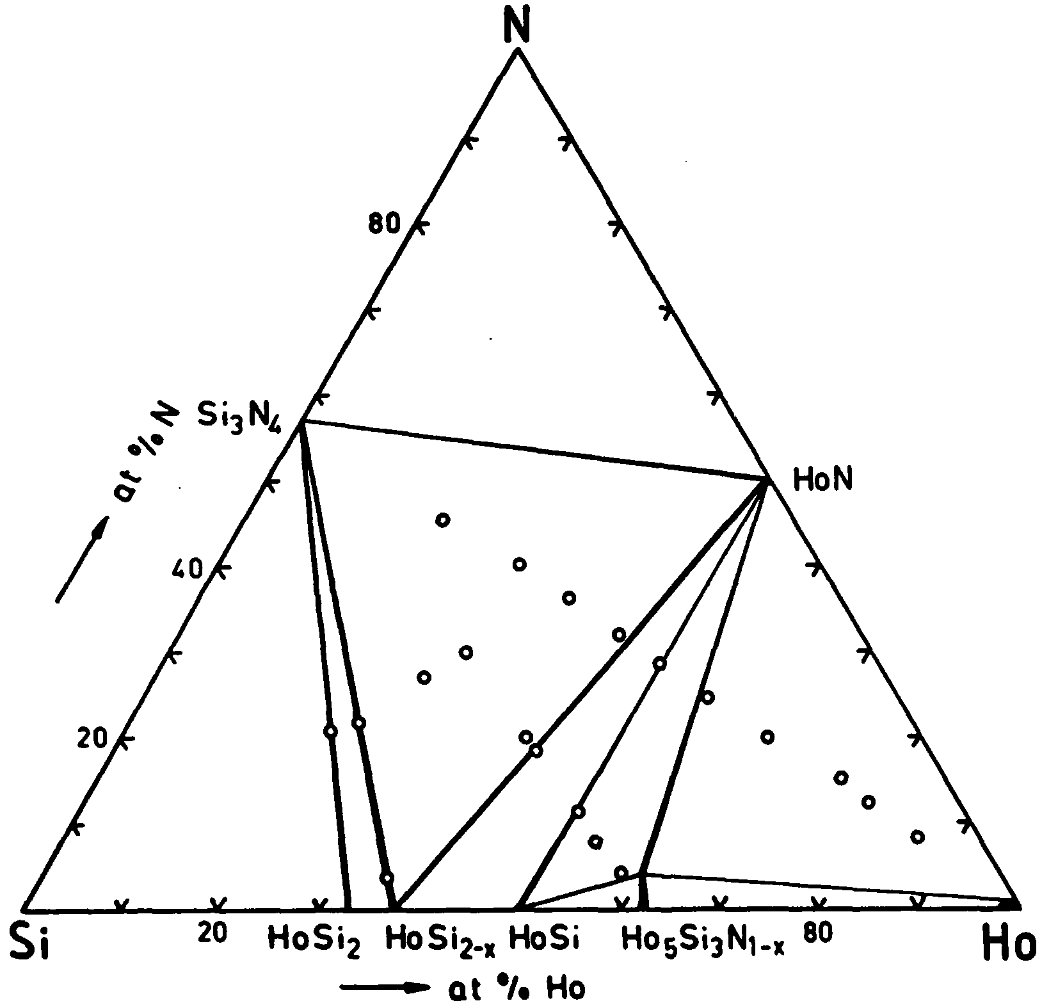
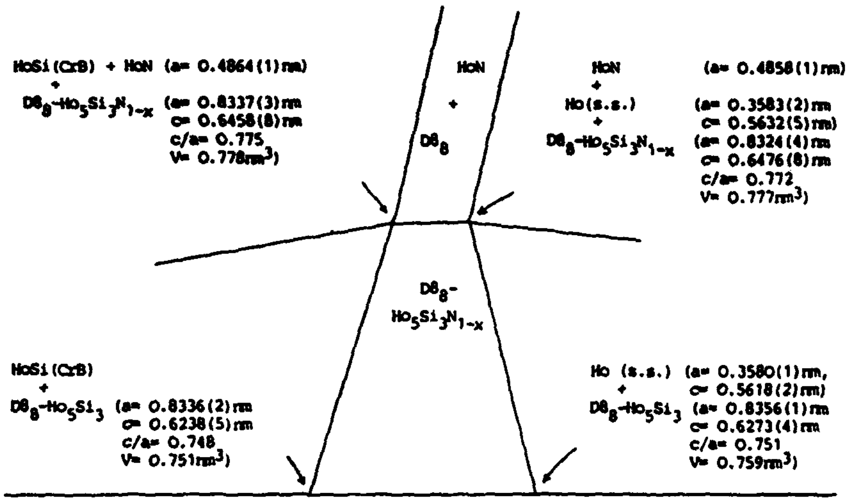


Fig.12.3: The homogeneity region of $Ho_5Si_3N_{1-x}$ at 1000°C



SYSTEM TITANIUM - SILICON - NITROGEN (Ti-Si-N)

INTRODUCTION / EXPERIMENTAL

The isothermal section of Ti-Si-N at 1000°C were calculated from thermodynamic data [84Bey] and are determined by x-ray analysis [85Sch].The alloys investigated in the latter work were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si), silicon (purity: 3N), titanium (purity: 2N, impurities in ppm: Ca 4000, Al 3500, Fe 1000, C 150, Si 30, other 30) and titanium nitride (purity 2N) all from Alpha Div.,Ventron Corp.,USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 550h at 1000°C or annealed at 1300°C ,48h in a r.f.furnace under argon (purity:5N+).

BINARY SYSTEMS

The phase diagram for the binary system Ti-Si given in [86Mas] shows the occurrence of four intermediate phases.However, the phase Ti_5Si_4 exists in two modifications (tab.13.1) as found by [69Nic]. The phase Ti_3Si is possibly impurity stabilized [89Paj][89Kiv].The Ti-Si system was thermodynamically modelled by [89Paj] as well as by [89Vah].The phase diagram of Ti-N given in [86Mas] needs to be updated (fig.13.1 [90Len]) to account for the newly discovered phases η-Ti_3N_{2-x} [86-1Len] and ζ-Ti_4N_{3-x} [86-2Len].No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.13.1). The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Ti-Si-N (tab.13.1).The isothermal section at 1000°C experimentally observed (fig.13.2 [85Sch]) shows TiN_{1-x} to be in equilibrium with Si_3N_4,$TiSi_2$ and Ti_5Si_3 which dissolves considerable amounts of nitrogen as is indicated by the increase of the lattice parameters relative to the values of the binary compound (fig.13.3). TiN_{1-x} coexists furthermore with α-Ti(containing 20 at% nitrogen in solid solution) and thus cuts off any phase fields containing ε-Ti_2N (fig.13.4).Analogously,the tie line between $TiSi_2$ and Ti_5Si_3(containing ≃4 at% nitrogen in solid solution) confines the occurrence of the phase TiSi and Ti_5Si_4 to compositions close to the binary Ti-Si.Exept for Ti_5Si_3,lattice parameters of neither titanium silicide coexisting with Si_3N_4 or TiN_{1-x} are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in these titanium silicides.These results are in perfect agreement with experimental data on the reaction of Si_3N_4 with titanium at 500°C < T < 2200°C [78Bor], [83Ore],[85Kag],[[86Mor],[86Sug],[87Bar],[90Des]; the reaction of titanium silicides with nitrogen [56Bre],[56Kie],[56Now],[69Fit], [89Jos],[90Des]; the reaction of TiN_{1-x} with silicon [84Kab] and the compatibility of TiN_{1-x} in contact with Si_3N_4 [81Som],[82Hay],[82Hir], [85Uch] or with $TiSi_2$ [73Cha],[83Nor],[85Ada],[86Tin].Using the thermodynamic data in tab.13.2 the phase equilibria at 1000°C can be calculated.At variance with [84Bey],but in agreement with [76Kri] the tie lines resulting for 1000°C confirm the experimentally observed isothermal section (figs.13.2).There is no pressure or temperature range where Si_3N_4 coexists in equilibrium with titanium.

MISCELLANEOIUS

Silicon nitride is not wet by $TiSi_2$ at 1500°C [73Cha].Additions of titanium enhance the nitridation reaction rate of silicon [81Muk].

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Table 13.1: Solid phases in the system Ti - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Ti(r) T<882	hP2 $P6_3/mmc$ Mg (A3)	a= 295.08 c= 468.55	[85Vil];powder pattern: ASTM file card # 5-682
β-Ti(h) T>882	cI2 $Im\bar{3}m$ W (A2)	a= 330.65	[85Vil];
Ti_3Si T<1170	tP32 $P4_2/n$ Ti_3P	a= 1019.6 c= 509.7	[85Vil];possibly impurity stabilized
Ti_5Si_3	hP16 $P6_3/mcm$ Mn_5Si_3 ($D8_8$)	a= 742.9 c= 513.92	[85Vil];powder pattern: ASTM file card # 29-1362
Ti_5Si_4(r)	tP36 $P4_12_12$ Zr_5Si_4	a= 670.2 c= 1217.4	[85Vil];powder pattern: ASTM file card # 27-907
Ti_5Si_4(h)	oP* Pbnm	a= 664.5 b= 650.6 c= 1269.0	[69Nic];powder pattern: ASTM file card # 23-1079
TiSi	oP8 Pnma FeB (B27)	a= 654.4 b= 363.8 c= 499.7	[85Vil];powder pattern: ASTM file card # 17-424
$TiSi_2$	oF24 Fddd $TiSi_2$ (C54)	a= 826.71 b= 480.00 c= 855.05	[85Vil];powder pattern: ASTM file card # 2-1120 35-785
ε-Ti_2N(r) T<1080	tP6 $P4_2/mnm$ TiO_2	a= 494.28 c= 303.57	[85Vil];powder pattern: ASTM file card # 17-386 31-33 at% N [87Len]
η-Ti_3N_{2-x}(h) 1066<T<1103	hR6 $R\bar{3}m$ $AgCrSe_2$	a= 297.95 c= 2896.5	[86-1Len]; gives powder pattern 29 at% N [86-1Len]

Tab.13.1 continued

ζ-Ti_4N_{2-x}(h)	hR8	a= 298.09	[86-2Len];
1078<T<1291	$R\bar{3}m$	c= 2166.42	gives powder pattern
	Ti_7S_{12}		31.5 at% N [86-2Len]
δ-TiN_{1-x}(r)	tI16	a= 414.0	[85Vil];powder pattern:
T<800	$I4_1/amd$	c= 880.5	ASTM file card # 23-1455
(metastable)			38 at% N [87Len]
TiN_{1-x}	cF8	a= 423.9	[85Vil];powder pattern:
	$Fm\bar{3}m$		ASTM file card # 38-1420
	NaCl (B1)		
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160

Tab.13.2:Thermodynamic data for the solid phases in Ti - Si - N

phase	ΔG_f^o (J/gramatom)	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 $TiSi_2$	-56967 + 2.23725 T	[89Vah]
.5000 TiSi	-68000 - 0.04119 T	[89Vah]
.5000 Ti_5Si_4	-71000 - 0.79164 T	[89Vah]
.1250 Ti_5Si_3	-72409.5 - 0.31694 T	[89Vah]
.2500 Ti_3Si	-66565.2 + 11.5143 T	[89Vah]
.5000 TiN	-167883 + 46.4424 T	(25°C<T<882°C) [76Fro]
	-169138.2 + 47.4884 T	(882°C<T<1200°C) [76Fro]

Fig.13.1: Phase diagram of the boundary system titanium - nitrogen

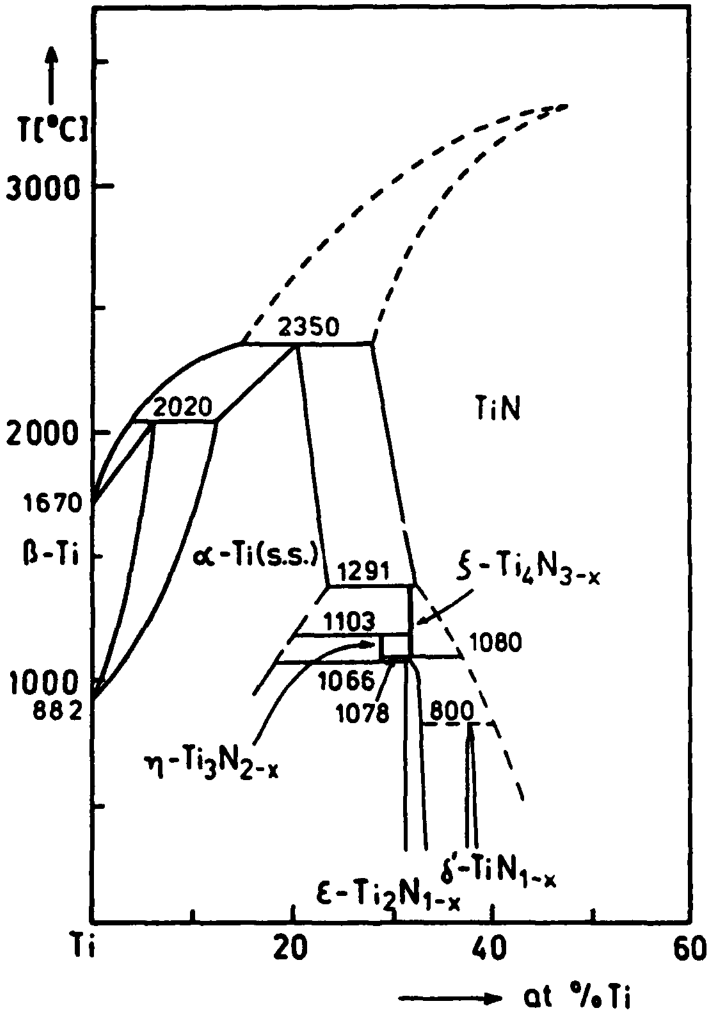


Fig.13.2: Isothermal section observed in the system Ti - Si - N at 1000°C (in the absence of external nitrogen pressure)

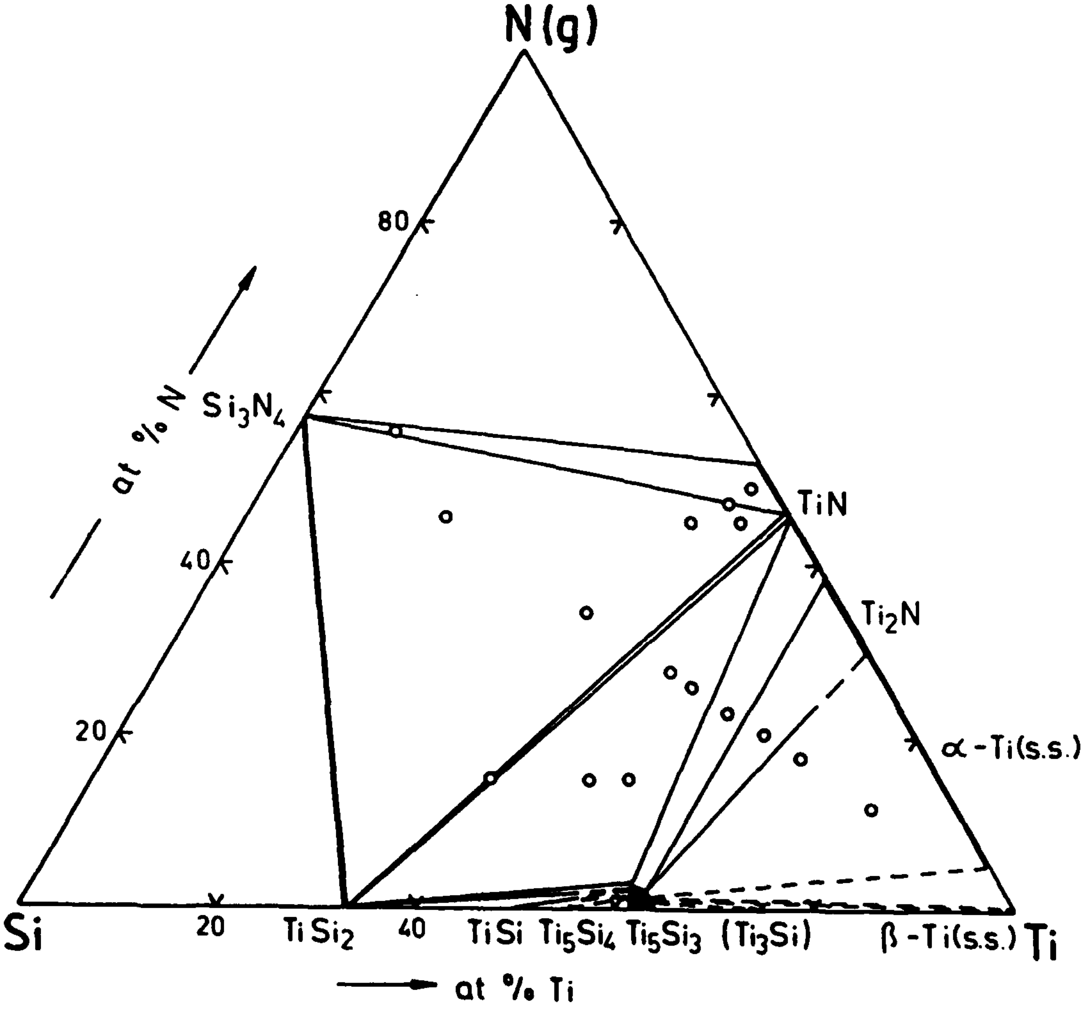


Fig.13.3: Lattice parameters,c/a ratios and unit cell volumes of the $D8_8$-type $Ti_5\,Si_3N_{5-x}$ phase field homogeneity limits at 1000°C

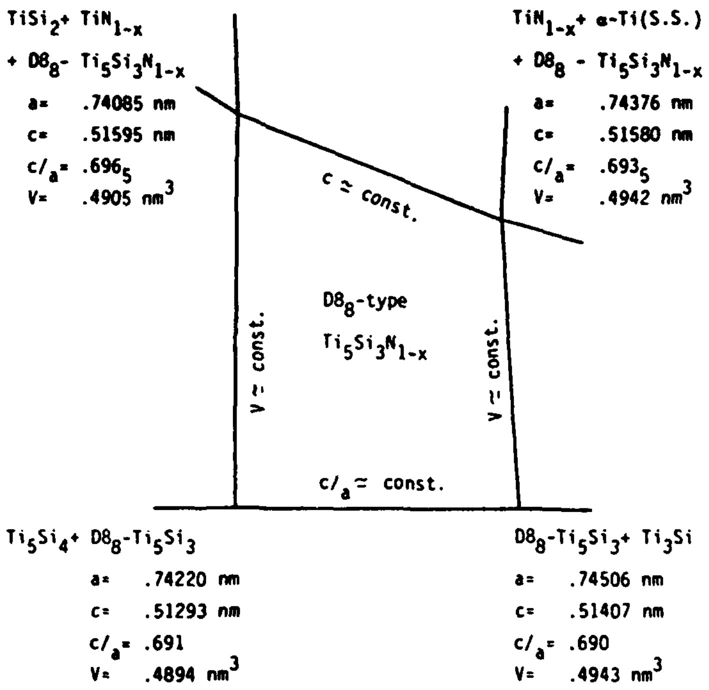
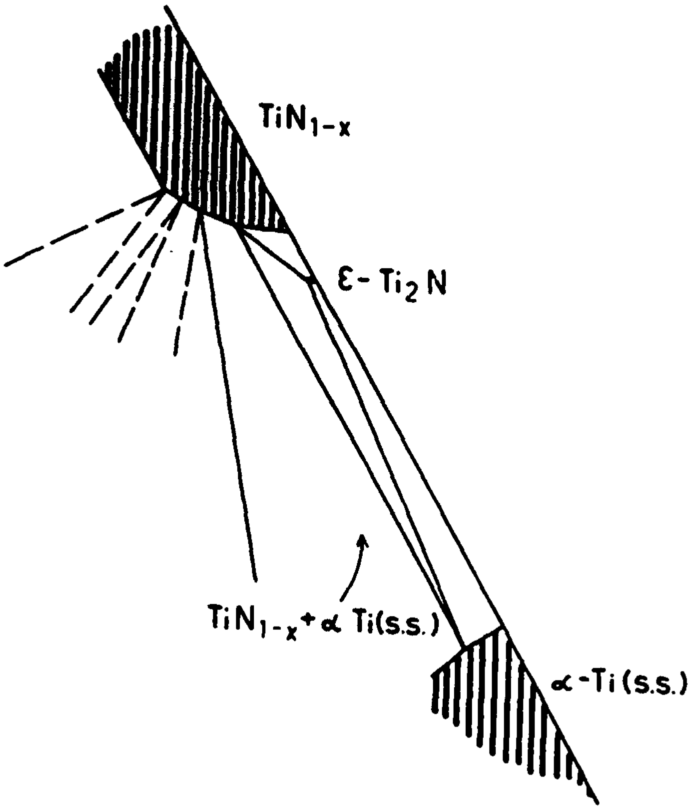


Fig.13.4: Detail of the phase field partition at 1000°C in Ti-Si-N close to the binary Ti-N (schematic)



SYSTEM ZIRCONIUM - SILICON - NITROGEN (Zr-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Zr-Si-N at 1000°C and 1300°C were determined by x-ray analysis [85-1Sch]. The alloys were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4, 58 at% Si), silicon (purity: 3N), zirconium (purity: m3N) all from Alpha Div., Ventron Corp., USA and zirconium nitride (purity 2N; from Materials Research Corp., USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at 1000°C or annealed at 1300°C, 48h in a r.f. furnace under argon (purity: 5N+).

BINARY SYSTEMS

The phase diagram for the binary system Zr-Si given in [86Mas] is a reproduction of [76Kub] which is based on [53Lun]. In the more recent experimental investigation by [76Koc], which is reproduced in [76Mof], the phase Zr_5Si_3 is found to decompose below 1745°C into Zr_3Si_2 and Zr_2Si. Furthermore, the composition of the intermediate phase most rich in zirconium is corrected from Zr_4Si to Zr_3Si. Using high purity materials (Zr bar, purity: 3N, impurities in ppm: O 450, H 260, C<200, Hf<200, Cr 60, Al 52, Si 45, other<30, from Cezus Puk Ugine, France; Si ingot, purity: 6N, from Alpha Div., Ventron Corp., USA) the decomposition of Zr_5Si_3 formed upon melting was corroborated [85-2Sch] but the occurrence of a zirconium silicide more rich in Zr than Zr_2Si could not be confirmed. Thus it is likely, that the phase Zr_3Si is impurity stabilized like the analogous phase in the Ti-Si system [89Paj], [89Kiv]. It was noted furthermore [85-2Sch], that ZrSi(h) having CrB type structure transforms only in Si rich ZrSi alloys into ZrSi(r) having FeB type structure, but not in Zr rich ZrSi alloys where it exists at 1000°C even after annealing for 550h. The phase diagram of Zr-N is given in [86Mas]. No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.14.1). The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Zr-Si-N (tab.14.1),but Zr_5Si_3(h) is stabilized by nitrogen to lower temperatures.Two experimentally determined isothermal sections are reported [85Sch]: At 1000°C as well as 1300°C (figs.14.1 and 14.2 resp.).$Zr_5Al_3N_{1-x}$ coexists at both temperatures with ZrN_{1-x},Zr_2Si,Zr_3Si_2,Zr_5Si_4 and ZrSi (CrB). Relative to the binary compound (tab.14.1) the lattice parameters are increased to a= 789.22 pm, c= 564.77 pm (coex. with ZrN_{1-x}). At 1000°C Si_3N_4 coexist with ZrN_{1-x},$ZrSi_2$ and ZrSi (FeB); at 1300°C no tie line exists between Si_3N_4 and ZrSi.These data confirm earlier reports on the interaction of Si_3N_4+ Zr [56-1Bre][76Kri],Si + ZrN_{1-x} [66Yas],$Zr_{.625}Si_{.375}$+ ZrN_{1-x}(fig.14.3 [56Now]) as well as on the coexistence of Si_3N_4 + ZrN_{1-x} [85Uch].With the exception of the above mentioned phase $Zr_5Si_3N_{1-x}$, in ternary alloys lattice parameters of neither binary zirconium silicide,Si_3N_4 or ZrN_{1-x} are altered with respect to the values of the pure binary alloys indicating virtual insolubility of the resp.third component.

The thermodynamic data for zirconium silicides in tab.14.2 are taken from [56-2Bre] (cited in part by [82Mur]) who critically reviewed and supplemented the measurements by [55Rob] rather than just citing their data (as done in more recent compilations ,e.g. [60Pop],[70Kar],[76Alc]).However,since the temperature dependency of the data for zirconium silicides are not known,only rough estimates are possible for the tie lines occurring in the ternary Zr-Si-N.The results of these estimates are generally consistent with the experimentally observed isothermal sections (figs.14.1 and 14.2). There is no pressure or temperature range where Si_3N_4 coexists in equilibrium with zirconium.

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Table 14.1: Solid phases in the system Zr - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Zr(r) T<863	hP2 $P6_3/mmc$ Mg (A3)	a= 323.2 c= 514.7	[85Vil];powder pattern: ASTM file card # 5-665
β-Zr T>863	cI2 $Im\bar{3}m$ W (A2)	a= 356.8	[85Vil];powder pattern: ASTM file card # 34-657
Zr_3Si	tP32 $P4_2/n$ Ti_3P	a= 1101 c= 545	[85Vil]; possibly impurity stabilized
Zr_2Si	tI12 I4/mcm Al_2Cu (C16)	a= 660.9 c= 529.8	[85Vil];powder pattern: ASTM file card # 25-757
Zr_5Si_3(h) T>1745	hP16 $P6_3/mcm$ Mn_5Si_3 ($D8_8$)	a= 788.6 c= 555.8	[85Vil];powder pattern: ASTM file card # 6-582
Zr_3Si_2	tP10 P4/mbm U_3Si_2 ($D5_a$)	a= 708.2 c= 371.5	[85Vil];powder pattern: ASTM file card # 14-368
Zr_5Si_4	tP36 $P4_12_12$ Zr_5Si_4	a= 712.25 c= 1300.0	[85Vil];powder pattern: given in [66Pfe]
ZrSi(r) T<1460	oP8 Pnma FeB (B27)	a= 699.5 b= 378.6 c= 529.6	[85Vil];powder pattern: ASTM file card # 9-226
ZrSi(h) T>1460	oC8 Cmcm CrB (B33)	a= 375.4 b= 989.2 c= 374.6	[61Sch]; gives powder pattern
$ZrSi_2$	oC12 Cmcm $ZrSi_2$ (C49)	a= 372.1 b= 1468 c= 368.3	[85Vil];powder pattern: ASTM file card # 32-1499

Tab.14.1 continued

ZrN_{1-x}	cF8	a= 458.5	[85Vil];powder pattern:
	$Fm\bar{3}m$		ASTM file card # 2-956,
	NaCl (B1)		31-1493,35-753
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160

Tab.14.2:Thermodynamic data for the solid phases in Zr - Si - N

phase	ΔG_f^o (J/gramatom)	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 $ZrSi_2$	ΔH_f^{298} = -53000	[56-2Bre]
.5000 ZrSi	ΔH_f^{298} = -77400	[56-2Bre]
.1111 Zr_5Si_4 (Zr_6Si_5)	ΔH_f^{298} = -78000	[56-2Bre]
.2000 Zr_3Si_2	ΔH_f^{298} = -77000	[56-2Bre]
.1250 Zr_5Si_3	ΔH_f^{298} = -72175	[56-2Bre]
.3333 Zr_2Si	ΔH_f^{298} = -69730	[56-2Bre]
.5000 ZrN	-183230 + 48.325 T	[76Fro]

Fig.14.1: Isothermal section observed in the system Zr - Si - N at 1000°C (in the absence of external nitrogen pressure)

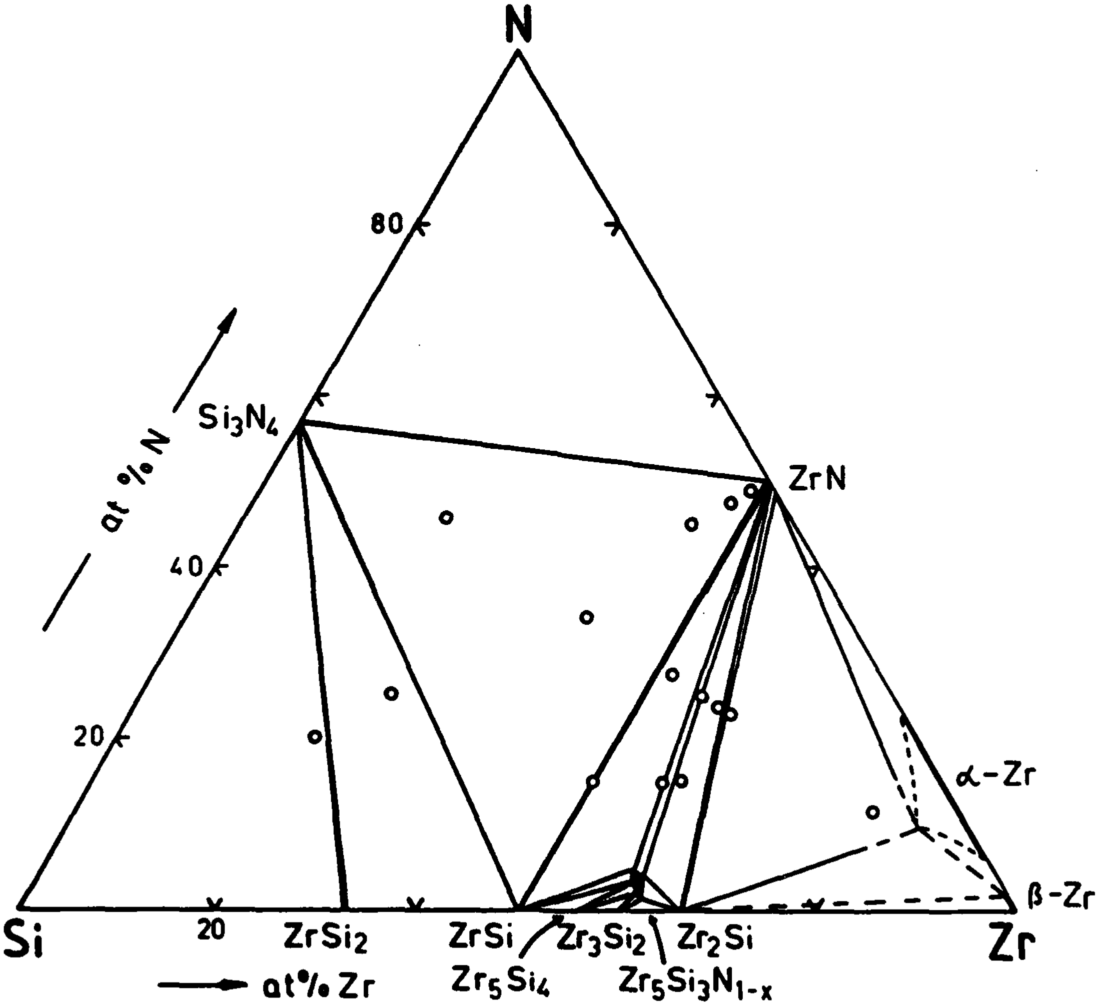


Fig.14.2: Isothermal section observed in the system Zr -Si - N at 1300°C (under argon)

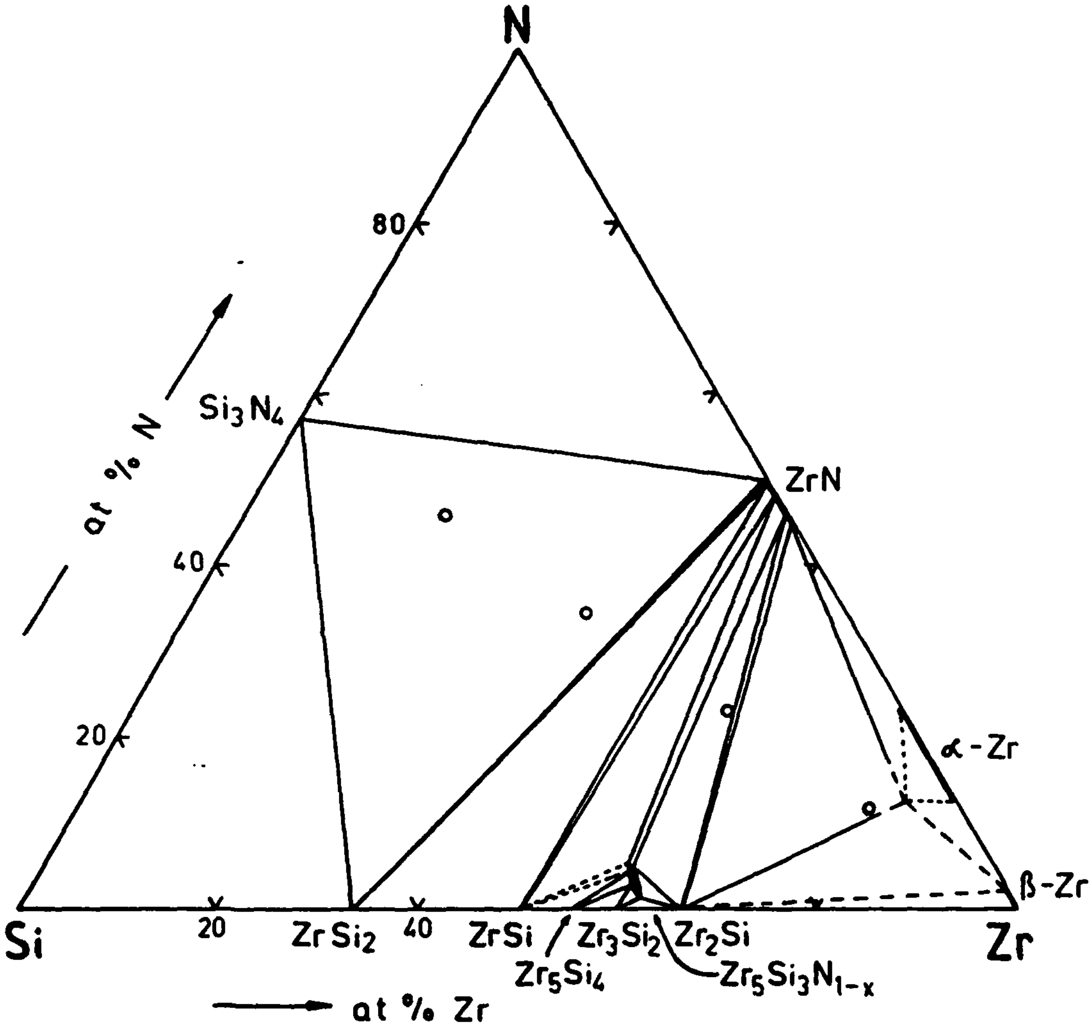
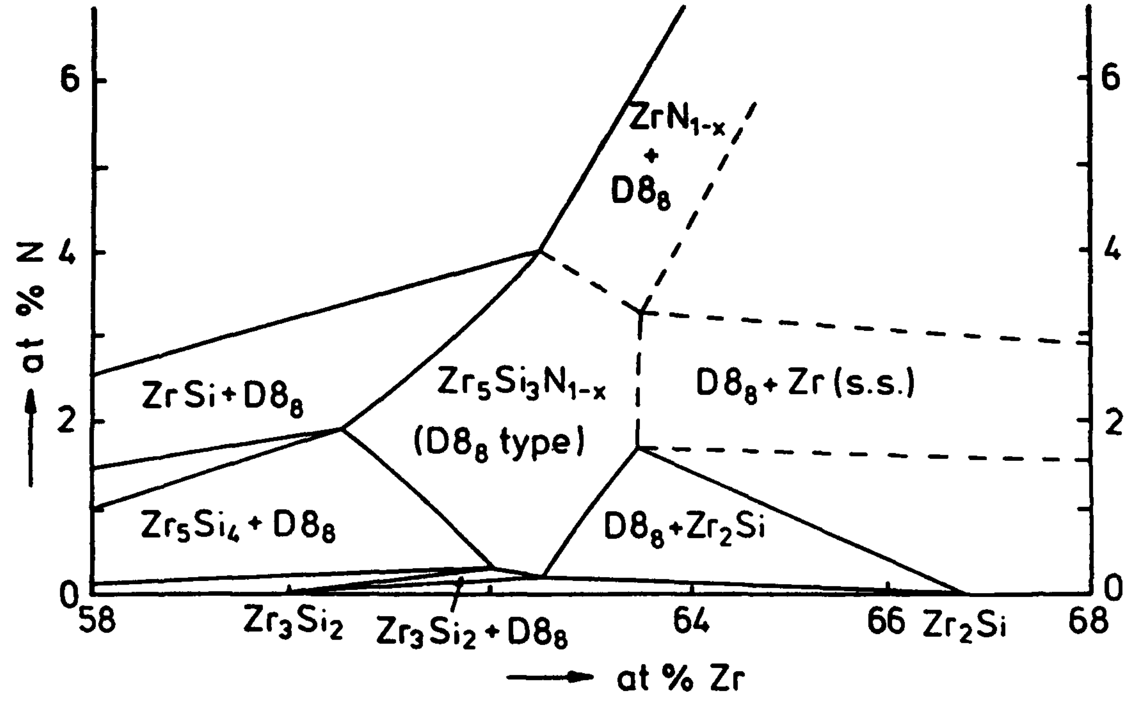


Fig.14.3 The phase field of $Zr_5Si_3N_{1-x}$ at 1400°C



SYSTEM HAFNIUM - SILICON - NITROGEN (Hf-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Hf-Si-N between 1000°C and 1300°C were determined by x-ray analysis [87Sch],[88Sch].The alloys investigated in were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si), silicon (purity: 3N) and hafnium (purity: 3N) all from Alpha Div.,Ventron Corp.,USA as well as hafnium nitride (purity: 2N; from Materials Reseach Corp.,USA). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at 1000°C or annealed at 1500°C,48h in a r.f.furnace under argon (purity:5N+).

BINARY SYSTEMS

For the system Hf-Si the phase diagram of [69Rud] (reproduced by [76Mof] as well as [89Gok]) is preferred over the diagram compiled by [81Kub] (reproduced in [86Mas]).According to [69Rud] neither Hf_5Si_3 (Mn_5Si_3-type) nor Hf_3Si (Ti_3P type) are binary eqilibrium phases (tab.15.1).The phase diagram of Hf-N (fig.15.1 [90Oka]) is based on [69Rud] but modified to account for the results of [70Rud] and [73Bil].No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.15.1). The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Hf -Si-N (tab.15.1).Isothermal sections are reported for 1000°C and for 1300°C (fig.15.2 [87Sch][88Sch]).At both temperatures HfN_{1-x} is the dominating phase coexisting with Si_3N_4 as well as all binary silicides.These data confirm earlier reports on the reaction of Si_3N_4 with hafnium [81Muk] and on the coexistence of Si_3N_4 with HfN during hot pressing at 1850°C [85Uch]. In ternary alloys lattice parameters of neither binary hafnium silicide, Si_3N_4 or HfN_{1-x} are altered with respect to the values of the pure binary alloys indicating virtual insolubility of the resp. third component.

Only limited thermodynamic data are available for binary hafnium silicides (tab.15.2). These allow only rough estimates of the tie lines which ,however, compare favorably with the experimentally observed equilibria.There is no pressure or temperature range where Si_3N_4 coexists in equilibrium with hafnium.

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Table 15.1: Solid phases in the system Hf - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Hf(r) T<1743	hP2 $P6_3/mmc$ Mg (A3)	a= 319.8 c= 506.1	[85Vil];powder pattern: ASTM file card # 38-1478
β-Hf(h) T>1743	cI2 $Im\bar{3}m$ W (A2)	a= 361.5	[85Vil];
Hf_2Si	tI12 I4/mcm Al_2Cu (C16)	a= 655.3 c= 518.6	[85Vil];powder pattern: ASTM file card # 12-467 25-371
Hf_3Si_2	tP10 P4/mbm ($D5_a$) U_3Si_2	a= 698.8 b= 367.5	[85Vil];powder pattern: ASTM file card # 14-427
Hf_5Si_4	tP36 $P4_12_12$ Zr_5Si_4	a= 703.9 c= 1283	[85Vil];
HfSi	oP8 Pnma FeB (B27)	a= 688.9 b= 377.2 c= 522.3	[85Vil];powder pattern: ASTM file card # 13-369
$HfSi_2$	oC12 Cmcm $ZrSi_2$ (C49)	a= 367.2 b= 1457 c= 364.1	[85Vil];powder pattern: ASTM file card # 10-202 38-1373
Hf_3N_2(h) 750<T<2000	hR6 $R\bar{3}m$ $AgCrSe_2$	a= 320.6 c= 2326	[85Vil];powder pattern: ASTM file card # 23-1097
Hf_4N_3(h) 750+ <T<2250	hR8 $R\bar{3}m$ Ti_7S_{12}	a= 321.4 c= 3112	[85Vil];powder pattern: ASTM file card # 24-465
HfN_{1-x}	cF8 $Fm\bar{3}m$ NaCl (B1)	a= 451.18	[85Vil];powder pattern: ASTM file card # 33-592

Tab.15.1 continued

Si	cF8 Fd$\bar{3}$m C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Tab.15.2:Thermodynamic data for the solid phases in Hf - Si - N

phase	ΔG_f^o (J/gramatom)	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 $HfSi_2$	ΔH_f^{298} = -50208	[82Mur]
.5000 HfSi	ΔH_f^{298} = -71130	[82Mur]
.1250 Hf_5Si_3 (Hf_5Si_4 + Hf_3Si_2)	ΔH_f^{298} = -69820	[82Mur]
.2500 Hf_3Si	ΔH_f^{298} = -62760	[82Mur]
.5000 HfN	-1845105 + 42.48 T	[76Fro]

Fig.15.1: Phase diagram of the boundary system hafnium - nitrogen

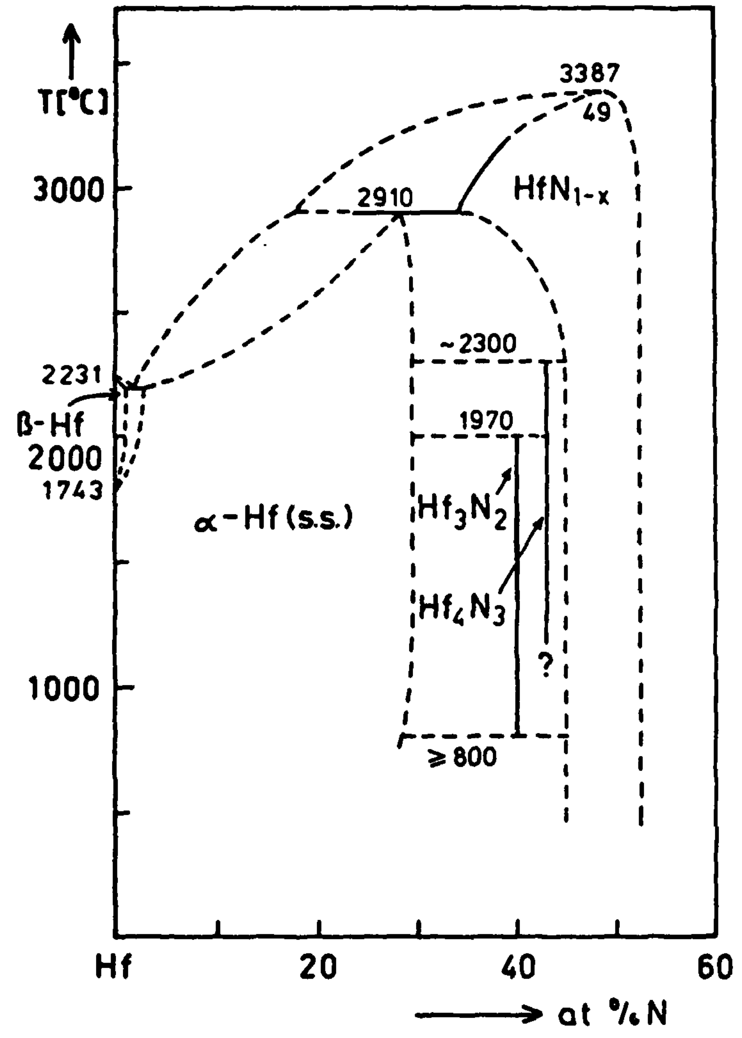
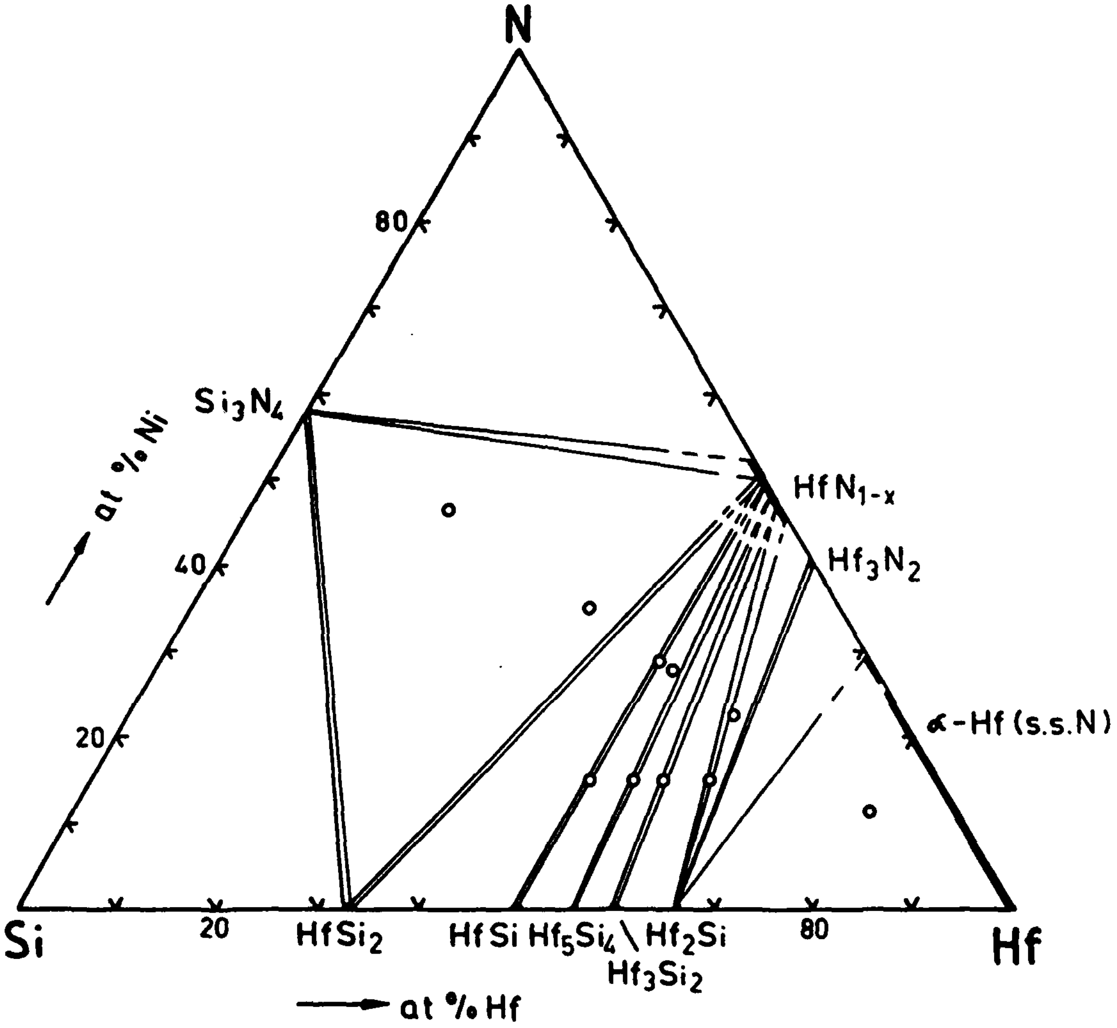


Fig.15.2: Isothermal section observed in the system Hf - Si - N at 1300°C under argon (at 1000°C identical tie lines exist)



SYSTEM VANADIUM - SILICON - NITROGEN (V-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of V-Si-N at 1000°C and 1500°C were determined by x-ray analysis [85Sch],[86And].The alloys investigated in the former work were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si), silicon (purity: 3N) and vanadium (purity: 2N5; impurities in ppm: C 900, Si 800, Cr 600, Fe 500, Al 200, others < 100) all from Alpha Div.,Ventron Corp.,USA and vanadiun nitride (purity 2N, from Materials Research Corp.,USA).Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 600h at 1000°C or annealed for 30h at 1500°C in a r.f.furnace under argon (purity:5N+).

BINARY SYSTEMS

Phase diagrams for the systems V-Si and V-N are given in [86Mas]. Although not shown in the V-N diagram [86Mas],with varying nitrogen content differently ordered structures occur within the "homogeneity range" of the subnitride β-V_2N_{1-x} (tab.16.1).No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.16.1). The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

The only ternary phase existing in The system V-Si-N is $V_5Si_3N_{1-x}$ (tab.16.1) which dominates the phase equlibria at 1000°C (fig.16.1 [85Sch]) and 1500°C (fig.16.2 [85Sch]).$V_5Si_3N_{1-x}$ coexists at 1000°C with Si_3N_4,V_2N_{1-x} and all binary vandium silicides stable at this temperature but not with VN_{1-x},silicon or vanadium.[86And] confirms these tie lines except they report $V_5Si_3N_{1-x}$ to coexist with VN_{1-x}. However,thermochemical calculations using the data in tab.16.2 corroborate the experimental findings reported in fig.16.1.Neither Si_3N_4 nor VN_{1-x} are stable at 1500°C under argon.Thus the tie lines directed from VSi_2,$V_5Si_3N_{1-x}$ as well as V_2N_{1-x} towards Si_3N_4 at 1000°C are changed toward N_2(gas) at 1500°C (fig.16.2 [85Sch]).These data confirm earlier reports on the interaction of Si_3N_4+ V [69Fel],Si_3N_4 + VN_{1-x} [85Uch],VSi_2 + N_2 [69Fit] and $V_{.625}Si_{.375}$+ N_2 [56Now].Lattice parameters of neither vanadium silicide coexisting with $V_5Si_3N_{1-x}$, Si_3N_4 or N_2(gas) are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in vanadium silicides.

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Table 16.1: Solid phases in the system V - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
V	cI2	a= 302.71	[85Vil];powder pattern:
	$Im\bar{3}m$		ASTM file card # 22-1058
	W (A2)		
V_3Si	cP8	a= 472.49	[85Vil];powder pattern:
	$Pm\bar{3}n$		ASTM file card # 19-405
	Cr_3Si (A15)		
V_5Si_3	tI32	a= 942.9	[85Vil];powder pattern:
	I4/mcm	c= 475.6	ASTm file card # 9-301
	Si_3W_5 ($D8_m$)		
V_6Si_5(h)	oI44	a= 1596.6	[85Vil];powder pattern:
T>1160±100	Ibam	b= 750.1	ASTM file card # 23-722
	Ge_5Ti_6	c= 485.8	27-611
VSi_2	hP9	a= 457.1	[85Vil];powder pattern:
	$P6_222$	c= 637.2	ASTM file card # 13-260
	$CrSi_2$ (C40)		38-1419
β-V_2N_{1-x} phases:			
V_9N_4	hP*	a= 491.0	[82Ono];
	$P6_322$	c= 455	powder pattern given
	V_9N_4		
V_2N	hP9	a= 491.7	[85Vil];powder pattern:
	$P\bar{3}1m$	c= 456.8	ASTM file card # 6-624
	V_2N		30-1420,32-1413,33-1439
$V_{32}N_{26}$	tP58	a= $2a_{VN}$	[78Ono];
T<500	$P4_2/nmc$	c= $2a_{VN}$	powder pattern given
	$V_{32}N_{26}$		
VN_{1-x}	cF8	a= 413.6	[85Vil];powder pattern:
	$Fm\bar{3}m$		ASTM file card # 25-1252
	NaCl (B1)		35-768
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		

Tab.16.1 continued

α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160
*$V_5Si_3N_{1-x}$	hP18 $P6_3/mcm$ filled Mn_5Si_3	a= 715.54 c= 485.21	[85Sch];powder pattern: ASTM file card # 8-379

Tab.16.2:Thermodynamic data for the solid phases in V - Si - N

phase	ΔG_f^o (J/gramatom)	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 VSi_2	-40700 + 3.15 T	[81Smi]
.0909 V_6Si_5	-49600 + 3.1 T	[81Smi]
.1250 V_5Si_3	-53800 + 4.1 T	[81Smi]
.2500 V_3Si	-43100 + 3.33 T	[81Smi]
V(s.s.10at% N)	-11175 (at 1773K)	estimated from plot ΔG_f^{1773} vs. x_N
V(s.s.5at% N)	-8000 (at 1273K)	estimated from plot ΔG_f^{1273} vs. x_N
.3431 $V_2N_{.93}$	-89591 + 30.55 T	[76Fro]
.5000 VN_{1-x}	-77404 + 46.024 T	[82Pom]

Fig.16.1: Isothermal section observed in the system V - Si - N at 1000°C (in the absence of external nitrogen pressure)

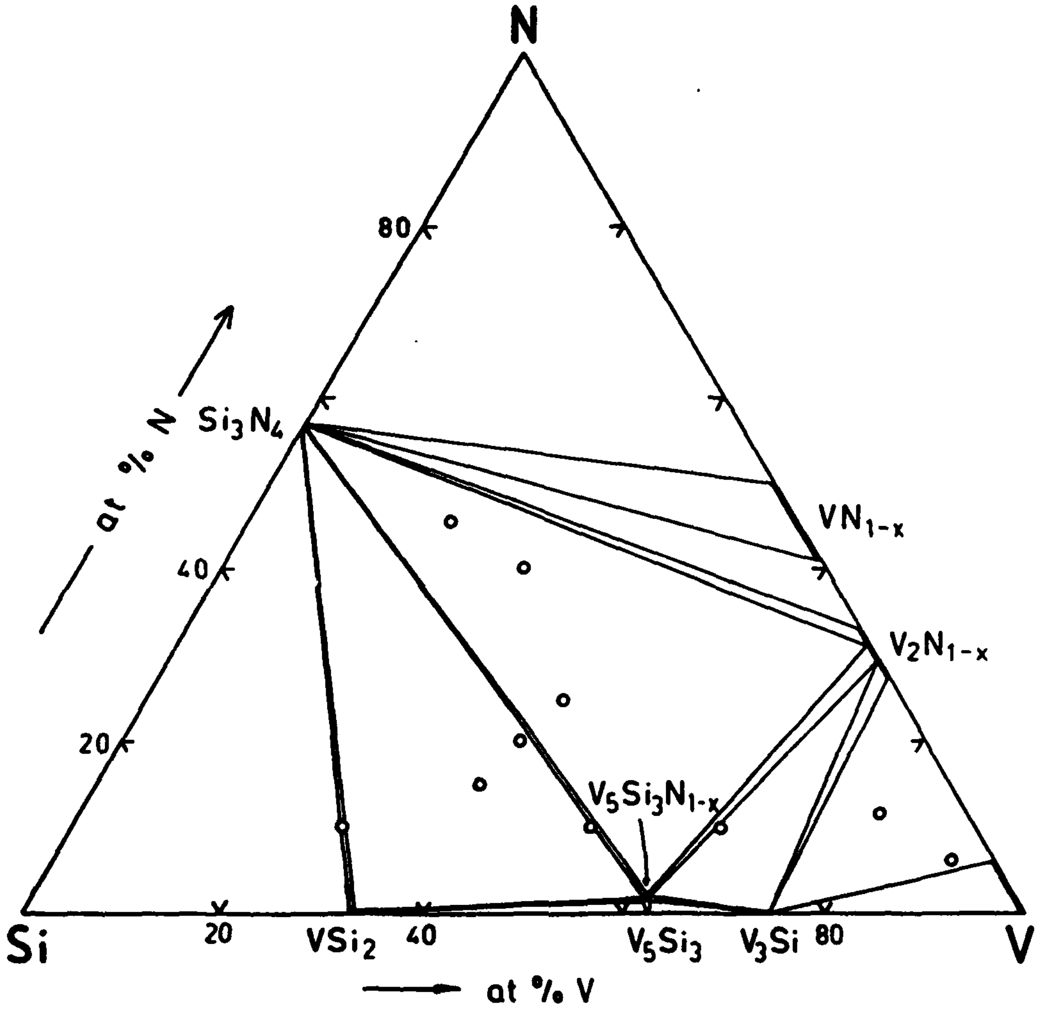
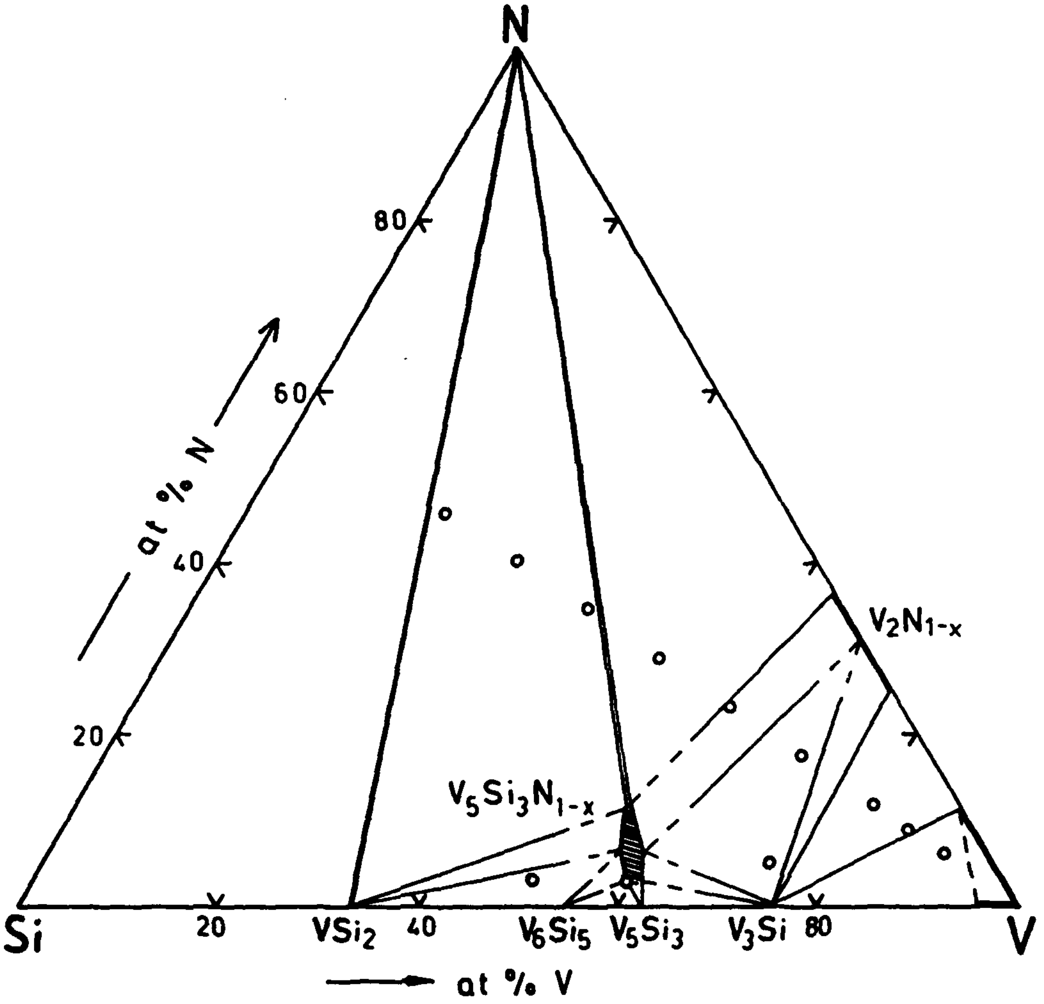


Fig.16.2: Isothermal section observed in the system V -Si - N at 1500°C (under argon)



SYSTEM NIOBIUM - SILICON - NITROGEN (Nb-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Nb-Si-N between 1000°C and 1500°C were determined by x-ray analysis [85-1Sch].The alloys investigated were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si), silicon (purity: 3N), niobium (purity: 2N8; impurities in ppm: Ta 800, Ti 100, Fe 80, O 80, c 50, W 50, other < 10) and niobium nitride (δNbN,purity: 3N) all from Alpha Div.,Ventron Corp.,USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 600h at 1000°C or annealed for 30h at 1500°C in a r.f.furnace under argon (purity:5N+).

BINARY SYSTEMS

The phase diagram of [80Koc] for the system Nb-Si (fig.17.1) is be preferred to the diagram given in [86Mas],because it shows in detail the stability ranges of the two modifications of Nb_5Si_3 (tab.17.1).The phase diagram for the system Nb-N (fig.17.2 [85-2Sch]) is based on [83Bra] as well as on the compilation by [79Pol].Phases stable only at nitrogen partial pressures higher than 10^5Pa [71Ter] are not included in this figure.No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.17.1). The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

The only ternary phase existing in the system Nb-Si-N is $Nb_5Si_3N_{1-x}$ (tab.17.1).$Nb_5Si_3N_{1-x}$ dominates the phase equilibria in the isothermal section at 1500°C (fig.17.3 [85-1Sch]) but does not occur at 1000°C (fig.17.4 [85-1Sch]).At this temperature Si_3N_4 coexist with ε-NbN, γ-Nb_4N_3 β-Nb_2N,Nb_5Si_3 and $NbSi_2$ but not with niobium. These data confirm reports on the interaction of Si_3N_4+ Nb or niobium compounds [56Bre][76Kri][85Uch][86Sug] as well as on the reactions of niobium silicides with N_2(gas) [56Now][69Fit]. Lattice parameters of neither niobium silicide coexisting with $Nb_5Si_3N_{1-x}$, β-Nb_2N, Si_3N_4 or N_2(gas) are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in niobium silicides.

Only limited thermodynamic data are available for binary niobium silicides (tab.17.2). These are not sufficient to allow calculation of tie lines to be compared with the experimentally observed equilibria. However, it is evident, that there is no pressure or temperature range where Si_3N_4 coexists in equilibrium with niobium.

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Table 17.1: Solid phases in the system Nb - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Nb	cI2 Im$\bar{3}$m W (A2)	a= 330.02	[85Vil];powder pattern: ASTM file card # 34-370
Nb_3Si	tP32 $P4_2/n$ Ti_3P	a= 1022.4 c= 518.9	[85Vil];powder pattern: ASTM file card # 22-763
Nb_5Si_3(r) T<1940	tI32 I4/mcm Cr_5B_3 ($D8_l$)	a= 657.0 c= 1188.4	[85Vil];powder pattern: ASTM file card # 30-874
Nb_5Si_3(h) T>1650	tI32 I4/mcm Si_3W_5 ($D8_m$)	a= 1002.6 c= 507.17	[85Vil];powder pattern: ASTM file card # 30-875
$NbSi_2$	hP9 $P6_222$ $CrSi_2$ (C40)	a= 481.9 c= 659.2	[85Vil];powder pattern: ASTM file card # 8-450
β-Nb_2N	hP9 P$\bar{3}$1m V_2N	a= 526.7 c= 498.8	[85Vil];powder pattern: ASTM file card # 30-869
γ-Nb_4N_3	tI14 I4/mmm Nb_4N_3	a= 438.2 c= 863.2	[85Vil];powder pattern: ASTM file card # 20-803
δ-NbN_{1-x}(h)	cF8 Fm$\bar{3}$m NaCl (B1)	a= 439.4	[85Vil];powder pattern: ASTM file card # 25-1361 34-337,38-1155
ε-NbN	hP8 $P6_3/mmc$ TiAs	a= 295.8 c= 1127.3	[85Vil];powder pattern: ASTM file card # 20-801
Nb_5N_6	hP22 $P6_3/mcm$ Nb_5N_6	a= 519.3 c= 1038.0	[85Vil];powder pattern: given in [71Ter]

Tab.17.1 continued

Nb_4N_5	tI18 I4/m $RhLi_4H_4$	a= 687.3 c= 429.8	[85Vil];powder pattern: given in [71Ter]
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160
*$Nb_5Si_3N_{1-x}$ T>1000	hP18 $P6_3/mcm$ filled Mn_5Si_3	a= 751.69 c= 531.03	[85-1Sch];powder pattern: ASTM file card # 8-422

Tab.17.2:Thermodynamic data for the solid phases in Nb - Si - N

phase	ΔG_f^o (J/gramatom)	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 $NbSi_2$	ΔH_f^{298} = -46000	[73Cha]
.1250 Nb_5Si_3	ΔH_f^{298} = -60700	[73Cha]
.2500 Nb_3Si		
.3333 Nb_2N	-90793 + 30.96 T	[76Fro]

Fig.17.1: Phase diagram of the boundary system niobium - silicon

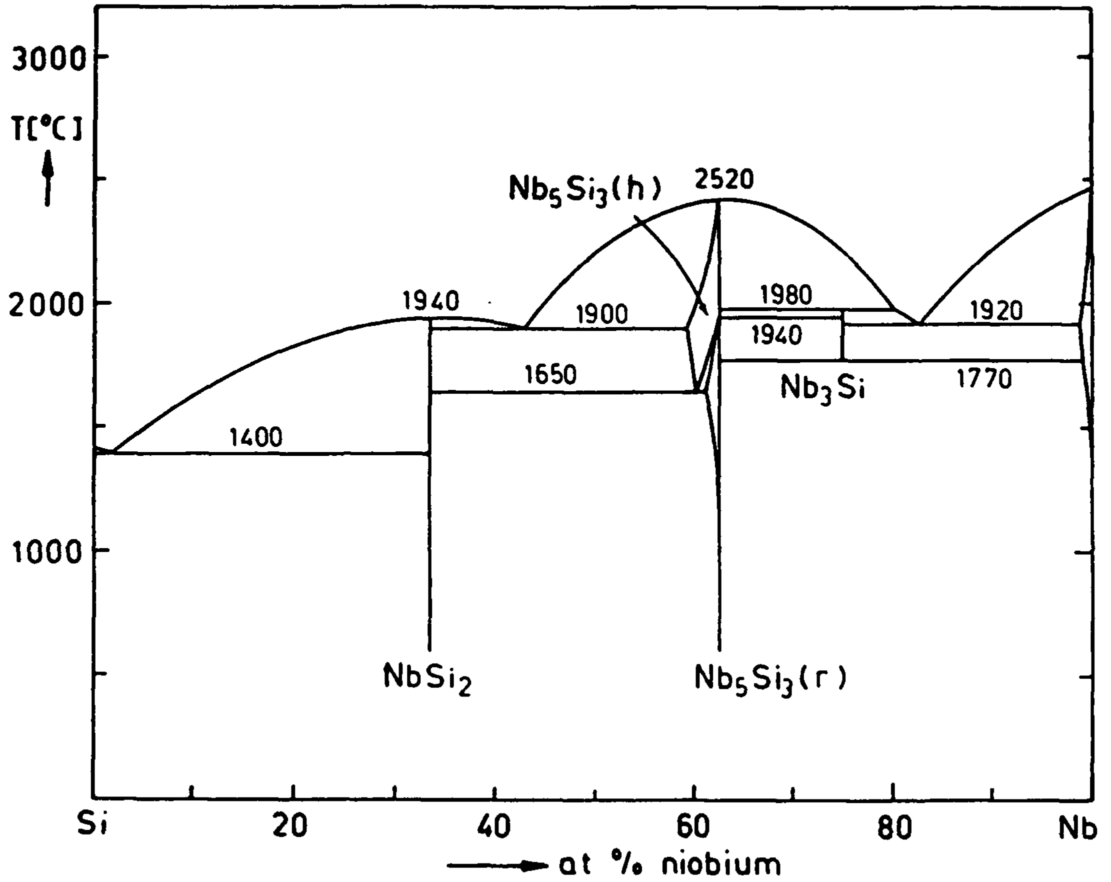


Fig.17.2: Phase diagram of the boundary system niobium - nitrogen

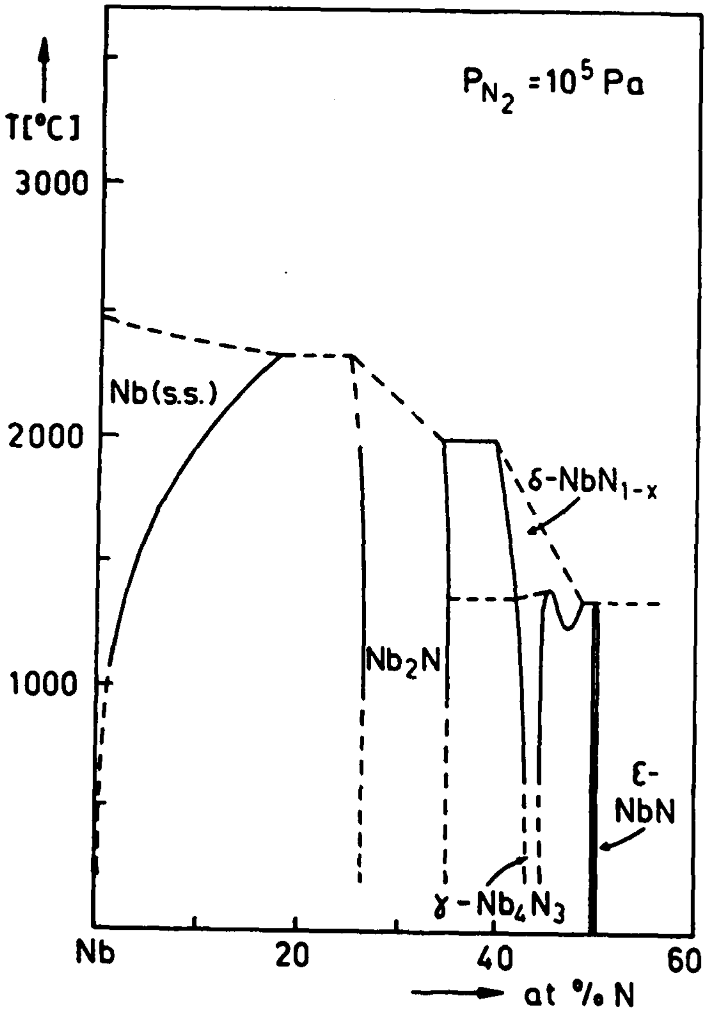


Fig.17.3: Isothermal section observed in the system Nb - Si - N at 1000°C (in the absence of external nitrogen pressure)

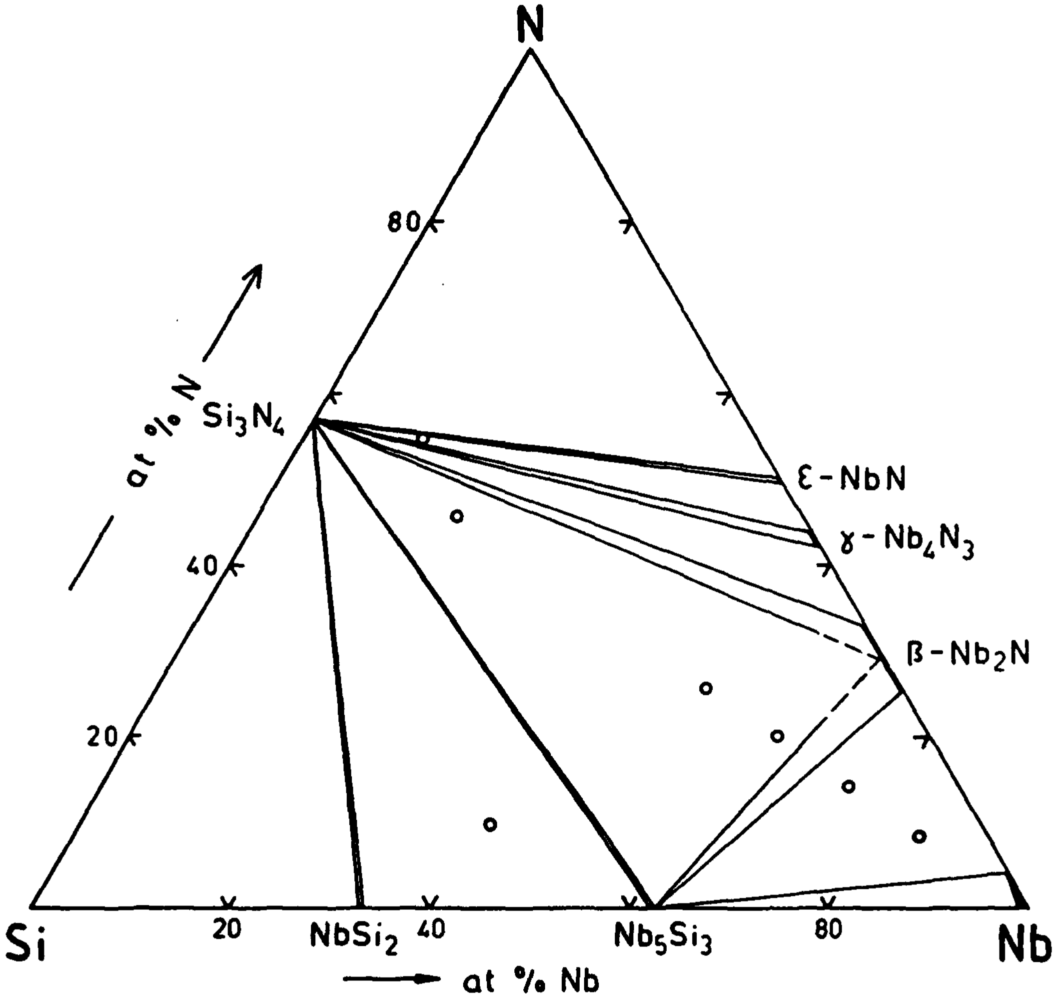
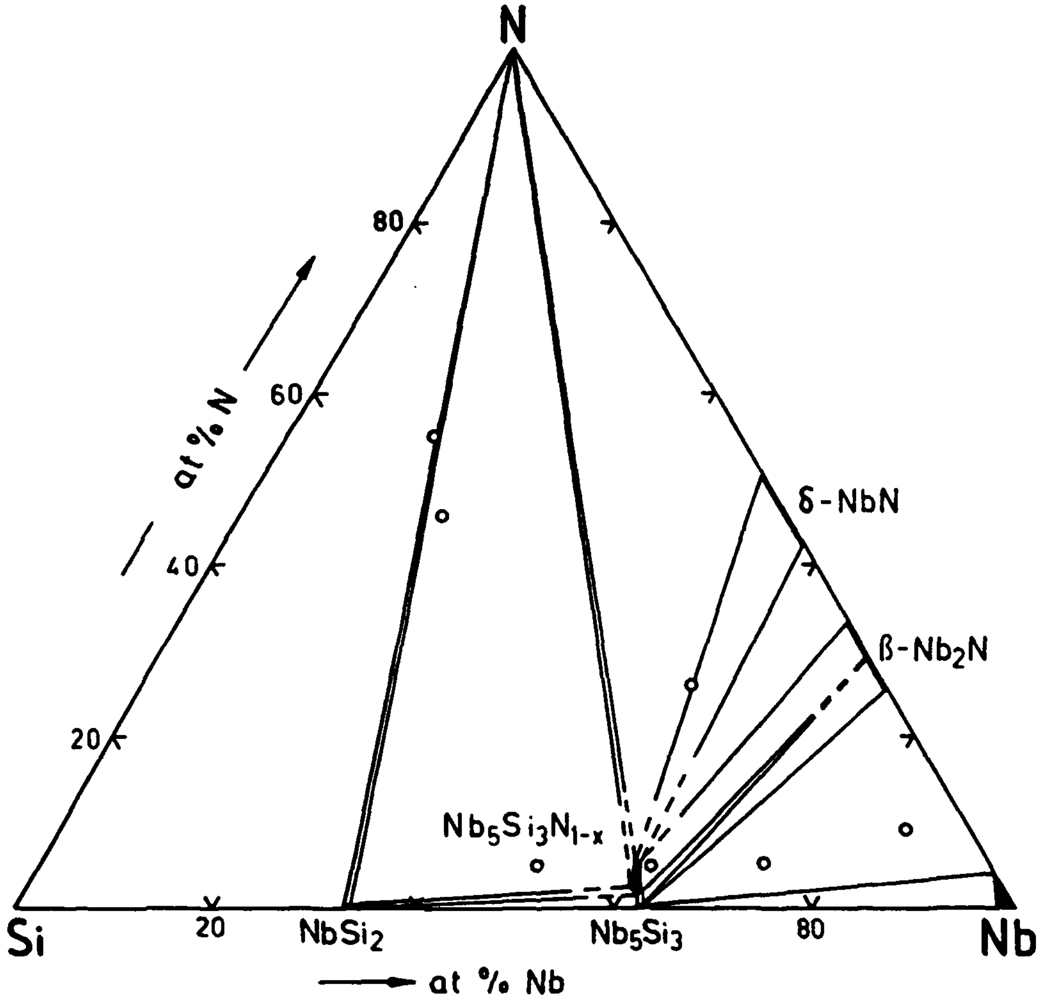


Fig.17.4: Isothermal section observed in the system Nb -Si - N at 1500°C (under argon)



SYSTEM TANTALUM - SILICON - NITROGEN (Ta-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Ta-Si-N between 1000°C and 1500°C were determined by x-ray analysis [56Bre],[85Sch].The alloys investigated in the latter work were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si), silicon (purity: 3N) and tantalum (purity: 3N6; impurities in ppm: O 1700, Fe 150, Nb 100, other < 10) all from Alpha Div.,Ventron Corp.,USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 600h at 1000°C or annealed for 30h at 1500°C in a r.f.furnace under argon (purity:5N+).

BINARY SYSTEMS

The tantalum-silicon phase diagram of [81Koc] (fig.18.1,thermodynamically modelled by [89Vah]) is preferred over the diagram given in [86Mas].Five intermediate phases exist (tab.18.1).The phase diagram for the system Ta-N (fig.18.2) is based on [83Ett] and supplemented by original information taken from [69Boo],[73Gei], [75Gat] and [84Koy].No phase diagram is reported for the system Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.18.1). The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

The only ternary phase existing in the system Ta-Si-N is $Ta_5Si_3N_{1-x}$ (tab.18.1).$Ta_5Si_3N_{1-x}$ dominates the phase equilibria in the isothermal section at 1500°C under argon (fig.18.3 [85Sch]) and 1327°C under nitrogen (fig.18.4 [56Bre]) but does not occur at 1000°C (fig.18.5 [85Sch]).At the latter temperature Si_3N_4 coexist with ε-TaN,β-Ta_2N, Ta_5Si_3 and $TaSi_2$ but not with Ta_2Si,Ta_3Si or tantalum.These data confirm reports on the interaction of Si_3N_4+ Ta or TaN [81Tam][85Uch] as well as on the reactions of tantalum silicides with N_2(gas) [56Now]

[69Fit].Lattice parameters of neither tantalum silicide coexisting with $Ta_5Si_3N_{1-x}$,β-Ta_2N,Si_3N_4 or N_2(gas) are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in tantalum silicides.

Using the thermodynamic data in tab.18.2 for the calculation of tie lines, the experimental results at 1000°C (fig.18.3) are corroborated.There is no pressure or temperature range where Si_3N_4 coexists in equilibrium with tantalum.

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Table 18.1: Solid phases in the system Ta - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ta	cI2 $Im\bar{3}m$ W (A2)	a= 330.25	[85Vil];powder pattern: ASTM file card # 4-788
Ta_3Si	tP32 $P4_2/n$ Ti_3P	a= 1019.3 c= 517.5	[85Vil];powder pattern: ASTM file card # 18-1312
Ta_2Si	tI12 I4/mcm Al_2Cu (C16)	a= 616 c= 505.6	[53Now];powder pattern: ASTM file card # 6-552
Ta_5Si_3(r) T<2160	tI32 I4/mcm Cr_5B_3 ($D8_l$)	a= 651.6 c= 1187.3	[85Vil];powder pattern: ASTM file card # 9-232
Ta_5Si_3(h) T>2160	tI32 I4/mcm Si_3W_5 ($D8_m$)	a= 988 c= 506	[85Vil];powder pattern: ASTM file card # 9-280
$TaSi_2$	hP9 $P6_222$ $CrSi_2$ (C40)	a= 478.21 c= 656.95	[85Vil];powder pattern: ASTM file card # 8-53 38-483
Ta_6N_2(r) T<790	c**	a= 1010	[85Vil]
β-Ta_2N(r) T<1850	hP9 $P\bar{3}1m$ V_2N	a= 528.5 c= 491.9	[85Vil];powder pattern: ASTM file card # 31-1370
β-Ta_2N(h) T>1650	hP3 $P6_3/mmc$ Fe_2N (L'3)	a= 304.76 c= 491.87	[85Vil];powder pattern: ASTM file card # 26-985
δ-TaN_{1-x}(h) T>1750	cF8 $Fm\bar{3}m$ NaCl (B1)	a= 433	[85Vil];powder pattern: ASTM file card # 32-1283

Tab.18.1 continued

ε-TaN	hP6	a= 519.6	[85Vil];powder pattern:
T<1950	P$\bar{6}$2m	c= 291.1	ASTM file card # 9-257
	TaN		
Ta_5N_6	hP22	a= 516	[85Vil];powder pattern:
	$P6_3/mmc$	c= 1027	given in [71Ter]
	Nb_5N_6		
Ta_4N_5	tI18	a= 683.1	[85Vil];powder pattern:
	I4/m	c= 426.9	given in [71Ter]
	$RhLi_4N_4$		
Si	cF8	a= 542.86	[85Vil];powder pattern:
	Fd$\bar{3}$m		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160
*$Ta_5Si_3N_{1-x}$	hP18	a= 750.88	[85Sch];powder pattern:
T> 1000	$P6_3/mcm$	c= 524.57	ASTM file card # 6-594
	filled Mn_5Si_3		

Tab.18.2:Thermodynamic data for the solid phases in Ta - Si - N

phase	ΔG_f^o (J/gramatom)	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 $TaSi_2$	-39700 + 5.084 T	[89Vah]
.1250 Ta_5Si_3	-41800 + 5.599 T	[89Vah]
.3333 Ta_2Si	-41800 + 6.391 T	[89Vah]
.2500 Ta_3Si	-38700 + 7.331 T	[89Vah]
.3333 Ta_2N	-67920 + 17.015 T	[76Fro]

Fig.18.1: Phase diagram of the boundary system tantalum - silicon

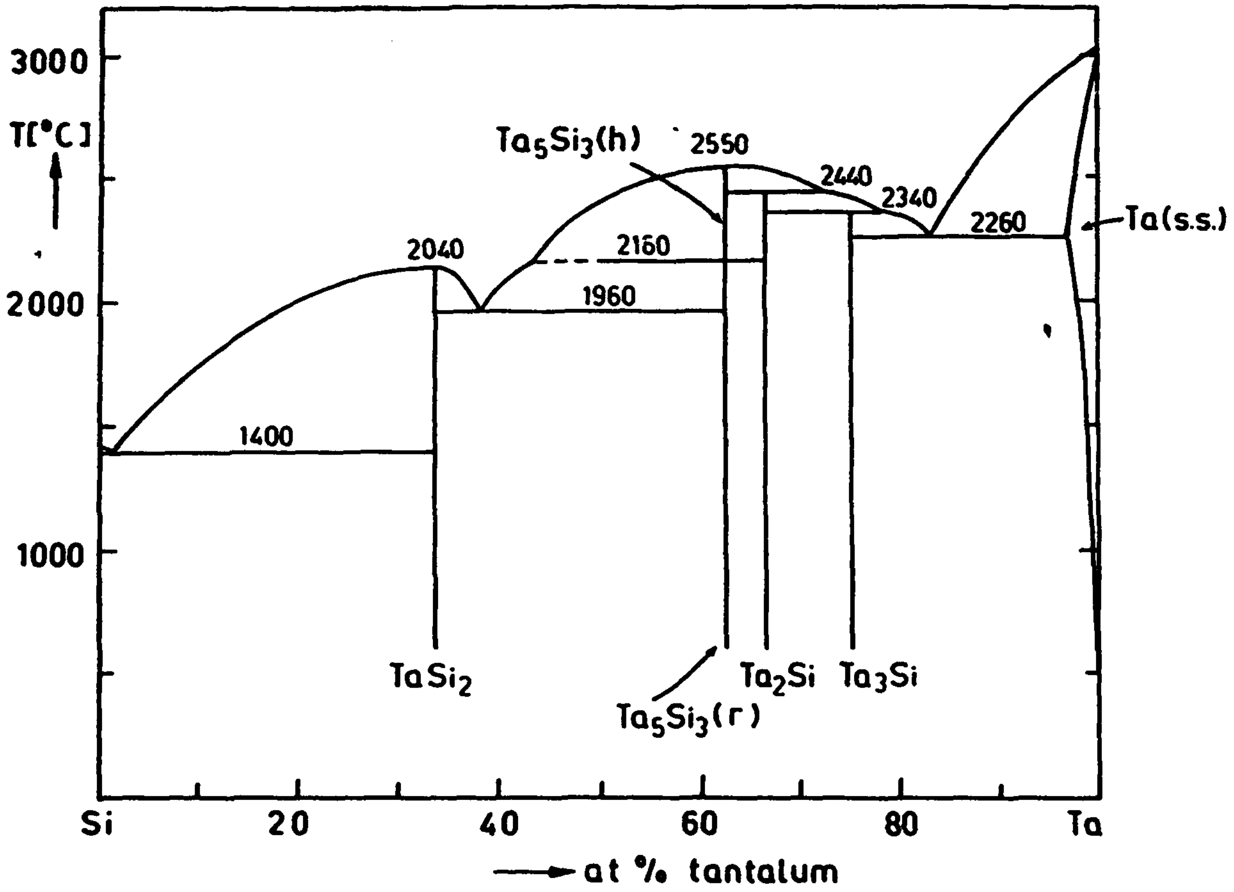


Fig.18.2: Phase diagram of the boundary system tantalum - nitrogen

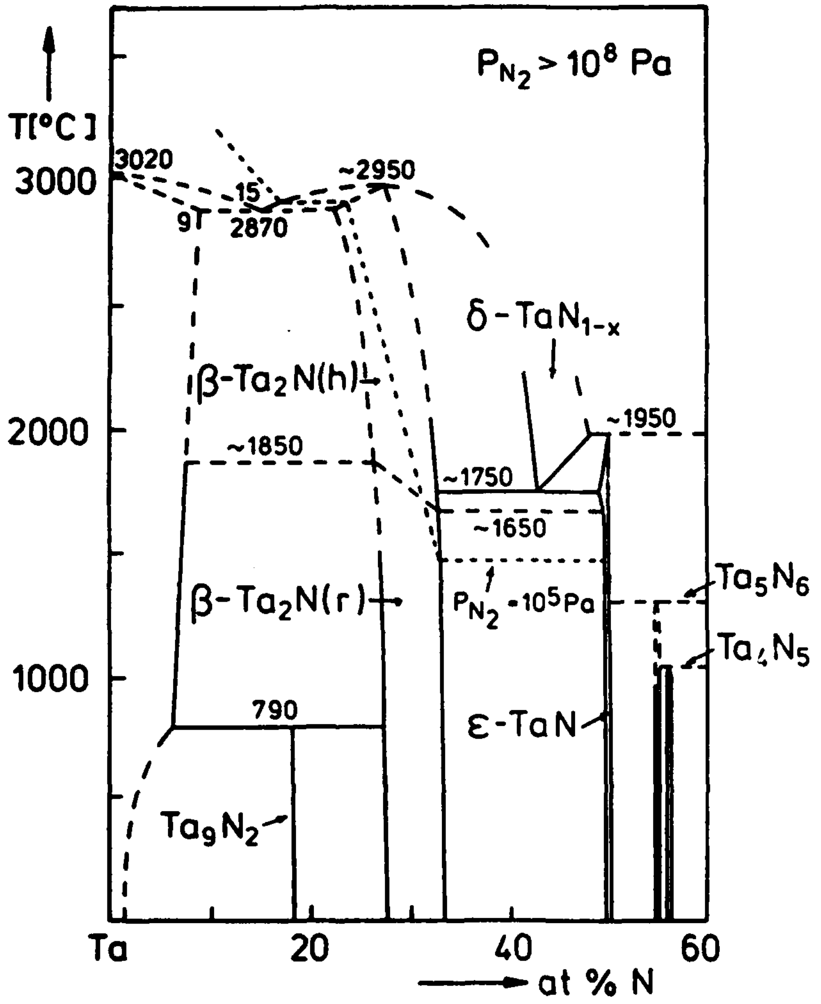


Fig.18.3: Isothermal section observed in the system Ta - Si - N at 1000°C (in the absence of external nitrogen pressure)

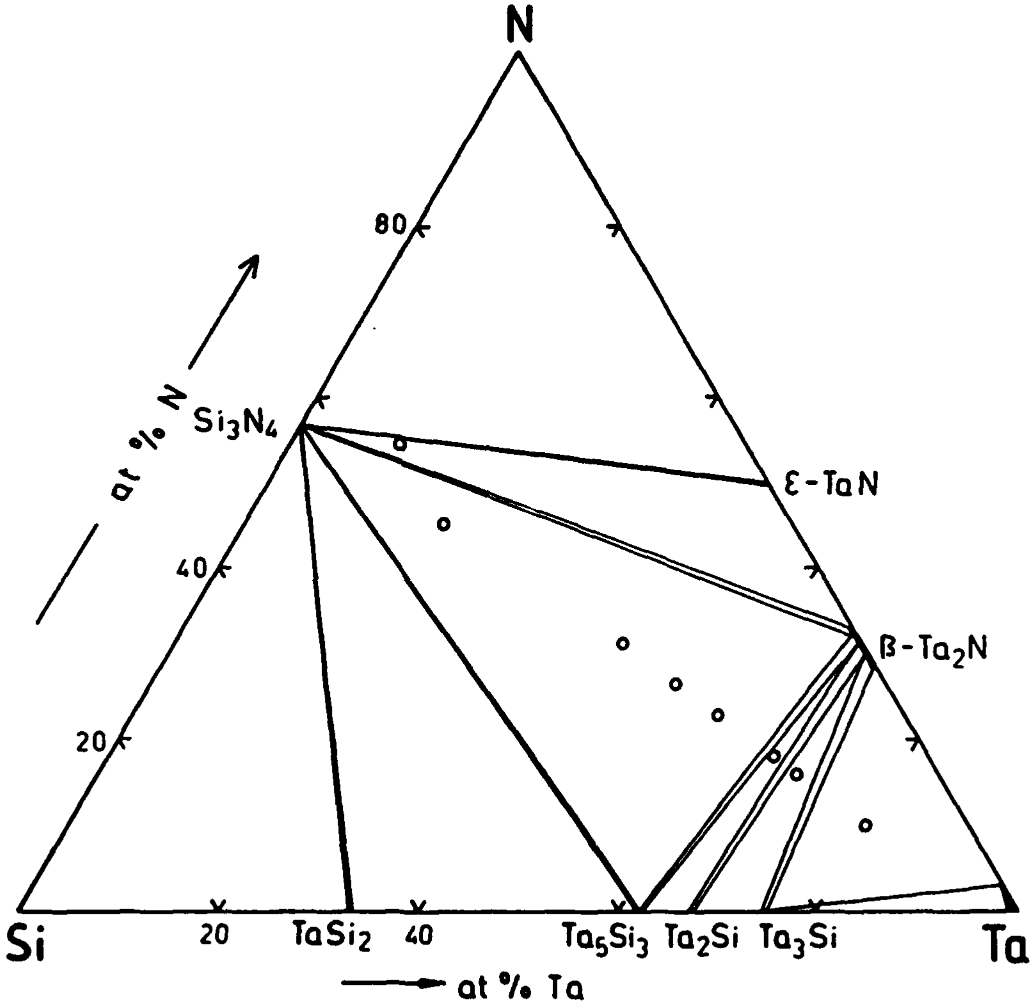


Fig.18.4: Isothermal section observed in the system Ta - Si - N at 1327°C (under nitrogen)

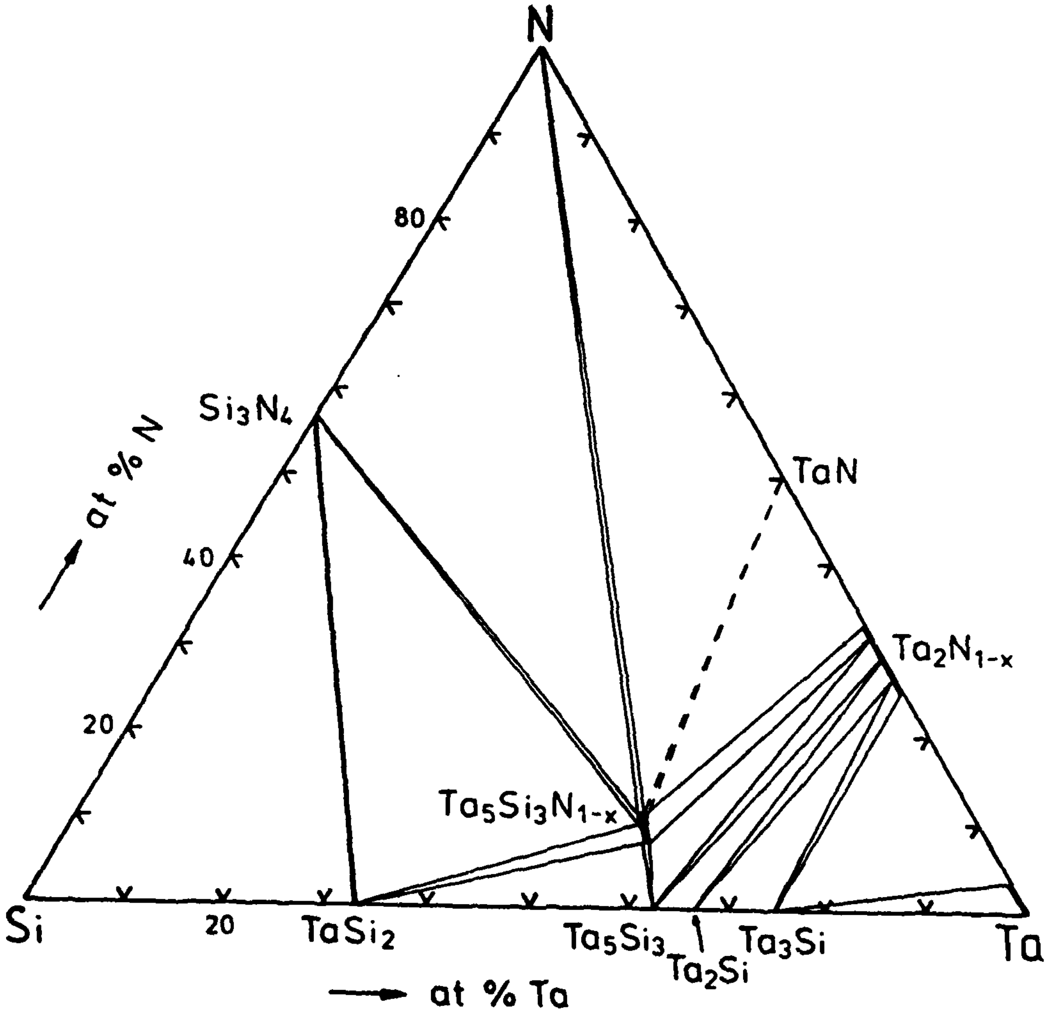
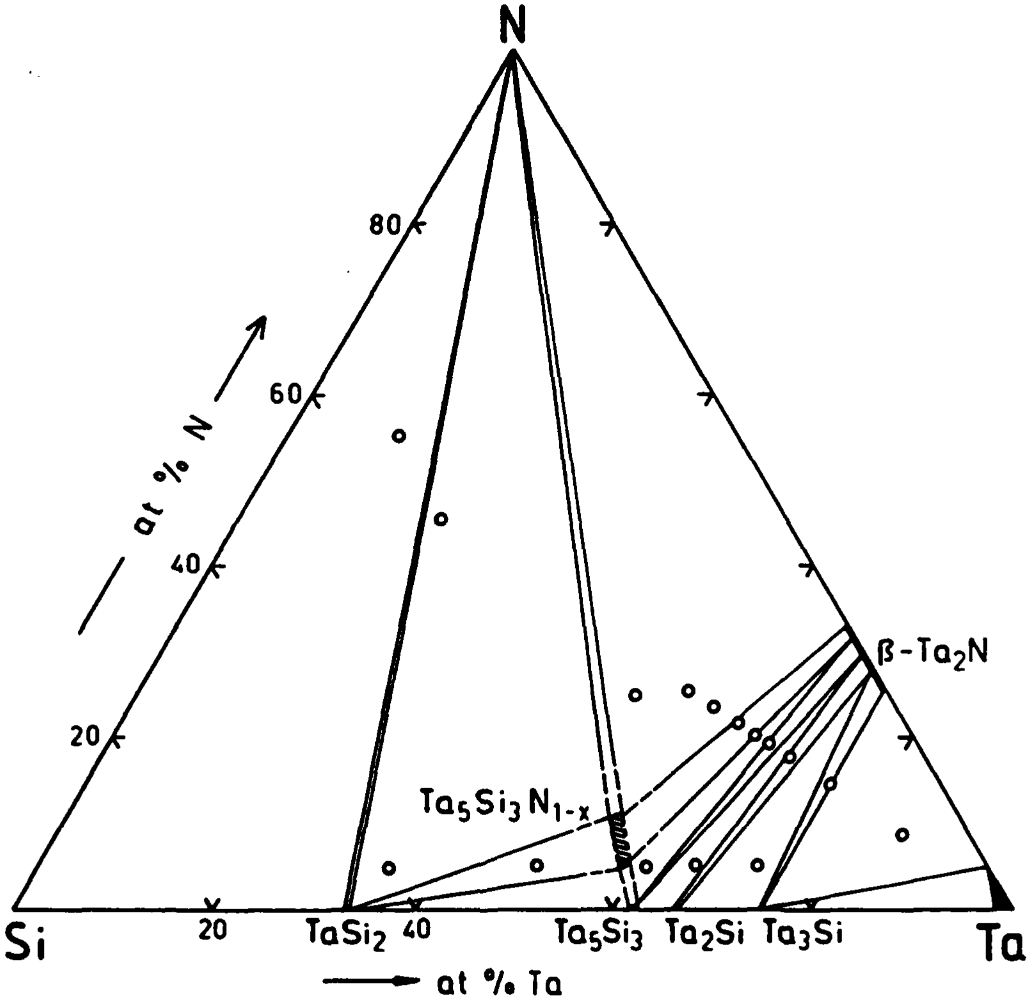


Fig.18.5: Isothermal section observed in the system Ta - Si - N at 1500°C (under argon)



SYSTEM CHROMIUM - SILICON - NITROGEN (Cr-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Cr-Si-N between 1000°C and 1600°C were determined by x-ray analysis [81Kat],[88Sch].The alloys investigated in the latter work were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si), silicon (purity: 3N) and chromium (purity: 3N5) all from Alpha Div.,Ventron Corp.,USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at temperatures up to 1000°C or annealed in an r.f.furnace under argon (purity:5N+) at temperatures up to 1400°C.

BINARY SYSTEMS

In the binary system Cr-Si [86Mas] four intermediate phases exist (tab.19.1).The phase diagram of *Cr-N (fig.19.1) is due to* [71Sve] (reproduced e.g. in [76Mof] and [81Kat]) but modified according to [76Fro].At 1000°C and $p(N_2)= 10^5$ Pa (tab.19.1) two intermediate phases, Cr_2N and CrN,exist.However neither phase is stable at this temperature and $p(N_2) \leq 70$ Pa [76Fro],[81Yam].No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.19.1). The solubility of nitrogen in silicon as well as in chromium is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Cr-Si-N (tab.19.1).Four experimentally determined isothermal sections are reported [81Kat],[88Sch]: At 1000°C as well as 1400°C in the absence of external nitrogen pressure (figs.19.2 and 19.4 resp.);at 1000°C under $p(N_2)$ exceeding ≅ 40 Pa (fig.19.3); and at 1600°C at $p(N_2)= 10^5$ Pa (fig.19.5). These data confirm earlier reports on the decomposition of Si_3N_4 in contact with chromium at temperatures of 900°C and above [56Now],[66Mue], [69Fel],[73Cha],[76Kri],[77Kha],[83Ore],[89Got].The silicide most rich in chromium coexisting with Si_3N_4 is Cr_3Si at 1000°C and Cr_5Si_3 at 1400°C and 1600°C.Lattice parameters of neither chromium silicide coexisting with Si_3N_4 or N_2 gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in chromium silicides.

Using the thermodynamic data in tab.19.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C as well as at 1400°C are calculated (tab.19.3).The resulting tie lines are consistent with the experimentally observed isothermal sections (figs.19.2 to 19.4).There is no pressure or temperature range where Si_3N_4 coexists in equilibrium with chromium.

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Table 19.1: Solid phases in the system Cr - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Cr	cI2 $Im\bar{3}m$ W (A2)	a= 288.4	[85Vil];powder pattern: ASTM file card # 6-694
Cr_3Si	cP8 $Pm\bar{3}n$ Cr_3Si (A15)	a= 455.5	[85Vil];powder pattern: ASTM file card # 7-186
Cr_5Si_3	tI32 I4/mcm Si_3W_5 ($D8_m$)	a= 917.0 c= 463.6	[85Vil];powder pattern: given in [55Par]
CrSi	cP8 $P2_13$ FeSi (B20)	a= 460.7	[85Vil];powder pattern:
$CrSi_2$	hP9 $P6_222$ $CrSi_2$ (C40)	a= 443.1 c= 636.4	[85Vil];powder pattern: ASTM file card # 12-596 35-781
Cr_2N	hP9 $P\bar{3}1m$	a= 479.6 c= 447.0	[85Vil];powder pattern: ASTM file card # 27-127 35-803
CrN	cF8 $Fm\bar{3}m$ NaCl (B1)	a= 414.8	[85Vil];powder pattern: ASTM file card # 11-65
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Tab.19.2: Thermodynamic data for the solid phases in Cr - Si - N

phase	ΔG_f^o (J/gramatom)	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 $CrSi_2$	-26700 + 1.0 T	[75Cha]
.5000 CrSi	-27400 - 0.6 T	[75Cha]
.1250 Cr_5Si_3	-27500 - 0.8 T	[75Cha]
.2500 Cr_3Si	-26400 + 0.6 T	[75Cha]
Cr(s.s.7at% Si)	-7200 (at 1673K)	estimated from plot ΔG_f^{1673} vs. x_{Si}
Cr(s.s.6at% Si)	-6700 (at 1273K)	estimated from plot ΔG_f^{1273} vs. x_{Si}
.3632 $Cr_2N_{0.76}$	-30663.4 + 15.22 T	[76Fro]

Tab.19.3: Calculated invariant equilibria in Cr - Si - N

a) at 1000°C (1273K):

$p(N_2)$ (Pa)	Reaction
5×10^{-3}	$Si_3N_4 = 3\ Si + 2\ N_2$
85×10^{-3}	$Si_3N_4 + 6\ Cr_{.5}Si_{.5} = 9\ Cr_{.333}Si_{.667} + 2\ N_2$
220×10^{-3}	$Si_3N_4 + 12\ Cr_{.625}Si_{.375} = 15\ Cr_{.5}Si_{.5} + 2\ N_2$
2.2	$Si_3N_4 + 15\ Cr_{.75}Si_{.25} = 18\ Cr_{.625}Si_{.375} + 2\ N_2$
42	$Cr_2N_{.76} = 2\ Cr + 0.38\ N_2$
830	$Si_3N_4 + 4.5\ Cr_2N_{.76} = 12\ Cr_{.75}Si_{.25} + 3.71\ N_2$

b) at 1400°C (1673K)

$p(N_2)$ (Pa)	Reaction
95	$Si_3N_4 = 3\ Si + 2\ N_2$
680	$Si_3N_4 + 6\ Cr_{.5}Si_{.5} = 9\ Cr_{.333}Si_{.667} + 2\ N_2$
1.7×10^3	$Si_3N_4 + 12\ Cr_{.625}Si_{.375} = 15\ Cr_{.5}Si_{.5} + 2\ N_2$
6.6×10^3	$Cr_2N_{.76} = 2\ Cr\ \ 0.38\ N_2$
13.8×10^3	$Si_3N_4 + 15\ Cr_{.75}Si_{.25} = 18\ Cr_{.625}Si_{.375} + 2\ N_2$
250×10^3	$Si_3N_4 + 4.5\ Cr_2N_{.76} = 12\ Cr_{.75}Si_{.25} + 3.71\ N_2$

Fig.19.1: Phase diagram of the boundary system chromium - nitrogen

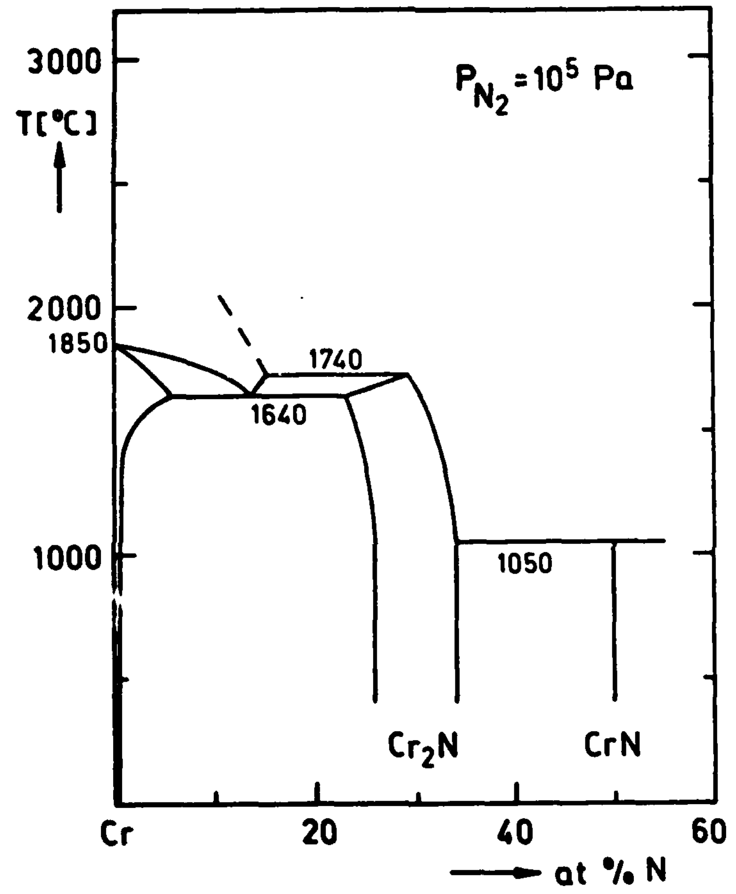


Fig.19.2: Isothermal section observed in the system Cr - Si - N at 1000°C (in the absence of external nitrogen pressure)

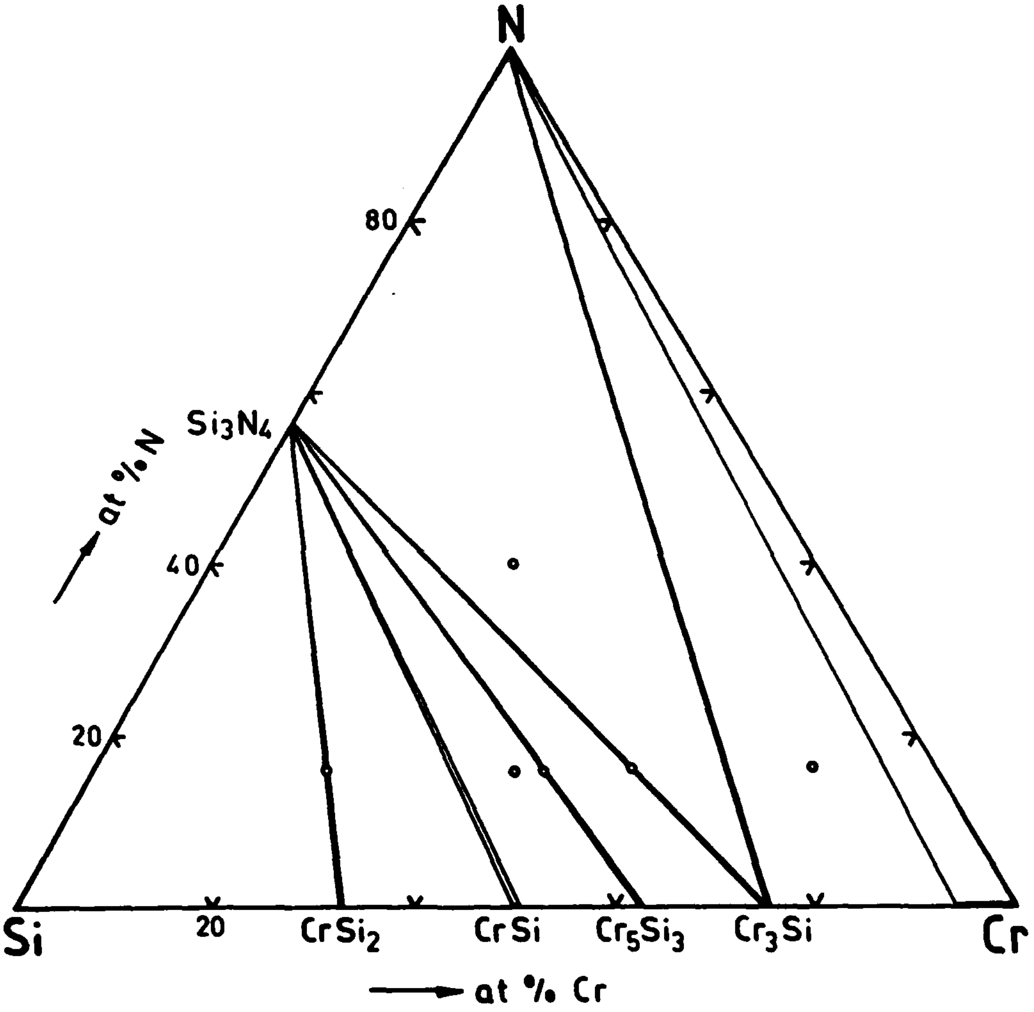


Fig.19.3: Isothermal section observed in the system Cr - Si - N at 1000°C (under a nitrogen partial pressure above ≅ 40 Pa)

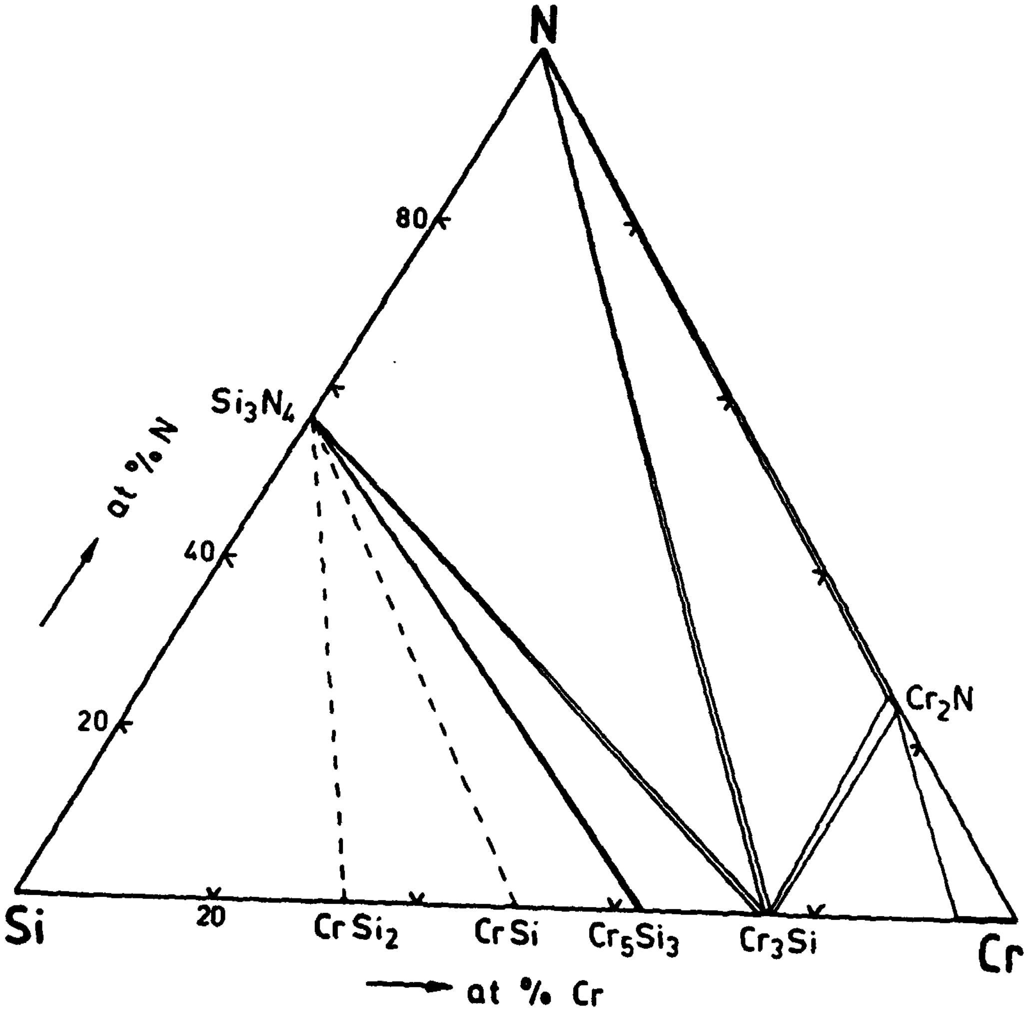


Fig.19.4: Isothermal section observed in the system Cr -Si - N at 1400°C (under argon)

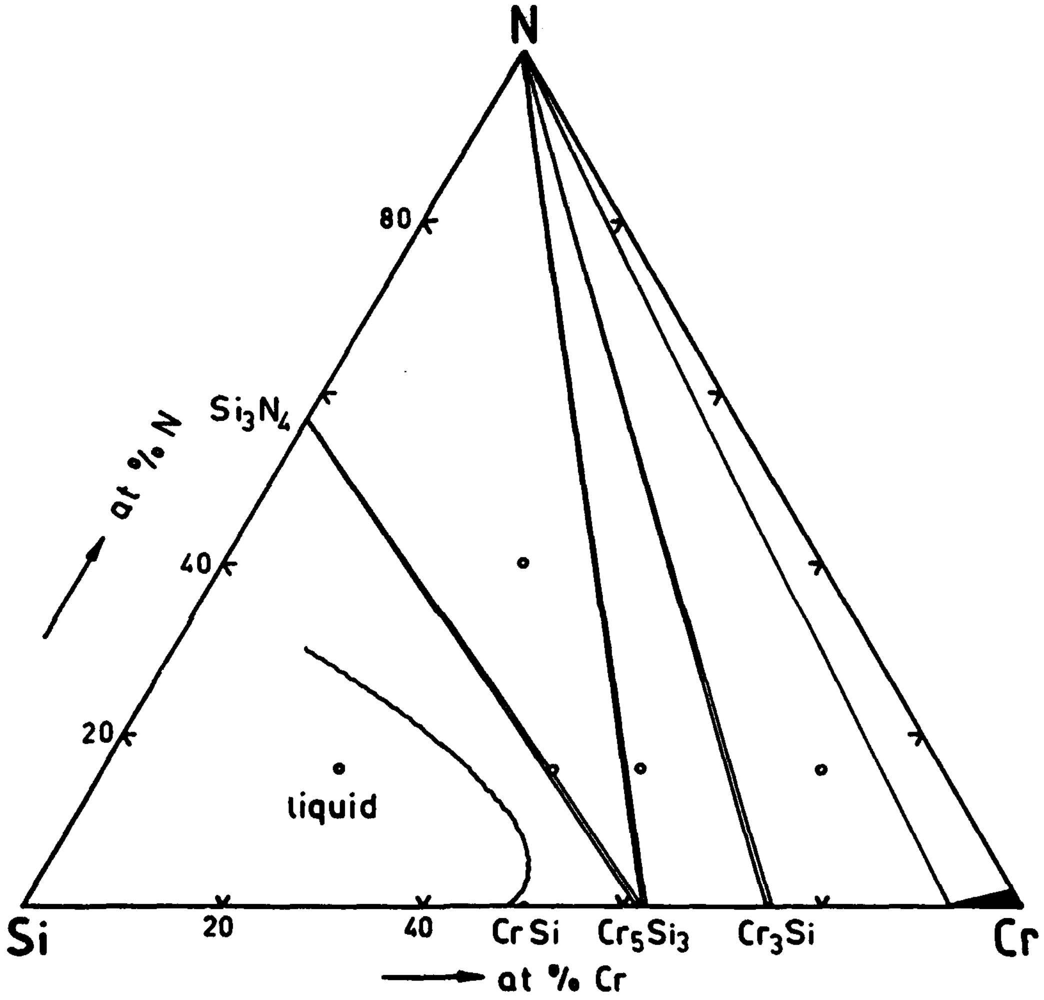
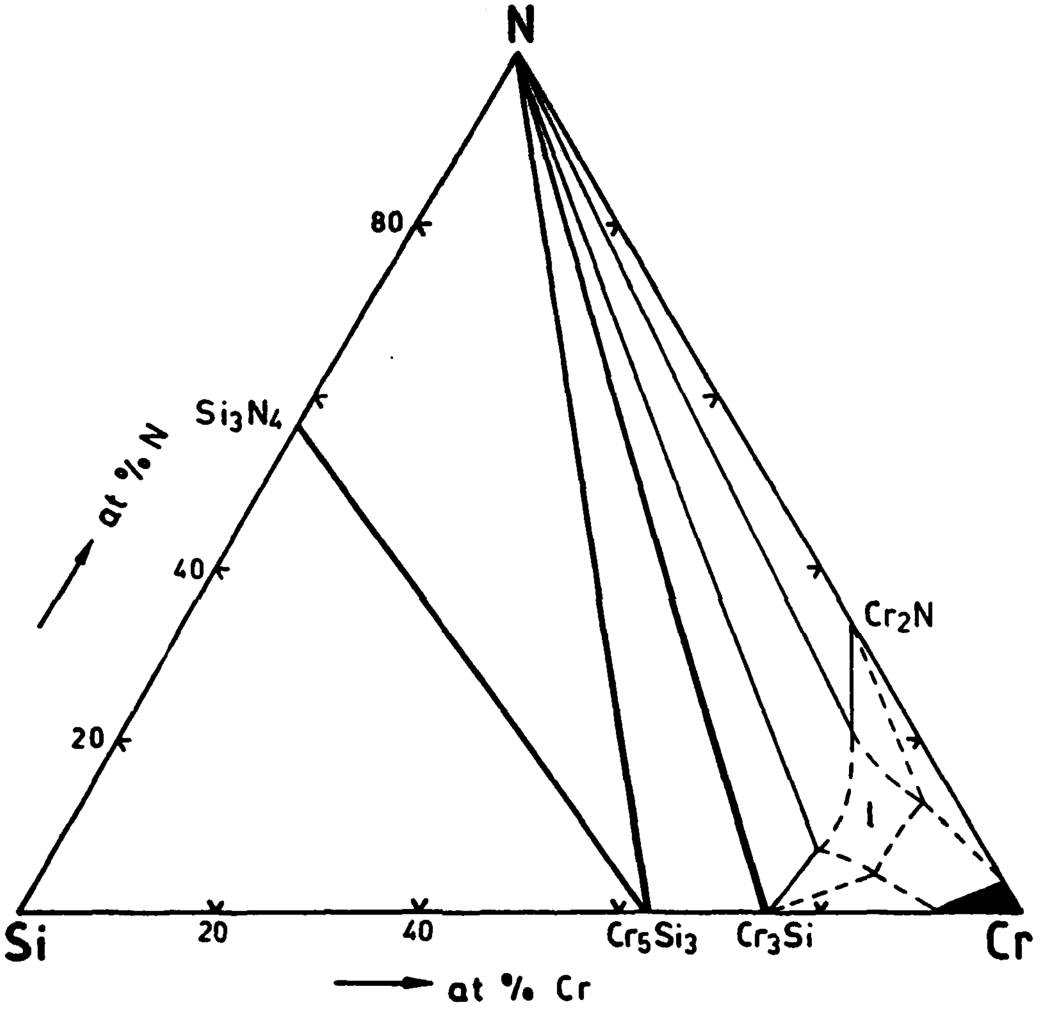


Fig.19.5: Isothermal section observed in the system Cr - Si - N at 1600°C (under $p(N_2) = 10^5$ Pa)



SYSTEM MOLYBDENUM - SILICON - NITROGEN (Mo-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Mo-Si-N between 1000°C and 1400°C were determined by x-ray analysis [88Sch].The alloys investigated were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si,from Alpha Div.,Ventron Corp.,USA),silicon (purity: 3N,from Alpha Div.,Ventron Corp.,USA) and molybdenum (purity: 3N,from Metallwerk Plansee,Austria).Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at temperatures up to 1000°C or annealed in an r.f.furnace under argon (purity:5N+) at temperatures up to 1400°C.

BINARY SYSTEMS

The phase diagram for the binary system Mo-Si given in [86Mas] (based on [72Koc], thermodynamically modelled by [89Vah]) needs to be modified with regard to the melting behavior of Mo_3Si [54Now], [80Zot],[83Chr]: Mo_3Si decomposes upon melting into Mo_5Si_3+ (liq.) rather than Mo + (liq.) (fig.20.1).Three intermediate phases occur (tab.20.1).The phase diagram for the system Mo-N given in [86Mas] is based on [70Ett] and [78Jeh] but does not include the occurrence of β-Mo_2N at $T \leq 850$°C as shown in the original diagrams (fig.20.2 due to [70Ett],[78Jeh],reviewed by [80Fer]).The intermediate phases are listed in tab.20.1.Neither is stable at 1000°C unless $p(N_2) > 10^5$Pa [78Jeh].No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.20.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Mo-Si-N (tab.20.1).At 1000°C as well as at 1400°C Si_3N_4 coexists with $MoSi_2$ and Mo_5Si_3 but not with Mo_3Si or Mo (fig.20.3).In the absence of external nitrogen pressure no molybdenum nitride is observed [88Sch].This confirms earlier reports on the decomposition of Si_3N_4 in contact with molybdenum at temperatures of 1000°C and above [56Now],[69Fit],[77Kha][79Mue][83Sug]. However at temperatures up to 1000°C this reaction is slow and incomlete even after 400h anneal [88Sch].Lattice parameters of neither molybdenum silicide coexisting with Si_3N_4 or N_2 gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in molybdenum silicides.

Using the thermodynamic data in tab.20.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C as well as at 1400°C are calculated (tab.20.3).The resulting tie lines are consistent with the experimentally observed isothermal section (fig.20.3).

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Table 20.1: Solid phases in the system Mo - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Mo	cI2 $Im\bar{3}m$ W (A2)	a= 314.70	[85Vil];powder pattern: ASTM file card # 4-809
Mo_3Si	cP8 $Pm\bar{3}n$ Cr_3Si (A15)	a= 489.0	[85Vil];powder pattern: ASTM file card # 4-814
Mo_5Si_3	tI32 I4/mcm Si_3W_5 ($D8_m$)	a= 964.25 c= 490.96	[85Vil];powder pattern: ASTM file card # 17-415
$MoSi_2$	tI6 I4/mmm $MoSi_2$ (C11)	a= 320.2 c= 785.1	[85Vil];powder pattern: ASTM file card # 6-681
β Mo_2N T<850	tI12 $I4_1/amd$ Mo_2N	a= 420 c= 801	[85Vil];powder pattern: ASTM file card # 24-768
γ Mo_2N (or Mo_3N_2) T>850	cP8 $Pm\bar{3}m$	a= 416.5	[85Vil];powder pattern: ASTM file card # 25-1366
δ MoN	hP16 $P6_3/mmc$ MoN	a= 572.5 c= 560.8	[85Vil];powder pattern: ASTM file card # 25-1367
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Tab.20.2: Thermodynamic data for the solid phases in Mo - Si - N

phase	ΔG_f^o [J/gramatom]	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 $MoSi_2$	-46515.7 - 2.832 T	[89Vah]
.1250 Mo_5Si_3	-37008 - 3.787 T	[89Vah]
.2500 Mo_3Si	-29710 + 0.510 T	[89Vah]
.3333 Mo_2N	-19107.4 + 17.96 T	[76Fro]

Tab.20.3: Calculated invariant equilibria in Mo - Si - N

a) at 1000°C (1273K):

$p(N_2)$ (Pa)	Reaction
5×10^{-3}	$Si_3N_4 = 3\ Si + 2\ N_2$
23.6	$Si_3N_4 + 3.429\ Mo_{.625}Si_{.375} = 6.429\ Mo_{.333}Si_{.667} + 2\ N_2$
6.4×10^3	$Si_3N_4 + 15\ Mo_{.75}Si_{.25} = 18\ Mo_{.625}Si_{.375} + 2\ N_2$
12×10^3	$Mo_2N = 2\ Mo + 0.5\ N_2$
39.5×10^3	$Si_3N_4 + 4.5\ Mo_2N = 12\ Mo_{.75}Si_{.25} + 4.24\ N_2$

b) at 1400°C (1673K)

$p(N_2)$ (Pa)	Reaction
95	$Si_3N_4 = 3\ Si + 2\ N_2$
64×10^3	$Si_3N_4 + 3.429\ Mo_{.625}Si_{.375} = 6.429\ Mo_{.333}Si_{.667} + 2\ N_2$
10×10^6	$Si_3N_4 + 15\ Mo_{.75}Si_{.25} = 18\ Mo_{.625}Si_{.375} + 2\ N_2$
11×10^6	$Mo_2N = 2\ Mo + 0.5\ N_2$
22×10^6	$Si_3N_4 + 4.5\ Mo_2N = 12\ Mo_{.75}Si_{.25} + 4.24\ N_2$

Fig.20.1: Phase diagram of the boundary system molybdenum - silicon

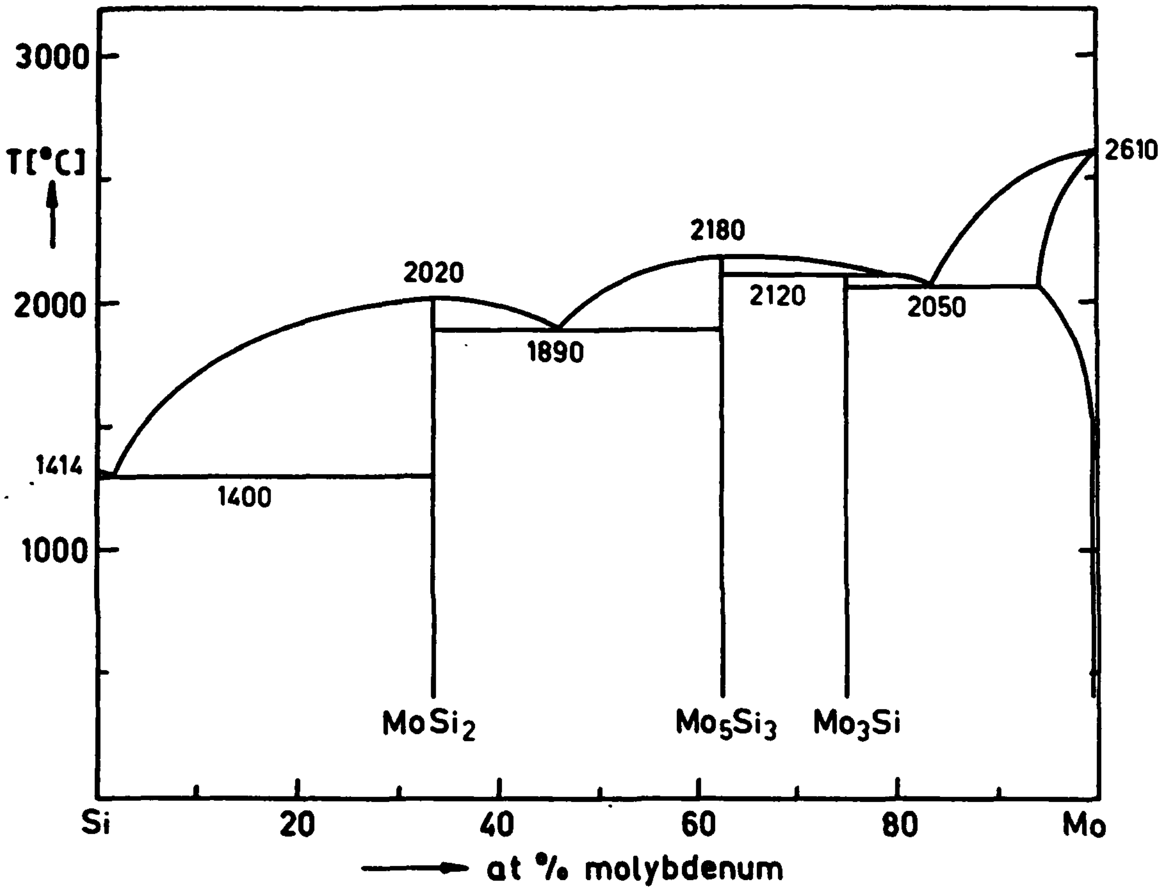


Fig.20.2: Phase diagram of the boundary system molybdenum - nitrogen

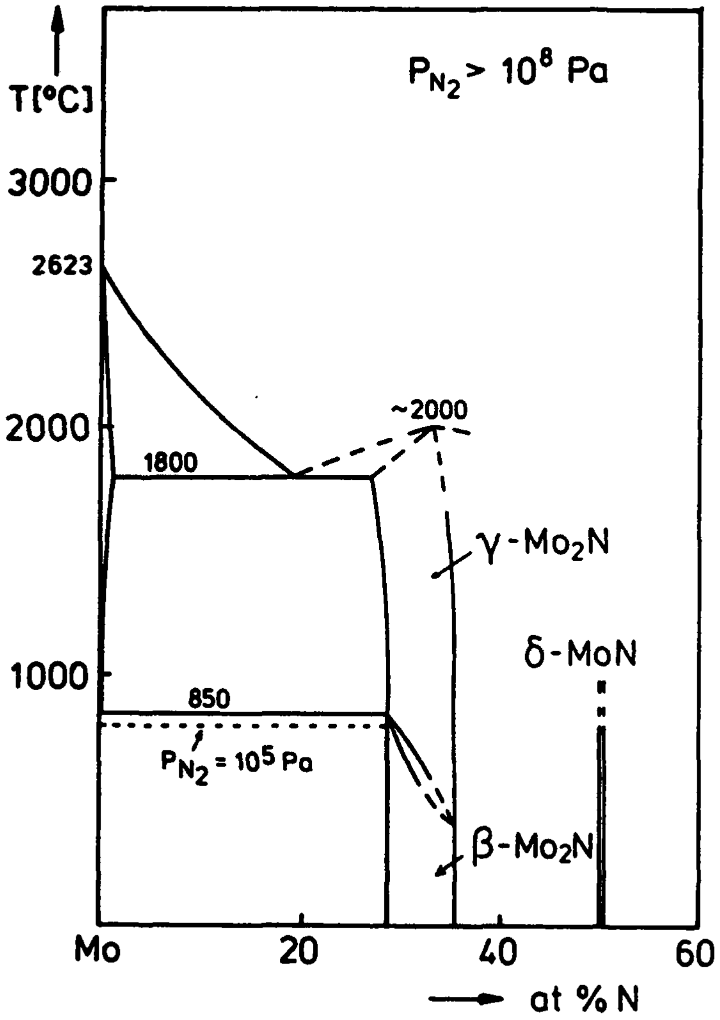
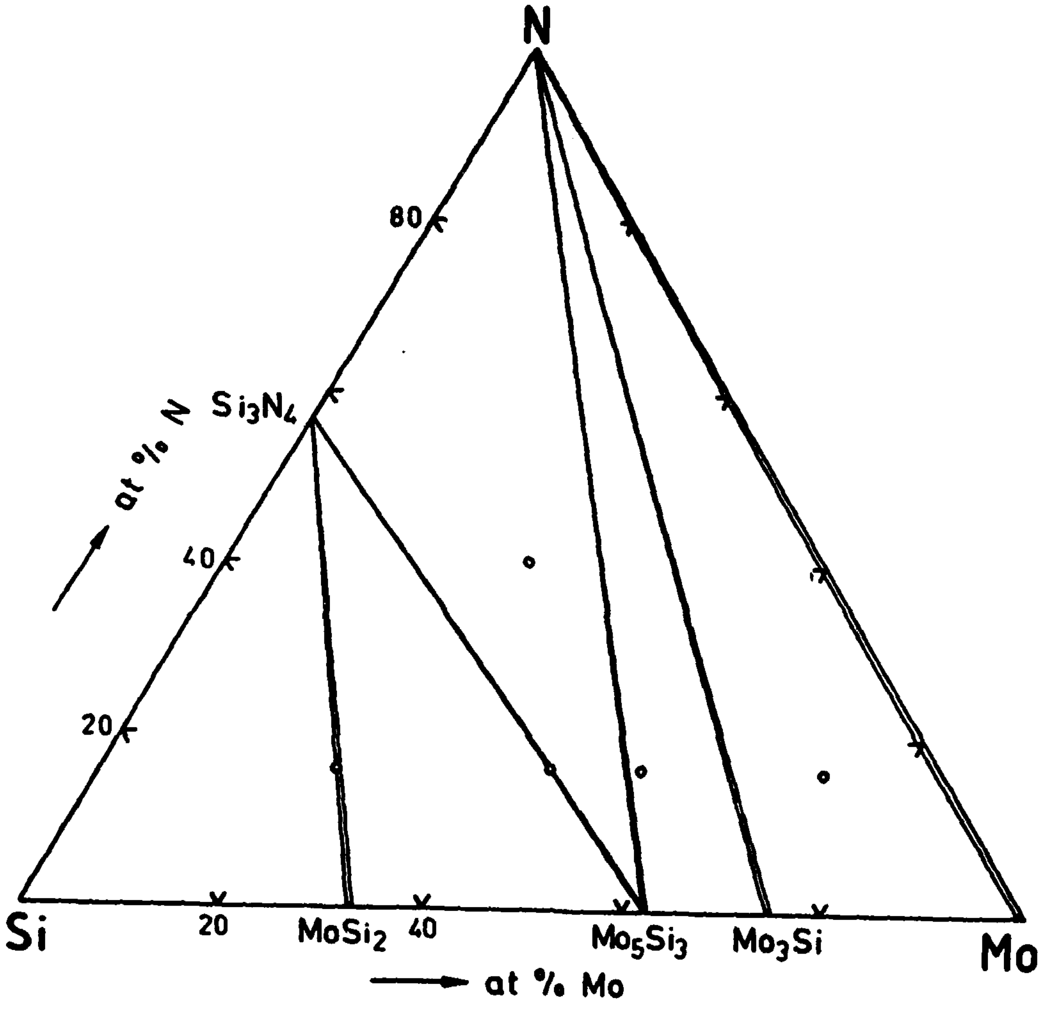


Fig.20.3: Isothermal section observed in the system Mo - Si - N at 1400°C under argon (At 1000°C identical tie lines exist)



SYSTEM TUNGSTEN - SILICON - NITROGEN (W-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of W-Si-N between 1000°C and 1400°C were determined by x-ray analysis [88Sch].The alloys investigated were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si,from Alpha Div.,Ventron Corp.,USA),silicon (purity: 3N,from Alpha Div.,Ventron Corp.,USA) and tungsten (purity: 3N,from Metallwerk Plansee,Austria).Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at temperatures up to 1000°C or annealed in an r.f.furnace under argon (purity:5N+) at temperatures up to 1400°C.

BINARY SYSTEMS

The phase diagram for the binary system W-Si is given in [86Mas] and was thermodynamically modelled by [89Vah].No phase diagram exist for the systems W-N or Si-n.Two supposedly stable [88Wri] tungsten nitrides are reported (tab.21.1).However,the cubic phase (β)-W_2N was shown to be an oxynitride [67Gue].Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.21.1). The solubility of nitrogen in silicon as well as tungsten is very low [76Fro],[81Jeh].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in W-Si-N (tab.21.1). Figs.21.1 and 21.2 show the phase equilibria in the absence of external nitrogen pressure at 1000°C and 1400°C resp. [88Sch].Si_3N_4 coexists with tungsten up to 1128°C [88Sch].Above this temperature Si_3N_4 is rapidly decomposed [69Fit],[70Sat],[77Kah],[79Mue],[88Sch] and a three phase field Si_3N_4+ W_5Si_3+ N_2(gas) exists.Lattice parameters of neither tungsten silicide coexisting with Si_3N_4 or N_2 gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in tungsten silicides.

Using the thermodynamic data in tab.21.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C as well as at 1400°C are calculated (tab.21.3).The resulting tie lines are consistent with the experimentally observed isothermal sections (figs.21.1 and 21.2).For the observed onset of the decomposition reaction of Si_3N_4 with tunsten at 1128°C the calculated nitrogen eqilibrium pressure is 376 Pa.

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Table 21.1: Solid phases in the system W - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
W	cI2 $Im\bar{3}m$ W (A2)	a= 316.52	[85Vil];powder pattern: ASTM file card # 4-806
W_5Si_3	tI32 I4/mcm W_5Si_3 ($D8_m$)	a= 964.5 c= 497.0	[85Vil];powder pattern: ASTM file card # 16-261
WSi_2	tI6 I4/mmm $MoSi_2$ (C11)	a= 321.1 c= 786.8	[85Vil];powder pattern: ASTM file card # 11-195
β-W_2N (W_3N_4)	cF8 $Fm\bar{3}m$ NaCl (B1)	a= 412.6	[85Vil];powder pattern: ASTM file card # 25-1257
δ-WN	hP2 $P\bar{6}m2$ WC (B_h)	a= 289.3 c= 282.6	[85Vil];powder pattern: ASTM file card # 35-1256
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Tab.21.2: Thermodynamic data for the solid phases in W - Si - N

phase	ΔG_f^o [J/gramatom]	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 WSi_2	-31039 + 0.697 T	[89Vah]
.1250 W_5Si_3	-19203.8 - 1.778 T	[89Vah]

Tab.21.3: Calculated invariant equilibria in W - Si - N

a) at 1000°C (1273K):

p(N_2) (Pa)	Reaction
5×10^{-3}	$Si_3N_4 = 3\ Si + 2\ N_2$
1.5	$Si_3N_4 + 3.429\ W_{.625}Si_{.375} = 6.429\ W_{.333}Si_{.667} + 2\ N_2$
17	$Si_3N_4 + 5\ W = 8\ W_{.625}Si_{.375} + 2\ N_2$

b) at 1400°C (1673K)

p(N_2) (Pa)	Reaction
95	$Si_3N_4 = 3\ Si + 2\ N_2$
6.22×10^3	$Si_3N_4 + 3.429\ W_{.625}Si_{.375} = 6.429\ W_{.333}Si_{.667} + 2\ N_2$
56.6×10^3	$Si_3N_4 + 5\ W = 8\ W_{.625}Si_{.375} + 2\ N_2$

Fig.21.1: Isothermal section observed in the system W - Si - N at 1000°C (in the absence of external nitrogen pressure)

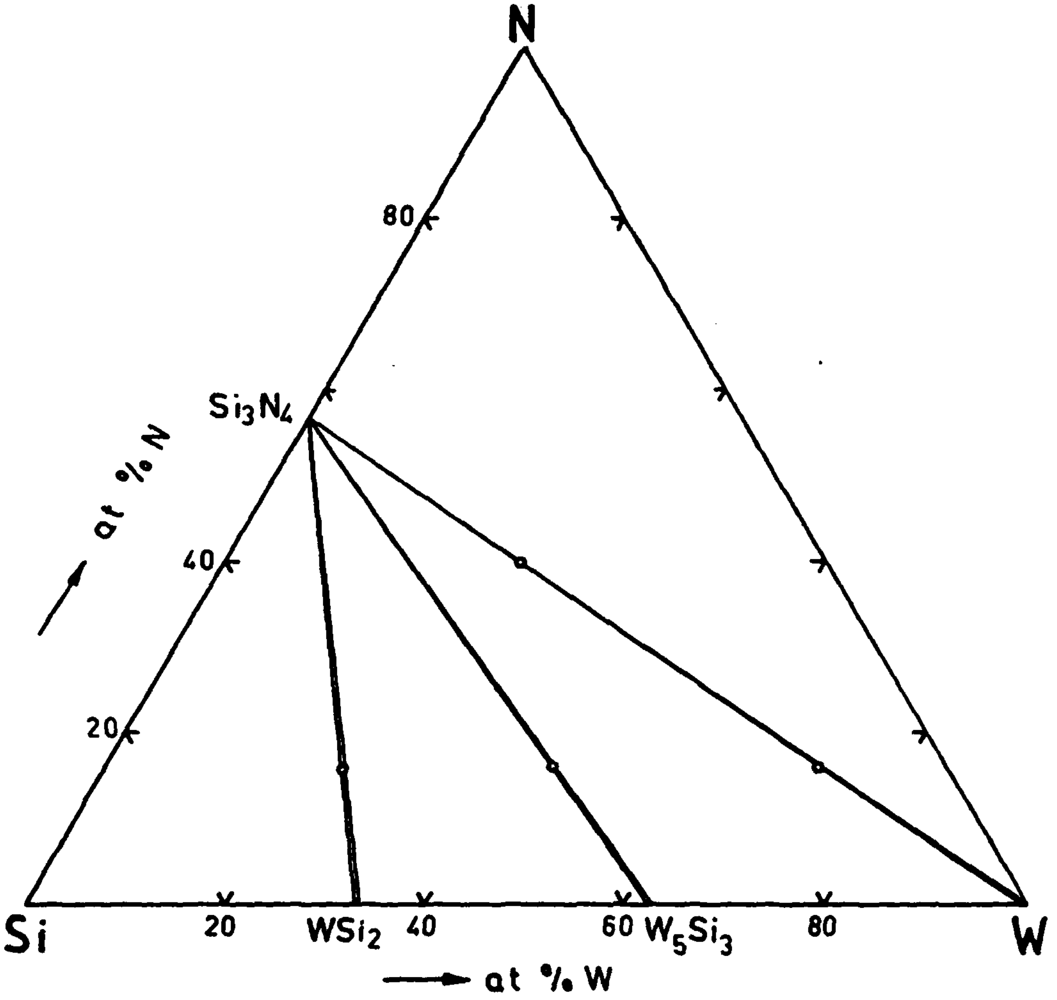
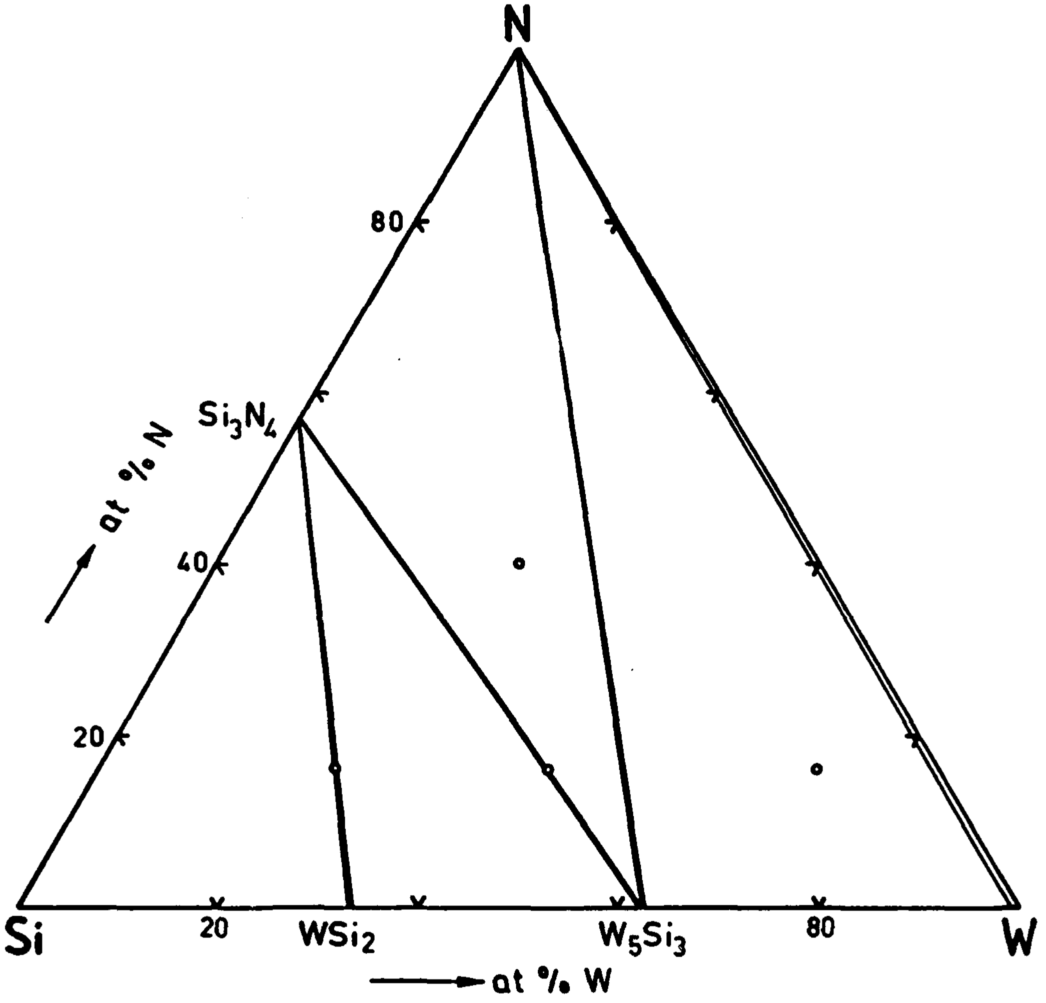


Fig.21.2: Isothermal section observed in the system W - Si - N at 1400°C (under argon)



SYSTEM MANGANESE - SILICON - NITROGEN (Mn-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of the system Mn-Si-N were investigated at 1000°C by x-ray analysis [87Wei]. Alloys were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4, 58 at% Si), silicon (purity: 3N), Mn_2N (purity: 3N) from Alpha Div., Ventron Corp., USA and manganese (purity: 2N5) from Fluka AG., Switzerland. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil and heat treated at 1000°C.

BINARY SYSTEMS

The phase diagram for the system Mn-Si is given in [86Mas] and was thermodynamically optimized by [89Cha]. The diagram for the system Mn-N given in [86Mas] was recently revised (fig.22.1 [90Gok]). Structural data for manganese silicides as well as the solid phases reported to form under nitrogen are listed in tab.22.1. No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.22.1). The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

The ternary phase $MnSiN_2$, discovered by [71Mar], (tab.22.1) forms above 700°C by reaction of manganese with silicon under nitrogen [79Pom]. This phase is stable up to 1300°C under $p(N_2) = 10^5$ Pa [79Pom]. The isothermal section at 1000°C [87Wei] (fig.22.2) shows $MnSiN_2$ to coexist with N_2(gas), Si_3N_4, Mn_3Si, β-Mn(s.s.Si) and γ-Mn(s.s.N) under their equilibrium nitrogen partial pressure. Under argon $MnSiN_2$ decomposes already above 800°C [79Pom]. Lattice parameters of $MnSiN_2$ do not vary significantly with variation of the ratio Mn/Si in the alloys. Thus at 1000°C $MnSiN_2$ is a line compound. The three phase field $MnSiN_2$ + Mn_3Si + β-Mn(s.s.Si) observed requires, that phase fields with Mn_5Si_2 participating must be cut off by a tie line between Mn_3Si and β-Mn(s.s.Si) at low nitrogen contents.Lattice parameters of neither manganese silicide coexisting with Si_3N_4 or $MnSiN_2$ are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in manganese silicides.Thus β-Mn(s.s.Si) is likely to dissolve N_2 .

Using the thermodynamic data in tab.22.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C are calculated (tab.22.3).The resulting tie lines are consistent with the experimentally observed isothermal section (fig.22.2).

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Table 22.1: Solid phases at 1000°C in the system Mn - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Mn(r) T<727	cI58 $I\bar{4}3m$ α-Mn (A12)	a= 891.39	[85Vil];powder pattern: ASTM file card # 32-637
β-Mn(h) 727<T<1100	cP20 $P4_132$ β-Mn (A13)	a= 631.5	[85Vil],powder pattern: ASTM file card # 33-887
β-Mn (s.s.15at% Si)		a= 628.3	[85Vil]
γ-Mn(h) T>1100	cF4 $Fm\bar{3}m$ Cu (A1)	a= 386.2	[85Vil];powder pattern: ASTM file card # 1-1202 tetrag.dist.upon quench: ASTM file card # 17-910
γ-Mn (s.s.10at% N)		a= 388	[75Kud]
$Mn_{44}Si_9$ (Mn_6Si,εMnSi) T<879	hR159 $R\bar{3}$	a= 1087.1 c= 1918.9	[85Vil];powder pattern: ASTM file card # 31-832 18-811,18-812
Mn_9Si_2 (ζMnSi)	oI186 Immm	a= 1699.2 b= 2863.4 c= 465.6	labeled Mn_4Si in [85Vil]; powder pattern: ASTM file card # 24-737
Mn_3Si	cF16 $Fm\bar{3}m$ BiF_3 (DO_3)	a= 572.2	[85Vil];powder pattern:
Mn_5Si_2 T<850	tP56 $P4_12_12$ Mn_5Si_2	a= 890.97 c= 871.53	[85Vil],powder pattern: ASTM file card # 29-896 30-826
Mn_5Si_3	hP16 $P6_3/mcm$ Mn_5Si_3 ($D8_8$)	a= 691.1 c= 481.3	[85Vil];powder pattern: ASTM file card # 3-1039
MnSi	cP8 $P2_13$ FeSi (B20)	a= 455.7	[85Vil]

cont.

Tab.22.1 continued:

$MnSi_{2-x}$ phases:

$Mn_{11}Si_{19}$	tP120	a= 551.8	[85Vil]
($MnSi_{1.729}$)	$P\bar{4}n2$	c= 4813.6	
$Mn_{26}Si_{45}$	t**	a= 551.5	[85Vil]
($MnSi_{1.730}$)		c= 1133.6	
$Mn_{15}Si_{26}$	tI164	a= 553.1	[85Vil];powder pattern:
($MnSi_{1.733}$)	$I\bar{4}2d$	c= 6531.1	ASTM file card # 20-724
$Mn_{27}Si_{47}$	tP296	a= 553	[85Vil];powder pattern:
($MnSi_{1.741}$)	$P\bar{4}n2$	c= 1179.4	ASTM file card # 26-1251
Mn_4Si_7	tP44	a= 552.5	[85Vil]
($MnSi_{1.75}$)	$P\bar{4}c2$	c= 1746.3	
ε-Mn_4N	cP5	a= 394.2	[75Kud]
	Fm3m		
	Fe_4N (L'1)		
ζ-Mn_2N phases :			
Mn_2N_{1-x}(h)	hP3	a= 281.60	[85Vil]
(0<x<0.33)	$P6_3/mmc$	c= 453.44	
at T ≳ 400°C	Fe_2N (L'3)		
$Mn_2N_{0.86}$(r)	hP12	a= 489.16	[85Vil];powder pattern:
($Mn_{12}N_5$)	$P6_222$	c= 455.45	ASTM file card # 31-824
at T ≲ 137°C	$Mn_{12}N_5$		
$Mn_2N_{0.98}$(r)	oP12	a= 453.7	[85Vil]
at RT	Pbcn	b= 566.8	
	PbO_2	c= 490.9	
Mn_2N	oC24	a= 485.52	[85Vil]
	$C222_1$	b= 840.88	
	Mn_2N	c= 453.27	

Tab.22.1 continued:

η-Mn_3N_2	tI10	a= 297.4	[84Jac]
	I4mmm	c= 1212.6	
	ThH_2 (L'2b)		
θ-Mn_6N_5(r)	t**	a= 421.5	[85Vil];powder pattern:
T<400		c= 414.5	ASTM file card # 1-1158
θ-Mn_6N_5(h)	c**	a= 422.5	[85Vil]
T>400			
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160
* $MnSiN_2$	oP16	a= 524.8	[85Vil];powder pattern:
	$Pna2_1$	b= 651.1	ASTM file card # 25-548
		c= 507.0	

Tab.22.2: Thermodynamic data for the solid phases in Mn - Si - N

phase	ΔG_f^o [J/gramatom]	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.0333 $Mn_{11}Si_{19}$	-9661.5 + 1.0 T	[89Cha]
.5000 MnSi	-12253.2 + 1.0 T	[89Cha]
.1250 Mn_5Si_3	-12874.5 + 1.25 T	[89Cha]
.1429 Mn_5Si_2	-11542.2 + 1.5 T	[89Cha]
.2500 Mn_3Si	-10897.0 + 1.5 T	[89Cha]
.0909 Mn_9Si_2	-8629.5 + 1.0 T	[89Cha]
.1429 Mn_6Si	-7101.0 + 0.75 T	[89Cha]
β-Mn(s.s.14at% Si)	-6000 (at 1273K)	estimated from plot ΔG_f^{1273} vs. x_{Si}
γ-Mn(s.s.10at% N)	-2000 (at 1273K) (or more negative)	estimated from 1) Mn + ε-$Mn_4N \overset{778K}{\leftrightarrow} \gamma$-$Mn_{.9}N_{.1}$ 2) $T_{decomp.}$ = 1573K for γ-$Mn_{.9}N_{.1}$ at $p(N_2) = 10^5$ Pa
.2000 ε-Mn_4N	-4534 + 3.266 T	calc. from data given in [75Gme]
.3333 ζ-Mn_2N	-83667.7 + 5.807 T	calc. from data given in [75Gme]
.2000 η-Mn_3N_2	-6680 + 5.696 T	calc. from data given in [75Gme]
* .2500 $MnSiN_2$	-42250 ± 500 (at 1273K)	estimated from the exp. obs. tie lines: 1) coex.(Si_3N_4 + Mn_3Si) but <u>not</u> ($MnSiN_2$ + Mn_5Si_3) 2) coex. ($MnSiN_2$+ Mn_3Si) but <u>not</u> (Si_3N_4+ Mn_9Si_2) or (Si_3N_4+ β-Mn(s.s.Si)) resp.

Tab.22.3: Calculated invariant equilibria in Mn - Si - N at 1000°C

$p(N_2)$ (Pa)	Reaction
5×10^{-3}	$Si_3N_4 = 3\ Si + 2\ N_2$
6×10^{-3}	$Si_3N_4 + 8.278\ Mn_{.5}Si_{.5} = 11.278\ Mn_{.367}Si_{.633} + 2\ N_2$
20×10^{-3}	$Si_3N_4 + 12\ Mn_{.625}Si_{.375} = 15\ Mn_{.5}Si_{.5} + 2\ N_2$
130×10^{-3}	$Si_3N_4 + 15\ Mn_{.75}Si_{.25} = 18\ Mn_{.625}Si_{.375} + 2\ N_2$
180×10^{-3}	$MnSiN_2 = .222\ Si_3N_4 + 1.333\ Mn_{.75}Si_{.25} + .556\ N_2$
200×10^{-3}	$MnSiN_2 + 7.333\ Mn_{.818}Si_{.182} = 9.333\ Mn_{.75}Si_{.25} + N_2$
330×10^{-3}	$MnSiN_2$ + 15.217 β-Mn (s.s.14at% Si) = 17.217 $Mn_{.818}Si_{.182} + N_2$
max. 2875	$MnSiN_2$ + 6.825 γ-Mn (s.s.10at% N) = 7.143 β-Mn (s.s.14at% Si) + 1.321 N_2

Fig.22.1: Phase diagram of the boundary system manganese - nitrogen

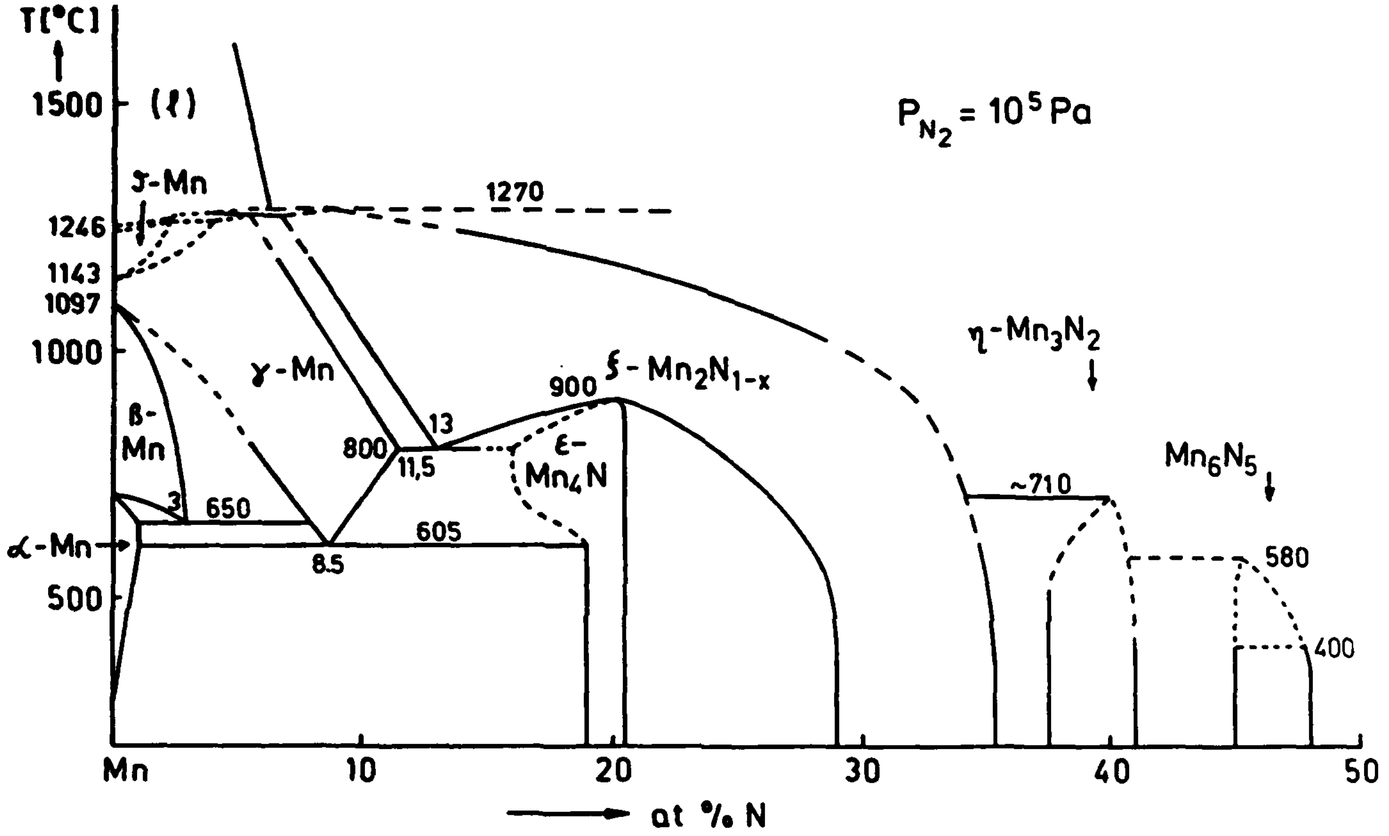
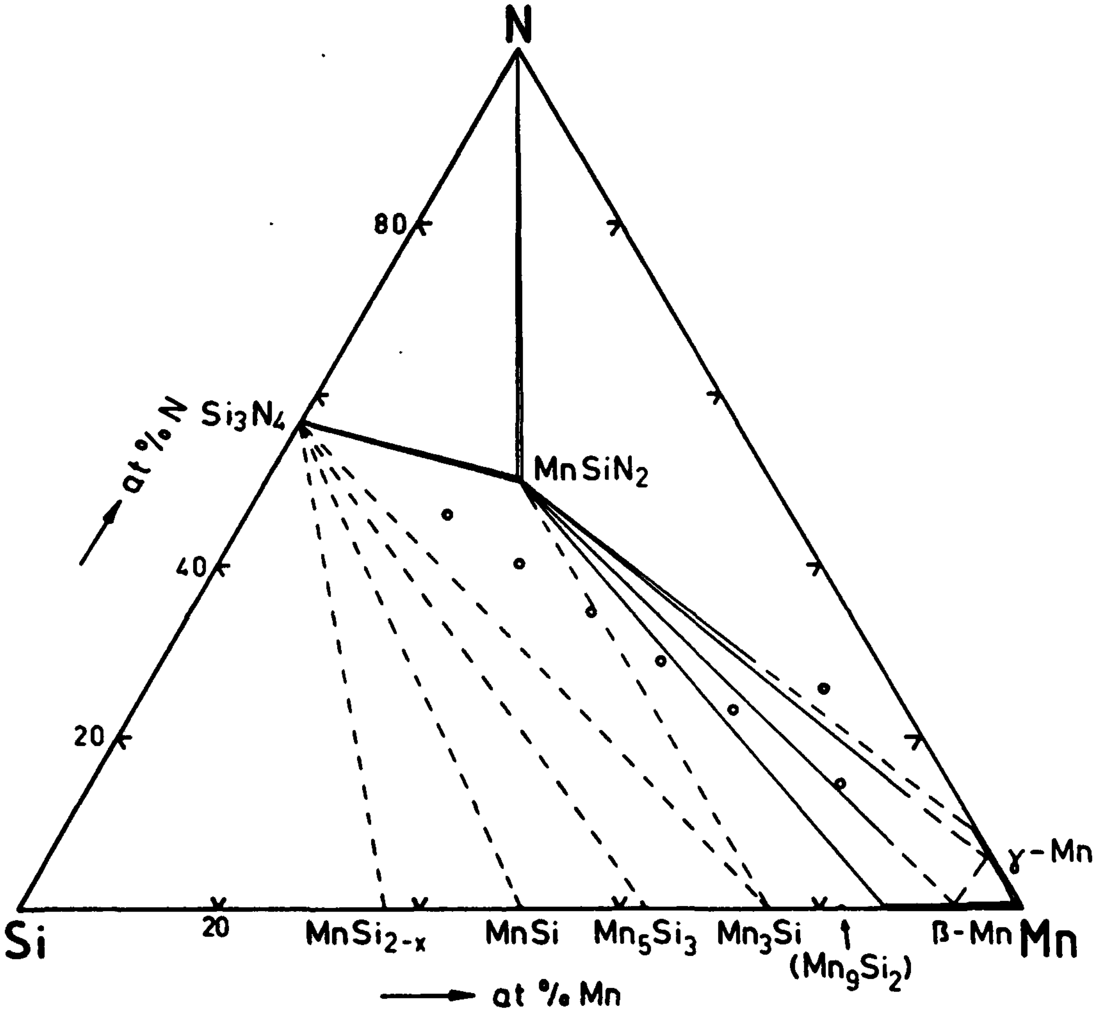


Fig.22.2: Isothermal section observed in the system Mn - Si - N at 1000°C (in the absence of external nitrogen pressure)



SYSTEM RHENIUM - SILICON - NITROGEN (Re-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Re-Si-N between 1000°C and 1400°C were determined by x-ray analysis [88Sch].The alloys investigated were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si,from Alpha Div.,Ventron Corp.,USA),silicon (purity: 3N,from Alpha Div.,Ventron Corp.,USA) and rhenium (purity: 4N,from Johnson, Mathey and Brandenberger,Switzerland).Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at temperatures up to 1000°C or annealed in an r.f.furnace under argon (purity:5N+) at temperatures up to 1400°C.

BINARY SYSTEMS

The phase diagram for the binary system Re-Si due to [82Jor] is reproduced in [76Mof].No phase diagram for the systems Re-N or Si-N is reported.It is likely,that the rhenium nitride reported to exist up to 370°C (tab.23.1) is stabilized by oxygen. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.23.1). The solubility of nitrogen in silicon as well as rhenium is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Re-Si-N (tab.23.1) Figs.23.1 and 23.2 show the phase equilibria in the absence of external nitrogen pressure at 1000°C and 1400°C resp. [88Sch].At 1000°C Si_3N_4 coexists with rhenium,but at 1400°C a three phase field Si_3N_4+ $Re_{17}Si_b$+ N_2(gas) exists.Thus the onset for the decomposition of Si_3N_4 by rhenium is between these temperatures.Lattice parameters of neither rhenium silicide coexisting with Si_3N_4 or N_2 gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in rhenium silicides.

Using the thermodynamic data in tab.23.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C as well as at 1400°C are calculated (tab.23.3).The resulting tie lines are consistent with the experimentally observed isothermal sections (figs.23.1 and 23.2).

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Table 23.1: Solid phases in the system Re - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Re	hP2 $P6_3/mmc$ Mg (A3)	a= 276.09 c= 445.76	[85Vil];powder pattern: ASTM file card # 5-702
$Re_{17}Si_9$ (Re_5Si_3)	mP24 $P2_1/b$	a= 645.11 b= 960.12 c= 539.38 β = 94.2°	[85Vil];powder pattern: ASTM file card # 32-891
ReSi T>1650	cP8 $P2_13$ FeSi (B20)	a=477.5	[85Vil];powder pattern: ASTM file card # 8-278
$ReSi_2$	oI6 Immm	a= 312.8 b= 314.4 c= 767.7	[85Vil];powder pattern: ASTM file card # 35-1384
ReN_{1-x}	cF8 $Fm\bar{3}m$ NaCl (defect)	a= 402	[83Haq];gives powder pattern
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Tab.23.2: Thermodynamic data for the solid phases in Re - Si - N

phase	ΔG_f^o [J/gramatom]	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 $ReSi_2$	-30100 + 0.0 T	[73Cha]
.5000 ReSi	-26400 + 0.0 T	[73Cha]
.1250 Re_5Si_3	-19700 - 2.1 T	[73Cha]
(~ .0385 $Re_{17}Si_9$)		

Tab.23.3: Calculated invariant equilibria in Re - Si - N

a) at 1000°C (1273K):

$p(N_2)$ (Pa)	Reaction
5×10^{-3}	$Si_3N_4 = 3\ Si + 2\ N_2$
1.3	$Si_3N_4 + 3.429\ Re_{.625}Si_{.375} = 6.429\ Re_{.333}Si_{.667} + 2\ N_2$
24	$Si_3N_4 + 5\ Re = 8\ Re_{.625}Si_{.375} + 2\ N_2$

b) at 1400°C (1673K)

$p(N_2)$ (Pa)	Reaction
95	$Si_3N_4 = 3\ Si + 2\ N_2$
5.8×10^3	$Si_3N_4 + 3.429\ Re_{.625}Si_{.375} = 6.429\ Re_{.333}Si_{.667} + 2\ N_2$
76.2×10^3	$Si_3N_4 + 5\ Re = 8\ Re_{.625}Si_{.375} + 2\ N_2$

Fig.23.1: Isothermal section observed in the system Re - Si - N at 1000°C (in the absence of external nitrogen pressure)

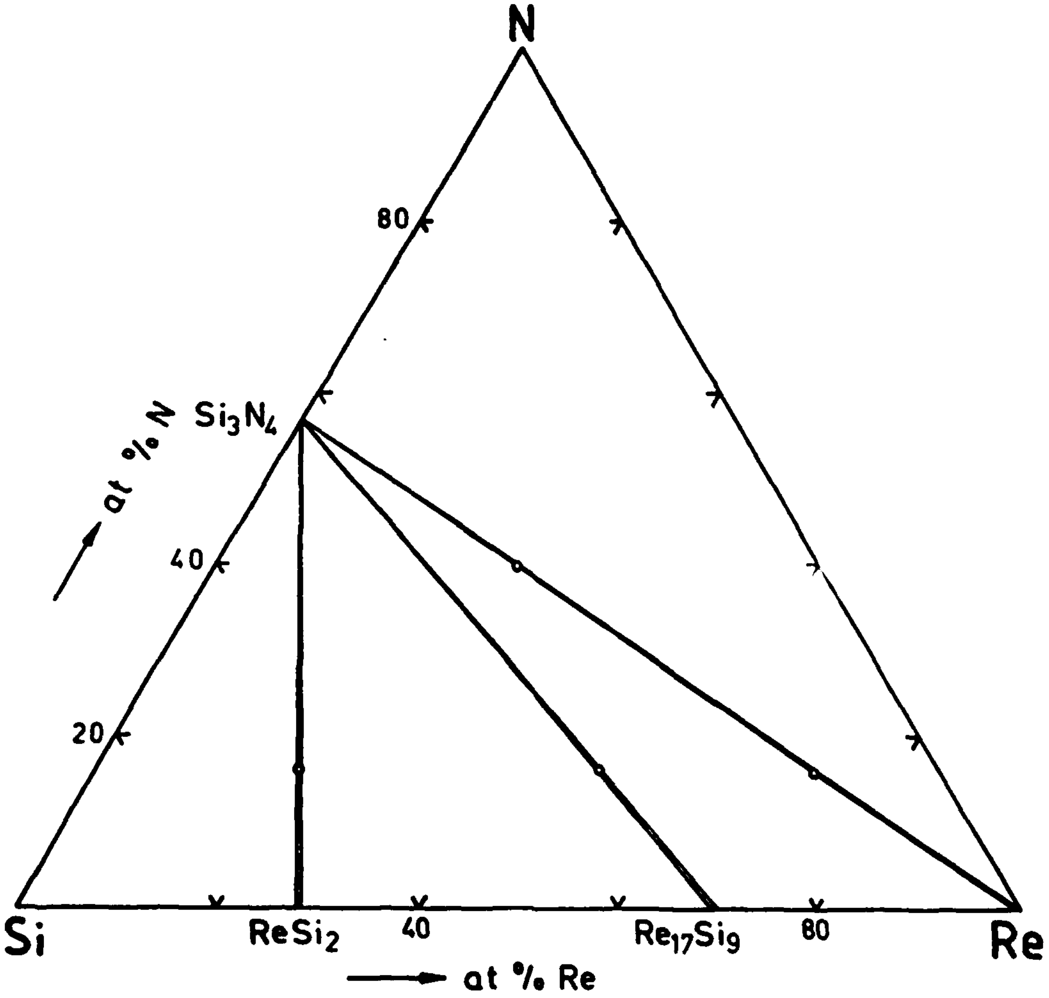
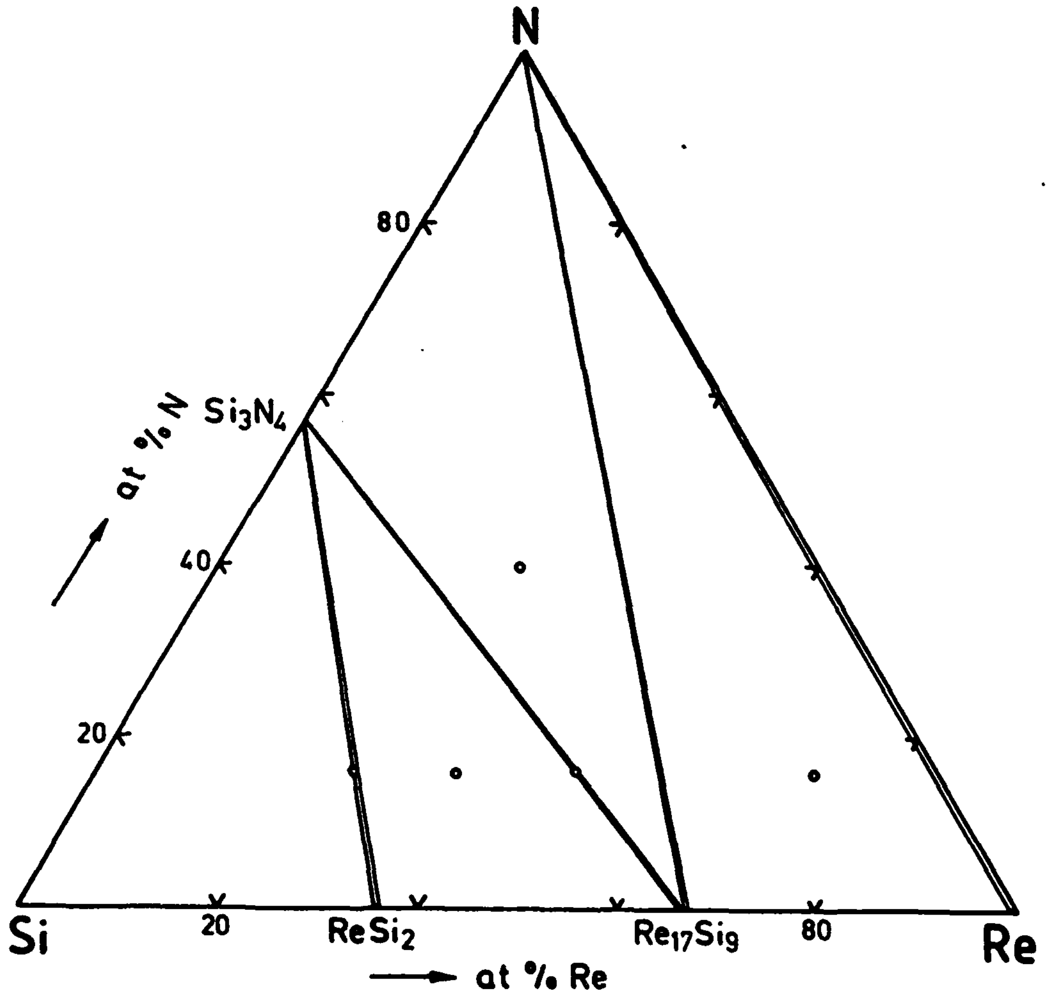


Fig.23.2: Isothermal section observed in the system Re - Si - N at 1400°C (under argon)



SYSTEM IRON - SILICON - NITROGEN (Fe-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Fe-Si-N between 900°C and 1150°C were determined by x-ray analysis [87Wei].The alloys investigated were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4, 58 at% Si,from Alpha Div.,Ventron Corp.,USA),silicon (purity: 3N, from Alpha Div.,Ventron Corp.,USA) and iron (purity: 2N5,impurities in ppm: Ni 600, C<600, O<2000; from Fluka AG,Switzerland).Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil,heat treated either at 900°C,340h or 1150°C,170h and quenched.

BINARY SYSTEMS

The phase diagram for the system Fe-Si given in [86Mas] is based on [80Sch].However,according to more recent data [89Hil] no α_2-Fe_3Si(h) exists (fig.24.1).The phase diagram for the system Fe-N is given in [86Mas].No phase diagram for the system Si-N is reported.Si_3N_4 occors in two modifications: α-Si_3N_4 and β-Si_3N_4. Crystal structure data for the solid phases are listed in tab.24.1.The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Fe-Si-N (tab.24.1).Two isothermal sections are reported [87Wei]: In the absence of external nitrogen partial pressure Si_3N_4 is found to coexist at 900°C with all binary silicides stable at this temperature and with α-Fe (fig.24.2).At 1150°C Si_3N_4 coexists with all stable binary silicides but is decomposed by iron forming α-Fe containing $\geq 7 \pm 1$ at% Si in solid solution (fig.24.3).Under pure argon the onset of this decomposition reaction is observed at 1120 ± 10°C [87Wei].This agrees with earlier,just qualitative observations [57Gle][66Mue][66Yas][67Cal][69Fel][76Mat] and is consistent with [75Sie].Lattice parameters of neither iron silicide coexisting with Si_3N_4 or N_2 gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in iron silicides.The solid solution of 6 at% Si in α-Fe, heat treated in a nitrogen atmosphere (95% N_2,5% H_2,P_{total}:10^5 Pa), dissolves 2 × 10^{-7} at% nitrogen at 900°C and 1.3 × 10^{-6} at% nitrogen at 1150°C resp.[63Pea].

MISCELLANEOUS

Joining of Si_3N_4 to steel by hot pressing resulted in excellent bonding due to the formation of iron silicides in the interface. However,due to thermal expansion mismatch low tensile strength (failure in the Si_3N_4) resulted [88Sug].Thus additional interlayers of other metals are preferred.

Iron is often used as addition in silicon to aid nitridation by promoting the formation of liquid phase at temperatures far below the melting point of pure Si [81Muk][81Shi].The reaction products found are Si_3N_4 and iron silicides [75Lei][85Bou],which however are recognized to be the primary cause of strength degradation in hot pressed silicon nitride [85Her].

Wetting angles under vacuum between Si_3N_4 and Fe_2Si_5 as well as FeSi are reported to be θ = 66° (at 1450°C) and θ = 76° (at 1500°C) respectively [73Cha].

Tennenhouse et al. [85Ten] investigated the interaction of Si_3N_4 cutting tools with iron and iron based alloys in air.They conclude that the low melting phase formed during machining is an oxide phase and does not occur in the ternary Fe-Si-N.

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Table 24.1: Solid phases in the system Fe - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Fe(r) T<911	cI2 $Im\bar{3}m$ W (A2)	a= 286.65	[85Vil];powder pattern: ASTM file card # 6-696
γ-Fe(h) 911<T<1392	cF4 $Fm\bar{3}m$ Cu (A1)	a= 366.60	[85Vil];powder pattern: ASTM file card # 31-619
Fe_3Si	cF16 $Fm\bar{3}m$ BiF_3 (DO_3)	a= 560.8	[85Vil];powder pattern: ASTM file card # 11-616
Fe_2Si T>1044	hP6 $P\bar{3}m1$	a= 405.2 c= 508.55	[85Vil];
Fe_5Si_3 825<T<1056	hP16 $P6_3/mcm$ Mn_5Si_3 ($D8_8$)	a= 675.52 c= 471.74	[85Vil];powder pattern: ASTM file card # 38-438
FeSi	cP8 $P2_13$ FeSi (B20)	a= 448.91	[85Vil];powder pattern: ASTM file card # 38-1397
$FeSi_2$(r) T<986	oC48 Cmca	a= 986.3 b= 779.1 c= 783.3	[85Vil];powder pattern: ASTM file card # 20-532
$FeSi_2$(h) (Fe_2Si_5) T>955	tP3 P4/mmm	a= 269.5 c= 509.0	[85Vil];powder pattern: ASTM file card # 22-1113 35-822
Fe_4N T<680	cP5 $Pm\bar{3}m$ Fe_4N (L'1)	a= 379.70	[85Vil];powder pattern: ASTM file card # 6-627
ζ-Fe_2N T<500	hP3 $P6_3/mmc$ Fe_2N (L'3)	a= 270.5 c= 437.6	[85Vil]powder pattern: ASTM file card # 1-1236 3-925

Tab.24.1 cont.

Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.24.1: Phase diagram of the boundary system iron - silicon

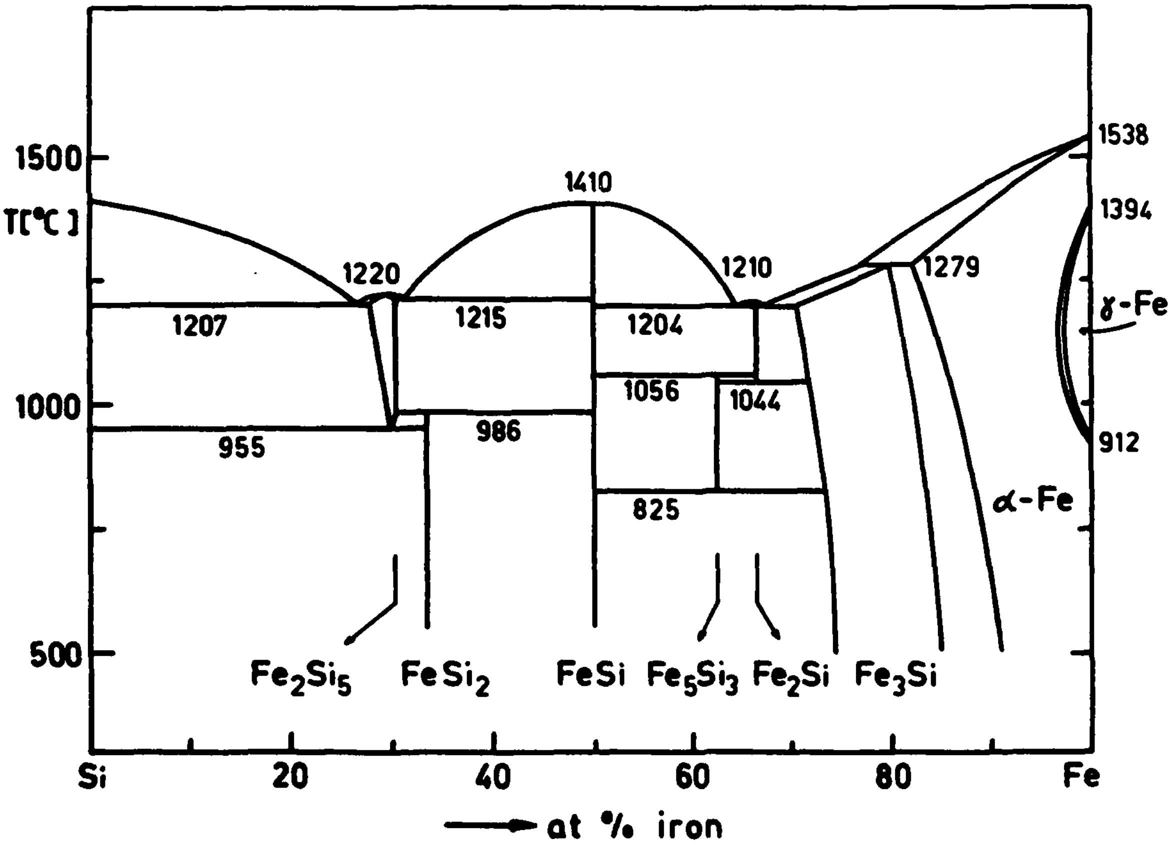


Fig.24.2: Isothermal section observed in the system Fe - Si - N at 900°C (in the absence of external nitrogen pressure)

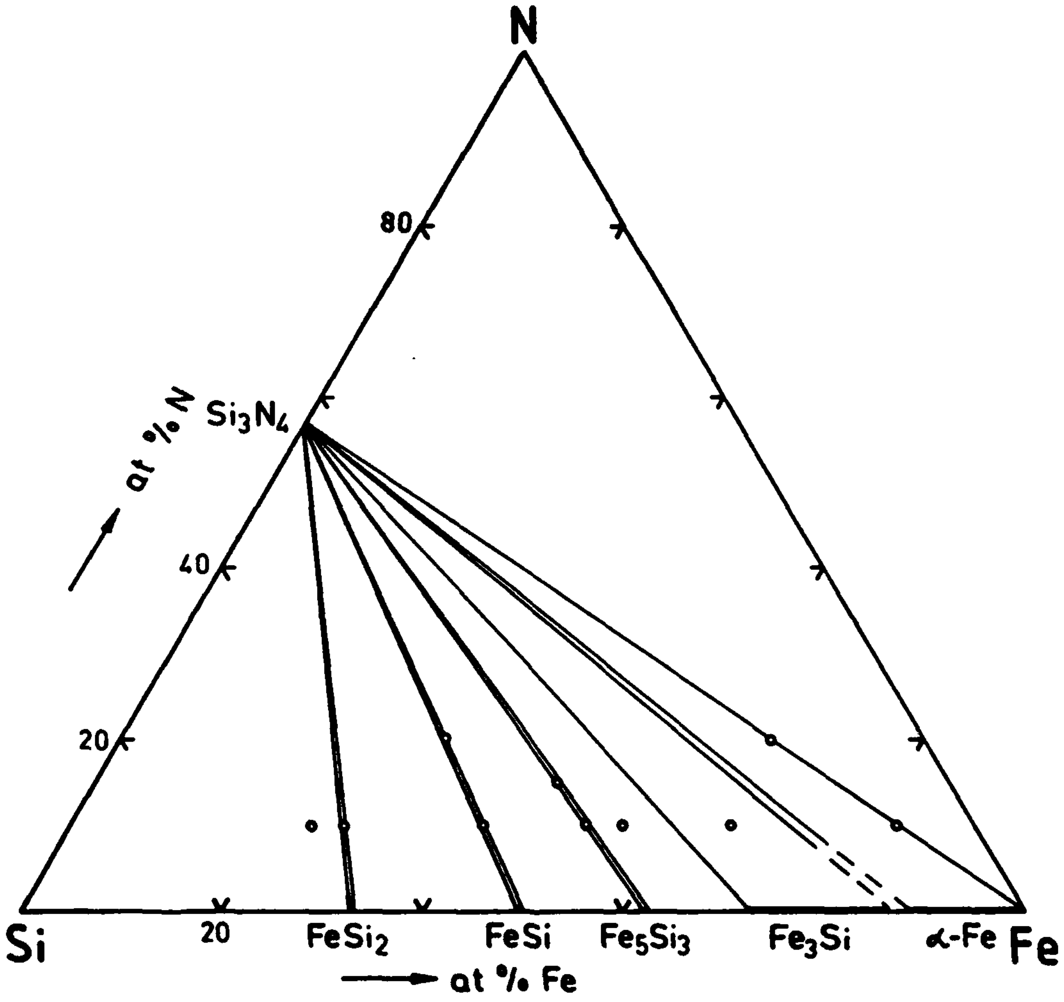
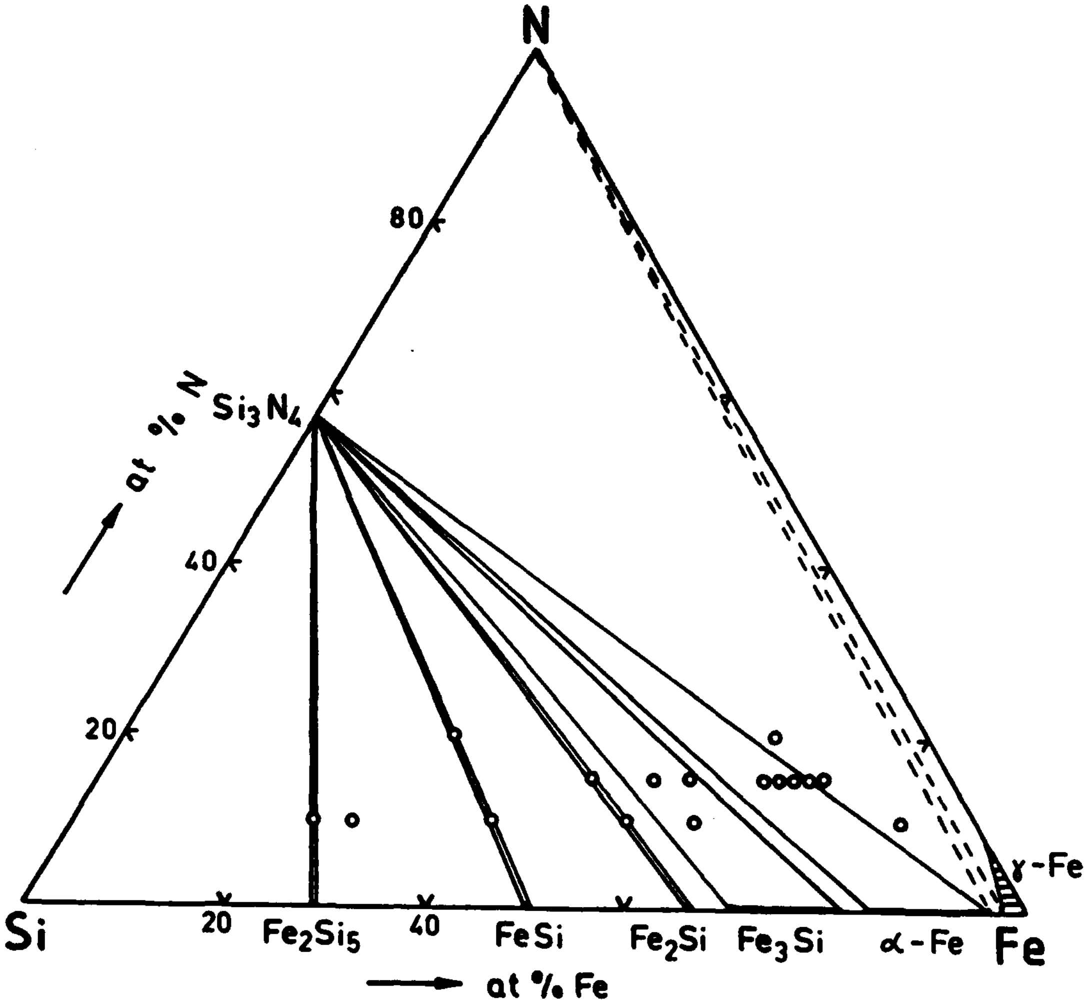


Fig.24.3: Isothermal section observed in the system Fe - Si - N at 1150°C (in the absence of external nitrogen pressure)



SYSTEM RUTHENIUM - SILICON - NITROGEN (Ru-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Ru-Si-N at 1000°C and 1250°C were determined by x-ray analysis [88Wei].The alloys investigated were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si, from Alpha Div.,Ventron Corp.,USA),silicon (purity: 3N,from Alpha Div.,Ventron Corp.,USA) and ruthenium (purity: 3N;from Engelhard Ind. Div.,USA).Mixtures of these powders and/or of powdered master alloys made thereof by arc melting were cold pressed and annealed in evacuated quartz tubes lined with Mo foil at 1000°C (170h) and 1100°C (up to 500h) folled by water quench.Heat treatments at higher tempe- retures (up to 1330°C,72h) were conducted in alumina crucibles placed in an rf-furnace under 10^5Pa high purity (5N) argon.Gas quenching after rf-treatment can be considered moderate only.

BINARY SYSTEMS

The phase diagram for the binary system Ru-Si (fig.25.1) was redetermined by [88Wei].No phase diagrams for the systems Ru-Si or Si-N resp. are reported.Si_3N_4 occurs in two modifications: α-Si_3N_4 and β-Si_3N_4.Crystal structure data for the solid phases are listed in tab.25.1. The solubility of nitrogen in silicon as well as in ruthenium is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Ru-Si-N (tab.25.1).Two isothermal sections are reported [88Wei]: In the absence of external nitrogen partial pressure Si_3N_4 is found to coexist at 1000°C with all binary silicides stable at this temperature and with Ru (fig.25.2).At 1250°C Si_3N_4 coexists with Ru_2Si_3 and RuSi but is decomposed by by alloys more rich in ruthenium (fig.25.3).Under pure argon the onset of this decomposition reaction is observed at 1210 ± 10°C [88Wei].Lattice parameters of neither ruthenium silicide coexisting with Si_3N_4 or N_2 gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in ruthenium silicides.

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Fig.25.1: Phase diagram of the boundary system Ru - Si

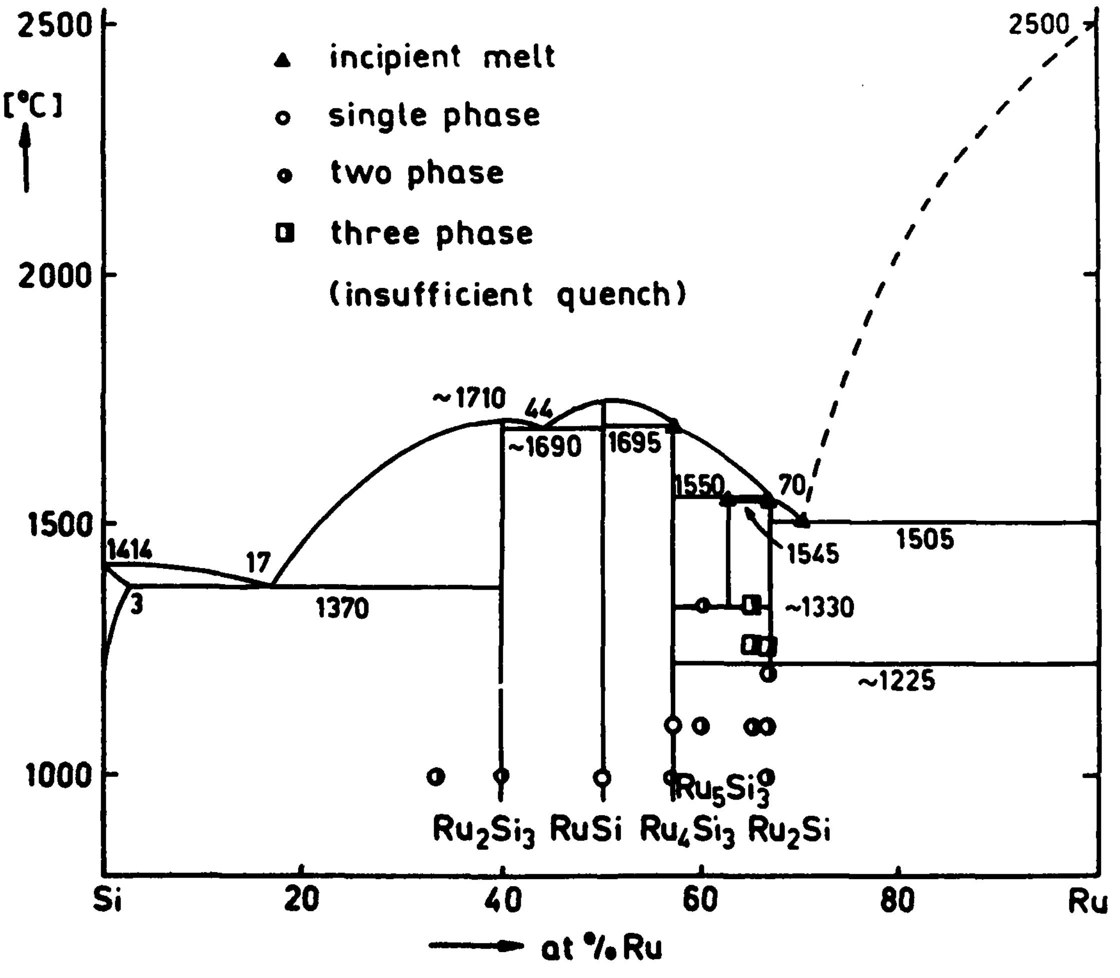


Table 25.1: Solid phases in the system Ru - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ru	hP2	a= 270.0	[85Vil];powder pattern:
	$P6_3/mmc$	c= 427.5	ASTM file card # 6-663
	W (A2)		
Ru_2Si	oP12	a= 527.9	[85Vil];powder pattern:
1255<T<1505	Pnma	b= 400.5	ASTM file card # 14-334
	Co_2Si (C23)	c= 741.8	
Ru_5Si_3	oP16	a= 524.6	[85Vil];
1330<T<1550	Pbam	b= 981.5	
	Rh_5Ge_3	c= 402.3	
Ru_4Si_3	oP28	a= 519.36	[85Vil];
	Pnma	b= 402.16	
	Rh_4Si_3	c= 1734.3	
RuSi	cP2	a= 290.9	[85Vil];powder pattern:
(Ru rich)	$Pm\bar{3}m$		ASTM file card # 10-213
	CsCl (B1)		
RuSi	cP8	a= 470.3	[85Vil];powder pattern:
(Ru poor)	$P2_13$		ASTM file card # 18-1140
	FeSi (B20)		
Ru_2Si_3	tP80	a= 1107.5	[85Vil];powder pattern:
	$P\bar{4}c2$	c= 895.4	ASTM file card # 32-978
	Ru_2Sn_3		
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160

Fig.25.2: Isothermal section observed in the system Ru - Si - N at 1000°C (in the absence of external nitrogen pressure)

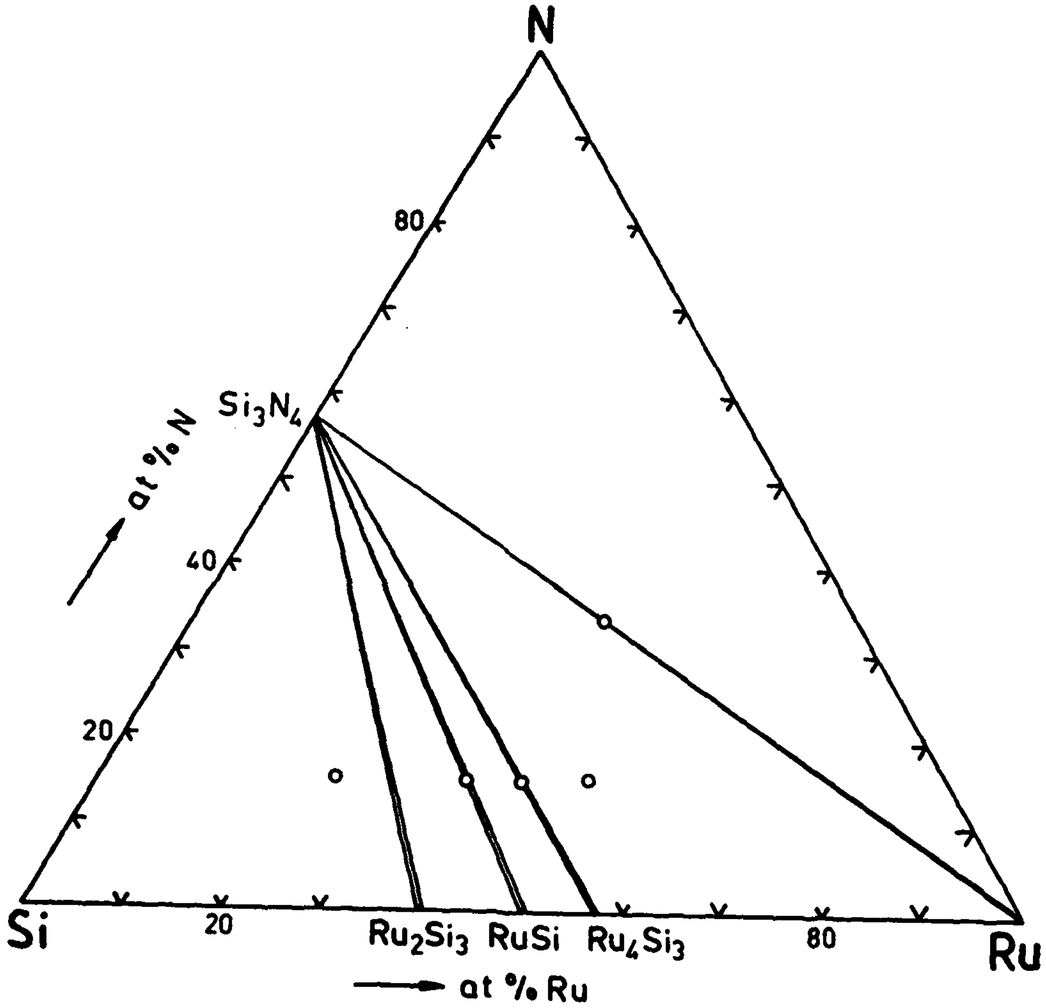
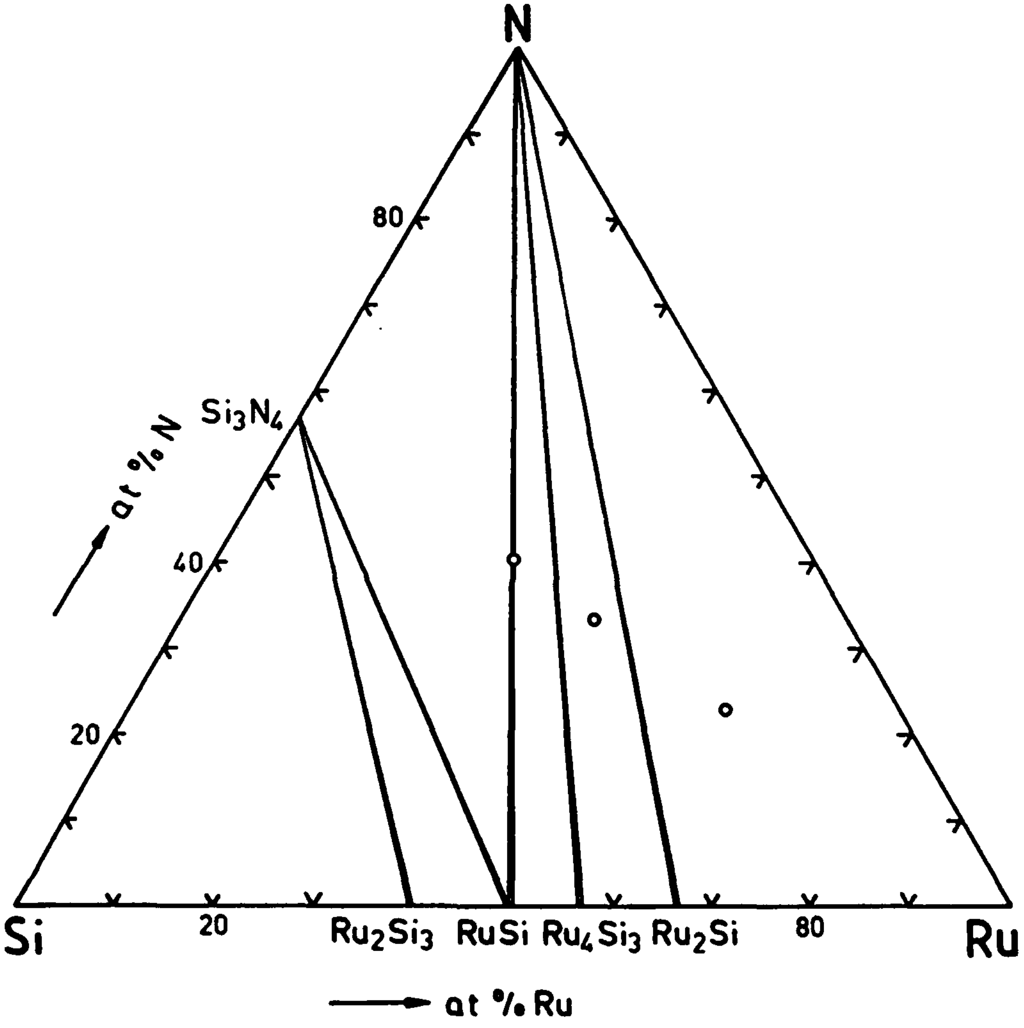


Fig.25.3: Isothermal section observed in the system Ru - Si - N at 1250°C (under argon)



SYSTEM COBALT - SILICON - NITROGEN (Co-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Co-Si-N between 1000°C were determined by x-ray analysis [87Wei].The alloys investigated were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si,from Alpha Div.,Ventron Corp.,USA),silicon (purity: 3N,from Alpha Div.,Ventron Corp.,USA) and cobalt (purity: 2N8,impurities in ppm: Fe<500,Ni<500,Mn<50,Cu<50; from Fluka AG,Switzerland).Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil,heat treated at 1000°C,170h and quenched.

BINARY SYSTEMS

The phase diagram for the binary system Co-Si in [86Mas] is a reproduction of [58Han],the Co rich section of which needs to be modified (fig.26.1) according to [72Boo] and [73Koe].No phase diagrams are reported for the systems Co-N or Si-N.None of the cobalt nitrides reported (tab.26.1) is stable at 1000°C,$p(N_2) \leq 10^5$ Pa [87Wei]. Si_3N_4 occurs in two modifications: α-Si_3N_4 and β-Si_3N_4.
Crystal structure data for the solid phases are listed in tab.26.1. The solubility of nitrogen in silicon as well as in cobalt is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Co-Si-N (tab.26.1).In the absence of external nitrogen partial pressure Si_3N_4 is found to coexist at 1000°C with all binary silicides stable at this temperature and with α-Co (fig.26.2).Under pure argon the onset of the decomposition of Si_3N_4 in contact with Co is observed at 1170°C [87Wei].This agrees with earlier,just qualitative observations [66Mue][66Yas].Lattice parameters of neither cobalt silicide coexisting with Si_3N_4 or N_2 gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in cobalt silicides.

Using the thermodynamic data in tab.26.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C are calculated (tab.26.3).The resulting tie lines are consistent with the observed isothermal sections (figs.26.2).

MISCELLANEOUS

Wetting angles of the silicides CoSi and "Co_2Si" on Si_3N_4 are reported to be $\theta = 62°$ and $\theta = 40°$ resp. under vacuum [73-1Cha].

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Table 26.1: Solid phases in the system Co - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Co(h) T>410	cF4 $Fm\bar{3}m$ Cu (A1)	a= 354.46	[85Vil];powder pattern: ASTM file card # 15-806
ε-Co(r) T<410	hP2 $P6_3/mmc$ Mg (A3)	a= 250.71 c= 406.95	[85Vil];powder pattern: ASTM file card # 5-727
Co_3Si(h) 1193<T<1214	t**	a= 842 c= 581	[85Vil];
Co_2Si(r) T<1238	oP12 Pnma Co_2Si (C23)	a= 491.8 b= 373.8 c= 710.9	[85Vil];powder pattern: ASTM file card # 4-847
Co_2Si(h) T>1238			
CoSi	cP8 $P2_13$ FeSi (B20)	a= 444.26	[85Vil];powder pattern: ASTM file card # 8-362
$CoSi_2$	cF12 $Fm\bar{3}m$ CaF_2 (C1)	a= 536.5	[85Vil];powder pattern: ASTM file card # 8-344 38-1449
Co_4N	c**	a= 373.8	[85Vil]
Co_3N	hP*	a= 274.6 c= 432.2	[85Vil];powder pattern: ASTM file card # 6-691
Co_2N	oP6 Pmnm Fe_2C	a= 460.56 b= 434.43 c= 285.35	[85Vil];powder pattern: ASTM file card # 6-647

Tab.26.1 continued

Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Tab.26.2: Thermochemical data for the solid phases in Co - Si - N

phase	ΔG_f^o [J/gramatom]	Comment
.1429 Si_3N_4	-124602 + 57.95 T	[76Fro]
.3333 $CoSi_2$	-32900 + 1.2 T	[73-2Cha]
.5000 CoSi	-47500 - 3.1 T	[73-2Cha]
.3333 $Co_2Si(r)$	-37700 - 0.0 T	[73-2Cha]
.2500 Co_3Si	ΔH_f^{298} = -28450	[84Pas]

Tab.26.3: Calculated invariant equilibria in Co - Si - N at 1000°C

$p(N_2)$ (Pa)	Reaction
5×10^{-3}	$Si_3N_4 = 3\ Si + 2\ N_2$
14×10^{-3}	$Si_3N_4 + 6\ Co_{.5}Si_{.5} = 9\ Co_{.333}Si_{.667} + 2\ N_2$
29.3	$Si_3N_4 + 9\ Co_{.667}Si_{.333} = 12\ Co_{.5}Si_{.5} + 2\ N_2$
....	Si_3N_4 + 12.275 ε-Co(s.s.17at% Si) = 15.275 $Co_{.667}Si_{.333} + 2\ N_2$
....	Si_3N_4 + 264 α-Co(s.s.11at% Si) = 267 ε-Co(s.s.12at% Si) + $2\ N_2$

Fig.26.1: Phase diagram of the boundary system Co - Si

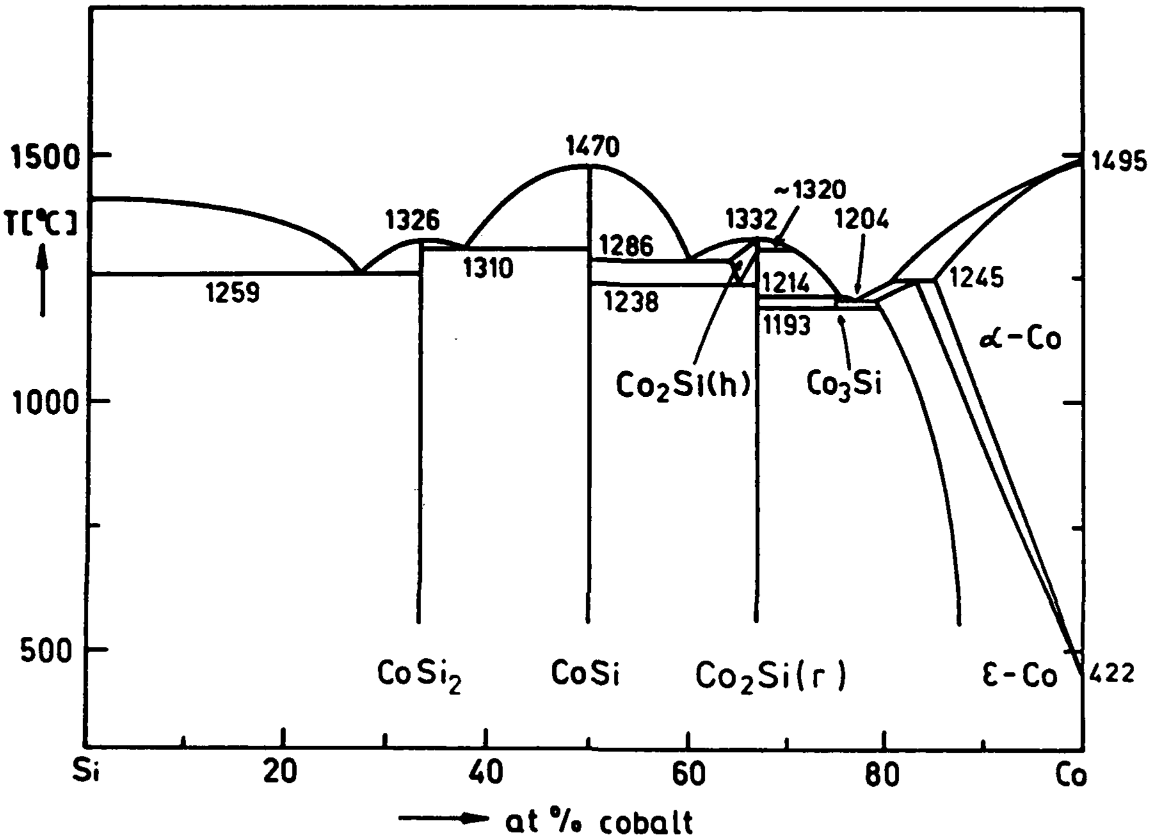
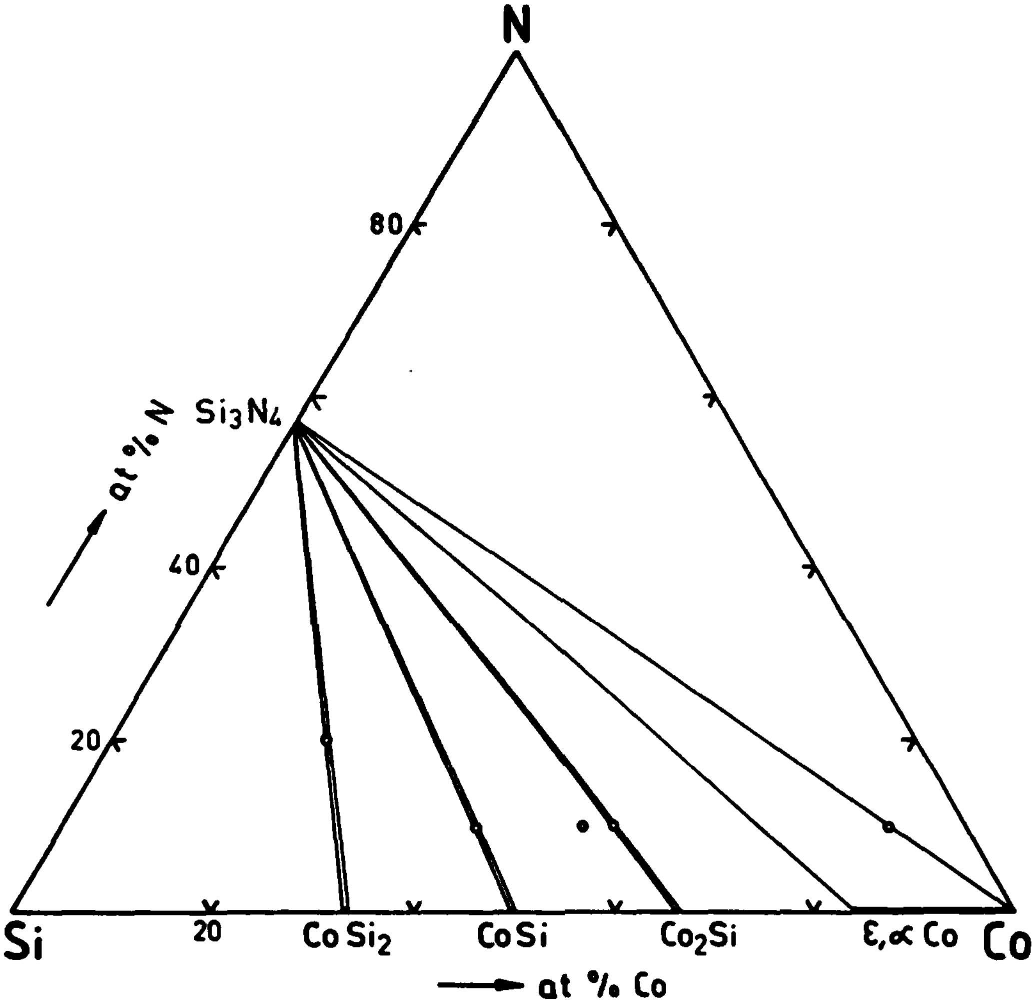


Fig.26.2: Isothermal section observed in the system Co - Si - N at 1000°C (in the absence of external nitrogen pressure)



SYSTEM RHODIUM - SILICON - NITROGEN (Rh-Si-N)

INTRODUCTION/EXPERIMENTAL

An isothermal section is derived for 1250°C.Two ternary alloys were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4, 58 at% Si),silicon (purity:3N),both from Alpha Div.,Ventron Corp.,USA and rhodium (purity:3N; from Degussa,FRG).Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were heat treated at 1250°C,72h in alumina crucibles placed in an rf-furnace under 10^5Pa high purity (5N) argon.Gas quenching after rf-treatment can be considered moderate only.

BINARY SYSTEMS

The phase diagram for the system Rh-Si due to [85Sch] is reproduced in [76Mof].Structural data for the intermediate phases are listed in tab.27.1.No phase diagrams are reported for the systems Rh-N os Si-N. Si_3N_4 occurs in two modifications: α-Si_3N_4 and β-Si_3N_4.Crystal structure data for the solid phases are listed in tab.27.1. The solubility of nitrogen in silicon as well as rhodium is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Rh-Si-N (tab.27.1).At 1250°C three rhodium silicides are stable (fig.27.1).Under argon Si_3N_4 is found to coexist at this temperature with RhSi but not with Rh_5Si_3,Rh_2Si or rhodium (fig.27.2).In accordance with the rather moderate quenching rate RhSi(x) rather than RhSi(h) is observed.

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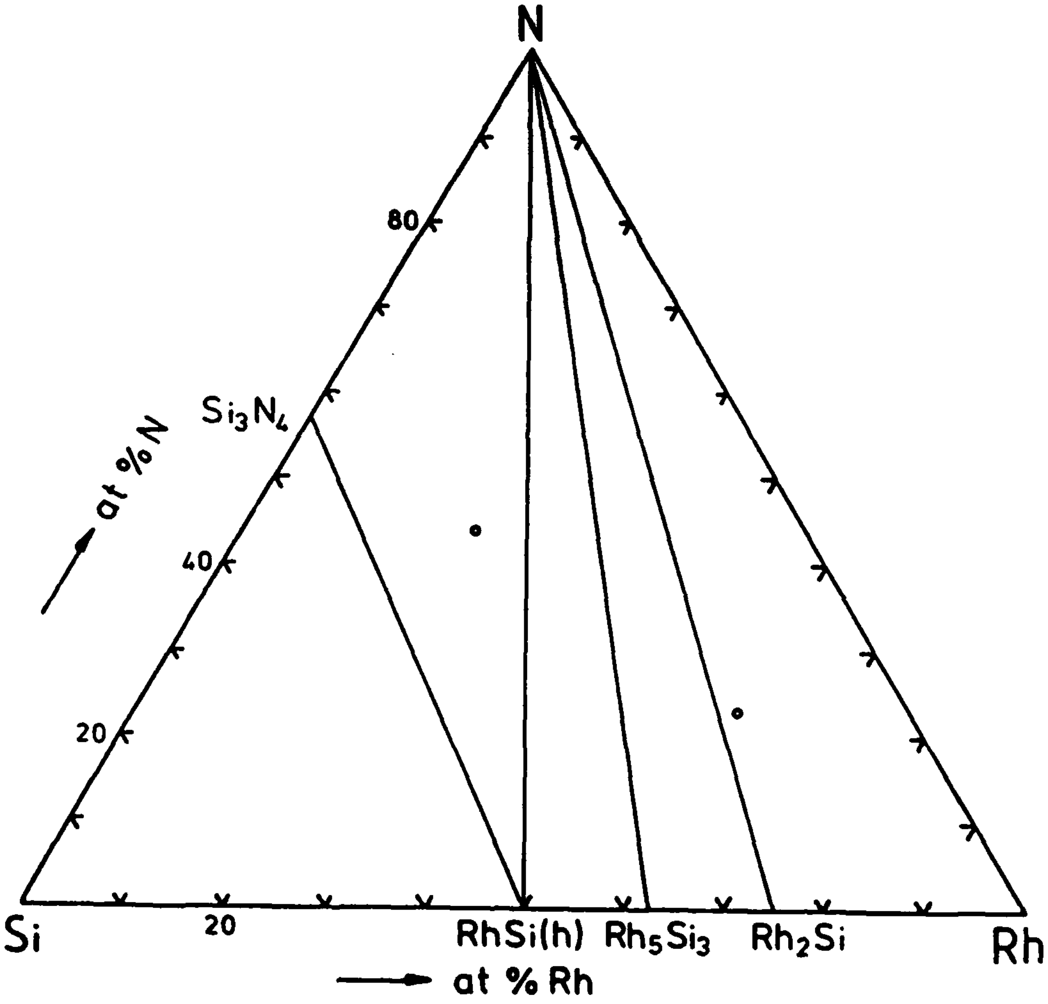
Tab.27.1: Solid phases in the system Rh - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Rh	cF4	a= 380.34	[85Vil];powder pattern:
	$Fm\bar{3}m$		ASTM file card # 5-685
	Cu (A1)		
Rh_2Si	oP12	a= 540.8	[85Vil];powder pattern:
	Pnma	b= 393	ASTM file card # 37-1316
	Co_2Si (C23)	c= 738.3	
Rh_5Si_3	oP16	a= 531.7	[85Vil];powder pattern:
	Pbam	b= 1013.1	ASTM file card # 37-1317
	Rh_5Ge_3	c= 389.5	
$Rh_{20}Si_{13}$	hP34	a= 1185.1	[85Vil];powder pattern:
1050<T<1225	$P6_3/m$	c= 362.3	ASTM file card # 37-1318
Rh_3Si_2	hP6	a= 394.2	[85Vil];powder pattern:
T<820	$P6_3/mmc$	c= 504.7	given in [85Sch]
	$InNi_2$ ($B8_2$)		
RhSi(h)	cP8	a= 467.4	[85Vil]
T>1030	$P2_13$		
(Rh rich)	FeSi (B20)		
RhSi(x)	mP*	a= 458.8	martens.transf. RhSi(h)
	$P2_1/c$	b= 456.8	[85Sch];powder pattern:
		c= 553.6	ASTM file card # 38-999
		β= 115.92	
RhSi(r)	oP8	a= 553.1	[85Vil];powder pattern:
T<1080	Pnma	b= 306.3	ASTM file card # 35-1075
(Si rich)	MnP (B31)	c= 636.2	
Rh_4Si_5	mP18	a= 1233.5	[85Vil];powder pattern:
	$P2_1/m$	b= 350.8	ASTM file card # 35-1076
	Rh_4Si_5	c= 592.4	
		β= 100.18	
Rh_3Si_4	oP28	a= 1881.0	[85Vil];powder pattern:
	Pnma	b= 361.4	ASTM file card # 35-1077
	Rh_3Si_4	c= 581.3	

Tab.27.1 continued

Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160

Fig.27.1: Isothermal section observed in the system Rh - Si- N at 1250°C (under argon)



SYSTEM NICKEL - SILICON - NITROGEN (Ni-Si-N)

INTRODUCTION / EXPERIMENTAL

Phase equilibria of Ni-Si-N at 900°C were determined by x-ray analysis [87Wei].The alloys investigated were prepared using powders of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si),silicon (purity: 3N) and nickel (purity: 3N) all from Alpha Div.,Ventron Corp.,USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil,heat treated at 900°C,340h and quenched.

BINARY SYSTEMS

The phase diagrams for the binary systems Ni-Si as well as Ni-N are given in [86Mas].The system Ni-Si was thermodynamically modelled [86Mey],[87Mey].No phase diagram for the system Si-N is reported. Si_3N_4 occurs in two modifications: α-Si_3N_4 and β-Si_3N_4.Crystal structure data for the solid phases are listed in tab.28.1. The solubility of nitrogen in silicon as well as nickel is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Ni-Si-N (tab.28.1).In the absence of external nitrogen partial pressure Si_3N_4 is found to coexist at 900°C with all binary silicides stable at this temperature and with Ni (fig.28.1).Under pure argon the onset of the decomposition of Si_3N_4 by nickel is observed at 1170 ± 10°C [87Wei].This agrees with earlier,just qualitative observations [66Mue][66Yas][69Fel][79Ben] and is consistent with [89Bri].Lattice parameters of neither nickel silicide coexisting with Si_3N_4 or N_2 gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in nickel silicides.

Using the thermodynamic data in tab.28.2 the nitrogen pressures for the invariant equilibria occurring at 900°C are calculated (tab.28.3).The resulting tie lines are consistent with the observed isothermal section (figs.28.1)

MISCELLANEOUS

The wetting angle under vacuum between Si_3N_4 and Ni_2Si is reported to be $\theta = 108°$ (at 1450°C)[73Cha].

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Table 28.1: Solid phases in the system Ni - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ni	cF4 $Fm\bar{3}m$ Cu (A1)	a= 352.32	[85Vil];powder pattern: ASTM file card # 4-850
Ni_3Si(r) ($Ni_{29}Si_9$) T<1031	cP4 $Pm\bar{3}m$ Cu_3Au ($L1_2$)	a= 350.4	[85Vil];powder pattern: given in [39Osa]
Ni_3Si(h) 1114<T<1164	cP2 $Pm\bar{3}m$	a= 280.8	[85Vil];
Ni_3Si(h) ($Ni_{25}Si_9$) 987<T<1114	hP*	a= 669.8 c= 2885.5	cited as $Ni_{37}Si_{13}$ in [85Vil] powder pattern: in [79Ell]
$Ni_{31}Si_{12}$ (Ni_5Si_2)	hP43 P321 $Ni_{31}Si_{12}$	a= 667.1 c= 1228.8	[85Vil];powder pattern: ASTM file card # 17-222 24-524
Ni_2Si(r) T<1217	oP12 Pnma Co_2Si (C23)	a= 500 b= 373 c= 704	[85Vil];powder pattern: ASTM file card # 3-943
Ni_2Si(h) (Ni_3Si_2(h)) T>806	hP6 $P6_3/m$	a= 380.5 c= 489.0	[85Vil];powder pattern: ASTM file card #3-1069
Ni_3Si_2(r) T<843	oC80 $Cmc2_1$ Ni_3Si_2	a= 1222.9 b= 1080.5 c= 692.4	[85Vil];powder pattern: ASTM file card # 17-881
NiSi	oP8 Pnma MnP (B31)	a= 518 b= 334 c= 562	[85Vil];powder pattern: ASTM file card # 38-844
$NiSi_2$	cF12 $Fm\bar{3}m$ CaF_2 (C1)	a= 540.6	[85Vil];powder pattern: given in [39Osa]

Tab.28.1 continued

Ni_4N	cP5	a= 374.0	[85Vil];powder pattern:
	Pm$\bar{3}$m		ASTM file card # 36-1300
	Fe_4N (L'1)		
Ni_4N	t**	a= 372	[85Vil];powder pattern:
		c= 728	given in [83Dor]
Ni_3N	hP*	a= 460.7	[85Vil];powder pattern:
T<400 in N_2	$P6_322$ or P312	c= 430.4	ASTM file card # 10-280
Si	cF8	a= 542.86	[85Vil];powder pattern:
	Fd$\bar{3}$m		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160

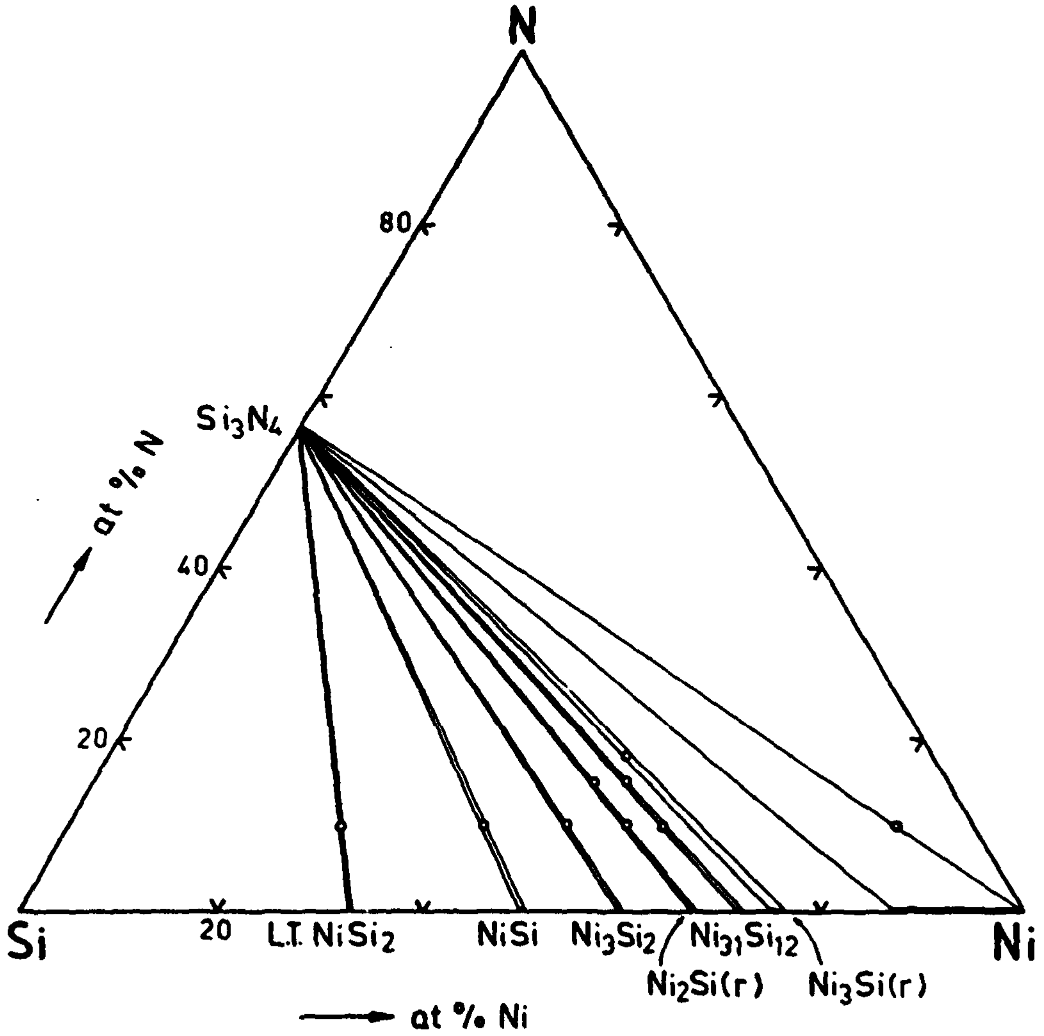
Tab.28.2: Thermochemical data for the solid phases in Ni - Si - N

phase	ΔG_f^o [J/gramatom]	Comment
.1429 Si_3N_4	$-124602 + 57.95\ T$	[76Fro]
.3333 $NiSi_2$(r)	$-36159.2 + 154.02\ T - 25.02\ T \ln T - .00185\ T^2 + 180498/T$	[86Mey]
.5000 NiSi	$-42442.1 + 145.95\ T - 24.38\ T \ln T - .00153\ T^2 + 162967/T$	[86Mey]
.2000 Ni_3Si_2(r)	$-45996.1 + 146.93\ T - 24.55\ T \ln T - .00222\ T^2 + 116002/T$	[87Mey]
.3333 Ni_2Si(h)	$-45666.1 + 146.28\ T - 24.71\ T \ln T - .00292\ T^2 + 69036/T$	[86Mey]
for $x_{Si}=0.4$:	-81000 (at 1173K)	(estimated from plot ΔG_f^{1173} vs. x_{Si})
.3333 Ni_2Si(r)	$-47668.2 + 132.10\ T - 22.19\ T \ln T - .00486\ T^2 + 69036/T$	[87Mey]
.1429 Ni_5Si_2 ($Ni_{31}Si_{12}$)	$-49358.8 + 149.68\ T - 24.76\ T \ln T - .00303\ T^2 + 60407/T$	[86Mey]
.2500 Ni_3Si(h') ($Ni_{25}Si_9$)	$-47801.4 + 150.00\ T - 24.81\ T \ln T - .00313\ T^2 + 51777/T$	[86Mey]
.2500 Ni_3Si(h)	$-42985.5 + 146.55\ T - 24.81\ T \ln T - .00313\ T^2 + 51777/T$	[86Mey]
.2500 Ni_3Si(r) ($Ni_{29}Si_9$)	$-49261.6 + 151.64\ T - 24.81\ T \ln T - .00313\ T^2 + 51777/T$	[86Mey]
Ni(s.s.12at% Si)	-76000 (at 1173K)	(estimated from plot ΔG^{1123} vs. x_{Si})

Tab.28.3: Calculated invariant equilibria in Ni - Si - N at 900°C

$p(N_2)$ (Pa)	Reaction
0.15×10^{-3}	$Si_3N_4 = 3\ Si + 2\ N_2$
.16	$Si_3N_4 + 6\ Ni_{.5}Si_{.5} = 9\ Ni_{.333}Si_{.667} + 2\ N_2$
.2	$Si_3N_4 + 15\ Ni_{.6}Si_{.4}(h) = 18\ Ni_{.5}Si_{.5} + 2\ N_2$
1.6	$Si_3N_4 + 27\ Ni_{.667}Si_{.333}(r) = 30\ Ni_{.6}Si_{.4}(h) + 2\ N_2$
77	$Si_3N_4 + 36.855\ Ni_{.721}Si_{.279} =$ $39.855\ Ni_{.667}Si_{.333}(r) + 2\ N_2$
6.7×10^3	$Si_3N_4 + 51.216\ Ni_{.763}Si_{.239} =$ $54..219\ Ni_{.721}Si_{.279} + 2\ N_2$
9×10^3	Si_3N_4 + 19.564 Ni(s.s.12at%Si) = $22.564\ Ni_{.763}Si_{.237} + 2\ N_2$

Fig.28.1: Isothermal section observed in the system Ni - Si - N at 900°C (in the absence of external nitrogen pressure)



SYSTEM COPPER - SILICON - NITROGEN (Cu-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Cu-Si-N at 700°C were determined by X-ray analysis [90Wei].The 8 alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4(mixture of α-Si_3N_4 and β-Si_3N_4;58 at% Si;from Alpha Div.,Ventron Corp.,USA) and Cu or arc melted Cu-Si alloys resp.(Cu powder,3N,from E.Merck A.G.,FRG; Cu rods,5N+,from Ventron GmbH,FRG; Si powder,m4N,from Fluka AG,Buchs, Switzerland).

BINARY SYSTEMS

The phase diagram for the system Cu-Si is given in [86Mas].No phase diagrams exist in the literature for Cu-N and Si-N.In the system Cu-N three intermediate phases are reported to exist: The most stable of these,Cu_3N (tab.29.1), decomposes around/above 310°C (in hydrogen atmosphere) [84Bai].Two azides,CuN_3 and CuN_6,were systhesized at room temperature [48Wil],[68Soe].Silicon nitride exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.29.1).The solubility of nitrogen in copper as well as in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Cu-Si-N at 700°C (tab.29.1). Fig.29.1 shows the isothermal section at 700°C in the absence of external nitrogen pressure.Cu as well as all binary Cu-silicides stable at 700°C coexist with Si_3N_4.This is in agreement with earlier data [69Fel],[75Lei].Lattice parameter measurements indicate insolubility of nitrogen in Cu or any of the Cu silicides nor of Cu in Si_3N_4.

MISCELLANEOUS

Liquid copper does not wet Si_3N_4 (θ= 144±10° under vacuum [66Yas], [66Mue],[87Nak],[Lju],[Tom]).

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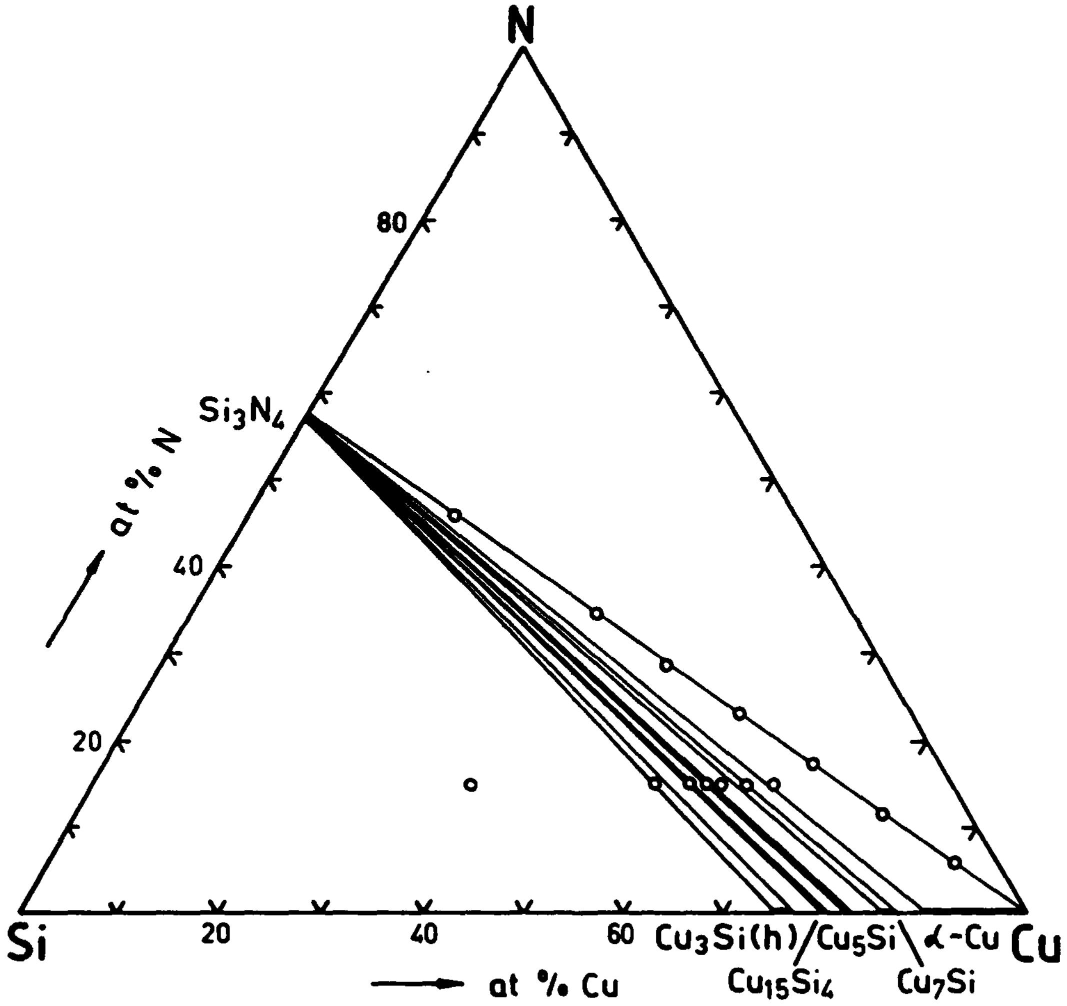
Table 29.1: Solid phases in the system Cu - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Cu	cF4 $Fm\bar{3}m$ Cu (A1)	a= 361.48	[85Vil];powder pattern: ASTM file card # 4-836
$\varkappa$-Cu_7Si 552<T<842	hP2 $P6_3/mmc$ Mg (A3)	a= 255.99 c= 418.49	[85Vil]; at 12 at% Si
β-Cu_6Si(h) T>785	cI2 Im3m W (A2)	a= 285.4	[85Vil]
γ-Cu_5Si(r) T<729	cP20 $P4_132$ βMn (A13)	a= 622.3	[85Vil];powder pattern: ASTM file card # 4-841
δ-Cu_5Si(h) ($Cu_{17}Si_3$) T>710	t**	a= 881.5 c= 790.3	[85Vil]
ε-$Cu_{15}Si_4$(r) T<800	cI76 $I\bar{4}3d$ $Cu_{15}Si_4$	a= 971.4	[85Vil];powder pattern: ASTM file card # 23-222
η-Cu_3Si(h) 558<T<859	hP72	a= 704.5 c= 2195.0	[85Vil]
$\eta'$$Cu_3Si$(h)	hR* $R\bar{3}$	a= 2540 c= 4420	[85Vil]
$\eta''$$Cu_3Si$(r)	t**	a= 726.7 c= 789.2	[85Vil];powder pattern: ASTM file card # 23-224
Cu_3N	cP4 $Pm\bar{3}m$ ReO_3 (DO_9)	a= 381.3	[85Vil];powder pattern: ASTM file card # 2-1156

Tab.29.1 continued

CuN_3	tI32 $I4_1/a$	a= 365.3 c= 559.4	[85Vil];powder pattern: ASTM file card # 4-622
CuN_6	oP28 Pnma	a= 1348.1 b= 308.4 c= 907.6	[85Vil];powder pattern: ASTM file card # 21-281
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.29.1: Isothermal section observed in the system Cu - Si - N at 700°C



SYSTEM SILVER - SILICON - NITROGEN (Ag-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Ag-Si-N at 700°C and 900°C were determined by x-ray analysis [90Wei].The alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si;from Alpha Div., Ventron Corp.,USA) and high purity ("puriss") Ag.

BINARY SYSTEMS

The equilibrium diagram for the simple eutectic (845°C,10 at%Si) system Ag-Si is given in [86Mas].Structural data of two metastable Ag-silicides are listed in [85Vil].No phase diagram exists in the literature for the systems Ag-N and Si-N.In the system Ag-N two intermediate phases are reported (tab.30.1).Neither phase is stable at 700°C or higher temperatures.Silicon nitride exists in two modifications :α-Si_3N_4 and β-Si_3N_4 (tab.30.1).The solubility of nitrogen in silver as well as in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Ag-Si-N at 700°C or 900°C (tab.30.1). Fig.30.1 shows the isothermal section at 900°C :Ag coexists with Si_3N_4 in equilibrium confirming earlier data [66Mue].Lattice parameter measurements indicate mutual insolubility of Ag and Si_3N_4.

MISCELLANEOUS

Liquid silver does not wet Si_3N_4 [69Fel] ($\theta = 145 \pm 10°$ under vacuum [66Mue],[87Nak],[89Lju].

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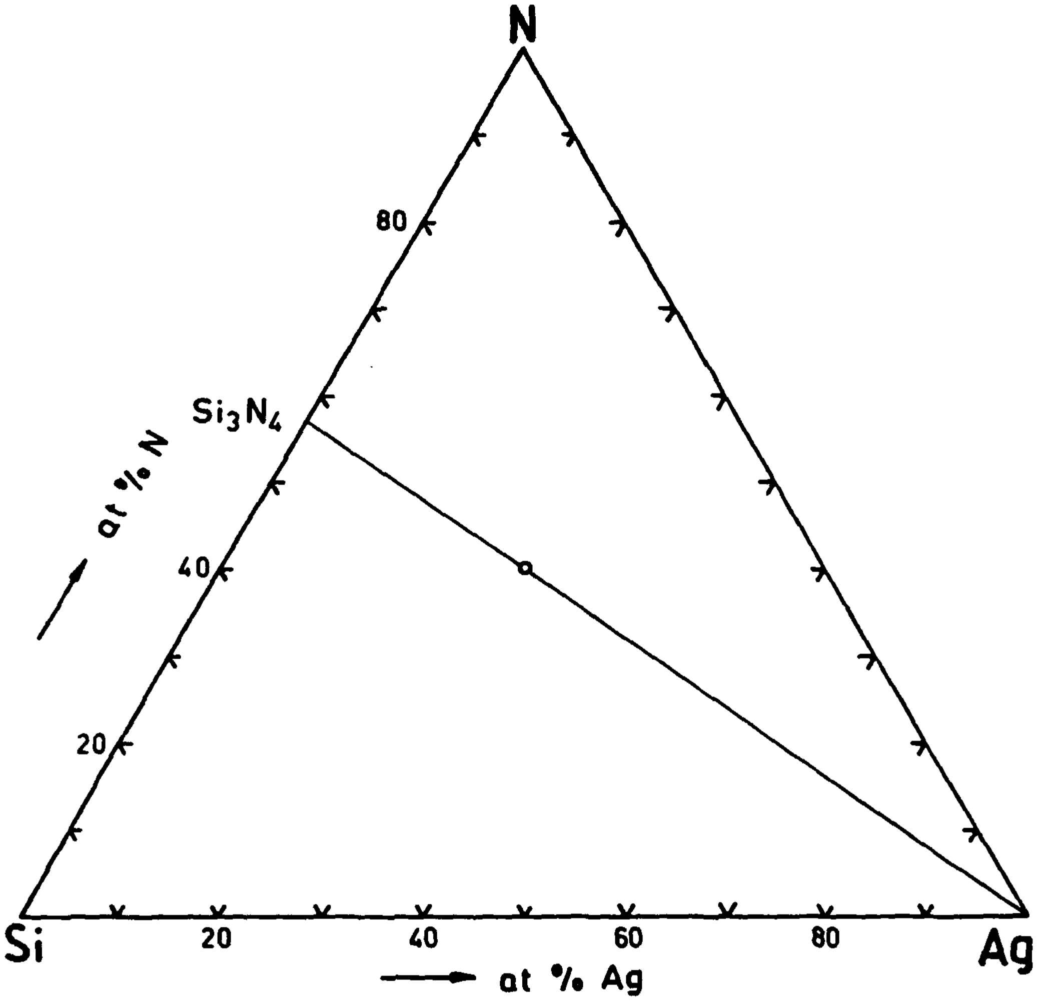
Table 30.1: Solid phases in the system Ag - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ag	cF4 $Fm\bar{3}m$ Cu (A1)	a= 408.53	[85Vil];powder pattern: ASTM file card # 4-783
Ag_3N	cF*	a= 437.8	[85Vil]
AgN_3	oI*	a= 561.7 b= 591.46 c= 600.57	[85Vil];powder pattern: ASTM file card # 3-906
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.30.1 : Isothermal section observed in the system Ag - Si - N at 900°C



SYSTEM GOLD - SILICON - NITROGEN (Au-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Au-Si-N at 900°C were determined by X-ray analysis [90Wei].The alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4;58 at% Si;from Alpha Div.,Ventron Corp.,USA) and high purity ("puriss.") Au.

BINARY SYSTEMS

The equilibrium diagram for the simple eutectic (363°C,18.6 at% Si) system Au-Si is given in [86Mas].The existence of several metastable Au-silicides is reported [85Vil],[81Tsa].No phase diagrams exist in the literature for the systems Au-N and Si-N.In the System Au-N no intermediate phase is reported [84Oka].Silicon nitride exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.31.1).The solubility of nitrogen in gold [84Oka] as well as in silicon [76Fro] is very low.

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Au-Si-N at 900°C (tab.31.1).Fig.31.1 shows the isothermal section at 900°C : Confirming earlier data [69Fel] Au and Si_3N_4 coexist in equilibrium.It should be noted,however,that mechanical stress in thin films of Au deposited on Si_3N_4 can cause the formation the metastable phase Au_5Si_2 (hex.,a=938.2pm,c=1545.9pm [81Tsa]; powder pattern: ASTM file card # 36-938) upon the partial decomposition of Si_3N_4 at low nitrogen partial pressure [89Ede].Lattice parameter measurements indicate mutual insolubility of Au and Si_3N_4.

MISCELLANEOUS

Gold does not wet silicon nitride (θ = 157°) [89Lju].

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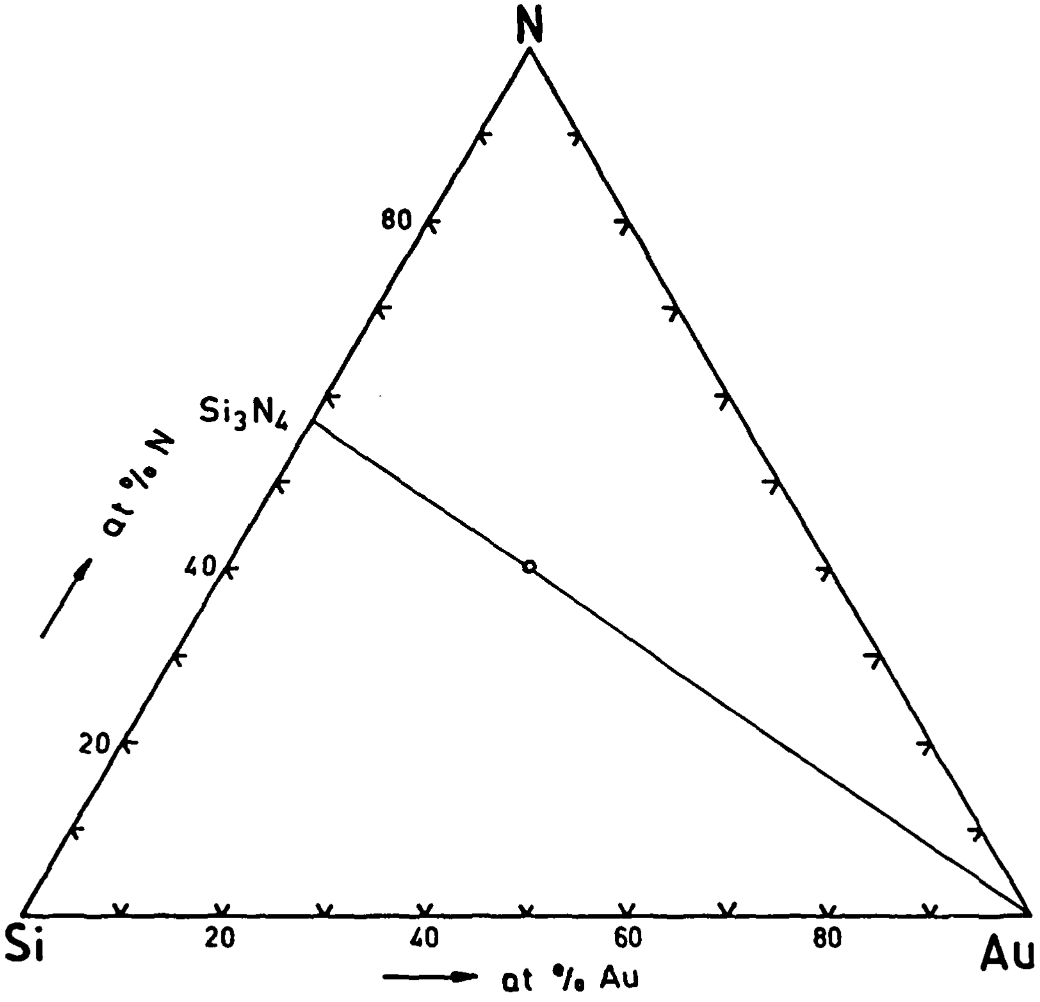
Table 31.1: Solid phases at in the system Au - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Au	cF4 $Fm\bar{3}m$ Cu (A1)	a= 407.89	[85Vil];powder pattern: ASTM file card # 4-784
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.31.1: Isothermal section observed in the system Au - Si - N at 900°C



SYSTEM ZINC- SILICON - NITROGEN (Zn-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Zn-Si-N at 350°C were determined by x-ray analysis [90Wei].The alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4;58 at% Si;from Alpha Div.,Ventron Corp.,USA) and Zn (m3N+,from Alpha Div.,Ventron Corp.,USA).

BINARY SYSTEMS

The phase diagram for the simple eutectic (419.3°C,0.045 at% Si) system Zn-Si is given in [86Mas].No Phase diagrams exist in the literature for Zn-N and Si-N.In the system Zn-N the phase Zn_3N_2 (tab.32.1) exists up to 700°C [88Wri].For the azide ZnN_6,which decomposes around 300°C [88Wri],two structures are reported (tab.32.1). Silicon nitride exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.32.1).The solubility of nitrogen in zinc [88Wri] as well as in silicon [76Fro] is very low.

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Zn-Si-N at 350°C (tab.32.1). Fig.32.1 shows the isothermal section at 350°C : Confirming earlier data [65Yas],[69Fel] Zn coexists with Si_3N_4 in equilibrium.Lattice parameter measurements indicate mutual insolubility of Zn and Si_3N_4.

MISCELLANEOUS

Liquid zinc does not wet Si_3N_4 [66Mue].

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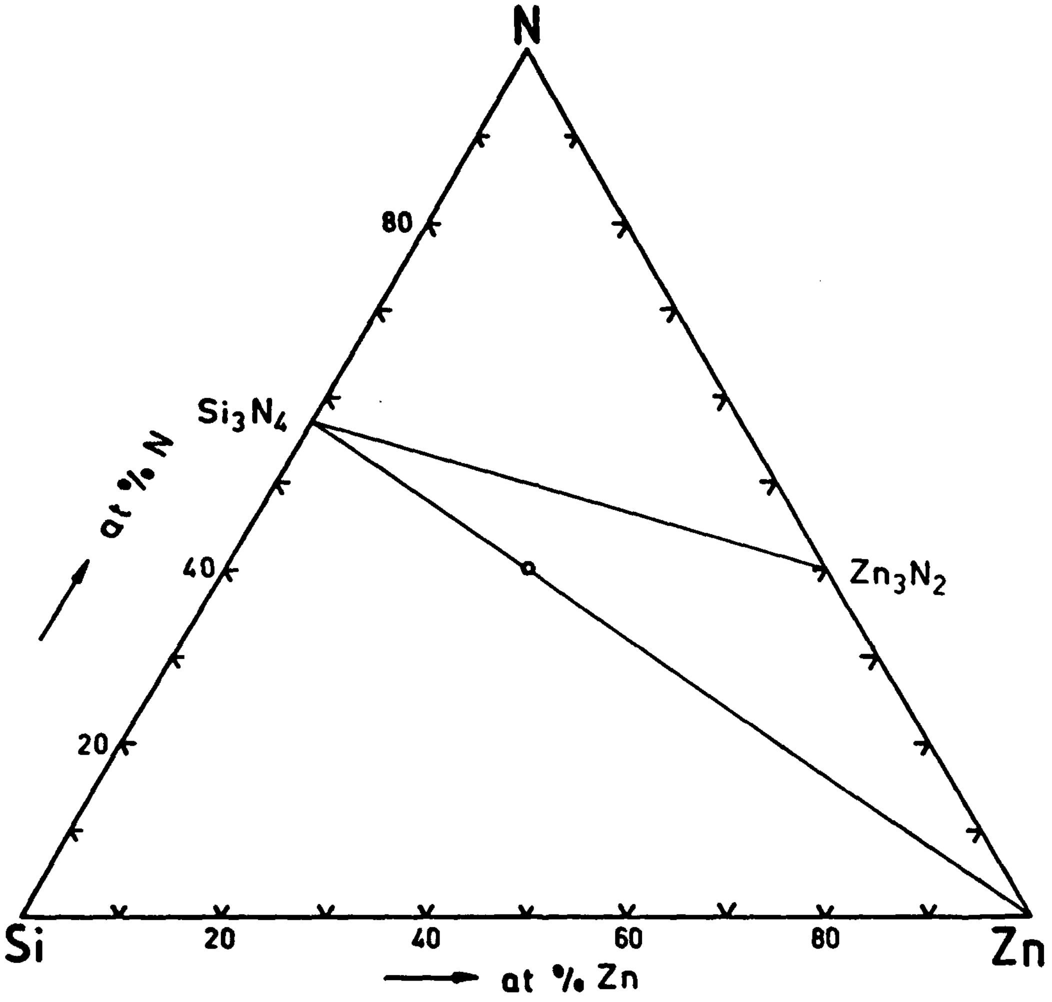
Table 32.1: Solid phases in the system Zn - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Zn	hP2 $P6_3/mmc$ Mg (A3)	a= 266.46 c= 494.61	[85Vil];powder pattern: ASTM file card # 4-831
Zn_3N_2	cI80 $Ia\bar{3}$ Mn_2O_3 ($D5_3$)	a= 976.3	[85Vil];powder pattern: ASTM file card # 35-762
α-ZnN_6	oP36 $P222_1$	a= 1098 b= 692 c= 1633	[85Vil];powder pattern: ASTM file card # 30-1473
β-ZnN_6	o*28	a= 735 b= 437 c= 1523	[88Wri];powder pattern: ASTM file card # 23-740
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.32.1 : Isothermal section observed in the system Zn - Si - N at 350°C



SYSTEM CADMIUM - SILICON - NITROGEN (Cd-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Cd-Si-N at 300°C were determined by X-ray analysis [90Wei].The alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4;58 at% Si;from Alpha Div.,Ventron Corp.,USA) and Cd (3N,from Alpha Div.,Ventron Corp.,USA).

BINARY SYSTEMS

The phase diagram for the simple eutectic (320°C,0.135 at% Si) system Cd-Si is given in [86Mas].No phase diagram exists in the literature for Cd-N and Si-N.The nitride Cd_3N_2 (tab.33.1) decomposes at 180°C in an atmosphere of NH_3 (pressure not specified)[88Wri].The azide CdN_6 decomposes around 100°C [88Wri].Silicon nitride exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.33.1).The solubility of nitrogen in cadmium [88Wri] as well as in silicon [76Fro] is very low.

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Cd-Si-N at 300°C (tab.33.1). Fig.33.1 shows the isothermal section at 300°C : Confirming earlier data [65Yas],[69Fel] Cd coexists with Si_3N_4 in equilibrium.Lattice parameter measurements indicate mutual insolubility of Cd and Si_3N_4.

MISCELLANEOUS

Liquid cadmium does not wet Si_3N_4 (θ= 157° under vacuum [66Mue]).

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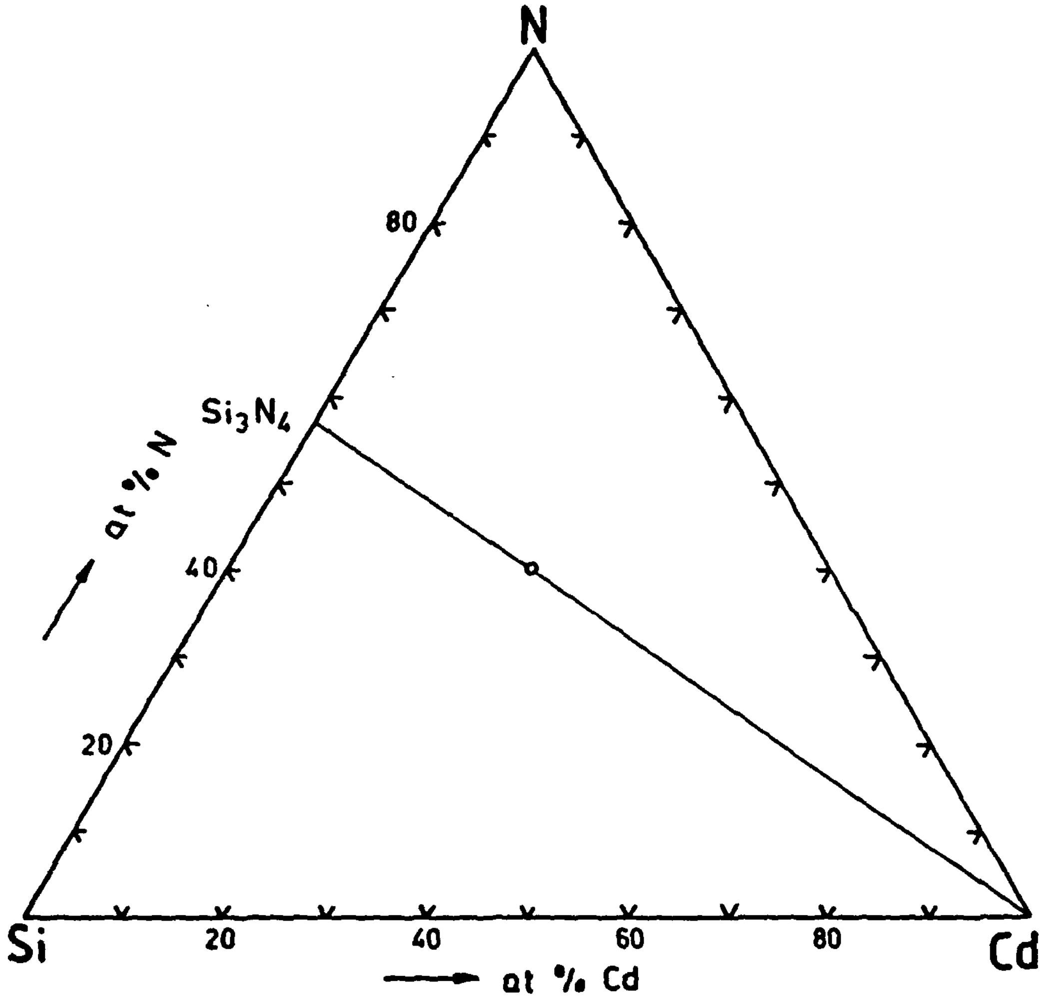
Table 33.1: Solid phases in the system Cd - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Cd	hP2	a= 297.87	[85Vil];powder pattern:
	$P6_3/mmc$	c= 561.66	ASTM file card # 5-674
	Mg (A3)		
Cd_3N_2	cI80	a= 1081	[85Vil];powder pattern:
	$Ia\bar{3}$		ASTM file card # 10-253
	Mn_2O_3 ($D5_3$)		
CdN_6	oP56	a= 782	[85Vil]
	Pbca	b= 646	
		c= 1604	
Si	cF8	a= 542.86	[85Vil];powder pattern:
	$Fd\bar{3}m$		ASTM file card # 5-565
	C (A4)		
α-Si_3N_4	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si_3N_4		
β-Si_3N_4	hP14	a= 760.8	[85Vil];powder pattern:
	$P6_3/m$	c= 291.1	ASTM file card # 29-1132
	Si_3N_4		33-1160

Fig.33.1 : Isothermal section observed in the system Cd - Si - N at 300°C



SYSTEM ALUMINIUM - SILICON - NITROGEN (Al-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Al-Si-N at 600°C were investigated by x-ray analysis [90Wei], transmission electron microscopy (TEM) and Auger electron spectroscopy (AES)[89Bre].The alloys investigated in [90Wei] were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4, 58 at% Si,from Alpha Div.,Ventron Corp.,USA), AlN (2N,from Koch Light Lab. Ltd.,UK), silicon (m4N,from Fluka AG,Switzerland) and aluminium (2N8,from Koch Light Lab. Ltd.,UK).

BINARY SYSTEMS

The phase diagrams for the systems Al-Si as well as Al-N are given in [86Mas]. AlN is the only stable intermediate phase (tab.34.1).No phase diagram is reported for Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.34.1).The solubility of nitrogen in aluminium as well as in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Al-Si-N (tab.34.1).Fig.34.1 shows the isothermal section at 600°C in the absence of external nitrogen pressure. Although expected from thermochemical data [76Fro],x-ray data of samples prepared from Al + Si_3N_4 did not show the formation of Si + AlN. However,the occurrence of this reaction was observed by AES [89Bre] and TEM [86Nak] [89Bre]: Around each grain of Al a thin layer of AlN is formed acting as a diffusion barrierand retarding further progress of the reaction.Thus the phases observed by x-ray (fig.34.1) coexist in metastable equilibrium even after anneal for several hundred hours.

MISCELLANEOUS

The wetting angle of liquid aluminium on Si_3N_4 is found to be θ= 126° [66Mue],[66Yas],[87Nak].However at temperatures above 1100°C Al wets Si_3N_4 (θ= 72°) [89Lju],[89Tom].

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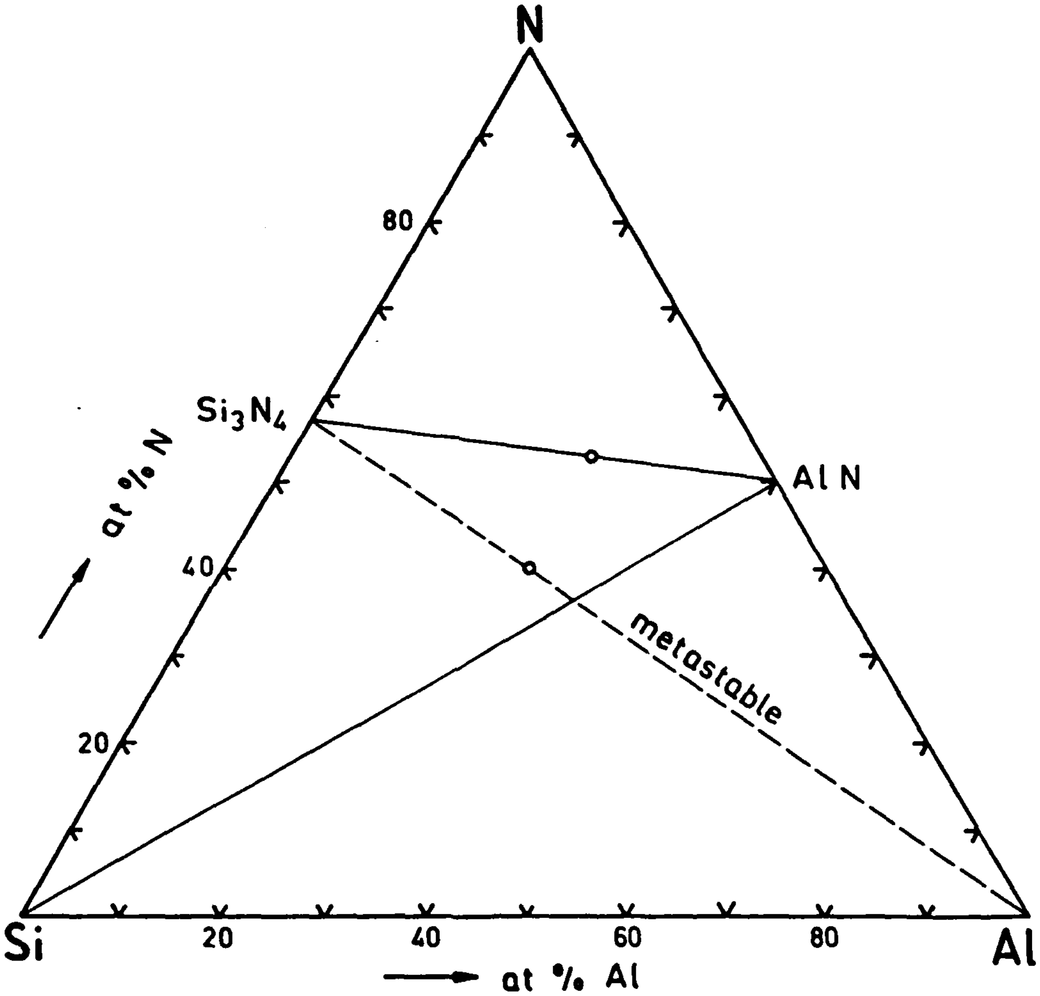
Table 34.1: Solid phases in the system Al - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Al	cF4 $Fm\bar{3}m$ Cu (A1)	a= 404.88	[85Vil];powder pattern: ASTM file card # 4-787
AlN	hP4 $P6_3mc$ SZn (B4)	a= 311.0 c= 498.0	[85Vil];powder pattern: ASTM file card # 25-1133
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.34.1: Isothermal section observed in the system Al - Si - N at 600°C



SYSTEM INDIUM - SILICON - NITROGEN (In-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of In-Si-N at 120°C were determined by x-ray analysis [90Wei].The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si,from Alpha Div., Ventron Corp.,USA) and indium (4N,from Fluka AG,Switzerland).

BINARY SYSTEMS

The phase diagrams for the system In-Si is given in [86Mas].No phase diagrams are reported for In-N or Si-N.The phase InN (tab.35.1) decomposes at 680°C under 10^5 Pa N_2 [38Juz],[87Jon].Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.35.1). The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in In-Si-N (tab.35.1). Fig.35.1 shows the isothermal section at 120°C in the absence of external nitrogen pressure.In agreement with thermochemical data [76Fro] indium coesists with Si_3N_4 in equilibrium.Lattice parameter measurements indicate mutual insolubility of In and Si_3N_4.

MISCELLANEOUS

Indium does not wet silicon nitride [89Lju],[90oe].

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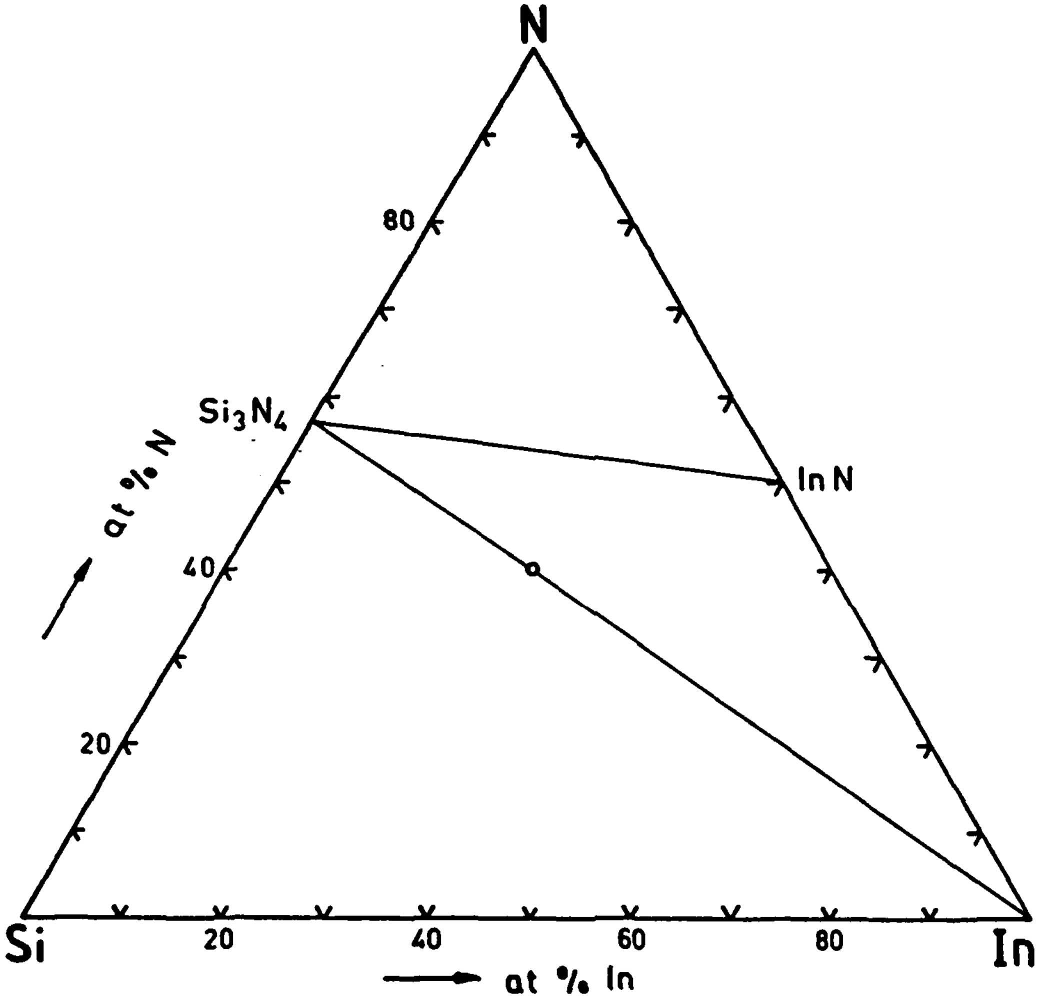
Table 35.1: Solid phases in the system In - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
In	tI2 F4/mmm In (A6)	a= 325.12 c= 494.67	[85Vil];powder pattern: ASTM file card # 5-642
InN	hP4 $P6_3mc$ SZn (B4)	a= 354.0 c= 570.4	[85Vil];powder pattern: ASTM file card # 2-1450
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.35.1: Isothermal section observed in the system In - Si - N at 120°C



SYSTEM THALLIUM - SILICON - NITROGEN (Tl-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Tl-Si-N at 200°C were determined by x-ray analysis [90Wei].The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si,from Alpha Div., Ventron Corp.,USA) and thallium (4N,from Fluka AG,Switzerland).

BINARY SYSTEMS

The phase diagrams for the system Tl-Si is given in [86Mas]. No phase diagrams exist in the literature for Tl-N or Si-N.The nitride TlN is reported (tab.36.1) without further specification of its stability with regard to temperature and nitrogen pressure.The azide TlN_3 exists at least up to 225°C [73Mau].Si_3N_4 occurs in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.36.1).The solubility of nitrogen in silicon as well as in thallium is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Tl-Si-N (tab.36.1). Fig.36.1 shows the isothermal section at 200°C in the absence of external nitrogen pressure: Tl coexists with Si_3N_4 in equilibrium.Lattice parameter measurements indicate mutual insolubility of Tl and Si_3N_4.

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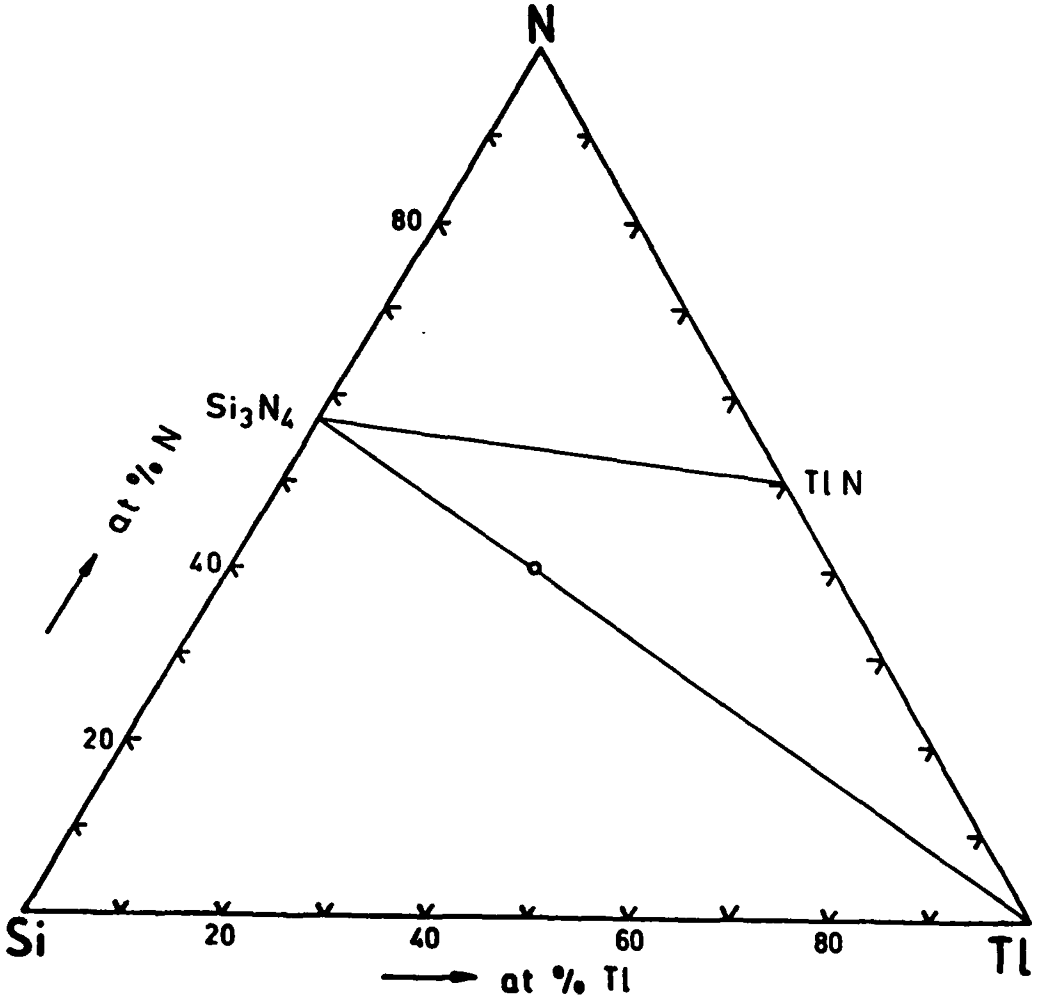
Table 36.1: Solid phases in the system Tl - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
α-Tl(r)	hP2	a= 345.66	[85Vil];powder pattern:
T<234°C	P6$_3$/mmc	c= 552.48	ASTM file card # 30-1341
	Mg (A3)		
β-Tl(h)	cI2	a= 387.1	[85Vil];powder pattern:
T>234°C	Im3m		ASTM file card # 2-876
	W (A2)		
TlN	hP4	a= 368	[85Vil]
	P6$_3$ mc	c= 601	
	SZn (B4)		
TlN$_3$(h=r)	tI16	a= 620.8	[85Vil];powder pattern:
-25<T<225+	I4/mcm	c= 735.5	ASTM file card # 21-1209
Si	cF8	a= 542.86	[85Vil];powder pattern:
	Fd$\bar{3}$m		ASTM file card # 5-565
	C (A4)		
α-Si$_3$N$_4$	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si$_3$N$_4$		
β-Si$_3$N$_4$	hP14	a= 760.8	[85Vil];powder pattern:
	P6$_3$/m	c= 291.1	ASTM file card # 29-1132
	Si$_3$N$_4$		33-1160

Fig.36.1: Isothermal section observed in the system Tl - Si - N at 200°C



SYSTEM TIN - SILICON - NITROGEN (Sn-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Sn-Si-N at 200°C were determined by x-ray analysis [90Wei].The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si,from Alpha Div., Ventron Corp.,USA) and tin (5N,from Alpha Div.,Ventron Corp.,USA).

BINARY SYSTEMS

The phase diagrams for the system Si-Sn is given in [86Mas]. No phase diagrams exist in the literature for Sn-N or Si-N.Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.37.1).The solubility of nitrogen in silicon as well as in tin is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Sn-Si-N (tab.37.1). Fig.37.1 shows the isothermal section at 200°C in the absence of external nitrogen pressure: Sn coexists with Si_3N_4 in equilibrium.This agrees with ealier literature [65Yas],[69Fel].Lattice parameter measurements indicate mutual insolubility of tin and Si_3N_4.

MISCELLANEOUS

The wetting angle of liquid tin on Si_3N_4 is reported to be $\theta = 155 \pm 15°$[66Mue],[89Lju],[89Tom],[90Loe].

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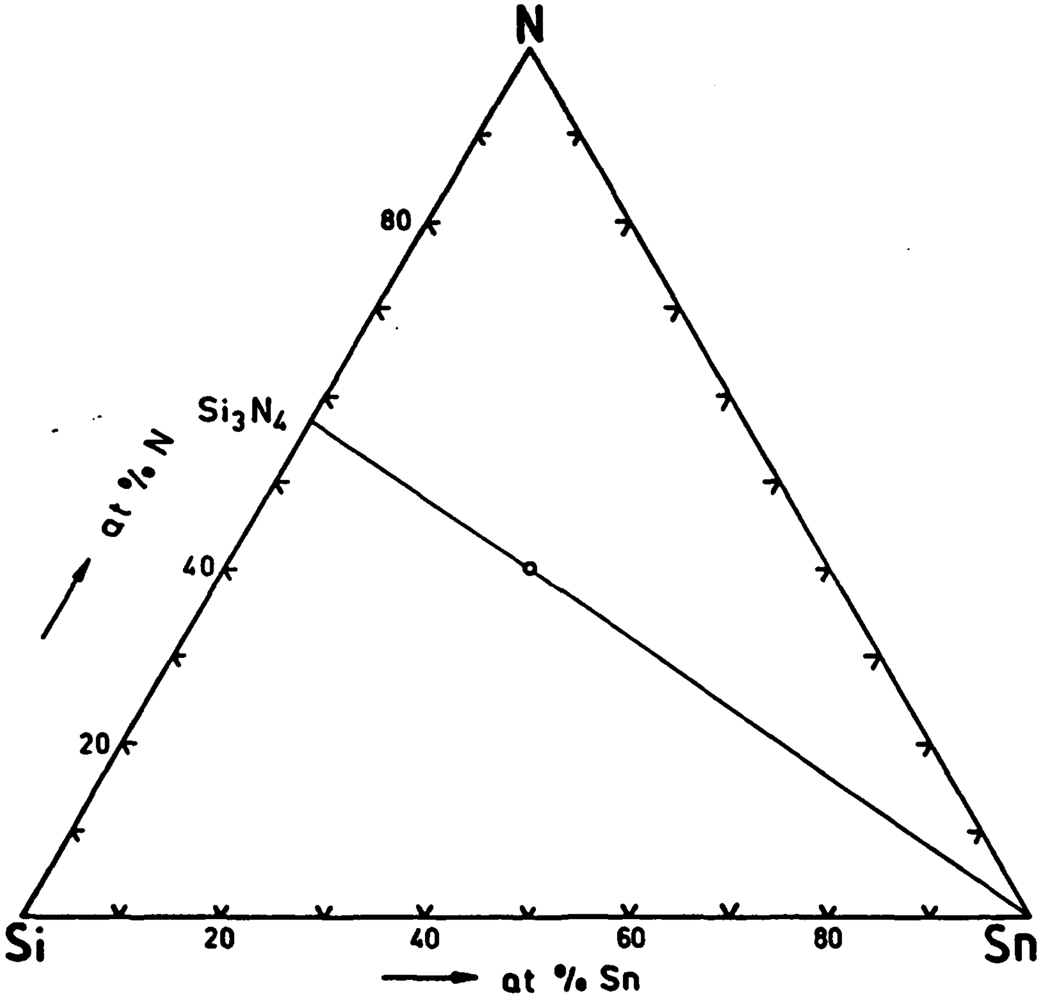
Table 37.1: Solid phases in the system Sn - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
β-Sn T>13°C	tI4 $I4_1/amd$ β-Sn (A5)	a= 583.15 c= 318.14	[85Vil];powder pattern: ASTM file card # 4-673
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.37.1: Isothermal section observed in the system Sn - Si - N at 200°C



SYSTEM LEAD - SILICON - NITROGEN (Pb-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Pb-Si-N at 200°C were determined by x-ray analysis [90Wei].The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si,from Alpha Div., Ventron Corp.,USA) and lead (2N8,from Alpha Div.,Ventron Corp.,USA).

BINARY SYSTEMS

The phase diagrams for the system Pb-Si is given in [86Mas]. No phase diagrams exist in the literature for Pb-N or Si-N.The azide PbN_6 (tab.38.1) decomposes upon aging at room temperature as well as upon heating to 128°C.Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.38.1).The solubility of nitrogen in silicon as well as in lead is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Pb-Si-N (tab.38.1). Fig.38.1 shows the isothermal section at 200°C in the absence of external nitrogen pressure: Pb coexists with Si_3N_4 in equilibrium.This agrees with ealier literature [60Coo],[65Yas],[69Fel],[77Ash].Lattice parameter measurements indicate mutual insolubility of lead and Si_3N_4.

MISCELLANEOUS

The wetting angle of liquid lead on Si_3N_4 is reported to be θ= 159° [66Mue].

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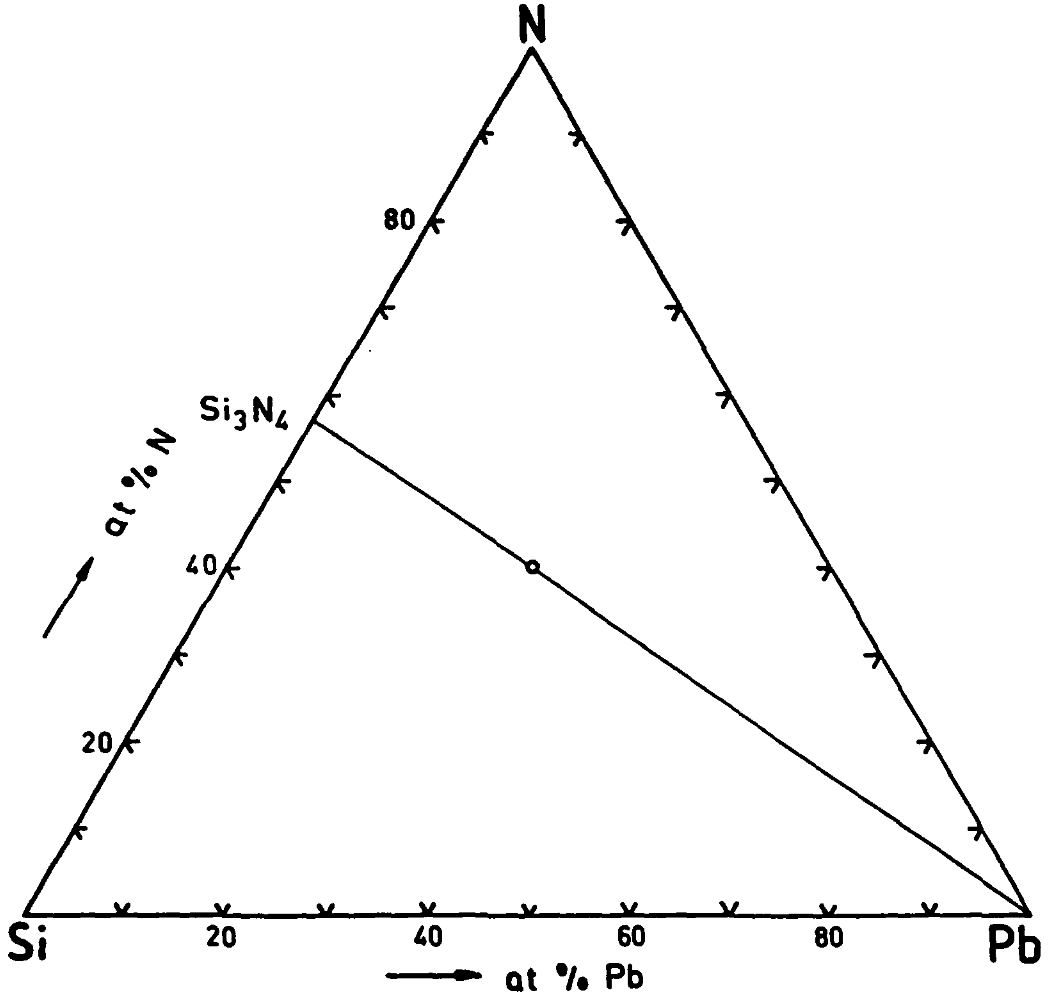
Table 38.1: Solid phases in the system Pb - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Pb	cF4 $Fm\bar{3}m$ Cu (A1)	a= 495.07	[85Vil];powder pattern: ASTM file card # 4-686
PbN_6	oP84 Pnma	a= 663 b= 1625 c= 1131	[85Vil];powder pattern: ASTM file card # 14-629 24-82
Si	cF8 $Fd\bar{3}m$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.38.1: Isothermal section observed in the system Pb - Si - N at 200°C



SYSTEM ANTIMONY - SILICON - NITROGEN (Sb-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Sb-Si-N at 600°C were determined by x-ray analysis [90Wei].The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4,58 at% Si,from Alpha Div., Ventron Corp.,USA) and antimony (4N,from Fluka AG.,Switzerland).

BINARY SYSTEMS

The phase diagrams for the system Sb-Si is given in [86Mas]. No phase diagrams exist in the literature for Sb-N or Si-N.Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.39.1).The solubility of nitrogen in silicon is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Sb-Si-N (tab.39.1). Fig.39.1 shows the isothermal section at 600°C in the absence of external nitrogen pressure: Sb coexists with Si_3N_4 in equilibrium.This agrees with ealier literature [88Ahn].Lattice parameter measurements indicate mutual insolubility of antimony and Si_3N_4.

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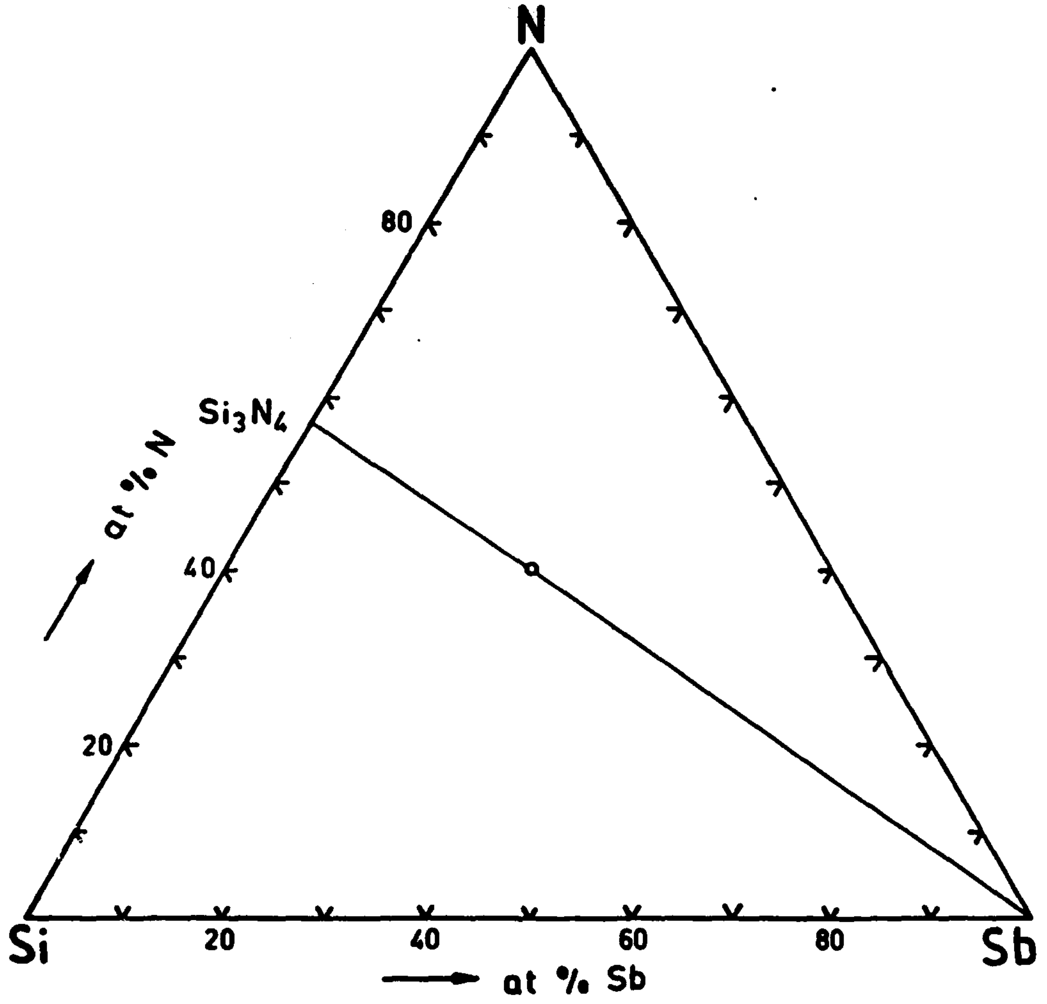
Table 39.1: Solid phases in the system Sb - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Sb	hR2 R$\bar{3}$m α-As (A7)	a= 430.84 c= 1127.4	[85Vil];powder pattern: ASTM file card # 35-732
Si	cF8 Fd$\bar{3}$m C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 $P6_3/m$ Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.39.1: Isothermal section observed in the system Sb - Si - N at 600°C



SYSTEM BISMUTH - SILICON - NITROGEN (Bi-Si-N)

INTRODUCTION / EXPERIMENTAL

The phase equilibria of Bi-Si-N at 200°C were determined by x-ray analysis [90Wei]. The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of Si_3N_4 (mixture of α-Si_3N_4 and β-Si_3N_4, 58 at% Si, from Alpha Div., Ventron Corp., USA) and bismuth (3N, from E.Merck, FRG).

BINARY SYSTEMS

The phase diagrams for the system Bi-Si is given in [86Mas]. No phase diagrams exist in the literature for Bi-N or Si-N. Si_3N_4 exists in two modifications: α-Si_3N_4 and β-Si_3N_4 (tab.40.1). The solubility of nitrogen in silicon as well as in bismuth is very low [76Fro].

SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Bi-Si-N (tab.40.1). Fig.40.1 shows the isothermal section at 200°C in the absence of external nitrogen pressure: Bi coexists with Si_3N_4 in equilibrium. This agrees with ealier literature [69Fel]. Lattice parameter measurements indicate mutual insolubility of bismuth and Si_3N_4.

MISCELLANEOUS

The wetting angle of liquid bismuth on Si_3N_4 is reported to be $\theta > 90°$ (non wetting) [65Yas].

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Table 40.1: Solid phases in the system Bi - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Bi	hR2 R$\bar{3}$m α-As (A7)	a= 454.60 c= 1186.2	[85Vil];powder pattern: ASTM file card # 5-519
Si	cF8 Fd$\bar{3}$m C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
α-Si_3N_4	hP28 P31c Si_3N_4	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
β-Si_3N_4	hP14 F6_3/m Si_3N_4	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Fig.40.1: Isothermal section observed in the system Bi - Si - N at 200°C