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Phase Diagrams of the Ternary Systems Mn, Fe, Co, Ni–Si–N*

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Phase equilibria in the ternary systems Mn, Fe, Co, and Ni–Si–N are investigated and isothermal sections at 900°C (Fe–Si–N, Ni–Si–N), at 1000°C (Mn–Si–N, Co–Si–N) and at 1150°C (Fe–Si–N) are presented. In the system Mn–Si–N, Si_3N_4 coexists with $MnSiN_2$, Mn_3Si, Mn_5Si_3, MnSi, and $MnSi_{2-x}$. In the systems Fe, Co, Ni–Si–N, Si_3N_4 coexists with all binary silicides but reacts rapidly with iron above 1120 ± 10°C, and cobalt and nickel above 1170 ± 10°C to form binary silicides and nitrogen gas.

Introduction

Silicon nitride is one of the most attractive advanced ceramic materials of today. Although much is known regarding wetting, metallizing, and joining Si_3N_4 to base metals no rationale of these data in the form of phase diagrams is available. This prompted a systematic investigation of such transition metal–silicon–nitrogen systems and the first set of ternary phase diagrams is presented here.

Literature Review

Liquid manganese wets silicon nitride (ϑ = 74°) (*1*) and is reported to react violently with Si_3N_4 at 1270°C under vacuum as well as in inert gas (*2*). The compounds identified as the reaction products are $MnSiN_2$, Mn_3Si, and Si_3N_4 (800°C, argon) and Mn_5Si_3 and Si_3N_4 (1200°C, argon), respectively (*3*). The ternary phase $MnSiN_2$ is orthorhombic, space group $Pna2_1$, a = 0.5258 nm, b = 0.6511 nm, and c = 0.5070 nm (*4*). $MnSiN_2$ was found to form as well by reaction of manganese with silicon under nitrogen (*3*). The decomposition of $MnSiN_2$ into MnSi and N_2 gas starts under nitrogen (10^5 Pa) above 1300°C and under argon above 800°C (*3*).

Silicon nitride is reported to decompose in contact with iron at temperatures above 700°C (*5*). This reaction is described to be fast and violent at higher temperatures, especially above the melting point of iron (*1, 2, 6*). At 1200°C, Si_3N_4 whiskers are observed to be dissolved in an Fe matrix (*7*). The reaction products found are binary iron silicides and nitrogen gas. A temperature of 1300°C is reported to be necessary to decompose the silicon nitride completely in an alloy Fe + 6 wt% Si_3N_4 in order to obtain an nitride-free alloy (*8*). The same author observed that at 1150°C the nitrogen evolution is reduced under vacuum compared to a hydrogen atmosphere. Tennenhouse *et al.* (*9*) investigated the interaction

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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. Joining Si_3N_4 to steel by hot pressing resulted in excellent bonding due to the formation of Fe-silicides in the interlayer. However, due to thermal expansion mismatching, low tensile strength (failure in the Si_3N_4) resulted (*10*). Iron is often used as an addition in silicon to aid nitridation. The reaction products found are Si_3N_4 and iron silicides (*11, 12*), which, however, are recognized to be the primary course of strength degradation in hot pressed silicon nitride (*13*). These results are in agreement with the observation that no bonding takes place and Si_3N_4 is apparently compatible with FeSi (at 1500°C, vacuum, wetting angle $\vartheta = 76°$) and Fe_2Si_5 (at 1450°C, vacuum, wetting angle $\vartheta = 66°$) (*14*). On the other hand nitriding $FeSi_2$ leads to the formation of Si_3N_4 + Fe at 1200°C according to Matsumoto *et al.* (*15*).

Liquid cobalt is reported to decompose Si_3N_4 (*1, 6*) by the formation of binary silicides and nitrogen gas. The binary silicides CoSi and "Co_3Si" were found to be compatible with Si_3N_4 (*14*). No bonding to the ceramic was observed. The wetting angles are $\vartheta = 62°$ and $\vartheta < 40°$, respectively. Silicon nitride acts as diffusion barrier between Co and Si in shallow-junction VLSI devices (*16*).

Liquid nickel is also reported to decompose Si_3N_4 (*1, 2, 6*) under the formation of binary silicides and nitrogen gas. This reaction was observed to already take place at temperatures above 1000°C (*17*). These observations are in accord with reports on the degradation of Si_3N_4 whiskers in a nickel matrix in the temperature range between 1000 and 1200°C (*7, 18–20*). The apparent compatibility of Si_3N_4 with Ni_2Si was concluded from the wetting angle of Ni_2Si on Si_3N_4 ($\vartheta = 108°$, no wetting) (*14*). Nitriding silicon with the addition of Ni results in the formation of nickel silicides besides Si_3N_4 (*11*).

Phase diagram data of the binary silicon–metal and nitrogen–metal systems are taken from literature references: Mn–Si from Moffatt (*21*); Fe–Si from Schürmann and Hensgen (*22*); Co–Si from Hansen (*23*) updated by the work of van den Boomgaard and Carpay (*24*) as well as Köster *et al.* (*25*); Ni–Si from Osawa and Okamoto (*26*), Oya and Suzuki (*27*), and Ellner *et al.* (*28*); Mn–N from Zwicker (*29*), Lihl *et al.* (*30*), and Kudielka and Grabke (*31*); Fe–N from Kubaschewski von Goldbeck (*32*).

No phase diagrams are reported for Co–N and Ni–N. Crystal structure data of the intermediate phases are compiled by Villars and Calvert (*33*).

Experimental Procedures

In order to identify all binary silicide phases and to obtain master alloys for further preparation, binary metal–silicon alloys were prepared by arc melting under argon (99.999% pure) from powders or ingots of the constituting elements using the starting materials listed below.[1] Ternary compositions were prepared by mixing powders of these master alloys and binary nitride powders. These ternary mixtures were cold pressed and sintered in evacuated quartz tubes lined with Mo or Ta foil.

X-ray diffraction (Co$K\alpha_1$ radiation, Cr$K\alpha$ radiation) was performed on all alloys using

[1] Silicon powder, purity m99.9%, from Alpha Div., Ventron Corp., USA; silicon lump, purity m99.9999%, from Alpha Div., Ventron Corp., USA; iron powder, purity 99.5%, impurities (in ppm): Ni 600, C < 600, O < 2000, from Fluka AG, Switzerland; cobalt powder, purity 99.8%, impurities (in ppm): Cu < 50, Pb < 50, Fe < 500, Zn < 50, Ni < 500, Mn < 50; from Fluka AG, Switzerland; nickel powder, purity m99.9%, from Alpha Div., Ventron Corp., USA; silicon nitride (mixture of α-Si_3N_4 and β-Si_3N_4), powder 58% Si; from Alpha Div., Ventron Corp., USA; manganese nitride (Mn_2N) powder, purity 99.9%, from Alpha Div., Ventron Corp.

Guinier or Debye–Scherrer cameras. In several ternary systems silicon nitride coexists with the transition metal at 1000°C. In order to determine the temperature at which reaction takes place, a large pellet (5–10 g) of the cold compacted powder mixture (Si_3N_4 + 30 at.% *Me*) was placed in an RF furnace under vacuum and heated slowly. Monitoring with an optical pyrometer the increase in temperature versus the gas pressure (on a logarithmic scale with arbitrary units) permits direct observation of the onset of gas evolution resulting from the reaction

$$Si_3N_4 + xMe \rightarrow Me_xSi_3 + 2N_2\uparrow .$$

Furthermore the nitrogen gas acts as transporting agents for metallic vapors which are deposited on the quartz window, therefore virtually bringing to an end the optical temperature measurements at the onset of the reaction.

Results and Discussion

The Ternary System Manganese–Silicon–Nitrogen

All phases and crystal structures reported for the binary system Mn–Si (*21*, *33*) could be corroborated and are confirmed. Mn_5Si_2, found at 700°C, could not be observed at temperatures of 800°C and above. No other discrepancies with the established phase diagram are observed. The lattice parameters found are Mn_6Si ($Mn_{0.855}Si_{0.195}$, ε-phase), a = 1.08916 nm, c = 1.92056 nm; Mn_9Si_2 ($Mn_{0.815}Si_{0.185}$, ξ-phase), a = 1.70195 nm, b = 2.86750 nm, c = 0.46675 nm; Mn_3Si a = 0.57242 nm; Mn_5Si_2 a = 0.89001 nm, c = 0.87084 nm, Mn_5Si_3 a = 0.68988 nm, c = 0.48096 nm; MnSi a = 0.45593 nm; and $Mn_{15}Si_{26}$ a = 0.55309 nm, c = 6.54763 nm. The lattice parameter of β-Mn(s.s) in an alloy $Mn_{0.90}Si_{0.10}$ annealed at 800°C was a = 0.62869 nm.

In the ternary system the phase $MnSiN_2$ was formed at 1000°C upon reaction of Si_3N_4 with manganese. $MnSiN_2$ coexists in the absence of external nitrogen pressure with Si_3N_4, Mn_3Si, β-Mn(s.s.), and nitrogen gas (Fig. 1). The lattice parameters found are a = 0.52656 nm, b = 0.65222 nm, c = 0.50737 nm (Si-rich) and a = 0.52678 nm, b = 0.65208 nm, c = 0.50693 nm (Mn-rich). $MnSiN_2$ may therefore be considered a line compound having only a very narrow homogeneity range. A three-phase field ($MnSiN_2$ + Mn_3Si + β-Mn(s.s.)) was observed. Hence the stability of Mn_9Si_2, which was found to exist in the binary Mn–Si system at this temperature, is confined to compositions close to the binary Mn–Si by a tieline between Mn_3Si and β-Mn(s.s.). Si_3N_4 coexists with $MnSi_{2-x}$, MnSi, Mn_5Si_3, and Mn_3Si besides $MnSiN_2$ (Table I). No solubility of nitrogen was observed in any of the manganese silicides. If the external nitrogen pressure is not negligible the formation of γ-Mn(s.s.) modifies the phase equilibria at the Mn-rich corner of the ternary system (Fig. 2). With further increase of the external nitrogen partial pressure, manganese nitrides richer in nitrogen coexist with $MnSiN_2$. Thus

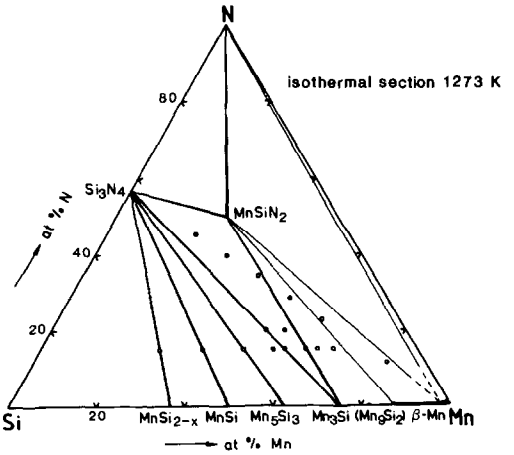

FIG. 1. Isothermal section of the ternary system Mn–Si–N at 1000°C (in the absence of external nitrogen pressure).

TABLE I

SOLID-STATE REACTION PRODUCTS OBSERVED IN THE SYSTEM Mn–Si–N UPON ANNEALING AT 1000°C, 120 h (EVACUATED QUARTZ TUBES)

$Mn_{0.366}Si_{0.634}$ (am) + Si_3N_4 (15 at.% N)	→	$Si_3N_4 + MnSi_{2-x}$
$Mn_{0.50}Si_{0.50}$ (am) + Si_3N_4 (15 at.% N)	→	$Si_3N_4 + MnSi + Mn_5Si_3$
$Mn_{0.625}Si_{0.375}$ (am) + Si_3N_4 (15 at.% N)	→	$Si_3N_4 + Mn_5Si_3$
$Mn_{0.714}Si_{0.286}$ (am) + Si_3N_4 (15 at.% N)	→	$Si_3N_4 + Mn_5Si_3 + Mn_3Si$
$Mn_{0.75}Si_{0.25}$ (am) + Si_3N_4 (15 at.% N)	→	$Si_3N_4 + Mn_3Si + MnSiN_2$
$Mn_{0.75}Si_{0.25}$ (am) + Si_3N_4 (20 at.% N)	→	$Si_3N_4 + Mn_3Si + MnSiN_2$
$Mn_{0.818}Si_{0.182}$ (am) + Si_3N_4 (20 at.% N)	→	$Mn_3Si + MnSiN_2$
$Mn_{0.85}Si_{0.15}$ (am) + Si_3N_4 (15 at.% N)	→	$Mn_3Si + MnSiN_2 + \beta$-Mn(s.s.)
$Mn_{0.90}Si_{0.10}$ (am) + Si_3N_4 (15 at.% N)	→	$Mn_3Si + MnSiN_2 + \beta$-Mn(s.s.)

Note. am stands for arc-melted.

room temperature X-ray diffraction of alloys annealed at 1273 K under 5×10^4 Pa nitrogen and quenched to liquid nitrogen temperature shows the formation of cubic ε-Mn_4N. However, *in situ* high-temperature X-ray diffraction of a specimen having the same nominal composition indicates the existence of a hexagonal phase at 1273 K, confirming Kudielka and co-workers (*31*).

The Ternary System Iron–Silicon–Nitrogen

All phases and crystal structures reported for the binary Fe–Si system (*22, 23*) are corroborated and confirmed. According to Kudielka (*34*) the high-temperature phase Fe_2Si is hexagonal; however, quenching in water was claimed to be insufficient to retain the hexagonal symmetry and a primitive cubic pattern is obtained instead (*35*). The lattice parameters found are for Fe_2Si_5: $a = 0.26879$ nm, $c = 0.51281$ nm; $FeSi_2$: $a = 0.98789$ nm, $b = 0.78038$ nm, $c = 0.78408$ nm; FeSi: $a = 0.44844$ nm; Fe_5Si_3: $a = 0.67426$ nm, $c = 0.47146$ nm; α_2-Fe_3Si: $a = 0.28100$ nm at the Si-rich phase boundary; α_1-Fe_3Si: $a = 0.5650$ nm (at 75 at.% Fe).

Two isothermal sections have been established in the ternary Fe–Si–N. At 900°C (Fig. 3) Si_3N_4 was found to coexist with all binary silicides stable at this temperature and α-Fe (Table II). At 1150°C (Fig. 4) Si_3N_4 is decomposed by pure iron, forming α-Fe containing 6–8 at.% Si in solid solution. The onset of this decomposition reaction was observed at 1120 ± 10°C. All other binary phases stable 1150°C were found to coexist with Si_3N_4 (Table II). However, as mentioned in the previous section, the phase Fe_2Si could not be observed, probably due to insufficient quenching. Specimens along the tieline Si_3N_4 + Fe_2Si showed the X-ray diffraction patterns of Si_3N_4, Fe_5Si_3, and Fe_3Si. It was not possible

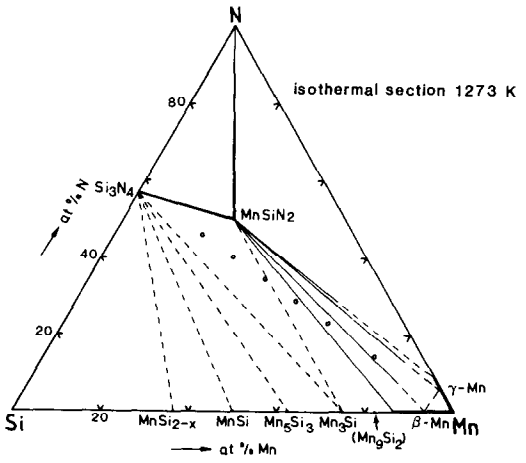

FIG. 2. Isothermal section of the ternary system Mn–Si–N at 1000°C (external nitrogen pressure not negligible).

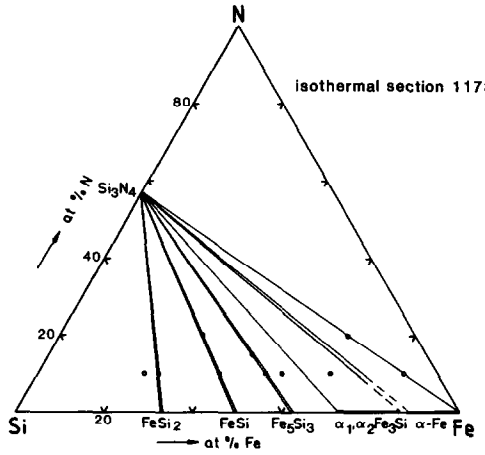

FIG. 3. Isothermal section of the ternary system Fe–Si–N at 900°C (in the absence of external nitrogen pressure).

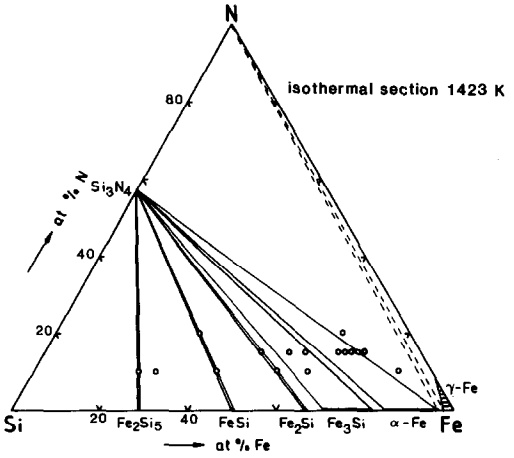

FIG. 4. Isothermal section of the ternary system Fe–Si–N at 1150°C (in the absence of external nitrogen pressure).

to distinguish between α_1- and α_2-Fe_3Si due to coincidences of X-ray diffraction lines of Si_3N_4 with the weak lines characteristic for the ordered α_1-Fe_3Si phase. However, the smaller lattice parameter of α_2-Fe_3Si (a = 0.282 nm) with respect to the α_1-Fe_3Si subcell ($a = 2 \times a_0 = 2 \times 0.283$ nm) served as an indicator.

TABLE II

SOLID-STATE REACTION PRODUCTS IN THE SYSTEM Fe–Si–N

Upon annealing at 900°C for 340 h (evacuated quartz tube)			
$Fe_{0.33}Si_{0.67}$ + Si_3N_4	(10 at.% N)	→	$FeSi_2$ + Si_3N_4
$Fe_{0.50}Si_{0.50}$ + Si_3N_4	(20 at.% N)	→	FeSi + Si_3N_4
$Fe_{0.625}Si_{0.375}$ + Si_3N_4	(15 at.% N)	→	Fe_5Si_3 + Si_3N_4
$Fe_{0.67}Si_{0.33}$ + Si_3N_4	(10 at.% N)	→	Fe_5Si_3 + α_2-Fe_3Si + Si_3N_4
$Fe_{0.75}Si_{0.25}$ + Si_3N_4	(10 at.% N)	→	α_1-Fe_3Si + Si_3N_4
Fe + Si_3N_4	(10 at.% N)	→	α-Fe + Si_3N_4
Fe + Si_3N_4	(20 at.% N)	→	α-Fe + Si_3N_4
Upon annealing at 1150°C for 170 h (evacuated quartz tube)			
$Fe_{0.285}Si_{0.715}$ + Si_3N_4	(10 at.% N)	→	Fe_2Si_5 + FeSi + Si_3N_4
$Fe_{0.33}Si_{0.67}$ + Si_3N_4	(10 at.% N)	→	Fe_2Si_5 + FeSi + Si_3N_4
$Fe_{0.50}Si_{0.50}$ + Si_3N_4	(20 at.% N)	→	FeSi + Si_3N_4
$Fe_{0.625}Si_{0.375}$ + Si_3N_4	(10 at.% N)	→	Fe_5Si_3 + α_2-Fe_3Si(a = 0.2834 nm) + Si_3N_4 (insufficient quench)
$Fe_{0.67}Si_{0.33}$ + Si_3N_4	(10 at.% N)	→	α_2-Fe_3Si (a = 0.2823 nm) + Si_3N_4
Upon annealing at 1150°C for 60 h (RF-furnace, 10^5 Pa argon)			
$Fe_{0.75}Si_{0.25}$ + Si_3N_4	(15 at.% N)	→	α_1-Fe_3Si(a = 0.56549 nm) + Si_3N_4
$Fe_{0.90}Si_{0.10}$ + Si_3N_4	(15 at.% N)	→	α-Fe (a = 0.28601 nm) + Si_3N_4

TABLE III

SOLID-STATE REACTION PRODUCTS OBSERVED IN THE SYSTEM Co–Si–N UPON ANNEALING AT 1000°C, 170 h (EVACUATED QUARTZ TUBES)

$Co_{0.33}Si_{0.67}$ + Si_3N_4	(20 at.% N)	→ $CoSi_2$ + Si_3N_4
$Co_{0.50}Si_{0.50}$ + Si_3N_4	(10 at.% N)	→ CoSi + Si_3N_4
$Co_{0.625}Si_{0.375}$ + Si_3N_4	(10 at.% N)	→ CoSi + L.T.-Co_2Si + Si_3N_4
$Co_{0.67}Si_{0.33}$ + Si_3N_4	(10 at.% N)	→ L.T.-Co_2Si + Si_3N_4
Co + Si_3N_4	(10 at.% N)	→ Co(α + ε) + Si_3N_4

The Ternary System Cobalt–Silicon–Nitrogen

The three intermediate phases reported to exist at 1000°C in the Co–Si system (*23–25, 33*) are corroborated and confirmed. The lattice parameters found are for $CoSi_2$: a = 0.53526 nm; CoSi: a = 0.44449 nm; L.T.-Co_2Si: a = 0.49073 nm, b = 0.37333 nm, c = 0.70963 nm. The high-temperature phases H.T.-Co_2Si and Co_3Si were not observed under the experimental conditions chosen.

At 1000°C Si_3N_4 coexists with cobalt and all binary cobalt silicides stable at this temperature (Table III). The onset of a reaction between Si_3N_4 and Co is found to be at 1170°C from log p versus temperature data. No ternary phase is observed. No solubility of nitrogen in the binary silicides is detected. An isothermal section at 1000°C is shown in Fig. 5.

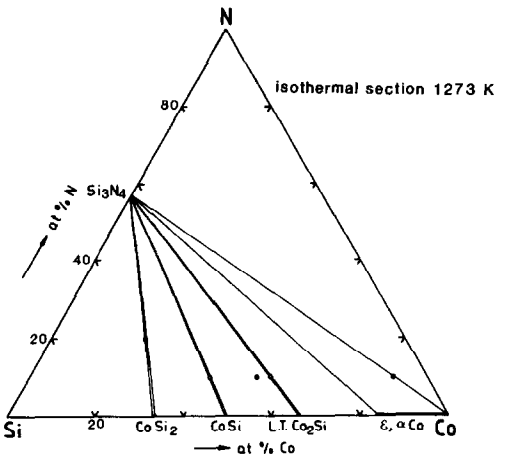

FIG. 5. Isothermal section of the ternary system Co–Si–N at 1000°C (in the absence of external nitrogen pressure).

The Ternary System Nickel–Silicon–Nitrogen

All the phases and crystal structures reported for the binary system Ni–Si (*26–28, 33*) are corroborated and confirmed with the exception of the high-temperature modifications of $NiSi_2$, Ni_2Si, and Ni_3Si. Attempts to obtain H.T.-Ni_2Si by quenching an alloy from 940 and 1020°C, respectively, into liquid nitrogen did not result in the formation of the desired phase. No specific effort was made to obtain H.T.-$NiSi_2$ or H.T.-Ni_3Si. The lattice parameters of the silicides found are for L.T.-$NiSi_2$: a = 0.54030 nm; NiSi: a = 0.51810 nm, b = 0.33365 nm, c = 0.56140 nm; Ni_3Si_2: a = 1.22363 nm, b = 1.08135 nm, c = 0.69213 nm; L.T.-Ni_2Si: a = 0.50040 nm, b = 0.37333 nm, c = 0.70715 nm; $Ni_{31}Si_{12}$: a = 0.66777 nm, c = 1.2280 nm; $Ni_{25}Si_9$: a = 0.67022 nm, c = 2.88954 nm; L.T.-Ni_3Si: a = 0.35098 nm.

In the ternary system Ni–Si–N Si_3N_4 coexists at 900°C with nickel and all binary nickel silicides stable at this temperature (Table IV). Decomposition of Si_3N_4 by Ni is very fast above 1170°C, but below this temperature Ni and Si_3N_4 seem to coexist. No ternary phase is observed. No solubility of nitrogen in the binary silicides is de-

TABLE IV

SOLID STATE REACTION PRODUCTS IN THE SYSTEM Ni–Si–N UPON ANNEALING AT 900°C UP TO 340 h (EVACUATED QUARTZ TUBES)

$Ni_{0.33}Si_{0.67}$ + Si_3N_4	(10 at.% N)	→ L.T.-$NiSi_2$ + NiSi + Si_3N_4
$Ni_{0.50}Si_{0.50}$ + Si_3N_4	(10 at.% N)	→ NiSi + Si_3N_4
$Ni_{0.60}Si_{0.40}$ + Si_3N_4	(10 at.% N)	→ Ni_3Si_2 + L.T.-Ni_2Si + Si_3N_4
$Ni_{0.67}Si_{0.33}$ + Si_3N_4	(15 at.% N)	→ L.T.-Ni_2Si + Si_3N_4
$Ni_{0.715}Si_{0.285}$ + Si_3N_4	(15 at.% N)	→ L.T.-Ni_2Si + Si_3N_4
$Ni_{0.75}Si_{0.25}$ + Si_3N_4	(18 at.% N)	→ L.T.-Ni_3Si + Si_3N_4
Ni + Si_3N_4	(10 at.% N)	→ Ni + Si_3N_4

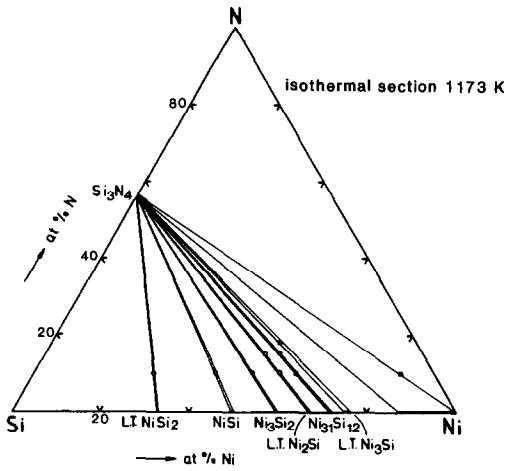

FIG. 6. Isothermal section of the ternary system Ni–Si–N at 900°C (in the absence of external nitrogen pressure).

tected. The isothermal section at 900°C is shown in Fig. 6.

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