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Silicon nitride–metal joints: phase equilibria in the systems Si_3Ni_4–Cr, Mo, W and Re

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Phase diagrams in the ternaries Cr–Si–N, Mo–Si–N, W–Si–N and Re–Si–N are established. No ternary phase is found. Si_3N_4 coexist under argon at 1273 K with all binary Cr-silicides but not with chromium, with $MoSi_2$ and Mo_5Si_3 but not with Mo_3Si or molybdenum, with WSi_2, W_5Si_3 and tungsten, and with $ReSi_2$, $Re_{17}Si_9$ and rhenium. At 1673 K, Si_3N_4 is found in coexistence with Cr_5Si_3, $MoSi_2$, Mo_5Si_3, WSi_2, W_5Si_3, $ReSi_2$ and $Re_{17}Si_9$. The implications of these phase equilibria for joining silicon nitride with low thermal expansion metals are discussed.

1. Introduction

Silicon nitride is one of the materials attracting attention due to its high strength at elevated temperatures. Practical applications frequently require these ceramics to be joined with structural metals. Upon thermal cycling, however, differences in thermal expansion cause considerable stress at the metal–ceramic interface. The use of metals with matching thermal expansion will reduce this internal stress to a level small enough to be accommodated by mechanical deformation of the metal rather than failure of the joint, but to ensure sufficient service lifetime of the joint at the temperatures of interest (> 1273 K), a higher chemical stability of Si_3N_4 compared to the metal at the interface is required. Because the coefficient of thermal expansion, α, for Si_3N_4 is $3.2 \times 10^{-6}\,{}^\circ C^{-1}$ [1], phase equilibria of Si_3N_4 with molybdenum, tungsten and rhenium, the metals with the smallest coefficient of thermal expansion, as well as with chromium were systematically investigated. The mechanical implications of the resulting reaction products in equilibrium with Si_3N_4 at the interface are discussed in terms of phase transformations and thermal expansion of these phases.

2. Literature review

2.1. Cr–Si–N System

Silicon nitride was found to react with chromium at temperature as low as 900° C [2]. The reaction was described as fast and violent at temperatures of 1830° C and above [3, 4]. The reaction products formed in an alloy Si_3N_4 + 50 vol % Cr after annealing at 1173 K (30 min, moderate vacuum of 10^{-2} torr) were Cr_3Si, Cr_5Si_3, Cr_2N and CrN. After annealing at 1373 K (30 min, moderate vacuum of 10^{-2} torr) the reaction products were Cr_3Si, Cr_5Si_3 and a trace of Si_3N_4 [2]. Krilov and Bronnikov [5] reported Cr_3Si, Cr_5Si_3, CrSi, $CrSi_2$, Cr_2N, CrN, silicon and nitrogen gas to be the products of the reaction of Si_3N_4 with variable amounts of chromium under otherwise not further specified conditions. From thermochemical data these authors calculate $Si_3N_4 + 17\,Cr$ to form $3Cr_3Si + 4Cr_2N$. Nitriding an alloy $Cr_{0.10}Si_{0.90}$ (wt %) resulted in the formation of Si_3N_4 and chromium nitride [6]. Earlier experiments [7] of heating for 12 h at 1673 K under hydrogen, a powder mixture of chromium, silicon and silicon nitride which had a composition along the tie-line Cr_5Si_3–N led to the formation of Cr_5Si_3 with W_5Si_3-type structure from an alloy initially containing 10 at. % nitrogen and to the formation of Cr_3Si from an alloy initially containing 20 at. % nitrogen. Champion *et al.* [8] report Si_3N_4 and "Cr_3Si_2", probably Cr_5Si_3, to be compatible under vacuum at 1773 K.

The reaction and phase relations in the system Cr–Si–N at 1873 K under 10^5 Pa nitrogen were investigated by Kato *et al.* [9] and their results are presented in an isothermal section (Fig. 1d). These data confirm all earlier observations in so far that all experiments which have led to the formation of chromium nitrides must have been performed under external nitrogen pressure (even if it was as low as 1 Pa). In the absence of external nitrogen, no chromium nitrides are found [7].

2.2. Mo–Si–N System

Molybdenum and silicon nitride seem to coexist up to 1273 K. Thin Si_3N_4 films deposited on hot molybdenum substrates in order to manufacture thin layer capacitors were described to be usable up to 1273 K [10, 11] and TZM alloy (which contains 94 wt % Mo) takes up only 1 wt % silicon and 350 p.p.m. nitrogen upon heat treatment in contact with Si_3N_4 over 1173 h at 1273 K or 1125 h at 1373 K [12]. However, Khalepa [2] reports the formation of Mo_2N upon annealing Si_3N_4 + 50 vol % Mo at 1273 K for 30 min under moderate vacuum (10^{-2} torr) and the formation of $MoSi_2$, Mo_5Si_3 and Mo_3Si upon heating at 1473 K. Nowotny *et al.* [7] observed that nitriding Mo_5Si_3 at 1673 K with NH_3 results in the formation of Mo +

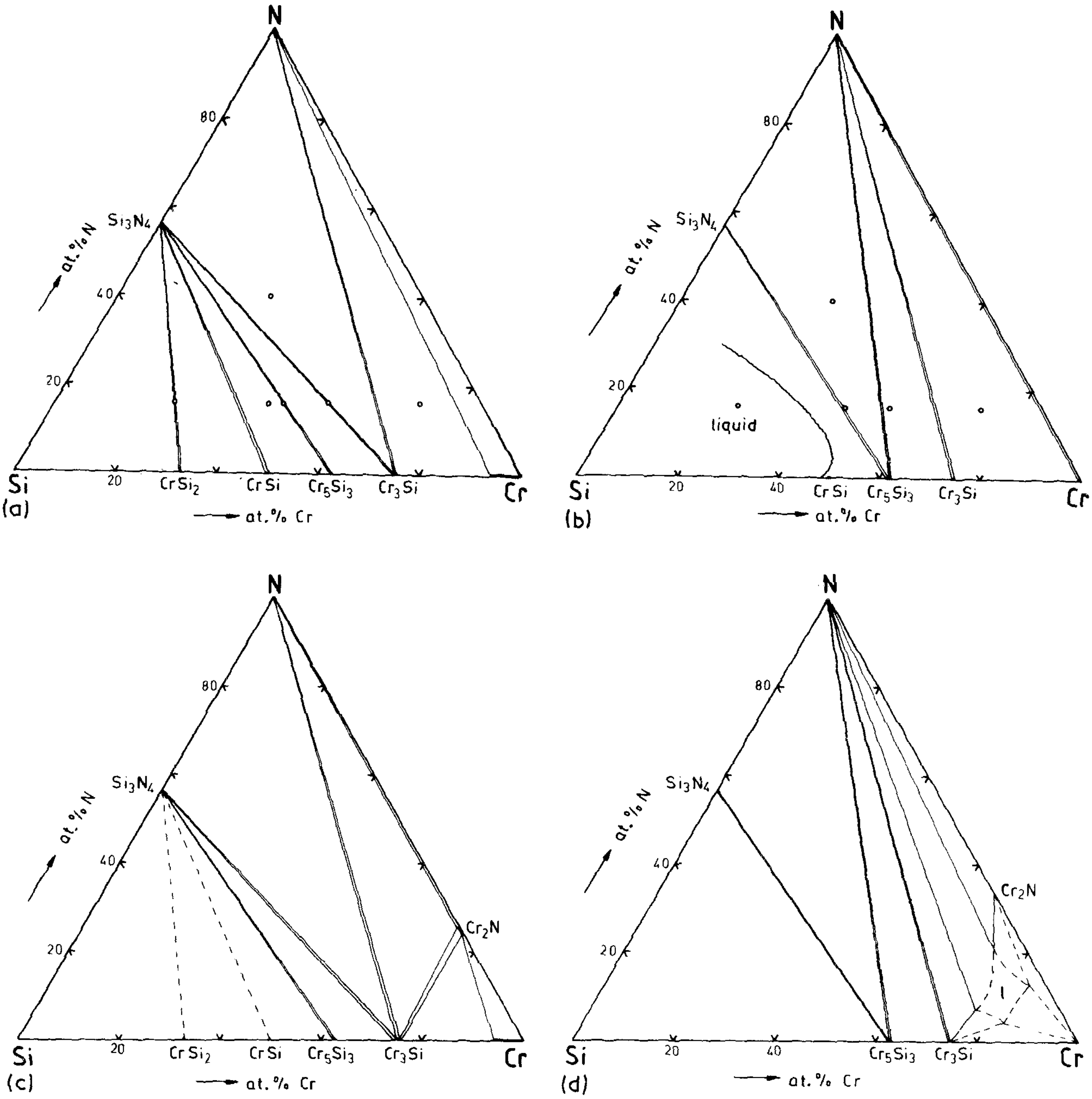

Figure 1 Cr–Si–N system. (a) Isothermal section at 1273 K (under argon), (b) isothermal section at 1673 K (under argon), (c) isothermal section at 1273 K (under small external nitrogen partial pressure), (d) isothermal section at 1873 K (under 10^5 Pa N_2).

Mo_3Si; nitriding $MoSi_2$ at 1673 K with NH_3 yielded Mo_5Si_3. On annealing an Mo–Si powder mixture (37.5 at. % silicon) blended with Si_3N_4 powder (nominal nitrogen content of the specimen: 20 at. %) at 1973 K, Mo_5Si_3 and nitrogen gas are formed.

Fitzer and Reinmuth [13] report that $MoSi_2$ react at 1553 K with nitrogen (1 atm) to form Mo_5Si_3 and Si_3N_4; at 1848 K the Si_3N_4 is decomposed with release of nitrogen and the freed silicon reacts with Mo_5Si_3 to form $MoSi_2$. Müller-Zell and Hennicke [1] prepared Si_3N_4 + Mo ceramic–metal joints by hot pressing at 2023 K under pressures varying from 1×10^{12} to 3×10^{12} Pa. In the intermediate layer formed, Mo_5Si_3 was identified. Suganuma and co-workers [14, 15] observed Si_3N_4–Mo couples in the interface Mo_5Si_3 and Mo_3Si after pressure sintering at 1990 K, 3×10^9 Pa.

2.3. W–Si–N System

The reaction of Si_3N_4 with tungsten has been investigated between 1573 K and 2373 K. In all cases the formation of the binary tungsten silicides W_5Si_3 and WSi_2 is reported [1, 2, 16, 17]. No ternary phase is observed. Fitzer and Reinmuth [13] report that WSi_2 reacts at 1523 K with nitrogen (1 atm) to form W_5Si_3 and Si_3N_4; at 1723 K the Si_3N_4 is decomposed with the release of nitrogen and the freed silicon reacts with W_5Si_3 to form WSi_2.

2.4. Re–Si–N System

No data have been found in the literature.

3. Experimental details

The starting materials used were silicon powder (purity 99.9%, Alpha Div., Ventron Corp., USA), chromium

TABLE I Solid state reaction products observed in the system Cr–Si–N

(a) Upon annealing at 1273 K for 400 h (evacuated quartz tube)

Si_3N_4 + 30 at.% Cr	→ Si_3N_4 + Cr_3Si
Si_3N_4 + 72 at.% Cr	→ Cr_3Si + Cr_2N
$Cr_{0.33}Si_{0.67}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + $CrSi_2$ + trace CrSi
$Cr_{0.625}Si_{0.375}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + Cr_5Si_3
$Cr_{0.75}Si_{0.25}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + Cr_3Si

(b) Upon annealing at 1673 K for 40 h (r.f. furnace, 10^5 Pa argon)

Si_3N_4 + 30 at.% Cr	→ Si_3N_4 + Cr_5Si_3
Si_3N_4 + 72 at.% Cr	→ Cr_3Si
$Cr_{0.625}Si_{0.375}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + Cr_5Si_3
$Cr_{0.75}Si_{0.25}$ + Si_3N_4 (16 at.% N)	→ Cr_5Si_3 + Cr_3Si

powder (purity 99.95%, Alpha Div., Ventron Corp., USA), molybdenum powder (purity 99.9%, Metallwerk Plansee, Austria), tungsten powder (purity 99.9%, Metallwerk Plansee, Austria), rhenium powder (purity 99.99%, Johnson, Matthey and Brandenberger, Switzerland) and silicon nitride powder ($\alpha + \beta Si_3N_4$, 58% Si; Alpha Div., Ventron Corp., USA).

Binary metal silicides were synthesized by arc melting appropriate powder mixtures under purified argon. Ternary powder compacts were prepared by mixing and cold pressing binary metal silicide powder and silicon nitride powder. The green compacts were heat treated at 1273 K, 400 h in evacuated, sealed quartz tubes lined with molybdenum foil. Heat treatment at higher temperatures (up to 1773 K, 40 h) was done in a r.f. furnace under pure argon (purity > 99.999%). All specimens were analysed by X-ray diffraction using 118 mm Debye-Scherrer and Guinier-Huber cameras. ($CuK\alpha_1$ radiation, internal standard: germanium.)

4. Experimental results

4.1. Cr–Si–N System

In agreement with literature data, Si_3N_4 is found to be decomposed on contact with chromium. At 1273 K, Si_3N_4 coexists with $CrSi_2$, CrSi, Cr_5Si_3 and Cr_3Si. This phase is in equilibrium with nitrogen gas. In the absence of external nitrogen pressure, no chromium nitride is stable at 1273 K. However, the nitrogen released upon Si_3N_4 decomposition by chromium provides sufficient nitrogen partial pressure inside an evacuated quartz tube to stabilize Cr_2N. Under these conditions Cr_3Si is found to coexist with Cr_2N (Table I). The respective phase equilibria, without external nitrogen pressure (Fig. 1a) and with small external nitrogen pressure (Fig. 1c) are presented in isothermal sections.

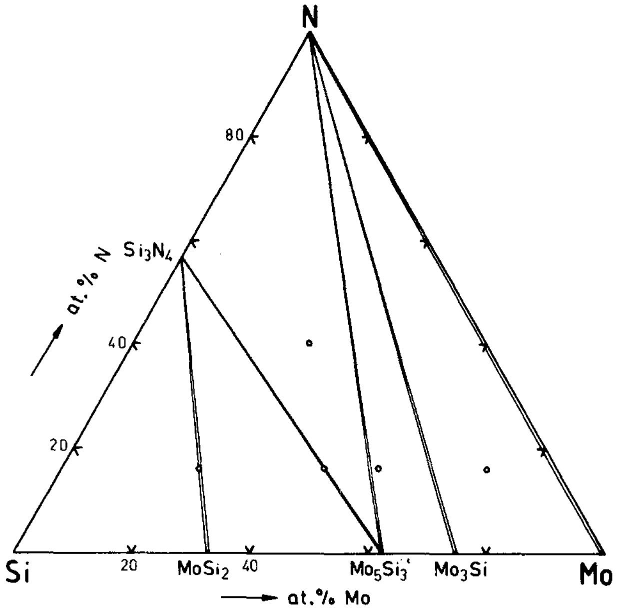

Figure 2 Mo–Si–N system. Isothermal section at 1673 K (under argon).

At 1673 K, a tie-line between Cr_5Si_3 and nitrogen gas exists. Therefore reaction between Si_3N_4 and Cr_3Si yields Cr_5Si_3 (and N_2) (Table I). The phase equilibria at this temperature in the absence of external nitrogen pressure are shown in Fig. 1b. No nitrogen solubility in binary chromium silicides is observed.

4.2. Mo–Si–N System

The reaction between Si_3N_4 and molybdenum proceeds very slowly at 1273 K. In the absence of external nitrogen pressure, Si_3N_4 coexists with $MoSi_2$ and Mo_5Si_3, but not Mo_3Si and Mo. However, even after 400 h, the reaction is incomplete (Table II).

At 1673 K the same equilibria are observed (Fig. 2); according to Fitzer and Reinmuth [13] at 1848 K the tie-line between Si_3N_4 and Mo_5Si_3 is reversed and $MoSi_2$ coexists with nitrogen gas at this and higher temperatures. No ternary phase was found.

4.3. W–Si–N System

At 1273 K, Si_3N_4 is found not to react with tungsten or any tungsten silicide (Table III). An isothermal section is presented in Fig. 3a. The Si_3N_4–W tie-line exists up to 1400 K. At this temperature a reaction

TABLE II Solid state reaction products observed in the Mo–Si–N system

(a) Upon annealing at 1273 K for 400 h (evacuated quartz tube)

Si_3N_4 + 30 at.% Mo	→ Si_3N_4 + Mo_3Si + Mo
$Mo_{0.33}Si_{0.67}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + $MoSi_2$
$Mo_{0.625}Si_{0.375}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + Mo_5Si_3
$Mo_{0.75}Si_{0.25}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + Mo_5Si_3 + Mo_3Si

(b) Upon annealing at 1673 K for 40 h (r.f. furnace, 10^5 Pa argon)

Si_3N_4 + 30 at.% Mo	→ Si_3N_4 + Mo_5Si_3
$Mo_{0.33}Si_{0.67}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + $MoSi_2$ + Mo_5Si_3
$Mo_{0.625}Si_{0.375}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + Mo_5Si_3
$Mo_{0.75}Si_{0.25}$ + Si_3N_4 (16 at.% N)	→ Mo_5Si_3 + Mo_3Si

TABLE III Solid state reaction products observed in the W–Si–N system

(a) Upon annealing at 1273 K for 400 h (evacuated quartz tubes)

Si_3N_4 + 30 at.% W	→ Si_3N_4 + W
Si_3N_4 + 72 at.% W	→ Si_3N_4 + W
$W_{0.33}Si_{0.67}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + WSi_2
$W_{0.625}Si_{0.375}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + W_5Si_3

(b) Upon annealing at 1673 K for 40 h (r.f. furnace, 10^5 Pa argon)

Si_3N_4 + 30 at.% W	→ Si_3N_4 + W_5Si_3
Si_3N_4 + 72 at.% W	→ W_5Si_3 + W
$W_{0.33}Si_{0.67}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + WSi_2 + W_5Si_3
$W_{0.625}Si_{0.375}$ + Si_3N_4 (16 at.% N)	→ Si_3N_4 + W_5Si_3

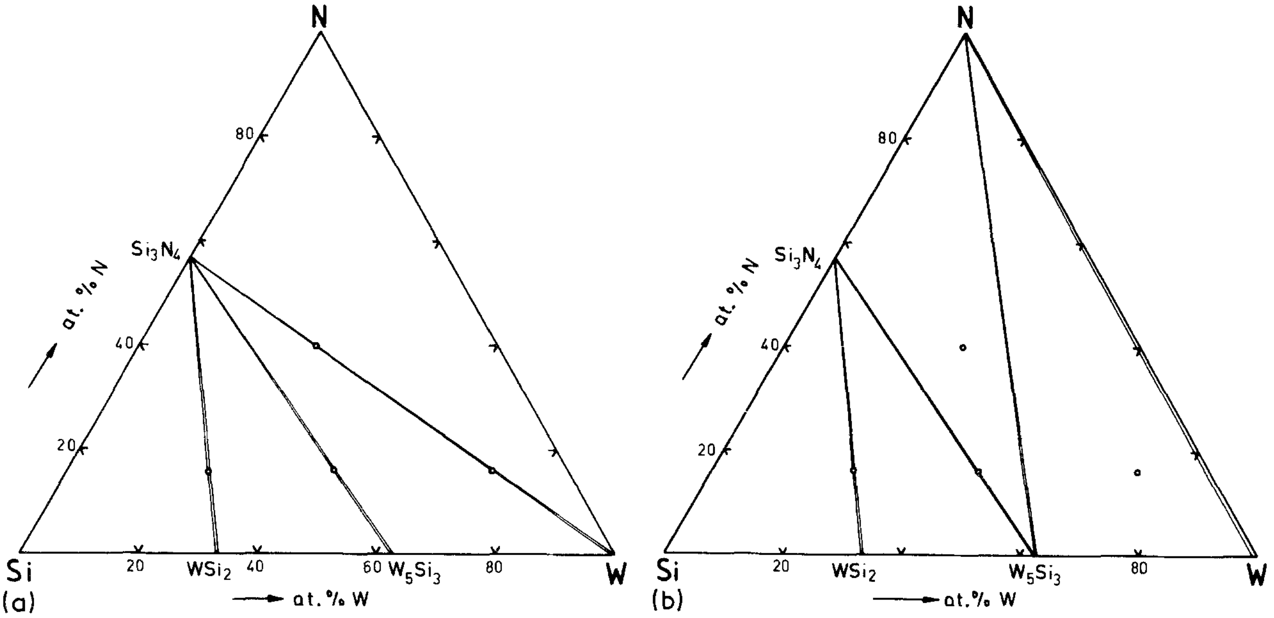

Figure 3 W–Si–N system. (a) Isothermal section at 1273 K (under argon), (b) isothermal section at 1673 K (under argon).

takes place with the formation of W_5Si_3 and nitrogen gas. The resulting phase equilibria (isothermal section at 1673 K) are shown in Fig. 3b. At 1773 K WSi_2, also, coexists with nitrogen [13].

4.4. Re–Si–N System

At 1273 K no reaction between Si_3N_4 and rhenium is observed (Table IV). Si_3N_4 is in equilibrium with $ReSi_2$, $Re_{17}Si_9$ and rhenium (Fig. 4a). No ternary phase exists. At 1673 K, Si_3N_4 reacts with rhenium and forms $Re_{17}Si_9$ and nitrogen gas (Table IV). The resulting phase equilibria are shown in Fig. 4b.

5. Discussion

Due to the chemical reaction of chromium, molybdenum, tungsten and rhenium with Si_3N_4, good chemical bonding results for such metal–ceramic joints. In fact, wetting experiments [8] for example, the pair Cr_5Si_3–Si_3N_4 yielded a contact angle of $\theta = 80°$ at 1773 K under vacuum. However, the formation of increasingly more silicon-rich silicides upon increasing the temperature causes increasingly higher internal stresses at the metal–ceramic interface of the joint. In Table V literature values of the coefficients of thermal expansion are compiled and the thermal mismatch for Si_3N_4–metal or silicide couples relevant for elevated temperature regimes are given. Athough the values of the coefficients of thermal expansion for the metal silicides are close to the values of the respective metals, the low ductility of the metal silicides formed, as compared to the respective metals, will result in low fracture toughness and brittle failure of such metal–

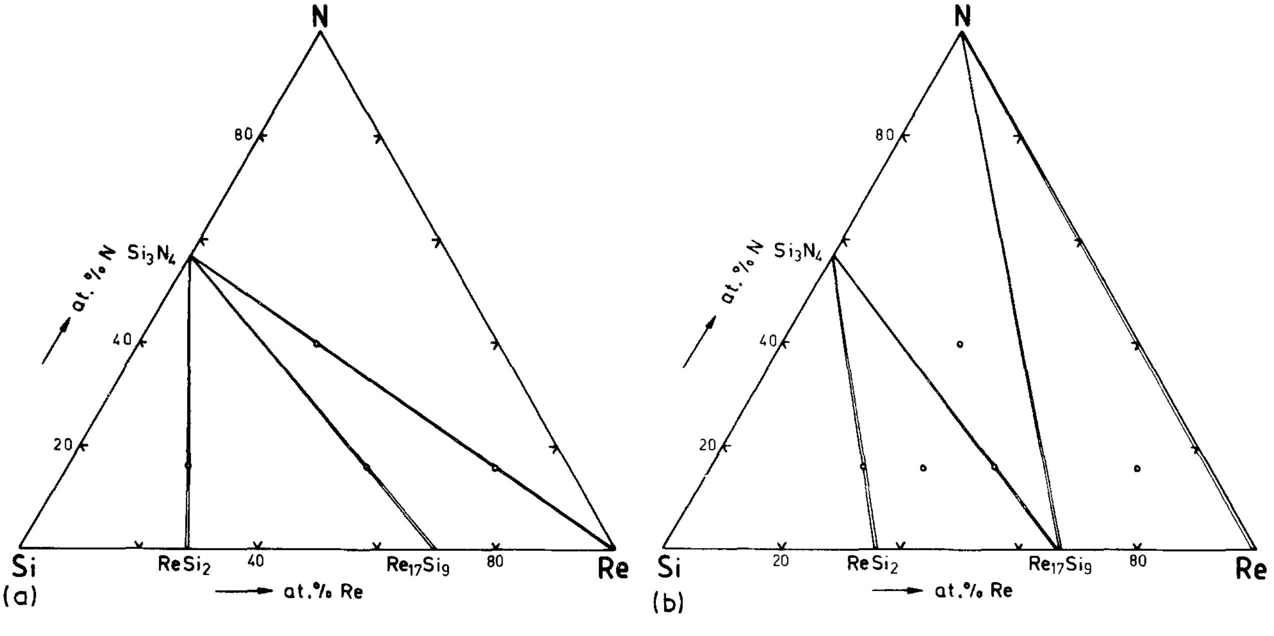

Figure 4 Re–Si–N system. (a) Isothermal section at 1273 K (under argon), (b) isothermal section at 1673 K (under argon).

TABLE IV Solid state reaction products observed in the Re–Si–N system

(a) Upon annealing at 1273 K for 400 h (evacuated quartz tubes)

Si_3N_4 + 30 at. % Re	→ Si_3N_4 + Re
Si_3N_4 + 72 at. % Re	→ Si_3N_4 + Re
$Re_{0.33}Si_{0.67}$ + Si_3N_4 (16 at. % N)	→ $ReSi_2$ + Si_3N_4
$Re_{0.50}Si_{0.50}$ + Si_3N_4 (16 at. % N)	→ $ReSi_2$ + $Re_{17}Si_9$ + Si_3N_4
$Re_{0.67}Si_{0.33}$ + Si_3N_4 (16 at. % N)	→ $Re_{17}Si_9$ + Si_3N_4

(b) Upon annealing at 1673 K for 40 h (r.f. furnace, 10^5 Pa argon)

Si_3N_4 + 30 at. % Re	→ $Re_{17}Si_9$ + Si_3N_4
Si_3N_4 + 72 at. % Re	→ $Re_{17}Si_9$ + Re
$Re_{0.33}Si_{0.67}$ + Si_3N_4 (16 at. % N)	→ $ReSi_2$ + Si_3N_4
$Re_{0.50}Si_{0.50}$ + Si_3N_4 (16 at. % N)	→ $ReSi_2$ + $Re_{17}Si_9$ + Si_3N_4
$Re_{0.67}Si_{0.33}$ + Si_3N_4 (16 at. % N)	→ $Re_{17}Si_9$ + Si_3N_4

ceramic joints. This view is supported by experimental evidence in the systems Si_3N_4–Cr [20], Si_3N_4–Mo and Si_3N_4–W [1].

Furthermore it can be seen from Table V, that only for the system Mo–Si–N does a pair of materials with relatively small thermal mismatch coexist over an extensive temperature range above 1273 K, not undergoing chemical reaction. Thus thermal cycling up to temperatures in the vicinity of 1650 to 1700 K, the operating temperatures desired for Si_3N_4 components and coatings, will cause thermal fatigue of Si_3N_4–Cr_3Si, W or Re joints due to silicide formation/decomposition within the temperature interval of interest.

6. Conclusions

It is concluded that the concept of strong and tough Si_3N–metal joints taking advantage of low thermal mismatch in specific material combinations fails due to the reaction of Si_3N_4 with the candidate metals chromium, molybdenum, tungsten and rhenium at elevated temperatures. Even at constant level of thermal mismatch between the ceramic and the silicide, the increased brittleness of the silicides formed relative to the respective metals as well as chemical transformations during thermal cycling, restricts the potential of such joints for structural applications at elevated temperatures.

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TABLE V Thermal mismatch $\Delta = \alpha_{phase} - \alpha_{Si_3N_4}$ of phases in the systems Si_3N_4–Cr, Mo, W, Re

Phase	Thermal expansion coefficient (20 to 1000° C) (10^{-6} °C^{-1})	Reference	Thermal mismatch, Δ (10^{-6} °C^{-1})	Comments
Cr	11.1	[18]	7.9	
Cr_3Si	10.5	[19]	7.1	Coexists with Si_3N_4 at 1273 K
Cr_5Si_3	11.1	[19]	7.9	Coexists with Si_3N_4 at 1273, 1673 K
Mo	6.2	[18]	3.0	
Mo_5Si_3	6.4	[19]	3.2	Coexists with Si_3N_4 at $T \leqslant 1848$ K
$MoSi_2$	8.3	[19]	5.1	
W	5.2	[18]	2.0	Coexists with Si_3N_4 at $T \leqslant 1400$ K
W_5Si_3	5.4	extrapolation	2.2	Coexists with Si_3N_4 at $T \leqslant 1773$ K
WSi_2	7.3	[19]	4.1	
Re	6.7	[18]	3.5	Coexists with Si_3N_4 at 1273 K
$Re_{17}Si_9$	n.d.	–	–	Coexists with Si_3N_4 at 1273, 1673 K

n.d. = not determined.