JOURNAL OF MATERIALS SCIENCE 32 (1997) 3031–3036

Interaction of Si_3N_4 with titanium at elevated temperatures

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In relation to the joining of silicon nitride ceramics to metal, the reaction products and the reaction mechanism between Si_3N_4 and titanium have been investigated under a nitrogen or an argon atmosphere at temperatures of 823–1573 K. Using Si_3N_4/titanium powder mixtures, reaction rates were determined by thermogravimetric (TG) analysis, and reaction products were examined by X-ray diffraction. At higher temperatures and on prolonged heating, reaction products were changed in the following orders: TiN_2, $TiN_2 + TiN$, $TiN + TiSi_2 + Si$, $TiN + Si$ and TiN (nitrogen atmosphere) and $TiN_2 + Ti_5Si_5$, $TiN_2 + TiN + Ti_5Si_3$ and $TiN + TiSi_2 + Si$ (argon). By relating these results to TG measurements, a full understanding of the reaction mechanism between Si_3N_4 and titanium was acquired.

1. Introduction

Silicon nitride ceramics, which have excellent high-temperature strength, good hardness, corrosion resistance and wear resistance, are important as the structural materials for high temperature applications. However, because of their brittle nature, the joining of the ceramics of metals is often adopted. During joining, the occurrence of new phases (reaction layer) are frequently observed as a result of the chemical reaction at the ceramic/metal interface, and the reaction layer grows further in service at elevated temperatures. The occurrence and the growth of the reaction layer strongly affects the mechanical properties of the joint. Therefore, information about the high temperature reactions that ultimately determine the integrity of the bond are considered to be necessary for obtaining successful joints. Furthermore, the compatibility between ceramics and metal is an important factor controlling the use of ceramics at elevated temperatures. However, the investigations from these aspects are incomplete. Thus, the authors have investigated the interaction of Si_3N_4 with nickel [1, 2], iron [3], chromium [4–6], molybdenum [7], niobium [8], tungsten [9] and manganese [10] in great detail.

Titanium is reactive with ceramics, and has a high level of toughness and a low thermal expansion coefficient. Therefore, in joining silicon nitride ceramics to metals or to ceramics, titanium is used as the insertion metal and brazing alloy [11–14]. In present work, using the powder mixture of Si_3N_4 and titanium, the reaction products and the reaction mechanisms were investigated by thermogravimetry and X-ray diffraction at temperatures of 823 to 1573 K and under a nitrogen or an argon atmosphere.

2. Experimental procedure

The starting materials were silicon nitride powder (α fraction: $\geqslant 95$, purity: 98.5%, mean particle size: 0.2 μm) and titanium powder (purity: 99.5%, mean particle size: 7 μm). They were thoroughly mixed in a silicon nitride mortar, and the mixture of 2 g of Si_3N_4 and 2 g of titanium was compacted into a tablet of 20 mm in diameter.

The thermobalance unit used for thermogravimetry (TG) consists of an analogue-type automatic recording balance (measurable limit: 100 g, sensitivity: 0.1 mg) and an SiC resistance furnace.

The temperature was measured with a Pt/Pt–13%Rh thermocouple positioned close to the sample. When the desired temperature was reached, either nitrogen or argon gas was flowed from the bottom of the furnace at $2.5 \times 10^{-5}\ m^3\,s^{-1}$. A tablet specimen was placed in a magnesia crucible of 26 mm in inner diameter and 35 mm in depth. The magnesia crucible was suspended in the hot zone of the furnace (alumina reaction tube of 44 mm in inner diameter) with a platinum wire connected to the balance. The mass change was recorded automatically during each experiment. Upon completion of the measurement, the specimen was quenched by raising the crucible rapidly to the lower temperature zone of the furnace. The reaction products were analysed by X-ray diffractometer (XRD).

3. Results

3.1. TG curve

Fig. 1 shows TG curves for Si_3N_4/titanium mixture heated continuously at heating rate of $1\ K\,min^{-1}$ under both Ar and N_2 atmospheres. For comparison with Si_3N_4/titanium mixture, TG curves for Si_3N_4/nickel, Si_3N_4/iron, Si_3N_4/chromium and Si_3N_4/molybdenum mixtures also are shown in Fig. 1. Under an argon atmosphere, no mass change was observed for Si_3N_4/titanium mixture, although the mass loss was observed for other mixtures. Under a nitrogen atmosphere, Si_3N_4/titanium mixture exhibited the mass gain above about 700 K, while other mixtures exhibited the mass loss. It may be noted that, above 1350 K, the mass loss changed to the mass gain for Si_3N_4/chromium mixture. Shapes of TG curves are greatly dependent upon the reactivity of metal to nitrogen. Titanium is one of the most reactive metals to nitrogen. Therefore, all of the nitrogen from Si_3N_4 reacted with titanium to form nitrides. No generation of nitrogen gas resulted in no mass change for Si_3N_4/titanium mixture heated under an argon atmosphere. In addition, the mass gain occurred under a nitrogen atmosphere, because titanium was nitrided by nitrogen gas.

Figs 2 and 3 show TG curves for Si_3N_4/titanium mixture heated isothermally under a nitrogen atmosphere. Below 1073 K, the mass increased monotonously with the lapse of time. Above 1123 K, TG curves were divided into three stages, as follows: first stage at which the mass increased rapidly; second stage at which the mass decreased abruptly; and third stage at which the mass increased again. All stages were shortened with increasing temperature. Below 1273 K, the third stage was completed earlier, and then no mass change observed. At temperatures of 1323 to 1423 K, the mass gain continued gradually. Above 1473 K, the drastic mass gain occurred immediately after the gradual mass gain. Fig. 4 shows TG curves for Si_3N_4/titanium mixture heated under an argon atmosphere. No mass change was found below 1273 K. Above 1373 K, a slight mass loss occurred rapidly within 100 s, and then the mass remains unchanged. As discussed later, the mass gain was attributed to the nitridation of titanium, while the mass loss was attributed to the decomposition of Si_3N_4 and the formation of $TiSi_2$.

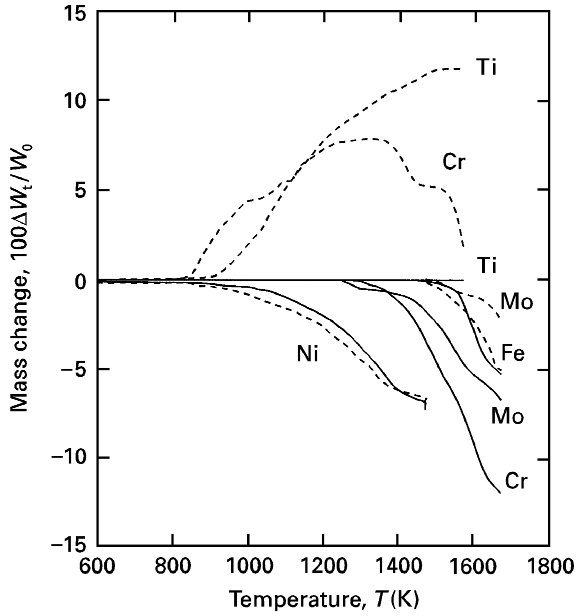

Figure 1 Mass change with reaction of Si_3N_4–Ti mixture heated continuously at $1\ K\,min^{-1}$. (——) Ar stream; (– – –) N_2 stream.

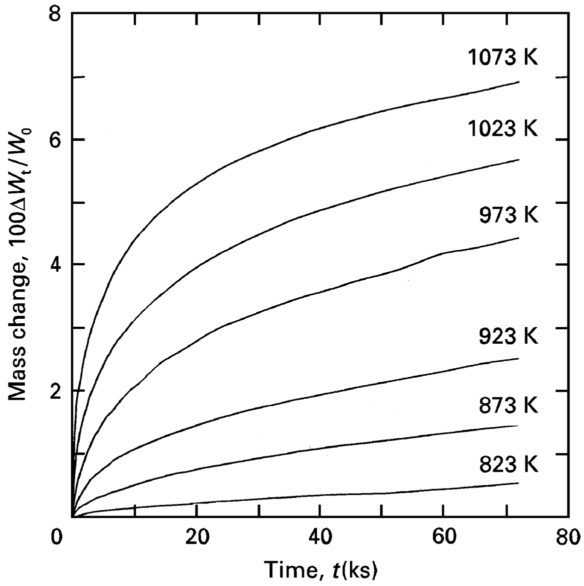

Figure 2 Mass gain with reaction of Si_3N_4–Ti mixture heated isothermally at temperatures from 823 to 1073 K in N_2 gas stream.

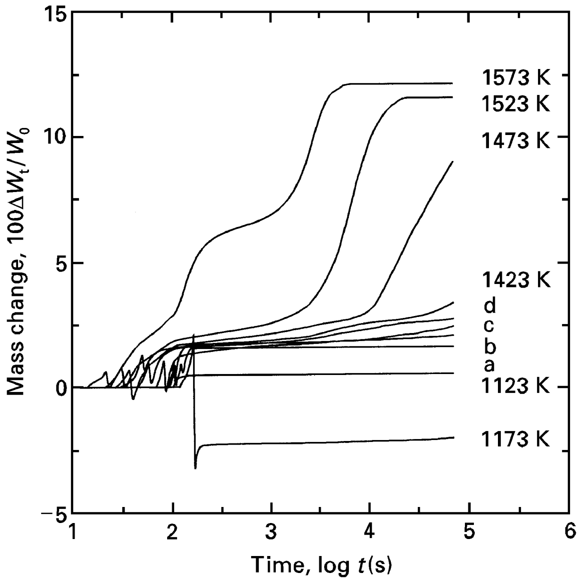

Figure 3 Mass change with reaction of Si_3N_4–Ti mixture heated isothermally at temperatures from 1123 to 1573 K in N_2 gas stream. (a) 1223 K; (b) 1273 K; (c) 1323 K; (d) 1373 K.

3.2. X-ray diffraction

Figs 5 and 6 show XRD patterns of Si_3N_4/titanium mixtures heated at temperatures of 873 to 1573 K for

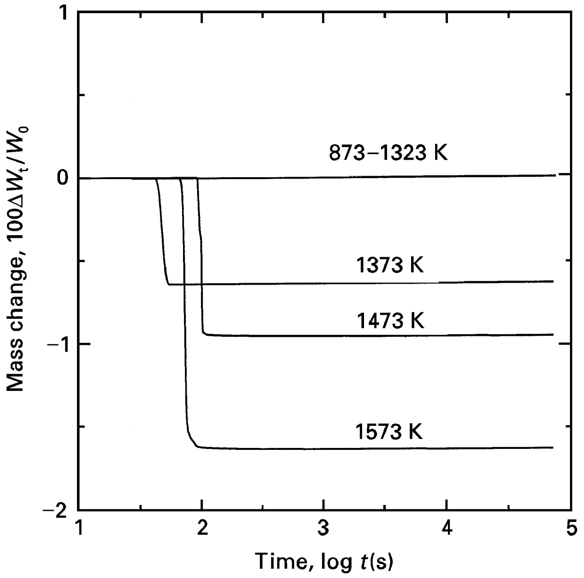

Figure 4 Mass change with reaction of Si_3N_4–Ti mixture heated isothermally at temperatures from 873 to 1573 K in Ar gas stream.

72 ks under a nitrogen atmosphere and an argon atmosphere, respectively. Titanium nitrides (Ti_2N, TiN), titanium silicides (Ti_5Si_3, $TiSi_2$) and Si were detected as the reaction products. The isothermal changes in reaction products are summarized in Figs 7 and 8. At higher temperatures and on prolonged heating, the reaction products changed in the following orders: TiN_2, TiN_2 + TiN, TiN + $TiSi_2$ + Si, TiN + Si and TiN (nitrogen atmosphere) and TiN_2, TiN_2 + TiN + Ti_5Si_3 and TiN + $TiSi_2$ + Si (argon atmosphere). Abrupt changes in reaction products were observed at 1073 to 1123 K under a nitrogen atmosphere and at 1323 to 1373 K under an argon atmosphere, respectively. The abrupt changes corresponded to the abrupt mass loss observed in TG curves (Figs 3 and 4).

4. Discussion

4.1. Reaction between Si_3N_4 and titanium under nitrogen atmosphere

Below 1073 K, TG curves showed a monotonous mass gain (Fig. 2). Then, Ti_2N alone was produced below 923 K, and it changed to TiN with rising temperature (Fig. 7). A similar result is reported for the reaction between titanium sheet and nitrogen gas [15]. At 823 K, a mass gain was observed (Fig. 2), though no titanium nitride was detected. The phase diagram suggests the formation of the Ti–N solid solution [16]. Thus the Ti–N solid solution and the titanium nitrides were produced by the reactions between titanium particles and nitrogen gas.

$$1/2\mathrm{N}_2(\mathrm{g}) = N(\text{in Ti}) \qquad (1)$$

$$2\mathrm{Ti(s)} + 1/2\mathrm{N}_2(\mathrm{g}) = \mathrm{Ti}_2\mathrm{N(s)} \qquad (2)$$

$$\mathrm{Ti(s)} + 1/2\mathrm{N}_2(\mathrm{g}) = \mathrm{TiN(s)} \qquad (3)$$

At temperatures from 1123 to 1573 K, TG curves were divided into three stages. At first stage, titanium reacted with nitrogen gas to form TiN, resulting in a mass gain. Then the solid state reaction between Si_3N_4 and titanium also occurred simultaneously, and consequently $TiSi_2$ and Si, as well as TiN, were produced (Fig. 7). These reactions are represented by the

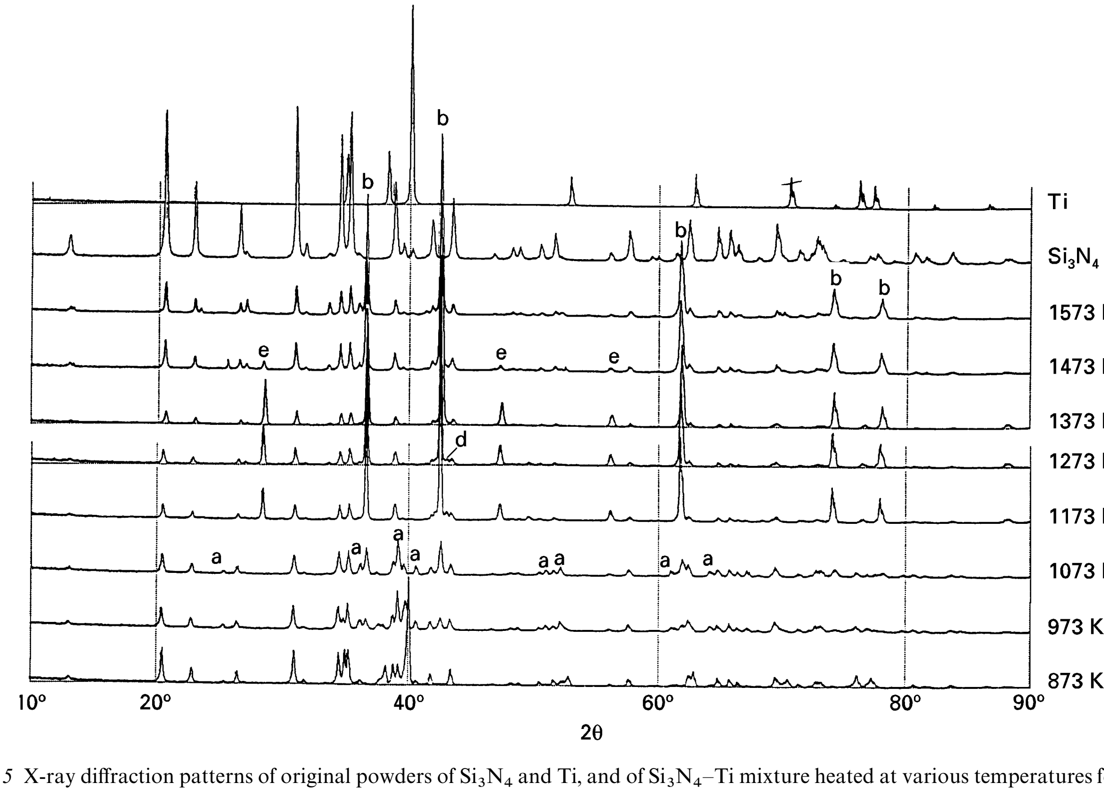

Figure 5 X-ray diffraction patterns of original powders of Si_3N_4 and Ti, and of Si_3N_4–Ti mixture heated at various temperatures for 72 ks in N_2 gas stream. (a) Ti_2N; (b) TiN; (c) Ti_5Si_3; (d) $TiSi_2$; (e) Si.

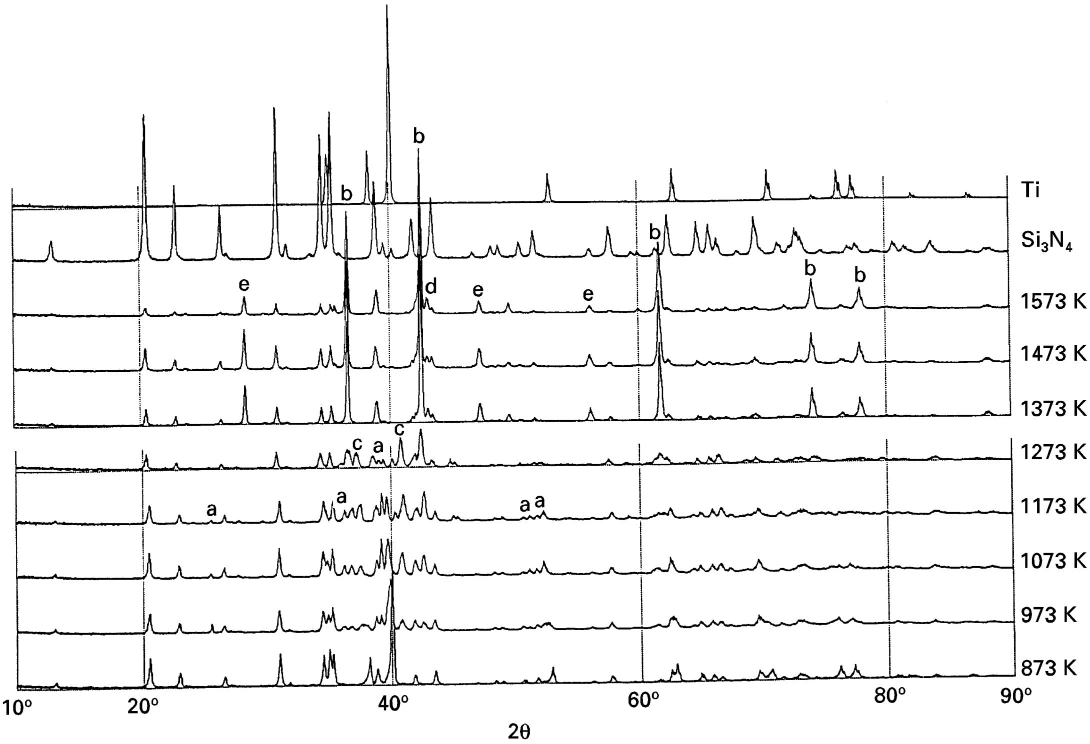

Figure 6 X-ray diffraction patterns of original powders of Si_3N_4 and Ti, and of Si_3N_4–Ti mixture heated at various temperatures for 72 ks in Ar gas stream. (a) Ti_2N; (b) TiN; (c) Ti_5Si_3; (d) $TiSi_2$; (e) Si.

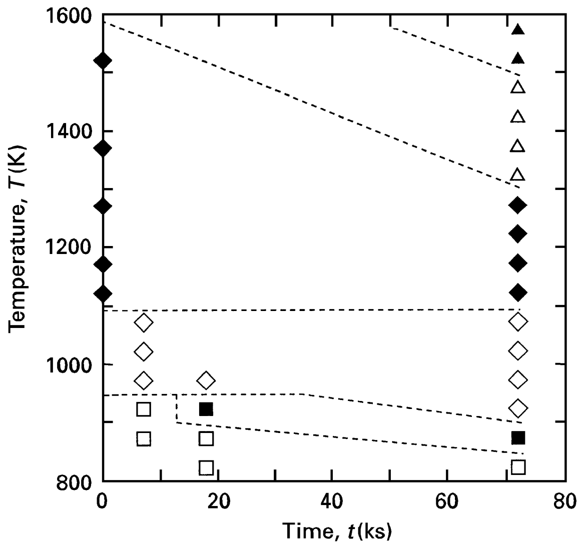

Figure 7 Temperature versus time diagram for reaction products of Si_3N_4 with Ti in N_2 gas stream. (▲) TiN; (△) TiN + Si; (◆) TiN + $TiSi_2$ + Si; (◇) TiN + Ti_2N; (■) Ti_2N; (□) Ti_2N.

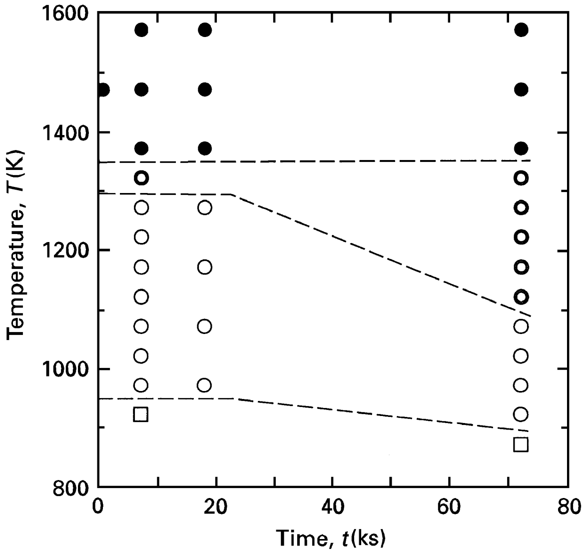

Figure 8 Temperature versus time diagram for reaction products of Si_3N_4 with Ti in Ar gas stream. (●) TiN + $TiSi_2$ + Si; (**O**) TiN + Ti_2N + Ti_5Si_3; (○) Ti_2N; (□) Ti_2N.

equations

$$Si_3N_4(s) + 4Ti(s) = 4TiN(s) + 3Si(s) \quad (4)$$

$$\Delta G^0(\mathrm{J\,mol^{-1}}) = -613\,000 + 40.80T(\mathrm{K}) \; [17]$$

$$Ti(s) + 2Si(s) = TiSi_2(s) \quad (5)$$

$$\Delta G^0(\mathrm{J\,mol^{-1}}) = -140\,200 + 5.44T(\mathrm{K}) \; [17]$$

Negative free energies (G) indicate that above reactions must proceed at the experimental temperatures.

At second stage, an abrupt mass loss occurred, indicating that nitrogen gas was generated. The X-ray diffraction showed the formation of $TiSi_2$ and free silicon. These results present the following reactions

$$4Si_3N_4(s) + 6TiN(s) = 6TiSi_2(s) + 11N_2(g) \quad (6)$$

$$\Delta G^0(\mathrm{J\,mol^{-1}}) = -451\,1540 - 1779.66T(\mathrm{K}) \; [17]$$

$$Si_3N_4(s) = 3Si(l) + 2N_2(g) \quad (7)$$

$$\Delta G^0(\mathrm{J\,mol^{-1}}) = -874\,460 - 405.01T(\mathrm{K}) \; [17]$$

The experimental temperatures are much lower than the temperatures at which Equations 6 and 7 can proceed thermodynamically under a nitrogen atmosphere of 1.01×10^5 Pa: 2535 and 2297 K higher, respectively. Since Equations 3, 4 and 5 are highly exothermic, the temperature of Si_3N_4/titanium mixture seems to exceed the initiation temperature of Equations 6 and 7. At higher temperatures and on prolonged heating, the reaction products changed in the sequence of TiN + $TiSi_2$ + Si, TiN + Si and TiN. Thus, $TiSi_2$ and Si disappeared and the mass increased significantly (Fig. 3). These results are attributed to the following reactions

$$6TiSi_2(s) + 11N_2(g) = 4Si_3N_4(s) + 6TiN(s) \tag{8}$$

$$\Delta G^0(\mathrm{J\,mol^{-1}}) = -451\,1540 + 1779.66\,T(\mathrm{K})$$

$$3Si(s) + 2N_2(g) = Si_3N_4(s) \tag{9}$$

$$\Delta G^0(\mathrm{J\,mol^{-1}}) = -723\,830 + 315.06\,T(\mathrm{K})$$

The temperature of Si_3N_4/titanium mixture decreased after the termination of second stage, and consequently Equations 6 and 7 proceeded in the reverse direction. Therefore, the temporary increase in temperature led to the transient production of free silicon. In addition, no $TiSi_2$ can coexist with Si_3N_4 and TiN at equilibrium below 2535 K. Finally, only titanium nitride was the stable phase under a nitrogen atmosphere. Therefore, the mass gain at third stage is responsible for the progress of Equations 8 and 9. This is substantiated in Fig. 9 which represents the relative X-ray intensities of Si and Si_3N_4. Since Ti was not detected in the reacted sample, it was adopted as the internal standard material. Thus, the relative X-ray intensity was the ratio of intensity for Si (1 1 1) and Si_3N_4 (2 0 1) to that for Ti (1 0 1). With a steep decrease of Si, Si_3N_4 increased significantly, and correspondingly the remarkable mass gain was observed. From this result, obviously, it could be seen that Equation 9 proceeded.

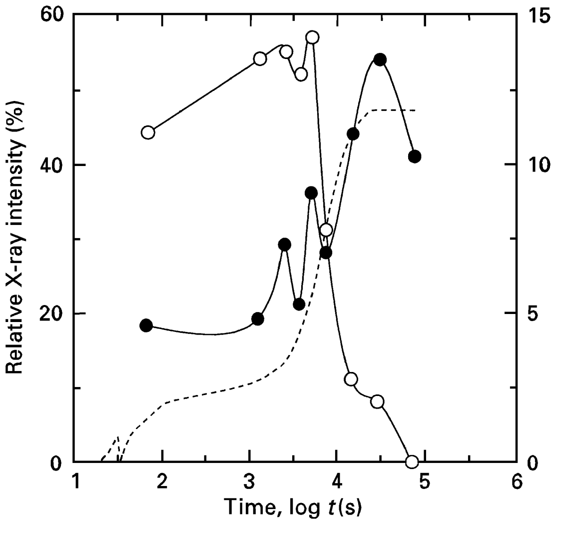

Figure 9 Relative X-ray intensities of reaction products at 1523 K in N_2 gas stream. (○) Si; (●) Si_3N_4; (- - - -) mass change.

4.2. Reaction between Si_3N_4 and titanium under argon atmosphere

Below 1323 K, the mass remained unchanged (Fig. 4), though Ti_2N, TiN and Ti_5Si_3 were produced (Fig. 8). From this result, the following reactions may be considered

$$Si_3N_4(s) + 8Ti(s) = 4Ti_2N(s) + 3Si(s) \tag{10}$$

$$Si_3N_4(s) + 4Ti(s) = 4TiN(s) + 3Si(s) \tag{4}$$

$$\Delta G^0(\mathrm{J\,mol^{-1}}) = -613\,000 + 40.80\,T(\mathrm{K})$$

$$5Ti(s) + 3Si(s) = Ti_5Si_3(s) \tag{11}$$

$$\Delta G^0(\mathrm{J\,mol^{-1}}) = -194\,140 + 16.74T(\mathrm{K})$$

All the reactions can proceed below 1323 K, since the free energy changes are negative. Because free Si reacted immediately with Ti to form Ti_5Si_3, it was not detected by the X-ray diffraction. The nitride changed from Ti_2N to TiN at higher temperatures and on prolonged heating. Elsewhere, similar results were obtained [4, 6, 8, 10].

Above 1373 K, TiN, $TiSi_2$ and Si were produced by Equations 4 and 5

$$Si_3N_4(s) + 4Ti(s) = 4TiN(s) + 3Si(s) \tag{4}$$

$$Ti(s) + 2Si(s) = TiSi_2(s) \tag{5}$$

The abrupt decreases in mass were observed after about 100 s. This phenomenon was caused by the occurrence of Equation 7.

$$Si_3N_4(s) = 3Si(l) + 2N_2(g) \tag{7}$$

Neither Equation 2 nor 3 proceed under an argon atmosphere. Therefore, it was the exothermic reactions (Equations 4 and 5) that raised the temperature of the Si_3N_4/titanium mixture up to the initiation temperature of Equation 7. Since Equations 4 and 5 were less exothermic than Equations 2 and 3, the temperature, at which Equation 7 occurred, was 250 K higher under an argon atmosphere than under a nitrogen atmosphere. The endothermic reaction (Equation 7) stopped immediately, owing to the temperature drop of the mixture. Therefore, the mass loss was momentary, as shown in Fig. 4. This is demonstrated in Fig. 10 which shows the relative X-ray intensities of the reaction products at 1523 K under an argon atmosphere. 100 s after the mass was lost rapidly, the intensities of TiN, Si, $TiSi_2$ and Si_3N_4 remained unchanged.

The abrupt decreases in mass were not observed, when the powder mixture was heated slowly (Fig. 1). A similar result is considered to be obtained in the reaction between Si_3N_4 and titanium block, which proceeds very slowly. This seems to be because the heat of reaction is sufficiently liberated and consequently no temperature rise of the mixture occurs.

5. Conclusions

Using a powder mixture of Si_3N_4 and titanium, the reaction products and the reaction mechanisms were

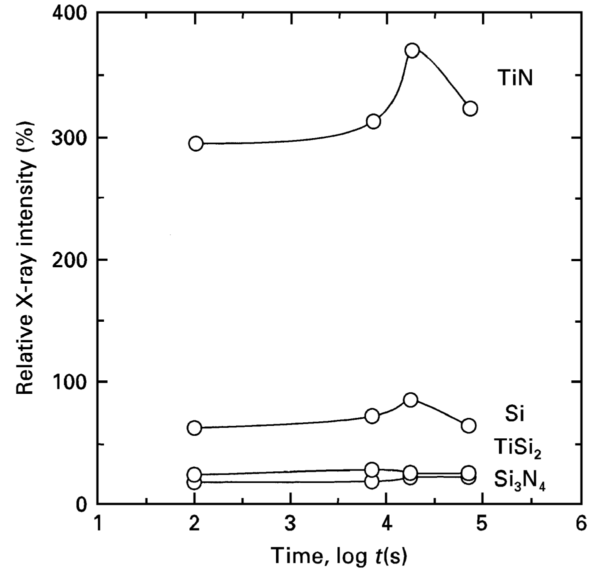

Figure 10 Relative X-ray intensities of reaction products at 1473 K in Ar gas stream.

investigated under a nitrogen or an argon atmosphere. The following results were obtained.

1. Under a nitrogen atmosphere and below 1073 K, Ti_2N and TiN were produced by the nitriding of titanium and a monotonous mass gain was observed. Above 1123 K, the reaction was divided into three stages. At the first stage, titanium was nitrided by nitrogen gas and consequently a mass gain was observed. At the second stage, the mass decreased abruptly, and TiN, Si and $TiSi_2$ were produced. At the third stage, the mass gain was observed, and both Si and $TiSi_2$ disappeared.
2. Under an argon atmosphere and below 1323 K, no mass change was observed, though Ti_2N, TiN and Ti_5Si_3 were produced. Above 1373 K, TiN, $TiSi_2$ and Si were produced, and the mass remained unchanged, except that the mass decreased abruptly at about 100 s.
3. The occurrence of exthothermic reactions raised temporarily the temperature of the Si_3N_4/titanium mixture, resulting in the decomposition of Si_3N_4 and the production of free silicon.

Acknowledgement

The authors thank the Tanikawa Foundation for financial support of this work.

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Received 18 October 1995
and accepted 20 January 1997