JOURNAL OF MATERIALS SCIENCE 29 (1994) 2231–2237

Interaction of Si_3N_4 with Cr

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The interaction of Si_3N_4 with chromium was investigated under an argon or nitrogen atmosphere at temperatures from 773–1573 K. Reaction rates were determined by thermogravimetric analysis, and reaction products were examined by X-ray diffraction. Cr_2N, Cr_3Si, Cr_5Si_3 and CrSi were produced under argon, while reaction products under nitrogen were Cr_2N, CrN and Cr_3Si. Possible reactions between Si_3N_4 and chromium have been discussed thermodynamically. The initial rate obeyed a linear rate law. When chromium particles were coated with the reaction layer, the rate was described by a parabolic rate law. The reaction mechanism and the rate-determining step have been proposed.

1. Introduction

Silicon nitride ceramics are regarded as important structural materials for excellent high-temperature strength, resistance to wear and oxidation. However, because of their brittle nature, joining of the ceramics to metal is frequently required [1, 2]. In such cases, metals react with Si_3N_4 to form the reaction layers consisting of nitrides and silicides at the interface. The growth of reaction layers will strongly influence the mechanical properties of the Si_3N_4–metal bond and silicon nitride ceramics themselves [3]. Although much is known regarding wetting, metallizing and joining of Si_3N_4 to metals, the reaction kinetics and reaction mechanism are not yet fully understood; further work is therefore required.

Using powder mixtures of Si_3N_4–metal, a kinetic study has been conducted on the reactions between Si_3N_4 and metals. Previously, reports have been published on Si_3N_4–Ni [4, 5] and Si_3N_4–Fe [6]. Of the many metals, in particular, chromium is the main alloying element in iron-, nickel- and cobalt-based heat-resistant alloys. Therefore, the interaction of chromium with Si_3N_4 is of great interest. In the present study, the reaction kinetics of Si_3N_4 powder with chromium powder has been investigated under an argon or a nitrogen atmosphere, and the reaction products and the reaction mechanism were examined.

2. Experimental procedure

The starting materials were silicon nitride powder (Ube Industries Ltd, α fraction $\geqslant 95\%$, purity 98.5%, particle size 0.2 μm) and chromium powder (Wako Pure Chemical Industries Ltd, purity 99.9%, particle size 29 μm). They were thoroughly mixed in a silicon nitride mortar, and the mixture of 2 g Si_3N_4 and 2 g Cr was compacted into a tablet of 20 mm diameter.

The thermobalance unit used for thermogravimetric analysis (TGA) consisted in 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 argon or nitrogen was flowed from the bottom of the furnace at 2.5×10^{-5} $m^3 s^{-1}$. A tablet specimen was placed in a magnesia crucible (inner diameter 26 mm, depth 35 mm). The magnesia crucible was suspended in the hot zone of a furnace (alumina reaction tube of 44 mm inner diameter) with a platinum wire connected to a balance. The mass change was recorded automatically during each experiment. Upon completion of the measurement, the specimen was quenched by raising the crucible into the low-temperature zone of the furnace. The reaction products were analysed by X-ray diffraction.

3. Results

Fig. 1 shows the TGA curves for a Cr–Si_3N_4 mixture heated isothermally at temperatures from 1373–1573 K, in an argon atmosphere. The mass loss is associated with the evolution of nitrogen gas from the reaction of chromium with Si_3N_4, followed by the formation of silicides. The reaction proceeds rapidly during the initial stage, and then slows down with time. As mentioned later, this result is based on the formation of the reaction layer around chromium particles.

The isothermal TGA curves under a nitrogen atmosphere are given in Fig. 2. Below 1273 K, a continuous increase in mass is observed. Above 1373 K, TGA curves turn to the mass loss via a maxima, after a remarkable mass gain in the early stage. The mass gain measured with a thermobalance is due to the nitridation of chromium particles with nitrogen gas. In particular, at lower temperatures, only the mass gain is observed because the reaction between Si_3N_4 and chromium is not able to occur. This nitridation rate increases with an increase in temperature. As discussed later, the mass loss accompanied by the formation of Cr–Si solid solution and chromium silic-

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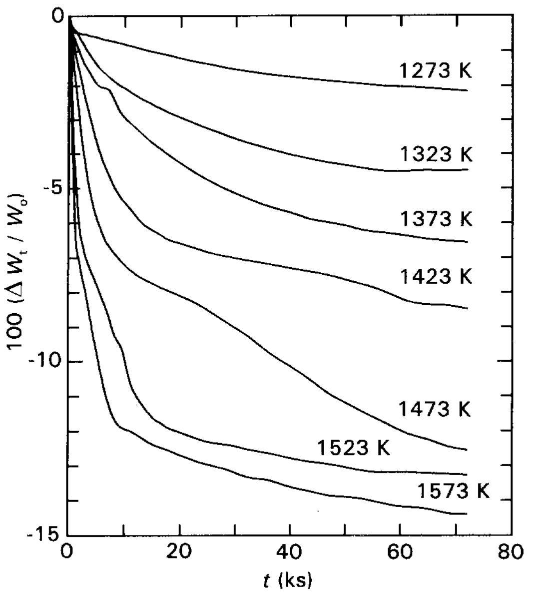

Figure 1 Mass loss with reaction of Si_3N_4–Cr mixture heated in an argon atmosphere at temperatures from 1273–1573 K.

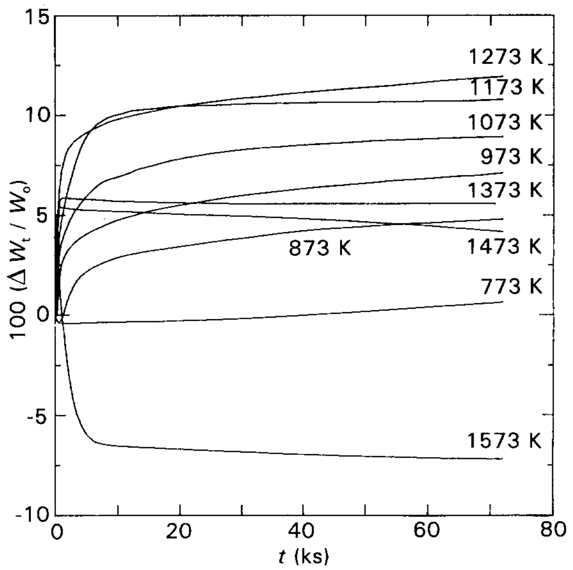

Figure 2 Mass change with reaction of Si_3N_4–Cr mixture heated in a nitrogen atmosphere at temperatures from 773–1573 K.

ide as a result of the reaction of Si_3N_4 with chromium nitrides at higher temperatures.

Figs 3 and 4 show the electron probe micro analysis (EPMA) line profiles for the coarse chromium particle (about 1 mm diameter) which was reacted with Si_3N_4 powder at 1423 K for 72 ks. The reaction layer of chromium silicide is observed at the surface of the chromium. The X-ray intensity fluctuates widely due to the pores which were formed by the generation of nitrogen gas.

Figs 5 and 6 show the relative X-ray intensities of the reaction products after heating for 72 ks. The relative X-ray intensity is the ratio of intensity for $Cr_2N(1\,1\,1)$, $CrN(2\,2\,0)$, $Cr_3Si(2\,1\,1)$, $Cr_5Si_3(0\,2\,2)$ or $CrSi(2\,1\,0)$ to that for $Si_3N_4(2\,1\,0)$, respectively. The X-ray diffraction intensity for $Si_3N_4(2\,1\,0)$, which was nearly constant in all samples, was adopted as a standard. Under an argon atmosphere, the reaction between Si_3N_4 and chromium yields Cr_2N, Cr_3Si, Cr_5Si_3 and CrSi. Cr_2N and Cr_3Si coexist at lower temperatures. With increasing temperature, Cr_2N disappears and the silicide changes from Cr_3Si to CrSi via Cr_5Si_3. Under a nitrogen atmosphere, the reaction products are Cr_2N, CrN and Cr_3Si. Below 1423 K, the reaction between chromium particles and nitrogen gas

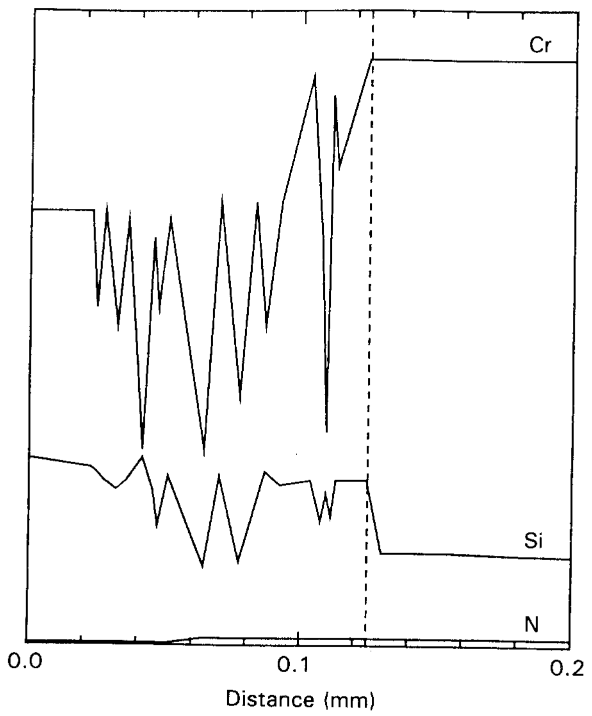

Figure 3 EPMA line analysis of a chromium particle reacted with Si_3N_4 in an argon atmosphere at 1423 K for 72 ks.

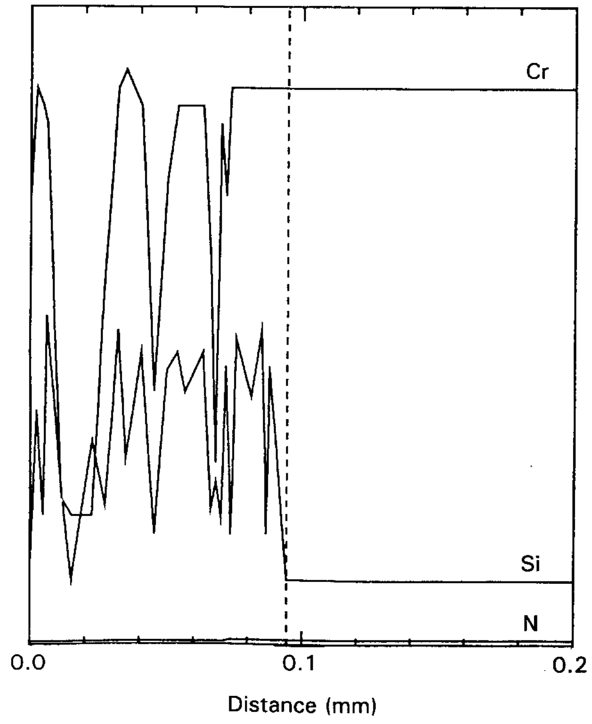

Figure 4 EPMA line analysis of a chromium particle reacted with Si_3N_4 in a nitrogen atmosphere at 1423 K for 72 ks.

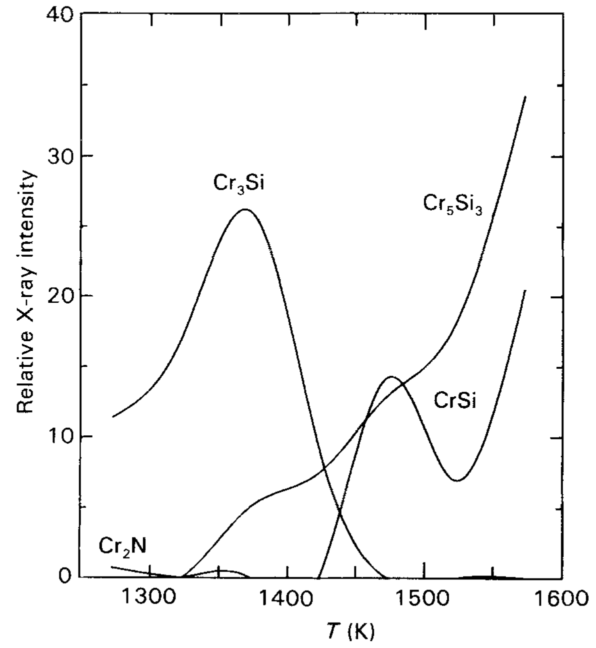

Figure 5 Relative X-ray intensities of reaction products in an argon atmosphere.

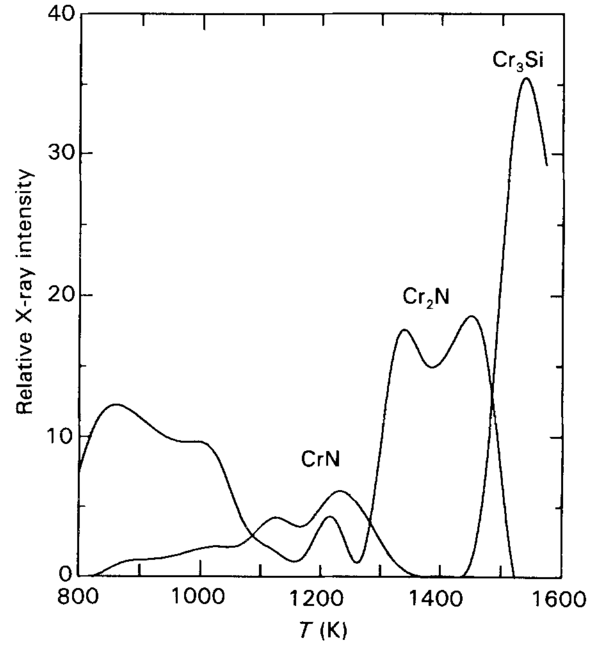

Figure 6 Relative X-ray intensities of reaction products in a nitrogen atmosphere.

yields only nitrides, as discussed later. Cr_3Si and Cr_2N coexist at 1473 and 1523 K. At 1573 K, Cr_2N disappears and Cr_3Si is only a product.

4. Discussion

4.1. Thermodynamic considerations

In general, thermodynamic equilibrium considerations may be used to predict the reactions which can proceed at the interface between Si_3N_4 and metal under given experimental conditions (temperature and partial pressure of nitrogen). The following reactions between Si_3N_4 and chromium are of particular importance [7]

$$Si_3N_4(s) + 9Cr(s) = 3Cr_3Si(s) + 2N_2(g) \quad (1)$$

$$\Delta G^\circ(\mathrm{J\,mol^{-1}}) = 405000 - 304.89\,T(\mathrm{K})$$

$$Si_3N_4(s) + 5Cr(s) = Cr_5Si_3(s) + 2N_2(g) \quad (2)$$

$$\Delta G^\circ(\mathrm{J\,mol^{-1}}) = 504600 - 330.62\,T(\mathrm{K})$$

$$Si_3N_4(s) + 3Cr(s) = 3CrSi(s) + 2N_2(g) \quad (3)$$

$$\Delta G^\circ(\mathrm{J\,mol^{-1}}) = 563200 - 326.73\,T(\mathrm{K})$$

$$2Si_3N_4(s) + 3Cr(s) = 3CrSi_2(s) + 4N_2(g) \quad (4)$$

$$\Delta G^\circ(\mathrm{J\,mol^{-1}}) = 1209200 - 624.21\,T(\mathrm{K})$$

Using free-energy data [8], equilibrium nitrogen pressure for possible reactions, p_{N_2} is calculated, and is given in Fig. 7 as a function of temperature.

At a nitrogen pressure of 1.01×10^5 Pa(= 1 atm), the formation temperatures of Cr_3Si, Cr_5Si_3, CrSi and $CrSi_2$ are 1328, 1526, 1723 and 1937 K, respectively. Thus, at the experimental temperatures lower than 1573 K, Cr_3Si and Cr_5Si_3 should be formed. However, all the above reactions will proceed in a flowing argon atmosphere, because the nitrogen pressure at the interface between Si_3N_4 and chromium is low. X-ray diffraction (XRD) confirms the formation of Cr_3Si, Cr_5Si_3 and CrSi. $CrSi_2$ is unable to be formed, because the mole ratio of silicon to chromium in the sample is smaller than 2. As indicated in Fig. 5, Cr_2N coexists with Cr_3Si at temperatures lower than 1473 K. Part of the nitrogen released in Reaction 1 provides sufficient nitrogen partial pressure to stabilize Cr_2N. Another nitride, CrN having larger equilibrium pressure of nitrogen is more unstable than Cr_2N, and hence is not produced in an argon atmosphere, as shown in Fig. 8.

$$4Cr(s) + N_2(g) = 2Cr_2N(s) \quad (5)$$

$$\Delta G^\circ(\mathrm{J\,mol^{-1}}) = -99200 + 46.99\,T(\mathrm{K})[8]$$

$$2Cr(s) + N_2(g) = 2CrN(s) \quad (6)$$

$$\Delta G^\circ(\mathrm{J\,mol^{-1}}) = -113400 + 73.22\,T(\mathrm{K})[8]$$

Cr_2N was not detected by XRD at temperatures higher than 1473 K. This result suggests that the following reaction has occurred

$$18Cr_2N(s) + 4Si_3N_4(s) = 12Cr_3Si(s) + 17N_2(g) \quad (7)$$

$$\Delta G^\circ(\mathrm{J\,mol^{-1}}) = 3405700 - 2065\,T(\mathrm{K})[8]$$

For example, on the basis of thermodynamic consideration, a nitrogen pressure less than 4.93×10^4 Pa is required for Reaction 7 to proceed at 1473 K. Therefore, this reaction is possible by the very small partial pressure of nitrogen in the argon stream.

Under a nitrogen atmosphere, chromium reacts with nitrogen in preference to Si_3N_4, and then Cr_2N and CrN are formed as detected by XRD. As a result, a mass gain is observed in the TGA curves. In particular, above 1473 K, the initial mass gain is due to the nitridation of chromium particles. At temperatures from 1373–1473 K, slight mass loss is measured after the initial increase in mass and CrN disappears (see

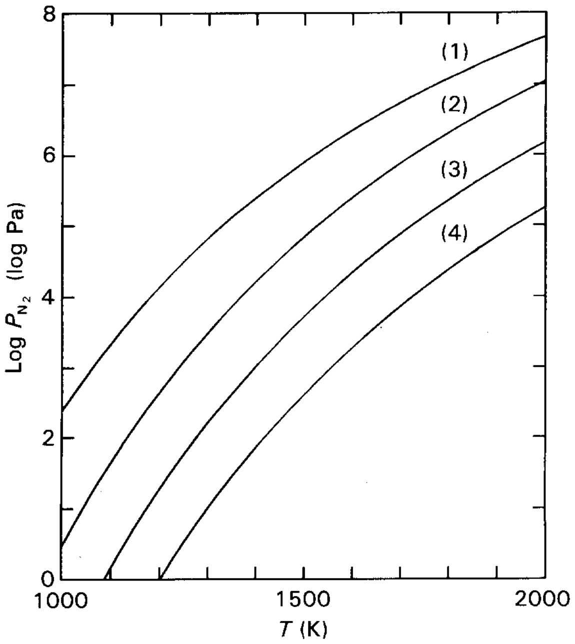

Figure 7 Log p_{N_2}–temperature diagram for Reactions 1–4.

Figs 4 and 6). This result indicates that Si_3N_4 interacts with the nitride layer formed around chromium particles, according to the following reaction

$$4CrN(s) + 2Si_3N_4(s) = 6\underline{Si}(\text{in Cr}) + 2Cr_2N(s) + 5N_2(g) \quad (8)$$

$$\Delta G^\circ(J\,mol^{-1}) = 1702\,800 - 829.02\,T(K)[8]$$

where $\underline{Si}$ stands for silicon dissolved in chromium as a solid solution. It is necessary for the progress of Reaction 8 that the value of Raoultian activity with respect to pure solid silicon is less than 2.6×10^{-4} at 1373 K and 1.4×10^{-3} at 1473 K. Because of very low solid solubility of silicon, very little mass loss is measured in TGA. Fig. 4 shows that chromium nitrides disappear and that Cr_3Si is produced on prolonged heating at high temperatures. Reactions 7 and 9 are considered to be the reaction occurring at the interface between nitride and Si_3N_4.

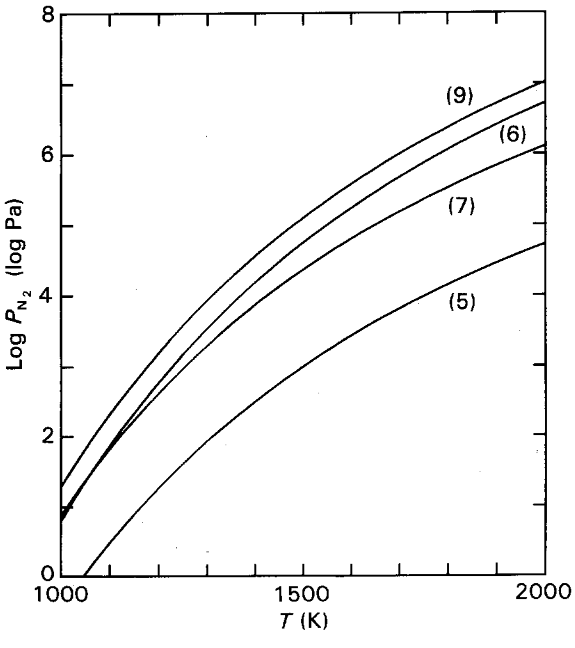

Figure 8 Log p_{N_2}–temperature diagram for Reactions 5–7 and 9.

$$18CrN(s) + 2Si_3N_4(s) = 6Cr_3Si(s) + 13N_2(g) \quad (9)$$

$$\Delta G^\circ(J\,mol^{-1}) = 2851\,000 - 1928\,T(K)[8]$$

According to Fig. 8, the nitrogen pressure for Reactions 7 and 9 exceeds 10^5 Pa (= 1 atm) at 1649 and 1479 K, respectively. The equilibrium data for Reactions 8 and 9 correspond to the disappearance of CrN above 1373 K. At 1573 K, Cr_2N cannot be identified by XRD, because of covering with a Cr_3Si layer. The formation of Cr_3Si causes a substantial decrease in mass, as shown in Fig. 4.

4.2. Reaction mechanism and rate-determining step

The reaction mechanism between Si_3N_4 and chromium under an argon atmosphere is illustrated schematically in Fig. 9. Si_3N_4 dissociates into silicon and nitrogen atoms at the contact points between Si_3N_4 and chromium particles. Nitrogen atoms desorb as nitrogen gas and silicon atoms react with chromium to produce the silicides. After the silicide layer is continuously formed around the chromium particles, both inward diffusion of silicon and outward diffusion of chromium allow the reaction layer to

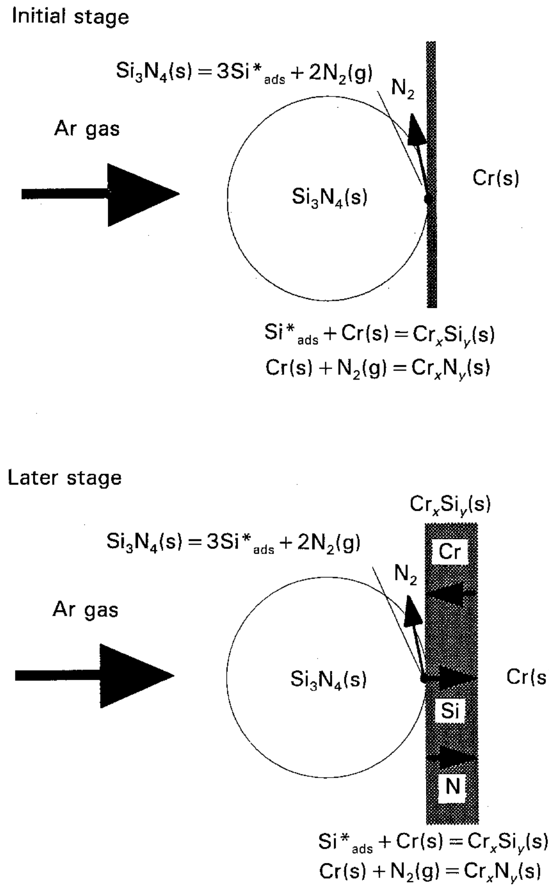

Figure 9 Schematic illustration of the reaction mechanism between Si_3N_4 and chromium in an argon atmosphere.

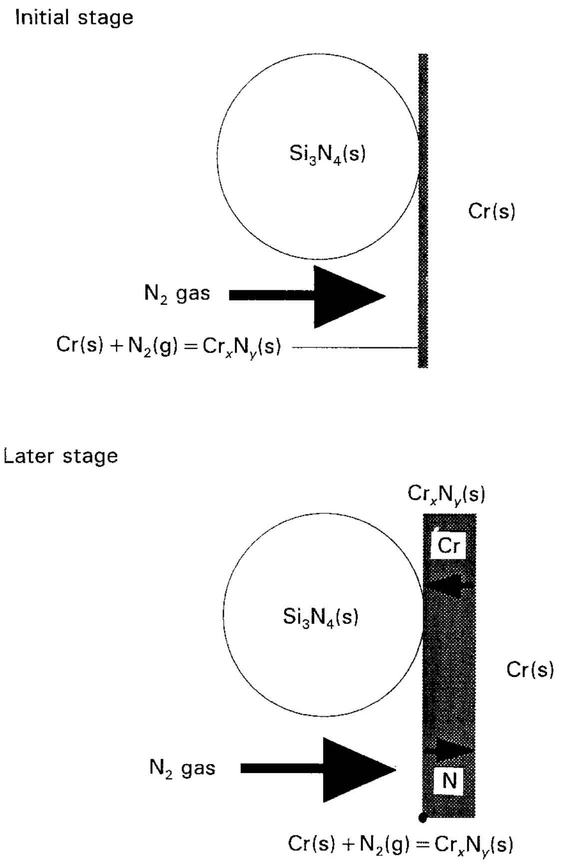

Figure 10 Schematic illustration of the reaction mechanism between Si_3N_4 and chromium in a nitrogen atmosphere at lower temperatures.

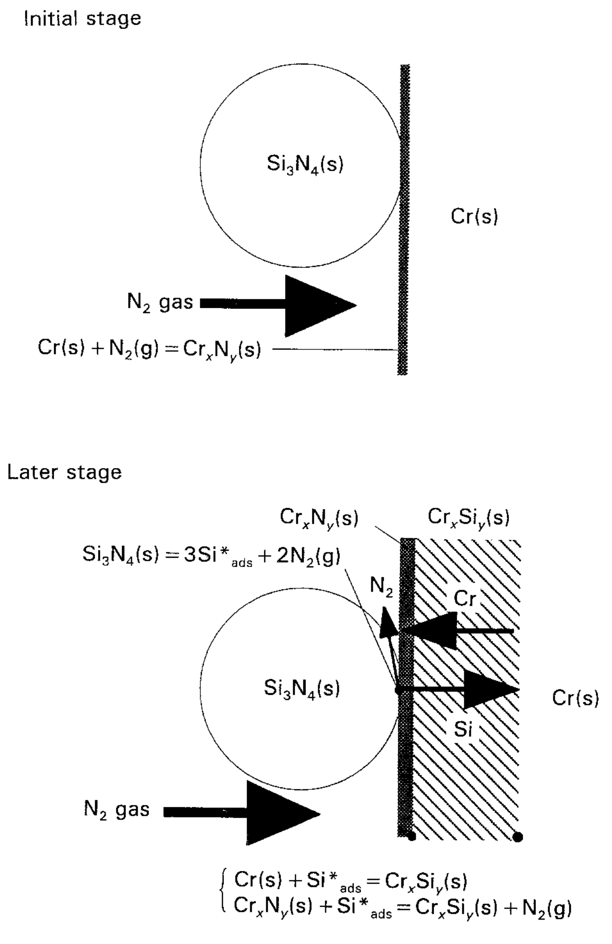

Figure 11 Schematic illustration of the reaction mechanism between Si_3N_4 and chromium in a nitrogen atmosphere at higher temperatures.

grow. Schematic illustrations of the reaction mechanism under a nitrogen atmosphere are given in Figs 10 and 11. Nitrogen gas diffuses to the surface of chromium particles and nitridation Reactions 5 and 6 proceed. After chromium particles are coated with the nitride layer, nitrogen diffuses inwards and chromium diffuses outwards through the reaction layer. At temperatures higher than 1323 K, Reactions 8 and 9 occur at the interface between Si_3N_4 and the nitride layer. Therefore, chromium diffuses inwards and silicon diffuses outwards through the reaction layer which is composed of Cr–Si solid solution or Cr_3Si.

The rate data given in Figs 2–4 follow approximately a linear rate law Equation 10 at the early stage of reaction

$$\Delta W_t / W_0 = k_1 t \tag{10}$$

Arrhenius plots of the linear rate constant, k_1, are shown in Fig. 12. The activation energies, E_1, calculated from the slopes of the Arrhenius line are 260 kJ mol^{-1} in argon and 35 kJ mol^{-1} in nitrogen, respectively.

The mass change initially obeys a linear law but then gradually deviates from it. Figs 13 and 14 show that the kinetics in the later stage can be explained by a parabolic rate law given by

$$\Delta W_t / W_0 = k_p^{1/2} t^{1/2} \tag{11}$$

Fig. 15 shows the Arrhenius plots of the parabolic rate constant, k_p, obtained from Figs 13 and 14. The activation energy, E_p, in an argon atmosphere is 365 kJ mol^{-1} over the entire temperature range. Three-step temperature dependence of k_p are linear, and the activation energy is calculated to be 149 kJ mol^{-1}. The value of k_p decreases abruptly at 1323 K, and indicates the linear dependence against

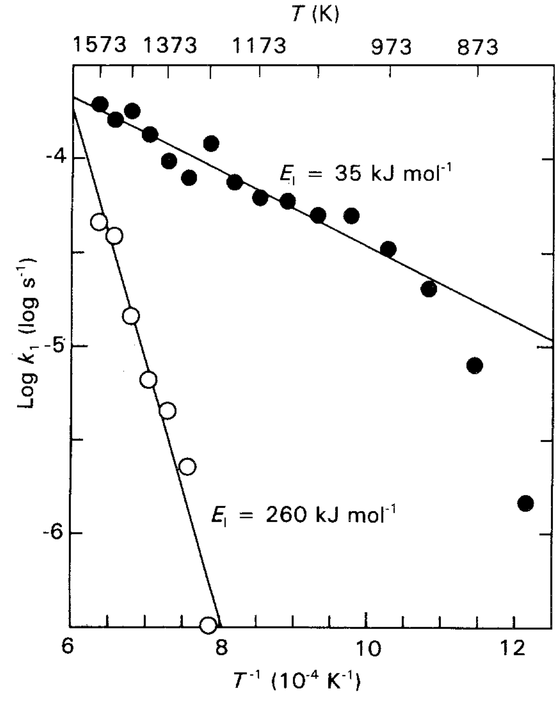

Figure 12 Arrhenius plots for the rate constant of the linear rate law, k_1, (○) in argon, (●) in nitrogen.

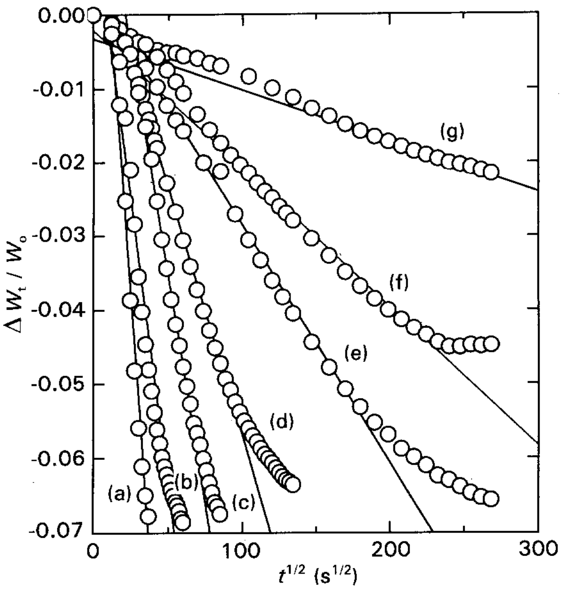

Figure 13 Application of the parabolic rate law to data shown in Fig. 1. (a) 1473 K, (b) 1523 K, (c) 1573 K, (d) 1423 K, (e) 1373 K, (f) 1323 K, (g) 1273 K.

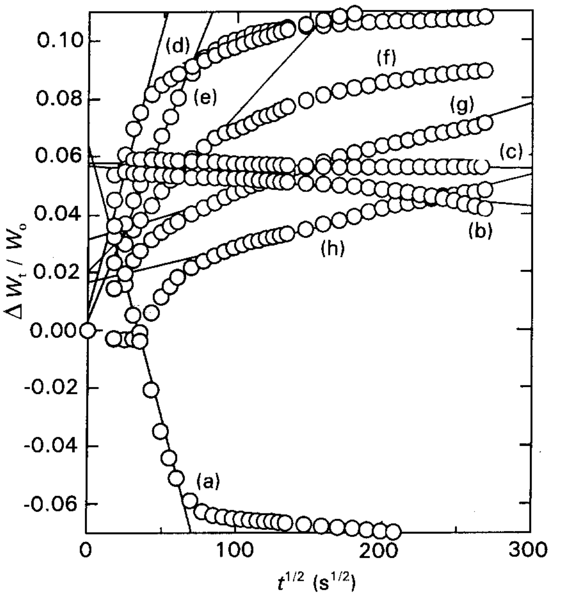

Figure 14 Application of the parabolic rate law to data shown in Figs 2 and 3. (a) 1573 K, (b) 1473 K, (c) 1373 K, (d) 1273 K, (e) 1173 K, (f) 1073 K, (g) 973 K, (h) 873 K.

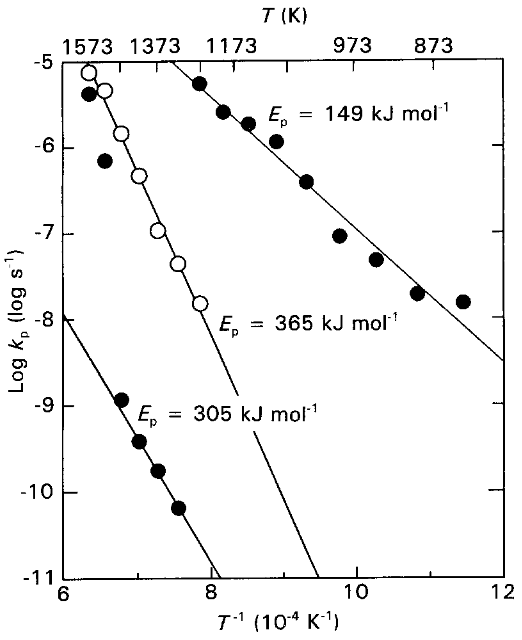

Figure 15 Arrhenius plots for the rate constant of the parabolic rate law, k_p, (○) in argon, (●) in nitrogen.

reciprocal temperature at 1323–1473 K. The slope of these plots yields the activation energy value of 305 kJ mol^{-1}. Above 1523 K, the rate constant, k_p, becomes nearly equal to the value obtained from the reaction in an argon atmosphere.

Under an argon atmosphere, the initial rate, which obeys a linear rate law, is considered to be controlled by the reaction at the interface between Si_3N_4 powder and chromium particles. The above value of 265 kJ mol^{-1} will usually be found reasonable as an activation energy for a chemical reaction. When the chromium silicide layer is formed around chromium particles, the reaction is determined by the diffusion through the reaction layer. The value 365 kJ mol^{-1} obtained from the present work compares favourably with the activation energies of the interdiffusion in various silicides [9–11].

Under a nitrogen atmosphere, chromium initially reacts with nitrogen to form Cr_2N and CrN. The linear rate law observed in the formation of nitride is interpreted in terms of either a chemical reaction control or a gaseous diffusion control. The low activation energy of 35 kJ mol^{-1} suggests the diffusion of nitrogen through interparticle pores of Si_3N_4–Cr compact as the rate-determining step. Below 973 K, the plots deviate downwards from the Arrhenius line, and a large activation energy of 202 kJ mol^{-1} is obtained. The nitridation of chromium is mixed-controlled by gaseous diffusion in the pores of the compact and reaction on the chromium particles, because of sluggishness of the chemical reaction at lower temperatures. As the thickness of the reaction layer grows, the subsequent reaction proceeds in accordance with the parabolic rate law, substantiating a solid-state diffusion control. Below 1273 K, the activation energy obtained in the present work is 149 kJ mol^{-1}, which is close to 115 kJ mol^{-1} for the diffusion of nitrogen in chromium [12]. This is consistent with the formation of Cr_2N and CrN. Above 1323 K, the main reaction product changes from chromium nitride to chromium silicide and Cr–Si solid solution as a result of the occurrence of Reactions 8 and 9. The change of diffusing species results in a decrease of the parabolic rate constant and an increase of the activation energy.

5. Conclusions

Reaction rates between Si_3N_4 and chromium under an argon or a nitrogen atmosphere were measured to investigate the reaction mechanism. The following results were obtained.

1. Under an argon atmosphere, a mass loss is observed, because the formation of silicides accompanies the generation of nitrogen gas. The reaction products are Cr_2N and Cr_3Si at low temperatures. At higher temperatures and on prolonged heating, Cr_2N disappears and the silicide changes from Cr_3Si to CrSi via Cr_5Si_3.

2. Under a nitrogen atmosphere, the nitridation of chromium particles with nitrogen gas results in a mass gain. Above 1373 K, a mass loss, which is due to the formation of Cr–Si solid solution and Cr_3Si, is observed after an initial mass gain.

3. The initial rate obeys a linear rate law. The reaction rate in an argon atmosphere is determined by the reaction at the interface between Si_3N_4 and chromium, whereas the reaction rate in nitrogen is mixed-controlled by the gaseous diffusion of nitrogen through both interparticle pores and the nitridation of chromium particles with nitrogen.

4. The rate is described by a parabolic rate law at the later stage of the reaction, when chromium particles are coated completely with the reaction layer. The rate-determining step is considered to be the solid-state diffusion through the reaction layer.

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Received 22 June
and accepted 29 October 1993