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Interaction of Si_3N_4 with Ni–Cr alloy under N_2 or Ar atmosphere

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In relation to the joining of silicon nitride ceramics to metal, the interaction of Si_3N_4 with Ni–Cr alloy was investigated at temperatures from 1073 to 1573 K under N_2 or Ar atmosphere. Reaction rates were determined by thermogravimetry and reaction products were examined by X-ray diffraction. CrN, Ni_3Si, Ni_5Si_2, Ni_2Si and $(Cr, Si)_3Ni_2Si$ were produced under N_2 atmosphere. In addition to these products, Ni_3Si_2, Cr_3Si and Cr_5Si_3 also were produced under Ar atmosphere. The reaction products were considered from the standpoint of thermodynamics. While the incubation period was observed under Ar atmosphere, it was not observed under N_2 atmosphere. The initial rates obeyed a linear rate equation. The rates at the later stage of reaction described a parabolic rate equation. The reaction mechanism model was proposed. *© 1998 Kluwer Academic Publishers*

1. Introduction

In recent years, silicon nitride ceramics have become of interest as high-temperature structural materials because of their excellent thermal and mechanical properties. However, large and complex-shaped components are difficult to fabricate because of brittleness and poor machinability in silicon nitride ceramics. One method of overcoming this difficulty is the joining technology of ceramics to metal [1–5]. Chemical reaction occurs between ceramics and metal during the joining process, and this often leads to the formation of a reaction layer with different properties. This reaction layer may grow further when the joints are exposed subsequently to high-temperature service conditions. Excessive growth of the reaction layer is thought to result in serious chemical and mechanical degradation of the joints. When silicon nitride ceramics are employed in high-temperature engineering applications, detailed knowledge is required of the compatibility with structural alloys, especially heat-resistant alloys.

Nickel-based super alloys show a high degree of resistance to creep at elevated temperature. The Ni–Cr binary system is of great importance as a basic type of heat-resistant super alloy. In addition, Ni–Cr alloy, which is highly refractory, is the promising joining media for ceramics in high-temperature applications [6–11]. However, silicon nitride ceramics decompose by reaction with Ni–Cr alloy and a reaction layer is formed at the interface between the ceramics–alloy. Solid-state reactions, therefore, have been investigated between silicon nitride and Ni–Cr alloys [6–14]. However, the reaction products and reaction mechanism have not yet been understood fully. The solid-state reaction at the ceramics–metal interface is very slow, which makes it difficult to clarify the development of the reaction layer. The use of powder samples in which the reaction can proceed rapidly enables one to predict the chemical stability of a joint used in long-time service at high temperatures.

In the present work, using a powder mixture of Si_3N_4 and Ni–Cr alloy, the reaction products and the reaction mechanism were studied by thermogravimetry (TGA) and X-ray diffraction (XRD) at temperatures of 1073–1473 K under a nitrogen or an argon atmosphere. In addition, chemical reactions between Ni–Cr alloy and Si_3N_4 were considered from the viewpoint of thermodynamics and the possible reaction products were determined from thermodynamic data for various reactions. Furthermore, based on kinematic analysis of TGA data, a reaction model was proposed.

2. Experimental procedure

The starting materials were silicon nitride powder (α-fraction $\geqq$ 95%, purity 98.5%, particle size 0.2 μm) and Ni–Cr alloy powder (30.9 mass % Cr, particle size 10 μm). This alloy is hereafter called Ni31Cr alloy. Two grams of Si_3N_4 and 2 g Ni31Cr alloy were thoroughly mixed in a silicon nitride mortar, and then a mixture was compressed into a tablet 20 mm in diameter. The thermobalance unit used for determining TGA consisted of a digital-type automatic recording balance and a silicon carbide resistance furnace.

The tablet specimen was placed in a magnesia crucible 26 mm in inner diameter and 35 mm in depth. The magnesia crucible was connected to the balance

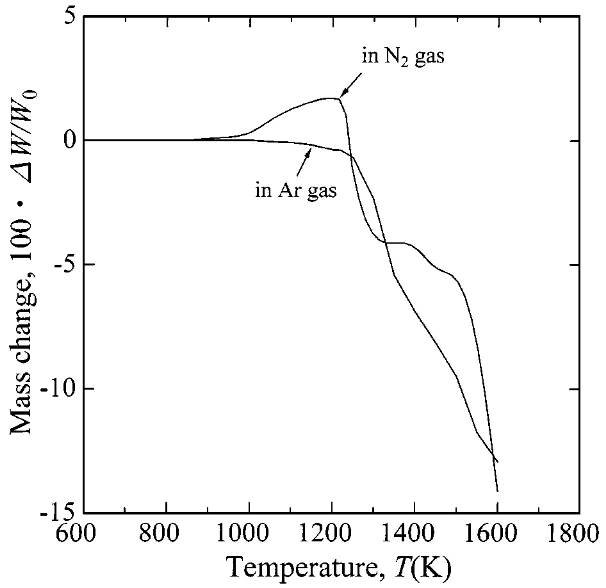

Figure 1 TGA curves for Si_3N_4–Ni31Cr alloy mixture heated continuously at $1\,K\,min^{-1}$.

with a platinum wire and was suspended in the alumina reaction tube of the furnace. The mass change was recorded automatically during each measurement. Either nitrogen or argon gas was introduced into the alumina tube from the bottom of the furnace at a flow rate of $2.5 \times 10^{-5}\,m^3\,s^{-1}$. Upon completion of the measurement, the specimen was cooled rapidly by raising the crucible into the low-temperature zone of the furnace. The reaction products were analysed by XRD.

3. Results

Fig. 1 shows TGA curves of Si_3N_4–Ni31Cr alloy mixtures heated continuously from room temperature to 1600 K at a heating rate of $1\,K\,min^{-1}$. The ratio of the mass change determined by TGA to the initial specimen mass is expressed as $100 \times \Delta W/W_0$. Under nitrogen atmosphere, the reaction that caused the mass gain began at 950 K. The mass gain is thought to be due to the nitridation of chromium as an alloying constituent with nitrogen gas [15–17]. Above about 1200 K, the TGA curve shows a change from mass gain to mass loss. This appears to be because the solid-state reaction between Si_3N_4 and Ni31Cr alloy proceeds at elevated temperature [15–17]. Thus, the mass loss is attributable to the formation of silicides and the resultant generation of nitrogen gas. Under an argon atmosphere, solid-state reaction between Si_3N_4 and Ni31Cr alloy started slowly at 1050 K and proceeded rapidly above 1300 K. The temperature of silicide formation is found to be lower under an argon atmosphere than under a nitrogen atmosphere.

Figs 2 and 3 show TGA curves of Si_3N_4–Ni31Cr alloy mixtures heated isothermally under a nitrogen atmosphere at temperatures from 1073 to 1473 K. A characteristic feature of such TGA curves is the rapid mass gain at early stages and the subsequent mass loss. As can be seen from Fig. 3, a brief time of mass gain was observed even at elevated temperatures. This seems to be because of the nitridation of chromium in the alloy with the nitrogen gas, and the subsequent generation of nitrogen gas as a result of the reaction between Si_3N_4 and Ni31Cr alloy, as mentioned above. With rising temperature, the turning time from the mass gain to the mass loss was significantly shortened. While the mass increased over a long period of 37.5 ks at 1073 K (Fig. 2), it decreased only 80 s after the mass gain at 1473 K (Fig. 3). It should be noted that each TGA curve had a tendency to approach a definite value, asymptotically i.e. an equilibrium value.

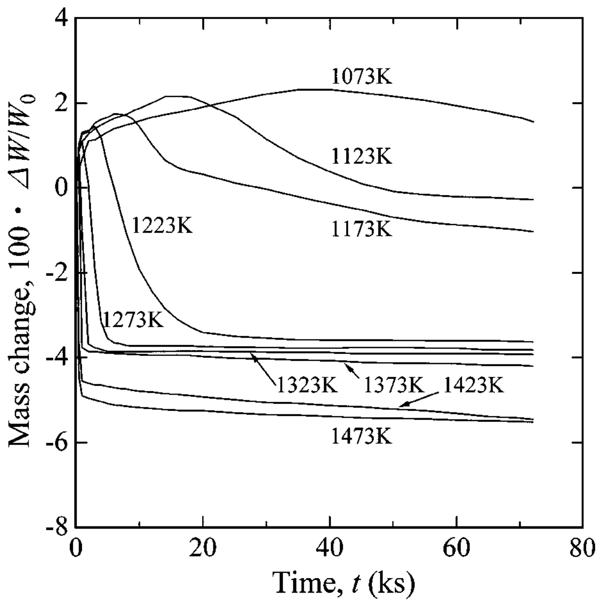

Figure 2 TGA curves for Si_3N_4–Ni31Cr alloy mixture heated isothermally for 72 ks under nitrogen atmosphere.

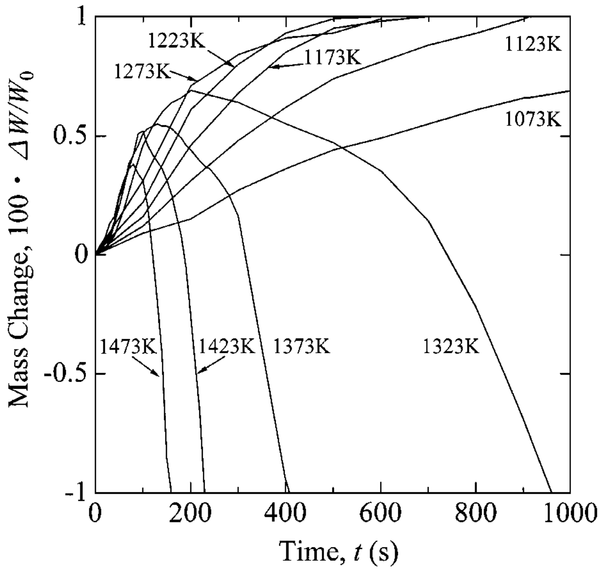

Figure 3 TGA curves for Si_3N_4–Ni31Cr alloy mixture heated isothermally for 1000 s under nitrogen atmosphere.

Fig. 4 shows TGA curves of Si_3N_4–Ni31Cr alloy mixtures heated isothermally under an argon atmosphere at temperatures from 1073 to 1473 K. The mass loss was observed at all temperatures, because the nitrogen-generating reaction occurred between Si_3N_4 and the Ni31Cr alloy. Below 1173 K, the reaction occurred gradually. At 1223 K, the reaction rate increased suddenly after about 15 ks. Such gradual reaction is

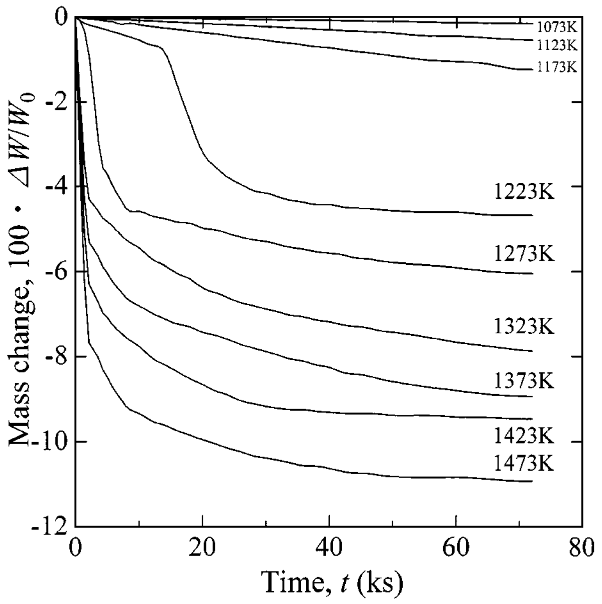

Figure 4 TGA curves for Si_3N_4–Ni31Cr alloy mixture heated isothermally for 72 ks under argon atmosphere.

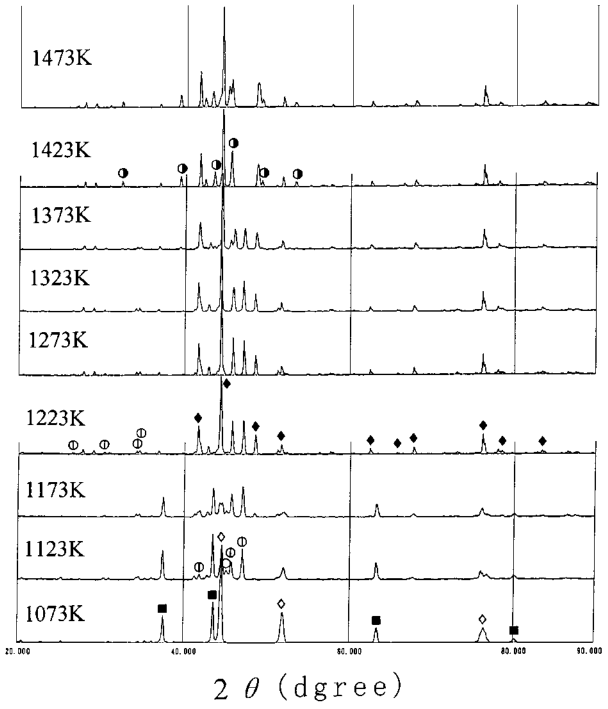

Figure 5 XRD patterns of Ni31Cr alloy interacted with Si_3N_4 for 72 ks under nitrogen atmosphere. (◇) Ni–Cr alloy, (○) Ni_3Si, (⦶) Ni_5Si_2, (◑) Ni_2Si, (■) CrN, (♦) (Cr, $Si)_3Ni_2Si$.

thought to correspond to the occurrence of an incubation period. The incubation period was remarkably shortened at higher temperatures. In addition, the reaction proceeded more quickly even after 72 ks, though it approached to equilibrium under a nitrogen atmosphere.

Fig. 5 shows XRD patterns of Ni31Cr reacted with Si_3N_4 at temperatures from 1073 to 1473 K for 72 ks under a nitrogen atmosphere. Si_3N_4 powder was removed from the Si_3N_4–Ni31Cr alloy mixture by suspension in acetone. The peaks of Si_3N_4, therefore, were not detected. Chromium nitride (CrN), nickel silicides [(Ni_3Si, Ni_5Si_2 ($Ni_{31}Si_{12}$), Ni_2Si)] and a Ni–Cr–Si ternary compound [(Cr, $Si)_3Ni_2Si$)] were detected as the reaction products [18–22]. The change of reaction products with temperature is summarized in Table I. Ni–Cr solid solution disappeared above 1223 K [23]. With rising temperature, of nickel silicide, which was the major constituent of the alloy, changed to silicide having a higher Si/Ni ratio in the following order: Ni_3Si, Ni_5Si_2 and Ni_2Si. On the other hand, chromium, i.e. another constituent of alloy, formed CrN at lower temperatures and (Cr, $Si)_3Ni_2Si$ at elevated temperatures.

TABLE I Reaction products in Si_3N_4 Ni31Cr alloy mixture heated for 72 ks under nitrogen atmosphere

Temperature, T (K)	Reaction product[a]					
	Ni–Cr	CrN	Cr_3Ni_2Si	Ni_3Si	Ni_5Si_2	Ni_2Si
1073	◎	◎	—	—	—	—
1123	○	◎	—	△	○	—
1173	○	○	△	△	○	—
1223	—	—	◎	—	○	—
1273	—	—	◎	—	○	—
1323	—	—	◎	—	○	—
1373	—	—	◎	—	○	○
1423	—	—	◎	—	—	○
1473	—	—	◎	—	—	○

[a] Undetected, △ weak, ○ strong, ◎ very strong.

Fig. 6 shows XRD patterns of Ni31Cr alloy reacted with Si_3N_4 at temperatures from 1073 to 1473 K for 72 ks under an argon atmosphere. Except for Ni–Cr solid solution, Cr_2N [24], Ni_3Si and (Cr, $Si)_3Ni_2Si$ were weakly detected at temperatures from 1073 to 1173 K. This corresponds to a minor mass loss in the TGA

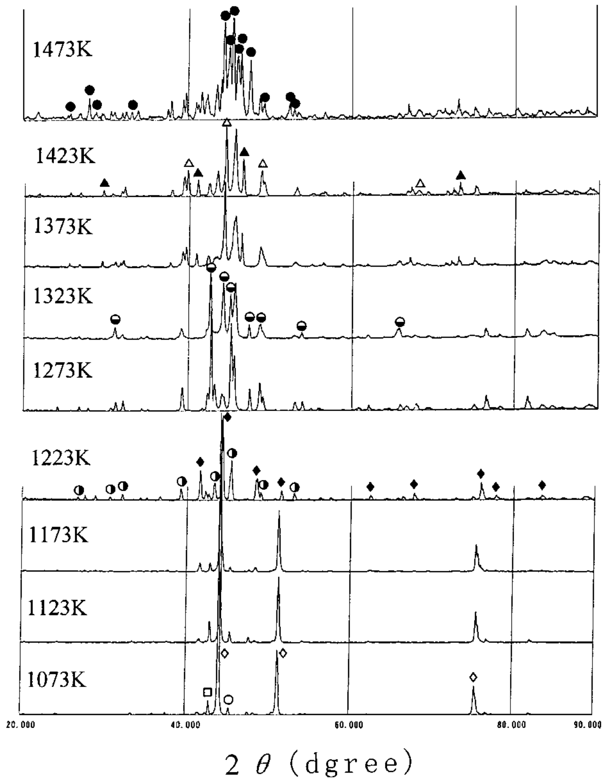

Figure 6 XRD patterns of Ni31Cr alloy interacted with Si_3N_4 for 72 ks under argon atmosphere. (◇) Ni–Cr alloy, (○) Ni_3Si, (◑) Ni_2Si, (●) Ni_3Si_2, (△) Cr_3Si, (▲) Cr_5Si_3, (□) Cr_2N, (♦) (Cr, $Si)_3Ni_2Si$, (◒) X.

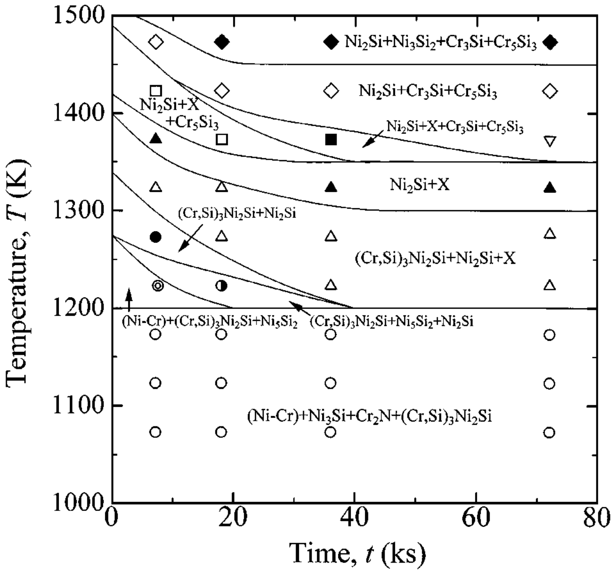

Figure 7 Temperature versus time relationship for reaction products in Si_3N_4–Ni31Cr alloy mixture heated under argon atmosphere.

curves (Fig. 4). Above 1223 K, the diffraction patterns of the products became sharp. The nickel silicide with a higher Si/Ni ratio, namely Ni_3Si_2 [25], was produced in addition to silicides such as Ni_3Si, Ni_5Si_2 and Ni_2Si, which were detected under a nitrogen atmosphere. Furthermore, chromium silicides such as Cr_3Si [26] and Cr_5Si_3 also were produced. The diffraction angle and intensity of Cr_5Si_3 were calculated from its crystal system, space group and lattice constant [27]. The reaction product denoted by X is the phase that was not identifiable from JCPDS cards. Fig. 7 indicates the temperature versus time relationship for products of the reaction between Si_3N_4 and Ni31Cr. At higher temperatures and on prolonged heating, the reaction products changed from Ni–Cr solid solutions + Ni_3Si + Cr_2N + $(Cr, Si)_3Ni_2Si$ to Ni_2Si + Ni_3Si_2 + Cr_3Si + Cr_5Si_3. The Si/Ni ratio of nickel silicides changed from a low to a high value. On the other hand, it may be noted that the formation of Cr_5Si_3 preceded that of Cr_3Si.

4. Discussion

4.1. Reaction products

Under a nitrogen atmosphere, an a consequence of the nitridation of chromium in alloy, the TGA curves show the mass gain at an early stage of reaction (Figs 2 and 3). Below 1223 K, CrN was detected by XRD (Fig. 5). The formation of CrN in Si_3N_4/Ni–Cr alloy system has been observed in other studies [7, 8, 11]. In addition, such nitridation also occurred in Si_3N_4/Cr, Si_3N_4/Fe–Cr alloy and Si_3N_4/stainless steel systems [15–17]. CrN is formed around Ni31Cr alloy particles, according to the following reaction

$$Cr(s) + 1/2N_2(g) = CrN(s)$$
$$\Delta G^\circ\ (J\ mol^{-1}) = -113\,400 + 73.22\ T\ (K)\ [28] \tag{1}$$

while ΔG° is the standard free energy change.

The Raoultian activity relative to a pure solid chromium should be used in thermodynamical consideration for the nitridation of chromium in Ni31Cr alloy. Assuming that the Ni–Cr alloy is an ideal solution, Raoultian activity is estimated to be 0.34. From thermodynamical calculation, CrN is stable below 1765 K. Therefore, CrN can be produced even above 1273 K, though it was not detected 72 ks after reaction (Fig. 5, Table I). The rapid mass gain also implies the formation of CrN at the earliest stage of reaction (Fig. 3). On prolonged heating, TGA curves showed the change from mass gain to mass loss. This appears to be because the nitridation was followed by the formation of silicides. The silicides were consequently produced in the following order. Ni_3Si, $(Cr, Si)_3Ni_2Si$, Ni_5Si_2 and Ni_2Si.

ΔG° (measured in joules per mole) is known for the following reactions

$$Si_3N_4(s) + 9Ni(s) = 3Ni_3Si(s) + 2N_2(g)$$
$$\Delta G^\circ = 308\,900 - 329T[29] \tag{2}$$

$$Si_3N_4(s) + 6Ni(s) = 3Ni_2Si(s) + 2N_2(g)$$
$$\Delta G^\circ = 269\,600 - 228T[29] \tag{3}$$

$$2Si_3N_4(s) + 9Ni(s) = 3Ni_3Si_2(s) + 4N_2(g)$$
$$\Delta G^\circ = 657\,800 - 437T[29] \tag{4}$$

$$Si_3N_4(s) + 9Cr(s) = 3Cr_3Si(s) + 2N_2(g)$$
$$\Delta G^\circ = 405\,000 - 305T[28] \tag{5}$$

$$Si_3N_4(s) + 5Cr(s) = Cr_5Si_3(s) + 2N_2(g)$$
$$\Delta G^\circ = 504\,600 - 331T[29] \tag{6}$$

where T is the temperature in kelvins.

The Raoultian activities relative to pure solid nickel and chromium, a_{Ni} and a_{Cr}, should be adopted in thermodynamical calculation. The values of a_{Ni} and a_{Cr} are approximated to be 0.66 and 0.34, respectively. Under a nitrogen atmosphere ($p_{N_2} = 101$ kPa), Ni_3Si, Ni_2Si and Ni_3Si_2 should be themodynamically produced at temperatures higher than 1037, 1302 and 1620 K, respectively. Naturally, Cr_3Si and Cr_5Si_3, which should be thermodynamically produced above 1808 and 1764 K, respectively, as well as Ni_3Si_2, were not produced at the experimental temperatures. In accordance with thermodynamical estimation, Ni_3Si and Ni_2Si were detected above 1123 and 1373 K by XRD, respectively (Fig. 5, Table I). Such small difference in the formation temperature of silicides may be attributable to errors in ΔG° and a_{Ni}. In general, the formation temperature of silicide has a tendency to increase with increasing Si/metal ratio [15–17]. Ni_5Si_2, therefore, is thought be produced at the formation temperature between Ni_3Si and Ni_2Si. Then, $(Cr, Si)_3Ni_2Si$ is thought to be produced at low temperature, because of a low Si/metal ratio. In fact, XRD indicates that Ni_5Si_2 and $(Cr, Si)_3Ni_2Si$ was produced at 1123 and 1173 K, respectively.

Under an argon atmosphere, Cr_2N was produced together with Ni_3Si and $(Cr, Si)_3Ni_2Si$ below 1173 K.

This is because chromium was nitrided by nitrogen gas evolved during the formation of the above silicides.

$$\begin{aligned} &2\mathrm{Cr(s)} + 1/2\mathrm{N_2(g)} = \mathrm{Cr_2N(s)} \\ &\Delta G^\circ = -99\,200 + 46.99T[28] \end{aligned} \tag{7}$$

From Equations 1 and 7, the equilibrium nitrogen pressure of the chromium nitrides at 1173 K is calculated to be 3.1 kPa for CrN and 0.89 kPa for Cr_2N, respectively. Thus, CrN with a high nitrogen equilibrium pressure was not produced under an argon atmosphere. Thermodynamical estimation indicates that the formation temperatures of silicides should be lowered by the establishment of a low nitrogen pressure. The formation temperatures of Ni_3Si, $(Cr, Si)_3Ni_2Si$ and Ni_2Si were 1073, 1073 and 1223 K under an argon atmosphere, respectively. As would be expected, they were lower than those under a nitrogen atmosphere. In addition, Cr_3Si, Cr_5Si_3 and Ni_3Si_2, which were not produced under a nitrogen atmosphere, were detected above 1373, 1373 and 1473 K, respectively. Cr_5Si_3 was produced at an early stage of reaction compared with Cr_3Si. This result corresponds with the above thermodynamical estimation: the formation temperature of Cr_5Si_3 (1764 K) is lower than that of Cr_3Si (1808 K) under a nitrogen atmosphere. The X phase, which was produced at temperatures from 1223 to 1423 K (Fig. 7), is not listed in JCPDS cards. With rising temperature and on prolonging the duration of heating, the X phase replaced the $(Cr, Si)_3Ni_2Si$ phase and was subsequently converted to Cr_5Si_3, Cr_3Si and Ni_3Si_2. From this result, the X phase can be estimated to be an Ni–Cr–Si ternary compound. The compounds to be considered are presented in the Ni–Cr–Si phase diagram as follows: Cr_2Ni_2Si, Cr_2Ni_3Si, $Cr_3Ni_3Si_4$, Cr_4Ni_2Si and $Cr_{11}Ni_6Si_3$ [30]. However, no crystallographic data exist concerning these compounds.

4.2. Incubation period

Under a nitrogen atmosphere, no incubation period was observed, because of the occurrence of gas–solid reaction, namely the nitridation of chromium in Ni31Cr alloy at the earliest stage of reaction (Figs 2 and 3). CrN is thought to act effectively as a bridging layer between Si_3N_4 and Ni31Cr alloy. Consequently, the subsequent solid-state reaction, i.e. the formation of silicides, did not show the incubation period.

Under an argon atmosphere, solid-state reaction begins between Si_3N_4 and Ni31Cr alloy. As shown in Fig. 8, therefore, TGA curves are characterized by the existence of an incubation period (period I). This is because Ni31Cr alloy particles are only brought into point contact with Si_3N_4 powders and the reaction proceeds very slowly. The gradual growth of the reaction layer leads to an increase in the contact area until the reaction proceeds rapidly (period II). Thus, TGA curves revealed a linear relationship in the period II. The subsequent heating caused the gradual decrease in reaction rate (period III). Fig. 9 shows the relationship between the duration of incubation period and heating temperature. The incubation period was markedly long at lower temperatures, but decreased drastically with increasing temperature. Below 1173 K, the incubation period continued throughout the duration of the experiment (72 ks).

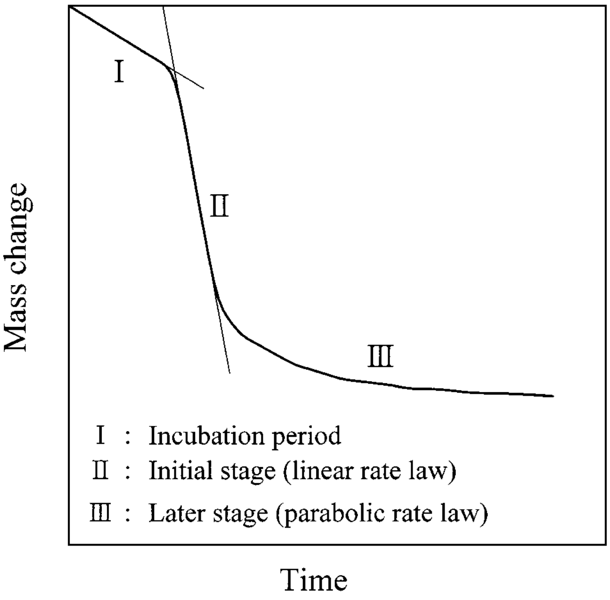

Figure 8 Schematic illustration of the TGA curve of Si_3N_4–Ni31Cr alloy mixture heated isothermally under argon atmosphere.

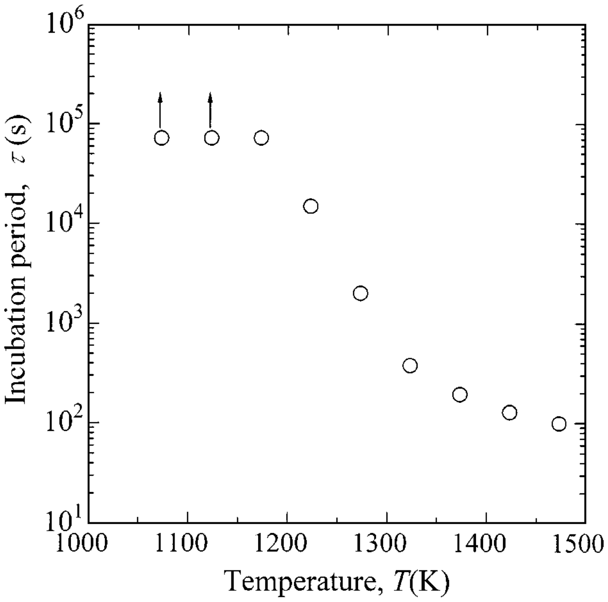

Figure 9 Incubation period for reaction between Si_3N_4 and Ni31Cr alloy.

4.3. Kinetic analysis

At an early stage of reaction, the rate of reaction between Si_3N_4 and metal obeyed the following linear rate law [15, 17, 31–36]

$$100 \times \Delta W/W_0 = k_l \times t \tag{8}$$

where $\Delta W/W_0$ is the ratio of the mass loss to the initial specimen mass and K_l is the rate constant for the linear rate law. From Fig. 8, it can be seen that the linear rate equation is applicable to TGA data in periods I

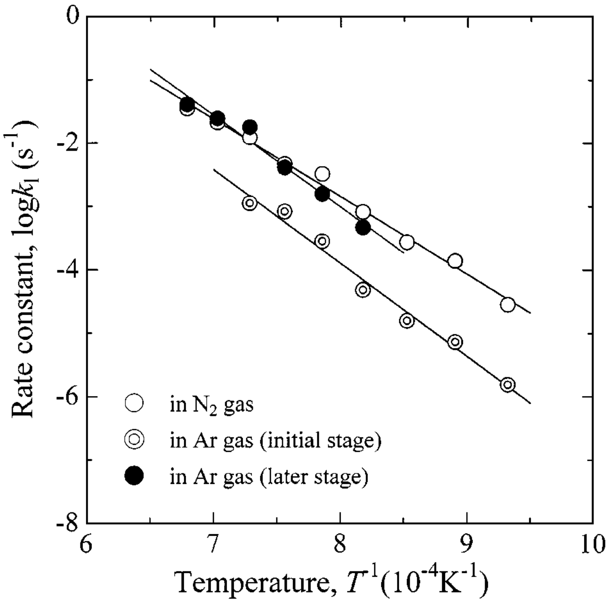

Figure 10 Arrhenius plots for rate constant of linear rate law, k_l.

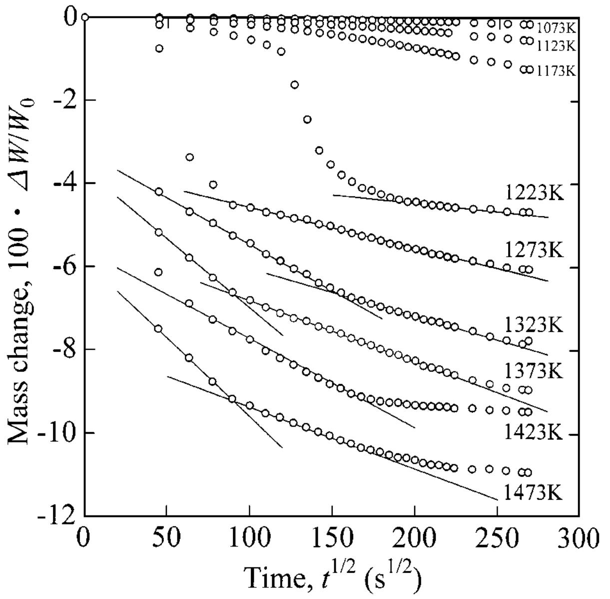

Figure 11 Application of parabolic rate law to TGA data shown in Fig. 4.

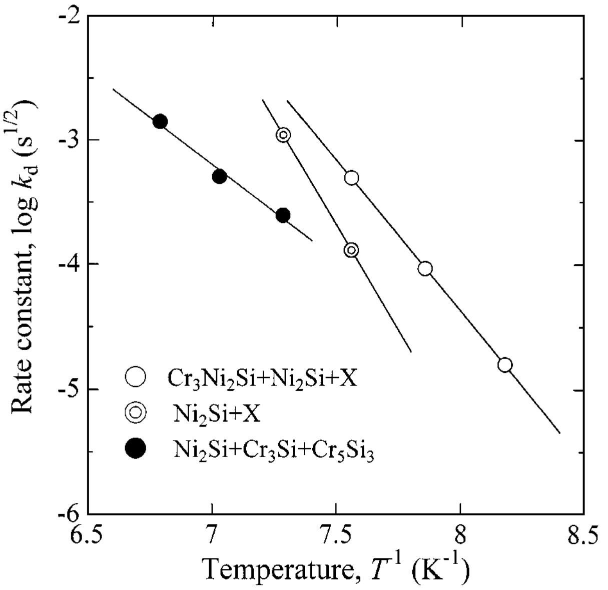

Figure 12 Arrhenius plots for rate constant of parabolic rate law, k_p.

and II. TGA curves under a nitrogen atmosphere also show the linear relationship at an initial stage of the reaction where mass loss occurs (Figs 2 and 3). The mass loss was due to reaction between Si_3N_4 and Ni31Cr alloy as well as under an argon atmosphere. Fig. 10 shows the relationship between K_l and the reciprocal of temperature. The rate constant under a nitrogen atmosphere was nearly equal to that under an argon atmosphere (period II). On the other hand, the rate constant at period I (i.e. incubation period) was one order of magnitude lower than that at period II. The plots give straight lines. From the Arrhenius equation, the activation energies were estimated to be 234 kJ mol^{-1} under a nitrogen atmosphere, 281 kJ mol^{-1} at period I (incubation period) and 277 kJ mol^{-1} at period II under an argon atmosphere, respectively. Similar activation energies suggest that the reaction rate is controlled by the same chemical process. The small value of K_l at the incubation period is thought to be attributable to the poor contact between Si_3N_4 and Ni31Cr alloy.

When metal particles are completely coated with the reaction layer, the rate-determining step changes from interfacial reaction to solid-state diffusion throught it. As a result, the reaction rate obeyed a parabolic rate law [15, 17, 31–36]

$$100 \times \Delta W/W_0 = k_p^{1/2} \times t^{1/2} \tag{9}$$

where k_p is the rate constant for the parabolic rate law. The application of the parabolic rate equation to TGA data under an argon atmosphere is shown in Fig. 11. Each plot yielded a linear relation with different slopes. This appears to be because the reaction products changed with the lapse of time (Fig. 6). Fig. 12 shows the Arrhenius plots of the parabolic rate constant, k_p. The linear relations were obtained in the regions of $Cr_3Ni_2Si + Ni_2Si + X$, $Ni_2Si + X$ and $Ni_2Si + Cr_3Si + Cr_5Si_3$, respectively. The activation energies in each region were 463, 644 and 292 kJ mol^{-1}, respectively. Such a difference in activation energy is thought to be attributable to the different diffusing species and the different product layers. The TGA data under a nitrogen atmosphere could not be described by the parabolic rate equation. This seems to be because the reaction rate was not controlled by a diffusion process alone. Fig. 2 shows that the reaction rate decreased rapidly to approach zero. Since the reaction was nearly at equilibrium, interfacial reaction proceeded very slowly. Therefore, the resistance of interfacial reaction to the overall reaction cannot be neglected. Finally, the rate is considered to be determined by both solid-state diffusion and the chemical process.

5. Conclusions

Reaction products and the reaction mechanism between Si_3N_4 and 69.1 mass % Ni–30.9 mass% Cr alloy (Ni31Cr alloy) were investigated under nitrogen or argon atmospheres. The following results were obtained.

1. Under a nitrogen atmosphere, the nitridation of chromium in the alloy with nitrogen gas caused the formation of CrN and a resultant mass gain at an early stage of reaction. At a later stage, silicides such as Ni_3Si, Ni_5Si_2, Ni_2Si and $(Cr, Si)_3Ni_2Si$ were produced by the solid-state reaction between Si_3N_4 and Ni31Cr alloy, and consequently a mass loss was observed after the initial mass gain.

2. Under an argon atmosphere, Ni_3Si_2, Cr_3Si and Cr_5Si_3 were produced in addition to silicides which were detected under a nitrogen atmosphere. The formaiton of such silicides resulted only in mass loss.

3. While the incubation period was not observed under a nitrogen atmosphere, it was observed, in particular over a long period of time at lower temperatures, under an argon atmosphere. Then the incubation time was drastically shortened with increasing temperature.

4. The initial rate obeyed a linear rate equation. The activation energies were estimated to be $234\,\text{kJ mol}^{-1}$ under a nitrogen atmosphere and $277\,\text{kJ mol}^{-1}$ under an argon atmosphere. The rate-determining step is thought to be the interfacial reaction between Si_3N_4 and Ni31Cr alloy.

5. At a later stage of reaction under an argon atmosphere, the rate was described by a parabolic rate equation. The activation energies in the regions of $Cr_3Ni_2Si + Ni_2Si + X$, $Ni_2Si + X$ and $Ni_2Si + Cr_3Si + Cr_5Si_3$ were 463, 644 and $292\,\text{kJ mol}^{-1}$, respectively. The reaction rate is considered to be determined by solid-state diffusion through the reaction layer.

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