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Effect of metal oxides addition on the preparation of Si_3N_4 whiskers by vaporization of amorphous Si_3N_4

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Abstract

The effect of metal oxides addition in the preparation of Si_3N_4 whiskers by reacting amorphous Si_3N_4 and metal oxides was investigated experimentally and thermodynamically. The compacted bodies of amorphous Si_3N_4 and a variety of metal oxides were heated at 1490°C, 700 torr in N_2. Of all the metal oxides, the addition of TiO_2, Cr_2O_3 and Fe_2O_3 produced a silicide and nitrides such as TiN, CrN and FeSi in the compacted bodies after heating, and produced large mass loss of the compacted bodies. α-Si_3N_4 whiskers were formed in only the TiO_2 addition system, and a Ti impurity was included in the whiskers. Thermodynamic calculation indicated that the decrease in Si_3N_4 amount and the increase in SiO (gas) amount with increasing temperature were pronounced with the three systems, and that TiO gas was formed in the system of TiO_2 addition. From these results, it was concluded that high affinity of metal atoms in additives with Si_3N_4 resulted in high partial pressure of SiO gas for nucleation of Si_3N_4 whiskers. Furthermore, it was presumed that nitridation of the transported TiO gas and the condensation of SiO gas on the resulting TiN nucleus produced Si_3N_4 whiskers.

1. Introduction

Silicon nitride ceramic has high promise for engineering applications due to its excellent properties such as high strength, high fracture toughness and high thermal shock resistance. It is widely known that sintered Si_3N_4 is fabricated by liquid phase sintering under N_2 pressures ranging from 1 to a few atm, because vaporization of Si_3N_4 occurs during sintering due to its high vapour pressure if pressureless sintering is used. On the other hand, the high vapor pressure of Si_3N_4 has been intentionally used to synthesize fine-grained Si_3N_4 whiskers [1]. Particularly, amorphous Si_3N_4 is easy to vaporize due to high degree of randomness in crystalline structure, compared to crystalline Si_3N_4 [1].

We reported that the addition of TiO_2 to an amorphous Si_3N_4 powder promoted mass loss of the Si_3N_4 at high temperature in N_2 and the resulting formation of α-Si_3N_4 whiskers [1]. The effect of TiO_2 on the whisker formation, however, has not been clarified. It is important to clarify the reason for the peculiar role of TiO_2 among various metal oxides.

Lin et al. [2] demonstrated the following in a study of nitridation of powder mixtures of Si and TiO_2. During the TiN formation in nitridation of the powder mixtures of Si and TiO_2, oxygen in TiO_2 is released, which reacts with Si, forming SiO_2. Rocabois et al. [3] demonstrated that the vapour pressures of SiO and N_2 gases were much larger than those of gas species such as Si, SiN, Si_2N in thermodynamic calculations of Si_3N_4–Si_2N_2O system. Considering the above works, the following mechanism is presumed for the formation of α-Si_3N_4 whiskers from amorphous Si_3N_4 and TiO_2. Silicon monoxide (SiO) gas is generated by the reaction of amorphous Si_3N_4 with TiO_2, which SiO gas is re-nitrided with N_2 on the surface of a substrate.

Thermodynamic calculation using computer simulations is frequently effective to resolve reaction mechanisms in gas phase processing such as chemical vapour deposition (CVD). It was also conducted on the formation of Si_3N_4 whiskers by carbothermal reduction of silica-based materials [4–8].

In the present study, we thermodynamically and experimentally investigated the effect of metal oxides addition on the preparation of Si_3N_4 whiskers from

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amorphous Si_3N_4 and TiO_2 by means of experiments and thermodynamic calculation using computer simulation, and discussed the effect of TIO_2 addition.

2. Experimental procedure

High purity amorphous Si_3N_4 (Mtsui–toatsu–kagaku Co., Ltd.) was used as starting Si_3N_4 powder. It had a specific surface area of 13.1 m^2/g, nitrogen content of 39.5 wt% and oxygen content of 6.0 wt%. The powder mixtures of the Si_3N_4 and various metal oxides as additives (see Table 1) were prepared by ball milling in ethanol for 24 h, and were then pressed to the dimension of 45 mm square after drying. The additional amount of metal oxides was 21.6 mol% against the Si_3N_4 powder.

As shown in Fig. 1, the compacted bodies were set in tubular graphite (IG–11, Toyo Tanso Co., Ltd.) with an outer diameter of 90 mm, and then were first heated up to 800°C at the heating rate of 20°C min^{-1} in vacuum. At this temperature, N_2 gas was subsequently introduced into the system up to initially set pressure, which was much lower than a final pressure of 700 torr due to the increase in pressure with temperature, and were finally heated to 1490°C at the same heating rate. At this temperature, N_2 gas was increased to result in a total pressure of 700 torr during the duration of the 2 h hold at temperature. Ale pressure of 700 torr was automatically maintained by a exhaust valve during the heating. After heating, the mass loss of the compacted

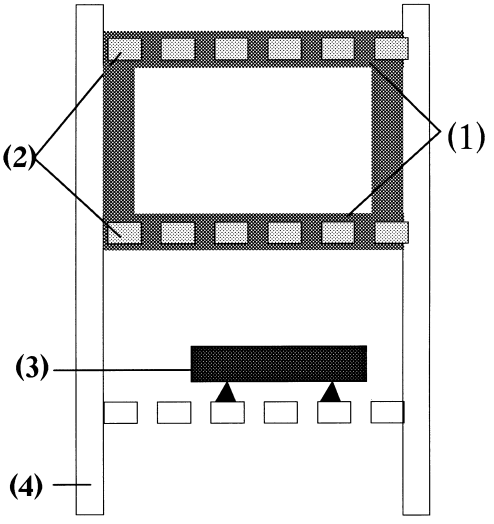

Fig. 1. Schematic apparatus for Si_3N_4 whisker synthesis; (1) Si_3N_4 whiskers, (2) graphite substrates, (3) source materials (amorphous–Si_3N_4/metal oxides), (4) tubular carbon with an outer diameter of 90 mm.

Table 1
Chemical species used in thermodynamic calculation

Additive	Nitrides(s)	Silicides(s)	Chemical species Another condensed phases (s and l)	Gas phases
TiO_2	TiN(s)	Ti_5Si_3(s), TiSi(s), $TiSi_2$(s)	Ti(α), Ti(β), Ti(1), TiO(α), TiO(β), TiO_2(1), TIO_2(anatase), TiO_2(rutile), Ti_2O_3(s), Ti_3O_5(p), Ti_4O_7(s), Ti_5O_9(s), Ti_6O_{11}(s), Ti_7O_{13}(s), Ti_8O_{15}(s), Ti_9O_{17}(s)	Ti(g), TiO(g), TiO_2(g)
Cr_2O_3	CrN(s), Cr_2N(s)	CrSi(s), $CrSi_2$(s), Cr_3Si(s), Cr_5Si_3(s)	Cr(s), Cr(1), CrO_2(s), CrO_3(s), CrO_3(1), Cr_2O_3(s), Cr_2O_3(1), Cr_8O_{21}(s),	Cr(g)
Fe_2O_3	Fe_2N(s), Fe_4N(s)	FeSi(S), $FeSi_2$(s)	Fe(α), Fe(β), Fe(γ), Fe(δ), Fe(1), $Fe_{0.89}O$(s), $Fe_{0.89}O$(s), $Fe_{0.947}O$(s), FeO(s), FeO(1), Fe_2O_3(s), Fe_3O_4(s), Fe_3O_4(1), Fe_2SiO_4(s), Fe_2SiO_4(1), $FeSiO_3$(s)	Fe(g)
HfO_2	HfN(s)			Hf(s), Hf(1), HfO_2(s), HfO_2(1)
B_2O_3	BN(s)		B(β), B(1), B(amorphous), B_2O_3(s), B_2O_3(1)	B(g), B_2(g), BN(g), BO(g), BO_2(g), B_2O(g), B_2O_2(g), B_2O_3(g)
$A1_2O_3$	AlN(s)		Al(s), $A1_2O_3$(s), $A1_2O_3$(1), $A1_2SiO_5$(andalusite), $A1_2SiO_5$ (kyanite) Al_2SiO_5(silimanite), $A1_2SiO_7$(s), Al_6SiO_{13}(mullite)	Al(g), $A1_2$(g), AlN(g), AlO(g), AlO_2(g), Al_2O(g), Al_2O_2(g)
Mgo	MgN(s), Mg_3N_2(s)	Mg_2Si(s)	Mg(s), Mg(1), $Mg(NO_3)_2$(s), MgO(s), MgO(1), Mg_2Si(1), $MgSiO_3$(s) $MgSiO_3$(1), $MgSiO_4$(s), Mg_2SiO_4(1)	Mg(g), Mg_2(g), MgN(g)
CaO	Ca_3N_2(s)	CaSi(s), $CaSi_2$(s), Ca_2Si(s)	Ca(a), Ca(b), Ca(1), $Ca(NO_3)_2$(s), CaO(s), CaO(1), CaO_2(s) $CaSiO_3$(s), $CaSiO_3$(1), Ca_2SiO_4(s), Ca_3SiO_5(s), $Ca_3Si_2O_7$(s)	Ca(g), Ca_2(g), CaO(g)
BaO	Ba_3N_2(s)		Ba(α), Ba(β), Ba(γ), Ba(1), $Ba(NO_3)_2$(s), BaO(s), BaO(1), BaO_2(s)	Ba(g)
Li_2O	Li_3N(s)		Li(s), Li(1), Li_2O(s), Li_2O(1), Li_2O_2(s), Li_2SiO_3(s), Li_2SiO_3(1), $Li_2Si_2O_5$(s), $Li_2Si_2O_5$(1), Li_4SiO_4(s), Li_4SiO_4(1)	Li(g), Li_2(g), LiO(G), Li_2O(g), Li_2O_2(g)
Another	Si_3N_4(α)		Si(s), Si(1), SiO_2(highquartz), SiO_2(lowquartz), SiO_2(lowcristobalite), SiO_2(highcristobalite), SiO_2(vitreous), N_2O_4(1)	Si(g), Si_2(g), Si_3(g), SiO_2(g), N(g), N_2(g), N_3(g), NO(g), NO_2(g), NO_3(g), N_2O(g), N_2O_3(g), O_3(g) N_2O_4(g), N_2O_5(g), O(g), O_2(g)

bodies was measured, and the formation of whiskers was confirmed. Impurities in the Si_3N_4 whiskers were quantified by chemical analysis.

3. Thermodynamic calculation

3.1. The principle [9] [10]

Phase equilibrium is calculated using Eq. (1) regarding free energy of the system and Eq. (2) regarding mass balance of the system. Chemical equilibrium applies when both the mass balance and the minimum of G/RT are satisfied. G is Gibbs' free energy of the system.

$$G/RT = \sum_{i}^{g} x_i^g \left[(g^0/RT)_i + \ln P + \ln(x_i^s/X)\right] + \sum_{i}^{c} x_i^c (g^0/RT)_i \quad (1)$$

$$\sum_{i}^{m} a_{ij} x_i^g + \sum_{i}^{s} a_{ij} x_i^c = b_j \quad (2)$$

Here, $X_i g^0$ are mol amount of chemical species i, standard Gibbs free energies of the i, respectively. R, T, P and X are gas constant, temperature (K), total pressure and total mol amount. The g, c, m and s show gas phase, condensed phase, the number of gas species and the number of condensed species, respectively. The a_{ij} is the number of element j in chemical species i, b_j is the sum of element j. In the present study, phase equilibrium was calculated using a commercial thermodynamic calculation program (EKVICALC) and database (EKVISYSTEM), produced by Svensk Energidata Co. Table 1 shows all chemical species used in this calculation.

3.2. The conditions of calculations

In thermodynamic calculation using computer simulation, it is important to confirm previously the kind of chemical species included in the database used in the calculation. Table 1 shows all the chemical species included in the database (EKVIBASE).

Thermodynamic data of amorphous Si_3N_4 is necessary for a series of calculations in the present study. However, thermodynamic data of amorphous Si_3N_4 as well as β-Si_3N_4 is not included in the database. We substituted the thermodynamic data of α-Si_3N_4 for that of amorphous Si_3N_4. Si_2N_2O is also not included in it. This inevitably leads to incorrectness of the calculation. However, we considered that intrinsic difference in reaction of Si_3N_4 with metal oxides, depending on the kind of them, could be estimated. The calculated compositions are summarized in Table 2. SiO_2 is derived from the surface of Si_3N_4. Metal atoms of 21.6 mol% against Si_3N_4 are included, similarly to the following experimental condition. The amount of N_2 was determined from the capacity of used apparatus. The calculation was performed at temperatures of 1000 to 1800°C, under a pressure of 700 torr.

4. Results and discussion

Fig. 2 shows temperature dependence of the calculated mass loss of Si_3N_4. Clearly, the mass loss depends on the kind of additive, and the addition of Fe_2O_3, Cr_2O_3 and TiO_2 lead to large mass loss. Significant mass loss starts at about 1500°C. Fig. 3 shows temperature dependence of the calculated amounts of solid SiO_2

Table 2
The conditions of thermodynamic calculation

Source	Material	Amount (g)
Si_3N_4	$Si_3N_4(\alpha)$	8.875
	SiO_2(vitreous)	1.125
Additive	TiO_2(rutile)	1.096
	Cr_2O_3	1.040
	Fe_2O_3	1.090
	Hf_2O_3	2.880
	B_2O_3	0.478
	$A1_2O_3$	0.700
	MgO	0.552
	CaO	0.772
	BaO	2.100
	Li_2O	0.204
Gas	N_2	28.000

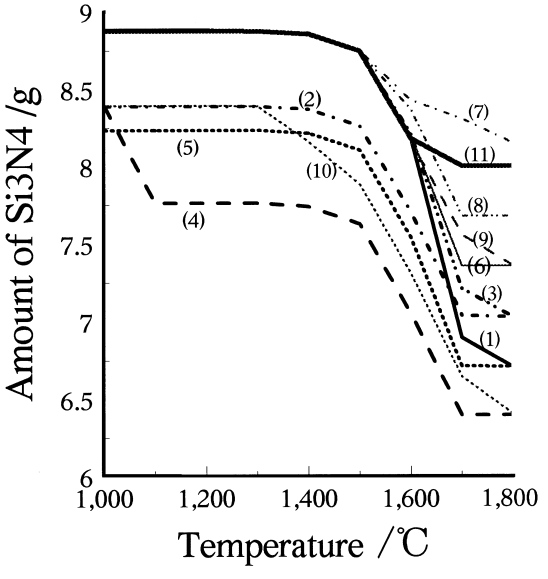

Fig. 2. The calculated amounts of Si_3N_4 in various Si_3N_4–metal oxide systems; (1) HfO_2, (2) B_2O_3, (3) $A1_2O_3$, (4)Fe_2O_3, (5) TiO_2, (6) MgO, (7) CaO, (8) Li_2O, (9) BaO, (10) Cr_2O_3 and (11) no additives.

phase. The addition of TiO_2, Cr_2O_3, Fe_2O_3 and B_2O_3 produces SiO_2 amount larger than the initial SiO_2 amounts of each system. Similarly to the results of Si_3N_4, significant decrease in SiO_2 amount starts at about 1500°C , and the SiO_2 disappears at 1700°C.

Figs. 4 and 5 show temperature dependence of the calculated amounts of gas phases of SiO and N_2. There is no significant difference in SiO amount below 1600°C. Above 1700°C, the addition of TiO_2, Cr_2O_3 and Fe_2O_3 produces large amounts of SiO gas. The increase in N_2 amount also starts at about 1500°C except TiO_2 addition, and the addition of Cr_2O_3 and Fe_2O_3 produces large amounts of N_2 gas, compared to the other additives.

Thus, we can summarize the above results of thermodynamic calculation as follows. The addition of TiO_2, Cr_2O_3 and Fe_2O_3 results in large mass loss of Si_3N_4, large decrease in SiO_2 amount, and the addition of Cr_2O_3 and Fe_2O_3 results in the formation of large amounts of N_2 gas. Table 3 shows the comparison of the experimental mass loss of specimens [11,12] and the calculated mass loss of Si_3N_4, which were ranked in order of mass loss. In addition, deposited phases identified experimentally and calculated are also written in the table.

Of all additives, the addition of TiO_2 experimentally produced the largest mass loss and large amounts of Si_3N_4 whiskers on graphite substrates and the inner wall of the tubular graphite. Chemical analysis of the Si_3N_4 whiskers indicated that titanium of 0.09 wt% was included as a impurity. Although additives such as Cr_2O_3 and Fe_2O_3 also promoted mass loss, no whiskers were formed.

From these experimental and the above calculated results, the formation of large amounts of SiO gas is presumed in the systems of TiO_2, Cr_2O_3 and Fe_2O_3 addition. However, this indicates that large mass loss is not enough for the whisker formation.

Si_2N_2O was experimentally formed in some systems (TiO_2, Cr_2O_3, Fe_2O_3 and Li_2O). Lin et al. showed that the addition of large amounts of TiO_2 forms not SiO_2 but Si_2N_2O in the reaction of Si_3N_4 with TiO_2 [2]. Probably, the formation of Si_2N_2O in the systems of TiO_2, Cr_2O_3 and Fe_2O_3 addition is because of the higher oxygen content in the oxides, compared to another

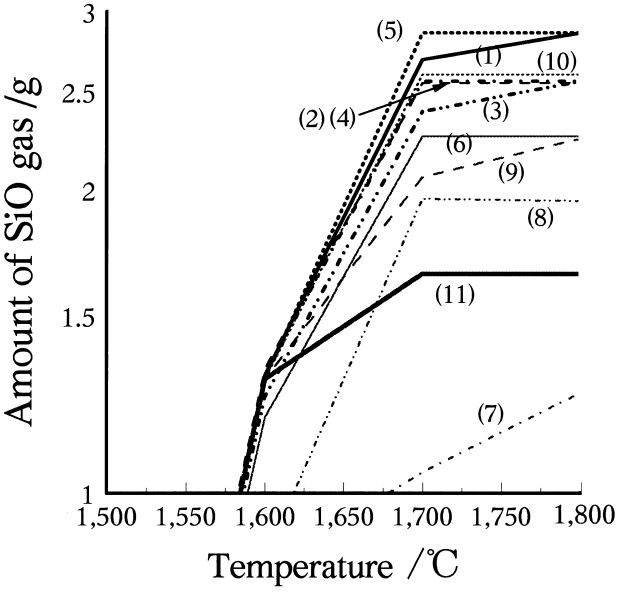

Fig. 4. The calculated amounts of SiO gas in various Si_3N_4–metal oxide systems; (1) HfO_2, (2) B_2O_3, (3) $A1_2O_3$, (4) Fe_2O_3, (5) TiO_2, (6) MgO, (7) CaO, (8)Li_2O, (9) BaO, (10) Cr_2O_3 and (11) no additives.

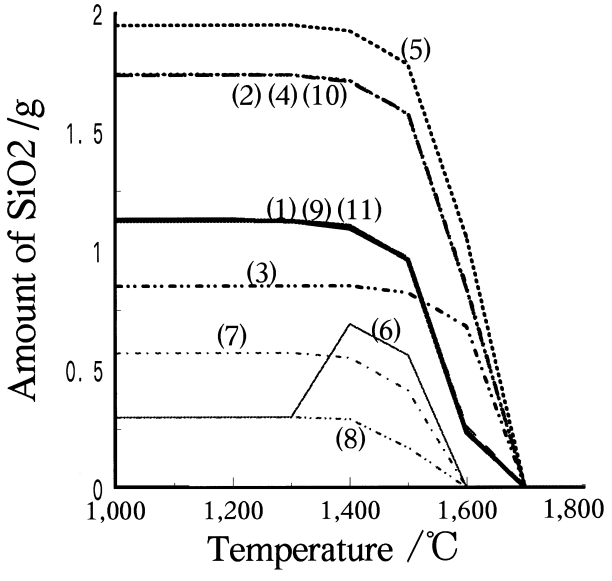

Fig. 3. The calculated amounts of SiO_2 in various Si_3N_4–metal oxide systems; (1) HfO_2, (2)B_2O_3, (3) $A1_2O_3$, (4) Fe_2O_3, (5) TiO_2, (6) MgO, (7) CaO, (8)Li_2O, (9) BaO, (10) Cr_2O_3 and (11) no additives.

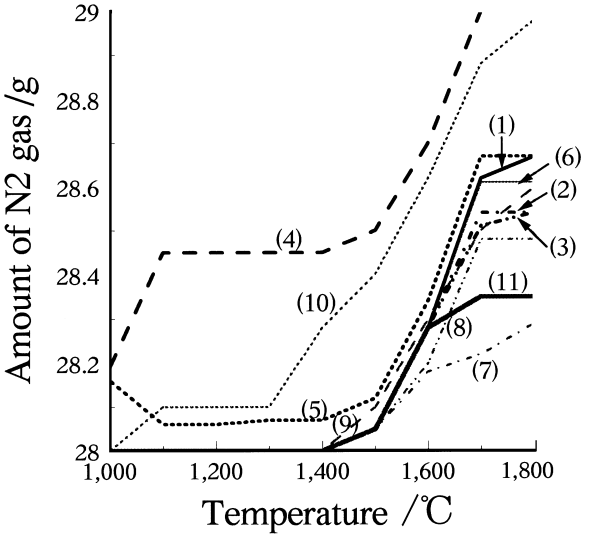

Fig. 5. The calculated amounts of N_2 gas in various Si_3N_4–metal oxide systems; (1) HfO_2, (2) B_2O_3, (3) $A1_2O_3$, (4) Fe_2O_3, (5) TiO_2, (6) MgO, (7) CaO, (S) Li_2O, (9) BaO, (10) Cr_2O_3 and (11) no additives.

additives. However, the reason for the formation of Si_2N_2O in the system of Li_2O addition is not clarified.

The addition of Cr_2O_3, Fe_2O_3, MgO, CaO, HfO_2 or $A1_2O_3$ produced β-Si_3N_4 in addition to α-Si_3N_4. Si_2N_2O and β-Si_3N_4 are not included in the database used in the present study. Thus, the phases deposited experimentally do not always correspond with the calculated phases. The ranking of the experimental mass loss, however, well corresponds with the calculated results. In particular, the additives such as TiO_2, Cr_2O_3 and Fe_2O_3 actually promoted mass loss of specimens.

Focusing on the three systems with large mass loss, we find that FeSi or metal nitrides such as TiN and CrN are experimentally formed in addition to Si_3N_4 and Si_2N_2O. On the other hand, any nitrides and silicides are not formed in the other systems. There are two possibilities regarding the formation of TiN or CrN. One is the reactions of TiO_2 or Cr_2O_3 with Si_3N_4, and another is reduction of the oxides with N_2 gas. We confirmed that TiN and CrN were formed enough in beating in Ar gas at the same temperature. This results shows that the formation of TiN and CrN is caused by the former reaction. This is probably because of high affinity of Ti and Cr atoms with N atom.

The formation of FeSi is not simply ascribed to the reaction of Fe_2O_3 with Si_3N_4 because of the possibility of the reaction of Fe_2O_3 with SiO_2 on the surface of Si_3N_4. However, the experimental large mass loss of Si_3N_4 in Si_3N_4–Fe_2O_3 system suggests that the formation of FeSi is caused by the former reaction. Thus, we consider that high reactivity of additives with Si_3N_4 produces large mass loss of Si_3N_4.

As shown in Fig. 4, however, the thermodynamic amount of SiO gas, which causes whisker formation, does not depend significantly on the kind of additive at the experimental temperature of 1490°C. Apparent difference in SiO amount appears above 1700°C, when the addition of TiO_2, Cr_2O_3 and Fe_2O_3 produces large amounts of SiO gas.

Thus, there is temperature misfit between the experimental and the calculated results regarding the formation of large amounts of SiO gas. The reason for this is considered as follows. One is the use of thermodynamic data of α-Si_3N_4. Amorphous Si_3N_4 is easy to react with TiO_2 than α-Si_3N_4 [1]. Therefore, actual temperatures, at which large amounts of SiO gas start to be formed, are possibly lower than those of the calculated temperatures. Another is kinetic. In the calculation, the addition of HfO_2, B_2O_3 and $A1_2O_3$ also produces large amounts of SiO gas. However, the experimental mass loss of these systems is much smaller than that of TiO_2, Cr_2O_3 and Fe_2O_3 system. It is possible that the formation rate of SiO gas in the former systems is much smaller than that in the latter systems.

No whiskers were formed in the systems of Cr_2O_3 and Fe_2O_3 addition, however, in spite of the formation of experimental large mass loss of specimens. For this phenomena, we consider as follows. Two steps are necessary for whisker formation. One is the formation of SiO gas, and another is its re-nitridation with N_2 gas. The vapour pressure of SiO gas is related to facility of nucleation. Among three additives, TiO_2 produces the largest SiO amount and the smallest N_2 amount. The resulting largest partial pressure of SiO gas possibly gives rise to the higher facility of nucleation.

Furthermore, a Ti impurity is contained in the Si_3N_4 whiskers. This is probably contained as TiN because of high affinity of Ti with N atom. Fig. 6 shows temperature dependence of the calculated partial pressure of TiO gas. Below 1400°C, the calculated values were zero. Although the values are much smaller than that of gas species such as SiO and N_2, some TiO gas seems to be transported to graphite substrates and nitrided on them. Si_3N_4 whiskers are possibly condensed on the TiN nucleus.

Table 3
The comparison of the experimental mass loss and the calculated mass loss of Si_3N_4 in various Si_3N_4–metal oxide systems

Experimental					Calculated			
Rank	Additive	Mass loss of specimen (wt%)	Deposited phases	Formation of whiskers	Rank	Additive	Mass loss of Si_3N_4 (wt%)	Deposited phases
1	TiO_2	19.2	α,Si_2N_2O, TiN	O	1	Fe_2O_3	13.8	α, SiO_2, FeSi
2	Cr_2O_3	14.1	α, β, Si_2N_2O, CrN	X	2	Cr_2O_3	11.0	α, SiO_2, Cr_5Si_3
3	Fe_2O_3	13.2	α, β, Si_2N_2O, FeSi	X	3	TiO_2	8.5	α, SiO_2, TiN
4	BaO	10.8	α, Ba_2SiO_4	X	4	B_2O_3	2.7	α, SiO_2, BN
5	Li_2O	8.8	α, Si_2N_2O	X	5	BaO	1.3	α, SiO_2
6	B_2O_3	7.7	α	X	5	Li_2O	1.3	α, SiO_2, Li_4SiO_5
7	MgO	8.4	α, β	X	5	MgO	1.3	α, SiO_2
8	Nothing	7.9	α	X	6	Nothing	1.2	α, SiO_2
9	CaO	5.4	α, β	X	6	CaO	1.2	α, SiO_2, $Ca_3Si_2O_7$
10	HfO_2	6.3	α, β[a]	X	6	HfO_2	1.2	α, SiO_2
11	$A1_2O_3$	4.9	α, β	X	6	$A1_2O_3$	1.2	α, SiO_2, $A1_6Si_2O_{13}$

α: α–Si_3N_4, β: β–Si_3N_4.
[a] Unidentified.

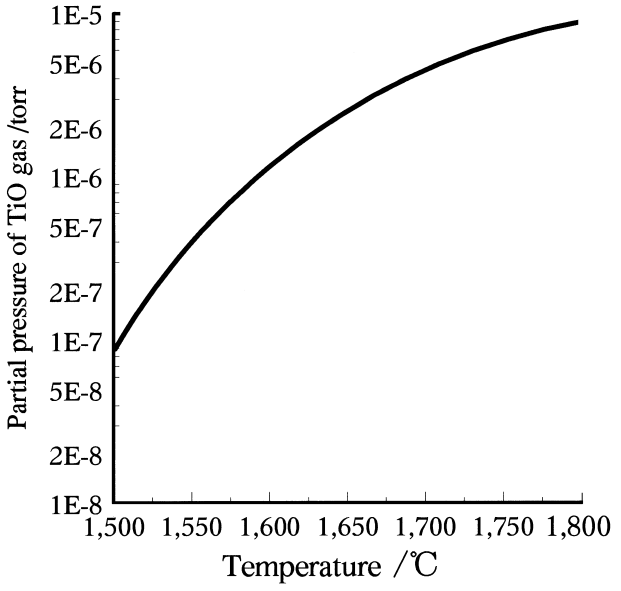

Fig. 6. The calculated partial pressure of TiO gas in Si_3N_4–TiO_2 system.

5. Conclusions

Mass loss and the formation phase after heating various amorphous Si_3N_4–metal oxide composites in N_2 were investigated, and the results was discussed compared to the results of thermodynamic calculation to clarify the mechanism for the formation of Si_3N_4 whiskers from amorphous Si_3N_4–TiO_2 source material. The conclusion is summarized as follows:

1. Among various metal oxides, the addition of TIO_2, Cr_2O_3 and Fe_2O_3 experimentally and thermodynamically produces large mass loss with increasing temperature.
2. The addition of TiO_2, Cr_2O_3 and Fe_2O_3 experimentally and thermodynamically forms silicides or nitrides of metal atoms in the oxides.
3. The formation of Si_3N_4 whiskers occurs in only the system of TiO_2 addition, and a Ti impurity is contained in the whiskers.
4. With increasing temperature, SiO gas is thermodynamically formed, and the formation is also pronounced with the systems of TiO_2, Cr_2O_3 and Fe_2O_3 addition.
5. TiO gas is thermodynamically formed in the system of TiO_2 addition although its amount is small. High reactivity between TiO_2 and Si_3N_4 produces high partial pressure of SiO gas and slight partial pressure of TiO gas. The TiO gas is transported to substrates, on which nucleation of TiN occurs. Finally, SiO gas is nitrided on the TiN nucleus, forming Si_3N_4 whiskers.

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References

[1] C. Kawai, A. Yamakawa. J. Mater. Sci. Lett. 14 (1995) 192–193.
[2] W. Lin, J.M. Yang, S.J. Ting, Journal of the American Ceramics Society. 75 (11) (1992) 2945–2952.
[3] P. Rocabois, C. Chatillon, C. Bernard. Journal of the American Ceramics Society 79 (5) (1996) 1351–1360.
[4] H. Wada, L. Wang. Ceram. Eng. Sci. Proc., 11 (9–10) (1990) 1463–1479.
[5] M.J. Wang, H. Wada. Journal Mater. Sci. 25 (1990) 1690–1698.
[6] H. Wada, L. Lang. Journal Mater. Sci. 27 (1992) 1528–1536.
[7] M.J. Wang, H. Wada. Mater. Sci. Forum 47 (1989) 267–281.
[8] H. Wada, M.J. Wang, T.Y. Tien. Journal of the American Ceramics Society 71 (10) (1988) 837–840.
[9] W.B. White, S.M. Holmson, G.B. Dantzig. Journal Chem. Phys. 28 (1958) 751–755.
[10] R.C. Oliver, S.E. Stephanou, R.W. Baier. Chemical. Enginearing. 69 (1962) 121–128.
[11] C. Kawai, A. Yamakawa. Proc. Spring Sym. Jpn. Soc. Powder and Powder Metallurgy, Tokyo, (1995) p. 71.
[12] C. Kawai, H. Takeuchi, T. Nishioka, A. Yamakawa. Proc. Spring Sym. Jpn. Soc. Powder and Powder Metallurgy, Tokyo, (1996) p. 51.