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Phase Equilibrium Studies in Si_2N_2O-containing Systems: II. Phase Relations in the Si_2N_2O–Al_2O_3–La_2O_3 and Si_2N_2O–Al_2O_3–CaO Systems

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SUMMARY

Sub-solidus phase relations have been studied in the Si_2N_2O–Al_2O_3–La_2O_3 and Si_2N_2O–Al_2O_3–CaO systems. The results show that no new compound is found in the Si_2N_2O–Al_2O_3–La_2O_3 system, but there exists a new compound CaO·Si_2N_2O and a continuous cubic solid solution between 3CaO·Si_2N_2O and 3CaO·Al_2O_3 in the Si_2N_2O–Al_2O_3–CaO system. In the Si_2N_2O-rich area of these two systems the excess Si_2N_2O reacts with La_2O_3 and CaO to form Si_3N_4, and either $La_{10}(SiO_4)_6N_2$(H-phase) or $CaSiO_3$, respectively. Several quaternary compatibility regions occur in the Si_2N_2O–Al_2O_3–La_2O_3 system:

H–Si_3N_4–La_2O_3·Si_2N_2O–La_2O_3·Al_2O_3
H–Si_3N_4–La_2O_3·Al_2O_3–La_2O_3·11Al_2O_3
H–Si_3N_4–La_2O_3·11Al_2O_3–Al_2O_3
H–Si_3N_4–Al_2O_3–O'ss
H–Si_3N_4–O'ss–Si_2N_2O

and in the Si_2N_2O–Al_2O_3–CaO system:

Si_3N_4–$CaSiO_3$–CaO·Si_2N_2O–3CaO·Al_2O_3
Si_3N_4–$CaSiO_3$–3CaO·Al_2O_3–2CaO·Al_2O_3·SiO_2
Si_3N_4–$CaSiO_3$–2CaO·Al_2O_3·SiO_2–Al_2O_3
Si_3N_4–$CaSiO_3$–Al_2O_3–O'ss
Si_3N_4–$CaSiO_3$–O'ss–Si_2N_2O

From the results of this work, the sub-solidus phase diagrams of the Si_2N_2O–Al_2O_3–La_2O_3 and Si_2N_2O–Al_2O_3–CaO systems are presented.

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1. INTRODUCTION

In our previous paper[1] the phase relations in the Si_2N_2O–Al_2O_3–Y_2O_3 system were presented. In order to understand the function of rare-earth oxides, lanthanum oxide has been chosen as a component for studying this series of systems. The phase relations in the Si_2N_2O–Al_2O_3–La_2O_3 system may be useful for the investigation of other rare-earth oxide systems and will be beneficial to the utilization of rare-earth oxides as densification aids in high technology ceramics.

As is well known, calcium, as one of the impurities usually occurring in the starting powders of silicon nitride and the sintering aids, is a harmful element which degrades the strength of silicon nitride-based ceramics at high temperatures. The study of the phase equilibrium of CaO-containing systems is beneficial for understanding the behaviour of calcium in advanced ceramics.

Phase relationships previously reported in the Al_2O_3–La_2O_3 system[2] show two stable compounds, $La_2O_3 \cdot Al_2O_3$ and $La_2O_3 \cdot 11Al_2O_3$. In the Si_2N_2O–La_2O_3 system[3,4] there are also two compounds, $2La_2O_3 \cdot Si_2N_2O$ (J-phase) and $La_2O_3 \cdot Si_2N_2O$ (K-phase), paralleling those found in the yttrium oxide-containing system.

In the Al_2O_3–CaO system compounds with the compositions Al_2O_3:CaO = 6:1, 2:1, 1:1, 7:12, 1:3 are well known,[5] and $3CaO \cdot Si_2N_2O$ has been found[6] with the same cubic structure as $3CaO \cdot Al_2O_3$ in the Al_2O_3–CaO system.

The limiting solubility of Al_2O_3 in Si_2N_2O ss in the Si_2N_2O–Al_2O_3 system has been reported to be 15 m/o Al_2O_3.[1]

2. EXPERIMENTAL

The starting materials used were lanthanum oxide, a reagent with 99·9% purity (Shanghai Yuolong Chemical Works), and calcium oxide, obtained by calcining calcium carbonate (99·99% purity) at 1100°C for 2 h. The details of the other starting materials used and all the experimental procedures have been described in the previous paper.[1]

3. RESULTS AND DISCUSSION

3.1. The Si_2N_2O–Al_2O_3–La_2O_3 system

In this system no new phase is found, except the two compounds reported earlier, $2La_2O_3 \cdot Si_2N_2O$ (J-phase) and $La_2O_3 \cdot Si_2N_2O$ (K-phase), with the same structures as $2Y_2O_3 \cdot Si_2N_2O$ (J-phase) and $Y_2O_3 \cdot Si_2N_2O$ (K-phase), respectively. In the Si_2N_2O-rich side, however, Si_2N_2O reacts with La_2O_3 to form Si_3N_4 and $La_{10}(SiO_4)_6N_2$(H-phase), as in the Si_2N_2O–Al_2O_3–Y_2O_3 system,[1] by the following reactions:

$$10Si_2N_2O + 6La_2O_3 \rightarrow La_{10}(SiO_4)_6N_2 + 4Si_3N_4 + La_2O_3 \cdot Si_2N_2O$$
$$9Si_2N_2O + 5La_2O_3 \rightarrow La_{10}(SiO_4)_6N_2 + 4Si_3N_4$$

These reactions are also extended into the ternary system Si_2N_2O–Al_2O_3–La_2O_3. Therefore, several quaternary compatibility areas are formed as follows:

H–Si_3N_4–$La_2O_3 \cdot Si_2N_2O$–$La_2O_3 \cdot Al_2O_3$
H–Si_3N_4–$La_2O_3 \cdot Al_2O_3$–$La_2O_3 \cdot 11Al_2O_3$
H–Si_3N_4–$La_2O_3 \cdot 11Al_2O_3$–Al_2O_3
H–Si_3N_4–Al_2O_3–O'ss
H–Si_3N_4–O'ss–Si_2N_2O

On the basis of the experimental results the sub-solidus phase diagrams of the Si_2N_2O–Al_2O_3–La_2O_3 system are as shown in Figs 1 and 2.

The results of this work show the phase diagram of the

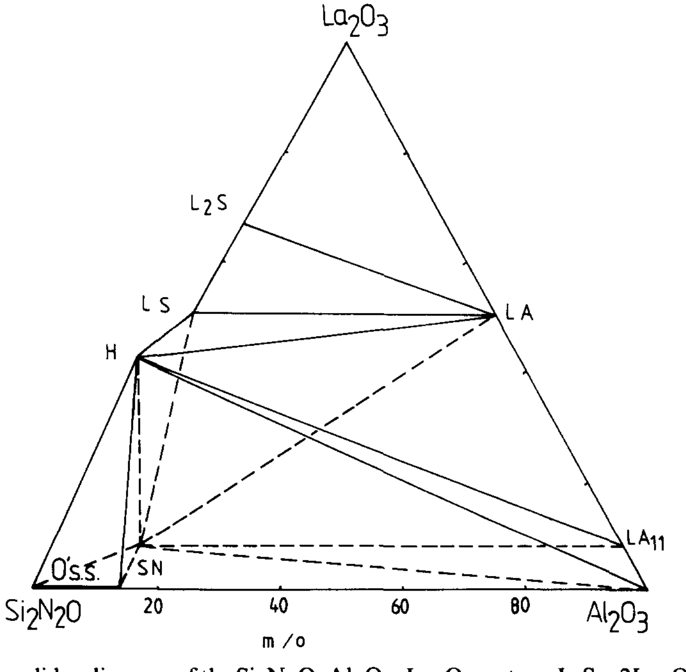

Fig. 1. Sub-solidus diagram of the Si_2N_2O–Al_2O_3–La_2O_3 system. $L_2S = 2La_2O_3 \cdot Si_2N_2O$; $LS = La_2O_3 \cdot Si_2N_2O$; $LA = La_2O_3 \cdot Al_2O_3$; $H = La_{10}(SiO_4)_6N_2$.

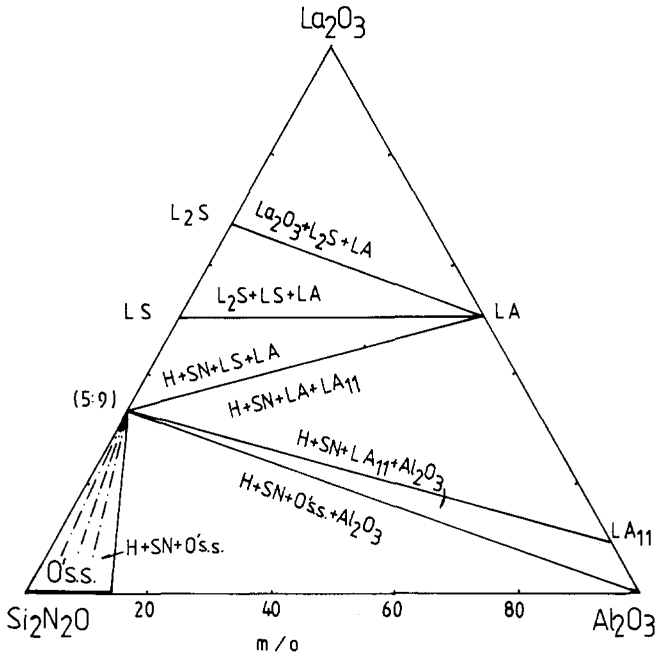

Fig. 2. Sub-solidus diagram of the Si_2N_2O–Al_2O_3–La_2O_3 system. 5:9 ($5La_2O_3 \cdot 9Si_2N_2O = 4Si_3N_4 + La_{10}(SiO_4)_6N_2$).

Si_3N_4–SiO_2–La_2O_3 system to be slightly different from that obtained by Mitomo *et al.*[4]

3.2. The Si_2N_2O–Al_2O_3–CaO system

One new stable compound, $CaO \cdot Si_2N_2O$, was found in this system. Its X-ray data without indexing are shown in Table 1. A continuous cubic solid solution between $3CaO \cdot Si_2N_2O$ and $3CaO \cdot Al_2O_3$ was observed. At the Si_2N_2O-rich end, however, Si_2N_2O also reacts with CaO to form Si_3N_4 and $CaSiO_3$ (which melts at 1415 °C) through the following reactions:

$$2CaO + 3Si_2N_2O \rightarrow Si_3N_4 + CaSiO_3 + CaO \cdot Si_2N_2O$$

$$CaO + 2Si_2N_2O \rightarrow Si_3N_4 + CaSiO_3$$

Such decomposition reactions of excess Si_2N_2O are also liable to occur with the additive Al_2O_3 in the ternary system Si_2N_2O–Al_2O_3–CaO. Therefore, several quaternary compatibility areas are formed as follows:

Si_3N_4–$CaSiO_3$–$CaO \cdot Si_2N_2O$–$3CaO \cdot Al_2O_3$

Si_3N_4–$CaSiO_3$–$3CaO \cdot Al_2O_3$–$2CaO \cdot Al_2O_3 \cdot SiO_2$

Si_3N_4–$CaSiO_3$–$2CaO \cdot Al_2O_3 \cdot SiO_2$–$Al_2O_3$

Si_3N_4–$CaSiO_3$–Al_2O_3–O'ss

Si_3N_4–$CaSiO_3$–O'ss–Si_2N_2O

TABLE 1
X-ray Data for $CaO \cdot Si_2N_2O$

d (obs)/Å	I/I_0	*d (obs)/Å*	I/I_0
4·720	vw	2·145	vvw
4·102	w	2·111	vvw
4·096	vw	2·099	vvw
3·405	ms	2·070	vvw
3·327	ms	2·026	vvw
3·250	vw	1·945	vw
3·176	w	1·907	w
3·089	w	1·881	vw
2·998	m	1·831	vw
2·922	m	1·790	vw
2·882	w	1·734	vw
2·810	w	1·705	vw
2·743	vw	1·675	vw
2·660	s	1·639	w
2·548	ms	1·600	vvw
2·515	m	1·556	m
2·411	w	1·540	vvw
2·350	vs	1·509	vw
2·293	w	1·502	vw
2·249	w	1·476	vvw
2·217	vw	1·447	vw
2·186	vvw		

Key. Notation for I/I_0: w, weak; vw, very weak; vvw, very very weak; m, medium; ms, medium strong; s, strong.

On the basis of the experimental results, the sub-solidus phase diagrams of the Si_2N_2O–Al_2O_3–CaO system investigated are as shown in Figs 3 and 4.

In addition, compositions within the region Al_2O_3–$3CaO \cdot Al_2O_3$–$2Si_2N_2O \cdot CaO$ (Fig. 4) always form the compound $2CaO \cdot Al_2O_3 \cdot SiO_2$ with some nitrogen-containing glass above 1250°C. Below this temperature the solid-state reaction could not occur and equilibrium could not be reached. Therefore, the phase behaviour in such a region is represented by dashed lines starting from $2CaO \cdot Al_2O_3 \cdot SiO_2$. In the Si_2N_2O-containing systems investigated excess Si_2N_2O decomposes easily and reacts with Y_2O_3, La_2O_3 or CaO to form Si_3N_4 and either H-phase or $CaSiO_3$. According to the following reaction[7,8] in a nitrogen atmosphere at high temperature:

$$4Si_2N_2O \rightarrow Si_3N_4(s) + 4SiO(g) + Si(l, g) + 2N_2(g)$$

the phenomenon of such reactions of excess Si_2N_2O with Y_2O_3, La_2O_3 and CaO is easy to understand.

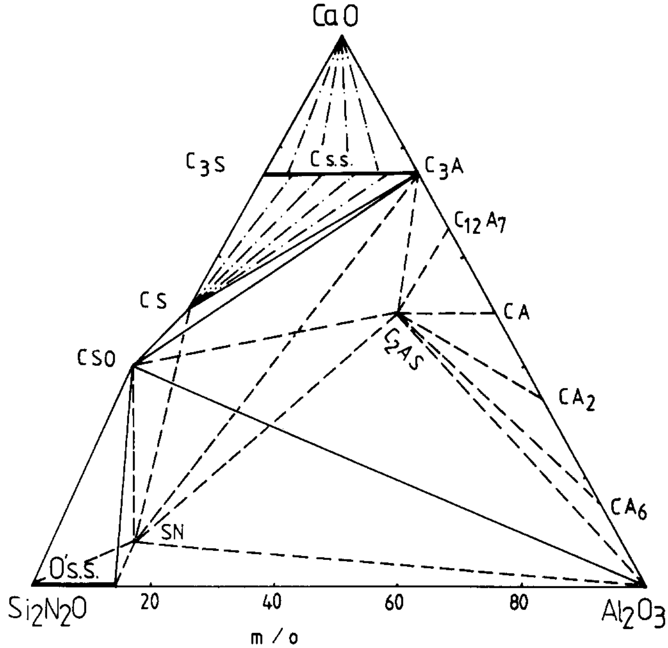

Fig. 3. Sub-solidus diagram of the Si_2N_2O–Al_2O_3–CaO system. $C_3S = 3CaO \cdot Si_2N_2O$; $CS = CaO \cdot Si_2N_2O$; $CSO = CaSiO_3$; $C_2AS = 2CaO \cdot Al_2O_3 \cdot SiO_2$; $CA_6 = CaO \cdot 6Al_2O_3$; $C_3A = 3CaO \cdot Al_2O_3$; $C_{12}A_7 = 12CaO \cdot 7Al_2O_3$; $CA = CaO \cdot Al_2O_3$; $CA_2 = CaO \cdot 2Al_2O_3$.

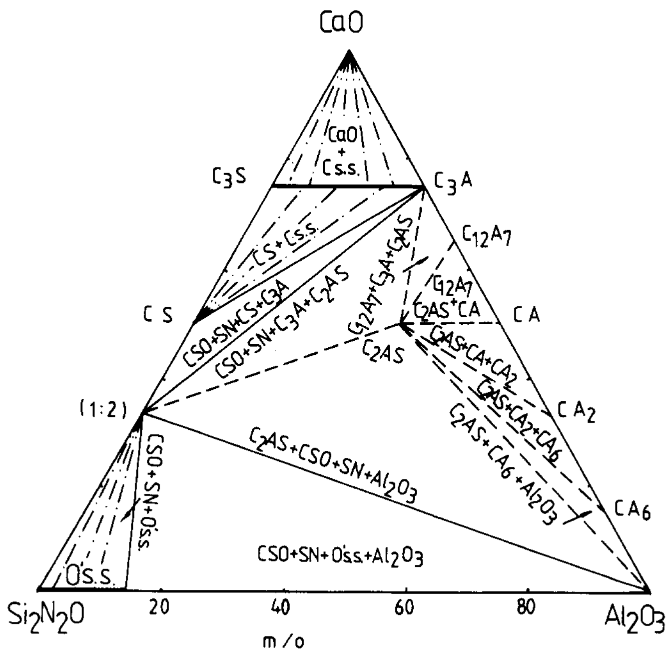

Fig. 4. Sub-solidus diagram of the Si_2N_2O–Al_2O_3–CaO system. 1:2, $CaSiO_3 + Si_3N_4$.

CONCLUSIONS

1. The sub-solidus phase diagrams of the Si_2N_2O–Al_2O_3–La_2O_3 and Si_2N_2O–Al_2O_3–CaO systems are presented. In the former system no new compound is found; in the latter system a new compound $CaO \cdot Si_2N_2O$ and a continuous cubic solid solution between $3CaO \cdot Si_2N_2O$ and $3CaO \cdot Al_2O_3$ are formed.
2. In the Si_2N_2O-rich area of these two systems the excess Si_2N_2O reacts with La_2O_3 and CaO to form Si_3N_4 and either $La_{10}(SiO_4)_6N_2$ (H-phase) or $CaSiO_3$, respectively, in a nitrogen atmosphere at high temperatures, and several quaternary compatibility regions are formed.

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