Thermal degradation behaviour of the layer-type complexes of montmorillonite/α-naphthylamine, saponite/α-naphthylamine and their mixtures

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Samples of montmorillonite/α-naphthylamine complex (MNC), saponite/α-naphthylamine complex (SNC) and their mixtures were heated at temperatures below 1473 K under a nitrogen atmosphere to examine macroscopic structural change and crystalline phases deposited after pyrolysis. SNC resulted in a dense structure after pyrolysis. Heating of samples of MNC/SNC mixtures gave a porous structure which became dense as the proportion of SNC increased. No porosity measured by the mercury porosimeter was detectable in samples pyrolysed from MNC containing more than 25% SNC. After pyrolysis, the MNC/SNC mixtures gave crystalline phases which were never formed in the pyrolysed pure MNC and SNC. The formation of these crystalline phases was explained by reference to the chemical compositions of the mixtures and the phase diagram.

1. Introduction

We have reported previously that thermal degradation behaviour of clay/organic complexes is strongly dependent on the combination of clay and organic compound. Typical examples are the formation of a homogeneous and porous material derived from the montmorillonite/α-naphthylamine complex (refered to as MNC) [1, 2] and a dense material derived from the saponite/α-naphthylamine complex (refered to as SNC) [3]. These phenomena aroused our interest in the thermal degradation behaviour of the MNC/SNC mixture for the following two reasons. First to examine the possibility of structural control of the porous material derived from the MNC by varying the proportion of SNC added. Second, we were interested in the crystalline phases formed in the mixture after decomposition of the complexes by heating. The present work was undertaken to clarify both points.

2. Experimental details

2.1. Raw materials and preparation methods of samples

Montmorillonite from Aterasawa, Yamagata, Japan, was used after purification by the conventional sedimentation method in this laboratory. The purified montmorillonite from this region is marketed by Kunimine Industries Co. Ltd (trade name Kunipia-F). Saponite is commercially available from the same company (trade name Smecton-SA). Table I lists the chemical compositions and cation exchange capacities (CEC) of Kunipia-F and Smecton-SA.

An equivalent amount of α-naphthylamine hydrochloride ($C_{10}H_7NH_2 \cdot HCl$) (measured by CEC) was

added to 3% montmorillonite aqueous solution, followed by stirring at 353 K for 4 days to convert it into MNC. The SNC was prepared under the same condtions as for the MNC, except that stirring was continued for 3 days. The resulting MNC and SNC were washed with deionized water until the Cl^- ion was no longer present. In addition to both complex samples, the MNC/SNC mixtures (MNC/SNC = 95/5, 90/10, 75/25 and 50/50 by weight) were heated at temperatures below 1473 K under a nitrogen atmosphere after drying at 333 K. The heating rate and residence time for a prefixed temperature were 5 K min^{-1} and 1 h, respectively.

TABLE I Chemical compositions (wt %) and cation exchange capacities (CEC) of montmorillonite and saponite

Component	Mont.*	Saponite*	MNC/SNC			
			95/5	90/10	75/25	50/50
SiO_2	57.96	54.71	57.8	57.6	57.2	56.3
Al_2O_3	21.87	5.02	21.0	20.2	17.7	13.5
Fe_2O_3	1.92	0.03	1.8	1.7	1.5	1.0
MgO	3.44	30.74	4.8	6.0	10.3	17.1
CaO	0.54	–	0.5	0.5	0.4	0.3
Na_2O	2.98	2.15	2.9	2.9	2.8	2.6
K_2O	0.14	–	0.1	0.1	0.1	0.1
SO_3	–	0.67				
Ig. loss	10.75	6.67				
Total	90.60	99.99				

CEC (meq/100 g) 119 71.2
These values were cited from the catalogues.
*Trade names Kunipia-F and Smecton-SA, produced by Kunimine Industries Co.

*Author to whom all correspondence should be addressed.
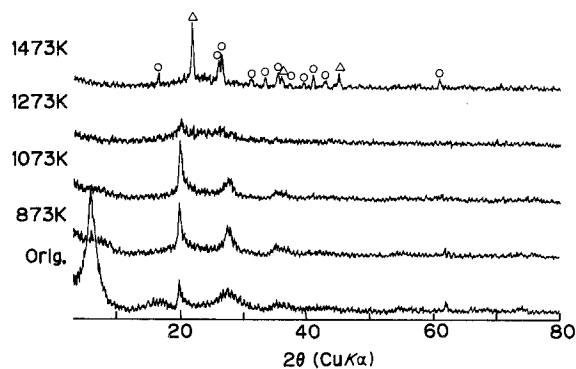‡ *Present address:* Kunimine Industries Co. Ltd, Nabekake, Kuroiso, Tochigi 325, Japan.

Figure 1 X-ray diffraction profiles of MNC before and after heating. (O) Mullite (ML), (△) α-cristobalite (CB).
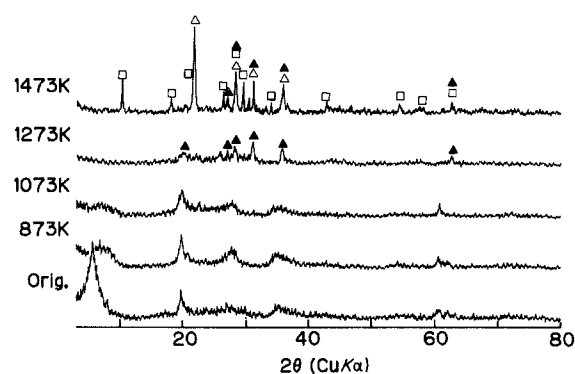

Figure 2 X-ray diffraction profiles of MNC/SNC = 50/50 before and after heating (△) α-cristobalite (CB), (▲) enstatite (ET), (□) cordierite (CD).

2.2. Measurements

Powder X-ray diffraction was carried out using nickel-filtered CuKα radiation. The polished surface of the block sample was etched with 7% NaOH solution for 40 min at room temperature, followed by scanning electron microscopy. Carbon content was measured by the combustion method using tin particles as a combustion accelerator. The porous structures of some samples were examined using a mercury porosimeter.

3. Results

3.1. X-ray diffraction analysis

Figs 1 to 3 show X-ray diffraction profiles of the MNC, the SNC and the mixture of MNC/SNC = 50/50 before and after heating, respectively. The (0 0 1) diffraction peak of MNC around 5° (2θ, CuKα) disappeared at 873 K, but the (0 0 3) peak at 28° and the (1 1 –, 0 2 –) peak at 20° remained after heating to 1073 K. The latter peak was still present faintly even after heating to 1273 K. At 1473 K, mullite (3Al₂O₃ · 2SiO₂) and α-cristobalite (SiO₂) were formed from the MNC.

After heating the SNC to 1073 K, the SNC remained bound with a small quantity of enstatite (MgO · SiO₂) being formed. At higher temperatures, enstatite was formed in greater quantities. As shown in Fig. 3, enstatite was formed in the mixture at 1273 K, and cordierite (2MgO · 2Al₂O₃ · 5SiO₂) and cristobalite in addition to enstatite were observed in the mixture after heating to 1473 K.

Table II lists crystalline phases in the samples before and after heating. Estimates of the relative amounts present were obtained by comparing the diffraction peak intensities. Formation of new crystalline phases

were first observed at 1473, 1073 and 1273 K in the MNC, the SNC and the mixture, respectively. The crystalline phases formed at 1273 K changed from magnesium aluminium silicate (MgO · Al₂O₃ · 4SiO₂) to enstatite as the proportion of SNC increased. After heating to 1473 K, cristobalite and mullite formed in the MNC sample but both these together with cordierite were deposited in the MNC with only 5% SNC added. In the MNC samples with 10 to 25% SNC added, cristobalite and cordierite formed. In addition to these phases, enstatite was observed in the mixture of MNC/SNC = 50/50. Only enstatite was formed in the SNC sample.

3.2. Carbon content

Table III shows the carbon contents of the samples. The content in the SNC before heating was ~7% which started to decrease at 873 K and fell to 5.6% at 1473 K. The MNC contains a larger amount of carbon, and a smaller decrease in the carbon content with the increase in temperature was observed. The carbon contents of the mixtures were intermediate between those of the MNC and the SNC regardless of temperature.

3.3. SEM observation

Figs 4a and b are scanning electron micrographs of samples after heating to 1073, 1273 and 1473 K. The structure of the SNC sample after heating to 1073 K has become considerably more dense although fine raw particles can still be observed in cracks. Such particles disappeared after heating to 11273 and 1473 K. However, the MNC after heating to 1073 K showed a characteristic porous structure which started to sinter at 1273 K. A homogeneous and dense struc-

TABLE II Crystal phases formed in the samples before and after heating

Sample	Heat-treatment temperature (K)				
	Orig.	873	1073	1273	1473
MNC	MNC	MNC	MNC	MNC	CB* > ML
MNC/SNC = 95/5	MNC, SNC	MNC, SNC	MNC, SNC	MA	CB ≫ CD > ML
MNC/SNC = 90/10	MNC, SNC	MNC, SNC	MNC, SNC	MA	CB > CD
MNC/SNC = 75/25	MNC, SNC	MNC, SNC	MNC, SNC	MA	CB > CD
MNC/SNC = 50/50	MNC, SNC	MNC, SNC	MNC, SNC	ET	CB > CD > ET
SNC	SNC	SNC	SNC, ET	ET	ET

*CB, α-cristobalite; ML, mullite; CD, cordierite; ET, enstatite; MA, MgAl₂Si₄O₁₂ (ASTM 27-716).
The relative amounts of formation were determined semi-quantitatively from the peak intensities. The peaks of MNC and SNC were not separated.

TABLE III Carbon contents (wt %) of the samples before and after heating

Sample	Heat-treatment temperature (K)				
	Orig.	873	1073	1273	1473
MNC	11.6	12.2	11.7	10.8	11.2
MNC/SNC = 95/5	9.9	9.6	10.1	9.5	9.4
MNC/SNC = 90/10	10.0	9.4	9.8	9.9	9.6
MNC/SNC = 75/25	10.5	10.6	9.4	9.1	9.1
MNC/SNC = 50/50	9.4	9.9	8.9	8.2	8.1
SNC	6.7	6.6	6.3	5.7	5.6

Figure 3 X-ray diffraction profiles of SNCs before and after heating. (▲) Enstatite (ET).

ture was observed at 1473 K. It should be noted that some areas in these photographs show planar particle surfaces. The structures formed from samples of the mixtures of MNC/SNC = 75/25 and 50/50 are intermediate between those observed for the MNC and the SNC or relatively more similar to the MNC derived structure. After heating to 1473 K, these structures sintered with the increase in temperature but narrow pores remained.

3.4. Pore size distribution diagram

Fig. 5 shows pore size distribution diagrams of the samples formed at 1073 K before sintering. The MNC showed a large pore volume ($0.6 \, ml \, g^{-1}$) consisting of the homogeneous pores (average pore radius 60 to 70 nm). In the case of the sample with 5% SNC added, the pore volume was reduced by half with a decrease in pore size. The mixture of MNC/SNC = 90/10 showed a small pore volume and pore size (average pore radius 10 nm). In samples with larger percentages
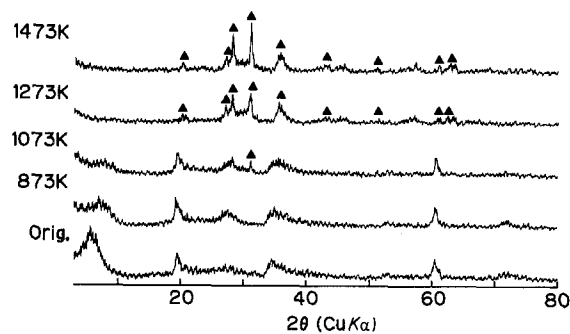
of SNC added, pores were no longer detectable using the mercury porosimeter.

4. Discussion

The first object of this work was to examine the structures derived from the MNC/SNC mixture. As shown in Fig. 4, even the mixtures of MNC/SNC = 50/50 and 75/25 resulted in relatively dense structures which are similar to those derived from SNC rather than MNC. This trend can be seen more clearly from the pore size distribution diagrams (Fig. 5) in which it can be seen porosity was not detectable in samples from the mixture of MNC/SNC = 75/25. It should be noted that some closed pores are included in this sample as observed in Fig. 4. It can be concluded that SNC has a stronger effect on the resultant structure of the MNC/SNC mixture.
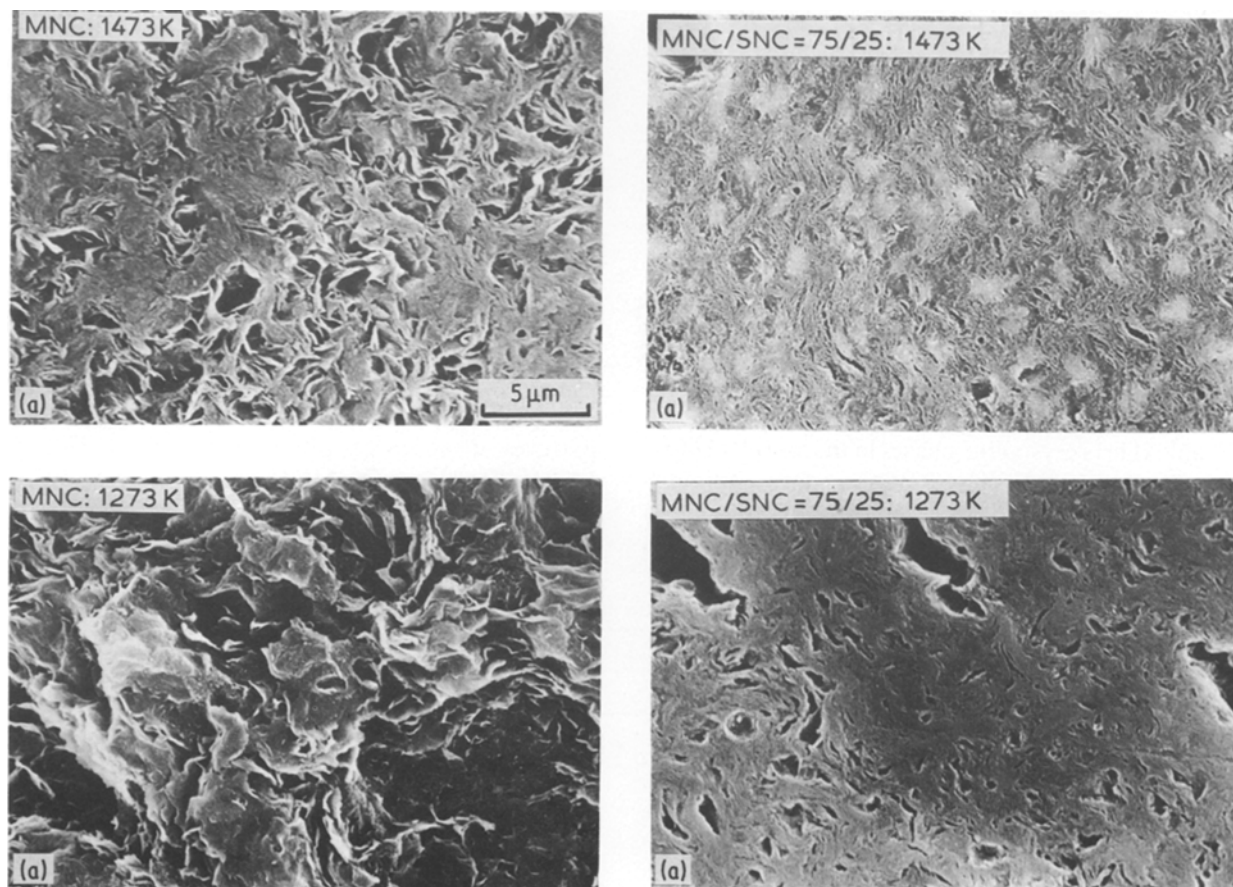

Figure 4 Scanning electron micrographs of (a) MNCs and MNC/SNC = 75/25 and (b) MNC/SNC = 50/50 and SNC, before and after heating.
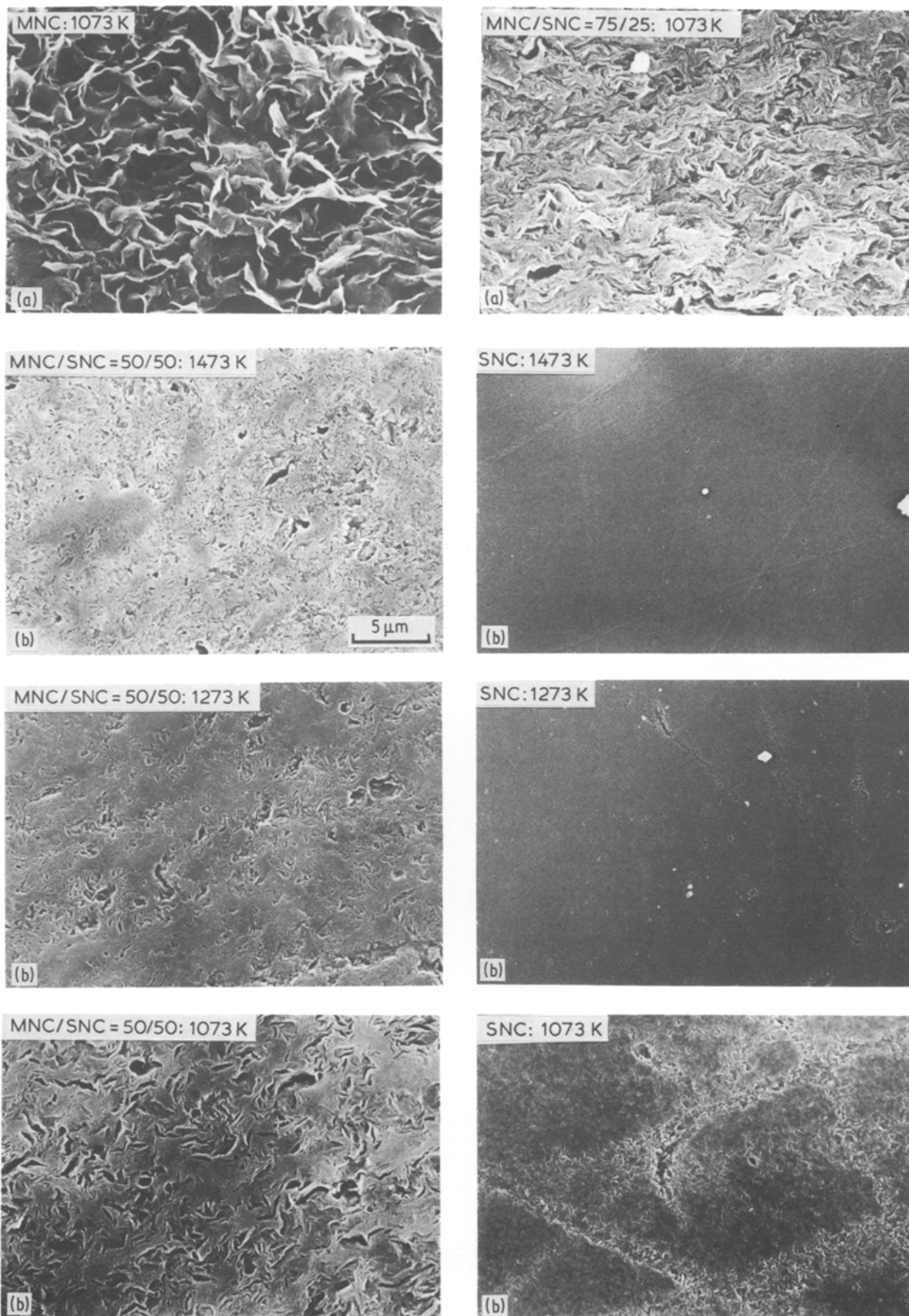
Figure 4 Continued.

We have reported previously that pyrolysis of MNC results in a characteristic card house-like porous structure with a large pore volume consisting of pores of several tens of nanometers in radius. The porous structure can be changed by the use of freeze-drying [4] and selection of the dispersion medium of the MNC [5]. These techniques, however, are effective only to increase the pore size and pore volume, whereas the addition of SNC to MNC was effective in reducing both the pore size and the pore volume. One
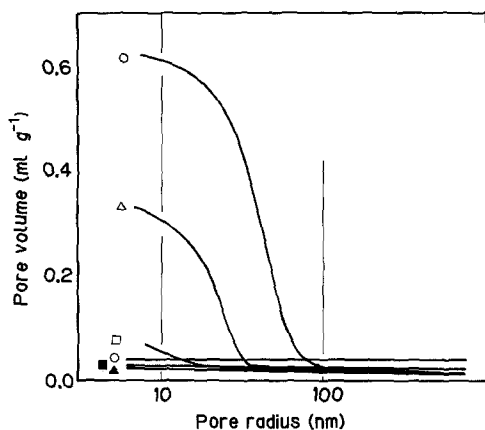
Figure 5 Pore size distribution diagrams of all samples after heating to 1073 K. (O) MNC, (△) MNC/SNC = 95/5, (□) MNC/SNC = 90/10, (■) MNC/SNC = 75/25, (▲) MNC/SNC = 50/50, (●) SNC.

problem is that large changes were caused by the addition of small amounts of SNC, i.e. control of the porous structure by this method is very sensitive.

The second object of this work was to investigate the kinds of crystalline phases formed in the pyrolysed MNC/SNC mixtures. After heating to 1273 K (Table II), enstatite was observed in SNC and the mixture of MNC/SNC = 50/50, and the mixtures including 5 to 25% of the SNC gave magnesium aluminium silicate which was not formed in either the MNC or the SNC. As far as these phenomena are concerned, the SNC seems to have the stronger influence on the kinds of crystalline phases formed. After heating to 1473 K, however, cristobalite was formed abundantly in the mixture of MNC/SNC = 50/50 as well as in the MNC. It is not easy to say which component governed the type of crystalline phase deposited.

As shown in Table II, some crystalline phases formed only in the MNC/SNC mixtures, which suggests a reaction between the MNC and the SNC.
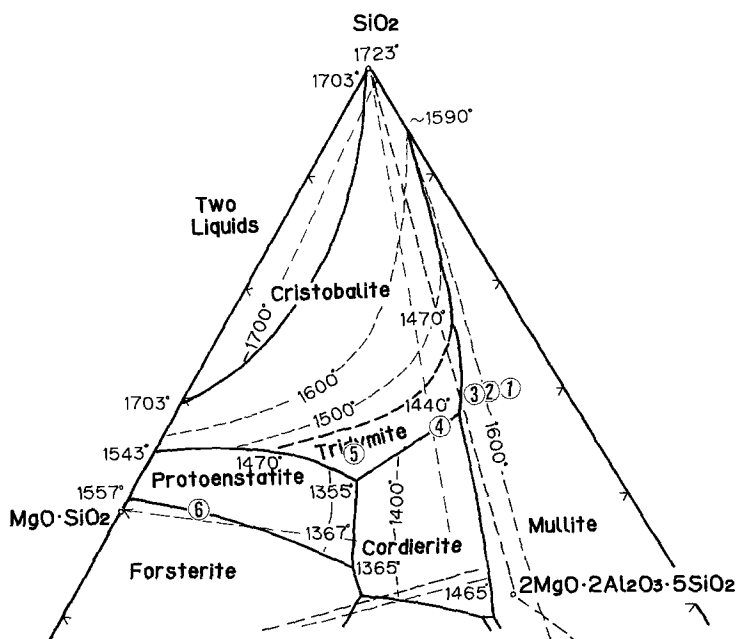
Based on the analytical data of Kunipia-F and Smecton-SA listed in Table I, chemical compositions of the mixtures were calculated and are shown in Table I. Of course, the samples contain some carbon (Table III), but the carbothermal reduction does not seem to occur at 1473 K when the crystalline phases and carbon contents are examined. Therefore, the relative ratio (in weight per cent) among the three main components, SiO_2, Al_2O_3 and MgO, were calculated and plotted in the SiO_2–Al_2O_3–MgO phase diagram (Fig. 6) [6]. The deposited crystalline phases formed in the MNC/SNC mixtures (Table II) were roughly consistent with those in the phase diagram. It is concluded that the original structures of individual components do not remain after heating to high temperatures.

Acknowledgements

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Figure 6 Phase diagram of the system MgO–Al_2O_3–SiO_2. 1, montmorillonite; 2, montmorillonite/saponite = 95/5; 3, montmorillonite/saponite = 90/10; 4, montmorillonite/saponite = 75/25; 5, montmorillonite/saponite = 50/50; 6, saponite.