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SEM study of the fractured surfaces of films and blocks prepared from montmorillonite and its complex with α-naphtylamine

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Four samples were heated under nitrogen to determine the relations between heat-treatment conditions and the topographies of the fractured surfaces of the resulting samples. The samples used were thin films (several $10\,\mu$m thick) of lithium-montmorillonite (Mont) and its complex (MNC) with α-naphtylamine, and the blocks of raw montmorillonite and its complex with α-naphtylamine (MNC). Two characteristic topographies were obtained from MNC film. They were of a very dense structure with the memory of a layered structure after heating to about 1173 K at 1 or $5\,\mathrm{K\,min^{-1}}$, and a homogeneous fine porous structure after heating to 1173 to 1273 K at $40\,\mathrm{K\,min^{-1}}$. An unique porous structure was also obtained from MNC block, several millimetres thick by heating to 873 K for 1 h. However, Mont, in both film and block, was not suitable for preparation of the homogeneous structure, regardless of porous or dense structures.

1. Introduction

Some clay minerals such as montmorillonite and halloysite are known to form intercalation compounds with organic compounds [1, 2]. The present authors were interested in carbonizing the organic compounds in this seriously restricted field in the expectation of developing a new functional material. The thermal degradation behaviour of montmorillonite–α-naphtylamine complex (MNC) film was examined as the first work of this series. MNC film resulted in a fine and homogeneous porous structure after heating to 1273 K under nitrogen, further details of which were reported elsewhere [3, 4]. This result suggests that MNC can be used as a raw material for a new porous ceramic with thermal stability. In order to complete such a trial, however, the structures of the MNC film must first be characterized in further detail with regard to heat-treatment conditions. Through such work, of course, other characteristic structures may be obtained. Next our interest is to endow these characteristic structures to the block.

The present work, therefore, was carried out with the following two purposes. One was to prepare MNC film from lithium-montmorillonite (Mont) as reported previously [3, 4] and to determine the relations between the structures of the fractured surfaces and heat-treatment conditions. The second purpose was to prepare MNC block and to reveal the relations stated above. Here, however, raw Mont without ion exchange was used from the practical point of view. For the references, lithium-Mont film and raw Mont block also served the same purpose.

2. Experimental details

Raw Mont from Aterasawa, Yamagata, Japan was used in the present work. Preparation procedures of the thin film and block are given below.

2.1. Films

A thin film, several $10\,\mu$m thick was prepared from lithium-Mont particles (smaller than 2 to $3\,\mu$m) of which further details were reported elsewhere [3]. A part of the resulting thin film was soaked in 0.1 N α-naphtylamine · hydrochloride($C_{10}H_7NH_2 \cdot HCl$: NA) aqueous solution at 353 K for 3 days to convert it into MNC film. After removal of NA from the film surface with acetone, the film was subjected to sealing in glass tubing under vacuum, followed by γ-ray radiation of 12 Mrad and by heating to 473 K for 1 h to induce polymerization of NA between the Mont layers. Another part of the Mont film was also subjected to γ-ray radiation and heated as stated above. Both films thus prepared were further heated in nitrogen under the following conditions:

heat-treatment temperature (HTT): 1073, 1173, 1273 and 1373 K
heating rate: 1, 5 and $40\,\mathrm{K\,min^{-1}}$
residence time: 1 min and 1 h

2.2. Blocks

NA was added to the suspension of raw Mont particles (smaller than 2 to $3\,\mu$m) without cation exchange to achieve 1.5 times the cation exchange capacity (108 meq/100 g) of raw Mont. After keeping at 353 K for 3 days, the resulting MNC particles were collected by centrifuging, followed by drying at 393 K for several days to prepare MNC block. Attempts were made to prepare raw Mont block but it was very difficult because of a remarkable preferred orientation

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TABLE I Crystal phases formed in Mont film

HTT (K)	Residence time 1 min, heating rate ($K\,min^{-1}$)			Residence time 1 h, heating rate ($K\,min^{-1}$)		
	1	5	40	1	5	40
1073	LAS Mont	LAS Mont	Mont	LAS Mont	LAS Mont	(LAS)
1173	LAS	LAS (Mont)	(LAS)	LAS	LAS	LAS
1273	LAS	LAS	LAS	LAS	LAS	LAS
1373	LAS (CB)	LAS	LAS	–	–	–

( ), a small degree of formation.
LAS, lithium–aluminosilicate type crystal.
CB, cristobalite.

TABLE II Crystal phases formed in MNC film

HTT (K)	Residence time 1 min, heating rate ($K\,min^{-1}$)			Residence time 1 h, heating rate ($K\,min^{-1}$)		
	1	5	40	1	2	40
1073	MNC	MNC	MNC	MNC	MNC	MNC
1173	MNC	MNC	MNC	MNC	MNC	MNC
1273	(MNC)	(MNC)	MNC	(MNC) (LAS)	MNC (LAS)	MNC (LAS)
1373	(MNC) (LAS)	(MNC) (LAS)	MNC (LAS)	–	–	–

( ), a small degree of formation.
LAS, lithium–aluminosilicate type crystal.
CB, cristobalite.

of the raw Mont particle. Therefore, as thick a part as possible was used in the following experiment. This specimen and an MNC block, several millimetres thick were heated in nitrogen under the following conditions:

HTT: 873, 1073, 1273 and 1473 K
heating rate: 1 and 40 $K\,min^{-1}$
residence time: 1 h

The fractured surfaces of the resulting films and blocks were observed by scanning electron microscopy (SEM). The crystal phases formed in the specimens were identified using X-ray diffraction analysis (nickel filtered Cu$K\alpha$-radiation).

3. Results and discussion

3.1. MNC and Mont films

The crystal phases in Mont and MNC films after heating are summarized in Tables I and II, of which further details will be reported later. As examples, changes of X-ray diffraction profiles of Mont and MNC films with HTT (heating rate 1 $K\,min^{-1}$; residence time 1 min) are shown in Figs. 1 and 2. Lithium-aluminosilicate-type crystal (LAS) appeared in the Mont films, except for one, at 1073 K and the original Mont disappeared completely at 1173 K with no LAS remaining. LAS alone was observed in Mont film heated to 1373 K with one exception in which cristobalite (CB) formed slightly.

However, MNC persisted up to 1173 K, although the gradual degradation of its crystal structure was presumed from a strengthening of the background of its X-ray diffraction profile (Fig. 2). Even after heating to 1273 K, MNC alone was slightly observed when the retention time was just 1 min. By extending the retention time to 1 h, however, LAS also formed faintly. As a result, it is clear that the layered structure of MNC has a higher thermal stability than Mont by about 200 K.

Fig. 3 shows the fractured surface (edge) of Mont (No. 1) and MNC (No. 2) films before heating. Both films have the layer stacking structures preferentially oriented parallel to the film surfaces, although MNC films is more dense. Except as specifically noted, the magnification of all photographs is equal to the scale shown in No. 1.

Fig. 4 shows scanning electron micrographs of the fractured surfaces of Mont films after heating to various HTTs for 1 min. With increasing heating rate, on the whole, a more porous Mont film was obtained, of which typical examples are Mont films heated to 1273 and 1373 K at 40 $K\,min^{-1}$ (Nos. 13 and 14). When the structures are examined in more detail, however, a difference is observed between Mont films heated at 1 $K\,min^{-1}$ and those heated at 5 or 40 $K\,min^{-1}$, that is, the former is more porous near the film surface, in comparison to the preferential pore formation near the centre in the latter films. When a larger heating rate is used, just the film surface is preferentially densified because it is heated more quickly than the interior. The delayed gas evolution from the interior, therefore, results in the pores between the dense film surfaces. Here, the memory of the layered structure in raw Mont remains in the resulting films. When the Mont film is heated slowly, on the other hand, the whole of the film is heated so uniformly that the evolved gas can escape more easily from the film,

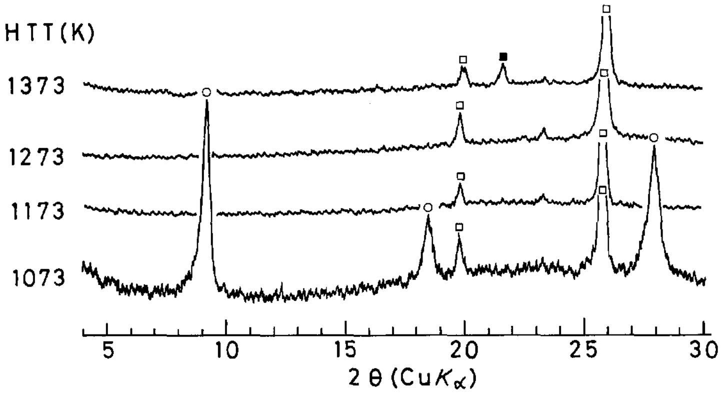

Figure 1 Changes of X-ray diffraction profiles of Mont film with HTT (heating rate 1 $K\,min^{-1}$; residence time 1 min). (○) Mont, (□) LAS, (■) CB.

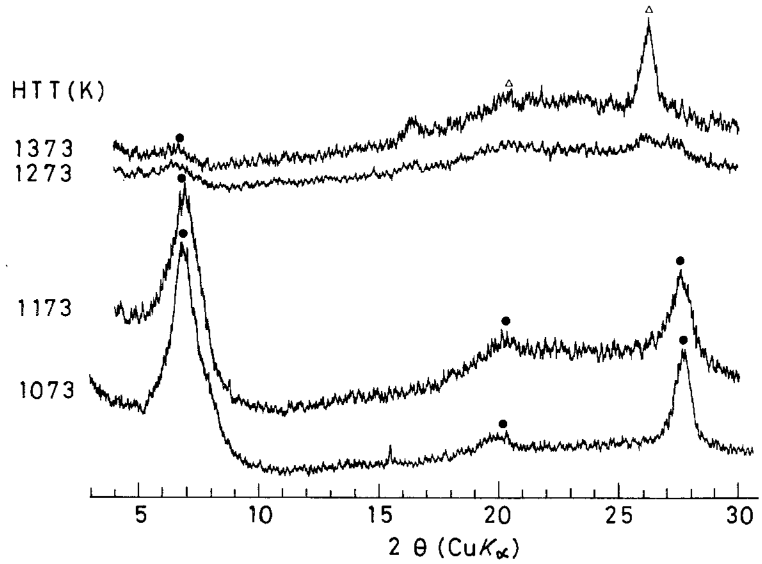

Figure 2 Changes of X-ray diffraction profiles of MNC films with HTT (heating rate 1 K min^{-1}; residence time 1 min). (●) MNC, (△) LAS.

resulting in the dense film centre. The effect of HTT was not so remarkable except for Mont films heated rapidly.

Mont films heated for 1 h are shown in Fig. 5. The observed structures are substantially same as those in Fig. 4, though with minor differences. For example, Mont films heated to 1073 or 1173 K at small heating rates for 1 h (Nos. 15, 16, 18 and 19) seem to be more dense than those heated for 1 min under the corresponding conditions (Nos. 3, 4, 7 and 8), respectively, possibly through further sintering during the longer residence period. The pores were formed abundantly in Mont films heated at 40 K min^{-1} (Nos. 21, 22 and 23). Needles were observed in No. 21, which must be formed by the rapid gas evolution when Mont film became considerably more fluid. In the more fluid state attained at higher HTTs, these needles were degraded and changed into the stalagmites (No. 23). From Figs. 4 and 5, as a result, it is clear that Mont films with homogeneous structures, regardless of density or porosity, are difficult to prepare.

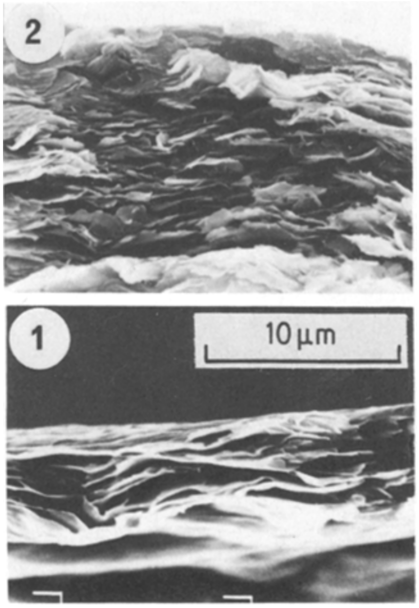

Figure 3 The fractured surfaces of (1) raw Mont and (2) raw MNC films.

Fig. 6 shows the fractured surfaces of MNC films heated to various HTTs for 1 min. One feature of MNC films, compared with Mont films, is the preferred retention of the memory of the layered structure. This must be attributable to the more thermally stable layered structure of MNC owing to the insertion of NA molecules between the Mont layers. In Fig. 6 there are two characteristic structures: they are the very dense structure with the memory of the layered strucutre (Nos. 25 and 29), and the homogeneous fine porous structure (Nos. 36 and 38). Such a difference is governed mainly by the heating rate. On the whole, a large heating rate is effective in producing the porous structure and smaller heating rate the dense structure. These structures are not derived from Mont film but from MNC film. It should be noted, in addition, that two different structures were obtained from the same raw MNC film after heating at 40 K min^{-1} (Nos. 33 to 38). This suggests that the resulting structure is considerably changeable under a large heating rate, details of which are not clear at present. We can also see the sintering process of MNC film from Fig. 6. The layered stacking becomes more dense with increase in HTT up to 1173 K, with no remaining pores. However, the structure becomes porous at 1273 K, which may be attributable to the dense film surface formation followed by gas evolution. The film is densified again at higher HTT.

The fractured surfaces of MNC films heated to various HTTs for 1 min are shown in Fig. 7. Similar structures to those in Fig. 6 are seen. For example, the structures of Nos. 47 and 48 are very similar to those of Nos. 36 and 37, respectively. HTTs for the former

TABLE III Crystal phases formed in Mont and MNC blocks

HTT (K)	Mont		MNC	
	1 K min^{-1}	40 K min^{-1}	1 K min^{-1}	40 K min^{-1}
873	Mont	Mont	MNC	MNC
1073	Mont	Mont	MNC	MNC
1273	CB	CB	(MNC)	MNC
1473	CB, CD, MU		CB, MU, CD	

( ): a small amount of formation.
CB, Cristobalite; CD; cordierite; MU, mullite.

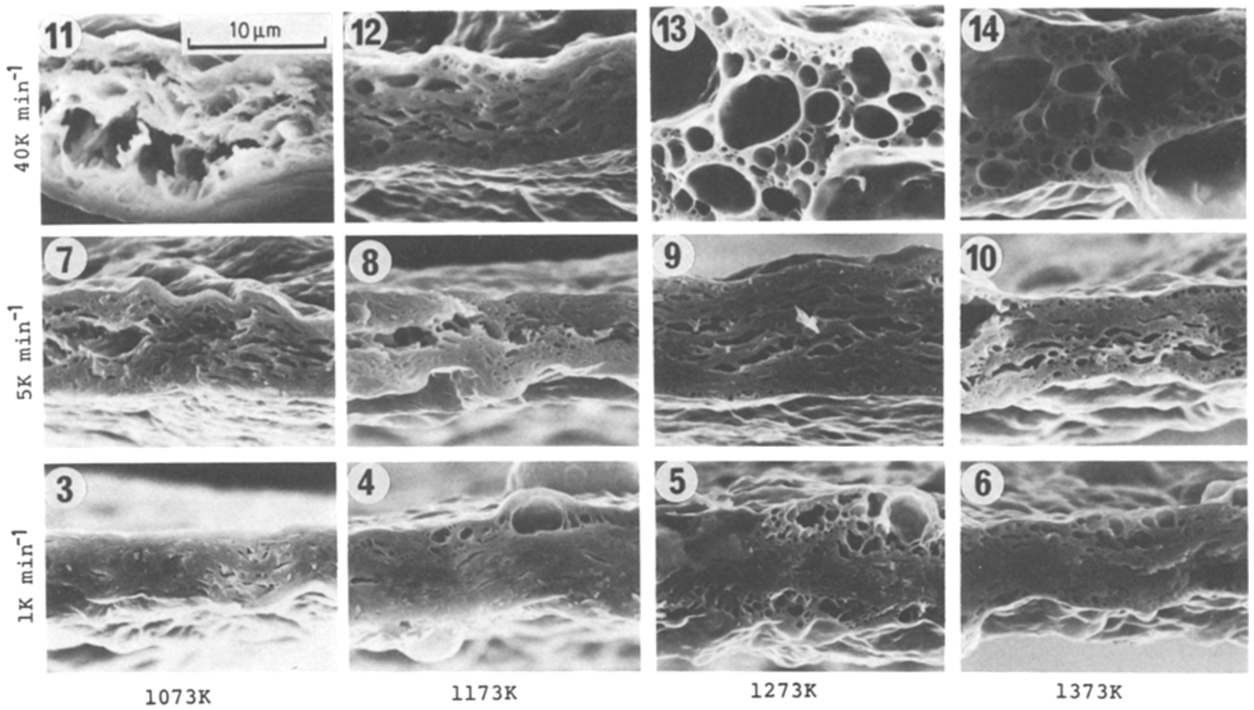

Figure 4 The fractured surfaces of Mont films after heating (residence time 1 min).

two, however, are lower than those for the latter two by 100 K; in other words, the sintering of MNC film proceeds during the residence period. Therefore, the fine and homogeneous porous structure we wished to prepare, was obtained by heating MNC film to 1173 to 1273 K at a heating rate as large as 40 K min^{-1}.

3.2. Mont and MNC blocks

The crystal phases formed in Mont and MNC blocks are summarized in Table III. Raw Mont block without ion exchange retained its layered structure up to 1073 K, with no formation of any other crystal, which is higher than the maximum HTT for lithium-Mont.

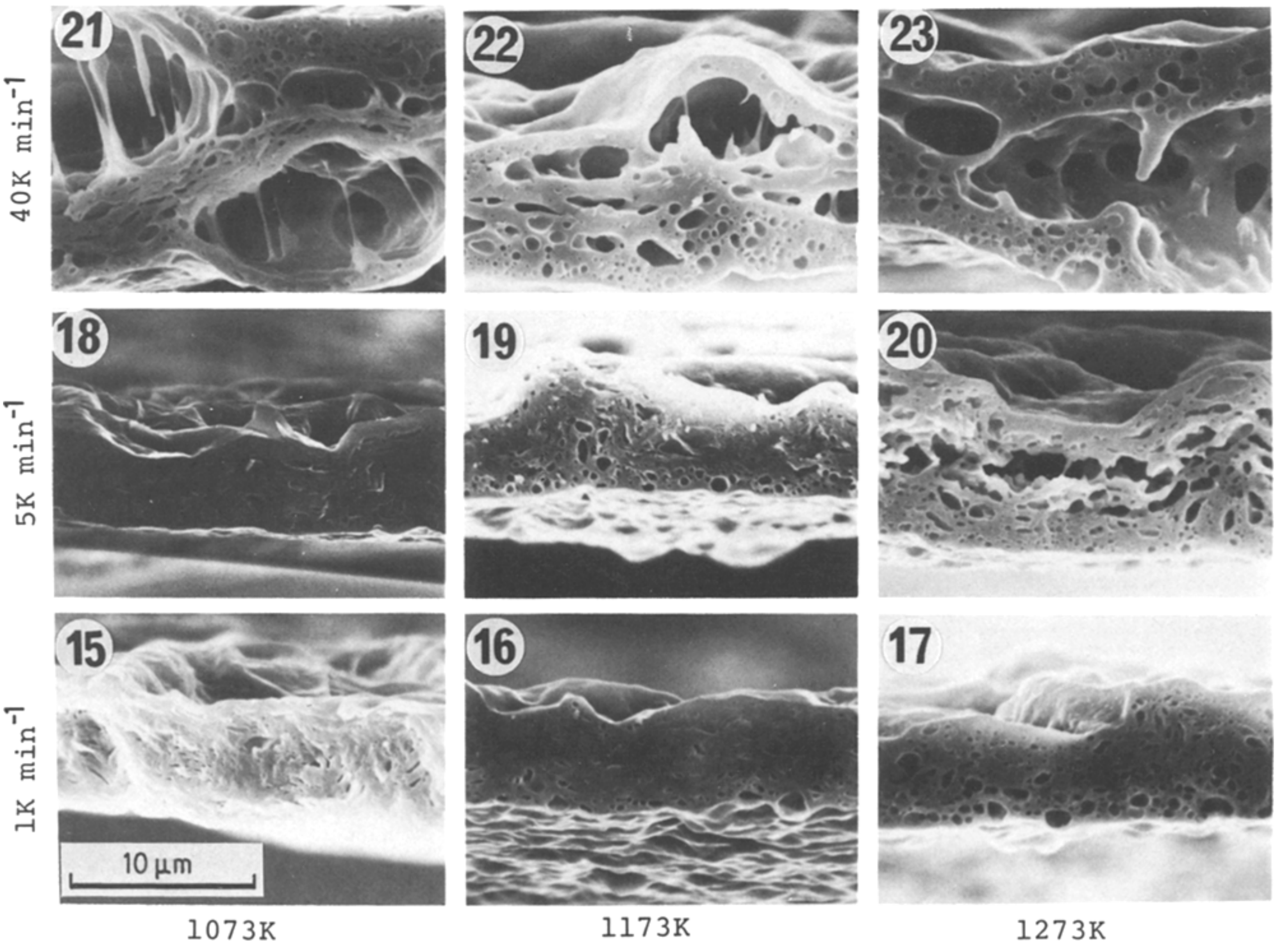

Figure 5 The fractured surfaces of Mont films after heating (residence time 1 h).

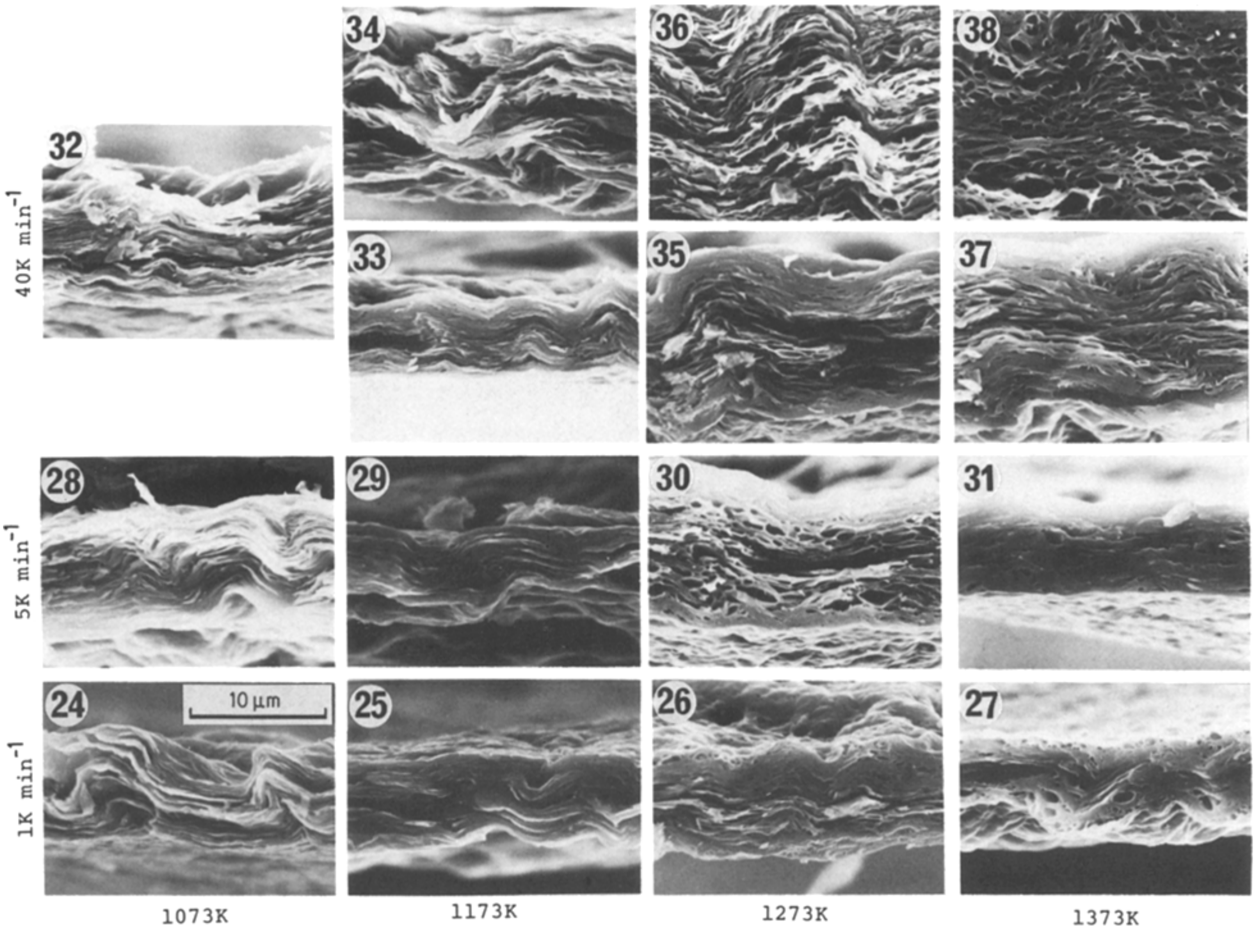

Figure 6 The fractured surfaces of MNC films after heating (residence time 1 min).

This Mont changed completely into CB at 1273 K; and at 1473 K, μ-cordierite (CD) and mullite (MU) also formed in addition to CB. However, MNC derived from Mont without ion exchange somewhat remained even after heating to 1273 K for 1 h without the formation of other crystals, which means that this MNC is slightly more thermally stable than MNC from lithium-Mont. At 1473 K, MNC changed completely into CB, MU and CD. LAS was never observed here.

Fig. 8 shows the fractured surfaces of raw Mont and MNC blocks before heating. Mont particles exhibited such a remarkable preferred orientation that it was difficult to prepare the block as stated above. The scanning electron micrograph of No. 49 shows the thickest part of the Mont sample obtained; here the layer stacking is clearly observed. On the other hand, MNC consists of the complexly entangled wavy planes, leading to the porous structure (No. 50).

The fractured surfaces of Mont blocks heated under various conditions are shown in Fig. 9. Mont presents different structures according to the visual angle because of its remarkable preferred orientation. In No. 54, for example, we can see the edge of the layer stacking in the upper part, and the surface of Mont plate in bottom part. A typical photograph of the edge of the layer stacking is shown in No. 51. This shows clearly that the layer stacking remains unchanged after heating to 873 K. This phenomenon corresponds well with results obtained by X-ray diffraction (Table III). The structures shown in Nos. 51 and 54 changed to the structures shown in Nos. 52 and 55 through heating at 1073 K. Here the edge of the layer stacking was apparently sintered (No. 55) and the individual plane particle could not be recognized (No. 52). The resulting structures of Nos. 52 and 55 are very heterogeneous. No. 56 is Mont block after heating to 1273 K at 40 K min^{-1}, in which the round pores appeared instead of the layered stacking. Its photograph at lower magnification is No. 57 from which it is clear that the block is very porous. No 53 is Mont block heated to 1473 K at 1 K min^{-1}. The conchoidal structure appeared on the fractured surface. This structure is usually observed on the fractured surface of such brittle materials as glass. When a photograph of No. 53 is taken at lower magnification, as for No. 57, a heterogeneous structure with many pores is observed. The effect of heating rate on the structures of the resulting Mont block has not been remarked upon, because its effect was negligibly small compared with the difference in the structures observed from different visual angles. As a result, it was not easy to prepare the homogeneous structure from Mont block, regardless of the porosity or density of the structures.

Fig. 10 shows the fractured surfaces of MNC blocks after heat-treatment. These structures are completely different from those shown in Fig. 9. The structure of No. 58 is very analogous to that of raw MNC block (No. 50). This is reasonable from the X-ray diffraction results. After heating to 1073 K at 1 min^{-1} (No. 59), however, a slightly less porous structure was obtained through sintering. The sintering which

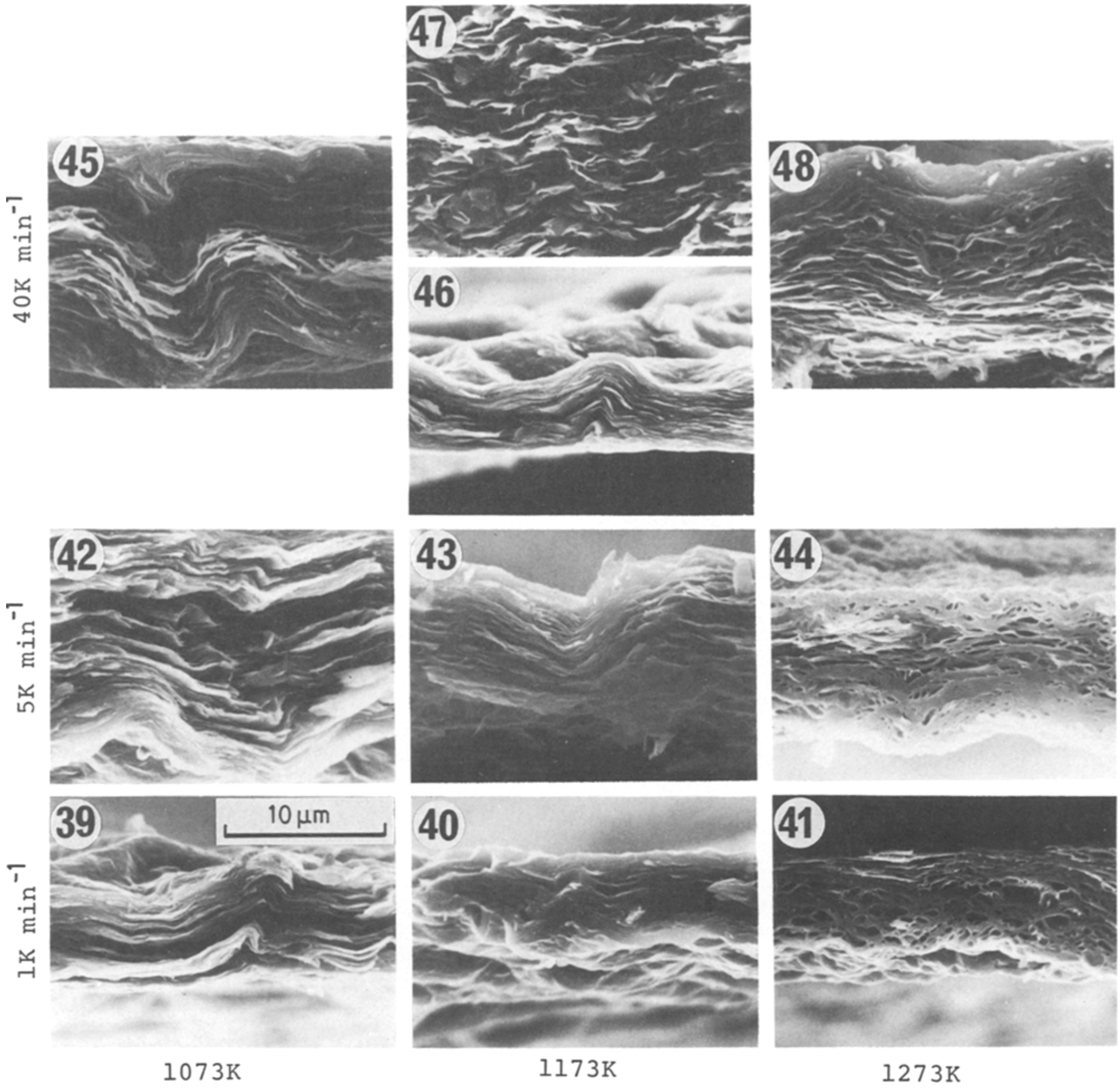

Figure 7 The fractured surfaces of MNC films after heating (residence time 1 h).

resulted in the less porous structure proceeded remarkably at higher HTT as can be seen from Nos. 60 and 61. The latter, especially, exhibited a very dense structure. When a heating rate of 40 K min^{-1} was used, a more porous structure consisting of the wavy planes was obtained (No. 62). At 1073 K in HTT, however, the effect of heating rate was not observed, neither was any difference observed at higher HTTs, though not presented here. The MNC blocks obtained are all considerably hard.

From the present work, the heat-treatment conditions for the preparation of a fine and homogeneous

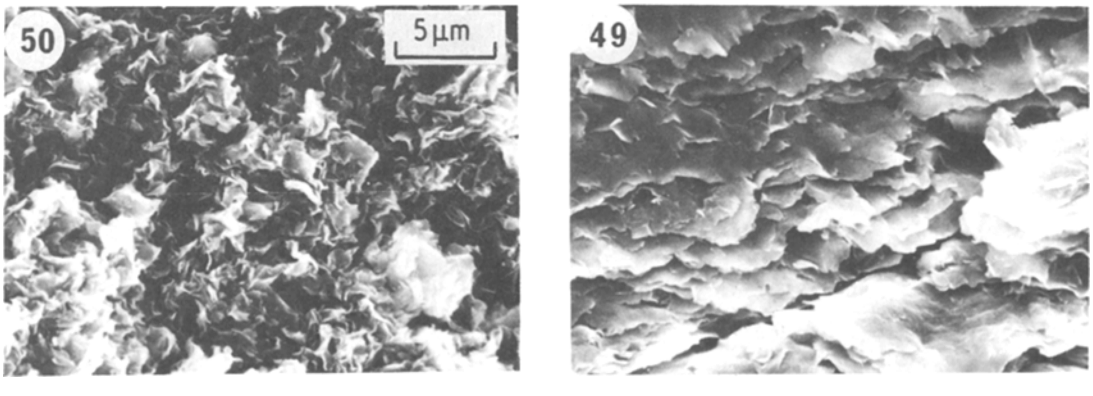

Figure 8 The fractured surfaces of (49) raw Mont and (50) MNC blocks.

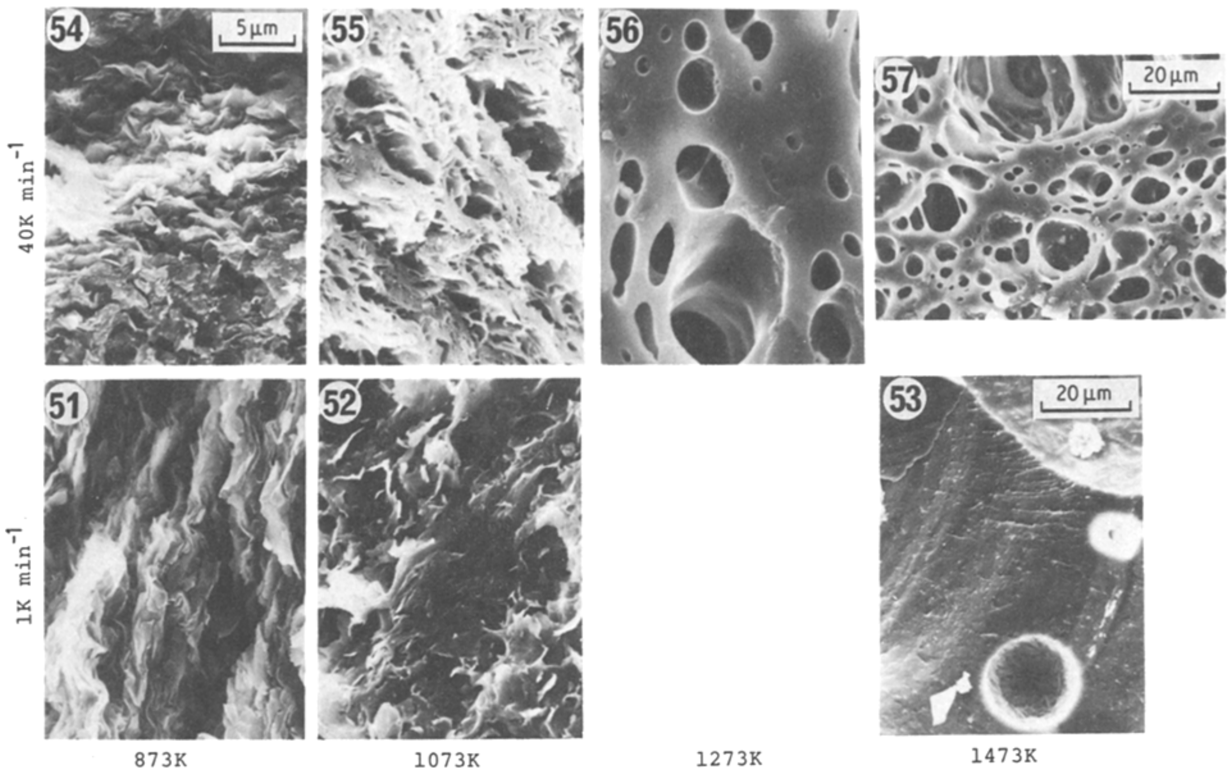

Figure 9 The fractured surfaces of Mont blocks after heating (residence time 1 h).

porous film or block from MNC were ascertained. In addition, how to prepare the dense film from MNC was also revealed. The next problems to be solved are the preparation of the bulk article with characteristic structures and to enhance the thermal stability of these structures. These studies are now in progress and will be reported in the future.

4. Conclusions

The following conclusions were obtained from this work.

1. Compared with Mont, in both film and block, MNC is far more suitable to obtain the homogeneous structures through heat-treatment.

2. Two characteristic structures were derived from

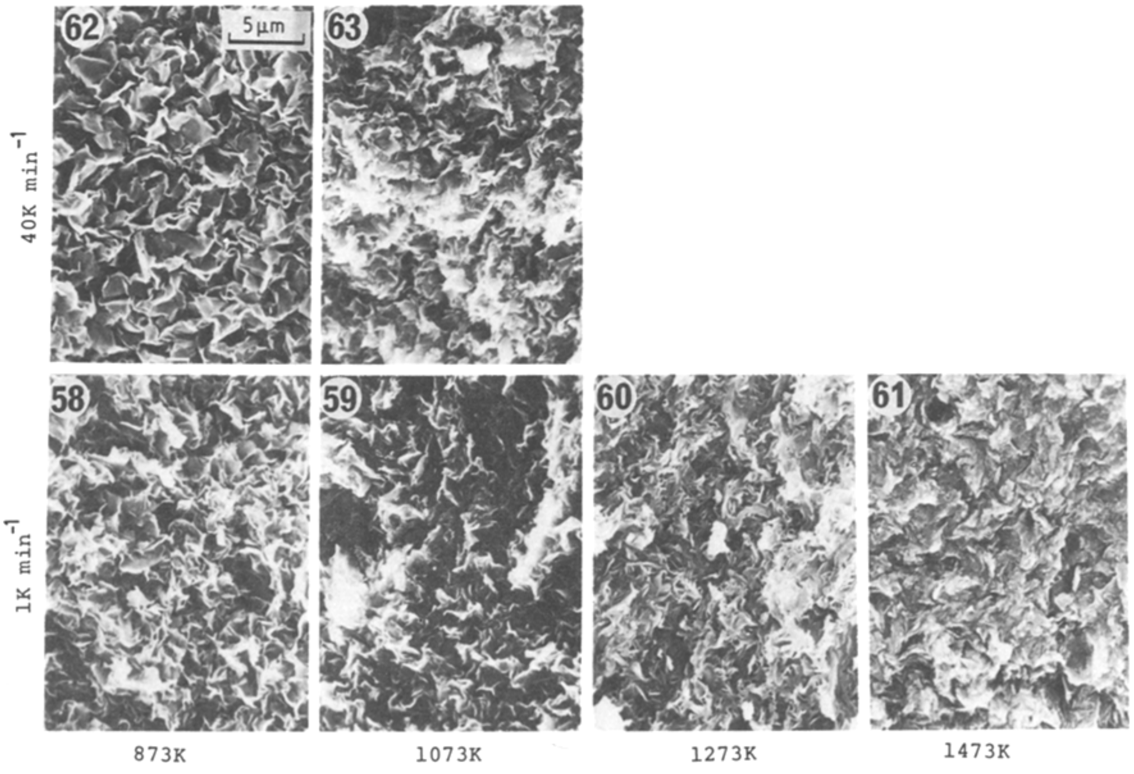

Figure 10 The fractured surfaces of MNC blocks after heating (residence time 1 h).

MNC films. One is the very dense film with the memory of a layered structure, and the other a homogeneous fine porous structure. The former was prepared by heating to about 1173 K at a small heating rate such as 1 or 5 K min^{-1}. Heating to 1173 to 1273 K at a large heating rate of 40 K min^{-1}, on the other hand, resulted in the latter structure. No significant effect of residence time was observed.

3. A unique porous structure consisting of wavy plates was prepared from MNC block by heating to about 873 K for 1 h. With increase of HTT, the porosity decreased.

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