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Characteristics of mouldings made from the saponite/acriflavine complex after heating under nitrogen

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Carbonization of the clay/organic layer-type complex produces the clay/carbon layer-type complex or clay (or its heat-treated derivative) together with finely dispersed carbon. To evaluate the characteristics of a moulding made from such structures, the saponite/acriflavine complex powder was pressed into a moulding (10 × 10 mm ϕ) under 1000 kg cm^{-2} and then carbonized below 1673 K under nitrogen. Some properties of the moulding, such as electrical resistivity, varied widely with carbonization temperature, but, on the whole, it behaved as an intermediate material between the ceramics and the carbon materials. Its most unique property is low electrical resistivity, in spite of its low carbon content. Structural changes that take place during the carbonization process are discussed in detail.

1. Introduction

During the course of an investigation into the carbonization behaviour of the clay/organic complexes [1–3], it became apparent that a saponite/α-naphthylamine complex (SNC) film, several tens of micrometres thick, results in a very dense and homogeneous structure after carbonization [2]. The resultant material consists microscopically of either the clay/carbon layer-type complex or contains finely dispersed carbon derived from the intercalated α-naphthylamine, depending on the carbonization temperature. This material, therefore, is expected to have unique properties which are different from those of clay that is simply mixed with carbon particles, such as carbon black. The present authors, however, were confronted with two problems, namely, α-naphthylamine is a carcinogenic material and a thin film is not suitable for measuring as many properties as possible. So we looked for an organic compound that could serve as an alternative to α-naphthylamine and found that acriflavine behaves in a similar manner. The purposes of this work are to describe the carbonization (heat-treatment) under nitrogen of a moulding made from the saponite/acriflavine complex and to determine the composition of carbonized moulding.

2. Experimental details

2.1. Preparation of the moulding and heat-treatment procedures

Saponite (Sap) was synthesized by the Kunimine Ind. Co. Ltd. It has a cation exchange capacity: (CEC) of 71 meq/100 g and its chemical composition is given in Table I. As a preliminary experiment, various amounts of acriflavine hydrochloride ($C_{13}NH_7(NH_2)_2 \cdot 2HCl$) were added to a 3.5 wt % aqueous solution of Sap. The solution was stirred at room temperature for one day to synthesize the saponite/acriflavine complex (SAC). The most thermally stable SAC was prepared from Sap solution by adding an amount of acriflavine that was 1.5 times the CEC of the Sap. This SAC was pulverized so as to pass through a 100 mesh sieve after drying and was then pressed into a moulding (10 × 10 mm ϕ) under 1000 kg cm^{-2} for 10 min. Here 4 wt % of water was added as a lubricant. The resultant moulding was heated to a prefixed temperature between 873 K and 1673 K at a heating rate of 5 K min^{-1} under nitrogen and held at that temperature for 1 h. Five mouldings were prepared for individual heat-treatment temperatures (HTT). After heating to 1673 K, however, the mouldings deformed so seriously that they were not subjected to any subsequent measurements.

2.2. Measurements

X-ray powder diffraction procedures using Cu*K*α-radiation and SEM observation of the fractured surface were conducted according to the conventional methods. SEM observation was also made of the polished surfaces before and after etching by HF for 7 min at room temperature. The carbon content was measured by the combustion method using tin particles to aid the combustion. The bulk density was calculated from the weight and size of the moulding. The apparent porosity was obtained by the Archimedes' method in water. The electrical resistivity was found by the conventional potentiometric method used at room temperature. The compressive strength was measured by applying a load along the pressing direction on the surface of the moulding with a crosshead speed of 2.5 mm min^{-1}. The thermal expansion coefficient was measured using a differential thermal expansion apparatus, employing alumina rod as a

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TABLE I Chemical composition of saponite

	Concentration (wt %)
SiO_2	54.71
Al_2O_3	5.02
Fe_2O_3	0.03
MgO	30.74
Na_2O	2.15
SO_3	0.67
ignition loss	6.67
Total	99.99

reference, with a heating rate of 5 K min^{-1} under nitrogen. The measurements of other thermal properties were made by the laser flash method at the Shinku Riko Co. Ltd. To evaluate oxidation resistivity, the SAC powder was subjected to thermogravimetric analysis with a heating rate of 10 K min^{-1} in a flow of air.

3. Results

Fig. 1 shows changes in the X-ray diffraction profiles of the SAC with HTT. The peaks from the SAC were clearly observed up to 873 K, but became weak with the formation of enstatite at 1073 K. The basal spacings of the SACs with no heating and after heating to 873 K are 1.38 and 1.30 nm, respectively. As reported previously [2], raw Sap under dehydration exhibited 0.98 nm. After heating to 1273 K, the deposited crystalline phase consisted of enstatite alone and, at higher HTTs, changed into forsterite, protoenstatite and clinoenstatite.

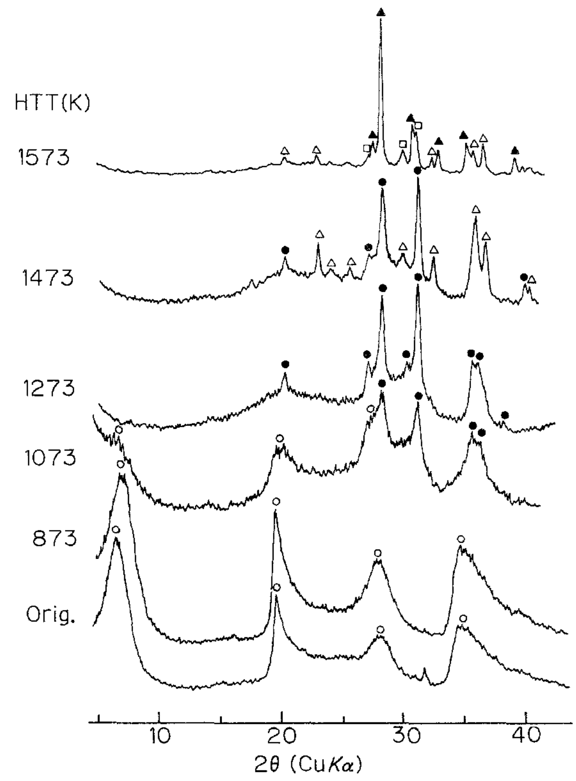


Figure 1 Changes of X-ray diffraction profiles of the SAC with HTT. (○) SAC; (●) enstatite; (△) forsterite; (▲) protoenstatite; (□) clinoenstatite.

Table II summarizes some properties and the carbon contents of the SAC mouldings. Although tin particles were used as stated above, the carbon content scattered considerably. On the whole, however, it is reasonable to conclude that the content decreased gradually from approximately 7 wt % to approximately 4 wt % with rising HTT.

The 873 K SAC moulding was so brittle and so unstable with water that only its bulk density and carbon content were measured. The bulk density of 1.9 g ml^{-1} at 873 K increased gradually with increasing HTT and reached 2.5 g ml^{-1} at 1573 K. Conversely, the apparent porosity decreased from approximately 20% to approximately 10% at 1573 K. In contrast to our expectation, which was based on the carbonization behaviour of the SNC reported previously [2], such porosities are large. Shore hardness decreased from 80 to 60 with increase in HTT. The values of the compressive strength scattered so widely that a clear relationship could not be obtained between the strength and HTT. Cracks in the moulding must be the main cause of this scattering as described later. The potentiometric apparatus used here can measure electrical resistivities below 10^{14} ohm-cm, but the 873 K SAC moulding had a higher resistivity. The resistivity decreased remarkably in the HTT range of 873–1273 K, and became less than 1 ohm-cm above 1473 K.

Fig. 2 shows the thermal expansion coefficients of the SACs changed with temperature. The value of the 1073 K SAC moulding decreased up to 500 K and then increased till it became zero at 700–950 K. It increased steeply again at 1000 K. The coefficients of the other three mouldings increased gradually, though to somewhat different extents, with increasing temperature up to 1150 K and steeply at higher temperatures.

The changes in the thermal conductivities are shown in Fig. 3. The conductivities of all the mouldings increased gradually with increase in temperature, but their absolute values were higher in the SAC that was subjected to heat-treatment at a higher temperature. A large difference, especially, was observed between the SAC mouldings heated to 1473 K and 1573 K. The specific heat, though not presented

TABLE II Some properties of specimens

HTT (K)	Bulk density ($g ml^{-1}$)	Apparent porosity (%)	Shore hardness	Compressive strength (MPa)	Resistivity (ohm cm)	Carbon content (%)
873	1.9	–	–	–	$> 10^{14}$	6.5
1073	2.2	21	77	170	2.8×10^4	5.3
1273	2.2	23	73	160	21	5.8
1473	2.3	15	74	130	0.67	3.7
1573	2.5	11	57	270	0.38	4.5

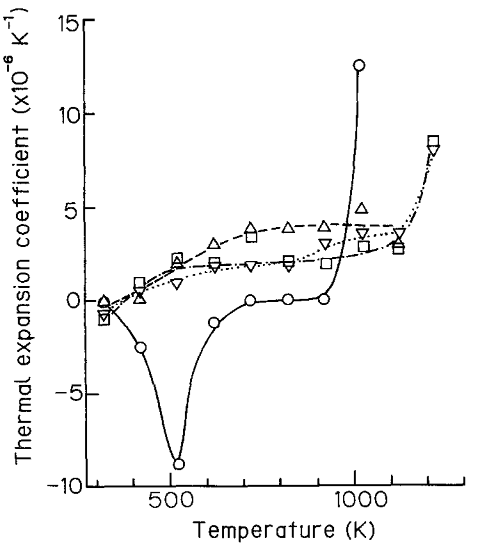


Figure 2 Changes in the thermal expansion coefficients of the SAC mouldings with temperature, after heating to various HTTs: (—○—) 1073 K; (– –△– –) 1273 K; (–·□·–) 1473 K; (···▽···) 1573 K.

here, exhibited similar trends to those of the thermal conductivity.

Fig. 4 shows the TG–DTA curves of the SAC powder samples in air. The 873 K SAC showed three weight decreases. The first one at around 400 K is attributable to the removal of adsorped and/or interlayed water. The second exothermic weight decrease at around 850 K and the third endothermic one at around 1050 K are the result of the combustion of the intercalated acriflavine (or its carbonaceous derivative) and dehydration of OH in the Sap layer, respectively [2]. After this dehydration, it crystallized into enstatite with a sharp exothermic peak just below 1100 K. In the SAC samples heat-treated to 1073 K or higher the exothermic weight decrease is observed clearly, but other weight decreases are not clear except for the small weight decrease resulting from the removal of water in the 1073 K SAC at around 400 K.

Fig. 5 shows the fracture surfaces of the SAC mouldings. The flaky particles or their stacking structure are observed in the 873 K SAC moulding. The particles became gradually rounded with increasing HTT. Fig. 6 consists of SEM photographs of the polished surfaces before and after etching. The surfaces shown before etching were not evaporated with thin gold film for SEM observation so that their photographs are not clear. However, many grooves appeared in the 1073 K SAC moulding after etching. The particles sintered more favourably with higher HTTs. Some places suggesting the stacking structure, however, were seen even in the 1273 K SAC moulding as arrowed. The more developed sintered-structure is suggested from the photograph of the 1573 K SAC moulding after etching.

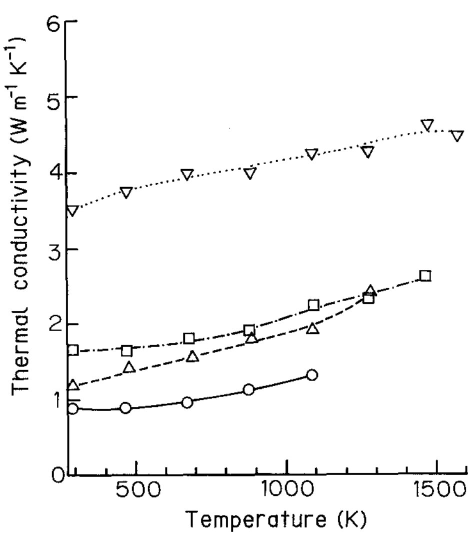


Figure 3 Changes in the thermal conductivities of the SAC mouldings with temperature, after heating to various HTTs: (—○—) 1073 K; (– –△– –) 1273 K; (–·□·–) 1473 K; (···▽···) 1573 K.

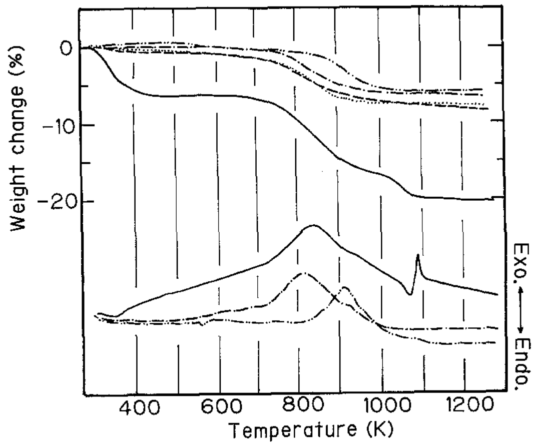


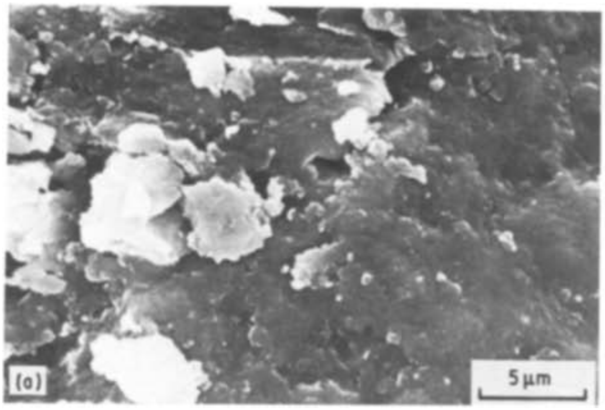
Figure 4 TG–DTA curves for the SAC mouldings in air, after heating to various HTTs: (·–··–) 1573 K; (·····) 1473 K; (·–·–·) 1273 K; (– – –) 1073 K; (——) 873 K.

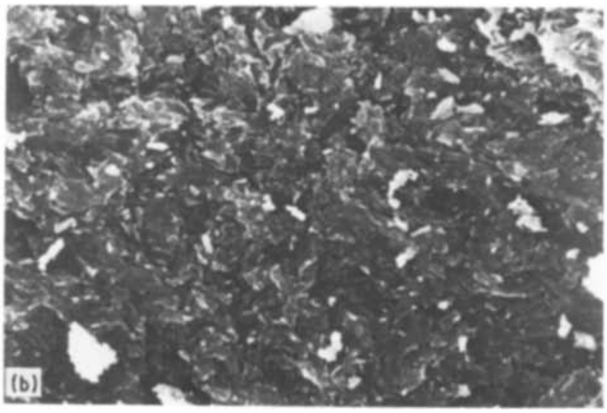
4. Discussion

4.1. Structural change of the SAC moulding with HTT

As shown by X-ray diffraction profiles (Fig. 1), the SAC layer structure remains unchanged up to 873 K. The layer structure at this stage is still capable of rehydrating (Fig. 4) so that the 873 K SAC moulding has quite low water-resistance [2]. Since the SAC particle doesn't sinter by being heated to 873 K, the moulding is also very mechanically brittle. One point to note here is the preferred orientation of the flaky SAC particles in this moulding (Fig. 5), such a structural factor is very important materially. According to Fig. 5, however, this orientation seems to disappear gradually with increase in HTT, and of course, it is also well known that the orientation can be eliminated by use of the isostatic-press technique.

At 1073 K, enstatite forms to some extent while some of the SAC remains (Fig. 1), which means sintering occurs of the SAC layer structure itself and among the SAC particles. The mechanical properties of the moulding are thereby improved remarkably (Table II). Two points to note here are the abrupt decrease in the electrical resistivity (Table II) and the characteristic behaviour of thermal expansion with temperature (Fig. 2). Some possible explanations for the former phenomenon have been considered. The first is the increase in bulk density, but this increase is too small to explain such a large decrease. The next possibility is the formation of the more perfect carbon layer in the





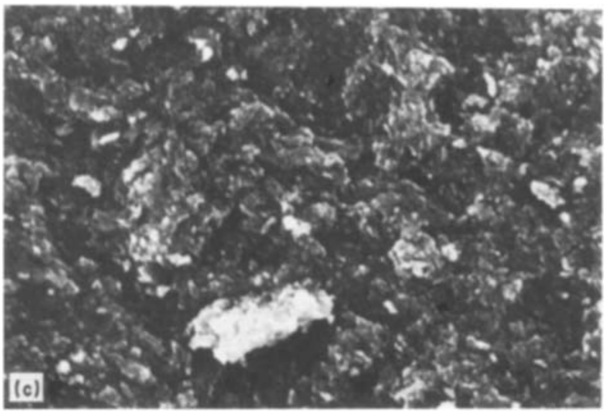


Figure 5 SEM photographs of the fractured surfaces of SAC mouldings after heating to various HTTs: (a) 873 K; (b) 1273 K; (c) 1573 K.

moulding. Such a development, however, is not favoured in this HTT range, as reported previously [2]. The third explanation seems to be the most plausible – namely, that the carbonized derivative of the acriflavine is still sandwiched between the insulating Sap layers at 873 K and, in addition, individual SAC particles do not connect with each other closely, which leads to high electrical resistivity. At 1073 K, however, the intercalating carbonaceous derivative is excluded on the surface of the deposited enstatite crystal and simultaneously, the SAC particles sinter to connect to each other. As a result of such structural changes, an electric circuit forms in the moulding and results in the remarkable lowering of the resistivity. For the characteristic behaviour of the thermal expansion coefficient, on the other hand, we have no clear explanation. The 1073 K SAC moulding, however, is distinguished from the SACs heated to higher HTTs by the remains of the SAC layer structure in which water is retained as suggested from the small endothermic weight decrease around 400 K (Fig. 4). The removal of the interlayered water is a plausible explanation for the thermal shrinkage (Fig. 2).

After heating to 1273 K, the moulding consists of enstatite alone. The structural changes at 1073–1273 K are substantially the same as those at 873–1073 K. The further decrease in the electrical resistivity can be reasonably explained by further transformation into enstatite. In fact, the moulding sintered more favourably at this HTT (Fig. 5). The characteristic thermal expansion behaviour must be eliminated by the complete transformation of the SAC layer structure to enstatite.

The moulding continues to sinter at 1273–1473 K, as can be seen from the increase in the density and the decrease in the porosity (Table II). The flaky particle becomes more rounded at 1473 K, though this is not presented here. At this point, enstatite converts to some extent to forsterite but this transformation has no substantial effect on the properties of the moulding. The decrease in electrical resistivity at this HTT range may be mainly caused by an increase in the density (Table II). After heating to 1573 K, enstatite changes completely to forsterite, protoenstatite and clinoenstatite (Fig. 1), and the sintering of the moulding subsequently continues because this is the stage just immediately before fusion (Figs 5 and 6). The resulting dense structure exhibits a higher resistivity to oxidation, possibly by suppressing the penetration of oxygen. In addition, the development of the well-sintered state at this HTT results in large increases in compressive strength (Table II) and thermal conductivity (Fig. 3).

4.2. Evaluation of the SAC moulding

As stated above, some properties of the SAC moulding change widely with HTT. In order to make a structural evaluation, however, the most highly sintered 1573 K SAC mouldings are compared with other commercially available materials. The values shown in Fig. 7 were cited from the catalogues of the various materials. The carbon material, conventionally, has been evaluated as an intermediate material between the metal and ceramic materials, because its high electrical and thermal conductivities are similar to those of the metals and its high chemical resistivity and high thermal stability (under inert atmosphere) are similar to those of the ceramics. Shore hardnesses for two ceramics references are not shown in Fig. 7, but they must be far larger than 100. As can be seen in Fig. 7, both ceramic and carbon materials exhibited irregular polygons, although their shapes are different from each other. Compared with other reference materials, the SAC moulding has a less irregular polygon and never has the maximum or minimum value of all properties in Fig. 7, which means that the SAC moulding, on the whole, is an intermediate material between ceramics and carbons. Such an evaluation can also be made to the SAC mouldings heated to lower HTTs.

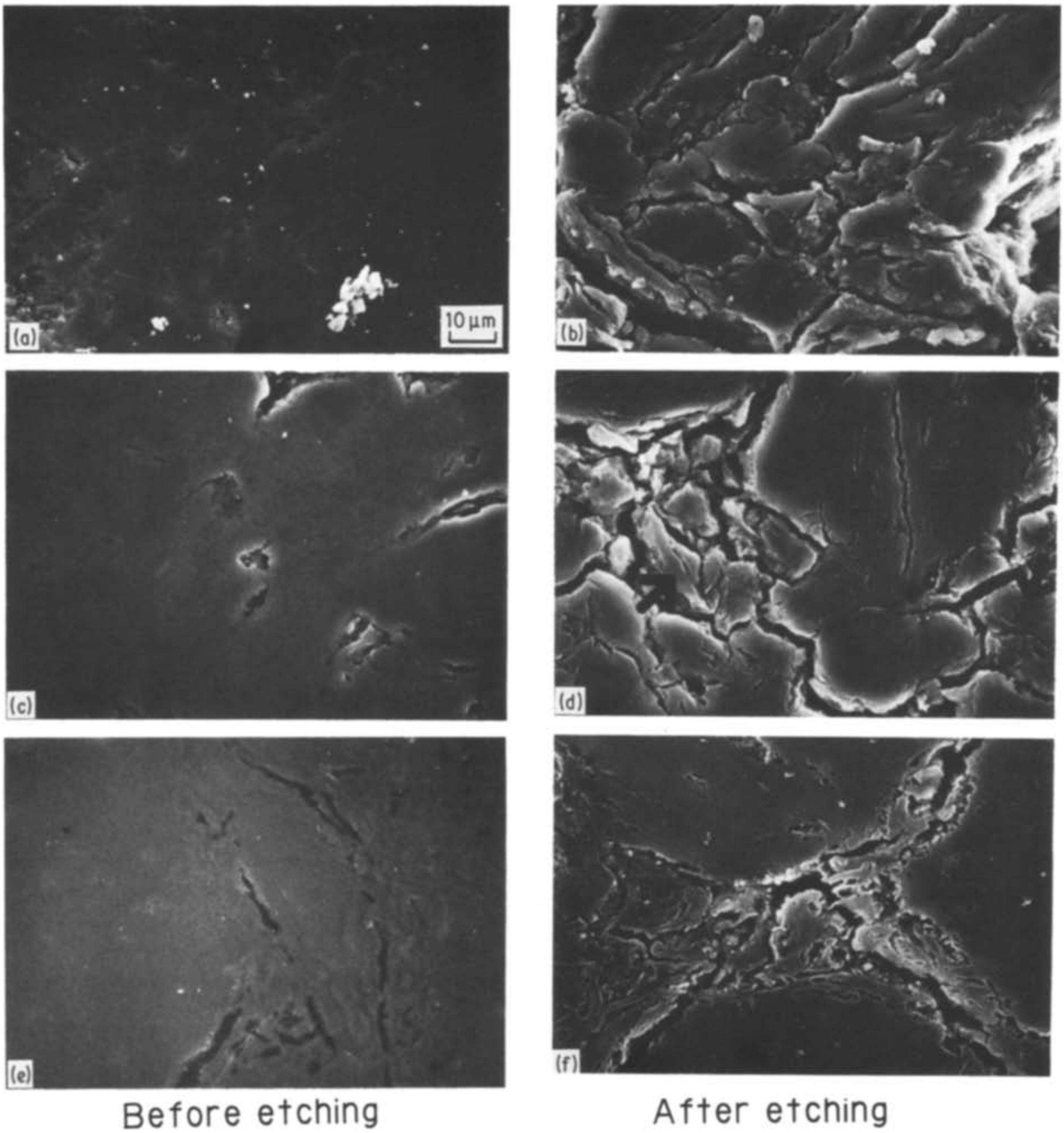


Figure 6 SEM photographs of the polished surfaces of the SAC mouldings before and after etching, after heating to various HTTs: (a) 1073 K; (b) 1273 K; (c) 1573 K.

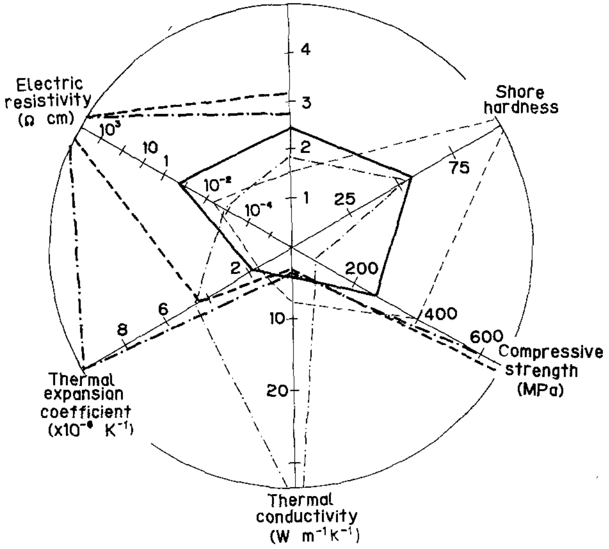


Figure 7 Comparison diagrams of the 1573 K SAC moulding and other reference materials. (——) 1573 K SAC; (–·–·–) forsterite (Kyo. Cera); (– – – –) silicon carbide (C-600, Asahi Glass); (– – –) glassy carbon (GC-20, Takai Carbon); (–·–·–) isotropic carbon (IG-11, Toyo Tanso).

An outstanding characteristic of the SAC moulding is its low electrical resistivity in spite of its low carbon content, which may be attributable to a specific structure derived from the clay/organic layer-type complex. The mechanical properties shown in Table II are relatively poor but, we think, can be improved remarkably by using the hot-press technique, because the serious cracks in the moulding (Fig. 6) can be removed by use of this technique. The oxidation resistivity of the SAC moulding at high temperatures is low (Fig. 4). This may be a serious disadvantage in its application as a refractory structural material.

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