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Discrimination of Ceramics—Study on the Microstructures of Ceramics

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ABSTRACT: A method for discrimination of alumina ceramics was developed based on the observation of the surface morphology of etched surfaces, density, X-ray diffraction line profiles and grain size distributions.

The experimental observations of the surface microstructure were made, using the scanning electron microscopy (SEM), on several different alumina ceramics with high (>99%), middle (96 to 98%) and low (approximately 92%) alumina content in order to identify them. The samples were prepared with a sulfuric acid (4.5 mol/L) etching method performed at 150 ~ 200°C for 2 h on low and middle purity alumina ceramics and for 4 h on high purity alumina ceramics.

The results indicate that the SEM observation coupled with computerized image analysis to determine grain size distribution is a powerful tool to discriminate among alumina ceramics that exhibit similar morphological characteristics.

The X-ray diffraction line profile study is suggested as an additional useful index for the determination of microcrystalline structure.

KEYWORDS: forensic science, ceramics

Ceramics are synthetic materials, produced from nonmetallic inorganic solid bound together by sintering at high temperature. Since they possess several useful characteristics such as heat-resistance, corrosion-resistance, reasonable strength, insulation, or semiconductivity, fine ceramics have become widely employed as industrial materials. These uses include alumina ceramics as IC substrates, translucent alumina as optical materials, zirconia ceramics as edge tools and silicon carbide and silicon nitride as a heat-resisting materials. Sapphire (alumina single crystal) and hydroxy apatite, which exhibit high strength, are referred to as bioceramics and are used as artificial teeth or bones [*1–3*]. The ever growing use of ceramics has resulted in these materials or articles composed of ceramics being encountered more commonly as physical evidence in criminal cases [*4,5*], in one case a fragment of the dental porcelain (artificial tooth) found in the murder site was identified the artificial tooth of the suspect in a murder case, and in another case the manufacturer was determined from a minute fragment of a zirconia ceramic cutleries

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by means of scanning micro photography. Establishment of forensic science methods for distinguishing the characteristics of these materials is needed for criminal investigations.

The scanning electron microscope (SEM) is well suited for the observation of the microstructure of ceramics materials. It is well known that size and shape of grains of sintered polycrystalline ceramics are affected by the condition of the sintering process and nature of the original ceramic powder [*6–12*].

In this study, the aim was to classify ceramics from different sources by SEM-observation of their microscopical surface characteristics which was cleared by acid or thermal etching method.

Materials and Methods

Materials

Nineteen alumina ceramic samples manufactured by nine ceramic companies in Japan were collected. Their alumina content varied and was divided into three groups according to alumina content (low purity approximately 92%, medium purity 96 to 98% and high purity more than 99%, see Table 1).

Measurement

Rectangular solid samples approximately 1 × 2 cm and 0.5 cm thick were prepared by cutting them from the exhibits with a diamond saw.

After the measurement of the density of samples by Archimedian method, the samples were ground in turn on #6000 diamond pad, with #4000 SiC powder and #6000 alumina powder. This polishing process is essential to make the grain boundary structure of the sample clear, because the irregular original surface (whether from cut surface, polished surface or broken surface) obscures the morphology of microstructures (Fig. 1).

TABLE 1—*Alumina ceramics.*

Manufacturer	Grade name	Purity (%)
S	A-392	92
	A-396	96
	A-399	99
NK	SSA-S	92
	SSA-999H	99
NT	KP-999	99
O	...	92
	...	97
	...	99.5
N	...	92
	...	96
	...	99.8
T	AL-170	97
	AL-197	99
K	A-471	97
OS	...	...
I	...	96
	...	99.5
	Porous (low density)	...

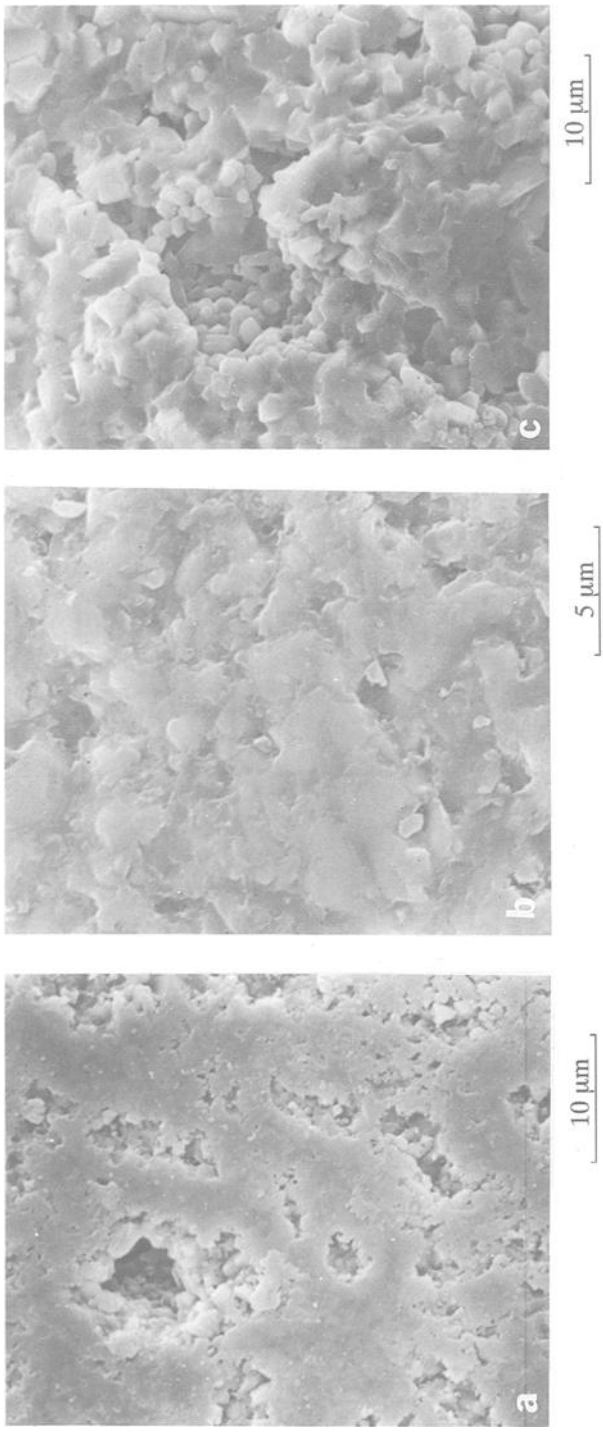

FIG. 1—*Comparison of micrograms of each surface:* (a) *cut off surface;* (b) *polished surface;* (c) *fractured surface. Samples are alumina (92%) from company S.*

After cleaning in an ultrasonic cleaner, each sample was treated to make grain boundary conspicuous by acid or thermal etching procedure (Fig. 2).

Each prepared sample was sputter coated with Pt-Au and observed with Hitachi S2500 SEM; secondary electron image operating at 25kV.

The image processing for determination of the area distributions of the micrograin structure was performed by the micrograin structure analysis program previously developed for metal crystals supplied by the Iron and Steel Institute of Japan [*13*].

The X-ray diffraction (XRD) measurements were made by using a Shimazu XD-D1 (X-ray diffractmeter) with Cu-k α source operating at 40kV-30mA, scanning rate is 0.125 deg/min and an integlating time is 4 s [*14–16*]. For this measurement, samples were cut to be a rectangular solid specimen approximately 1 × 2 cm and 0.5 cm thick fixed on the holder with a clay compound.

Etching Procedure

Two kinds of chemical etching and thermal etching were evaluated for their usefulness in elucidating morphological structure.

Phosphoric acid etching was evaluated by dipping samples on 60% and 80% boiling phosphoric acid under standard atmospheric pressure for several minutes. Typical SEM micrographs are shown in Fig. 3*a* and 3*b*.

Control of the etching time and temperature of this phosphoric acid etching procedure was found to be too difficult to obtain reproducible results. Either increasing the acid strength from 60 to 80% or extending of etching time from 5 to 15 min caused an excessive amount of grain boundary etching (Fig. 3*a*,3*b*).

For the thermal etching, samples were heated at 1400°C for 10 min. The temperature is 100°C lower than the sintering temperature, Tamman temperature, of alumina ceramics.

A long time—half a day—was needed for heating and cooling of the sample. This etching treatment gave a desirable result for the purpose, however slight grain growth due to the heating was observed (Fig. 3*c*).

According to these results, it was concluded that both phosphoric acid etching and thermal etching were not suitable for the observation of the microstructure of surfaces in the present study.

Sulfuric acid etching produced favorable results for grain structure analysis by SEM.

To evaluate sulfuric acid etching, samples were immersed in 4.5 mol/L or 6 mol/L sulfuric acid in a teflon capsule, sealed in a stainless steel pressure vessel and heated to between 150 and 200°C for 2 to 4 h. Etching with 4.5 mol/L sulfuric acid at 200°C for 2 h generated good grain boundary etching, while the increase of acid concentration to 6 mol/L resulted in attack of the internal portions of grains (Fig. 4).

Experiments with high temperature sulfuric acid enchants resulted in the adoption of 4.5 mol/L sulfuric acid at 150 to 200°C as the best alternative. The degree of etching depended on the Al_2O_3 purity of ceramics. Two hour treatments for low alumina samples seemed adequate, while up to four hours were required for the high alumina materials (Fig. 5).

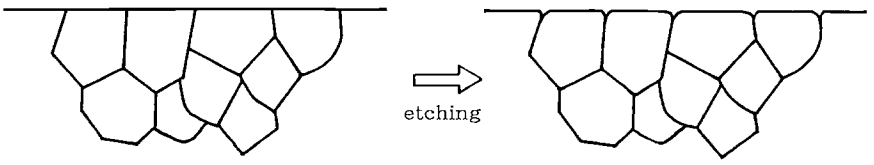

FIG. 2—*Grain boundary etching of polished surfaces.*

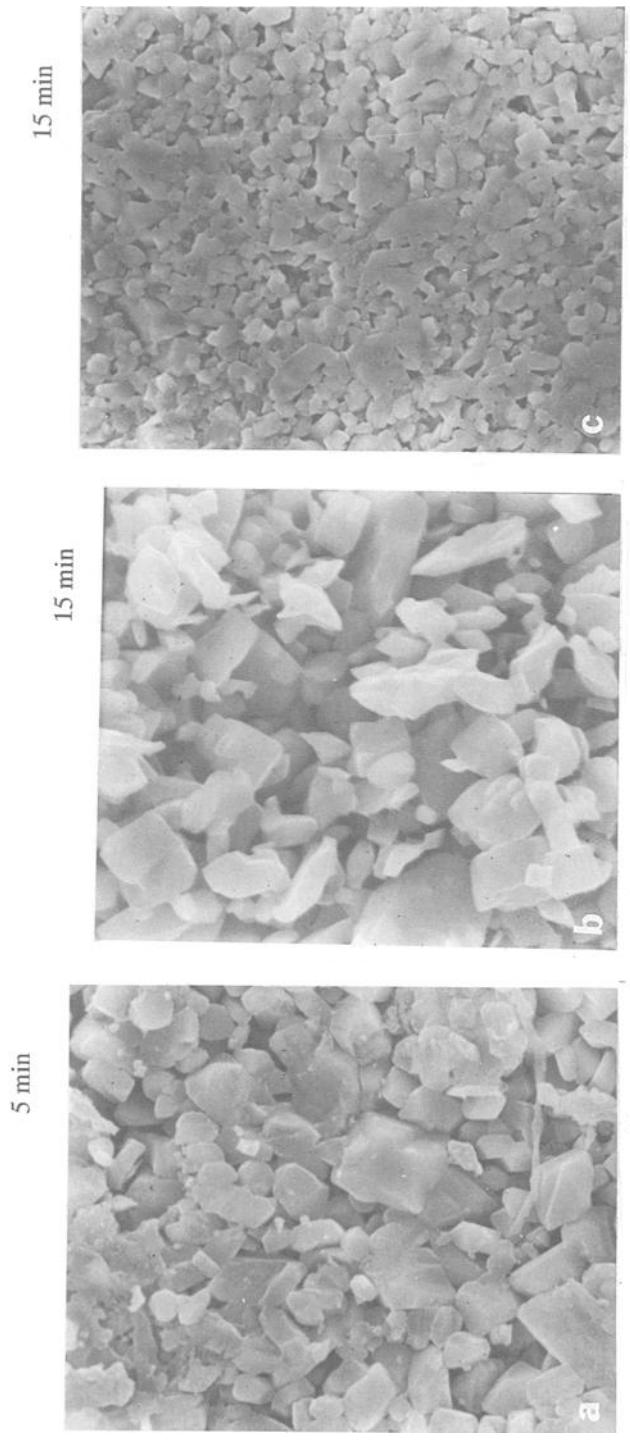

FIG. 3—*Comparison of each etching method:* (a) *boiling phosphoric acid (60%);* (b) *boiling phosphoric acid (80%);* (c) *thermally etched at 1400°C. Samples are alumina (92%) from company S.*

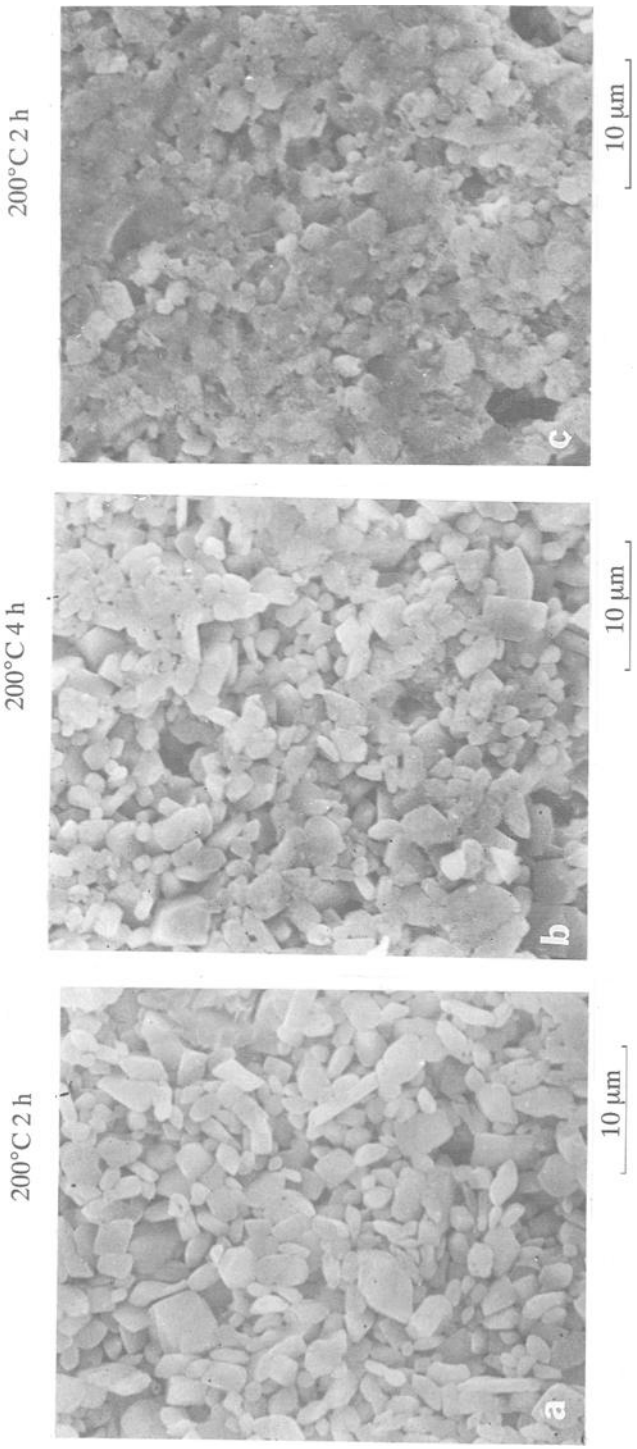

FIG. 4—*Comparison of conditions of sulfuric acid etching:* (a) H_2SO_4 *(4.5 mol/L);* (b) H_2SO_4 *(4.5 mol/L);* (c) H_2SO_4 *(6 mol/L). Samples are alumina (92%) from company S.*

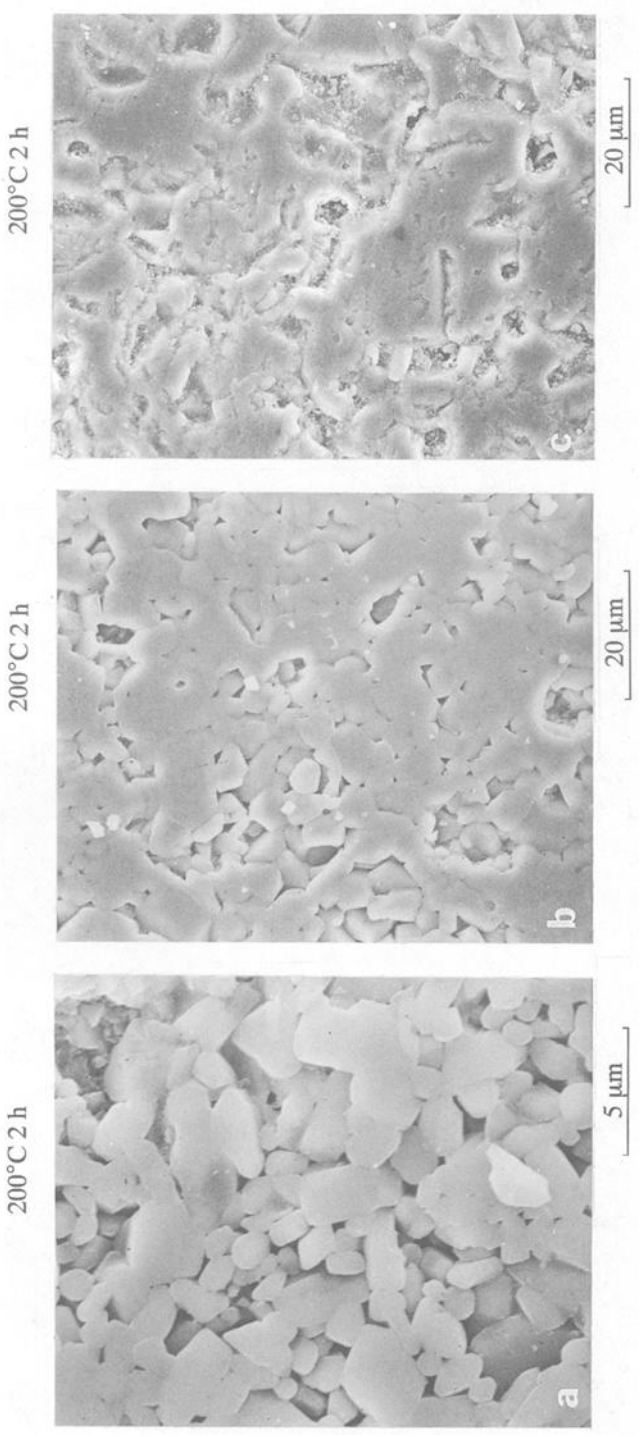

FIG. 5—*Comparison of clarity of sulfuric acid etching on different purity:* (a) *alumina (92%);* (b) *alumina (97%);* (c) *alumina (99%). Samples are alumina from company S.*

These results suggest that etching for long time makes it difficult to identify grain boundary, and high concentrations of sulfuric acid is not suitable for alumina ceramics etching.

Based on these results, the most suitable conditions for chemical etching of alumina ceramics was determined; to be, sulfuric acid (4.5 mol/L) at a temperature range is of 150 to 200°C, carried on for 2 h on low purity alumina ceramics and for 4 h on high purity alumina ceramics.

Therefore, it is apparent that for sample of unknown content of Alumina, suitable etching conditions must be established.

Results and Discussion

Observation of Grain Morphology

Photomicrographs of low alumina content ceramics samples (92%) manufactured by three companies (O, N, S) are shown in Fig. 6. In them the one from company S was discriminated from other makers through feature of grain morphology.

The surface morphology of middle purity alumina ceramics samples (96–97%) manufactured by five companies (S, O, N, I, T) are shown in Fig. 7. Distinct differences of grain morphology were observed among makers.

Pits in the grain brought from the grain growth were observed for the sample from company T.

The existence of pits enabled discrimination between samples from T and O, although those had similar aspects in their grain morphology.

Photomicrographs of high alumina content ceramic samples (>99%) manufactured by six companies (N, NT, I, O, T, S) are shown in Fig. 8. The large size of grains in the sample from company I was similar to that from the company T.

The sample from company I, however, contained some small size grains, and it indicated that the raw ceramic powder had different particle size distribution, or the ceramic was sintered in different conditions from others. Although the grain size distribution in sample from company NT was similar to that from company O, some grain growth in that from company O resulted in discrimination between them.

The microstructure of low alumina content ceramics is distinguishable by the SEM observation, because of clear differences in their grain boundary structures. Increase in the alumina content of the ceramics produces less grain boundary differences therefore identification of microstructure differences of the high and middle alumina content ceramics were problematic.

Grain size becomes large as the purity of alumina powder increases, because the lack of impurities at the grain boundary promotes large grain growth during sintering process. Because increase in the purity of alumina ceramics produces less grain boundary etching, identification of microstructure on high and middle purity of alumina ceramics is more difficult.

Density

Table 2 shows the measured density of alumina ceramics. The density generally increased proportionally with the increase of the purity of alumina in the ceramics. The grain growth observed in the high alumina content ceramics decreased the porosity.

These density measurements showed the possibility of generating information about the different manufacturing processes thereby leading to identification of the source manufacturer.

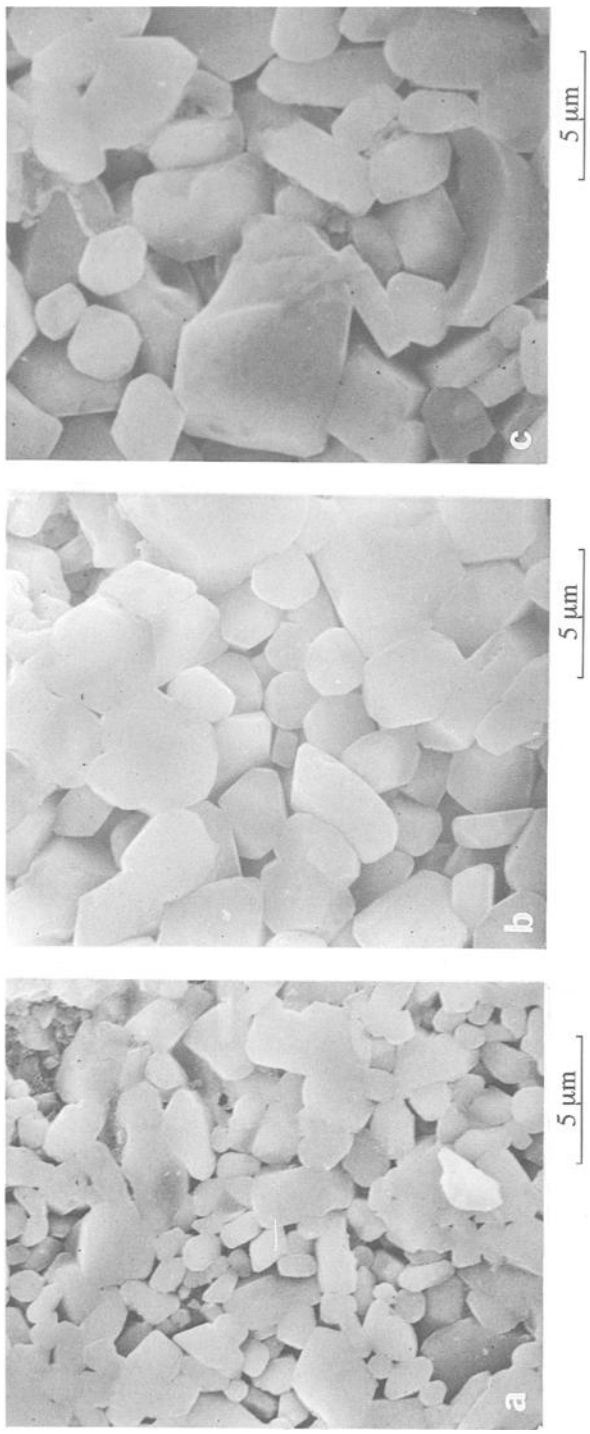

FIG. 6—*Comparison of microstructure of alumina ceramics (92%) from different supplier:* (a) *company S;* (b) *company O;* (c) *company N.*

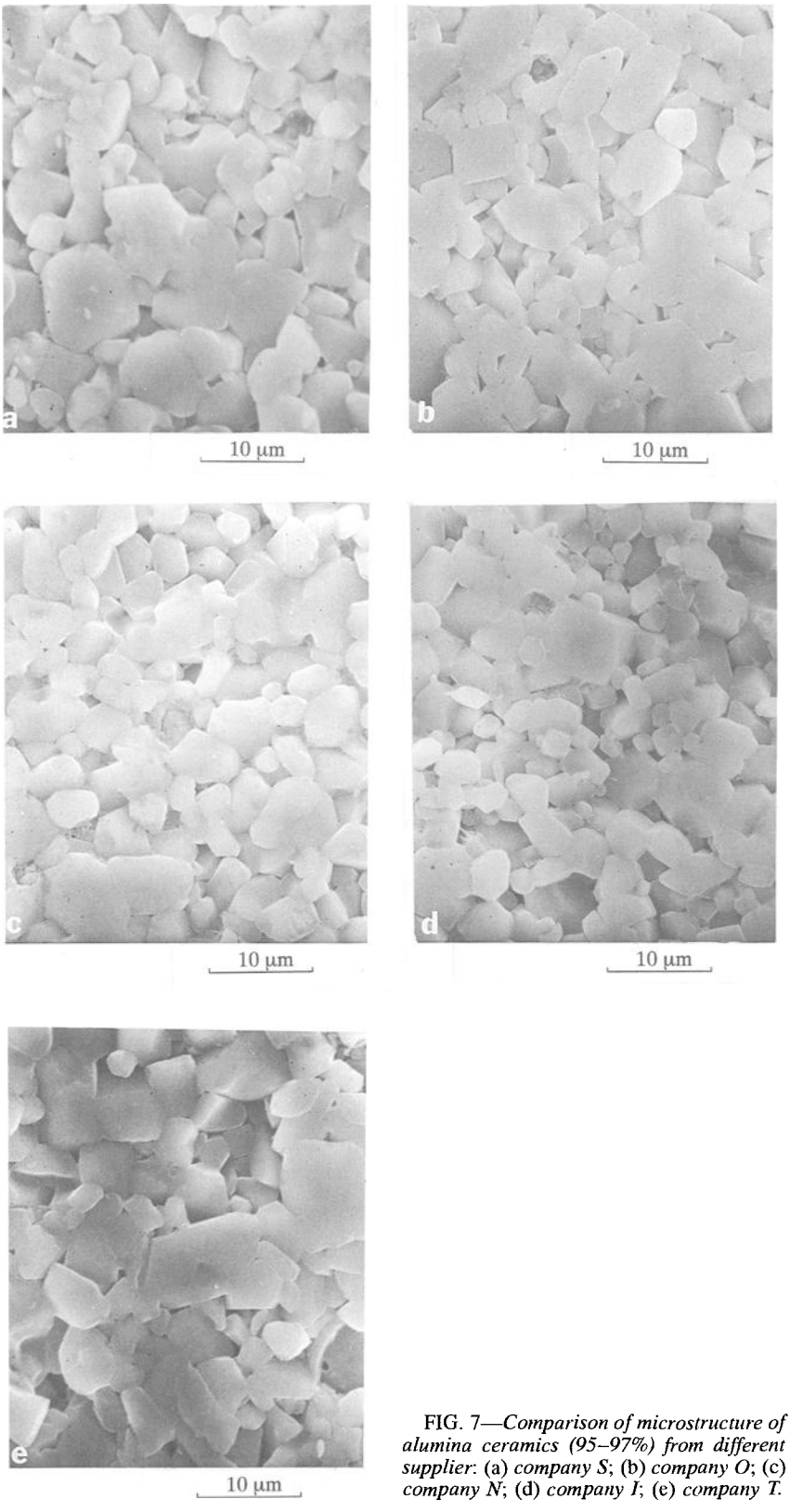

FIG. 7—*Comparison of microstructure of alumina ceramics (95–97%) from different supplier*: (a) *company S*; (b) *company O*; (c) *company N*; (d) *company I*; (e) *company T*.

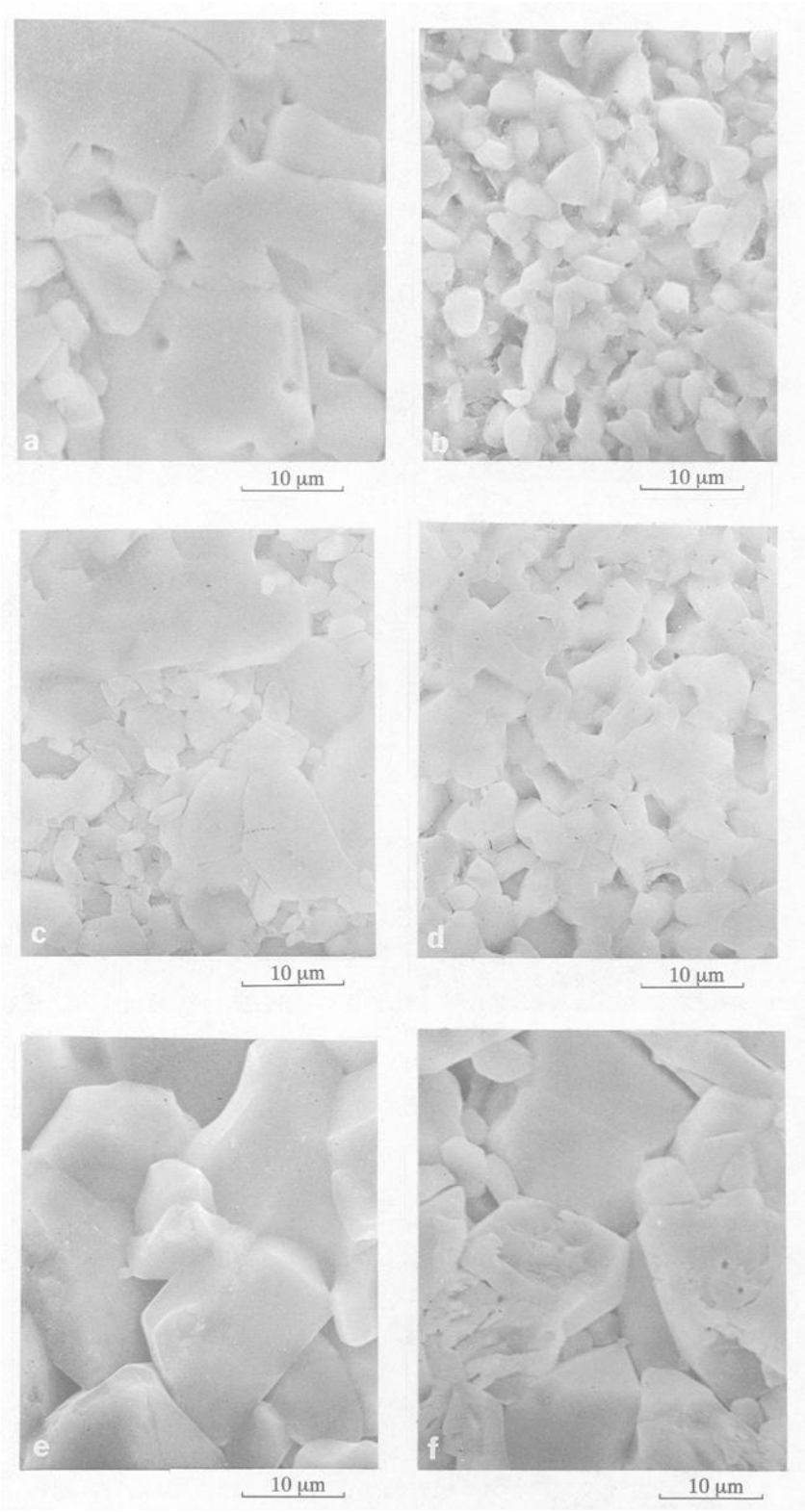

FIG. 8—*Comparison of microstructure of alumina ceramics (>99%) from different supplier*: (a) *company N*; (b) *company NT*; (c) *company I*; (d) *company O*; (e) *company T*; (f) *company S.*

TABLE 2—*Density of alumina ceramics.*

Supplier	Grade name	Purity (%)	Density
S	A-392	92	3.627
	A-396	96	3.736
	A-399	99	3.997
NK	SSA-A	92	3.895
	SSA-999	99	3.904
NT	KP-990	99	3.859
I	...	96	3.753
	...	99.5	3.911
N	...	92	3.545
	...	96	3.768
	...	99.8	3.919
O	...	92	3.618
	...	97	3.770
	...	99.5	3.920
T	AL-170	97	3.767
	AL-197	99	3.882
K	A-471	97	3.686

Image Analysis

Figure 9 shows results of grain size distribution analysis for low alumina content ceramics from companies O and N, which is one of typical results derived from some analysis. They exhibited less morphological differences, therefore discrimination between them seemed difficult.

However the pattern of grain area distribution for them were different apparently. The sample from company N had higher percentage of large grain size than that from company O. This result indicates that the analysis of particle area distribution is a powerful tool to support morphological discrimination of alumina ceramics with the similar morphological characteristics.

For the future, data accumulation regarding the pattern of grain area distribution should be desired for applying this method to the discrimination of ceramics.

X-Ray Diffraction Analysis

Table 3 shows results of the half wave width, a measure of band broadening in X-ray diffraction.

Because the half wave width is reflected mainly by the average crystallite size, the half wave width by X-ray diffraction analysis seems to be good index along with grain observations to discriminate the microstructure of alumina ceramics.

The sample (alumina content 92%) from company N showed large half wave width of three diffraction peaks, in comparison with that from company O (Table 3).

Although these samples showed almost the same morphology of grain structures on SEM observation, the crystallite size of alumina in the ceramics from company N was twice as large as that from company O. X-ray diffraction gives some informations about the internal pits of the particles while the SEM observations deal with the surface.

For these samples, the shift of d-value spacing of lattice plane, caused by a crystalline strain was not observed.

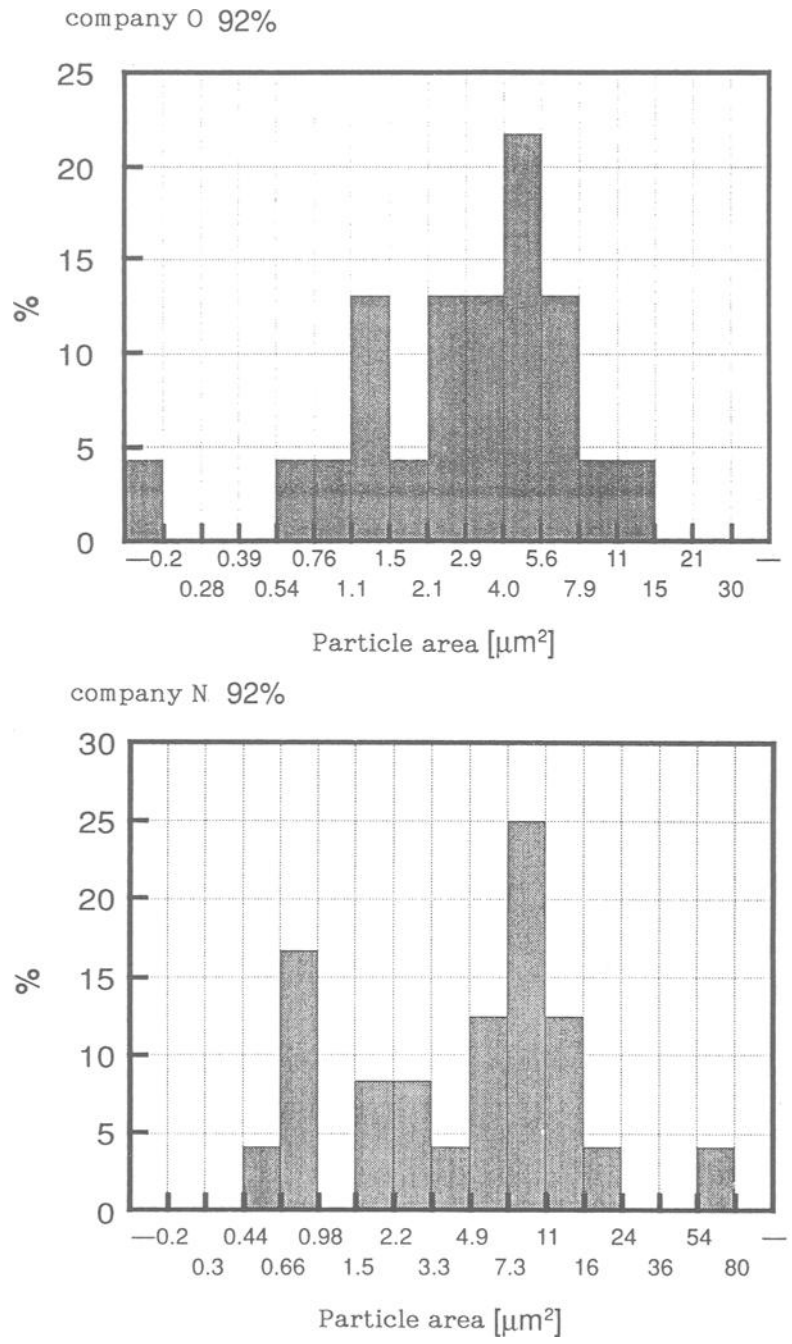

FIG. 9—*Particle area distribution.*

TABLE 3—*Half wave width of three X-ray diffraction peaks for two alumina ceramics that show similar morphology of microstructures. Alumina content: 92%.*

Plane Index (hkl)	(116)	(113)	(104)
Company O	0.125	0.106	0.184
Company N	0.277	0.267	0.275

Conclusion

The morphological observation of ceramics surfaces was preformed to discriminate their microstructure. The etching during preparation of samples was an important factor in determining morphological differences among specimens. Image analysis and X-ray diffraction analysis supported the results obtained by examining microstructure. Density measurements suggested the degree of grain growth, which was related to the purity of alumina powder.

Further analytical determinations of the elements which are added to ceramic formulations in order to control the grain growth on sintering, or to improve ceramics' characteristics may be useful. Surface study would support the discrimination of ceramics established by the morphological observation [*3–6*]. And therefore these further studies are recommended.

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