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Ceramic material processing by electrical discharge in electrolyte

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New ceramic materials receive a great deal of attention as machine components, but they are hard to work. So a hybrid processing which combines electrical discharge processing with grinding is proposed. In this study, in order to examine the possibility of this hybrid processing, the electrical discharge processing on four kinds of ceramics was carried out with a needle electrode. The ceramic materials were alumina and three kinds of silicon nitride series to which are added alumina (ASN), magnesia (MSN), yttria and alumina (YASN). The results obtained showed that a pit can be formed on any ceramic and the pit depth apparently varies with the ceramic material. The removal rates of ASN, alumina, YASN and MSN become low in turn, and are independent of their mechanical properties. In the case of the silicon nitride series, the removal rates depended on their sintering additives, and the higher the applied voltage, the greater was the volume removed. High removal rate and low electrode loss are obtained when the needle electrode is negative. The ceramic materials are mainly removed by etching the grain boundary in a high-temperature electrolyte during the discharging process.

1. Introduction

New ceramic materials, namely alumina, silicon nitride and silicon carbide, have many advantages for mechanical uses because of their high strength at high temperature, high hardness and high stability in corrosive environments. But they are usually nonconductive materials and electrical discharge processing, which is usually used for cemented carbide, cannot be adopted. In addition they are hard to grind even with a diamond grinding wheel, because they have not only high hardness but also high sensitivity on strength by induced cracks. Therefore, it is necessary to develop some new means of processing. Hybrid processing in which two or more processes are combined, may be a way of overcoming the difficulties. In this paper, we propose a hybrid processing which combines electrical discharge processing with grinding. Because the ceramic materials are nonconductive, it is impossible to cause electrical discharge by using nonconductive fluid and it is necessary to use electrolyte as the processing fluid.

Many studies on the electrical discharge processing for nonconductive materials in electrolyte have been carried out. These were on diamond die making by Chauncy *et al.* [1], on hole making in ruby by Kurafuji *et al.* [2], glass cutting by Tsutsui [3], etc. However, these studies were almost solely on single-phase materials.

In order to examine the possibilities of the proposed hybrid grinding, in this study electrical discharge processing was carried out on nonconductive ceramics in an electrolyte using a needle electrode.

2. Ceramic materials

Ceramic materials for machine components are mainly produced by a sintering process. On sintering, additives are used to prevent grain growth and to aid the sintering process. It is especially difficult to sinter silicon nitride or silicon carbide ceramics without additives. Moreover, sintering additives have a great influence on the mechanical properties of the products. For this reason, many studies have been carried out on sintering additives [4]. Therefore, it is important to know the compositions, preparation method and conditions, in addition to the mechanical properties of the materials.

Bearing this in mind, we produced all the ceramic materials in a hot-pressing method. These ceramic materials were alumina (Alumina) and silicon nitride series which included alumina (ASN), magnesia (MSN), yttria and alumina (YASN), as additives. The compositions of the starting materials are shown in Table I.

On sintering silicon nitrides, Si_3N_4 powder and the additives were weighed, and then mixed with methyl alcohol for 48 h. A plastic pot mill was chosen for mixing in order to prevent changes to the composition. After drying, the mixture was sieved with a 50-mesh plastic sieve. Hot-pressing was carried out at a compacting pressure of 35 MPa at certain temperatures and for certain durations, using a graphite mould. The dimensions of the obtained compact were 50 mm diameter and 7 mm thick. A four-point bending test was carried out on each compact 3 mm × 4 mm × 40 mm in size. Vickers hardness was also measured with 9.8 N load and the density was obtained by Archimedes' method. The sintering conditions and the properties of the ceramics are shown in Table II. The bending strengths of YASN and MSN are relatively large, and the hardness of Alumina is relatively high.

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TABLE I Compositions of the ceramics used (%)

	Si_3N_4	Al_2O_3	MgO	Y_2O_3
Alumina	–	99.5	–	–
ASN	89	11	–	–
MSN	95	–	5	–
YASN	91	1	–	8

3. Experimental procedure

The experimental apparatus used for discharge is shown in Fig. 1. One electrode is a nickel needle of 0.5 mm diameter. The end of this electrode was finished flat with a WA no. 1000 oil stone and set in a socket attached to the end of a copper plate spring in order to be observed easily. The other electrode was a graphite vessel, in which the electrolyte was kept, of 60 mm inside diameter. The ceramic material (5 mm × 5 mm × 3 mm) was mirror-finished with 3 μm diamond paste and was fixed on the centre of this vessel. By using a balance system, the needle was pressed down on the ceramic material. The power source for electrical discharge was a direct current of single-phase full-wave rectification and its voltage was variable from 0 to 70 V. NaOH solution was used as the processing fluid and the dipping from the ceramic material was 2 mm. The electrical voltage and current waves were observed with an oscilloscope. Experimental conditions are shown in Table III.

4. Results and discussion

4.1. Material removal

By taking the needle electrode as a negative pole, graphite vessel as a positive pole and applying 50 V between these poles for 3 min in 20% NaOH solution, the needle was surrounded by an orange-coloured flame. In order to confirm electrical discharge, the flame was analysed by a spectrometer and the result is shown in Fig. 2. It can be seen that this result shows the characteristic spectrum of natrium as well as a continuous spectrum. The result can be interpreted that the flame results from the discharge which can be generated by applying 50 V.

The scanning electron micrographs of ceramic materials after processing are shown in Fig. 3. Pits are formed on the ceramic materials, but their shape and dimensions differ from each other.

TABLE II Sintering conditions and the properties of ceramics

Material	Alumina	ASN	MSN	YASN
Firing temperature (°C)	1500	1750	1800	1850
Firing time (min)	30	60	60	60
Density ($g\,cm^{-3}$)	3.966	3.131	3.178	3.284
Bending strength (MPa)	500	500	800	800
Hardness (Hv)	2200	1750	2100	1850

TABLE III Experimental conditions

Workpiece	Alumina, ASN, MSN, YASN
Electrode	0.5 mm diameter Ni-wire
Power source	d.c. 0–70 V
Load	0–0.3 N
Electrolyte	5% NaOH, 20% NaOH
Dipping	2 mm

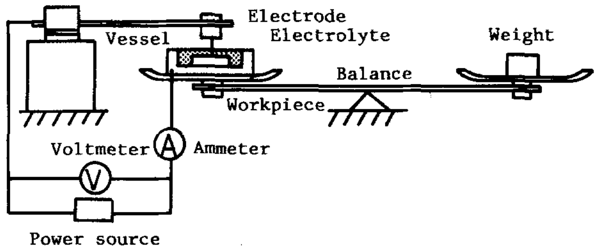


Figure 1 Schematic drawing of the experimental apparatus.

The profile curves of the pits are shown in Fig. 4. On Alumina and ASN, the pits are clearly recognized and their maximum depths are 85 and 230 μm, respectively, but the pit depth of YASN is about 0.25 μm. On MSN, the pit can be observed by SEM, however, it can hardly be recognized from the profile curve.

On ASN, the pit-forming process with processing time was observed by SEM and the result is shown in Fig. 5. The ceramic material removal starts at the edgeline of the needle electrode and spreads outwards. At this time, little charge can be observed on the specimen just below the electrode. After the pit reaches a certain depth, the removal proceeds beneath the electrode and a pit, as shown in Fig. 3, is formed. The diameter of the pit is larger than that of the needle.

It is clear that the removal rates of ASN, alumina, YASN and MSN become low in turn. It seems that the removal rates are independent of material hardness, but dependent on the compositions of ceramic materials. The pit can be clearly recognized both by SEM observation and in the profile curve when the sample contains alumina. However, the greater the alumina content does not necessarily imply a larger removal rate, because the removed volume of alumina is smaller than that of ASN.

We prepared other sintered compacts similar to ASN whose alumina content was changed to 5%, 20% in addition to 11%. The hardnesses of these compacts were HV 1770 and HV 1750. Their porosities were 1.4%, 8%, 0.2%, and the greater the alumina content, the lower the porosity.

Electrical discharge processing was also carried out on these compacts for 3 min at 50 V in 20% NaOH solution. The volumes removed calculated from the profile curves of the pits were 9×10^{-3}, 33×10^{-3} and $145 \times 10^{-3}\,mm^3$ for alumina contents of 5%, 11% and 20%, respectively. It is clear that the removed

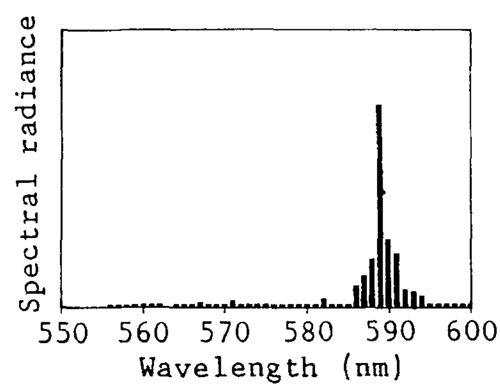


Figure 2 Spectrum of the flame.

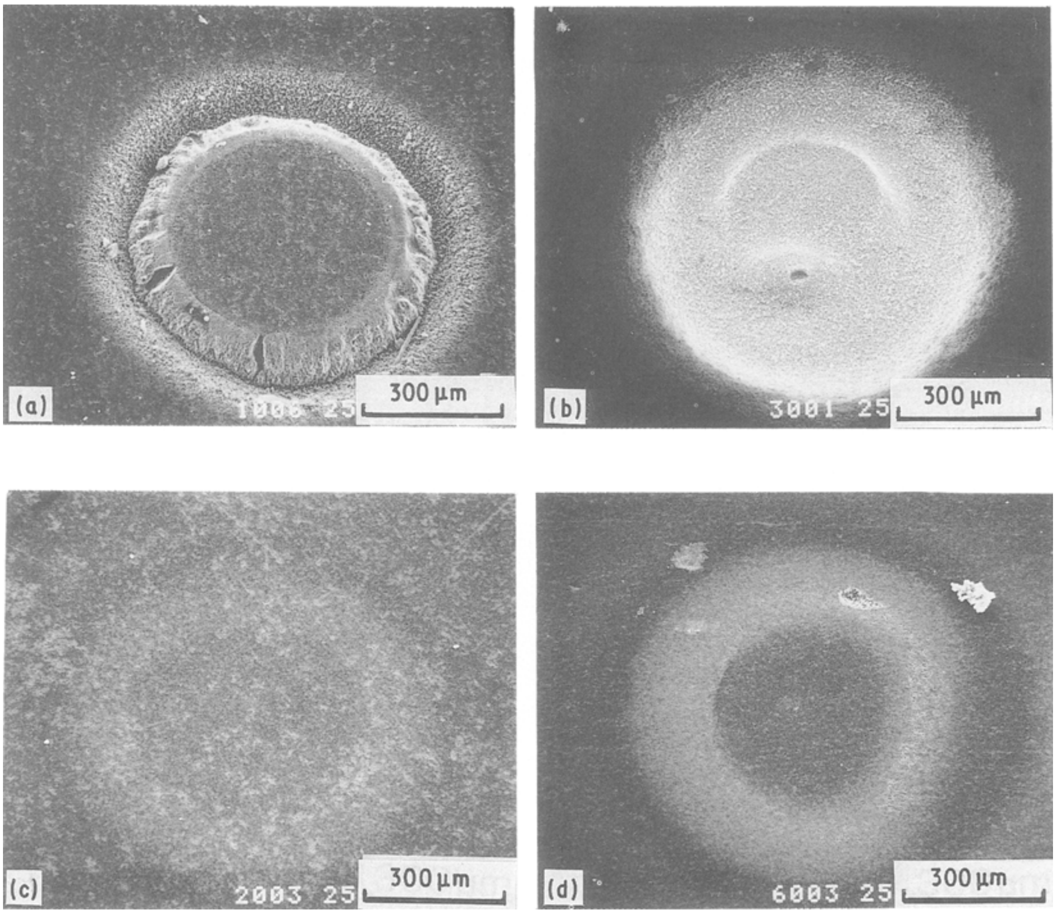


Figure 3 Pits formed by the electrical discharge in 20% NaOH (50 V, 3 min). (a) Alumina, (b) ASN, (c) MSN, (d) YASN.

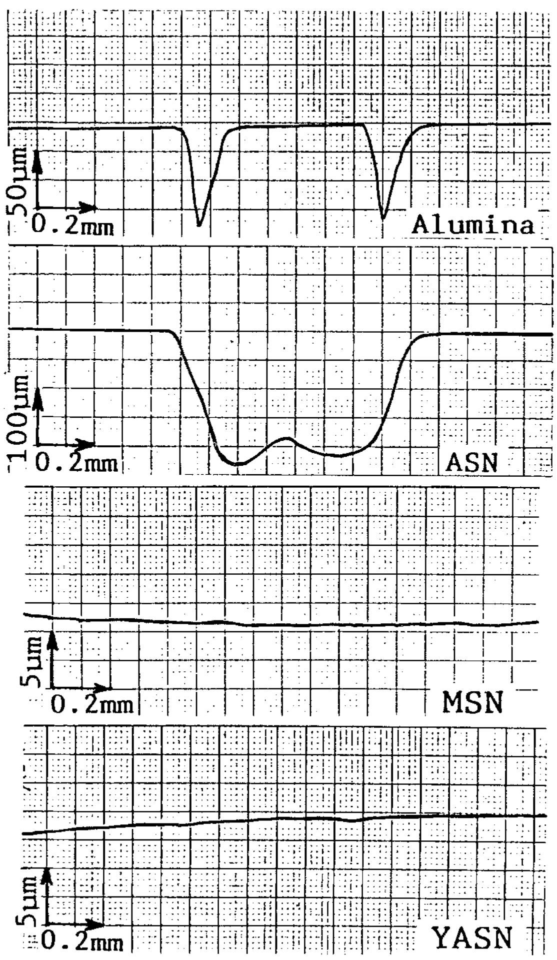


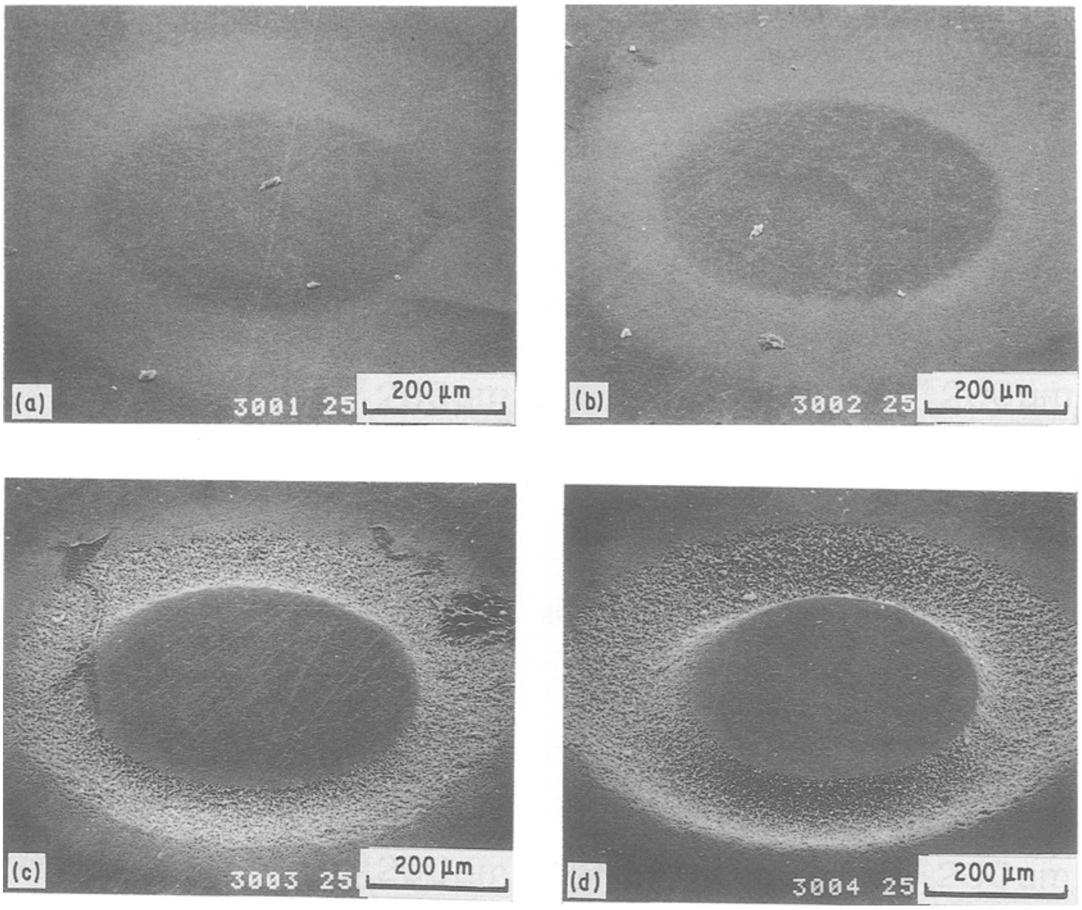
Figure 4 Pit profiles (20% NaOH, 50 V, 3 min).

volume is proportional to alumina content, and has no relation to the hardness. Differences in the removal rates of these compacts may have resulted from the amount of glassy phase which is composed of alumina, and SiO_2 around the silicon nitride powder.

4.2. Effects of applied voltage on the volume removed

In order to make the effects of applied voltage on the removal clear, current and voltage waves were recorded. In the case of Alumina, typical waves obtained with discharging voltages of 20, 30 and 40 V are shown in Figs 6a, b and c, respectively. At 20 V, a pit could not be formed, the voltage and current waves reaching their peaks at the same time. In Figs 6b and c, the waves are almost the same as the case in (a) except that when the instantaneous voltage was above 50 V, the current wave dropped rapidly and both waves fluctuated greatly. At this moment, the electrode was surrounded by an orange-coloured flame, and the level of processing fluid around the needle electrode rose and was stirred by blowing bubbles. It is understood that hydrogen gas generated from the negative pole surface formed the electrical insulating layer, and electrical discharge was generated between the needle electrode and the processing fluid through this layer.

A similar electrical discharge could not be observed in Fig. 6a, whereas it could be recognized in both Figs 6b and c. The discharging duration in (c) was longer than that in (b). These voltage and current waves were



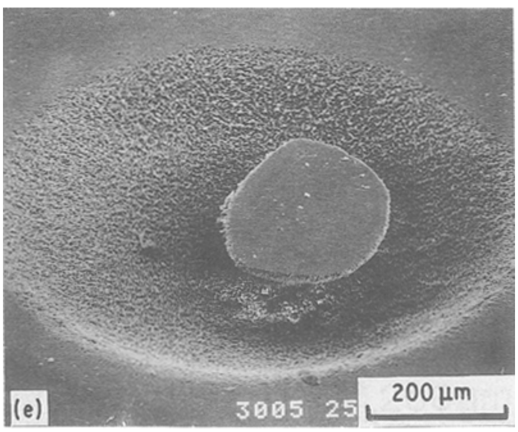


Figure 5 Pit forming process on ASN. (a) 5 sec, (b) 10 sec, (c) 30 sec, (d) 60 sec, (e) 120 sec.

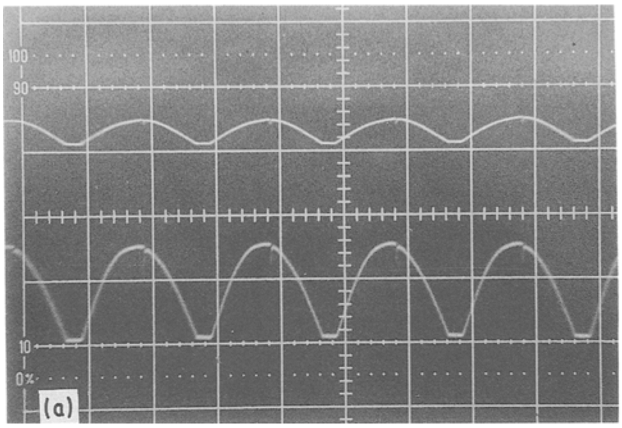
similar to other ceramics. However, when 5% NaOH was used, the voltage at which the electrical discharge started was higher than in the case of using 20% NaOH. It is understood that the electrical conductivity decreases in proportion to the concentration of the electrolyte and a high voltage is needed to generate sufficient hydrogen gas to form the electrical insulating layer. It is proved that to make a pit, the voltage and current waves shown in Fig. 6b or c are indispensable.

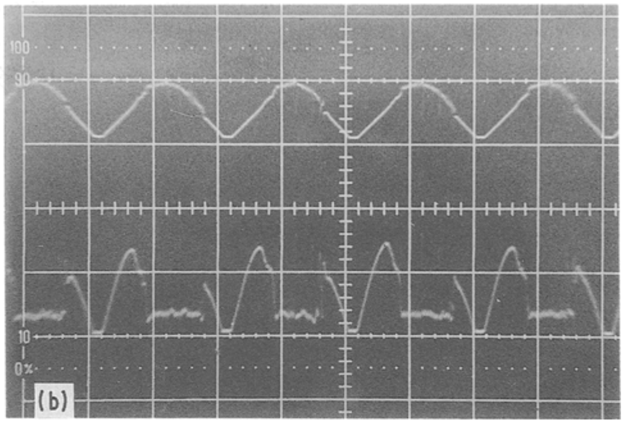
To investigate the relation between the removed volume and the applied voltage, variations of removed volume which were calculated from the profile curves with the applied voltage for a range of NaOH concentrations are shown in Fig. 7. The removed volume increases rapidly with increasing applied voltage. It is for this reason that the discharging duration can be lengthened, the cooling duration shortened and the discharge itself can be strengthened by increasing the applied voltage. In doing so, the temperature of the NaOH solution will rise and remain high. The removed volume becomes larger as the NaOH concentration increases. However, the pit could not be formed when the voltage was below a certain value in any NaOH concentration. The minimum voltages necessary to form pits increased with decreasing NaOH concentration.

4.3. Removal mechanism

Fig. 8 shows SEM observations of pit bottoms. Alumina and ASN grains seem to be disconnected as observed in Fig. 8a and b. Comparing these disconnected grains with those observed in the microstructure of ceramics as-sintered, the grain sizes were almost the same. The ceramic materials might be removed by separating their grains from the boundaries by discharging. Even in a small pit of YASN in Fig. 8c and MSN in Fig. 8d, the grain boundaries seemed to be slightly etched. However, in our experiments, melted trace, which could be produced by laser irradiation in chemical solution could not be found.

In the above observations, the pits showed etched features, so the etched volume of the ceramics soaked in 20% NaOH solution were measured. On being soaked at 30° C for 30 h, no weight change was measured. When the temperature of the NaOH solution was increased 120° C for 30 min, the weight loss of each ceramic could be measured. The weight losses of ASN, Alumina, YASN and MSN were 35×10^{-3},





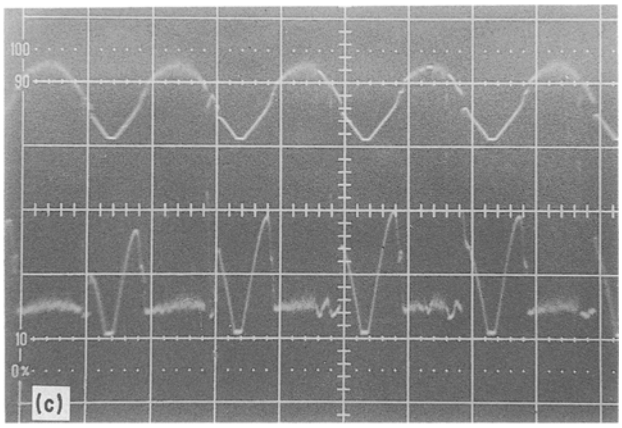


Figure 6 Typical current and voltage waves: upper waves, voltage, 50 V/div; lower waves, current, 0.5 A/div. (a) D.c., 20 V; (b) d.c., 30 V; (c) d.c., 40 V.

5.16×10^{-3}, 5.1×10^{-4} and 2.4×10^{-4} mg mm^{-2} respectively. The order was the same as that in electrical discharge. Therefore, it is demonstrated that the removal mechanism of electrical discharge in NaOH solution is mainly based on etching by chemical solution. In the case of ASN, the volume removed by discharge of 50 V for 3 min was approximately 0.2 mg mm^{-2}, while that by soaking in 20% NaOH solution was much less, even after 30 min at 120° C. It is thus understood that removal by electrical discharge proceeds above 120° C.

As the material removal is considered to be etching

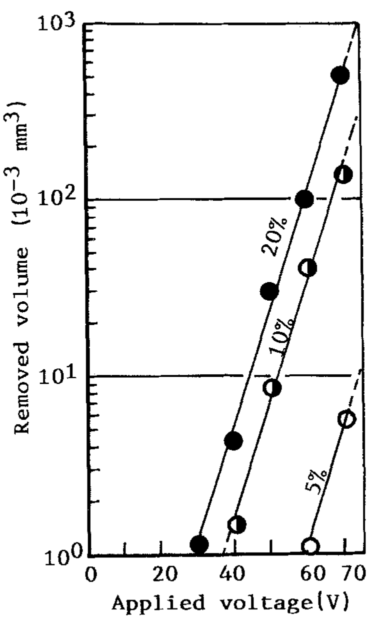


Figure 7 Variations of the removed volume with the applied voltage for a range of NaOH concentrations.

by the processing fluid, the effect of the electrolyte on the removal rate was examined. NaF and $NaNO_3$, as well as NaOH, were selected as processing fluids. In order to achieve similar discharging states, the experiments were carried out using the following procedure. To generate a discharge, it is necessary for the insulating gas layer resulting from electrolysis to surround a needle electrode. The amount of gas generated depends on the electrolytic current. So if the conductivities of the electrolytes are almost the same, a similar discharging state can be obtained. Each electrolyte was prepared under the same conductivity of 60 S cm^{-1} which was obtained in NaF saturated solution. The concentrations of the electrolyte were 4.0%, 6.2%, and 1.2%, respectively. In these electrolytes, the electrical discharge processing was carried out at 70 V for 5 min. It was checked with an oscilloscope that the discharge began at 65 V and continued during the experiments.

The pits obtained are shown in Fig. 9. In spite of similar discharging states, the pit depth varies apparently with the electrolyte, and the volumes removed become smaller in NaF, $NaNO_3$ and NaOH, in turn. It is proved that this processing is governed by etching in the heated electrolyte with an electrical discharge other than the electrical discharge itself.

The appearance observation of the needle after discharging on Alumina in 20% NaOH for 3 min is shown in Fig. 10. At the end face of the needle, the finished marks by the oil stone are clearly recognizable and the contour is also clear. Almost no change can be observed on the needle in comparison with the ceramic materials. Considering the large difference between the hardness of Alumina and the nickel needle, a pit can be formed without any mechanical means.

To investigate the effect of pressure of the needle electrode on removal, by varying the pressure, electrical discharge processing on Alumina was carried out, but the effect could not be estimated. Electrical discharge was generated, by leaving a 0.3 mm gap between the ceramic material and the needle; however, no pit could be obtained even on ASN. Thus it can be understood that the pit can be obtained only when the needle electrode either touches the ceramic material or is located very near the ceramic.

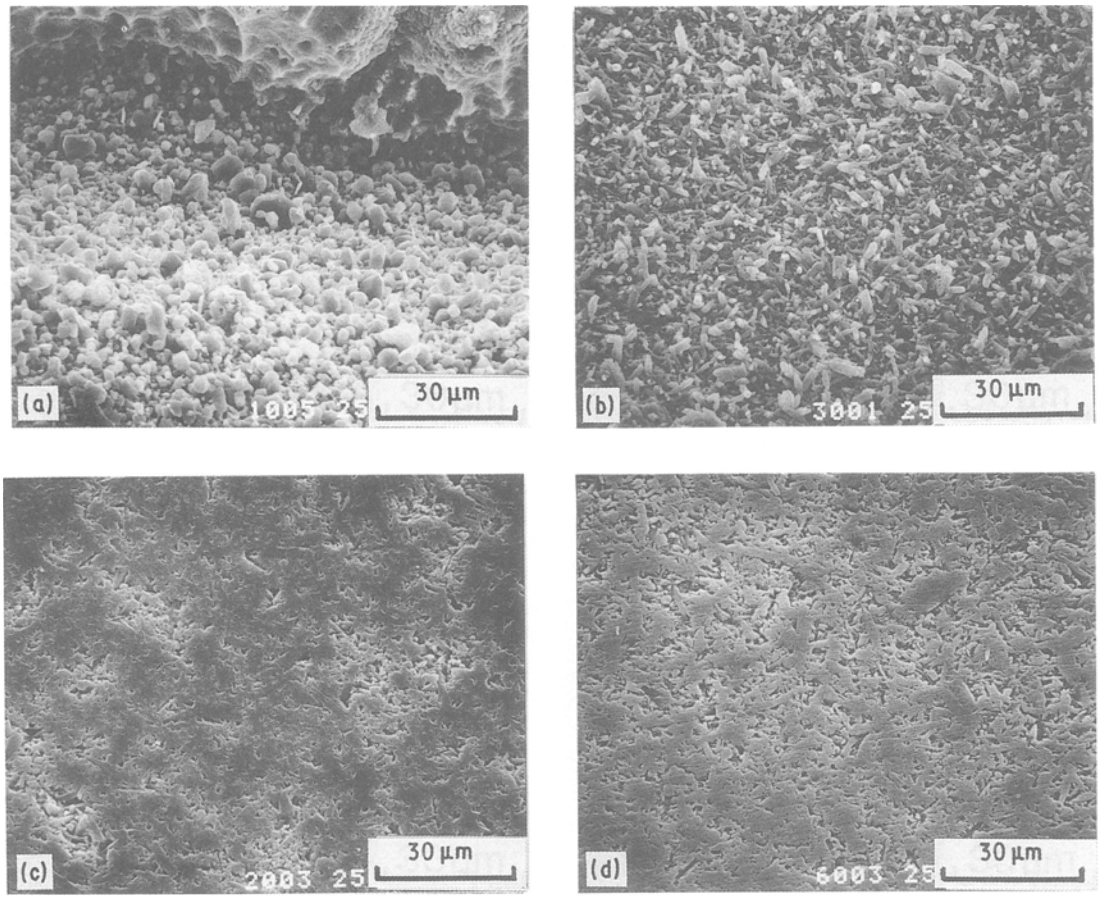
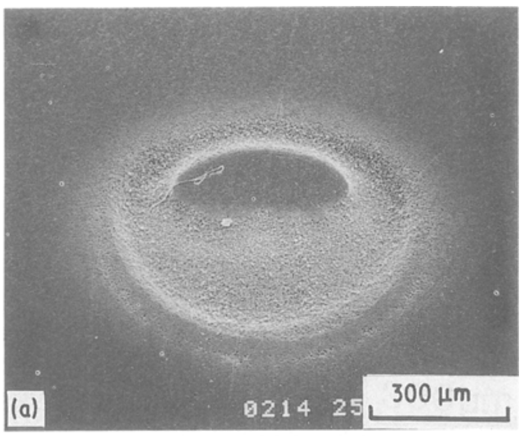


Figure 8 SEM observations of the pit bottoms. (a) Alumina, (b) ASN, (c) MSN, (d) YASN.

4.4. Polarity of the needle electrode

In the paper on hole making in ruby [2], it was reported that it was impossible to make a hole when the needle electrode was in a positive pole. As mentioned above, electrical discharge processing mainly consists of the etching effect of the heated electrolyte, so it may be possible to form a pit even if the polarity is reversed. Electrical discharge processing in reversed porarity was tried with 50 V for 3 min in 20% NaOH on ASN which was the most removed among the materials used. Electrical discharge was generated but was



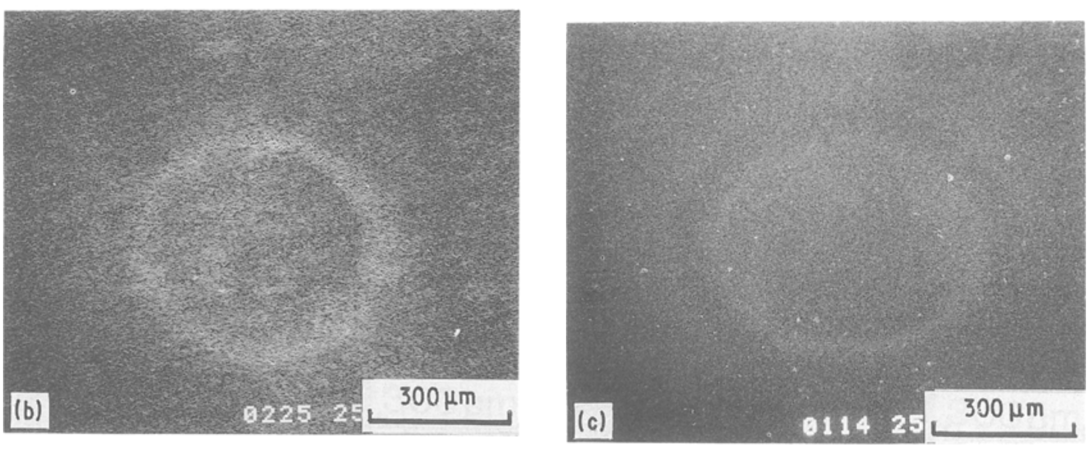


Figure 9 Pits formed by the electrical discharge in different solutions. (a) NaF, (b) $NaNO_3$, (c) NaOH.

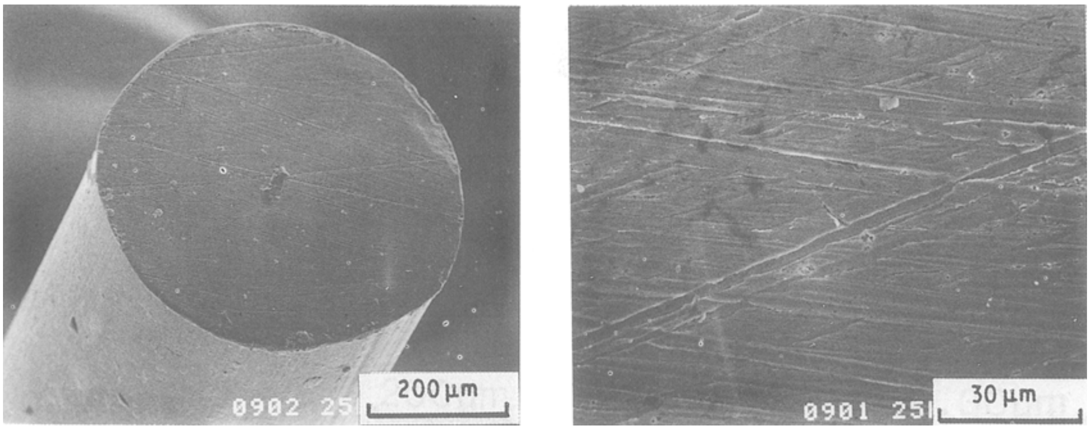


Figure 10 Needle electrode after the discharge for 3 min.

weak, and the volume removed was also less. SEM observation of the pit formed and the cross-sectional profile are shown in Fig. 11. The depth and the diameter of the pit were 150 μm and 0.5 mm, respectively, the diameter being almost equal to that of the needle electrode. For other kinds of ceramics, similar experiments were performed. In the case of Alumina, a pit was formed slightly, but not formed with YASN and MSN.

Fig. 12 shows the appearance of the needle electrode after discharging in the same conditions. The needle end changed and looked rough. It is understood that the needle electrode not only dissolved during electrolysis but also is damaged by electron impact during electrical discharge. When the electrode was positive, however, pits were formed on ASN and Alumina. The reason for this may be that the temperature of the processing fluid around the needle was raised, not as high as that of the negative pole, by the needle electrode which was heated by electron impact. The diameter of the pit is almost the same as that of the needle.

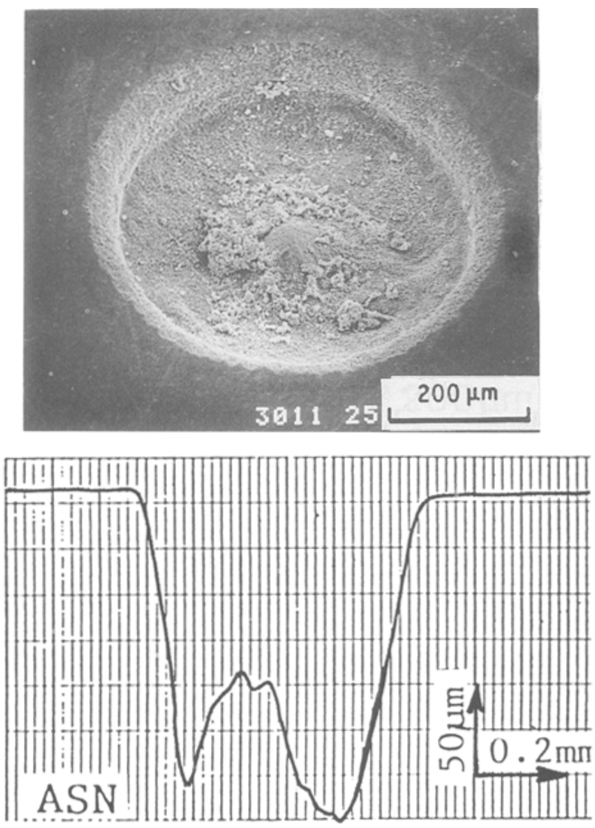


Figure 11 SEM observation and profile of a pit in reversed polarity (20% NaOH, needle electrode positive).

4.5. Removal model

Based on the above observations, a removal mechanism is proposed in Fig. 13. The gas generated from the needle electrode by electrolysis forms an insulating layer as shown in Fig. 13 (1), then the electrical discharge begins through this insulating layer as shown in (2). The needle electrode plays the role of electron supplier. At this time the electrolyte around the needle electrode is heated by electron impact. As a result, ceramic material is etched off by the heated electrolyte, as shown in (3). The removal continues with the stirring of the electrolyte, and material removal proceeds towards the area below the needle electrode with permeating of the electrolyte to the part removed previously, as shown in (4).

5. Conclusions

In this study, electrical discharge processing in chemical solution for nonconductive ceramic materials was carried out in order to examine the adoption for the hybrid processing of new ceramic materials. The following results were obtained.

1. A pit can be formed on any ceramic, but pit depth varies apparently with the ceramic material.

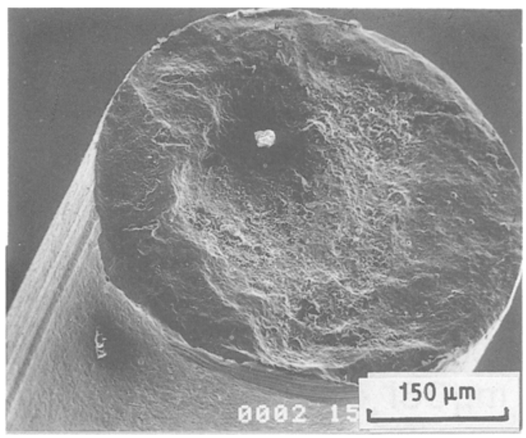


Figure 12 Needle electrode after the discharge for 3 min in reversed polarity (20% NaOH, needle electrode positive).

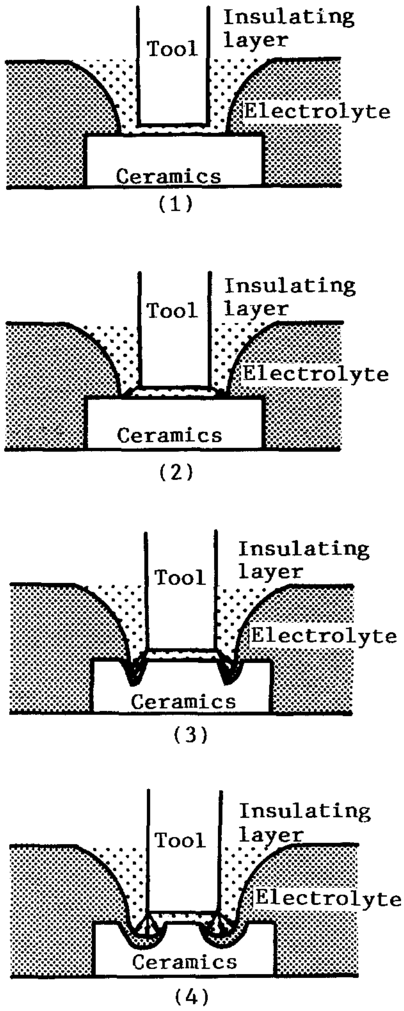


Figure 13 A removal model of ceramic material by electrical discharge in the electrolyte.

2. The removal rates of ASN, Alumina, YASN and MSN become low in turn and are independent of their mechanical properties.
3. In the case of silicon nitride series, the removal rates depend on their sintering additives.
4. The higher the applied voltage, the greater the volume removed.
5. High removal rate and low electrode loss are obtained when the needle electrode is negative.
6. Ceramic materials are mainly removed by etching of the grain boundary in a high-temperature electrolyte during discharging.
7. There is a possibility that electrical discharge processing is one of the elements of a proposed hybrid grinding of ceramic materials.

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