Preparation of Ceramic Surfaces for Microscopic Observation by Penning Discharge Microetching

Eiichi NISHIKAWA, Toshio SUGITA, Toshiyuki TAKAHASHI,* Hitoshi IDA** and Yuuko TSUYA**

Department of Electrical Engineering, Science University of Tokyo, 1-3, Kagurazaka, Shinjuku-ku, Tokyo 162-8601
*Toshiba Tungsten Co., Ltd., 580, Harima-cho, Saiwai-ku, Kawasaki-shi, Kanagawa 210-8503
**Moruto Instrument Co., Ltd., 1-1-10, Yashima, Bunkyo-ku, Tokyo 113-0034

In this study, a new microetching technique for the observation of ceramic surfaces by Penning discharge microsputtering is developed and applied to ceramic surfaces. Each ceramic surface was prepared by mechanical polishing and subsequent etching and the resultant surfaces were examined under both an optical and a scanning electron microscope. The results in the case of using with a gold target revealed high-definition images of the surface structure of the Si₃N₄, ZrO₂ and Al₂O₃-ZrO₂-Al₆Si₂O₁₃ ceramics after surface etching using this process. However, in the case of using a gold target, high-purity Al₂O₃ ceramics and Al₂O₃-ZrO₂ complex ceramics, the resultant surface preparation was unsuccessful. However, when using a titanium target, the procedure in both cases, was successful. This difference could be attributed to the difference in the effect of oxygen on both metals.

Keywords: Microetching, Microscopic observation, Surface preparation, Si₃N₄ ceramics, ZrO₂ ceramics, Al₂O₃ ceramics, Al₂O₃-ZrO₂ complex ceramics, Al₂O₃-ZrO₂-Al₆Si₂O₁₃ ceramics

1. Introduction

The mechanical and electrical properties of ceramic materials are extremely sensitive to the ceramic microstructure. For the microscopic study of morphology, a suitable etching method must be applied on a polished surface in order to develop the microstructure. In the case of metals, soft chemical etching is typically used. However, it is difficult to apply the same method to corrosion-resistant materials such as ceramics. The microstructure of ceramics is usually examined by observation of the characteristics of a fractured surface (fractography), a strong chemical etched surface, or a thermally etched surface.1)2) In the case of these observations, there remains a small doubt that some of the detailed microstructure might be lost. Another possible process for the microscopic study of morphology is cathode sputtering. In sputtering using the conventional apparatus, the etching rate is too slow. Therefore, a new etching process for ceramics is desired so as to accurately observe the microstructure. The Penning discharge microsputtering technique has been developed by Sugita et al.3)-6) This technique, called "microetching," permits the removal of a small area of the surface by etching any substrate material, be it an insulator, a semiconductor or a metal and is also utilized for inlays on hard materials as well as to flatten the surface of diamond films. In the present research, the application of this microetching technique to the etching of ceramic materials, is examined for the study of the microstructure of some ceramic materials.

2. Experimental procedure

Figure 1 depicts a cross section of the microetching apparatus that is divided into a discharge chamber and a specimen chamber. In the discharge chamber, there are two parallel flat cathodes (C₁, C₂) and located between them is a cylindrical anode (A). A magnetic field of 0.1 T is applied vertically by external magnets (B). The specimen (S) is placed so as to be centered on between a hole (H) on C₂, and a mask (M). The pinhole of M is approximately located within the anode circumference. The chambers are evacuated to 1×10⁻³ Pa by a vacuum system, and then filled with argon gas to 3×10⁻² Pa. A d.c. voltage of 1.0 kV is applied to the anode while the cathode is held at the earth potential. Because of the vertical magnetic field, Penning discharge occurs and the etching beam arrives at the surface of the specimen. After microetching, the surfaces were observed using an optical microscope and a scanning electron microscope (SEM).

The ceramic specimens investigated in this study are listed in Table 1. These specimens were fabricated by the hot isostatic pressing (HIP) method. The surfaces to be etched were prepared by mechanical polishing using a diamond
paste with grains of diameter of 0.3 μm.

The operational conditions for each experiment are summarized in Table 2. For ceramics, the basic operation conditions involved the use of a gold target in argon gas of 3 × 10^-2 Pa with an etching time of 10 min. When the specimen could not be satisfactorily microetched under these conditions, the effects of various etching times and target materials were examined.

### Table 1. Components and Sintering Temperatures of Specimens

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Component</th>
<th>Sintering temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃N₄ ceramic</td>
<td>Si₃N₄(add:Y₂O₃)</td>
<td>1800</td>
</tr>
<tr>
<td>ZrO₂ ceramic</td>
<td>ZrO₂(add:Y₂O₃)</td>
<td>1650</td>
</tr>
<tr>
<td>Al₂O₃ ceramic</td>
<td>100%Al₂O₃</td>
<td>1600</td>
</tr>
<tr>
<td>Al₂O₃-ZrO₂ ceramic</td>
<td>60%Al₂O₃:40%ZrO₂</td>
<td>1500, 1600, 1650, 1700</td>
</tr>
<tr>
<td>Al₂O₃-ZrO₂-Al₂SiO₅ ceramic</td>
<td>Al₂O₃:20%ZrO₂:15%Al₂SiO₅</td>
<td>1550</td>
</tr>
</tbody>
</table>

### Table 2. Basic Operational Conditions for the Microetching of Each Ceramic

<table>
<thead>
<tr>
<th>Argon pressure</th>
<th>3 × 10^-2 Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic field</td>
<td>0.1 T</td>
</tr>
<tr>
<td>Anode voltage</td>
<td>+1.0 kV</td>
</tr>
<tr>
<td>Discharge current</td>
<td>10 mA</td>
</tr>
<tr>
<td>Etching time</td>
<td>10, 20 or 30 minutes.</td>
</tr>
<tr>
<td>Target</td>
<td>Au, Ti</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Silicon nitride ceramics (Si₃N₄)

The optical and SEM micrographs of Si₃N₄ etched by the microetching technique for 20 min are shown in Figs. 2(a) and 2(b). A dendritic microstructure surrounding needle-like grains was observed. There appears to be a glassy formation surrounding the grains in the silicon nitride ceramic. It is well known that on a fractured surface (Fig. 2(c)), during conventional observation, only needle-like grains can be recognized among the small round grains, but the dendritic microstructure on the microetched surface of the same material is not observed.

3.2 Zirconia ceramics (ZrO₂)

Figure 3(a) shows an optical micrograph of a partially stabilized zirconia (PSZ) surface etched by the microetching technique for 30 min. It shows small grains (approximately 1 μm in diameter) which can distinctly be observed using the optical microscope. Figures 3(b) and 3(c) show SEM micrographs of the same specimen microetched for 10 min and for 30 min, respectively. Some traces of diamond polishing remained as shallow scratches after microetching for 10 min (Fig. 3(b)), but after etching for 30 min these were completely removed to yield a perfectly flat surface (Fig. 3(c)). Moreover, in each grain, a group of parallel-stripe-like etch pits, which was dependent on the crystal orientation, was observed. These patterns are not observed on the fractured surfaces of the same material. This preponderance of these parallel stripes may correspond to the strain on the grain caused by the residual stress in the PSZ.

3.3 Alumina ceramics (Al₂O₃)

By microetching under the basic conditions employing the Au target, the microstructure of a high-purity HIP Al₂O₃ ceramic did not develop and the removal rate appeared to be very slow. Considering the oxidation activity of metals, Cu, Mo and Ti were used as target materials for etching the Al₂O₃ ceramic. It was only with Ti, the most active metal, that a satisfactory etching was achieved. A sharp grain boundary and a group of etch pits depending on crystal orientation were observed, as shown in Figs. 4(a) and 4(b). The etched surface was analyzed by EPMA to examine the effect of the Ti oxide that might have developed on the specimen surface; the result was quite negative.

3.4 Alumina zirconia complex ceramics (Al₂O₃-ZrO₂)

The highest bending strength and fracture toughness of the Al₂O₃-ZrO₂ ceramics were obtained by sintering at 1650 °C and 1700°C. In the examination of the effect of sintering temperature on microstructure, microetching under the basic conditions with the Au target did not result in the development of any structure. The target Ti was then tested instead.
of the Au one. Microetching using the Ti target developed the microstructure of a complex ceramic. Comparison of SEM micrographs (Fig. 5) before and after etching, reveals that the grain size is smaller at lower sintering temperatures. After the microetching, the microstructures of weak materials sintered at temperatures below 1600°C were revealed to have rough topography. This finding indicates insufficient binding between each grain. Sharp and fine boundaries between large grains on a microetched surface were observed due to the perfect binding of the strong materials sintered at temperatures above 1650°C.

3.5 Alumina zirconia mullite complex ceramics (Al₂O₃-ZrO₂-Al₆Si₂O₁₃)

A SEM micrograph of the surface of the Al₂O₃-ZrO₂-Al₆Si₂O₁₃ complex ceramic after microetching for 20 min is shown in Fig. 6(a) (In this case, there is no coating on the
Grains of three different types, surrounded by sharp and rather straight grain boundaries, are observed. It is confirmed that the microstructure developed by the microetching (Fig. 6(a)) was similar to that observed in a backscattered electron SEM image (Fig. 6(b)). The three grain types, namely light, gray and dark, correspond to zirconia, alumina and mullite, respectively. Each zirconia grain appears to be surrounded by mullite grains to modify the binding between the zirconia and alumina grains. On the other hand, in the case of thermal etching at 1300°C for 1 h in air (Fig. 6(c)), only two types of grains, light and dark, are evident. These grains have a rounded structure and are surrounded by broad grain boundaries. Thus, it is obvious that this microetching process is superior to the thermal process for determining the exact microstructures of ceramic surfaces.

4. Conclusions

The microetching technique provides a larger amount of useful information regarding the detailed morphology of ceramics, compared with other, more conventional, techniques. In addition, this technique removes stains and shallow scratches from the ceramic surfaces more easily than conventional techniques. The use of target materials that are more easily oxidized than gold enhances the microetching process and produces a surface that is more readily observable.

Acknowledgments The authors are grateful to Mr. Akio Kurose of JEOL, Ltd. for assistance with the SEM observations. They would also like to thank Professor Yukio Nakamura of Tokyo University of Agriculture for his helpful advice in the preparation of this manuscript.

References