Vacuum Electrical Breakdown Characteristics and Surface Condition of Ti Electrodes with Oxidation Conditions

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ABSTRACT

Outgassing from an electrode surface is regarded as a major factor leading to electrical breakdowns in vacuum. Recently oxidation treatment at 200 ^{o}C was reported as an effective means of reducing Ti outgassing. In this paper, we report our measurement and comparison of the electrical breakdown characteristics of Ti electrodes with different oxidation conditions (without oxidation, oxidation at 200 ^{o}C, oxidation at 450 ^{o}C). In addition, we analyzed electrode surfaces before and after breakdown experiments in situ with X-ray photoelectron spectroscopy (XPS). Before oxidation, we machined the electrode's surfaces to the roughness of 0.8μm Rmax with diamond turning. Breakdown experiments demonstrated that the breakdown field is highest at the first application of voltage to electrodes with oxidized at 200 ^{o}C. Before breakdown experiment, surface analysis revealed that all the sample electrodes had a large amount of carbon originating from the hydrocarbons of contaminants, and after the experiments, they revealed that the carbons had disappeared. To obtain breakdown characteristics of electrodes with smoother surfaces, we conducted experiments on electrodes with a surface roughness of 0.05 μm Ra. For these electrodes, the breakdown field was higher at first breakdown; the repetitions required to achieve saturated breakdown fields were significantly fewer, and the amount of carbon on electrode surfaces before breakdown was less.

Index Terms — **Vacuum breakdown, Ti, mechanochemical polishing, X-ray photoelectron spectroscopy, conditioning, oxidation.**

1 INTRODUCTION

THE insulating ability of a vacuum is used for high-power devices such as particle accelerators, and vacuum interrupters. In an accelerator, a high breakdown field is required to achieve higher reliability and higher accelerating energy. Many studies have clarified factors leading a vacuum gap to electrical breakdown, and have tried to establish a surface treatment for electrodes [1]. Gases released from electrode surfaces are regarded as one of the major factors leading to electrical breakdown in a vacuum. Reducing the outgassing rate of electrode surfaces must be one of the effective means of increasing the breakdown field.

Titanium is recognized as a potential electrode material for the beam duct of an accelerator because of its antiferromagnetism, low residual radioactivity, light weight, and high electric resistivity. Huguenin and Dubois reported the breakdown characteristics of Ti [2]. Recently, Morimoto et al. found that oxidation treatment at 200 ^{o}C is effective for reducing outgassing of Ti because of the thin and fine oxide layer created on its surface [3]. Therefore this oxidation treatment is expected to enable achieving higher hold-off voltage with Ti electrodes in a vacuum gap. We undertook our investigation to clarify the dependence of breakdown characteristics on this oxidation treatment.

We investigated and compared breakdown characteristics of Ti electrodes with different oxidation conditions (natural oxidation, oxidation at 200 ^{o}C, oxidation at 450 ^{o}C). We also analyzed electrode surfaces in situ with X-ray photoelectron spectroscopy (XPS) before and after breakdowns. In addition we examined them with a scanning electron microscope (SEM) after breakdowns.

Another factor that influences the breakdown field is surface roughness. Mechanochemical polishing (MCP) in conjunction with diamond turning makes a Ti electrode surface smoother. Using these processes, we obtained a surface roughness of

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about 0.05 μm Ra. In our breakdown experiments, we analyzed surfaces on electrodes treated by diamond turning, MCP, and oxidation at 200 °C, and compared the results with those obtained for electrodes without MCP.

2 EXPERIMENTAL

2.1 SAMPLE ELECTRODE PREPARATION

Table 1 lists the processing parameters and properties for all sample electrodes. Sample electrodes were machined from pure titanium (Japan Industrial Standards JIS 2). Figure 1 illustrates the geometry of the sample electrodes. All the sample electrode surfaces were finished with precision machining with a natural diamond bit (diamond turning) to the roughness of 0.8 μm R-max. Then the samples were oxidized under the conditions given in Table 1 to clarify how the different oxidation influenced the breakdown field. Ti electrodes machined with the diamond turning followed by MCP were also prepared to investigate how surface roughness influences the breakdown field. The MCP is a polishing way that mechanical polishing is carried out in particular liquid solution which chemically reacts with electrode material. The polishing provided surface roughness of 0.05 μm Ra. Kobe Steel Ltd. (KOBELCO), the manufacture, conducted all these treatment processes at their facilities, and then transferred the processed electrodes to Saitama University in a container filled with N_2 gas.

Table 1. Properties of sample electrodes

	Sample A	Sample B	Sample C	Sample D
Oxidation temperature [°C]	-	450	200	200
Processing procedure	1.Machine lathing with diamond bite	1.Machine lathing with diamond bite 2.Oxidation at 450 °C	1.Machine lathing with diamond bite 2.Oxidation at 200 °C	1.Machine lathing with diamond bite 2.MCP 3.Oxidation at 200 °C
Material	Pure Ti JIS2			
Geometry	φ 25, R30			
Surface roughness [μm] (Rmax)	0.8	0.8	0.8	0.05
Oxidation atmosphere	Ar + O_2 (8%)			
Thickness of oxidation layer [nm]	10 (Natural oxidation layer)	80	10	10
Crystal Structure of oxidation layer	Not Crystallized	Rutile (TiO_2)	Not Crystallized	Not Crystallized

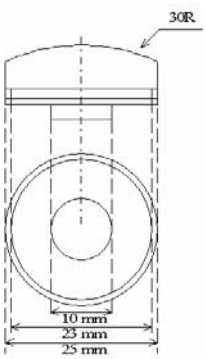


Figure 1. Geometry of sample electrode.

2.2 EXPERIMENTAL APPARATUS

Figure 2 is a schematic drawing of the apparatus used for measurements of breakdown characteristics and surface analysis of the electrodes. This apparatus consists of five vacuum chambers: sample-entry chamber (chamber 1), surface-treatment chamber (chamber 2), surface analysis chamber (chamber 3), voltage-application experiment chamber (chamber 4), and surface-charge distribution measurement chamber (not used in this experiments). We analyzed electrode surfaces with XPS in chamber 3. These five vacuum chambers are connected to each other with gate valves. All the chambers, except chamber 1, are evacuated continuously. When sample electrodes are introduced in the vacuum chamber, only the chamber 1 is exposed to air. Sample electrodes are transferred between chambers with transfer rods. A feature of this apparatus is that breakdown measurements and surface analysis can be conducted without exposing sample electrodes to air (in situ investigation). The applied voltage was an impulse voltage (rise time 64 μs / time to half value 700 μs / peak value 80 kV), and same voltage is used on all breakdown

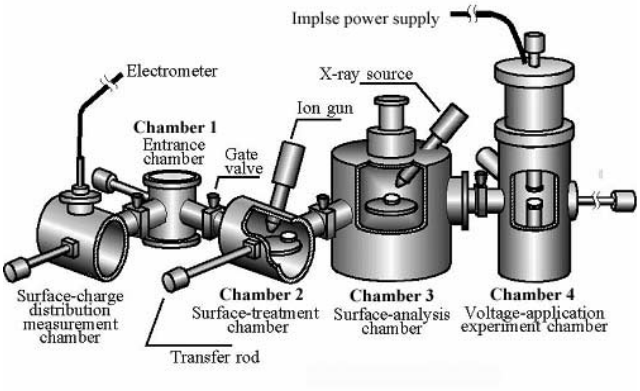


Figure 2. Apparatus for in-situ experiment

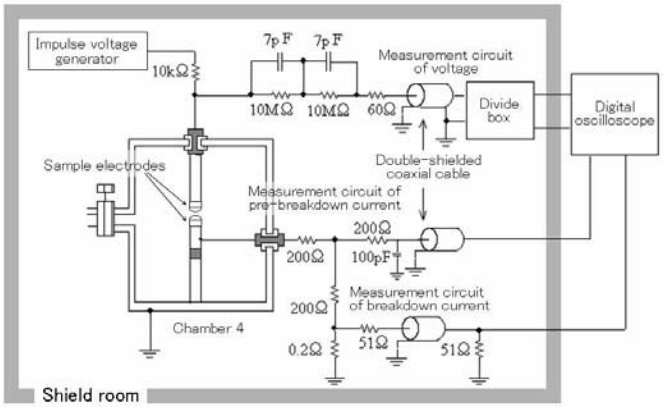


Figure 3. Circuit diagram of breakdown test

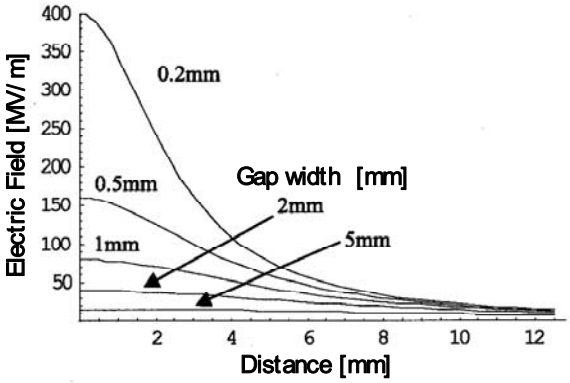


Figure 4. Changes of electric field intensity at the electrode surface with the distance from the center axis of the gap [4]. Applied voltage:80 kV.

tests. The residual pressure in each chamber was maintained in the range of 10^{-7} to 10^{-8} Pa by using a sputter ion pump and a Ti-getter pump.

Breakdown test was carried out in chamber 4. Figure 3 shows the circuit diagram of breakdown test. The measurement method of breakdown electric field is as follows. First, we set electrodes face to face with gap width 5 mm in chamber 4, and apply impulse voltage. The peak value is 60 kV at first and it is increased by 2 kV up to 80 kV until breakdown occurred. If breakdown occurred, we record the voltage-current waveforms and evaluate breakdown strength by calculating breakdown field, dividing the peak voltage by gap width. If breakdown didn't occurred at 80 kV gap width was shortened by 20% using micro meter, and voltage was applied from 60 kV.

Figure 4 shows changes of electric field intensity at the electrode surface with the distance from the center axis of the gap at a given gap width [4]. Applied voltage was 80 kV. It is confirmed that the effective area where the electric field intensity is stronger than 90% of the peak value becomes smaller for smaller gap width.

2.3 PROCEDURE

First, sample electrodes were introduced into the chamber 1 immediately after breaking the container's seal to avoid exposing them to air for a long time. Next, to analyze electrode surfaces with XPS, the samples were transferred to chamber 3 via chamber 2 by using the transfer rods. Then, they were transferred to chamber 4, where repetitive breakdown tests were performed by the way described in 2.2. Thereafter, electrodes were transferred back to chamber 3 to analyze their surface again. After the series of experimental steps, electrodes were taken from chamber 1, and their surfaces were observed with a scanning electron microscope (SEM) in the Molecular Analysis and Life Science Center of Saitama University.

3 RESULTS AND DISCUSSION

3.1 BREAKDOWN CHARACTERISTICS

Figure 5 shows the escalation of breakdown fields with the number of repetitive breakdowns for samples prepared under different conditions. Three pairs of electrodes treated with

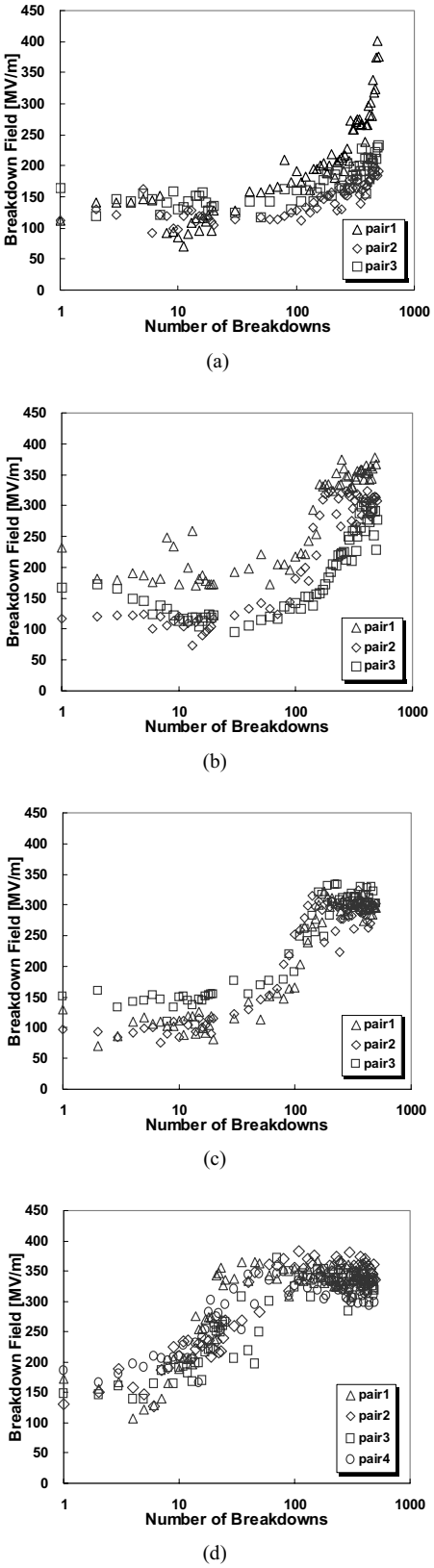
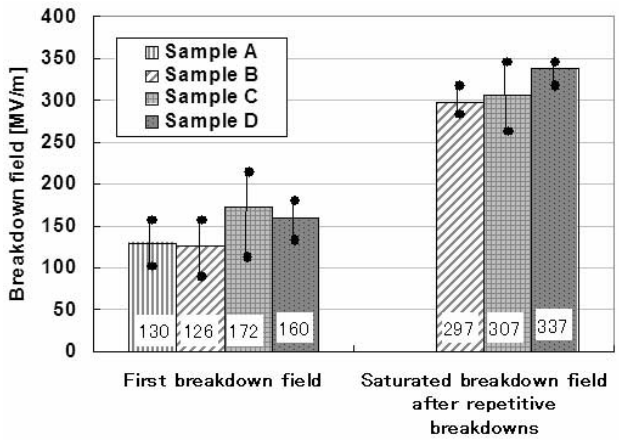
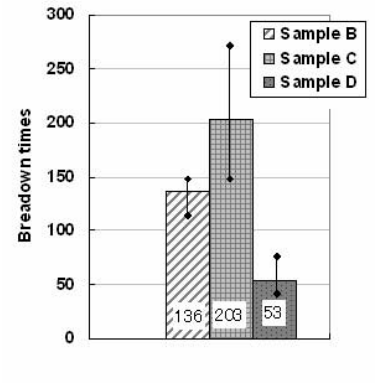


Figure 5. Breakdown characteristics.
(a) without oxidation (Sample A)
(b) oxidation at 450 °C (Sample B)
(c) oxidation at 200 °C (Sample C)
(d) oxidation at 200 °C after MCP (Sample D)



(a)



(b)

Figure 6. Summarized breakdown characteristics.
(a) Breakdown fields of each sample electrode
(b) Number of breakdowns required to achieve saturated breakdown field (Breakdown field for Sample A was not saturated)

same oxidation conditions were prepared and subjected to breakdown experiments to investigate the variation in breakdown fields. Under the same oxidation condition, the breakdown field escalation and number of breakdowns were similar. Average values of principal parameters for these results are summarized in Figure 6. Average breakdown fields at the first breakdown of Ti electrodes with oxidation at 200 ^{o}C, i.e. Sample C and Sample D, are 172MV/m and 160 MV/m respectively, and these values are much higher than those for the other electrodes oxidized under different conditions. This result corresponds to the findings of Morimoto et al. [3] that describe the reduction of outgassing from the surface layer created by oxidation at 200 ^{o}C.

Owing to the conditioning effect of the repetitive breakdowns, breakdown field was increased and then saturated after a certain number of breakdowns. The average values of saturated fields were in about 300 MV/m for all samples, and their values were not so different. This may have been caused by the phenomena that contaminants on electrode surfaces were removed and the microscopic geometry of the surfaces was changed by the repetitive breakdowns (This will be discussed in section 3.2 and section 3.4). Sample D required the least number of breakdowns to achieve a saturated breakdown field. This result indicates that the MCP treatment of Ti electrodes is significantly effective for achieving a conditioned breakdown field with fewer repetitive breakdowns.

3.2 CHEMICAL COMPOSITIONS OF ELECTRODE SURFACE

Figure 7 shows the chemical compositions found by XPS analysis of the electrode surface before and after repetitive breakdowns. Before breakdown (Figure 7a), spectra for all electrodes without MCP show clear peaks of C1S and O1S; in particular, the C1S peak is extremely high, while the peak of Ti2P originating from the electrode material is very weak. For electrodes with MCP (Sample D), the peak height of C1S is lower than those of Samples A, and C. These spectra reveal that the surfaces of as received electrodes were covered with oxide films and carbon based compounds. After breakdown experiments (Fig. 7(b)), on the other hand, the C1S peak almost disappears and peaks of Ti2P and Ti2S become clearer and higher for all the electrodes.

To look at carbon on the surface in detail, narrow XPS spectra near C1S of each sample are shown in Fig.8. The C1S peak originating from $(CH_2)_n$ is clearly confirmed at 284.6eV of binding energy[5] for Sample A before breakdown. After repetitive breakdowns, this peak decreases and a peak corresponding to TiC (281.2eV[5]) appears. According to the depth profile shown in the Morimoto et al.[3] the highest amount of carbon was observed at the top-most surface layer and then the amount decreased with the depth. Therefore, the results shown in Fig. 8(a) suggest that the breakdown removed the top-most carbon layer and exposed a TiC layer. The lathing done with a natural diamond bit may have created this

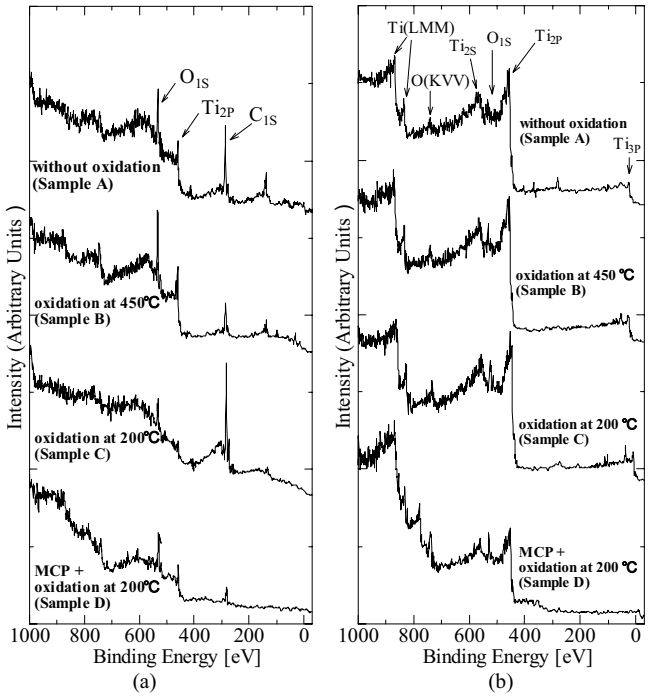


Figure 7. XPS spectra of electrode surfaces before and after repetitive Breakdowns.
(a) Before breakdown
(b) After breakdowns

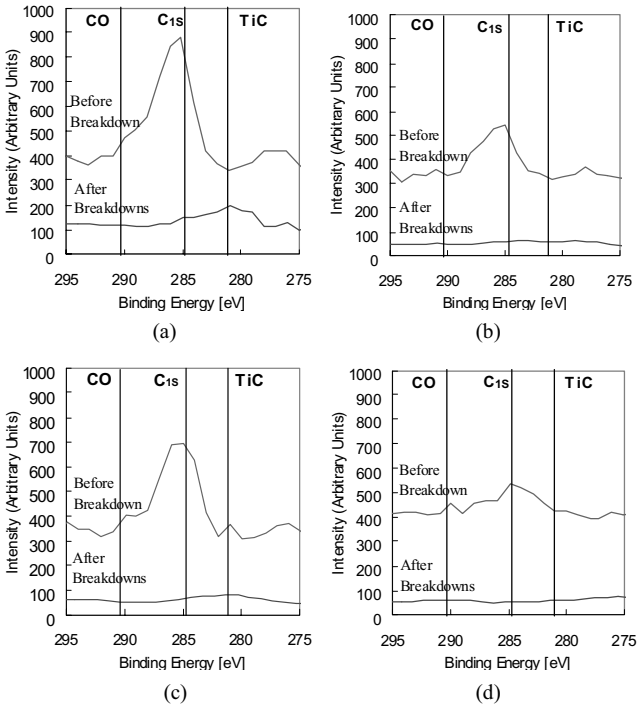


Figure 8. XPS spectra near C1S.
(a) without oxidation (Sample A)
(b) oxidation at 450 °C (Sample B)
(c) oxidation at 200 °C (Sample C)
(d) oxidation at 200 °C after MCP (Sample D)

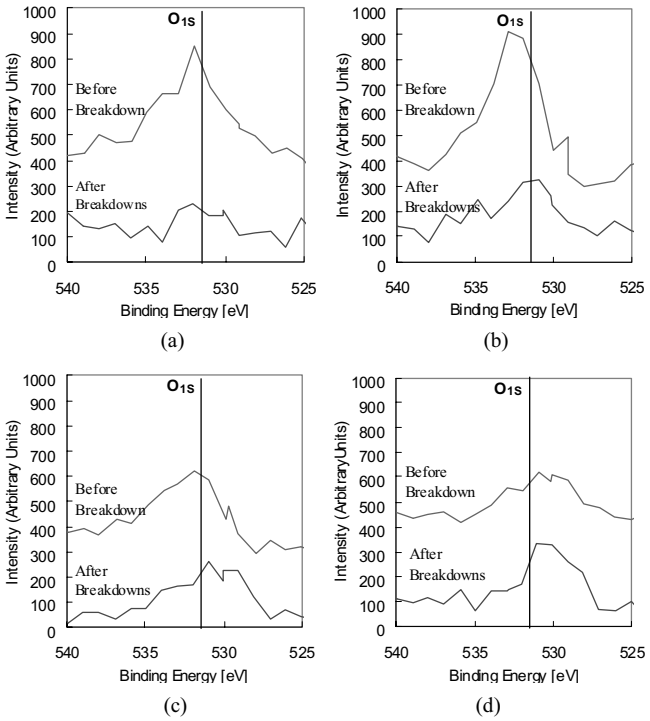


Figure 9. XPS spectra near O1S.
(a) without oxidation (Sample A)
(b) oxidation at 450 °C (Sample B)
(c) oxidation at 200 °C (Sample C)
(d) oxidation at 200 °C after MCP (Sample D)

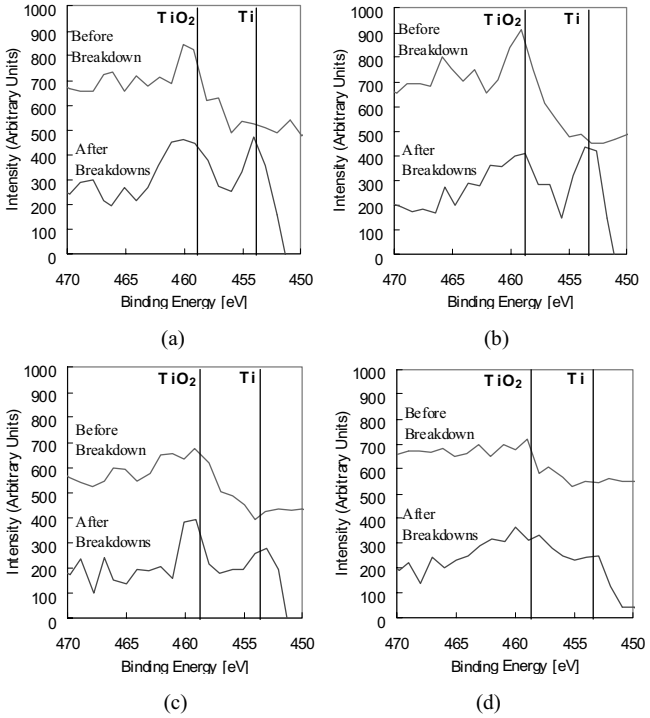


Figure 10. XPS spectra near Ti2P.
(a) without oxidation (Sample A)
(b) oxidation at 450 °C (Sample B)
(c) oxidation at 200 °C (Sample C)
(d) oxidation at 200 °C after MCP (Sample D)

TiC. A TiC peak was also observed in the spectra of Sample C before breakdown. A TiC peak was not found on the surface of Sample B, probably because of a thick oxygen layer. For Sample D, the C1S peak height before breakdowns was much lower than those of the other electrodes without MCP, and the TiC peak was not found after breakdowns. From these results, we found that MCP is effective not only to obtain a smooth surface but also to remove TiC and a large amount of carbon from the surface.

Narrow spectra near O1S and Ti2P of each sample are presented in Fig.9 and Fig.10, respectively. The spectra of Sample B before breakdowns show a higher O1S peak (Fig. 9(b)) and TiO_2 peak (Fig. 10(b)) owing to a thick oxide layer created by oxidation at 450 **°C.** After repetitive breakdowns, the heights of the oxygen peaks of all were lower and the Ti peaks became clear. This means that oxide and organic layers due to contaminations were removed by repetitive breakdowns, and the electrode material of Ti appeared on the surface similar to those for Cu [6].

3.3 RELATIONSHIP BETWEEN VOLTAGE AND CURRENT WAVEFORMS

We investigated voltage and current waveforms, which had been recorded in the process of repetitive breakdown test, to consider the breakdown mechanism based on the changes in electrode surface condition resulting from the process of repetitive breakdown conditioning. Figure. 11 shows the waveforms of applied voltage and current. The pre-breakdown current I_p waveform consists of displacement

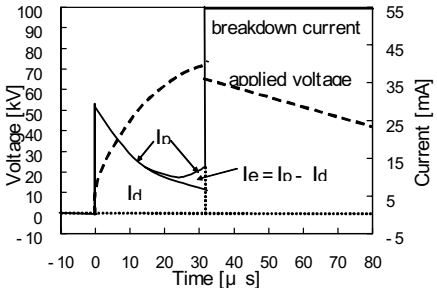


Figure 11. Components of pre-breakdown current (Model waveform: at 40th breakdown for Sample C).

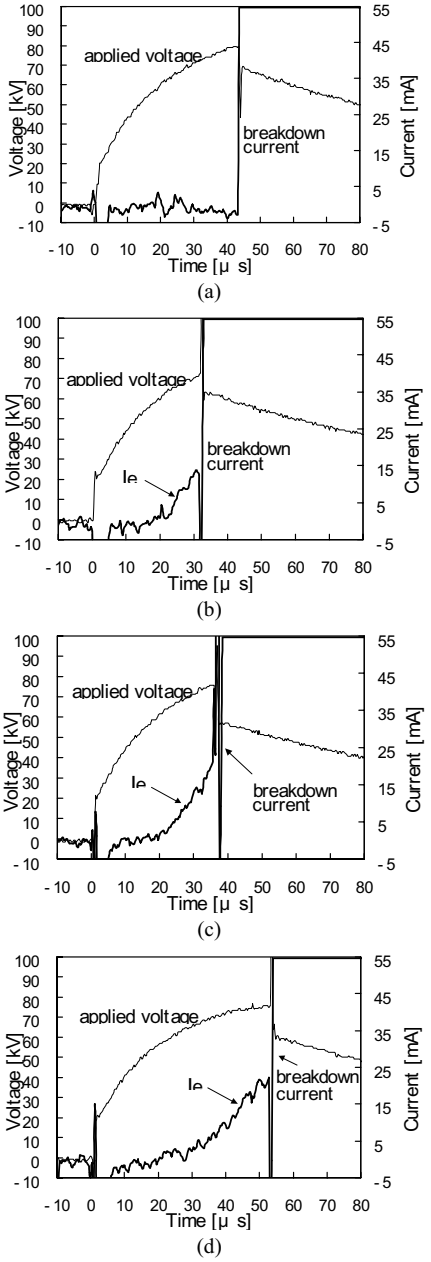


Figure 12. Voltage and current waveforms (Sample C).
(a) At first breakdown
(b) At 40th breakdown
(c) At 120th breakdown
(d) At 230th breakdown

Table 2. Number of breakdowns at which electron emission was observed

	Number of Breakdowns
Without oxidation (Sample A)	80
With oxidation at 450 °C (Sample B)	80
With oxidation at 200 °C (Sample C)	40
With oxidation at 200 °C after MCP (Sample D)	28

current I_d and a current corresponding to an increase of the applied voltage. This latter current gradually increasing over time is due to field electron emission current I_e. The current I_e can be estimated by subtracting I_d from I_p. Figures 12a to 12d show waveforms of applied voltage, calculated I_e and breakdown current in the process of 500 times of breakdown tests. Field emission current I_e cannot be seen in Figure 12a. This breakdown is accompanied by a sudden current increase. This kind of breakdown may be caused by clumps on the electrode surface [7]. These breakdowns are confirmed for the early stage of repetitive breakdown tests. The waveforms including field electron emission current can be seen after 40th to 500th breakdown for Sample C as shown in Figures 12b-12d. Table 2 shows the numbers of breakdowns at which electron emission was observed for all samples. Based on the work of Xu and Latham [8] this type of breakdown may be called electron emission based.

3.4 MICROSCOPIC PICTURE OF ELECTRODE SURFACE

Electrode surfaces were observed by using a SEM after the series of experiments. Figures 13a and 13b show the undamaged area of the electrode surface of Sample C and Sample D, respectively. On electrode surface of Sample C

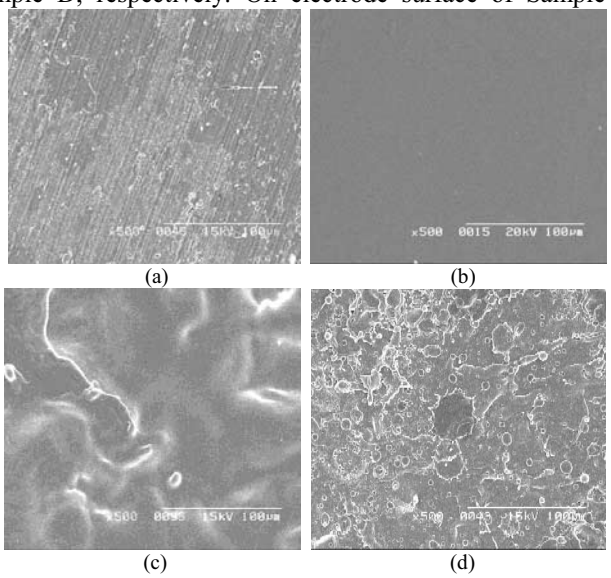


Figure 13. SEM image of electrode surfaces of Ti oxidized at 200 °C.
(a) Lathing traces on electrode surface prepared without MCP (Sample C)
(b) Electrode surface of Ti electrode prepared with MCP (Sample D)
(c) Electrode surface after repetitive breakdowns (Sample C: anode)
(d) Electrode surface after repetitive breakdowns (Sample C: cathode)

lathing traces from machining can be seen, while on surface of Sample D such traces cannot be found. Figures 13c and (d) show the center area of the anode and the cathode after repetitive breakdowns, respectively. This image confirms that the surface feature of the anode is different from that of the cathode. In particular, obvious traces of melt can be seen on the anode surfaces, while there are many particles on the cathode surfaces. The following mechanism explains these features. When the high voltage was applied between electrodes, electrons emitted from the cathode collided with the anode surface. The anode surface was then heated and melted by electrons. The molten or vaporized anode materials were deposited on the cathode surface.

4 CONCLUSION

Titanium electrodes treated with 200 ^{o}C oxidation exhibited highest breakdown field. This result corresponds to outgassing characteristics of oxidized Ti. After conditioning, no significant difference occurred in the breakdown fields among electrodes treated with different procedures. The MCP treatment of Ti is effective for reducing the number of breakdowns required to achieve a conditioned breakdown field.

The TiC layer remains under the layer of organic contaminants on the electrode without MCP, and the TiC may be related to the conditioning characteristics. Repetitive breakdowns removed contaminants of hydrocarbon and oxides for all samples. The MCP treatment reduced the amount of carbon on the electrode surface.

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