EFFECT OF OZONIZED WATER TREATMENT ON ELECTRICAL BREAKDOWN OF OXYGEN-FREE COPPER ELECTRODES OF A VACUUM GAP

S. Kobayashi*, K. Sekikawa*, K. Ohira*, K. Asano and Y. Saito****

*Dept. of Electrical and Electronic Systems, Saitama University,
255 Shimo-Okubo, Urawa 338-8570, JAPAN
**KEK-High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba 305-0801, JAPAN

Abstract - A recently developed ozonized water treatment technique was applied to surface treatment of oxygen-free copper electrodes. Breakdown characteristics of the electrodes were measured in a vacuum by applying impulse voltages. Results showed that the breakdown field at the first voltage application was not improved, but the conditioning effect of the gap by repetitive breakdowns was significant. The value of breakdown field after conditioning was arround 250 MV/m (for a 0.3-mm gap length) . Breakdown fields were lowered to values similar to those of the first voltage application, after the conditioned electrodes were exposed to air for two to three weeks. Reconditioning, however, was achieved rapidly.

1. INTRODUCTION

Electrical breakdown phenomena in ultrahigh vacuum have a great effect on the performance and reliability of high-power devices, such as particle accelerators, vacuum interrupters, and electron tubes. Repetitive breakdowns have been reported to cause the breakdown strength of a vacuum gap to rise (the "conditioning effect"). It has been pointed out that a significant conditioning effect can only be obtained if the electrode surface is cleaned *in situ* [1]. However from a practical point of view, it is preferable that electrode surface treatment be performed in air and that the treated surface condition is kept in air.
It is known that ozonized water treatment is effective in removing organic contaminants on surfaces and in creating oxidized film [2]. Recently, new regalations that order a reduction in the usage of SF_6 gas have come into effect, and the development of an alternative insulating medium is expected. Therefore, it will be necessary to develop practical surface treatment techniques. This paper reports on the effect that ozonized water treatment has on the electrical breakdown of oxygen-free copper electrodes in a vacuum.

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2. OZONIZED WATER TREATMENT

The outline of changes to the surface layer caused by ozonized water treatment is shown in Fig. 1. Ozonized water reduces and removes organic contaminants from surfaces and has the strong effect of creating an oxidized film. This oxidized film is resistant to gas adsorption. It is, therefore, able to keep the surface clean even if the surface is exposed to air [3]. In addition, ozonized water never damages the metallic surface, unlike acids, and the liquid waste disposal process is simple because ozonized water doesn't include toxic substances.

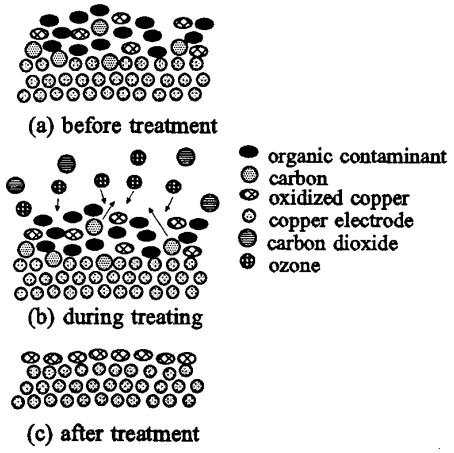

Fig. 1. Changes in surface condition caused by ozonized water treatment.

3. EXPERIMENTAL

3-1 Ozonized water

Ozone was added to ultra-purewater (over 17.5 M Ωcm, flow rate 1 or 2 l/min) by a water electrolysis method that used an ion exchange film. The concentration of ozone was 2.8 ppm. The electrodes were treated with the ozonized water for 15, 30 and 60 minutes.

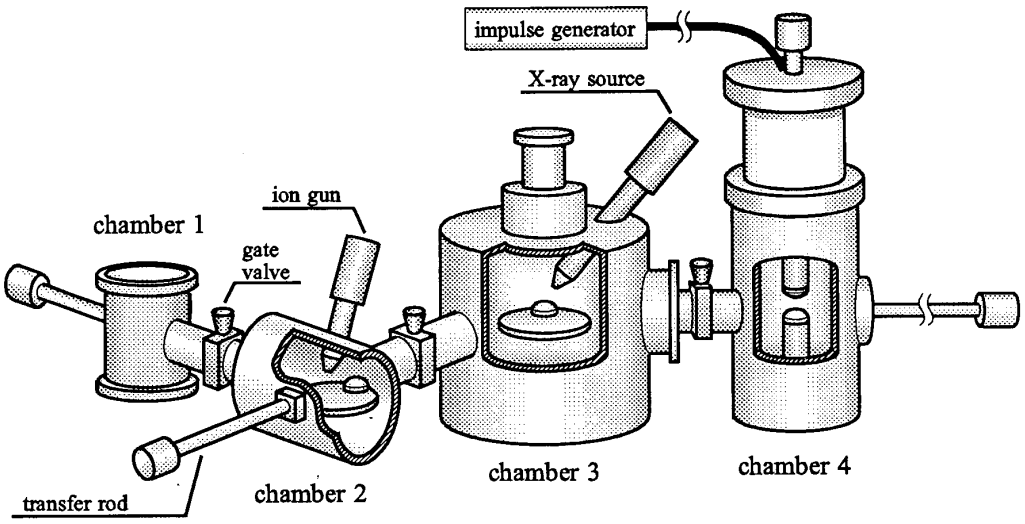

Fig. 2. *In situ* experimental apparatus.

3-2 In situ breakdown and surface analysis system

A schematic drawing of the experimental apparatus is shown in Fig. 2. This system has four vacuum chambers which eliminate the affects that air has on surface condition. Electrodes areintroduced into chamber 1. Only this chamber was exposed to air. Electrode surfaces are then analyzed by X-ray photoelectron spectroscopy (XPS) in chamber 3. Five-hundred repetitive breakdowns are then performed in succession on electrode in chamber 4. The applied voltage is an impulse voltage (rise time 64 μs / time to half value 700 μs). The residual pressure in each chamber was maintained in the range of 10^{-7}-10^{-8} Pa by using a sputter ion pump and a Ti-getter pump.

3-3 Procedure

Oxygen-free copper (class 1, purity $\geqq$ 99.996%) was used as the electrode material (diameter: 22 mm, curvature of electrode surface: 18 mm). After ultrasonic cleaning in acetone, the electrodes were mounted on a holder made of teflon. The electrodes were then treated in ozonized water for the time described above. The ozonized water was changed every five minutes during the treatment period. After treatment, the electrodes were rinsed with ultra-purewater, and then their surfaces were dried by dry nitrogen gas. Finally, the electrodes were kept in a desiccator until they were placed in vacuum chamber 1 of the experimental system (for a few days or several weeks).
The electrodes were put inside the vacuum chamber and their surfaces were analyzed by XPS, then, 500 breakdowns were performed, and their surfaces were analyzed again. After the experiment, the electrodes were taken out of the chamber and kept in the desiccator. Several weeks later, the experiment was performed again in order to determine how exposure to air affected them.

4. RESULTS

4-1 Breakdown characteristics

The difference in the breakdown characteristics with ozonized water treatment conditions is shown in Fig. 3. Ozonized water treatment for 15 minutes was performed on the A_1 electrodes; the A2 electrodes were treated for 30 minutes; the A3 electrodes were treated for 60 minutes; and the A_4 electrodes were kept in the dessicator for three weeks after the 30-minute treatment.

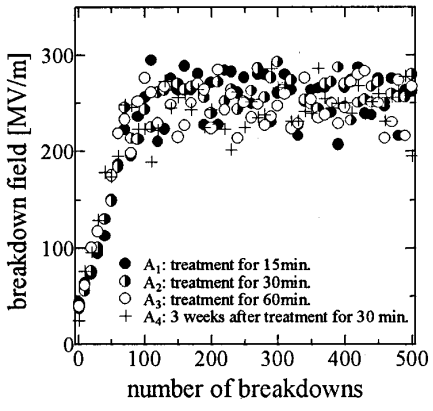

Fig. 3. Breakdown characteristics of electrodes treated with ozone.

All the electrodes showed an obvious improvement in breakdown strength. The effect of the repetitive breakdowns was obvious (excellent conditioning effect) , and the conditioned breakdown fields were high. The breakdown fields of the A_4 electrodes were as high as those of the other electrodes (A_1-A_3). This result exhibits that the effect of ozonized water treatment can be maintained in the air.

The average breakdown fields after saturation of the improvement in the breakdown field (about 130 breakdowns) are as follows (at 0.3-mm gap length): for electrode A_1; 257 MV/m, for A_2; 261 MV/m, for A_3; 247 MV/m and for A_4; 247 MV/m.

4-2 Surface conditions

Figure 4 shows XPS wide-scan spectra of the cathode of A_2 electrode before and after 500 breakdowns. The spectra before breakdowns had clear peaks due to oxygen (O_{1S}) and carbon (C_{1s}) , and the spectra of Cu_{2P}, Cu_{Auger} and Cu_{3P} are scarcely observed. Therefore, the electrode surface was covered with oxidized film and organic contaminants. The intensites of oxygen spectra were higher than those obtained in our past results. No carbon spectra were expected to be observed, because the electrode was treated with ozonized water. Carbon spectra, however, are clearly observed. After 500 breakdowns, the oxygen and carbon spectra due to contaminants on the electrode surface were removed completely, and the copper spectra clearly appeared. Therefore, the repetitive breakdown process was able to completely clean the electrode surfaces.

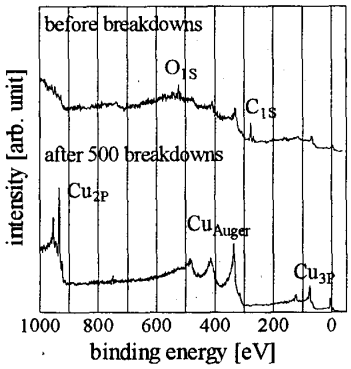

Fig. 4. XPS wide-scan spectra of the cathode of A_2 before and after 500 breakdowns.

4-3 Breakdown characteristics after exposure to air

The breakdown fields of conditioned electrodes after exposure to air for two to three weeks are shown in Fig. 5. The electrodes were kept in the desiccator (20 ℃, humidity: 25%) after being subjected to 500 breakdowns (Fig. 3). Ozonized water treatment was done on the A_1', A_2' and A_3' electrodes for 15, 30 and 60 minutes, respectively. These results demonstrate that exposing the surface to air after 500 breakdowns (conditioned) lowers the breakdown strength and the reconditioning of breakdown fields can be easily achieved. The average electric field after saturation of the breakdown field (about 90 breakdowns) was: 239 MV/m for electrode A_1', 270 MV/m for A_2', and 250 MV/m for A_3', and the first breakdown fields were lower than those shown in Fig. 3.

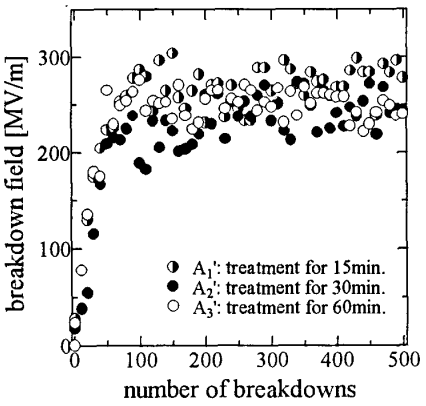

Fig. 5. Breakdown characteristics of conditioned electrodes after exposure to air.

5. DISCUSSION

5-1 Influence of ozonized water treatment

As can be seen in Fig. 3, varying the treatment time had little effect on the breakdown fields. After the saturation of conditioning all he breakdown fields were around 250 MV/m. In previous experiments [1], such a high breakdown field could only be achieved after *in situ* surface cleaning. The ozonized water treatment, however, can give higher breakdown fields without any *in situ* treatments.

The first breakdown field of the A_4 electrode was lower than those of the other electrodes (A_1-A_3). This result may be due to surface contamination caused by longer exposure to air. The breakdown fields of the A_4 electrodes after saturation of the conditioning, however, was as high as those of A_1-A_3.

5-2 Electrode surface condition

A small peak can be seen between $Cu_{2P1/2}$ and $Cu_{2P3/2}$ lines in the spectra shown in Fig. 6. This

peak usually originates from CuO. The peak ratio of x-ray satellite to $Cu_{2P3/2}$ after 500 breakdowns was 0.14 (Fig. 6). For the spectra before breakdown, the ratio was 0.41. The value of the ratio before breakdown was somewhat fairly larger than that after breakdown. In addition, from Fig. 7, the Auger peak shift due to Cu_2O is not observed. Therefore, in this experiments ozonized water treatment creates CuO films.

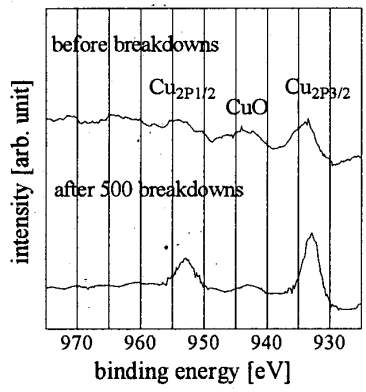

Fig. 6. XPS narrow-scan spectra of $Cu_{2P1/2}$, $Cu_{2P3/2}$ and CuO before and after 500 breakdowns.

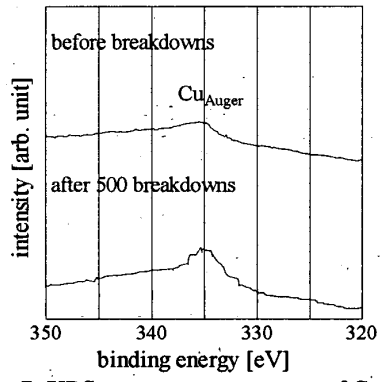

Fig. 7. XPS narrow-scan spectra of Cu_{Auger} before and after 500 breakdowns.

5-3 Changes in breakdown characteristics due to air exposure after the conditioning

Figure 8 shows XPS wide-scan spectra of the cathode of the A_2' electrode that was exposed to air after conditioning. Before the breakdowns were performed, oxygen and carbon spectra were observed and copper spectra were not observed. Therefore, the electrode surface was recontaminated by exposure to air after conditioning. The first breakdown fields of the electrodes A_1'-A_3' were lowered, as shown in Fig. 5. The values are lower than those shown in Fig. 3 for A_1-A_3. After 500 breakdowns, the surfaces were completely clean, and the breakdown fields recovered rapidly.

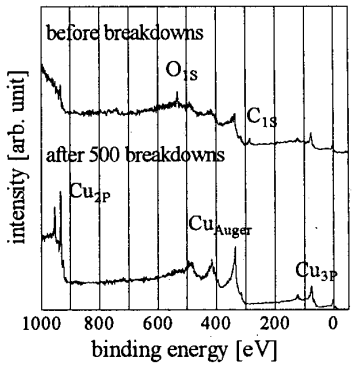

Fig. 8. XPS wide-scan spectra of the cathode of the A_2' electrodes. Here, " before breakdowns" means that the conditioned electrode was kept in the desiccator before the breakdown experments.

6.CONCLUSION

- Electrodes treated with ozonized water were significantly affected by repetitive breakdowns.
- The results confirmed that CuO was created on the electrode surfaces by the ozonized water treatment.
- Exposure of the conditioned electrodes to air reduced their breakdown fields; however, the breakdown characteristics were easily reconditioned afterwards .

ACKNOWLEDGMENTS

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REFERENCES

[1] Shinichi Kobayashi, "Recent Experiments on Vacuum Breakdown of Oxygen-fre e Copper Electrodes", IEEE Transactions on Dielectric and Electrical Insulation, Vol. 4, No. 6, 1997, pp. 841-847.

[2] Yasuchika Nagai and Kiyomitsu Asano, "Surface Analysis of Oxygen Free Copper Treated with Ozonized Water", J. Vac. Soc. of Japan, Vol. 38, No. 3, 1995, pp. 278-281. (in Japanese)

[3] Kiyomitsu Asano, Shinji Mitsunobu, Takaaki Furuta, Tsuyosi Tajima and Eiji Ezura, "Elimination Effects of Surface Carbon Contaminations on Field Emission in Superconducting RF Cavities", KEK Preprint 97-126, 1997. (in Japanese)