J Electroceram (2008) 21:214–217
DOI 10.1007/s10832-007-9100-z

Effects of manganese and chromium doping on the surface properties of alumina insulators

Y. J. Lei · D. Q. Xiao

Abstract Bulk doping was taken into consideration to improve the surface voltage hold-off performance of alumina insulators in vacuum. The as-blended 95% alumina powder was selected as initial powder to be doped with proper Cr_2O_3 and $MnCO_3$. The results of properties measurements and experiments showed that samples doped with proper Cr_2O_3 and $MnCO_3$ possessed better surface properties compared with original 95% alumina insulators. The doped samples displayed higher surface breakdown strength and performed better metallization properties after being metallized through a newly designed method. Both the surface resistivity and the secondary electron emission coefficient of alumina were decreased significantly after manganese and chromium doping, which resulted in the improvement of surface insulating performance. In addition, some points concerning the influences of manganese and chromium doping on the structures and properties of alumina insulators were also briefly discussed upon analyses on composition and structure of ceramic samples.

Keywords Alumina insulator · Doping · SEE coefficient · Surface hold-off voltage · Metallization

1 Introduction

The voltage hold-off capability of alumina in vacuum is usually far below that of a similar-sized vacuum gap and also lower than the dielectric breakdown strength of the insulator body because of the occurrence of surface flashover, which severely restricts further practical application of alumina ceramics as insulators in vacuum devices. With the development of vacuum devices to miniaturization, finding ways to improve the surface voltage, withstanding performance of alumina ceramics, has become of great importance.

When trying to improve the surface hold-off voltage of alumina insulators, their metallization performances must be taken into consideration because the insulating strength and metallization property of insulator are always the two vital parameters for vacuum devices. Surface treatment is by far the most prevalent and most reported methods to increase the surface hold-off voltage of alumina insulators. Surface polishing, surface quasimetallization, surface depositing, and surface ion implantation were found to be effective in improving the flashover performance of the ceramic insulator [1–6]. Surface treatment holds great advantages to increase the surface flashover voltage of alumina without changing any of its bulk properties, but it is very difficult to maintain the properties of the treated surface because the ceramic insulator will usually undergo metallization under high temperature. In the present work, bulk doping is taken into consideration to improve the surface insulating performance of alumina significantly and hardly modify its basic properties.

2 Sample preparation

A conventional manufacturing process beginning with blending of a mixture of starting materials was applied to prepare ceramic samples. The as-blended 95% alumina powder was selected as initial powder to be doped with proper Cr_2O_3 and $MnCO_3$. Ceramic samples with designed structure and dimension were obtained after a lot of manufacturing steps, including batching, presintering,

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grinding, dry pressing, dewaxing, final sintering, and machining. Note that the sintering temperature of alumina ceramics was decreased with the addition of Cr_2O_3 and $MnCO_3$. Accordingly, a series of 95% alumina samples were also manufactured for comparing with the doped samples in every experiment. All samples were ultrasonically cleaned in acetone and deionized water for more than half an hour before measurements.

3 Properties measurements and experiments

The surface resistivity, the secondary electron emission (SEE) character, the surface hold-off voltage, and the surface metallization performance of alumina insulator are the main properties we are interested in. The surface resistivity was measured using a high resistance test instrument.

A special system for insulating performance test in vacuum was used to measure the flashover voltage of ceramic samples. A test sample was placed between two parallel electrodes in a vacuum chamber and pulsed voltages (~5.5 μs) were applied during the test process. To ensure the comparability of the measured results, an identical test procedure was adopted in every measurement because the experimental procedure had obvious influences on the test results as we have reported before [7].

An equipment of electron-beam-induced SEE was applied for SEE coefficient test of ceramic specimens in our work. The beam current was about 10^{-7} A with a diameter of 8 mm and the pulse duration was 1 ms. The energy of incident electrons could be adjusted from 100 to 5,000 eV. The vacuum degree was maintained at around 6×10^{-8} Torr during the whole testing process. To gain a believable result, all experimental conditions should be maintained identical because SEE yield measurement is very sensitive to these conditions [8].

To discuss the effects of manganese and chromium doping on the metallization performance of 95% alumina, a slurry for doped specimens metallization was designed according to the general mechanism of ceramic metallization and penetrating of glass phase between ceramic and its surface coating. A common technology was adopted to fulfill the metallization of test samples. A helium leak detector was used for seal checking and an LJ-1000 model tension test machine for measurement of metallization strength.

4 Results and discussion

4.1 Results of properties measurements

The SEE curves of two alumina specimens were plotted in Fig. 1, where it was obvious that the Cr- and Mn-doped sample possessed a lower SEE coefficient (3.12) than the 95% alumina sample (6.04). The corresponding energy of incident electrons yielding the maximum secondary electrons was 800 eV for 95% alumina sample and 500 eV for the Cr- and Mn-doped specimen respectively.

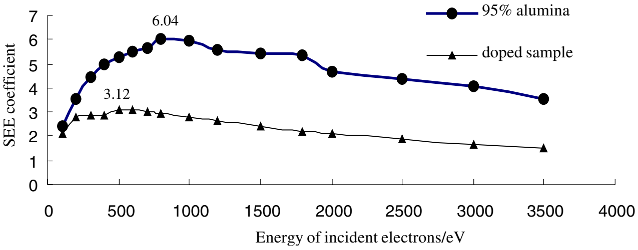

Fig. 1 SEE curves of alumina samples

The measured results of basic surface properties of alumina samples were listed in Table 1, in which it was shown that the surface hold-off voltage of Cr- and Mn-doped alumina was obviously higher than that of 95% alumina, whereas both the surface resistivity and SEE coefficient of the former was far below that of the latter.

The doped sample showed bad metallization effects after being metallized with the metallization slurry and corresponding technology for 95% alumina ceramic that it failed to pass seal checking and its metallization strength was far below that of 95% alumina. However, both samples passed leak checking and possessed considerably high metallization strength when they were metallized under the newly designed metallization method and it was found that the Cr- and Mn-doped sample had higher metallization strength than 95% alumina in this case.

4.2 Discussion

To study the effects of Cr_2O_3 and MnO additives on the structure and composition of alumina surface, both alumina samples were analyzed through SEM, x-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD). We have analyzed SEM photographs of both alumina samples elsewhere that the surface of Cr_2O_3- and MnO-doped alumina had smaller and more homogeneously distributed crystal grains than 95% alumina [9]. Here the XPS and XRD patterns of ceramic specimens were provided, as

Table 1 Results of surface properties measurement.

Sample	Surface resistivity/ Ω	SEE coefficient	Surface hold-off voltage $kV^{-1}\cdot mm^{-1}$
95% alumina	1.57×10^{13}	6.04	2.11
Alumina doped with Cr and Mn	5.99×10^{10}	3.12	2.83

shown in Figs. 2, 3, and 4. There was no difference in surface composition of two alumina specimens from their XPS spectra except that there existed the characteristic peak of manganese in the spectrum of the surface of doped sample. It is obvious in Fig. 4 that there mainly existed corundum—Al_2O_3 in 95% alumina sample whereas both corundum—Al_2O_3 and galaxite—$MnAl_2O_4$ were detected in Cr_2O_3- and MnO-doped sample. There was some difference in diffraction angles and in grating space between two corundum—Al_2O_3 spectra. The SEM, XPS, and XRD results of the doped sample indicated that the addition of Cr_2O_3 and MnO facilitated lessening of grain size and led to forming of a new crystal phase and induced distortion of corundum crystal lattice. The form of $MnAl_2O_4$ during sintering restrained the excessive growth of grain size and enhanced the densification of ceramic body. It is supposed that chromium atom probably attaches itself to the development of grains and mainly exists in the crystal lattice of corundum, resulting in the distortion of crystal lattice because Cr_2O_3 has the same type of crystalline as Al_2O_3 and the ion radius of Cr^{3+} is very close to that of Al^{3+}. Therefore, the doping of Cr_2O_3 facilitates the sintering process of alumina ceramic. In addition, the decrease of sintering temperature of alumina after doping also contributed to the development of small-sized grains.

The results of properties measurements and experiments indicated that the Cr- and Mn-doped alumina possessed better surface performances, compared with the original 95% alumina. We consider that the doping of Cr_2O_3 into alumina helps to reduce the SEE coefficient of the insulator effectively because Cr_2O_3 has an extremely low SEE coefficient. During the sintering of the doped sample, a glass phase will be formed by some MnO, Al_2O_3, and SiO_2. Similar glass may also be formed in the sintering process of metallization coating. So the combination of metallizing layer to ceramic surface is enhanced through mutual diffusion of glass phase with identical composition between them so that fine metallization effects are promised. As to the decrease of surface resistivity, changes of surface structure and composition should be the best answers. However, this still needs to be studied and discussed further [10–12].

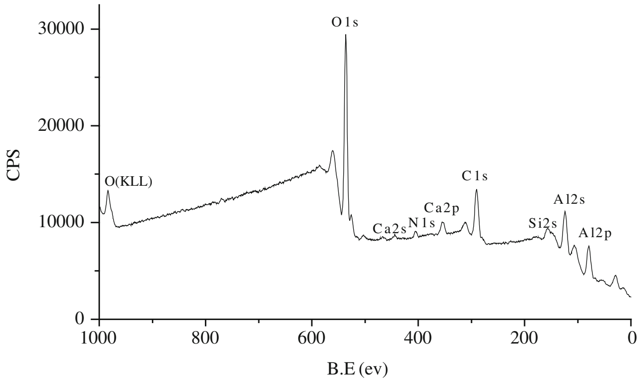

Fig. 2 XPS pattern of 95% alumina

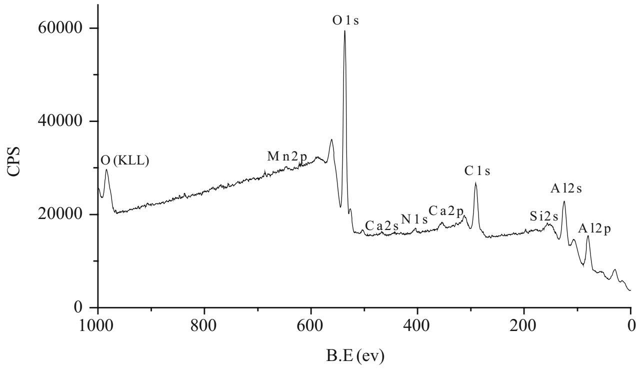

Fig. 3 XPS pattern of Cr- and MN-doped alumina

5 Conclusions

It was found from present work that bulk doping had obvious influence on the surface structures and properties of alumina insulators. The surface properties of 95% alumina were significantly improved after Cr and Mn doping. The doped sample had homogeneously distributed smaller crystal grains. The surface hold-off voltage was greatly improved by about 30%. With the addition of Cr_2O_3 and MnO, the surface resistivity and the SEE coefficient of the original alumina insulator were decreased significantly, which resulted in the improvement of surface hold-off voltage. In addition, Cr and Mn doping did not ruin the metallization performance of alumina insulator, although it brought about obvious changes to its surface structure and surface electrical properties. Moreover, better metallization

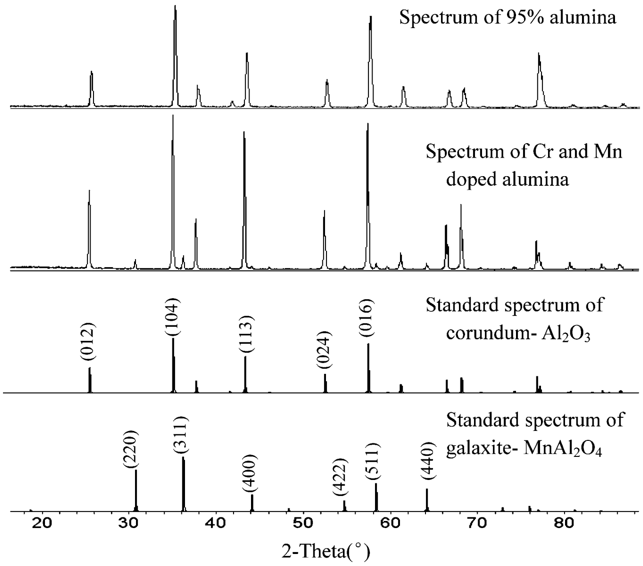

Fig. 4 XRD patterns of alumina samples

effects were obtained after suitable adjustments to the coating slurry and technology for metallization.

Acknowledgement This work was supported in part by the Institute of Electronic Engineering in China Academy of Engineering and Physics under Project S20041310.

References

1. H.C. Miller, IEEE Trans. Electr. Insul. **28**, 512 (1993)
2. H.C. Miller, IEEE Trans. Electr. Insul. **15**, 419 (1980)
3. H. Brettschneider, IEEE Trans. Electr. Insul. **23**, 33 (1988)
4. L.L. Hatfield, E.R. Boerwinkle, G.R. Lerker et al., IEEE Trans. Electr. Insul. **24**, 985 (1989)
5. Hanna Moscicka-Grzesiak, Zbigniew Banaszak, in *3rd International Conference: Properties and Applications of Dielectric Materials.* (Japan, 1991), p. 627
6. F. Liu, I. Brown, in *Proceedings of the 1997 Conference: Particle Accelerator.* (Vancouver, Canada, 1998), p. 3752
7. Y.J. Lei, D.Q. Xiao, Insulating Materials (in Chinese). **37**, 29 (2004)
8. Juan M. Elizondo, Keith Meredith, Neil Lapetina, IEEE Trans. Plasma Sci. **30**, 1955 (2002)
9. Y.J. Lei, D.Q. Xiao, Journal of the Chinese Ceramic Society (in Chinese). **33**, 91 (2005)
10. J.Z. Lu, L.J. Ding, C.R. Li et al., in *2002 IEEE International Symposium on Electrical Insulation.* (Boston, MA, USA, 2002), p. 290
11. L.J. Ding, C.R. Li, J.C. Wang et al., IEEE Trans. Dielectr. Electr. Insul. **9**, 182 (2002)
12. T. Shioiri, T. Shindo, T. Kamikawaji et al., IEEE Trans. Dielectr. Electr. Insul. **9**, 416 (2002)