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Electrical insulating property of ceramic coating materials in radiation and high-temperature environment

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Abstract

The electrical insulating performance of Er_2O_3, Y_2O_3 and $CaZrO_3$ disc specimens made by a sintering method has been examined under gamma-ray irradiation at high temperature. The conductivities without irradiation, which were on the order of 10^{-14}–10^{-13} S/m at room temperature, increased during heating. In contrast, the conductivities under the irradiation of 4.5–8.8 Gy/s were on the order of 10^{-12}–10^{-10} S/m and significant temperature dependence of the conductivities was not observed up to ~250 °C for Er_2O_3, ~400 °C for Y_2O_3 and ~250 °C for $CaZrO_3$, respectively. At higher temperatures, the conductivities without and under irradiation were of almost the same magnitude and increased with temperature. Similar behavior in insulating performance was observed also for an Er_2O_3 coating layer of 1.6 μm in thickness. The present results indicate that the degradation of insulating performance due to the radiation induced conductivity (RIC) weakly depends on temperature and would be negligible for maintaining of the required performance in the radiation and high-temperature environment of a fusion blanket.

1. Introduction

In the development of ceramic coating materials for the liquid lithium cooled blanket system [1–4], the irradiation effect is one of the important factors affecting their electrical insulating performance. Previously, neutron and gamma-ray irradiations using a DT neutron source, a fission reactor and a ^{60}Co gamma-ray source have been performed on the candidate materials such as Er_2O_3, Y_2O_3 and $CaZrO_3$ at low temperature (<50 °C) [5,6]. The results indicated that degradation of the insulating property due to radiation induced conductivity (RIC) would not prevent the candidate materials from maintaining the required performance ($<10^{-2}$ S/m) [7] at high dose rate (several kGy/s) in the fusion blanket [8].

Since ceramic materials have excellent initial insulating performance, the effect of the RIC dominates their performance in a radiation environment at low temperature. However, the inherent insulating performance degrades at high temperature due

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to motion of ions and electrons through the matrix and grain boundaries. Therefore, examination of the irradiation effect has been required at high temperature conditions where the conductivity without irradiations exceed the magnitude of the RIC observed at low temperature. In the present study, the electrical insulating performances of sintered disc specimens of Er_2O_3, Y_2O_3 and $CaZrO_3$ have been examined under gamma-ray irradiation at high temperature of up to 550–600 °C.

In the development of insulating coatings, recent studies indicate that a thin Er_2O_3 layer on a structural material such as a vanadium alloy is stable in liquid Li at 1073 K and has a potential of self-healing and thus is a most promising candidate [9]. Since the electrical properties of a thin coating layer will be affected by the existence of cracks and pits in addition to the properties of the matrix and grain boundaries, gamma-ray irradiation at high temperature has also been performed on a thin Er_2O_3 coating layer made by RF sputtering.

2. Experiment

Disk specimens of Er_2O_3 (supplied from TYK Corp.), Y_2O_3 (T.E.P. Corp.) and $CaZrO_3$ (TYK Corp.) were made by a sintering method with powders of 99.9% purity. The dimensions were 10 mm in diameter and 1 mm in thickness. As shown in Fig. 1(a), a center electrode and a guard electrode were made on the surface by Pt sputtering for current measurement and prevention of the leakage current through the side surface, respectively. On the other surface, an electrode was made for voltage supply. The thickness of the electrodes was ~200 nm. The conductivities were examined by measuring the induced current through the bulk of the specimens. The conductivities before irradiation were 1.3×10^{-13} S/m (Er_2O_3), 4.0×10^{-14} S/m (Y_2O_3) and 4.5×10^{-14} S/m ($CaZrO_3$) at room temperature.

A specimen coated with thin Er_2O_3 layer was prepared at the University of Tokyo by RF sputtering [10]. A coating layer of 1.6 μm in thickness was made on a polished stainless steel substrate. Small electrodes of 2–4 mm^2 were made on the layer by painting with silver paste or sputtering of Pt as shown in Fig. 1(b). The electrode was connected to an electrometer and bias voltage was applied to the substrate for the conductivity measurement. Since the electrical current flowing through the surface was considered significantly lower than that in the bulk specimens, no guard electrode was made on

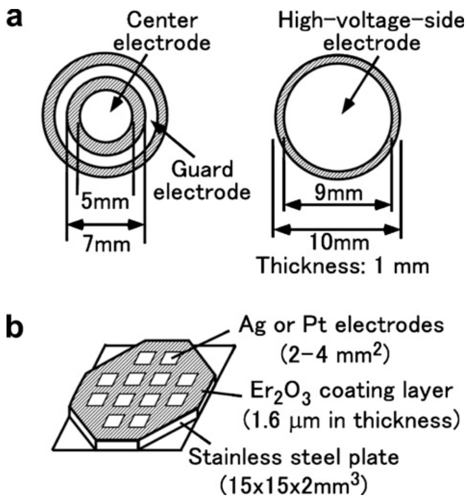

Fig. 1. Dimensions of specimens and electrodes. (a) Bulk specimen; (b) coated specimen.

the coated specimen. The typical conductivities for the coating layer were on the order of 10^{-14}–10^{-13} S/m before irradiation at room temperature and similar to those for the disc specimens with the guard electrodes. The temperature dependence of conductivity for an electrode with a conductivity of 7.8×10^{-14} S/m was examined and designated 'Coating #1'. For some of the electrodes on the coating layer, high initial conductivities were obtained before the irradiation at room temperature. This was due to metal particles of the electrode entering into small pits, which were found under observation with an optical microscope and had opening of 1–2 μm in diameter at the coating surface. To examine the irradiation effect on the large leakage currents through the pits, irradiation on the electrode with a conductivity of 4.1×10^{-7} S/m was also performed and designated 'Coating #2'.

The gamma-ray irradiation was performed in the ^{60}Co irradiation facility of ISIR (Institute of Scientific and Industrial Research) of Osaka University. Fig. 2 shows the schematic arrangement of the irradiation experiment. The insulating performances of the specimens were examined in the vacuum chamber evacuated to $< \sim 5 \times 10^{-2}$ Pa. The specimen and a thermocouple were mounted at the surface of a ceramic plate on a heater with ceramic adhesive. The ^{60}Co gamma-ray source was located in a holder in front of the chamber. The dose rates at the specimen position were estimated to be 4.5–8.8 Gy/s by transport calculation using the MCNP-4C code [11]. The conductivities of the specimens under irradiation were evaluated from

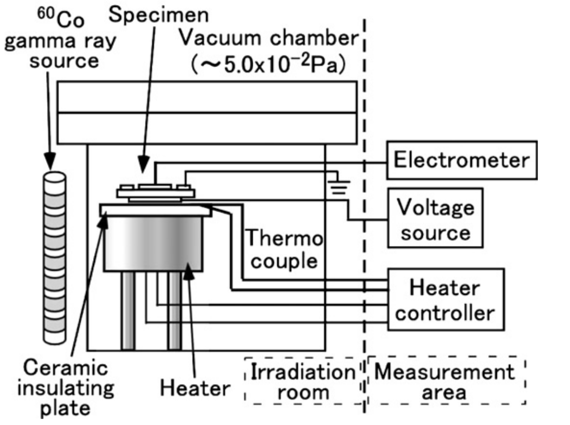

Fig. 2. Schematic arrangement of conductivity measurement under gamma-ray irradiation at high temperature.

the relation of the applied voltage and the induced current during heating. The typical heating speed was ~2.5 °C/min. In all the measurements except for the Y_2O_3 disc specimen, the gamma-ray source was removed to a storage area at several points during the heating and the conductivities without irradiation were measured. For the Y_2O_3 disc specimen, the temperature dependence of the conductivity was measured separately before and during irradiation. The magnitude of the RIC was examined by comparison of the conductivities without and under the irradiation. The bias voltages applied during the examination were 250 V or 300 V for the bulk specimens and 0.5 V for the Er_2O_3 coated specimen.

3. Results

Fig. 3 shows the temperature dependence of the electrical conductivities of the disc specimens examined without and under the gamma-ray irradiation. The evaluated radiation induced conductivities (RIC) were 5.1×10^{-12} S/m for Er_2O_3 (4.5 Gy/s), 3.0×10^{-10} S/m for Y_2O_3 (5.1 Gy/s) and 2.2×10^{-11} S/m for $CaZrO_3$ (8.8 Gy/s) at room temperature. The induced currents at room temperature were almost proportional to the bias voltages in both the measurements without and under the irradiation [6]. During heating, the conductivities without irradiation gradually increased with temperature. In contrast, a significant increase was not observed in the conductivities under the irradiation in the low temperature region, although the values fluctuated with heating. The conductivities without irradiation

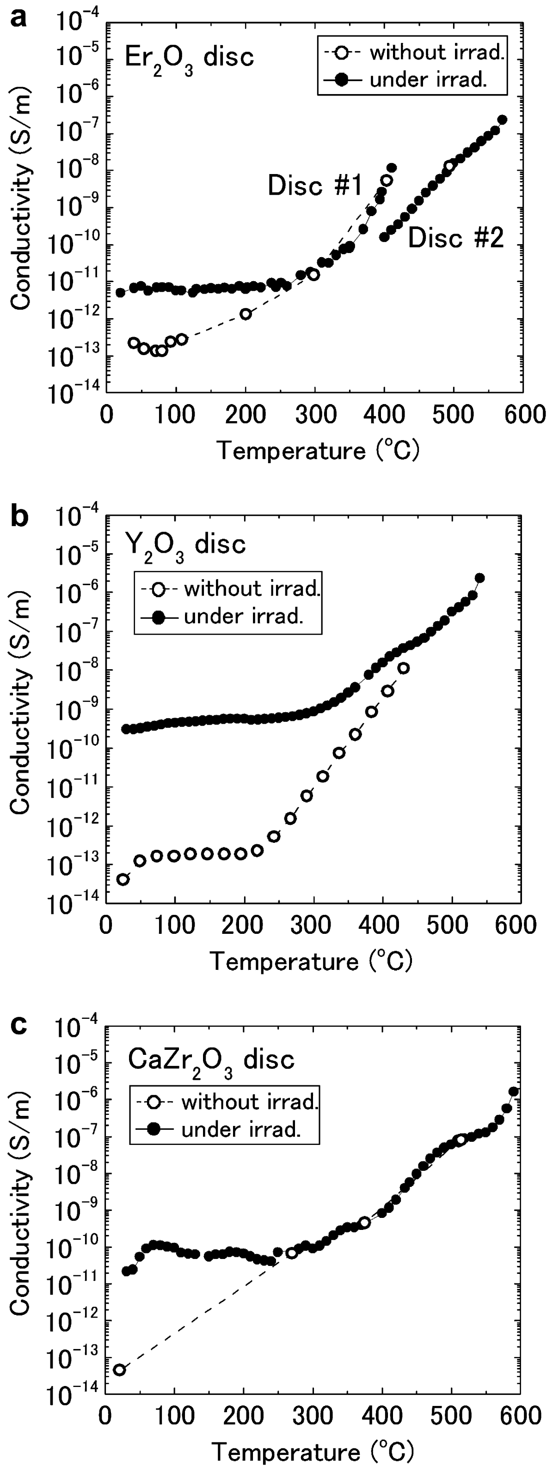

Fig. 3. Temperature dependence of conductivities without and under gamma-ray irradiations for bulk specimens.

exceeded the levels of the RICs, i.e. the increases in the conductivities due to irradiation, at the temperatures of 250 °C (Er_2O_3), 400 °C (Y_2O_3) and 250 °C ($CaZrO_3$). In the high temperature region, the values of the conductivities were at almost the same level in the measurements without and under irradiation for the three materials. During the measurement for the Er_2O_3 disc specimen, the load for the voltage source exceeded the capability of the system at ~400 °C and could not continue. It is possible that the leakage current through the ceramic plate below the specimen increased largely due to the contamination of the surface. The data at higher temperature were obtained for other disc specimen.

Results of similar examination on the Er_2O_3 coating layer were shown in Fig. 4. The coating layer made by RF sputtering had a high insulating performance of almost the same level as the Er_2O_3 sintered bulk specimens. In the examination for Coating #1, the evaluated RIC was 1.2×10^{-12} S/m (4.5 Gy/s) at room temperature. The effect of the RIC dominated the insulating performance in the low temperature region below ~100 °C. In the higher temperature region of 100–650 °C, the conductivities without and under the irradiation were almost of the same magnitude and the temperature dependence was similar to those for the bulk specimens. In the measurement of Coating #2 with high initial conductivity, the insulating performance was dominated by leakage current through the pits on the coating layer and no significant effect of the RIC was observed. In observation of the coating surface with an optical microscope, no crack or peeling was found after heating, although the thermal expansion coefficient of stainless steel is almost twice that of a vanadium alloy. In all of the measurements for the bulk specimens and the coated specimen, the electrical currents were almost proportional to the bias voltages and showed ohmic behavior.

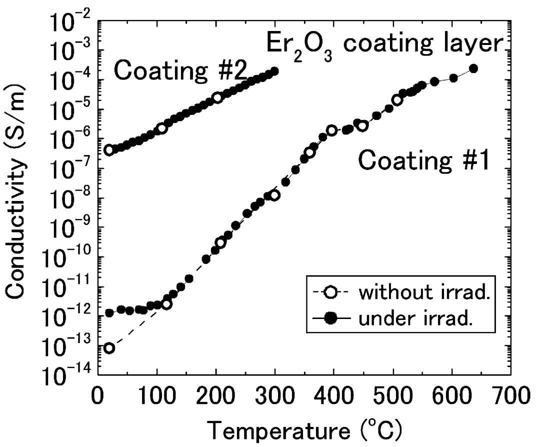

Fig. 4. Temperature dependence of conductivities without and under gamma-ray irradiations for Er_2O_3 coated specimens.

4. Discussion

The present results indicate that the degradation of insulating performance due to RIC in the candidate coating materials weakly depends on temperature and the inherent performance of the materials without irradiations will dominate the performance in the intense radiation and high-temperature environment. In the fusion blanket environment, the dose rate will be about 3 orders of magnitude higher than the present experiment [8]. Extrapolation from the present and previous results on the dose rate dependence [5,6] gives the RIC levels between 10^{-9} and 10^{-7} S/m for the environment. In the case of Y_2O_3, which showed the largest RIC, RIC will dominate the insulating performance up to ~500 °C in the fusion blanket. The result for the coating layer also indicated that the leakage current through the pits and cracks would not be affected by RIC.

The dominant factors determining the magnitude of RIC is the motion of electrons in the matrix excited by irradiation, i.e. drift of electrons according to the electric field, and stopped by recombination with holes or trapping [12]. The present results indicate that the motion of the excited electrons is not enhanced dramatically with temperature in the candidate materials. For detailed examination of electrical properties relating to the band structure of the materials, more accurate temperature control and irradiations using high-energy charged-particle beams are considered to be effective as reported for high quality Al_2O_3 and $MgAl_2O_4$ spinel crystals [12,13]. In the present results, it is possible that the fluctuation of the conductivities under the irradiation at low temperature was due to release of accumulated electrons or the effect of humidity in the specimens, since the data were obtained for the first heating treatment for the specimens.

5. Conclusion

The electrical insulating performances of Er_2O_3, Y_2O_3 and $CaZrO_3$ disc specimens made by a sintering method and an Er_2O_3 coating layer made by an RF sputtering method have been examined under gamma-ray irradiation at high temperature. The evaluated values of the radiation induced conductivity (RIC) for the disc specimens were 5.1×10^{-12} S/m for Er_2O_3 (4.5 Gy/s), 3.0×10^{-10} S/m for Y_2O_3 (5.1 Gy/s) and 2.2×10^{-11} S/m for $CaZrO_3$ (8.8 Gy/s) at room temperature. For the Er_2O_3 coating layer, it was 1.2×10^{-12} S/m (4.5 Gy/s). Although the conductivities without irradiation, which were on the order of 10^{-14}–10^{-13} S/m at room temperature, increased during heating, significant temperature dependence was not observed under the irradiation up to ~250 °C for Er_2O_3, ~400 °C for Y_2O_3 and ~250 °C for $CaZrO_3$, respectively. At higher temperature, where the inherent conductivities without irradiation exceeded the magnitudes of the RICs observed at room temperature, the conductivities without and under irradiation were of almost the same magnitude and increased with temperature. The present results for the candidate coating materials indicate that the degradation of insulating performance due to the RIC weakly depends on temperature and is almost independent of the conductivities enhanced by heating due to motion of ions and electrons inside of grains, in grain boundaries, pits and cracks. Extrapolation from the present and the previous results on the dose rate dependence of the RICs gives the values between 10^{-9} and 10^{-7} S/m for the dose rate of several kGy/s in the fusion blanket. The present examination of temperature dependence indicated that the effect of the RIC would be negligible for maintaining of the required performance (<10^{-2} S/m) [7] in the intense radiation (several kGy/s) and high temperature (~650–700 °C) environment of the fusion blanket system [8].

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