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**The Effect of Cesium Vapour on the Bulk Conductivity of
Plasma - Sprayed Alumina**

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The Effect of Cesium Vapour on the Bulk Conductivity of Plasma - Sprayed Alumina

P. Agnew and J.L. Ing

1. Introduction

The thermionic fuel elements (TFEs) of the TOPAZ-II space nuclear power system sit in cylindrical channels in the reactor core and are separated from the NaK coolant channels by a 50 μm gap filled with helium at around 100 Torr. Ideally there would be no contact between the outer metallic surface of the TFE collector and the coolant channel. However in practice mechanical forces and thermal expansion make it difficult to maintain the 50 μm gap over the full length of the TFE. Therefore in order to maintain electrical isolation of the collector from the reactor body the outside of the molybdenum collector is coated with a thin layer of plasma-sprayed (ps) alumina, around 150 μm thick. Under normal operational conditions this insulating layer has a temperature of around 900 K and must hold off a maximum of 15 V. Under non-standard conditions this may rise to 30 V. Thus the insulator may be exposed to electric fields up to $2 \times 10^5 \text{ Vm}^{-1}$. In a nuclear heated system this combination of temperature, high electric fields and radiation may be a cause of some concern in the light of recent investigations of the so-called 'RIED' effect (radiation induced electrical degradation) <1,2,3>. In the present work we wish to consider the possibility of another potential failure mechanism for this insulator, that of cesium penetration.

Cesium is contained within the inter-electrode gap by a metal-ceramic seal at each end of the TFE. Therefore under normal operating conditions the ps insulator is not exposed to cesium. However if a seal should start to leak it is possible for Cs to flow into the helium gap and come into contact with the surface of the ps insulator. Recent investigations <4> have shown that the ps material has a high degree of porosity. In fig. 1 we show an optical microscopy cross section of this material, at 200x magnification.

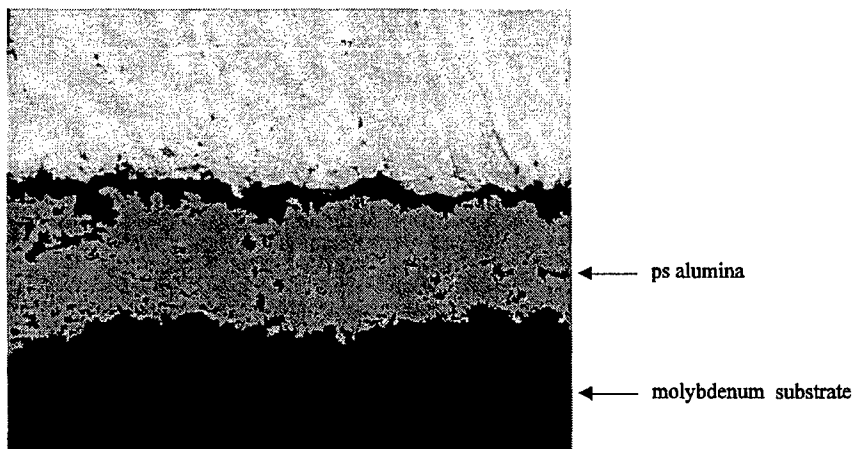


Fig. 1. Cross section of TOPAZ-II TFE ps alumina

A large number of pores are clearly visible as dark areas in the alumina layer. If cesium is able to move beyond the surface and penetrate the bulk of the material it might lead to a significant increase in its bulk conductivity, leading to loss of performance of the thermionic system. In the light of this scenario, the experiments described in this report were performed to assess the effect of Cs vapour on the bulk electrical conductivity, σ_b , of ps alumina. We have determined σ_b (i) as a function of sample temperature from 560 K to 970 K at a constant Cs pressure of 0.1 Torr, and (ii) as a function of Cs pressure from 10^{-3} Torr to 1 Torr at a constant sample temperature of 673 K.

2. Experimental Details

These experiments were performed in our general purpose Cs facility, which allows a variety of experiments to be performed in an atmosphere of cesium vapour at pressures up to 2 Torr. The major features of the facility are a six-way cross vacuum chamber, a high temperature all metal valve, a cesium reservoir and heater block, and a vacuum pumping system consisting of a 220 l/s ion pump and two 80 l sorption pumps. This combination of pumps ensures hydrocarbon free operation and has no moving parts. It is thus vibration-free and reliable. After baking to 523 K the residual chamber pressure is typically around 5×10^{-9} Torr. The six-way cross is surrounded by an oven, constructed of 2" -thick marinite. Temperatures are monitored at a number of points throughout the rig by a computerized data acquisition system, to ensure there are no 'cold spots' where Cs can condense out. The high temperature valves and Cs piping are heated with heater tapes and manually controlled by variable transformers.

A special sample stage is utilized for making conductivity measurements. It consists of a stainless steel block containing two cartridge heaters. The block is welded after installation of the heaters and in this way the heaters are unable to contaminate the vacuum. It is important to reduce sources of contaminants in the chamber to a low level since the system cannot be pumped when Cs is present. The sample is mounted on the heater block and held in place by an insulating fixture. This fixture blocks the line of sight path between the heater block and the sample, which considerably reduces the probability of contaminants originating from the heater block reaching the sample surface. It also provides mechanical fixing of the sample to the heater block. The sample is electrically isolated from the heater block by a disc of 0.5 mm thick BeO. This material has good electrical insulation properties but is a relatively good thermal conductor. All of the heaters used in the system are DC, to minimize electrical interference at low measurement current levels.

Cesium is supplied to the vacuum chamber by heating a reservoir of the liquid metal. The reservoir consists of a one inch diameter stainless steel cylinder clamped between two copper blocks. Cartridge heaters placed in the block allow the temperature of the reservoir to be raised to around 670 K. Under equilibrium conditions the following equation has been shown to give a good fit to experimental data :

$$P_{Cs} = 2.45 \times 10^8 T^{-1/2} \exp\left(-\frac{8910}{T}\right) . \quad (1)$$

In this equation the temperature of the Cs reservoir T is in Kelvin and the equilibrium vapour pressure P_{Cs} is in Torr.

2.1 Sample Preparation

Circular discs of 1" diameter niobium were cut from a 1mm thick sheet. A small hole was then drilled into the edge of the disc for later insertion of a stainless steel wire electrode lead. The plasma-sprayed coatings were produced by the staff of the Sandia National Laboratory plasma-spray facility, under the supervision of Dr. R. Neiser <4>. The surface to be coated was grit blasted to improve adhesion and then sprayed with the alumina coating. The coatings were sprayed in air using a computer controlled deposition system. Ten samples were produced, with a mean coating thickness of 211 μ m.

Two niobium electrodes were applied to the surface of the coatings in a ring pattern, as shown in fig. 2.

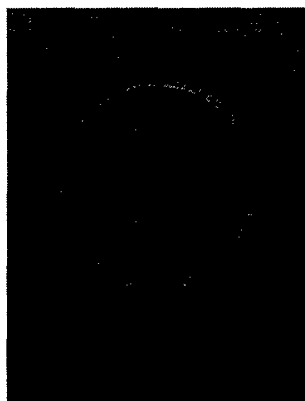


Fig. 2. Sample of ps alumina with niobium electrodes

The inner electrode diameter was 9.0 mm and the inner diameter of the outer electrode was 15 mm. Masks of magnetic stainless steel were machined and held in place over the masked areas by magnets. The niobium electrodes were then sputter deposited, to a thickness of around 500 nm. This electrode thickness of 500 nm was chosen after experience with polished single crystal samples had shown that it was sufficient to give good adhesion and low resistance (<1 Ω) electrodes. However with the rough surface of the ps material this electrode thickness resulted in significantly higher electrode resistance, of around 50 Ω . This does not lead to a significant error in the sample conductivity determination when the sample resistance is much higher than this value. However in future work it would be desirable to increase the electrode thickness, perhaps to a value of 1 μ m.

2.2 Electrical Measurements

The guarded electrode pattern, shown in fig. 2, was chosen to allow separation of bulk and surface conduction. The bulk conductivity σ_b was computed from measured values of the bulk conductance G_b . The relationship between the two for the guarded electrode configuration is

$$\sigma_b = G_b \left(\frac{t}{\pi(r_0 - \delta)^2} \right) . \quad (2)$$

In this equation t is the coating thickness and r_0 is the radius of the centre electrode plus D , where D is one half of the difference between the centre and guard electrode radii. δ is a correction factor which accounts for fringing fields. It is given by the following equation <5>

$$\delta = \frac{2t}{\pi} \ln \left\{ \cosh \left(\frac{\pi D}{2t} \right) \right\} . \quad (3)$$

For our samples the values of these parameters are: $t=211 \mu\text{m}$, $r_0 = 6.0 \text{ mm}$, $D = 1.5 \text{ mm}$. Using these values the numerical relationship between bulk conductivity and conductance is determined to be

$$\sigma_b = 3.188 G_b \quad (\Omega\text{m})^{-1} . \quad (4)$$

3. Initial Sample Characterization

Prior to exposure to Cs vapour the bulk electrical conductivity, σ_b , of the ps alumina was measured. There was significant variability in the sample conductance during the first two days over which measurements were made. This is thought to be due to the gradual release of water vapour and other adsorbed gases from the internal pores of the material. After this initial instability the conductance reached steady, reproducible values and measurements were made as a function of sample temperature. These results are shown in fig. 3.

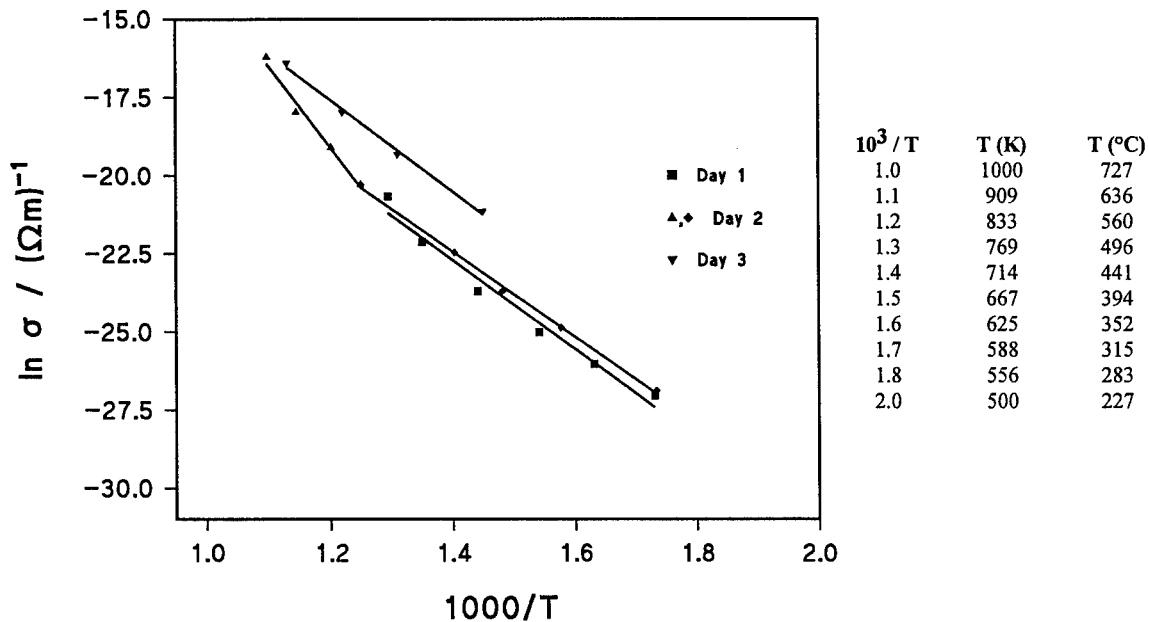


Fig. 3. Bulk conductivity of ps alumina prior to Cs exposure.

This figure shows data taken over a period of three days. The data have an Arrhenius form, with an activation energy of approximately 1.2 eV.

4. Effect of Exposure to Cs Vapour

Exposure to Cs vapour was achieved by rapidly heating the Cs reservoir to the required temperature. The effect on σ_b is a rapid increase in its magnitude. In fig. 4 we show compare the pre-exposure σ_b data with that obtained shortly after exposure.

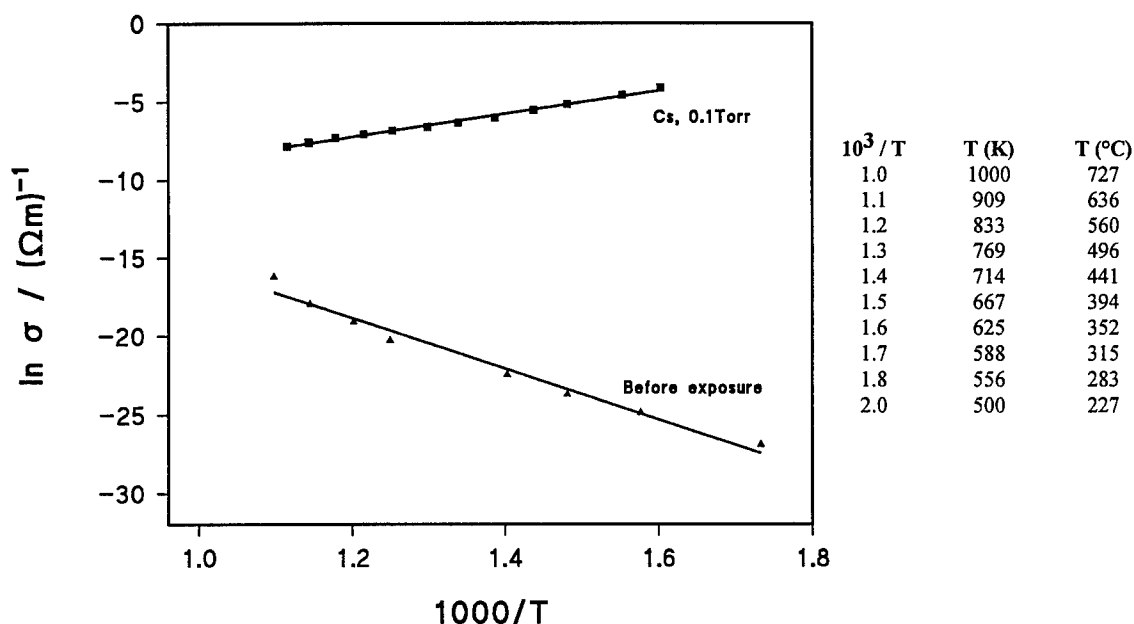


Fig. 4. Effect of Cs on the bulk conductivity of ps alumina

At the lower temperatures σ_b has increased by about eight orders of magnitude. At higher temperatures, more relevant to TFE operations, the increase is around four orders of magnitude. Not only has the magnitude of σ_b increased but the trend in the temperature dependence has reversed. It is still approximately 'Arrhenius', but the sign of the exponent has changed. In fig. 5 the effect of Cs is shown on a closer scale. Actually the experimentally measured I-V characteristics change slope slightly above about 3 V and so depending on which slope one uses the values of σ_b vary somewhat. However the effect is small. For completeness we have evaluated σ_b both ways and presented the results in fig. 5.

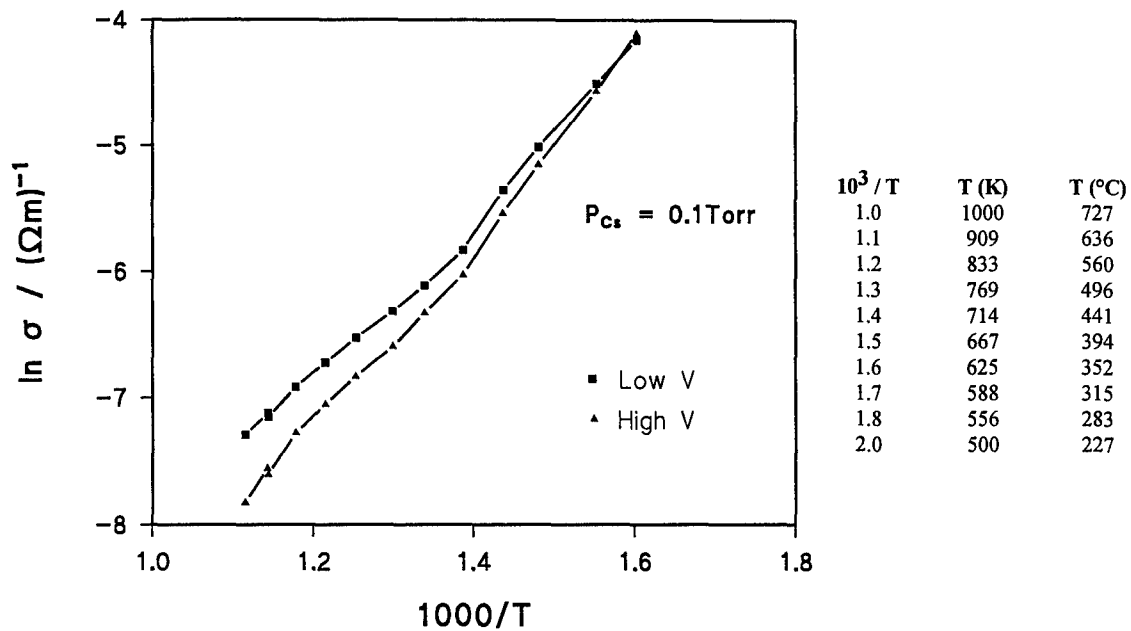


Fig. 5. Bulk conductivity of ps alumina in Cs vapour at 0.1 Torr

5. Pressure Dependence

Measurements of σ_b were made as a function of Cs pressure over the range 10^{-3} to 1 Torr, at a constant sample temperature of 673K. The results are shown in fig. 6.

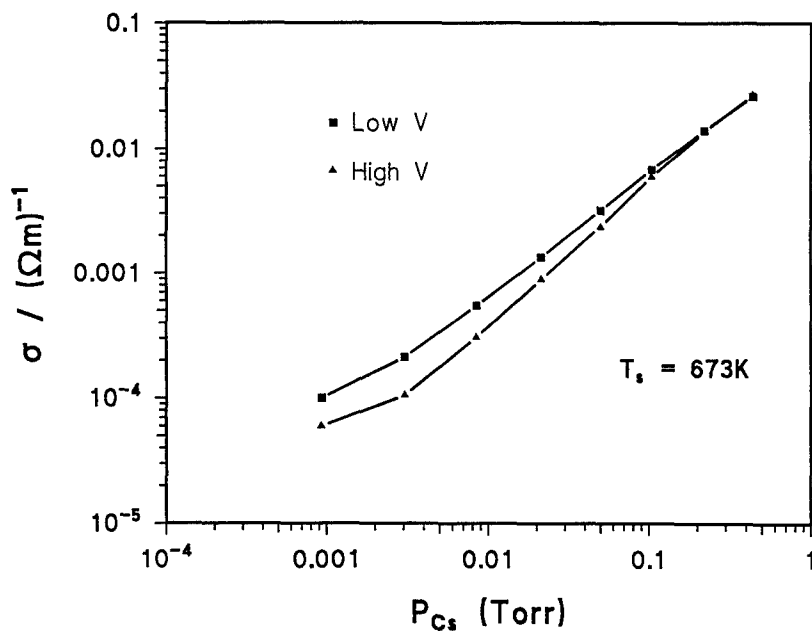


Fig. 6. Variation of σ_b with Cs pressure at a constant sample temperature of 673K

Again, we have evaluated σ_b using both slopes of the I-V characteristics for completeness. The linearity of the data on a log-log plot indicate a power law dependence of σ_b on Cs pressure. In fact the dependence is of the form

$$\sigma_b \propto P_{Cs}^{1.13} \quad (7)$$

6. Discussion

As a check on the validity of the results a similar experiment was performed with a single crystal sample of alumina. In this case it is clearly impossible to have significant penetration of Cs into the bulk. We were not able to detect any increase in the bulk conductivity of this sample, in sharp contrast to the observations for plasma-sprayed material. It is clear from our results that Cs vapour can easily penetrate the interior of plasma-sprayed alumina, leading to large increases in the bulk conductivity.

The dependence of the bulk conductivity on Cs pressure is quite different to that of the surface conductivity. We have shown in a previous report <6> that the surface conductivity exhibits a very weak dependence on P_{Cs} . The present work shows that in ps alumina, σ_b varies approximately linearly with P_{Cs} over three orders of magnitude. One possible explanation of this is that higher pressures force Cs into successively smaller pores in the material. It would be desirable to confirm this by means of some micro-analytical technique. However we have no plans to do this at the present time.

In the introduction we suggested that leaking TFE seals might lead to the coating of ps alumina with Cs, resulting in much larger leakage currents to ground. These experiments suggest that this failure/degradation mechanism is indeed feasible. At present we are unable to say precisely what level of conductivity should be regarded as unacceptably high for this material. To put the results in context we have re-plotted the conductivity data of fig. 4 in base ten and added some data of the intrinsic conductivity of silicon to the graph. This should give a more familiar reference point by which to judge the modified conductivity of our ps material.

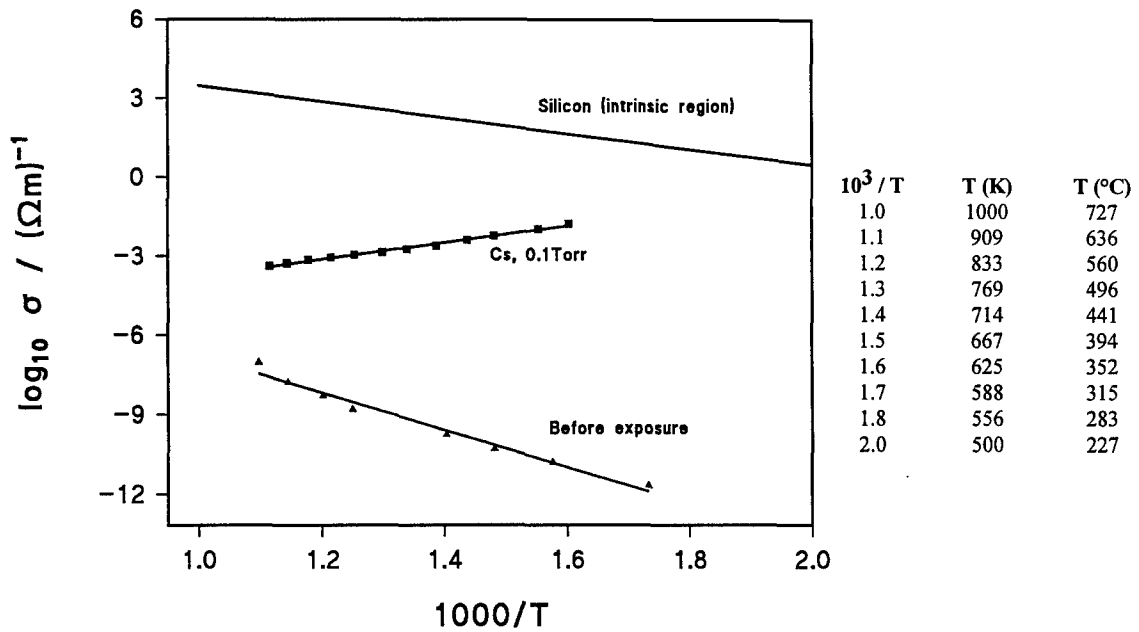


Fig. 7. Comparison of the effect of Cs on the bulk conductivity of ps alumina with silicon

Clearly the modified material has a much lower bulk conductivity than semiconducting silicon. However values of conductivity above $10^{-4} (\Omega\text{m})^{-1}$ would usually be considered poor for electrical insulators. Thermionic devices are invariably low voltage, high current devices and are much more capable than most electronic devices of withstanding large leakage currents to ground. But there is clearly some cause for concern here.

7. Summary

We have shown that Cs vapour is able to easily penetrate the bulk of plasma-sprayed alumina, leading to large increases in the bulk conductivity of the material. We have determined the temperature and pressure dependencies over a significant and technologically relevant range. In contrast to the surface conductivity we have found that the bulk conductivity exhibits a significant dependence on Cs pressure, varying approximately linearly with P_{Cs} . We believe that this effect represents a potentially significant degradation mechanism for single cell thermionic fuel elements which utilize this material.

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