DEVELOPMENT OF ELECTRICALLY INSULATING COATINGS BY MOCVD TECHNIQUE

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OBJECTIVE

The objectives of this task are to (a) develop electrically insulating coatings by the metallorganic vapor deposition (MOCVD) technique, with emphasis on understanding the basic thermodynamic conditions and kinetic processes needed to develop stable coatings that are compatible with an Li/Li-Ca environment; (b) perform detailed postexposure analysis of the surface layers by several electron/optical techniques to characterize the elemental and phase compositions, quantify stratification in the layers, and establish the roles of compositional changes in the coating and microstructure; and (c) measure the electrical resistance of the coatings before and after exposure to Li.

SUMMARY

As part of the U.S. Department of Energy's Fusion Reactor Program, studies have been in progress at Argonne National Laboratory (ANL) to develop electrically insulating coatings on V-Cr-Ti alloys, in particular on V-4Cr-4Ti, the primary candidate for use in various structural applications, including in the first-wall structure/blanket of a fusion reactor. The first wall will be in contact with liquid Li coolant, and electrical conductivity across the wall will lead to magnetohydrodynamic pressure losses during flow in the magnetic field. Hence, among the critical requirements of the rather stringent design criteria for the first wall material are that the coating on it be nonporous, tenacious, electrically insulating, and capable of maintaining its structural integrity while in use in a liquid Li environment at temperatures of 400-700°C. More information on the material requirements of fusion reactors is reported in Ref. 1.

This report addresses the development and characterization of CaO and Y_2O_3 coatings that were applied on V-4Cr-4Ti alloy by an MOCVD process. Several coupon specimens were coated with CaO or Y_2O_3 by the process developed at ANL. The specimens were analyzed and the coatings were characterized before exposure to a liquid Li environment. The analysis and characterization used one or more of scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), and X-ray diffraction (XRD) techniques. Results are presented, with emphasis on microstructural analysis and electrical resistivity of the coatings. We plan to expose the coated specimens in liquid Li of varying chemistry at temperatures of 500-700°C.

BACKGROUND

A review of available information on electrical resistivity values for several oxides, nitrides, and mixed oxides showed that oxides such as CaO, MgO, BeO, Y_2O_3, and $MgAl_2O_4$, and nitrides such as BN, AlN, and Si_3N_4 exhibit resistivities of $>10^6$ Ω·cm at temperatures below ≈700°C.[1] The requirement is that the product of the electrical resistivity of the insulator coating and the

thickness of the coating should exceed a nominal value of 100 Ω·cm^2 under operating conditions. This translates to a

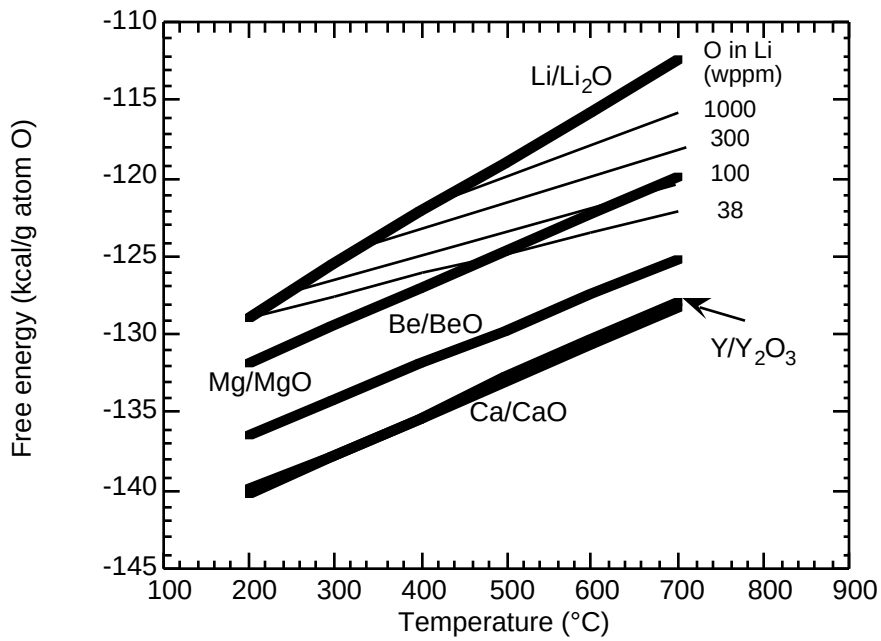

Fig. 1. Thermodynamic stability of several candidate oxide coatings in Li environment.

minimum resistivity value of 10^6 Ω·cm for a coating thickness of 1 µm, or 10^5 Ω·cm for a coating thickness of 10 µm. Based on the resistivity values of materials listed above, a coating layer of <1 µm in thickness of any of these materials would be adequate from the insulating standpoint, provided that resistivity is not reduced during operation, e.g., by irradiation.

A majority of oxides that form from the constituents (e.g., V, Cr, Ti, Si, Al, etc.) of structural materials are unstable in an Li environment. The distribution coefficient for O between these metals and Li is such that O will transfer from the metals into Li and that O concentration in Li has no consequence in the corrosion performance of these metals and their alloys. Therefore, from the standpoint of stable oxides in an Li environment, very few candidates are feasible. Figure 1 shows the thermodynamic stability of several oxides (CaO, MgO, Y_2O_3, BeO) that are possible candidates for insulator application in an Li environment. It is evident that all four oxides are stable in O-saturated Li at temperatures of >200°C. Also shown in the figure are free energy values for Li that contains various concentrations (1000, 300, 100, and 38 wppm) of O. The lowest value of 38 wppm O corresponds to an O concentration that is established by cold-trapping Li at 200°C. Under these conditions, all except MgO are thermodynamically stable over the wide temperature range (200-700°C) of interest for fusion systems.

Coating approaches such as the physical vapor deposition (PVD) technique and in-situ coating in a Ca/Li environment have been investigated to prepare CaO coating on vanadium alloys[2] which

are candidate materials for structural application in a fusion system. In both approaches, a layer of calcium is deposited on the surface of V alloys by vapor- or liquid-phase transport methods. CaO

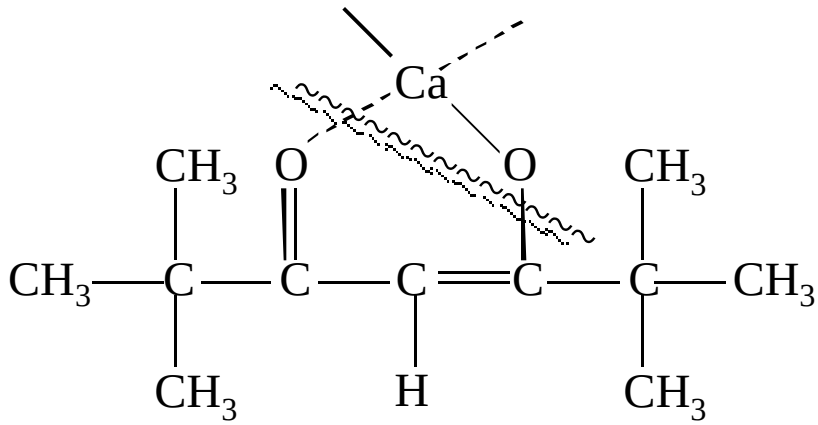

Fig. 2. Diagram of bond breaks in Ca precursor used in MOCVD technique.

coatings were obtained after oxidation of the deposited Ca layer. There may be a small amount of V in the film since Ca-deposited specimens were oxidized at elevated temperature to obtain the electrically insulating coating. Vanadium enrichment can decrease the resistance of the coating, especially if it is bound with oxygen, since the O will transfer to Li thereby leaving V metal in the coating. Furthermore, oxidation of the deposited Ca layer to CaO can lead to volume increase and may debond the coating from the substrate. To overcome these problems, an alternate method (MOCVD) was examined for the development of electrically insulating coatings.

The MOCVD technique allows preparation of a CaO film on the surface of a V alloy without using the two-step Ca deposition/oxidation process. CaO can be directly deposited on the surface of V alloy by MOCVD. For example, when the Ca precursor, calcium bis(2,2,6,6-tetramethyl-3,5-heptanedionate), is heated to high temperature, the C and O bonds will break as shown in Fig. 2.

The MOCVD approach will not only reduce the concentration of V and O enrichment in the coatings, but will also minimize the possibility of cracking during oxidation of deposited Ca. The method also has an additional advantage in that coatings can be applied in structures with complex geometry. In this report, we discuss the preparation of CaO and Y_2O_3 coatings by MOCVD.

EXPERIMENTAL PROGRAM

Calcium bis(2,2,6,6-tetramethyl-3,5-heptanedionate) [$Ca(TMHD)_2$] was selected as the precursor to prepare the CaO coating by the MOCVD method. However, [$Ca(TMHD)_2$] has a low vapor pressure and decomposes easily. To obtain a reasonable rate of film growth, the precursor must be heated to a high temperature (usually above 200°C) for a suitable vapor pressure, whereas significant decomposition of this compound is observed at 240°C. Therefore, only a narrow

temperature window is available for vaporizing the precursor. To accomplish the precursor vaporization and deposition of the coating in a narrow temperature range, we developed an MOCVD system in which the residence time and temperature for the process were controlled better than that possible with commercial MOCVD equipment.

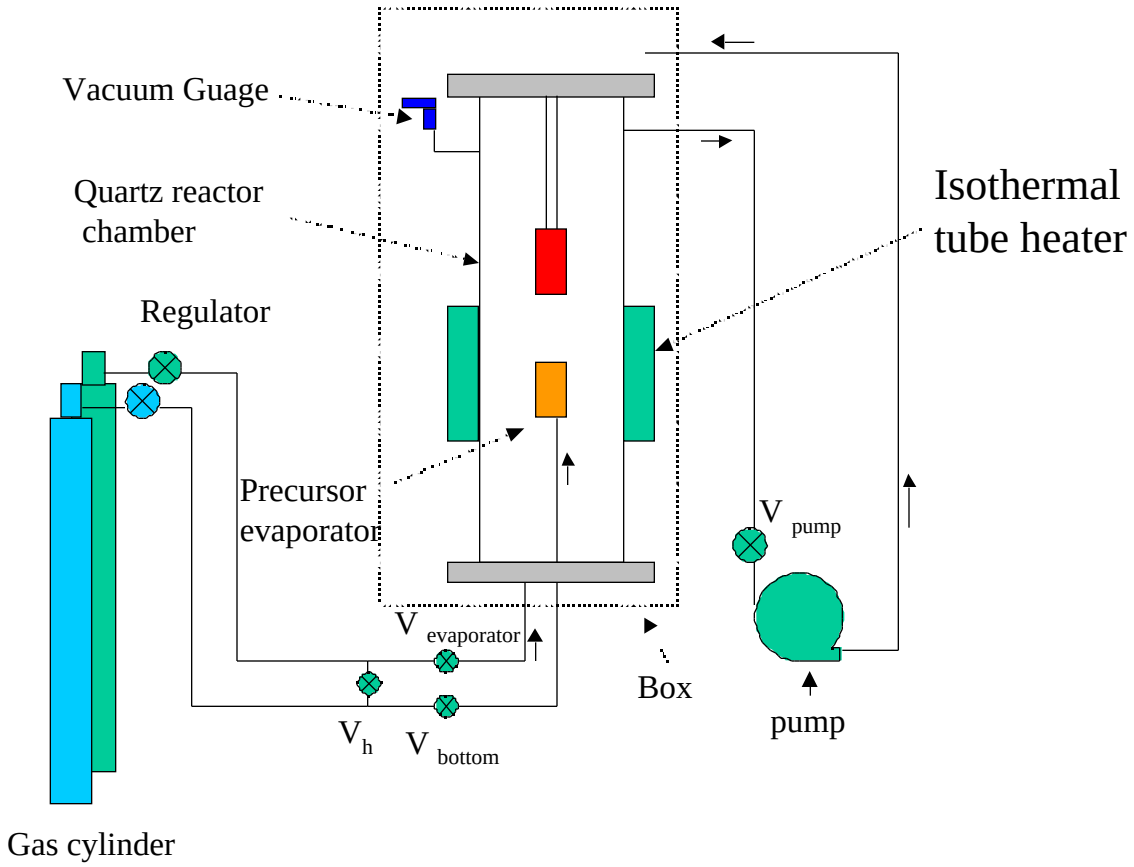

Fig. 3. Schematic of MOCVD system with assembled reactor and precursor evaporator.

The system we developed at Argonne National Laboratory consists of gas supply lines, precursor evaporator, isothermal tube heater, quartz reactor chamber, sample heater, vacuum meter, and pump. Figure 3 is a schematic representation of the entire system. The difference between this system and commercial MOCVD equipment is that the precursor evaporator is located within the quartz reaction chamber. Since the distance between the precursor evaporator and the sample heater is short, it is easy to control the temperature over this short distance with the isothermal tube heater, so that the precursor will not condense or decompose before it reaches the sample heater. The sample holder is made of a Ni-base alloy with a resistance heater. The precursor evaporator is covered by Al foil and 99.999% purity He is introduced into the precursor evaporator to minimize oxidation of the precursor. Oxygen flow enters from the bottom of the quartz reactor chamber.

Vanadium alloy coupons were glued to the sample heater by Ag paste. [$Ca(TMHD)_2$] was positioned in the precursor evaporator. 99.999% purity Ar was introduced into the chamber from bottom at the beginning to prevent precursor from oxidation. The reactor chamber was evacuated to 0.5 torr by a mechanical pump. The isothermal tube heater was kept at 220-240°C, the samples were heated to 650-850°C, and the precursor evaporator was heated to 200-240°C. After all temperatures were stabilized, Ar was introduced into the precursor evaporator from the bottom of the chamber and then the flow was switched to O gas. The O reacted with $Ca(TMHD)_2$ and deposited CaO on the surface of each V alloy coupon.

RESULTS

Figure 4 is an SEM image of the coating developed by MOCVD. The surface of the V alloy specimen is covered by condensed fine particles (≤1 µm in size) of CaO. The SEM cross-sectional photomicrograph of the CaO coating shows that the thickness of CaO layer is ≈20 µm (Fig. 5). Figure 6 shows the X-ray diffraction pattern of the coating and clearly indicates the coating to be pure CaO. Figure 7 shows the concentration of Ca and V as a function of distance from surface. There is almost no V in the CaO layer.

A two-probe method was used to measure the electrical resistance of these specimens by deposition of Au film over areas of 2 x 2 mm and use of Pt wire for electrical leads. The specimen assembly was inserted in a furnace and resistance measurements were made in an Ar environment between room temperature and ≈700°C. The variation in the product of resistance times area (i.e., R x A, which is equivalent to the product of resistivity times coating thickness) as a function of temperature obtained on specimens of V-4Cr-4Ti alloy was measured. For some of the specimens, the measurements were conducted during several heating and cooling cycles to establish the mechanical integrity of the coatings under thermal cycling. The R x A value of the coating decreases with increasing temperature (see Fig. 8). The value is $>10^7$ $\Omega\cdot cm^2$ at 700°C, which is much higher than the minimum requirement of 100 $\Omega\cdot cm^2$ for fusion application.

REFERENCES

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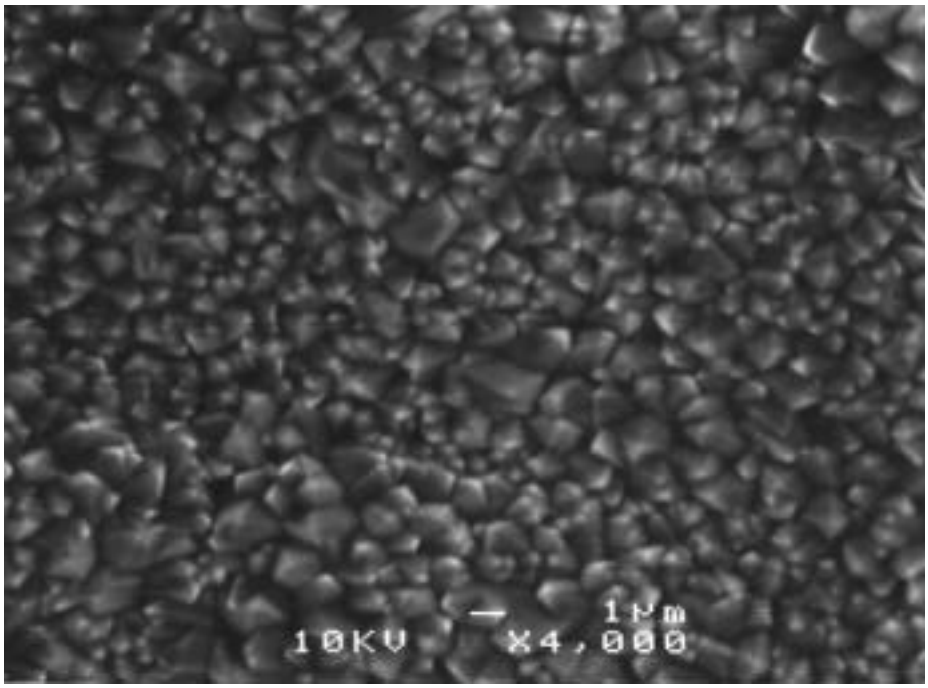

Fig. 4. SEM photomicrograph of surface of CaO coating developed by MOCVD.

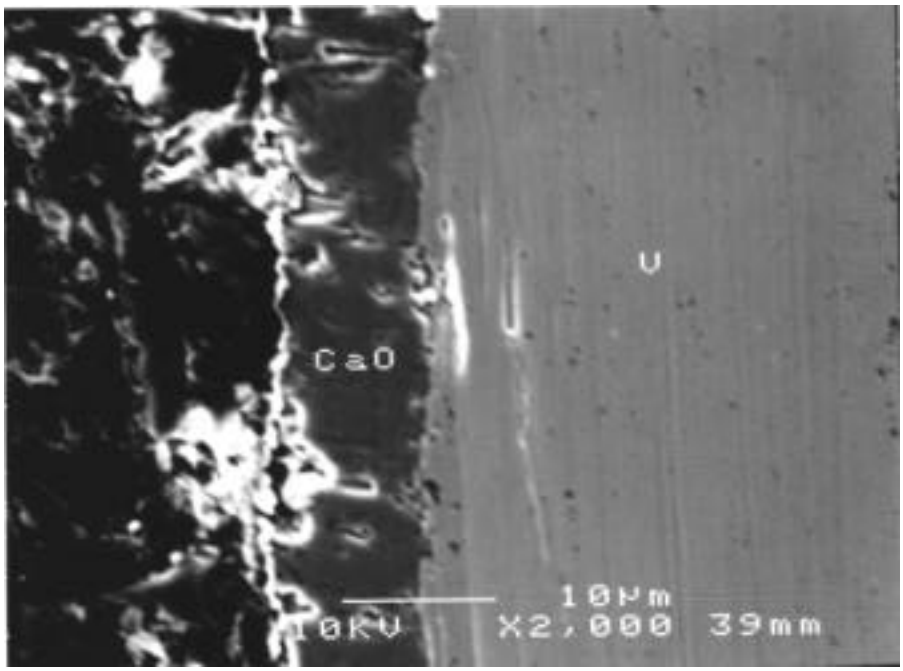

Fig. 5. SEM photomicrograph of cross section of CaO coating developed by MOCVD.

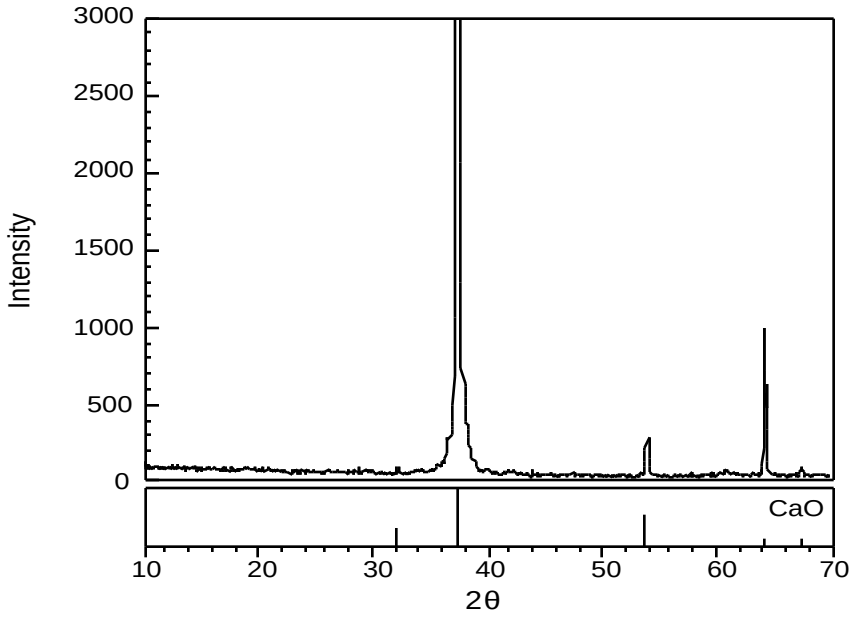

Fig. 6. XRD pattern of coating developed by MOCVD, indicating a composition of CaO.

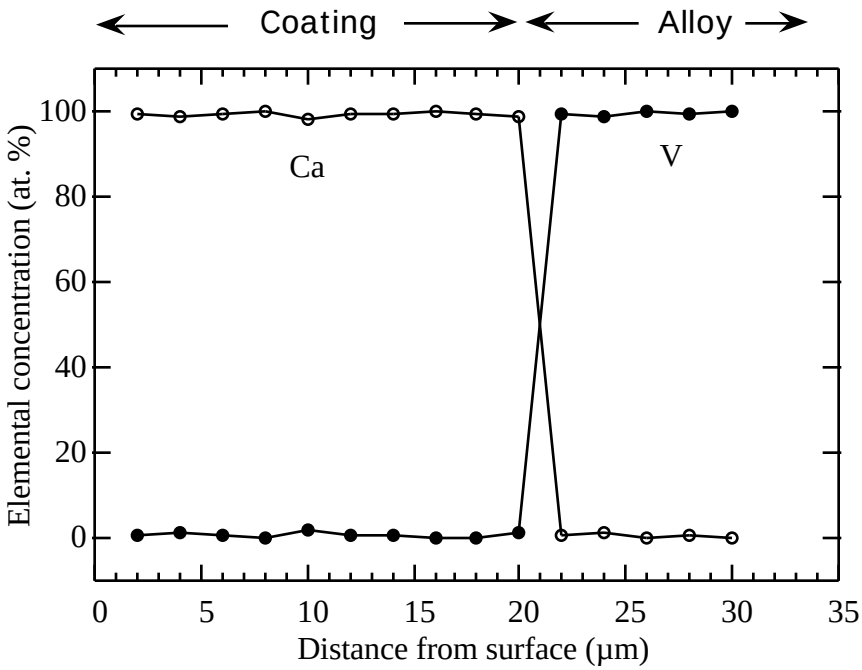

Fig. 7. Concentration of Ca and V as a function of distance from surface of CaO coating developed by MOCVD.

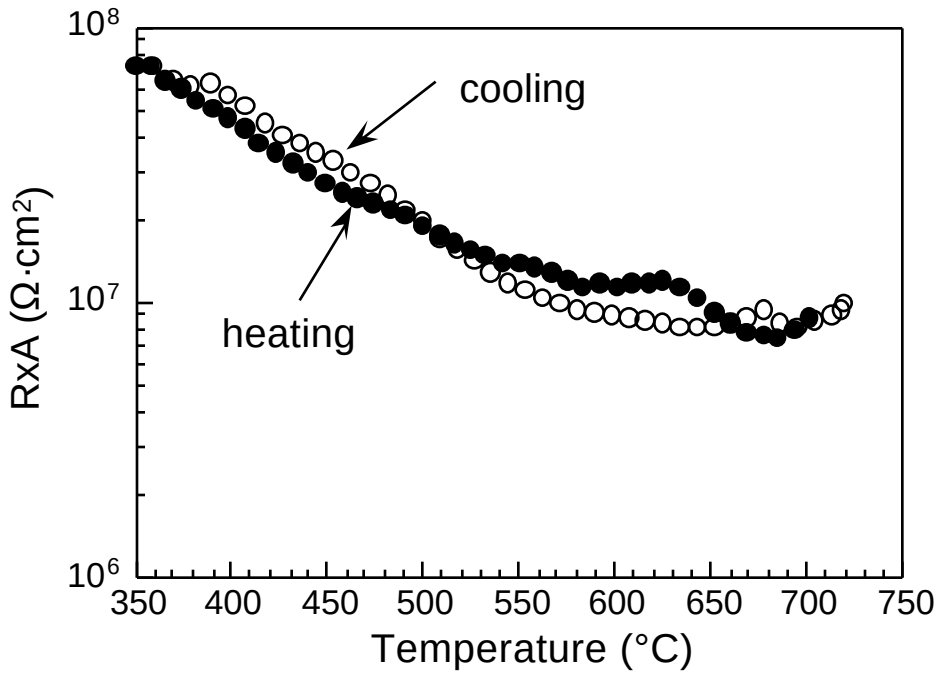

Fig. 8. Resistance times area (R x A) as a function of temperature for CaO coating developed by MOCVD.