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Non-destructive evaluation of thermal barrier coatings using impedance spectroscopy

Xin Wang, Junfa Mei, Ping Xiao *

Materials Research Group, Department of Mechanical Engineering, Brunel University, Uxbridge UB8 3PH, UK

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Abstract

Determining the oxidation of thermal barrier coatings (TBCs) non-destructively is essential for monitoring the performance of TBCs and predicting the lifetime of TBCs in service. In this research, impedance spectroscopy was used, as a non-destructive tool, to examine the oxidation of thermal barrier coatings (TBCs). Impedance diagrams obtained from impedance measurements at 623 K, were analysed according to equivalent circuit models of the oxidised TBCs. TBCs after oxidation at 1373 K consist of yttria stablised zirconia as a top coat, an alumina layer from the oxidation and a MCrAlY alloy as a bond coat. When the oxidation time is less than 200 h, the impedance spectra of TBCs can be fitted by using an equivalent circuit model, which represents a discontinuous layer of alumina between the top coat and bond coat. When the oxidation time is between 400 and 1500 h, the impedance spectra of TBCs can be fitted by using a simple equivalent circuit model, which represents a three-layer structure consisting of a continuous alumina layer, a mixed oxide layer and the top coat. In this case, the thickness of the alumina layer can also be measured by simulating the electrical modulus spectra of TBCs. Therefore, impedance spectroscopy is a powerful tool for non-destructive evaluation of oxidation of TBCs.

Keywords: Alloy; Al_2O_3; Impedance spectroscopy; Oxidation; Thermal barrier coatings; ZrO_2

1. Introduction

Thermal barrier coatings (TBCs) typically consist of yttria stablised zirconia (YSZ) as top coat and a MCrAlY alloy as bond coat. The bond coat between YSZ and the substrate superalloy is designed not only to promote adhesion of the YSZ to the substrates, but also to provide oxidation resistance.[1] The oxidation of bond coat is a dominant factor leading to the failure of TBCs.[2,3] As the oxidation proceeds, more and more aluminium element diffuses outward to the bond coat/YSZ interface to form a alumina layer. It has been observed that the spallation of YSZ can be associated to the phase conversion of the initially formed α-alumina to mixed spinal phase, which in turn is directly related to the depletion of aluminium in bond coating.[4] Since the content of aluminium in bond coat is limited, the thickness of the alumina layer can be an indicator of extent of aluminium depletion in bond coat. Therefore, non-destructive characterisation of the alumina layer in TBCs is very important in predicting the lifetime of TBCs in service.

Our previous research[5] has shown that the impedance spectra of TBCs obtained at room temperature are related to the growth of the oxide layer in TBCs due to isothermal oxidation. Other researchers,[6] by making impedance measurements at 469 K, found that impedance spectra were sensitive to the thickness of different layers in TBCs. In this work, impedance measurements were made at 623 K to determine the oxide growth in TBCs due to oxidation at 1373 K for a period up to 1500 h. At measuring temperature of 623 K, YSZ is a moderate ionic conductor whereas the alumina layer is a good insulator. The large difference in electrical properties of the alumina and YSZ lead to the distinction of impedance spectra of the alumina layer and YSZ in the impedance measurements of TBCs. In order to examine the detailed microstructure of TBCs after oxidation, different equivalent circuit models representing different microstructures of TBCs were established to simulate impedance spectra of TBCs after oxidation for different periods. Electrical modulus spectra were used to monitor the growth of the alumina layer.

* Corresponding author. Fax: +44-1895-812636.
E-mail address: ping.xiao@brunel.ac.uk (P. Xiao).

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2. Experimental procedure

The Haynes 230 alloy (for composition see Table 1) with a thickness 2mm was sprayed with a HVOF MCrAlY bond coat (38.5 wt.% Co–32 wt.% Ni–21 wt.% Cr–8 wt.% Al–0.5 wt.% Y) and a Metco 204 NS TBC top coat (8 wt.% yttria stabilised zirconia) at Sermatech, Lincoln, UK. The coated plates were cut into 10 by 10 mm squares by using a precision diamond cutting saw at low speed to avoid any mechanical damage to the coating. The samples were oxidised in a chamber furnace at 1373 K for up to 1500 h.

Four samples for each oxidation time were prepared, one of which was examined by SEM coupled with energy dispersive X-ray spectroscopy (EDS) and the remaining three samples were used for impedance measurements. One electrode for impedance measurements was applied by painting a thin layer of silver ink on YSZ and subsequent firing at 673 K for 15 min. The substrate (Haynes 230 alloy) acted as another electrode. The painted area is 8 by 8 mm and is 2 mm away from the edge to avoid possible current leakage.

Impedance measurements were made by using a Solartron SI 1255 HF Frequency Response Analyser coupled with a 1296 Dielectric Interface (Solartron, UK). AC voltage was applied to TBCs with amplitude of 1 V and frequency from 10^6 to 10^{-3} Hz with 5 readings per decade of frequency. Impedance measurements were made after the samples had been placed in a furnace at 623 K for 30 min. Impedance measurements were made at 623 K in air. ZView Impedance Analysis software (Scribner Associates, Inc., Southern Pines, NC) was used to simulate impedance spectra based on equivalent circuit models.

Table 1
The composition of Haynes 230 alloy (wt.%)

Ni	Cr	W	Mo	Fe	Co
57[a]	22	14	2	3[b]	5[b]
Mn	Si	Al	C	La	B
0.5	0.4	0.3	0.10	0.02	0.015[b]

[a] As balance.
[b] Maximum.

3. Results and discussions

3.1. Microstructure of TBCs

Fig. 1 shows the SEM back-scattered images of TBCs after oxidation at 1373 K for 100 and 800 h respectively. According to analysis using EDS, the dark layer between the top coat and bond coat is nearly pure alumina layer, while the grey region contains mixed oxides, i.e. alumina, chromium oxide, cobalt oxide and nickel oxide. Previous studies on oxidation of TBCs also showed similar microstructures of TBCs after oxidation.[4,6,7] In most areas, the alumina layer is continuous whereas the mixed oxides are present between the alumina layer and top coat, with sporadic distribution and non-uniform growth. Both the alumina layer and mixed oxides grew with the increase of oxidation time. In the samples that have been oxidised for less than 200 h, the alumina layer is not uniform and in some parts the mixed oxides were formed between top coat and bond coat (as shown in Fig. 1a). For the samples that have been oxidised for more than 400h, the alumina layer is continuous and relatively uniform (Fig. 1b).

3.2. Impedance spectra and the equivalent circuit models

Figs. 2 and 3 show the Bode plots from impedance measurements at 623 K. There is a significant difference in the impedance spectra of TBCs oxidised for less than

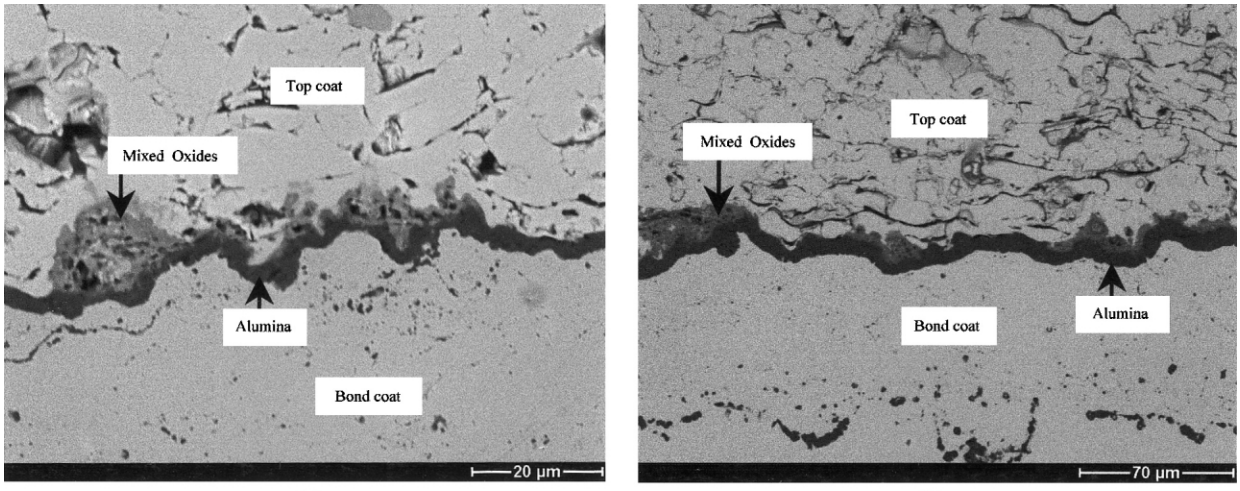

Fig. 1. SEM back-scattered image of TBC samples oxidised at 1373 K (a) for 100 h and (b) for 800 h.

200 h and more than 400 h. When TBCs were oxidised for more than 400 h, impedance spectra of TBCs have three relaxation processes shown in the phase angle plots where their relaxation frequencies are $\sim 2\times10^5$ Hz, $\sim 4\times10^2$ Hz and ~ 10 Hz respectively. However, when TBCs were oxidised for less than 200 h, there are only two relaxation processes, at $\sim 2\times10^5$ Hz, $\sim 4\times10^2$ Hz respectively.

Based on the SEM observation, oxidised TBC samples consist of five layers, which are top coat, mixed oxides, alumina layer, bond coat and substrate. Since the substrate and bond coat are highly conductive, the electrical impedance from these materials is negligible. Thus the equivalent circuit should consist of three units in series as shown in Fig. 4, where each unit consists of one resistor and one constant phase element (CPE) being connected in parallel. CPE is used here since CPE is more suitable to describe the behaviour of a non-ideal capacitor, which contains various phases as dielectric materials.[8] The impedance of CPE is given by:[9]

$$Z_{\mathrm{CPE}}(j\omega) = A^{-1}(j\omega)^{-n} \tag{1}$$

Where A is a constant that is independent of frequency, ω is angular frequency and $j = \sqrt{-1}$, and n is an exponential index which represents a dispersion of relaxation frequency. When $n = 1$, CPE represents an ideal capacitor; when $n = 0$, CPE acts as a pure resistor. Thus CPE can represent a wide variety of non-ideal elements that closely reflect the electrical properties of oxide layers in TBCs.

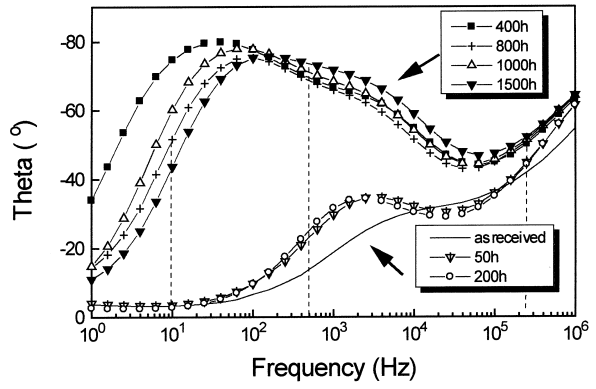

Fig. 2. Phase angle plot from impedance measurements of TBC samples oxidised for different periods.

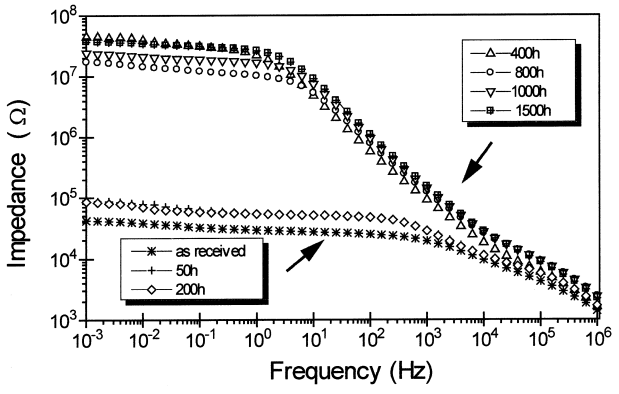

Fig. 3. Impedance plot from impedance measurements of TBC samples oxidised for different periods.

The model shown in Fig. 4 was employed to simulate the measured impedance spectra. The simulation fits the measured spectra of the TBCs oxidised for more than 400 h very well. However, it does not fit the impedance spectra of TBCs oxidised for less than 200 h. Fig. 5a–c show that the CPE parameters of the top coat, mixed oxides and alumina layer in the TBCs oxidised from 400 to 1500 h, change as a function of the oxidation time. For the top coat (Fig. 5a), the index n is basically consistent, which may indicate that no significant microstructural or compositional change occurred during oxidation. Meanwhile the parameter A appears to show a slight decrease during oxidation from 400 to 1000 h and then increase from 1000 to 1500 h. However, the magnitude of change is comparable to the error range. Thus we can assume that top coat does not have significant microstructural change during oxidation treatment.

For the mixed oxides (Fig. 5b), the parameter A does not show significant change during oxidation from 400 to 1500 h, since the variation of this parameter is within error range. But the index n shows a decreasing trend with increasing oxidation time. As the index n represents the non-uniformity of current density as consequence of inhomogeneous microstructure, the decreasing n might indicate the homogeneity of mixed oxides decreased during the oxidation experiment.

The CPE parameters of the alumina layer (Fig. 5c) shows that the index n is close to 1 and nearly constant for TBCs oxidised from 400 to 1500 h. This indicates that the alumina here is a uniform layer with high purity and behaves as a dielectric material in a nearly ideal capacitor. The capacitance of the CPE here can be roughly represented by the parameter A. The decreasing of the parameter A with oxidation time (Fig. 5c) is due to the increase in the thickness of the alumina layer during oxidation.

In the TBCs oxidised for less than 200 h, the mixed oxides penetrate into the alumina layer in some parts (Fig. 1a). In this case, the equivalent circuit model of the

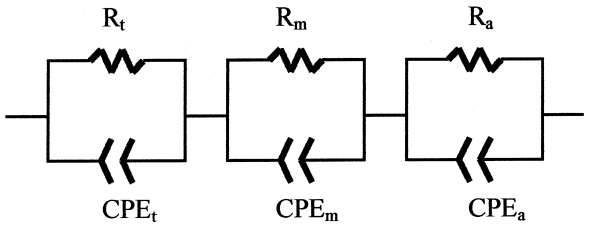

Fig. 4. Equivalent circuit model of TBC samples oxidised for periods of 400–1500 h.

TBCs can be described as shown in Fig. 6 where R_t and CPE_t represent the top coat, R_m and CPE_m represent the mixed oxides and R_a and CPE_a represent the alumina layer. This model was found to fit the impedance spectra of the TBCs oxidised for less than 200 h (Fig. 2). According to microanalysis by using EDS, the mixed oxides contain the chromium oxide, cobalt oxide and nickel oxide. Cr_2O_3 is a p-type semiconductor and is quite conductive at 623 K.[10] Both cobalt and nickel oxides are also much more conductive than alumina at high temperature.[11] Thus $R_{m'}$ is expected to be much smaller in value than R_a. Therefore, electrical current would mainly pass through mixed oxides when electrical voltage was applied to the TBCs. In this case it is difficult to determine the contribution of the alumina to the impedance spectra of TBCs. The two relaxation processes shown in the impedance spectra (Fig. 2) correspond to the mixed oxide layer and the top coat layer. It is difficult to examine the microstructure of the alumina layer in this case.

3.3. Determining thickness of alumina layer

Electrical modulus is defined as:[9]

$$M = j\omega C_e Z \tag{2}$$

Where ω is the angular frequency, C_e is the capacitance of the empty cell between electrodes, i.e. the space which the YSZ and alumina layer occupy in the TBC, $j = \sqrt{-1}$, and Z is impedance. Electrical modulus spectra can be plotted as imaginary part vs real part.[9] Fig. 7 shows the modulus spectra of the as-received sample and TBCs oxdised for 400–1500 h, where the left semicircle was obtained at low frequency and the right one was obtained at high frequency. As expected, only one semicirclular curve is shown in the modulus spectrum of an as-received sample, whereas two semicircles appear in the spectra of the oxidised samples. The large semicircle at right corresponds to YSZ and the small semicircle at left corresponds to the oxide layer. The diameters of the right semicircle are similar for all of spectra. However, the diameter of the left semicircle increases with the oxidation time (Fig. 6). SEM observation also indicated

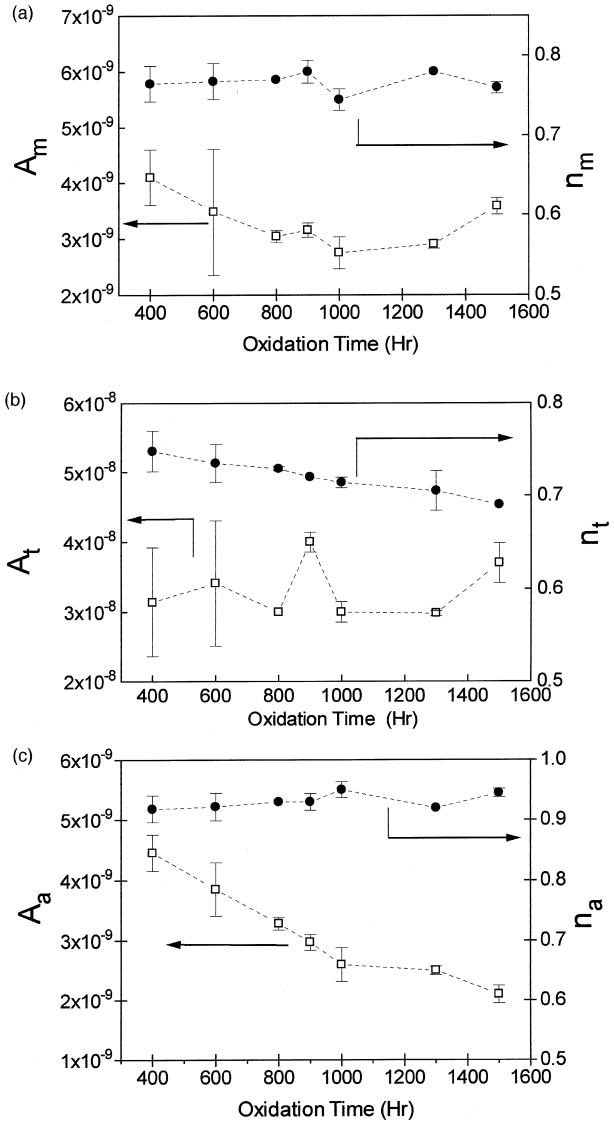

Fig. 5. CPE parameters of (a) top coat; (b) mixed oxide; (c) alumina as a function of oxidation time.

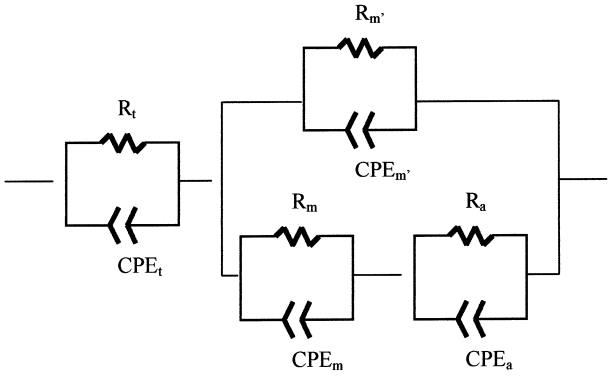

Fig. 6. Equivalent circuit model of TBC samples oxidised for less than 200 h.

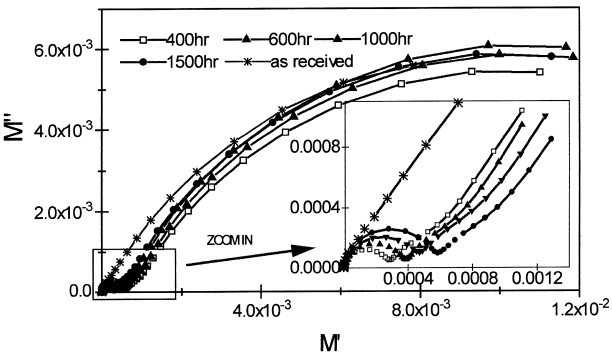

Fig. 7. Electrical modulus spectra of TBC samples oxidised for 400–1500 h with a detailed spectra at low frequency.

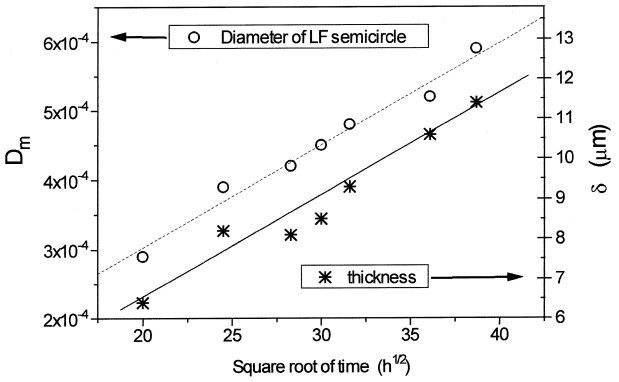

Fig. 8. Diameter of LF semi-circle corresponding to alumina layer and the thickness of alumina layer as a function of square root of oxidation time.

that the thickness of the oxide layer increased with increasing oxidation time.

To estimate the left semicircle without consideration of the right semicircle, we assume the equivalent circuit of the oxide layer in the TBCs oxidised for 400–1500 h as a single RC circuit. According to Eq. 1, the equation relating M'' to M' can be established as following:[12]

$$(M'')^2 + (M' - \frac{C_e}{2C})^2 = (\frac{C_e}{2C})^2 \quad (3)$$

When M'' equals to zero for the left semicircle, M' equals to C_e/C as the diameter of the left semicircle. The electrode area on TBCs is the same for all of impedance measurements. The thickness of YSZ is about 300 μm, and is much thicker than that of the alumina layer formed due to oxidation. Therefore, we can assume $C_e = \varepsilon_o A/\delta$ (A: areas of electrode; δ: thickness of cell) as a constant. Thus the diameter (D_m) of the left semicircle is inversely proportional to the capacitance ($D_m = C_e/C$) with the alumina layer as a dielectric material. The capacitance is inversely proportional to the thickness of the alumina layer ($C = \varepsilon\varepsilon_o A/\delta$). Therefore, the diameter in modulus spectrum (D_m) is proportional to the thickness (δ) of the alumina layer in TBCs:

$$D_m = \frac{C_e \cdot \delta}{\varepsilon \cdot \varepsilon_o \cdot A} \quad (4)$$

The thickness (δ) of oxidation layer for different oxidation time has been obtained by image analysis based on SEM photos. Plotting both the diameter of LF semicircle (D_m) and thickness of oxidation layer (δ) against the square root of oxidation time resulted in good linear relationship as shown in Fig. 8. This indicates the growth of oxidation layer follows parabolic law ($\delta \sim \sqrt{t}$; t: time), which agrees with a previous study.[7]

4. Conclusion

Thermally grown oxide layer developed in TBC during isothermal oxidation at 1373 K consists of a layer of alumina and a layer of mixed oxides. Impedance spectra of oxidised TBCs showed either two or three relaxation processes depending on oxidation time. When the oxidation time is above 400 h, impedance spectra show three relaxation processes, indicating the presence of top coat, alumina layer and the mixed oxide layer. When the oxidation time is less than 200 h, only two relaxation processes appear in impedance spectra which suggests that the alumina layer is not continuous with the penetration of the mixed oxides.

Modulus spectrum has been proven to be a very useful non-destructive approach to examine the growth of the alumina layer in TBC. When a continuous alumina layer was formed in TBC, the impedance spectra of TBCs can be used to determine the thickness of alumina layer in TBCs.

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