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Non-Destructive Evaluation for Material of Thermal Barrier Coatings

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단열 코팅재료의 비파괴 평가기법

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Abstract

Material degradation is a multibillion-dollar problem which affects all the industries amongst others. The last decades have seen the development of newer and more effective techniques such as Focused-ion beam(FIB), Transmission electron microscopy(TEM), Secondary-ion mass spectroscopy(SIMS), auger electron spectroscopy(AES), X-ray Photoelectron spectroscopy(XPS), Electrochemical impedance spectroscopy(EIS), Photo-stimulated luminescence spectroscopy(PSLS), etc. to study various forms of material degradation. These techniques are now used routinely to obtain information on the chemical state, depth profiling, composition, stress state, etc. to understand the degradation behavior. This paper describes the use of these techniques specifically applied to materials degradation and failure analysis.

Key Words : Transmission electron microscopy(TEM), X-ray Photoelectron spectroscopy(XPS), Non-destructive evaluation(NDE) Thermal barrier coatings(TBCs)

1. 서 론

Materials degradation is a global problem, which has huge impact on world's economy with direct and indirect losses due to materials loss running into billions of dollars every year. The past 15 to 20 years have seen greater awareness of the significance of materials degradation leading to improvements in materials and coatings to combat the problem.

However, ever-increasing need to mitigate the problem demands a better understanding of the degradation processes and mechanisms involved therein. While the conventional techniques such as optical microscopy(OM), X-ray diffraction(XRD), scanning electron microscopy(SEM)

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and energy-dispersive X-ray analysis(EDX) are still being used for the corrosion characterization and failure analysis, the last decade have seen the application of newer and advanced techniques to get better insight into the problem.

The nature of the surface film and its breakdown during the degradation process are very important aspects of these studies. Surface sensitive techniques such as the Auger electron spectroscopy(AES) and X-ray Photoelectron spectroscopy(XPS) have become extremely effective for both qualitative and quantitative analysis in terms of composition and chemistry of corrosion films[1~6]. The two techniques often compliment each other and can provide an insight into the changes in surface chemistry as a function of materials composition and environmental conditions, which can be ofimmense value in elucidating the corrosion mechanisms and failure analysis. The inability of XPS and AES to detect H and He can be a limitation because hydrogen(as the hydrates and hydroxides) is an important constituent. Secondary-ion mass spectroscopy (SIMS) can be used to overcome this problem. The capability of the technique to detect all elements in ppm to ppb level makes it very effective to determine the trace impurities in corrosion film.

Focused-ion beam(FIB) technique is an emerging tool for degradation studies in complex shapes. FIB is also being successfully used for the preparation of thin TEM samples in matter of hours, which otherwise is very difficult. Raman spectroscopy is yet another technique for the routine analysis of corrosion products. The technique allows the identification of materials based on their molecular vibrational spectra, obtained by excitation with visible laser light. The technique is non-destructive and the Raman spectrum with high spectral resolution can be acquired within a few seconds. Furthermore, no specific sample preparation is required. Photo-stimulated luminescence spectroscopy(PSLS), which makes use of a micro-Raman system, is fast emerging as a powerful non-destructive tool for the stress analysis of the alumina scale(with Cr impurities) formed on alloys and coatings in high temperature environment[6]. Additionally, the well-developed Electrochemical impedance spectroscopy(EIS) technique used extensively in aqueous corrosion to study degradation of coatings, etc. is now being adapted for high-temperature studies such as evaluation and monitoring of thermal barrier coatings[7,8].

The objective of this paper is to emphasize the use of modern techniques for the characterization and failure analysis of materials. An attempt will be made in the following to describe the usefulness of some of these modern analytical tools for studying the various aspects of materials degradation and failure analysis. The kind of information that can be obtained using each of these techniques will be illustrated with specific examples.

2. XPS ANALYSIS OF DEGRADATION PRODUCT

The scope of surface chemistry related to materials degradation is very broad and the XPS is extensively used for characterizing the surface corrosion film[1,3,10]. Usage of XPS in corrosion studies include, but are not limited to, the distinction of oxide structures lying near the outer surface from those deeper in the bulk phase, oxidation of Ti-Al-N alloys, oxidation of stainless steels and binary Fe-Cr alloys, and oxidation-resistant coatings.

Chromium content in steel plays an important role in terms of its resistance to high temperature. Following example illustrate the use of XPS technique to study the chromium and cerium surface chemistry of the oxide scale on steel. XPS spectrum of $Cr(2p_{3/2})$ is presented in Fig. 1 for the bare, oxidized and coated oxidized steel at 923 K for 24 hours.

The bare steel(Fig. 1(a)) shows the main peak at 576.2 eV along with 2 small shoulder peaks at 574.3 eV and 578.0 eV, corresponding to Cr_2O_3, Cr^0, and Cr-hydroxide type species, respectively[30]. The surface oxide and hydroxide formation is due to the natural passivation and physisorbed OH from air exposure. The FWHM of Cr ($2p_{3/2}$) in Fig. 1(b) and (c) increases to 2.7 and 3 eV, as compared to the Cr(2p) line in the bare sample, indicating the presence of multiple Cr-containing oxide species due to high temperature exposure. The decrease in Cr(2p) B.E (575.5 + 0.2 eV) in Cr_2O_3 is possibly due to the formation of Cr-Fe-Mn mixed oxides. A further decrease in Cr(2p) B.E

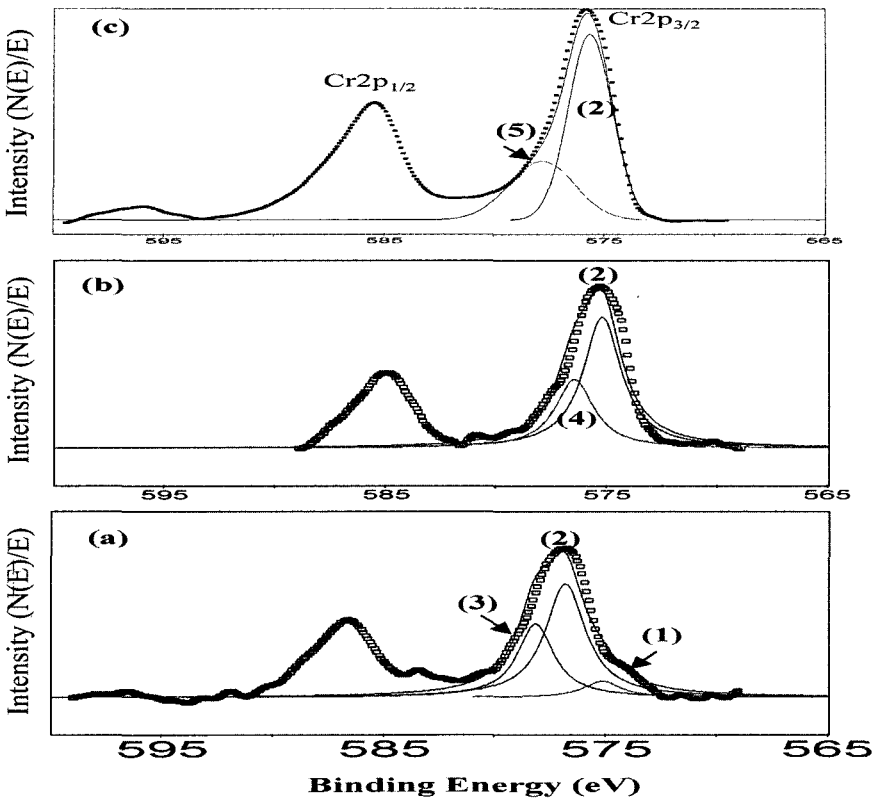


Fig. 1 XPS Cr(2p) Spectra for (a) high Cr steel, (b) high Cr steel - oxidized (c) high Cr steel - oxidized and coated. Experimental core level spectra (...), and the result of computer fitted spectra (—). Suggested peak identification: (1) Cro, (2) Cr_2O_3, (3) Cr-OH (4) Fe-Mn-chromates, (5) Cr-Ce-O type

to 577.4 eV in Fig. 1(c) is due to the possible formation Cr-Ce-O type oxides. Formation of chromia in the presence of ceria is responsible for preventing the material degradation and is consistent with the observed decrease in oxide growth rate.

3. RESIDUAL STRESS ANALYSIS IN THERMALLY GROWN OXIDE SCALE

Knowledge of stress in Thermally grown oxide(TGO) is very important as Thermal barrier coatings(TBCs) typically fail due to the spalling of the Thermally grown oxide (TGO) scale caused by residual stresses.

Photo-stimulated luminescence spectroscopy, pioneered by Clarke et al. is emerging as a powerful non-destructive technique to measure the stresses in the -Al_2O_3 TGO buried under the yttria-stabilized zirconia(YSZ) top coat in TBCs. The Cr^{3+} Photo-luminescence in -Al_2O_3 occurs by the excitation and subsequent relaxation of electrons from impurity Cr^{3+} ions resulting in a photon emission. Two distinct photo-luminescence peaks(R1 and R2) are observed at frequencies of 14,402 and 14,432cm^{-1}, respectively if the TGO is stress free. However, if TGO is stressed the R-lines exhibit a systematic shift, known as the piezo-spectroscopic effect. The frequency shift, and the local stress within the Al2O3lattice can be phenomenologically related by the coefficients of the piezo-spectroscopic tensor; and the stress within the crystal can be can be calculated based on the position of the luminescence peaks. The schematic of the PSLS technique is shown in Fig. 2.

For a more detailed discussion of the principles of Cr^{3+} Photo-luminescence, the reader is referred to the literature[6].

PSLS measurements were carried out on a thermally cycled EB-PVD TBC specimen. Photo-stimulated R1-R2 luminescence, exhibiting the stressed(shifted) and stress-free(not shifted) -Al_2O_3(i.e., bimodal luminescence) was observed from the intact and spalled TGO regions, respectively. The SEM micrograph of the top view of the NiCoCrAlY bond coat showing the intact and spalled region of the TGO is shown in Fig. 3(a).

A typical example of a bimodal R1-R2 luminescence spectrum is presented in Fig. 3(b). From the stressed component of the -Al_2O_3 R1-R2 luminescence, the average compressive residual stress in the intact region of the TGO layer was found to be between 4.5-5.0 GPa. On the other hand, PSLS spectra analysis from the regions of the bond coat where scale has spalled off shows very little or no residual stress. This result is very significant in that it tells us the TGO underneath the YSZ ceramic topcoat has compressive residual stress. The compressive stress in the TGO ultimately causes the spallation of the scale and in the process, the stress is relaxed. This is evident from the near zero stress values in the spalled region of the TGO.

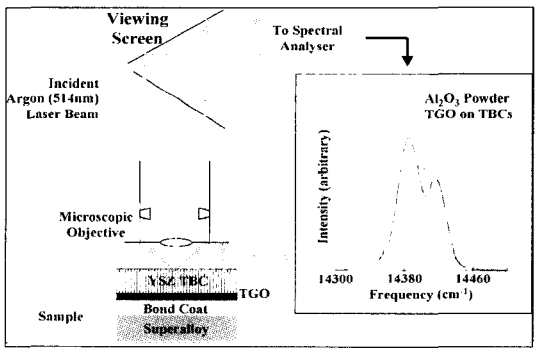


Fig. 2 Schematic of the PSLS technique used for stress measurement in thermally grown oxide (TGO) in TBCs

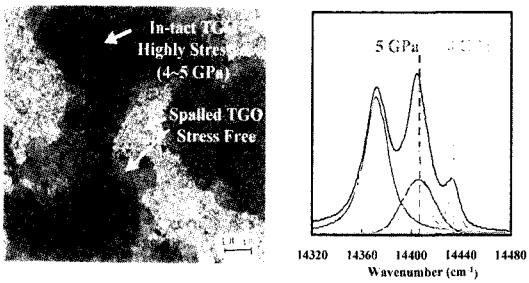


Fig. 3 Stress assessment of TBC by photo-stimulated luminescence spectroscopy; (a) Top of NiCrAlY bond coat surface after the spallation of 7 wt. % YSZ TBC, and (b) Bimodal stress state associated with the spallation of TBC as observed by the PSLS

4. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF TBC

The electrochemical impedance spectroscopy(EIS) is a powerful technique for characterizing electrical properties of electrified interface. The technique has gained popularity in the field of aqueous corrosion[13], inhibitors and organic paints[12~14], variously coated reinforcing concrete rods and Al alloys. The technique can be used to monitor the process of degradation and is capable of providing information about the location of degradation activity, type and extent of damage[12]. The capability of EIS technique to study a system with multiple interfaces can be of great value in the multi-layer systems such as TBC.

The schematic of EIS measurement system on TBCs is shown in Fig. 4, with TBC sample as working electrode (WE), a Pt- mesh as the counter electrode(CE), and an Ag/AgCl electrode as the reference electrode(RE). A 0.01 M solution of $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ is the electrolyte.

The system response(as a result of sinusoidal voltage perturbation of 20 mV in the frequency range of 1 m-1 MHz) can be recorded as either a Nyquist or Bode plot[9].

The effectiveness of the technique lies in the correct interpretation of the EIS data represented by Nyquist or Bode plot, which is accomplished by generating an a.c. equivalent electric circuit model for the electrified interface system corresponding to the TBC.

EIS can be very effectively used for the quality evaluation of the TBC[9]. The as-received TBC consists of ceramic top coat with porosity, bond coat and the superalloy sub-

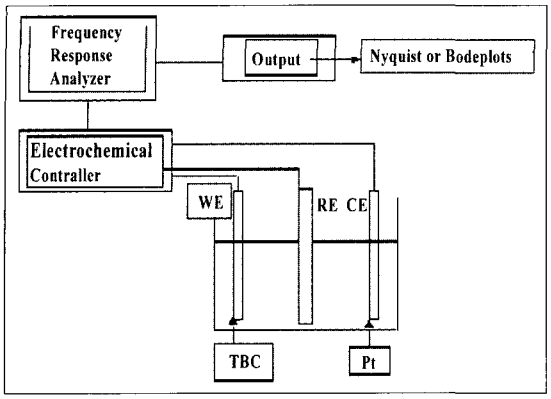


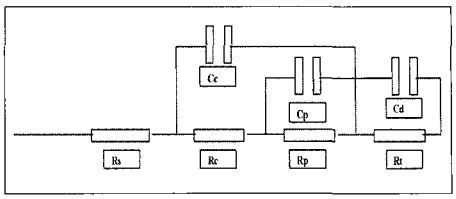
Fig. 4 A typical set up of electrochemical impedance measurement system

strate. As a result, the electrical impedance measurement of such a system can be attributed to the electrolyte, ceramic top coat. porosity in the top coat and the top coat/bond coat interface. Accordingly, an EIS a.c. equivalent circuit for the TBC system can be modeled as shown in Fig. 5(a).

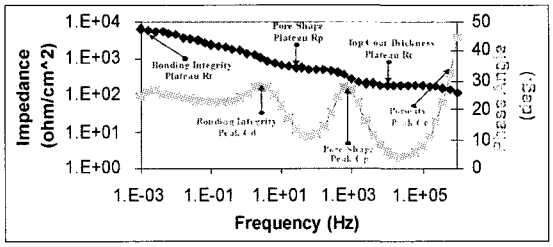
The total impedance Z(ω) of the equivalent circuit can be given by:

$$Z(\omega) = R_s + \{[R_c + (j\omega C_p + R_p^{-1})^{-1}]^{-1} + j\omega C_c\}^{-1} + (j\omega C_d + Rt^{-1})^{-1}$$

where Z is the impedance of the system; Rs the solution resistance between the reference electrode and top coat surface; R_c the resistance of the ceramic top coat; C_c the capacitance of the ceramic top coat; R_p the pore resistance; C_p the pore capacitance, Rtthe transmission resistance of the double layer at the interface between the ceramic top coat and metallic bond coat; C_d the capacitance of the double layer at the interface between the ceramic top coat and metallic bond coat; the angular frequency of the input sinusoidal wave; and finally j is the sign of the imaginary part of complex. Using this model, the experimental EIS spectra in the form of Bode or Nyquist plot can be simulated. A typical EIS Bode plot from an as-processed air-plasma sprayed TBC specimen is shown in Fig. 5(b). Based on the morphological structure of the TBC specimen(not shown here), the EIS equivalent circuit and the Bode plot, a mathematical relationship between TBC morphological properties(YSZ thickness, porosity, pore shape, etc.) and the EIS equivalent circuit parameters



(a)



(b)

Fig. 5 Quality evaluation of TBCs using EIS; (a) A typical EIS equivalentcircuit for as-Received air-plasma sprayed TBC; (b) The EIS Bode plot showing mathematical relationship between TBC morphological properties and EIS equivalent circuit parameters

(TBC electrical resistance, TBC top layer capacitance and pore resistance could be established. It has been shown that the top coat thickness has a linear relationship with R_c and the top coat porosity(P) is proportional to the C_c. Similarly, pore shape and size could be correlated with the values of R_p.

The EIS can also be used for the monitoring the evolution of defects in the top coat, porosity, the growth of TGO and thermal conductivity of TBC(9). Fig. 6(a) shows the Nyquist plot for a free-standing TBC sample exposed to various high-temperature tests. It can be seen that the electrochemical impedance has increased with the exposure temperature, in conjunction with the increase in thermal conductivity and increased sintering. In another example (Fig. 6(b)), the effect of exposure time at 1000°C on the electrochemical impedance behavior of a free-standing TBC is presented. Longer exposure time results in a decrease in electrochemical impedance. In addition, the technique can also be used to monitor the growth of TGO and increase in thermal conductivity.

To summarize, it can be said that the EIS has shown

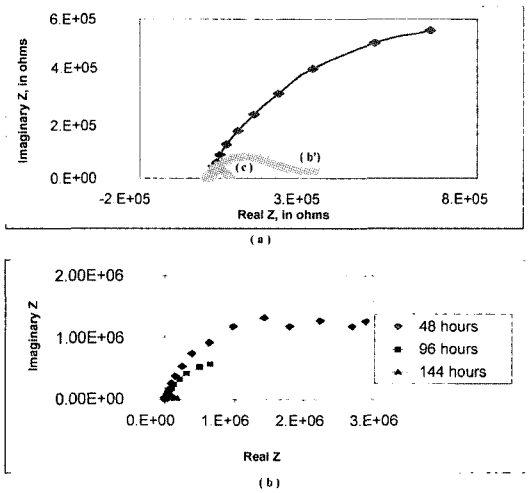


Fig. 6 Post-exposure evaluation of TBC; (a) Nyquist plots for TBC samples: (a) oxidized at 1200°C in air, (b') oxidized at 1000°C, (c) Hot corroded at 950°C for 96 hrs; and (b) Nyquist plots of free standing TBC showing the effect of exposure time at 1000°C on the electrochemical impedance behavior

great promise to be developed into a non-destructive technique for not only the quality evaluation of as-processed TBC but also for the monitoring of damage in exposed TBCs. The quantitative evaluation of TBC damage and life-time prediction is also feasible by the EIS. A sustained research effort in this direction is continued for the further consolidation and authentication of the results so that the EIS could be developed into a NDE tool for the evaluation and monitoring of high-temperature coatings.

5. DEGRADATION OF CERAMIC MATRIX COMPOSITES

Degradation of a Nextel-720 fiber/alumina Ceramic matrix composite(CMC) after exposure in air and water vapor (90%water vapor and 10% oxygen) in the temperature range of 1000-1200°C for up to 2000 hours was investigated using SEM and XPS.

Exposure of the CMC in air and water vapor environments between 1000-1200°C up to 1000 hours has not caused any significant changes in terms of mechanical strength. The composite material has, in fact, almost retained the original strength as can be seen from stress-strain response curve of the alumina-Nextel 720 CMC system after exposure to various temperatures for 1000 hours in both air and water vapor in Fig. 7.

During high-temperature exposure in presence of water vapor, volatile $Si(OH)_4$ was formed on the surface of alumina-Nextel 720 CMC system as indicated by XPS surface analysis(Fig. 8), consistent with the previously reported literature on silica-forming ceramics in water vapor environment. It is believed that the formation of $Si(OH)_4$, which occurs due to the decomposition of mullite phase in Al_2O_3 and SiO_2, and subsequent reaction of SiO_2 with water vapor is responsible for the surface degradation of the Nextel-720/alumina CMC.

XPS analysis also revealed that aluminosilicate film has developed on the surface of the Nextel-720/alumina CMC exposed to water vapor at 1100°C within 1000-hour (Inset, Fig. 8).

Formation of aluminosilicate layer at the surface can retard the further reaction with water vapor and suspend

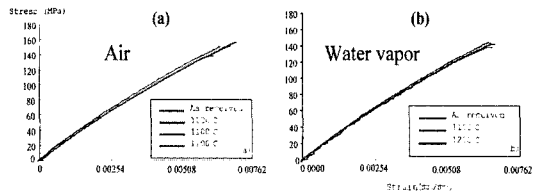


Fig. 7 Stress-strain response curve of the alumina-Nextel 720 CMC system after exposure at various temperatures for 1000 hours in (a) air and (b) in water vapor

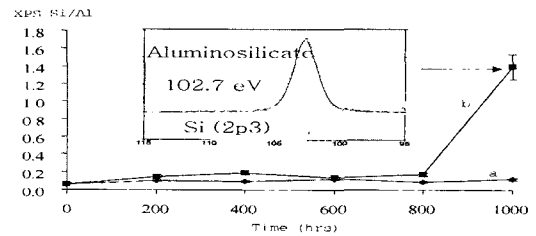
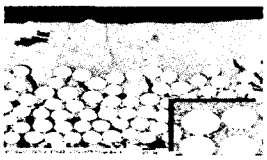
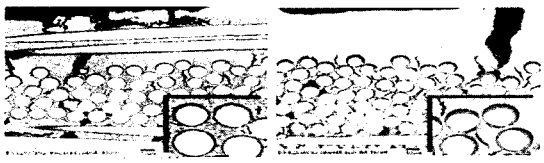


Fig. 8 XPS Si/Al ratio of Nextel-720/Alumina CMC exposed to (a) air and (b) water vapor at 1100°C for 1000 hrs. Inset shows the formation of alumino silicate phase in the case of water vapor exposure for 1000 hrs.



(a) As-received



(b) After 1000hrs (c) After 1500hrs

Fig. 9 Cross-sectional back scattered electron micrographs of Nextel-720 fiber/alumina CMC in (a) as-received condition, (b) after 1000 hrs, and (c) after 1500 hrs exposure at 1100°C in water vapor

the degradation of the bulk materials.

Back-scattered electron micrograph of the cross-section of the as-received CMC and post-exposed The CMC at 1100°C for 1000 and 1500 hrs are presented in Fig. 9. Progressive materials degradation due to loss of Si from the fiber is evident from the dark regions surrounding the fibers as seen from insets in Fig. 9(b) and (c).

6. CONCLUSION

Recently Non-destructive evaluation(NDE) techniques used for lifetime prediction and life-remain assessment of TBCs. Both Photo-stimulated luminescence spectroscopy (PSLS) and Electrochemical impedance spectroscopy(EIS) were introduced along with selected results in addition, TBC specimen preparation for TEM analysis by Focused ion beam(FIB) was demonstrated along with selected microstructural observations, carried out by TEM and STEM. These results can provide better understanding of TBC failure mechanisms and promote more efficient application of TBCs.

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