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Fourier transform infrared reflection absorption spectroscopy and microspectroscopy, a tool to investigate thermally grown oxide scales

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Abstract

The main goal of this work is to show the interesting contribution of reflectance infrared spectroscopy to determine the composition of oxide films on metal surfaces. Illustration is reported on oxidation of α_2-TiAl (Ti75-Al25 at.%) and γ-TiAl (Ti50–Al50 at.%) alloys, carried out at 650 °C under laboratory atmosphere. Reflectance infrared spectra were recorded on an FTIR 710 Nicolet spectrophotometer, equipped with a Nicolet IR plan microscope. The knowledge of the infrared optical constants makes it possible to predict the infrared reflection spectra of different thin layers. As there is a lack of data in literature, theoretical calculations have been made in order to study experimental spectra. To illustrate these computations the first band observed for a thin film (200 nm) of Al_2O_3 is the higher longitudinal optical (LO) mode, the position of which is 920 cm^{-1} for α-Al_2O_3, 930 cm^{-1} for γ-Al_2O_3 or a broad band at 980 cm^{-1} for amorphous Al_2O_3. In the case of TiO_2/alloy system, the LO mode moves from 830 cm^{-1} for rutile TiO_2 to 880 cm^{-1} for anatase TiO_2. A peak fit program was applied to the spectra in order to extract each oxide contribution. The position of the fitted single absorption bands makes it possible to identify the different oxides. The oxide grown on α_2-TiAl phase, consists of α-Al_2O_3 and rutile TiO_2 (24 h to 500 h of oxidation treatment), γ-Al_2O_3 and rutile TiO_2 for 1000 h of oxidation treatment. Chemical maps reveal heterogeneous distribution of the oxides in the layer. A detailed surface characterization showed that the surface was principally covered with α-Al_2O_3 and locally with an Al_2O_3/TiO_2 mixture. In the case of γ-TiAl oxidation, the oxide film consists of α-Al_2O_3, γ-Al_2O_3 and rutile TiO_2 mixture. FTIR spectroscopy provides important information about amorphous, poor or well crystallized materials when X-ray diffraction is only convenient for crystallized phases.

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1. Introduction

The deterioration of alloys which occurs in air at elevated temperature is often complex and it is important to characterize oxides, especially at the beginning of the oxidation. Several tools have been used to identify the different types of oxides in the thermally grown scales as Scanning Electron Microscopy (SEM), X-ray diffraction to identify crystallographic phases or Transmission Electron Microscopy to observe alumina phase morphology. Other techniques like X-ray photoelectron spectroscopy, Raman spectroscopy or luminescent spectroscopy are available [1–6].

For a better understanding of the oxidation behavior of Ti–Al alloys, knowledge of the chemical and physical properties of the oxide layer compounds formed at low temperature is necessary. From Scanning Electron Microscopy analysis, it follows that the oxidation of TiAl alloys generally leads to a complex scale with a layered structure consisting of an outer layer of mainly TiO_2 while an inner layer was composed of a mixture of TiO_2 and α-Al_2O_3.

The main goal of this work is to show the complementary contribution offered by reflectance infrared spectroscopy (IRRAS) to determine the composition of oxide films on metal surfaces. The knowledge of the infrared optical constants makes it possible to predict the infrared reflection spectra of different thin layers.

2. Experiments

The α2-Ti_3Al and γ-TiAl polycrystalline substrates were grown at the ONERA by arc fusion under argon atmosphere. Their bulk composition (at.%) was measured to be $Ti_{75}Al_{25}$ and

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$Ti_{45.5}Al_{55.5}$ for the α_2 and γ phases, respectively. Annealing at 1400 °C for 4 h was performed on γ-TiAl in order to eliminate the dendritic inclusions of $\alpha_2+\gamma$ observed by SEM after synthesis. Samples (20 × 8 × 3 mm) were cut by spark-machining. Their surfaces were prepared by mechanical polishing (1000 grit SiC paper then 6 μm diamond paste). Afterwards, the samples were cleaned ultrasonically with ethanol.

Isothermal oxidation experiments were performed at 650 °C for 24, 168, 500 and 1000 h under laboratory atmosphere.

Total reflectance was measured in the 200–2500 nm wavelength range by the use of a double beam Perkin Elmer Lambda 9 spectrophotometer equipped with an integrating sphere. The recordings of reflectance were performed at near normal incidence (8°).

Optical data, refractive index and absorption coefficient, of TiAl alloys were obtained with a spectroscopic infrared ellipsometer SE900 from SENTECH. Oxide layer composition has been made by glow discharge optical emission spectroscopy (GDOES). GDOES used in this work is JY 5000 RF manufactured by JOBYN-YVON. Each profile analysis has been obtained after a purging time of 3 min under (Ar-CH_4) atmosphere to remove residual atmospheric nitrogen from the plasma compartment. Cross section of samples was observed by scanning electron microscope SEM DSM 982 Gemini under 15 keV.

Reflectance infrared spectra were recorded on an FTIR 710 Nicolet spectrophotometer, equipped with a reflectance accessory for near grazing incidence of 80°, and a Nicolet IR plan microscope at the external port. The microscope was equipped with a video camera and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector.

The spectral point by point mapping of the surface of the specimens was done in a grid pattern with the use of the computer controlled microscope stage and Omnic Atlus microscope software in reflectance mode.

3. Results and discussions

3.1. Computation of reference spectra

Interpretation of reflectance spectra is more difficult than interpretation of transmission spectra since the effects of radiation incidence angle, optical constants of surface compounds, and phase changes during the reflection process are critical considerations in reflectance spectroscopy. In counterpart, no sample preparation is required and non destructive analysis is possible. Films can be studied directly on the metal surface, thus minimizing possible structural change caused by operations such as electron bombardment or high-vacuum pumping at elevated temperatures. In order to study the spectra, theoretical calculations have been made with the infrared optical constants (or with the dielectric constants) obtained from literature. The complex expression of the specular part of the reflectance can be calculated by considering a thin film of dielectric material on an infinitely thick substrate [7,8].

The calculations utilize a physical value of the oxidation layer like the thickness. The measurement of film thickness using reflected light is a well-established process. This technique is dependent upon the interference pattern resulting from partial reflection/transmission through two partially reflecting surfaces.

In the case of a thin dielectric film on the metallic substrate, both the top and bottom surfaces of the film reflect light, with the total amount reflected being dependent upon the sum of these two reflections. Furthermore, these two reflections may add together constructively or destructively depending upon their phase relationship. This phenomenon is due to the wavelike nature of light, with the phase relationship determined by the difference in optical path lengths of the two reflections. The resulting interference fringes can be used to determine the thickness of the probed film, assuming that refractive index and angle of incidence are both known. Film thickness can thus be calculated using the following expression [9]:

$$d = \frac{m}{2D_n\sqrt{n^2 - \sin^2\theta}} \qquad (1)$$

where: d = film thickness, m = number of fringes in wavenumber region used, n = refractive index, θ = angle of incidence, D_n = wavenumber region used (ν_1–ν_2; cm^{-1}).

The spectra display interference fringes, more pronounced for the γ-TiAl samples than the α_2-TiAl (Fig. 1). The interference fringes become less pronounced due to scattering from a rough surface, the macroscopic surface topography of the γ-TiAl samples are much smoother than the surfaces of α_2-TiAl thermally oxidized samples.

The refractive indices which can be used to evaluate the oxide layer thickness are dependent on the structure and the

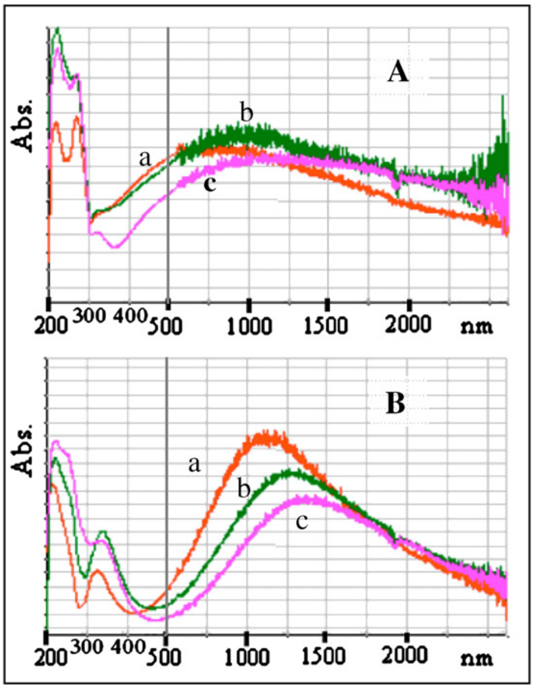

Fig. 1. Near normal absorbance in the UV–Vis–NIR range (scale change at 500 nm) of α_2-Ti_3Al (A) and γ-TiAl (B) samples after oxidation treatment during: a)168 h b) 500 h c) 1000 h.

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