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Optical fluorescence spectroscopy for identification of minor oxide phases in alumina scales grown on high temperature alloys

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Abstract

In the present study laser induced fluorescence optical spectroscopy (LIFOS) has been used for characterization of alumina based surface scales formed during oxidation of high temperature alloys. Prior to the analysis of oxide scales, a set of reference data has been obtained on single crystals of α-Al_2O_3 and several oxide phases ($Y_3Al_5O_{12}$, $YAlO_3$ and $MgAl_2O_4$) frequently found as minor constituents in the alumina scales. A number of effects, which can affect the fluorescence spectra has been studied on the single crystals. Hence the analyses were carried out at different temperatures in the range of 77 to 303 K, at different laser powers and using two primary laser wavelengths.

The reference spectra were used as a basis for phase analyses of the oxide scales formed on FeCrAl-alloys during air oxidation at 1200 °C. The spectrometry results of the oxide scales were compared with the data obtained with SEM and XRD. Although identification of the minor alumina scale phases using LIFOS appears to be possible, care should be taken when interpreting the results. The main reason is by far stronger fluorescence from alumina, however other important effects are also discussed, which are responsible for discrepancies between the spectra obtained from “ideal” reference specimens and those from the minor phases in oxide scales.

Keywords: YAG; YAP; Alumina; Luminescence spectroscopy; Oxidation; FeCrAlY

1. Introduction

Most metallic materials designed for application at and above 1273 K rely for their resistance against oxidizing environments on the formation of protective alumina films or scales [1]. The alumina scales forming on high-temperature alloys at these temperatures generally possess an α-Al_2O_3 structure [1]. In addition to the scale-forming element Al, the high temperature alloys are frequently doped with minor (up to 0.1 wt.%) alloying elements such as Y, La, Ti, Zr etc. These elements, termed Reactive Elements (RE) tend to be incorporated in the alumina scale and have a profound effect on the scale protective properties, such as adhesion to the metal substrate and (to a less extent) the scale growth rate [2]. In the alumina

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scales the REs have been found to form their own oxides or mixed oxides e.g. $Y_3Al_5O_{12}$, which frequently precipitate at the alumina grain boundaries [3]. In most cases the alloy compositions also contain unavoidable impurities, such as Mg, which alike intentionally added REs have a tendency for incorporation in the alumina scale, thereby forming oxide phases such as $MgAl_2O_4$ [4,5].

Laser Induced Fluorescence Optical Spectroscopy (LIFOS) has been recently employed by many researchers for identification of the various crystallographic modifications of alumina formed during high temperature oxidation of the metallic materials [6–9]. This method not only allows a fast, non-destructive identification with a high lateral resolution of different aluminas, but also measurements of the mechanical stresses arising in the scales upon cooling from the oxidation temperature due to thermal expansion mismatch between the oxide and metal [6,10].

There have been several studies concerning R-line luminescence from Cr^{3+} doped α/θ-Al_2O_3 [6–14] and oxide phases such as $Y_3Al_5O_{12}$ (Yttrium–Aluminium garnet YAG) [15–21], $YAlO_3$ (Yttrium–Aluminium perovskite YAP) [22–25], $MgAl_2O_4$ (Magnesium–Aluminium spinel) [26–30] etc. In all these phases the R-lines Cr^{3+} luminescence is related to substitution of the native oxide cation in octahedral coordination by Cr^{3+} ions [14,21,30]. The exact shape of the fluorescence spectra can be described by 11 parameters [11]. Moreover, a number of additional factors listed below can affect the Cr^{3+} luminescence spectra [6,11,14,16,22,25,26,31,32]:

a) concentration of Cr^{+3} doping ions,
b) presence of other doping ions,
c) presence of various types of defects in the crystal structure,
d) mechanical stresses,
e) temperature,
f) excitation wavelength.

All these factors can cause significant shifts of the characteristic peaks, changes in the peak intensity and FWHM (full width at half maximum) of the Cr^{3+} fluorescence bands. As a result, the interpretation of the spectra obtained from oxide scales formed during oxidation of alloys is frequently difficult and data reported by different laboratories tend to show substantial discrepancies.

In the present study, LIFOS has been used for investigation of Cr^{3+} fluorescence in single crystals of α-Al_2O_3, $MgAl_2O_4$, YAG, YAP. The effect of temperature in the range of 77 to 298K, of the excitation wavelengths and of the laser power on the fluorescence spectra of the single crystals have been studied (Part I). The spectra obtained from the single crystals were compared with those measured in oxide scales formed during high temperature oxidation of FeCrAl alloys, containing minor additions of Y and Mg (Part II). Besides the oxide scales were characterized by SEM and XRD. Differences between the spectra measured on the single crystals and oxide scales are discussed in terms of implications for the analysis methodology and interpretation of the spectral data obtained on the scales.

2. Experimental

The single crystals of α-Al_2O_3, $MgAl_2O_4$, YAG and YAP procured by the Czochralski method were supplied by MaTeck GmbH. Samples were cut by diamond saw in the form of square coupons of $10\times10\times1$ mm in size in pre-defined crystallographic directions and subsequently mirror polished.

The investigated oxide scales were formed by high temperature exposure of a commercial and a model FeCrAl alloys respectively. The chemical compositions of the two alloys are given in Table 1. Coupons in size $20\times10\times1$ mm were cut from the wrought alloy sheets, polished to mirror surface finish and ultrasonically cleaned in a detergent prior to oxidation. The isothermal and discontinuous oxidation exposures were performed in a resistance heated furnace at 1200 °C in laboratory air with air cooling of the specimens after the high-temperature exposure.

For analysing the chemical and phase compositions of the formed surface scales the specimens after exposure were studied by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX — *Leo 440/Oxford INCA*) and X-ray diffraction (XRD — *Siemens D5000*). For the fluorescence measurements a *Dilor HR800* spectrometer equipped with a controlled temperature stage chamber (Linkam THMS 600) was used. The fluorescence properties of