Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia 59 (2011) 2723–2730

Acta MATERIALIA

www.elsevier.com/locate/actamat

Experimental and ab initio study of vibrational modes of stressed alumina films formed by oxidation of aluminium alloys under different atmospheres

W.W. Peng [a,c], P. Roy [a,*], L. Favaro [b], E. Amzallag [b], J.B. Brubach [a], A. Congeduti [a], M.A. Guidi-Cestelli [d], A.M. Huntz [b], J. Barros [a], R. Tétot [b,*]

[a] *Synchrotron SOLEIL, L'Orme des Merisiers, BP 48, Gif-sur-Yvette Cédex F-91192, France*
[b] *ICMMO (LEMHE), UMR 8182 CNRS, Université Paris-Sud 11, Orsay F-91405, France*
[c] *Institute of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China*
[d] *Laboratori Nazionali di Frascati—INFN, Via E. Fermi 40, 00044 Frascati (Roma), Italy*

Received 5 August 2010; received in revised form 30 November 2010; accepted 4 January 2011

Abstract

A comprehensive study of the alumina films formed from heating Fe_3Al under different oxidizing atmospheres is conducted using Fourier transform IR spectroscopy in the complete mid-IR and far-IR ranges on the IR/THz synchrotron beamline of the SOLEIL facility. In addition, density functional theory is used to simulate α-alumina vibrational spectra for both bulk structure and thin slabs. The experimental absorbance spectra of films extend in a narrow energy range and present characteristic features similar to crystalline alpha-alumina (corundum structure). Moreover, the films spectra show a very good general agreement with the ab initio calculations for the alpha-alumina bulk structure. Nevertheless, in addition to transverse vibrations, extra modes, compared to the sapphire spectrum, can originate from either remnant transition alumina or from intense longitudinal-like modes present in the thin slab simulations. Furthermore, the dependence of film dynamical properties on oxygen and water partial pressures is addressed, and the strain induced by the film growth on the metal substrates is evaluated. This combination of simulated and measured absorbance spectra allows the precise determination of the crystalline nature of alumina thin films grown by oxidation under different atmospheres.
© 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Alumina; Thin films; Stress; Infrared spectroscopy; Ab initio simulations

1. Introduction

The applications of aluminium oxide thin films range from protection against friction and corrosion to optical applications, because of their high wear resistance. Moreover, these films are increasingly finding their way into micro-electromechanical systems as dielectric layers to prevent electrical shorting. The most stable crystalline phase, α-Al_2O_3 or sapphire, is exceptionally hard and optically transparent from the near-IR through the visible region into the UV, and hence it has a large and still increasing number of applications. In the IR range, this crystal presents several absorption characteristics resulting from AlO_6 octahedron deformations which allow α-Al_2O_3 to be distinguished from other metastable forms of alumina, such as γ-, κ- or θ-Al_2O_3, in which both AlO_6 octahedron and AlO_4 tetrahedron are present [1]. The spectral signatures of both α-Al_2O_3 and metastable forms have been thoroughly addressed in the literature using both experimental and theoretical simulations [2–5]. Some optical properties of alumina films prepared by different techniques have also been investigated [6–8].

Because of its importance for technological applications as a protective barrier against corrosion, several reports discuss the formation of aluminium oxide thin films from

* Corresponding authors.
E-mail addresses: pascale.roy@synchrotron-soleil.fr (P. Roy), robert.tetot@u-psud.fr (R. Tétot).

1359-6454/$36.00 © 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2011.01.010

oxidation of aluminium alloys [9–12]. The dependence of the structural and mechanical characteristics of the layers on oxygen partial pressure is well known, but its influence on the formation of multiple alumina phases remains an open question. Huntz et al. [11,12] exploited the deflection technique, a technique based on the curvature of an asymmetrical film during oxidation at high temperatures, to determine the influence of oxygen and water partial pressure in the formation of alumina from alumina forming steels. This technique suggested that, although the transformation rate is not strongly modified by the atmosphere in the furnace, the alumina layer forming varies: α-alumina forms directly in air, while in a low oxygen content atmosphere, a metastable form of alumina develops first and transforms into α-alumina. Moreover, it was shown that a compressive stress is induced by the growth of transition alumina, while the transformation to α generates a tensile stress due to a volume contraction of ~14% [10]. Other strong differences in the morphology and microstructure were also evidenced using imaging transmission electronic microscopy (TEM), but the formation of metastable phases of alumina under low oxygen pressures could not be established. Despite the suitability of vibrational study [4,5] for determining the nature of the different phases of alumina, the IR absorption of alumina films formed by oxidation remained unexplored because of the lack of sensitivity of widely available laboratory set-ups. Using the high brilliance of synchrotron radiation can help circumvent this limitation [13]. Specifically, in the present study the vibrational characteristics of the crystal structure of alumina films are investigated in the complete IR range. In turn, this experimental vibrational study is combined with density functional theory (DFT) simulation to allow for the first measure of the crystalline structure of alumina thin films formed by oxidizing Al alloys. Furthermore, the dependence of film dynamical properties on oxygen and water partial pressure is addressed, and the strain induced by the film growth on a metal substrate is evaluated.

2. Experimental and modelling technique

2.1. Experimental

2.1.1. Metal substrate and forming of alumina layers

The alumina layers were formed by oxidation of the Fe_3Al intermetallic alloy at 1000 °C under different atmospheres. All details can be found in Huntz et al. [11]. The main features are reported here. The substrate is a Fe–28Al–5Cr alloy doped with 0.01 at.% Zr with traces of B, C, N, O and S (⩽0.04 at.%) [11]. With this composition, it has been demonstrated that only aluminium oxidation occurs, and no iron or chromium oxides are formed [14,15]. All Fe_3Al samples used (~10 × 10 mm, 0.3 mm thick) were oxidized in a furnace with a controlled atmosphere, following the temperature cycle of heating to 1000 °C at 400 °C h^{-1}, held at 1000 °C for 4 h, then cooled to 450 °C at 300 °C h^{-1} and finally cooled to room temperature [11]. Three different oxidation atmospheres were used: synthetic air, argon (both from alpha gas) and an atmospheric pressure mixture of argon and H_2 ($pH_2 = 10^{-4}$ atm). The estimated partial pressures pO_2 and pH_2O at 1000 °C for the three atmospheres are reported in Table 1. These processes give rise to ~1-μm-thick alumina layers almost independent of the gaseous atmospheres used. Over the IR investigated area, the thickness is expected to vary by less than 5%. The oxidation of metal samples was followed by means of in situ deflection tests and thermogravimetric experiments. The deflection technique is based on the measurements of the deformation of an elongated metallic surface substrate covered on one side. These two techniques are sensitive to change in layer stress induced by either phase transformation or mass gains during oxidation, respectively. The analysis using deflection, thermogravimetry and TEM imaging suggests differences in the phase transformation pattern and in the microstructure of the film, depending on the oxygen and water pressures, although at the end of the heating cycle all three samples are mainly composed of α-Al_2O_3. Moreover, under a low oxygen atmosphere, growth of transition alumina occurs and, at 700 °C, the transition alumina transforms into α-alumina. In air, the oxidation is less efficient at low temperatures, and the alumina grows mostly into its stable α-Al_2O_3 from 800 °C. Information on the stress induced by the oxidation and phase transformations could also be extracted from the deflection measurements. This suggests that the direct formation into α-alumina gives rise to a tensile stress. In contrast, the formation of initial metastable alumina which induces compressive stress will be partially removed through the subsequent formation of α-Al_2O_3 at higher temperature. This, in turn suggests that all three alumina layers may present vibrational absorption characteristic of a sample under stress. Moreover, the microstructural observations show that the films are polycrystalline and randomly oriented [11]. Furthermore the presence of water in the atmosphere during oxidation favours the growth of needle-like structures of high interface to volume ratio [16].

2.1.2. IR measurements and set-up

IR spectra were obtained by the Fourier transform infrared (FTIR) technique using a Bruker IFS55 interferometer at 4 cm^{-1} resolution. The apparatus was adapted to work using either synchrotron radiation from the third-generation synchrotron radiation source SOLEIL (in the far-IR range) or globar (in the mid-IR range) as continuum sources. In addition to using intense synchrotron radiation from the optimized edge emission type

Table 1
Oxygen and water partial pressures in the three atmospheres used for oxidation of Fe_3Al (according to Huntz et al. [11]).

Pressure (atm)	Air	Argon	Ar–H_2–H_2O
pO_2	0.21	$\sim 10^{-6}$	8×10^{-18}
pH_2O	$\sim 10^{-6}$	$\sim 10^{-6}$	5×10^{-6}

Download English Version:

https://daneshyari.com/en/article/1447347

Download Persian Version:

https://daneshyari.com/article/1447347

Daneshyari.com