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Chemical, morphological and nano-mechanical characterizations of Al_2O_3 thin films deposited by metal organic chemical vapour deposition on AISI 304 stainless steel

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Abstract

Amorphous alumina coatings of different thickness have been deposited on AISI 304 stainless steel substrates by MOCVD in a hot wall reactor at 380 °C under O_2/H_2O atmosphere. The used aluminium precursor was the high volatile and easy to prepare dimethyl-aluminum-isopropoxide. Selected films were annealed in N_2 and O_2 atmosphere at 500 and 700 °C to evaluate the effects of the thermal treatments on the morphology and on the nano-mechanical properties of the coatings. X-ray diffraction and Rutherford backscattering spectroscopy measurements indicated that both the as grown and annealed films were amorphous and very pure with the correct Al_2O_3 stoichiometry. The surface morphology, investigated by atomic force microscopy, was free of cracks with a roughness of the films that increases with deposition time and with annealing in oxygen atmosphere. The hardness and the elastic modulus of the films and of the AISI 304 stainless steel substrate were measured by load-depth nano-indentation tests. The results highlighted a significant increase in the Berkovich hardness of the coated samples compared to that of the bulk AISI 304 stainless steel.

Keywords: Alumina coatings; MOCVD; Wear protection; Hardness; Nano-indentation

1. Introduction

Alumina has gained a great attention as a coating material. This interest is based on its high performance as functional material in wear [1] and corrosion [2] protection, in thermal barrier [3] applications and in microelectronics [4]. In particular, because of the excellent properties such as chemical inertness, corrosion resistance, good mechanical strength, high hardness, and transparency, Al_2O_3 is a good material for the wear protection of metal surfaces [5]. In the case of stainless steel substrates, the deposition temperature must not exceed the tempering temperature in order to avoid the softening process of the steel. For that reason hard α-Al_2O_3 films are not suitable for the coating of stainless steel as they can be obtained by CVD [6] at high substrate temperatures (>900 °C). Instead, amorphous Al_2O_3 coatings can be obtained at lower temperatures using different deposition processes such as r.f. magnetron sputtering [7], plasma deposition [8], physical vapour deposition [9], ion beam assisted deposition [10], sol–gel [11] and MOCVD. The last is particularly interesting because of its large potential for mass production and the ability to coat complex shaped samples. However, for its successful implementation the development of new highly volatile non-pyrophoric liquid sources is advisable to make the whole process more controllable and safer. So far, several aluminium precursors have been proposed for MOCVD of alumina films [12], however, the most common aluminium sources are homoleptic aluminum compounds such as trimethylaluminum [13], aluminium-tri-isopropoxide [14] and aluminum-tri-sec-butoxide [15]. These sources present several important drawbacks; the alkyls are

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highly pyrophoric while the alkoxides are solid and have low volatility. On the contrary, a good compound with a high volatility and a lower dangerousness is the heteroleptic dimethyl-aluminium-isopropoxide. With this precursor, amorphous Al_2O_3 depositions occur at moderate temperature (<400 °C) in a atmosphere of oxygen mixed with water vapour [16]. The obtained films are crack and pore free and present good surface uniformity.

For the wear protection of the alumina coatings it is also important to characterize the nano-hardness of the obtained deposit as the surface and near-surface mechanical properties of thin films can be critical for their final performances. In this regard, several studies concerning the deposition and the characterization of protective alumina coatings on stainless steel substrates have been reported [11,17–20], but most investigations concern alumina used as anticorrosion coating and, to our knowledge, only few data have been reported about the micro- and nano-hardness of the obtained coatings of the system Al_2O_3/stainless steel [21,22].

Therefore, in the present work, we report the results of an investigation of the compositional, morphological and nano-mechanical properties of alumina films obtained by MOCVD on AISI 304 stainless steel, using the volatile dimethyl-aluminium-isopropoxide as aluminum source. The films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS) and profilometer scans. The nano-hardness and elastic properties of both the film and substrate were evaluated using the load-depth curve measured by depth sensing indentation technique and finally, the study of the effects of different annealing conditions on the surface morphology and nano-mechanical properties of the coatings have been considered.

2. Experimental

Alumina coatings were grown in a horizontal hot wall reactor at a reduced pressure (2 Torr) at a temperature of 380 °C using dimethyl-aluminium-isopropoxide. The carrier gas was nitrogen (10 scc/min) flowing through the bubbler containing the aluminium source, thermostatically set to a temperature of 10 °C, while the reactant gas ($O_2 + H_2O$ vapour mixture, 200 scc/min) was introduced into the main flow, after the precursor evaporation zone, in close proximity to the entry of the reaction chamber, in order to avoid the decomposition of the precursor. The substrate used in the experiments was AISI 304 stainless steel. The stainless samples were ground on SiC paper with a final size of 4000 grit and polished, and all samples were cleaned and degreased with hot trichloethylene. Annealing of the samples was performed in the same reactor in an N_2 and O_2 atmosphere.

RBS measurements were performed at the CN accelerator at LNL-Legnaro, Italy, using a 2 MeV He^{2+} beam. Fixed random spectra were recorded and the film stoichiometry and thickness obtained by simulating the spectra with the RUMP software. ERDA measurements were performed using the HVEC 2.5 MeV AN 2000 accelerator, with a 2.2 MeV He^+ beam, in order to investigate Hydrogen content. AFM characterization of surface morphology was performed with a DME Dualscope™ instrument using silicon cantilever tips with nominal tip radius of 10 nm in non-contact mode. X-ray diffraction measurements were made with a Philips PW1830 powder diffractometer using Cu Kα radiation. Film thicknesses were determined using a Tenkor P-10 surface profiler by analysing the film height steps on partially masked samples. The obtained thickness values were cross-checked for selected with the values obtained from RBS spectra.

Nano-indentation was used to determine film hardness and elastic modulus using a Nano-test 600 instrument from Micromaterials Ltd, with a Berkovich (three-sided pyramidal) diamond indenter. The following peak loads were used, for each sample: 2.5, 5, 7.5, 10, 15, 17.5, 20, 30, 40, 50, 65, 80, 100, 120, 160, 200 mN with loading rate = unloading rate that were varied in proportion to the peak loads starting at a value of 0.1 mN/s for the 2.5 indentations, while common experimental conditions as initial (contact) load 0.05 mN and holding period at peak load 10 s were used for all the measurements. The indentations were repeated at least five times at each load on different regions of the sample surface apart 50 μm. The hardness and reduced modulus have been determined from these indentation curves using a method originally proposed by Oliver and Pharr which fits a power-law function to the unloading curve [23]. The Young's modulus of the samples has been calculated from the reduced modulus via the equation which includes the effects of non-rigid indenters on the load-displacement behaviour: $1/E_r = (1 - \nu^2)/E + (1 - \nu_i^2)/E_i$ where E and ν are the Young's modulus and Poisson's ratio for the specimen, respectively; E_i (1141 Gpa) and ν_i (0.07) the corresponding indenter quantities; and E_r is the reduced modulus which has been obtained by the initial slope of the unloading curve.

3. Results and discussion

3.1. Coating characterization

Both the as grown and the annealed films were amorphous as determined by X-ray diffraction. From RBS analysis (see Fig. 1) only Al and O film signals, floating on a background of Fe and Cr from the substrate, were detected and a stoichiometry of Al:O ∼ 2:3 was found. No carbon contamination was detected within the RBS detection limit that we estimate to be about 2 at.%. Moreover, from ERDA measurements also the hydrogen content of the films was found to be below 2 at.%. As well together with the absence of C impurities this indicates that organic residues that may be produced during the precursor decomposition process, fully desorbs from the growth surface.