Materials Chemistry and Physics 143 (2014) 1446–1451

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Pulsed laser deposition of alumina coating for corrosion protection against liquid uranium

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HIGHLIGHTS

- Alumina films deposited on stainless steel via pulsed laser deposition (PLD) technique.
- PLD alumina films investigated as potential corrosion protective coatings.
- Deposited coatings have been characterized in terms of their microstructure and crystalline phase.
- Corrosion resistance of coatings against liquid uranium was tested.
- Results suggest PLD alumina films have a promising potential for containment of molten uranium.

ARTICLE INFO

Article history:
Received 25 February 2013
Received in revised form
24 October 2013
Accepted 29 November 2013

Keywords:
Coatings
Ceramics
Thin films
Corrosion

ABSTRACT

Alumina coatings find wide applications as tribological coatings and as corrosion protective coatings for structural materials against chemical attack. We have investigated alumina coatings deposited on Stainless Steel (SS) substrates via pulsed laser deposition (PLD) technique. Characterization tests performed on these coatings including their compatibility with liquid uranium suggests alumina to be a potential candidate as a coating material for handling and containment of liquid uranium. We present here results of our detailed parametric study including dependence of average mass removal rate on laser fluence and ablation geometry and average deposition efficiency during PLD. These measurements provide vital inputs facilitating proper choice of process parameters for PLD runs. Deposited coatings have been characterized in terms of their microstructure, surface profile, adhesion to substrate, crystalline phase and corrosion resistance against liquid uranium. Our PLD based alumina coatings have shown a high degree of compaction and excellent corrosion resistance to molten uranium even upto a temperature of 1165 °C.

1. Introduction

Among various physical vapor deposition techniques, Pulsed Laser Deposition (PLD) is a simple and convenient method for deposition of films and coatings [1]. In this technique, focused laser radiation is used to vaporize material from a target and this ablated vapor is then deposited on a desired substrate [2]. The evaporation process of the target can be either thermal or non-thermal determined largely by the laser conditions. PLD technique has numerous advantages over other conventional techniques of film deposition. This technique enables deposition of coatings having precise stoichiometry and crystalline purity, offering at the same time, flexibility and control over the deposition rate [1,2]. Properties such as surface morphology, crystalline phase and density of defects in deposited film can be tailored by controlling PLD process parameters such as, laser wavelength, fluence, pulse duration and pulse repetition rate, distance between substrate and target and the environment of deposition [3,4]. In addition, PLD technique allows facile process automation and is also environment friendly [5]. In PLD process congruent removal of material from the target leads to preservation of stoichiometry in the deposited film. Thus PLD is widely used for deposition of chemically inert and complex oxide films with accurate stoichiometry [1,6]. However, PLD technique does have its limitations too. Narrow angular spread and inhomogeneous flux of species within the ablated plume restricts scaling up of PLD technique for deposition of large area uniform coatings [7]. A technical difficulty with PLD arises on account of presence of macroscopic particulates (size ~ few micron) in the deposited film

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http://dx.doi.org/10.1016/j.matchemphys.2013.11.063

due to splashing effect [1,7]. Despite these drawbacks researchers have developed techniques to deposit large area coatings (up to 200 mm diameter substrates) having reduced density of macroscopic particulates [8].

Refractory materials, organic compounds, metals, dielectrics, semiconductors and superconductors, deposited as thin films over a wide range of substrates serve many applications. Thin film dielectric coatings are deposited on glass substrate for optical components such as optical wave-guides, reflecting and anti-reflecting coatings [9]. Various coatings on structural components provide protection against harsh environmental conditions. Ceramic coatings used in automobile industry lead to economical and ecological benefits through reduced weight of the components and enhanced service life of various parts of the vehicle [10]. Also, in nuclear technology corrosion resistant coatings are necessary for containment and handling of highly corrosive liquids such as molten uranium, actinide wastes, and liquid lithium blankets in fusion reactors [11,12].

Alumina is an excellent ceramic material, which is employed in the form of coating for a wide range of applications owing to its properties such as high hot hardness [13,14], high mechanical strength [13], high melting point (2053 °C) [15] and good oxidation resistance [13,16]. Alumina also shows very good corrosion resistance against chemical attack [17]. Many polymorphic phases of alumina exist [18]. Of these polymorphs only α-alumina is thermodynamically stable above 1050 °C and it is also the densest amongst all polymorphs [19]. Therefore, coatings grown of polymorphs other than α-alumina catastrophically fail to provide corrosion protection at temperatures above 1050 °C as irreversible conversion of the unstable polymorphs to the densest α-alumina occurs at these elevated temperatures resulting in formation of cracks and pores in the coating. These cracks and pores formed in the coating due to phase transformation allow penetration of the corrosive chemicals to the structural material. Hence for high temperature (above 1050 °C) corrosion protection application, alumina coating having pure α-phase is essential.

In the study reported here, coatings of α-alumina have been deposited on surface roughened stainless steel (SS) substrates, employing PLD technique at room temperature and ambient atmospheric pressure. The deposited coatings have been characterized in terms of their surface profile, surface microstructure, adhesion to substrate, crystalline phase and corrosion resistance against molten uranium. Parametric investigation of PLD process including dependence of mass removal rate on laser fluence and ablation geometry, variation of ablation depth with laser fluence and average deposition efficiency (ratio of the mass deposited on substrate to mass ablated from target during PLD) during the PLD runs have also been studied. Results of our investigation enable proper choice of PLD process parameters facilitating deposition of alumina coatings demonstrating excellent corrosion protection capability.

2. Experiment

For our PLD studies sintered alumina pellets (diameter 10 mm and thickness 10 mm) have been used as targets and surface roughened SS discs as substrates. Surface roughening via sand-blasting of substrate improves mechanical adhesion of the coating with substrate surface. Both, the target and substrate were mounted on individual translational stages in order to have independent translation of both the target and the substrate maintaining, at the same time, a constant separation between the two. In this manner, deposition of coatings of uniform thickness over large area of the substrate was achieved. A focused beam of Nd:YAG nanosecond (ns) laser delivering laser pulses typically having pulse energy in the region of 18–20 mJ, pulse duration of 6 ns (FWHM) at 10 Hz pulse repetition rate and a wavelength of 532 nm has been used to ablate the target. Evaporation of material from the target occurs largely normal to the target surface. Therefore, the target was irradiated with the laser beam incident at an angle of 45 . In this configuration, spatial overlap between the incident laser beam and the vapor plume could be reduced, hence restricting attenuation of the incident laser beam by the plume [20,21]. The substrate and the target surface were maintained parallel to each other, separation between the two being ~3 mm. A schematic of our experimental setup is shown in Fig. 1.

PLD technique for film deposition typically employs high vacuum conditions. However, our studies involved PLD carried out in atmospheric air. Not being restricted by a vacuum chamber meant greater experimental flexibility and technical advantages when coating substrates having complex geometrical shapes [22]. However, PLD in air results in restricted plume length on account of collisions between the vaporized particles and ambient atmosphere which consequently limits the maximum allowable separation between substrate and target. Separation between target and substrate being restricted lead to critical demands on precise scanning movement of the substrate ensuring at the same time, that the incident laser beam does not get blocked during scanning of the substrate. Therefore, substrate could be moved only over a distance of ~3 mm in horizontal direction although movement in vertical direction had no such restrictions. In the present work, typically an area of ~0.15 cm^2 was coated at a time. By sequentially coating a portion of the substrate and then rotating the substrate to access a fresh uncoated region, SS substrates having diameter of 5–6 mm could be completely PLD coated with alumina in our setup.

For different ablation configurations average mass removal rate as a function of laser fluence was systematically investigated and average deposition efficiency (ratio of the mass deposited on substrate to mass ablated from the target) averaged over 18,000 laser pulses was measured using a micro-balance with measuring accuracy of 10 μg. Microstructure of the deposited coatings and their crystalline phases were investigated using a Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) technique, respectively. Adhesion of the coating to the substrate was tested by adhesive tape test and scratch tests employing a diamond indenter of 200 μm diameter. Corrosion resistance of the deposited coating against molten uranium has been characterized using Differential Thermal Analysis (DTA) technique [23]. DTA signal, which is a measure of temperature difference between a reference sample and the test sample when subjected to identical thermal cycles, was recorded. Observed peaks and dips in DTA signal provide signatures of phase transitions and chemical reactions in the test specimen. A laser fluence of 11 J cm^{-2} has been typically employed for ablation of Al_2O_3 target and subsequent deposition of these ejected species on surface roughened SS substrates.

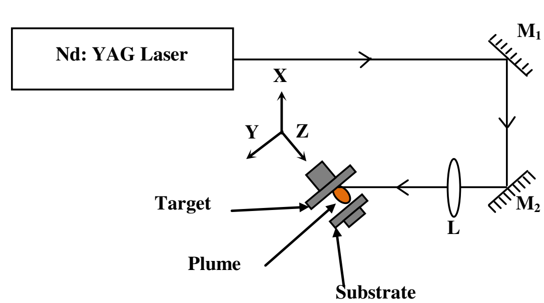

Fig. 1. Schematic of the PLD setup with folding mirrors M_1, M_2 and convex lens (L) having focal length of 50 cm. Target and substrate both have been translated in the *X*–*Y* plane while rotation is about *z*-axis.