Surface & Coatings Technology 240 (2014) 7–13

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Thermally activated transformations in metastable alumina coatings prepared by magnetron sputtering

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ARTICLE INFO

Article history:
Received 27 September 2013
Accepted in revised form 7 December 2013
Available online 15 December 2013

Keywords:
Alumina coatings
Metastable phases
Phase transformations
Differential scanning calorimetry
Sputtering

ABSTRACT

An as-deposited metastable structure of alumina coatings can be of essential importance for the transformation processes occurring in the coatings during their annealing. The present study focuses on thermal stability and phase transformations in magnetron sputtered alumina coatings with different as-deposited structures characterized by different ratios of an amorphous a-Al_2O_3 to crystalline γ-Al_2O_3 phase. Purely amorphous, purely γ-phase and γ-phase/amorphous coatings were investigated by a combination of differential scanning calorimetry (40 °C/min in air) and ex-situ X-ray diffraction analyses. Indentation testing and optical characterization were also carried out. In the coatings with a purely or partially amorphous as-deposited structure two exothermic transformations occurred. An a-to-γ transformation proceeded at ~900 °C while a γ-to-α transformation proceeded at ~1200 °C. In the crystalline γ-phase as-deposited coating the γ-to-α transformation was the only exothermic transformation observed at the same temperature of ~1200 °C. Independently of the as-deposited structure, the γ-to-α transformation was accompanied by the formation of the intermediate metastable θ phase without any detectable heat released. Measured changes in transformation enthalpies for the a-to-γ and γ-to-α transformations were close to each other while the activation energy was higher for the γ-to-α transformation. Hardness, effective Young's modulus and refractive index showed a tendency to increase with a decreasing amount of an amorphous phase in the coating.

1. Introduction

Machining of materials with low thermal conductivity, such as stainless steel or nickel superalloys, demands the use of cutting tools with an enhanced performance. Crystalline alumina coatings with high hot hardness and high chemical inertness are promising candidates for surface modification of these tools. Reactive magnetron sputtering, as a non-equilibrium deposition process, is a suitable method for the fabrication of alumina coatings at temperatures not exceeding 550 °C. Higher temperatures might be detrimental to high-speed steel substrates due to the softening of tempered steel.

Present trends in the research of reactive sputtering of crystalline alumina coatings include two areas: (i) the deposition of thermodynamically stable α-Al_2O_3 coatings at temperatures as low as possible and (ii) the deposition of metastable γ-Al_2O_3 coatings with thermal stability as high as possible. The formation of alumina coatings with the predominant α-Al_2O_3 phase at relatively low temperatures (≤650 °C) is still not commonly mastered and is limited to only special advanced magnetron sputtering techniques such as high-power impulse magnetron sputtering (HiPIMS) [1,2] and ac inverted cylindrical magnetron sputtering (ICMS) [3,4], or to sophisticated approaches such as an application of a Cr_2O_3 isostructural seed interlayer [5]. Wallin et al. [1] successfully deposited a well-crystalline α-Al_2O_3 phase by reactive HiPIMS at 650 °C on WC/Co substrates but Selinder et al. [2] observed by means of electron diffraction that this coating is of a two-phase (α + γ)-Al_2O_3 structure near the coating–substrate interface. Cloud et al. [3] prepared a pure α-Al_2O_3 coating even at 480 °C by reactive ac ICMS but only for the maximum coating thickness of 100 nm. Thicker coatings contained more γ-phase constituents. The application of a Cr_2O_3 seed interlayer aids the growth of α-Al_2O_3 at temperatures lower than 500 °C but only in combination with highly energetic bombardment of the growing coating under appropriate deposition conditions [5].

Although α-Al_2O_3 is the only thermodynamically stable phase of alumina, it is much easier to sputter nanocrystalline coatings with a metastable cubic γ-Al_2O_3 phase. This follows from the fact that γ-Al_2O_3 has a lower surface energy than α-Al_2O_3 and becomes energetically stable at surface areas greater than 125 $m^2\ g^{-1}$ at standard pressure and temperature conditions [6]. Comparable hardness and low work material affinity of γ-Al_2O_3 to α-Al_2O_3 coatings make them also attractive for high speed cutting. The limitation is, however, their thermal stability due to phase transformations resulting in a coating cracking. Hence, a few papers have been published on this topic recently. Eklund et al. [7] observed that all as-deposited alumina coatings with different fractions of the amorphous to γ-Al_2O_3 phase were transformed to α-Al_2O_3 between 1100 °C and 1150 °C during 1 h of annealing in air but the transformation paths depended on the phase fraction. Trinh

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http://dx.doi.org/10.1016/j.surfcoat.2013.12.004

et al. [8] found that annealing in vacuum for 5 h leads to the γ-to-α transformation in the coatings between 950 °C and 970 °C without any presence of an intermediate phase. The results of Edlmayr et al. [9] showed that the γ-to-α transformation in argon proceeds through a δ-Al_2O_3 intermediate phase and is shifted by about 100 °C to 1200 °C as the coatings are prepared with an ion bombardment. Bobzin et al. [10] demonstrated that thermal stability of γ-Al_2O_3 coatings is higher in vacuum (1200 °C) than in air (900 °C) during 1 h of annealing and can be controlled by choosing an interlayer.

In our previous work [11], we observed that an alumina coating with the γ-Al_2O_3 phase in the as-deposited state is thermally stable to 1000 °C even after 5 h of annealing in air. The γ-to-α transformation started at 1050 °C via the formation of an intermediate θ-Al_2O_3 phase which existed only in a narrow temperature range.

The present work is linked to our parallel paper [12], which is strictly focused on non-isothermal kinetics of solid-state processes in a purely amorphous a-Al_2O_3 and a purely crystalline γ-Al_2O_3 coating prepared by reactive magnetron sputtering. In this paper, we combine differential scanning calorimetry and X-ray diffraction to systematically investigate thermal stability and phase transformations in three metastable alumina coatings with different initial as-deposited structures prepared at variable discharge power and substrate temperature. Our intention is to identify all transformation processes in the coatings, correlate them with an initial as-deposited structure and extend knowledge in transformation phenomena in magnetron sputtered alumina coatings being attractive for the machining industry.

2. Experimental

Alumina coatings were prepared by reactive dc pulsed magnetron sputtering in an Ar + O_2 mixture using a dual magnetron system equipped with two Al targets (99.5% purity) of 50 mm in diameter. The magnetrons were driven by a pulsed dc power supply (Huettinger Electronic RMP-10) operating at a repetition frequency of 50 kHz. Other technical details are given in our previous paper [11]. All the coatings, with a thickness of approximately 4 μm, were deposited in the oxide mode of sputtering onto chemically cleaned aluminum and Si(100) substrates held at a floating potential at the following constant values of the deposition parameters: the substrate-to-target distance of 110 mm, the oxygen partial pressure of 0.2 Pa and the total pressure of 1.5 Pa. The substrate temperature and discharge power were selected as the important parameters affecting an initial as-deposited structure of the coatings. Two different discharge powers (0.6 and 1.2 kW) were used for sputtering of coatings on substrates ohmically heated to 500 °C during the depositions. Furthermore, the lower discharge power (0.6 kW) was also used for sputtering of a coating on an unheated substrate. In this case the substrate temperature, however, increased from room temperature (RT) to approximately 70 °C during the deposition by plasma heating. The deposition conditions are summarized in Table 1.

Thermal transformations in the alumina coatings were investigated by differential scanning calorimetry (DSC) using a Setaram Labsys DSC 1600 system. The calorimeter was calibrated by the melting of Al, Ag and Ni standards with a purity of 99.998 ± 0.001. The DSC analysis was carried out in synthetic atmospheric air flowing with a rate of 1 l/h under non-isothermal linear regimes in the temperature range from RT up to 1300 °C. The heating and cooling rates were set to 40 °C/min.

Table 1
Variable deposition parameters (discharge power, substrate temperature) used for the deposition of magnetron sputtered alumina coatings with different as-deposited structures.

Coating	Discharge power (kW)	Substrate temperature (°C)
I	0.6	RT → 70
II	0.6	500
III	1.2	500

To obtain a sufficient DSC signal and to exclude an influence of a substrate, approximately 4 μm thick coatings were deposited onto aluminum foils (50 mm × 50 mm × 0.1 mm), which were subsequently chemically removed using hydrochloric acid with a concentration of 19%. After substrate dissolving (approximately 2 h), diluting by distilled water, washing, filtering and drying, freestanding coating fragments were mechanically ground in an agate mortar to provide a fine powder. A mass of approximately 4 mg of the powder was charged into a 100 μl alumina crucible covered with a lid and used for each DSC measurement. An identical uncharged crucible was used as a reference. Each run was immediately followed by a second run under the same conditions to serve as a baseline.

X-ray diffraction (XRD) measurements of as-deposited and annealed powdered coatings after their cooling down to RT were carried out on a PANalytical X'Pert PRO diffractometer working in the Bragg–Brentano configuration using Cu Kα radiation (λ = 0.154187 nm). The data were collected using an ultrafast detector X'Celerator in the 2θ range of 15–95° with a scanning speed of 0.036°/s. The elemental composition of the coatings on the Si(100) substrate was measured with an accuracy of 10% by a PANalytical wavelength dispersive X-ray fluorescence (WDXRF) spectrometer MagiX PRO equipped with a 4 kW Rh-target X-ray tube, analytical software SuperQ v4.0 used for data collection and FP-MULTI software used for calibration and data analysis. A pure solid-state Al_2O_3 sample was used as a calibration standard. Hardness and effective Young's modulus of the coatings on the Si(100) substrate were determined from the load vs. displacement curves measured by a Fischerscope H100 microhardness tester with the Vickers diamond indenter at a load of 20 mN. The ratio of the penetration depth to the coating thickness was kept below 0.1 for all indentations in order to eliminate the effect of the substrate. The refractive index and extinction coefficient of the coatings on the Si(100) substrate were investigated by means of a J.A. Woollam variable angle spectroscopic ellipsometer between 300 and 2000 nm. The measured data were fitted using an optical model of the system composed of the Si substrate and alumina coating described by a Cauchy dispersion formula and surface roughness layer.

3. Results and discussion

In the following, the effect of a varying initial as-deposited structure of magnetron sputtered alumina coatings on thermal stability and transformation processes of metastable phases is investigated. Three coatings (I–III) were deposited at appropriate combinations of the discharge power and substrate temperature (see Table 1) in order to get materials with different ratios of crystalline to amorphous phases. As will be shown later, lower values of the discharge power and substrate temperature result in a structure with a higher disorder due to limited surface diffusion processes of impacting atomic species. All the coatings were well adherent to the substrates used, Al foils and Si(100) wafers, with respect to all analyses performed. The coatings were also highly transparent with colorful interference patterns. High optical transparency in the visible range indicates the coatings to be close to the stoichiometric composition of Al_2O_3. This was corroborated for all three coatings by analyzing their elemental composition by WDXRF spectrometry taking into account an accuracy of 10% of this method. Namely, the coatings possessed approximately the same composition of 37 at.% Al and 63 at.% O corresponding to the atomic ratio O/Al = 1.7.

3.1. As-deposited structure

XRD patterns of the as-deposited alumina coatings are shown in Fig. 1. All the coatings were analyzed in the form used afterwards for DSC measurements, i.e., as fine powders obtained by dissolving the Al substrates and grinding the free-standing coating fragments. Since the rate of dissolution of the metallic Al substrate is expected to be significantly higher than that of amorphous alumina in the coatings, we