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Formation of intermetallics in Pt/Al system as a function of Pt layer thickness

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ABSTRACT

The properties of metals and alloys are of critical importance and bulk alloying is one of the possibilities to enhance their properties. An alternative method to improve their surface characteristics is surface coating. In the system of our interest, Pt/Al, the formation of intermetallics and their spatial distribution was investigated in thermally annealed systems as a function of coating thickness using intense synchrotron X-ray beams. Whereas the detection of intermetallics within depths was examined by synchrotron μ-X-ray diffraction, changes in coating morphology were studied by scanning electron microscopy. Our results show that the $Al_{21}Pt_6$, Al_2Pt, Al_3Pt_2, AlPt, $AlPt_2$ intermetallics were formed irrespectively of coating thickness. However, the formation of the most dominant phases was strongly influenced by the coating thickness. They also provide new routes to generate specific Pt_xAl_y phases with desirable properties based on controllable experimental conditions, opening directions towards properties tunability of a coated system.

1. Introduction

The platinum group metals (PGMs) and their intermetallics have attracted great interest in many technological and industrial fields [1–6]. Considering the binary system of our research interest, Pt/Al, the main applications range from electronics where both metals are used as interconnects, through jewellery, and aerospace industry in which they are used as constituents of protective coatings. The importance of coatings in high temperature applications has increased tremendously because of their use for gas turbine blades. Various ways to improve the PtAl coating system, including both the bond coat and the thermal barrier coatings were investigated by several authors [7–8]. They reported the problems related to the PtAl coating' failure and the measures to improve the coating performance by addition of Zr, Hf and/or Si. This modification improves the yield strength, as well as the growth kinetics of the coating. Considering the jewellery application, pure platinum is too soft to be used for the fabrication of jewellery, so alloying additions are made to increase the hardness. It has been reported by several authors that the hardness of platinum can be increased by a factor of 6 when alloyed with Co or Cu [5,9–10]. An alternative method is to improve the surface properties is surface coating. Our previous study showed that Pt-Al intermetallics formed by annealing a Pt substrate coated with Al significantly increased the surface hardness [11]. The process of hardening by formation of intermetallics without compromising the purity of pure platinum is of great importance for jewellery and other applications where the properties such as hardness and scratch resistance are crucial. The intermetallics exhibit variety of colours used in jewellery making and has potential use as radiation sensing devices and selective solar absorbers because of reasonable transparency in the visible region [12]. In addition, thin Pt-based coatings are widely used for applications in microelectronics and semiconductor devices [13–16]. Degradation of coating morphology is an unwanted phenomenon that complicates the fabrication of thin film-based devices. The success of coating technology and reliability of electric devices depend on the ability to maintain coating integrity during processing and service. However, the morphological instability in some Pt-based coatings (e.g. Pt-Si system) can play an important role in nanotechnology to fabricate the solids at the nanoscale on solid substrates and specially to produce well-ordered catalysts necessary to control nanowire growth [17–18].

The research interest of this study was focused on morphological stability of thermally annealed Pt/Al coated systems as a function of their thickness. Continuity of coatings is very often difficult to preserve due to their thermodynamic instability at elevated temperature; thermal annealing at high temperature can result in structural defects, so that the coating formed is non-uniform, discontinuous and degraded in morphology [19–21].

Although there are several reports on the mechanisms and sequence of multiple phase formation in Pt-Al system, it remains controversial

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whether the coating formation is uniform or with clusters and precipitates. The role of multiple structures, small embedded domains with weak signals and/or heterogeneities, and/or phase separation effects at micrometer levels can be only achieved using analytical techniques which rely on intense X-ray pencil beams with high sensitivity (signal/background ratio), and capable of detecting up to micrometric aggregates within deep escape depths. Therefore, the aim of this study is to investigate the effects of Pt coating thickness and thermal annealing on the formation of intermetallic phases and to obtain better understanding on their distribution across the coating surface by synchrotron micro-X-ray diffraction (μ-XRD) and scanning electron microscopy (SEM) techniques.

2. Experimental details

In this study, pre-annealed pure Al substrates (10 × 10 × 0.125 mm) were coated with pure Pt at room temperature using an electron beam source. The electron beam was generated by a tungsten filament and magnetically led to the crucibles in a circular trajectory. The aluminium substrates were cleaned prior deposition in several solvents such as methanol, acetone, trichlorethanol, water, and diluted perchloric acid for a duration of 10 min for each step prior deposition. The samples were transferred to evaporation chamber immediately after washing. The coatings were deposited on unpolished substrates with surface roughness of approx. $R_a = 0.15$ μm as measured by surface profilometer. The samples were placed at the distance of 100 mm from the crucible where the Pt was placed and deposition was performed at a rate of 4.6 Å/s under high vacuum conditions (1×10^{-6} Torr) and current of 40 mA. The thickness of Pt layers was monitored using a quartz crystal sensor. Two systems were studied: 0.1 μm Pt and 0.3 μm Pt layer deposited on Al substrates. The coatings were subsequently thermally annealed in vacuum conditions at 500 °C for 2 h. The synchrotron based measurements were carried out using μ-XRD at the microprobe station ID18F of the European Synchrotron Radiation Facility (ESRF). The beamline is equipped with a three undulators source, and a fixed-exit double Si (111) crystal monochromator with an energy resolution of $\Delta E/E \sim 10^{-4}$. The monochromatic beam is focused on the sample surface by means of Al compound refractive lenses (~10^9 phot/s in the focused beam at 14.4 keV). The optical stack uses 56 lenses with parabolic profile and a radius of curvature of 196 μm. The intensity of the incident beam is monitored with a mini-ionization chamber, while a single element solid state Si(Li) detector (150 eV/channel measured at Mn-K_α X-ray line energy resolution at 4 μs shaping time; 30 mm^2 active area; 4 mm active thickness) collects the characteristic X-ray fluorescence lines. In transmission geometry, the diffraction patterns were recorded with a two-dimensional CCD detector (a 2 k × 2 k Mar CCD camera, with 78 μm × 78 μm pixel size and 165 mm diameter) positioned at a distance of 11 cm behind the sample. By creating a secondary source using the beamline slits (0.1 × 0.1 mm), the beam dimensions estimated by the Au knife-edge scan method were 2 × 2 μm^2 at 14.4 keV. The samples were measured in “single-point” and “line-scan” modes. The single-points at the distance of 2 mm were randomly chosen, while “line-scan” measurements were performed along a line with 30 measurements separated by 5 μm. The XRD data were analysed using Fit2D [22]. The coating morphology was investigated by SEM (Nova NanoSEM 230). The micrographs were acquired at an accelerating voltage of 20 keV in secondary electron (landing) mode. In order to investigate the microstructural changes in the substrate material (Al), the polished samples were anodized using the solution of 5 ml of HBF (48% concentrated) and 95 ml of distilled water. The samples were suspended in the mixture and connected to the circuit at a potential of 20 V for 90 s. Anodising process was conducted at room temperature using a current of 05 to 1.5 A. The anodized samples were dried and subsequently investigated using the polarised filter of the Reichert MeF3A microscope.

3. Results and discussion

3.1. Substrate microstructure and coating morphology

The microstructure and surface morphology of Al substrate are shown together with morphology of deposited Pt layers (0.1 μm and 0.3 μm) in Fig. 1. The optical microscope image, Fig. 1(a) revealed the microstructure of Al substrate supplied in annealed condition; the grains are mainly equiaxed with average size of approximately 5 μm. The presence of the parallel ridges formed during Al foil rolling are revealed by scanning electron microscope, Fig. 1(b). The surface roughness of approx. $R_a = 0.15$ μm was measured in as-received foil. The Pt layer morphology “followed” the substrate surface roughness and relatively rough surface (between $R_a = 0.2$ μm and $R_a = 0.25$ μm) was measured after deposition of 0.1 μm and 0.3 μm Pt layers, Fig. 1(c–d). It is due to the fact that the substrates were not polished prior to Pt deposition. In addition to small Pt splats of approx. 2 nm, the clusters of approx. 300 nm were observed in both coated systems.

3.2. Synchrotron μ-XRD analysis

Fig. 2(a) shows the μ-XRD (single-points) spectra of as-deposited Pt coatings. Apart from the expected Pt and Al related peaks, the XRD diffractograms show the presence of Al_3Pt_2 and $AlPt_2$ phases although in relatively small volume fractions. Except for the background signal, there are no significant differences between both spectra. A combination of several factors such as heat evolved during Pt evaporation, a small distance between the samples and crucible (50 mm), low deposition rate (deposition time of approx. 10–15 min per sample) and relatively thick Pt layers to be deposited (0.1 μm and 0.3 μm) it appears to be sufficient to trigger the phase transformation at the Al/Pt interface. Similar phenomenon, the phase formation during coating deposition at room temperature, was published by several authors [23–24]. They reported that the amorphous Al-Pt phase is formed during evaporation (at approx. 70 °C) at the Al/Pt interface. The amorphous Al-Pt phase has a compositional range between that of the equilibrium $Al_{21}Pt_8$ and Al_3Pt_2 phases. At higher temperatures (225 °C) the crystalline Al_3Pt_2 phase generates. It has also been shown that the initially amorphous layer crystallizes upon reaching a certain critical thickness. Amorphous layers formed by solid state reaction typically have thicknesses ranging from between 10 and 100 nm and are generated at relatively low temperature (typically 300 °C), although growth temperatures as high as 600 °C have been reported in the Ti-Si system [23]. As the thickness of the amorphous layer increases to a critical value, the nucleation of the more stable crystalline phase is favoured and the formation of amorphous phase stops [23]. Fig. 2(b) and (c) display the phase analysis of thermally annealed coatings obtained by single-point measurements, which show similar results for 0.1 μm Pt and 0.3 μm Pt coatings. In addition to Al_3Pt_2 and $AlPt_2$ formed during deposition, annealing of the samples transformed them into a mixture of new phases $Al_{21}Pt_6$, Al_2Pt, and AlPt. The volume fractions of the phases varied between measuring points in both coated systems. However, the major difference between thermally annealed coatings having different thickness of Pt layer is in the presence of the most dominant phase. The most dominant phase in thin coating was $Al_{21}Pt_6$ while the Pt-richer phase (Al_2Pt) appears to be the most dominant phase in thicker Pt layer. Fig. 2(d) shows the μ-XRD results obtained in line-scanning mode, which were similar for all 30 measurements taken along the line of 150 μm length and they are thus, presented as single XRD pattern for each coated system. The presence of same phases determined in a single-point mode (points separated 2 mm from each other), and in line-scanning mode indicates homogeneous distribution of intermetallics across the coating surface.

It should be noted that some weak peaks were not identified, suggesting formation of oxides and/or presence of unidentified phases. Further investigations with more intense beams are required to achieve a full understanding of the nature of these unidentified peaks and