Annealing effects on Pt coating morphology

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Abstract. The formation of intermetallic phases and coating surface morphology of Pt thin films deposited on thick Al substrates has been studied. Coatings were prepared under high vacuum using an electron beam evaporation system. Scanning electron microscopy (SEM) and the Particle Induced X-ray emission (PIXE) were used to study the surface morphology of the coatings while the X-ray diffraction (XRD) technique was used to study phase formation in the Al-Pt system after annealing at elevated temperatures in an unprotected atmosphere. The scanning electron microscope studies revealed that the morphology of thin platinum coatings is affected by annealing parameters such as temperature and time. Coating wrinkling/rumpling and increased surface roughness were the main features observed in the annealed coated systems considered in this study. The investigation of phase formation by XRD and RBS revealed the formation of the following intermetallic phases: Al_2Pt, Al_6Pt, $Al_{21}Pt_8$, and $Al_{21}Pt_6$ when annealed at different temperatures and times. The change in coating morphology has been attributed to the formation of the platinum/aluminium intermetallic phases.

1. Introduction

Platinum and aluminium-platinum coatings of heat treated substrates possess excellent properties including high resistance to corrosion, good thermal stability and an appealing appearance.

It is known that platinum and aluminium readily form intermetallic compounds during heat treatment. Intermetallic compounds based on platinum and platinum group metals have unique properties such as high temperature and environmental resistance[1]. Pt-Al coated systems find a broad application in the electronics (in integrated circuits as contacts or interconnects)[2], and in the aerospace industry[3,4] (inside gas turbine engine to sacrifice for oxidation and corrosion), and in catalytic converters. Pure Pt is remarkably too soft for fabricating jewellery and alloying it with other elements results in hard but workable alloys and this property makes the Pt-coated systems suitable candidates for the jewellery and plating industry[4].

The Al-Pt system is very complicated with many equilibrium phases[5,6]. However, despite the extensive work on these materials, the principles underlying the formation of various phases are still not fully understood. Apart from the obvious academic interest, knowledge of phase formation sequence should enable the materials scientist to control experimental parameters in such a way as to form specific phases with desirable properties. Therefore, the main aim of this research was to study the effects of annealing parameters on kinetics and thermodynamics of intermetallics formation and their effects on Pt-Al coating morphology.

2. Experimental

The electron beam evaporation system was used for Pt coatings deposition. Prior to deposition Al substrates were mechanically polished and chemically cleaned in an ultrasonic bath. Organic compounds such as methanol, acetone, trichloroethylene, de-ionized water and 5 % HF acid were used in the experimental cleaning process. Thin Pt coatings with thickness of 0.1 µm were deposited on the Al substrates in vacuum of better than 10^{-7} Torr. Annealing was performed in an unprotected atmosphere with vacuum of better than 10^{-7} Torr for annealing time periods ranging from 30 min to 1 hr. The surface morphology of the coatings were studied using SEM (Oxford Stereoscan 440 operated at acceleration voltage of 20 kV and a beam current of 100 pA at an average working distance of 17 mm) using secondary electrons. The particle induced X-ray emission (PIXE) was used to study elemental distribution of Al and Pt after annealing. A 2 MeV beam of alpha particles was used to probe a sample area of $0.5 \times 0.5 mm^2$ with a beam spot size of $3 \times 4 \mu m^2$. Phase analysis was performed by the Bruker Advance 8 X-ray diffractometer operated at voltage of 40 *kV* and a current of 40 *mA*. The Rutherford Backscattering Spectroscopy was also used to investigate solid-state interaction between Al and Pt. RBS spectra were obtained using a surface barrier detector with energy resolution of approximately 15 keV placed at an angle of 165º with respect to the incident beam. The Rutherford Backscattering Utilities and Manipulation Program (RUMP) which is a computer program was used to analyze RBS spectra.

3. Results and discussion

The scanning electron microscope was used to study the effects of annealing parameters (temperature and time) on the morphology of Al-Pt coated systems. Figures 1-2 show the changes in coating morphology of the 0.1 μ*m* Pt layers deposited on Al substrates after being annealed. The samples were annealed at different annealing temperatures and different annealing times.

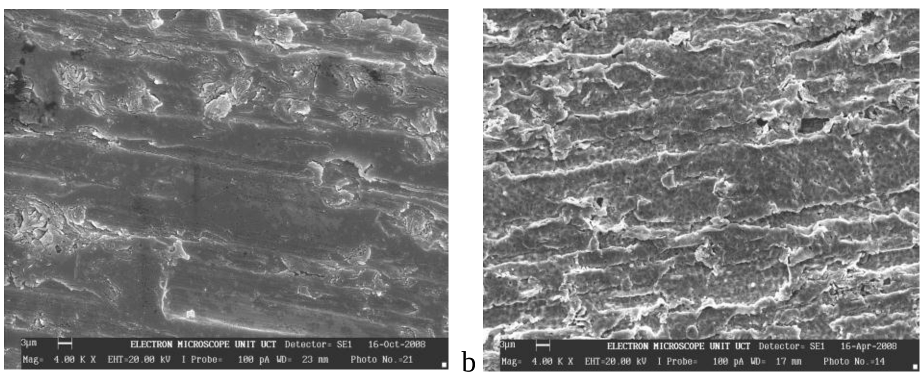
a 

Figure 1: Scanning electron micrographs of 0.1 μm Pt layer annealed at: (a) 200˚C and (b) 400˚C for 30 min. The sample annealed at 200˚C appeared smooth and some morphological changes occurred when annealing at 400˚C.

The SEM micrographs in figure1 show different morphologies of thin platinum coatings (0.1 μm) after heat treatments at 200 °C and 400°C. The coating surface appeared quite smooth after annealing at 200°C (figure 1 a) while a slight change in morphology has been observed after treatment at 400°C and one notes the start of coating rumpling at 400 °C shown by arrow in figure 1 (b). At the low annealing temperature of 200°C diffusion between Pt and Al was not sufficient to cause morphological changes. However, at 400°C there was effective interaction between elements (Pt and Al) which resulted in the formation of intermetallic compounds as confirmed by X-ray diffraction.

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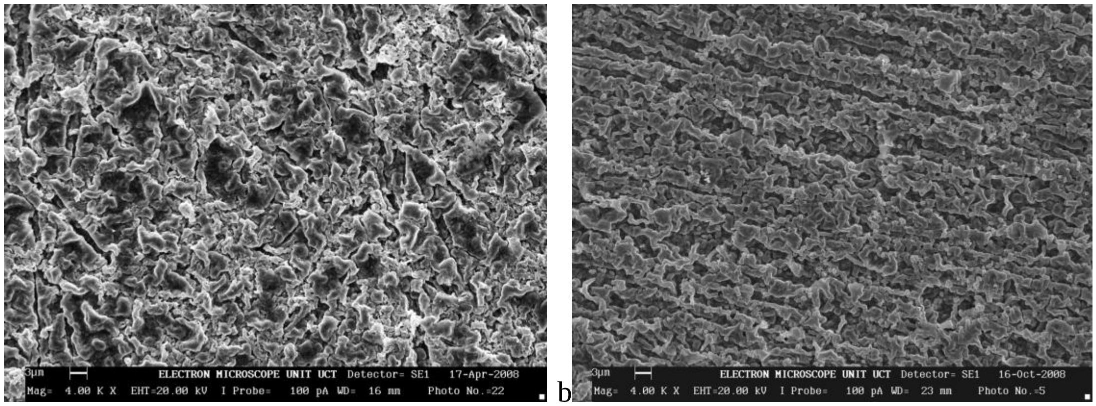

Figure 2: Surface coating morphology of the 0.1 µm Pt coating after heat treatment at: (a) 500˚C, (b) 560˚C for 30 min. Morphological changes induced by high temperature annealing caused significant increase in surface coating roughness.

The microscopical studies showed that the morphology of the coatings (0.1 μm Pt layer) changed significantly after annealing at high temperatures of 500°C and 560°C (figure 2). The surface roughness was increased significantly in comparison to the coating surfaces annealed at lower annealing temperatures and coating wrinkling is clearly visible in figure 2 (a) and (b) (shown by arrows). Solid-solid interfaces often provides exceptionally rapid paths for diffusion[7] and during diffusion atoms may jump across grain boundary, causing the grain boundary to move[8] and grain boundary movements are usually the result of uneven growth during the crystallization of the intermetallic phases. The distortion of planes during diffusion as a result of atoms forcing their way to interstitial site[8] can result in an irregular or uneven surface morphology. Although the atomic size factor cannot be avoided but annealing at a specific temperature can bring atoms at the right lattice site positions[8] and the surface of the coating can be improved. The mismatch in coefficients of thermal expansion of Al and Pt can also be one of the reasons which contribute to increased surface roughness[8]. The two materials do not expand and contract in the same way during heating and cooling: The thermal expansion coefficients for platinum and aluminium (at 20 ºC) are $23 \times 10^{-6} / ^{o}C \quad and \quad 9.1 \times 10^{-6} / ^{o}C$ respectively[9]. In addition, different Pt/Al intermetallic compounds have different mechanical properties and they can induce the residual stresses (tensile or compressive) in coated systems. Therefore, all these factors affect the morphology of coated systems subjected to annealing conditions. In general, the surface morphology of the coating such as roughness can be affected by many factors, including the substrate surface roughness, the thermal coefficient mismatch between the substrate and the coating. Pedraza et al[10] reported that rumpling or "roughening" is a defect that results not only from the differences between the thermal expansion coefficients but also due to different mechanical properties of the coating and substrate. They found that the coating volume changes during annealing and consequently, rumpling of coatings occurs, this was also observed by Yin et al[11]. The results of morphological study are in consistence with the rumpling behavior on the aluminium modified coatings observed by Wen et al.[12]. The formation of more than one intermetallic phase creates an environment where the reaction rate for each phase is different and the resulting growth of the phases will be dissimilar[11]. This will give rise to uneven surfaces. Surface rumpling is the mechanism which is believed to be responsible for the observed flaws (cracks). The effect of surface rumpling on formation and propagation of cracks has been reported by Panat et al[13] and Wen et al[12]. Another feature which can give rise to morphological changes in the coatings is the manner in which the Al-Pt intermetallic phases grow during heat treatment. The dependants of surface roughness on the manner in which phases grow in a system was reported by Li et al[14]. The results of their study showed that the film roughness was due to the manner in which the PtSi phases grow.

In addition, the presence of “precipitates” has been observed at higher annealing temperatures (e.g. 590 °C). The energy dispersive x-ray (EDX) analysis show that these precipitates consist of approximately 64 *at%* Al and 36 *at%* Pt. This corresponds to the chemical composition of Al_2Pt ($Al_{0.66}Pt_{0.33}$) intermetallic compound.

Elemental distribution of the Pt and Al was investigated in the sample (0.1 μm Pt layer deposited on Al substrate) annealed at 590°C for 30 *min*. The PIXE maps show that the concentration of Al was not uniform. The coating layer (Pt) is believed to be consumed by the Al substrate which under vacuum and at these high temperatures begins to melt. The concentration of Pt was between 40-60 *wt%* in the most of surface coatings. The consumption of the coating material by the thick substrate was also observed by Topić et al.[15] and they suggested that the coating material which was Al in their case was consumed by two processes: (a) by interdifussion between Al and Pt and subsequent intermetallic phase formation and by (b) oxidation due to exposure to high temperatures in an air environment (unprotected atmosphere).

The interfacial reactions and phase transformations in the Al-Pt coated system were studied by X-Ray Diffraction (XRD) and Rutherford Backscattering Spectrometry (RBS). The formation of aluminium-platinum intermetallic compounds was investigated as a function of annealing parameter (temperature) was studied. Considering the annealing process, the samples were annealed at different temperatures (from 300 °C to 560 °C) in duration of 30 minutes and an hour. Figure 3 shows the XRD spectra of the as-deposited and annealed coated systems consisting of a thin Pt layer (0.1 μm) deposited on Al substrate.

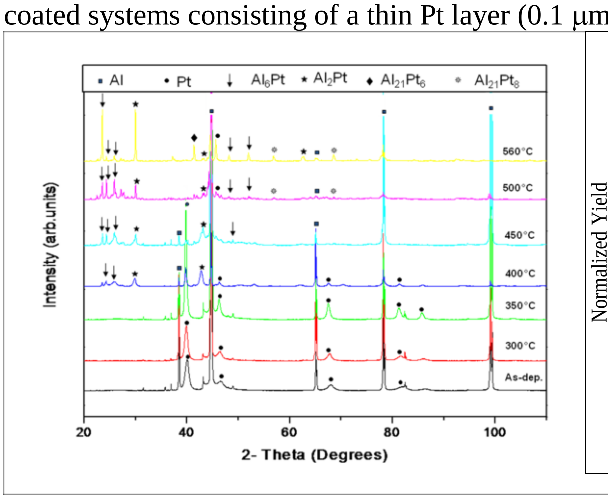

Figure 3: X-ray diffraction results of 0.1 μm Pt coatings for as-deposited and samples annealed at 300°C, 350°C, 400˚C, 450˚C, 500˚C and 560°C for 30 min. There were no intermetallic compounds formation observed when annealing at 350°C and temperatures below. Annealing at temperatures from 400˚C resulted in the formation of Al_2Pt, Al_6Pt, $Al_{21}Pt_8$ and $Al_{21}Pt_6$ intermetallic phases.

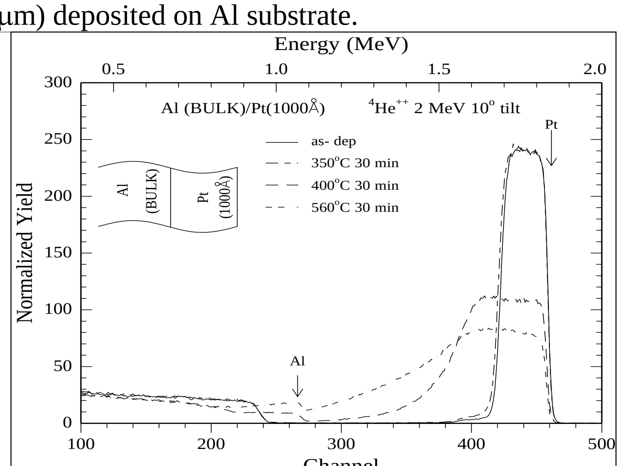

Figure 4: RBS spectra of samples of the 0.1 μm Pt layer deposited on thick Al substrate. RBS shows that there is no reaction between Pt and Al when annealing at temperatures below 350°C for 30 min. There has been interdifussion between Al and Pt for the sample annealed at 400°C and 560°C which resulted in the formation of Al-Pt intermetallic phases.

The phase analysis results show no formation of the Al/Pt intemetallic compounds when the samples were annealed at 300°C and 350 °C for 30 minutes while two phases, Al_2Pt and Al_6Pt, were detected for samples annealed at 400 °C and 450°C for 30 minutes. After annealing at higher temperature (500°C) for 30 minutes the additional phase $Al_{21}Pt_8$ was found. The XRD spectra annealed at 560˚C show the same phases as found after annealing at 500˚C/30 min. Considering the phase formation of the thin Pt coating (0.1 μm) subjected to annealing; it is evident that all the phases formed at different annealing temperatures are the aluminium rich phases. The limiting element in this system is Pt and the relative concentrations of the reactants was expected to go to the Al rich side after the Pt has been consumed according to the Walser-Bene and effective heat of formation models[16,17,18]. The formation of the $Al_{21}Pt_8$ at 500˚C showed that the relative concentration of the reactants has moved to the Al rich side of the effective heat of formation diagram.

However, the results obtained in this study do not correspond fully to the findings of other researchers. Topić et al[15] reported the formation of the Al_3Pt_2 phase around 250˚C in nitrogen atmosphere and at 300˚C in air conditions. The thickness of Pt layer could be one of the possible reasons. Namely, thin layer (0.1 μm) of Pt deposited on thick Al substrate (Al>Pt) was studied in this project while the other researchers used the coated system with significantly thicker Pt coating. On other hand, the other researchers studied thin Pt films deposited on Si wafer. The other possible reason for this discrepancy could be attributed to larger annealing steps (50°C) used in this study and thus, the formation of particular phase could have been missed.

Besides the phase analysis by XRD the other technique, RBS was also used to study the reactions between Al and Pt. Figure 4 shows RBS results for the 0.1 μm Pt thick coating subjected to elevated temperatures. In the RBS spectrum the heights of the Pt signal for the as-deposited and 350°C samples are very close. The results show a shift of the Pt signal to lower energies while the Al signal remained unchanged which implies that no Al-Pt compound was formed during annealing at 350°C for 30 min. These findings are consistent with the phase analysis results. X-ray diffraction confirmed that no compound formation occurred at 350°C. The slight shift to lower energy of the Pt signal on the 350°C annealed sample indicates that interaction (interdiffusion) between the Al and Pt occurred. However, the broadening of the Pt signal and the change in the Al signal observed for 400°C and 560°C annealed samples indicated the formation of Al-Pt intermetallics. This is also consistent with the XRD findings.

4. Summary and conclusion.

The characterisation of Aluminum/Platinum coated systems of platinum layers (0.1 μm) deposited on thick aluminium substrates annealed up to 590°C have been performed by several complementary techniques. The formation of intermetallic phases has been studied as a function of annealing parameters (temperature and time). The following conclusions can be draw from this study:

Annealing temperature significantly affects the coating morphology, the coatings became significantly rougher after annealing at higher temperatures

Annealing process promotes phase transformation and formation of intermetallic phases through thermally-activated atomic diffusion induced by furnace annealing between 300 °C and 560 °C.

Four Al-rich intermetallic compounds have been determined in the Al/Pt coated systems: Al_2Pt, Al_6Pt, $Al_{21}Pt_8$ and $Al_{21}Pt_6$

The annealing heat treatment at temperatures of up to 350 °C does not lead to the formation of Al/Pt intermetallic phases while two phases (Al_2Pt and Al_6Pt) were detected at 400 °C and 450 °C: Additional phase, $Al_{21}Pt_8$, was detected when the system was annealed at 500 °C for 30 minutes. Four Al-rich intermetallic phases, Al_2Pt, Al_6Pt, $Al_{21}Pt_8$ and $Al_{21}Pt_6$, have been formed by annealing at 560 °C.

The changes in morphology of heat treated coatings have been attributed to the rather complex Al-Pt system which comprises of several intermetallic phases, which the kinetics of crystallization process of these intermetallics is different.

The phase analysis results show that the phases determined in the Al/Pt coated systems are not fully in agreement with predictions made by effective heat of formation (EHF) model. However, this can be due to the fact that the experimental methodology included high measuring steps (50°C) and the formation of some phases could have been missed out.

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