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**Gudla, Visweswara Chakravarthy; Canulescu, Stela; Schou, Jørgen; Ambat, Rajan; Rechendorff, Kristian
; Christensen, Bjarke; Pleth Nielsen, Lars**

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Anodization of sputter deposited Al-Zr coatings and microstructural issues

Chakravarthy G.V., Stela Canulescu, Jørgen Schou, Rajan Ambat, Technical University of Denmark, Kongens Lyngby, 2800 Denmark
Kristian Rechendorff, Bjarke Christensen, Lars Pleth Nielsen, Danish Technological Institute, Århus C, 8000 Denmark

Summary

The anodization and optical appearance of magnetron sputtered Al-Zr coatings with Zr concentration varying from 6 wt. % to 23 wt. % on AA6060 substrates are studied. Heat treatment of the coated samples was carried out at 550 °C for 4 hours and the resulting microstructure showed uniform precipitation of Al-Zr based second phase particles. Anodization was performed in a 20 wt. % sulphuric acid (12.5 V constant voltage and 18 °C). Effect of coating composition and microstructures resulting from heat treatment upon appearance of the anodized samples were analysed by scanning electron microscopy, grazing incidence X-ray diffraction analysis, glow discharge optical emission spectroscopy and spectrophotometry. Microstructure of the coating is found to have clear influence on the appearance of anodized layer due to incorporation of partially oxidized second phase particles in the anodized layer, which modified the light absorption and scattering effects.

1   Introduction

Anodized aluminium alloy components are extensively used in various technological areas such as architectural, decorative, and automobile sectors either for corrosion protection, optical appearance or both [1]. Sulphuric acid anodizing is the most commonly used process for decorative anodizing of aluminium and the thicknesses used are in the range of 10 – 15 μm [2]. The anodized layer is usually transparent and the appearance depends on the composition of aluminium alloy being anodized, anodizing parameters and the surface condition prior to anodization [3, 4]. Also, anodization in sulphuric acid results in an anodized layer with nano-sized pores that can be impregnated with dyes both organic and inorganic to impart different colours to the anodized layer [2]. With the increasing use of recycled aluminium alloys for cost effectiveness and sustainability, the control of optical appearance of anodized components is becoming difficult. This is due to the increase and potentially fluctuating amount of intermetallic phases in recycled aluminium alloys, which behave differently from the aluminium matrix during the anodization process [1]. The electrochemical behaviour of various second phases in aluminium alloys during anodization has been studied extensively [5 - 8], but very little is known on the effect of these phases on the optical appearance after anodization [9]. Recently, authors have evaluated the use of sputtered coatings for anodization [10]. Sputtering deposition techniques provide coatings with a wide range of compositions compared to conventional melt and cast techniques. Also the coatings can be deposited on any kind of aluminium alloy without affecting the appearance after anodization due to second phases. The composition of these coatings can be tailored to suit the requirements and a further controlled heat treatment will cause the formation of well controlled second phases.

These second phases after anodization will modify the scattering phenomenon of light in the anodized layer and thus provide the desired optical appearance.

The anodization behaviour of various alloys systems like Al-Ti, Al-Cu, Al-Mg and Al-Mn has been reported earlier [10 - 13], but the anodization of Al-Zr system has not been reported yet. This paper describes the behaviour of Al-Zr coatings during sulphuric acid anodization. The coatings were obtained by magnetron sputtering and heat treated to form second phase precipitates. The effect of heat treatment, composition, microstructure and morphology on the appearance of anodized layer is investigated.

2 Experimental

2.1 Materials and methods

Aluminium substrates (AA6060) of dimensions 200 x 40 x 10 mm^3 were obtained from Erbslöh Aluminium GmbH, Germany. Al-Zr coatings with a composition gradient from 6 wt. % to 23 wt. % Zr were deposited using magnetron sputtering (Model CemeCon 800/8) at Tribology Centre, Danish Technological Institute, Denmark. All depositions were performed with a bias voltage of -50 V. One commercial AA1050 and one AA1050 target with Zr inserts were used in the chamber for obtaining the desired Zr fraction during the coating process. The thickness of the coatings obtained was approximately 16 μm.

Heat treatment of the coated samples was performed in a muffle furnace in ambient atmosphere at a temperature of 550 °C for 4 h. The samples were then removed from the furnace and cooled in ambient air. The heat-treated and as coated samples were then mechanically polished, buffed, and degreased in a mild Alficlean™ solution at 60 °C before being subjected to anodization. The samples were then subsequently desmutted by immersing in diluted HNO_3 followed by demineralised water rinsing. The surface preparation process resulted in removal of 5 - 6 μm of the coating thickness. Anodization was carried out in a 20 wt. % sulphuric acid bath maintained at 18 °C. Anodization voltage was fixed at 12.5 V and the process was carried out for 30 min followed by rinsing with demineralized water. Sealing of the anodized layer was performed in water at 96 °C for 25 min. followed by drying with hot air.

2.2 Spectrophotometry

Spectrally resolved optical reflectance of the coatings was measured using an integrating sphere – spectrophotometer setup. The samples were illuminated with a collimated beam from a deuterium tungsten-halogen light source (type DH2000 from Ocean Optics) at an angle of incidence of 8° with respect to normal. The reflected light was collected using an optical fibre coupled to an optical spectrometer (QE 65000 from Ocean Optics). Each reflectance spectrum was averaged over 4 s over the wavelength range from 350-750 nm. Diffuse reflectance of a sample can be measured directly using a gloss trap coated with a dark absorbing material in the specular light port of the sphere. The specular reflectance spectrum is then obtained by subtracting the diffuse reflectance from total reflectance of each sample. The spectrophotometer was calibrated using high specular and high diffuse reflectance standards.

2.3 Microstructural characterization

The morphology and microstructure of sputtered coatings and anodized layer was observed using scanning electron microscopy (Model Quanta 200 ESEM FEG, FEI) equipped with an EDS (Oxford Instruments 80 mm^2 X-Max). The samples were mounted in an epoxy and polished to reveal the cross section.

2.4 X-ray Diffraction

Grazing incidence X-ray diffraction (GI-XRD) (Model Bruker Discover D8) analysis was performed using Cu K$_\alpha$ radiation at 40 kV and 40 mA for the phase analysis of deposited and heat treated coatings before and after anodization. XRD patterns were recorded in the 2θ range from 25° to 160° with an incidence angle of 1˚, step size of 0.03° and a scan step time of 4 s.

2.5 Radio Frequency Glow Discharge Optical Emission Spectroscopy

Compositional depth profiling of the coated, heat treated, and anodized samples was performed using RF-GDOES (Model GD-Profiler 2, Horiba Jobin Yvon). The instrument was coupled with a software package (Quantum XP) for analysing and quantifying the data.

3 Results
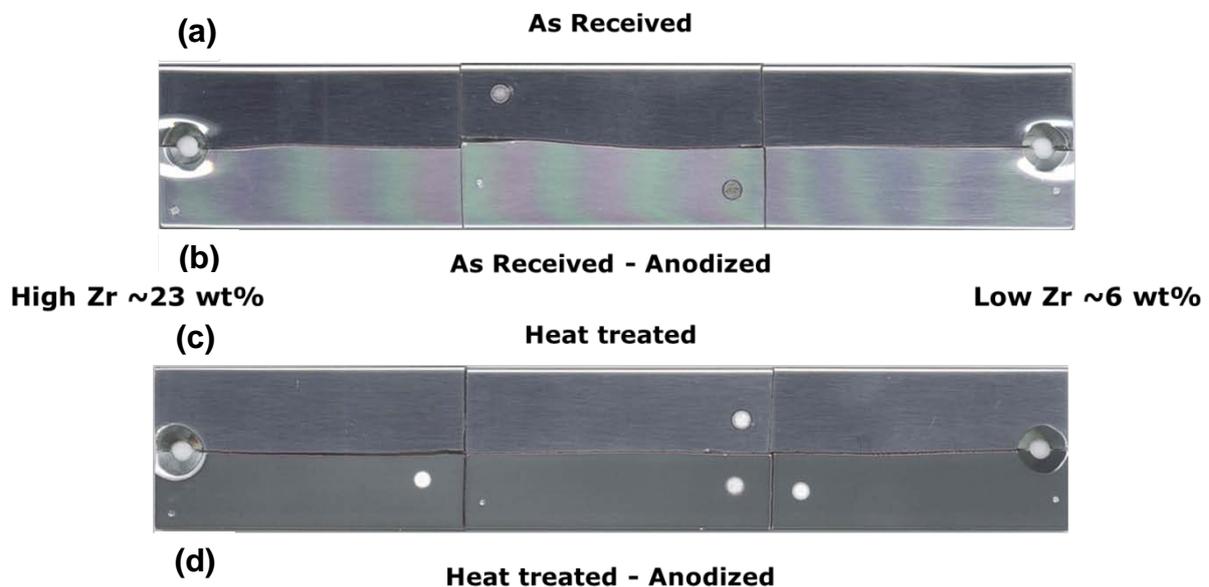
3.1 Visual appearance

Figure 1: Optical images of the Al-Zr coatings of different compositions deposited on AA6060 substrates (a) as received and polished, (b) as-received, polished, and anodized, (c) heat treated and polished and (d) heat treated, polished, and anodized condition. The Zr concentration in the coatings decreases from left to right. The white spots on the samples are due to GD-OES characterization.

Figure 1 shows the appearance of the coated samples before and after anodization, with and without heat treatment. It can be clearly seen that the heat treated sample after anodization looks dark throughout the range of Zr concentrations, whereas the

samples which were anodized in as-received condition show a transparent anodized layer. The colours appearing in the anodized layer of the non-heat treated sample are interference colours from a transparent anodized layer.

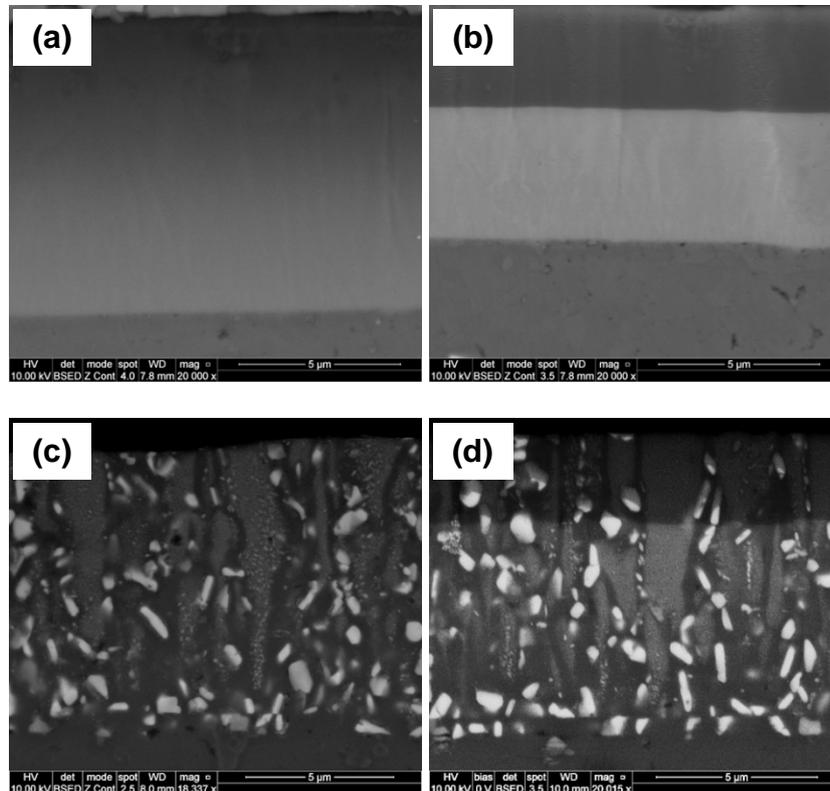## 3.2 Scanning electron microscopy

Figure 2: Back scattered electron images of Al- 17 wt. % Zr coatings cross section on AA6060 in (a) as coated, (b) as coated and anodized, (c) heat treated and (d) heat treated and anodized condition.

Figure 2 (a) shows the thickness of the coating after mechanical polishing is approx. 10 µm. Anodization of the sputtered coating resulted in an anodized layer of approx. 4 µm (Fig. 2 (b)). Also, it can be observed that there is a contrast within the coating in the form of bright columns which is attributed to variation in the Zr concentration arising out of the deposition process. The heat treated coating shows formation of secondary phases with different morphology, size and distribution (Figure 2 (c)). One type of second phase particles is in the size range of 300 – 400 nm which are homogenously distributed across the coating thickness and the others are in the nanometre size range (< 100 nm). The nanometre sized secondary phases are precipitated along certain regions and seem to follow the columnar structure arising out of the sputter deposition process. Preferential precipitation of these particles is due to the difference in Zr concentration as shown in figure 2 (b).

EDS data (not shown) of these second phases revealed the presence of Al, Zr, and Si. The presence of Si in the sputtered layer after heat treatment is attributed to diffusion from the Si containing substrate. The coating microstructure after heat treatment is similar throughout the composition range of Zr consisting of nano and submicron sized second phase particles.

Anodization of heat treated samples resulted in an anodized layer thickness of approx. 3 µm (Figure 2 (d)). It can be seen that in the anodized layer, the second phases are only partially affected which is reflected in the brightness contrast in individual particles in the anodized layer. The nano sized second phases are completely anodized as there is no observable contrast in the appearance of these particles in the anodized layer. EDS analysis of the partially anodized second phases does not show any appreciable changes in the concentration of the constituting elements, but presence of oxygen.
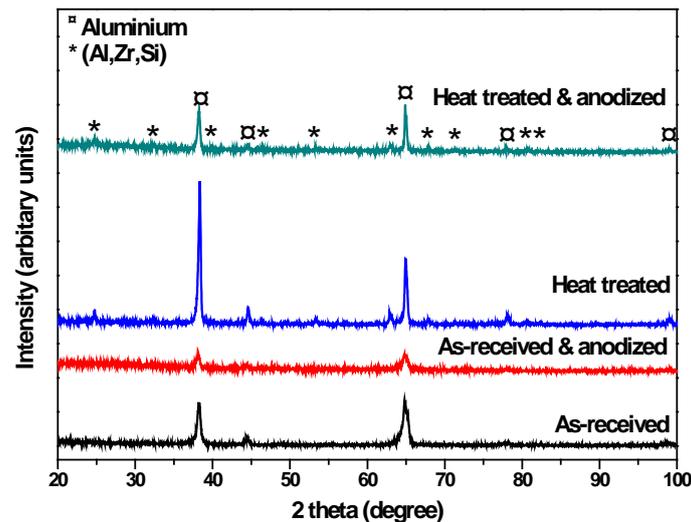
3.3 X-ray diffraction

Figure 3: GI-XRD pattern of the samples in as received and anodized condition with and without heat treatment taken from a composition of approximately 16-17 wt. % Zr.

GI-XRD pattern of the as-coated, heat treated, and anodized samples are shown in Figure 3. The diffraction pattern from the as-coated samples show peaks which correspond to pure aluminium. There are no separate peaks which correspond to Zr or related phases, showing that all the Zr is dissolved into the aluminium matrix. The diffraction pattern of the heat treated samples shows peaks corresponding to aluminium and a phase which was indexed from the JCPDS data as (Al, Zr, Si) (Pattern No. 14-0625, Stoichiometric data for this compound is not available in the JCPDS library). This is in accordance with the data obtained from the EDS results. It can also be observed that the anodization process does not give rise to any new peaks in the pattern as it transforms the surface to an amorphous phase.

3.4 GD-OES

The GD-OES depth profile analysis for the heat treated sample (not shown) revealed a higher concentration of Si when compared to that of the as-coated samples. The concentration of Si in the heat treated samples was measured to be 1.28 ± 0.21 wt. % and 0.08 ± 0.01 wt. % for the as coated sample. As mentioned earlier, the presence of Si in the PVD layer is due to diffusion from the substrate to the coating during heat treatment.
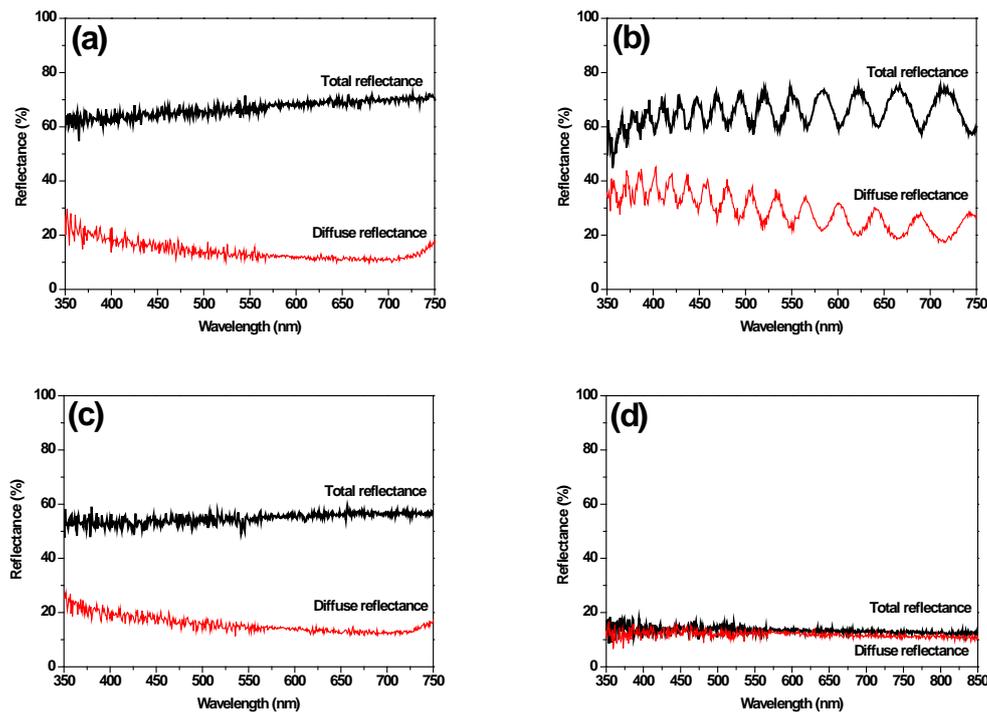
3.5   Spectrophotometry

Figure 4: Reflectance spectra of Al- 15 wt. % Zr coatings on AA6060 in (a) as coated, (b) as coated and anodized, (c) heat treated and (d) heat treated and anodized condition.

The diffuse and total reflectance spectra of the samples containing Zr concentration of 15 wt. % are shown in Figure 4. Optical reflectance of the coatings in the visible wavelength spectral range shows a weak dependence on wavelength. The as-received sample after polishing treatment has a high total reflectance and a diffuse reflectance value corresponding to approximately 1/3 the total reflectance value. The specular reflectance of these samples is the difference between the total and diffuse reflectance and is hence the remaining 2/3 of total reflectance in this case. After ano-dization (Figure 4(b)) the total reflectance remains nearly the same and interference fringes arise due to the formation of a uniform anodized layer (thickness value ~4 μm). The diffuse reflectance of the coatings increases after anodization. This may be ascribed to the structure and creation of pores in the anodized aluminium during the anodization process, which also serves as defects for the incoming light. The heat treated samples (Figure 4(c)) have a similar total and diffuse reflectance spectra as the as-received samples in the visible wavelength range. Upon anodization, the opti-cal reflectance of the heat treated sample (Figure 4(d)) decreases considerably. Also the specular reflectance is minimal for these samples implying that the samples lose their glossy nature. The same behaviour was observed across all the Zr concentra-tion values. The total reflectance of the samples decreases slightly with increasing Zr content from 6 to 23 wt. %.

4   Discussion

From the SEM, XRD, and RF-GDOES results it is clear that the heat treatment of the sputter coated samples gives a microstructure containing (Al-Zr-Si) phase in an Al matrix with a homogenous and dual size distribution, i.e. large second phase parti-

cles in the size range of 300 - 400 nm and small particles in the nanometer size range (<100 nm). After anodization, the particles with a higher size distribution are partially oxidized while the ones with a lower size distribution are completely oxidized. The un-anodized region of the large-size particles (300 - 400 nm) is metallic in nature, while the anodized region is essentially a mixture of oxides and hydroxides of Al, Zr, and Si. The refractive index in crystalline nature of these oxides is approximately 1.72, 2.17, and 1.52 over the visible wavelength range respectively [14]. The anodized Al matrix has a refractive index which is lower than that of zirconium oxide. Assuming that the refractive index of the anodized (Al-Zr-Si) layer of particles is larger than that of anodized Al, more particles different from the matrix in terms of refractive index will result in more scattering of light. Homogenous distribution of such scattering centres in the anodized aluminium matrix results in multiple scattering of light, which disperses the incident light in all directions and creates a diffuse appearance of the surface. However, the un-anodized particles consisting of (Al-Zr-Si) phase are metallic. The refractive indices of metals have a high extinction coefficient, which is responsible for their absorption characteristics. This becomes prominent when the size ranges are comparable to the wavelengths of visible light, where metal particles are absorbing due to surface plasmon effects [15]. This implies that multi-component metallic particles containing (Al-Zr-Si) phase serve as centres of absorption for the incoming light and will contribute to a dark appearance of the heat treated and anodized specimens. Thus, the anodized region of the large-size particles scatters light, whereas the un-anodized region absorbs the light. Multiple scattering events thus results in an increased absorption of light and gives the dark appearance to anodized surface. This phenomenon of reflective scattering by anodized region of the particles and absorption by un-anodized region is elucidated in Figure 5. Further work is under progress and will be the focus of a more detailed journal paper.
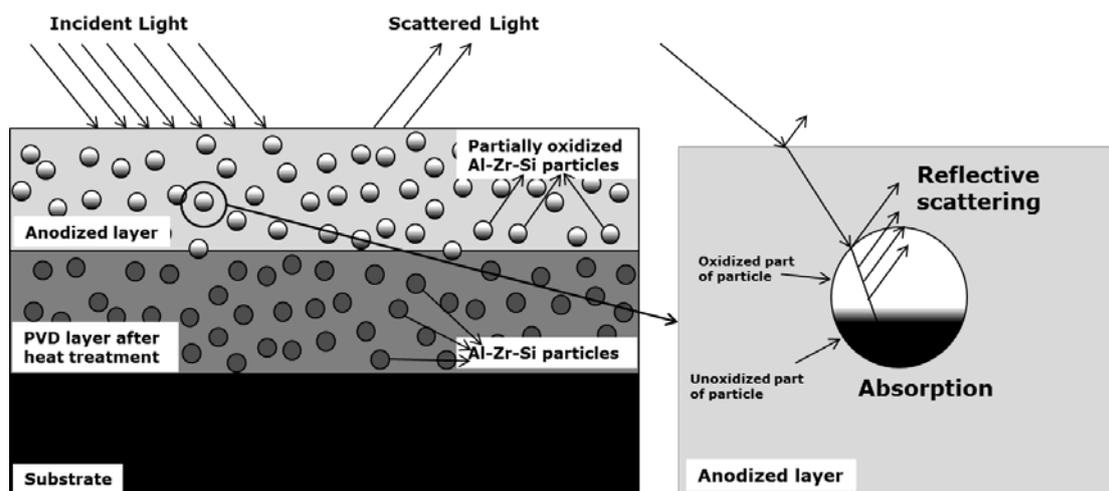

Figure 5: Schematic showing the reflective scattering and absorption of light from the second phase particles in the anodized layer (modify the schematic).

Conclusions

Thick Al-Zr coatings with Zr concentration varying from 6 wt. % to 23 wt. % on AA6060 substrates were studied. The optical reflectivity of the anodized samples with and without heat treatment was found to be similar throughout the composition gradient of Zr. Silicon diffusion from the substrate during heat treatment promotes the formation of (Al-Zr-Si) phase with a dual size distribution. Upon heat treatment, small

size second phases (<100 nm) and large size particles (300 - 400 nm) were formed. Anodization in sulphuric acid electrolyte at a voltage of 12.5 V results in complete oxidation of small size second phase particles, while the larger particles are only partially oxidized. Upon anodization, oxides of (Al-Zr-Si) serve as scattering centres in anodized aluminium matrix, but as they are only partially anodized they still act as absorption centres and lead to the dominantly absorbing behaviour of the specimen.

Acknowledgements

5   References

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