Formation of Alumina gradient coatings by Ion Beam Assistant Deposition

Xue Jianming[1] and G.K. Wolf[2]

1 Institute of Heavy Ion Physics, Peking University, 100871 Beijing
2 Physical Chemistry Institute, Heidelberg University, 69120 Germany

Abstract: $Al_2O_x(0<x<3)$ coatings and $Al-Al_2O_3$ gradient coatings were formed by evaporating pure aluminium(99.9%) in O_2 environment with an IBAD facility, 12 keV Ar^+ was used to irradiate the coatings simultaneously during the deposition. Sample's composition and depth profile were analysed by RBS and AES measurement, and their microhardness and porosity property were also measured in the experiment. Results show that, the oxygen concentration in the deposited coatings has a nearly linear relationship with the inputting gas flow before O_2 partial pressure in the target chamber reaches 1.2×10^{-3} mbar under which stoichiometric Al_2O_3 could be formed; and sample's microhardness and porosity property is affected significantly by the oxygen concentration in the coatings.

Key Words: IBAD, Alumina Coating, Gradient Coating, Corrosion Protection

1. Introduction

Aluminium and alumina coatings are widely used to modify material surface properties, such as corrosion resistant ability, tool surface hardening and ceramic surface metallization[1,2,3,4]. However, since aluminium is very soft and alumna is fragile, they are easily to be damaged in some practising environment. Aluminium/alumina multilayer coatings and alumina gradient coatings are expected to inherit the good properties of both aluminium and alumna and over come their weakness. Study on the formation and property of $Al_2O_x(0<x<3)$ coatings and Aluminium-Alumina gradient layers is necessary for this purpose.

Coatings made by IBAD method usually have high adhesion and good porosity property which is very important in material surface modification applications. Some papers have studied the formation of Al_2O_3 , Al and Al/Al_2O_3 coatings with IBAD technique[5,6,7,8,9], but no report on nonstiochoimetric and gradient alumina coatings had been published.

In this work, $Al_2O_x(0<x<3)$ coating and Aluminium-Alumina gradient layer will be deposited by using an IBAD facility, and their properties will also be discussed in this paper.

2. experiment details

The IBAD facility used in this work is equipped with a large target chamber of $1.1M^3$ and a MUCIS ion source which can provide high current with beam of diameter of 250mm, details about this facility had been described elsewhere[10].

Substrates were CK45 steel cylinders with diameter of 8mm and height of 10mm, and were polished mechanically to a mirror-like surface with roughness less than $1\mu m$. Coatings were also deposited on silicon wafer in purpose of RBS measurement. The assistant ion beam was 12keV Ar^+ with current density of $20\mu A/cm^2$, and its incident angle was $45°$; The deposition rate was always kept at $4Å/s$ and the coating thickness was monitored by a quartz crystal microbalance which had been calibrated by RBS method[11]. This set of parameters was chosen to enable the coatings have good porosity and adhesion properties[11].

The deposition was performed by evaporating Al of purity 99.9% in Oxygen environment, and the pressure in the target chamber was controlled with a digital flowmeter. Two series of coatings had been made in the experiment. The first series were four kinds of Al_2O_x coatings, which were deposited under O_2 pressure of 2×10^{-5}, 4×10^{-4}, 8×10^{-4} and 1.2×10^{-3} mbar respectively, the thickness of all these coatings was $1\mu m$; The another series includes five kinds of gradient coatings which composes of three layers: aluminium layer, $Al-Al_2O_3$ gradient layer and allumina layer, while the aluminium layer is always the most inner layer and Al_2O_3 layer is the most out one. This series of

coatings have the same thickness of 450nm, the alumina layer was always 50nm thick in all the samples, but the thickness of the gradient layers was 0nm, 100nm, 200nm, 300nm and 400nm respectively; The gradient layer were formed by increasing the O_2 inputting flow linearly until the pressure in the chamber reaches 1.2×10^{-3}mbar within a certain time, and its thickness could be determined by this time since the deposition rate was kept at 0.4nm/s.

Coating's porosity property was evaluated by the total area of its microholes which can be measured with electrochemical method. The measurement was performed by a conventional three electrodes system with a saturated Calomel electrode as reference electrode and potentialdynamiclly controlled in acetic aqueous buffer solution ($0.1MCH_3COONa + 1MCH_3COOH$), the scanning potential varied between -1200mV and 1200mV(vs SCE) at speed of 10mV/s. Critic corrosion current density (Icp) can be gained in this measurement, then the total area of microholes(S) in the coating can be derived as: $S=Icp/K$, where K is a constant(for CK45 steel, K is about $14mA/cm^2$)[12].

Alumina is corrosive in Cl^- contained aqueous solution but Al_2O_3 is very stable, it is interesting to study the corrosive behaviour of Al_2O_x(<0x<3) coatings in this kind of solution. In the experiment, corrosion resistance of samples with Al_2O_x coatings were measured; 0.1M NaCl was put into the acetic aqueous buffer solution; The potential scanned from -950mv(vs SCE) to the negative direction at speed of 0.25mV/s. Corrosion current as a function of the scanning potential was recorded.

Sample's microhardness were measured by a Vickers indentor under load of 15mN, and the final value is the average of eight different spots'. RBS and AES experiments were performed to investigate sample's composition and depth profile.

3.Results and discussion

3.1. Coating composition

RBS spectra were simulated with RUMP program. The results of the first series samples show that, under pressure of 2×10^{-5}, 4×10^{-4}, 8×10^{-4} and 1.2×10^{-3} mbar, the deposited coatings have a composition of Al, $Al_2O_{1.8}$ $Al_2O_{2.5}$ and Al_2O_3 respectively. The results of the second series samples are shown in Fig.1, Fig.1a is the depth profile of 300nm gradient layer, the other four kinds of samples have similar depth profile but their thickness are different as shown in Fig.2b. It can be seen that the O concentration increases linearly with the depth from the background value to 60%, but thickness of these gradient layers is larger than the expected values. This is because that the ion beam mixing effect enhanced O diffuse into aluminium layer and thus enlarge the gradient layer.
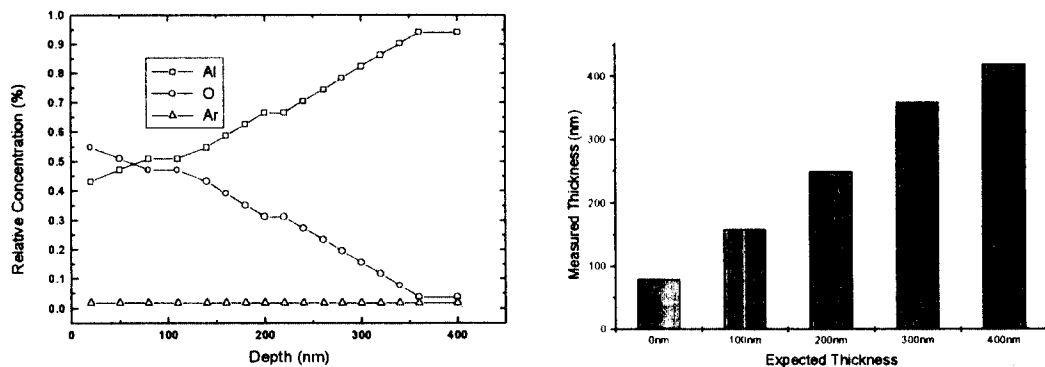
a) Depth profile of 300nm gradient layer b) Measured thickness of gradient layers

Fig.1 RBS measurement results of the gradient coatings

AES measurement results of the gradient coatings with 100nm and 400nm gradient layers are shown in Fig.2. It confirms that the O concentration changes gradually from 60% to its background value in the gradient layer; The concentration of O does not change linearly with the sputtering

charges, this is because the sputtering coefficient at different depth is not a constant due to the differential coating composition. Though it is impossible to get the accurate value of layer thickness, it is obvious that thickness of 400nm gradient layer is about two times larger than that of the 100nm gradient layer.
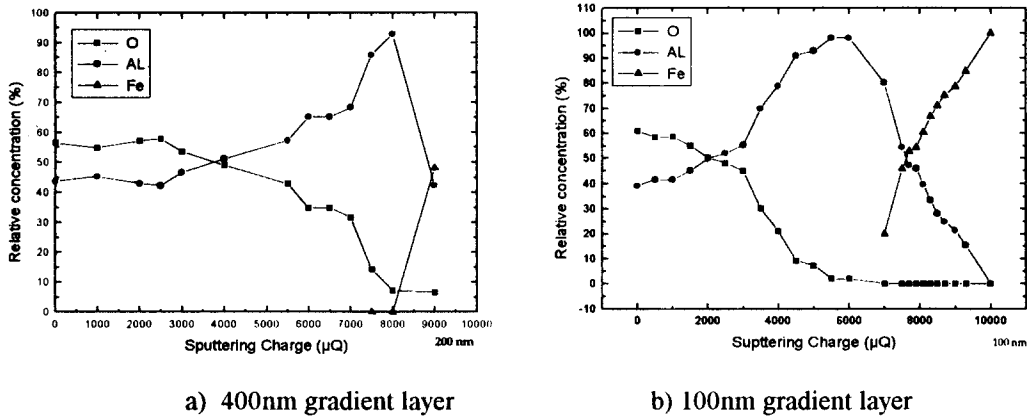

a) 400nm gradient layer   b) 100nm gradient layer

Fig.2 Depth profile of samples with 400nm and 100nm gradient layers measured by AES
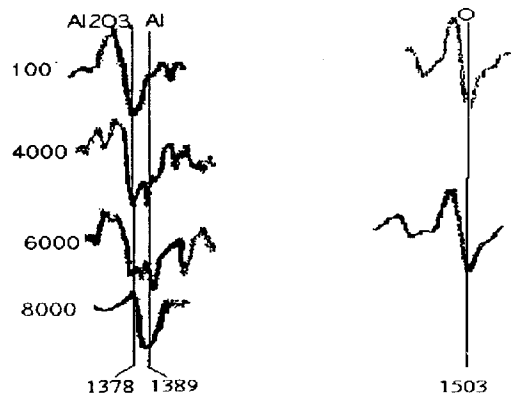

Fig.3 Al Auger electron peaks at different depth(μQ) of the 400nm gradient layer.

The chemical state of Al in the gradient coatings was also studied by AES. Fig.3 is the Al Auger peaks measured in different sputtering charges. Only two peaks were found in the experiment, one stands for metallic aluminium and the another for stiochoimetric Alumina; When O concentrate varied, only changes the height of these two peaks, but no new peaks appearing. This indicates that the Al_2O_{3x} coatings and the gradient layers is the mixture of metallic Al and Al_2O_3, no other compound exists.

The above results show that, it is possible to form Al_2O_x ($0<x<3$) coatings and design gradient Al-Alumina layers with expected composition and depth profile by carefully controlling of the O_2 inputting flow with an IBAD facility.

3.2. microhardness and porosity property

Sample's microhardness was measured under load of 15mN and the elastic effect was not recorrected. The results are shown in Fig.4. The Al_2O_x coatings of 1μm thick becomes harder with higher O concentration inside; As to the gradient coatings, sample's microhardness improves slightly when the gradient layer becomes thicker. According to the above AES results, Al_2O_x is the mixture of aluminium and Alumina, therefore, higher concentration of O or thicker aluminium-alumina

gradient layer means the coating composed of more alumina and less aluminium, as a result, sample's microhardness increases.
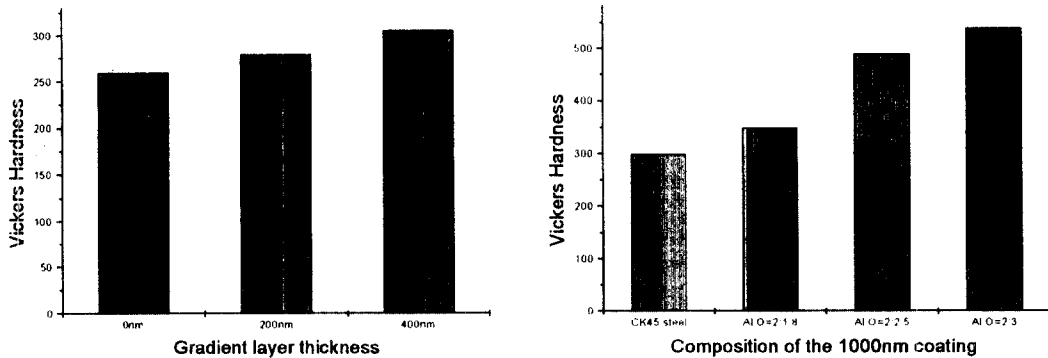

Fig.4 Sample microhardness measured with a Vickers indentor under 15mN load

As one of coating's important features, the total area of coating microholes had been gained as shown in Fig.5. Among the first series of coatings, $Al_2O_{1.8}$coating and $Al_2O_{2.5}$ coating is less porous than Al_2O_3 and Al coatings; In the second series of coatings, the one with 100nm or 200nm gradient layer shows better porosity property, and the coating becomes more porous increasing or decreasing the gradient layer thickness.

Since Aluminium grain dimension is smaller than the Alumina grain in this kind of coatings[11], the mixture of them is beneficial to reduce the formation of microholes; In case of the second series samples, the coating composition changes from Al_2O_3 to Al through the gradient layer part, a rapidly change could cut off some of the microholes, thus the microholes which can penetrate the whole coating become less, the measured area of the microholes decreases.
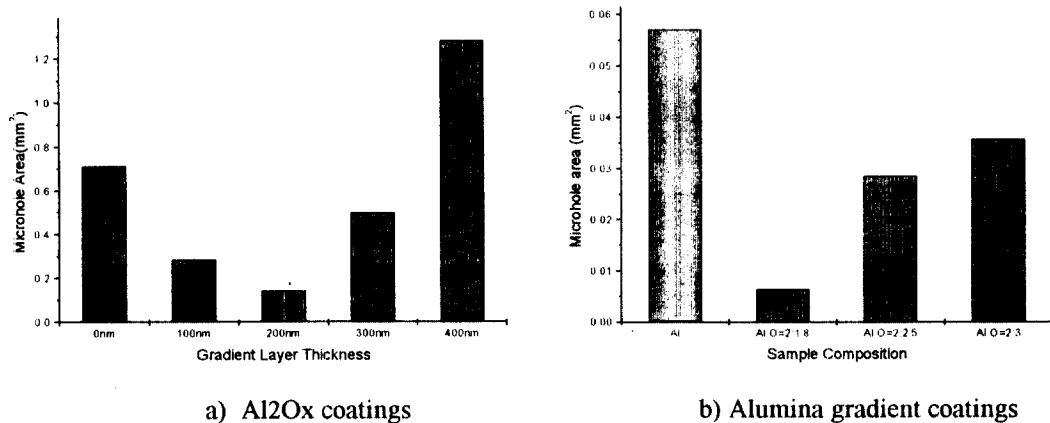

a) Al2Ox coatings   b) Alumina gradient coatings

Fig.5 Total area of coating microholes measured by electrochemistry method

3. Al_2O_x coating's corrosion protection ability in Cl⁻ contained solution

Cl⁻ contained solution is the most popular corrosive environment in the nature. Since aluminium is not stable so it can not be used to provide corrosion protection to corrosive materials, but Al_2O_3 coatings is widely used. It is very interesting to investigate the corrosive behaviour of Al_2O_x coatings in this kind of solution. Fig.6 is the electrochemistry measurement results and it can be seen that the $Al2O1.8$ coating can provide the best protection to 45 steel substrate while the Al_2O_3 coating does the worst; microscopy observation found no corrosion had occurred in the coating themselves, this means that the $Al_2O_x(x>1.8)$ material is stable in this solution. The $Al_2O_x(x>1.8)$ is also a suitable material to be used in this kind of environment, even it is better than the Al_2O_3 coating does.
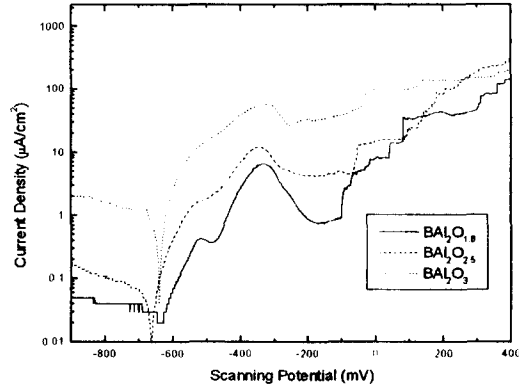
121

Fig.6 Corrosion resistance of Al_2O_x coating with different O concentration on CK45 steel

4.Conclusion

$Al_2O_x(0<x<3)$ and $Al-Al_2O_3$ gradient layers in different thickness can be formed by carefully controlling of the O2 inputting flow with an IBAD facility. The concentration of O in the deposited coating has a near linear relationship with the inputting flow before stiochoimetric Al_2O_3 can be formed.

Al_2O_x coating's microhardness is affected significantly by the O concentration, the higher the O concentration in the coating, the harder the coating is. Coating's porosity property is also influenced by the O concentration, the $Al_2O_{1.8}$ and $Al_2O_{2.5}$ coatings has less microhole compared with Al or Al_2O_3 coating's in same thickness; Electrochemistry measured in Cl contained solution show that the $Al_2O_{1.8}$ and $Al_2O_{2.5}$ coatings can provide better corrosion protection to CK45 steel substrate than the stiochoimetric Al_2O_3 does.

The above results show that, Al_2O_x $(0<x<3)$ and gradient alumina coatings with expected composition and depth profile can be formed with using IBAD facility, and some of their properties is better than Al or Al_2O_3 coatings.

Reference

[1]W.Ensinger and G.K. wolf, Mater. Sci. Eng. 116 (1989)p.1
[2]B.Enders, S. Krauss, K. Baba and G.K. Wolf, Surf. Coat. Technol 74-75(1995)p.995
[3]Ensinger, A. Schroer and G.K.Wolf, Nucl. Instrum. Methods B80/81(1993)p.445
[4]R.Emerich, B.Enders, G.K.Wolf, Proc. Int. Conf. on Ion beam modification of materials, Canberra, Feb.1995, p.732
[5]G.S. Was , J.W. Jones, C.E. Kalnas etal. Nucl. Instrum. Methods. B(80/81)(1993) p.1356
[6]G.S. Was, J.W.Jones, C.E. Kalnas etal. Surf. Coat. Technol. 65(1994)p.77
[7]R .S. Bhattachaya, A.K. Rai, A.W. McCormick, Surface Coat. Technol. 46(1991) p.155
[8]W. Kubler, Thin Solid Films 199(1983)p.257
[9]R. Emmerich, Dissertation, Heidelberg University(1994)
[10] R. Emmerich, B. Enders, W.Ensinger, Ion Beam Assisted Deposition: Process Parameters and Controll, in T.S. Sudarsh(ed.), Surface Modification Technologies VI, TMS Warrendale USA(1993).
[11] Xue Jianming, Doctoral dissertation, Peking University(1997).
[12] Xue Jianming, Zhao Weijiang etal., Surf. Coat. Technol, (in press).