Effects of tantalum ion implantation on the surface properties of Al–Mg alloy

D.Y. Zhang\textsuperscript{a,*}, Q.Y. Fei\textsuperscript{a}, H.M. Zhao\textsuperscript{a}, M. Geng\textsuperscript{a}, X.C. Zeng\textsuperscript{a,b}, P.K. Chu\textsuperscript{b}

\textsuperscript{a}National R&D Center for Surface Engineering of China, 2F, 531 building, Bagualing Industrial Zone, Futian District, Shenzhen 518029, PR China
\textsuperscript{b}Department of Physics & Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

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Abstract

The effects of tantalum ion implantation on the corrosion resistance, wear resistance and friction coefficient on Al–10% Mg alloys used in molds by the jelly food industry in China were investigated. The experimental results showed that the electrochemical passivation zone of the Al–Mg alloy specimens subjected to a citric acid solution was enlarged by tantalum ion implantation when the tantalum ion dose was more than $3.77 \times 10^{17}$ ions/cm$^2$. The hardness of implanted surface was elevated from 60 to 110 HV. The friction coefficient between the implanted surface and stainless steel was decreased from more than 1–0.33. Results obtained by X-ray photoelectron spectroscopy and Auger electron spectroscopy revealed the formation of a new Ta$_2$O$_5$ phase in the implanted layer.

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1. Introduction

Implantation of N, O, C, Fe, W, Mo, Ta, Cr has been used to enhance the surface properties of aluminum [1–19]. For example, it has been reported that implantation of these elements into Al can improve its surface characteristics such as wear resistance [5,6,8,13,14,18] and corrosion resistance [1–3,7,15–17]. Wei et al. have reported that the formation of a new Al$_3$Ta compound in tantalum implanted aluminum alloy [19]. Tantalum exhibits excellent corrosion resistance against most acidic solutions except HF and Al–10% (atomic) Mg alloy is one of the most corrosion resistant materials against an acidic environment among aluminum alloys. In the jelly food industry, Al–10% Mg is commonly used as the mold materials and better corrosion and wear resistance is needed. In the work described in this paper, we aim at lengthening the lifespan of jelly food molds made of Al–Mg alloy by using ion implantation.

2. Experimental details

Al–Mg alloy specimens (composition in wt.\%: Mg—10.8; Mn—0.3; the rest Al) were cut from a used mold as die-cast, ground, mechanically polished to roughness, $R_a$, of 0.6 $\mu$m that is the same as the surface of a new mold, and cleaned ultrasonically in acetone. Ion implantation was carried out in an ion implanter equipped with a metal vapor vacuum arc ion source. The cathode was made of industrial grade tantalum (composition in wt.\% Ta $\geq$ 99.6; the rest Nb, Ti). The ion accelerating voltage was 30 kV, and the average ion current density was 0.7 $\mu$A/cm$^2$. The working vacuum was about $2 \times 10^{-3}$ Pa during implantation. Under these implantation conditions, the sample temperature was lower than 60 $^\circ$C thereby ensuring that the sample microstructure remained unchanged. The implantation doses were $3 \times 10^{17}$, $5 \times 10^{17}$, or $7 \times 10^{17}$ cm$^{-2}$. 

\* Corresponding author.
E-mail addresses: deyuanzhang@sina.com (D.Y. Zhang), paul.chu@cityu.edu.hk (P.K. Chu).

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The electrochemical corrosion resistance experiments were conducted using a Gamry PCI4/750 electrochemical measurement system. The corrosion medium was an aqueous citric acid solution with a pH value of 3.3 and the temperature was 50 °C in order to simulate the practical working conditions of jelly food molds. The voltage was scanned from −660 to about −100 mV with a saturated calomel electrode (SCE) at a voltage scanning speed of 0.5 mV/min. The reference electrode was SCE whereas the working electrode was platinum.

The friction and wear experiments were carried out using the Sciland TS-0011 Tribometer in dry air at a relative humidity of 43%, temperature of 25 °C, normal load of 100 g, and speed of 25 mm/s. The measurement was made using JIS SUS303 stainless steel balls with the hardness of 900 HV. The friction force was recorded with a PCD-30 A computerized data treatment system at a recording frequency of 300 points/min. The surface hardness was measured using HXD-1000 TC micro-hardness tester under a normal load of 25 g and each test was performed for 15 s. The hardness values reported here are the mean values of 15 measurements on three samples.

The surface compositions and depth profiles were measured using the PHI-5300 X-ray photoelectron spectrometer (XPS) and PHI-610 Scanning Auger electron spectrometer. The operating parameters of AES were as follows: vacuum was $3.8 \times 10^{-7}$ Pa. The bias of coaxial electron gun was 3 kV, the angle of incidence was 30°. The CMA energy analyzer was used. Its energy resolution was 0.3%. A 3 kV argon ion beam with a current of 25 mA was used to acquire the depth profiles. The sputtered area was $1 \times 1 \text{ mm}^2$. The depth scale was estimated using a sputtering rate of 30 nm/min based on crater depth measurements in previous experiments conducted under similar sputtering conditions. The operating conditions of XPS are as follows. The working vacuum of analysis chamber was $3 \times 10^{-9}$ Pa and an aluminum anode was used. The energy resolution was 0.8 eV and sensitivity was $8 \times 10^4$ counts/s. The binding energies were calibrated based on the 285 eV carbon peak to compensate for sample charging.

### 3. Results

#### 3.1. Surface compositions and depth profiles

The AES depth profiles of tantalum, oxygen and aluminum in the Al–Mg alloy implanted with $7 \times 10^{17} \text{ cm}^{-2}$ Ta are depicted in Fig. 1. The implantation depth is about 300 nm, and the maximum tantalum concentration is about 22 at.%. It should be noted that since Ta is quite heavy and can cause some sputtering of the Al–Mg surface. However, our results show that a substantial amount of tantalum remains in the sample but as discussed later in this paper, sputtering does play a role in the depth of the Ta distribution. The amount of surface oxygen is very high (>50%) and is roughly about 2.5 to 3 times that of tantalum. It appears that a new Ta–O phase is formed in the implanted layer. The Gaussian fitting of the XPS spectrum shows that the binding energy of the Ta 4f$_{7/2}$ peak is about 25.501 eV, as shown in Fig. 2.

#### 3.2. Corrosion resistance

The passivation curves measured from the Al–10% Mg alloy samples implanted with different Ta doses in a citric acid solution of pH = 3.3 at 50 °C are displayed in Fig. 3. It can be observed that the passivated zone is expanded when the dose is higher than a critical value, while the activated corrosion current density of the implanted sample is much lower than that of the original Al–Mg alloy and does not change with the implant dose. Defining the first turning point, $V_c$, to be the highest voltage at which the surface layer remains passivated and based on the relationship between $V_c$ and the implantation dose shown in Fig. 4, a critical dose of $3.77 \times 10^{17} \text{ cm}^{-2}$ can be derived based on regression.
analysis. In other words, the aluminum samples implanted with a tantalum dose higher than the critical dose possess better corrosion resistance in a citric acid solution than the unimplanted ones.

3.3. Hardness, friction coefficient and wear resistance

The hardness results depicted in Fig. 5 illustrate that the surface hardness increases with the tantalum implantation dose. Our results show that when the implantation dose increases to $3 \times 10^{17}$ cm$^{-2}$, the surface hardness attains the maximum and little additional enhancement can be achieved by further increasing the implantation dose.

The typical friction coefficient variation with testing time acquired from the implanted sample is shown in Fig. 6. It can be readily observed that the implanted surfaces have much lower friction coefficients than the unimplanted samples. The friction coefficient decreases from more than 1 to 0.3 after tantalum implantation. During our test, after the implanted surface had been worn and punched through, the friction coefficient quickly reverted back to the original level. If the wear resistance is defined as the time when the friction coefficient begins to rise, the relationship between the wear resistance and Ta implant dose is quite similar to that of the hardness (Fig. 5).

4. Discussion

The AES depth profile reveals that the surface oxygen concentration is about 2.5 to 3 times that of tantalum, and deconvolution of the XPS peak using Gaussian fits shows that the tantalum peak is composed of a Ta 4f$_{7/2}$ peak at 25.501 eV and a Ta 4f$_{5/2}$ peak 27.405 eV. According to the spectra published in Ref. [20] as well as the published chemical shifts published in the Handbook of XPS published by Physical Electronics [21], these two peaks can be attributed to Ta$_2$O$_5$. Our results thus suggest that the implanted zone is mainly composed of Ta$_2$O$_5$, and our observation is different from that reported on Al$_3$Ta compounds [19]. This phenomenon can be explained by the normal free enthalpy of Ta$_2$O$_5$ that is $-1908$ kJ/mol [22] and that tantalum has a great chemical affinity to oxygen. The high surface oxygen concentration is due to leaks in the vacuum chamber and the long implantation time to achieve a high dose during when the tantalum surface becomes oxidized. The AES depth profiles show
that the concentrations and depths of the tantalum are smaller than the values calculated using TRIM implying that there is indeed a sputtering limited effect on the implantation process.

The passivation curves acquired in the citric acid solutions show that with increasing voltage, the sample is initially passivated but pitting corrosion ensues finally leading to activation. We can define $V_c$ as the voltage at which pitting corrosion occurs. When a small amount of tantalum is present on the surface, the local tantalum-rich area becomes the cathode forcing the adjacent area to be corroded as an anode, and so the stable zone is narrowed. That is to say, $V_c$ decreases. When the tantalum surface concentration is high enough to form a tantalum-rich film, $V_c$ becomes larger than that of the original surface. When the voltage forces the entire sample to the activated state, the corrosion current densities of all the samples become the same. It implies that the activated corrosion density has very little to do with the Ta concentration in the sample. However, this value is much smaller for samples that have not undergone Ta implantation. Hence, we believe that even when pitting corrosion emerges, the surface immersed in the acid solution remains tantalum-rich. In other words, tantalum does not dissolve substantially into the solution retaining the protection while most other elements tend to dissolve in the solution reducing the corrosion resistance.

5. Conclusion

The formation of $\text{Ta}_2\text{O}_5$ is observed in Ta implanted Al–Mg alloys. Tantalum implantation enhances the corrosion resistance in citric acid solutions at 50 $^\circ$C when the Ta dose exceeds a critical dose of $3.77 \times 10^{17}$ cm$^{-2}$. The surface hardness and wear resistance are also enhanced by about one fold, and the friction coefficient is reduced by 70%. The corrosion resistance of the implanted Al–Mg alloy in the citric acid solutions decreases initially with increasing Ta implantation dose and then increases when the Ta dose is higher than $2 \times 10^{17}$ cm$^{-2}$. Our study suggests an optimal dose of $3 \times 10^{17}$ cm$^{-2}$ for maximum efficacy.

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