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Surface alloying of aluminum with molybdenum by high-current pulsed electron beam

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ABSTRACT

The surface alloying of pre-coated molybdenum (Mo) film on aluminum (Al) substrate by high-current pulsed electron beam (HCPEB) was investigated. The microstructure and phase analysis were conducted by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results show that Mo particles were dissolved into Al matrix to form alloying layer, which was composed of Mo, Al and acicular or equiaxed Al_5Mo phases after surface alloying. Meanwhile, various structure defects such as dislocation loops, high-density dislocations and dislocation walls were observed in the alloying surface. The corrosion resistance was tested by using potentiodynamic polarization curves and electrochemical impedance spectra (EIS). Electrochemical results indicate that all the alloying samples had better corrosion resistance in 3.5 wt% NaCl solution compared to initial sample. The excellent corrosion resistance is mainly attributed to the combined effect of the structure defects and the addition of Mo element to form a more stable passive film.

1. Introduction

Aluminum (Al) and its alloys have been extensively used in various industries because of their excellent mechanical and physical properties (high specific strength, good ductility, low density, excellent thermal and electrical conductivity) [1,2]. However, they suffer from poor surface properties which severely restrict their further applications in many fields [3]. A major concern of Al and its alloys is the poor resistance to localized attack, particularly the pitting corrosion caused by the breakdown of passive film in the presence of halide ions. In order to overcome this deficiency, surface alloying of Al with transition metals like Mo, Cr, W and Ta is considered to be an efficient method to improve the stability of passive film [4,5]. However, the solid solubility of these metals in Al is less than 1 at.%, which makes it extremely difficult to synthesize transition metal aluminides by conventional metallurgical methods such as casting. Besides, these elements also fail to obey the Hume-Rothery rules to form solid solution with Al [6]. Therefore, the surface alloying process is only obtained by non-equilibrium techniques such as laser beam [7,8] and ion implantation [9]. These techniques are however energy and time consuming, and even may introduce undesirable impurities on the material surface.

High-current pulsed electron beam (HCPEB) is a relatively new non-equilibrium technique developed for surface modification and has been widely investigated in recent years [10–13]. HCPEB irradiation is carried out in a chamber with high vacuum which can efficiently prevent the material surface from oxidation and contamination. In addition, it can provide a narrow energy distribution, short duration time, widely chosen energy density range and good surface finishing. The interaction of the pulsed electron beam with the material can induce dynamic temperature fields in the surface layers, leading to ultra-fast melting, mixing and solidification. As a result, the modified surface after HCPEB treatment can exhibit outstanding mechanical properties and corrosion resistance [14–19]. Therefore, there is no doubt that HCPEB is a promising surface alloying method. Many researchers have investigated surface alloying of film-substrate systems by HCPEB technique. Rotshtein et al. [20] studied the Cu/stainless steel 316 system. Their results suggested that the formation of nano-Cu particles in the alloying layer led to the increase in hardness and wear resistance. In another study, Zhang et al. [21] investigated the Ti/AISI 316L stainless steel system, indicating that the enhancement in corrosion resistance was mainly attributed to the high homogeneity of Ti distribution in the melted layer after HCPEB irradiation. Luo et al. [22] examined the microstructure and wear resistance of Ta alloying layer on M50 steel. The results clearly showed that the friction coefficient was only 50% of the original samples under the circumstance of high temperature and heavy load. Accordingly, previous studies evidently demonstrated that HCPEB

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technique had a tremendous potential in surface alloying to improve the surface properties.

Molybdenum (Mo) is a kind of promising alloying element that can not only form hard intermetallic compounds with Al but also improve the corrosion performance. Nevertheless, to date, there is almost no report on detailed analysis of microstructure and phase evolutions in Mo/Al system alloyed by HCPEB irradiation. In light of this, the aim of present contribution is to investigate the relationship between the microstructural evolution and corrosion resistance of irradiated Mo/Al system.

2. Experimental procedure

2.1. Specimen preparations and Mo coating on Al

The as-received commercial Al 1100 with chemical composition (0.95 Si + Fe, 0.05–0.20 Cu, 0.05 Mn, 0.10 Zn and balance Al, all in wt. %) used in present study was cut into small (10 mm × 10 mm × 5 mm) square plates. All the samples were grounded with sand papers, polished with diamond paste and cleaned ultrasonically in acetone. Mo powder of 99.99% purity (5–10 μm particle size) was used. The slurry was prepared by mixing Mo powder (5 g) with organic binder (100 mL) (Nitrocellulose lacquer: diluent is 1:2). An agitator was used to mix the prepared slurry for about 20 min to get uniform mixing. The slurry was then sprayed onto Al samples using an air-pressurized spray gun. Later, they were dried in a vacuum oven at room temperature for 10 h. Before HCPEB irradiation, the thickness of the Mo coating measured by a Vernier Caliper was about 200 μm for all samples. The HCPEB irradiation was carried out with a HOPE-I type HCPEB apparatus. The parameters of the HCPEB irradiation were chosen as follows: working vacuum 5×10^{-3} Pa, accelerating voltage 27 keV, pulse duration 1.5 μs, energy density 4 J/cm^2, beam diameter 60 mm, pulse interval 10 s, and the number of pulses 15, 25.

2.2. Microstructural characterization

The phases at the sample surface were analyzed by X-ray diffraction (XRD) using a Rigaku D/max-2500/pc X-ray diffractometer with CuKα radiation. The microstructure of the modified surface was observed using a JEOL JSM-7001F type field emission gun scanning electron microscope (SEM) equipped with an Inca energy 350 type energy dispersive spectrometer (EDS) with accelerating voltage 15 kV. A transmission electron microscope (TEM, JEM-2100F) was also used to further investigate the microstructure and phases within the alloying layer. Thin foils used for TEM observation were prepared by one-sided milling, dimpling and subsequent ion thinning.

2.3. Electrochemical measurements

The electrochemical measurements were performed using a CHI660C electrochemical workstation. In order to ensure the accuracy of the corrosion test results, each experiment parameter was tested with three samples. A conventional three-electrode cell was used, containing the work electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum sheet as the counter electrode. The geometrically exposed area of the working electrode was 1 cm^2 and the electrolyte solution was 3.5 wt% NaCl (0.6 M). Standard potentiodynamic polarization and electrochemical impedance spectroscopy measurements were conducted after samples exposed to electrolyte solution under open circuit potential for 30 min at room temperature. The cyclic polarization (CP) tests were performed at a sweep rate of 0.333 mV/s. The electrochemical impedance spectra (EIS) were obtained at a frequency ranging from 10^{-2} Hz to 10^5 Hz at open circuit potential with an alternating current (AC) excitation amplitude of 10 mV.

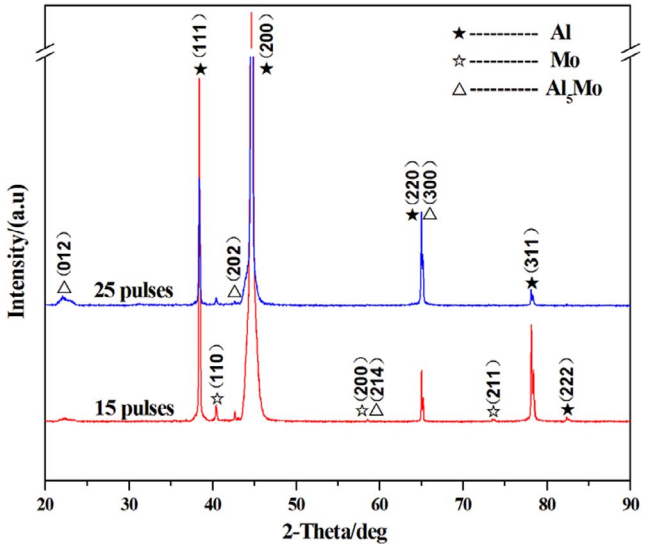

Fig. 1. XRD patterns of the samples after HCPEB irradiation with different pluses.

3. Results

3.1. Microstructure characterization

Fig. 1 shows the X-ray diffraction patterns of the irradiated samples with different pluses. It is clear that besides Al and Mo, the peaks of Al_5Mo intermetallic phase were also detected for both 15-pulsed and 25-pulsed samples. In addition, all of the Mo diffraction peaks were decreased in intensity after irradiation with 25 pulses while the intensity of Al_5Mo (0 1 2) peak was tremendously increased. It reveals that Mo atoms were largely dissolved into the Al substrate with increasing number of pulses, which resulted in the formation of Al_5Mo phase. The Mo-rich intermetallic phase such as Al_5Mo (Mo-16.7 at.%) hardly synthesized by the conventional methods was obtained indicating the ability of non-equilibrium HCPEB technique to significantly increase the solubility of Mo in solid Al. However, it is worth noting that there exist nine intermetallics in the Al-Mo phase diagram at different compositions and temperatures [23]. The absence of other intermetallics was probably owing to the most stable Al_5Mo phase with very low Gibbs free energy [24] under the HCPEB irradiation processing and material parameters employed in the present work.

Fig. 2 gives the secondary electron images of the samples after HCPEB irradiation. As shown in Fig. 2a, numerous volcano-like carters with small holes in their centers were observed on the surface of 15-pulsed sample. The presence of craters has been considered as a typical feature of HCPEB irradiation [25,26], suggesting the melt of Al matrix. The formation mechanism of craters has been investigated by many researches [27–30]. It has been well established that the craters are preferentially nucleated at the microstructure irregularities such as various structure defects, impurities and second phase particles. Besides, some large un-melted or partially melted white Mo powder was still visible on the melted surface of Al matrix. As the number of pulses increased to 25, as seen in Fig. 2b, the density of craters occurring on the surface was significantly reduced compared to the 15-pulsed sample. Meanwhile, the remaining Mo powder was further melted into Al substrate and rarely seen on the surface. In addition, it turned out that the surface of 25-pulsed sample became much smooth and compact. Table 1 gives the density and size of craters after HCPEB irradiation with different pulses. The evolution of crater density in present experiment was in good agreement with the work of Grosdidier et al. [31], which reported that the crater density for the alloys was decreased at high numbers of pulses. Therefore, the experiment results reveal that a sufficient number of pulses were favorable to remove