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Beneficial effects of yttrium on mechanical failure and chemical stability of the passive film in 6061 aluminum alloy

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Abstract Recent studies demonstrated that oxygen-active elements such as yttrium improved the resistance of some alloys to wear and corrosive wear. In this work, the breakdown of passive film and chemical resistance of the passive film in Y-free and Y-containing 6061 aluminum alloy samples were studied. It was demonstrated that critical load that caused failure of the passive film on Y-containing specimens was higher than Y-free samples. Also, penetration depth showed that indentation resistances of Y-containing samples were less than Y-free samples. Polarization behavior of Y-containing samples was improved in contrast of Y-free samples in water and acid environments. Y-containing samples had more power to stabilize the oxide film and make it more inert to electron transfer. Results showed that there was an optimum yttrium addition for improving the properties of Al 6061. Results showed that the best percent of yttrium addition was between 1.5 and 4% and more than this the properties of alloy did not improved

Introduction

Aluminium alloys are used widely in various industrial products such as vehicles, aircrafts, boats, and space shuttles thanks to their great formability, low density, and high corrosion resistance [1]. However, if the corrosion and wear properties of these alloys were be improved, it could be more useful for various products.

Recently positive effects of oxygen-active elements (OAEs) on corrosion and corrosive wear have been well demonstrated and documented. It has been shown that oxygen-active elements such as yttrium are very beneficial to passive metallic materials. Radu and Li [2] demonstrated that alloying Stellite 712 with a small amount of yttrium rendered the oxide scale on the alloy stronger with higher adherence to the substrate, which was largely beneficial to wear performance of alloy at elevated temperatures. Ahmadi and Li [3] reported that yttrium improved mechanical properties and high-temperature wear behavior of surface aluminized 1045 steel. Wang and Li [4] showed that yttrium enhanced the mechanical failure resistance and chemical stability of the passive film on 304 stainless steel. Other oxygen-active element, cerium, may also play a role similar to that of yttrium. Zhang and Li showed that cerium remarkably improved the protective efficiency of the aluminide coating on 1030 steel against dry sand erosion and corrosion in dilute NaCl and H_2SO_4 solutions [5]. The beneficial effect of the oxygen-active elements could be attributed to their high oxygen affinity, which helps to form a strong and adherent passive film.

The passive and oxide films are too thin and investigating their mechanical and physical properties is very difficult. This difficulty arises from the lack of suitable instrumentation. In recent years, some techniques have been developed for characterization of thin films. For instance, the nano-indentation technique has been widely used to investigate the mechanical behavior of thin films, including elasticity and hardness [6]. Another attractive technique for investigation the resistance of thin films is the nano/micro-scratch technique, which can be used to investigate the resistance of a thin film to wear, scratch, and

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delaminating [7]. These two techniques have been used to study wear and hardness of thin film coatings [8]. Iwasa et al. [9] used a nano-indentation technique to investigate thin films of indium-tin oxide and of chromium deposited on soda-lime-silica glass substrates.

Scanning Kelvin Probe is another method which is used to study the passive film. The chemical stability of surface coating could be evaluated using a Scanning Kelvin Probe by determining their surface Electron Work Function (EWF) [10]. EWF represents the energy required to activate the electron from the Fermi surface to the state of free electron. This parameter may be related to the stability of electron in a material or the inertness of the material against electron transfer.

The objective of this work was investigating effects of yttrium on mechanical failure and chemical stability of passive film in 6061 aluminium alloy. Various techniques were used in this research to study the effects of yttrium on properties of passive film in 6061 aluminum alloy modified with Yttrium.

Experimental procedure

Pieces of commercial 6061 aluminum and Y powder were mixed by melting in an arc melting furnace. Before melting, the furnace was evacuated to 5×10^{-2} T and then filled with argon gas to a pressure of 1 atm. The argon flow was maintained at a rate of 2 L/min during melting and solidification processes. All samples were turned over, remelted and cooled for four times in order to reduce microstructural inhomogeneity. The samples were mechanically polished using SiC sand paper and finally polished using 0.05 μm alumina.

Optical microscopy and scanning electron microscopy (SEM) were used to study microstructures. Chemical composition of samples was analyzed by energy dispersive X-ray spectroscopy (EDS).

Resistance of the oxide films against scratch was evaluated by universal micro-tribometer which had a mechanical testing probe made of tungsten carbide. Figure 1 shows shape of the probe. During scratch test, normal load was increased linearly from 0 to 10 g. Tip velocity under the applied load was 0.07 mm s^{-1}. Duration of scratch process was 60 s. During scratch, variation of electrical contact resistance with respect to load was recorded. When the oxide film was broken down under the applied force, electrical contact resistance dropped suddenly. Critical load resulting in drop of electrical contact resistance reflected to resistance of oxide film to failure.

The mechanical properties of passive films were evaluated using a tribo-scope (a combination of a nano-mechanical probe and an atomic force microscope). This test performed in tap water (10 h), NaCl solution (5 h), and H_2SO_4 solution (10 min). The probe was a four-sided pyramidal Vickers indenter made by diamond. The maximum applied load was 10 mN. Before nano-indentation test, Y-free and Y-containing samples were polished to roughness of 0.05 μm and etched using Keller's reagent for 10–15 s in order to remove the deformed layer caused by polishing.

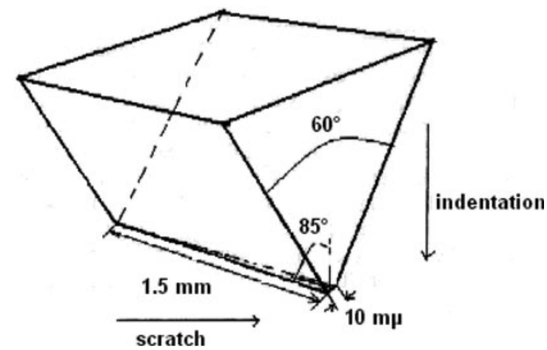

Fig. 1 Shape of the probe for indentation and scratch tests

A Gamry PC4/750 electrochemical measuring system was employed for test at a scanning rate of 0.33 mV/s under an applied potential of 0.5 V. Polarization test was performed in tap water, NaCl solution, and H_2SO_4 environments. In all electrochemical measurements, a Saturated Calomel Electrode (SCE) was employed as a reference electrode and a platinum wire as an auxiliary electrode.

A Scanning Kelvin Probe was used to measure the Electron Work Function (EWF) of the oxide films. Measurement was performed by applying a DC potential, termed the backing potential (V_b), to the sample and detecting the output signal via an amplifier connected to the tip electrode. A data acquisition system was used to measure the average peak to peak height (V_{ptp}) over a number of cycles as a function of V_b. The fractional change in capacity and then EWF were calculated. The EWF tests were carried out in open air after holding samples at 600 °C for 2 h. During the test, an area of 0.12×0.12 mm^2 was scanned.

Results and discussion

Microstructure of the samples

Figure 2 illustrates microstructures of Y-free and Y-containing samples. This figure shows a dendritic characteristic observed in all the specimens. The light and dark domains are dendritic and interdendritic regions, respectively. As shown, with increase the amount of yttrium, the dendritic structure was grown in the microstructure and a finer structure was shaped.

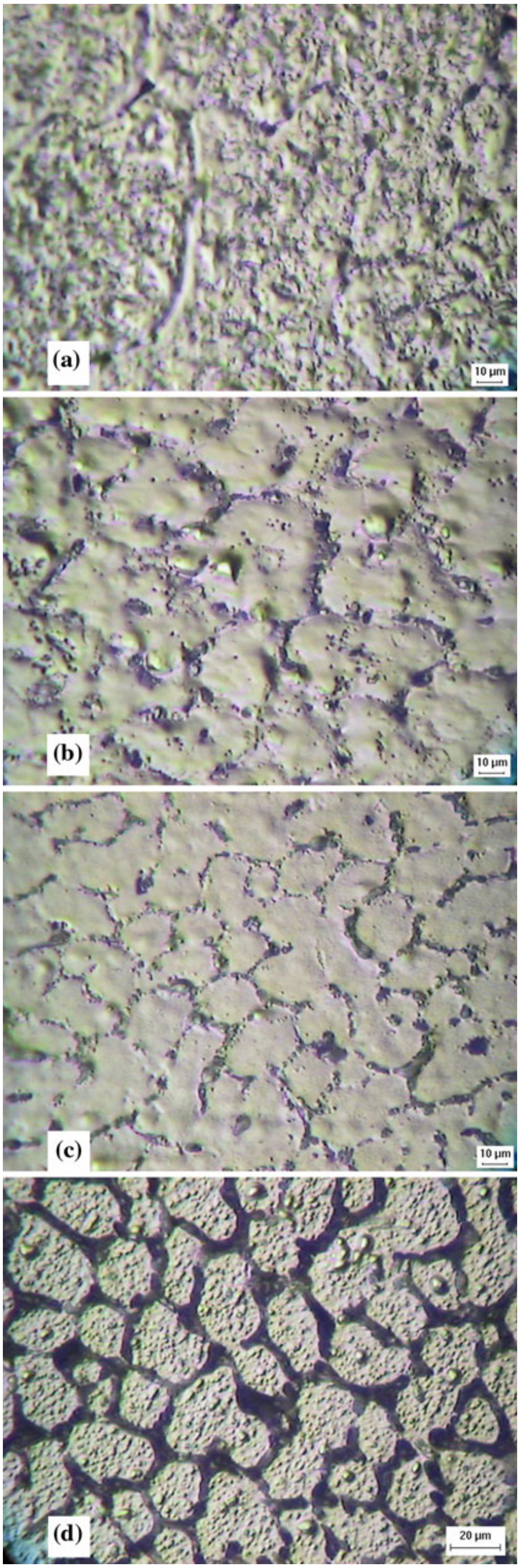

Fig. 2 Optical microstructures of 6061 alloy samples with **a** 0% Y, **b** 0.5% Y, **c** 1.5% Y, and **d** 4% Y. The light and dark domains are dendrite and inter-dendrite regions, respectively

Figure 3 shows SEM micrographs of Al 6061 samples without Ytrrium and containing 0.5, 1.5, and 4% Y, respectively. It can be seen with addition of yttrium, dendritic regions were grown in microstructure of the alloy. This dendritic structure is obvious especially in case of 1.5 and 4% Y addition. Compositions of various areas of the specimens (Fig. 3b–d) are given in Table 1. It can be seen that inter-dendritic regions contained different compositions from the matrix. White regions between grains of the dark Al matrix in Fig. 3 show Y congregation in the interdendritic regions. Although characterization of these new regions needs more investigations by the authors but according to some investigations [3, 11] these Y-rich phases may contain AlY, AlY_2, and AlY_3.

Scratch resistance of oxide film

The failure resistance of passive films in Y-free and Y-containing specimens was evaluated using micro-scratch technique. During the micro-scratch test, when the normal load was increased to a critical value, the passive film failed. A drop accompanied this failure in the contact electrical resistance. The critical load, corresponding to the drop in contact electrical resistance, was a measure of failure resistance of the oxide film. Figure 4 illustrates changes in contact electrical resistance of the oxide films of Y-free and Y-containing samples, as the indentation load was linearly increased. The drop in the contact electrical resistance of Y-free and Y-containing samples occurred when the passive film failed.

Figure 4 indicates that scratch resistance of the oxide film on Y-containing samples was superior to Y-free samples. This failure resistance was certainly beneficial for resistance against wear and corrosive wear. So, yttrium obviously enhanced the resistance of the oxide film to scratch failure. However, when Y addition was 4%, there was no more improvement in failure resistance of the oxide film in contrast with 1.5% addition. So it seems, there is an optimum content for addition of yttrium between 1.5 and 4% addition and more than this content yttrium addition would not improve the scratch resistance.

Mechanical properties of passive film

In order to evaluate the effect of yttrium on mechanical properties of the oxide passive film, the oxide film was investigated using a nano-mechanical probe with very light loads. Figure 5 presents load versus displacement curves of oxide film of Y-free and Y-containing samples formed under maximum load 10 mN. Nano-indentation tests performed in tap water, NaCl solution, and H_2SO_4 solution.

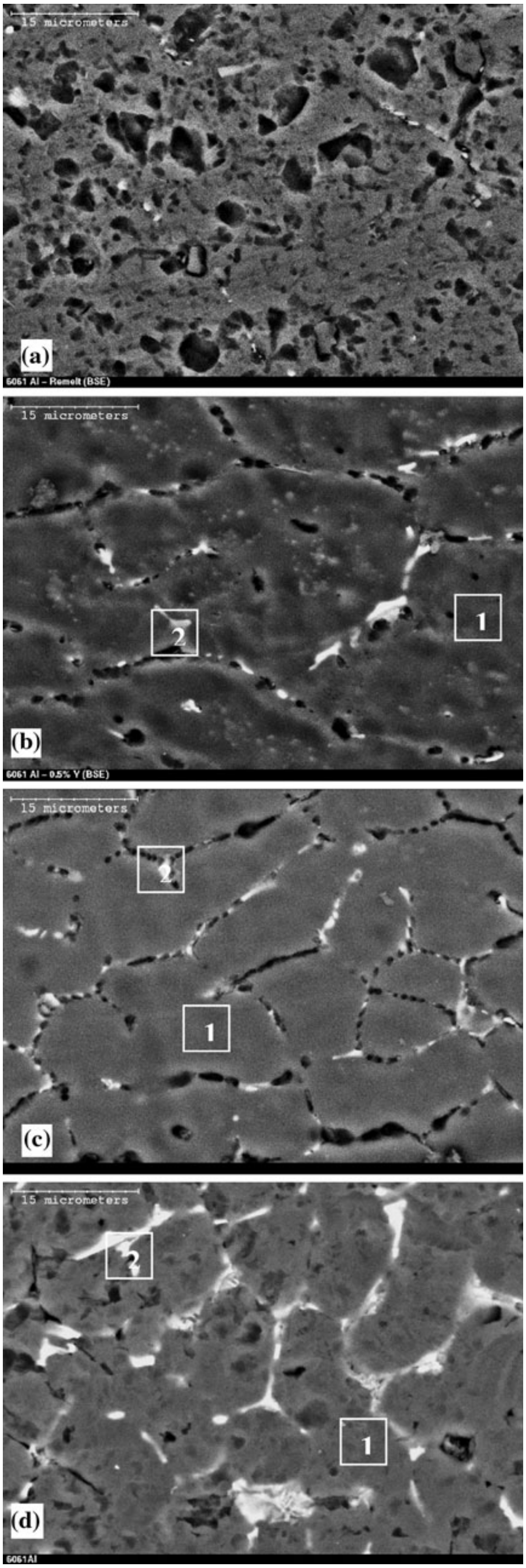

Fig. 3 Micrographs of cross-section of 6061 alloy samples with **a** 0% Y, **b** 0.5% Y, **c** 1.5% Y, and **d** 4% Y

Table 1 EDS analysis of selected areas (Fig. 3, atomic %)

Specimen	Area	Al	Si	Mg	Cu	Y
Y-free (Fig. 3a)	Overall	97.51	1.37	0.69	0.20	–
0.5% Y (Fig. 3b)	1	97.42	0.80	0.28	0.39	1.11
	2	99.43	–	0.57	–	–
1.5% Y (Fig. 3c)	1	88.61	5.97	0.57	–	4.86
	2	99.54	–	0.47	–	–
4% Y (Fig. 3d)	1	77.86	6.25	0.56	1.52	13.53
	2	99.55	–	0.46	–	–

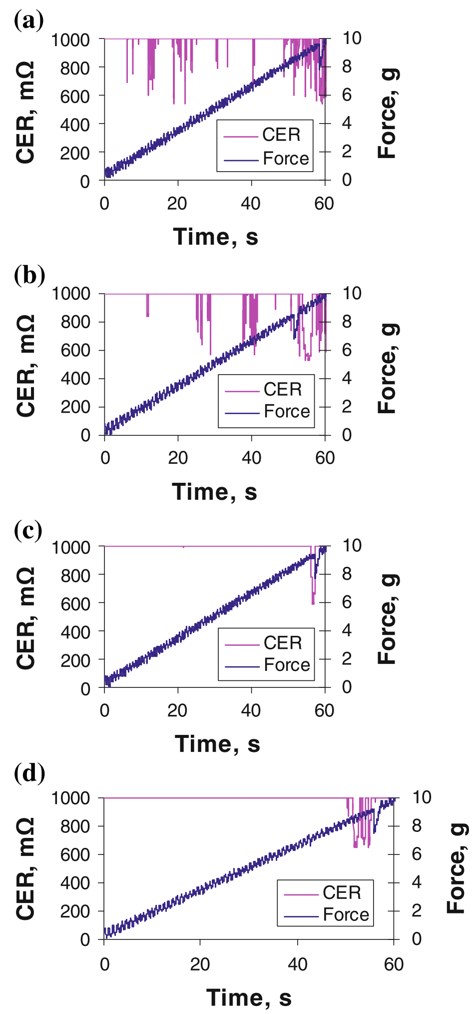

Fig. 4 Changes in the CER during micro-scratch in: **a** Al remelted, **b** Al + 0.5% Y, **c** Al + 1.5% Y, and **d** Al + 4% Y

In general, under a certain maximum load, the smaller the indentation depth, the harder is the material. In addition, the higher the slope of the unloading curves near the maximum load, the higher is the elastic modulus [12]. It should be indicated that since the oxide film on the surface of samples was very thin, the maximum depth could be

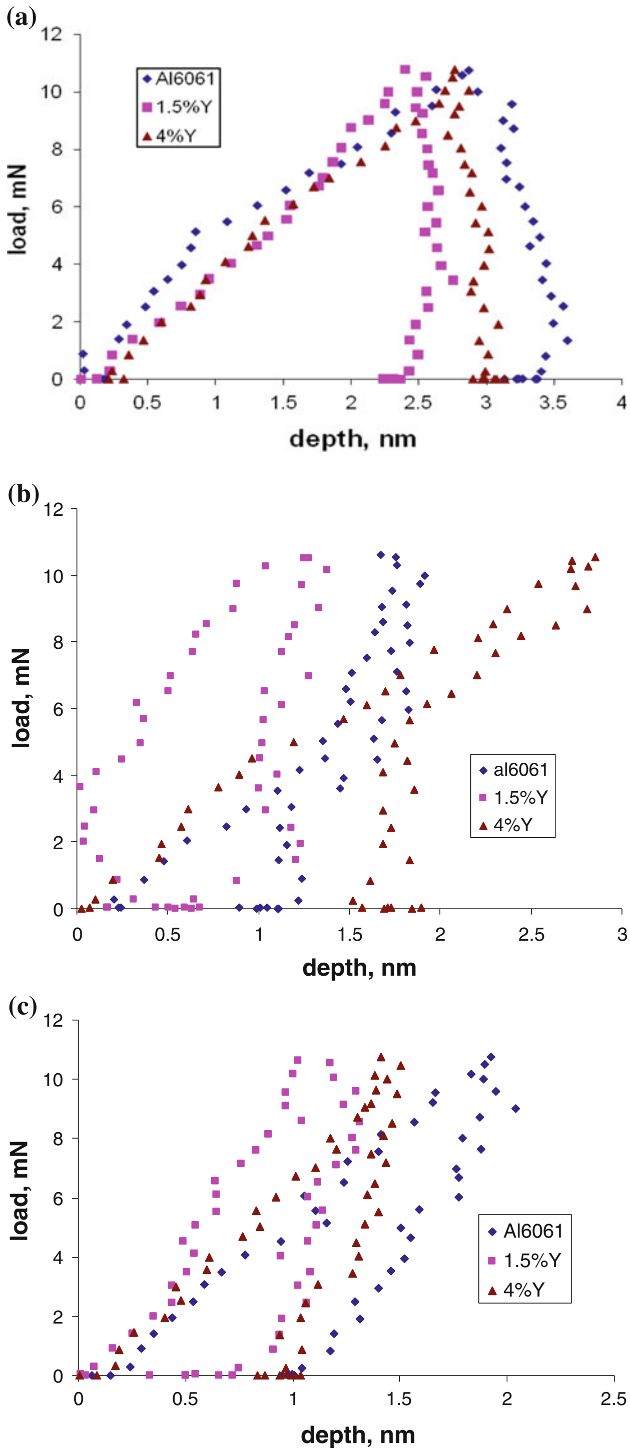

Fig. 5 Load-depth curves during nano-indentation test for the samples after being, **a** Tap water (10 h), **b** NaCl solution (5 h), and **c** H_2SO_4 solution (10 min)

influenced by the substrate. However, the measured results more or less reflected the mechanical behavior of the oxide film. According to Fig. 5, the oxide film in the Y-containing samples in all three environments had smaller penetration. In all three environments, Y-free sample had

Table 2 Nano-indentation test of different samples

Environment	Material	Maximum depth (nm)
Tap water (10 h)	Y free Al 6061	2.93
	Al 6061 +% 1.5	2.55
	Al 6061 +% 4	2.86
NaCl solution (5 h)	Y free Al 6061	1.76
	Al 6061 +% 1.5	1.27
	Al 6061 +% 4	2.85
H_2SO_4 solution (10 min)	Y free Al 6061	1.92
	Al 6061 +% 1.5	1.19
	Al 6061 +% 4	1.50

more indentation depth and therefore, less resistance to indentation than 1.5 and 4% added samples (Table 2).

Results showed that oxide film of Y-containing samples was harder than Y-free samples. The results showed that Yttrium improved the mechanical properties of oxide film. There was another notable effect in Fig. 5. It could be seen that 1.5% Y containing sample had smaller penetration than 4% Y containing sample. This result demonstrated this idea about existence an optimum content for addition of yttrium between 1.5 and 4% which more than this content, yttrium addition would not improve the nano-indentation resistance.

Electrochemical behavior

Electrochemical polarization behavior of the samples in tap water, 0.1 M H_2SO_4, and 3.5 wt% NaCl solutions was evaluated. Before tests, samples were prepared by connecting them with conductive copper wires, mounting them in epoxy followed by polishing to roughness of 0.05 μm. Polarization curves of samples with various amounts of Y and various environments were illustrated in Fig. 6a–c. As shown in Fig. 6a, although the addition of Y did not significantly influence the corrosion potential in tap water, the passivation behavior of the samples was improved when Y was added and the passive range extended to higher potentials. In this case, 1.5% Y-added sample had more improvement in passivation range than 4% sample. Figure 6b shows that polarization curves of various samples in 3.5 wt% NaCl solution. In this case, no considerable improvement in corrosion potential (E_{corr}) and passivation behavior of Y-added samples occurred.

Figure 6c shows that obtained polarization curves of samples added with different amounts of Y tested in a H_2SO_4 solution. The added yttrium did not change significantly the corrosion potential but there was a notable effect in passivation behavior of Al 6061 with addition of Y. The results showed that yttrium addition extended

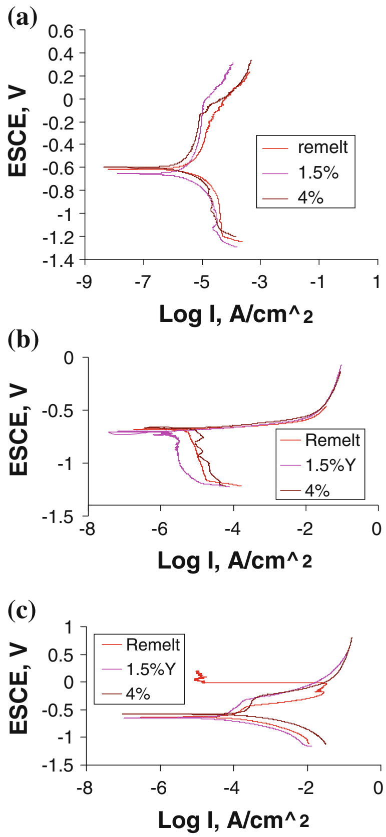

Fig. 6 Polarization curves of Y-free and Y-added samples in: **a** tap water, **b** 3.5 wt% NaCl solution, and **c** 0.1 M H_2SO_4 solution

passivation range of Al alloy considerably. There was no significant difference between passivation behavior of 1.5 and 4% Y-added samples.

Efforts were made to explain the effect of rare elements (RE) in improving the corrosion resistance of Al alloys [13] and pure aluminum. It was also found that a small amount of yttrium, e.g., 0.5%, markedly improved the polarization behavior of 304 stainless steel [14, 15] as well as the mechanical properties and the adherence of its passive film [4, 15]. The improvement in polarization behavior of the samples added with Y could be attributed to formation of a stronger and more adherent passive film due to the high oxygen affinity of yttrium. This enhanced passive film could improve polarization behavior of Y-added Al 6061 in contrast of Y-free alloy. It seems that a second phase was detrimental to the corrosion resistance of an alloy due to the formation of local galvanic cells. But such a negative effect could be compensated by possible beneficial effect of the enhanced passive film.

Electron work function

For oxide films and coatings, the degree of ease for an electron to escape from the Fermi surface to the state of free electron is related to the chemical stability and the protective role of the oxide film. In this work, a Scanning Kelvin Probe apparatus was used to determine the EWF of the oxide films on Y-free and Y-containing specimens.

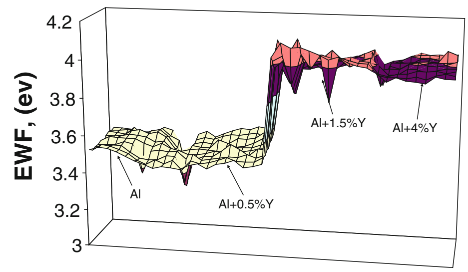

Fig. 7 Electron work function diagram of Al 6061, Y-free, and Y-containing samples

Table 3 Average electron work functions (eV) of different samples

Conditions	Al-remelted	Al-0.5% Y	Al-1.5% Y	Al-4% Y
Oxide film	3.50	3.51	3.99	3.98

The data is an average value over four measurements

Figure 7 presents EWF diagram of the oxide films of the aluminum samples. Table 3 presents results of the tests. According to the results, yttrium addition could improve the EWF of the oxide film on the samples. The best improvement was in the 1.5% yttrium case and after that in 4% addition, no more improvement was observed. This suggested that yttrium stabilized the oxide film and made it more inert to electron transfer, demonstrated by the electron work function measurement so the samples would be more protective against electrochemical attack.

Conclusions

Effects of yttrium on the resistance of passive film 6061 aluminum alloy to mechanical failure were investigated using micro-scratch, nano-indentation, polarization, and electron work function testing techniques. Microstructure studies showed that with addition of yttrium, new Y-rich regions created and dendritic structures were formed. According to the results of the tests, addition of yttrium delayed failure of passive film in samples to higher times and so improved scratch resistance of the samples. Also, this addition decreased indentation depth of samples in nano-indentation testing and so improved mechanical resistance of passive film. It was observed that between 1.5 and 4% addition of yttrium, there was an optimum content which more than it, there was not more improvement effect by yttrium.

Passivation behavior of the aluminum alloy was investigated by polarization tests. In water and H_2SO_4

environment, addition of yttrium extended the passivation range. Moreover, in case of water media, this addition improved corrosion potential. However, Y addition did not show improving effect on polarization behavior in NaCl media. The electron work function of the passive film was also determined using a Scanning Kelvin Probe apparatus. It was demonstrated that the electron work function of the passive film in Y-containing samples was higher than that in Y-free samples, implying that yttrium stabilized the passive film, thus leading to stronger and more chemically stable passive film. In both polarization and electron work function testing, it was observed again that more than 1.5% of yttrium, there was not more improvement effect by yttrium.

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