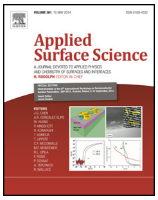
Applied Surface Science 301 (2014) 142–148

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc



Effects of copper and titanium on the corrosion behavior of newly fabricated nanocrystalline aluminum in natural seawater

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ARTICLE INFO

Article history:
Received 28 December 2013
Received in revised form 25 January 2014
Accepted 5 February 2014
Available online 16 February 2014

Keywords:
Aluminum alloys
Corrosion
Electrochemical investigation
Mechanical alloying
Seawater

ABSTRACT

Fabrication of a newly nanocrystalline Al and two of its alloys, namely Al–10%Cu; and Al–10%Cu–5%Ti has been carried out using mechanical alloying (MA) technique. The corrosion behavior of these materials in aerated stagnant Arabian Gulf seawater (AGSW) at room temperature has been reported. Cyclic potentiodynamic polarization (CPP), chronoamperometric current-time (CCT) and electrochemical impedance spectroscopy (EIS) measurements along with scanning electron microscopy (SEM) and X-ray energy dispersive (EDX) investigations were employed to report the corrosion behavior of the fabricated materials. All results indicated that Al suffers both uniform and localized corrosion in the AGSW test solution. The presence of 10%Cu decreases the corrosion current density, the anodic and cathodic currents and corrosion rate and increases the corrosion resistance of Al. The addition of 5%Ti to the Al–10%Cu alloy produced further decreases in the corrosion parameters. Measurements together confirmed that the corrosion of the fabricated materials in AGSW decreases in the order Al > Al–10%Cu > Al–10%Cu–5%Ti.

Introduction

Aluminum and its alloys have many characteristic properties like their low density, excellent workability, high thermal and electrical conductivities, and good corrosion resistance [1–5]. Therefore, Al and Al base alloys have been widely used as materials in the fields of transport, building, electrical engineering, household appliances, containers, aircraft, aerospace, etc. The use of these alloys in industry is limited by their relatively low yield stress and corrosion problems when exposed to harsh environments such as chloride solutions and natural seawater [6–8]. It has been reported [6–12] that Al and its alloys develop a compact, adherent, and continuous oxide film on their surfaces upon exposure to the atmosphere or aqueous solutions. The formation of aluminum oxide film does not have the ability to protect the surface in corrosive media such as natural seawater and solutions containing high chloride concentrations where, aluminum suffers both uniform and pitting corrosion [10–14]. This occurs because of the breakdown of the oxide film as a result of the corrosiveness attack of chloride ions that present in those media.

Mechanical alloying (MA) technique is a solid-state powder processing technique which involves repeated welding, fracturing, and re-welding of powder particles in a high-energy ball mill. A variety of equilibrium and non-equilibrium alloy phases could be synthesized using mechanical alloying starting from elemental powders. The advantages of using mechanical alloying technique in materials production include several benefits [15–19] such as (1) producing fine dispersoid of second phase particles; (2) extending the equilibrium solubility limit; (3) refining the grain sizes to the nanoscale; (4) producing new phases; and (5) alloying of immiscible alloying elements. MA technique, however, is a complicated process and requires an adequate control of several parameters to reach the desired properties of the products. These are some significant variables which influence the final properties of mechanically alloyed products: speed of milling; time of milling; grinding medium; ball-to-powder weight ratio; extent of filling the container; atmosphere of milling; process control agent; and milling temperature. Optimizing the previously-mentioned variables is a critical process for achieving the desired properties/microstructure of the processed alloys.

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http://dx.doi.org/10.1016/j.apsusc.2014.02.019
0169-4332/

The aim of the present work is twofold. The first is at developing thermally stable nanocrystalline pure aluminum and some of its alloys using MA technique. The design of the new alloys was achieved by adding 10%Cu and 5%Ti. Titanium is considered as a low diffusivity alloying element in aluminum in equilibrium conditions. The use of mechanical alloying technique in producing these alloys was to make use of the advantages of this technique in extending the solid solubility of copper and titanium in aluminum; refining the grain sizes to nanoscale and formation of thermally stable second phase particles. The extension of solid solubility limit of Ti and Cu in aluminum gives a chance for forming a super-saturated solid solution and also thermally stable nanosized precipitates. The second objective is to study the effect of Cu and Ti as alloying elements on the corrosion behavior of the fabricated nanocrystalline Al in the aerated stagnant Arabian Gulf seawater, which is known as the most corrosive medium for Al, at room temperature using cyclic potentiodynamic polarization, chronoamperometric current-time and electrochemical impedance spectroscopy measurements along with scanning electron microscopy and X-ray energy dispersive investigations.

Experimental setup

Fabrication of nanocrystalline Al and Al alloys

The as-received metal powder (size ≈100 μm) of aluminum, copper and titanium were used to synthesis the different nanocrystalline aluminum (Al; Al–10%Cu; and Al–10%Cu–5%Ti) alloys using mechanical alloying technique. The mechanical alloying procedure in the present study was carried out using 1S-attritor machine. Where, the ball milling process was performed under inert atmosphere of high purity argon (99.999%); ball-to-powder weight ratio (BPR) of 90:1; speed of rotation of 300 rpm, and milling time of 6 h. An amount of 3 wt% of stearic acid was added, as a process control agent (PCA), to the aluminum powder to prevent its agglomeration and welding during ball milling process. Powder consolidation was carried out using a high-frequency induction heat sintering (HFIHS) machine, where the processed powders were sintered into a dense and strong bulk material. The mechanically alloyed powders were placed in a graphite die and then introduced into the HFIHS. The obtained alloys were in a cylindrical shape with dimensions of 10 mm in diameter and 12 mm in length.

Chemicals, materials and electrochemical cell

The naturally aerated stagnant seawater was Arabian Gulf seawater and was obtained from the eastern region of the Arabian Gulf (eastern coast, Jubail, Dammam, Kingdom of Saudi Arabia). An electrochemical cell with a three-electrode configuration was used; a platinum foil and an Ag/AgCl electrode (in the saturated KCl) were used as the counter and reference electrodes, respectively. The newly fabricated nanocrystalline Al, Al–10%Cu, and Al–10%Cu–5%Ti rods were used as the working electrode. The working electrode for electrochemical measurements was prepared by welding a copper wire to a drilled hole was made on one face of the rod; the rod with the attached wire were then cold mounted in resin and left to dry in air for 24 h at room temperature. Before measurements, the other face of the working electrode, which was not drilled, was first ground successively with metallographic emery paper of increasing fineness up to 1000 grit and further polished with 5, 1, 0.5, and 0.3 mm alumina slurries. The electrodes were then cleaned using doubly-distilled water, degreased with acetone, washed using doubly-distilled water again and finally dried with dry air.

Electrochemical measuring techniques

An Autolab Potentiostat (PGSTAT20 computer controlled) operated by the general purpose electrochemical software (GPES) version 4.9 was used to perform the electrochemical experiments. The cyclic potentiodynamic polarization (CPP) curves were obtained by scanning the potential in the forward direction from −1800 to −250 mV against Ag/AgCl at a scan rate of 1.0 mV/s. For the back scan, the potential was reversed from −250 mV in the backward direction at the same scan rate in order to complete the cycle test. Potentiostatic current-time (CCT) experiments were carried out by stepping the potential of the aluminum samples at −500 mV vs. Ag/AgCl for 60 min. The electrochemical impedance spectroscopy (EIS) tests were performed at corrosion potentials (E_{OCP}) over a frequency range of 100 kHz–100 mHz, with an ac wave of ±5 mV peak-to-peak overlaid on a dc bias potential, and the impedance data were collected using Powersine software at a rate of 10 points per decade change in frequency. All measurements were carried out at room temperature and after 1 h immersion of the working electrode in the Arabian Gulf seawater except the open-circuit potential curves were collected from the first moment of the electrode immersion.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) investigations

The SEM investigation and EDX analysis were obtained for the surface of Al, Al–10%Cu and Al–10%Cu–5%Ti after their immersions in the AGSW for 60 min before applying and amount of −0.50 V vs. Ag/AgCl on the electrodes' surfaces for another 60 min. The SEM/EDX data were collected by using a JEOL model JSM-6610LV (Japanese made) scanning electron microscope with an energy dispersive X-ray analyzer attached.

Results and discussion

Cyclic potentiodynamic polarization (CPP) measurements

In order to study the effect of adding Cu and Ti on the corrosion behavior of the nanocrystalline Al after 60 min exposure in aerated stagnant AGSW, CPP measurements were carried out. Fig. 1 shows the CPP curves obtained for (a) Al, (b) Al–10%Cu, and (c) Al–10%Cu–5%Ti, respectively. The values of cathodic (βc) and anodic (β·a) Tafel slopes, corrosion potential (E_{Corr}), corrosion current density (j_{Corr}), passivation current (j_{Pass}) pitting potential (E_{Pit}), protection potential (E_{Prot}), polarization resistance (R_p), and corrosion rate (R_{Corr}) that were obtained from the CPP curves as previously reported in our studies [3,11,20,21] are listed in Table 1. It is clearly seen from Fig. 1 that the cathodic current of the tested materials decreases with increasing the potential in the less negative potential till the current reaches its minimum at the corrosion current density, j_{Corr}. The cathodic reaction for Al and its alloys at these conditions is believed to be the oxygen reduction as follows [3,11]:

$$O_2 + 2H_2O + 4e^- = 4OH^- \tag{1}$$

Further increasing the potential towards the positive direction leads to rapid increases of current in the anodic reaction due to the dissolution of aluminum metal, Al(0), into aluminum cations, Al(III), with the release of electrons according to the following reactions [11]:

$$Al = Al^{3+} + 3e^- \tag{2}$$

After the rapid increases of current, the polarization curve shows a large passivation region, which is most probably due to the formation of an oxide film and/or a corrosion product layer on the