Electrochimica Acta 203 (2016) 426–438

Contents lists available at ScienceDirect

Electrochimica Acta

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

Combining the Electrochemical Microcell Technique and the Electron Backscatter Diffraction method to study the electrochemical behaviour of polycrystalline aluminium in sodium chloride solution

Halina Krawiec*, Zbigniew Szklarz

AGH-University of Science and Technology, Faculty of Foundry Engineering, Department of Chemistry and Corrosion of Metals, ul. Reymonta 23, 30-059 Krakow, Poland

ARTICLE INFO

Article history:
Received 15 January 2016
Received in revised form 3 March 2016
Accepted 5 March 2016
Available online 7 March 2016

Keywords:
Plastic deformation
microstructure
crystallographic orientation
pitting corrosion

ABSTRACT

The corrosion behaviour of pure aluminium was studied at the microscale in 0.1M NaCl by combining the electron backscatter diffraction technique and the electrochemical microcell technique. The microstructure was first described. It was found that plastic strain has little influence on these microstructural parameters. After surface preparation, the crystallographic orientation of grains plays a significant role in their corrosion behaviour. Grains oriented along (001) planes are the most resistant to pitting corrosion whereas those oriented along (111) planes are the most susceptible to pitting. After plastic deformation, the susceptibility to pitting corrosion of Al grains is significantly increased and there is no influence of the crystallographic orientation of grains. It was proposed that the presence of a high density of statistically stored dislocations (which cannot be detected by EBSD) affects the physical chemical properties of the oxide film formed on grains. This oxide film degenerates, leading to high susceptibility of pure Al to pitting corrosion.

1. Introduction

Metals and alloys are usually used in engineering systems as a polycrystalline materials. They contain grains having their own crystallographic orientation and grain boundaries. Many studies have been performed to explain the influence of the crystallographic orientation of single grains on the electrochemical behaviour of metals and metallic alloys. These include zirconium [1], zinc [2,3], iron [4–7], niobium [8], copper [9], magnesium [10,11], titanium [12], pearlitic steel [13], ferritic steel [14], martensitic stainless steel [15], austenitic stainless steel [16], austenitic-ferritic stainless steel [17,18], Mg-Al-Zn alloys [19] and Ni-Cr-Mo-W-Fe alloys [20]. It appears that the crystallographic orientation plays a significant role in the electrochemical response of materials. However, an overview of this literature indicates that no general trends emerge. Results depend closely on the material and the electrolyte selected. In addition, results derived from different electrochemical techniques on the same couple material/electrolyte are generally consistent. For example, it was found both from scanning electrochemical microscopy [7] and polarisation curves plotted with a classical three-electrode cell [21] that that the active-dissolution current in borate solution of iron (110) planes is larger than that of iron (100).

Similar studies have also been performed on pure aluminium [22–29]. It was found [25] that the susceptibility of single aluminium crystals to the onset of pitting attack in chloride containing solutions (NaCl-based media for example) varies in the order (111) > (110) > (100). This was explained in terms of differences in the surface energy of (111), (110) and (100) planes [25]. The surface energy of aluminium crystal faces differ in the order (100) > (110) ≈ (111) [28]. It was also proposed that the formation of a pit on the (100) surface requires the dissolution of (111) subsurface atoms, while pit formation on the (111) surface requires the removal of the less tightly bound (100) subsurface atoms [28]. When a polarisation in the cathodic domain (at −2.5 V vs. SCE) is previously applied, Al crystals show little dependence of pit initiation on the surface orientation in HCl solutions [27,29]. During pit growth, the (110) planes dissolves more rapidly among the (100), (111) and (110) surfaces. Electrochemical studies on single aluminium crystals have also revealed the preferential occurrence of cathodic reactions on an (100) crystal in neutral chloride solution [25]. It was suggested that the more open

---

* Corresponding author.
E-mail address: krawiec@agh.edu.pl (H. Krawiec).

http://dx.doi.org/10.1016/j.electacta.2016.03.030

arrangement of atoms on the (100) plane facilitates reduction reactions and incorporation of reduced species into the (100) lattice.

The application of mechanical stress can significantly change the corrosion susceptibility of metals. Several studies have been performed to understand the corrosion fatigue behaviour [30,31], the corrosion wear resistance [32], the slurry erosion-corrosion behaviour [33] of pure aluminium. The development of stress induced by hydrogen absorption during cathodic polaristion has also been investigated [34]. The corrosion behavior of ultra-fine grained industrial pure Al fabricated by ECAP has been quantified [35]. Previous works [36,37] have shown that strain gradients developed near grain boundaries play a significant role in the corrosion behaviour of Al alloys. To our knowldege, no investigations have been conducted on single grains or mono-crystals of pure Al to understand the influence of crystallographic orientation on the electrochemical behaviour of strained specimens.

In this paper, the influence of the crystallographic orientation of grains in pure aluminium is first investigated in NaCl-based medium using the electron backscatter diffraction (EBSD) technique and the electrochemical microcell technique. The influence of strain applied in the plastic domain is then studied. Results are discussed considering the crystallographic orientation of grains and the nature of dislocations generated during plastic deformation

2. Experimental

2.1. Material and surface preparation

All experiments were carried out on polycrystalline aluminium plates of 99,99% purity (provided by Goodfellow Metals). Specimens were ground using 800, 1200, 4000 SiC emery papers followed by smoothing in silica colloidal suspension. They were then electropolished in an electrolyte containing 700 ml of ethanol, 100 ml of 2-butoxyethanol, 80 ml of perchloric acid and 120 ml of distilled water. The electrolyte temperature was 25 °C. A potential of 20 V was applied for 7 seconds.

2.2. Electron backscatter diffraction measurements

The crystallographic texture of polycrystalline Al specimens was determined after surface preparation and after applying 5.5% plastic strain using the EBSD technique. These experiments were performed using the INCA Crystal EBSD System coupled with a FEI Quanta 3D field-emission scanning electron microscope (FE-SEM). The post-process of EBSD measurements was carried out using the TSL orientation imaging microscopy (OIM) version 7 software package.

2.3. Electrochemical investigations

Local electrochemical measurements were performed on single aluminium grains using the electrochemical microcell technique. The set-up of this technique consists of an electrolyte-filled glass capillary whose tip is adhered to the specimen surface with a layer of silicon rubber. Note that the deformation of the silicon rubber is controlled when there is contact with the substrate using a high-spatial resolution video system. The same deformation is applied to the silicon gasket during a set of measurements. The electrolyte used is aerated. The microcell is mounted onto a microscope to enable precise positioning of the capillary on the specimen surface. In our experiments, the capillary tip has a diameter of 70 μm. The counter electrode is a platinum wire and the reference electrode is Ag/AgCl (3 M KCl). All electrochemical measurements were performed using a potentiostat AUTOLAB PGSTAT 302 N electrochemical interface with the Extreme Low Current Detection (ECD) module.

Local polarisation curves were plotted from −2000 mV vs. Ag/AgCl to the anodic direction at a scan rate of 1 mV s^{-1}. The electrolyte is 0.1 M NaCl at 25 °C. Local polarisation curves were interrupted when stable pitting was observed. Local Electrochemical Impedance Spectroscopy (LEIS) diagrams were plotted at the open circuit potential (OCP) value within a frequency range of 100 kHz to a few mHz (70 points) using 10 mV peak-to-peak sinusoidal potential difference. Samples were previously immersed in the solution at the OCP value for 90 minutes.

3. Results and discussion

3.1. Microstructure after mechanical polishing

EBSD measurements were first performed after electropolishing. These measurements were performed on a large surface area (72 mm^2) with a high spatial resolution (step of 5 μm). In the post-process of EBSD results, the grain tolerance angle used to define grain boundaries was set at 5° and the minimum grain size at 6 pixels. Under these conditions, both low-angle grain boundaries and high-angle grain boundaries are considered. In the case of low-angle grain boundaries, the angle θ between the two adjoining grains is low enough to accommodate this misorientation by an array of dislocations [38–40]. With increasing θ, the dislocation spacing decreases to such an extent that the dislocation model of the grain boundary structure fails because individual dislocations are no more distinguishable and overlap one with the other. This is the case of high-angle grain boundaries. Generally, it is assumed that the limit for successful application of the dislocation model lies between 13 and 15° [41]. This limit is supported experimentally on different materials [42,43]. According to structural unit model [44], a high-angle grain boundary is formed by repeated structural units that represent particular arrangements of limited number of atoms. High-angle grain boundaries containing coincidence sites are called coincidence site lattice boundaries. In this case, the grain boundary energy is low when the coincidence of atomic positions in both adjoining grains is high.

The fraction of high-angle grain boundaries within the analysed region was estimated to 80%. Coincidence site lattice boundaries represent less than 5% of these grain boundaries. They mainly correspond to $\Sigma3$ (roughly 2% of the coincidence site lattice boundaries) and $\Sigma5$ (roughly 1.2% of the coincidence site lattice boundaries). Other high-angle grain boundaries correspond to random grain boundaries.

Fig. 1(a) shows the inverse pole figure map derived from EBSD measurements. Grain boundaries were also plotted in this figure: white lines representing low-angle grain boundaries and black lines representing random grain boundaries. The average grain surface area calculated from this microstructure is 0.105 ± 0.04 mm^2. In addition, a majority of grains (52%) was found to appear in the red color, indicating that the specimen surface is preferentially oriented along (001) planes. A tolerance angle of 20° was used to calculate the fraction. This result was confirmed when constructing the (001) pole figure from EBSD measurements. The obtained pole figure (Fig. 1(b)) corresponds to the pole figure of a cubic system with the out-of-plane in the [001] direction.

Fig. 1(c) shows the grain orientation spread (GOS) map calculated within the investigated region from the inverse pole figure. The GOS gives the average misorientation angle between all measurement points in a grain (defined as a region completely surrounded by boundaries with a misorientation > 5°). It can be considered as a measure for the average dislocation density in grains [45]. Values between 0 and 6° were found, Fig. 1(c).