



Ionic motion during field-assisted oxidation of aluminium studied by molecular dynamics simulations



Astrid Gubbels-Elzas, Barend J. Thijsse *

Delft University of Technology, Department of Materials Science and Engineering, Mekelweg 2, 2628 CD Delft, The Netherlands

ARTICLE INFO

Article history:

Received 23 February 2014

Accepted 28 March 2014

Available online 4 May 2014

Keywords:

Oxidation

Alumina

Anodization

Molecular dynamics

Electric field

ReaxFF

ABSTRACT

Molecular dynamics simulations with the REAX force field were performed to model the growth of an oxide layer on (100)-oriented aluminium in three different oxidation environments: atomic oxygen gas, liquid water, and an aqueous ammonium tartrate solution. The anodizing behaviour was studied at two different temperatures (300 K and 600 K), in the absence of an external electric field and with field strengths of 0.5–2.0 V/Å applied over the growing oxide. The aim of this study is to determine how the ion motion in the oxide layer is affected by an electric field and by the oxidizing medium. The principal findings are that (1) O and Al ions move through the oxide via interrupted sequences of short replacement steps rather than as a continuous motion across the oxide, (2) dissociation of H₂O molecules at the surface is crucial, and (3) the dependence of the ion motion on the electric field strength exhibits steps in the growth behaviour.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In environmental conditions aluminium (Al) rapidly reacts with the oxygen (O) in air to form an oxide layer which protects the material from further reactions with the environment. Since this layer is very thin, it will often be necessary to increase the thickness of this layer in order to improve the surface hardness and corrosion resistance or the appearance of the Al product. This can be done by anodizing. The oxidation is then enhanced by placing the Al product in an electrolyte bath and applying an electric field over the growing oxide layer.

Since in industrial practice the field draws massive currents, anodizing is an energy intensive process, and improvements in process control would lead to massive energy reductions [1]. In order to accomplish this, it is necessary to obtain more insight in the anodization process. Not just the nature of the ion motion in the oxide layer needs to be determined, also the influence the electric field has on this motion as well as the influence of temperature and environment need to be studied. A large number of studies has been performed regarding the ion motion in an oxide layer. Campbell et al. [2] studied the oxidation of an aluminium nanocluster with molecular dynamics (MD) simulations and concluded that ion diffusion is promoted by pressure variations in the oxide layer. Wang and Hebert [3] developed a model for ionic conduction

in amorphous oxide films which they based on the hypothesis that oxygen and aluminium ion diffusion takes place by a so-called defect cluster mechanism. Experiments with markers have shown that the ion diffusion in the oxide layer consists of both anion and cation transport, while the cation transport number, which is the ratio between cation and anion transport, is around 0.4 [4,5, and references therein]. Hasnaoui et al. [6] studied the oxidation of aluminium with MD simulations and found the ion movement to proceed through the presence of mobile pores, that form during the formation of the oxide layer. In a later study [7] the influences of both pressure and temperature were taken into account. A layer-by-layer growth was found, which was also reported by Sankaranarayanan and Ramanathan [8]. For the growth of an anodic barrier layer Hebert and Houser [9] developed a model that describes the transport in planar anodic films. In their model ion migration is driven by gradients of mechanical stress and electrical potential. Henz et al. [10] found the major part of the mass flux of aluminium ions through the oxide to result from a built-in electric field induced by the oxide.

The influence of an external electric field on the ion motion in an oxide layer as well as on the resulting growth of the layer was determined in several studies. An experimental study by Popova et al. [11] showed that the presence of an electric field enhances ion migration for the oxidation of aluminium under influence of oxygen, following the Cabrera–Mott theory [12]. The ion transport in the pore surface of a porous anodic alumina under the influence of an electric field was investigated with MD simulations [13]. The

* Corresponding author. Tel.: +31 15 27 82221.

E-mail address: b.j.thijsse@tudelft.nl (B.J. Thijsse).

influence of an applied electric field on the oxidation behaviour of zirconia was studied [14], as well as on the oxidation of nickel in pure water [15]. The oxidation behaviour of iron was studied under the influence of different temperatures and electric field strengths [16].

Despite the large number of studies regarding the growth of an alumina layer, the nature of the ion motion leading to the initial development and growth of an alumina layer and the influence of an electric field on this process, as well as the influence of temperature and environment, are still unclear. A majority of the previously performed studies aims to describe the ion motion in an already formed alumina layer. In the present study we want to get more insight in the initial growth of an alumina layer on a bare Al surface and the influence of the process conditions on this growth. To achieve this, MD simulations are performed with a reactive force field [17,18] to model the growth of an oxide layer in three different environments: atomic O, H₂O, and an aqueous ammonium tartrate solution. We will find, among other things, that (1) O and Al ions are transported through the oxide layer via interrupted sequences of many short replacement steps rather than as a continuous motion from one side to the other, (2) dissociation of H₂O at the surface is critical, and (3) the dependence of the ion motion on the electric field strength exhibits steps in the growth behaviour.

2. Computational

MD simulations are performed in LAMMPS [19,20] with the ReaxFF potential [21], in which an Al crystal is exposed to three different environments. In all simulations a FCC Al crystal with a lattice constant of 4.041 Å at 300 K, containing 1000 atoms, is placed in a simulation box of 20.2 × 20.2 × 68.8 Å. The crystal consists of 20 atomic planes and has the (100) surface facing upward (z-direction). Above the crystal different atoms or molecules are placed to simulate different environments. In all cases the structure is first let to relax (10 ps) before starting the actual simulations. During the simulations the volume of the system is kept constant and the temperature is controlled with a Langevin thermostat [22]. A timestep of 0.1 fs is employed to correctly capture the atomic movements. The simulation box has periodic boundary conditions in x- and y-direction and is bounded in the z-direction by a reflecting wall. A uniform electric field is applied in the z-direction over the growing oxide layer (automatically adjusted to the increasing thickness), which produces an additional force \mathbf{F}_i on each particle in the oxide layer,

$$\mathbf{F}_i = Q_i \mathbf{E}, \quad (1)$$

where Q_i is the instantaneous charge of the particle and \mathbf{E} the electric field strength. The layer thickness is defined as the distance between the highest Al atom and the lowest O atom, the field is active over the layer thickness plus 2 Å on each side.

To study the influence of the electric field on the ion motion in a growing oxide layer, the growth of this layer is first studied in an atomic O environment. By studying the growth of alumina in atomic O, rather than in a more realistic environment like an electrolyte, we intend to determine the direct influence of the electric field on the ion motion in the oxide layer. In an environment like molecular oxygen, water or an electrolyte, the electric field will also influence the molecular dissociation and with that conceal the direct influence of the electric field on the ion motion.

The growth of the oxide layer is also studied in both pure water and in an electrolyte, which is an acid dissolved in water, to determine the influence of the different environments. The electrolyte applied in this study is ammonium tartrate dissolved in water. This

is a weak acid, applied in the anodization practice to grow a dense anodic oxide layer.

The growth of an alumina layer in an O environment is modelled by introducing O atoms in the simulation box above the Al sample with a velocity directed downward. The insertion frequency of O atoms is determined from the collision frequency of atoms from a gas with the wall, taking into account the system size, atomic mass, desired temperature and pressure (1 atm). The velocity of the atoms is chosen equal to the root mean square velocity of atomic O at 1 atm and at the desired temperature (300 K and 600 K). O atoms returning from the Al surface are removed from the simulation box in order to retain the desired collision frequency and velocity of the O atoms. To model oxidation in a water environment, water molecules are placed above the Al crystal, resulting in a water density of approximately 1 g/cm³. For anodizing in an ammonium tartrate solution part of the initial water molecules are replaced by ammonium tartrate molecules to obtain a 20 wt% solution.

3. Results and discussion

3.1. Oxidation in atomic oxygen

For the simulations performed in an atomic O environment, Fig. 1 shows the number of O atoms adsorbed at the Al surface versus time for all field strengths and temperatures. In this work all O atoms that are either at the Al surface or have moved inside the material are considered 'adsorbed'. One monolayer surface coverage results in an oxide thickness increase of approximately 4.0 Å. In all simulations the resulting oxide layer is an amorphous oxide layer.

To understand the influence of the electric field on the oxidation behaviour of Al, the ion movement in the oxide layer is studied in detail. Initially all atoms that reach the Al surface are adsorbed. Charge is transferred, resulting in positively charged Al ions and negatively charged O ions. New atoms that approach the Al surface are then attracted by the positively charged Al ions as well as repelled by the negatively charged O ions. Initially this leads to some grouping of O ions around an Al ion. When the number of O ions in the surface plane increases, the number of available surface sites for O adsorption decreases, which is reflected in a decrease in adsorption rate. However, if an electric field is present, its downward force on the O ions and upward force on the Al ions will refresh available adsorption sites by field-assisted ion motion, increasingly so for higher field strengths (Fig. 1).

Much can be learned about the ion movement in the growing oxide layer by looking at Fig. 2, where results are shown for different field strengths, at 600 K (at 300 K a similar, but less pronounced, behaviour is seen). Since the lowest O ions at the end of the simulation are those that arrived at the surface first (Figs. 2b, e and h), and not those that arrived last, we conclude that O ions do not travel all the way through the growing oxide layer immediately after adsorption and then remain virtually immobile. If this would be the case, atoms reaching the surface at a later moment in time would end up at lower z-positions since they had to cross a thicker oxide layer. Similarly, the increasing standard deviation of the Al atom positions per plane versus time (Figs. 2c, f and i) shows how the Al becomes part of the oxide layer plane by plane. Since the order of the Al planes (Figs. 2a, d and g) is retained and the standard deviation is larger for planes at a higher z-position, we can also conclude that single Al atoms do not travel all the way through the oxide layer once the oxide/Al interface reaches their position. If the Al ions would travel all the way through the oxide layer, two scenarios would be possible. (1) All

Download English Version:

<https://daneshyari.com/en/article/1560523>

Download Persian Version:

<https://daneshyari.com/article/1560523>

[Daneshyari.com](https://daneshyari.com)