



Origin of the Zn-induced Al intergranular corrosion of the outermost surface layer of the aluminium grain boundary: An ab initio study



Ming Zhao^{a,*}, Hongquan Song^b, Jianguo Li^c, Guangping He^a, Yanghai Gui^d

^a College of Mechanical and Material Engineering, North China University of Technology, Beijing 100144, China

^b School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, China

^c School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

^d Department of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, China

ARTICLE INFO

Article history:

Received 14 December 2014

Received in revised form 3 February 2015

Accepted 11 February 2015

Available online 3 March 2015

Keywords:

Aluminium grain boundary

Zinc segregation

Intergranular corrosion

Electrode potential shift

Ab initio calculation

ABSTRACT

The effects of zinc segregation on intergranular corrosion of the outermost surface layer of the AlΣ5 (012)/[100] grain boundary (GB) in an aluminium alloy have been investigated based on first-principles density functional calculations. It is demonstrated that the outermost surface of an Al GB with Zn atom segregation is less stable than that of the pure Al GB, and the first or second nearest-neighbour Al atom of a segregated Zn atom is more prone to corrosion dissolution than those in other sites. The electronic structure analysis shows that a charge reduction region forms along the grain boundary, which causes a more negative electrode potential shift than the pure Al GB. The Zn–Al bond has a metallic character that is similar to the Al–Al bond regardless of the degree of Zn segregation. It is confirmed that the corrosion of the outermost surface of the Al grain boundary with Zn segregation is enhanced because of the charge depletion among Al atoms and Zn atoms. This work contributes to our understanding of the comprehensive effects of Zn segregation on stress corrosion cracking of aluminium alloys.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Al alloys with zinc are the major alloying element that constitutes a group of heat-treatable alloys with low density and excellent weldability and processability. Unfortunately, the use of aluminium–zinc alloys is limited by their susceptibility to stress corrosion cracking (SCC) [1–3]. Zinc segregation to the GB of aluminium alloys has been analysed using many types of experimental techniques [4–6]. Because SCC in aluminium–zinc alloys is characteristically intergranular, the Zn grain boundary segregation is believed to be closely linked to SCC in aluminium–zinc alloys. Hydrogen and Mg segregation at the GB is also observed when Zn segregates [7]; hence, it is difficult to experimentally investigate the direct effect of zinc alone at the grain boundary on the stress corrosion cracking susceptibility of aluminium–zinc alloys. First-principles calculations are suitable to study the effect of one impurity alone without the effect of other impurities at the electronic scale. Zhang et al. investigated zinc segregation at the AlΣ5 (012)/[100] grain boundary using first-principles calculations. They found that the Zn segregation decreased the work of

separation of the AlΣ5 (012)/[100] GB by only 3% [8]. In fact, the SCC resulted from the simultaneous effects of mechanical stress and corrosion [9]. Intergranular corrosion significantly depends on the grain-boundary structure and microchemistry. Song et al. demonstrated that corrosion preferentially originated at the outermost surface layer of the GB region because of a tendency toward crack formation in the presence of stress [10]. In addition, some previous studies show that Zn segregates to the Al surfaces [11] and electrochemically activates the aluminium alloys, which is characterized by a sharp negative shift in the corrosion potential with respect to pure Al [12]. The decrease in the electrode potential implies that the segregated alloys corrode more easily than pure Al. Greeley et al. introduced a thermodynamic formalism to estimate the potential shift of surface alloys using density functional theory [13]. The electrode potential shift of the alloys relative to pure metal is used to measure the tendency to corrosion dissolution of the alloys in comparison to pure metal surfaces. Many studies of corrosion properties based on Greeley's method yield satisfactory results [14–16]. Although the dissolution trends of Zn-segregated Al (110) surfaces have been calculated [17], the origin of the Zn-induced Al intergranular corrosion of the outermost surface layer of the Al GB with zinc segregation, which is of crucial importance in understanding the stress corrosion cracking of Al–Zn alloys, is absent from previous works.

* Corresponding author. Tel./fax: +86 1088803160.

E-mail address: zmncut@126.com (M. Zhao).

In this work, the electrode potential shift of the outermost surface layer of the Al GB with different amounts of segregated Zn was investigated using first-principles pseudopotential total-energy calculations with Greeley's method. By substituting Zn atoms for different amounts of Al atoms in the outermost surface layer of the GB region, a single Al atom was removed to simulate the corrosion dissolutions of the outermost surface layer of the GB region. In addition, we calculated the vacancy formation energy needed to remove one neighbour Al atom of the Zn atoms at different sites in Al GB with Zn segregation to evaluate the stability of the material. Then, the electronic features are used to analyse the origin of the Zn-induced Al intergranular corrosion of the outermost surface layer of the Al GB with zinc segregation.

2. Computational methods

The $\Sigma 5$ (012)/[100] symmetrical tilt grain boundary (GB) was selected to study the effect of zinc segregation on Al intergranular corrosion of the outermost surface layer of Al GB with zinc segregation because it has been experimentally proven to be one of the high-energy GBs in Al [18], and it remains observed in relative abundance [19]. All of our calculations were performed using density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [20,21]. The interaction between ions and electrons is described using ultrasoft pseudopotentials [22]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was used as the exchange–correlation functional [23]. The cell structure was fully optimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique [24]. The cut-off energy of the plane wave was set to 300 eV, and the Brillouin zone sampling was performed using a $2 \times 4 \times 1$ set of the Monkhorst–Pack mesh. The convergence thresholds of geometry optimization were set to be 1×10^{-5} eV/atom for the energy change and 0.001 eV/Å for the maximum force. The optimization would stop when these criteria were satisfied.

To assess the accuracy of our computation method, we performed a series of calculations on the bulk Al and Zn phases. The lattice constants, elastic constants and bulk modulus are listed in Table 1, all of which are consistent with previous results.

We constructed a 120-atom surface model of an Al $\Sigma 5$ (012)/[100] tilt grain boundary, as shown in Fig. 1, with the x, y and z axes along the [012], [0–21] and [100] directions. Each surface model contains six layers of (100) GB surface, which is perpendicular to the (012) grain boundary plane, where two consecutive slabs are separated by a vacuum of 1.2 nm to avoid the interaction between the (100) GB surface and the corresponding lattice lengths of 18.110, 9.055 and 22.124 Å. As shown in Fig. 1, seven atomic sites were selected at the outermost surface layer of the GB region, which corresponds to different local segregation amounts of Zn. Site 1 was on the GB plane; sites i and $-i$ ($i = 2–10$) have mirror symmetry. The atomic sites 1, 2/–2, 3/–3, and 4/–4 were selected for the zinc grain boundary segregation because all segregation energies for those sites are negative, and there is a driving force for Zn segregation to those sites from the Al bulk [8]. In addition, previous studies show that Zn easily segregates to the Al surfaces [11]. In order to confirm

this conclusion, we replace the site 6 in the outermost layer and the third layer of the surface model with one Zn atom, respectively, where the Zn atom locates away from GB in the outmost surface layer and away from the outmost surface layer. The segregation energies of a Zn atom from the site 6 in the outermost layer and the third layer of the surface model to site i ($i = 1–4$) were calculated using the computational method described by Zhang et al. respectively [8]. The results are shown in Table 2. It is confirmed that all values of the segregation energy for the atomic sites 1, 2 or –2, 3 or –3 and 4 or –4 are negative. Therefore, there is a driving force for Zn segregation to those sites from the outermost surface layer and the inner layer of Al GB. Moreover, the segregation energy can be arranged in the following order: site 2 or –2 < site 3 or –3 < site 1 < site 4 or –4. Zn atoms segregate progressively to the Al GB according to the order of segregation energy. Specifically, sites 3 or –3 are not occupied by Zn atom until two Zn atoms occupy both sites 2 and –2, and so on.

So we only investigated the case for Zn atom in the outmost surface layer of the GB region, and the surface model was set up by replacing the outermost surface layer Al atoms with different numbers of Zn atoms. We performed the calculations of the following cases: one-Zn-atom segregation (site –2), two-Zn-atom segregation (sites 2 and –2), three-Zn-atom segregation (sites 2, –2 and –3), four-Zn-atom segregation (sites 2, –2, 3 and –3), five-Zn-atom segregation (sites 1, 2, –2, 3 and –3), six-Zn-atom segregation (sites 1, 2, –2, 3, –3 and 4) and seven-Zn-atom segregation (sites 1, 2, –2, 3, –3, 4 and –4). During the geometry optimization of the surface model of an Al $\Sigma 5$ (012)/[100] tilt grain boundary, we fixed the coordinates of the bottommost three Al layers to simulate the bulk-like environment; all atoms on the topmost three layers were allowed to fully relax by minimizing the atomic force.

To investigate the effect of the zinc grain boundary segregation on the corrosion properties of the Al GB region, we calculated the electrode potential shifts ΔU of Al in the outermost surface layer of Al $\Sigma 5$ (012)/[100] GB with Zn segregation relative to pure-Al GB for the reaction $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$ using the following formula [14]:

$$\Delta U = U_{\text{Al,Zn-GB}} - U_{\text{Al,pure-GB}} = \frac{\mu_{\text{Al,pure-GB}}^{\text{surf}} - \mu_{\text{Al,Zn-GB}}^{\text{surf}}}{3e} \quad (1)$$

where $\mu_{\text{Al,pure-GB}}^{\text{surf}}$ and $\mu_{\text{Al,Zn-GB}}^{\text{surf}}$ are the chemical potentials of Al atoms in the outermost surface layer of pure and zinc-segregated Al $\Sigma 5$ (012)/[100] grain boundaries, respectively. Note that the chemical potentials that we calculated are those of the surface layer, which are much different from the bulk ones. $U_{\text{Al,Zn-GB}}$ is the electrode potential of Al in the Al $\Sigma 5$ (012)/[100] grain boundary with segregated Zn atoms versus the standard hydrogen electrode, and $U_{\text{Al,pure-GB}}$ is the electrode potential of the pure grain boundary. Because metal dissolution always occurs on the surface area, we used a surface model of pure Al $\Sigma 5$ (012)/[100] grain boundary and Al $\Sigma 5$ (012)/[100] grain boundary with segregated Zn atoms to estimate the chemical potential. An Al atom was removed from the outmost surface of the model to produce a new surface model with a surface vacancy. The chemical potential was estimated by calculating the total energies of the optimized original model and new surface model with a vacancy [14].

$$\mu_{\text{Al,pure-GB}}^{\text{surf}} \approx E_{\text{pure-GB}} - E'_{\text{pure-GB}} \quad (2)$$

$$\mu_{\text{Al,Zn-GB}}^{\text{surf}} \approx E_{\text{Zn-GB}} - E'_{\text{Zn-GB}} \quad (3)$$

where $E_{\text{pure-GB}}$ and $E_{\text{Zn-GB}}$ are the total energies of the surface model of the pure Al GB and the Al GB with segregated Zn atoms, respectively, and $E'_{\text{pure-GB}}$ and $E'_{\text{Zn-GB}}$ are the total energies of the corresponding surface model with a removed Al atom. Because $E'_{\text{pure-GB}}$ and $E'_{\text{Zn-GB}}$ vary with the position of the removed Al atom and

Table 1
Lattice constants, elastic constants and bulk modulus B of Al and Zn.

Metals		a	c	a/c	C_{11}	C_{12}	C_{44}	C_{13}	C_{33}	B
		(Å)	(Å)							(GPa)
Zn	Exp. [25]	2.67	4.95	1.86	179	38	46	55	69	70
	Cal.	2.67	4.98	1.87	155	49	53	48	50	61
Al	Exp. [26,27]	4.05			114	61	31			76
	Cal.	4.03			126	52	40			77

Download English Version:

<https://daneshyari.com/en/article/1560265>

Download Persian Version:

<https://daneshyari.com/article/1560265>

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