

## Corrosion Behavior of the Al<sub>2</sub>Cu Intermetallic Compound and Coupled Al<sub>2</sub>Cu/Al

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The corrosion behavior of intermetallic Al<sub>2</sub>Cu has been investigated using polarization, electrochemical impedance spectroscopy (EIS), scanning kelvin probe (SKP), local electrochemical impedance (LEIS) and scanning electron microscopy. The corrosion potential of intermetallic Al<sub>2</sub>Cu is measured to be -473.04 mV in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution with pH 4.3. The highest corrosion rate over the immersing time between 0 and 96 h is observed at 48 h according to the EIS results. The potential results of coupled Al<sub>2</sub>Cu/Al reveal that the Al<sub>2</sub>Cu potential becomes positive during the immersion time and is higher than that of pure Al near the interface. The local impedance value of intermetallic Al<sub>2</sub>Cu increases greatly and is higher than that of pure Al. Thus, the corrosion degree of pure Al is more severe than that of intermetallic Al<sub>2</sub>Cu because of the galvanic corrosion of coupled Al<sub>2</sub>Cu/Al.

**Keywords:** intermetallic Al<sub>2</sub>Cu; corrosion behavior; EIS; SKP; LEIS

### 1. INTRODUCTION

The 2A12 alloy has been widely used in the industry due to its high strength and yield ratio and economic efficiency compared to the other Al–Mg–Cu alloy systems. However, 2A12 alloy is easily susceptible to local corrosion in the industrial or marine atmospheric environment because of the high number amount of structural defects and intermetallic compounds. Intermetallic compounds such as Al<sub>2</sub>Cu, Al<sub>2</sub>CuMg, and (Al,Cu)<sub>6</sub>Mn improve the material mechanical properties of the 2A12 alloy [1-3] but also lead to pits and intergranular corrosion because of the difference in the potential between the intermetallic and the aluminum (Al) matrix [4-6].

Intermetallic Al<sub>2</sub>Cu is an important intermetallic compound that greatly influences the corrosion behavior of the 2A12 alloy. Unfortunately, it is very difficult to continuously investigate the corrosion

behavior and its mechanism for the  $\text{Al}_2\text{Cu}$  intermetallic compound in bulk Al alloy using electrochemical methods because of the small size of intermetallic  $\text{Al}_2\text{Cu}$  [7-21]. SEM micrographs and the potentials of intermetallic  $\text{Al}_2\text{Cu}$  in the AA2017 alloy have been studied [7]. The coarse  $\text{Al}_2\text{Cu}$  crystallite had a strong influence on the cathodic process of the 2024 alloy and was related to the pitting susceptibility [8]. The  $\text{Al}_2\text{Cu}$  phase in the 2024 alloy was very important for micro-corrosion and local corrosion according to the results obtained by F. M. Queiroz<sup>[10]</sup>. The selective dissolution of Al in the  $\theta$  ( $\text{Al}_2\text{Cu}$ ) phase resulted in a porous copper-rich remnant and the de-alloying of the  $\theta$  phase. The de-alloying in the  $\theta$  phase could preferentially occur below the sample surface and was related to the local low pH environment [12]. A. C. Vieira [18] has considered effect of the  $\text{Al}_2\text{Cu}$  phase size on the mass transport dependent kinetics of oxygen reduction. On the other hand, smelting the same component materials as those in the intermetallic is a common approach for the study of the corrosion resistance of intermetallics [21-24]. The  $\text{Al}_2\text{Cu}$  phase was found to be the origin of corrosion and promoted the corrosion in Al - copper complex structure material, with the copper content showing little effect on the open circuit potential according to the results of W. R. Osorio [21]. The bulk Al-Cu alloy improved the corrosion resistance of the alloy as seen by polarization and electrochemical impedance spectrum experiments [22]. However, the method for studying the corrosion behavior of molten intermetallic  $\text{Al}_2\text{Cu}$  is rarely used in a certain environmental medium.

Galvanic corrosion in an Al alloy has been studied [24-26]. The authors had developed a finite-element model in order to study the influence of the microstructure on the micro-galvanic corrosion of Al alloys [24]. The influence of cerium cinnamate on the galvanic corrosion of the coupled  $\text{Al}_2\text{Cu}$  and Al was studied and cerium cinnamate played an inhibitory role in the coupling corrosion of  $\text{Al}_2\text{Cu}$ -Al on the basis of cerium oxide/hydroxide production [25]. However, the corrosion behavior and mechanism of intermetallic  $\text{Al}_2\text{Cu}$  are still unclear due to the influence of different structures in the material.

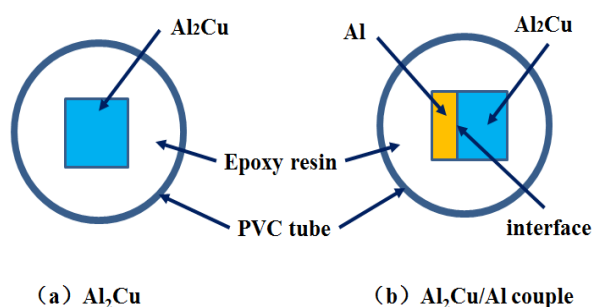
Environment pollution has very important influence on the corrosion behavior of Al alloys. Industrial environmental pollution media such as sulfur dioxide, haze, and ash are found in high concentrations in some economically developed regions or big cities in China. In particular, sulfur dioxide shows one of the strongest effects on the corrosion of Al materials such as the 2A12 alloy. The Jiangjin district is a typical location for studying the industrial atmospheric pollution of metallic materials in China with a perfect atmosphere monitoring system available for such studies. The 2A12 alloy is widely used in many fields such as high-speed rail, aircraft, and equipment and its corrosion behavior directly affects the service life of many types of equipment. The corrosion behavior and mechanism of intermetallic  $\text{Al}_2\text{Cu}$  in the 2A12 alloy need to be studied in detail in the industrial pollution atmospheric environment in the Jiangjin district in China.

## 2. EXPERIMENTAL

### 2.1. Experimental material

Pure Al (100%  $\alpha$  phase), intermetallic  $\text{Al}_2\text{Cu}$  and coupled  $\text{Al}_2\text{Cu}/\text{Al}$  were used in the experiments. The bulk form of intermetallic  $\text{Al}_2\text{Cu}$  was prepared from commercially pure Al (99.99%) and Cu (99.95%). The alloy was synthesized by combining the relevant proportions of Al (45.96 wt.%)

and Cu (54.04 wt.%) in a crucible. The process involved blending raw materials according to the Al-Cu phase diagram of the ratio, smelting these metal materials in the intermediate frequency vacuum induction furnace (version ZG001), pouring into the die, cooling by water, and then acquiring and annealing the cast ingot. The  $\text{Al}_2\text{Cu}$  intermetallic compound material was cut into the sample with the dimensions of 10 mm×10 mm×5 mm by line cutting for the test. Pure Al with the thickness of approximately 5 mm was deposited on the surface of the  $\text{Al}_2\text{Cu}$  sample with the dimensions of 10 mm×10 mm×5 mm in order to simulate the couple of intermetallic  $\text{Al}_2\text{Cu}$  and Al matrix ( $\alpha\text{-Al}$ ) in the 2A12 alloy. Thus, coupled  $\text{Al}_2\text{Cu}/\text{Al}$  is prepared for tests (Fig. 1).



**Figure 1.** Schematic representation of  $\text{Al}_2\text{Cu}$  (a) and  $\text{Al}_2\text{Cu}/\text{Al}$  couple electrode (b) model

The electrode samples for electrochemical testing were sealed by epoxy, leaving one of the surfaces with 1 cm×1 cm area open to the air to serve as the working electrode. Prior to the experiments, the exposed surface was sanded and polished by diamond paste, then degreased in acetone, and finally washed by distilled water and dried with a blower.

## 2.2 Polarization tests and EIS measurements

Polarization and EIS tests were performed on a multi-channel electrochemical workstation (model VMP3) using a three-electrode system. To study the  $\text{SO}_2$  corrosion behavior of intermetallic  $\text{Al}_2\text{Cu}$  in the Jiangjin district in China, the  $\text{SO}_2$  concentration in the Jiangjin district is used for data support to prepare the simulation solution. The simulation solution was 0.1 M  $\text{Na}_2\text{SO}_4$  with pH 4.3. The polarization curves were determined by increasing the potential from about  $-1.0$  V (SCE) to  $+0.2$  V (SCE) related to the open-circuit potential at the 0.166 mV/s scan rate. The working electrode was intermetallic  $\text{Al}_2\text{Cu}$  or pure Al, with Pt wire as the counter electrode and a saturated calomel electrode as the reference electrode.

The electrode samples of the  $\text{Al}_2\text{Cu}$  intermetallic compound used for the EIS tests were immersed in 0.1 M  $\text{Na}_2\text{SO}_4$  solution with pH 4.3 for approximately 96 h. EIS measurements were always conducted from high frequency to low frequency with the frequency range of 100 kHz–10 mHz at  $20\pm 2$  °C. The amplitude of the used sinusoidal signal was 5 mV relative to the open-circuit potential. The impedance experimental data were analyzed in terms of an appropriate equivalent circuit using the ZSimpWin program. The parameters were determined by the simulation.

### 2.3 SKP and LEIS tests

A  $\text{Al}_2\text{Cu}/\text{Al}$  couple specimen was immersed in 0.1 M  $\text{Na}_2\text{SO}_4$  solution with pH 4.3 for approximately 96 h and prepared for surface potential tests and local AC impedance measurement. Surface potential tests were performed with a SKP electrochemical workstation (model SKP370) at approximately  $20 \pm 2$  °C. The scanning mode is used with the step length of 150  $\mu\text{m}$ , the probe vibration frequency of 80 Hz and the amplitude of 30  $\mu\text{m}$ . LEIS measurement was carried out on a local electrochemical workstation (model LEIS370) at approximately  $20 \pm 2$  °C. The scanning mode was applied with a step length of 150  $\mu\text{m}$ , a probe vibration frequency of 10 Hz and an amplitude of 30  $\mu\text{m}$ .

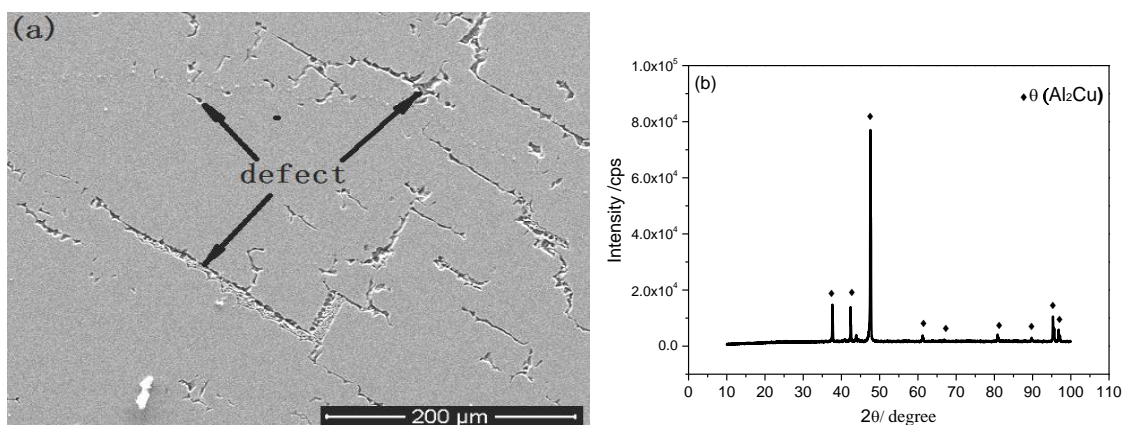
### 2.4. SEM observations and XRD and EDS analyses

The structure and corrosion morphology of the sample was observed using SEM. The compositional analysis for corrosion product was performed by energy dispersive spectroscopy (EDS) on the SEM instrument (model JSM6480LV). X-ray diffraction (XRD) was performed using a PHI Quantera SXM.

## 3. RESULTS AND DISCUSSION

### 3.1 The $\text{Al}_2\text{Cu}$ intermetallic compound preparations and analysis

Fig. 2 shows the results of the analysis for the  $\text{Al}_2\text{Cu}$  intermetallic compound. The SEM image of intermetallic  $\text{Al}_2\text{Cu}$  contains some pits and cracks as shown in Fig. 2a, and the intermetallic  $\text{Al}_2\text{Cu}$  is very hard and brittle. Intermetallic  $\text{Al}_2\text{Cu}$  consists of only Al and Cu elements as shown by the EDS analysis results (Table 1). The mass percentage of the Al and Cu elements in intermetallic  $\text{Al}_2\text{Cu}$  is 45.6:54.4. Its atomic ratio is 66.4:33.6 and is close to 2:1. The diffraction peak of intermetallic  $\text{Al}_2\text{Cu}$  is consistent with the characteristic peaks of the theta ( $\theta$ ,  $\text{Al}_2\text{Cu}$ ) phase (Fig. 2b).



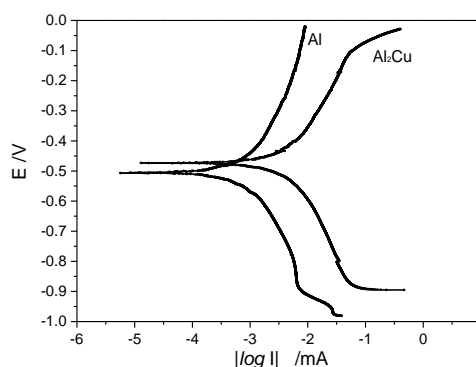
**Figure 2.** Analyses of intermetallic  $\text{Al}_2\text{Cu}$  (a) SEM image; (b) XRD analysis

**Table 1.** Chemical and atom composition of intermetallic Al<sub>2</sub>Cu

Element	Wt %	A <sub>t</sub> %
Al	45.6	66.4
Cu	54.4	33.6

### 3.2 Open circuit potential and potentiodynamic polarization curves analysis

Fig. 3 shows the polarization curves of intermetallic Al<sub>2</sub>Cu and pure Al immersed in the 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution. Table 2 shows the free corrosion potentials ( $E_{\text{corr}}$ ) and corrosion current densities ( $i_{\text{corr}}$ ) calculated by the Tafel extrapolation method. The  $E_{\text{corr}}$  value of intermetallic Al<sub>2</sub>Cu is approximately -473.04 mV (vs. SCE) and is higher than that for pure Al (about -507.16 mV (vs. SCE)). However, the  $i_{\text{corr}}$  value of intermetallic Al<sub>2</sub>Cu in Table 2 is 0.77  $\mu\text{A}$  higher than that of pure Al (approximately 0.22  $\mu\text{A}$ ) in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution with pH 4.3.

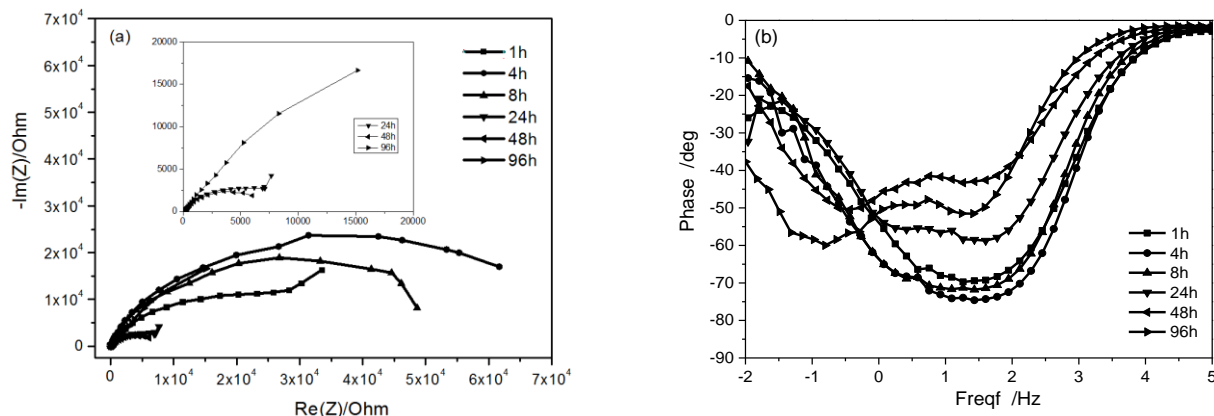
**Figure 3.** Polarization curves of Al<sub>2</sub>Cu and pure Al in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution**Table 2.** Polarization curve fitting parameter value

Parameter	$E_{\text{corr}}$ (V)	$I_{\text{corr}}$ ( $\mu\text{A}$ )
Pure Al	-507.16	0.22
Al <sub>2</sub> Cu ( $\theta$ )	-473.04	0.77

### 3.3 AC impedance curve of intermetallic Al<sub>2</sub>Cu

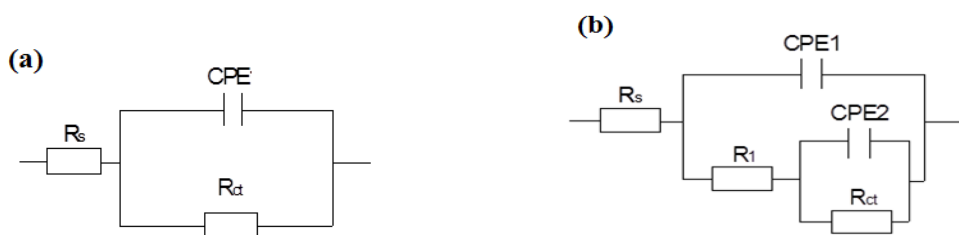
The EIS measurement of the samples as a function of time was carried out and the results are shown in Fig. 4. The Nyquist curves in Fig. 4a include an apparent capacitive semicircle in the high frequency region and one diffusion arc in the low frequency region between 1-8 h. Thus, one time constant is visible according to the Bode phase angle plots in Fig. 4b. However, one apparent capacitive semicircle is present, and two time constants are obtained from the Nyquist and phase plots

over the immersion time between 24-96 h. These EIS results suggest that the state of the surface of the  $\text{Al}_2\text{Cu}$  intermetallic compound electrode has been changed.



**Figure 4.** EIS plots of  $\text{Al}_2\text{Cu}$  with the increase of the immersion time (a) Nyquist plot; (b) bode plot

Figs. 5a and 5b show two equivalent circuits that were obtained by fitting the EIS spectra in Figs. 4a and 4b, respectively. Thin alumina films and corrosion products are present on the surface of the working electrode after long immersion. In the first equivalent circuit (Fig. 5a),  $R_s$  is the solution resistance, CPE is the double layer capacitance, and  $R_{ct}$  is the charge transfer resistance of the double layer. On the other hand, in the second equivalent circuit (Fig. 5b),  $R_s$  is the solution resistance, CPE1 is the outer layer capacitance including the passive film corrosion products,  $R_1$  represents the resistance of the corrosion products, CPE2 represents the double layer capacitance of the anodic area, and  $R_{ct}$  corresponds to the charge transfer resistance of the double layer.



**Figure 5.** Equivalent circuits of  $\text{Al}_2\text{Cu}$  electrode surface (a) equivalent circuits over the immersion time between 2 and 8 h; (b) equivalent circuits over the immersion time between 24-96 h

The typical EIS parameters can be determined using the equivalent circuits and are listed in Tables 3 and 4. In the equivalent circuits (Figs. 5a and 5b),  $R_s$  is the solution resistance. It is obvious that the  $R_s$  value becomes stable during the immersion time as expected. The capacitance is replaced by the so-called constant phase angle element (CPE,  $Z_{\text{CPE}} = 1/Y_0(j\omega)^n$ , where  $Z_{\text{CPE}}$  is the impedance of the constant phase element ( $\Omega \cdot \text{cm}^2$ ),  $\omega$  is the angular frequency of ac-voltage ( $\text{rad s}^{-1}$ ), and  $Y_0$  and  $n$  are the frequency independent parameters). The presence of CPE has been often explained by dispersion

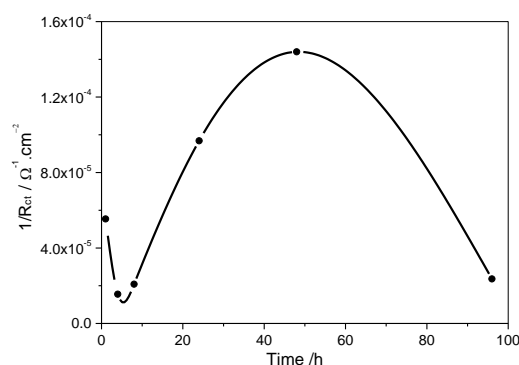
effects that can be caused by microscopic surface roughness [27, 28]. The value of  $(Y_0)_1$  can be regarded as the value of the outer layer capacitance (CPE1) including the passive film and corrosion products. The value of  $(Y_0)_2$  is thought to be an approximation of the double layer capacitance of the anodic area (CPE2). The values of  $n$  are usually related to the electrode surface roughness. For a perfectly smooth electrode,  $n$  will have a value of 1, and the impedance of a CPE will be equal to that of a pure capacitor. In corrosion studies, a low value of  $n$  can be ascribed to a roughening of the electrode due to corrosion. The rougher the electrode is, the lower the value of  $n$  becomes. This is because the real area of the corroded electrode is varied in the corrosion process, causing the deviation from smooth electrode [29].

**Table 3.** Parameters from EIS measurements over the immersion time between 2-8 h

Time	1 h	4 h	8 h
$R_s, \Omega \cdot \text{cm}^2$	27.66	26.71	30.97
$Y_0, \Omega^{-1} \text{cm}^{-2} \text{S}^{-n_1}$	1.97E-5	2.298E-5	2.768E-5
$n$	0.8059	0.8343	0.8278
$R_{ct}, \Omega \cdot \text{cm}^2$	1.189E5	6.474E4	4.818E4

**Table 4.** Parameters from EIS measurements over the immersion time between 24-96 h

Time	24 h	48 h	96 h
$R_s, \Omega \cdot \text{cm}^2$	26.58	29.59	26.72
$(Y_0)_1, \Omega^{-1} \text{cm}^{-2} \text{S}^{-n_1}$	5.039E-5	1.731 E-4	1.565 E-4
$n_1$	0.82	0.74	0.81
$R_1, \Omega \cdot \text{cm}^2$	852.2	424.5	568
$(Y_0)_2, \Omega^{-1} \text{cm}^{-2} \text{S}^{-n_2}$	7.718E-5	3.19 E-4	3.022 E-4
$n_2$	0.62	0.76	0.81
$R_{ct}, \Omega \cdot \text{cm}^2$	1.033E4	6929	4.424E4

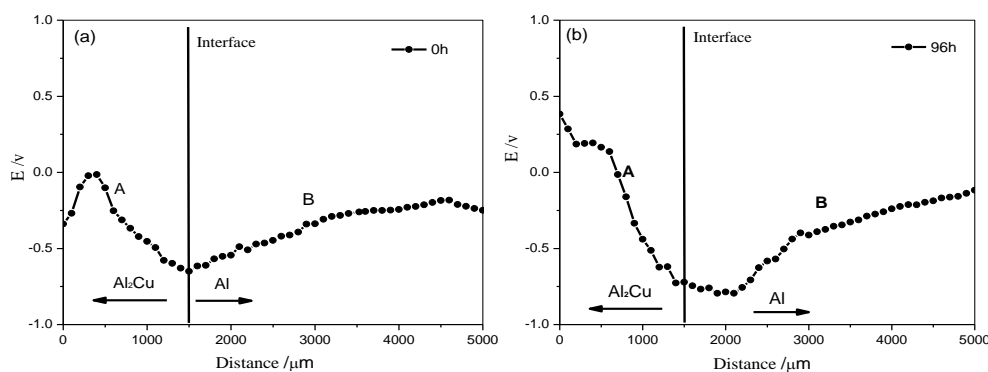


**Figure 6.** Variation of the corrosion rates of intermetallic  $\text{Al}_2\text{Cu}$  as a function of different immersion time

The reciprocal of the charge transfer resistance  $R_{ct}$  is used as a parameter to characterize the corrosion rate in this paper [30].  $1/R_{ct}$  Values for different immersion times are calculated from the medium frequency range as shown in Fig. 6. The corrosion rates vary with the immersion time. The corrosion rate of intermetallic  $Al_2Cu$  declines continuously in the initial stage of immersion (1-4 h), increasing during the immersion time of 4-48 h and decreasing gradually in the late stage of immersion (48-96 h). The highest corrosion rate is observed at 48 h.

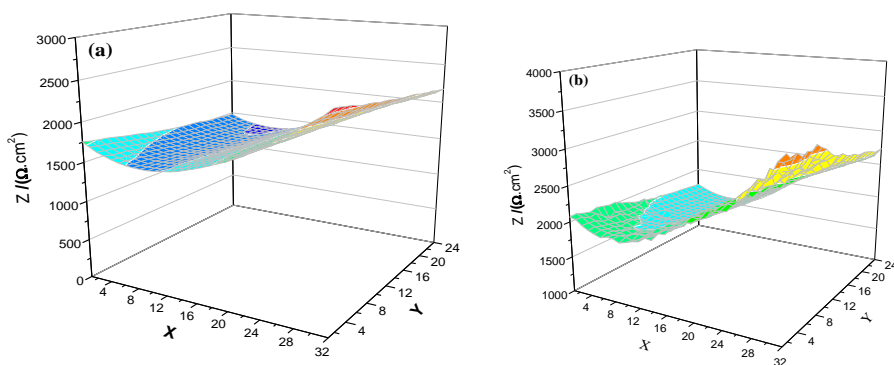
### 3.4 Surface potential change of the coupled $Al_2Cu/Al$ electrode

The line scan potential of the coupled  $Al_2Cu/Al$  electrode before and after the immersion is shown in Fig. 7. The  $Al_2Cu$  potential is higher than that of pure Al near the interface before the immersion (Fig. 7a) and this result is identical to the corrosion potential in Fig. 3. The potential of coupled  $Al_2Cu/Al$  at the interface is -0.651 V at 0 h and became -0.721 V after 96 h of immersion. The potential of the pure Al region remained stable before and after the immersion. However, the  $Al_2Cu$  potential value at the local area (dot A) increased significantly to approximately 0.384 V. The corrosion area of the coupled  $Al_2Cu/Al$  interface is close to the side of the pure Al expanded. The corrosion degree of coupled  $Al_2Cu/Al$  at the interface is aggravated after the immersion and after the pure Al is highly dissolved.

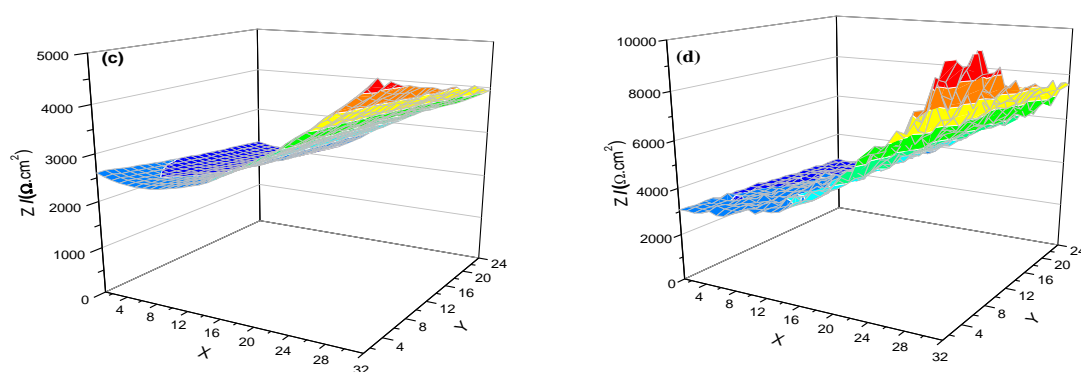


**Figure 7.** Potential of  $Al_2Cu/Al$  electrode before and after the immersion (a) 0 h; (b) 96 h

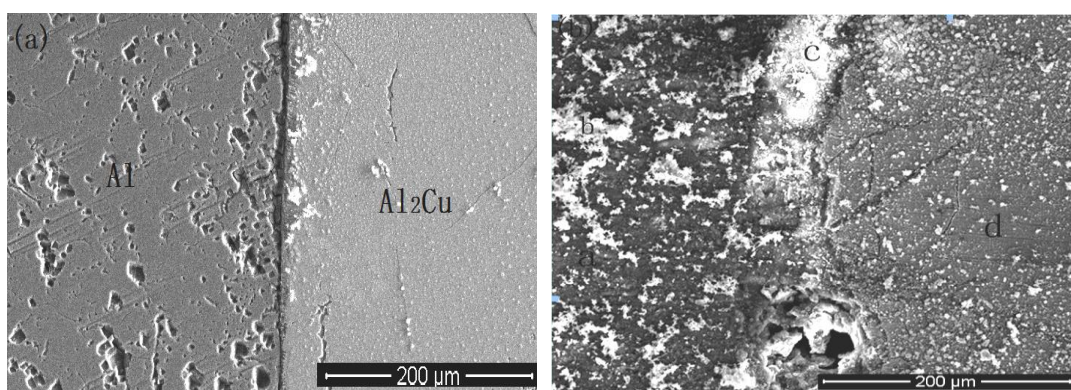
### 3.5 Local impedance change of $Al_2Cu/Al$ electrode



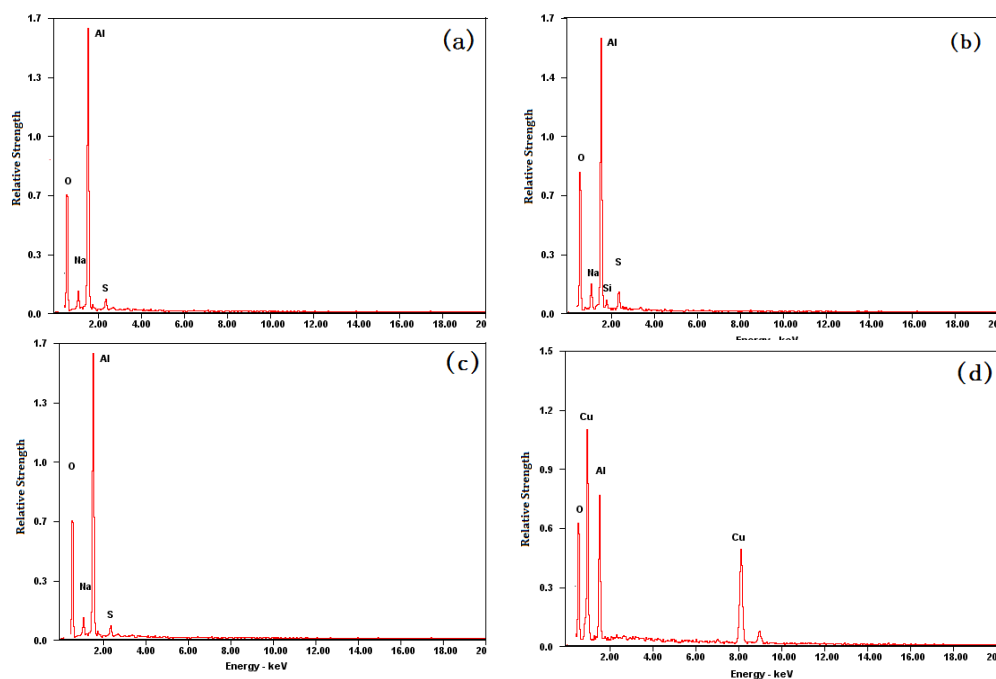




**Figure 8.** Local impedance values of  $\text{Al}_2\text{Cu}/\text{Al}$  electrode immersed for different time (a) 2 h; (b) 16 h; (c) 48 h; (d) 96 h



**Figure 9.** Surface image of coupled  $\text{Al}_2\text{Cu}/\text{Al}$  before and after immersion (a) 0 h; (b) 96 h



**Figure 10.** Energy spectrum of the corrosion products near the  $\text{Al}_2\text{Cu}/\text{Al}$  interface after the immersion (a) dot a; (b) dot b; (c) dot c; (d) dot d

Local impedance values of coupled  $\text{Al}_2\text{Cu}/\text{Al}$  immersed in solution for different time (scanning area  $5\text{ mm}\times 5\text{ mm}$ ) are shown in Fig. 8. The impedance values of pure Al vary from approximately  $1700\ \Omega\cdot\text{m}^2$  to  $2500\ \Omega\cdot\text{m}^2$  during the immersion. Meanwhile, the  $\text{Al}_2\text{Cu}$  impedance value increases greatly from approximately  $2200\ \Omega\cdot\text{m}^2$  to  $7500\ \Omega\cdot\text{m}^2$  and is higher than that of the pure Al. Therefore, the pure Al is dissolved easier than the  $\text{Al}_2\text{Cu}$  by the corrosion potential. This shows that the  $\text{Al}_2\text{Cu}$  region in coupled  $\text{Al}_2\text{Cu}/\text{Al}$  immersed in a solution is more difficult to dissolve relative to pure Al. This result is consistent with line scan potential and corrosion potential results.

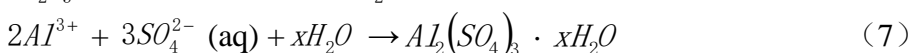
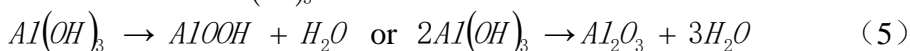
The surface morphology of coupled  $\text{Al}_2\text{Cu}/\text{Al}$  before and after the immersion is shown in Fig. 9. The sample surface is covered with a few corrosion products as shown by the corrosion morphology observation in Fig. 9b. The corrosion products are uneven and thick in the local regions due to corrosion product accumulation. There are many corrosion pits and holes, and the pitting in the Al region is more severe than in the  $\text{Al}_2\text{Cu}$  region. The corrosion products in the Al region mainly contain Al, Na, O and S elements as shown from EDS analysis in Figs. 10a and 10b and Al, Cu, O and S elements in the  $\text{Al}_2\text{Cu}$  region as shown in Fig. 10d. However, corrosion products mainly contain Al, O and S elements in the coupled  $\text{Al}_2\text{Cu}/\text{Al}$  interface in Fig. 10c. The corrosion products are mainly Al oxide and Al sulfate [31].

### 3.6 Analyses and discussion

When intermetallic  $\text{Al}_2\text{Cu}$  or coupled  $\text{Al}_2\text{Cu}/\text{Al}$  is immersed in  $0.1\text{ M Na}_2\text{SO}_4$  acidic solution simulating an industrial pollution atmospheric environment, the reduction of oxygen and dissolution of Al mainly occurs. The surface dissolution reaction on the sample surface is as follows [22, 31]:



At the same time, the following reaction also occurred due to the weak acid environment:



These reactions could explain the corrosion behavior of the intermetallic  $\text{Al}_2\text{Cu}$  or coupled  $\text{Al}_2\text{Cu}/\text{Al}$  sample surface. When intermetallic  $\text{Al}_2\text{Cu}$  or coupled  $\text{Al}_2\text{Cu}/\text{Al}$  is immersed in the solution, the dissolution of Al and Al oxide occurs primarily at the initial stage of the immersion. The Al oxide is dissolved and formed at the same time. The formation of Al oxide is the main results of the consumption of the hydrogen ions. Therefore, the Al oxide is the main corrosion product and covers the sample surface. A small amount of Al sulfate also appears among the Al oxide.

The potential of intermetallic  $\text{Al}_2\text{Cu}$  is approximately  $-473.04\text{ mV}$  in Fig. 3 and is similar to the potential in the  $0.5\text{ M H}_2\text{SO}_4$  solution [32]. This is different from the potential in the  $\text{NaCl}$  solution [22, 23]. The potential of pure Al is more negative than the potential of intermetallic  $\text{Al}_2\text{Cu}$ , and this is

in accordance with the previous result reported in the references [22, 23, 32]. Pure Al is more easily dissolved than intermetallic  $\text{Al}_2\text{Cu}$  in 0.1 M  $\text{Na}_2\text{SO}_4$  solution according to thermodynamics analysis of the potential order. It appears that this is not completely correct if the dissolution of  $\text{Al}_2\text{Cu}$  appears faster than Al according to the  $I_{\text{corr}}$  values. The origin of this effect is related to the structural characteristics of intermetallic  $\text{Al}_2\text{Cu}$  and the selective dissolution of Al in intermetallic  $\text{Al}_2\text{Cu}$  [9].

The corrosion behavior of intermetallic  $\text{Al}_2\text{Cu}$  varies for 96 h in accordance with the impedance spectrum. Nyquist spectra (Fig. 3a) show one apparent capacitive semicircle and one diffusion arc at the time of 1 h. This phenomenon can be explained as follows: after the sample is immersed in 0.1 M  $\text{Na}_2\text{SO}_4$  solution with pH 4.3, the oxidation film on the sample surface is in contact with the solution ions and then reacts with hydrogen ions. The hydrogen ion far away from the sample surface could transfer into the sample surface when hydrogen ion concentration near the sample surface decreases because of reaction consumption. This indicates that the reaction on the double layer surface is controlled with the diffusion of the hydrogen ion and the Nyquist spectra curve of low frequency is the diffusion arc. When the sample is immersed in solution for approximately 4 hours, the diffusion of hydrogen ions is not the primary factor. Therefore, the low frequency diffusion arc disappears (Fig. 3b) and the corrosion rate on the sample surface decreases. The reaction between the hydroxyl ion and Al primarily occurs on the sample surface due to the consumption of hydrogen ions from 1 h to 8 h. The anodic reaction is the reduction of Al and the cathodic reaction is the oxidation of oxygen. The corrosion rate on the sample surface increases. There is one apparent capacitive semicircle and two time constants obtained from the Nyquist spectra curve and Bode phase angle plots of 24–48 h of immersion. This means that the corrosion products of Al, e.g., Al oxide and Al sulfate, are deposited on the sample surface and change the structure of the double electric layer on the surface. At this time, because there is only a small amount of the corrosion product, the anodic reaction and cathodic reaction on the surface are influenced less. The corrosion rate increases. With the increase of the immersion time, the thickness of the corrosion products increases due to the rising amount of the corrosion product; this hinders the dissolution of Al and the diffusion of hydrogen and oxygen. Therefore, the corrosion rate on the sample surface decreases again.

When the coupled  $\text{Al}_2\text{Cu}/\text{Al}$  electrode is immersed in solution, the pure Al and  $\text{Al}_2\text{Cu}$  in the coupled  $\text{Al}_2\text{Cu}/\text{Al}$  electrode are dissolved. However,  $\text{Al}_2\text{Cu}$  and Al in the vicinity of the coupled  $\text{Al}_2\text{Cu}/\text{Al}$  interface have different potentials (Fig. 3), giving rise to galvanic corrosion. The galvanic corrosion of the coupled  $\text{Al}_2\text{Cu}/\text{Al}$  interface induces the strong dissolution of pure Al, while intermetallic  $\text{Al}_2\text{Cu}$  is protected as a cathode because the potential of the pure Al is more negative than that of intermetallic  $\text{Al}_2\text{Cu}$ . This result is similar to the potential analysis of  $\text{Al}_2\text{Cu}$  particle in Al-10 wt.% Si-3 wt.% Cu alloy, where the Volta potential map is between +350 mV and +450 mV relative to the matrix as found by scanning Kelvin probe force microscopy (SKPFM) [19]. The galvanic corrosion results in coupled  $\text{Al}_2\text{Cu}/\text{Al}$  are the current density results of the coupled  $\text{Al}_2\text{Cu}$  and Al in 0.005 M NaCl [25] and the micro-current values between IMP and Al [24], confirming that Al served as an anode, involving the dissolution of aluminum as described by Eq. (1), and  $\text{Al}_2\text{Cu}$  served as a cathode, involving the reduction of dissolved oxygen. The amount of corrosion product at the coupled  $\text{Al}_2\text{Cu}/\text{Al}$  interface increases (Fig. 9b). This result is identical to the local impedance value. The local impedance value of intermetallic  $\text{Al}_2\text{Cu}$  in coupled  $\text{Al}_2\text{Cu}/\text{Al}$  increases over the immersion time, and

pure Al local impedance remains stable. Simultaneously, the dissolution of Al or Al<sub>2</sub>Cu far from the coupled Al<sub>2</sub>Cu/Al interface continued. Therefore, while some corrosion products are present on the Al or Al<sub>2</sub>Cu surface [25], their amount is smaller than that at the coupled Al<sub>2</sub>Cu/Al interface. The corrosion degree on the coupled Al<sub>2</sub>Cu/Al interface is more serious than at the Al<sub>2</sub>Cu intermetallic compound or pure Al surface (Fig. 9b). Therefore, coupled Al<sub>2</sub>Cu/Al promotes localized corrosion of the 2A12 alloy.

#### 4. CONCLUSIONS

The mass percentage of Al and Cu elements for intermetallic Al<sub>2</sub>Cu is 45.6:54.4, and its atomic ratio is 66.4:33.6. The corrosion potential of intermetallic Al<sub>2</sub>Cu is approximately -473.04 mV and is higher than that of pure Al in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution with pH 4.3. The EIS results for intermetallic Al<sub>2</sub>Cu reveal that the highest corrosion rate over the immersing time between 0 and 96 h is observed at 48 h. The potential of intermetallic Al<sub>2</sub>Cu is higher than that of pure Al near the interface as obtained by the scan potential of coupled Al<sub>2</sub>Cu/Al. Local impedance results of coupled Al<sub>2</sub>Cu/Al indicate that the local impedance of intermetallic Al<sub>2</sub>Cu increases greatly from approximately 2200 Ω.m<sup>2</sup> to 7500 Ω.m<sup>2</sup> and is greater than that of pure Al. To summarize, the corrosion mechanism of coupled Al<sub>2</sub>Cu/Al is such that pure Al is highly dissolved and acts as the anode and intermetallic Al<sub>2</sub>Cu is protected as the cathode because of the galvanic corrosion of coupled Al<sub>2</sub>Cu/Al.

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