氧化鋁強化鋁基複合材料
在 3.5％鹽水中之腐蝕特性[†]

李輝隆*・連楠梓*・陳立業* 論著

Corrosion Behavior of
Al₂O₃ Reinforced Al　Composite in 3.5% NaCl Solution[†]

Huei-Long Lee, Nan-Tsu Lian and Sammy Lap-Ip Chan

摘　　要

　　本文主要在探討溶於水中之氧對氧化鋁強化鋁基複合材料在 3.5％ 鹽水中之腐蝕特性。實驗之進行乃採取簡單之 3.5％ 鹽水浸泡試驗，測量開路電位之變化以及不同浸泡時間後的重量變化，表面孔蝕數量之定量金相。結果發現於溶氧的鹽水溶液中，複合材料的抗腐蝕性較鋁為差，孔蝕的情形亦較為嚴重，浸泡期間開路電位也較不穩定。於不含氧的水溶液中之情況，鋁及複合材料之腐蝕現象大為改善，兩者之腐蝕特徵相近。然而，在電化學極化之實驗中，複合材料依然顯現較差之抗腐蝕性。氧化鋁強化相在不含氧水溶液之環境中對腐蝕之行為並無影響，反而水溶液中的氧對複合材料之抗腐蝕性有很大之效應。

ABSTRACT

　　The main objective of this work is to study the effect of the dissolved oxygen on the corrosion behavior of Al₂O₃/Al composite in a 3.5% aqueous NaCl solution. The corrosion behaviors of the Al and its composite were evaluated by a simple immersion test for 3 weeks in 3.5% NaCl solution. The open circuit potentials of the Al and its composite were recorded continuously through the immersion duration with and without the purging of dissolved oxygen. After different periods of immersion, the weight losses, surface pitting and its amount and metallographs in the metal and composite were measured and examined quantitatively. The results show that the composite has less corrosion resistance when the solution contained dissolved oxygen, and the pitting was more severe than that in the cor-

responding control Al. The composite also exhibited an unstable open circuit potential during the immersion. In the absence of dissolved oxygen, pitting corrosion resistance of the composite and aluminum was largely improved, and both materials exhibited the same corrosion behavior. However, the electrochemical test result showed that the composite showed the less corrosion resistant behavior than that of the Al. The Al_2O_3 reinforcements apparently had no effect on the pitting behavior of the Al matrix if oxygen was absent in the solution. In summary, the dissolved oxygen exhibits a significant influence on the corrosion behavior of Al matrix than does the Al_2O_3 reinforcement.

1. Introduction

Recent advances in the fabrication and characterization of metal matrix composities (MMCs) have resulted in a new development of engineering materials for a variety of applications, such as structural, defense, automobile and aerospace industries. These materials consist of lightweight metal or alloy (usually aluminum alloy) matrix, and incorporate with ceramic reinforcements to enhance the mechanical and physical properties of the matrix. The addition of the reinforced phase to a metal or alloy would significantly change the corrosion behavior of the matrix. The surface variations could affect the integrity of the protective oxidized film of the metal or alloy and promote the increased localized or general attack.

In general, composite can become more corrosion susceptible as a result of the following three causes. The first, galvanic coupling since the reinforcing phase may act as a cathode. The second, selective corrosion in the interfacial region or from crevice corrosion when gaps exist in the interfacial region. And the third, metal matrix defects such as voids. Literatures[1-8] concerning the corrosion behavior of metal matrix composite in sea water indicated a significant increase in the corrosion rate of composite, as compared to the respective unreinforced metals or alloys. These system included SiC/Al, graphite/Al and Al_2O_3/Al. The increased corrosion rate and localized attack were found to be a result of crevice corrosion promoted by galvanic coupling between the matrix and ceramic reinforcements. However, the effect of dissolved oxygen in the solution on the corrosion behavior of composite have scarcely been mentioned. The purpose of this work is to study the effect of the dissolved oxygen on the corrosion behavior of Al_2O_3/Al composite using an immersion test in NaCl solution. For comparison, the test on control commercial pure aluminum was also carried out. Finally, corrosion protection methods for metal matrix composites are reviewed[4-8].

2. Experimental details

2.1 Materials

The Al_2O_3/Al composite and control Al samples were fabricated by the powder metallurgy process, and extruded into rods of 17 mm in diameter. The composite material contained 10 volume percent of Al_2O_3 particulates of 10-15 μm. The purity of the aluminum was about 99.5%. All specimens studied here were in an as-extruded condition and were sectioned perpendicularly to the extruded direction. The specimen prepared for the immersion test was in the form of a disk, which was ground, polished and mounted inside a plastic ring. The two flat surfaces of the disk were exposed to the test solution.

2.2 Immersion test

The immersion test was carried out in 3.5% NaCl test solutions, which were made from reagent-grade NaCl and distilled water. All test specimens were cleaned with acetone and dried prior to the immersion test. During the immersion, continuous bubbling of the oxygen in the NaCl solution so that the oxygen saturation can be maintained. In another solution, nitrogen bubbling was used instead of oxygen so that the oxygen can be eliminated. The open circuit potential (OCP) was measured with a saturated calormel electorde (SCE) connected to the solution by using a Luggin Capillary, and recorded continuously as a function of time over a period of three weeks. In addition, after different immersion periods, samples were removed from the test solutions and the corrosion products were scrubbed, ultrasonically cleaned in distilled water and dried. The weight losses of the specimens were measured quantitatively, so that the effect of the dissolved oxygen on the degree of corrosion of the composite and Al in the test solution can be established.

2.3 Electrochemical polarization test

A potential range of -1 to 1 volt was selected at a scan rate of 2 mV/sec. Generally, before the beginning of the polarization measurement, the steady state OCP was made. After solution degassing, the potential scan was initiated as soon as the specimen was placed in the test solution. The electrochemical polarization was performed according to the ASTM Standard G5.

2.4 Microstructural analysis

In order to examine the degree of pitting and the pit distribution, optical microscopy (OM) and scanning electron microscopy (SEM) were performed on the materials after immersion in the salt solution. The amount of corrosion pits of the samples were measured quantitatively using an optical microscope equipped with a viewed monitor system. Specimens were also sectioned and polished for the observation of the pitting penetration into the materials.

3. Results and discussions

It has been indicated[1~4] that two types of corrosion can occur for the Al matrix composite when immersed in the NaCl solution at room temperature: the galvanic

corrosion between the matrix metal and reinforcement, and the pitting corrosion of the matrix itself. The galvanic corrosion is a characteristic of the aluminum matrix composites, since the difference in the electrochemical potentials between the matrix and reinforcement provides a local cell (short circuit) when immersed in aqueous solutions. Once the protetive surface of the aluminum was broken by pitting, galvanic corrosion will commence, leading the weight loss of aluminum.

The results of the weight losses of Al and composite materials after different immersion periods in the NaCl solutions is shown in Fig. 1. It illustrates the strong effect of immersion time and the presence of oxygen in the 3.5% NaCl solution on the weight losses of both the Al and composite specimens. It can also be seen from the figure that the weight losses were more significant for the composite and Al materials when immersed in the solution with the presence of oxygen than that without oxygen. The composite exhibited a larger weight loss than that of Al, and both increased linearly with the immersion time. On the other hand, both composite and Al showed the same weight loss behavior if the test solution contained no dissolved oxygen. For longer immersion periods, the weight losses did not increase linearly with time. Thus, it can be suggested that the dissolved oxygen has a significant influence on the general corrosion of both the composite and Al.
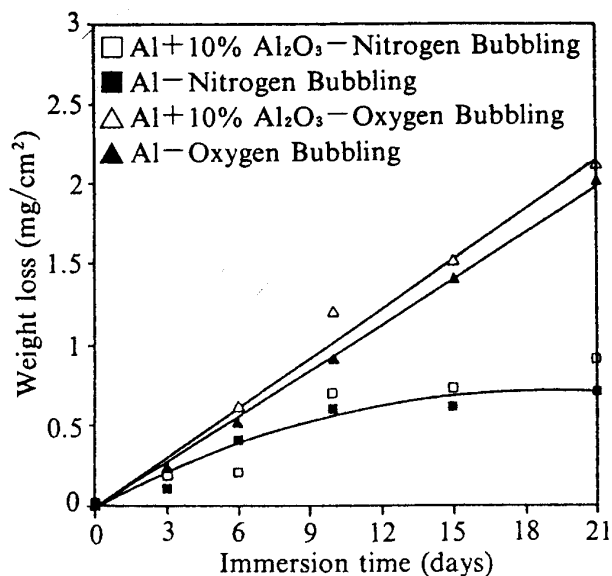

Fig. 1 The weight losses of Al and composite with and without the presence of oxygen in 3.5% NaCl solution.

Effect of the Al_2O_3 reinforcements and dissolved oxygen on the pitting rate of the composite and Al immersed in the salt solution can be seen from Fig. 2. The results indicate a similar tendency of corrosion rate as compared with that shown in Fig. 1. For the composite in the test solution with dissolved oxygen, its pitting rate was greater than that of the Al. As compared with those in the test solution without dissolved oxygen, both composite and Al exhibited a better pitting resistance. There was no evidence to show that the corrosion of the Al matrix was accelerated by the Al_2O_3 reinforcement in oxygen-free solution. This finding is in consistent with that indicated by Trzaskoma et al.[1]

Fig. 3 shows the results of the open circuit potentials vs. immersion time of Al and composite during immersion. It is no-
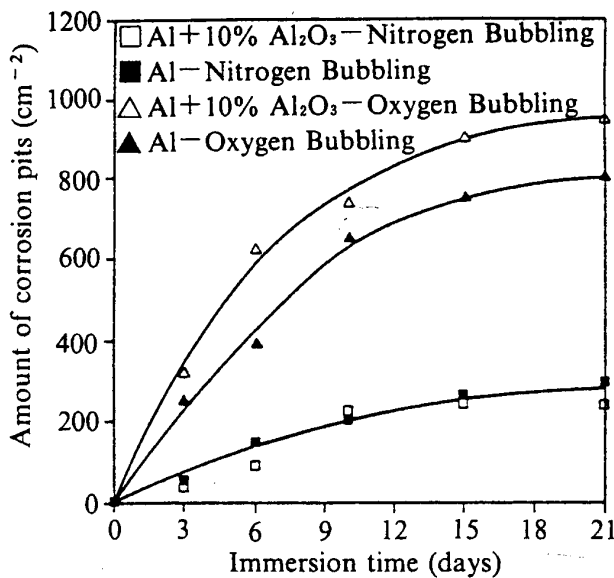
Fig. 2 The amount of corrosion pits in Al and composite after immersion in 3. 5% NaCl solution with and without dissolved oxygen.

Fig. 3 The open circuit potentials of Al and composite with and without the presence of oxygen in 3.5% NaCl solution.

ted that initially the open circuit potentials of Al and composite immersed in the test solution with and without dissolved oxygen were nearly the same. However, the potential of the composite immersed in the 3.5% NaCl solution with the presence of dissolved oxygen soon dropped with increasing immersion time. Finally, there exhibited a more stable potential value which may possibly be the covering of corrosion products in the aluminum surfaces. The control Al material also showed similar behavior as the composite when immersed in the oxygen-saturated NaCl solution. The more anodic open circuit potential of the composite suggests the combination of oxygen affects the kinetics of the anodic reaction. This effect could be due to an increase of reaction sites on the material surfaces.
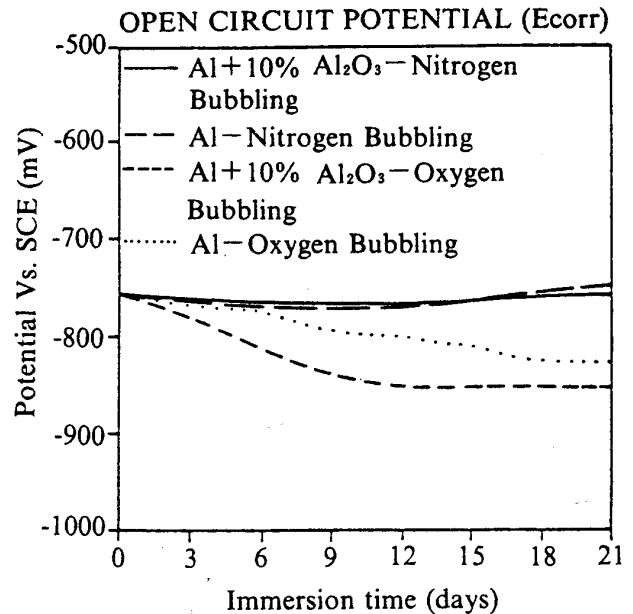
For the composite and Al materials immersed in the oxygen-free salt solution, the open circuit potential in the immersion test show high and constant stability throughout the three weeks duration.

Potentiodynamic polarization curves generated for Al and its composite reinforced with 10% Al_2O_3 in the deaerated 3.5% NaCl solution are shown in Fig. 4. These results were obtained by beginning the polarization scan as soon as the test specimen was immersed in the test solution. The curves show that the polarization behavior of the Al and its composite is different. Galvanic coupling between the Al matrix and ceramic reinforcement promoted the anodic polarization current significantly. Continuous protective oxide film formed
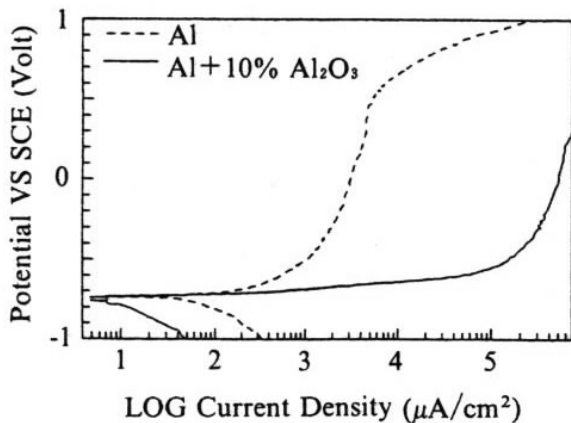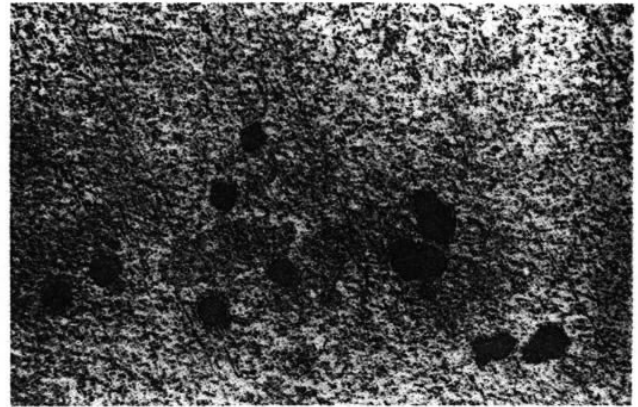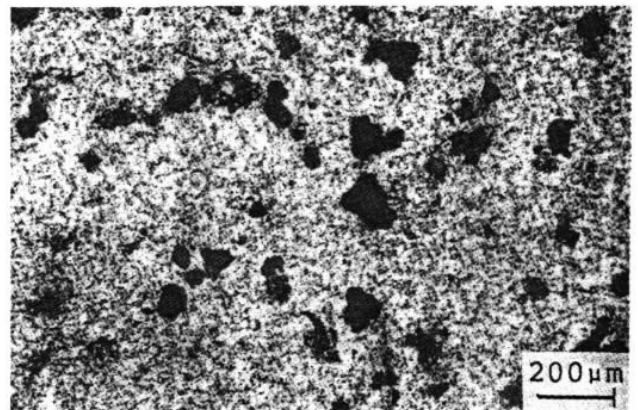
Fig. 4 Potentiodynamic polarization behavior of the Al and Al+10% Al₂O₃ composite.

(a)

(b)

Fig. 5 OM photos showing the pitting morphology of (a) Al and (b) composite after 3 weeks immersion in 3.5% NaCl solution.

on the Al surface destroyed by the reinforcement addition also increased the corrosion current. The composite is somewhat more susceptible to corrosion than that of the Al itself.

The corrosion surfaces of the composite and Al after immersion in 3.5% NaCl solution with oxygen have been examined and are shown in Fig. 5. Both Al (Fig. 5 (a)) and composite (Fig. 5(b)) reveal the same pitting size and shape, i.e., round and irregularly shaped pits were formed on both composite and Al materials. It can be seen that the size and shape of the pits were unaffected by the presence of Al₂O₃ particles. In addition, Fig. 6 and 7 shows some more detail SEM micrographs of pits formed in Al and composite after immersion in the salt solution. Fig. 6 shows that the pits developed on the composite in regions with relatively low density of Al₂O₃. However, a few larger particle reinforcements (e. g. 50μm) were also found to be
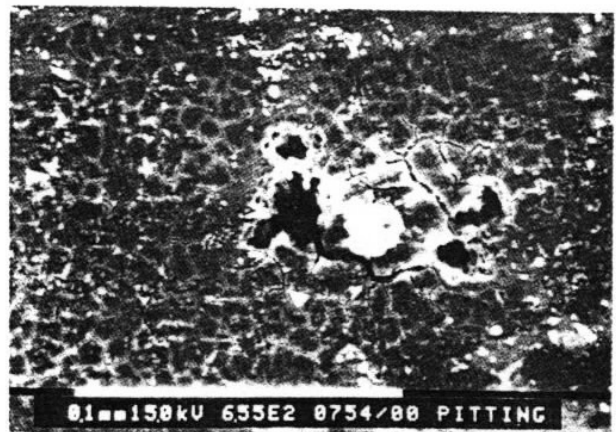

Fig. 6 SEM photo showing the pits of composite were initiated in the reinforcement-free matrix.

sensitive to the pitting as shown in Fig. 7. The decohesion from the matrix of the particles because of corrosion make them separated from matrix. The pitting in the composite did not all concentrate on the Al_2O_3/Al interfaces.


Fig. 7 SEM photo showing the pits of composite were initiated in a few larger Al_2O_3 interface.

The typical cross-sectional view through Al and composite disks after immersion in the salt solution are shown in Fig. 8, which reveals both the pitting shape and penetration or the attack orientation. In Fig. 5, there shows the similar type or pitting, but the depth of penetration was not the same.

Pitting corrosion of Al and composite exposed in the test solutions were identified on both Al and composite surfaces. Although the pitting may possibly be accelerated by the crevices created by the reinforcement in the Al matrix, most of the pits of the composite and Al were distributed throughout the matrix and did not
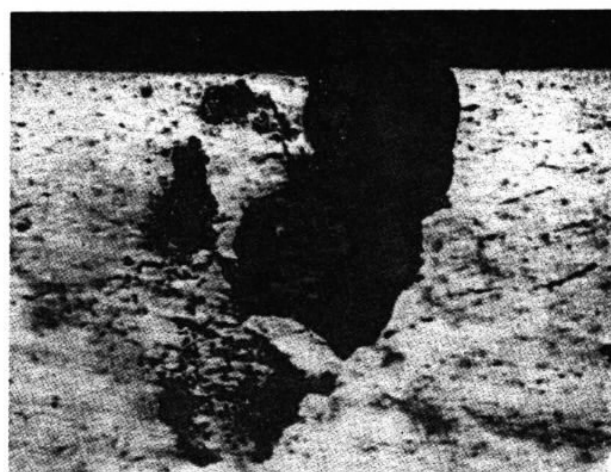
(a)
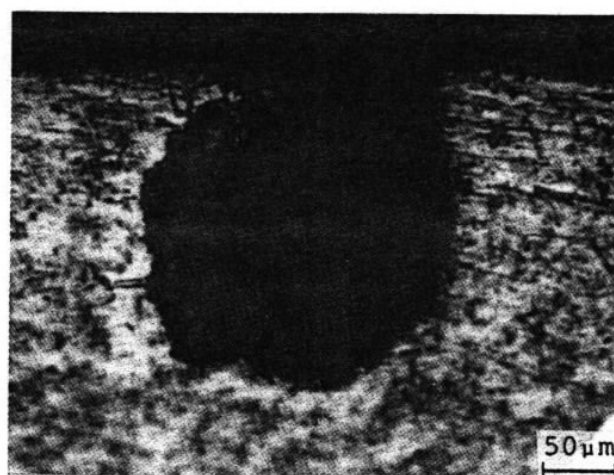
(b)

Fig. 8 OM photos showing the cross-sectioned views of the pitting penetration mode of (a) Al and (b) composite.

concentrated around the Al_2O_3 reinforcements. There was, however, some exceptions as found around the large particles. The similar observation was also reported by Mansfeld et al. [5] and Aylor et al.[6] The exact reason for this observation requires further research.

4. Corrosion protection methods

A variety of surface treatments[4-8], including organic and inorganic methods, has been applied to metal matrix composites to identify adequate corrosion protection systems. The purpose of this section is to provide an indication of coatings that look promising after exposure in the marine or sodium chloride environments for a variety of periods. Of the coating systems evaluated on the composites, the electroless nickel plating was the least successful due to the galvanic corrosive interaction between the cathodic nickel plating and thd anodic aluminum matrix. The sulfuric acid anodizing provided good protection for the composites in all environmental exposure. The chromate/phosphate conversion and the electro-deposited Al/Mn coatings experienced minimal degradation during the exposure. Composites immersed in $CeCl_3$ solution produced very corrosion resistant surfaces. Al_2O_3 plasma spray and organic epoxy coatings also exhibited the better corrosion resistance during the immersion in the corrosion environments.

5. Conclusions

1. The composite exhibited the less corrosion resistance, such as decreasing open circuit potential, susceptible pitting corrosion and larger weight loss during the immersion in 3.5% NaCl solution with the presence of oxygen.

2. In the absence of dissolved oxygen, pitting corrosion resistance of composite and aluminum was improved, both materials showed the same corrosion behavior.

3. The Al_2O_3 reinforcements did not significantly influence the pitting corrosion susceptibility of the Al matrix when the NaCl solution was free of oxygen.

Acknowledgment

References

1. P. P. Trzaskoma, E. C. McCafferty and C. R. Crowe, J. Electrochem. Soc., 130 (1983) 1804-1809.

2. D. M. Aylor and D. Taylor, "Metals Handbook 9th edition", ASM, vol. 2, pp. 859-865.

3. T. Otani, B. McEnaney and V. D. Scott, "Proceedings of the Int. Sym. on Advances in Cast Reinforced Metal Composite", ed. by S. G. Fishman and A. K. Dhingra, ASM, 1989, pp. 383-388.

4. D. M. Aylor and R. M. Kain, "Recent Advances in Composites in the United States and Japan", ASTM STP 864, ed. by J. R. Vinson and M. Taya, 1985, pp. 632-647.

5. F. Mansfeld and S. L. Jeanjaquet, Corr. Sci., 26 (9) (1986) 727-734.

6. D. M. Aylor, R. J. Ferrara and R. M. Kain, Materials Performance, 23 (7) (1984)32-38.

7. F. Mansfeld, S. Lin, K. Kim and H. Shih, Corr. Sci., 27 (9) (1987) 997-1000.

8. M. S. N. Bhat, M. K. Surappa and H. V. Nayak, J. Mater. Sci., 26 (1991) 4991-4996.