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Influences of Li on Corrosion Resistance of 7075 and 7055 Aluminum Alloys

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Abstract

Pitting, intergranular and exfoliation corrosion behaviors of 7075 and 7055 aluminum alloys with and without Li subjected to different tempers (T6 and multi-aging) were studied. Li addition decreases the corrosion resistance to intergranular corrosion (IGC) and exfoliation corrosion (EXCO), while the multi-aging process improves it. Microstructural observations reveal that Li addition obviously influences the microstructures of 7075 and 7055 aluminum alloys. It makes the grain boundary precipitates more coherent and finer, and the precipitate free zones (PFZ) narrower. The anodic dissolution theory might explain the relationship between microstructures and corrosion resistance here.

1. Introduction

Al-Zn-Mg-Cu alloys have been widely used for structural materials in aerospace industry due to their high strength. Addition of Li to aluminum alloys will decrease their density and increase their Yong' modulus. Z.K. Zhao [1] testified that Li-containing 7075 and 7055 treated with multi-aging process had good mechanical properties. However, the corrosion resistance of Al-Zn-Mg-Cu alloys must be taken into consideration. Besides compositions, the heat treatment can also greatly influence the corrosion behaviors of 7000-series aluminum alloys. For example, 7000-series aluminum alloys with peak-aged state (T6 temper) are very susceptible to stress corrosion cracking (SCC), while retrogression and re-aging (RRA) can greatly improve the corrosion resistance to SCC [2,3].

The main purpose of this work was to investigate the influences of Li on corrosion resistance of 7075 and 7055 aluminum alloys, and tried to give an explanation in a microscopic view. The influences of temper on corrosion resistance were also studied.

2. Experimental Methods

2.1 Materials

The chemical compositions are listed in Table 1 [1]. All the aluminum alloys were solution heat-treated at 485℃ for 2 hours, followed by quenching in water at room temperature.

Two kinds of aging processes were performed after that: T6 (120℃×24h) and multi-aging (80℃×5h+100℃×5h+150℃×18h).

Table 1: Chemical compositions (weight percent) of the alloys investigated [1].

Alloys	Zn	Mg	Cu	Cr	Zr	Li	Al
7075	5.6	2.8	1.6	0.24	-	-	Bal.
7055	8.0	2.4	2.4	-	0.18	-	Bal.
7075Li	5.6	2.8	1.6	0.24	-	1.1	Bal.
7055Li	8.0	2.4	2.4	-	0.18	1.1	Bal.

2.2 Pitting Corrosion

Potentiodynamic measurements were carried out in a three-electrode electrochemical cell. A saturated calomel electrode was the reference electrode, while the auxiliary electrode was made of Pt. The working surface area was about 40 mm^2. This test was conducted in 3.5 mass% NaCl solution with CHI600A electrochemical workstation, and the potential scanning rate was 9 mV/min. The scanning reversed when the current density reached 1 uA/mm^2.

2.3 Intergranular Corrosion

The IGC test was in accordance with the guidelines in ASTM B597 [4]. The corrosive solution was made up of NaCl 30 g/L, HCl (1.19g/ml) 10 ml/L and pure water. The ratio of solution volume to working area was 30 ml/cm^2. All specimens immersed in corrosive solution were maintained at 35℃ for 24 hours. After the test, they were taken into 30% HNO_3 for about 5 to 10 seconds to get rid of the superficial corrosion products. Then, they were sectioned and observed under the optical microscope.

2.4 Exfoliation Corrosion

The EXCO test was prepared according to ASTM G34 [5]. The corrosive solution was made up of NaCl 234 g/L, KNO_3 50 g/L, HNO_3 6.5 ml/L and pure water. The ratio of solution volume to working area was 30 ml/cm^2. All specimens immersed in corrosive solution were maintained at 25℃, and were visually inspected at regular intervals(5h, 12h, 24h, 48h). The development of exfoliation corrosion was assessed by reference to the standard photographs in ASTM G34: N, indicates no appreciable attack, P represents pitting corrosion and EA-EC describes a range from superficial to severe exfoliation. Besides visual rating, some samples were observed under the optical microscope in the same way as IGC test.

2.5 Microstructural Observations

Thin foils of aluminum alloy 7055 with and without Li for transmission electron microscopy (TEM) were prepared using the same method as in the previous study [6]. The samples were observed using a H8100 at 200 kV.

3. Results

3.1 Pitting Corrosion

The susceptibility to pitting corrosion is usually evaluated by the breakdown potential (E_b) and the protection potential (E_{prot}) [7]. Both E_b and E_{prot} of all specimens are listed in Table 2 and 3. They show that Li decreases the pitting resistance of 7075 and 7055 aluminum alloys subjected to T6 temper, while no obvious decreases occur in multi-aging temper.

Table 2: Pitting corrosion properties of Li-free AA 7075 and AA 7055 with T6 or multi-aging temper.

Material(Temper)	7075(T6)	7075(Multi)	7055(T6)	7055(Multi)
E_b(mV/SCE)	-790	-797	-790	-812
E_{prot}(mV/SCE)	-825	-834	-823	-826

Table 3: Pitting corrosion properties of Li-containing AA 7075 and AA 7055 with T6 or multi-aging temper.

Material(Temper)	7075Li(T6)	7075 Li (Multi)	7055 Li (T6)	7055 Li (Multi)
E_b(mV/SCE)	-829	-815	-815	-805
E_{prot}(mV/SCE)	-843	-842	-826	-825

3.2 Intergranular Corrosion

Table 4: Maximum intergranular corrosion depths of tested specimens. (unit: um)

Temper\ Material	7075	7075 Li	7055	7055 Li
T6	260	350	250	270
Multi-aging	190	240	200	200

Table 4 shows that Li addition greatly increases the susceptibility of AA 7075 to intergranular corrosion, but only a little increase is found in AA 7055. In comparison with T6 temper, the multi-aging temper increases the intergranular corrosion resistance to different extents. Figure 1 (a) shows a relatively typical micrograph of intergranular corrosion.

3.3 Exfoliation Corrosion

All EXCO test results are displayed in Table 5. This table shows that Li addition increases the EXCO susceptibilities of both AA 7075 and AA 7055 with T6 or multi-aging temper. In addition, the influences of temper on EXCO resistance are also obvious that multi-aging temper is better than T6 temper.

Table 5: Visual rating of exfoliation testing specimens.

Temper\ Material	7075	7075 Li	7055	7055 Li
T6	EB	ED	EC	ED
Multi-aging	EA	EC	EA	EB

Figure 1 (b) illustrates that exfoliation corrosion progresses essentially along the grain boundary. It indicates that the EXCO was mainly intergranular. Compared with Figure 1（a）, Figure 1 (b) is more serious in intergranular corrosion. The corrosion depth of Figure 1 (b) (370 um) is much bigger than that of Figure 1 (a) (210 um), even apparently exceeds the maximum intergranular corrosion depth of AA 7075Li with multi-aging temper (240 um) which is shown in Table 4. Comparisons of other specimens also indicate that the corrosion depths of samples in EXCO test are much bigger than that in IGC test.

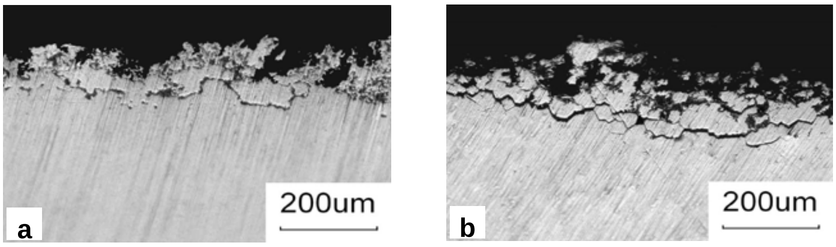

Figure 1: Micrographs of AA 7075Li (multi-aging)（a）in IGC solution after 24h (IGC test: ASTM B597)（b）in EXCO solution after 48h (EXCO test: ASTM G34).

3.4 Microstructural Observations

High density of fine precipitates distribute homogeneously in AA 7055Li matrix, as can be seen in Figure 2 (a). P.C. Bai [9] testified that they were η^1 ($MgZn_2$) phase and GP zones by means of X-ray diffraction (XRD) method. Large η phase particles in the range from 20 to 100 nm are sparsely scattered in the matrix too. The high strength of the aluminum is believed to arise from the high concentration of fine η^1 particles, while the η phase hardly contributes to it [10].

Figure 2 (a) also illustrates that the grain boundary (GB) precipitates of AA 7055Li about 4 nm in width are coherent. In contrast with AA 7055Li, the grain boundary precipitates of AA 7055 are wide and incoherent, as is shown in Figure 2 (b). In fact, they are made up of a string of small particles about 11 to 15 nm in diameter. With X-ray photoelectron spectroscopy (XPS) analysis, P. C. Bai [9] found that Al and Cu were rich in the grain boundary of AA 7055Li, and inferred that it was θ^1 (Al_2Cu) phase. The precipitate free zones (PFZ) of AA 7055Li (about 20 nm) are also narrower than that of AA 7055 (about 24 nm).

From Figure 2 (c) [1] and (d) [8], the influences of Li on the microstructures of 7075 aluminum alloy can also be seen. The grain boundary precipitates width of AA 7075Li (15 nm) is slightly larger than that of AA 7075 (10 nm). However, the PFZ width of Li-free 7075 is about 25 nm, while the PFZ of Li-containing 7075 is too tiny to be seen. It should be noted that the PFZ of Li-containing 7075 alloy still exist, because the segregation of solute atoms, such as Cu atoms, to the grain boundary must cause concentration reduction of solute atoms in adjacent area.

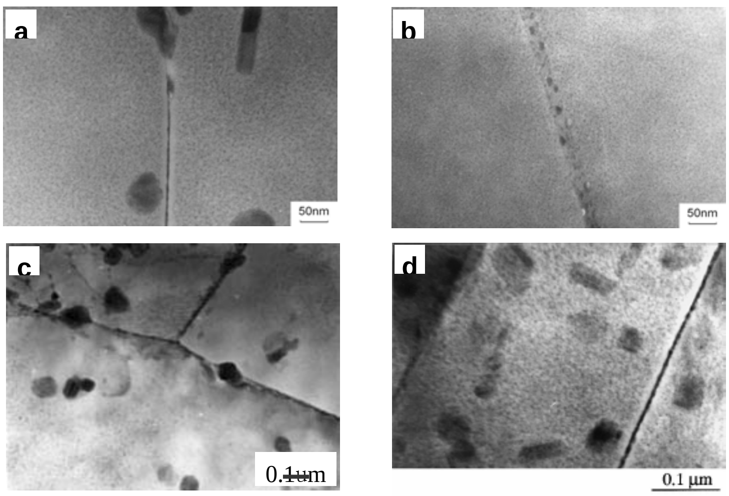

Figure 2: Microstructures of (a) AA 7055Li (b) AA 7055 (c) AA 7075Li [1] (d) AA 7075 [8] with T6 temper.

4. Discussion

The intergranular corrosion and the EXCO have been widely believed to be correlated in mechanism. This paper also proves their correlation. But in some cases, such as the influences of Li on 7055 aluminum alloy with different tempers, the IGC test results are not as explicit as EXCO test results. Comparisons of corrosion depths between IGC and EXCO suggest that corrosion of EXCO test is much severer than that of IGC test, which is caused by more corrosive solutions and longer test time. This might suggest that severer corrosion would make influences caused by any factor, e.g. Li or temper, more obvious.

From an electrochemical point of view, both pitting and IGC seem to be very similar in nature [12]. But the results of the pitting corrosion in this paper are complicated and show no apparent correlation with IGC, especially in the influences of temper.

Microstructural observations reveal that Li addition can apparently modify the precipitation process and the microstructures of 7000-series aluminum alloys. Li atoms preferentially trap vacancies during aging and slow down the diffusion and clustering of Zn, Mg atoms [9,11]. The results show that Li addition retards aging kinetics process and coarsening of precipitates, and thus makes the precipitate free zones (PFZ) narrower than that of Li-free 7000-series aluminum alloys [9,11].

The anodic dissolution theory [13] might explain the relationship between microstructures and corrosion resistance here. The grain boundary precipitates which are relatively rich in Cu solute atoms have a higher electrode potential than the precipitate free zones (PFZ) which are relatively poor in Cu. They locally formed numerous and very tiny corrosion cells in the presence of corrosive medium. The macroscopic corrosion behaviors depend on how these tiny corrosion cells work.

At least 2 factors influence these cells: the electric potential difference between the two electrodes inside the cell and the distribution of these cells.

From this point of view, the cells along the grain boundary of Li-containing 7055 are coherent and large, while the cells of Li-free 7055 are dispersed and small. Thus the cells of Li-free 7055 aluminum alloy seemingly has a better distribution, which is beneficial to improve corrosion resistance.

As for AA 7075 with and without Li, they both have coherent and similar width of grain boundary precipitates, but the precipitate free zones (PFZ) of Li-containing 7075 alloy are much narrower than that of Li-free 7075 alloy. The narrower the precipitate free zones (PFZ) are, the more serious the concentration reduction of Cu atoms in the PFZ is. And bigger concentration difference of Cu atoms between the grain boundary precipitates and the precipitate free zones (PFZ) determines larger electric potential difference between the two electrodes inside the cell. As a result, the grain boundary of Li-containing 7075 alloy is more likely to be susceptible to corrosion.

5. Conclusions

1. Li addition decreases the corrosion resistance of 7075 and 7055 aluminum alloys with T6 or multi-aging temper to both IGC and EXCO.

2. In comparison with T6 temper, the multi-aging temper increases the corrosion resistance of 7075 and 7055 aluminum alloys with and without Li.
3. Microstructural observations reveal that Li addition obviously influences the microstructures of 7075 and 7055 aluminum alloys. It makes the grain boundary precipitates more coherent and finer, and the precipitate free zones (PFZ) narrower. The anodic dissolution theory might explain the relationship between microstructures and corrosion resistance here.

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