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Consistent Variation of Stress Corrosion Cracking Susceptibility and Passive Film-induced Stress for 7050 Aluminum Alloy with Polarization Potential

Qi Xing[1,2,3],   Song Renguo[1,2,3],   Qi Wenjuan[1,2,3],   Jin Jirong[1,2,3],   Wang Chao[1,2,3],

Li Hai[1,2,3],   Xiong Ying[4]

[1] School of Materials Science and Engineering, Changzhou University, Changzhou 213164, China; [2] Jiangsu Key Laboratory of Materials Surface science and Technology, Changzhou University, Changzhou 213164, China; [3] Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, Changzhou University, Changzhou 213164, China; [4] Zhejiang University of Technology, Hangzhou 310014, China

Abstract: The film-induced stress and susceptibility to stress corrosion cracking (SCC) of 7050 aluminum alloy in the chloride solution at various potentials was investigated. The results show that large tensile stress is generated by the passive film during original corrosion. The passive film induced tensile stress increases obviously with an increase in potential under anodic potential; however, it decreases with an increase in potential when the potential $E \geq -1100$ mV$_{SCE}$ while it increased when $E < -1100$ mV$_{SCE}$ under cathodic potential. The variation of film-induced stress with potential is consistent with that of the susceptibility to SCC with potential.

Key words: 7050 aluminum alloy; stress corrosion cracking; passive film-induced stress; polarization potential

Aluminum alloys of 7000 series (Al- Zn-Mg-Cu) have been introduced since 1943 and used extensively as airframe structures due to their high specific strength [1]. In the numerous studies reported in the scientific literatures on this subject, two basic mechanisms have been proposed to model SCC (stress corrosion cracking): anodic dissolution and hydrogen embrittlement. However, there is currently no consensus on the precise mechanism [2,3]. Recently, many researchers have proposed a new mechanism to explain SCC that the corrosion process promotes localized plastic deformation and finally results in SCC. Chu Wuyang's [4-7] work shows that the corrosion process can facilitate dislocation emission and motion during SCC of brass, type 304 stainless steel, α-Ti and Ti$_3$Al+Nb, and cracks of SCC will nucleate in a dislocation-free zone (DFZ) only when the corrosion-enhanced dislocation emission and motion develop to a critical condition. It has been mentioned that vacancies induced by anodic dissolution can facilitate the climb of edge dissolutions, which result in anodic polarization- enhanced ambient creep[8].

Many experiments show that metal foils with a protective layer formed on one side are concave or convex during anodic polarization using a potentiostat because of tensile or compressive stress, respectively, generated at or near the passive film interface [9]. For aluminum alloy there is a passive film formed during corrosion in a 3.5%NaCl solution impressed an anodic polarization potential; however, when impressed a cathodic polarization potential, there is still a passive film formed.

When the aluminum alloy is immersed in a chloride solution, the metallic ions cross the passive film into solution and dissolve constantly through exchanging with anions [10]; at

the same time, great additional tension is generated at the interface of film and matrix which can facilitate dislocation emission and motion. When the dislocation emission and motion reaches to a critical value, the localized stress concentration will be equal to the atomic bonding force and then leads to breaking of atomic bonds, correspondingly, making the SCC micro-cracks nucleate[11,12]. So far, there have been few reports on the passive film and its relationship with susceptibility to SCC of 7050 aluminum alloy.

The aim of the present study is to determine the relationship between the passive film-induced stress and the susceptibility to SCC by a flowing stress difference method and slow strain rate testing (SSRT) in 3.5%NaCl solution impressed an anodic or cathodic polarization potential coupling electrochemical impedance spectroscopy (EIS) with energy dispersive spectroscope (EDS).

1 Experiment

The 7050 high strength aluminum alloy tested was supplied by Alcoa Co. in the form of smooth specimens machined from a 40 mm thick rolled plate. The chemical composition of the alloy is listed in Table 1. The specimens were 2 mm in thickness and 15 mm in gauge length with the tensile axis parallel to the short transverse direction which is known to be the most sensitive orientation to SCC [13]. They were heat-treated with over aging: solid solution at 470 ℃ for 2 h and then aging at 135 ℃ for 24 h after water quenching. All of the specimens were abraded with a sequence of emery papers from 500# to 1200#, rinsed in de-ionized water, degreased in acetone and dried prior to testing.

The susceptibility to SCC was evaluated in terms of the percent strength loss I_σ measured through SSRT tests.

$$I_\sigma = (1 - \sigma_{SCC}/\sigma_F) \times 100\% \qquad (1)$$

where, σ_F and σ_{SCC} are the strength to fracture of tensile specimens during SSRT in air and in the 3.5%NaCl solution, respectively, at a strain rate of 1×10^{-6} s^{-1}. The specimens were etched in a 2% NaOH solution for 1 min in order to remove the air-formed oxide. After cleaning in diluted HNO$_3$ solution, the specimens in the solution were kept at various constant potentials from −640 to −1300 mV$_{SCE}$ (including anodic and cathodic polarization). The stable open-circuit potential was −730 mV$_{SCE}$.

The specimens were strained in air to a plastic strain $\varepsilon_P \geq 1\%$ under a strain rate of 1×10^{-6} s^{-1}. After unloading, the specimens were immersed in the 2% NaOH solution for 1 min to remove the oxide and cleaned in diluted HNO$_3$ solution, then put into the 3.5% NaCl solution and impressed various constant potentials for 24 h to form different passive films. After that, the specimens with passive film were again strained in air to yield. The yield stress of the specimen with passive film, σ_{ys}, was less than the flow stress of the specimen before unloading, σ_f. The difference between σ_f and σ_{ys} is the film-induced stress i.e., $\sigma_P = \sigma_f - \sigma_{ys}$.

Table 1 Chemical composition of the 7050 aluminum alloy (wt%)

Element	Al	Zn	Mg	Cu	Zr	Fe	Si	Ti	Mn
Content	Bal.	6.42	2.25	2.02	0.13	0.11	0.07	0.03	0.10

A potentiostat-galvanostat (PAR273A, Shanghai, China) and a frequency response analyzer were used together with a Faraday cage to avoid external interferences. The traditional EIS three electrode set-up was employed using Ag/AgCl, KCl (saturated) as the reference electrode, platinum gauze as the counter electrode and the 7050 aluminum alloy substrate as the working electrode. To control the exposed area of metal, a poly (methylmethacrylate) cylindrical tube was clamped to the metallic substrates. The area exposed to the electrolytes was 1 cm^2 and the volume of the electrolyte was 120 cm^3. The measurement of EIS was carried out in the frequency ranging from 10^{-2} Hz to 10^{5}Hz and the amplitude deviation within 5 mV at OCP.

The film surface was studied with SEM (JEOL JSM6360-LA, Tokyo, Japan).

2 Results

2.1 Susceptibility to SCC of 7050 aluminum alloy in 3.5% NaCl solution

The maximum stress and time to fracture of the specimen during extending in air are σ_F =500 MPa, and t_F = 40.6 h, respectively. The stress and time to fracture of the specimen during SSRT at open circuit and various potentials are listed in Table 2. The susceptibility to SCC, I_σ is also listed in Table 2. Table 2 indicates that polarization potential has a great influence on the susceptibility to SCC, especially under an anodic potential.

Fig.1 shows the fracture surface of 7050 aluminum alloy immersed in air, in 3.5% NaCl solution and impressed various potentials. The fracture surface of the alloy extending in air is dimple, and there has some inclusions inside. The open-circuit condition has a brittle dimple rupture surface and the fracto-graphy of SCC at a cathodic polarization of −1100 mV$_{SCE}$ is interpreted as mixed intergranular and quasicleavage trans-

Table 2 Susceptibility to SCC of 7050 aluminum alloy at various potentials

E/mV$_{SCE}$	σ_{SCC}/MPa	I_σ/%	t_{SCC}/h
−640	214	57.2	15
−670	275	45	17.1
−700	288	42.4	17.5
−730*	340	32	24
−800	324	35.2	19
−900	291	41.8	17.8
−1100	260	48	16.4
−1200	282	43.6	17.3
−1300	300	40	18

* Open circuit potential
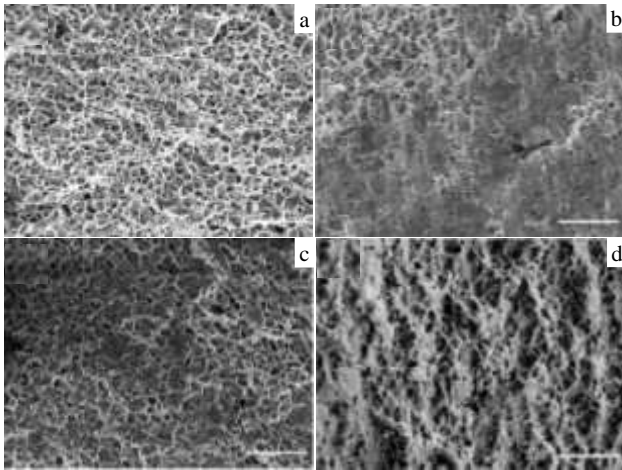
Fig.1 Fracture surface of 7050 aluminum alloy under various conditions: (a) in air, (b) at open circuit, (c) at a cathodic polarization potential of −1100 mV, and (d) at an anodic polarization potential of −670 mV
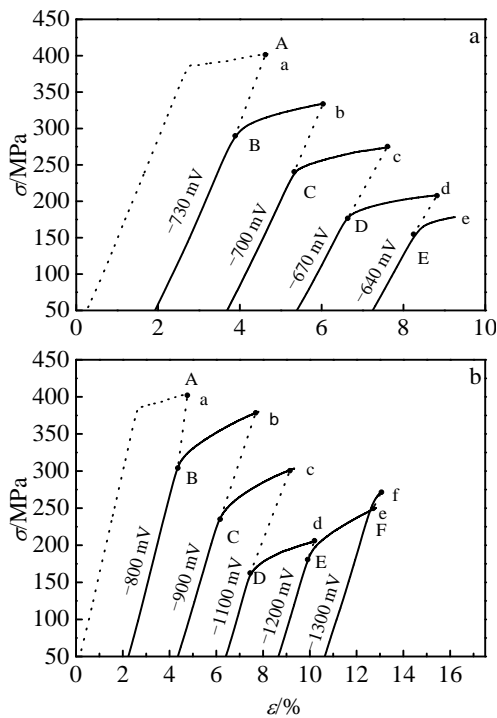

Fig.2 Stress-strain curves of 7050 aluminum alloy extended in air before and after immersing at various potentials: (a) at anodic polarization potentials and (b) at cathodic polarization potentials

granular. At an anodic polarization of −670 mV$_{SCE}$, it is typically intergranular with many corrosion products.

2.2 Passive film-induced stress

Stress-strain curves for specimens with various potentials before or after the passive film formed during slow tensile tests in air are shown in Fig.2. The dotted lines are the stress-train curves extending in air and the solid lines are those extending again in air after unloading at point A and forming a passive film through corrosion in the 3.5% NaCl solution impressed a polarization potential. The difference between the flow stress at the point A and the yield stress at the point B is an additive stress induced by the passive film. The difference between point A and point C is an additive stress induced by passive film impressed a different polarization potential, i.e., $\sigma_P = \sigma_f - \sigma_{ys}$. σ_P for the specimens are listed in Table 3.

It can be concluded from Fig.2 that there exists an additional tensile stress induced by the passive film no matter at an anodic or at cathodic potential which can assist the applied stress to facilitate SCC. Anodic polarization has a so great influence on the passive film-induced stress that even a little increase of the potential can make a large rise of the additional stress. For cathodic polarization, the plots become much more gradual. Moreover, there exists a special tendency: when the potential $E \geq -1100$ mV$_{SCE}$, the film-induced tensile stress decreases with an increasing potential; correspondingly, the film -induced tensile stress increases.

The variation of the stress induced by the passive film formed at various constant potentials and the variation of susceptibility to SCC with potential are shown in Fig.3. The variation of film-induced stress with potential is consistent with that of susceptibility to SCC with potential and at the open-circuit potential of −730 mV$_{SCE}$, both film-induced tensile stress and susceptibility to SCC have a minimum value.

2.3 Electrochemical impedance spectroscopy (EIS) tests

Fig.4 depicts the open-circuit potential as a function of time in the chloride solution in the absence of load for the specimens. The variation of the potential against time was monitored in 40 h. In Fig.4, the potential increases rapidly within 20 h, and gradually from 24 h to 40 h. The immersing time change in aluminum alloy usually causes an appreciable shift on the corrosion potential in a chloride solution before 24 h. So we choose a moderate time 24 h as the immersion time.

Electrochemical impedance spectrum (EIS) was conducted once the specimens had been immersed in the chloride solution and under various polarization potentials for 24 h. Fig. 5 exhibits the Nyquist plots where Z_{re} and Z_{im} are the real imaginary components, respectively, of the impedance, and Z_{re}

Table 3 Stress induced by the passive film formed during corrosion at various constant potentials

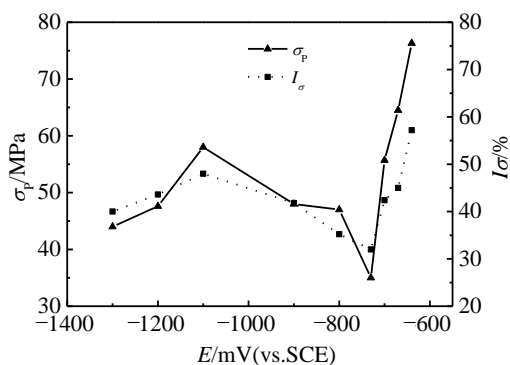| Potential/mV$_{SCE}$	−640	−670	−700	−730	−800	−900	−1100	−1200	−1300
$\sigma_P = \sigma_f - \sigma_{ys}$/MPa	76.3	64.5	55.7	35	47	52	58	47.6	44

Fig.3 Passive film-induced stress and susceptibility to SCC of 7050 aluminum alloy in 3.5% NaCl solution at various constant potentials
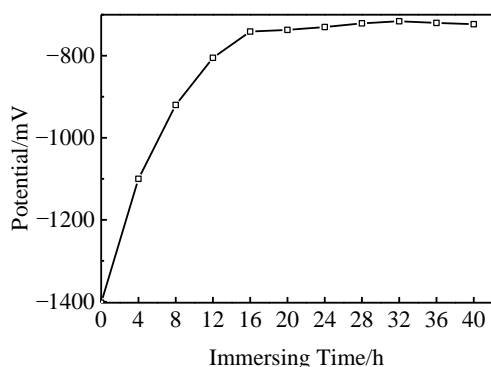

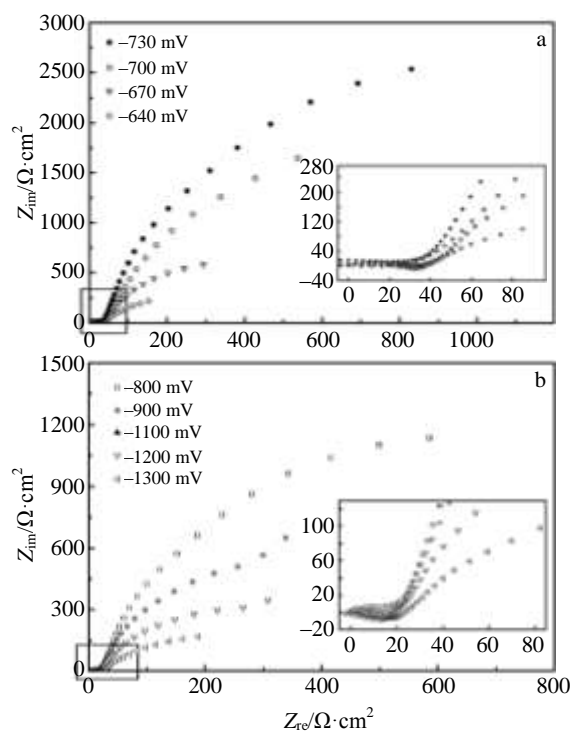Fig.4 Free corrosion potential of 7050 aluminum alloy *vs* corrosion time

Fig.5 Nyquist plots resulted from electrochemical impedance spectroscopy for specimens immersed in 3.5% NaCl solution and at various polarization potentials: (a) at anodic polarization potentials and (b) at cathodic polarization potentials
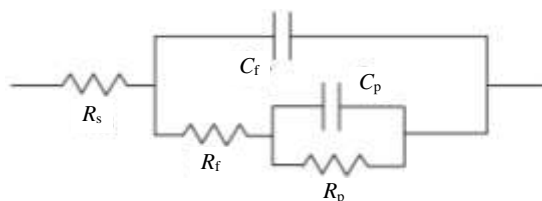

Fig.6 Schematic drawing of the equivalent circuit (where R_s is the solution resistance between the reference electrode and the working electrode, C_f is the capacitance of the film, R_f is the pore resistance of the film, C_p is the capacitance of the double layer of the aluminum alloy, R_p is the polarization resistance of the electrode)

indicates the SCC resistance of the specimens. The bigger the Z_{re} value, the more resistance to SCC of the specimen. Two capacitive contributions can be resolved when the high frequency behavior is magnified. The shorter time constant probably arises from the dielectric property of the passive film. The impedance data should be analyzed in either graphical or equivalent circuit modeling [14]. The latter was found more satisfactory to this work. An equivalent circuit model, drawn in Fig.6, was proposed to describe the ac behavior of 7050 aluminum alloy coated with a passive film. The resistance and capacitance are varied until the predicted ac behavior matches the corrosion experimental data as closely as possible. The physical meaning of equivalent circuit elements is as following: R_s is the solution resistance between the reference electrode and the working electrode, C_f is the capacitance of the film. R_f is the pore resistance of the film, C_p is the capacitance of the double layer of the aluminum alloy, and R_p is the polarization resistance of the electrode. The data for the elements under a variety of potentials are listed in Table 4. From Table 4 it can be indicated that all specimens reveal a similar magnitude of R_s. It is generally believed that a system with lower C_f and C_p but higher R_f and R_p is more resistant to corrosion, as a metallic system involving film-formation is concerned. On the other hand, a system with higher C_f and C_p but lower R_f and R_p facilitates attraction. According to Table 4, the corrosion resistance is much better for open circuit condition than others, and the corrosion resistance is better for cathodic polarization conditions than anodic polarization conditions at a macro level.

3　Discussions

Fig.3 indicates that the variation of susceptibility to SCC of 7050 aluminum alloy in the chloride solution with potential is

Table 4   Electrochemical impedance data of the electrical elements proposed in the equivalent circuit

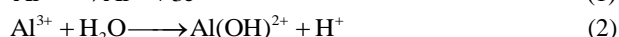| Potential/mV	−640	−670	−700	−730	−800	−900	−1100	−1200	−1300
R_s/Ω cm^2	1.208	2.434	1.768	1.004	1.367	1.573	1.082	2.301	1.644
C_f/×10^{-3} µF cm^{-2}	2.445	1.795	0.3986	0.1511	0.1902	0.4224	0.6496	0.5673	0.2768
R_f/Ω cm^2	276.2	9.986	21.35	32.79	188.3	19.84	7.983	16.65	19.44
C_p/×10^{-3} µF cm^{-2}	68.75	0.4900	12.37	6.004	2.896	8.577	23.65	17.35	8.988
R_p/×10^2 Ω cm^2	2.224	4.330	17.62	9.153	5.741	18.39	3.298	4.984	6.122

consistent with that of the passive film-induced stress. This means that a large tensile stress induced by the passive film is a necessary condition for SCC of 7050 aluminum alloy in the chloride solution. The original of the film-induced stress and its role in SCC should be discussed. The passive film formation involves either the inward diffusion of anions or outward immigration of cations [15,16]. If only the anions move, the anion transport number β=1, new passive film is generated at the metal/passive film interface, i.e., the passive film grows inward. Since the volume of oxide is greater than the volume made available by the ionization, the lattice of the surface layer expands. The metal matrix of the specimen hinders the surface layer consisting of the passive film to elongate, resulting in a compressive stress. If only cations move outward, the anion transport number β =0, new passive film is generated only at the passive film-solution interface, and there are many free spaces (vacancies) left at the metal side of the inner interface produced by the oxidation of 7050 aluminum alloy. The other part of specimen hinders the metal layer containing vacancies to contract, resulting in a tensile stress at the inner interface. Actually $0<\beta<1$. When impressed various potentials there is always a tensile stress generated by passive film.

For anodic polarization, $0<\beta<1$ there are many micro batteries formed and the ions transport actively during the process of polarization; at the same time the passive film is formed, and the stress induced by the passive film increases with the anodic potential increases. For cathodic polarization, there has a special tendency of the passive film-induced stress which increases first and then decreases with the cathodic polarization potential shifts negatively, and the inflection point is −1100 mV$_{SCE}$ (see Fig.2b).
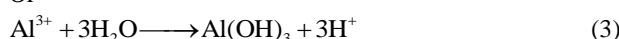
The EIS experiment is a representation of corrosion resistance of the passive film formed in the 3.5% NaCl solution with various potentials. The smaller the impedance value and the capacitance arc are, the worse the specimen's corrosion resistance is, moreover, the susceptibility to SCC is become higher and therefore the yield strength decreases with increasing the SCC susceptibility. As we can see from Fig.2 and Fig.5, there is a consistent variation of yield stress and EIS parameters with potentials, which proves that the existence of a film-induced stress is the directly reason of the yield strength increase. Table 4 is the fitting parameters of equivalent circuit. The lower C_f, C_p values and higher R_f, R_p values mean that the specimen is much easier to be corroded. R_s is the resistance of electrolyte, and there is a small difference among various pH values.
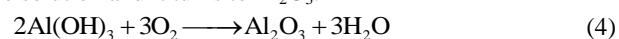
The anodic dissolution reaction of 7050 aluminum alloy in 3.5% NaCl solution is [17]:

$$Al \longrightarrow Al^{3+} + 3e^- \tag{1}$$

$$Al^{3+} + H_2O \longrightarrow Al(OH)^{2+} + H^+ \tag{2}$$

Or

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+ \tag{3}$$

Al(OH)$_3$ is white floccules. Oxidation reaction will occur in the solution and it turns to Al$_2$O$_3$:

$$2Al(OH)_3 + 3O_2 \longrightarrow Al_2O_3 + 3H_2O \tag{4}$$

Al$_2$O$_3$ is black oxide which will attach on the alloy matrix surface to form a passive film during immersing. However, the film cannot be absolutely sealed so the solution with Cl$^-$ ions could enter into the layer between alloy surface and passive film despite of a fraction. Cl$^-$ ions and aluminum alloy would take electrochemical reaction which generates a film-induced stress at the metal/passive film interface. The stress is parallel to the applied stress and helps the applied stress make the specimen fracture in an early stage.

The tensile stress induced by the passive film formed during SCC is the same with that during original corrosion, and can assist the applied stress to facilitate SCC. The passive film-induced stress measured in this work is an average value over the entire cross-section of the specimen. In fact, the maximum film-induced stress should exist at or near the interface between the passive and alloy, which is larger than the average value, σ_p, as shown in Table 3. The maximum film-induced stress is $\alpha\sigma_P$ ($\alpha>1$), and will assist the applied stress σ_a to generate SCC in a local zone. When the local stress concentration $\sigma_a + \alpha\alpha\sigma_P$ is equal to the failure stress extending in air, σ_F, the applied stress necessary for SCC, σ_{SCC}, will be $\sigma_{SCC} = \sigma_F - \alpha\sigma_P$. If $\sigma_P \leq 0$, $\sigma_F = \sigma_{SCC}$, no SCC occurs. For 7050 aluminum alloy no matter at anodic or cathodic potential, always $\sigma_P > 0$, and then SCC occur. The larger the film-induced stress σ_P is, the greater the susceptibility to SCC as shown in Fig.3.

4   Conclusions

1) There is a passive film formed after immersing in 3.5% NaCl solution at various polarization potentials for 24 h and can generate a passive film-induced tensile stress.

2) At anodic potential, the film-induced stress increases with increasing the potential; at cathodic potential, the film-induced stress is of a tendency of increases first and then decreases with the cathodic polarization potential shifting

negatively, and the inflection point is −1100 mV$_{SCE}$.

3) The variation of film-induced stress with potential is consistent with that of the susceptibility to SCC with potential.

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7050 铝合金应力腐蚀敏感性和钝化膜引起的膜致应力随电位变化的一致性

祁　星 [1,2,3]，宋仁国 [1,2,3]，祁文娟 [1,2,3]，金骥戎 [1,2,3]，王　超 [1,2,3]，李　海 [1,2,3]，熊　缨 [4]

(1. 常州大学 材料科学与工程学院，江苏 常州 213164)

(2. 常州大学 江苏省材料表面科学技术重点实验室，江苏 常州 213164)

(3. 常州大学 江苏省光伏科学与工程协同创新中心，江苏 常州 213164)

(4. 浙江工业大学，浙江 杭州 310014)

摘　要：用流变应力差值法测量了不同极化电位下 7050 铝合金在 3.5%NaCl 水溶液（pH=10）腐蚀过程中表面钝化膜形成的拉应力，并用慢应变速率拉伸法测量了不同极化电位下的应力腐蚀敏感性。结果表明:7050 铝合金在溶液中自然腐蚀时，表面钝化膜会产生一定的拉应力；阳极极化使表层拉应力明显上升，且随着电位升高应力增大；阴极极化时，当电位 $E \geq$-1100 mV 时表层拉应力随着电位的升高而降低，当电位 $E \leq$−1100 mV 时拉应力随着电位升高而升高。应力腐蚀敏感性随外加电位变化规律和钝化膜引起的附加拉应力变化完全一致。

关键词：7050 铝合金；应力腐蚀；膜致应力；极化电位

作者简介：祁　星，男，1988 年生，硕士生，常州大学材料科学与工程学院，江苏 常州 213164，电话：0519-86330069，E-mail: qixing321@outlook.com