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Correspondence between Susceptibility to SCC of 7050 Aluminum Alloy and Passive Film-induced Stress at Various pH Values

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Abstract: The passive film-induced stress and the susceptibility to SCC of 7050 aluminum alloy in 3.5% sodium chloride solution at various pH values were investigated by slow strain rate testing (SSRT) and flowing stress differential method. The results showed that the passive film-induced stress and the susceptibility to SCC decreased with increasing pH values when pH≤7, while they increased with increasing pH values when pH ＞7. However, the corrosion type was interpreted as exfoliation corrosion when pH=1 and 14, and there was no film formed on the surface of the specimens. The whole variation plots of film-induced stress and the SCC susceptibility with pH values were both presented as a valley shape. The symbol and amount of the film-induced stress were related to the compositions of the passive film, which were analyzed using X-ray photoelectron spectroscopy (XPS).

Key words: 7050 aluminum alloy; susceptibility to SCC; pH value; passive film-induced stress

1 Introduction

7000 series aluminum alloys (Al-Zn-Mg-Cu) have been introduced since 1943 and used extensively as airframe structures due to their high strength/density ratio[1]. However, the stress corrosion cracking (SCC) is a factor limiting their more widespread application[2-6]. Recently, many researchers have proposed a new mechanism to explain SCC that the corrosion process promotes localized plastic deformation and finally results in SCC. A series research works of W.Y. Chu's group[7-10] showed that the corrosion process can facilitate dislocation emission and motion during SCC of brass, type 304 stainless steel, α-Ti and Ti_3Al+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[11]. A passive film or de-alloy layer formed on the surface in most SCC controlled by anodic dissolution has a remarkable influence on SCC. The experiments showed that the passive film or dezincification layer could generate a large tensile stress[12,13], which is parallel to the applied stress during SCC. *In situ* TEM observation showed that the corrosion process could facilitate dislocations emission and motion during SCC[14]. Perhaps, it is due to the film-induced additive stress, which assists the applied stress to enhance local plastic deformation during SCC.

Up till now, the relationship between susceptibility to SCC and passive film-induced stress of aluminum alloy has not been investigated. The aim of the present study is to determine this relationship and the mechanism by using flowing stress difference method and slow strain rate testing (SSRT) in 3.5% sodium chloride solution at various pH values coupling electrochemical impedance spectroscopy (EIS) with scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) is also used to analyze the composition and structure of the passive film formed at various pH values.

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2 Experimental

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 7050 aluminum alloy is listed in Table 1. The specimens were 2 mm thick and 15 mm gauge long with the tensile axis parallel to the short transverse direction which is known to be the most sensitive orientation to SCC. They were heat-treated with over aged: 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 1 200, 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 by SSRT tests. $I_t = (1-t_{SCC}/t_F)\times 100\%$ and $I_\sigma = (1-\sigma_{SCC}/\sigma_F)\times 100\%$, where σ_F, t_F and t_{SCC}, σ_{SCC} were fracture strength and fracture time of tensile specimens during SSRT in air and in the 3.5% sodium chloride solution at various pH values at a strain rate of $1\times10^{-6}\ s^{-1}$, respectively. The specimens were etched in a 1% sodium hydroxide solution for 1 min in order to remove the air-formed oxide. After cleaning in diluted HNO_3 solution, the specimens in the chloride solution were kept at various pH values. The pH value was adjusted using sodium hydroxide or sulfuric acid.

The specimens were strained in air to a plastic strain $\varepsilon_P \geqslant 1\%$ at a strain rate of $1\times10^{-6}s^{-1}$. After unloading, the specimens were immersed in the1% sodium hydroxide solution for 1 min to remove the oxide and cleaned in diluted nitric acid solution, then put into the 3.5% sodium chloride solution with various pH values for 6 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*, $\sigma_P = \sigma_f - \sigma_{ys}$.

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} to 10^5 Hz and the amplitude deviation within 5 mV at open circuit potential.

X-ray photoelectron spectra (XPS) were obtained with an ESCALABMKLL spectrometer (VG Scientific Ltd. West Sussex, Britain). A magnesium anode source produced the Mg Ka X-ray source. Electrons taken off the film surface were captured by an electron multiplier.

The film surfaces were observed by a scanning electron microscope (SEM) (JEOL JSM6360-LA, Tokyo, Japan).

3 Results

3.1 Immersion surface and susceptibility to SCC of 7050 aluminum alloy

Table 1 Chemical composition of 7050 aluminum alloy/wt%

Elements	Al	Zn	Mg	Cu	Zr	Fe	Si	Ti	Mn
Content/ wt%	Bal	6.42	2.25	2.02	0.13	0.11	0.07	0.03	0.10

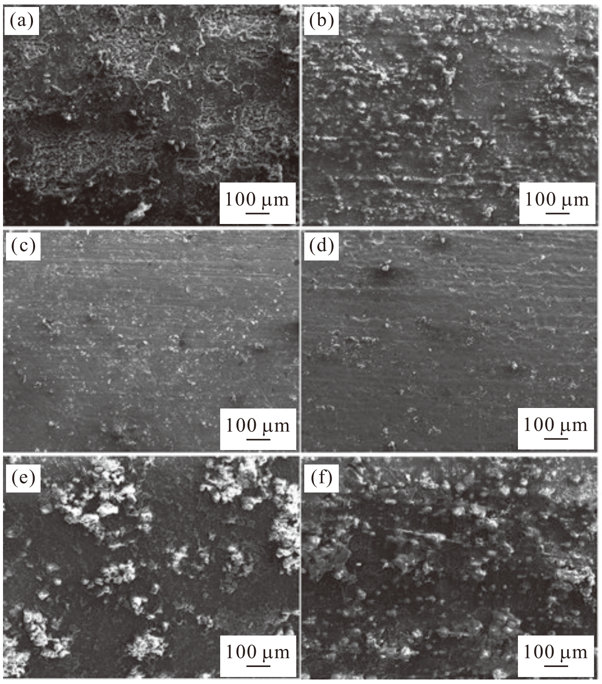

Fig.1 Surface of 7050 aluminum alloy after immersed in 3.5% sodium chloride solution for 6 h under various pH values: (a) pH=1; (b) pH=2; (c) pH=7; (d) pH=9; (e) pH=13; (f) pH=14

Fig.1 shows the surface of the specimens after immersing in 3.5% sodium chloride solution at various pH values for 6 h. When pH =1 and 14, the surface of the specimens is peel off thus exposing the substrate to be attacked, the phenomenon is interpreted as exfoliation, therefore, there is not any passive film formed at the surface; When pH = 7 and 9, as shown in Figs.1 (c) and (d), the passive film is very flat and there are little corrosion products on the surface; however, there are many vacancies in the film when pH =2 and 13, resulting in a very loose and uneven passive film, usually, the passive film of this type can generate a large additive stress.

Table 2 Susceptibility to SCC of 7050 aluminum alloy after immersed in 3.5% sodium chloride solution under various pH values

pH	$t_{\rm SCC}$/h	$\sigma_{\rm SCC}$/MPa	$I_{\rm t}$	I_σ
2	16.0	145	0.62	0.71
3	18.9	205	0.55	0.59
4	23.9	230	0.43	0.54
5	29.4	320	0.3	0.36
6	31.5	335	0.25	0.33
7	31.9	345	0.24	0.31
8	29.4	340	0.3	0.32
9	27.3	295	0.35	0.41
10	18.9	220	0.55	0.56
11	11.4	150	0.73	0.7
12	10.9	100	0.74	0.8
13	5.0	80	0.88	0.84

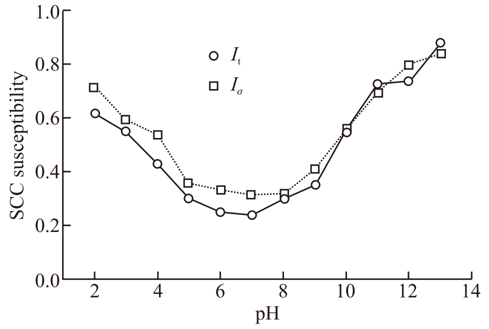

Fig.2 Variation of susceptibility to SCC uner various pH values of 7050 aluminum alloy

The average fracture stress and time to fracture of the specimen during extending in air were σ_F =500 MPa and t_F = 42 h, respectively. The stress and time to fracture of the specimen during SSRT in the chloride solution at various pH values are listed in Table 2. The susceptibility to SCC, I_σ and I_t are also listed in Table 2. Fig.2 shows the SCC susceptibility at various pH values. I_σ and I_t are of the same change tendency with changing pH values although their absolute values are different. It can be seen from Fig.2 that the plots have a valley shape and the susceptibility to SCC has a minimum value when pH=7. The change tendency of the plots is much more gradual when 5⩽pH⩽9 compared with that when pH<5 or pH>9.

3.2 Passive film-induced stress at various pH values

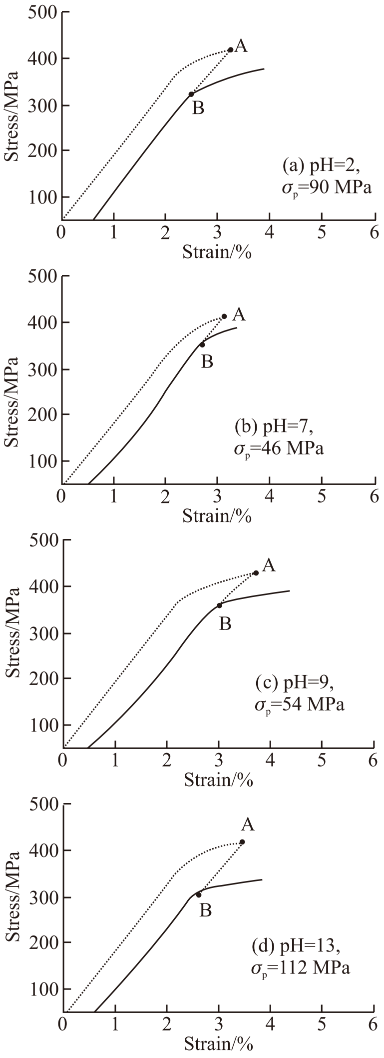

Fig.3 Stress-strain curves before or after the passive film forming on the same specimen (a) pH=2, (b) pH=7, (c) pH=9, (d) pH=13

Table 3 Stress induced by passive film during corrosion at various pH values

pH	2	3	4	5	6	7	8	9	10	11	12	13
$\sigma_{\rm P}$/MPa	90	86	71	63	49	46	46	54	76	83	96	112

Stress-strain curves for specimens at various pH values before or after the passive film formed during slow tensile tests in air are shown in Fig.3. The dotted line is the stress-train curve extending in air and the solid line is that extending again in air after unloading at point A and forming a passive film through corrosion in the 3.5% sodium chloride solution with various pH values. The difference between the flow stress at point A and the yield stress at point B after forming the passive film is the additive stress induced by passive film, *i e*, $\sigma_{\rm P} = \sigma_{\rm f} - \sigma_{\rm ys}$. $\sigma_{\rm P}$ for the specimens are listed in Table 3. It should be pointed out that the passive film-induced stress measured by the flowing stress difference method is an average stress along the cross-section of a whole specimen[15]. It can be seen form Fig.3 that the passive film-induced stress values at pH=7 and 9 are very close, meanwhile, the passive film-induced stress values at pH=2 and 13 are also very close but much larger than the values at pH=7 and 9. That means the type of film formed when pH=7 and 9 has a big difference with that at pH=2 and 13. Fig.3 indicates that the direction of passive film-induced stress is parallel to the direction of applied stress and therefore can assist the applied stress to promote the alloy’s plastic deformation. The stress intensity factor K_{Ip} generated by film-induced stress superimposes upon the stress intensity factor K_{Ia} generated by applied stress and promotes the dislocation emission and motion developing, eventually leads to the cracks initiation and propagation[16].

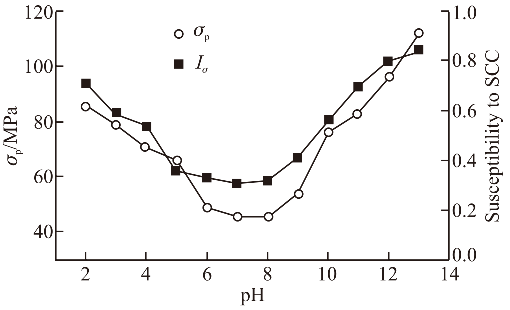

Fig.4 Passive film-induced stress and susceptibility to SCC at various pH values

The variation of passive film-induced stress and susceptibility to SCC at various pH values are shown in Fig.4. The variation of film-induced stress with pH values is consistent with that of susceptibility to SCC with pH values, and both film-induced tensile stress and susceptibility to SCC have a minimum value when pH=7. The presence of a large additive stress is an essential condition to the anodic dissolution type of SCC of 7050 aluminum alloy in the chloride solution.

3.3 Electrochemical impedance spectroscopy

Fig.5 is the Nyquist plots of 7050 aluminum alloy after forming various films in 3.5% sodium chloride solution when pH=2, 7, 9 and 13. As the figure shows, when pH=7 and 9, the capacitance arc of the film appears at the high frequency part, however, the low frequency part has a much bigger radius and the impedance value is also higher than that at the high frequency part. When pH=2 and 13, the radius of capacitance arc and the impedance value are significantly less than the values at pH=7 and 9 at the same frequency level. It means that SCC resistance of the loose passive film formed after immersion when pH=2 and 13 is weaker than that of the flat and dense film when pH=7 and 9. Fig.6 is Bode plots when pH=2, 7, 9 and 13. There exists an obviously difference among the four pH values at low frequency stage (10^{-2}-

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

Item	pH=2	pH=7	pH=9	pH=13
$R_s/(\Omega\cdot cm^2)$	1.082	1.004	1.768	1.208
$C_f/(\mu F\cdot cm^2)$	6.496×10^{-4}	1.511×10^{-4}	3.986×10^{-4}	2.445×10^{-3}
$R_f/(\Omega\cdot cm^2)$	7.983×10^{0}	3.279×10^{1}	2.135×10^{1}	2.762×10^{2}
$C_p/(\mu F\cdot cm^2)$	2.365×10^{-2}	6.004×10^{-3}	1.237×10^{-2}	6.875×10^{-2}
$R_p/(\Omega\cdot cm^2)$	3.298×10^{2}	9.153×10^{2}	1.762×10^{3}	2.224×10^{2}

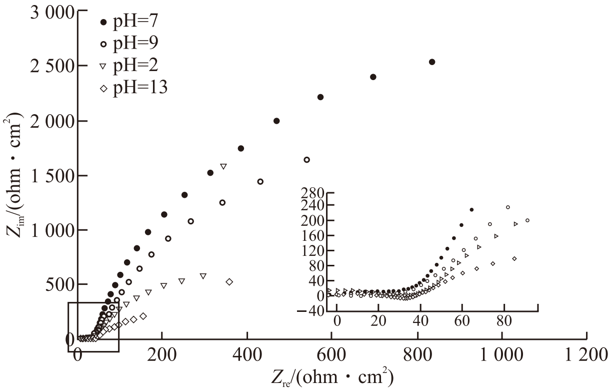

Fig.5 Nyquist plots of 7050 aluminum alloy at various pH values

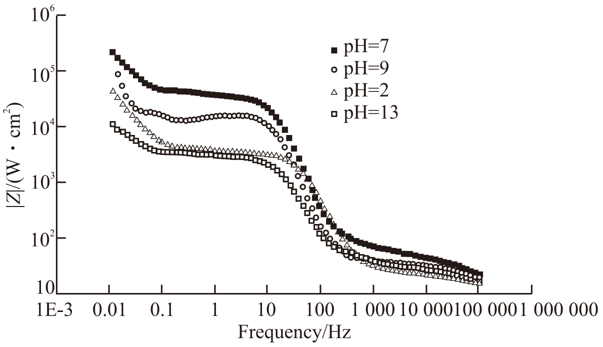

Fig.6 Bode plots of 7050 aluminum alloy under various pH values

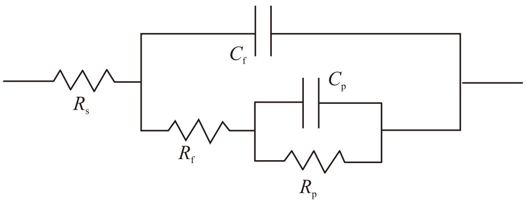

Fig.7 Equivalent circuit of 7050 aluminum alloy specimens in 3.5% sodium chloride solution

10 Hz), the ∣ Z ∣ value at pH =2 and 13 is lower than the value at pH=7 and 9. At the middle frequency part (10-1 000 Hz), the ∣ Z ∣ value increases sharply and at the high frequency part (10^3-10^5Hz) there is little difference among them. Fig.7 is the equivalent circuit where R_S is the resistance of electrolyte, C_f is the component representing the passive film of alloy, C_p-R_p is the component representing the corrosion reaction. The parameters of every component are in Table 4.

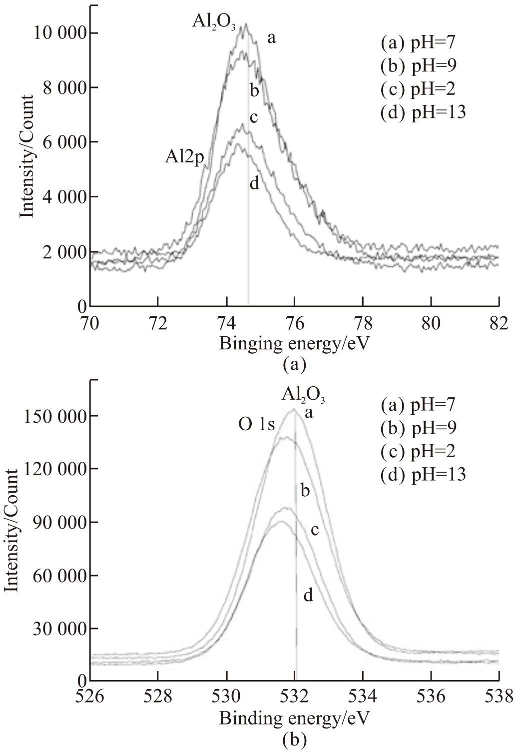

Fig.8 XPS spectra of Al 2*p* and O 1*s* of 7050 aluminum alloy passive film: (a) Al 2p; (b) O 1*s*

3.4 X-ray photoelectron spectra

Fig.8 shows the XPS chemical peak position and integrated intensity of the elements in passive film changing with the pH values. The vertical lines in the figures are the standard peak position of elements' chemical state. It can be seen from Figs.8 (a) and (b) that the peak positions of Al 2*p* and O 1*s* have different changes with various pH values, however the two peak positions both have an obvious chemical state, *i e*, aluminum oxide. The binding energy of aluminum oxide corresponding to Al 2*p* peak position is 74.3 eV, and for O 1*s* peak position is 532.1 eV. Apparently, the amount of aluminum oxide when pH=7 and 9 is larger than that when pH=2 and 13 which again demonstrates the conclusion obtained before. On the other hand, it means that aluminum oxide has a significant influence on the quality of passive film.

4 Discussion

Fig.4 indicates that the variation of susceptibility to SCC of 7050 aluminum alloy in the chloride solution at various pH values is 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 origin of the film-induced stress and its role in SCC should be discussed.

The EIS experiment is a representation of corrosion resistance of the passive film formed in the 3.5% sodium chloride solution with various pH values. The smaller the impedance value and the capacitance arc are, the worse of the specimen's corrosion resistance is, moreover, the susceptibility to SCC becomes higher and therefore the yield strength decreases with increasing SCC susceptibility. As we can see from Fig.3 and Fig.5, there is a consistent variation of yield stress and EIS parameters with pH values 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. RS is the resistance of electrolyte, there is small difference among various pH values.

The anodic dissolution reaction of 7050 aluminum alloy in 3.5% sodium chloride solution is[17]:

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3\mathrm{e}^- \qquad (1)$$

$$\mathrm{Al}^{3+} + \mathrm{H_2O} \rightarrow \mathrm{Al(OH)}^{2+} + \mathrm{H}^+ \qquad (2)$$

$$\text{Or} \quad \mathrm{Al}^{3+} + 3\mathrm{H_2O} \rightarrow \mathrm{Al(OH)_3} + 3\mathrm{H}^+ \qquad (3)$$

Al $(OH)_3$ is white floccule, it will undergo oxidation reaction in the solution and turn to aluminum oxide:

$$2\mathrm{Al(OH)_3} + 3\mathrm{O_2} \rightarrow \mathrm{Al_2O_3} + 3\mathrm{H_2O} \qquad (4)$$

Aluminum oxide is a black oxide which will attach on the alloy matrix surface formed 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 generated 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. As the XPS results show (see Fig.8), when pH=7 and 9, the amount of oxide aluminum oxide is very rich, forming a flat and dense film and can reduce the solution permeation into the metal/passive film interface to some extent, moreover, the newly produced aluminum oxide will block the original crack, hindering the entrance of solution into the metal/passive film interface. However, when pH=2 and 13, the balance between H^+ and OH^- is broken, aluminum oxide produced at the beginning starts to dissolve which makes the film become loose and more solution with Cl^- ions enters into the metal/passive film interface, eventually, the interaction speed between passive film and matrix increases, leading to the passive film-induced stress to increase. When pH=1 and 14, the dissolution speed of aluminum oxide is greater than the production speed, the aluminum alloy matrix is exposed to the solution and continues dissolving in the strong acid or base environment, therefore, there is no passive film-induced stress.

When the SCC of 7050 aluminum alloy in 3.5% sodium chloride solution at various pH values occurs, as we can see in Fig.4, the film-induced stress increases with increasing pH values when pH$>$7, simultaneously, the susceptibility to SCC also increases; while there exists an opposite change tendency when pH$\leqslant$7, but the passive film-induced stress varies with pH values which is consistent with that of SCC susceptibility with pH values.

5 Conclusions

a) The difference of the flow stress before unloading and the yield stress after unloading and forming a passive film is the passive film-induced stress. The passive film-induced stress can assist the applied stress to promote the plastic damage.

b) The film-induced stress is related to the amount of aluminum oxide in the film. When pH$>$7, the film-induced stress increases with increasing pH values, at the same time, the susceptibility to SCC also increases with increasing pH values; there exists an opposite change tendency when pH$\leqslant$7.

c) When pH=1 and 14, the corrosion type is exfoliation and no passive film has formed.

References

[1] Li J F, Peng Z W, Li C X, *et al.* Mechanical Properties, Corrosion Behaviors and Microstructure of 7075 Aluminum Alloy with Various Aging Treatment[J]. *Trans. Nonferrous Met. Soc. China*, 2008, 18: 755-762

[2] Alarm A, Bahr D F, Michael J. Effects of Alloy and Solution Chemistry on the Fracture of Passive Films on Austenitic Stainless Steel[J]. *Corr Sci.*, 2006, 48: 925-936

[3] Najjar D, Magnin T, Warner TJ. Influence of Critical Surface Defects and Localized Competition between Anodic Dissolution and Hydrogen Effects during Stress Corrosion Cracking of 7050 Aluminum Alloy[J]. *Mater. Sci. Eng. A*, 1997, 238: 293-302

[4] Wang D, Ni D R, Ma Z Y. Effect of Pre-strain and Two-step Aging on Microstructure and Stress Corrosion Cracking of 7050 Alloy[J]. *Mater. Sci. Eng. A*, 2008, 494: 360-366

[5] Li J F, Peng Z W, Li C X, *et al.* Mechanical Properties, Corrosion Behaviors and Microstructure of 7075 Aluminum Alloy with Various Aging Statements[J]. *Trans. Nonferrous Met. Soc. China*, 2008, 18: 755-762

[6] Chen S Y, Chen K H, Peng G S, *et al.* Effect of Heat Treatment on Strength, Exfoliation, Corrosion and Electrochemical Behavior of 7085 Aluminum Alloy[J]. *Mater. Design*, 2012, 35: 93-98

[7] Guo XZ, Gao K W, Chu W Y, *et al.* Correlation Between Passive Film-induced Stress and Stress Corrosion Cracking of α-Ti in a Methanol Solution at Various Potentials[J]. *Mater. Sci. Eng. A*, 2003, 346: 1-7

[8] Lu H, Gao K W, Chu W Y. Determination of Tensile Stress Induced by Dezincification Layer during Corrosion for Brass[J]. *Corr Sci.*, 1998, 40: 1 663-1 670

[9] Chen H, Guo X Z, Chu W Y, *et al.* Martensite Caused by Passive Film-induced Stress during Stress Corrosion Cracking in Type 304 Stainless Steel[J]. *Mater. Sci. Eng. A*, 2003, 358: 122-127

[10] Gao K W, Chu W Y, Li H L, *et al.* Correspondence between Hydrogen Enhancing Dezincification Layer-induced Stress and Susceptibility to SCC of Brass[J]. *Mater. Sci. Eng. A*, 2004, 371: 51-56

[11] Li J X, Chu W Y, Wang Y B, *et al. In situ* TEM Study of Stress Corrosion Cracking of Austenitic Stainless Steel[J]. *Corr Sci.*, 2003, 45: 1 355-1 365

[12] Qiao L J, Chu W Y, Miao H, *et al.* Strength Effect in Stress Corrosion Cracking of High Strength Steel in Aqueous Solution[J]. *Metall. Trans. A*, 1993, 24: 959-963

[13] Li Q K, Zhang Y, Chu W Y. Molecular Dynamics Simulation of Stress Corrosion Cracking in Cu_3Au[J]. *Comput. Mater. Sci.*, 2002, 25: 510-518

[14] Guseva O, Schmutz P, Suter P, *et al.* Modelling of Anodic Dissolution of Pure Aluminum in Sodium Chloride[J]. *Electrochim. Acta*, 2009, 54: 4 514-4 524

[15] Guo XJ, Gao K W, Qiao L J, *et al.* The Correspondence between Suscetibility to SCC of Brass and Corrosion-induced Tensile Stress with Various pH Values[J]. *Corr. Sci.*, 2002, 44: 2 367-2 378

[16] Ramamurthy S, Lau W M L, Atrens A. Influence of the Applied Stress Rate on the Stress Corrosion Cracking of 4340 and 3.5NiCrMoV Steels under Conditions of Cathodic Hydrogen Charging[J]. *Corr. Sci.*, 2011, 53: 2 419-2 429

[17] Lin J C, Liao H L, Jehng J C. Effect of Heat Treatments on the Tensile Strength and SCC-Resistance of AA7050 In an Alkaline Solution[J]. *Corr. Sci.*, 2006, 48 : 3 139-3 156