Hydrogen-increased dezincification layer-induced stress and susceptibility to stress corrosion cracking of brass [①]

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Abstract: Dezincification layer formed during corrosion or stress corrosion cracking (SCC) of brass in an ammonia solution could induce an additive stress. The effect of hydrogen on the dezincification layer-induced stress and the susceptibility to SCC were studied. The dezincification layer-induced stress was measured using the deflection method and the flowing stress differential method, respectively. The latter measures the difference between the flowing stress of a specimen before unloading and the yield stress of the same specimen after unloading and forming a dezincification layer. The susceptibility to SCC was measured using slow strain rate test. Results show that both the dezincification layer-induced stress and the susceptibility to SCC increase with increasing hydrogen concentration in a specimen. This implies that hydrogen-enhanced dezincification layer-induced stress is consistence with the hydrogen-increased susceptibility to SCC of brass in the ammonia solution.

Key words: hydrogen; dezincification layer-induced stress; stress corrosion cracking; brass

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1 INTRODUCTION

During stress corrosion cracking (SCC) controlled by anodic dissolution, a passive film or dezincification layer forms on the surface[1]. Experimental results exhibited that a foil of α-Ti or brass with one end fixed and another side protected with a protective layer formed on it was concave during corrosion in a methanol and an ammonia solutions, respectively[2, 3]. This means that a tensile stress exists on the interface between the passive film or dezincification layer and the matrix [2, 3]. Extensive experiments showed that the dependence of the dezincification layer-induced tensile stress on the applied potential and pH value in the solution was in a good agreement with that of the susceptibility to SCC of brass in the ammonia solution[4-6]. Both the dezincification layer-induced stress and the susceptibility to SCC had a maximum value at open-circuit potential, decreased slightly under anodic polarization, and reduced remarkably under cathodic polarization. When the cathodic potential was below − 460 mV (SCE), the dezincification layer-induced stress was zero or compressive, and correspondingly no SCC occurred[4]. The passive film induced-stress and the susceptibility to SCC of α-Ti in a methanol solution decreased with increasing amount of water in the methanol solution; when the amount of water is about 10%, the passive film-induced

stress was zero, at the same time, no SCC occurred [7]. So, the essential condition for the happening of SCC controlled by anodic dissolution under the conditions mentioned above is the presence of a big enough tensile stress induced by the passive film or the dezincification layer.

Hydrogen could facilitate corrosion and SCC of type 310 austenitic stainless steel in a boiling $MgCl_2$ solution [8]. For example, the threshold stress for SCC of a precharged specimen decreased by 20%, and the crack propagation rate increased by ten times as compared with that of uncharged one[8].

Because the stress induced by the passive film or the dezincification layer is closely related to the susceptibility to SCC, an increase in the susceptibility to SCC by hydrogen might imply that hydrogen can increase the passive film-induced or the dezincification layer-induced tensile stress. The aim of this study is to investigate the influence of hydrogen on the dezincification layer-induced stress and the susceptibility to SCC of brass in the ammonia solution, and the relationship between them is discussed.

2 EXPERIMENTAL

The material used here was brass containing 38% Zn. Foil specimens in a dimension of 0. 2 mm × 5 mm × 90 mm and smooth tensile specimens with the

gauge length of 50 mm and cross section of 0. 2 mm × 5 mm were used to investigate the dezincification layer-induced stress. The single-edge notched specimens with a size of 0. 2 mm × 10 mm × 95 mm containing a notch of 5mm in depth and 0. 1 mm in radius of semi-cycular tip were used to study the hydrogen embrittlement and the susceptibility to SCC. All specimens were polished using 1000-grit finish, and then annealed in vacuum at 280 ℃ for 1. 5 h followed by air cooling. Some specimens were precharged in a solution of 0. 5 mol/L H_2SO_4+ 0. 25 g/L As_2O_3 for 48 h, with current densities of 2, 20 and 200 mA/cm^2 respectively. Hydrogen concentration (C_0) of small samples charged with various current densities, was measured by heat extraction method at 800 ℃[9].

Hydrogenated and hydrogen-free notched specimens were slowly extended in air and in a solution of 1 mol/L NH_4OH+ 5 g/L $CuCl_2$ respectively to fail with a displacement speed of 1. 89 × 10^{-5} mm/s. The susceptibility to hydrogen embrittlement is I_{HE}= [1 − σ_{air}(H)/ σ_{air}] × 100%, where σ_{air}(H) and σ_{air} are fracture stresses of the hydrogenated and hydrogen-free specimens, respectively. The susceptibility to SCC of the specimens with various hydrogen concentrations is I_{SCC}= (1− σ_{sol}/ σ_{air}) × 100%, where σ_{air} (H) and σ_{sol} are fracture stresses of the specimens with the same hydrogen concentration extended in air and in the solution, respectively.

Two methods were used to measure the dezincification layer-induced stress. The first one is deflection method. i. e. , a hydrogenated or hydrogen-free foil specimen with a protective layer formed on one side and another end fixed deflected gradually during immersed in the above mentioned ammonia solution. The dezincification layer-induced stress averaged over the thickness of the dezincification layer is defined as[2, 10]

$$\sigma_p^* = \frac{Eh^2 \delta}{3(1- v^2)Ld} \qquad (1)$$

where δ is the deflection at the free end of the foil, E= 108 GPa, v= 0. 35 are the elastic modulus and Persion's ratio of brass, h= 0. 2 mm, L= 60 mm are the thickness and the length of the specimen immersed in the solution, and d is the thickness of the dezincification layer, d= s/L, where s is the cavity area inside the dezincification layer measured by scanning electron microscopy (SEM).

The second one is the flowing stress differential method, i. e. , a hydrogenated or hydrogen-free specimen was extended in air to the plastic strain $\varepsilon_p \geqslant$ 1%. After unloading, the specimen was immersed in the ammonia solution for 1 h to form a dezincification layer through corrosion. After cleaned and dried, the same specimen with the dezincification layer was extended in air to yield. The yield stress of the specimen with the dezincification layer σ_{ys}, is different to the flowing stress before unloading, σ_f, and the difference between them[11] is the additive stress induced by the dezincification layer, i. e. , σ_p= σ_f− σ_{ys}.

3 RESULTS

3. 1 Influence of hydrogen on dezincification layer-induced stress

Hydrogen content in the hydrogen-free specimen was measured to be 1. 6 × 10^{-6} after the specimen heated to 800 ℃. The hydrogen must exist in irreversible traps, that is, can not diffuse out of the specimen at room temperature. After precharged in a H_2SO_4 solution with current densities of i= 2, 20 mA/cm^2 and 200 mA/cm^2 for 48 h, hydrogen concentrations measured at 800 ℃ were 3. 2 × 10^{-6}, 4. 5 × 10^{-6} and 8. 4 × 10^{-6}, respectively. Correspondingly, the diffusible hydrogen concentrations (C_0) in the hydrogenated specimens were 1. 6 × 10^{-6}, 2. 9 × 10^{-6} and 6. 8× 10^{-6}, respectively, as listed in Table 1.

Table 1 Dezincification layer-induced stress in brass containing hydrogen

$i/(mA \cdot cm^{-2})$	$C_0/10^{-6}$	δ/ mm	d/ μm	σ_p^*/ MPa	σ_p/ MPa
Uncharged	0	0. 565	3. 85	65. 6	13. 1
2	1. 6	0. 685	4. 44	68. 9	17. 8
20	2. 9	0. 75	4. 51	74. 3	28. 7
200	6. 8	1. 8	5. 03	134. 1	45. 7

The deflections of the hydrogenated and hydrogen-free specimens corroded for 40 min in the above mentioned ammonia solution increases linearly with corrosion time, as shown in Fig. 1. And the morphologies of the dezincification layer are shown in Fig. 2. The cavity area in the dezincification layer has been measured by SEM and then the average thickness d of the dezincification layer was calculated and listed in Table 1. The dezincification layer-induced stress averaged over the thickness of the dezincification layer, σ_p^*, was calculated based on Eqn. (1) and also listed in Table 1.

Stress-strain curves for specimens with various hydrogen concentrations before or after the dezincification layer formed during slow tensile tests in air are shown in Fig. 3. The dotted lines are the stress-strain curves extending in air and the solid lines are those extending again in air after unloading at point A and forming a dezincification layer through corrosion in the ammonia solution. The difference between the flowing stress at the point A and the yield stress at the point B is an additive stress induced by the dezin-
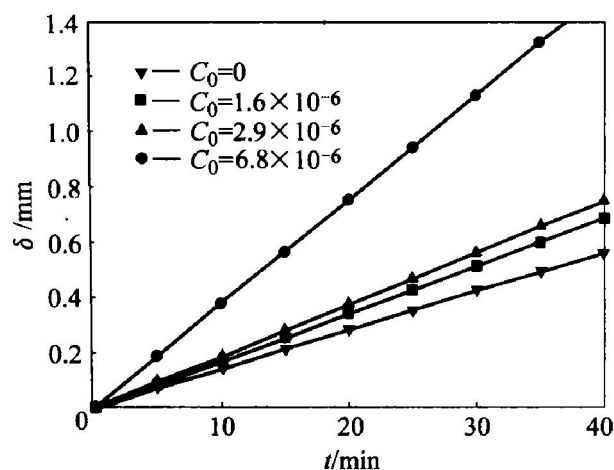
Fig. 1 Deflection of brass containing various hydrogen concentrations vs corrosion time
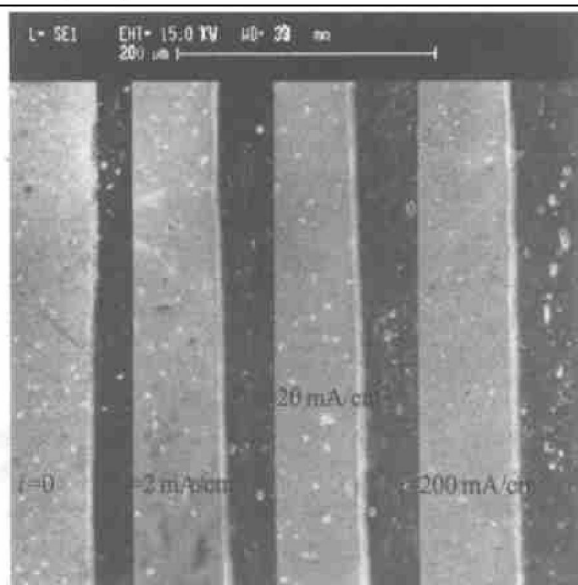

Fig. 2 Dezincification layers of specimens containing hydrogen
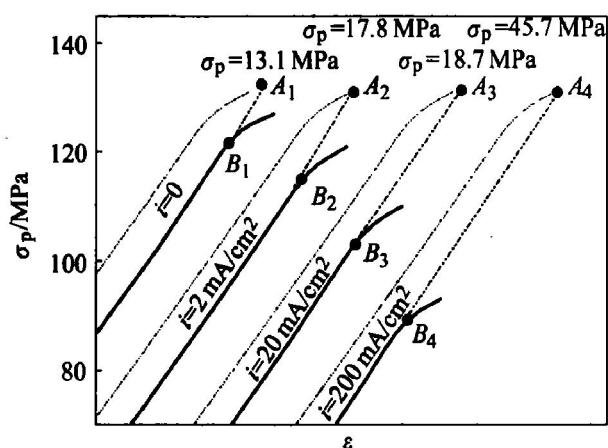

Fig. 3 Stress vs strain curves before and after dezincification layer forming for uncharged and charged specimens

cification layer, i. e., $\sigma_p = \sigma_f - \sigma_{ys}$. σ_p for the hydrogenated and hydrogen-free specimens are also listed in Table 1. Experiments showed that the yield stresses of the specimen without the dezincification

layer after unloading were the same with the flowing stresses before unloading, and the differences were less than 2 MPa, which was less than the dezindification layer-induced stress listed in Table 1. It should be pointed out that σ_p measured by the flowing stress differential method is that over the thickness of the whole specimen, and σ_p^* measured by the deflection method is the dezincification layer-induced stress averaged over the thickness of the dezincification layer. The thickness of the dezincification layer is much smaller than that of the whole specimen. So, the latter, i. e., σ_p^* is far higher than the former, i. e., σ_p. Since the measurement error of the dezincification layer thickness is big, the measurement precision of σ_p^* is far lower than that of σ_p. The dezincification layer-induced stress increases with increasing hydrogen concentration, as shown in Fig. 4.
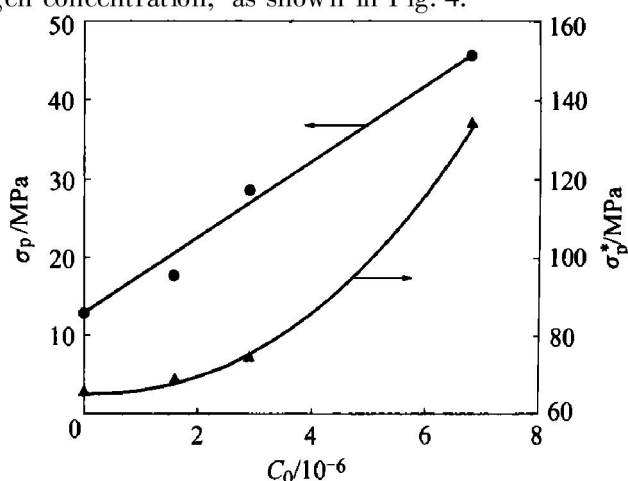

Fig. 4 Dezincification layer-induced stress measured using two methods vs hydrogen concentration

3. 2   Susceptibility to hydrogen embrittlement of hydrogenated specimen

The results in slow strain rate tests (SSRT) with displacement rate of 1. 89 × 10^-5 mm/s for the notched specimens with various hydrogen concentrations are listed in Table 2. The fracture stress σ_{air} and fracture time t_{air} of the hydrogenated specimens in air increased slightly as compared with that of hydrogen-free specimen, instead of decreasing. This result indicates that brass has no sus-

Table 2 SSRT results of brass containing various hydrogen concentrations

$i/$ (mA·cm^{-2})	$C_0/$ 10^{-6}	$\sigma_{air}/$ MPa	$t_{air}/$ min	$\sigma_{sol}/$ MPa	$t_{sol}/$ min	$I_{SCC}/\%$
Uncharged	0	218	1 950	60	248	72. 6
2	1. 6	225	2 040	52	214	76. 9
20	2. 9	227	2 100	46	192	79. 7
200	6. 8	226	2 100	38	170	84. 8

ceptibility to hydrogen embrittlement in SSRT of the hydrogenated specimen.

3.3 Influence of hydrogen on susceptibility to SCC

If the hydrogenated and hydrogen-free specimens were slowly extended in the ammonia solution with the displacement rate of 1.89×10^{-5} mm/s, the fracture stress σ_{sol} and fracture time t_{sol} decreased greatly as compared with that in air, as shown in Table 2. The susceptibility to SCC of the specimens with various hydrogen concentrations, I_{SCC}, is also listed in Table 2. It can be seen that the susceptibility to SCC of brass in the ammonia solution increased with increasing hydrogen concentration. The variation of the susceptibility to SCC of the specimens with various hydrogen concentrations with the dezincification layer-induced stress averaged over the whole specimen is shown in Fig. 5. Fig. 5 indicates that the susceptibility to SCC increases linearly with increasing the dezincification layer-induced stress.
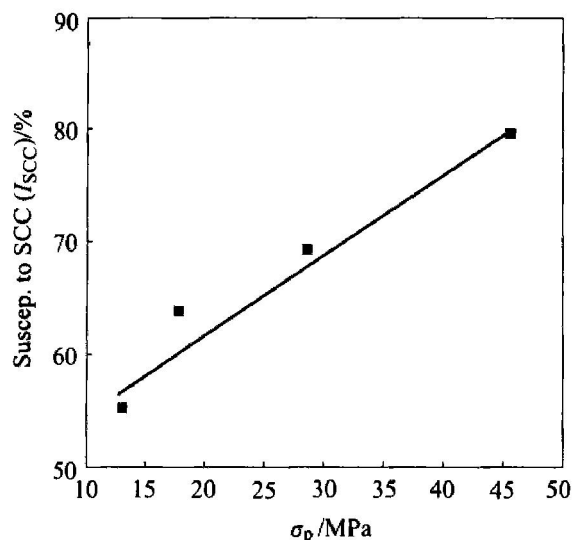

Fig. 5 Susceptibility to SCC vs dezincification
layer-induced stress

4 DISCUSSION

The results in SSRT in air indicate that brass does not exhibit hydrogen embrittlement. So, the remarkable decrease in the fracture stress and fracture time of brass in the ammonia solution is induced by SCC controlled by anodic dissolution. A passive film or a dezincification layer forms on the surface during SCC controlled by anodic dissolution resulting in an additive tensile stress generating, which may be measured by experiments. Why does an additive tensile stress generate after a passive film or a dezincification layer forms on the surface during original corrosion and SCC? For brass, a lot of vacancies or even voids generate in the dezincification layer because of the selective dissolution of zinc. The vacancies and voids will make the porous dezincification layer near the

surface shrink, the middle part of the specimen, however, will hinder the shrinkage of the dezincification layer, resulting in a big tensile stress generated at or near the interface between the dezincification layer and the matrix. The dezincification layer-induced stress is parallel to the dezincification layer[10], and has the same orientation with the applied stress σ during extending. Therefore the dezincification layer-induced tensile stress σ_p will assist the applied stress σ to facilitate plastic deformation, as shown in Fig. 3. Mon et al[12] calculated the stress distribution of Au-Cu alloy with de-alloying porous layer using the continium eigenstrain analysis method. The result indicated that the stress induced by the de-alloying layer distributed inhomogeneously along the cross section of the specimen, and the maximum tensile stress existed near the interface but in the matrix[12]. The dezincification layer-induced stress measured in this study is averaged over the thickness of the dezincification layer, or over the whole specimen, which is smaller than the maximum additive stress near the interface. So, the maximum additive stress in local area during original corrosion or SCC should be $\alpha\sigma_p$, where $\alpha > 1$, which has the same orientation with the applied stress σ. When the resultant stress $\sigma + \alpha\sigma_p$ is equal to the critical stress for dislocation generation and motion, local plastic deformation occurs under a lower applied stress. The observation in transmission electron microscope (TEM) showed that new dislocations generated continuously and the static dislocations moved again during SCC under constant deflection condition[13]. When the SCC-enhanced dislocation emission and motion developed to a critical condition, a microcrack of SCC initiated and propagated[13]. Maybe, the stress concentration in some local area (such as dislocation free zone ahead a crack tip or the front of pile-up dislocations) is equal to the cohesive strength and causes the atomic bond to break, resulting in initiation and propagation of a stress corrosion crack. When the local macroscopic stress concentration $\sigma + \alpha\sigma_p$ is equal to the fracture stress in air σ_{air}, SCC occurs. At the same time, the corresponding applied stress is the fracture stress extended in solution, σ_{sol}, i.e.,

$$\sigma_{sol} = \sigma_{air} - \alpha\sigma_p \qquad (2)$$

According to the definition of the susceptibility to SCC $I_{SCC} = (1 - \sigma_{sol}/\sigma_{air}) \times 100\%$, then,

$$I_{SCC} = \frac{\alpha\sigma_p}{\sigma_{air}} \times 100\% \qquad (3)$$

Since hydrogen does not affect remarkably the fracture stress of brass in air σ_{air}(see Table 2), the hydrogen increasing the additive stress σ_p induced by the dezincification layer causes hydrogen increasing the susceptibility to SCC I_{SCC}. Because σ_{air} is basically

a constant, Eqn. (3) shows that the susceptibility to SCC of the specimens with various hydrogen concentrations increases linearly with increasing the dezincification layer-induced stress, which is consistent with the experimental results shown in Fig. 5.

Previous studies indicate that the dependence of the susceptibility to SCC of brass in the ammonia solution on the applied potentials[4] or on the pH value of solution[6] is in a good agreement with that of the dezincification layer or passive film-induced stress. Further, the results of the present study exhibit that the variation of the susceptibility to SCC with hydrogen concentration is consistent with that of the dezincification layer-induced stress. So, the dezincification layer-induced stress is an essential condition to SCC of brass in the ammonia solution.

5   CONCLUSIONS

1) A dezincification layer formed during corrosion of brass with various hydrogen concentrations in an ammonia solution could generate an additive tensile stress, which increased with increasing hydrogen concentration in the specimen.

2) Slow strain rate tests indicate that brass do not exhibit hydrogen embrittlement, but hydrogen facilitates SCC of brass in the ammonia solution, and the susceptibility to SCC increases with increasing hydrogen concentration in the specimen.

3) The susceptibility to SCC of brass with various hydrogen concentrations increases linearly with increasing the dezincification layer-induced stress.

REFERENCES

[1]   Chu W Y, Qiao L J, Chen Q Z, et al. Fracture and Environmental Fracture [M]. Beijing: Science Press, 2000. 156 - 232. (in Chinese)

[2]   Lu H, Gao K W, Chu W Y. Investigation of tensile stress induced by dezincification layer during corrosion of brass [J]. Corrosion Sci, 1998, 40(10): 1663 - 1670.

[3]   Lu H, Gao K W, Qiao L J, et al. Stress corrosion cracking caused by passive film-induced tensile stress [J]. Corrosion, 2000, 56(11): 1112 - 1118.

[4]   Guo X Z, Gao K W, Qiao L J, et al. Stress corrosion cracking relation with dezincification layer-induced stress [J]. Metall Mater Trans A, 2001, 32A(6): 1309 - 1311.

[5]   Guo X J, Gao K W, Qiao L J, et al. Stress Corrosion cracking of brass in ammonia solution [J]. Trans Nonferrous Met Soc China, 2001, 11(1): 22 - 25.

[6]   Guo X J, Gao K W, Qiao L J, et al. The Correspondence between susceptibility to SCC of brass and corrosion-induced tensile stress with various pH values [J]. Corrosion Sci, 2002, 44(11): 2367 - 2378.

[7]   Lu H, Gao K W, Liu H, et al. Stress Corrosion cracking and passive film-induced tensile stress [J]. J Mater Sci Tech, 2001, 17(4): 413 - 416.

[8]   Qiao L J, Chu W Y, Hsiao C M. hydrogen-facilicated corrosion and stress corrosion cracking of austenitic stainless steel of type 310 [J]. Metall Trans A, 1993, 24A(4): 959 - 964.

[9]   Li H L, Gao K W, Qiao L J, et al. Strength effect in stress corrosion cracking of high strength steel in aqueous solution [J]. Corrosion, 2001, 57(4): 295 - 299.

[10]   Nelson J C, Oriani R A. Stress generation during anodic oxidation of titanium and aluminum [J]. Corrosion Sci, 1993, 34(2): 307 - 311.

[11]   Guo X Z, Gao K W, Qiao L J, et al. Correlation between dezincification layer-induced stress and susceptibility to SCC of brass [J]. Acta Metall Sinica, 2000, 36(7): 753 - 756. (in Chinese)

[12]   Mon K, Ferrari M. On corrosion-induced stress states in binary noble metal alloys [J]. Mater Sci Eng, 1997, A232(1): 88 - 102.

[13]   Gao K W, Chu W Y, Gu B, et al. In situ transmission electron microscope observation of corrosion-enhanced dislocation emission and crack initiation of stress corrosion [J]. Corrosion, 2000, 56(5): 515 - 522.

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