EFFECTS OF CONTENT OF FERROMAGNETIC PHASES ON PIT CORROSION BEHAVIOR OF AUSTENITE STAINLESS STEEL

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In this paper the correlation between pit corrosive sensitivity of metastable austenite stainless steel (1Cr18Ni9Ti) with different deformation at lower temperature and the content of ferromagnetic phases is discussed. The test results show that this kind of stainless steel may induce α'-Martensite (ferromagnetic phase) and α'- Martensite when deformed at low temperature. Furthermore, the deformation-induced martensite has strong effect on its pit corrosive sensitivity when the ferromagnetic phase content is lower than 4.6%. The pit corrosive sensitivity increases with the ferromagnetic content. But when the content is within 4.6%~20.5%, it decreases with the content finally. When the content is higher than 20.5%, it increases again. This regularity can also be proved by electrochemical test and immersing test.

Metastable austenite stainless steel is a kind of corrosion resistant metal material used widely in many fields. With appearance of a large number of defects, cold deformation can induce stainless steel to transform partly into martensite, which will decrease largely the corrosion resistance of the materials.

Pit corrosion is generally a common corrosive form, which is a very harmful for the use of materials. It was regarded as a source of crack inducing stress corrosion fracture. Especially in the medium containing chloride, pit corrosion occurs very easily in metastable austenite stainless steel and can further induce stress corrosion fracture with the operation of stress, resulting in paroxysmal destruction and invalidation.

Therefore, the study of correlation between pit corrosive sensitivity of metastable austenite stainless steel and its content of ferromagnetic phases plays an important role on controling corrosion resistance of stainless steel.

1. Experimental methods

1.1 Sample preparation

Commercial 1Cr18Ni9Ni stainless steel plates were used in the experiment. The chemical composition is: 0.08wt%C, 0.87wt%Si, 0.77wt%Mn, 0.030wt%P, 0.013wt%S, 17.27wt%Cr, 10.34wt%Ni, 0.60wt%Ti.

The stainless steel plate was first cut into a long strip of 140mm x 25mm x 3mm. Then the long strip was cooled to below zero 70°C in liquid nitrogen and drawn at invariable temperature on stretch machine of the type INSTRON-1185. Inorder to prepare samples with different Martensite content. Stretch elongation was respectively 5, 10, 13, 15, 20, 25, 30% etc. After elongation, the samples were made into electrochemical testing samples of 40mm x 25mm x 3mm and metallographic samples of 20mm x 25mm x 3mm. Moreover, the content of α'-Martensite (ferromagnetic phase) was measured through austenite measuring appliance of the type TSJ-1A. No less than four samples were used for each measurement.

Samples of electrochemical testing was processed by nitric acid passivation methods, then encapsulated by rosin paraffine to avoid disturbance of crevice corrosion.

1.2 Experimental solution

3.5% NaCl solution confected diluted deionizing water was utilized as electrochemical testing solution. GB4334.7-84 prescriptive concentration $FeCl_3$-HCl solution was used as immersion test solution.

1.3 Test methods

Pit corrosive laging annulus was mensurated and corrosive resistance was measured by M350A corrosive testing system. Experimental temperature was 50±1°C. 217 type of saturated calomel electrode was chosn as reference electrode. Assisted electrode was platina electrode. Nitrogen was aerated into electrolytic cell continuously, which was used to avoide disturbance of oxygen.

Pit corrosive sensitivity samples with different elongations in $FeCl_3$-HCl solution was mensurated in twenty-four hours. Experimental temperature was 50±1°C. The surface area and weight of the sample before and after immersion was measured accurately and corrosive rate was calculated precisely.

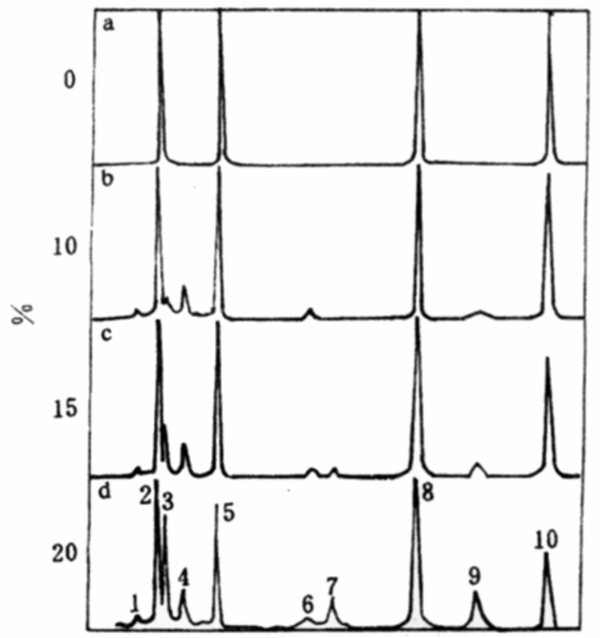


Fig.1. X-ray diffraction pattern of samples with different deformation: 1-ε(100); 2-A(111); 3-M(110); 4-ε(011); 5-A(200), 6-ε(102); 7-M(200); 8-A(220); 9-M(211); 10-A(311)

2. Experimental results and discussion

2.1 Correlation between Martensite content and deformation

From X-ray diffraction patterns of the samples with different deformations as shown in Fig.1, it can be concluded that 1Cr18Ni9Ti stainless steel did induce body centered cubic α′-Martensite and hcp ε′- Martensite after deformations. And α′-Martensite content increases constantly with the increase of deformation, while ε′- Martensite content is basically a constant value during deformation. It is reported that ε′-phase is a intermediate phase in the transformation from austenite to α′-Martensite. Transformation sequence is from γ to ε′ and then to α′.

Fig.2 and Fig.3 are TEM micrograph and diffraction patern of corresponding α′-Martensite and ε′-Martensite respectively.

Fig.4 shows the correlation between α′-Martensite (ferromagnetic phase) content and deformation. One can see that α′-Martensite content increases monotonously with the increase of deformation. Therefore, α′-Martensite content can reflect deformation magnitude. Thus, the relationship among α′-Martensite content, the deformation and the corrosive resistance can be determined.

2.2 Experimental results of immersion in FeCl3 solution

The samples of different α′-Martensite content were dipped into a solution containing 6%FeCl and 0.05mol/dm3 HCl at 50±1°C. Twenty -four hours later, the samples were taken out of the solution and corrosive production in corrosive pits was eliminated through ultra-sonic cleaning. Then pit corrosive weight loss on per unit area was calculated. And the final results can be seen in Fig.5.

When ferromagnetic phase content is lower than 4.6%, pit corrosive sensitivity of stainless steel increases with the increase of ferromagnetic phase content. The reason is that with the increase of ferromagnetic phase content micro-defects on the surfaces of the samples increase which lead to the increase of active spots for pit corrosion. The same rule can be obtained through observation of distribution of corrosive pits.

While ferromagnetic phase content is in the scope of 4.6%~20.5%, pit corrosive weight loss

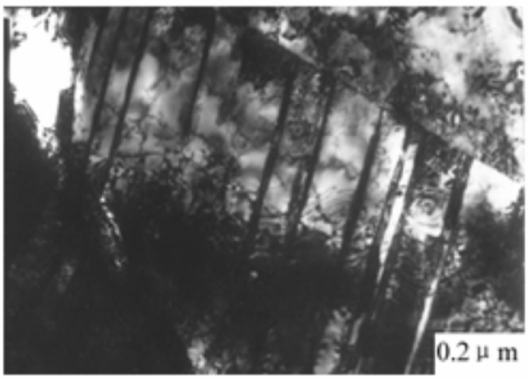


Fig.2. TEM micrograph and diffraction spots of α′-Martensite

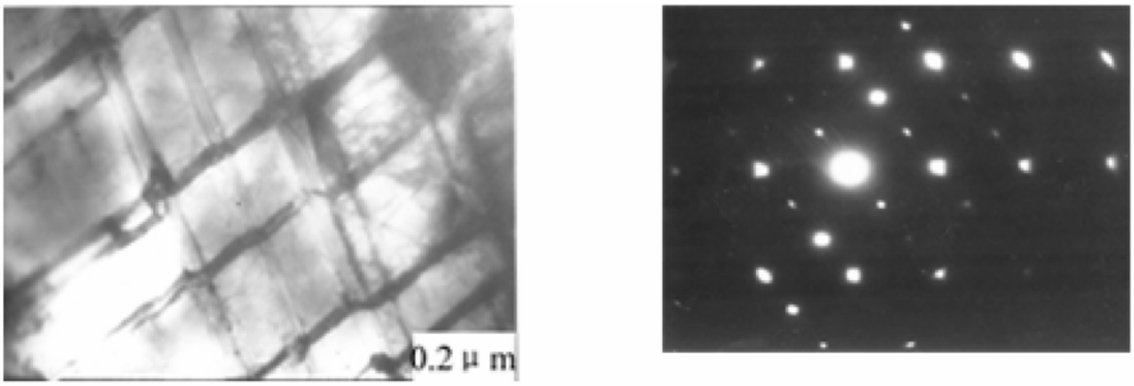
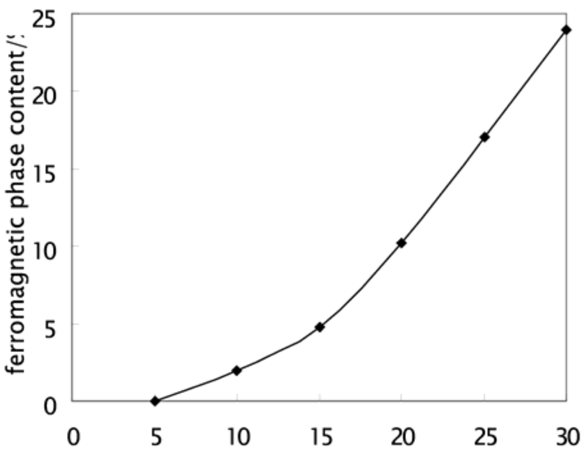


Fig.3. TEM micrograph and diffraction spots of ε′-Martensite

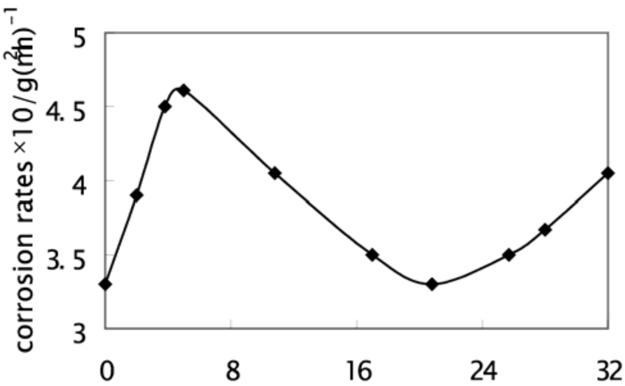
decreases with the increase of ferromagnetic phase content. In this scope, pit corrosive sources increase with the increase of ferromagnetic phase content. But decrease of austenite area will cause decrease of relative area ratio between non-pit corrosive region(cathode area) and pit corrosive region(anode area). Accordingly, self-catalysis effect of pit corrosion was weaken. The results is that pit corrosive sensitivity decreases with the increase of ferromagnetic phase content.

When ferromagnetic phase content is larger than 20.5%, corresponding to a higher deformation microscopic cracks inside the samples are stretched greatly. Thin passivation film on the surface of samples is destroyed severely and pit corrosion occurs easily. Redemption of the thin film becomes more and more difficult. Hence, once pit corrosion appears, it is difficult to recover the damage on



tensile deformation, %

Fig. 4. Amount of tensile deformation vs ferromagnetic phase content

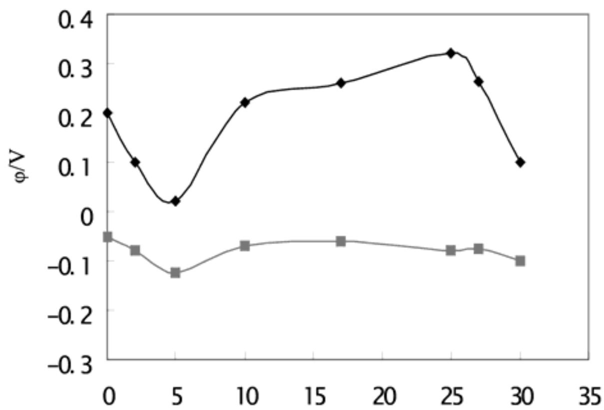


ferromagnetic phase content, %

Fig. 5. Corrosion rates vs ferromagnetic phase content

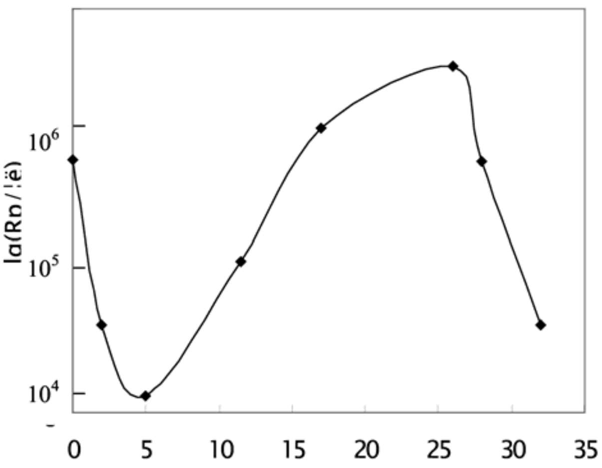
the surface, which results in the increase of pit corrosive weight loss with the increase of α′-Martensite content.

The above viewpoints were also proved



ferromagnetic phase content, %

Fig. 6. Pitting corrosion characteristic electrical potential vs ferromagnetic phase content



ferromagnetic phase content, %

Fig. 7. Ferromagnetic phase content vs polarizing resistance

through measuring results of pit corrosive potential (φ_b), protective potential (φ_p) and polarization resistance (R_p).

2.3 Measurement of pitting corrosion characteristic electrical potential and polarization resistance

Fig.6 shows that the relation among φ_b, φ_p and α'-Martensite content is the similar to that of Fig.5. The difference in Fig.5 is that the breakdown potential of pit corrosion decreased because of the size increase of microscopic cracks, which is led by heavy deformation. The critical point of decrease of φ_p is 16.7 in Fig.6. That is, self-renovation ability of corrosive pit begins to lower when ferromagnetic phase content is more than 16.7%. Pit corrosive sensitivity depends on both occurrence of pit corrosion (φ_b) and development of pit corrosion (φ_p). In Fig.5 the critical point of on the curve of weight loss of pit corrosion vs α'-Martensite content appears at the point where ferromagnetic phase content is 20.5%, which is in the middle between the critical point of φ_b (25.5%) and the critical point of φ_p (16.7%).

Fig.7 shows the relation between R_p measured by linear polarization methods and ferromagnetic phase content. Compared with Fig.6, R_p and φ_b have the same rule as in Fig.7. As pointed out by Ref. 7, macro-batteries producing anode region of local selecting corrosion and the other cathode region appear when local corrosion takes place. Under the conditions of nature corrosion, anode reaction electric current is always equal to cathode reaction electric current by mixing electricity theory, that is , I_a=I_c. However, because of formation of local corrosion, cathode area is much smaller than anode area, that is, S_a<<S_c.Thereby, cathode reaction electric current density is much bigger than anode reaction electric current density, that is, Ia>>Ic, which indicates local anode reaction rate is big and reaction resistance is small and reaction occurs easily. When potential of polarization is invariable, because of the equation ΔE_a=ΔE_c, local anode reaction resistance is small and electric current is big, which indicates the relation $R_{p,a}$<<$R_{p,c}$. Moreover, $R_{p,a}$ and $R_{p,c}$ are parallel connection on the interface, so R_p depends largely on properties of the passivation thin film of pit corrosive regions.

The above analysises show that Rp and φ_b are also stability parameters of pit corrosive active point (pit corrosive sources), which hence have the same rules with change of ferromagnetic phase content.

From the comparison among Fig.5, Fig.6 and Fig.7, one can notice that it is incorrect to utilize a single electrochemical parameter (φ_b or φ_p etc.) to estimate pit corrosive sensitivity because pit corrosive rate is determined by both pit corrosive occurrence and the further development of the corrosion. In other words, overall consideration is necessary.

3. Conclusions

3.1 Elongation deformation of metastable austenite stainless steel at a low temperature can induce partial austenite transformation into α'-Martensite (ferromagnetic phase) and α'-Martensite. α'- Martensite is an intermediate phase, whose content is invariable basically with the increase of deformation. However, α'-Martensite content increases monotonously with increase of deformation.

3.2 Deformation induced Martensite plays an important role on pit corrosive sensitivity of stainless steel. When α'-Martensite content is lower than 4.6%, pit corrosive sensitivity increases with the increase of α'-Martensite content. When ferromagnetic phase content is in the scope from 4.6% to 20.5%, pit corrosive sensitivity decreases with the increase of ferromagnetic phase content. When ferromagnetic phase content is more than 20.5%, pit corrosive sensitivity increases again with the increase of ferromagnetic phase content.

3.3 Deformation has a remarkable influence on pit corrosive breakdown potential, pit corrosive protective potential and polarization resistance, whose rules are consistent with that of pit corrosive weight loss in $FeCl_3$ solution.

REFERENCES

1. W.L. Zhen, Q. Yu. Steel Surrounding Sensitivity Fracture, Beijing: chemical industry press, 1988: 38~39.(in chinese).
2. A. Cigada, B. Mazza, G. Pedeferri, et al. Stress Corrosion Cracking of 304L Austenitic Steel and the Martensite Transformation. Corrosion Science, 1982, 22(6): 559~578.
3. JIS G0577-1981. Pit Corrosive Potential Test Standard of Stainless Steel in Japanese.
4. V. Seetharaman. Influence of the Martensitic Transformation on the Deformation Behavior of an AISI 316 Stainless Steel at low Temperatures, Materials Science, 1981,16(1): 523~530.
5. M. Pat. The Martensite Phases in 304 Stainless Steel, Metallurgical Transactions, 1970,1(6): 1577~1586.

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