

Galvanic effects on electrochemical behaviors of bare surface of 304 stainless steel^①

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Abstract: The bare surface of 304 stainless steel is produced by the fast fracture method. The influence of the surface galvanic cell on the electrochemical behaviors of bare surface of 304 stainless steel has been investigated in H_2SO_4 solutions with different concentrations. The results show that the solution corrosivity level and the area ratio influence the surface galvanic effects caused by the inhomogeneity between the free-film surface of alloy and the passive surface. The surface galvanic effects can speed up the dissolution rate of the bare surface of the alloy and will change the electrochemical behavior of bare surface. With the increase of the area ratio between passive surface and fractured surface, the galvanic potential becomes more positive and, in the range of passive potential, both galvanic current and the peak fracture current increase evidently.

Key words: stainless steel; alloy; galvanic effect; electrochemistry

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1 INTRODUCTION

There are many ways to produce fresh bare surface of metals at a certain speed by the dynamic methods^[1~9] and the fast fracture method is one of these. The electrochemical information about the bare surface in corrosive solution can be obtained by this method to study the repassivation kinetics of bare metals.

When the surface film of passive metals is removed in the electrolyte, anodic dissolution, passivation and/or repassivation processes instantly carry out on the exposed bare surface^[10,11]. The repassivation ability and the repassivation kinetics of the bare surface of metals are the keys to the study of local corrosion and passivation theory.

On the surface of the metals, especially the passive alloy, in the fast fracture process in electrolyte, due to the nonexistence of the passive film on the fractured surface (bare surface), the electrochemical inhomogeneity can be induced between its bare surface and its passive surface.

The fractured surface, with lower potential, can be called anode. In contrast, the passive surface around is cathode with higher potential. Thus surface galvanic cell comes into being between the cathode area and anode area on the surface of same alloy^[12]. In general, the area of fracture surface is much less than that of the passive surface around. So the area effect of the galvanic cell will have an important influence on the electrochemical behaviors of the bare sur-

face of alloy. So, the study to the electrochemical behaviors of alloy in the fast fracture process has both theoretical and practical importance.

2 EXPERIMENTAL

In this article, the galvanic effect on the electrochemical behaviors of the bare surface of 304 stainless steel in the fast fracture process was investigated respectively at the open circuit potential and under the applied potential. In experiment, the area of the fractured surface was defined as S_A , the area of the coupled passive surface was called S_C .

The wire of 304 stainless steel (d 0.3 mm) was used as electrode, its chemical content (mass fraction, %) was: 18.160Cr, 8.620Ni, 0.027S, 0.026P, 1.240Mn, 0.510Si, 0.052C and Fe balance. The experimental solutions were 0.1 mol/L, 0.2 mol/L, 0.5 mol/L H_2SO_4 . Before the experiment, a notch was prepared as the preformed crack for the wire of stainless steel. Then the part of sample A, which submerges into solution, was insulated using glue (Nanda 704) except for the preformed crack. Sample C prepared by the same material, with changeable surface area, was used as the galvanic couple to sample A in parallel. Their distance was 1 cm. In applied potential fast fracture experiment, sample A and C were electrically short-circuited by a wire. Fig.1 is the schematic of the fast fracture apparatus. Under the rapid action of the lever, sample A fractured at the notch instantly under certain load.

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The maximum galvanic potential between sample A and C during the fracture process was defined as φ_g and the maximum galvanic current was called I_{Lg} . The fractured galvanic current density J_{Lg} can be obtained when the area of the fractured surface divides I_{Lg} . In applied potential experiment, the peak value of the fractured current recorded was I_{peak} .

The CR-3 multifunction corrosion measuring equipment was used in experiment to monitor the change of φ_{Lg} and I_{Lg} . PS-I potentialstat was used to apply potential on the specimen and record the I_{peak} in the fast fracture process. The data was collected by the AD/DA interface and corresponding electrochemical measuring software.

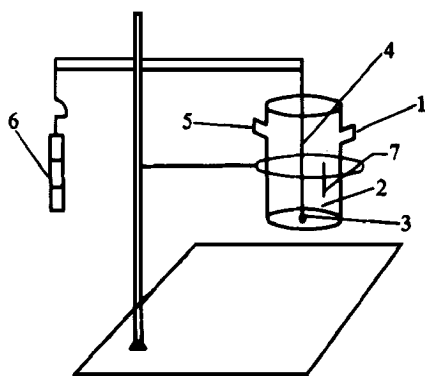


Fig.1 Schematic of testing apparatus

- 1 — Pt; 2 — H_2SO_4 solution;
3 — Plug; 4 — Working electrode (Sample A);
5 — Reference electrode (SCE); 6 — Load; 7 — Sample C

Fig.2 shows the typical $\varphi-t$, $I-t$ curves recorded in the experiment. It is seen from the curves that there are peaks of the potential and current in the $\varphi-t$ and $I-t$ curves during the fast fracture process of 304 stainless steel in H_2SO_4 solutions. These peak values are the important electrochemical parameters of the bare surface of alloy. At the same time, the recorded $\varphi-t$, $I-t$ curves represent the process of passive film's removal, dissolution and the subsequent repassivation occurred on the fresh surface, and

the setup of new dynamic equilibrium on the surface of 304 stainless steel. Thus the change of φ_{Lg} , J_{Lg} and I_{peak} represents the electrochemical behaviors of 304 stainless steel bare surface.

3 RESULTS AND DISCUSSION

The bare surface of 304 stainless steel is produced in the fast fracture process. Because the potential at the interface between the bare surface and solution is lower than that at the interface between the passive film surface and solution^[12], there exists an electrochemical inhomogeneity for the same material due to the different surface states, which results in the appearance of surface galvanic cell. Fig.3 and Fig.4 show the relation between the fractured galvanic potential and the logarithm area ratio (S_C/S_A) and between the logarithm fractured galvanic current density and the logarithm area ratio (S_C/S_A) in H_2SO_4 solutions with different concentrations. The curves indicate that φ_g is directly in proportion to $\lg(S_C/S_A)$ and, on the other hand, the relationship between $\lg(J_{Lg})$ and $\lg(S_C/S_A)$ is also linear. As increasing the area ratio (S_C/S_A), φ_g approaches to the steady potential of sample C, and the anodic current density grows evidently, which leads to speed up the dissolution rate of bare surface. The results obtained above are similar to that, deduced by Mansfeld^[12], about the relationship between the galvanic current and the area ratio coupled as well as between the galvanic potential and the area ratio for the galvanic couple of different metals. It proves that the galvanic effect can exist on the surfaces, with different electrochemical states, of the same material, and this kind of galvanic effect is similar to that between two different metals. So the existence of surface galvanic cell must have great effect on the electrochemical behaviors of the bare surface of alloy.

Seen from Fig.3 and Fig.4, it is obvious that the effect of area on the surface galvanic cell is the weakest in 0.1 mol/L H_2SO_4 , the strongest in 0.2

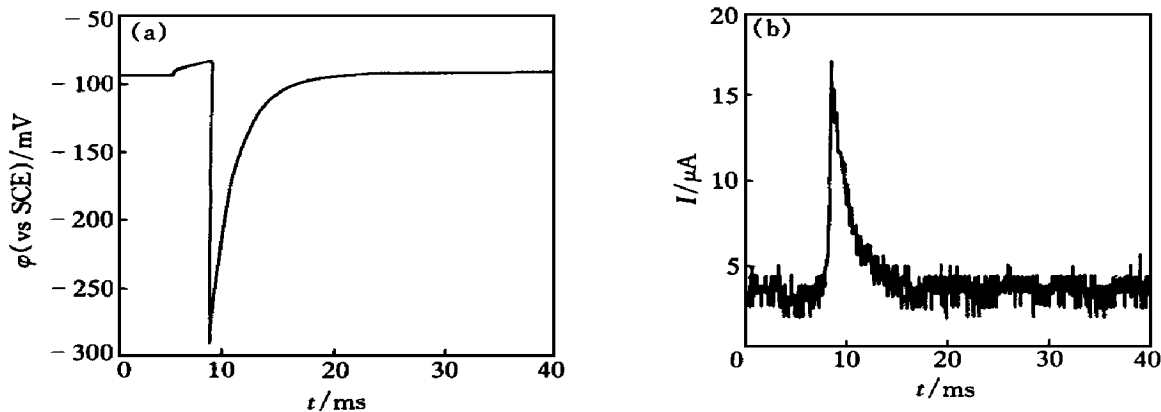


Fig.2 Typical variation of potential φ and current I with time during surface breaking process

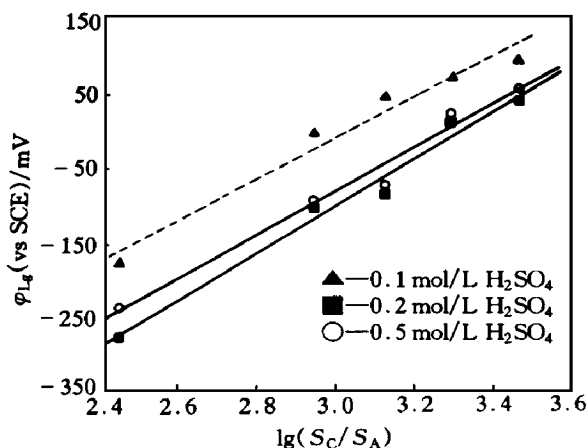


Fig. 3 Relationship of $\varphi_{Lg} - \lg(S_C/S_A)$ of 304 stainless steel in H_2SO_4 solutions with different concentrations

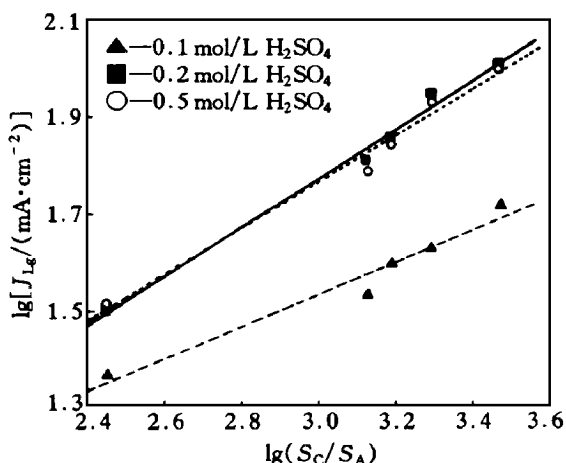


Fig. 4 Relationship of $\lg(I_{Lg}) - \lg(S_C/S_A)$ of 304 stainless steel in H_2SO_4 solutions with different concentrations

mol/L H_2SO_4 . By comparing the polarization curves of 304 stainless steel in the H_2SO_4 solutions with three different concentrations, it is shown that 304 stainless steel has the greatest corrosion current density in 0.2 mol/L H_2SO_4 , the lowest that in 0.1 mol/L H_2SO_4 . So it can be concluded that the extent of galvanic effect is related to the corrosivity of the experimental solutions.

In applied potential experiment, the potential of the fractured surface of alloy will deviate from the potential applied instantly when the fracture occurred. At this moment, the galvanic cell forms between the fractured surface and the passive surface around, which has influence on the electrochemical behaviors of the fractured alloy. Fig. 5 shows the variation of I_{peak} of 304 stainless steel with S_C/S_A under the applied passive potential 200 mV. It can be seen that, in all the H_2SO_4 solutions of different concentration, as increasing S_C/S_A , I_{peak} grows and anodic dissolu-

tion rate becomes faster. But the extents of galvanic effect in these solutions are much different. The degrees of galvanic effect (area ratio effect) in 0.2 mol/L H_2SO_4 and 0.5 mol/L H_2SO_4 are evidently higher than that in 0.1 mol/L H_2SO_4 . This indicates that, for the passive alloy, the stronger the aggressiveness of the solutions, the more obvious the galvanic effect with the change of the area ratio S_C/S_A .

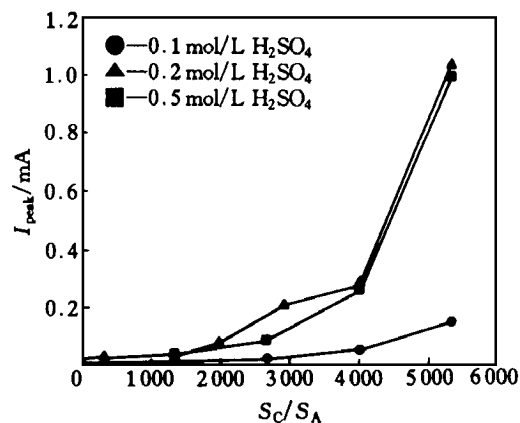


Fig. 5 Relationship of $I_{peak} - S_C/S_A$ of 304 stainless steel in H_2SO_4 solutions with different concentrations under applied potential 200 mV (vs SCE)

Fig. 6 shows that the relationship between the breaking current I_{peak} of 304 stainless steel in 0.2 mol/L H_2SO_4 solution and the applied potential under the condition of certain area ratio. It can be seen that I_{peak} grows slowly as the increase of S_C/S_A , which indicates that, in the passive range, the potential has a little effect on the peak current. Comparing with the result under $S_C/S_A = 0$, the bigger the area ratio, the greater the fractured current, from which it is learnt that the galvanic cell formed due to the surface electrochemical inhomogeneity has important

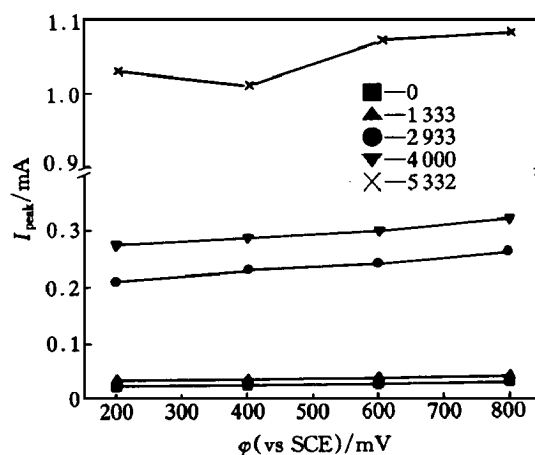


Fig. 6 Relationship between I_{peak} and applied potential φ of 304 stainless steel in 0.2 mol/L H_2SO_4 solution with different values of S_C/S_A

influence on the fractured current of alloy in the fast fracture process.

From the results above, the galvanic effect, formed on the 304 stainless steel surfaces with different surface states, affects greatly the electrochemical behavior during the fracture process of 304 stainless steel. Because the fractured surface area is so small, the area ratio of S_C to S_A can reach a very high value. So the area effect on the experimental results can not be ignored when studying the electrochemical kinetics of the alloy's bare surface which is produced through fast fracture method.

The analysis above demonstrates that there exists surface galvanic effect between the fractured surface and the passive surface around during the fast fracture process. The existence of the area ratio effect evidently influences the electrochemical kinetics of the bare surface of alloy. This leads to the increase of dissolution rate of alloy.

4 CONCLUSIONS

1) There is surface galvanic cell in the fast fracture process, due to the electrochemical inhomogeneity between the bare surface of alloy and the passive surface of alloy. And the effect of area ratio (passive surface to fractured surface) on the electrochemical galvanic behavior is particularly important and evident.

2) The surface galvanic effect has obvious effect on the electrochemical behaviors of the bare surface of 304 stainless steel. It speeds up the dissolution rate of the bare surface.

3) With the increase of S_C/S_A , ϕ_{Lg} moves towards positive direction and I_{Lg} increases substantially.

4) Under the passive potential of 200 mV, the fractured current I_{peak} increases with S_C/S_A . The applied potential doesn't have strong effect on the I_{peak} .

5) In passive system, the stronger the corrosivity of the corrosion medium, the more obvious the sur-

face area effect on the galvanic behavior.

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