Passivity Breakdown Studies of Chromium Steels with Progressive Addition of Chloride Ions*

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Passivity breakdown characteristics of Cr steels have been studied by adding chloride ions progressively in sulfuric acid solutions. Effects of holding time at different potentials on the film growth have also been studied by adding a fixed quantity of chloride ions in sulfuric acid solution after a passive layer has been formed. Comparative study of corrosion kinetics has been made for different modes of experimentation. SEM studies have also been done to examine the nature of breakage of passive layers.

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I. Introduction

It is generally believed that an oxide film is the reason for passivity and the breakdown of this protective film is the reason for passivity breakdown.

The main factors controlling the formation and growth of oxide layers are the potential of the metal and concentrations of metallic and hydroxyl ions⁽¹⁾. It has been reported that the breakdown of the oxide layers are reported to depend on the concentration of chloride ions in the solution⁽²⁾⁽³⁾, and the higher the chloride ion concentration, the lower is the potential at which the breakdown of these oxides takes place⁽⁴⁾⁻⁽⁶⁾.

In the present investigation it is found that once a passive layer is formed, the stability of oxide seems to increase with progressive addition of chloride ions. The breakdown of the passive layer is not only dependent upon potential but also upon the experimental conditions.

II. Experimental

Experiments were performed with 9.52% Cr

and 12.10% Cr steels. In the first set of experiments a freshly prepared sample was mounted in a polarization cell set-up according to GS-72 and containing 0.5 kmol/m³H₂SO₄ solution. Fixed potential was applied and the steady current was measured. To this solution a weighed amount of KCl was added to make it 0.5 kmol/m³H₂SO₄ + 1 molCl⁻/m³ and again the steady current was noted. Further additions of chloride ions were made to measure the steady current. It was observed that for each addition of chloride ions it took about 600 s (10 min) to reach the steady current state. In this manner chloride ions were added progressively to make the solution 1, 50, 100 and 200 molCl⁻/m³, and for each stage steady current values were noted.

For the second set of experiments, like the previous set of experiments, a freshly prepared sample was mounted in a polarization cell containing 0.5 kmol/m³H₂SO₄ solution. A fixed potential was applied to passivate the sample and the variation of anodic current was noted as a function of time. After 1.2 ks (20 min) the weighed amount of KCl was added to this solution to make it 0.5 kmol/m³H₂SO₄ + 1 mol/m³Cl. Again the variation of current was noted as a function of time. In this manner similar experiments were done for both of the steels and kinetic data were recorded for the following solutions: 0.5 kmol/m³H₂SO₄ plus additions of 50 mol/m³Cl⁻, 100 mol/m³Cl⁻, and 200 mol/m³Cl⁻. For the first three solu-

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tions experiments were conducted at 0.90 V (vs SCE), whereas for the solution containing highest concentration of Cl^- ions experiments were conducted at three different potentials.

Finally, experiments were done for 12.10% Cr Steel with $0.5 \text{ kmol/m}^3 \text{H}_2\text{SO}_4 + 100 \text{ mol/m}^3 \text{Cl}^-$ solution. In the same potentiostatic set up the current density was measured once by applying a fixed potential directly to the sample (mode A), and once for the same potential but reaching it by changing potential quasistationarily after starting from zero current potential (mode B). SEM photographs of pits were taken for the above two modes but care was taken so as to make the potential applied higher than the pitting potential.

III. Results and Discussion

Experiments were so designed that effect of progressive addition of Cl^- ions on pitting characteristics of two Cr Steels could be studied.

From Figs. 1 and 2 it can be seen that when Cl^- ions are added progressively in $0.5 \text{ kmol/m}^3 \text{H}_2\text{SO}_4$ solution just like potentiostatic diagram inflations are obtained which suggest

Fig. 1 Progressive addition of Cl^- ions 9.52% Cr steel.

Fig. 2 Progressive addition of Cl^- ions 12.10% Cr steel.

that for a fixed potential a critical amount of Cl^- ions may be found at which pitting starts. For example in Fig. 1 for applied potential 0.80 V (vs SCE), critical amount of Cl^- ions is found to be $100 \text{ mol/m}^3 \text{Cl}^-$ and in Fig. 2 for applied potential 0.80 V (vs SCE) critical amount of chloride ions is found to be slightly above $100 \text{ mol/m}^3 \text{Cl}^-$. Thus it seems that resistance against pitting increases as Cl^- ions are added progressively in $0.5 \text{ kmol/m}^3 \text{H}_2\text{SO}_4$.

To find out whether this increase in resistance is due to the increase in holding time at a fixed potential, experiments were carried out to obtain Figs. 3–6. Figures 3 and 4 show that once the sample is passivated for 1 mol/m^3 of Cl^- ion addition there is a decrease in current density. For 50 mol/m^3 of Cl^- addition the current density remains unchanged, while for 100 mol/m^3 of Cl^- addition there is an increase in current density. Figures 5 and 6 show that under similar experimental conditions for higher additions of Cl^- (200 mol/m^3) the current density increases rapidly and the incubation time decreases with increasing potential. These results indicate that the holding time in-

Fig. 3 Change in current density with time at a fixed potential of 0.90 V (vs SCE) for 9.52% Cr steel and for different Cl^- addition.

Fig. 4 Same as Fig. 3 except the sample is 12.10% Cr steel.

Table 1 Steady currents at fixed potential when the potential is applied directly on the specimen (mode A) and when the potential is quasistationarily changed through passive region to trans-passivity (mode B). Sample 12.12% Cr Steel, Medium $0.5 \text{ kmol/m}^3 \text{H}_2\text{SO}_4 + 100 \text{ mol/m}^3 \text{Cl}^-$.

	Current in mA/m^2	
	0.40 V	0.60 V
Mode A	21230	57510
Mode B	4160	8710

Fig. 5 Change in current density with time at different potentials for 9.52% Cr steel & for $200 \text{ mol/m}^3 \text{Cl}^-$ addition in $0.5 \text{ kmol/m}^3 \text{H}_2\text{SO}_4$ solution.

Fig. 6 Same as Fig. 5 except the sample is 12.10% Cr steel.

Fig. 7 Passive layer formed on the 9.52% Cr steel ($\times 1600 \times 6/7$).

Fig. 10 Pits formed on 9.52% Cr steel due to direct application of potential more than pitting potential ($\times 3200 \times 6/7$).

Fig. 8 Pits formed on 9.52% Cr steel due to continuous polarization through trans passive region ($\times 1600 \times 6/7$).

Fig. 11 Same as Fig. 10 except the sample is 12.10% Cr steel. ($\times 6/7$).

Fig. 9 Same as Fig. 8 except here sample is 12.10 Cr steel rather than 9.52% Cr steel ($\times 1600 \times 6/7$).

creases the passive film thickness only when the solution concentration remains unchanged at a

fixed potential.

Thus it may be said that the stability of passive oxide increases with the progressive addition of chloride ions.

From Fig. 2, the current density obtained for 0.60 V (vs SCE) at the $0.5 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4 + 100 \text{ mol/m}^3 \text{ Cl}^-$ solution is 1.8 mA/m^2 . This value is considerably smaller than the values obtained for mode A and mode B as tabulated in Table 1. It is worthwhile to mention that the pitting potential of this sample in this medium is 0.325 V (vs SCE). From this comparison it becomes clear that with the progressive addition of Cl^- ions pitting has not initiated even at 0.60 V (vs SCE).

It is seen that mode A gives a current density somewhat higher than mode B. There can be

two reasons for this high current density for mode A. Either passive layer does not form at all, or it forms but its rate of destruction is much faster. SEM photographs of pits obtained for the two modes reveal that oxide layers do form in both cases. However, Figs. 10 and 11 reveal that the pit formation is due to some sort of tearing of the passive layer as if the breakdown is abrupt, whereas Figs. 8 and 9 show that pits formed by a gradual process suggesting some sort of nucleation and growth.

IV. Conclusion

(1) After a passive layer is formed when chloride ions are added progressively, the stability of passive oxide increases.

(2) Rate of corrosion varies with experimental conditions, it being maximum when a

potential is applied directly and minimum when chloride ions are added progressively.

(3) Nature of breakdown of passive layer also varies with experimental condition. For the quasistationary mode of change of potential, pitting is regular or gradual, whereas when a potential is applied directly breakdown of the passive layer is abrupt.

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