OXIDATION AND CORROSION BEHAVIOUR OF MAGNETITE COATED CARBON STEEL AFTER CHEMICAL CLEANING

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Effect of chemical cleaning on oxide growth and subsequent corrosion behaviour of carbon seel was evaluated. Magnetite film was grown on carbon steel specimens in argon saturated lithium hydroxide solution of pH 10.5 at 300°C for 7 days. The specimens were then chemically cleaned in a solution containing 5% citric acid, 3% ammonium citrate, 0.2% disodium EDTA and 0.001% phenyl throurea. The entire oxide dissolved in this solution within 30 minutes at 60°C. Specimens thus cleaned were again exposed to deoxygenated lithium hydroxide solution to grow magnetite film as stated above. The thickness of the magnetite film formed after cleaning treatment was found to be ca. 1.8 μm as compared to 1.4 μm that formed on specimens initially.

The corrosion rate of the carbon steel with magnetite layer of 1.4 μm in double distilled water at room temperature was found to be 0.3 mdd for a ten day exposure while that of chemically cleaned and reoxidised was found to be 2.4 mdd indicating thereby, an increase. Potentiostatic polarisation on the unoxidised & oxidised specimens with and without chemical cleaning, in lithium hydroxide solution of pH 10.5 did not show any significant difference. However, in 1M potassium sulphate solution, cathodic polarization showed lower current for plain carbon steel than that for de-scaled one and the one with initial magnetite layer showed lesser current than that on descaled and subsequently oxidised.

Chemical claning of iron oxide deposits is sometimes necessary to enhance the service life and to reduce occurence of pitting of industrial equipment like heat exchangers, boilers and steam generators. The solvents used for the dissolution of corrosion products are usually based on chelating agents which are agressive towards unalloyed steels and corrosion inhibitors are therefore added to protect them.

In water cooled nuclear pressurised heavy water reactors where carbon steel is the main construction material, Fe_3O_4 is the main oxidation product whereas in BWRs, where stainless steel is the main construction material, the oxide will consist of Ni^{2+} and Cr^{3+} also in addition to Fe^{3+} and Fe^{2+}. Considerable work has been reported <1-8> on the chemical cleaning of corrosion products and the mechanism of dissolution of deposits on industrial equipment. A suitable chemical cleaning process must ensure the effective dissolution of the oxide deposits without unacceptably high corrosion rates thereafter, which is likely to be the result of residual chemicals left over in the system.

However, the literature on the effect of chemical cleaning on subsequent formation of magnetite film and the corrosion behaviour of carbon steel is scanty. In an earlier work, <9>, the authors have reportd a suitable formulation for chemical cleaning of carbon steel which consists of citric acid, EDTA, ammonium citrate and phenyl thiourea. This paper deals with effect of chemical cleaning using this formulation on the oxidation and corrosion behaviour of carbon steel.

EXPERIMENTAL

Carbon steel coupons of dimension 25 mm x 20 mm x 2 mm having a composition C= 0.11, Mn=0.35, S=0.03, Si=0.04 were polished and exposed to a lithium hydroxide (argon saturated) solution of pH 10.5 at 300°C for 7 days. These conditions lead to the formation of magnetite film which was then dissolved in the cleaning solution containing 5% citric acid, 3% ammonium citrate, 0.2% disodium EDTA and 0.001% phenyl thiourea at 60°C. Some of the specimens, were cleaned and then the magnetite film was again developed on them by using the procedure described above.

Weights of the specimens were recorded after every treatment.

Corrosion rates of untreated carbon steel as well as after various treatments described above were evaluated by exposing the specimens in double distilled water at room temperature (28°C) for 10 days. Cathodic and anodic polarizaation experiments were carried out on various specimens in deoxygenated 10.5 pH LiOH and 1 M K_2SO_4 solutions. Corrosion potentials were measured against saturated calomal electrode and then were stepped up in steps of 40 mV at a time and current was recorded each time after one minute.

RESULTS AND DISCUSSION

The results of magnetite growth on carbon steel at 300°C in deoxygenated lithium hydroxide solution initially as well as after chemical cleaning are shown in Table 1. It can be seen that the base metal

TABLE 1

MAGNETITE GROWTH ON THE PLAIN AND ON THE DISCALED COUPONS OF CARBON STEEL IN LITHIUM HYDROXIDE SOLUTION OF pH 10.5 (ARGON SATURATED) AT 300 C.

Treatment	Base metal (mdd)	Total Oxide um	Adherent Oxide um	Crud Release Rate (mdd)
Nil	9.26	1.72	1.43	2.15
Oxidised & Chemically Cleaned	11.48	2.14	1.81	2.42

loss, total oxide thickness, adherent oxide thickness and crud release rates were slightly higher after chemical cleaning but not high enough to cause any alarm The thickness of the adherent oxide formed initially was found to be in agreement with the work reported elsewhere <10> and there was not significant deviation even after chemical cleaning. Magnetite formation under the conditions mentioned above takes place as per Schikorr Reaction:

$$3\ Fe(OH)_2 \longrightarrow Fe_3O_4 + H_2 + 2H_2O \quad --(1)$$

The fact that the initially developed magnetite film completely dissolved in 5% citric acid, 3% ammonium citrate, 0.2% EDTA and 0.001% phenyl thiourea at 60 C within 30 minutes can be explained as follows:

Manetite film is believed to contain numerous microcracks <11> and anodic reaction of reductive dissolution leading to the oxidation of base metal at the expense of ferric reduction in the scale takes place through these cracks <12-14>. Figure 1 shows the schematic representa-

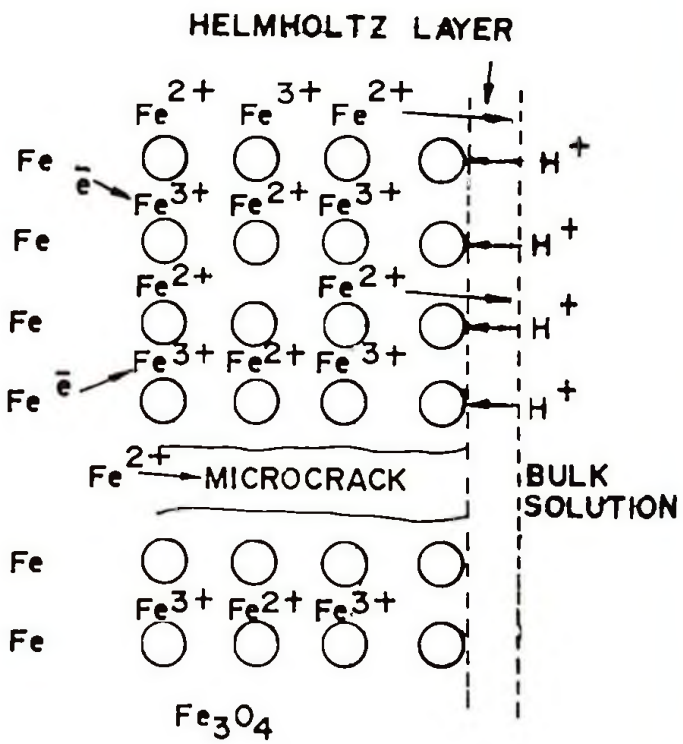


Fig. 1 Dissolution of magnetite on iron surface

tion of magnetite dissolution from a ferrous metal surface. The iron is oxidised at the microcracks, releasing electrons that reduce Fe^{3+} in the scale. The Fe^{2+} ions can pass across the Helmholtz layer into the bulk solution. Protons also cross the double layer to react with the oxide ions forming OH ions initially. The passage of the products across the interphase is considered the rate determining step. Factors that are known to influence the reaction rate include the presence of strong complexing agents such

as ammonium citrate and EDTA, and the pH. The complexing ions affect the rate by removing Fe^{2+} ions from the region around the double layer or by changing the surface charge, thereby changing the potential. Many authors show a 1/2 order dependence on $[H^+]$ in the absence of complexing solutions, but the pH dependence in presence of complexing ions is not straight forward <16>.

The overall equation for magnetite dissolution in presence of chelating ions can be written as follows:

$$Fe_3O_4 + Fe + 8H^+ + 4Chel \rightarrow Fe(II)Chel + 4H_2O \quad \ldots\ldots\ldots (2)$$

The corrosion rates of polished, initially oxidised, chemically cleaned, and reoxidised carbon steel coupons in double distilled water at room temperature (28°C) have been represented in Table 2. It can be seen that chemically cleaned carbon steel had slightly higher corrosion rate than initially polished one and this could be due to the effect of residual chemicals or even the surface roughness caused as a result of dissolution process. Similarly, chemically cleaned and subsequently oxidised carbon steel specimens had a corrosion rate of 2.42 mdd (ca.0.44 mpy) as against 0.28 mdd (ca.0.05 mpy) of that which was oxidised after polishing. Though these values show an eight fold increase in corrosion rate as a result of chemical cleaning to the value of 0.44 mpy in distilled water open to air (which is fairly aggressive towards carbon steel), it shows excellent protection provided by the surface film formed on reoxidised specimen. It has been reported, as discussed earlier in equation (1), that magnetite is usually formed on carbon steel surfaces in deareated lithium hydroxide solution of pH 10.5 at temperatures greater than 150°C; however, x-ray diffraction <10> and XPS studies <17> have indicated that small amount of α-Fe_2O_3 could also be formed alongwith magnetite layer. The amount of α-Fe_2O_3 formed along with magnetite is dependent upon three factors viz. surface roughness, the contaminants on the surface and the environment (dissolved oxygen content in the medium). It is possible that the residual chemicals and roughness left on the surface after chemical cleaning in the present investigation causes the formation of slightly more amount of α-Fe_2O_3, thereby leading to higher thickness of the film and increase in corrosion rate.

TABLE 2

CORROSION OF VARIOUS PRETREATED CARBON STEEL IN DISTILLED WATER AT ROOM TEMPERATURE (28°C)

Pretreatment of carbon steel	Corr.rate mdd
Nil	14.95
Magnetite Coated	0.28
Chemically Cleaned	19.66
Reoxidised(Magnetite coated)	2.42

Potentiostatic cathodic and anodic polarization curves for different carbon steel specimens in deoxygenated lithium hydroxide (pH 10.5) and 1 M K_2SO_4 solution have been shown in figures 2 and 3. Anodic polarization in lithium hydroxide

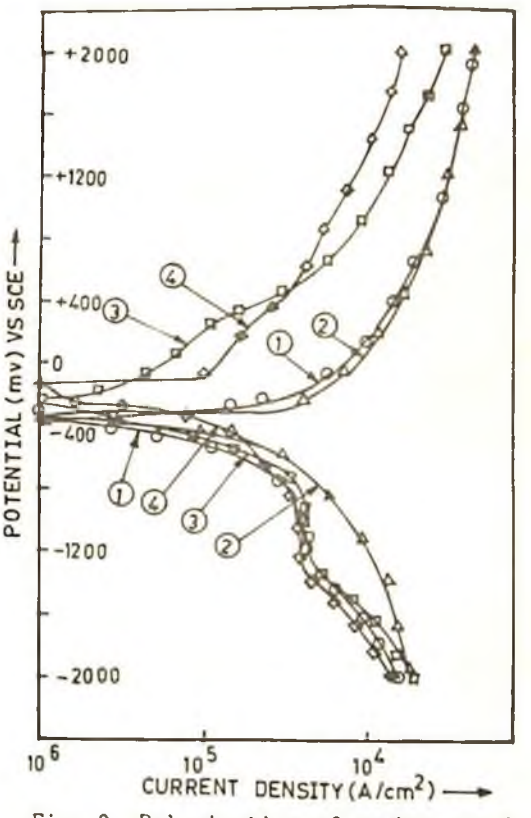


Fig. 2 Polarization of carbon steel in argon saturated lithium hydroxide of pH 10.5 at room temperature. 1) Plain carbon steel 2) chemically cleaned carbon steel 3) Magnetite coated carbon steel 4) chemically cleaned and reoxidised carbon steel

solution (Fig.2) indicates that the currents on intially polished as well as on chemically cleaned carbon steel were

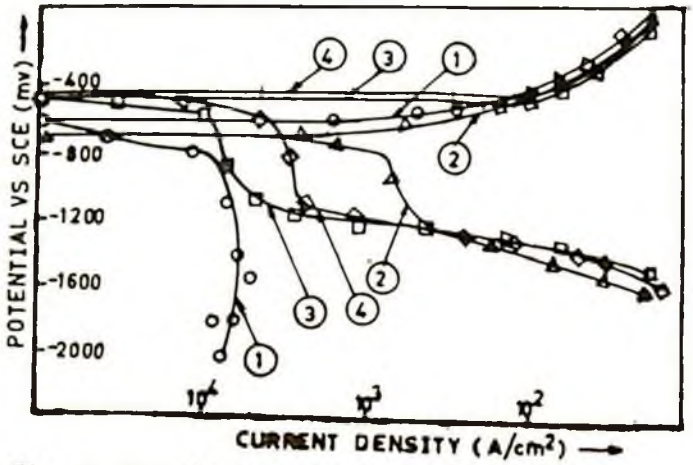


Fig. 3 Polarization of carbon steel in argon saturated 1 M K SO at room temperature 1) Plain carbon steel 2) Chemically cleaned carbon steel 3) Magnetite coated carbon steel 4) Chemically cleaned cleaned and reoxidised carbon steel.

higher than those on magnetite coated specimens. This is because magnetite coating prevents carbon steel from dissolution. These results are consistent with weight loss data obtained on these samples. No other significant differences are apparent in the polarization behaviour of various specimens in the solution. In 1 M K_2SO_4 solution, anodic polarization curves for various specimens did not show any significant difference, but, in cathodic region, polished carbon steel showed much less current than the chemically cleaned one, justifying thereby the weightloss data of Table 2. Similarly, initially oxidised carbon steel showed less current than the chemically cleaned and reoxidised. This explains the higher corrosion rate for reoxidised. This explains the higher corrosion rate for reoxidised specimen.

CONCLUSIONS

Chemical cleaning formulation containing 5% citric acid, 3% ammonium citrate, 0.2% disodium EDTA and 0.001% phenyl thiourea ia good for chemical cleaning of corrosion products on carbon steel in industrial equipment. Oxidation and corrosion rates increases slightly as a result of chemical cleaning but not enough to warrant any alarm.

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