Pickling Treatment of Hot Rolled Stainless Steel (304) – Problem of Pitting Corrosion in Local Industry

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SYSTEMATIC experiments have been carried out with an aim to find out the proper pickling treatment of hot rolled S.S. (304) sheets which is a serious problem of a local stainless steel industry. A mixture of 10% HNO and 1% HF at 65°C has been recommended as the proper pickling treatment. Dislodgement of the oxide scale from the S.S. seeets in the presence of nitric acid has been explained with the concept of reduction of nitric acid at the oxide surface. Reasons for pitting of S.S. during the pickling treatment with a mixture of 10% HNO and 3% HCl (as followed by the industry are explained.

PICKLING of the mill-scale formed by oxidation during hot working of a metal is done by immersing in a suitable acid, e.g. warm dil HCl or H_2SO_4 for mild steel, nitric acid for copper alloys. For pickling of the oxide scale formed over hot rolled stainless steel, a mixture of HNO_3 and HCl has been recommended in 'Corrosion Engineering'[1] (Fontana and Green) and a mixture of H_2SO_4 and HCl at 65°C is given in the 'Engineering Chemistry[2] (P.C. Jain). The local stainless steel industry has been pickling the hot rolled S.S. sheets (304) in two stages ; first with 10% H_2SO_4 and then with a mixture of 10% HNO_3 and 3% HCl (by volume) at room temperature. In some of the sheets, terrible pitting has been reported. This paper presents the results of systematic studies with an aim to suggest the proper pickling treatment to the industry.

EXPERIMENTAL

Small samples (3 x 5 cm) of the hot-rolled and annealed 304 S.S. sheets obtained from the industry were treated separately with 10% solutions (by volume) of H_2SO_4, HCl and HNO_3. Pickling tests were also carried out with mixtures of (i) HNO_3 and HCl (ii) HNO_3 and H_2SO_4 and (iii) HCl and H_2SO_4. In another experiment pickling was done exactly as it is being done by the industry in two steps, first with 10% H_2SO_4 and then with a mixture of 10% HNO_3 and 3% HCl. Another experiment was done with a mixture of 10% HNO_3 and 1% HF. All the acids used, were of B.D.H., AnalaR grade and the solutions were prepared with double distilled water.

RESULTS

The results are included in Table 1. From these results it was found that nitric acid alone (of the acids reported here) could remove the oxide scale over the hot rolled S S. (304) sheets. As with the addition of 1% HF, the sheets appeared to be relatively brighter, a mixture of 10% HNO_3 and 1% HF at 65°C has been recommended as the proper pickling treatment to the industry. Stainless steel sheathed electrical heaters were recommended for heating purpose as S,S. is resistant to corrosion in 10% HNO_3. A mixture of H_2SO_4 and HCl at 65°C as given by Jain[2] did not remove the oxide scale ; instead it caused a high rate of corrosion of stainless steel itself. Pitting was observed in the mixture of HNO_3 and HCl (the treatment recommended by Fontana and Green) and the rate of pickling was also reduced.

Advantages of our pickling treatment over the one being followed by the industry :

1. No pitting at all
2. High rate of pickling
3. Saving of the acid
4. Saving of labour
5. Relatively brighter sheets

DISCUSSION

During hot working of 304 S.S., there is formation of oxides of Fe, Ni and Cr as a scale. Electron microprobe analyses[3],[4] confirm marked enrichment of Cr_2O_3 adjacent to the metal phase in the case of iron-chromium alloys. For austenitic 18-8 steels, the highest corrosion resistance is obtained at a film thickness of 30-50 Å as the oxide film is then of amorphous nature[5]. But, the thicker films obtained during the hot rolling process have higher ionic conductivity and are less protective.

TABLE 1

Results of all the experiments conducted

Acid	Time of immersion	Temperature	Result
10% H_2SO_4	30 min. to 2 hrs.	30°C	Partial removal of the scale.
10% HCl	30 min. to 2 hrs	30°C	Partial removal
10% *HNO_3*	*30 min.*	*30°C*	*Complete removal*
10% H_2SO_4	One hour	65°C	Partial removal
10% HCl	One hour	65°C	Partial removal
10% *HNO_3*	6 min.	*66°C*	*Complete removal*
10% HNO_3 + x% HCl (x = 1%, 3%, 5%, 7%, 10%)	30 min.	30°C	Effect of pickling was reduced with increasing concentration of HCl, tendency for pitting
As above	6 min. to 30 min.	65°C	Same as above
10% HNO_3 + x% H_2SO_4 (x = 1%, 3%, 5%, 7%, 10%)	6 min. to 30 min.	65°C	Effect of pickling was reduced with increasing concentration of H_2SO_4
x% H_2SO_4 + y% HCl (x + y = 10%)	One hour	65°C	Partial removal of the scale.
First with 10% H_2SO_4 and then with 10% HNO_3 + 3% HCl (As done by the industry)	30 min.	30°C	Complete removal, but tendency for pitting in the first batch of sheets and severe pitting in the second batch (cf-Fig. 1)
10% HNO_3 + 1% HF	6 min.	65°C	Complete removal, No pitting, Brighter sheets when compared to 10% HNO_3 alone (cf-Fig. 2)

Dislodgement of the oxide scale from the metal : A) *Concept of reductive dissolution*[6] : Metal/acid/oxide.

At cathode in the presence of an acid :

$$H^+ + e^- \longrightarrow H \text{ (ads)} \quad (1)$$

$$2H(\text{ads.}) + \underset{\text{(oxide lattice)}}{O^{2-}} \longrightarrow H_2O + 2e^- \quad (2)$$

$$2H^+ + \underset{\text{(lattice)}}{O^{2-}} \longrightarrow H_2O \quad (3)$$

In case of iron oxide, at cathode :

$$Fe_2O_3 + 6\,H^+ + 2\,e^- \longrightarrow 2\,Fe^{2+} + 3\,H_2O \quad (E_1^0 = +0.73\text{ V})$$

at anode :

$$Fe \longrightarrow Fe^{2+} + 2\,e^- \quad (E_2^0 = -0.44\text{ V})$$

$\therefore E_1^0 - E_2^0 = 1.17$ V. The net result is that Fe^{3+} ions in the lattice are either removed directly into the solution as Fe^{2+}_{aq} or reduced to the ferrous state while still in the lattice. In both the ways, there is formation of vacancies in the surface and hence facilitates dissolution of the oxide scale.

The dislodgement of the oxide scale from mild steel in the presence of an acid can be explained with the concept of reductive dissolution. But HCl or H_2SO_4 or the mixtures of the two acids could not affect the removal of oxide scale over 304 S.S., while HNO_3 could do so easily. According to the concept of reductive dissolution, HCl and H_2SO_4 also should be able to remove the oxide scale. Hence, this concept cannot explain the dislodgement of oxide scale of 304 S.S. in the presence of nitric acid.

B) *Nitric acid reduction*[7] : Nitric acid is described as an oxidizing acid which itself is reduced at cathode.

The over all reaction at cathode is :

$$3\,H^+ + NO_3^- + 2e^- = HNO_2 + H_2O$$

The successive steps are :

$$H^+ + NO_3^- = HNO_3$$

$$HNO_3 + HNO_2 = N_2O_4 + H_2O$$

$$N_2O_4 = 2\,NO_2$$

$$2\,NO_2 + 2\,e^- = 2\,NO_2^-$$

$$2\,NO_2^- + 2H^+ = 2\,HNO_2$$

Thus the cathodic reduction of nitric acid is autocatalytic, i.e., the final reduction product, nitrous acid is consumed in the initial stages of reaction so that the more nitrous acid is produced, the faster is it formed in fresh reaction.

Reduction of nitric acid takes place at the adherent oxide (rich in Cr_2O_3) surface and during the process of reduction, there is evolution of brown fumes of NO_2 and eventual dislodgement of the oxide scale. The results of pickling treatment with another oxidizing acid, chromic acid confirm that the oxidizing acids could affect the removal of oxide scale over S.S. 304, the mechanism being reduction of these acids at the oxide surface. Simultaneously the stainless steel surface undergoes oxidation forming a thin, invisible, inert, nonporous and adherent film of Cr_2O_3 which is highly protective and hence no further dissolution of stainless steel.

Pitting Corrosion in the presence of HCl : In the first batch of the sheets, pickled in a freshly prepared 10% HNO_3 and 3% HCl solution, there was only a tendency for pitting. But when the industry used the same solution for the second time, visible pits were observed (Cf. Fig. 1). This can be explained as follows. It has been known for years[5,7] that pitting corrosion of stainless steel takes place in enviroments containing appreciable concentration of chloride ions ; pitting is very fast if active depolarizing ions like Fe^{3+} are also present in the environment. Eg. $FeCl_3$ solution causes severe pitting of 304 s.s. within a very short time[8]. Here in the present case the environment contains a high concentration of chloride ions and also Fe^{+3} ions when the second batch goes for pickling, and hence severe pitting of the sheets even within 30 minutes, Neverthless, metallurgical inhomogenity, and improper heat treatment (causing precipitation of carbide) also contribute to the tendency of pitting of these stainless steels and hence such terrible pitting in a very short time.



Fig. 1



Fig. 2

Fig. 1 Picking treatment : First with 10% H_2SO_4 and then with a mixture of 10% HNO_3 and 3% HCl. White spots are to be noted as pits (×100)

Fig. 2. Pickling treatment with a mixture of 10% HNO_3 and 1% HF. No Pitting at all (X 100)

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REFERENCES

1. M. G. Fontana and N. D. Green, Corrosion Engineering, Mc Graw Hill Book Company, New York, (1976)
2. P. C. Jain, Engineering Chemistry, Dhanpat Rai and Sons, Delhi (1976).
3. D. Lal, R. Borg, M. Brabers, J. Mackenzie and C. Birchenall, Corrosion, 17, (1961) 357 t.
4. G. Wood and D. Melford, *J. Iron Steel Inst.*, 198, (1961), 142.
5. Gosta Wranglen, An Introduction to Corrosion and Protection of Metals, Halsted Press, A division of John Wiley and Sons (1972)
6. J. M. West, Electrodeposition and corrosion processes 2nd edition, Van Nostrand Rienhold Co., London (1970).
7. H. H. Uhlig, Corrosion and corrosion control, John Wiley and Sons Inc., (1971)
8. H. H. Uhlig and J. Gilman, Corrosion, 19, (1973) 261 t.