

CHEMICAL BLACKENING OF STAINLESS STEEL

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ABSTRACT

Chemical blackening of stainless steel from a chromic acid-sulphuric acid bath containing selenium compound as addition agent has been investigated. The effect of temperature, sulphuric acid concentration and additive concentration on the blackening characteristics as well as the potential-time behaviour of the system have been studied. The corrosion resistance of the coating is also reported.

Key words: chemical blackening, corrosion resistance

INTRODUCTION

Stainless steel contains a minimum of 9% chromium in addition to varying amounts of nickel, molybdenum, titanium, niobium, manganese, silicon etc.

18% chromium-8% nickel stainless steel has become industrially and technologically an important material and is used with and without surface finishing. For instance, stainless steel is finished with a coating from oxalic acid-boric acid-thio salt based solution [1] to facilitate wire-drawing operations and is also coated with copper, silver, gold, lead [2] for improved thermal and electrical conductivities, appearance, flow properties and drawing operations. Besides, the stainless steel is blackened for reduced light glare, for improved safety and minimal eye fatigue on moving tooling and machine parts [3]. Blackening of stainless steel does not make any dimensional changes as the oxide coating is less than a micron thick. Recently it is reported that oxide coated stainless steel finds applications in solar-energy systems because of its good light absorption and poor emission properties [4].

In this paper, a method of blackening of stainless steel of type 304 AISI from a chromic acid-sulphuric acid bath with selenium as an additive is reported though many other methods are cited in literature [5]. The method reported in this paper has many advantages over other methods from the point of view of cost, simplicity, temperature of operation (below 100°C) and the degree of blackness obtained.

EXPERIMENTAL

Stainless steel rods of AISI 304 type with a diameter of 1-2 mm was used. The preparation of the blackening electrolyte needs a special mention. The required quantity of selenium compound was dissolved in hot sulphuric acid (kept at 150°C) slowly and it resulted in a pale pink coloured solution. This solution in hot condition was poured into the chromic acid salt and mixed well. There is no chance for explosion. The whole mass was cooled and the pasty mass was added to water slowly. It was heated near to the boiling temperature, cooled and stocked.

The experimental set up is shown in Fig. 1. The potential of stainless steel was measured with reference to a saturated calomel electrode (SCE) using high impedance digital voltmeter. The potential-time behaviour of the system was studied at different concentrations of selenium compound and sulphuric acid as well as temperature.

The following sequence of operations was used for blackening of stainless steel: i) polishing and buffing ii) degreasing with benzene/trichloroethylene iii) electrocleaning at 50°C in an alkaline solution cathodically iv) rinsing and drying v) blackening vi) rinsing and drying.

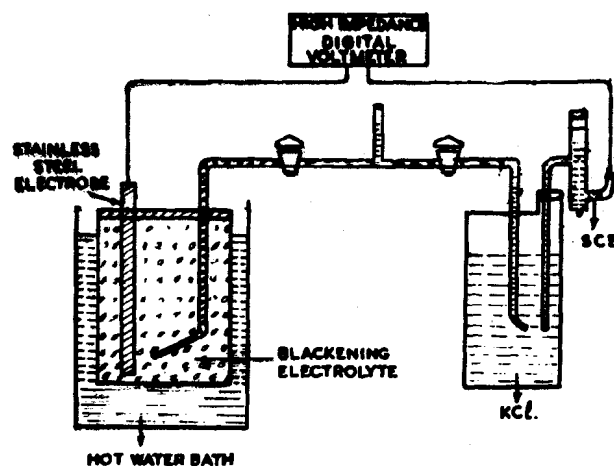


FIG.1 EXPERIMENTAL SET-UP

Adhesion and corrosion resistance of the coatings were assessed.

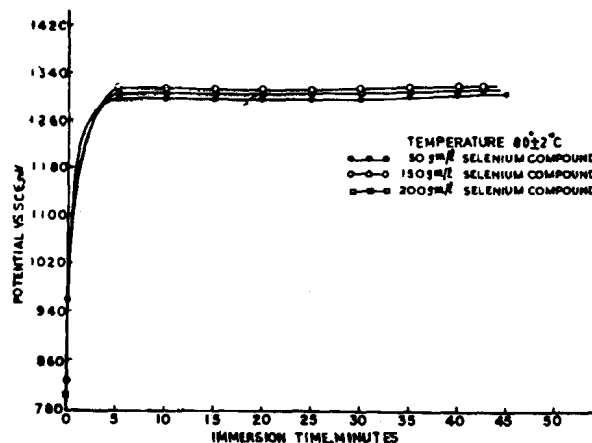


FIG.2 EFFECT OF SELENIUM CONCENTRATIONS ON POTENTIAL BEHAVIOUR WITH TIME

RESULTS AND DISCUSSION

Fig. 2 shows the relationship between the electrode potential and the immersion time from a bath containing chromic acid: 200 gpl, sulphuric acid: 275 gpl, selenium compound: 50 gm/l or 150 gpl and temperature: $80^{\circ} \pm 2^{\circ}\text{C}$. The electrode potential increases very sharply in the first five minutes of immersion in the bath and tends to remain almost constant. Thereafter, this behaviour is same for all the concentrations of the selenium compound, except for the fact that the potential increase is slightly higher at higher concentration of selenium compound in the bath. Figs.3 and 4 show the potential-time behaviour of the electrode for different temperatures from the above bath with selenium compound. The behaviour of the system is similar to the one in Fig.2 and the potential increases with increase of

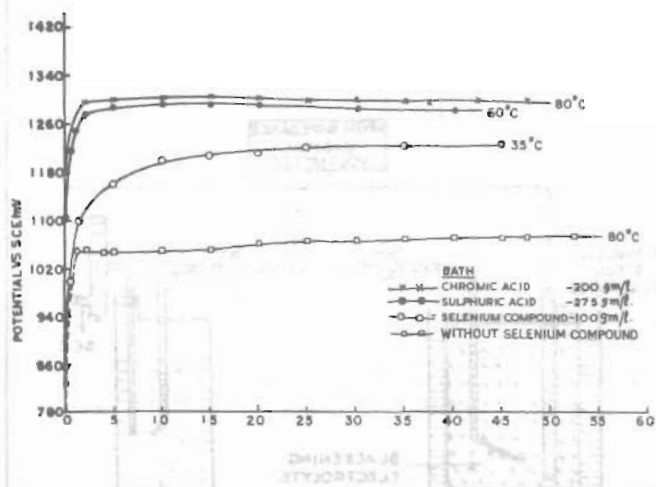


FIG.3 POTENTIAL MEASUREMENTS WITH AND WITHOUT SELENIUM COMPOUND IN THE BATH AT DIFFERENT TEMPERATURES.

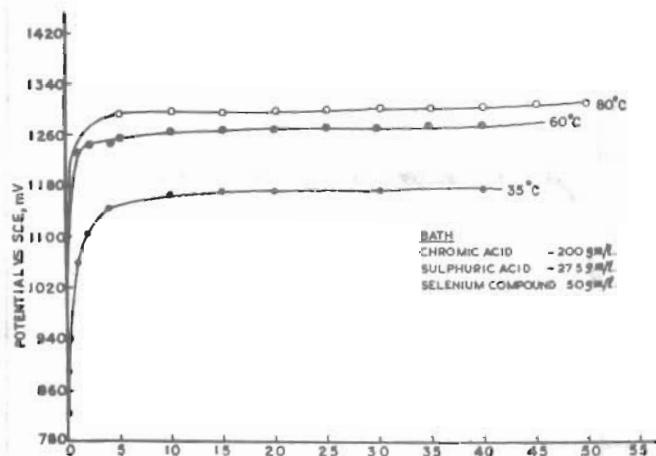


FIG.4 POTENTIAL MEASUREMENTS AT DIFFERENT TEMPERATURES WITH 50 gm/l SELENIUM COMPOUND IN THE BATH.

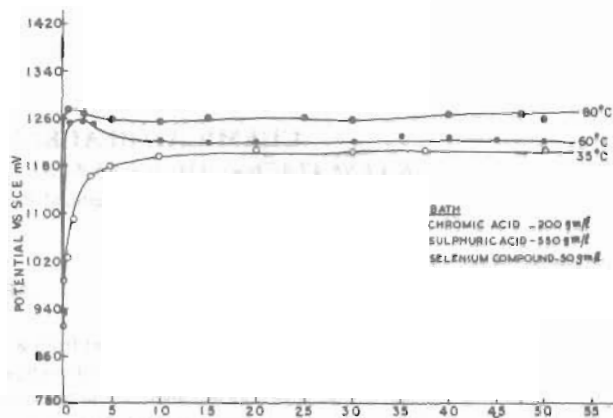


FIG.5 POTENTIAL MEASUREMENTS AT DIFFERENT TEMPERATURES WITH SULPHURIC ACID CONCENTRATION AT 550 gm/l IN THE BATH.

temperature. At 35°C, the horizontal part of the curve is in the potential range of about +1200 mV for both the concentrations of selenium compound (see also Fig. 4). For the system without selenium, the horizontal portion of the curve is around +1050 mV even when the bath temperature is at $80^{\circ} \pm 1^{\circ}\text{C}$. This shows clearly that the potential of the electrode shifts to a more positive value in the presence of selenium compound. A similar finding has been reported in the case of stainless steel electrode in phosphoric acid solution in the presence of sodium selenite salt [6] in the temperature range of 100° to 110°C .

Fig. 5 shows the potential change of the electrode with time from a bath containing chromic acid: 200 g/l, sulphuric acid: 550g/l and selenium compound 50 g/l at temperatures 35°, 60° and 80°C respectively. At temperatures of 60 and 80°C a hump (peak) is seen in the time limit of five minutes. But at 35°C such a hump is not observed. A similar hump has been reported [7] in colouring of stainless steel from a highly concentrated chromic-sulphuric acid bath temperatures above 70°C. Also it is noted that panels are blackened only when the potential of the electrode attains a value above +1300 mV in 5-10 minutes of immersion. If this value is not attained within this time, only greyish colours are obtained.

Figs. 6(a) and (b) show the scanning electron micrographs of stainless steel specimens treated in the bath with and without selenium compound, at the magnification of 2000 X.

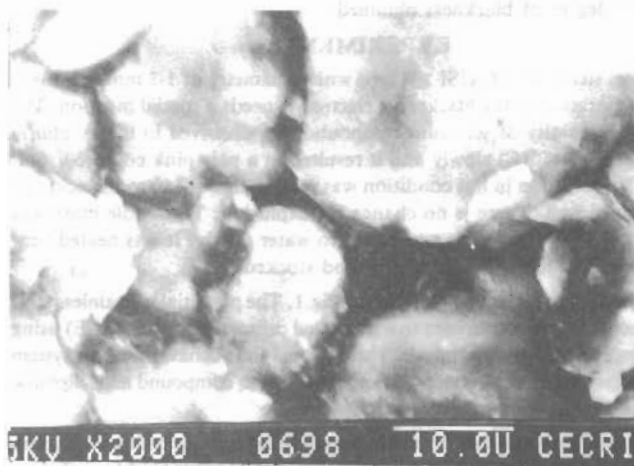


Fig.6 (a)

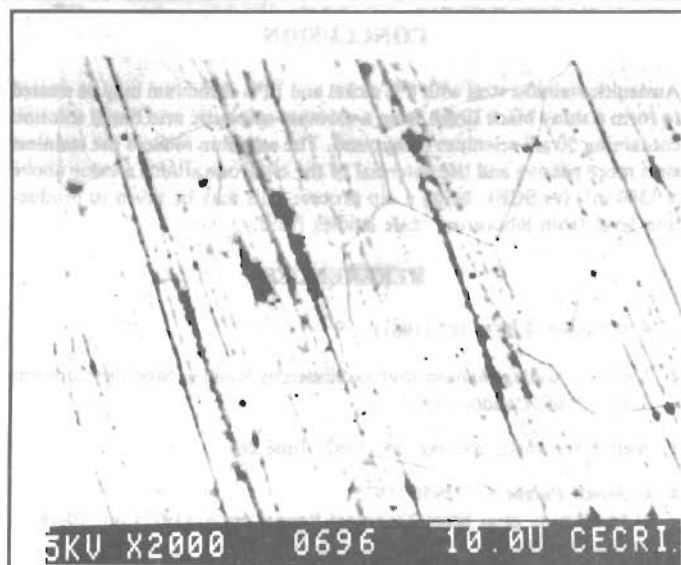


Fig.6(b)

The specimen treated in the absence of selenium shows grain boundaries distinctly whereas the one treated in the presence of selenium compound (blackened specimen) shows black and white regions in the form of islands. Fig. 6(c) shows the photograph of some blackened stainless steel samples.

In the place of selenium compound, compounds like molybdc acid, vanadic acid have been tried with little success. The phenomenon of blackening starts after 10 minutes and the degree of blackening improves with immersion time.

Although we have not made measurements of the film thickness, it is reported that the thickness does not exceed 0.8 micron. Without selenium compound in the bath, blackening does not take place in spite of the treatment at higher temperatures and longer immersion periods. Therefore, it appears that selenium plays a vital role in the blackening process. Similar role of selenium was reported [8] in the case of blackening of copper in acid media. Also in the blackening of stainless steel from concentrated alkali solution with mercury salt addition, it was reported [9] that the presence of HgO^- ions are responsible for black film formation.

The adhesion of the film to the metal surface was good as shown by the conventional adhesive tape test. Also the blackened stainless steel had good corrosion-resistance in various media as shown in the Table I.

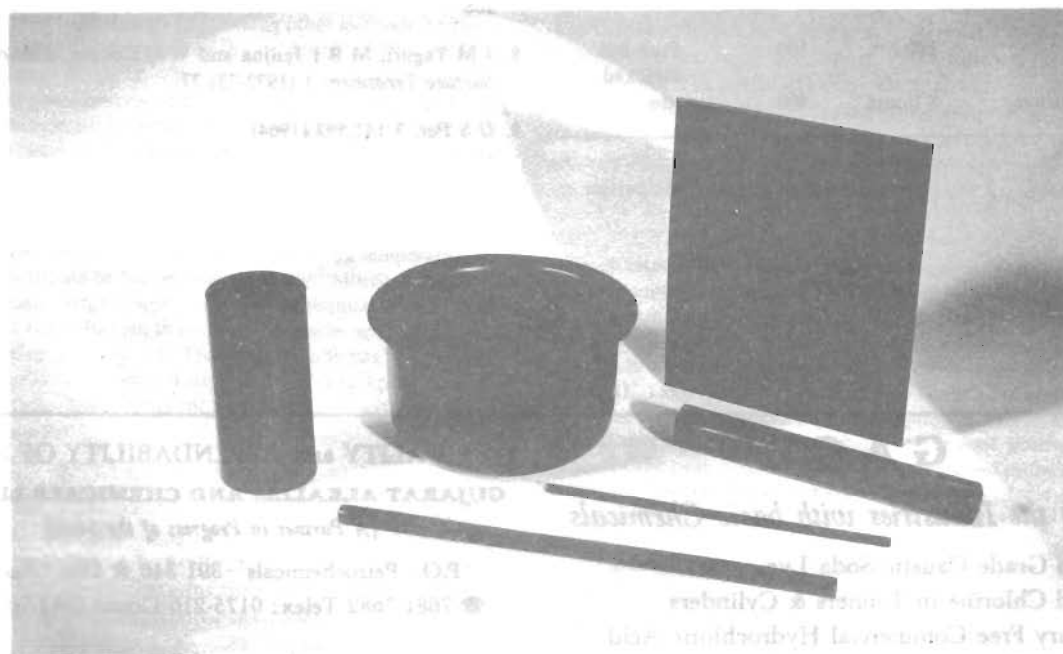


Fig.6(c)

Table 1: Corrosion-resistance tests on the blackened stainless steel specimens

No. Test conditions	Time (days)	Temp (°C)	Observations made
<i>I. Immersion in</i>			
a) Conc. H ₂ SO ₄ (Sp.Gr 1.84)	7	35	Film is not attacked Finish is also retained.
b) Conc. HNO ₃ (Sp. Gr. 1.42)	7	35	-do-
c) Acetic acid (glacial)	7	35	-do-
d) 5M sodium hydroxide	7	35	-do-
e) Triethanolamine	7	35	-do-
f) Acetone	7	35	-do-
g) Benzene	7	35	-do-
h) Saturated sodium chloride solution	7	35	-do-
i) Conc. HCl 10 N	—	—	Film is attacked immediately
j) 5% HCl (by vol)	1 hr.	35	Film is attacked in an hour
<i>2. Heat-test</i>			
a) Boiling water	100 hrs.	100	Film not attacked
b) Heating in a furnace	5 hours	400	-do-

CONCLUSION

Austenitic stainless steel with 8% nickel and 18% chromium may be treated to form a shiny black finish from a chromic-sulphuric acid based solution containing 50 g/l selenium compound. The selenium renders the stainless steel more passive and the potential of the electrode attains a value above +1300 mV (vs SCE). Being a dip process, this may be taken to production level from laboratory scale studies readily.

REFERENCES

1. *U S Patent*, 2,953, 487 (1961)
2. 'Surface finishing stainless steel' published by Stainless Steel Development Association, London (1967)
3. Walter Schwartz, *Plating*, 69 (1982) June 26
4. a) *Japan Patent* 52/72950 (1975)
b) M Haroda et al *Steel Technical Report No.6*, (1977) pp. 70-76
5. a) *Chemical Abstracts* 50 (1956) 11210c
b) *U S Patent* 2,542,994 (1951)
c) *Brit Patent* 834834 (1960)
d) *Brit Pat* 1009822 (1966)
e) *U S Pat* 3,314,812 (1967)
6. V P Khvostov and I P Anoshchenko, *Soviet Electrochemistry*, 16 (1980) 918
7. T E Evans, A C Hart and A N Skedgell, *Trans Inst of Met Fin*, 51 (1973) 108
8. J M Taguri, M B I Janjua and W C Cooper, *Electrodeposition and Surface Treatment* 1 (1972-73) 77
9. *U S Pat.* 3,142,592 (1964)