Studies on newer chemical passivation treatment for stainless steel

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An attempt has been made to develop a chemical passivation treatment for AISI 304 stainless steel based on nitric acid in the presence of various oxidising agents such as sodium molybdate, potassium dichromate and potassium permanganate. The stability of the passive film formed through different chemical passivation treatments has been studied by potential–time measurement in 0·5 M sulphuric acid and the operating parameters of chemical passivation have also been optimised by this technique. Results of the study show that chemical passivation of stainless steel in nitric acid shifts the open circuit potential in the positive direction. Increase of concentration of nitric acid, treatment time and temperature further ennobles the potential. Addition of either dichromate or permanganate ions to nitric acid helps in forming a more stable passive film whereas molybdate, even at higher concentrations does not have any beneficial effect on passive film formation.

Keywords: Passivation, Chemical treatment, Stainless steel, Nitric acid, Sulphuric acid

Introduction

Stainless steels are self-passivating upon exposure to air and moisture, as a result of their high chromium content. Passivation treatments by chemical or electrochemical methods are useful in augmenting the naturally occurring protective oxide films. The passive film so formed is somewhat thicker and more corrosion resistant than that formed by autopassivation.

The presence of foreign matter on a stainless steel surface is the root cause of localised corrosion. Common contaminants include embedded iron or iron oxide, heat tints (superficial oxide from either internal or external welding) and paint and/or crayon markings. These can cause rupture of the passive film and help in adsorption of chlorides from the environment or by decomposition of organic compounds such as polyvinyl chloride in the marking materials. Scratches and grinding marks can also initiate pitting corrosion.

Acid cleaning is commonly employed in industry to remove the contaminants from the surface. For this purpose, 20–40 v/v% nitric acid solutions are often used at temperatures ranging from 20 to 70°C. Even for surfaces free from metallic contaminants, treatment in dilute nitric acid greatly increases their resistance to pitting.[1–5] In this investigation, attempts have been made to develop a chemical passivation treatment based on nitric acid, which for ecological reasons can be operated at room temperature without the use of toxic dichromate.

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Experimental

Electrodes

AISI 304 stainless steel of nominal composition of size 1 cm × 5 cm was used. Specimens were lacquered so as to expose 1 cm^2.

Electrolyte

For passivation, nitric acid of concentrations 10, 20 and 30 v/v-% containing 0·1–0·5 wt/v-% of sodium molybdate or potassium permanganate or potassium dichromate were used. For evaluating the stability of the passive film formed 0·5 M H$_2$SO$_4$ was used.

Technique used

Potential–time measurements were made in 0·5 M H$_2$SO$_4$ for the stainless steel passivated in different solutions using a digital multimeter with a saturated calomel electrode as the reference electrode.
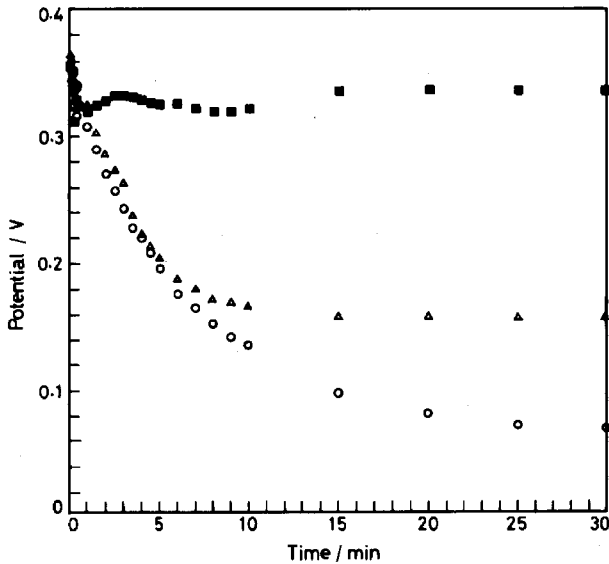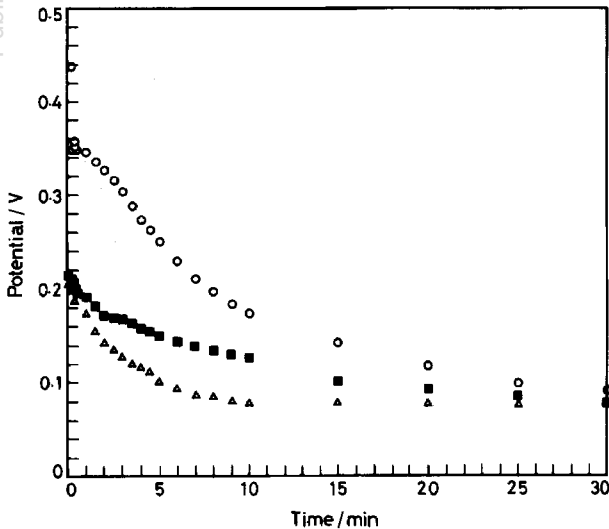
Results

Effect of nitric acid concentration

Figure 1 shows the variation of open circuit potential with different immersion time in various concentrations of nitric acid at room temperature. In 30 v/v% nitric acid, the potential shifts immediately towards the more noble direction and it is stabilised at +320 mV. With increasing time of immersion, the potential is little changed. In 10 and 20 v/v% nitric acid, the potentials are noble initially (+370 mV) but are stabilised at +170 and +85 mV for 20 and 10 v/v% nitric acid respectively.

To evaluate the stability of the passive film formed, the potential–time behaviour of passivated stainless steel has been studied in 0·5 M H$_2$SO$_4$ and the values are shown in Fig. 2. Stainless steel is passivated in 10 and

○, 10 v/v% HNO₃; △, 20 v/v% HNO₃; ■, 30 v/v% HNO₃

1 Potential–time behaviour of 304 stainless steel during passivation

20 v/v% nitric acid. Initially the potential is around $+220$ mV falls to a value of $+120$ mV within 10 min. In the case of specimens passivated in 30 v/v% nitric acid, though initially the potential is at $+350$ mV, it also stabilises to the same value of $+120$ mV after 30 min of immersion. From the above data, it is clear that sufficient passivation is attained even at a 10 v/v% concentration of nitric acid.
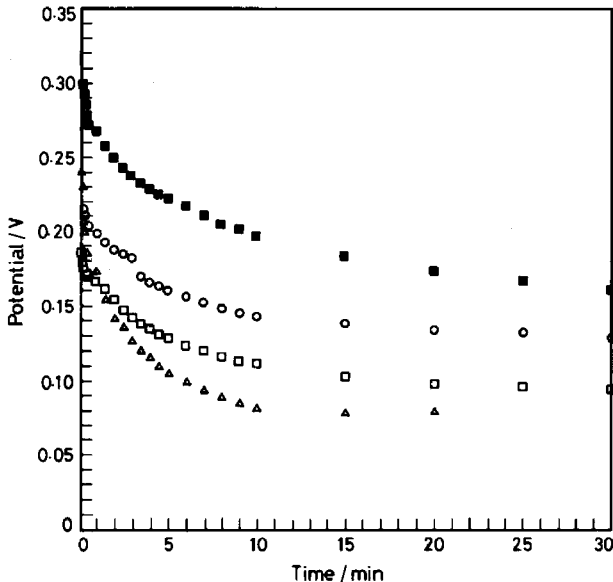
Effect of temperature

Figures 3 and 4 show the potential–time behaviour of stainless steel in 0·5 M H₂SO₄ after passivation in 10 and 20 v/v% nitric acid for 30 min at different temperatures (30, 40 and 50°C).

For stainless steel passivated in 10 v/v% nitric acid, treatment at higher temperature shows an increase in the initial potential in the more noble direction. The values after a period of 30 min are more negative than those obtained at room temperature.
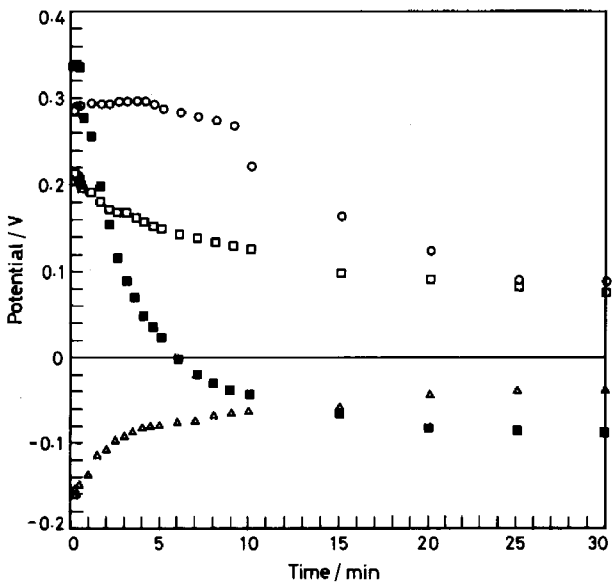

▲, 30°C; □, 40°C; ○, 50°C; ■, 60°C

3 Potential–time behaviour of 304 stainless steel in 0·5 M H₂SO₄ after passivation in 10 v/v% HNO₃

In the case of stainless steel passivated in 20 v/v% nitric acid, passive films formed at 40 and 50°C stabilise at potentials of -100 to -50 mV within 10 min, whereas the passive film formed at 30°C stabilises at $+100$ mV within 30 min. These data confirm that passivation treatment at 30°C forms a stable film and treatment at higher temperature has no beneficial effect.

Effect of various oxidising agents

Oxidising agents such as potassium dichromate, sodium molybdate and potassium permanganate were added to 10 and 20 v/v% nitric acid in the concentration range of 0·1–1 wt/v% and the potential–time behaviour of passivated stainless steel in 0·5 M H₂SO₄ studied. The results are summarised in Tables 1 and 2.

○, 10 v/v% HNO₃; ■, 20 v/v% HNO₃; ▲, 30 v/v% HNO₃

2 Potential–time behaviour of passivated 304 stainless steel in 0·5 M H₂SO₄

□, 30°C; ▲, 40°C; ■, 50°C; ○, 60°C

4 Potential–time behaviour of 304 stainless steel in 0·5 M H₂SO₄ after passivation in 20 v/v% HNO₃

Table 1 Potential–time behaviour of passivated* stainless steel in 0·5 M H_2SO_4

Type of oxidising agent	Concentration / %	Initial potential v. SCE / mV	Stabilised potential v. SCE (after 30 min) / mV
10 v/v-% nitric acid	–	+230	+80
Potassium dichromate	0·05	+300	+380
	0·10	+350	+380
	0·50	+350	390
Sodium molybdate	1·00	+250	+100
Potassium permanganate	0·05	+570	+400
	0·10	+985	+780
	0·50	+1000	+855

*Passivated in 10% nitric acid containing various concentrations oxidising agents at room temperature for 30 min

Table 2 Results of potential–time study of passivated* stainless steel in 0·5 M H_2SO_4

| Type of oxidising agent	Concentration / %	Initial potential v. SCE / mV	Stabilised potential v. SCE (after 30 min) / mV
20 v/v-% nitric acid	–	+250	+120
Potassium dichromate	0·05	+300	+200
	0·10	+340	+260
	0·50	+400	+300
Sodium molybdate	0·10	+260	+130
	0·50	+280	+140
	1·00	+300	+140
Potassium permanganate	0·05	+290	+350
	0·10	+805	+500
	0·50	+1100	+800

*Passivated in 20% nitric acid containing various concentrations oxidising agents at room temperature for 30 min

From the tables, it is clear that addition of molybdate even at a higher concentration (1 wt/v%) does not have a significant beneficial effect, whereas permanganate as well as dichromate addition stabilises the potential at more noble values.

Discussion

The majority of the results of stability studies on stainless steel especially localised corrosion, indicates that sulphide inclusions and in particular MnS particles act as preferential sites for attack.[6–9]

Passivation in nitric acid removes the MnS inclusion responsible for pit initiation because MnS is thermodynamically unstable below pH 5.[8] In acid media, MnS dissolves according to the reaction

$$MnS\,(s) + 2H^+\,(aq) \rightarrow H_2S\,(g) + Mn^{2+}\,(aq) \qquad (1)$$
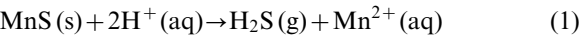
In addition to the dissolution of MnS inclusions, nitric acid treatment favours chromium enrichment on the metal surface by the preferential dissolution of iron.[4,5] Moreover, the strong oxidising condition favours the thickening of natural oxide film. An X-ray photoelectron spectroscopy (XPS) study[10] showed that for a nitric acid passivated sample, sputtering for a period of 8 min was necessary to remove all the oxidised iron, while total removal of the oxide from the sample passivated in nitric acid containing sodium dichromate required a period of 35 min. No evidence was found for incorporation of dichromate ion in the passive film. It seems, therefore, that the oxidising dichromate or permanganate ions to polarise stainless steel to higher potentials as observed. This ennoblement of potential enhances the stability of the stainless steel.

Conclusions

The present investigation has shown that even a simple potential–time monitoring technique is useful in evaluating stability of metals, in this case the passivation treatment of AISI 304 stainless steel. It has been shown that sufficient passivation is attainable even at 10 v/v% nitric acid compared to 20 and 30 v/v% concentrations.

Good passivation is ensured at 30°C and an increase of temperature up to 50°C does not confer any additional beneficial effect.

Addition of either dichromate or permanganate ions to the nitric acid further shifts the potential in the noble direction as a result of the formation of more stable passive films but addition of molybdate, even at higher concentrations, does not have any beneficial effect.

Acknowledgement

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