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THE ANODIC BEHAVIOUR OF MOLYBDENUM IN BASIC, ACIDIC AND CHLORIDE CONTAINING MEDIA

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ABSTRACT

It is a long known fact that molybdenum increases the corrosion resistance of steels in chloride containing media. However the mechanism of this effect is yet to be determined. This study is concerned the investigation of the anodic behavior of Mo in a wide potential range in order to clarify this protective effect. The potential range employed was chosen between-1500mV and 2300mV covering active, passive and transpassive region of iron.

1. INTRODUCTION

The theoretical aspects of molybdenum's corrosion behaviour are complex and there is as yet no clear cut, generally applicable picture. There are, however, a large number of literature references which include data on passivation and potential of molybdenum under widely assorted conditions[1]. Molybdenum is widely used as an alloying addition to stainless steels to facilitate the formation of the passive film on steel surface and to improve resistance to pitting attack. Papers have been published concerning the electrochemical behaviour of Mo[2,3]. In order to discuss the Mo dissolution, it is important to determine species dissolved from Mo electrode at various potential ranges. Itagaki et al[4] have determined the species dissolved from Mo electrode by the chemical analysis and discussed the dissolution behaviour of Mo in sulfuric acid solution.

In this study a cyclic voltammetric method of Mo electrode have been performed in a wide potential range of –1500mV and 2300mV and the results were compared with the data given in literature.

EXPERIMENTAL

The experiments were carried out with 1mm diameter Mo wire supplied with Murex Company embedded into resin. It was polished with sand papers with decreasing roughness, degreased with acetone, washed with bi-distilled water and reduced at.-1500 mV for 15 minutes. The experimental solution was purged with purified nitrogen and stirred with magnetic stirrer prior and throughout the experiment. The cyclic voltammograms were taken with Wenking Model VSC72 voltage scan generator with a scan rate of 1mV/s. The reference and counter electrodes were saturated calomel (SCE) and Pt plate respectively. All the potentials were given against SCE.

RESULTS AND DISCUSSION

Figure 1, Figure 2 and Figure 3 are the cyclic voltametric curves of 0.1 M NaOH(1) and 0.1M NaOH +3.0M NaCl(2); 0.05 M H_2SO_4(1) and 0.05 M H_2SO_4+3.0M NaCl(2) and 0.1 M HCl (1) and 0.1 M HCl+3.0 M NaCl respectively.

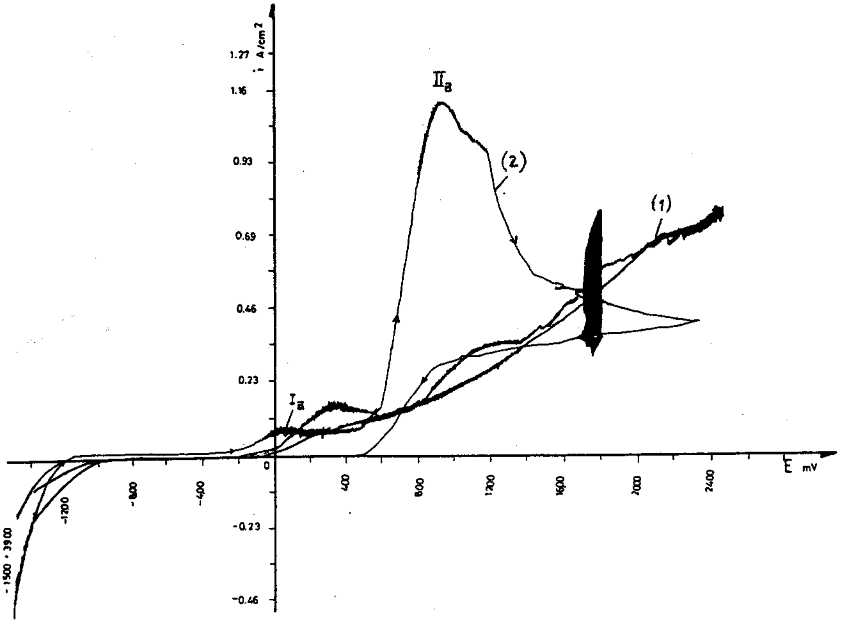

Figure 1. Cyclic current-potential curves of molybdenum in 0.1 M NaOH(1) and 0.1 M NaOH+3 M NaCl(2)

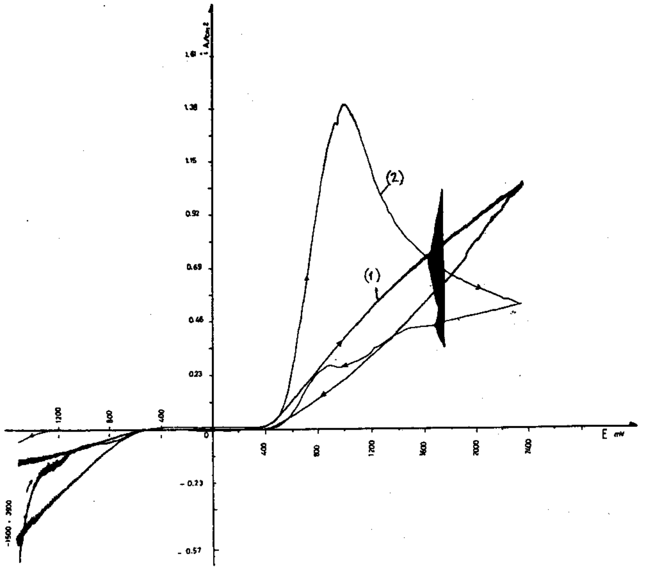

Figure 2. Cyclic current-potential curves of molybdenum in 0.05 M H_2SO_4 (1) and 0.05 M H_2SO_4+3 M NaCl(2)

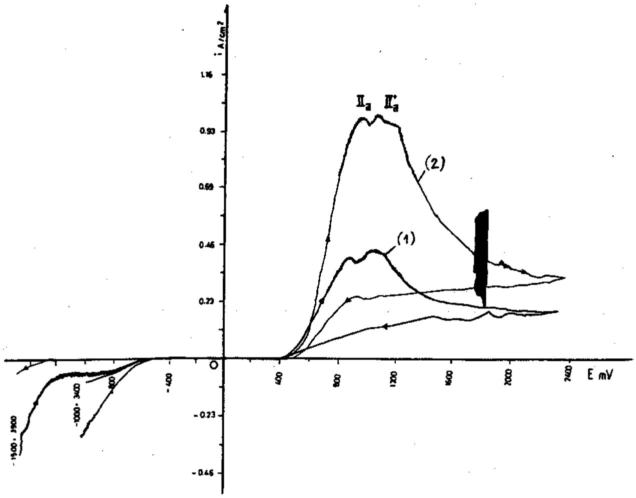

Figure 3. Cyclic current-potential curves of molybdenum in 0.1 M HCl(1) and 0.1 M HCl(1)+3 M NaCl(2)

In the cyclic voltammetric curve obtained in NaOH solution (curve 1 in Figure 1) the passive region is reached with the passage of a very small anodic current (too small to be shown on this scale). The transpassive dissolution starts at-200mV followed by two peaks followed by waves merged with each other as the potential is increased. The voltammogram in 0.5 M NaOH gives three distinctive peaks[5]. The addition of $\overline{Cl}$ (curve 2 in Figure 1) causes the passivation to be reached at more negative potential of- 1220 mV, the transpassive dissolution to start at- 200 mV and the peak I to be replaced with a small current oscillating wave. The small peak observed at 500 mV is followed by peak IIa with rapid increase in current. The current decreases after this peak making a shoulder and O_2 evolution occurs at 1700 mV.

In both curves in H_2SO_4 (Figure 2) and HCl (Figure 3) it is observed that the passive region starts at- 500 mV and the transpassive region at 400 mV. The small IIa peak in H_2SO_4 solution (curve 1 in Figure 2) is followed with a oscillating increase in current. The peak in HCl is much more distinctive (curve 1 in Figure 3). The curves obtained after the addition of NaCl are similar in both these acids which display oxygen evolution with wild oscillations. There is no oxygen evolution in media containing no chloride ions, which shows that the film formed in non-chloride ion containing media has much better coverage properties.

Figure 4 clearly shows that molybdenum is passive where active iron dissolution takes place but shows a stepwise transpassive dissolution at the passive region of iron. The H_2SO_4 curve reveals that Mo passes to passivation region without showing any active dissolution. The curves obtained with pure NaOH and H_2SO_4 show no active Mo dissolution region. The transpassive dissolution of Mo manifests itself with increasing peaks with increasing potentials. This must be due to the higher oxides of Mo. Thus the second passivation phenomena observed with Cr or Ni takes place multi stepwise with Mo especially in basic media[1]. The peak Ia turns into a small step after the addition of NaCl to basic media (curve 2 in Figure 1), this region falls into passivation region in the reverse scan. The peak I_a is not observed in HCl and H_2SO_4 and this region corresponds to the passivation region. The extension of passivation region in acidic media can be explained by the formation of the protective MoO_2 layer in acidic media according to Pourbaix diagrams[6,7] and the dissolution of Mo as MoO_4^{2-} in the basic media.

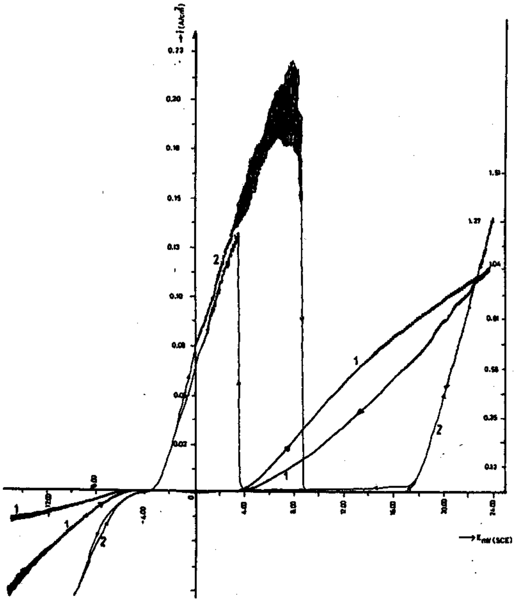

Figure 4. Cyclic current-potential curves of molybdenum and iron in 0.05 M H_2SO_4

The Ia peak is most probably due to the dissolution of Mo as Mo^{3+} and its precipitation as $Mo(OH)_3$ and/or Mo_2O_3 (dissolution-precipitation mechanism). The peak IIa must correspond the formation of protective MoO_2 or/and $Mo(OH)_4$. The merged peaks at higer potentials must be due to the Mo^{5+},Mo^{6+} or non stoichiometic oxides of Mo.

Hull[8] who obtained three peaks in KOH solutions starting from the corrosion potential and increasing up to 2.0 V claimed that the main species formed was Mo^{3+} up to 0.2V, MoO_2 up to 0.95 V and $Mo^{5+}$and Mo^{6+} at higher potentials. Povey and Metcalfe[9] who made XPS surface analysis in NaOH reported that mostly Mo^{3+} species were formed up to -0.4 V Mo^{3+} and Mo^{4+} up to 0.4 V and Mo^{6+} species potentials above that.

The Mo films formed in acidic media were investigated by Lu et al[10] using XPS, Yang et.al[7] with AES and XPS and Urgen et al[11] with ESCA. However the voltammetric curves obtained by these workers were up to 0.6 V and the surface analysis were made only up to this potential.

The peak Ia is not effected by the addition of 0.1 M NaCl to 0.1 M NaOH. However the addition of 5.0 M NaCl makes all the peaks observed in curve 2 in Figure 1 smaller and the reverse scan completely coincides with the passivation region.

The increase $\overline{\mathrm{Cl}}$ concentration causes the current of peak IIa to increase and become pointed. The addition of the 5.0 M NaCl resulted in the lower current density at 2300 mV which signifies that the film obtained under this condition has the best coverage properties. The formation of this sort of protective film can only be explained by the precipitation of highly insoluble chloride salt upon the electrode surface.

The facts that the peak IIa becomes much more distinctive after the addition of 3.0 M NaCl to H_2SO_4 solution and becomes pointed as it is in HCl can only be attributed to the formation this sort of insoluble Mo-Cl salt. The IIa and IIa' peaks obtained by the addition of same concentration of NaCl in curve of Figure 3 being bigger than those observed in curve 2 of Figure 1 shows that the Mo-Cl compounds formed in HCl solution are much more protective. The peak IIa must be due to the formation of Mo-chloride or Mo-oxychloride while peak IIa' must be result of Mo-oxide or Mo-hydroxide. The chloride compounds of Mo are known to be highly insoluble[12]. The study of Schneider et al[13] also support this hypothesis. These workers determined the presence of Mo and $\overline{\mathrm{Cl}}$ at the bottoms of the pits they formed at the surface of FexMo (x=1,2,3%) and Fe 17Crx Mo(x=1,3,7%) alloys in $H_2S0_4+\overline{\mathrm{Cl}}$ media and attributed this to the formation of highly insoluble Mo-CI species.

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