

Passivity and pitting of austenitic stainless steel AISI 316 in the $\text{CH}_3\text{OH}-\text{H}_2\text{SO}_4$ system

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The passivity and pitting behaviour of AISI 316 stainless steel in methanol containing different concentrations (0.001 to 1 M) of H_2SO_4 has been investigated by an electrochemical method. Higher concentrations of sulphuric acid have been found to facilitate the passivation process and influence the passivity current and passivation range. The studies reveal the peculiarities of steel pitting and predicts the protective properties of the surface by a process of repassivation in this system. The kinetics of pitting, morphology of the pits and repassivation of the surface have been investigated for this steel. The beneficial effect of molybdenum as an alloying element of steel, on corrosion behaviour has been noticed.

1. Introduction

The passive state of many metals and alloys can be destroyed by some anions, leading to pitting. Although many papers [1-13] had been devoted to the influence of organic solvents on the dissolution of metals and alloys, the peculiarities of the influence on the initial stage of metal/alloy pitting are not well studied. Meanwhile a partial change of medium composition from organic to aqueous-organic can markedly influence the kinetics of the reaction on the surface of passive metal, i.e. composition and thickness of the passive layer; double layer structure and reaction ability of anions.

Pitting corrosion has long been a serious problem for metals and alloys. The stainless steels rely on the formation of a passive film. The localized breakdown in passivity by aggressive anions can lead to very high rates of penetration, even when the overall corrosion rate is minimal. The microstructure of stainless steels and, in particular, the chemical inhomogeneity at the metal surface plays an important role in determining the pitting susceptibility. A great deal of experimental work has been devoted to the study of pitting corrosion and the effect of different alloying elements on pitting susceptibility. Kolotyrkin [14] has described the decrease in susceptibility of steels when alloyed with chromium and molybdenum.

In view of the growing interest in corrosion studies of metals and alloys in organic solvents, a systematic investigation has been undertaken in this laboratory to understand the peculiarities involved in corrosion, passivity and pitting behaviour of metals and alloys. Our earlier results [15-17] on AISI 304 in different alcohols and H_2SO_4 mixtures revealed some interesting features and prompted us to extend the work for other austenitic stainless steels. Because austenitic stainless steel AISI 316 is industrially important and

also it contains molybdenum, it might indicate the role of the alloying element (molybdenum) in usual stainless steels, on corrosion, passivation and pitting behaviour in the methanol- H_2SO_4 system.

In the present investigation, the cathodic and anodic behaviour of AISI 316 has been evaluated in deaerated methanol containing different concentrations of H_2SO_4 at $30 \pm 1^\circ\text{C}$ along with studies of passivity, pitting and repassivation.

2. Experimental procedure

The experimental set up and working procedures are the same as adopted earlier [15-18]. The solutions were prepared with concentrated H_2SO_4 (analytical reagent) in dried distilled methanol. The experiments were conducted in a three-necked assembly using a test electrode of AISI 316 stainless steel (18Cr 8Ni 3Mo) with an exposable area of 2 cm^2 and platinum counter electrode of the same area. The reference electrode was an SCE.

3. Results and discussion

The results of cathodic and anodic polarization studies for AISI 316 stainless steel and the electrochemical parameters derived from these curves (Fig. 1) are given in Table I at different concentrations of H_2SO_4 in methanol. The cathodic polarization curves clearly reveal the diffusion-controlled nature in the lower concentrations of acid in methanol while in the case of solution mixtures having high concentrations of acid (0.1 and 1 M) a linear nature is observed due to higher concentrations of H^+ ions. The cathodic reaction appears to be hydrogen evolution. The cathodic tafel slope (b_c) decreases with increasing acid concentration.

It can be seen that AISI 316 stainless steel shows a greater noble corrosion potential than AISI 304 and

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TABLE I Corrosion parameters of AISI 316 SS in methanol-H₂O₄ mixtures

	Concentration of H ₂ SO ₄ in methanol			
	0.001 M	0.01 M	0.1 M	1.0 M
E_{corr} (mV)	+60	+40	-60	-135
i_c ($\mu\text{A cm}^{-2}$)	2.4	4.0	8.0	16.0
i_{corr} ($\mu\text{A cm}^{-2}$)	negligible	negligible	negligible	0.25
i_p ($\mu\text{A cm}^{-2}$)	1.3	0.8	0.42	0.25
E_c (mV)	+180	+100	+60	-40
Passivation range (mV)	+200 to 1060	+300 to 1100	+200 to 1200	+100 to 1320
E_b (mV)	+1120	+1200	+1280	+1360
b_a (mV/dccdl)	60	55	50	45
b_c (mV/dccdl)	165	150	140	125
E_{pn} (mV) 0.5 mV sec ⁻¹	+1120	+1180	+1260	+1300
5 mV sec ⁻¹	+1040	+1100	+1185	+1220
E_{pr} (mV) 0.5 mV sec ⁻¹	+940	+985	+1080	+1100
5 mV sec ⁻¹	+860	+920	+980	+1020

302 which indicates that molybdenum renders more corrosion resistance to the 18/8 stainless steels [15-17]. The marked improvement in corrosion resistance and shift in corrosion potential towards the noble direction due to molybdenum have been reported earlier [19-23].

The anodic polarization curves show distinct active-passive transition in each solution mixture (Fig. 1). The critical current density for passivity (i_c) increases regularly with increasing concentration of H₂SO₄ in methanol. Such an increase in i_c can be associated with the influence of increasing acidity

which can lead to the increased metal dissolution rate. The lowest value of i_c is found for this stainless steel in comparison with the AISI 304 and 302 at the same respective concentrations of acid in methanol [15-17]. It has been reported [20, 24, 25] that when molybdenum is used as an alloying element in stainless steels it offers an additional passivating effect and thus the lowest critical current has been obtained in the present investigations. Newman and France [26] observed that molybdenum acts at a submonolayer level in its primary inhibiting action on active dissolution of stainless steel in H₂SO₄. The tafel slope

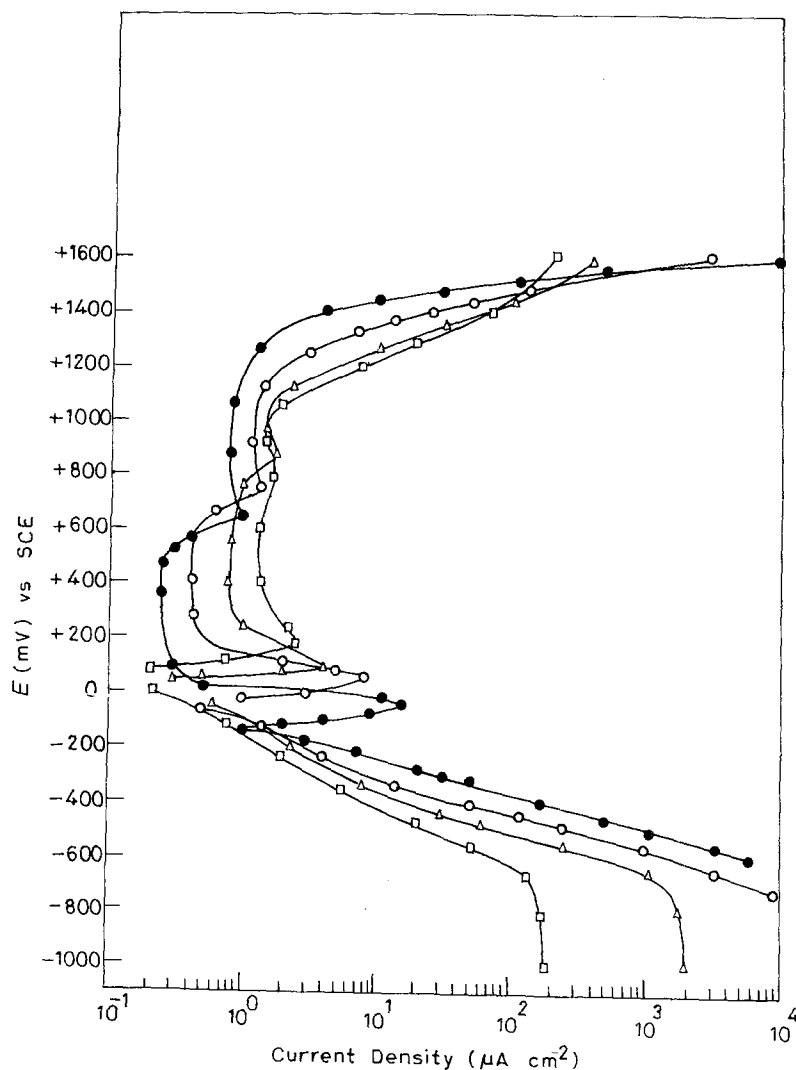


Figure 1 Cathodic and anodic polarization curves of AISI 316 SS in solution of H₂SO₄ in methanol. (●) 1.0 M, (○) 0.1 M, (Δ) 0.01 M, (□) 0.001 M.

obtained for the anodic reaction compares favourably with the metal dissolution in the active region [27].

Fig. 1 shows that the passivity current decreases and the passivation range increases with increasing concentration of acid in methanol. It is also significant to compare the I_p values obtained for AISI 316 SS and AISI 304 SS and AISI 302. The lowest I_p and the widest passive range have been obtained for AISI 316 SS rather than those without molybdenum [15–17]. Such observations are likely to arise from the fact that molybdenum may allow much protective film to be formed. It has been suggested [24, 28] that molybdenum holds the lattices together very tightly and thereby reduces the passive current significantly.

The formation of passive film on the surface at each concentration of acid in methanol and the decrease in passivity current and broadening of the range of passivity with increasing concentration of acid in methanol, indicate the progressive growth of a more protective nature of the film with acid concentration. It is inferred that the water content present in the highest concentration of H_2SO_4 in methanol is sufficient to satisfy the conditions required for the

formation of a more stable, coherent and protective passive film. This also suggests that the water present in the medium plays a more important role in conditioning the passive film than the acidity effect of H_2SO_4 . The need and importance of water up to certain limit, in passive film formation have been greatly emphasized by various workers [1, 2, 4, 9, 10, 29–31]. The shorter range of passivity has been observed in methanol containing lower H_2SO_4 concentration (0.01, 0.001 M). In this case, a small amount of water existing in solution is probably bound by ions present in the solution or by methanol, and is thus insufficient for proper stabilization of the anodic film. Such an explanation has also been given by Banas [32].

A feeble secondary passivity peak is observed in each solution mixture (Fig. 1) which moves towards the noble potential direction with decreasing acid concentration in methanol. This occurs possibly due to the formation of lower valence molybdenum in the lower potential region which is subsequently oxidized to higher valence molybdenum at higher potentials [33, 34]. Clayton and Lee [34] investigated the role of molybdenum in stainless steel and found that a more

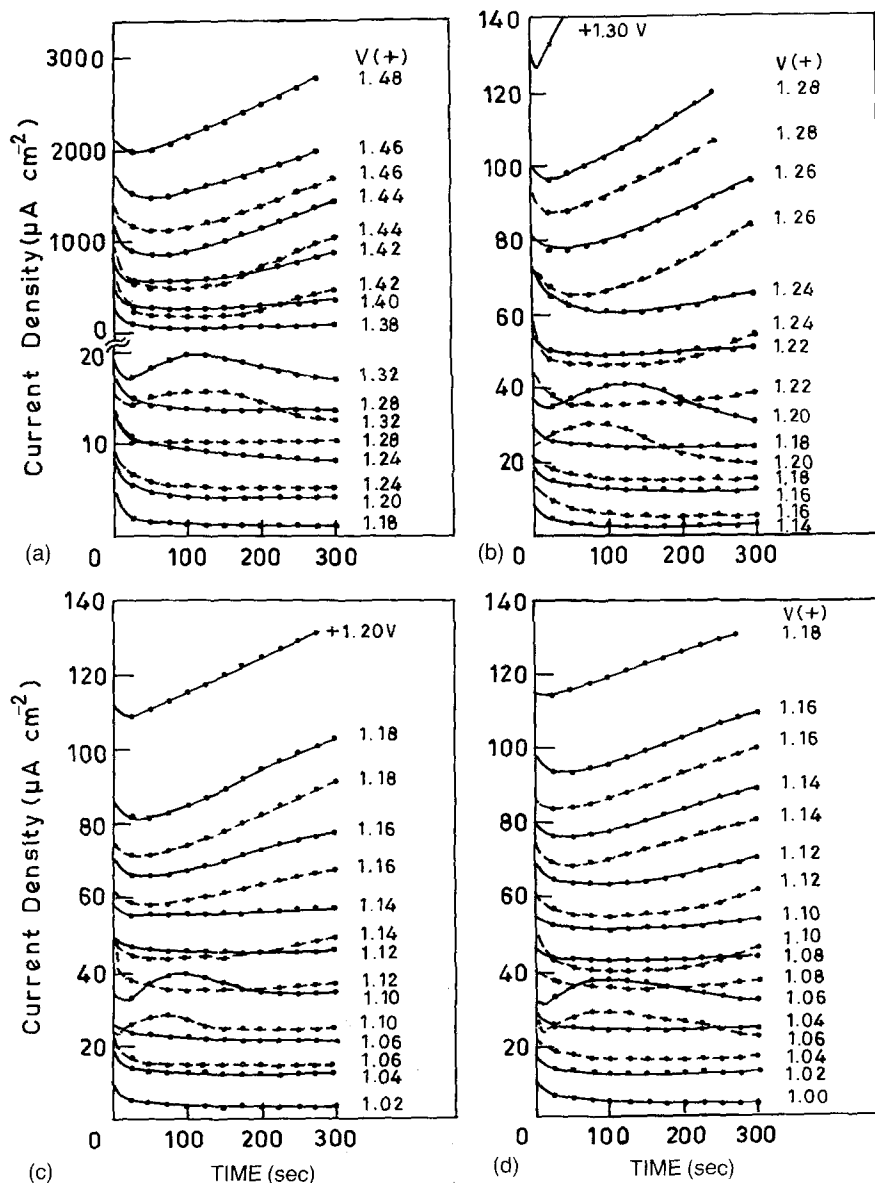


Figure 2 Current transients at constant potential in methanol containing H_2SO_4 : (a) 1 M, (b) 0.1 M, (c) 0.01 M, (d) 0.001 M.

highly developed interfacial film composed of mainly Cr_2O_3 containing CrO_3 , in solid solution of a glassy phase was formed.

The breakdown potential (E_b) shifted in the noble direction in the transpassive region as the acid concentration increased in methanol (Fig. 1). The observed rapid increase in current at the said potential is not due to oxygen evolution but it may be due to the reactivation of the surface. A careful examination of the surface of the test electrode in this potential region revealed localized damage of the surface in the form of pitting.

In order to determine the pitting potential more accurately some additional experiments were performed in the passive region up to the breakdown potential; current-time at various constant applied potential in the passive region was studied. The potential was successively increased in steps and corresponding $i-t$ plots are shown in Fig. 2. The current initially decreases sharply with respect to the time and after a certain time (t_i , induction time) it increases sharply at constant potential. The rapid increase in current, at applied potential, can be assigned to the nucleation of the pits; this is characterized as the pitting potential (E_{pn}). Microscopic examination clearly revealed the existence of the pits on the surface. The extent of attack in terms of pitting intensity increased linearly with the concentration of H_2SO_4 . A previous study [35] also found sulphate aggressiveness towards carbon steel in alcohol- H_2SO_4 solution.

To investigate the kinetics of pitting some effort has been made to derive more information from $i-t$ transients. The plots of $(I - I_p)$ against $(t - t_i)$ at different constant potentials show a linear nature (Fig. 3)

and the current related to pitting fits the following equation given by Engell and Stolica [36]

$$(I - I_p) = K(t - t_i)^b$$

where I_p is the background current, t_i the induction time, K and b are constants. The value of b is found to lie between 1.2 and 1.8 in our case. The above equation also predicts the exponent b slightly greater than unity. Thus the overall current can be assigned to the pitting in the present study.

Fig. 4 illustrates that the induction time decreases as the applied potential is made more noble. Such a relationship of induction time with applied potential has earlier been observed by other investigators [37-39].

In the present case the early stage of pitting should be associated with the induction time, resulting from $i-t$ transients, and can be attributed to the adsorption and initiation process preceding pit nucleation. The adsorption of anions (perhaps SO_4^{2-}) should promote the electro-dissolution of the passive film to create sites for localized attack on the metal.

The dependence of the induction time (t_i) on applied potential (E) is given by the equation [40]

$$\log t_i/t_0 = K'(E - E_b)^{-1}$$

where E_b is the breakdown potential, taken from the $i-t$ curves; t_0 and K' are constants. This equation is satisfactorily obeyed in the present studies (Fig. 5) and provides a clue that the primary step in the pitting of stainless steel 316, corresponds to the local accumulation of the aggressive species at the corrosion sites. However, in solutions having lower concentrations of acid (0.01 and 0.001 M), the aggressive action is

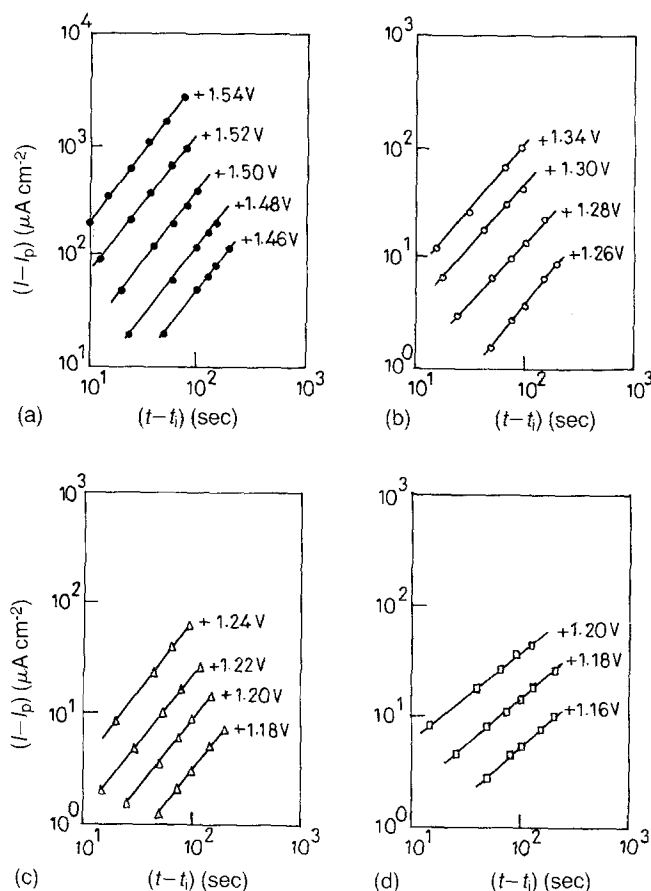


Figure 3 Log $(I - I_p)$ against log $(t - t_i)$ plots for AISI 316 in methanol containing H_2SO_4 : (a) 1 M, (b) 0.1 M, (c) 0.01 M, (d) 0.001 M.

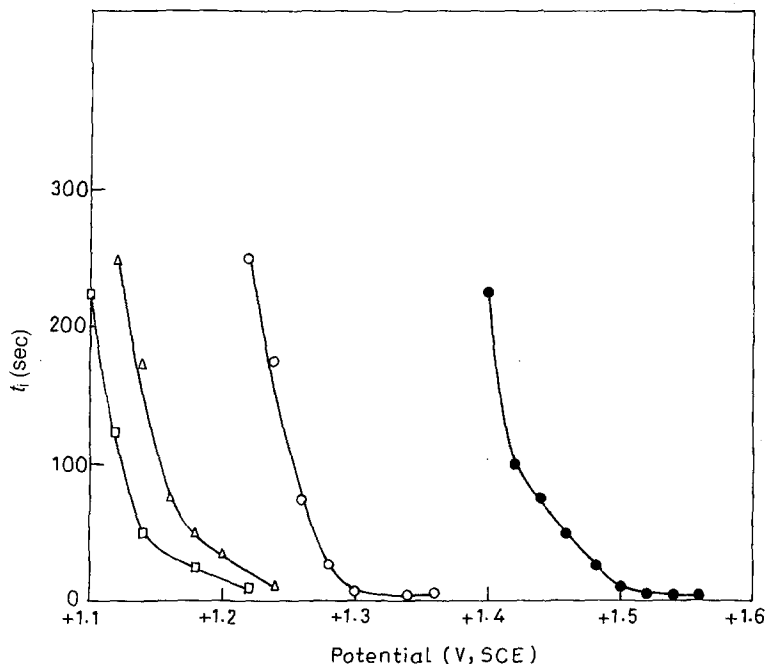


Figure 4 Induction time (t_i) against E plots for AISI 316 SS in methanol H_2SO_4 solution mixtures. (●) 1.0 M, (○) 0.1 M, (△) 0.01 M, (□) 0.001 M.

probably not intense enough, as $(E - E_b)^{-1}$ deviates from $[(E - E_b)^{-1} = 0]$. It is also evident from the microscopic observations because only etch-type pits are formed at this particular concentration of H_2SO_4 in methanol.

The SEM examination of the experimental stainless steel 316 reveals that the intensity of pitting is greater in higher concentrations of acid. It can be seen (Fig. 6) that the corrosion products are soluble within the pits and the surface assumes a nature similar to that

accompanying electropolishing. Some hexangular pits are formed (indicated by arrow (c)).

For studies of repassivation in stainless steel 316 (after determining the pitting potential by $i-t$ experiments), the potential was quickly brought back to the initial potential in the passive region (up to +100 mV value) and the test electrode held at this potential for some time. Similar experiments were performed again at the same constant potentials for $i-t$ and the plots are depicted by the dashed line in Fig. 2. Although the

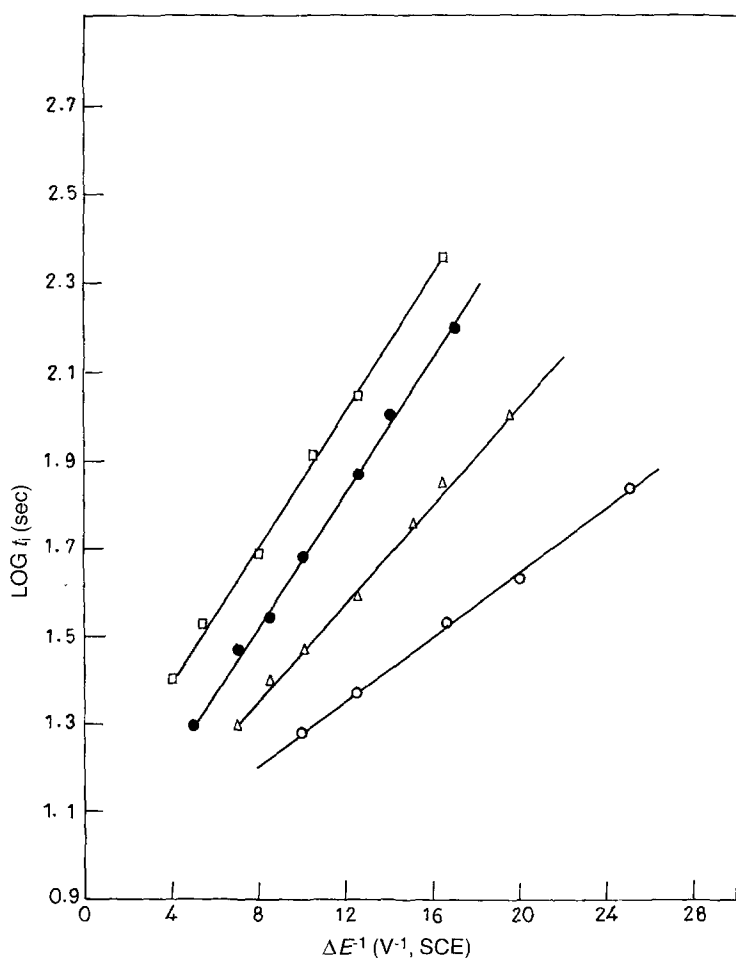


Figure 5 $\text{Log } t_i$ against $(E - E_b)^{-1}$ plots for AISI 316 SS in methanol- H_2SO_4 solution mixtures. (●) 1.0 M, (○) 0.1 M, (△) 0.01 M, (□) 0.001 M.

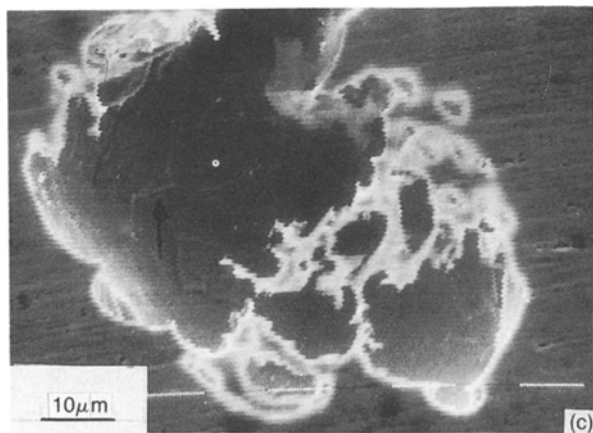
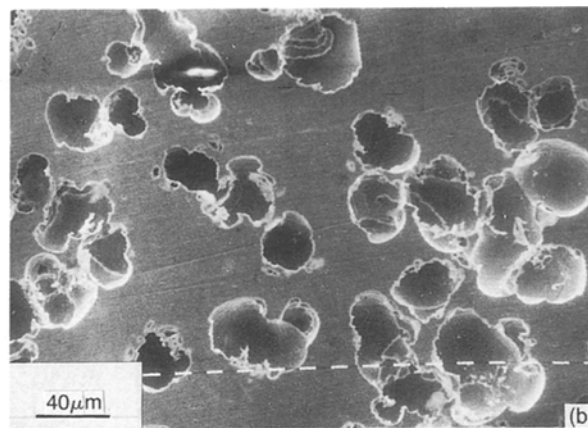
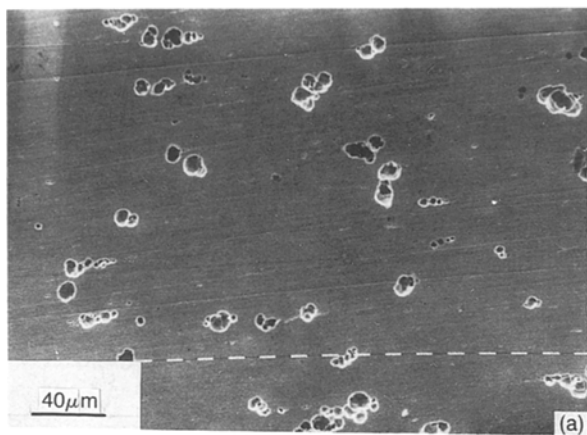


Figure 6 Scanning electron micrographs of AISI 316 in methanol containing (a) 0.01 M H_2SO_4 , (b) 1 M H_2SO_4 , (c) 1 M H_2SO_4 .

nature of the curves in both cases is found to be almost identical at each chosen potential, the magnitude of the current is always found to be lower during the course of repeated polarization. This clearly shows that the surface is following repassivation. The lower value of current obtained at each potential suggests the repair of the film leading to more protective film

formation. Once the repassivation of the surface is inferred, cyclic anodic polarization experiments were performed to determine the protection potential (E_{pr}). The protection potential is found to be less noble than the pitting potential and also it depends on the scan rate and concentration of acid in methanol (Fig. 7, Table I).

It has been observed that stainless steel 316 shows the most noble pitting potential and offers a wider passive range in comparison to the other stainless steels [15–17] at each concentration of H_2SO_4 in methanol. It is noted that such characteristics are due to the marked improvement in the corrosion resistance to pitting, mainly because of the presence of a small amount of molybdenum in the base stainless steels. It seems that some changes in the film composition or structure have taken place which either reduce the likelihood of the passive film breakdown or

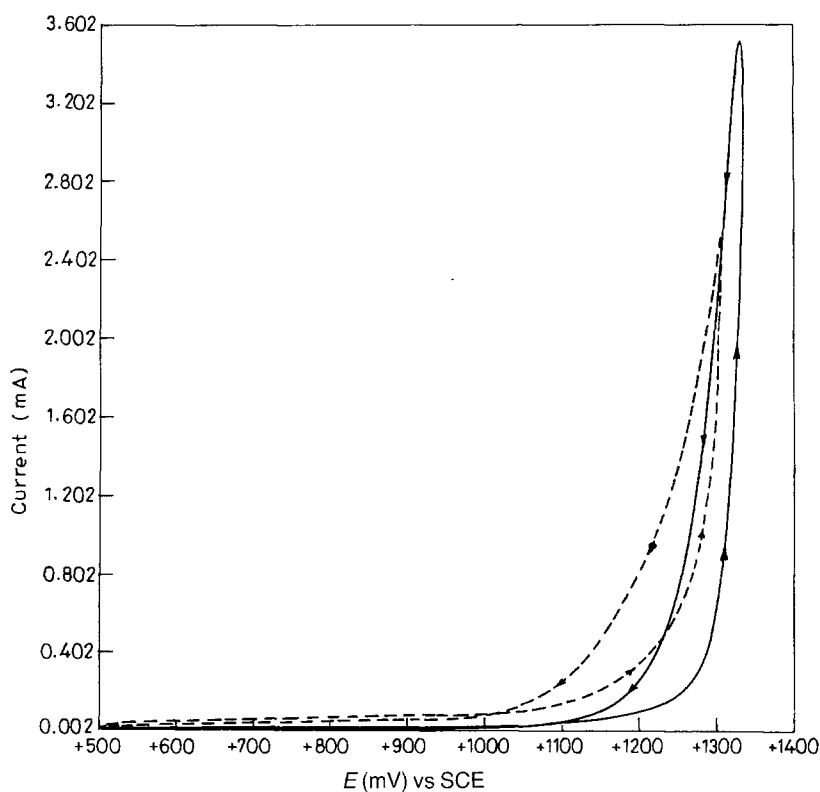


Figure 7 Typical cyclic anodic polarization curve for AISI 316 in methanol-1.0 M H_2SO_4 . Scan rate: (—) 0.5, (---) 5.0 $mV\ sec^{-1}$.

enhance the repassivation at the incipient pit sites. Several explanations [41–43] have been given for the noted improvement in corrosion resistance due to the molybdenum addition in stainless steels. Marshall and Burstein [42] noted the enhanced corrosion resistance of stainless steel containing molybdenum arising from the accelerated production of chromium-rich film, while some other workers [43] thought it was due to molybdenum dissolution from the oxide film followed by the adsorption of molybdate species on to the surface. It has also been suggested [39] that either molybdenum inhibits the formation of the critical nuclei or it slows down the reaction of aggressive ions with the passive films and also it makes difficult for the critical aggressive nuclei to form in the presence of molybdenum.

4. Conclusion

The electrochemical studies of the corrosion behaviour of AISI 316 stainless steel in H₂SO₄–methanol solution mixtures show an interesting active passive and pitting nature which is influenced by the concentration of H₂SO₄ in methanol. The existing water in the solution mixtures offer conducive conditions for the formation of a protective and stable passive film. The molybdenum appears to play a significant role in rendering more corrosion resistance to the stainless steel in this medium. The most probable cause of pitting is due to the participation of H₂SO₄ and is evident by the study of kinetics of pitting. Owing to the repassivation, the surface of the steel becomes more protective.

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