

# Electrochemical behaviour of AISI 321 stainless steel in methanol-H<sub>2</sub>SO<sub>4</sub> mixtures

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The electrochemical corrosion behaviour (passivity, pitting and repassivation) of austenitic stainless steel AISI 321 containing titanium has been investigated in methanol containing different concentrations of sulphuric acid (0.001-1 M). The cathodic reaction is observed to be hydrogen evolution. Anodic polarization of the stainless steel reveals a characteristic 'cathodic loop' in methanol with higher concentrations of H<sub>2</sub>SO<sub>4</sub> (0.1 M and 1 M). A clear and stable passivity is also observed in each solution mixture which breaks down at higher potentials due to pitting. The passivation current, passivity range, pitting intensity and pitting potential are found to vary with variation of acid concentration in the methanol. The kinetics of pitting and the morphology of the pits have been studied. A variation in concentration of acid and scan rate has been found to influence the protection potential of the stainless steel.

## 1. Introduction

The corrosion behaviour of metals and alloys in organic solvents has received much attention in the recent past and interesting behaviour is reported in the literature [1-15]. This communication is a part of our programme of investigation of the corrosion behaviour of austenitic stainless steels in different organic solvents, particularly in alcohols containing mineral acids. Our previous [14] studies with some stainless steels (AISI 302, 304, 347) in methanol, ethanol, isopropanol and *t*-butanol containing varying concentrations of H<sub>2</sub>SO<sub>4</sub> showed interesting results. The alloying elements (Mo, Ti or Nb) may also influence the corrosion behaviour of stainless steel in methanol-H<sub>2</sub>SO<sub>4</sub> mixtures. It is intended to investigate the influence of trace amounts of titanium (as an alloying element) in stainless steel on its corrosion in alcohol-H<sub>2</sub>SO<sub>4</sub> mixtures.

The present paper deals with the studies of corrosion, passivity, pitting and repassivation of stainless steel AISI 321 in deaerated methanol-H<sub>2</sub>SO<sub>4</sub> solution mixtures at 30 ± 1°C.

## 2. Experimental details

The experimental set up, working procedures and preparation of the solutions and specimen are the same as described earlier [14, 15]. The test electrode of AISI 321 SS, with chemical composition 18Cr-8Ni-1.8Mn-0.07C-0.28Ti of 2 cm<sup>2</sup> exposed surface area in conjunction with a platinum counter electrode and an SCE reference electrode were employed for the electrochemical studies. The experiments were per-

formed at 30 ± 1°C in deaerated methanol containing different concentrations (0.001-1 M) of H<sub>2</sub>SO<sub>4</sub> under still conditions. The potentials are reported against SCE after making corrections for *IR* drop.

## 3. Results and discussion

### 3.1. Polarization studies

The cathodic and the anodic polarization curves of AISI 321 SS in different mixtures of methanol-H<sub>2</sub>SO<sub>4</sub> are shown in Fig. 1a. The cathodic curves show an almost linear behaviour in solution mixtures containing higher concentrations (0.1 M and 1 M) of H<sub>2</sub>SO<sub>4</sub> in methanol while a limiting nature is observed in solutions having lower H<sub>2</sub>SO<sub>4</sub> concentrations (0.01, 0.001 M). The limiting nature is due to diffusion control of the reaction.

The observed cathodic Tafel slopes (*b<sub>c</sub>*) indicate that in each case the cathodic reaction is hydrogen evolution (Table 1). The present values of *b<sub>c</sub>* agree with the usually reported values for hydrogen evolution.

A cathodic loop, i.e. negative current was observed (Fig. 1b) during the early stage of the anodic polarization (starting from -260 and -220 mV) in the solutions having higher H<sub>2</sub>SO<sub>4</sub> concentrations (0.1 M, 1 M) in methanol. Such a cathodic loop within the anodic region has also been found earlier [16-22] and it has been considered as being due to metastable passivity [18, 19]. In the present case the loop is observed probably due to the reduction of residual oxygen in the solution as suggested earlier [14, 16, 20]. In the solutions containing lower concentrations of

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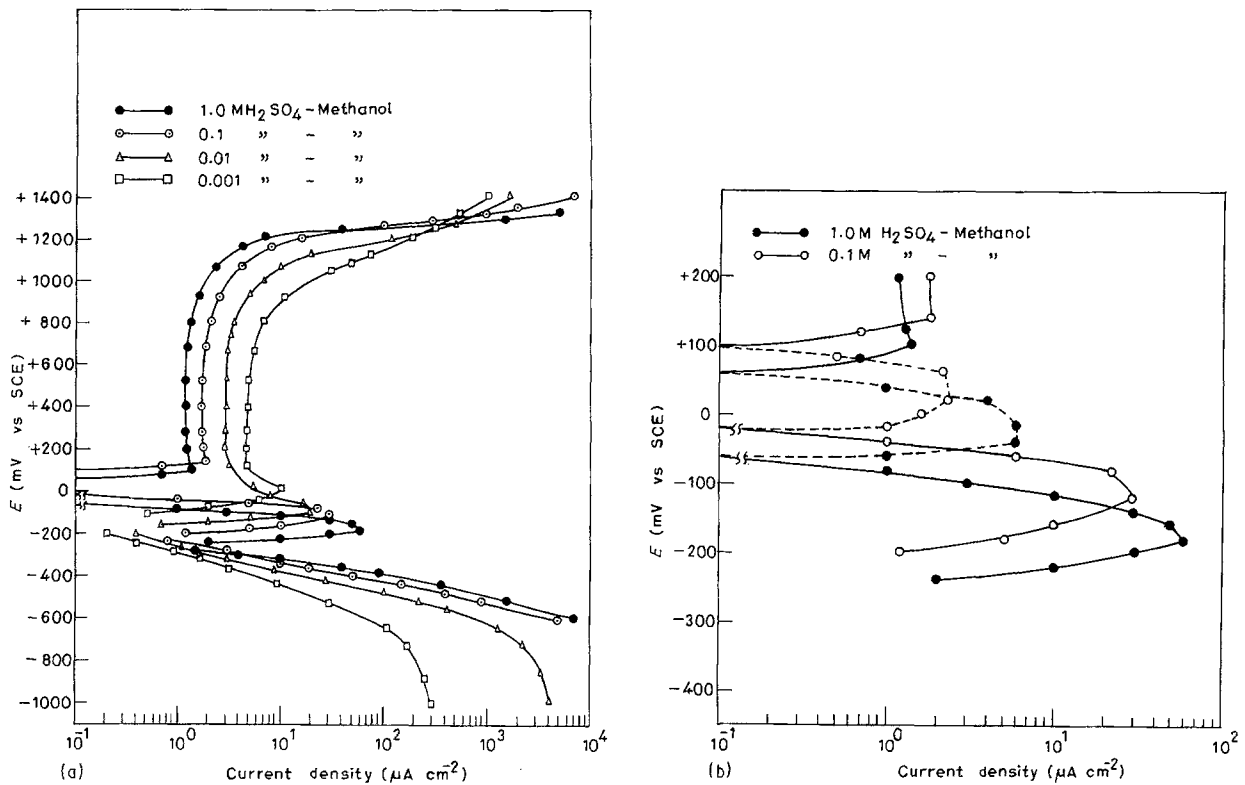


Fig. 1. (a) Cathodic and anodic polarization curves for AISI 321 SS in different concentrations of  $H_2SO_4$  (0.001–1 M) in methanol. (b) Anodic polarization curves for AISI 321 in solutions of  $H_2SO_4$  in methanol. --- represents the cathodic current.

acid (0.01, 0.001 M) in methanol, the surface of the stainless steel probably does not provide an oxide-free surface (due to low solubility in lower acid concentration) to facilitate the reduction of oxygen, as a result of which no such loop is observed in these solution mixtures.

It can be seen from Fig. 1a and Table 1 that the critical current density ( $i_c$ ), passivation current ( $i_p$ ), critical potential for passivity ( $E_c$ ) and the range of passivity are influenced by the variation of acid concentration in methanol. The anodic Tafel slope also varies with the concentration of acid. The  $b_a$  values resemble the usually reported values for active dissolution of metal in the active region. The range of passivity is enlarged as the concentration of  $H_2SO_4$  in methanol is increased and a wider range of passivity

has been offered by AISI 321 stainless steel than 302 SS, in methanol containing the same concentrations (0.001–1 M) of  $H_2SO_4$  [23]. An improvement in the passivation range and a substantial decrease in the passivation current for this stainless steel over 302 SS, in the solution mixture of methanol– $H_2SO_4$ , can be ascribed to the beneficial influence of titanium present in the stainless steel. The range of passivity increased with increase in  $H_2SO_4$  concentration. The important role played by water in passive film formation and/or breakdown can also be realized in the present case as has been emphasized earlier [2, 5–7, 9–12].

Reactivation of the surface of stainless steel can be inferred at above +1000 mV (Fig. 1a) in the solution mixtures. Above this potential, the current increased considerably even with slight increase in the potential. No gas evolution was apparent at this potential. A few pits appeared on the surface.

Table 1. Corrosion parameters of AISI 321 stainless steel in methanol– $H_2SO_4$  mixtures

	Concentration of $H_2SO_4$ in methanol			
	0.001 M	0.01 M	0.1 M	1.0 M
$E_{corr}$ (mV)	–120	–160	–220	–260
$i_c$ ( $\mu A cm^{-2}$ )	10	20	30	60
$i_p$ ( $\mu A cm^{-2}$ )	4.6	3.0	1.7	1.2
$E_c$ (mV)	+20	–100	–120	–140
$E_b$ (mV)	+1000	+1080	+1180	+1200
$b_a$ (mV dec <sup>-1</sup> I)	55	50	45	35
$b_c$ (mV dec <sup>-1</sup> I)	150	145	130	120
$E_p$ (0.5 mV s <sup>-1</sup> )	+1060	+1160	+1140	+1200
(5.0 mV s <sup>-1</sup> )	+940	+1020	+1080	+1120
$E_{pr}$ (0.5 mV s <sup>-1</sup> )	+820	+880	+940	+1020
(5.0 mV s <sup>-1</sup> )	+760	+820	+900	+960

### 3.2. Pitting potential

As pitting of the stainless steel has thus been inferred, a precise determination of the pitting potential was carried out by performing current vs time studies at various constant potentials applied between the passive region and transpassive region in each case (Fig. 2). It can be seen that the current decreases with increase in time when polarized within the passive region (Fig. 2). This clearly indicates the formation of a stable passive film in this region until the breakdown potential is approached. Microscopic examination of the specimens within the passive region revealed an absence of

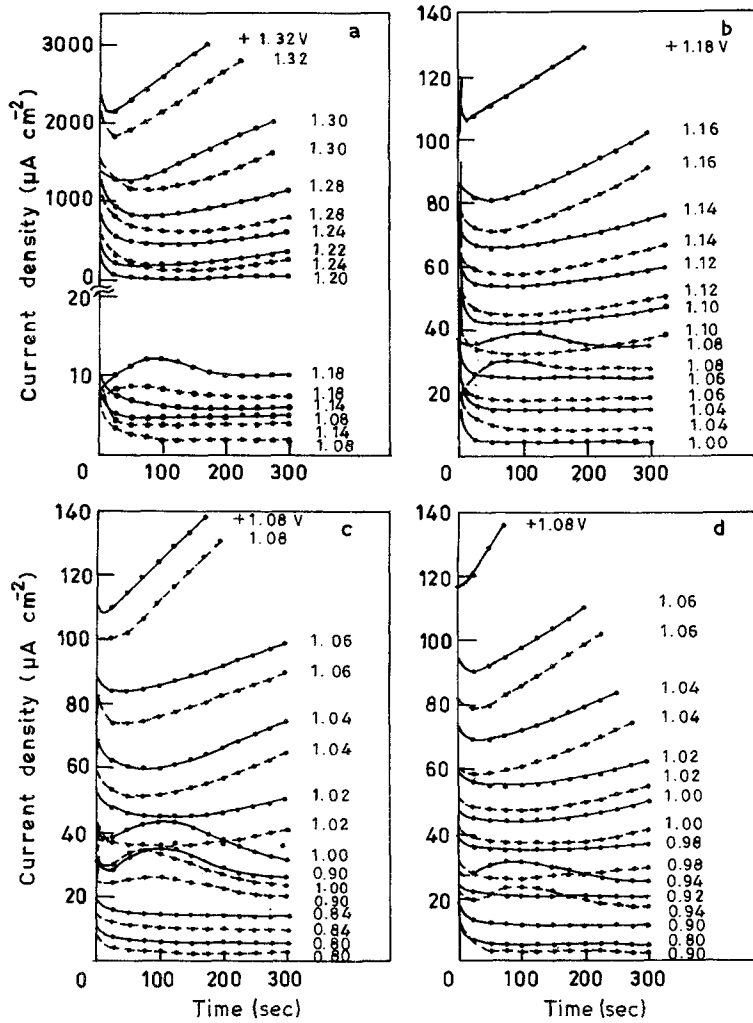


Fig. 2. *i* vs *t* transients for AISI 321 in different concentrations of H<sub>2</sub>SO<sub>4</sub>: (a) 1; (b) 0.1; (c) 0.01; (d) 0.001 M in methanol.

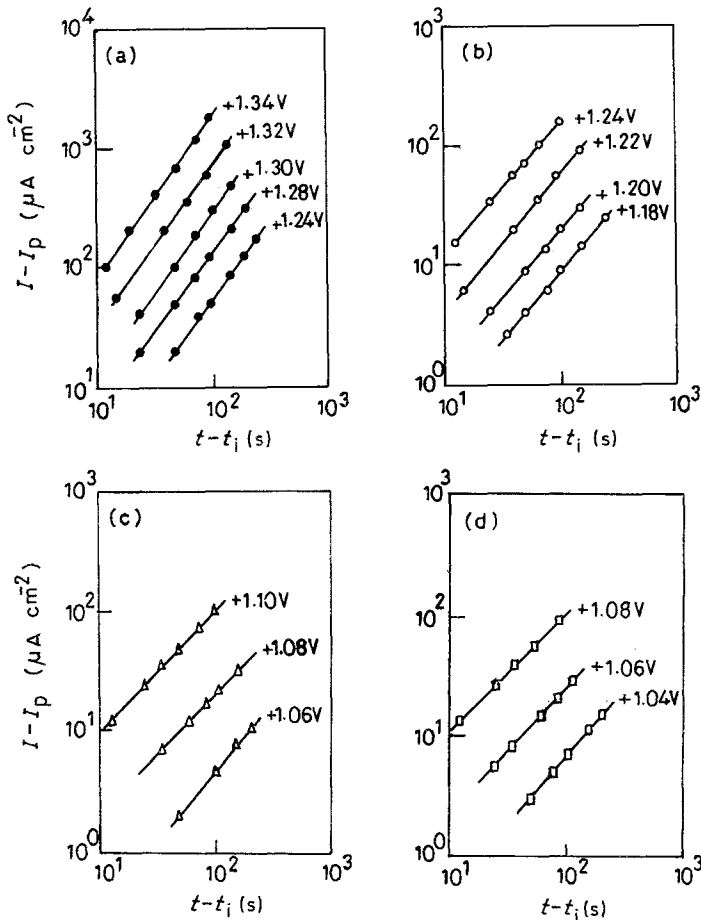


Fig. 3.  $\log(I - I_p)$  vs  $\log(t - t_i)$  plots for the transients recorded in different concentrations of H<sub>2</sub>SO<sub>4</sub>: (a) 1; (b) 0.1; (c) 0.01; (d) 0.001 M in methanol.

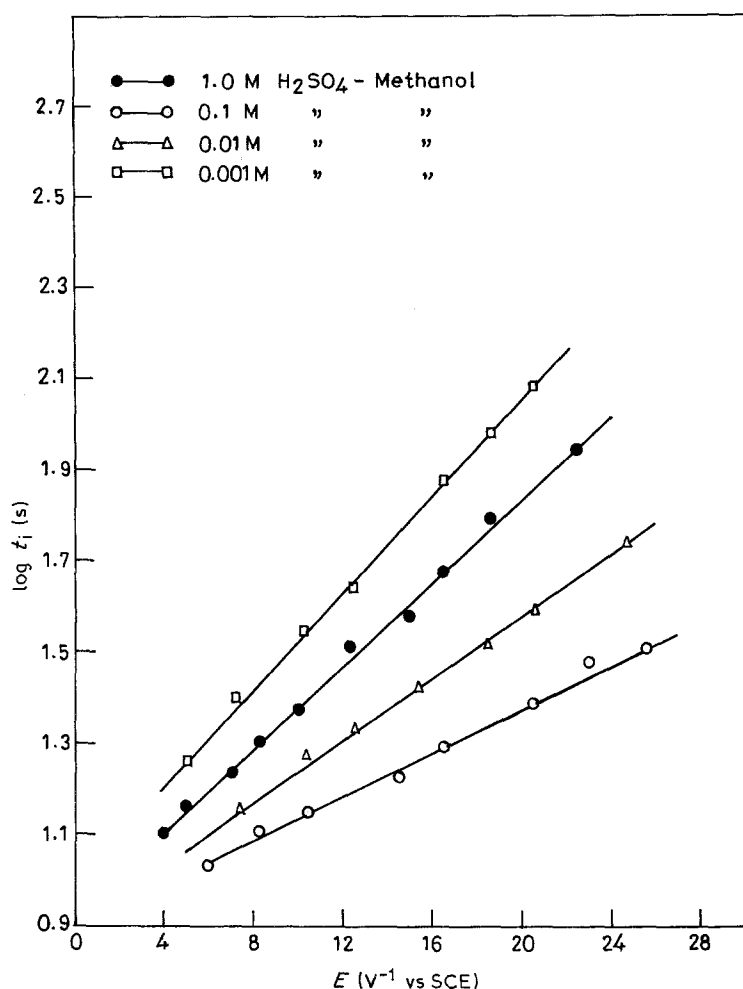


Fig. 4.  $t_i$  vs  $E$  plot in different concentrations of  $H_2SO_4$  (0.001–1 M) in methanol.

pits. It is seen from Fig 2 that at the breakdown potential, the current initially increased sharply and then decreased slightly for a while and ultimately became constant after some time in each solution. Such a trend of variation of current with respect to time in the vicinity of the breakdown potential suggests that there is competition between pit initiation and repair of the passive film. At potentials slightly nobler than the breakdown potential, the current initially decreased slightly and, after a certain time ( $t_i$ , the

induction time), increased rapidly. At this potential clear pits were formed. The pitting potential ( $E_p$ ) thus obtained was seen to shift in the noble direction as the concentration of acid in methanol increased (Table 1). It is worth noting that the pitting potential was always found to be nobler than that of AISI 302 under similar experimental conditions and in the same solution [23].

The value of  $b$ , derived from the plots of  $\log(I - I_p)$  vs  $\log(t - t_i)$  based on the Engell and

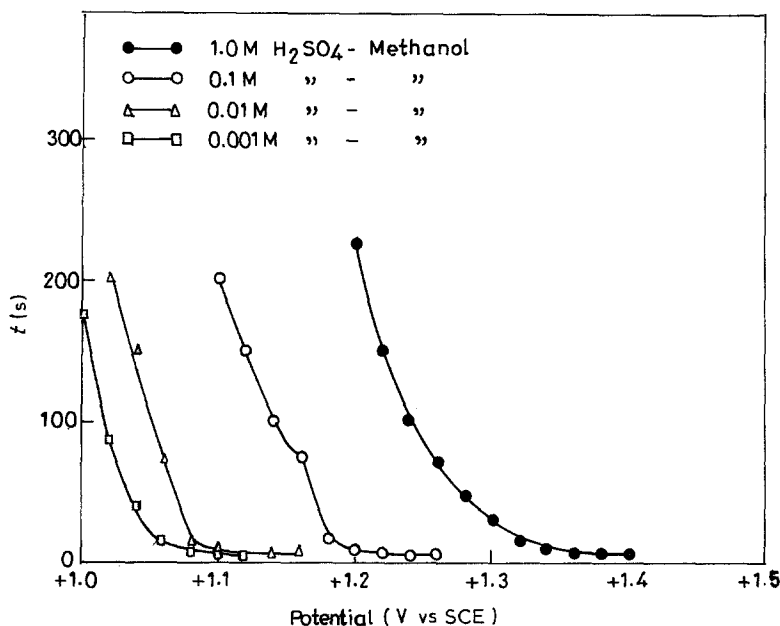


Fig. 5.  $\log t_i$  vs  $(E - E_b)^{-1}$  plot in different concentrations of  $H_2SO_4$  (0.001–1 M) in methanol.

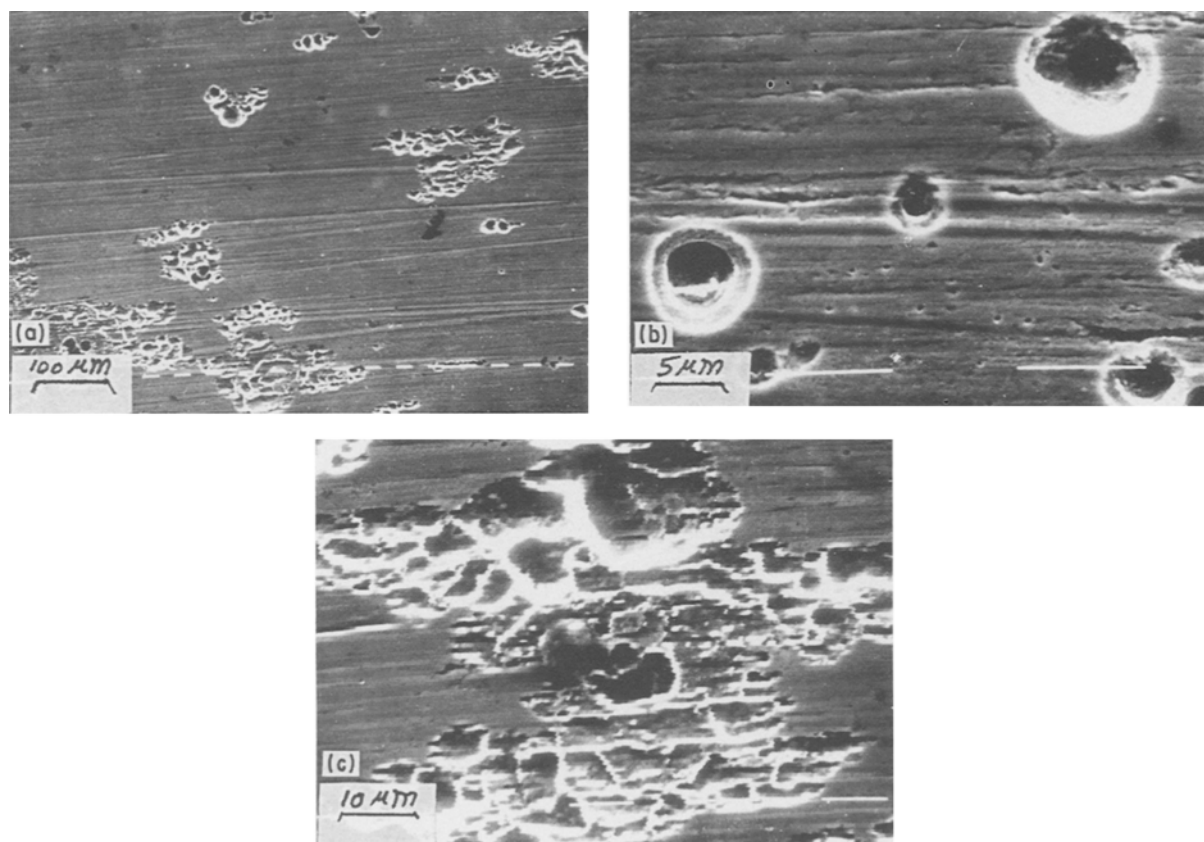


Fig. 6. SEM micrographs showing pitting of AISI 321 in different concentrations of H<sub>2</sub>SO<sub>4</sub> in methanol: (a) 0.01; (b) 0.01; (c) 1 M.

Stolica [24] equation

$$(I - I_p) = K(t - t_i)^b \quad (1)$$

was found to lie between 1.2 and 1.8 in each solution mixture of methanol-H<sub>2</sub>SO<sub>4</sub> (Fig. 3). It is seen that the above equation holds well in the present case and relates the current to the occurrence of pitting only. The values of  $b$  suggest that the overall current should be assigned only to pitting. The present results are similar to the observations of several other workers [25–28]. The induction time is found to decrease as the applied potential is made more anodic than the breakdown potential (Fig. 4). The following equation [29]

$$\log t_i/t_0 = K'(E - E_b)^{-1} \quad (2)$$

relates  $t_i$  to the applied potential ( $E$ ) and is fully obeyed in the present case. The plot of  $\log t_i$  vs  $\Delta E^{-1}$  (Fig. 5) for the AISI 321 SS in each solution clearly satisfied the primary condition for the initiation of pits due to accumulation of aggressive species at the corrosion sites on the passive film.

The surface examination by SEM clearly revealed grown pits on the surface. These are scattered and circular (Fig. 6). Sometimes many micropits join together and are partially covered with insoluble corrosion products (Fig. 6c). The pitting intensity is maximum in the solution containing higher acid concentrations.

### 3.3. Repassivation

To further explore repassivation and repair of the pits,

the potential was brought abruptly back to a definite potential in the passive region and the same specimen was subjected to repeated polarization at various constant applied potentials between the passive region and the breakdown potential and again  $i$  vs  $t$  transients were recorded at the same respective potentials as applied earlier (shown by dashed line, Fig. 2). It may be observed (Fig. 2a–d) that under repeated polarization, the current is always lower in magnitude at each chosen potential and usually the nature of the curve is similar. This indicates that the surface has undergone repassivation.

Since the surface of the stainless steel appeared to have undergone repassivation, the protection potential was determined by applying cyclic anodic polarization (Fig. 7). The protection potential was found to be nobler in each case and to depend on the scan rate and acid concentration in methanol (Table 1). The protection potential confirmed the repassivation of the surface and also the formation of a more protective layer.

The present results have shown that AISI 321 SS is more corrosion resistant than AISI 302 SS under similar experimental conditions in methanol-H<sub>2</sub>SO<sub>4</sub> mixtures. The most likely reason for the improvement in the localized corrosion resistance appears to be the presence of titanium as an element in the solid solution, which assists the formation of a highly resistive passive film and delays the formation of M<sub>23</sub>C<sub>6</sub> carbide by its higher carbide-forming tendency. It has been reported [30] that titanium improves the pitting corrosion resistance of the stabilized steels,

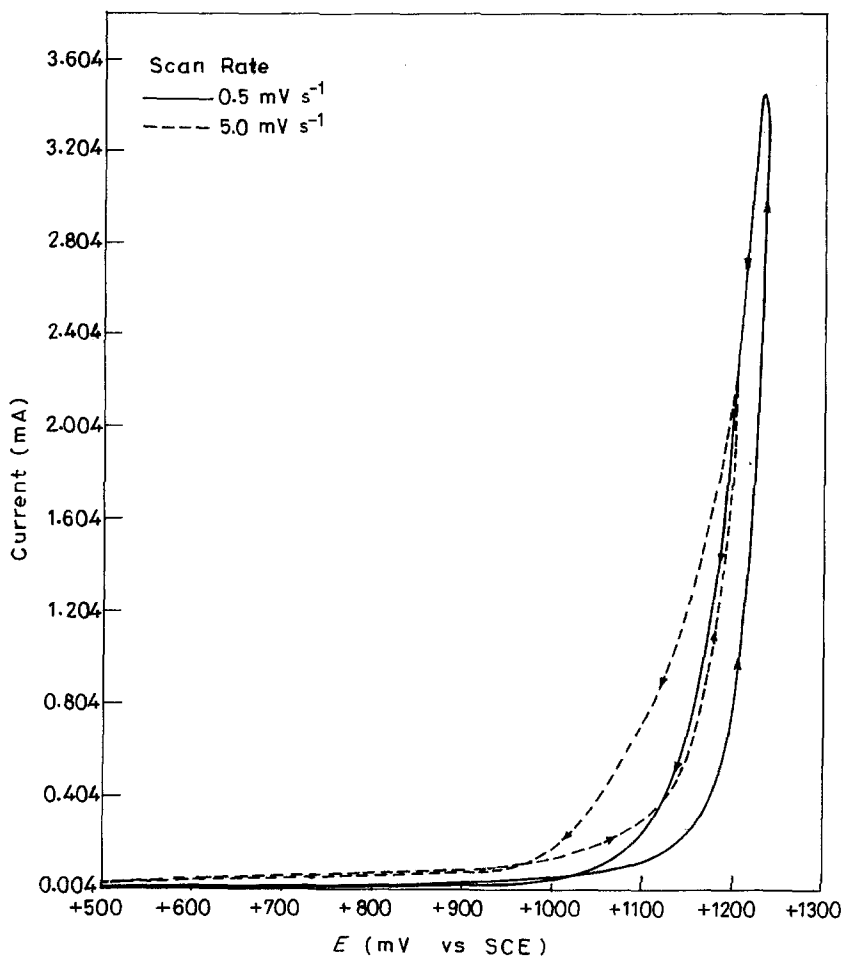


Fig. 7. Typical cyclic anodic polarization curve of AISI 321 in methanol-1 M H<sub>2</sub>SO<sub>4</sub> mixture.

where Ti is partially present in solid solution. It seems that Ti may be playing a more prominent role in stabilizing the passive film to improve the pitting corrosion resistance. On anodic polarization, titanium may also dissolve along with the other constituents of the stainless steel and may enter the Cr-rich mixed oxide passive film. In general the passive films of the stainless steels have a high defect density. The presence of Ti in the passive film may reduce the defect concentration by occupying the vacant sites.

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