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**A STUDY ON THE ELECTROCHEMICAL BEHAVIOUR OF 416  
AND 440C MARTENSITIC STAINLESS STEELS IN ALCOHOLS**

دراسة السلوك الكهروكيميائي للصلب ٤١٦، ٤٤٠، المارتينسيطي المقاوم للتآكل في الكحوليات

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تم في هذا البحث دراسة السلوك الكهروكيميائي للصلب ٤١٦، ٤٤٠ المارتينسيطي المقاوم للتآكل في محاليل من الكحوليات (إيثانول - إيزوبروبانول، بيثانول، والتي تحتوي على نسب مختلفه من حامض الكبريتيك (1 to 2M) بواسطة منحنيات الاستقطاب الأتودي - الكاثودي. لقد لوحظ من منحنيات الاستقطاب وجود السلوك الفعال - الخامل وكذلك مقاومه للتآكل تعتمد على تركيز الحامض في الكحوليات . كما تم دراسة تأثير إضافة الماء بنسب مختلفه (٥، ١٠، ١٥٪) إلى حامض كبريتيك (1M) - كحول على السلوك الكهروكيميائي للصلب. لقد وجد أن إضافة الماء المقطر يؤثر تأثيرا كبيرا على حاله الخامله (Pssivation) للصلب ٤١٦ وكذلك ٤٤٠.

المدخلات :

مارتينسيطي ، مقاوم للتآكل ، صلب ، كهروكيميائي ، كحول ، حامض كبريتيك، تآكل ، أتودي ، إستقطات ، فرق الجهد ، ماء ، كاثودي ، خامل ، تركيز .

**ABSTRACT**

The electrochemical behaviour of AISI 416 and 440 martensitic stainless steel in alcoholic solutions (ethanol, iso-propanol and t-butanol) containing different concentrations of sulfuric acid (0.1 to 2M) has been investigated using potentiostatic anodic-cathodic polarization techniques.

An activ- passive transition behaviour were observed and the critical current density (CD) for passivity was found to be dependent on the concentration of acid in alcohols.

The effect of water additions (5, 10, 15%) to 1M H<sub>2</sub>SO<sub>4</sub> alcohols has been also investigated. It was found that the presence of water strongly influences the passivation of both steels in 1M H<sub>2</sub>SO<sub>4</sub> - alcoholic solutions.

**Key Words**

Martensitic, Stainless, Steel, Electrochemical, Alcohol, Sulfuric acid, Corrosion, Potentiostatic, anodic, polarization, potential, current, Water, Cathodic, Passivity, Concentration.

**Introduction : -**

There is an increasing interest on the corrosion of metals and alloys in non-aqueous solvents (1) because of the newly developing electrochemical energy sources. Apart from this, the corrosion processes in organic solvents are different from those in aqueous media. This is not only caused by the different electric and bond interaction between the metal and the solvents, but is also because of the physicochemical properties of the solvent itself i.e., its dielectric constant, the dissociation equilibrium, and the solubility of reactants and products of the corrosion reaction. The electrochemical investigations have been reported in methanolic solution containing inorganic acid (HCl or H<sub>2</sub>SO<sub>4</sub> or a mixture of both) and the conducting salts (2-4). The role of water on the passivity and the passivity break down has been examined in methanol + HCl or H<sub>2</sub>SO<sub>4</sub> system (5,7).

Potentiodynamic studies have shown that the presence of water, even at a low concentration, strongly influences the passivation of iron and AISI 3.4L stainless steel (SS) in protic alcoholic solution(8).

Tajima et al (9) studied the anodic behaviour of types 304 and 430 stainless steels in solutions of various organic acids in methanol and found that pitting occurred in methanolic solutions of tartaric, malic, lactic, and acetic acid, but not in formic and benzoic acids. Therefore this programme has been developed to study the corrosion and problems associated with non-aqueous solvents.

**Experimental :**

Experiments were conducted using cubes of AISI 416 and 440. Martensitic stainless steels solution annealed at 1100°C for 2hrs. followed by oil quenching, the chemical compositions are as follows.

Steel	C	Mn	P	S	Si	Cr	Mo
416	0.15	1.25	0.06	0.15	1	12-14	0.6
440c	1	0.44	0.015	0.012	0.27	16.91	0.45

The test electrode with an area of 1 cm<sup>2</sup> was mechanically polished and then was sequentially finished using 1/0 - 2/0-3/0 and 4/0 grade emery papers. Then, the electrode was dipped in a detergent which saponified the particulate material sticking to the surface and the edges. The electrode was then rinsed in flowing water and degreased in acetone. After washing with redistilled water, the electrode was pickled for a while to ensure the removal of any residual oxide. The solutions were prepared with H<sub>2</sub>SO<sub>4</sub>

and dried distilled ethanol, iso-propanol, and T-butanol. The solutions was deaerated with purified nitrogen for 2 hrs. The corrosion studies were conducted potentiostatically (Potentiostatic Wenking pos 73).

The experiments have been conducted in a three- necked assembly, in which platinum counter electrode of area  $1\text{cm}^2$  was placed 3 cm away from the working electrode. The reference electrode was saturated calomel electrode.

The potentiostatic tests were carried out by recording current densities at various constant values of applied potentials by quasi-stationary anodic polarization technique.

### **Results and Discussion .**

The corrosion potential ( $E_{\text{corr}}$ ) of 440 and 416 (MSS) in deaerated solution tends towards a more negative potential as the concentration of  $\text{H}_2\text{SO}_4$  increased in ethanol and iso-propanol (Tables 1,2) .

The shift in the corrosion potential may be explained in terms of the dissolution of air-formed oxide that is believed to be formed at the time of immersion of the test specimen in the solution.

The dissolution of oxide is favored more and more as the acid concentration is increased in ethanol and iso-propanol solutions and the resulting surface assumes a more negative corrosion potential value and a more current density (Fig 1, 2, 3) .

1- The cathodic polarization curves (figures 1, 2, 3, 4, 5, 6, 7) reveal that these are fairly linear up to - 800 mv. The cathodic curves for each solution mixture containing 0.1 to 2M  $\text{H}_2\text{SO}_4$  exhibited a limiting nature towards a more negative potential from - 800 mv, such limiting nature is found to be pronounced particularly in the low concentration of acid in all alcohols. Such a limiting current density (CD) can be attributed to the diffusion controlled phenomenon that is probably a result of the presence of a lower  $\text{H}_2\text{O}$  content in the solution with the lower acid concentration than in 2 and 1 M  $\text{H}_2\text{SO}_4$ . The cathodic polarization curves exhibited a well defined tafel region in ethanol, iso-propanol and T- butanol.

The cathodic polarization curves for 440 MSS (Fig 1, 2, 3) exhibited a well defined tafel region with the same average slope for the 0.1 M  $\text{H}_2\text{SO}_4$  - T- butanol, ethanol and isopropanol, also the same average slope for iso-propanol and ethanol with different  $\text{H}_2\text{SO}_4$  concentrations (0.1 to 2M).

The cathodic polarization curves for 416 MSS (Fig 4, 5, 6) exhibited also well defined tafel region with an average slope which did

not depend on the  $H_2SO_4$  concentration (Fig 5) but greatly depend on the type of alcohols at constant  $H_2SO_4$  content (0.1 M) (Fig 4) .

2- The anodic polarization curves for AISI 440 and 416 Mss. in deaerated ethanol, isopropanol and T- butanol containing different concentrations of  $H_2SO_4$  (0.1 to 2M) are shown in figures (1, 2, 3, 4, 5, 6, 7,) ..

### **2-a- Corrosion Characreristics of 440 MSS.**

The anodic polarization curves (Fig 1,2,3,) exhibited active - passive and transpassive features.

From table (1) it is observed that; the corrosion current ( $I_{corr}$ ), critical current ( $I_c$ ) and the passivation current ( $I_p$ ) increases with increasing the concentration of  $H_2SO_4$  in ethanol and isopropanol alcohols, also the passivation range affected by the change in acid concentration. This may result from the enhanced solubility of pre-existing oxide film and an increase of the metal dissolution with increasing acid concentration.

Also from the anodic polaritation curves (Fig. 1) and Table (1) we can detect that, the alcohol type at constant acid concentration has a significant effect on the corrosion characteristics of 440 MSS. it was found that, the corrosion current ( $I_{corr}$ ), critical current ( $I_c$ ) and passivation current ( $I_p$ ) in isopropanol alcohol are smaller than in T-butanol and ethanol respectively, which means that ethanol is a more corrosive solution than T-butanol and isopropanol alcohols respectively.

### **2-b. Corrosion characteristics of 416 MSS:**

The anodic polaritation curves (Fig. 4,5,6) for 416 MSS exhibited active-passive features. From table (2), it is observed that, the corrosion characteristics of 416 MSS in alcohols affected by the type of alcohol and the acid concentration in alcohols such as 440 MSS.

From Fig. (7) and Tables (1,2) we can found that, the corrosion current ( $I_{corr}$ ) for 440 MSS in 2M  $H_2SO_4$ -isopropanol solution is  $0.12 mA/Cm^2$  and the passivation rang from 400 to 1200 mV/SCE while for 416 MSS the corrosion current is  $0.05 mA/Cm^2$  and the passivation range from 100 to 1600 mV/SCE.

This means that 416 MSS is more resist to corrosion attack in alcohols than 440 MSS.

Mazza, et al (10) have discussed the role of water on the stability of the passive film of iron and steel fomed in deaerated, fairly acidic methanolic solution and have reported on the maximum beneficial effect with a water centent 0.5 to 1.5% ; beyond this range ; it resulted in

an unstable poorly protective film. It is understood that for each alcohols containing a higher concentration of acid, the existing water content in the solution is sufficient enough to provide the condition for the stable passive film formation on the studied specimen.

In the present work , fig (8) shows the anodic polarization curves for 440 Mss in 1M H<sub>2</sub>SO<sub>4</sub> - ethanol+ different percentages of dist. water (5 to 15%) . It was found that the presence of water with percentages 5 to 15% have an important effect on the stability of protective film. Also increasing the water content to 15% resulted in an unstable poorly protective film.

### **Conclusion**

- 1- The corrosion characteristics of 440 MSS and 416 MSS depend on the type of alcohols and the concentration of H<sub>2</sub>SO<sub>4</sub> in alcohols.
- 2- 416 Mss have better corrosion resistance in alcohols with different concentrations of H<sub>2</sub>SO<sub>4</sub> than 440 Mss.
- 3- The addition of dist. water by percentages ranged from 5 to 15% to alcohols with certain percentage of H<sub>2</sub>SO<sub>4</sub> resulted in an unstable poorly protective film.

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**Table(1): Corrosion characteristics of AISI 440 MSS in different concentrations of  $H_2SO_4$  - alcohols from cathodic and anodic polarization curves.**

Solution	Corrosion potential $E_{corr}$ , mV/SCE	$I_c$ mA/Cm <sup>2</sup>	$I_p$ mA/Cm <sup>2</sup>	$I_{corr}$ mA/Cm <sup>2</sup>	$E_p$ mV/SCE	passivation rang, mV/SCE
0.1 M $H_2SO_4$ - ethanol	-200	-	$3.84 \times 10^{-3}$	0.013	000	000 to 1200
1 M $H_2SO_4$ - ethanol	-330	$6.9 \times 10^{-2}$	$7.69 \times 10^{-3}$	0.15	200	200 to 1000
2 M $H_2SO_4$ - ethanol	-340	14	$25 \times 10^{-2}$	0.4	-150	-150 to 1000
0.1M $H_2SO_4$ - isopropanol	330	-	$2 \times 10^{-3}$	$1.6 \times 10^{-4}$	-200	-200 to 1600
1M $H_2SO_4$ - isopropanol	-270	$6.5 \times 10^{-3}$	$3 \times 10^{-2}$	$3 \times 10^{-2}$	400	400 to 1300
2 M $H_2SO_4$ - isopropanol	-260	$2.3 \times 10^{-2}$	0.01	0.12	400	-400 to 1200
0.1 M $H_2SO_4$ - T- butanol	-210	-	$3.84 \times 10^{-3}$	0.008	000	000 to 1400

**Table (2): Corrosion characteristics of AISI 416 MSS in different concentrations of  $H_2SO_4$  - alcohols from cathodic and anodic polarization curves.**

Solution	Corrosion potential $E_{corr}$ , mV/SCE	$I_p$ mA/Cm <sup>2</sup>	$I_{corr}$ mA/Cm <sup>2</sup>	passivation rang, mV/SCE
0.1 M $H_2SO_4$ - butanol	-100	0.002	0.003	100 to 1600
0.1 M $H_2SO_4$ - ethanol	-330	0.001	0.035	100 to 1600
0.01 M $H_2SO_4$ - isopropanol	100	0.004	0.003	1000 to 1600
1M $H_2SO_4$ - isopropanol	-100	0.04	0.007	100 to 1600
2 M $H_2SO_4$ - isopropanol	-200	0.06	0.05	100 to 1600

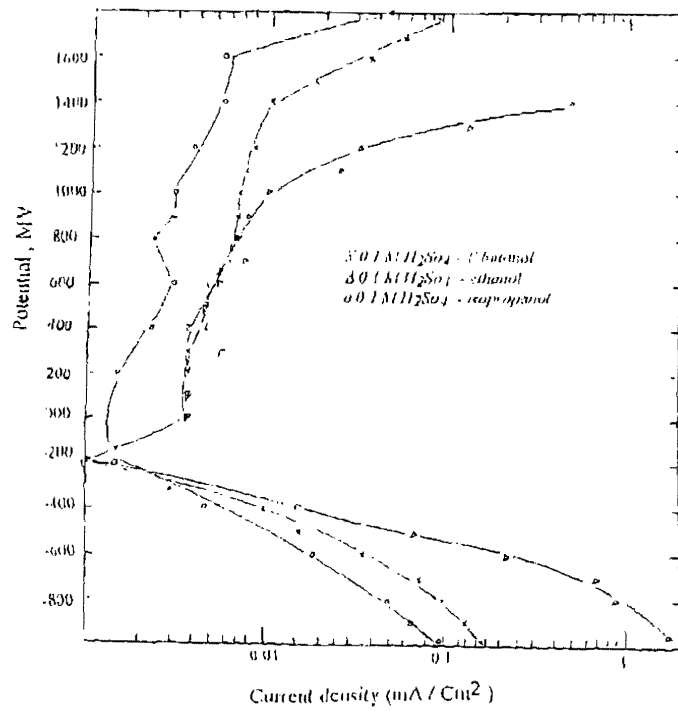
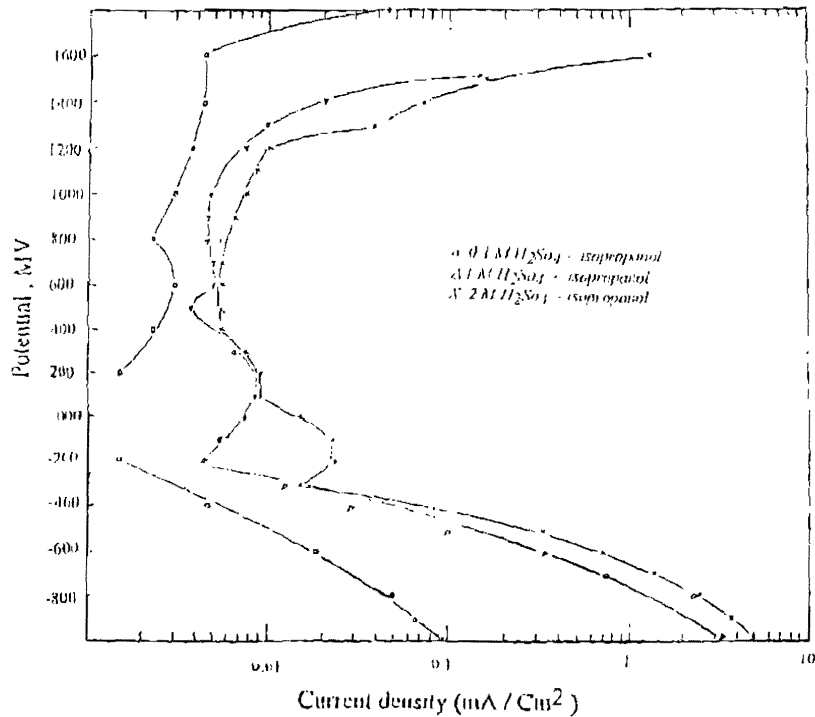


Fig ( 1) Cathodic and anodic polarization curves of AISI 440 stainless steel in deaerated H<sub>2</sub>SO<sub>4</sub> (0.1M) + F-butanol, ethanol and isopropanol solutions.



Fig(2) Cathodic and anodic polarization curves of AISI 440 stainless steel in deaerated H<sub>2</sub>SO<sub>4</sub> (0.1 to 2M) + isopropanol solutions.



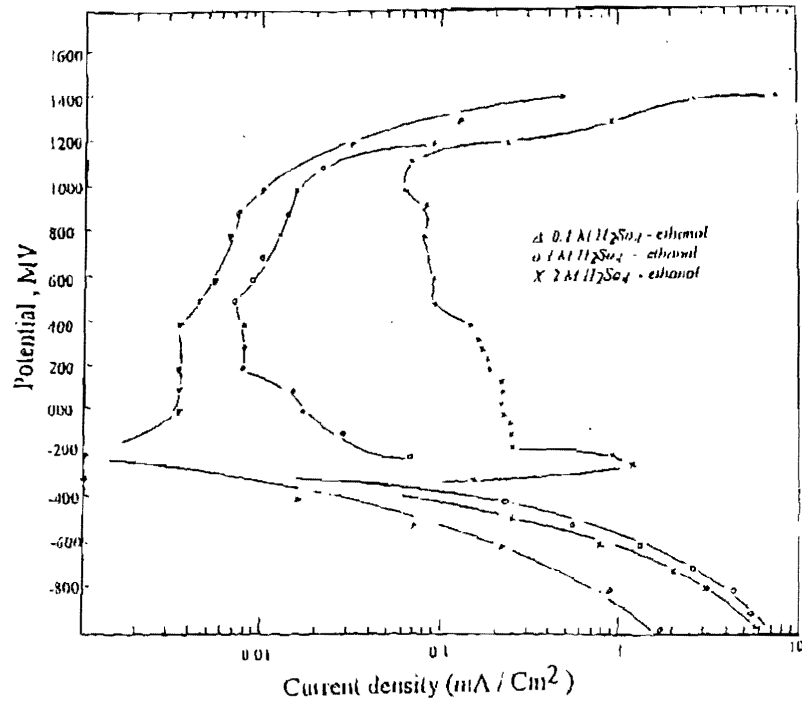


Fig (3) Cathodic and anodic polarization curves of AISI 440 MSS in deaerated H<sub>2</sub>SO<sub>4</sub> (0.1 to 2M) + ethanol.

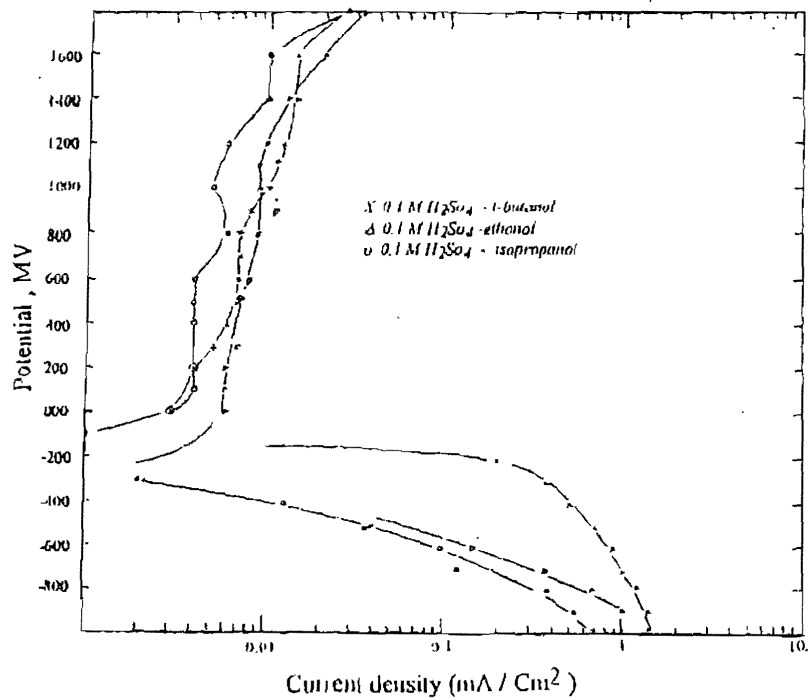


Fig (4) Cathodic and anodic polarization curves of AISI 416 MSS in deaerated H<sub>2</sub>SO<sub>4</sub> (0.1 M) + T-butanol, ethanol, and isopropanol solutions.

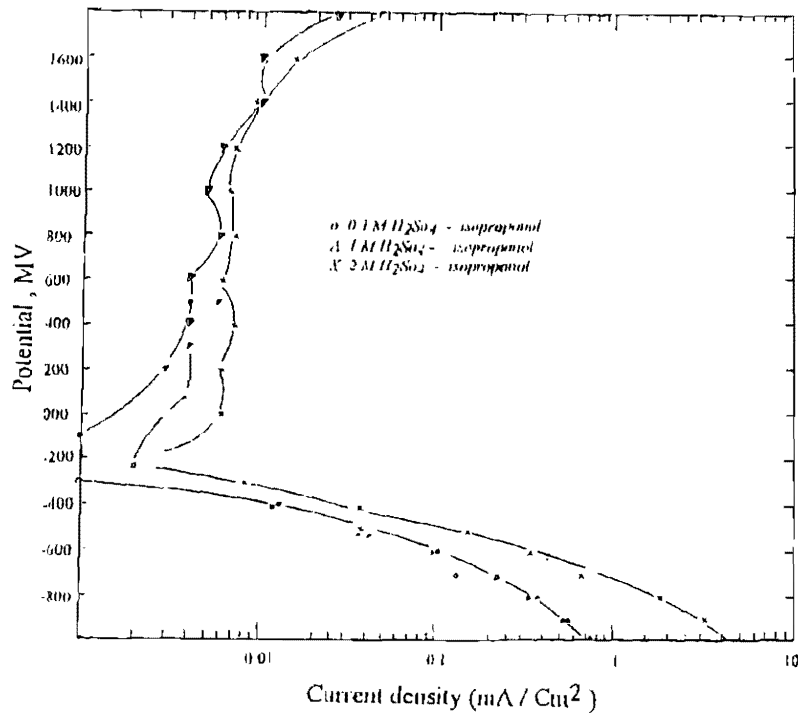


Fig (5) Cathodic and anodic polarization curves of AISI 416 MSS in deaerated H<sub>2</sub>SO<sub>4</sub> (0.1 to 2M) + isopropanol solution .

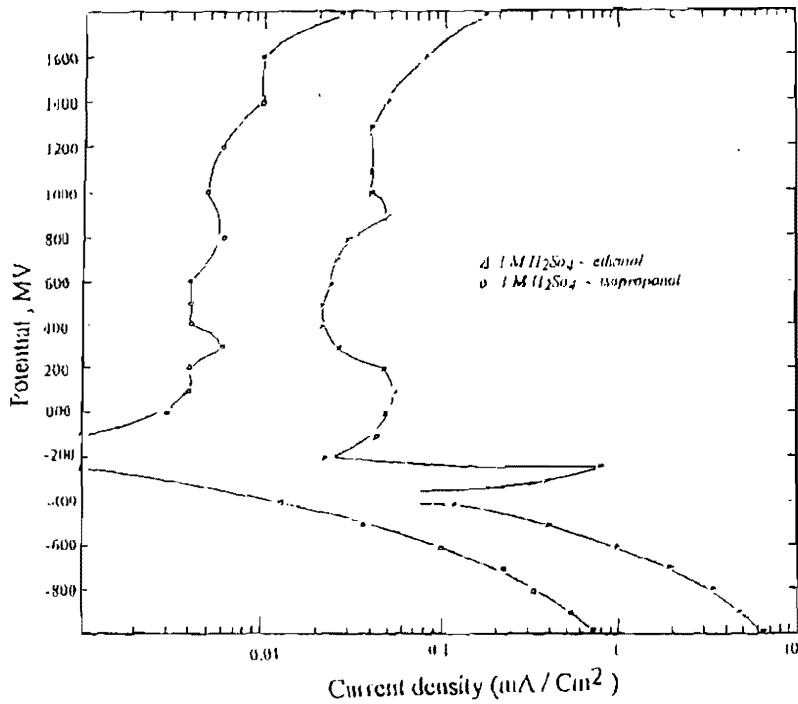


Fig (6) Cathodic and anodic polarization curves of AISI 416 MSS in deaerated H<sub>2</sub>SO<sub>4</sub> (1M) + ethanol and isopropanol solutions .

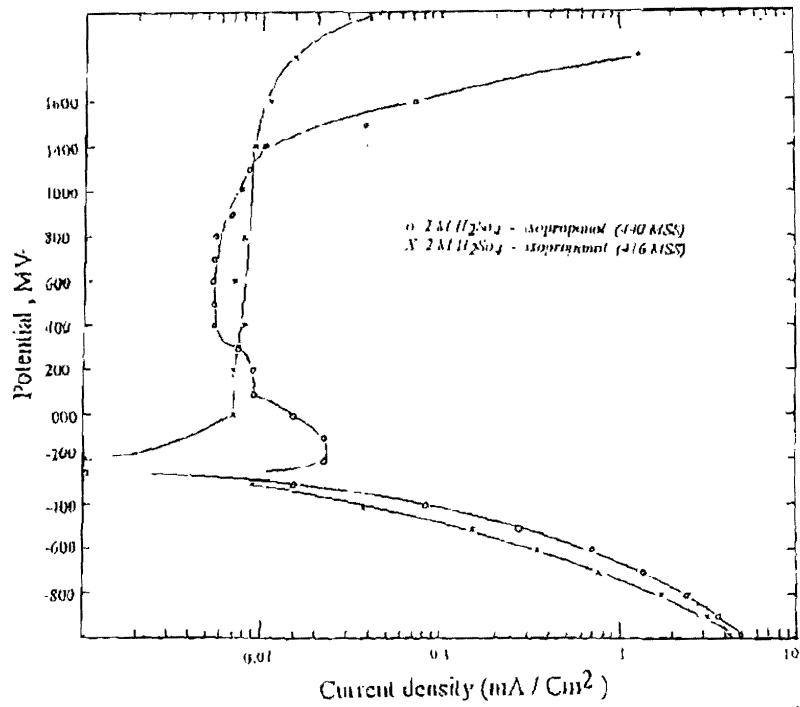


Fig (7) Cathodic and anodic polarization curves of AISI 416 and 440 MSS in deaerated H<sub>2</sub>SO<sub>4</sub> (2M) + isopropanol solution.

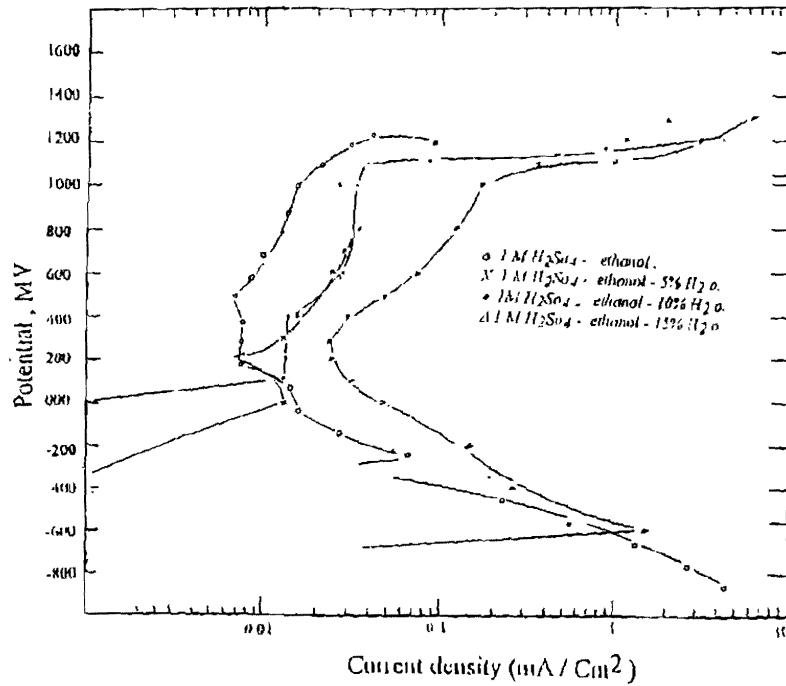


Fig (8) Effect of water content on the potentiostatic anodic polarization curves of AISI 440 MSS at 25°C in 1 M H<sub>2</sub>SO<sub>4</sub> + ethanol.