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

دراسة السلوك الكهروكيميائى للصلب ٤١٦، ٤٤٠ المارتينسيتى المقاوم للتأكل فى الكحوليات

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تم فى هذا البحث دراسة السلوك الكهروكيميائى للصلب ٤١٦، ٤٤٠ المارتينسيتى المقاوم للتأكل فى محاليل من الكحوليات (إيثانول - أيزوبروبانول، بيتانول ، والتى تحتوى على نسب مختلفه من حامض الكبريتيك (1.to 2M) بواسطه منحنيات الاستقطاب الانودى - الكاثودى. لقد لوحظ من منحنيات الاستقطاب وجود السلوك الفعال - الخامل وكذلك المقاومه للتأكل تعتمد على تركيز الحامض فى الكحوليات .

كما تم دراسة تأثير إضافة الماء بنسب مختلفه (٥، ١٠، ١٥٪) إلى حامض كبريتيك (1M)- كحول على السلوك الكهروكيميائى للصلب. لقد وجد أن إضافه الماء المقطر يؤثر تأثيرا كبيرا على الحاله الخامله (Pssivation) للصلب ٤١٦ وكذلك ٤٤٠

المدخلات :

مارتينسيت ، مقاوم للتأكل ، صلب ، كهروكيميائى ، كحول ، حامض كبريتيك، تأكل ، أنودى ، إستقطات ، فرق الجهد ، ماء ، كاثودى ، 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 concentractions 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 IM H_2So_4 alcohols has been also investigated. It was found that the presence of water strongly influences the passivation of both steels in IM H_2So_4 - 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 interst on the corrosion of metals and alloys in non-aqueous solvents (1) because of the newly developing electro-chemical 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 constent, the dissociation equilibriun, and the solubility of reactants and products of the corrosion reaction. The electrochemical investigations have been reported in methanolic solution containing in organic acid (HCl or H_2SO_4 or a mixture of both) and the conducting salts (2-4). The role of water on the passivity and the passivity break dowen has been examined in methanol + Hcl or H_2SO_4 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 occured in methanolic solutions of tartaric , malic, lactic , and acetc 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.

Expermental :

Experiments were conducted using cubes of AISI 416 and 440. Martensitic stainless steels solution aannealed 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 electrod with an area of 1 cm^2 was mechanically polished and then was sequence 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 electrod 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_2SO_4

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

The experiments have been conducted in a three- nackad assembly, in which platinum caunter electrod of area $1 cm^2$ was placed 3 cm a way from the working electrode. The refrence electrode was saturated calomel electrode.

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

Results and Discussion .

The corrosion potential (Ecorr) of 440 and 416 (MSS) in deaerated solution tends towards a more negative potential as the concentration of H_2SO_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 H_2SO_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 H_2O content in the solution with the lower acid concentration than in 2 and 1 M H_2SO_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 averag slope for the 0.1 M H_2SO_4 - T- butanol, ethanol and isopropanol, also the same averag slope for iso-propanol and ethanol with different H_2SO_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 (Icorr), critical current (Ic) and the passivation current (Ip) increases with increasing the concentration of H_2SO_4 in ethanol and isopropanol alcohols, also the passivation range affected by the change in acid concentraction. This may result from the enhanced solubility of pre-existing oxide film and an increase of the metal dissolution with incresing acid concentraction.

Also from the anodic polaritation curves (Fig. 1) and Table (1) we can detect that, the alcohol type at constant acid concentraction has a significant effect on the corrosion characteristics of 440 MSS. it was found that, the corrosion current (Icorr), critical current (Ic) and passivation current (Ip) in isopropanol alcohol are smaller than in T-butanol and ethanol respectively, which means that ethanol is a more corrosive solution than T-butabol 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 concentraction in alcohols such as 440 MSS.

From Fig. (7) and Tables (1,2) we can found that, the corrosion current (Icorr) for 440 MSS in 2M H_2SO_4-isopropanol solution is 0.12mA/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 lM H_2SO_4 - 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_2SO_4 in alcohols.
2- 416 Mss have better corrosion resistance in alcohols with different concentrations of H_2SO_4 than 440 Mss.
3- The addition of dist. water by percentages ranged from 5 to 15% to alcohols with certain percentage of H_2SO_4 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 Ecorr, mV/SCE	Ic mA/Cm^2	Ip mA/Cm^2	I corr mA/Cm^2	Ep mV/SCE	passivation rang, mV/SCE
0.1 M H_2SO_4 - ethanol	-200	-	3.84 X10^{-3}	0.013	000	000 to 1200
1 M H_2SO_4 - ethanol	-330	6.9 X 10^{-2}	7.69 X10^{-3}	0.15	200	200 to 1000
2 M H_2SO_4 - ethanol	-340	14	25 X10^{-2}	0.4	-150	- 150 to 1000
0.1M H_2SO_4 - isopropanol	330	-	2 X 10^{-3}	1.6x10^{-4}	-200	-200 to 1600
1M H_2SO_4 - isopropanol	-270	6.5 X10^{-3}	3 X 10^{-2}	3x10^{-2}	400	400 to 1300
2 M H_2SO_4 - isopropanol	-260	2.3 X 10^{-2}	0.01	0.12	400	400 to 1200
0.1 M H_2SO_4 - T- butanol	-210	-	3 84 X 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 Ecorr, mV/SCE	Ip mA/Cm^2	I corr mA/Cm^2	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

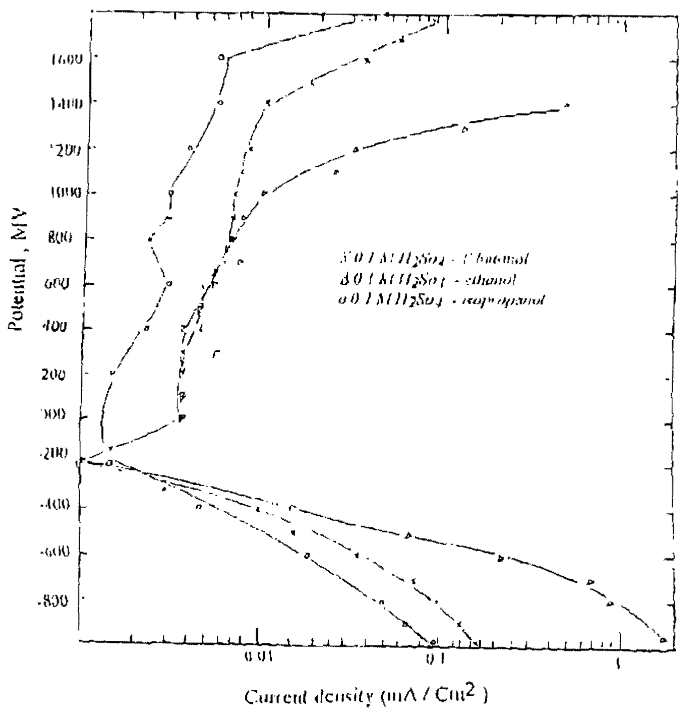
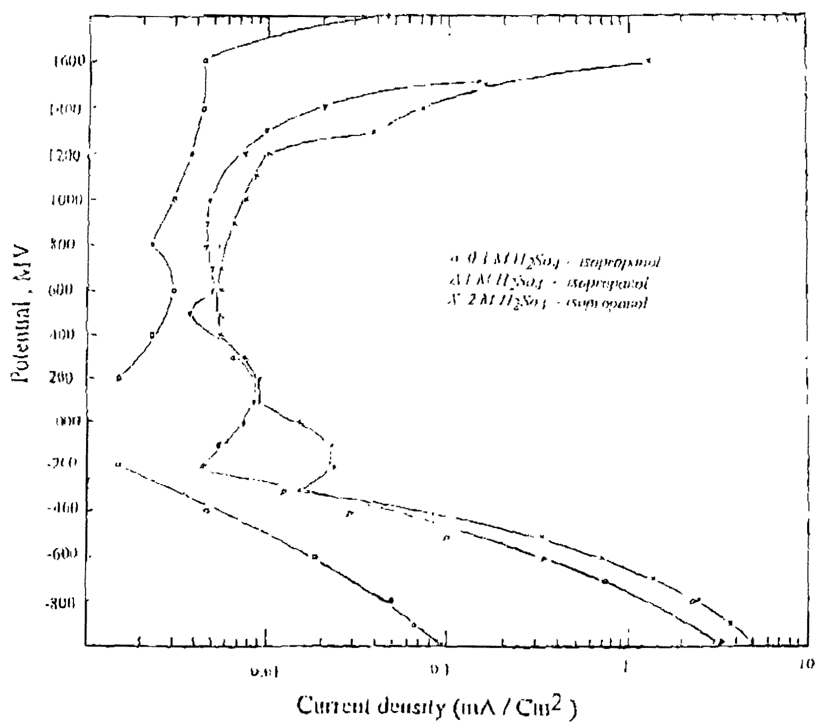


Fig (1) Cathodic and anodic polarization curves of AISI 440 MSS in deaerated H_2SO_4 (0.1M) + t-butanol, ethanol and isopropanol solutions.



Fig(2) Cathodic and anodic polarization curves of AISI 440 MSS in deaerated H_2SO_4 (0.1 to 2M) + isopropanol solutions.

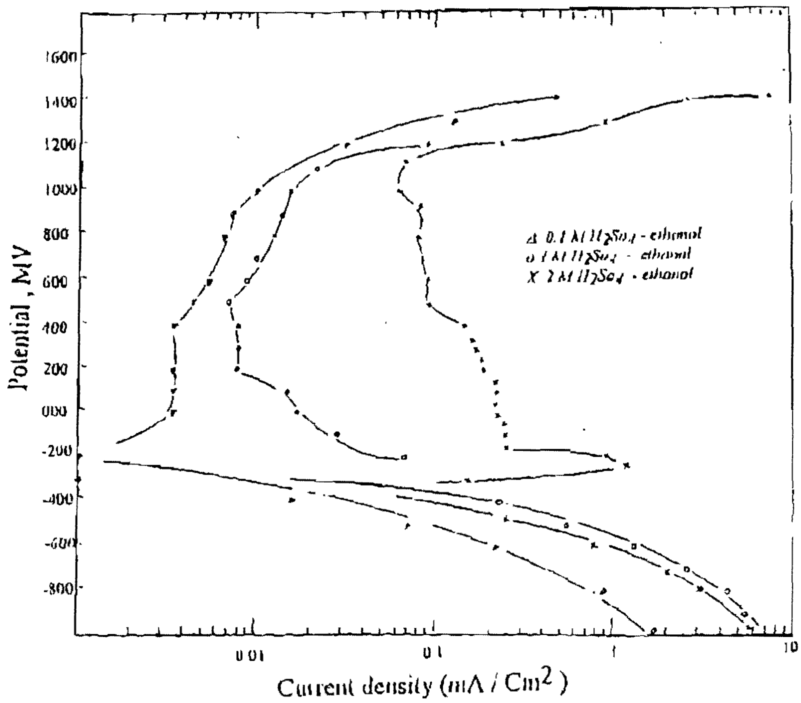


Fig (3) Cathodic and anodic polarization curves of AISI 440 MSS in deaerated H_2So_4 (0.1 to 2M) + ethanol.

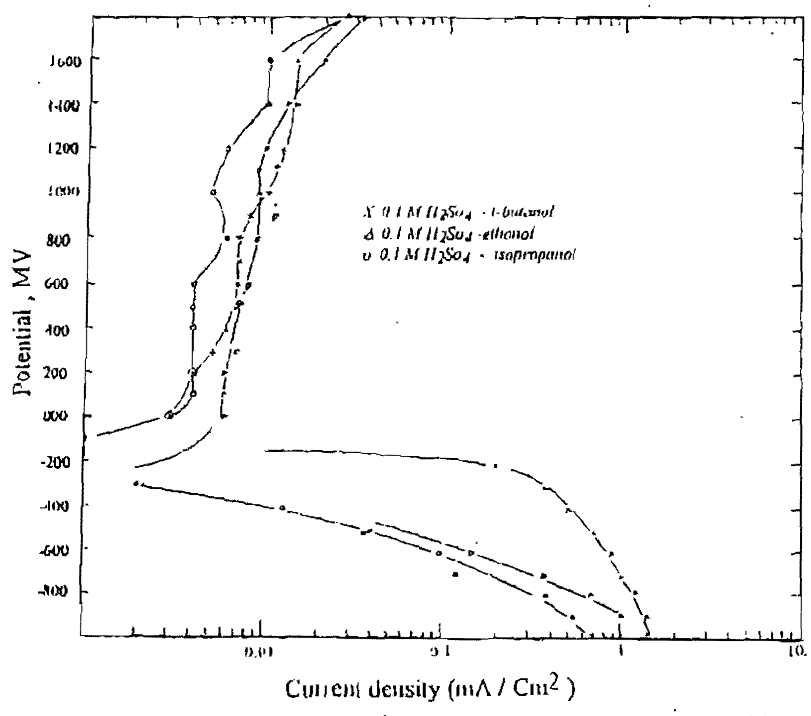


Fig (4) Cathodic and anodic polarization curves of AISI 416 MSS in deaerated H_2So_4 (0.1 M) + .T-butanol, ethanol, and isopropanol solutions.

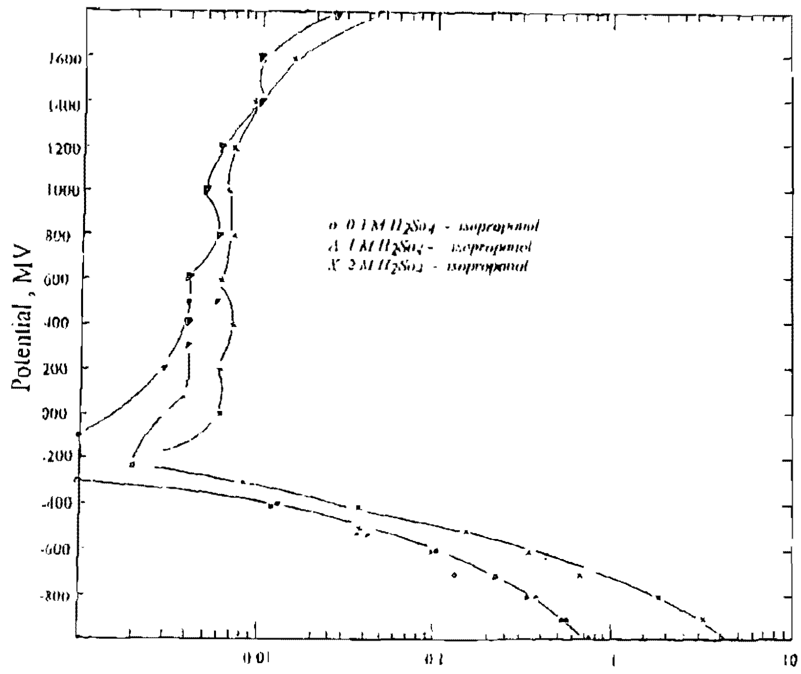


Fig (5) Cathodic and anodic polarization curves of AISI 416 MSS in deaerated H_2SO_4 (0.1 to 2M) + isopropanol solution.

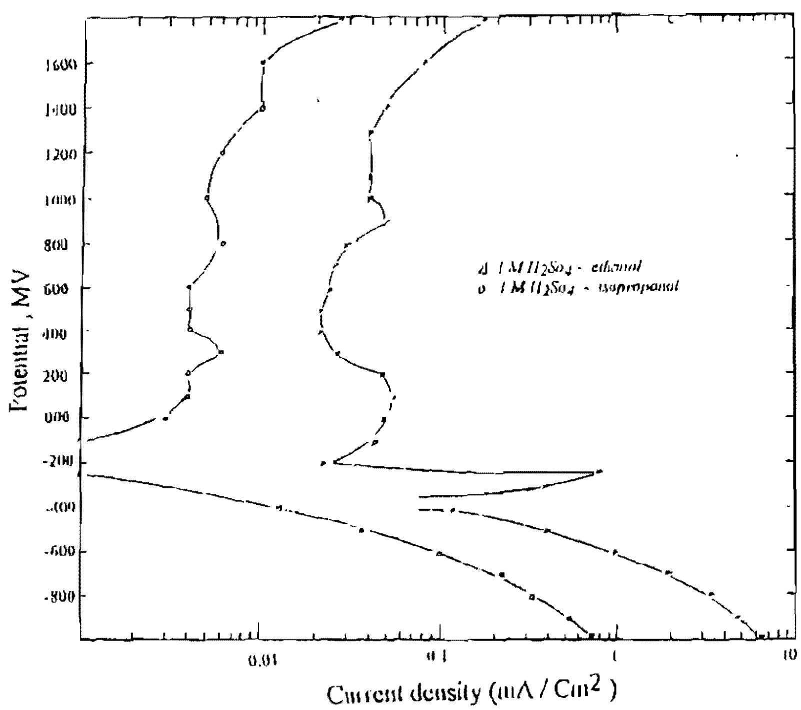


Fig (6) Cathodic and anodic polarization curves of AISI 416 MSS in deaerated H_2SO_4 (1M) +ethanol and isopropanol solutions.

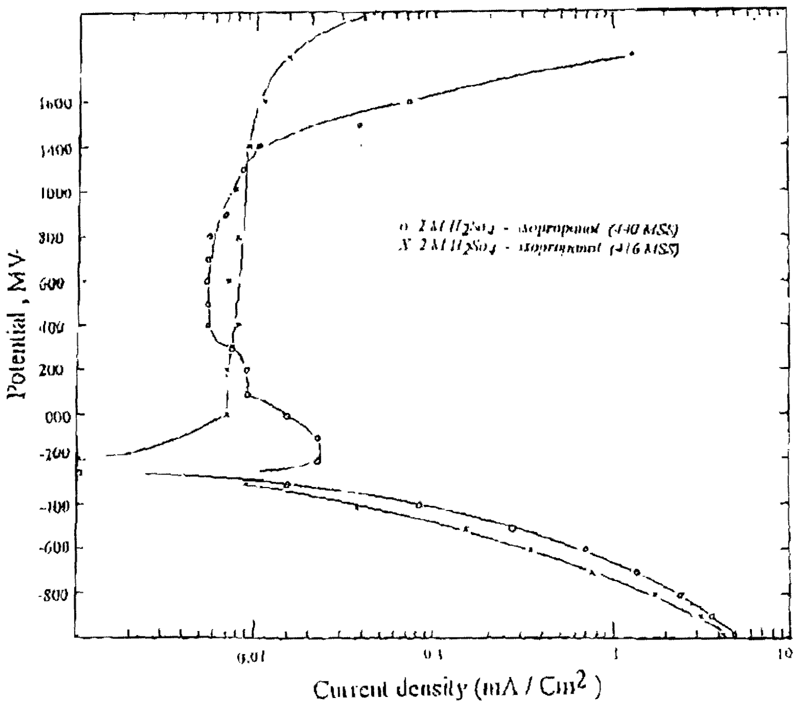


Fig (7) Cathodic and anodic polarization curves of AISI 416 and 440 MSS in deaerated H_2So_4 (2M) + isopropanol solution.

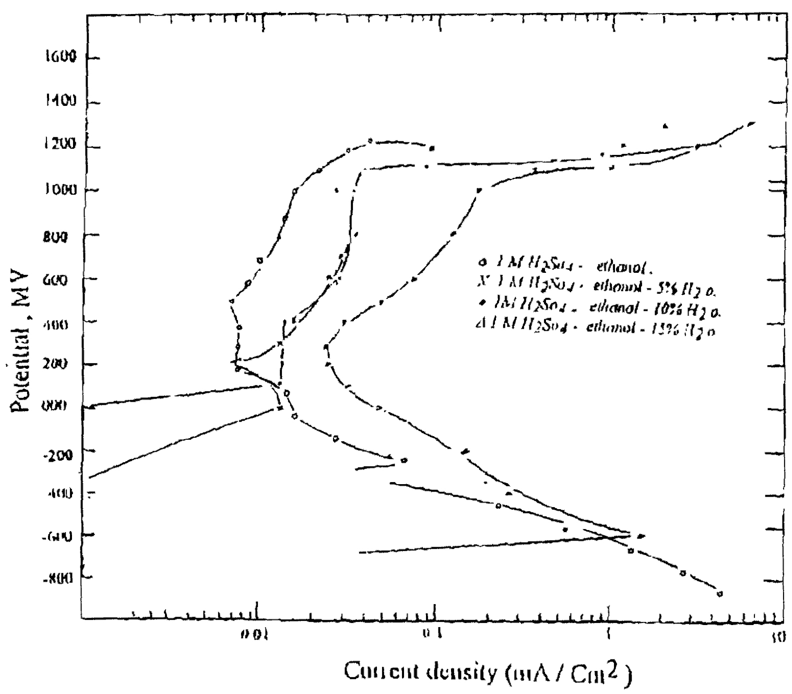


Fig (8) Effect of water content on the potentiostatic anodic polarization curves of AISI 440 MSS at 25 °c in 1 M H_2So_4 + ethanol .