

Surface analysis of steel samples polarized anodically in H_3PO_4 –HCl mixtures by SEM and EDAX techniques

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Abstract

Potentiodynamic polarization experiments were performed on 304 stainless steel in 14M H_3PO_4 containing 0-20000 ppm HCl at 298, 308 and 318 °K. Photomicrographs of the test samples were obtained from Scanning Electron Microscopy after performing anodic polarization experiments on steel samples in 14M phosphoric acid and in 14M phosphoric acid containing critical concentration of HCl at 298, 308 and 318 °K. It is witnessed that severe pitting of the surface occurs when chloride ions are added to phosphoric acid. Morphology of pits is studied and pits are found to be partially hemispherical with some corrosion product spread unevenly. The increase in temperature results in increased number of pits but the size of pits becomes smaller. The composition of passive film formed on 304SS is investigated by the Energy Dispersive x-ray analysis (EDAX) technique. The analysis of alloy samples after interrupting polarization of samples in the passive region at critical concentration of HCl shows the presence of chlorine atoms in the film (0.23 -0.36%). The result supports the Point Defect Model proposed by Macdonald et al to explain pitting phenomenon.

Key words: Stainless steel; pitting; Scanning Electron Microscopy; Energy Dispersive x-ray analysis.

Introduction

Present study involves surface analysis of AISI 304SS after treatment in H_3PO_4 –HCl medium. It is observed that stainless steels which are quite resistant to corrosion in various media [1] and also in presence of H_3PO_4 (due to formation of passive film), suffer severe destruction in the form of pitting if the medium has aggressive ions like Cl^- . This type of situation is faced during manufacture, storage and transport of phosphoric acid as HCl is added during acidulation process of its manufacture [1,2]. This added impurity (HCl) makes medium highly corrosive leading to pitting attack on alloy surface.

The corrosion behaviour of 304SS in concentrated phosphoric acid having different concentrations of added impurity in the form of HCl at different temperatures has been described earlier [3,4]. It was inferred from these studies that at a certain temperature,

there is a certain critical concentration of HCl below which pitting doesn't occur but at and above critical concentration of HCl localized attack on alloy surface in the form of pitting is witnessed. Hence the presence of aggressive ion in the form of HCl limits the utilization of 304SS in this medium.

Surface analysis of steels has been done earlier by investigators but Scanning Electron photomicrographs of steels having other compositions are available in literature [5,6]. Furthermore earlier studies were carried out primarily to study stress corrosion, cracking and pitting in other media. Hence it seems desirable to study the severity of pitting and effect of temperature on it by surface analysis of steel samples after exposing them to H_3PO_4 -HCl medium. The Present study is done with a view to study the morphology of pits and its dependence on temperature. Energy Dispersive X-Ray Analysis (EDAX) is carried out to ascertain if there is any change in alloy composition on steel surface and to investigate whether chlorine atoms are present on alloy surface.

Materials and Methods

Test samples were prepared from stainless steel sheets obtained from M/s Goodfellow Metals Ltd, England. The composition of 304SS was 18 Cr, 10 Ni and balance Fe. Test samples were polished and cleaned as mentioned elsewhere [3,4]. The electrode system consisted of the austenitic stainless steel working electrode, a counter electrode of platinum and a saturated calomel electrode (SCE) with KNO_3 salt bridge. The electrochemical experiments were carried out in an air thermostat maintained at 298, 308 and 318 °K under still condition. The solution consisted of 14M phosphoric acid with different ppm of HCl (BDH AR Grade) added to it. Potentials were impressed on the working electrode by a fast power potentiostat Wenking model POS 73.

Potentiodynamic polarization experiments were recorded at scan rate of $1mV.sec^{-1}$. Steady state potential of the steel sample in H_3PO_4 was determined and starting from E_s (steady state potential), potential was increased automatically with a scan rate of $1mV.sec^{-1}$ and polarization was stopped when potential was well in the transpassive region. Scanning Electron Microscopy of the steel samples was carried

out after the anodic polarization experiments. For this Scanning Electron Microscope JEOL-JSM 840A was used. The samples for such studies were mounted on studs using silver paste and photographs of the desired locations were taken at various magnifications.

Energy dispersive x-ray analysis (EDAX) of the steel samples was carried out after polarization was stopped within the passive region. EDAX was employed for studying point to point composition and elemental distribution of a variety of samples. It was accomplished by employing a detector which was a negatively biased Si chip into which lithium has been diffused and onto which a thin contact Au layer had been evaporated – rays from the specimen entered a wafer of pure silicon carefully treated with lithium. As the x-rays entered the silicon, each one gave up its energy by creating photoelectrons. Electrons were collected in less than a microsecond by an applied bias voltage and integrated by a field – effect – transistor preamplifier. Signal was further amplified to produce a string of pulses. Since the time was proportional to pulse height and thus to x ray energy, the result was build up of a spectrum of counts verses x-ray energy. The energy at which peaks occurred was identified with the elements that produce x-rays. The size of peaks is used to determine the amount of various elements present.

Results and Discussion

The Potentiodynamic polarization curves obtained by anodic polarization of 304SS at different temperatures have been shown elsewhere [3]. It is observed that irrespective of concentration of HCl and temperature, nature of the potentiodynamic polarization curves is same. It has an active region followed by a passive range and then the curves enter into transpassive region indicating dissolution of passive film. When the concentration of HCl is less than certain critical value steel surface doesn't undergo pitting attack but at and above critical concentration of HCl pitting corrosion takes place (it is ascertained by SEM analysis of alloy surface after the experiment). The critical concentration of HCl at which pitting starts is found to be 7600 ppm at 298⁰K, 3800 ppm at 308⁰K and 2900 ppm at 318⁰K [3,4]. It is observed that at a lower temperature a higher concentration of HCl may be tolerated by alloy without suffering destructive attack in the form of pitting. It has been discussed earlier that the resistance against pitting offered by Mo containing stainless steel alloy in this medium also depends on temperature in a similar manner [7,8].

The photomicrographs of test samples obtained from Scanning Electron Microscopy after performing polarization experiments on 304SS in 14M phosphoric acid and in phosphoric acid containing 7600 ppm HCl

at 298⁰K are shown in fig -1. In Fig 1 (B) a few large scattered pits are shown to be formed on alloy surface. The morphology of pits is same i.e. they are partially hemispherical (Fig 1C). Some corrosion product is spread in and around the pits. It is evidenced from Fig 1(D-E) that at a higher temperature (318⁰K), number of pits formed on alloy surface is increased but the size of pits is smaller.

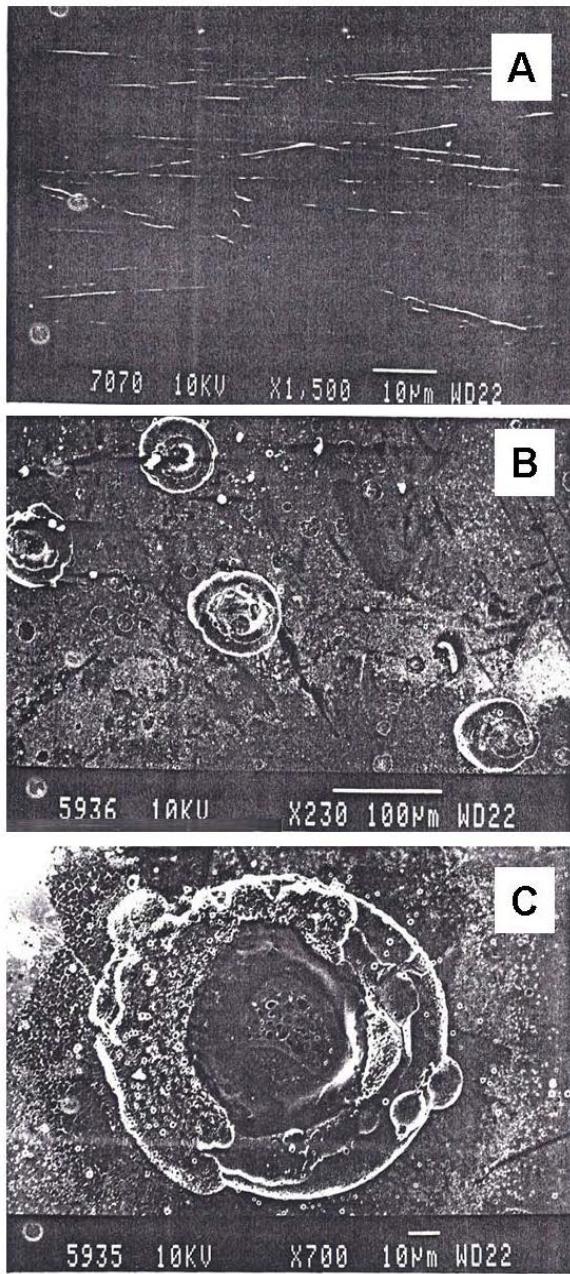
Table 1 Atomic percentage of different elements in 304SS obtained from EDAX.

Electrolyte Composition	Atomic percentage(%)					
	Cl	Cr	Fe	Ni	Cr/Fe	Ni/Fe
14M H ₃ PO ₄	-	19.32	70.58	10.10	0.273	0.143
	-	19.31	70.74	9.95	0.272	0.140
14M H ₃ PO ₄ + 7600 ppm HCl	0.36	19.55	70.17	9.92	0.278	0.141
	0.23	20.31	70.74	8.72	0.267	0.133

When Cl⁻ ions are present in the medium, a very small amount of corrosion takes place in spite of the passive state of the alloy [9]. As the formation of metal oxide film progresses, anodic areas are reduced to very small dimensions. The film growth is due to interaction among metal cations and oxygen ions. The rate of transport of cation vacancies and anion vacancies decide the growth of passive film. Anion vacancies are generated at metal film interface and consumed at film solution interface. At a higher temperature, rate of generation of anion vacancies is more but rate of their consumption by oxygen ions slows down. This is due to the presence of aggressive chloride ions in the medium, which adsorb competitively at anion vacant sites. This in turn creates cation vacancies [10]. At a higher temperature, cation vacancies are generated rapidly due to stronger chemisorptions of halide ions at film solution interface. Due to presence of more cation vacancies and anion vacancies the formation of compact passive film is restricted. This leads to the formation of more porous passive film at a higher temperature as anodic areas are more and density of vacancies is greater [7]. At more noble potentials when metal holes start piling up, formation of void takes place at metal film interface and pitting starts when void grows beyond a certain size. At a higher temperature, pitting starts at several local sites resulting in more number of pits. Size of pits is smaller at a higher temperature as adsorption of halide ions on film surface is limited.

Spectra of 304SS obtained by EDAX analysis after treatment in 14M H₃PO₄ and in 14M H₃PO₄-HCl are shown in Fig-2 and Fig-3 respectively. It is clear from results that when treated in HCl containing medium, chlorine atoms are found to be present on

surface of steel samples besides Fe, Cr and Ni. From EDAX analysis of steel samples it is found that 0.23% - 0.36% chlorine atoms are present in passive film



(Table-1). Presence of less than 1% chlorine atoms indicates that passive film has defects and oxygen ion vacancies are occupied up to some extent by halide ions. The result supports Point Defect Model proposed by Macdonald et al [10], according to which chloride ions occupy anion vacancies present in the passive film leading to creation of cation vacancies. When the rate of growth of cation vacancies is more than the rate of their submergence in the bulk, pits are formed.

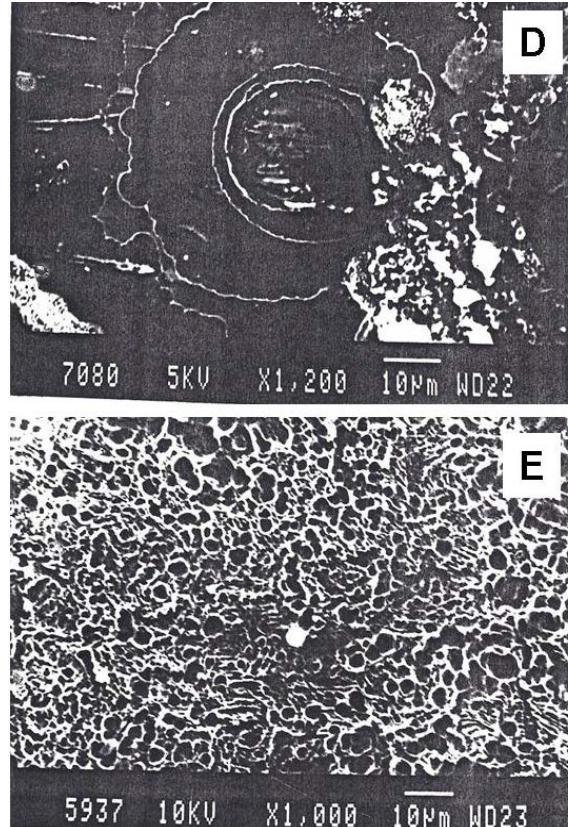


Fig. 1: Photomicrographs obtained by SEM analysis of 304SS samples in 14M phosphoric acid. A. No HCl, at 298⁰K; B-C: with HCl, at 298⁰K; D-E: with HCl at 318⁰K

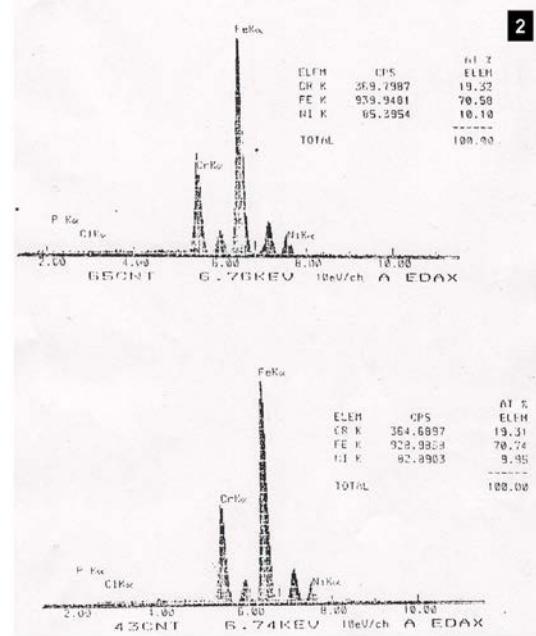


Fig. 2: EDAX spectra of 304SS after treatment in 14M phosphoric acid.

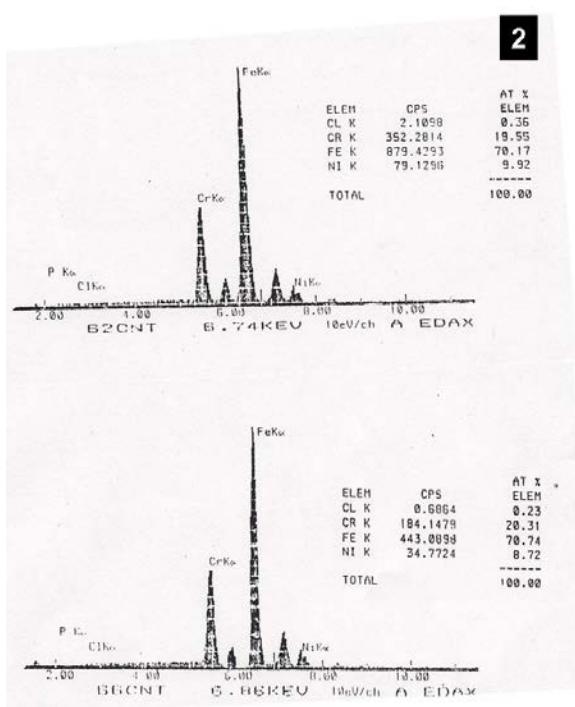


Fig. 3: EDAX spectra of 304SS after treatment in 14M phosphoric acid containing HCl.

Conclusions

It is found from SEM analysis that when concentration of HCl is below critical concentration, pitting doesn't take place. At and above critical concentration pitting corrosion is evidenced. The morphology of pits formed remains the same in all the cases i.e. they are partially hemispherical. At higher temperature more pits having smaller size are found to be present. Porosity of passive film depends on the temperature being more porous at a higher temperature.

It is inferred from EDAX analysis that when steel samples are treated in HCl containing medium, chlorine atoms are present in the passive film. This

supports the view that oxide ion vacancies are occupied by chloride ions up to some extent from the very beginning and continues so long as the passive film formation is completed. The defect density in the passive film leads to the formation of pits ultimately.

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