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Effect of the direction of the inclusions on the tested surface on susceptibility to pitting corrosion in stainless steels

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A study was made of the induction time of pitting (t_i) at constant potential in a stainless steel 316 L specimen in deareated NaCl solutions. The influence of the inclusion content in the steel on t_i was examined, in particular the effect of the inclusions' orientation on the surface of the specimen tested. It was found that the induction time at constant potential and under similar experimental conditions depends on the inclusions' orientation on the test specimen surface; when the direction of the inclusions is transverse to the rolling direction, t_i is shortened in comparison with the tested surface planes containing the rolling direction. The pitting initiation sites were the matrix–sulphide inclusions interphase. The microcavities associated with them could be preferential sites for pit nucleation.

1. Introduction

The passivity breakdown of stainless steels in solutions containing chlorides motivated many academic as well as industrial studies, because the main failure associated with the use of this material is pitting corrosion. In spite of the numerous investigations on the subject, the corrosion mechanism by pitting is not yet quite clear and has often been subject to discussions by many investigators working in this field. Several questions raised up were therefore in the selection criteria. The inclusions content effect in steel on corrosion by pitting is not yet at all clear, especially for such aspects as the role of chemical composition of the inclusion, in which there are controversial opinions concerning the effect of chromium content substitution manganese in MnS inclusions [1, 2]. To date the effect on size, shape, distribution and microcavities associated with the inclusions and the direction the inclusions' orientation on the tested surface have not been taken into account.

It has been emphasized that the stable passivity is not at rest but is alive in a dynamic balance between cracking and repassivation of the film, in different places over the surface. There are two points of view of the passivation process which include depassivation. Some authors consider cracking of the passivating film in pitting initiation by some mechanism.

The other group do not hold the actual cracking of the film itself. Therefore, the two points of view could be summarized in the following way.

(a) Cracking and repassivation of the passivating film in different sites of the film at random [3, 4].

(b) The surface of the stainless steel is formed by an inhomogeneous passivating film [5, 6]. The sulphides are electronic conductors and can be polarized to the potential of the passive stainless steel surface. At this potential, the sulphides are not thermodynamically stable and tend to dissolve. When such a dissolution takes place, virgin metal is exposed to the environment which will tend to regenerate the passivating film if certain critical conditions are not provided.

Basic investigative works (a), above mentioned, were carried out to consider the cracking of the flawless passivating film, without taking into account the structural and or compositional heterogeneities in the passivating film. In these theories the initiation of pitting is the result of interactions between aggressive species in the electrolyte, e.g. chloride ions, and the passivating film. From the kinetic point of view, the passivating destruction is explained in terms of competitive adsorption between chloride and oxygen ions, while thermodynamic focusing considers the pitting potential, E_p, as that in which the chloride ion is in equilibrium with the oxide.

Szklarska *et al.* [7] and Shreir *et al.* [8] examined and discussed these theories. On the other hand, numerous investigations [5, 6, 9, 10] consider the compositional heterogeneities (inclusions) of the passivating film at the initiation and propagation of pitting in stainless steels. A balance of the contributions of both criteria should be made with the intention of predicting the onset and spreading mechanism of pitting.

However, the probabilistic models on pitting corrosion in stainless steels given in the literature [3, 4] do not incorporate the microstructural aspects of the

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steel. In a previous work a probabilistic model to forecast corrosion by pitting was shown, which took into account the inclusion content in the initiation of pitting [11].

Here we intend to evaluate the influence of the inclusions' orientation on the specimen surfaces on the induction time of pitting (t_i) as well as the influence of the microcavities associated with inclusions on (t_i) and the pitting initiation site.

2. Experimental procedure

Stainless steel 316 L specimens were used which fulfilled the ISO specification for use as metallic orthopaedic implants. The chemical composition of the steel was (wt %): C 0.07, Si 0.24, S 0.005, Mn 1.2, Mo 2.2, Cr 17.3, Ni 13.3, Cu 0.15.

The microstructure was revealed by polishing with diamond paste to 3 µm, and exposure to an oxalic acid solution. The main phase is austenite with some martensite. This is shown in Fig. 1, the material has 1.2% ferrite δ as shown in Fig. 2.

2.1. Characterization of inclusions in the material

Characterization of inclusions (size, shape, quantity and distribution) was made by conventional techniques (light microscopy, scanning electron microscopy (SEM)). Figs 3 and 4 show the inclusions present in steel.

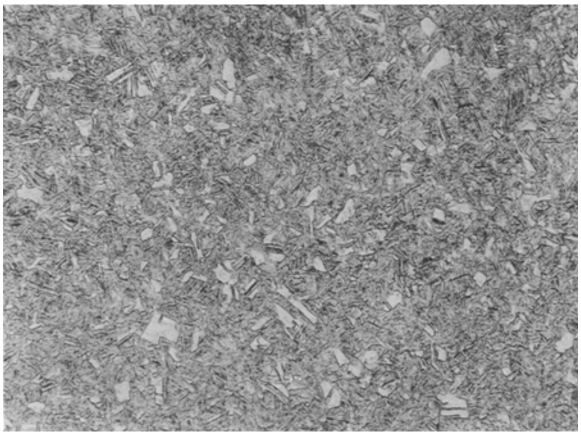

Figure 1 Microstructure observed in 316 L SS specimen under an optical microscope austenite and martensite × 72.

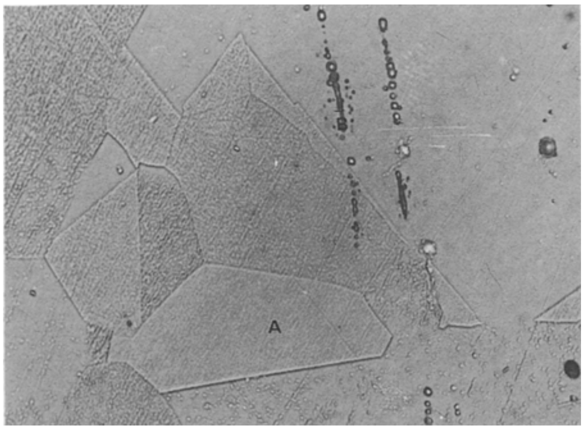

Figure 2 Microstructure of 316 L SS specimen observed by optical microscope. (A) Austenite, (B) Ferrite δ. × 720.

In order to study the chemical compositions of the phases that comprise the inclusions, a non-conventional technique [12] was used. Inclusions were removed from the matrix by epoxy replicas, etched with Br/CH_3OH solution and analysed by energy dispersive of X-rays (EDAX). The Br/CH_3OH solution was chosen in order to avoid the dissolution of the inclusion, given that the inclusion phases are nobler than the matrix. The same formalism of thin foil analysis was used in our work. Stoichiometric calculations were possible due to the absence of matrix effects.

The chemical composition of sulphide inclusions is shown in Table I.

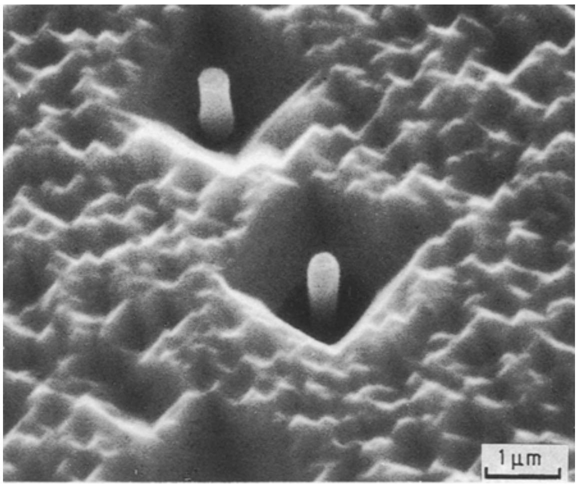

Figure 3 Scanning electron micrograph of a 316 L SS etched with Br/CH_3OH solution. Inclusion is composed of (Mn, Cr) S.

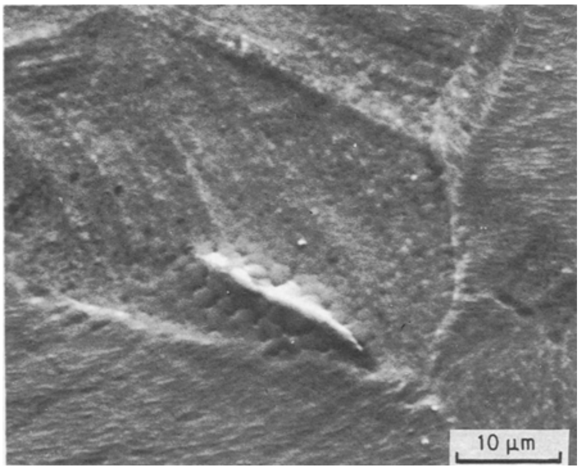

Figure 4 Scanning electron micrograph of a 316 L SS etched with Br/CH_3OH solution. Inclusion is composed of (Mn, Cr) S.

TABLE I The chemical composition of sulphide inclusions

Steel	Composition (%)	Phases	Size (µm)
316 L	Cr content, substituting Mn in MnS inclusions 20–30	(Mn, Cr) S	0.1–20

2.2. Electrochemical measurements

A conventional electrochemical cell was used. For the test specimen preparation epoxy resin was used. The exposed area of the specimen was approximately 0.25 cm^2. The induction time for pit generation at a constant potential was measured in 3.5 wt % NaCl solution deaerated with nitrogen gas for 2 h before applying the chosen potential during the whole experiment.

In each of the experiments at constant potential the induction time was measured on those surfaces of the sample that were planes containing the rolling direction and transverse to the rolling direction. This is shown schematically in Fig. 5.

Experiments at room temperatures and 2 °C were carried out on a specimen polished to a 600 grit finish and diamond paste to 3 µm. Superficial finishing paper 600 results are shown in Table II and the results for polishing to 3 µm with diamond paste are shown in Table III.

Logarithms of induction times at different potential values are shown in Table II. Note that at equal corrosion conditions (electrolyte, potential, temperature, surface treatment) t_i depends on the inclusion orientation relative to the direction of steel working on the test specimen surface. Under the same experimental conditions t_i is lower when inclusions are transverse to the rolling direction. It must also be noted that if corrosion conditions are constant for the same orientation of inclusions on the surface, t_i then depends on temperature.

In all experiments, pitting is caused in the sulphur matrix inclusion interphases (Figs 6 to 8). No variation, due to superficial finishing, polished to a 600 grit finish and diamond paste to 3 µm, of t_i could be seen. Comparing Figs 7 and 8 it is noted that t_i is similar.

3. Results and discussion

The pitting initiation site of stainless steels has stimulated many discussions. It was suggested that disturbances on the oxide film, e.g. grain boundaries and other flaws, could provide preferential sites for adsorption of Cl$^-$ anions [3, 4] and cause cracking of the film and thus initiation of pitting. In pure iron (Fe 99.99%), pitting appears at random on the surface with no special preference for sites, e.g. on grain boundaries or scratches.

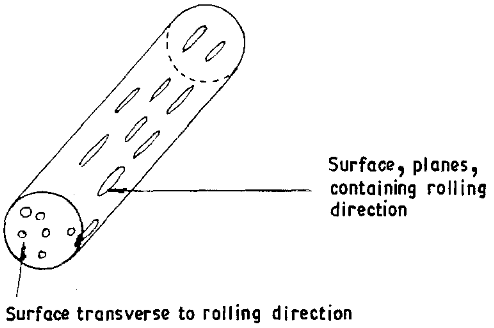

Figure 5 Schematic representation of the orientation of the inclusions in both surfaces tested.

TABLE II Electrochemical measurements of induction time for pit generation at a constant potential. The surface was polished to a 600 grit finish

Temperature (°C)	Potential (mV SCE)	Induction time for pit generation (t_i) log t_i (log sec): Parallel to rolling direction	Perpendicular to rolling direction
Room (~25)	50	5.15	Time too long
		5.33	
		5.25	
		5.04	
		$\sigma_n^a = 0.1087$	
	150	4.55	4.5
		4.63	4.46
		4.70	4.47
		$\sigma_n = 0.0784$	$\sigma_n = 0.0082$
	200	4.20	3.15
		4.25	3.17
		4.22	3.12
		4.24	3.28
		$\sigma_n = 0.0192$	$\sigma_n = 0.0604$
	250	3.38	2.73
		3.47	2.73
		3.41	2.77
		3.49	2.68
		$\sigma_n = 0.0444$	$\sigma_n = 0.0319$
	300	2.95	2
		3.19	2.26
		3.04	2.17
		3.09	2.23
		$\sigma_n = 0.0867$	$\sigma_n = 0.1006$
	370	2	
		2.20	
		0.60	
		2.33	
		$\sigma_n = 0.0698$	
2	50	Time too long	5.17
			5.25
			$\sigma_n = 0.04$
	150	Time too long	4.79
			4.79
			4.80
			4.77
			$\sigma_n = 0.0109$
	200	5.10	4.32
		5.20	4.33
		5.10	4.32
		5.10	4.52
		$\sigma_n = 0.0026$	0.0043
	250	4.72	3.98
		4.95	4.3
		4.90	3.97
		4.93	4
		$\sigma_n = 0.0942$	4.11
			$\sigma_n = 0.1245$
	300	4.33	2.92
		4.42	3.13
		4.34	2.21
		4.42	3.13
			2.77
		$\sigma_n = 0.0427$	$\sigma_n = 0.3238$

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[a] σ_n = standard deviation.

TABLE III Electrochemical measurements: surface polished with diamond paste to 3 μm

Applied potential (mV SCE)	Polishing with diamond paste	Temperature (°C)	Induction time (t_i in min)
(a) 250	up to 3 μm	2–3	2208
(b) 250	up to 3 μm	2–3	2150
(c) 250	up to 3 μm	2–3	2025
(d) 250	up to 3 μm	2–3	365
(e) 250	up to 3 μm	2–3	360

(a, b, c) Tested surface containing the rolling direction. (d, e) Tested surface transverse to the rolling direction.

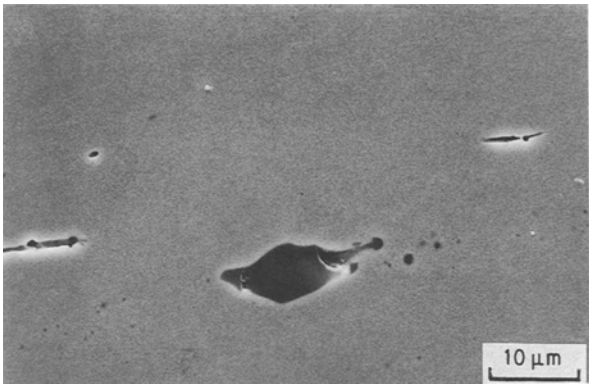

Figure 6 Scanning electron of the observed pitting initiation site. The potential applied was 250 mV SCE. Electrolyte deaerated 3.5 wt % NaCl solution, $t_i = 2208$ min. Polished with diamond paste to 3 μm.

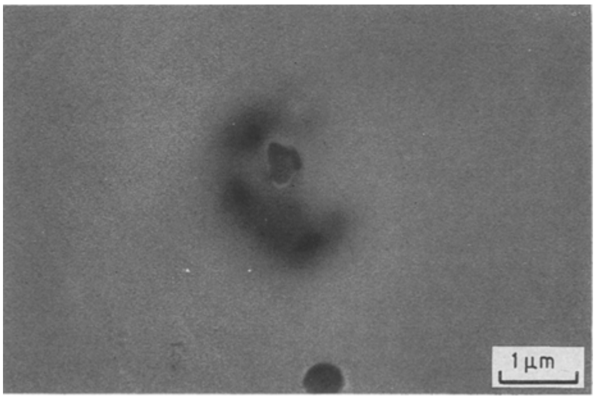

Figure 7 Scanning electron micrograph of the observed pitting initiation site. The experimental conditions are the same as in Fig. 5. $t_i = 365$ min.

Streicher [13] and Uhlig [14] reported that non-metallic inclusions could be pitting initiation sites, while Wilde and Armijo [5] and Ecklund [6] reported that the only pitting initiation sites in stainless steels were the MnS inclusions confirming that pitting starts on the non-metallic inclusions. Two aspects are discussed.

1. The oxide layer close to inhomogeneities such as inclusions has a composition slightly different from the rest of the surface. Therefore a potential difference can exist which is then amplified by preferential adsorption of the anions.

2. The sulphides in a commercial stainless steel containing manganese comprise manganese sulphides with variable amounts of dissolved iron and chromium. Sulphides are electronic conductors and can polarize at approximately the potential of the passivating film. At this potential the sulphides are thermodynamically unstable and tend to dissolve.

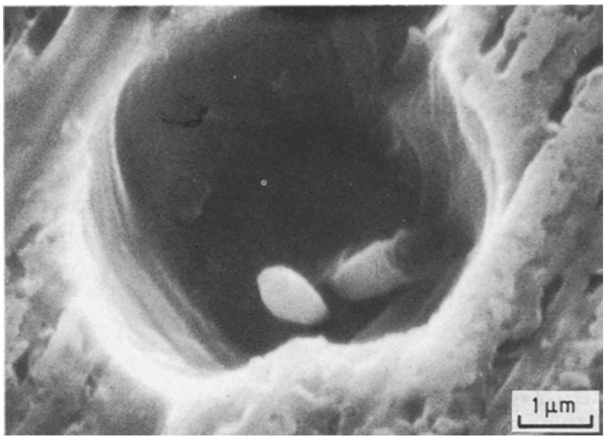

Figure 8 Scanning electron micrograph of the observed pitting initiation site. Experimental conditions as in Figs 6 and 7. Surface treatment: 600 emery polished; $t_i = 300$ min.

The experimental results showed that the pitting initiation site was in all cases in the interphase sulphide matrix. These observations are shown in Figs 6 to 8 in specimens where the exposed surface was transverse or parallel to rolling direction.

3.1. The effect of microcavities or microcracks associated with inclusions

The shape, size and distribution of the inclusions and microvoids and/or microcracks associated with the inclusions depend mostly on the conditions of solidification, rolling (and/or other working process) and thermal treatments. The influence of the surface roughness on pit nucleation was studied by Williams *et al.* [3]. However, the ability of microcavities associated with inclusions to nucleate pitting by a crevice corrosion mechanism, perhaps associated with another mechanism, has not been considered in the literature.

It was noted that microcavities or microcracks associated with oxisulphide inclusions are preferential pit initiation sites, and they shorten the induction time in the direction transverse to that of steel rolling. Microcrevices associated with oxide particles such as Al_2O_3 do not initiate pitting.

The influence of certain surface treatments, such as that reported by Shibata and Takeyama [4], with polishing to a 600 grit finish, corroded in 20% HNO_3 solution at 35 °C for 1 h, as suggested by the present authors as a crevice corrosion prevention treatment in plastic-metal union, should also be considered. This type of treatment dissolves the MnS inclusions, generating crevices, the size of which depends on the inclusion content of the steel, which seems to be unrelated to the pitting initiation site.

3.2. Inclusion direction effect on the tested surface

In the literature, the random occurrence of pitting was widely reported by the majority of investigators working on corrosion by pitting in stainless steel and ferrite alloys based on nickel. Szklarska and Smialowska [15] reported a wide scatter of results in measurements of E_p (the pitting potential) under potentiostatic conditions. Shibata and Takeyama [4] reported a statistical variation of E_p and a large variation, greater even than that of E_p, for the induction time (t_i) at constant potential. Freiman and Kharitonava [16] attributed the scatter in the results to poor control of experimental conditions. Shibata suggested that even with a strict control of experimental conditions, a wide scatter in the results, especially in t_i at constant potential, would still be seen.

Shibata and Takeyama [4], however, makes reference to experimental control and special care in electrochemical measurements and surface preparation, but they do not refer to the microstructural aspects of the material nor the orientation of the inclusions on the tested surface, which are examined in this work and based on achieved results. It is suggested that this may be an important cause of the scatter in the results.

From the experiments carried out it could be seen that t_i depends on corrosion conditions, temperature, regeneration, capacity of the film and inclusion orientation in the specimen surface. For similar corrosion conditions and temperature, at a given potential value, the induction time is reduced when the tested surface is transverse to the rolling direction, comparing with when the tested surface is parallel to the rolling direction. From the pitting initiation and spreading mechanisms suggested by Ecklund [6], the operating mechanism is possibly the same in both directions, but for geometrical reasons, on the surface of the sample, in the planes containing the transverse rolling direction, the reduction of H^+ ion concentration, generated in the interphase matrix inclusions by diffusion phenomena and electro-migration, is smaller.

4. Conclusions

1. The pitting initiation sites are the matrix–sulphide inclusion interphases.

2. Only the microcavities associated with sulphide inclusions could have a certain influence on the promotion of corrosion by pitting.

3. Microcavities generated by superficial preparation, etching by acids and/or microcavities associated with inclusions of the Al_2O_3 type do not behave as preferential sites for pitting.

4. The induction time at a constant potential and under similar corrosion conditions depends on the inclusion's orientation on the test specimen surface. When the direction of the inclusions is transverse to the direction of the steel rolling t_i is shortened.

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