PASSIVITY BREAKDOWN ON INDUSTRIAL STAINLESS STEELS: ROLE OF THE NATURE OF INCLUSIONS

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ABSTRACT

The role of manganese sulfide and titanium sulfide inclusions in the breakdown of the passivity occurring on two ferritic stainless steels was studied by metallographic and electrochemical techniques. The solubility of inclusions present in the alloy played a large part in the passive film stability.

INTRODUCTION

The passive films established on stainless steels are due to the presence of chromium in the alloy, and their stability is depending both on the alloy composition and the medium in which these metals are used. The local breakdown of the passive film leads to pitting which occurs in most cases at the inclusion-matrix interphase. Thus, the nature of these inclusions can play a role in pit initiation, and particularly sulfide inclusions [1]. We have studied and compared in this work the influence on pitting of the presence in the alloy of manganese or titanium sulfide inclusions, for two industrial ferritic stainless steels in neutral sodium chloride media. Manganese sulfide is well known as a very efficient accelerator of pit initiation [2, 3]. The role of titanium sulfide is not so clear : it can be an accelerator [4] or it can lead to a pitting resistance [5].

In order to clarify this point, several tests were performed : electrochemical measurements of the stable pitting probability [6], current-time curves at different potentials to observe metastable pitting [7], and metallographic observations of the pitted inclusions.

EXPERIMENTAL

The two alloys studied are AISI 430 ferritic stainless steels, and their composition is reported in Table I. One of these, AISI 430Ti, contains 0.435% Ti, compared with a conventionnal 430 ss containing 0.018% Ti. In these conditions, the microstructure of inclusions is different : in the AISI 430, one has MnS, and in the AISI 430Ti, one has TiS_2, as shown by previous surface microanalysis. The aggressive media are sodium chloride deaerated solutions with concentrations between 0,02 and 0,5 mol. L^{-1}

The pitting probability versus the applied potential, g(E), was obtained by the classical method based on the stochastic approach of Shibata and Takeyama [8], and developed by

Baroux [9]. It permits to deduce - by using a stochastic pit generation rate g_E - a conventional pitting potential, E_g, which can be written [10]:

$$E_g = Eo_g - a_i \ln [Cl^-] \qquad (1)$$

with Eo_g a constant depending on the alloy, and $[Cl^-]$ the chloride content. a_i is the slope of a line on a plot $E_g = f(\ln [Cl^-])$, which will be discussed later in this paper.

Table 1: Composition (wt.%) of the two studied industrial stainless steels.

grade	C	Si	Mn	Ni	Cr	Mo	S	Ti	N	Cu	Al
430	0.045	0.37	0.45	0.16	16.25	0.023	0.003	0.018	0.043	0.056	0.037
430Ti	0.025	0.36	0.44	0.11	17.4	0.003	0.005	0.365	0.014	0.002	0.002

The current vs. time curves were performed at fixed potentials corresponding to the passive region on the polarization curves. By using this technique it is possible to obtain in each case the pitting induction time at the potential E : if pits are unstable, the passive current decreases but peaks are observed, and when stable pitting is observed, the current increases. The number, N, of peaks present can be counted versus E [11 ; 12].

Metallographic observations were performed by SEM, combined with Energy Dispersive Spectroscopy (EDS) microanalysis.

RESULTS

As shown in Figure 1, the pit generation rate g(E) is depending on the potential by :

$$g(E) = g_o \exp E/\varphi \qquad (2)$$

where $1/\varphi$ is the slope of the lines obtained on these figures.

If one defines that the critical stable pitting is initiated when $g(E) = 0{,}1\ s^{-1}cm^{-2}$, the functionnal relationship $E_g = Eo_g - a_i \ln [Cl^-]$ is observed for the two stainless steels (Fig. 2), with two values of a_i . They correspond to 120 mV/decade for AISI 430 and 180 mV/decade for AISI 430Ti. If one considers the experimental φ value for each g(E) curve, one has for the two steels :

$$g(E) = k [Cl^-]^n \exp E/\varphi = k [Cl^-]^3 \exp E/\varphi \qquad (3)$$

The transfer coefficient, α., can be obtained from the relation

$$\varphi = k_B.T / n.\alpha.q \qquad (4)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and q is the charge transfered by the corrosion reaction.

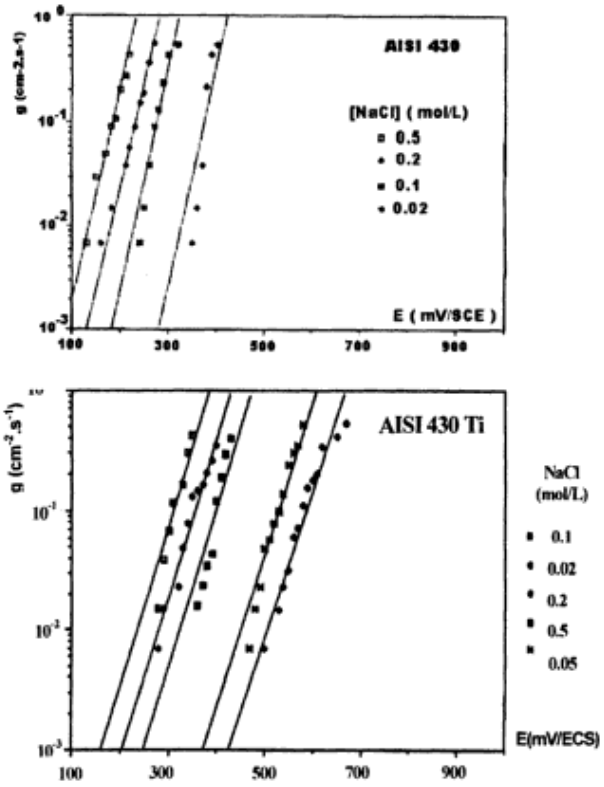

Figure 1 : Elementary pitting probability g(E) for the two stainless steels in deaerated neutral sodium chloride solutions

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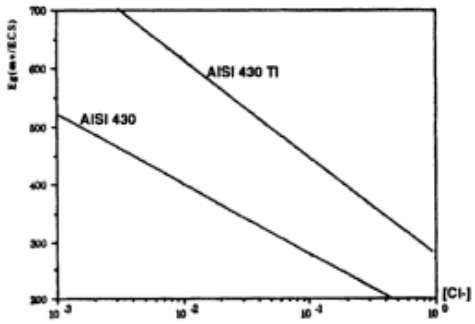

Figure 2 : Conventional pitting potentials for AISI 430 and 430 Ti in deaerated neutral sodium chloride solutions

CONCLUSION

The pitting initiation of stainless steels is depending on the passive film stability, but this stability is modified by the nature of inclusions present at the surface of the alloy. In particular, the sulfide solubility is an important parameter, which governs the passive film resistance to pitting corrosion. By comparison with previous tests performed in thiosulfate solutions, it appears that MnS and $Na_2S_2O_3$ play a similar role : that can be explained by MnS dissolution with thiosulfate formation in the medium. Titanium sulfide inclusions are non-soluble: pit initiation is due to matrix dissolution, and corresponds to a local depassivation.

Thus, passive film resistance to breakdown is greatly modified by the nature and the solubility of sulfide inclusions in industrial stainless steels. The interface between matrix and inclusion is the weakness point of the passive film and the inclusion can be considered as an anode if the inclusion is soluble (the MnS case) or cathode if the inclusion is insoluble (the TiS_2 case).

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