

Chemical Descaling of High Temperature Oxides Formed on Low Alloy Steels

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Introduction

The dissolution processes of “low temperature” thermal oxide layers ($\text{Fe}_3\text{O}_4|\text{Fe}_2\text{O}_3$) on iron and steels have been studied in acid solutions for over 80 years^{1, 2}. Even though, many questions about the pickling mechanism of high temperature $\text{Fe}_{(1-x)}\text{O}$ -containing scales remain open. It was early proposed^{2, 3} that the cathodic reactions involved in the dissolution of Fe_3O_4 and Fe_2O_3 in HCl solutions are most probably: 1) the reductive dissolution of ferric oxide, 2) oxygen reduction reaction (ORR) and 3) the hydrogen evolution reaction (HER). In the case of the acid pickling of the same oxides in 0.1 M H_2SO_4 solution, it was suggested⁴ that the rapid dissolution of the oxide films, when in contact with the metal substrate would be due to the formation of the cell “metal|acid|ferric oxide”. In this cell, the cathode would be the ferric oxide and could be quickly reduced to ferrous oxide, which would dissolve.

It was early identified by Pryor and Evans² that during the dissolution of Fe-oxides in HCl solutions, thicker Fe_3O_4 films result in a higher ohmic resistance and thus electron transport parallel to the Fe|oxide interfaces is more probable to occur.

It was further proposed that the reductive dissolution takes place near on oxide defects or on places where the film is abnormally thin. This could explain the slow and irregular form of self-reduction observed for thick films. Finally, it is proposed that the reductive dissolution occurs in three parallel steps: (1) Electron transport across the oxide, (2) reduction of the oxide layers to the ferrous valence, and (3) rapid dissolution of the direct reduction product. In this work we use the Scanning Vibrating Electrode Technique (SVET) to identify the mechanism of the chemical descaling. In a previous work⁵ results on thermal oxides formed on carbon steels under laboratorial conditions were reported, while now microelectrode techniques were used to describe the mechanisms of the chemical descaling of hot-rolling industrially formed scales.

Experimental

In this work the industrial process of chemical descaling of two low alloy steels was studied in 6M HCl at room temperature. For this, wire rods of the steels AISI 1095 (1 %C) and AISI 52100 (1 %C, 1.5 %Cr) were hot-rolled in a steel plant under controlled conditions of rolling temperature and cooling rate after coiling. For the microcharacterization of the high temperature scales the techniques XPS, grazing angle DRX and quantitative SEM–EDS with standards were used. The descaling performance of the steels was evaluated by mass loss measured continuously during descaling and voltammetry in the 6 M HCl solution, while *i*-maps were measured in more dilute solutions by the Scanning Vibrating Technique (SVET). Cross section preparation from hot-rolled wire rods is schematically shown in **Fig. 1** and the Electrochemical cell assembly for SVET measurements, respectively, in **Fig. 2**.

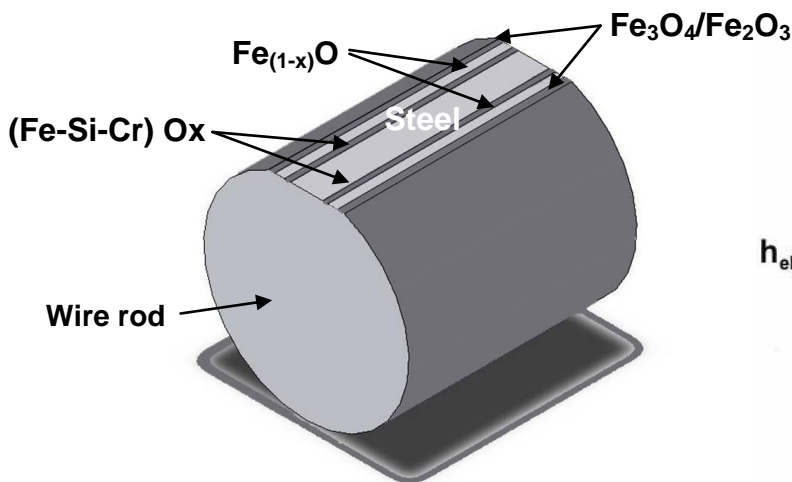


Fig 1 Schema of the preparation of cross section samples for SVET.

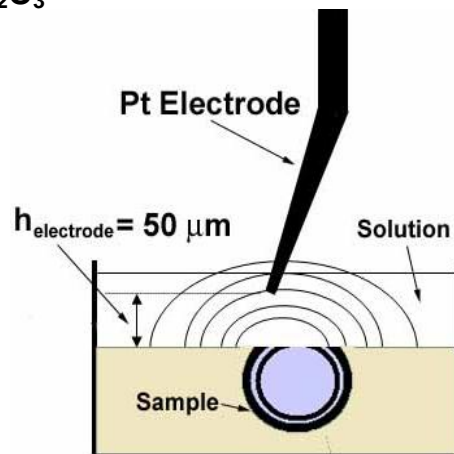


Fig 2 Electrochemical cell assembly for SVET measurements

Results and Discussion

Fig. 3 shows the mass loss during descaling of the two steels in 6 M HCl. A fast descaling rate is measured initially during the first 500 to 600 seconds (region 1) probably associated to the chemical dissolution of the scale, followed by a lower rate (2) characterized by strong H₂ evolution and low frequency weight oscillations. It was observed that these oscillations result from sample floating due to formation and detachment of H₂ bubbles, and are related to a strong attack of the metallic substrate. The optical observation during descaling revealed that the trend from region (1) to (2) is associated to the delamination and detachment from the surface of scale lamella that do not dissolve completely in the solution. The 1.5% Cr steel, even after 3h exposure, still shows scale residue on the surface, while the AISI 1095 is completely free of visible oxides after 20 min.

Fig. 4 shows an example of cyclic voltammetry measured on the oxidized AISI 1095 steel covered with a thick scale. In the first cycle, a low intensity *i*-plateau starting at potentials ca. 150 mV below E⁰(Fe³⁺/Fe²⁺) is observed, which can be attributed to the oxidation of wustite. In the following cycles this plateau is shifted to potentials above E⁰(Fe³⁺/Fe²⁺) and an *i*-peak of Fe oxidation is increasingly observed. XPS measurements showed that wustite contains small amounts of reduced Fe, which is probably formed by the eutectoid decomposition of wustite (4 FeO => Fe₃O₄+Fe).

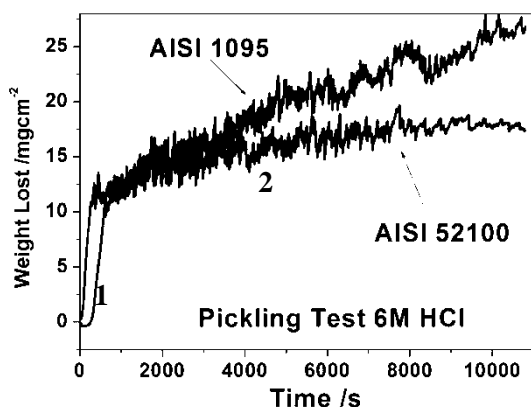


Fig. 3 Weight Loss Test for AISI 1095 & 52100 at 6M HCl solution

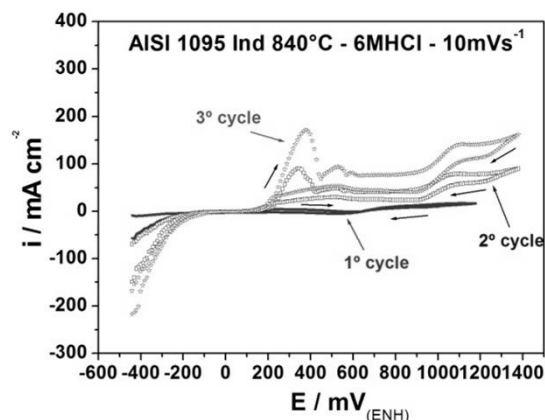


Fig. 4 Voltammetric measures for AISI 1095 at 6M HCl solution

Fig. 5 a and **c** show the cross section surface of the AISI 1095 steel, before and after exposure to a dilute descaling solution of 0.01 molL⁻¹ HCl, while in **Fig. 5b**, the corresponding *i*-map acquired after 1 hour is shown. The obtained *i*-values vary between 140 on the steel and -60

$\mu\text{A}\cdot\text{cm}^{-2}$ on the wustite surface. After the exposure during SVET measurement it was observed that a deep attack of the wustite occurs close to thtial interfacee me, while the magnetite/hematite surface is not attacked. This means that at least in dilute HCl solution descaling occurs by chemical dissolution of wustite under a strong hydrogen evolution and delamination of the upper magnetite/hematite layer.

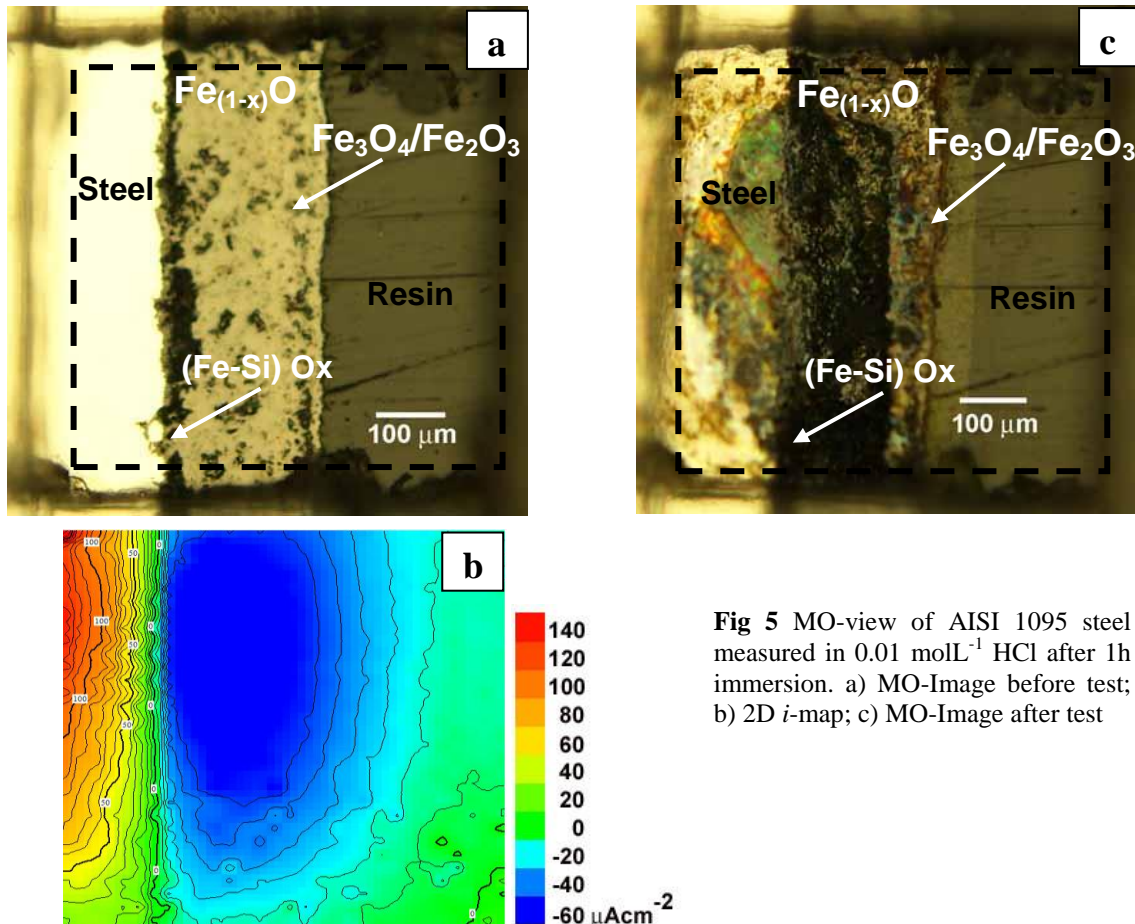


Fig 5 MO-view of AISI 1095 steel measured in 0.01 molL^{-1} HCl after 1h immersion. a) MO-Image before test; b) 2D *i*-map; c) MO-Image after test

Conclusions

The descaling process occurs by the chemical dissolution of the inner $\text{Fe}_{(1-x)}\text{O}$ layer, close to the metal surface, where the Fe content is higher. The outer $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ layer and attached undissolved Fe-poor $\text{Fe}_{(1-x)}\text{O}$ can then delaminate. A galvanic couple is formed between Fe and $\text{Fe}_{(1-x)}\text{O}$ and thus, very high anodic current densities occur on the steel surface close to the wustite interface, while the cathodic currents are more homogeneously distributed on the whole $\text{Fe}_{(1-x)}\text{O}$ surface. This intense Fe dissolution probably contributes to the descaling process.

Acknowledgements

The authors acknowledge the CAPES-COFECUB International Cooperation Program and the Microscopy Centre of UFRGS.

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