Contribution of electrochemical dissolution during pickling of low carbon steel in acidic solutions

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ABSTRACT

An electrochemical cell coupled with ICP-OES chemical analysis was used to explore the role of chemical and electrochemical reactions in pickling of low carbon steel in acidic media. Impedance spectroscopy was used to highlight scale properties. Dissolution of hematite is shown to be mainly of chemical nature, whereas the dissolution of magnetite and wüstite is both chemical and electrochemical. Initially, chemical dissolution of the scale dominated. The electrochemical reactions included oxidation of magnetite and wüstite and reduction of ferric ions formed by chemical dissolution. After the electrolyte reached the steel substrate, electrochemical dissolution of the iron was the main reaction.

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1. Introduction

Removal of scale from a steel surface concerns important industrial processes. In the hot strip mill process, steel surface is in contact with humid air at high temperatures, from nearly 1200 °C (reheating furnace) to nearly 700 °C (coiling). In these conditions, an oxide layer called commonly "scale" is formed [1]. It is usually removed by dissolution in an acid bath to recover a clean, bare, and smooth steel surface compatible with surface quality requirements. For non alloyed steels, scale is mainly composed of a mixture of iron oxides, which are soluble in pickling baths such as hydrochloric acid. The challenging aim of this process is to remove the scale completely without dissolving and thus roughening the steel substrate (over-pickling).

A good control of the dissolution process requires an accurate understanding of the mechanism of pickling and over-pickling. Such a study in real industrial conditions is difficult to be performed, since the pickling treatments on a mild steel fabrication line is very rapid, usually less than one minute. Another problem for such a study is the need to obtain well-defined systems reproducing the industrial scale composition, i.e. continuous parallel sub-layers deposited on the substrate and made of wüstite (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3) [2]. In order to obtain

information on the behaviour of passive films, a large amount of work has been carried out on pure iron oxides (bulk oxides, sintered powders or sputtered layers on a membrane) [3–9], and it has been shown that the electronic properties of synthetic iron oxides are in good agreement with the behaviour of natural passive films on iron. Compared to the large amount of data on the mechanism of pure iron oxide dissolution, there is much less information available on the dissolution of oxides from steel surface. In Ref. [10], oxides have been thermally formed on steel in different atmospheres and were only characterised in their initial state in a neutral medium. They have been shown to consist of an inner magnetite scale covered by a hematite layer, both with semiconducting properties that could be varied significantly by changing the atmosphere during thermal treatment.

Since it is known that iron oxide dissolution in acid solutions is simultaneously a chemical and an electrochemical process [5,7–9], another difficulty is to find experimental methods which allow the two mechanisms to be distinguished. While electrochemical methods provide information on the rate of electrochemical dissolution, additional analytical techniques are necessary to determine the total dissolution rate. In Refs. [5,7], *in situ* X-ray absorption near-edge spectroscopy (XANES) has been used simultaneously with electrochemical methods on synthetic oxide to determine the nature of the dissolution reaction, leading to the conclusion that dissolution of hematite and magnetite is mainly chemical in the anodic potential range, and that electrochemical dissolution of magnetite has to be taken into account in the cathodic range. Inductively coupled

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plasma-atomic emission spectroscopy (ICP-OES) has been shown to be a useful method for the *in situ* determination of material dissolution, using solution analysis in a flow cell [11–13]. A similar approach was used in the present work on oxide layers grown on a steel substrate. In order to reproduce the composition of the scale obtained in a hot strip mill, the oxide layer was thermally grown in a furnace. Electrochemical methods such as polarisation curves and impedance spectrometry were applied to estimate the rate of electrochemical dissolution, whereas the overall rate of iron dissolution in the pickling solution was followed *in situ*, using an analytical set-up composed of an inductively coupled plasma optical emission spectrometer (ICP-OES) placed downstream from the electrochemical flow. To allow measurements at a reasonable time scale, a 1 molar hydrochloric acid solution was used as pickling solution (1–3 M in industrial conditions) and all the experiments were performed at 20 °C (instead of 50–90 °C), assuming that a temperature increase does not modify the mechanisms, but only the rate of the reactions. Addition into the pickling bath of inhibitors often used on industrial lines was not considered in the present work and could be the aim of a future paper.

From the comparison between the electrochemical dissolution rate and the rate of total iron enrichment in the pickling bath, estimation of the chemical dissolution rate could be performed.

2. Experimental

2.1. Sample elaboration

A disc of 25 mm diameter was extracted from a low carbon steel black coil sheet and ground with SiC paper to a grit of 800 on both faces to remove scale and rust of hot rolling. The composition of the low carbon steel sample under investigation is given in Table 1.

2.2. Oxidation process

The oxidation process was conducted in an Orion® Pilot furnace. Both disc surfaces of all samples were ground with a SiC-paper to a grit of 800, cleaned in ethanol and then dried in air before oxidation tests. The samples were heated in a nitrogen atmosphere at a rate of 40 °C/min. The rate was reduced to 5 °C/min for the last 50 °C to avoid exceeding the desired oxidation temperature. Once the desired temperature was reached, the oxidation was isothermal at temperature 850 °C with 15% relative humidity for duration of 15 min. The pilot furnace chamber was subsequently cooled in a N_2 atmosphere to room temperature at a rate of 40 °C/min. The whole oxidation process is described in [14].

2.3. Electrochemical measurements

A classical three-electrode cell immersed in an air-saturated acid bath (HCl 1 mol L^{-1}) cell was used for pickling and over-pickling experiments at room temperature (20 °C). A saturated calomel electrode and a platinum electrode were used as reference and auxiliary electrodes, respectively. The oxidised disk electrode was integrated in a sample-holder, with the scale covered face in contact with the electrolyte. The back-face was polished to ensure good electrical contact with the stainless steel central piece of the sample holder. An electrochemical interface (Solartron SI 1287) and a frequency response analyzer (Solartron 1250) were

Table 1
Chemical composition of the steel as obtained by optical emission spectroscopy (OES).

Element	C	Si	Mn	P	Cr	Ni	Cu	N	Fe
wt%	0.04	0.02	0.19	0.01	0.025	0.017	0.025	0.01	Balance

monitored by a computer using Zware and Zplot software for electrochemical measurements. Impedance experiments were performed over frequencies ranging from 65 kHz to 0.2 Hz, using a 10 mV sinusoidal potential modulation peak to zero. The potential scan rate for the potentiodynamic experiments was 1 mV s^{-1}. All the electrochemical tests were performed in static conditions (rotation rate = 0 rpm).

2.4. ICP-OES experiments

An ICP-OES spectrometer, located in the ArcelorMittal Research Centre, has been adapted for electrochemical experiments as described in detail by Ogle and Weber [15]. The coupling of a flow cell and ICP-OES spectrometer allows the multi-element analysis in the electrolyte downstream from a dissolution cell, but, in the present case, only the iron concentration was followed. The spectrometer is a commercial apparatus from Jobin-Yvon, Inc. (Ultima 2000) using a polychromator, an argon plasma source consisting of a 40 MHz, 1 kW inductively coupled plasma, into which the electrolyte sample is continuously aspirated. In the flow cell used, the working electrode of the electrochemical cell was placed in a small compartment (0.2 mL of electrolyte), which is separated by a membrane from an adjacent compartment containing the reference. The electrolyte passed through the cell with a flow rate of about 2 mL/min, and the iron composition of the electrolyte was measured in real time. Previous calibration of the set-up allowed the establishment of the relationship between dissolution rate and concentration, taking into account the time resolution of the hydraulic system. The detailed procedure is described in Ref. [15]. The sample surface in contact with the electrolyte was 5×15 mm^2.

3. Results

3.1. Scale characterisation

After oxidation in the pilot furnace, the samples were moulded in a cold resin and ground with SiC-paper to a grit of 4000 to obtain cross-section micrographs. The resulting steel scale was homogenous and was essentially composed of wüstite covered by a magnetite layer (Fig. 1a). The mean thickness of the scale was about 70 μm. Below 570 °C, wüstite is known to be unstable and to transform into iron and magnetite eutectoid [16,17]. However, this transformation needs very low cooling rates, and, since in these experiments the cooling rate was about 40 °C/min, it can be assumed that this transformation only affected a small part of the scale volume [14,15].

On the top of the scale surface, Raman analysis shown in Fig. 1b revealed the presence of a hematite layer with intense peaks at 220 cm^{-1}, 290 cm^{-1} and 410 cm^{-1}, as well as small peaks at 500 and 610 cm^{-1}. This hematite layer was very thin and not visible on SEM micrograph of sample cross-section.

Raman characterisations performed on cross-section did not allow clear differentiation of magnetite and wüstite. The Raman spectrum obtained on the external layer corresponds well to the spectrum of magnetite (Fe_3O_4) with characteristic peaks at 310 cm^{-1}, 540 cm^{-1} and 670 cm^{-1} (Fig. 1b). The wüstite phase (FeO) is cubic and should not be visible on Raman. However, a peak at 660 cm^{-1} was observed from the Raman analyses of the internal layer (Fig. 1b) [18,19]. This peak could be due to the presence of lacunas in wüstite microstructure (wüstite $Fe_{1-x}O$ with relatively large x variation according to the phase diagram [17]) or partial wüstite transformation during cooling into $Fe + Fe_3O_4$ eutectoid (presence of magnetite areas).