Applied Surface Science 293 (2014) 24–36

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Behaviour of tetramine inhibitors during pickling of hot rolled steels

Marie-José Cornu[a], Alexey Koltsov[a,*], Sabrina Nicolas[a,b], Lydia Colom[a], Manuel Dossot[b]

[a] ArcelorMittal Maizières Research, Voie Romaine, 57280 Maizières-lès-Metz, France
[b] Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME) – UMR 7564 CNRS – Université de Lorraine, 405 rue de Vandoeuvre, 54602 Villers-lès-Nancy, France

ARTICLE INFO

Article history:
Received 1 August 2013
Received in revised form 24 October 2013
Accepted 6 December 2013
Available online 15 December 2013

Keywords:
Steel
Raman spectroscopy
XPS
Acid corrosion

ABSTRACT

To avoid the dissolution of steel in industrial pickling process, tetramine inhibitors are added to the pickling bath. This study is devoted to the understanding of the action mechanism of these inhibitors in hydrochloric and sulphuric baths on non-alloyed and alloyed steels. Pickling experiments and characterization with XPS, Raman and infrared spectroscopies have shown that inhibitors work only in acid media and leached out from the steel surfaces during the rinsing operation just after pickling. The effectiveness of inhibitors depends on the acid media and the temperature. Experimental data are consistent with a surface mechanism, i.e., the so-called "outer-sphere" adsorption.

1. Introduction

In the industrial process of flat carbon steel production, after hot rolling the steel strip is covered by scale, an oxide layer a few μm thick. It is removed by the pickling operation in order to obtain a satisfactory surface quality for subsequent cold rolling steps. The pickling process consists in the immersion of the hot rolled steel strip into the baths containing a concentrated hydrochloric (HCl) or sulphuric (H_2SO_4) aqueous acid solution. HCl is preferred in industry over H_2SO_4 because the ferrous chloride formed on the surface is highly soluble in water and there is no smut formation on the surface [1,2].

For classical low alloyed steels, the scale is composed of three layers of iron oxides: a thick wüstite (FeO) layer adjacent to the steel, an intermediate magnetite (Fe_3O_4), and a thin outlying hematite (Fe_2O_3) layer [1,3–5]. The scale microstructure is influenced by different parameters, such as the temperature during the hot rolling operation, the subsequent cooling rate and the storage conditions. According to the coiling temperature and cooling rate, the wüstite (FeO) layer of the scale can be decomposed partly or almost completely in $Fe + Fe_3O_4$ eutectoid [2,4].

During the pickling process in an acid medium, these different oxides react with protons according to the following chemical reactions:

$$FeO + 2H^+ \rightarrow Fe^{2+} + H_2O \tag{1}$$

$$Fe_3O_4 + 8H^+ \rightarrow Fe^{2+} + 2Fe^{3+} + 4H_2O \tag{2}$$

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O \tag{3}$$

The reaction products are iron cations and water. Iron cations can further combine with chloride or sulphate ions. When the scale is eliminated from the steel surface, protons react with the base steel:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{4}$$

The production of hydrogen gas is characteristic of the corrosion of base steel and has to be avoided. For this purpose a corrosion inhibitor is introduced into the pickling bath [1,2,6–9]. To play this role, molecules enabling electron donation such as π electrons in aromatic rings [2,8–10] or electrons from non-bonding *n* orbitals are the most efficient. Amines are a well-known class of inhibitors containing non-bonded *n* orbitals [7]. They are successfully employed for acid solutions due to their significant inhibitive efficiency given by nitrogen atoms that are electronegative.

Two amine molecules are typically used in commercial inhibitor solutions for pickling baths: hexamethylenetetramine (HMTA, IUPAC name 1,3,5,7-tetraazatricyclo[3.3.1.1(3,7)]-decane) and triethylenetetramine (TETA, IUPAC name N,N′-bis(2-aminoethyl)-1,2-ethane-diamine). HMTA is a cyclic tetramine molecule (Fig. 1a).

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* Corresponding author. Tel.: +33 387 70 48 95; fax: +33 387 70 47 13.
E-mail addresses: marie-jose.cornu@arcelormittal.com (M.-J. Cornu), alexey.koltsov@arcelormittal.com, koltsow@yahoo.fr (A. Koltsov), sabrina_nicolas@live.fr (S. Nicolas), Lydia.colom@sfr.fr (L. Colom), manuel.dossot@univ-lorraine.fr (M. Dossot).

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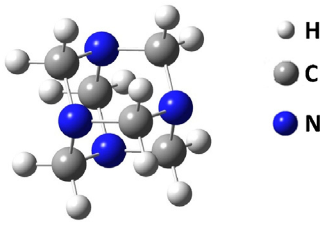
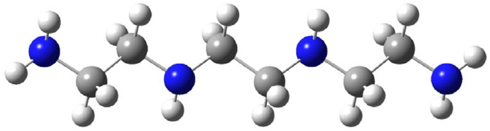
http://dx.doi.org/10.1016/j.apsusc.2013.12.024



a) Hexamethylenetetramine HMTA
($C_6H_{12}N_4$, MW = 140.19 g mole^{-1})



b) Triethylenetetramine TETA
($C_6H_{18}N_4$, MW = 146.23 g mole^{-1})

Fig. 1. Structure of HMTA (a) and TETA (b) molecules.

It is produced via reaction of formaldehyde and ammonia [11]. The molecule has only one p*K*a in water which means that only one nitrogen atom can be protonated in aqueous solution. TETA is a linear analogue of the HMTA molecule (Fig. 1b) [2]. Contrary to HMTA, TETA has four p*K*a values in water and the four nitrogen atoms can be protonated in aqueous solutions. According to Singh et al. [12], in the case of pickling in hydrochloric acid, the protonated HMTA molecule is adsorbed on the surface via electrostatic interaction with chloride anions sorbed on the surface, which defines an “outer-sphere” sorption mechanism. The inhibition efficiency of HMTA is a function of its concentration and the bath temperature [13]. Sathiyanarayanan et al. [2] presumed that the adsorption of TETA molecules is generally parallel to the steel surface. All the TETA molecules can form a bond with two iron atoms and effectively cover the surface even at a low concentration (10^{-2} mol L^{-1}) [2]. The inhibition efficiency of TETA is independent of its concentration contrary to HMTA, which has a maximum efficiency at high concentrations. This difference is explained by the higher surface coverage by one TETA molecule leading to the more efficient surface protection even at low concentrations. In the case of HMTA, the cage structure is thought to reduce the coverage efficiency [2].

Since these two corrosion inhibitors are widely used in pickling baths, the present work aims at comparing their respective mechanisms of corrosion inhibition under the conditions of a pickling bath for two different grades of steels. The pickling kinetic rates of the steel samples are first studied using two acids (HCl and H_2SO_4) and the role of the counter-ions Cl^- and $SO_4{}^{2-}$ is examined. Then the inhibitor efficiency is measured in these acidic solutions for HMTA and TETA. In order to understand the inhibition mechanism, the spectral properties of the corrosion inhibitors as a function of solution pH are studied. Finally, the steel surfaces after pickling are examined, and the rinsing steps after pickling are also studied. The information collected ex situ after pickling allows proposing a mechanism of corrosion inhibition for both inhibitors in the two acidic media studied.

2. Materials and methods

This study is focused on two model steel grades: a low carbon steel (grade A, containing 0.117 wt.% Mn, 0.074 wt.% Ti and 0.002 wt.% C) and an alloyed carbon steel (grade B, containing 1.6 wt.% Mn, 1.6 wt.% Si, and 0.22 wt.% C). The samples came from a hot rolling operation and were covered by a scale layer. The sample cross-sections are presented on Fig. S1 in the supporting information. The average scale thicknesses of 8 ± 2 μm and 14 ± 3 μm respectively for the A and B grades were estimated using the weight loss method described below. These thicknesses are in good agreement with those measured by optical images of the cross-sections in Fig. S1 in the supporting information.

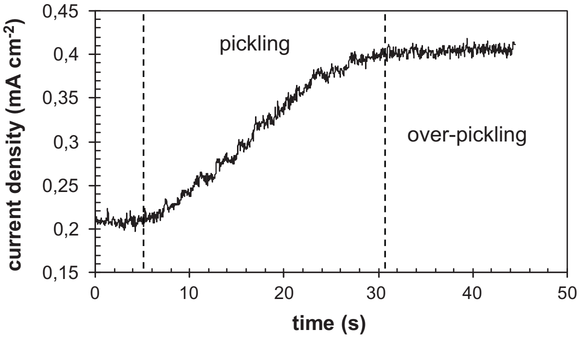


Fig. 2. Typical current vs. time curve for a pickling experiment in HCl acid containing inhibitor. The current increase corresponds to the pickling step and its stabilization corresponds to the full scale removal. Over-pickling step corresponding to iron dissolution is limited by pickling inhibitor in this case.

Before pickling, the samples were washed in ethanol and dried in air. They were then immersed in an agitated solution, at 70 °C. This solution contained HCl at 150 g L^{-1} (4.1 mol L^{-1}) or H_2SO_4 at 200 g L^{-1} (2.1 mol L^{-1}) and the inhibitor (HMTA or TETA from Sigma–Aldrich of the best purity) at 7×10^{-3} mol L^{-1}. The solutions were prepared using HCl 37% and H_2SO_4 96%. After pickling, the samples were rinsed in two demineralised water baths, first a hot bath (70 °C) and then a cool bath (ambient temperature). They were then dried under a flow of air. The pickling and rinsing conditions reproduce those typically employed in industry.

The pickling time was determined visually for square samples and by electrochemical measurement for disks. The experimental system used for electrochemical characterization of pickling time is composed of three electrodes, a working one of glassy carbon, a calomel reference (potential +0.248 V vs. normal hydrogen electrode NHE) or mercury-sulphate (potential +0.651 V vs. NHE) and an auxiliary one in platinum. The calomel electrode is used for the HCl solution and the mercury-sulphate electrode for H_2SO_4. A potential is applied between the working and reference electrodes. No potential or current is applied to the sample. Hence, the pickling is not disturbed by electrochemical reactions. In the hydrochloric acid bath, the potential applied is fixed at 800 mV/Ref (+1.048 V/NHE), whereas in the sulphuric acid bath, it is fixed at 400 mV/Ref (+1.051 V/NHE). These values are higher than the oxido-reduction potential of the redox couple Fe^{2+}/Fe^{3+} (+0.77 V/NHE) so as to provoke a total transformation of Fe^{2+} cations into Fe^{3+} by the reaction:

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^- \qquad (5)$$

The current produced between the working and auxiliary electrodes is therefore proportional to the concentration of the Fe^{2+} cations formed in the acid bath due to the dissolution of scale (Eqs. (1)–(3)) or iron (Eq. (4)). The pickling time was then measured as shown in Fig. 2 and corresponds to the total scale removal from the sample surface as detected visually (Fig. S2 in the supporting information).

In this study the pickling experiments were performed with a sample rotation speed of 450 rpm that corresponds to the industrial line speed of about 230 m min^{-1} and the same hydrodynamics regime. The scale thickness (e) is determined by weight loss measurements using the following formula:

$$e = \frac{W_1 - W_2}{\rho \cdot S} \qquad (6)$$