Materials Chemistry and Physics 143 (2014) 996–1004

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Effect of silicon content in steel and oxidation temperature on scale growth and morphology

Amine Alaoui Mouayd [a,b,c,*], Alexey Koltsov [c], Eliane Sutter [a,b], Bernard Tribollet [a,b]

[a] CNRS, UPR15, Laboratoire Interfaces et Systèmes Electrochimiques, F-75005 Paris, France
[b] UPMC Univ Paris 06, UPR15, LISE, 4 Place Jussieu, F-75005 Paris, France
[c] ArcelorMittal Maizières Research, voie Romaine, F-57280 Maizières-lès-Metz, France

HIGHLIGHTS

- A passivation period appears during oxidation of silicon steels at temperatures lower than 1177 °C due to silica formation.
- Silicon oxides concentrate at metal scale interface, their morphology depends on oxidation temperature.
- High silicon content leads to silica formation and long passivation of oxidation at temperatures lower than 1177 °C.
- Molten fayalite–wüstite eutectic at high temperatures enhances iron diffusion and cancels oxidation passivation.

ARTICLE INFO

Article history:
Received 6 August 2013
Received in revised form
9 October 2013
Accepted 29 October 2013

Keywords:
Alloys
Oxidation
Thermogravimetric analysis (TGA)
Raman spectroscopy and scattering

ABSTRACT

The effect of high silicon content in steel, 1.6 wt.%Si and 3.2 wt.%Si, and high oxidation temperatures (850–1200 °C) on scale growth rate and morphology were investigated. The steels were oxidized in a 15% humid air with short isothermal oxidation times (15 min). The scale growth rate of the non-alloyed steel follows a parabolic law with time; it is an iron diffusion controlled oxidation. The presence of silicon delays scale growth by forming a silica SiO_2 barrier layer at the scale/metal interface, this effect is more important for the steel containing 3.2 wt.%Si and induces a discontinuous scale. Silicon oxides are concentrated at the scale/metal interface; their morphology depends on the oxidation temperature. For temperatures lower than 950 °C, silica is formed. Between 950 °C and 1150 °C, fayalite (Fe_2SiO_4) grains appear in the wüstite matrix close to the scale/metal interface. For temperatures higher than 1177 °C, a fayalite–wüstite eutectic is formed; this molten phase favours iron diffusion leading to high scale growth. After cooling, a continuous fayalite layer with small wüstite grains is obtained at the scale/steel interface.

1. Introduction

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). At these conditions, an oxide layer called commonly "scale" is formed. It is usually removed by dissolution in an acid bath to recover a clean steel surface. For nonalloyed steels, scale is mainly composed of iron oxides and dissolved easily in pickling baths.

Some alloying elements such as Si, Mn and Al are added to steel to reach high level of mechanical properties like elasticity limit, strain strength, elongation, formability and crash worthiness. These elements segregate at high temperatures towards the scale/metal interface forming mixed oxides for silicon and aluminium or solid solutions in scale for Mn [1–3]. The presence of these oxides in the scale and at the steel/metal interface affects the pickling efficiency.

In this study, the focus is put on silicon effect on scale formation kinetics and chemistry during oxidation at hot strip mill temperatures. Silicon is present in Alloyed High Strength Steels (AHSS) to improve their mechanical and corrosion resistance, as well as in electrical steels for improving the electrical resistivity, which is an important property for applications as the core material of electromagnetic devices such as motors [4–6].

The elaboration of new silicon alloyed steel grades and the difficulties to pickle them triggered many recent studies on the effect of silicon on oxidation kinetics and final scale morphology. Some of these studies proposed some oxidation mechanisms for silicon alloyed

---

* Corresponding author. LISE, UPMC, 4 Place Jussieu, 75005 Paris, France. Tel.: +33 1 44 27 43 24.
E-mail address: amine.alaoui_mouayd@upmc.fr (A. Alaoui Mouayd).

0254-0584/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matchemphys.2013.10.037

samples but were limited to medium silicon alloyed grades and did not correspond completely to the Hot Strip Mill conditions [7–11].

According to Atkinson [12] and Adachi et al. [13] silicon contained in steel is first oxidized into silica which forms an interfacial sub-layer between wüstite and steel. The internal oxidation of steel can be also observed (oxide particles inside the steel), especially for the steel containing more than 0.3 wt.%Si. Genève [14] pointed out that scale adhesion is lower on Si steels than in that of FeO on pure Fe. On the contrary, the adhesion between silica or fayalite and the substrate is strong: leading to an increased difficulty to remove scale containing silicate phases during pickling. Above 1177 °C, the FeO–Fe_2SiO_4 [15] eutectic melts and infiltrates scale and steel grain boundaries. The penetration depth into the scale increases with the Si content, while that into the substrate varies slightly. The presence of liquid phase improves the scale adhesion for steels containing less than 0.5 wt.%Si, but for higher Si contents (up to 1.5 wt.%) the tendency is inversed.

In our study, high temperature and humidity conditions corresponding to those in the hot strip mill were applied on a medium and a highly silicon alloyed steel grades to determine the silicon effect on scale formation kinetics and mechanism. The chemistry and morphology of the resulting scale as well as the oxidation mechanism are demonstrated by crossing different characterization methods.

2. Experimental implementation

2.1. Samples elaboration

Samples of steels with different grades were elaborated in a 1 kg furnace where a bloc of nonalloyed steel melts and adequate masses of alloying elements were added to create the desired grades. After each addition, pencils were extracted with depressurized glass tubes. The pencils have a cylindrical form with a 4 mm diameter and a 120–150 mm length. The final samples form is a cylinder of a 5–10 mm length with a hook welded on its top disc for suspension in a thermo-gravimetric analyser, the studied surface is then the cylinder's bottom disc. Grades with silicon contents 0.02 wt.%Si (Si00), 1.6 wt.%Si (Si16) and 3.2 wt.%Si (Si32) were targeted, their chemical composition is given in Table 1.

2.2. Oxidation tests

The oxidation tests were conducted in a Linseis® Thermo-Gravimetric Analyser (TGA). The bottom disc surface of all samples was ground with a SiC-paper up to grade 800, cleaned in ethanol and then dried in air before the oxidation tests. The mass change was recorded continuously (1 point/second) during the entire thermal cycle. The sample was heated in a Nitrogen atmosphere at a rate of 40 °C min^{-1} and 5 °C min^{-1} for the last 50 °C to avoid over-heating once the desired oxidation temperature was reached. All oxidations were isothermal in the temperature range 850–1200 °C, in a 15% humid air during 15 min. Some additional experiments have been performed at lower durations for characterization purposes. After the test, the TGA chamber was cooled in a N_2 atmosphere down to room temperature with a 40 °C min^{-1} rate.

Table 1
Chemical composition of the three steel grades with optical emission spectroscopy (OES).

Sample	Elements (wt.%)							
	C	Si	Mn	P	Cr	Ni	Cu	N	Fe
Si00	0.04	0.02	0.19	0.01	0.025	0.017	0.025	0.01	Balance
Si16	0.04	1.55	0.19	0.01	0.025	0.017	0.025	0.01	Balance
Si32	0.04	3.25	0.19	0.01	0.025	0.017	0.025	0.01	Balance

2.3. Scale characterisation

After oxidation in the TGA, the samples were moulded in a cold resin and ground with SiC-papers up to grade 4000 to obtain cross-sections micrographs. Scale phases were observed with optical microscopy and scanning electrons microscopy. The phase nature was identified using Raman spectroscopy analyses and the estimation of elements content given by energy dispersive spectroscopy (EDS). Some samples were analysed by X-rays photoelectron spectroscopy (XPS) and Auger-FEG. The XPS setup used for characterizations was a Perkin–Elmer PHI 5500 with monochromatic Al Kα X-ray source of 187 eV (for survey spectra) and 11 eV (for high resolution spectra) pass energies of the analyzer. XPS characterizations showed depth resolution of 10 nm; analysed area was of 0.8 × 2 mm^2. Auger-FEG characterizations were performed with a Jeol Jamp 9500F device. Analyses were done at an acceleration voltage of 15 kV, a beam current of 1×10^{-8} A and a sample tilt of 0°.

3. Results and discussion

3.1. Scale growth kinetics

The mass gain per surface unit ($\Delta m/S$) of the non-alloyed sample Si00 during oxidation in a 15% humid air, at temperatures 900–1200 °C is reported in Fig. 1. For the non-alloyed sample Si00 at all oxidation temperatures, scale growth first follows a linear law (1) then a parabolic law (2).

The mass gain laws can be described by the following formulae:

- First linear step:

$$(\Delta m/S) = k_l \cdot t \tag{1}$$

- Parabolic step:

$$(\Delta m/S)^n = k_p \cdot t \tag{2}$$

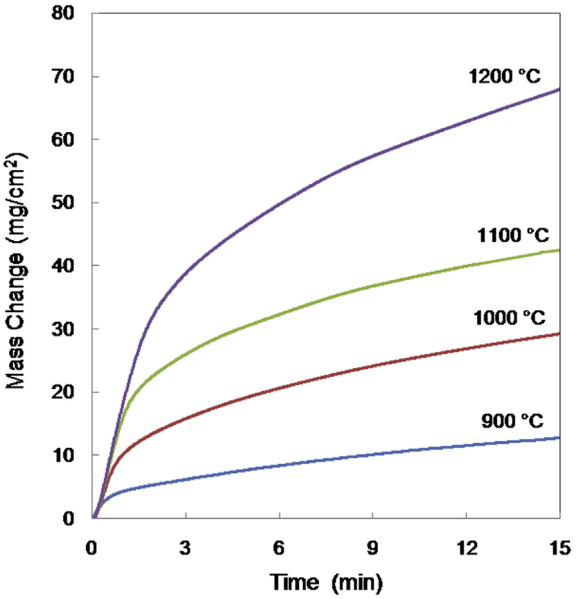

Fig. 1. Mass gain of Si00 during oxidation in 15% humid air at temperatures 900–1200 °C.