Corrosion Science 98 (2015) 507–515

Contents lists available at ScienceDirect

Corrosion Science

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

Anomalous oxidation of Fe–Si alloys under a low oxygen pressure at 800 °C

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ARTICLE INFO

Article history:
Received 19 December 2014
Accepted 23 May 2015
Available online 4 June 2015

Keywords:
A. Iron
B. SEM
C. Internal oxidation
C. Amorphous structures

ABSTRACT

The oxidation of three Fe–xSi alloys (x = 5, 9, 13 at.%) under 10^{-20} atm O_2 at 800 °C formed in all cases SiO_2 layers. For Fe–5Si this layer broke down and healed up periodically forming an anomalous internal oxidation zone with spherical and net-shaped SiO_2 particles. The SiO_2 layer formed on the other two alloys spalled off due to the growth and thermal stress accumulated. The critical silicon content needed for its external oxidation on Fe–Si alloys calculated according to an extension of Wagner's theory under the present experimental conditions is significantly smaller than the experimental results.

1. Introduction

Silicon is one of the most important alloying elements in commercial steels used in the manufacture of automobile bodies and frames and in the cores of motors and transformers. However, the oxidation properties of silicon steels seriously affected their application. Up to now, the oxidation of Fe–Si alloys with different silicon contents has been the subject of many investigations in different atmospheres, including air [1–6], pure O_2 [7–9], CO_2 + CO [10–12], air + H_2O [4,13], CO + H_2 + H_2O [14,15], H_2 + H_2O [16,17], CO_2 + H_2O [18,19], H_2 + N_2 + H_2O [20,21]. In these studies, the internal oxidation of silicon in Fe–Si alloys has been observed both in the presence [2,5,7,13,16–20] and in the absence [14,15,21] of external iron oxides. In the latter case, when the silicon content was less than 2 at.%, the shape of the SiO_2 particles was spherical [21], while for larger silicon contents, for example 5 at.% and 9 at.%, dendritic SiO_2 particles started to appear and were associated with the appearance of a thin continuous SiO_2 layer at the interface between the internal oxidation zone (ioz), and the base alloy [14]. This structure of the ioz, differing from the classical type which does not involve the presence of a nearly continuous layer of internal oxide at the interface between the ioz and the alloy but only a direct transition to an alloy matrix free from oxide particles, is named here as an anomalous ioz. However, the formation mechanism of this peculiar internal oxidation zone was not considered in details in the previous paper [14]. The present study examines the oxidation behavior of three Fe–Si alloys with rather high silicon contents under an oxygen pressure below the decomposition of the iron oxides. The critical silicon content required for the exclusive external oxidation of silicon is calculated and compared with the experimental results. The scale evolution is presented for different reaction times and silicon contents: in particular, the anomalous type of internal oxidation has been observed for the two more dilute alloys.

2. Experimental

Three Fe–Si alloys with nominal silicon contents of 5, 9 and 13 at.% (Fe–5Si, Fe–9Si and Fe–13Si, respectively) were prepared by repeated melting by vacuum induction mixtures of appropriate amounts of the two pure elements (99.8% Fe and 99.99% Si). The alloy ingots were subsequently annealed in 1 atm argon at 1000 °C for 36 h to remove the residual mechanical stresses and achieve a better alloy equilibration. The actual composition of the alloys, measured by inductively coupled plasma (ICP) spectrometry, is shown in Table 1. In agreement with the Fe–Si phase diagram, Fe–5Si and Fe–9Si are single-phase α, while Fe–13Si is single-phase α_1 [22]. The average grain sizes of the three alloys were 1.59 (Fe–5Si), 1.12 (Fe–9Si) and 0.506 mm (Fe–13Si) calculated according to the procedure described in GB/T 6394-2002.

Specimens with a size of 10 mm × 8 mm × 1.5 mm were cut from the ingots using a line saw and a 1 mm hole was drilled near one edge. All the specimens were mechanically abraded on successively

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http://dx.doi.org/10.1016/j.corsci.2015.05.055
0010-938X/

Table 1
Nominal and actual compositions of three Fe–*x*Si alloys measured by ICP spectrometry analysis.

Nominal	Actual (at.%/wt.%)
Fe–5Si	Fe–5.35/2.75Si
Fe–9Si	Fe–9.47/4.97Si
Fe–13Si	Fe–13.00/6.96Si

finer abrasive papers down to 2000 grit and finally cleaned with water, acetone and ethanol and dried immediately before each test. Prior to the experiment, each specimen was first suspended in the reaction chamber by quartz fibers and a Pt wire. The reaction tube was then flushed with the gas mixture from below with a counter flow of nitrogen from the top for about half an hour. A Pt gauze was placed below the sample at a distance of less than 1 cm in the hot zone to facilitate reaching equilibrium. After reaching the reaction temperature, the vertical furnace was raised to locate the specimen in the hot zone. The mass changes of the specimens were continuously recorded with a microbalance Setaram B-92. The mass of each specimen was also measured with an electronic balance before and after oxidation as a check of the recorded mass changes. The oxidized samples were examined by SEM (FEI INSPECT F 50, USA) attached with EDS (OXFORD X-Max, UK) and by X-ray diffraction (Panalytical X' Pert PRO, Holland). In addition, the oxidized samples prepared for observing the cross sections were ground down mechanically by 5000 emery paper after being mounted by resin and then polished by emery and diamond pastes. By equilibration at 800 °C the reacting gas, composed of 13.2 vol.% CO_2 balance H_2, provided an oxygen pressure of 10^{-20} atm. To identify the structure of the internal oxide particles in three dimensions, some samples, mounted in a direction parallel or perpendicular to the large face (10 mm × 8 mm), were etched with a $CuSO_4$ solution to remove iron from the internal oxidation zone to different degrees.

3. Results

3.1. Kinetic results

Parabolic plots of the kinetic curves obtained for the three alloys oxidized under the present conditions are shown in Fig. 1. The mass gains of these alloys after a fixed reaction time decreased with an increase of the silicon content, an effect which was particularly large in shifting from Fe–5Si to Fe–9Si. The kinetic curves did not follow the conventional parabolic rate law, which involves linear parabolic plots, and were generally rather irregular, presenting values of the instantaneous slope of the parabolic plot, denoted as instantaneous parabolic rate parameter (iprp), changing with time. In particular, the iprp of Fe–5Si decreased continuously with time from an initial value of $1.1 \times 10^{-11}\ g^2\ cm^{-4}\ s^{-1}$ to a limiting value of $6.5 \times 10^{-14}\ g^2\ cm^{-4}\ s^{-1}$, reached after about 10 h, which then remained constant up to the end of the experiment.

The oxidation of Fe–9Si showed a continuous increase of the iprp with time and followed approximately two parabolic stages with parabolic rate constant k_p of the first stage, lasting from 2 to 17 h, equal to 4.9×10^{-14}, while that of the second stage, lasting from 18 to 24 h, equal to $9.9 \times 10^{-14}\ g^2\ cm^{-4}\ s^{-1}$. Conversely, the oxidation of Fe–13Si showed a continuous decrease of the iprp with time and was more irregular (Fig. 1b), showing a first faster stage of about 2 h with a $k_p = 2.3 \times 10^{-13}\ g^2\ cm^{-4}\ s^{-1}$, followed by a second approximately parabolic stage lasting from 4 to 24 h with a $k_p = 1.7 \times 10^{-15}\ g^2\ cm^{-4}\ s^{-1}$.

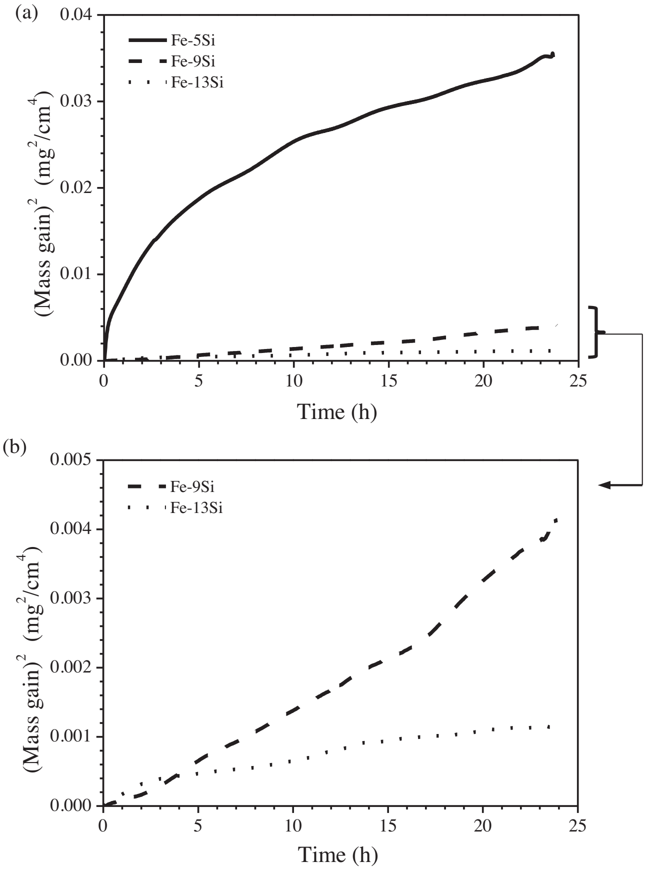

Fig. 1. Parabolic plots of the kinetic curves for the Fe–*x*Si (*x* = 5, 9, 13 at.%) oxidized in the H_2–CO_2 mixture at 800 °C for 24 h. (a) General plots; (b) enlarged plots for Fe–9Si and Fe–13Si.

3.2. Scale structure and composition

Cross sections of Fe–5Si oxidized for 4 different times (1.5, 4, 18 and 24 h) are shown in Fig. 2. In all cases iron oxides did not form, as shown in Fig. 3, while an SiO_2 layer containing some iron (the oxide layer is too thin to obtain an accurate analysis) formed at the front of the internal oxidation zone; this layer was discontinuous for samples oxidized for 1.5 and 4 h (Fig. 2a and b) but became continuous after longer reaction times (Fig. 2c–e). Actually, the structure of the zone formed between the SiO_2 layer and the gas phase was different from the classical model of internal oxidation [23,24] for different reasons, thus presenting an anomalous internal oxidation zone. In fact, the SiO_2 particles in the ioz were not only spherical, with radii ranging from tens to several hundreds of nm, but also vermicular. In addition, the content of SiO_2 particles with vermicular shape increased with an increase of the oxidation time (Fig. 2a–e). Finally and most importantly, a continuous layer of SiO_2 tended to form at the base of the ioz and in contact with the alloy, completely different from the classical structure of the ioz which corresponds to the presence of a uniform volume fraction of the precipitated oxide within the alloy in the absence of a layer of oxide intermediate between the ioz and the alloy. Moreover, the depth of the ioz was not uniform, especially after 24 h oxidation and had no relationship with the orientation of the grains (Fig. 2f). This is not considered a result of changes in the alloy composition in a lateral direction (the alloys were annealed for long times to avoid this possibility), but of the presence of the SiO_2 layer at the base of the ioz, which may have formed at different reaction stages over different locations over the surface.