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Nucleation and growth of selective oxide particles on ferritic steel

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ABSTRACT

In the continuous annealing process, steel sheets are annealed at 800 °C in an atmosphere of nitrogen and hydrogen (5 vol.%) containing low partial water pressure (20–50 Pa). Under these conditions, the most oxidizable alloying elements in the steel segregate towards the surface where they form oxide particles. The nucleation and growth of those oxides were examined. Oxide nucleation mainly occurs between 650 and 750 °C. During their growth, the oxides take the form of a spherical cap and are composed of MnO, Mn_2SiO_4 (or $MnSiO_3$), $MnAl_2O_4$, SiO_2, Al_2O_3 and B_2O_3. Particle nucleation and growth are favored on grain boundaries.

1. Introduction

Steel is often coated with a layer of zinc in order to protect it against corrosion. One of the most commonly used coating processes is hot-dip galvanizing, frequently performed in a continuous treatment line [1,2]. Before immersion in a bath of molten zinc or zinc alloy, steel sheets are annealed in an atmosphere of N_2 and H_2 (5–15 vol.%), containing only traces of water (approximately −40 °C dew point). Before annealing, the steel surface mainly consists of iron oxide. The main purposes of the heat treatment are to (1) recrystallize the steel substrate after cold rolling and (2) reduce iron oxides in order to improve wettability by liquid zinc. At the same time, the less noble steel alloying elements such as Al, Mn, Si, Cr, Ti and P segregate to the surface where they form oxide particles or films that are poorly wetted by liquid zinc [2].

Increasingly, the steel sheets being used in automotive applications are thinner than in the past in order to reduce both the weight of car bodies and the raw material costs. Mechanical properties of high strength combined with formability are retained or improved by using steels with higher levels of alloying elements [3]. Traditional annealing treatment works well for steels with low levels of alloying additions because few oxide particles are then formed on the surface. When steels with higher levels of alloying additions are annealed in the conventional way, many more oxides are formed, resulting in problems of wettability by liquid zinc [3].

Studies conducted on continuous annealing show that the iron oxides spontaneously formed in air during cold rolling are completely reduced in an atmosphere of N_2 and H_2 (5–20 vol.%) with a dew point from −60 to 0 °C and at a temperature from 780 to 840 °C [4–9]. At the same time, steel surfaces are covered in oxide particles [7,10–15] or films [7,15–17] containing the most oxidizable steel alloying elements. The chemical nature of the oxides formed chiefly depends on the dew point of the furnace atmosphere and the composition of the steels. For conditions close to industrial annealing, the most frequently analyzed oxides are MnO [5–7,12,17,18], SiO_2 [6,16–18], $MnSiO_3$ [7,10,17], Mn_2SiO_4 [10,16,17,19], Al_2O_3 [8,14,16], $MnAl_2O_4$ [8,14,16] or boric oxides such as B_2O_3 [8,13,16,18–21]. In agreement with other published papers, these oxides are called selective oxides in the present paper (even if they are not composed of the most oxidizable alloying element of the steel only).

In order to limit the formation of these selective oxides during annealing, oxide nucleation and growth mechanisms must be understood. To our knowledge, no study on the kinetics of selective oxide formation has been conducted to date in the context of continuous annealing. More generally, there are very few studies on the early stages of oxidation [22,23]. The primary goal of our study, therefore, is to examine the first stages in the formation of selective oxides on the surface of ferritic steel. The work is divided into the following stages:

(1) Annealing the chosen steel in conditions close to industrial annealing, with an oxidation reaction dip providing samples at different annealing times.

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(2) Characterization of the samples obtained to estimate geometrical parameters describing oxide particles and measure the chemical composition of those oxides.

2. Experimental procedure

2.1. Materials

The composition of the commercial steel substrate investigated is listed in Table 1. The annealing experiments were performed on a cold rolled Interstitial-Free Titanium *IF Ti* grade. Before the experiments, the substrates measuring $20 \times 20 \times 0.675\ mm^3$ are mirror-polished up to 1 μm diamond paste, leading to an average roughness of 4 ± 1 nm (measured by atomic force microscope), and cleaned in an ultrasonic bath with ethanol.

2.2. Annealing treatment

The samples are annealed in the quartz chamber of an infrared radiation furnace (*Ulvac Sinku-Riko* parabolic tubular furnace). The chosen temperature profile simulates the conditions of industrial continuous annealing (thick line profile 8, Fig. 1). The sample is first heated to 800 °C at a rate of approximately 6 °C s^{-1}. It is kept at that temperature for 60 s before being cooled to room temperature. The temperature scatter of the furnace is estimated by means of two thermocouples which are spot-welded to two diametrically opposite corners of the samples. The two temperature profiles obtained are in good agreement. The maximum temperature difference is obtained at 800 °C. It varies from 10 to 20 °C from one sample to another, with a mean value equal to 15 °C. Uncertainty in the temperature is then low (less than 3% at 800 °C). We have checked that the influence of this temperature scatter was negligible on the oxide parameters.

The gas atmosphere in the furnace is a commercial high purity N_2 and 5 vol.% H_2 mixture (*Air Liquide* with less than 3 ppm of H_2O and 2 ppm of O_2) and is introduced at a flowrate of $1.25 \times 10^{-5}\ m^3\ s^{-1}$ at standard temperature and pressure conditions (0 °C; 100 kPa). For our tests, the atmosphere dew point is -40 ± 2 °C (i.e. water partial pressure close to 19 ± 4 Pa, which corresponds to oxygen partial pressure of approximately 5.3×10^{-19} Pa at 800 °C), a comparable value to that of industrial furnaces on hot-dip galvanizing lines. Water partial pressure is adjusted using a humidity controller (*Panametrics*), which mixes streams of dry and moist gas in appropriate proportions. The actual dew point in the furnace chamber is measured using two aluminum oxide moisture probes (*Panametrics*) located at the gas inlet and outlet.

To obtain information on the nucleation and growth of oxide particles, we interrupted annealing at different points in the temperature profile, during the heating phase at 550, 600, 650, 700, 750 and 800 °C and during the holding phase at 800 °C for a hold lasting 30, 60 and 120 s. The nine temperature profiles are shown in Fig. 1. It is considered that the rapid cooling of samples that takes place when the annealing furnace is stopped acts like a dip for selective oxidation reactions. The selective oxides formed on the samples are then characterized by various techniques.

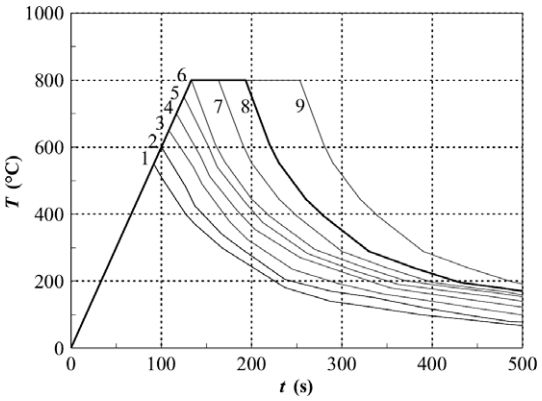

Fig. 1. Temperature profiles experienced by samples, 8: representative profile of industrial continuous annealing, 1–7 and 9: temperature profiles for the study of nucleation and growth of selective oxides.

2.3. Characterization procedure

2.3.1. Geometric description of oxides

After the annealing treatment, the commercial steels are observed in a Field Emission Gun Scanning Electron Microscope (FEG-SEM *LEO 1530*). All FEG-SEM micrographs are given at the same magnification ($2.2 \times 1.4\ \mu m^2$). Image analysis is used to obtain the geometric parameters that characterize oxide particles in two dimensions. First, oxide particle contours are drawn by hand. The particle drawing is then scanned and analyzed with *Visilog 5.0* software. This image analysis provides the oxides' surface density n_{oxides} and the equivalent diameter of each oxide (the equivalent diameter D_{eq} corresponds to the diameter of the circle with the same surface area as the oxides). From 10 to 20 SEM micrographs were carried out on several (2–4) samples that underwent the same temperature treatment to estimate the average and the standard deviation for the measurements.

To obtain a full description of the oxides' 3D geometry in direction z perpendicular to the sheet plane, the samples are observed by means of an Atomic Force Microscope (AFM *Digital Instruments Nanoscope IIIa*). The AFM cartographies ($2 \times 2\ \mu m^2$) were carried out using the tapping mode with etched silicon tips (*TESP Nanoprobe Digital Instruments*). The local maxima obtained from the raw data heights correspond to the maximum oxide heights H_{max}. From 5 to 10 cartographies per sample were carried out for several (2–4) samples that underwent the same temperature profile.

2.3.2. Chemical analysis

The oxide particles formed during annealing are analyzed by Energy Dispersive Spectroscopy (EDS *Princeton Gamma-Tech*).

The depth distribution of the elements is measured by Glow Discharge Optical Emission Spectroscopy (GDOES *LECO GDS-850A*). The surface of the specimen is gradually eroded in the shape of a disc with diameter 4 mm. Experimental erosion parameters for the analyses are 600 V and 9 torr. Erosion rate is estimated on the basis of the total depth of the eroded zone after analysis, which lasts 90 s. Erosion depth is measured by means of a contactless optical measurement device (*STIL CHR150-N*). The erosion rate is estimated at $1.8 \pm 0.4\ \mu m\ min^{-1}$ and corresponds to the average erosion rate of iron. During analysis (0–90 s), erosion depth is

Table 1
Average composition of the *IF Ti* steel studied (wt.%).

C	Si	Mn	P	Al	Cr	Ti	B	S	N	V	As	Cu	Ni	Sn
0.005	0.074	0.450	0.034	0.049	0.034	0.072	0.0005	0.012	0.0047	0.003	0.002	0.025	0.033	0.008