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CHARACTERIZATION BY ELECTRON DIFFRACTION OF OXIDE PARTICLES FORMED DURING ANNEALING

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ABSTRACT

In hot-dip galvanizing, before immersion in the bath of molten zinc or zinc alloy, steel sheets are annealed in a H_2-N_2 atmosphere containing traces of water with a controlled frost point. In addition to recrystallization of the steel substrate and reduction of iron oxides, this heat treatment induces segregation to the surface and the selective oxidation of the less noble alloying elements of the steel such as aluminum, manganese and silicon.

Selective oxidation of both Fe-Si (0.1 wt.%) alloy and commercial *IF Ti* steel was studied with different annealing conditions: a long-time annealing at low frost point (approx. -54°C) in order to favor external selective oxidation and a short-time annealing at higher frost point (approx. -40°C) relevant to galvanizing line practice. The oxide particles were extracted from the surface and characterized by Electron Diffraction in the Transmission Electron Microscope.

Keywords: electron diffraction, TEM, annealing, selective oxidation, steel

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 to 15 vol.%), containing only traces of water (approx. -30°C frost point). The main purposes of this 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 alloying elements of the steel such as Al, Mn, Si, Cr, Ti and P segregate to the surface where they form discrete oxide particles that are poorly wetted by liquid zinc [2-13].

Experiments were carried out to determine the identity of oxide species found on the steel surface (by XPS, electron diffraction or XRD) as a function of dew point and steel composition [3,4,6-13]. For steels containing high levels of manganese (respectively high levels of silicon), MnO [6,8-10,12,13] (respectively SiO_2 [6,10,11,13]) is the main oxide formed at any dew point of the furnace atmosphere. For the other steels, the oxidation phenomena are less simple. If the dew point of the furnace atmosphere is less than -20°C, complex oxides such as $MnSiO_3$ [4,12,13] or Mn_2SiO_4 [4,7,11,13] are formed together with single oxides such as MnO [3,7,12,13] and SiO_2 [7,11,13]. An increase in the dew point leads to oxidation of other elements (e.g., $(Mn,Cr)_3O_4$, $Mn_3(PO_4)_2$, PO_2, $MnPO_4$, $Mn_3P_6O_{18}$, Al_2O_3, Cr_2O_3) [6,7,12,13]. For steels containing high levels of aluminum and manganese, the main oxide formed is Al_2O_3 at low dew point and $MnAl_2O_4$ at -35°C dew point [11]. The oxidation phenomena are complicated further by additions of alloying elements such as boron that lead to the formation of boron oxides [6,7] which could be $Mn(BO_2)_2$ [6].

It is not currently possible to predict the chemical nature of oxide particles from the dew point of the annealing treatment or the composition of the steel. In the present study, the oxidation behavior of various steels has been investigated with the aim of gaining better understanding of the internal structure and morphology of the oxides. In order to facilitate characterization, it was decided to first study single oxide particles and large complex oxide particles formed during long-time annealing at low dew point. The results obtained are then used to characterize the small complex oxide particles present on the steel surface after a short annealing time in line with the galvanizing line practice.

The work comprised the following stages: 1) development of the experimental protocol aimed at characterizing the oxide particles, based on electron diffraction; 2) determination of the chemical nature of the oxide particles formed during both long and short-time annealing.

EXPERIMENTAL PROCEDURE

Materials

The composition of the substrates investigated is listed in Table 1. The annealing experiments were performed on an iron and silicon (0.08 wt.%) alloy and on a commercial steel. The iron and silicon alloy is a laboratory steel. The

commercial steel is a cold rolled *IF-Ti* grade. Before the experiments, the substrates measuring 20 x 20 mm^2 are mirror-polished up to 1 µm with diamond paste and cleaned in an ultrasonic bath with ethanol.

Table 1 Average composition of the alloys

Average content (x 10^{-3} wt.%)	C	Si	Mn	P	Al	Cr	Ti	B	S	N
IF-Ti steel	5	74	450	34	49	34	72	5	12	47
Fe-Si alloy	3	80	<5	4	<5	<2	<5	<5	2	3

Annealing treatment

The first step of the research work was aimed at obtaining the electron diffraction patterns of the different oxide particles that could be formed during continuous annealing. In order to foster growth of oxide particles, the specimens were annealed in a resistance furnace (*Pyrox*), at low frost point (-54 ± 3°C) with the temperature profile shown in Fig. 1a (long-time annealing).

The results obtained are then used to characterize the oxide particles formed at higher frost points (-40 ± 3°C), during short-time annealing in line with galvanizing line practice. The samples are annealed in the quartz chamber of an infrared radiation furnace (*Ulvac Sinku-Riko* parabolic tubular furnace) with the temperature profile shown in Fig. 1b.

In both cases, after establishing a primary vacuum in the furnace chamber, a controlled atmosphere is introduced, consisting of 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) at a flow rate of 45 $ln.h^{-1}$. The frost point in the furnace chamber is measured using an aluminum oxide moisture probe (*Panametrics*) located at the gas outlet. The annealing treatment is started when the targeted frost point of the experiment is reached.

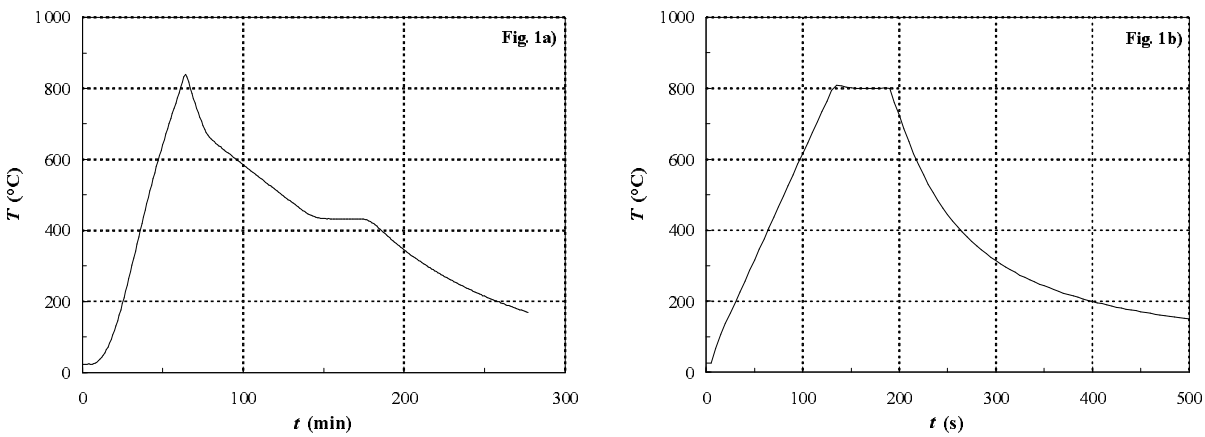

Figure 1 Temperature profile experienced by a sample in a) the resistance furnace (long-time annealing) and b) the infrared radiation furnace (short-time annealing)

CHARACTERIZATION PROCEDURE

Analysis techniques

After cooling, the surfaces of both laboratory and commercial steels are observed in a field emission gun scanning electron microscope (FEG-SEM *LEO 1530*). The oxide particles formed during annealing are analyzed by energy dispersive spectroscopy (EDS *Princeton Gamma-Tech*).

The oxide particles are then extracted from the steel surface using the double replica methodology. The chemical nature of the oxides is determined by electron diffraction in the transmission electron microscope (TEM *JEOL 1200 EX*) at 120 kV. In some cases, the electron diffraction patterns obtained are compatible with two different oxides, one of them containing iron. EDS analyses performed directly on the replica are used to choose between the two possibilities.

Extraction replica methodology

The analysis of the oxide particles by electron diffraction requires their extraction on fine carbon films by means of

a replica technique. This is a two-stage process:

• In the first step, the oxide particles are extracted onto a polymer film. The oxidized sample is immersed for about one minute in a solution of ethanol containing 3 vol.% nitric acid in order to decrease adhesion between oxides and steel substrate. A piece of cellulose acetate polymer is softened in acetone for a few seconds and then used to cover the sample surface. Once dry, the deposited polymer film is peeled off to extract the oxide particles.

• In the second step, the polymer film is put on a clean microscope glass slide to be transferred easily to a vacuum evaporator (*LADD*). The side of the polymer film covered by the oxides is then coated with an approximately 20 nm-thick layer of carbon. The oxide particles are embedded between the carbon and the polymer films. This double replica is inserted in a copper grid and the polymer film is dissolved carefully in acetone.

TEM observation and interpretation

The carbon film with the extracted oxide particles is finally ready to be studied by TEM using selected area diffraction and conventional bright field and dark field techniques. For each sample, about ten oxide particles are selected to be analyzed by electron diffraction. For each particle, diffraction patterns corresponding to different diffracting plans are obtained by tilting the replica.

These experimental diffraction patterns are then compared with theoretical ones in order to determine the chemical nature and orientation of the particle (Fig. 3). The crystal structure of the possible oxides (lattice parameters and atom positions) is found in the Inorganic Crystal Structure Database (ICSD) [14]. Based on the crystal parameters, theoretical electron diffraction patterns are calculated by means of the Java Electron Microscopy Simulation (JEMS) software [15].

RESULTS AND DISCUSSION

Long-time annealing of the Fe-Si alloy (Table 1)

After long-time annealing, the iron and silicon alloy is covered with both spherical and elongated compounds (Fig. 2a). Iron and silicon are detected by EDS analysis of the oxidized samples. The particles present on the replicas contain silicon only or, more rarely, both iron and silicon (Table 2).

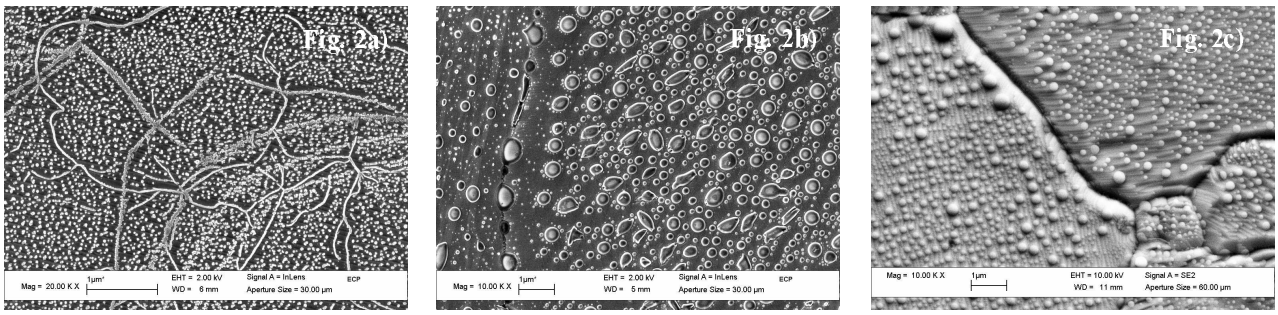

Figure 2 Micrographs of the specimen surface after long-time annealing for a) Fe-Si alloy and b) *IF Ti* steel and after short-time annealing for c) *IF Ti* steel

Table 2 Results of EDS analysis performed on oxidized steel surfaces (before extraction of the oxides) and on replicas

Substrate	Annealing	Sample	detected elements
Fe-Si alloy	long-time	oxidized steel surface	Fe, Si
		replica	Si or Fe, Si
IF Ti steel	long-time	oxidized steel surface	Fe, Mn, Al, Si, Ti
		replica	Mn, Al, Si, Ti
IF Ti steel	short-time	oxidized steel surface	not detected
		replica	Al, Si, Mn, Ti, S

Electron diffraction patterns corresponding to two different chemical compounds have been measured. According to thermodynamic calculations of Gibbs free energies [16,17] and earlier observations [10,11,13], the compounds could be metallic iron, iron oxides (Fe_3O_4), silicon oxides (SiO_2) and oxides of silicon and iron (Fe_2SiO_4). As explained earlier, for each possible case, theoretical diffraction patterns have been calculated and compared with the experimental ones.

The same electron diffraction pattern is measured for most analyzed particles (Fig. 3a). The measured distances and angles are characteristic of crystalline silica SiO_2, in the form of quartz (trigonal crystal structure, P3221 space group, lattice parameters $a = b = 4.91$ Å, $c = 5.40$ Å [14]), in the [001] incidence electron plane, as illustrated by the simulation shown in Fig. 3b. The preferred crystal orientation in the [001] direction could be explained by the epitaxial growth of SiO_2 on the Fe-Si alloys.

Another chemical compound, a spinel Fd3mS structure, was detected in a few particles. Considering the lattice parameters, this cubic spinel could be Fe_3O_4 ($a = 8.39$ Å [14]) or Fe_2SiO_4 ($a = 8.23$ Å [14]). EDS analysis shows that silicon is combined with iron in some oxide particles (Table 2), which suggests the presence of the Fe_2SiO_4 cubic form on the replicas.

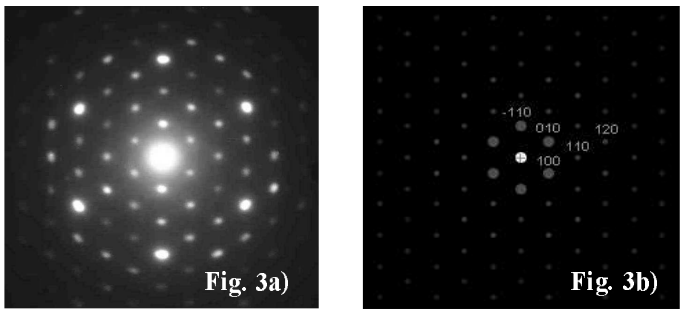

Figure 3 Comparison of a) the experimental electron diffraction micrograph and b) the simulation for quartz in the [001] electron incidence

Long-time annealing of *IF Ti* steel (Table 1)

After long-time annealing, the commercial steel is covered with spherical or elongated compounds, larger than those obtained on the Fe-Si alloy (Fig. 2b). A depletion zone can be noticed at each side of the grain boundary. The presence of this zone suggests the segregation of oxidized elements at the grain boundaries, which constitute easy paths of diffusion. However the observations of the particles formed at the grain boundaries and at the top of the grain do not show any differences concerning the nature of the oxides. EDS analysis of the replicas reveals the presence of Mn, Al, Si and in some cases Ti and the absence of iron in the particles (Table 2).

Conventional bright and dark field techniques reveal that the spherical particles can be composed of either several oxides or several grains of the same oxide with different orientations (Fig. 4). This result illustrates the complexity of the oxides' nucleation and growth within a particle. The elongated particles were found to be of one orientation or nature (Fig. 5).

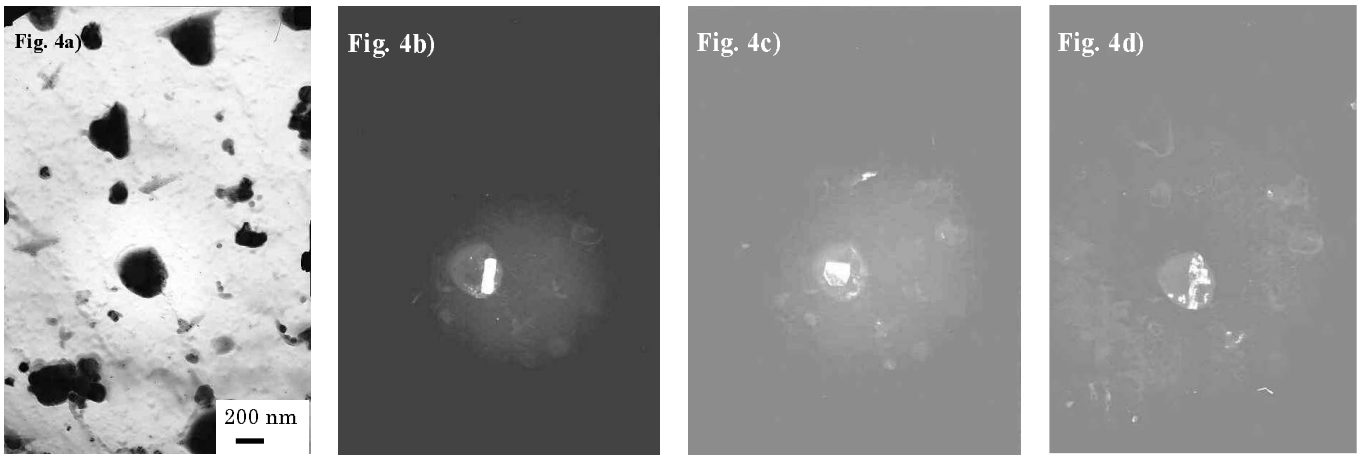

Figure 4 a) Bright and b), c), d) dark fields revealing different parts of the same particle

Electron diffraction patterns corresponding to four main different chemical compounds were measured and compared with the theoretical patterns obtained for the numerous possible oxides (SiO_2, TiO_2, Al_2O_3, MnO and complex oxides such as $MnAl_2O_4$, Mn_2SiO_4, $MnSiO_3$, $TiAl_2O_5$, Al_2SiO_5).

Characteristic distances corresponding to (111), (022), (113), (004) planes of a cubic Fd3mS spinel structure are found on the replicas. The corresponding diffraction rings often constitute the background of the diffraction patterns measured for a single spherical particle. This spinel structure can be attributed to the complex oxide of aluminum and

manganese, $MnAl_2O_4$ (a = 8.20 Å [14]). The other oxides that can be found in the spherical particles are described below.

Silica in the high temperature form of cristobalite (cubic crystal structure, Fd3mS space group, a = 7.135 Å [14]) is also present on the surface as shown in Fig. 6. Due to the various orientations of silica in the selected area, the diagram corresponds to a transition to a powder diagram generated by the first diffraction planes (111), (022) and (113).

Diffraction configurations characteristic of large lattice parameters (i.e., short distances from the transmitted beam) were also measured on the patterns. These short distances are thought to correspond to the first diffraction plane (110) of the complex oxide $TiAl_2O_5$ (orthorhombic crystal structure, Cmcm space group, a = 9.48 Å, b = 9.74 Å, c = 3.58 Å [14]). Other patterns are attributed to first diffraction planes of the tephroite Mn_2SiO_4 (orthorhombic crystal structure, Pnma space group, a = 4.90 Å, b = 10.60 Å, c = 6.26 Å [14]).

Some squared particles were also recognized as TiC precipitates by EDS analysis.

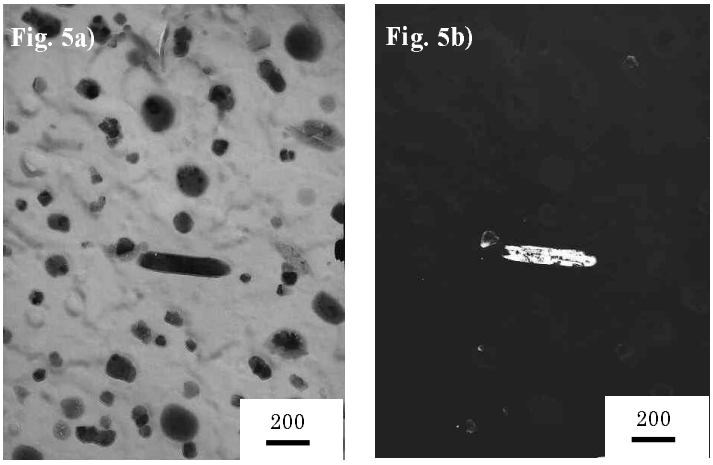

Figure 5 a) Bright and b) dark fields revealing a compact elongated structure

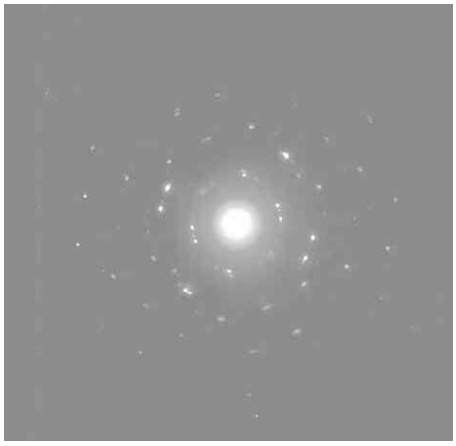

Figure 6 Diffraction electron micrograph representing silica in the form of cristobalite

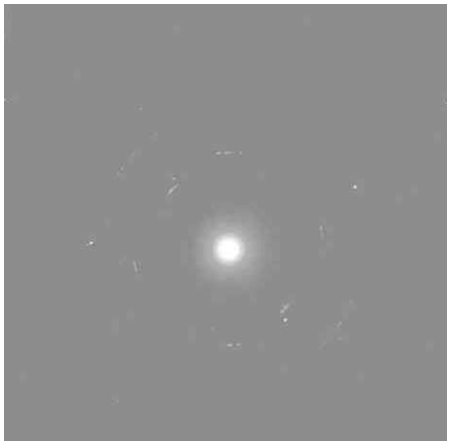

Figure 7 Diffraction electron micrograph representing MnO characteristic distances

Short-time annealing of *IF Ti* steel (table 1)

After short-time annealing relevant to galvanizing line practice, the commercial steel is covered with spherical compounds, from a few nanometers to 200 nm in diameter with a large number of particles less than 100 nm in diameter (Fig. 2c). EDS analysis of the largest particles extracted from the steel surface reveals the presence of Al, Si, Mn and in some cases Ti and S and the absence of iron (Table 2).

Electron diffraction patterns are more difficult to interpret than those obtained after long-time annealing. As the particles are small or composed of small parts of various orientation or nature, the diffraction signal associated with one particle is weak and the selected analyzed area has to be large enough to obtain visible diffraction spots or rings. As a consequence, the dark fields are composed of a lot of small diffracting zones spread out over the surface and the diffraction patterns are in the shape of rings, characteristic of different chemical compounds or orientations. Most of the time, the characterization of a single particle is complicated by the presence of parasitic oxides. In spite of these difficulties, the main oxides were characterized based on the interpretation of the electron diffraction patterns.

Parts of rings corresponding to the first (111), (002), (022) diffraction planes of MnO (cubic crystal structure, Fm3m space group, a = 4.44 Å [14]) are present most of the time (Fig. 7). The diffraction patterns also contain diffraction spots characteristic of corundum Al_2O_3 (trigonal crystal structure, R3CH space group, $a = b$ = 4.76 Å, c = 13.00 Å [14]). The spinel structure attributed to $MnAl_2O_4$ is occasionally found. Complex oxide of manganese and silicon described in the literature for the same annealing conditions [7] has not been detected.

Silica in the form of cristobalite Fd3mS was detected in some particles. Squared precipitates of MnS and TiC detected by EDS analyses are also present on the replicas.

CONCLUSION

Selective oxidation of both Fe-Si (0.1 wt.%) alloy and commercial *IF Ti* steel was studied in different annealing conditions: a long-time annealing at low frost point (approx. -54°C) in order to foster external selective oxidation and a short-time annealing at higher frost point (approx. -40°C) in line with galvanizing line practice. In all cases, less noble alloying elements such as Si, Al and Mn segregate to the surface where they form oxide particles.

During long-time annealing, the Fe-Si alloy becomes covered with numerous spherical and elongated particles of silica in the form of quartz. The growth of silica occurs in the [001] preferred direction, probably in epitaxy with the steel substrate. $FeSiO_4$ is occasionally detected in that case.

During long-time annealing, the commercial steel becomes covered with particles that can contain either several oxides or several grains of the same oxide with different orientations. Two main oxides were analyzed: $MnAl_2O_4$ and SiO_2 in the form of cristobalite. Mn_2SiO_4 and $TiAl_2O_5$ were also thought to be present on the steel surface.

During short-time annealing, oxide particles are very small, leading to difficulties in characterizing isolated particles. MnO and SiO_2 in the form of cristobalite were detected. Corundum Al_2O_3 was also thought to be present on the replicas.

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