Formation of Surface and Subsurface Oxides during Ferritic, Intercritical and Austenitic Annealing of CMnSi TRIP Steel

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The equilibrium external oxidation of CMnSi TRIP steel at different annealing temperatures in a low dew point N$_2$–10%H$_2$ atmosphere of −30°C was investigated for the first time by means of high resolution transmission electron microscopy of cross-sectional samples. Annealing in the ferrite stability temperature range below the Ae1 temperature resulted in the formation of 300–600 nm size crystalline internal MnO in the matrix. In the subsurface region, 10–20 nm size SiO$_2$ particles were detected. Large amorphous lens-shaped xMnO·SiO$_2$ oxides, with x<0.5, were present at the surface, and thin films of crystalline xMnO·SiO$_2$ oxides, with 1<x<2, were formed between these large lens-shaped oxides. The amorphous lens-shaped xMnO·SiO$_2$ oxides were covered by a continuous thin layer of crystalline xMnO·SiO$_2$ oxide, with x>2. Amorphous 15–50 nm size internal SiO$_2$ particles covered with a thin layer of crystalline MnO·SiO$_2$ and MnO·Al$_2$O$_3$ oxides were found in the subsurface matrix region and at the grain boundaries after annealing in the intercritical and the fully austenitic temperature ranges. A discontinuous amorphous SiO$_2$ layer covered by a layer of crystalline 2MnO·SiO$_2$+MnO·SiO$_2$ mixed oxide was present at the surface after annealing in the intercritical Ae1–Ae3 temperature range. This changed to a continuous layer of amorphous SiO$_2$ on the steel surface covered by a continuous layer of crystalline 2MnO·SiO$_2$+MnO·SiO$_2$ mixed oxide after annealing in the austenitic stability range. The results clearly show an increased tendency for the xMnO·SiO$_2$ and SiO$_2$ oxides to form two separate surface oxide films covering the entire steel surface during continuous annealing at the higher annealing temperatures used to process advanced high strength steels. The presence of these film-forming oxide layers will prevent the formation of the inhibition layer and its wetting by the liquid Zn, and cause galvanizing surface defects.

KEY WORDS: TRIP steel; dew point; selective oxidation; external oxidation.

1. Introduction

TRansformation-Induced Plasticity (TRIP) steels are formable high strength steels which allow for the design of car bodies with an improved passenger safety combined with a lower weight. The galvanisability of Advanced High Strength Steels (AHSS) such as Transformation-Induced Plasticity (TRIP) steels is a key factor to promote this trend as thinner gauge sheet will be used which must be resistant to perforation corrosion. The gas atmosphere of the annealing furnace in continuous galvannealing or galvanizing lines leads to the reduction of the iron oxides formed after the acid pickling process during cold rolling. It also results in the selective oxidation of the less noble key alloying additions of Si, Al and Mn. Selective external oxidation during annealing may result in surface defects on hot dip galvanizing products because the oxides deteriorate the wettability of the steel by molten Zn. The surface oxides on TRIP steels during annealing have been studied previously by Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectroscopy (SIMS), and Energy Dispersive Spectrometry (EDS). Internal selective oxides have been studied by means of XPS, SIMS and Glow Discharge Optical Emission Spectroscopy (GDOES). A review of the oxides observed on TRIP steels using these various micro-analytical methods are reviewed in Table 1. The methods used for oxides characterization usually give the average composition on a macro scale. The morphology, size and distribution of oxides are rarely reported. In the present contribution, High Resolution Transmission Electron Microscopy (HR-TEM) of Focused Ion Beam (FIB) cross-sectional samples was therefore used to carry out an in depth analysis of the composition and micro-structure of surface and internal oxides formed on a CMnSi TRIP steel after annealing in a N$_2$–10%H$_2$ atmosphere with a low dew point of −30°C. These gas atmosphere conditions correspond to those used during the intercritical annealing of AHSS in industrial continuous hot dip galvanizing lines. The annealing temperatures were 700°C, 870°C and 930°C, corresponding to ferritic, intercritical and austenitic annealing temperatures, respectively. The selection of temperatures made it possible to observe the effect of an increasing annealing temperature on the structure of the surface oxides. An extended annealing time was chosen to allow for the precise determination of the equilibrium oxide phases in conditions of external
oxidation.

2. Experimental Procedure

The TRIP steel used in the present study was full hard cold rolled steel. The composition was 0.11% C, 1.53% Mn, and 1.46% Si. Samples with size of 10×10×1.1 mm were cut by a wire-cutting machine to minimize mechanical damages and strain effects. The sample surface was mirror-polished with a 0.5 μm diamond suspension prior to annealing to avoid effects related to the roughness of the strip surface.

The heat treatments were carried out in a vacuum tube furnace with a controlled 10%H2/N2 atmosphere. The oxygen content in the gas mixture was less than 1.7 ppm. Prior to the mixture gas entering the furnace, the system was pumped to less than 5 mbar vacuum to remove residual gases and avoid oxidation by oxygen and moisture. The flow rate of the gas mixture through the furnace during the annealing process was 0.7 L/min and the dew point was carefully controlled at a constant value of −30°C. The annealing temperatures were 700°C, 870°C and 930°C. The selective oxidation of Mn and Si occurs in the atmosphere during annealing and Fe is not oxidized because the oxygen partial pressure of the atmosphere is lower than that of Fe but higher than that of Mn and Si. It should be noted that 870°C is a typical intercritical annealing temperature used for the processing of TRIP steel. 700°C is close to Ae1 and 930°C is in the single phase austenite stability range above Ae3. The heating and cooling rates were +5°C/min and −4.5°C/min, respectively. After annealing the samples were kept in the furnace until the temperature reached room temperature. The annealed samples were prepared for cross-sectional TEM analysis by coating with Pt, to avoid both further oxidation and altering the surface oxides during the FIB milling process.

The annealed samples were investigated in a JEOL JEM-2100F field emission transmission electron microscope. The cross-sectional samples prepared by FIB allow for the analysis of composition, crystal structure, morphology, size, and distribution of the oxides on the steel surface and in the subsurface region. The determination of the composition of the internal and surface oxides was done by means of Energy Dispersive Spectroscopy (EDS). The crystal structure of the various oxides and the interface structure between oxides and matrix were investigated by HR-TEM.

3. Results

TEM cross-sectional micrographs of a sample annealed at 700°C are shown in Fig. 1. Large lens-shaped oxide particles and thin oxide films were formed on the surface during annealing (Fig 1(a)). The high-resolution micrograph of the interface area between a lens-shaped oxide particle and the steel surface indicates that these larger oxide particles were amorphous (Fig. 1(b)). The diffuse intensity rings in the diffraction patterns (Fig. 1(b)) obtained from the hemispherical particles also prove that these oxides were amorphous. An outer layer was covering these lens-shaped particles, as can be seen in Fig. 1(d). The size of the lens-shaped amorphous oxides on the surface varied from 30 to 240 nm. In addition, a thin oxide film, with the thickness of about 20 nm, was formed on the free surface area not occupied by the larger lens-shaped oxide particles. This discontinuous film-like oxide was crystalline (Fig. 1(c)). The EDS analysis revealed that the lens-shaped particles had a complex composition corresponding to xMnO·SiO2, with the atomic ratio of Mn to Si, x, less than 0.5 in the core of the particles. The large lens-shaped particles were therefore amorphous SiO2 with MnO in solution. In the outer crystalline layer covering the amorphous oxide particles, x was larger than 2. The composition of thin crystalline film-like oxides on the surface was a mixture of 2MnO·SiO2 and MnO·SiO2, with an atomic ratio of Mn to Si between 1 and 2. The film-like 2MnO·SiO2 oxide was easily recognized by the periodic contrast from the (112) lattice planes with the inter-planar spacing of 0.29 nm (Fig. 1(c)). The results are in good agreement with the results of Mahieu et al. and Bellhouse et al. who analyzed the composition of the surface oxides on TRIP steels by means of XPS. The 2MnO·SiO2 and MnO·SiO2 oxides seemed to have been formed first on the surface during the annealing process and the amorphous silicon oxide particles, which were covered by the outer Mn-rich xMnO·SiO2 layers grew in a later stage at the interface between oxide layer and matrix. In the discussion section it will be shown that this is confirmed by the absence of a xMnO·SiO2 oxide film at the interface between the hemispherical particles and the matrix, as shown in the high resolution image (Fig. 1(b)). Internal oxide particles were observed in the subsurface close to the surface.

| Type of TRIP steel | Dew point (°C) | Observed oxides | Annealing temperature (°C) | Analysis methods | Ref. |
|-------------------|---------------|-----------------|--------------------------|-----------------|------|
| C MnSi            | 50            | 2MnO·SiO2, 2MnO  | 870                      | HR-STEM         | [5]  |
| C MnSi            | 50            | 2MnO·SiO2, 2MnO  | 930                      | HR-STEM         | [6]  |
| C MnSi            | 50            | 2MnO·SiO2, 2MnO  | 870                      | HR-STEM         | [7]  |
| C MnSi            | 50            | 2MnO·SiO2, 2MnO  | 930                      | HR-STEM         | [8]  |
and at grain boundaries (Fig. 2). The internal oxides within a depth of 50 nm below the surface were mainly SiO₂ particles with a diameter of about 20 nm. At the grain boundaries larger MnO oxide particles with diameter in the range of 300–600 nm were observed at 1 μm below the surface. These MnO particles were crystalline, as shown in micrograph Fig. 2(b). In this micrograph the TRIP steel matrix is revealed by the (110) inter-planar distance of 0.20 nm. The presence of the internal oxide MnO was inferred from the lattice planes with the (220) interplanar distance of 0.16 nm (Fig. 2(b)).

TEM micrographs of cross-sectional samples intercritically annealed at 870°C are shown in Fig. 3. The oxides formed on the surface had a two-layer structure (Fig. 3(a)). The inner layer was a discontinuous amorphous SiO₂ layer (Fig. 3(b)). The outer 2MnO·SiO₂ layer was crystalline, as shown in zone A of Fig. 3(c). There was a transition zone between the outer layer and the inner layer on the surface. There were also some coarse MnO oxides on the top surface of the outer crystalline oxide layer. In addition, small Al oxides were present on these outer MnO particles. These Al₂O₃ oxides were not observed in the samples annealed at 700°C.

Below the surface, internal oxide particles with a diameter of about 200 nm were present at grain boundaries. They had a multi-layer structure: the core of the oxide was amorphous and their outer shell, i.e. the interface layer between the oxide particle and the Fe matrix, was crystalline. Closer to the surface, smaller internal oxide particles with a diameter less than 50 nm, were also observed. They had a similar multi-layer structure consisting of an amorphous core and a crystalline outer shell. An elemental map for O, Al, Si and Mn is shown in Fig. 3(d). The analysis revealed that the outer layer was a mixture of the crystalline phases 2MnO·SiO₂ and MnO·SiO₂ covering an amorphous SiO₂ oxide core. Internal oxide particles located at grain boundaries had a multi-layer structure with amorphous SiO₂ at the core and a crystalline MnO·Al₂O₃ and MnO·SiO₂ oxide mixture covering the SiO₂ oxide. These layered oxides were not observed in the samples annealed in the ferrite stability range. It must however be mentioned that amorphous silicon oxides were recently reported by Li et al. ⁵

The TEM cross-sectional micrographs of samples an-
Fig. 2. Cross-sectional TEM micrographs for CMnSi TRIP steel annealed at 700°C. (a) Overview with the lens-shaped $\alpha$MnO·SiO$_2$ oxides particles on the surface and a larger subsurface MnO oxide. (b) Interface structure between the internal oxide and the matrix in zone A, and (c) corresponding diffraction pattern.

Fig. 3. Cross-sectional TEM micrographs for CMnSi TRIP steel annealed at 870°C. (a) Overview of the oxide layers at the surface and a large subsurface multi-layer oxide particle. The latter oxide has an amorphous SiO$_2$ core and a crystalline MnO·SiO$_2$ and MnO·Al$_2$O$_3$ mixed oxide shell. (b) Interface structure between an amorphous SiO$_2$ surface oxide and the steel surface in zone B. (c) Interface structure between an amorphous SiO$_2$ surface oxide and a crystalline 2MnO·SiO$_2$+MnO·SiO$_2$ mixed oxide in zone A. (d) O, Si, Mn and Al elemental mapping of zone C.
nealed at 930°C are shown in Fig. 4. A layered surface oxide structure was clearly visible during the TEM observations (Fig. 4(a)). The total surface oxide layer thickness was about 130 nm. This was appreciably thicker than the oxide thickness after annealing at 700°C. The surface layers formed in the austenite stability range had a similar layer structure as the oxide layer observed after intercritical annealing. The detailed oxide analysis revealed that the outer surface oxide layer consisted of a crystalline oxide mixture of 2MnO·SiO₂, MnO·SiO₂, and MnO·Al₂O₃. In the HR-TEM micrographs of the outer crystalline oxides the (224) planes of 2MnO·SiO₂ with a 0.25 nm inter-planar distance were clearly observed (Fig. 4(b)). The inner amorphous oxide formed a continuous layer with a thickness of about 50 nm, while the corresponding layer was discontinuous after intercritical annealing at 870°C. The inner layer was composed of amorphous SiO₂.

Compared with the images in Fig. 2 and Fig. 3, many more oxide particles with a diameter 30–100 nm were found along grain boundaries within a range of about 500 nm below the surface. Figure 5 is a detailed schematic comparing the observed evolution of the selective oxidation during the annealing of CMnSi TRIP steel in conditions of oxidation used in the present work.

4. Discussion

Recently Huin et al.\textsuperscript{10} proposed a general extension of Wagner’s model for the an-isothermal oxidation of steels which takes into account an arbitrary number of elements and oxides, and the possible formation of mixed oxides. In addition, the effect of the Mn/Si ratio and the presence of
Al were systematically analyzed by the authors. Their model predicts that only 2MnO·SiO₂ and SiO₂ will ultimately be formed for TRIP steel compositions. The model does not take into account the formation and morphology of the oxides, i.e. it does not account for the possibility of surface oxide film formation. The effect of Al is also described by the authors; they conclude that Al has only a very minor influence and that no Al₂O₃ or MnO·Al₂O₃ can be formed. The formation of two separate layers, a 2MnO·SiO₂+MnO·SiO₂ mixed oxide layer and an amorphous SiO₂ layer, and the very similar multi-layer structures of the internal oxide particles below the surface and at the grain boundaries, cannot as yet be predicted by a numerical model, and a qualitative explanation is proposed for the observation reported here.

At the initial stage of oxidation, Mn and Si formed external oxides on the surface and a continuous 2MnO·SiO₂+MnO·SiO₂ oxide mixture film was formed because these mixed oxides have a much lower Gibbs free energy of formation than either MnO or SiO₂. In the case of annealing in the austenite stability range, the growth of these oxides is believed to be by a two-stage mechanism.

In the initial stage, 2MnO·SiO₂ was the most likely oxide to form on the CMnSi TRIP steel. The rate of Mn oxidation required to form this compound is twice the rate of oxidation for Si. In addition, the diffusivity of Si in austenite is much higher than that of Mn. Si therefore diffuses from the matrix to the surface oxide at a faster rate than Mn when the CMnSi TRIP steel is annealed in the austenite stability range (Table 2). The two phenomena result in a depletion of Mn, and cause a gradual decrease of the Mn/Si ratio, \( x \), in the mixed oxide xMnO·SiO₂.

In the second stage, a critically low Mn concentration was reached and a pure SiO₂ oxide layer grows at the interface between the mixed oxides and the steel matrix. The growth of this SiO₂ oxide layer is due to oxygen anion diffusion through the oxide layers and its reaction with Si at the SiO₂/steel interface. A two-layer oxide structure consisting of an outer crystalline xMnO·SiO₂ layer and an inner amorphous SiO₂ layer was therefore observed.

Prior to the formation of the surface-covering oxide layers, solute oxygen atoms could still diffuse into the steel matrix to react with Si atoms, which had already diffused to grain boundaries and subsurface regions. At the grain boundaries and in the grains close to the surface where internal amorphous SiO₂ particles were formed in the initial stages of the oxidation, Mn and Al atoms reacted with oxygen to form the crystalline MnO·SiO₂ and MnO·Al₂O₃ outer layers on the SiO₂ particles, leading to the formation of the observed multi-layer oxides particles.

At the ferritic annealing temperature of 700°C, Mn and Si have a comparable diffusivity. In this case, Mn and Si diffused to the surface and reacted with oxygen, leading to the formation of 2MnO·SiO₂+MnO·SiO₂ mixed oxides at the start of the oxide formation process. In this case the decrease of the Mn and Si subsurface matrix concentration as a result of their oxidation was simultaneous and no separate pure amorphous SiO₂ oxide layer was found to have grown at the interface between the mixed oxide and the steel matrix. In these conditions, lens-shaped amorphous xMnO·SiO₂ mixed oxide particles were formed, with a gradual depletion of the Mn/Si ratio. When the value of \( x \) was below the critical value of 0.5, the xMnO·SiO₂ oxide was observed to become amorphous.

At the intercritical annealing temperature of 870°C, an intermediate situation occurred, which was complicated by the simultaneous presence of both ferrite and austenite. During intercritical annealing, it is known that Si and Al tend to partition to ferrite, while Mn partitions to austenite. The diffusivity of Si and Al in ferrite is much higher than that of Mn in austenite at this annealing temperature.

Having said that, the similarities between the oxides formed in the intercritical temperature range and those formed in the austenite stability range are striking: after the initial formation of the 2MnO·SiO₂+MnO·SiO₂ mixed oxide at the surface, a discontinuous layer of amorphous SiO₂ was formed at the interface between the initial mixed oxide and the steel surface. In the subsurface and at the grain boundaries oxides particles were present which had an amorphous SiO₂ core covered with a layer of MnO·SiO₂ and MnO·Al₂O₃ oxide. The high temperature ferrite and austenite phases present at the surface could not, for obvious reasons, be observed. It is at present unclear why the observations did not seem to be influenced by the presence of the ferrite and austenite at the surface. This may be related to the fact that, in addition to the oxidation of Mn, Si and Al, the surface oxidation of C may lead to a steel surface composition considerably different from the bulk composition. The oxidation of C to gaseous CO during continuous annealing is usually not given much attention, as it is too small to cause a measurable deterioration of the mechanical properties. The surface properties of a CMnSi TRIP steel may however be considerably influenced by it. In the present case, it may have caused the decarburization of a surface layer of a few micrometers thick. As a result most of the surface would have been ferritic during annealing and this may explain the gradual tendency for xMnO·SiO₂ and SiO₂ oxides to form thin surface oxide films covering the entire steel surface during continuous annealing at higher annealing temperatures.

### Table 2. Diffusivity of alloying elements in TRIP steel matrix (cm²/s)³)

| T (°C) | Dₓₓₓ in α | Dₓₓₓ in α | Dₓₓₓ in α | Dₓₓₓ in γ | Dₓₓₓ in γ | Dₓₓₓ in γ |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| 700   | 6.39255E-13 | 6.05288E-13 | 3.11543E-13 | /         | /         | /         |
| 870   | 3.99287E-11 | 3.46723E-11 | 2.88066E-11 | 1.46197E-13 | 1.53479E-12 | /         |
| 930   | /         | /         | /         | 5.85743E-13 | 5.50064E-12 | /         |

5. Conclusions

The present work has revealed that the current understanding of the oxidation phenomena occurring at the surface of CMnSi TRIP steel during intercritical annealing in industrial continuous galvanizing lines, in which the atmosphere favors external oxidation, is still not fully understood.
The selective oxidation of Si and Mn on the surface of a CMnSi TRIP steel annealed in conditions of external oxidation in a (10%)\(\text{H}_2\)+\(\text{N}_2\) atmosphere with a low dew point of \(-30^\circ\text{C}\) leads to the formation of a complex multilayer surface oxide and internal oxide particles. After annealing in the austenitic and intercritical temperature range, two distinct oxide layers are formed: an outer crystalline \(2\text{MnO} \cdot \text{SiO}_2 + \text{MnO} \cdot \text{SiO}_2\) mixed oxide layer and an inner amorphous \(\text{SiO}_2\) layer. During annealing in the ferrite stability range, a crystalline oxide film and amorphous lens-shaped oxide particles are formed at the surface. Both have a composition which can be written as \(x\text{MnO} \cdot \text{SiO}_2\); whereas the crystalline oxides have \(1 < x < 2\), the amorphous oxide has \(x < 0.5\). The latter can be considered a solid solution of MnO in SiO\(_2\). Internal oxide particles formed both in the grain matrix and at the grain boundaries were also detected after intercritical annealing and annealing in the austenitic stability range, despite the pronounced external oxidation conditions. The oxide particles had a multi-layer structure, consisting of an amorphous SiO\(_2\) oxide core and a crystalline MnO-Al\(_2\)O\(_3\)+MnO-SiO\(_2\) mixed oxide layer. Despite a very low alloy content (0.028 mass%), Al still showed a pronounced tendency to form internal oxides particles during annealing in the austenitic temperature range.

The external MnO-SiO\(_2\)-2MnO-SiO\(_2\) mixed oxide layer and the amorphous SiO\(_2\) layer are expected to have a negative effect on the galvanisability of CMnSi TRIP steel as they are expected to act as effective barriers to the Fe\(_2\)Al\(_5\)-Zn\(_x\) inhibition layer formation, which requires the reaction of Fe atoms at the steel surface with solute Al atoms in the liquid Zn. This may also explain why internal oxidation in higher dew point atmospheres has been shown to improve the galvanisability of TRIP steels by causing internal rather than external oxidation.

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