Effects of Surface Microstructure on Selective Oxidation Morphology and Kinetics in $N_2 + 5\%H_2$ Atmosphere with Variable Dew Point Temperature

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(Received on October 31, 2018; accepted on December 19, 2018)

Starting surface microstructure has been shown to influence selective oxidation morphology and kinetics on cold-rolled grades of CMnSi advanced high strength steels (AHSSs). The research presented below examined this phenomenon after 120 and 1 800 s and under $N_2 + 5\%H_2$ with 0°C and –30°C dewpoint temperatures (DPTs). Starting microstructures were altered by pre-annealing, which led to decarburization and grain growth. All samples were oxidized in a high temperature confocal scanning laser microscope (CSLM) at 850°C. External oxides were subsequently examined using secondary electron scanning electron microscopy (SE SEM) and energy-dispersive spectroscopy (EDS). Cross-sections were produced and examined in a focused ion beam scanning electron microscope (FIB-SEM). Oxidizing atmosphere, surface microstructure, and time all influenced selective oxidation behavior. High and low DPT atmospheres had expected effects. Variation between microstructures was only apparent in 1 800 s samples oxidized in a high DPT atmosphere. Decarburized samples oxidized at higher DPTs exhibited surfaces covered with discrete iron nodules which may facilitate reactive zinc wetting.

KEY WORDS: advanced high-strength steel (AHSS); selective oxidation; high-temperature confocal scanning laser microscope (HT-CSLM).

1. Introduction

The development of AHSS grades was an answer to the automotive industry's need to comply with corporate average fuel economy (CAFE) standards established by the United States Congress in 1975 and produce lightweight, fuel-efficient cars that maintained or improved safety standards.^{1–3)} AHSS grades are characterized by good combinations of ductility and strength, which enables improved crashworthiness even with a thinner sheet gauge. To achieve such properties in steel, a highly engineered, multi-phase microstructure is required. Attention to annealing time, temperature, and heating/cooling rates is needed, but so are alloying element additions such as silicon and manganese. These elements are necessary to stabilize certain phases required to achieve characteristic AHSS properties.^{4,5)} However, because of these additions, many grades of AHSS prove challenging to galvanize due to selective oxidation.^{6–8)}

Traditional industrial annealing cycles run between 700°C and 900°C in an $N_2 + H_2$ atmosphere with a dewpoint of around –30°C to –20°C.^{9–11)} These conditions are sufficient to prevent iron from oxidizing but not silicon or manganese.¹²⁾ At the relatively high temperatures and low dewpoints found in annealing furnaces, silicon and man-

ganese are prone to external oxidation, or the formation of oxides on the surface of the bare metal.⁹⁾ Silicon and manganese surface oxides reduce the ability of liquid zinc to wet the steel surface in a hot-dip galvanizing line and result in poor coating quality. Several methods have been developed to overcome the galvanization challenges posed by AHSS with varying degrees of success for many first-generation grades.^{4,7,13–18)} Development of new AHSS grades are still underway and a fundamental understanding of the thermodynamics and kinetics of selective oxidation is paramount to designing and developing strategies to hot-dip galvanize new alloys. To enable prediction of oxidation behavior, all contributing factors need to be identified and accounted for. The effect of certain parameters such as atmospheric dewpoint^{6–8,15,17–20)} and microstructure^{10,14,21–23)} have been studied but many questions remain.

The objective of this set of experiments was to investigate whether variations in the starting microstructure can influence selective oxidation in a way that will improve zinc adherence to a hot-dip galvanized product intended for use in the automotive industry. For the scope of this report, improvements included reducing external oxidation or increasing internal oxidation. Prior work by the current authors suggested steel microstructure can influence selective oxidation behavior,²³⁾ however this work was conducted under conditions that were not industrially relevant. In this report, the effect of microstructure was tested under anneal-

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DOI: <https://doi.org/10.2355/isijinternational.ISIJINT-2018-727>

ing conditions that were more industrially relevant. Specific objectives for this report were:

- (1) Characterize selective oxidation behavior (internal or external, morphology, and chemistry) resulting from different atmospheric DPTs.
- (2) Characterize selective oxidation behavior resulting from different starting microstructures.
- (3) Make a comparison between the results generated from this set of experiments to prior results.
- (4) Establish if modifications to surface microstructure can change selective oxidation in way considered favorable to hot-dip galvanization.

2. Materials and Experimental Methods

A CMnSi AHSS with 0.09 wt% C, 0.91 wt% Si, 2.02 wt% Mn, and 0.04 wt% Al was used for all experiments. Starting material was originally in 1.5 mm thick cold-rolled sheets. Blank discs of this material were prepared with a circular 6 mm diameter punch, and then ground down to approximately 1 mm thickness. Samples with three different microstructures were then prepared from the blank discs prior to studying oxidation behavior. One microstructure remained in the as-received, cold-rolled state (CR) and two were annealed at different temperatures for different lengths of time (1 200 A and 850 A). Micrographs collected by light optical microscopy (LOM) of each sample type after heat treatment are below in **Fig. 1** (surfaces etched with 2% nital). Parameters used to achieve each microstructure and results from Vickers hardness tests to assess changes to near-surface microstructure are reported elsewhere.²³⁾ Grain size measurements were collected from pre-annealed specimens in the decarburized zone near the surface. Measured grain sizes per ASTM standard E112 were $52.8 \pm 8 \mu\text{m}$ for 1 200 A samples and $7.0 \pm 1 \mu\text{m}$ for 850 A samples. Grain size measurements were not collected from CR samples because the grains were too small and deformed to be sufficiently resolved in the LOM to make accurate grain size measurements. Post-anneal, the edges were ground off all samples to remove any iron oxide which may have formed.

This was done to eliminate any unintended oxygen sources during later oxidation experiments. Afterwards, all samples were polished flat through 1 μm diamond suspension with a Struers automatic polisher in preparation for oxidation. Care was taken when preparing the 850 A type samples to not grind through the thin ($\sim 250 \mu\text{m}$) decarburized layer at the surface.

Samples with each microstructure discussed above were oxidized at 850°C in a CSLM infrared furnace with a ramp up and cool down rate of 600°C/min. A schematic of the furnace configuration is below in **Fig. 2**. During oxidation, samples were placed on 8 mm diameter alumina discs inside of a fused quartz reaction tube. Gas was passed directly over the sample surface at a rate of 0.25 L/min with linear velocity 6.4 cm/s. Oxidation was performed in an $\text{N}_2 + 5\%\text{H}_2$ atmosphere at either 0°C or -30°C dewpoint. Hold times at 850°C were 2 minutes, with a second set of samples exposed at 0°C for 30 minutes. A table outlining individual sample starting conditions as well as experimental conditions is below in **Table 1**. Atmospheric dewpoint was controlled with an Edgetech Instruments DewGen and monitored with an Edgetech Instruments DewMaster chilled mirror hygrometer, equipped with a S2 two stage chilled stainless steel mirror sensor with 65°C depression range. Based on relations from²⁴⁾ Eqs. (1) and (2), the partial pressure of oxygen at 850°C for the -30°C dewpoint was 2.78×10^{-22}

Fig. 2. Schematic of the sample setup inside the CSLM infrared furnace. (Online version in color.)

Fig. 1. LOM images of the starting surface (top) and internal (bottom) microstructures for a) CR, b) 1 200 A, and c) 850 A samples; etched with 2% nital to reveal grain boundaries.²³⁾

Table 1. All samples oxidized at 850°C in $\text{N}_2 + 5\%\text{H}_2$ environment; specific conditions listed.

Sample Type	Pre-Annealing Temperature (°C)	Pre-Annealing Time (s)	Oxidation Time (s)	Oxidation DPT (°C)
CR	—	—	120	0
CR	—	—	120	-30
1 200 A	1 200	7 200	120	0
1 200 A	1 200	7 200	120	-30
850 A	850	7 200	120	0
850 A	850	7 200	120	-30
CR	—	7 200	1 800	0
CR	—	7 200	1 800	-30
1 200 A	1 200	7 200	1 800	0
1 200 A	1 200	7 200	1 800	-30
850 A	850	7 200	1 800	0
850 A	850	7 200	1 800	-30

atm and 7.18×10^{-20} atm for the 0°C dewpoint.

$$\log_{10} p_{\text{sat } H_2O} = 9.80 DP / (273.8 + DP) - 2.22 \dots (1)$$

$$0.5 \log_{10} p_{O_2} = 3.00 - \frac{13\,088}{T} + \log_{10} \left(\frac{p_{\text{sat } H_2O}}{p_{H_2}} \right) \dots (2)$$

In these equations, partial pressures are in atmospheres, “DP” stands for “dewpoint” and is used in units of °C, and “T” is oxidizing atmosphere temperature in Kelvin. Details regarding the specific parameters used in each experiment are below in Table 1.

After oxidation, sample surfaces were examined with a FEI Nova 600 Dual Beam FIB or a Quanta 600 SEM in SE mode to observe external oxide morphology and coverage variations between samples. For samples oxidized for two minutes, the FIB was used to mill into the sample surface and expose a cross section approximately 15–50 μm wide and 6–8 μm deep. Minimum, maximum, and average internal oxidation depths were obtained from each sample and compared to one another. The 52° sample tilt in the FIB was accounted for in internal oxidation measurements. Average oxidation depths were obtained from five measurements across the length of the exposed interior. Internal oxidation for samples oxidized for 30 minutes were cross-sectioned using a diamond saw, mounted in bakelite, and polished through 1 μm diamond with a Struers automatic polisher. These samples were observed with the Quanta 600 SEM in SE mode. An average internal oxidation depth was obtained for each sample by averaging five measurements collected

across each sample. Selected area EDS analyses were performed on sample surfaces to collect oxide and surface feature chemistry information.

3. Results

3.1. External Oxidation

Images of external oxidation from samples oxidized for 120 s are below in **Fig. 3**. Oxide layers and nodules were observed, as was preferential oxidation at grain boundaries. Surface nodules were not observed on the CR sample oxidized at –30°C DPT but were for 1 200 A and 8 500 A samples. Distinct morphological differences between grains were observed for 1 200 A and 850 A samples oxidized at –30°C DPT and also for the 1 200 A sample oxidized at 0°C DPT.

Images of external oxidation from samples oxidized for 1 800 s are below in **Fig. 4**. Surface nodules were larger, more numerous, and again absent from the CR sample oxidized at –30°C DPT. Instead of nodules, the surface was covered with discrete patches of lacy oxide. Similar to samples oxidized for 120 s, distinct morphological differences were observed between grains for 1 200 A and 850 A samples oxidized at –30°C DPT and also for the 1 200 A sample oxidized at 0°C DPT. Preferential oxidation at grain boundaries was again observed.

EDS performed at 5 and 20 kV accelerating voltage on grain boundary features indicated high manganese and oxygen content for all samples oxidized at 0°C DPT (**Figs. 5 and 6**), regardless of oxidation time. Samples oxidized

Fig. 3. SEM images of the surfaces of samples oxidized for two minutes at 850°C; columns describe DPT atmosphere; rows describe starting microstructure.

Fig. 4. SEM images of the surfaces of samples oxidized for 1 800 s at 850°C; columns describe DPT atmosphere; rows describe starting microstructure.

Fig. 5. EDS maps of 1 200 A type samples oxidized for 1 800 s in both a) -30°C and b) 0°C DPT atmospheres; iron, oxygen, and silicon maps were collected at 5 kV and manganese maps were collected at 20 kV. (Online version in color.)

Fig. 6. EDS maps of 850 A type samples oxidized for 120 s in both a) -30°C and b) 0°C DPT atmospheres; iron, oxygen, and silicon maps were collected at 5 kV and manganese maps were collected at 20 kV. (Online version in color.)

at -30°C DPT tended to have grain boundaries rich in manganese, silicon, and oxygen. The exception was 1 200 A samples, which had iron-rich grain boundaries poor in silicon, manganese, and oxygen. EDS performed on grain interior nodules resulted in spectra similar to the unoxidized bulk material. Discrete patches with a lacy appearance found only on the CR sample oxidized at -30°C DPT for 1 800 s were rich in manganese and oxygen. At -30°C DPT there were variations in surface morphology that were either iron-rich or silicon/oxygen-rich. For samples oxidized at 0°C DPT there was no variation in chemistry between grains regardless of morphological variation.

3.2. Short Timescale Internal Oxidation

Images of internal oxidation for each sample oxidized for 120 s can be found below in **Fig. 7**. Little variation was apparent between the three microstructure conditions. Samples oxidized at a DPT of -30°C had shallower internal oxidation compared to those oxidized at 0°C (depth measurements consolidated in **Fig. 8**). Oxides formed within grains (intragranular) and at grain boundaries (intergranular). Intragranular oxides were often spherical although larger, irregularly shaped oxides were also observed (see **Fig. 7(d)**). Intergranular oxides were film-like, but protrusions from the film were sometimes observed as in **Fig. 7(d)**. Samples of type 850 A and 1 200 A oxidized at -30°C DPT appeared to have larger and more numerous intragranular oxides (**Figs. 7(d)** and **7(f)**).

3.3. Long Timescale Internal Oxidation

Samples oxidized for 1 800 s at 0°C DPT showed different internal oxidation behavior with more intragranular oxidation in the 1 200 A and 850 A samples (see **Fig. 9** below). Similar to samples oxidized for 120 s, samples oxidized at -30°C DPT for 1 800 s showed minimal variation in internal oxidation depth between microstructures and sparse or absent intragranular oxidation.

A baseline for purely intragranular internal oxidation depth was difficult to determine for the 850 A type sample, so average intergranular depths were collected: 9.7, 13.7, and $7.1\text{ }\mu\text{m}$ for 1 200 A, 850 A, and CR samples oxidized at 0°C DPT respectively (see **Fig. 10**). Average intergranular depths for samples oxidized at -30°C DPT were 5.1, 5.2, and $5.8\text{ }\mu\text{m}$ for 1 200 A, 850 A, and CR samples respectively.

There were noticeable differences between individual grains as shown in **Fig. 11** for the 1 200 A sample oxidized at 0°C DPT. This figure also showed a relationship between deep internal oxidation and rougher surfaces. The preferential alignment of oxide particles observed in 1 200 A was also observed in grains of the 850 A sample.

4. Discussion

The purpose of this experiment was to study the selective oxidation behavior of different microstructure conditions in industrially relevant environments. Oxidation occurred for 120 s in forming gas atmospheres ($\text{N}_2 + 5\%\text{H}_2$) with con-

Fig. 7. SEM images of internal oxidation of samples oxidized for two minutes at 850°C; columns describe DPT atmosphere; rows describe starting microstructure.

Fig. 8. Summary of internal intergranular oxidation depth measurements after 120 s; error bars represent ± 1 standard deviation from the average.

trolled DPTs of -30°C and 0°C . A second set of samples was annealed for 1 800 s to examine effects of hold time and to compare with previous results²³⁾ where gaseous oxygen at very low partial pressures was the only oxidant.

SEM images of external surfaces showed differences in coverage with both DPT and starting microstructure. Iron-rich nodules in grain interiors were common to all samples oxidized at 0°C DPT and pre-annealed samples oxidized at -30°C DPT. For both atmospheres, nodules were largest on the 1 200 A and 850 A samples. Grain boundary oxides were silicon-rich at -30°C DPT and manganese-rich at 0°C DPT. Samples oxidized at a DPT of -30°C had more

prominent grain boundary features and overall a higher EDS oxygen signal than samples oxidized at 0°C . Samples oxidized for 1 800 s had larger surface features than their 120 s counterparts.

Both manganese and silicon oxides were expected, as they have been observed to form in relevant literature.^{15,21,25,26)} The occurrence of pure iron nodules, which was seen on several samples, is somewhat less reported but has been observed in other internally oxidizing systems.^{27,28)} The appearance of surface nodules on pre-annealed samples oxidized at -30°C DPT has interesting implications regarding prospects for zinc adherence or galvanization. For successful galvanization to occur, bare iron must be exposed at the surface to react with the molten zinc and form the protective coating. The formation of iron nodules from increased internal oxidation may provide a sufficiently large surface area of bare iron to improve the materials ability to be galvanized. Two formation mechanisms for surface nodules with pure base metal composition have been proposed: Nabarro-Herring creep²⁷⁾ and pipe-diffusion controlled creep.²⁸⁾

Creep occurs because compressive stress (due to formation of higher volume internal oxides) at the internal oxidation front leads to locally lower vacancy concentration and therefore a vacancy concentration gradient between the internal oxidation front and the alloy surface. Diffusion of vacancies toward the internal oxidation front results in a flux of iron atoms to the surface, leading to nodule or surface layer formation. This is a form of Nabarro-Herring creep if lattice diffusion controls the rate. A study in the Ag-In system found that transport rates were too high for lattice

Fig. 9. SEM images of internal oxidation of samples oxidized for 1 800 s at 850°C; columns describe DPT atmosphere; rows describe starting microstructure.

Fig. 10. Intergranular internal oxidation measurements for samples oxidized for 1 800 s; error bars indicate ± 1 standard deviation from the average.

diffusion to be controlling and proposed that fast-path diffusion occurred at dislocations.²⁸⁾ Both mechanisms result in the transport of bulk metal to the surface where the formation of discrete nodules can occur.

The internal oxidation that led to the formation of pure iron surface nodules appeared to be somewhat influenced by steel microstructure. This was particularly evident for samples oxidized at -30°C DPT. Though intergranular oxidation depths were not significantly affected by steel microstructure, the overall volume fraction appeared to be greater for pre-annealed samples. This was likely the reason surface nodules were observed. Internal oxides in samples

Fig. 11. SEM image of 1 200 A sample oxidized for 1 800 s in 0°C DPT atmosphere; image is a cross section of two grains, internal oxidation appears dark against bulk material; illustration of more surface features on a grain with greater internal oxidation depth.

oxidized at 0°C DPT often had dendritic morphologies that were oriented or aligned relative to the surrounding grain. This was particularly evident in 1 200 A and 850 A samples oxidized for 1 800 s.

Dendritic oxide morphologies have been previously observed in the solid state, though not frequently. In a study on internal SiO_2 formation in copper, the initial SiO_2 morphology was dendritic and over time spheroidization occurred.^{29,30)} The presence of a non-spherical morphology such as a dendrite could lead to changes in oxygen transport into the metal at short times, as oxide/metal interfaces are often fast-paths for oxygen diffusion. Formation of a dendritic structure is dependent on interfacial instability and a preferred growth direction derived from anisotropy.

Fig. 12. SE SEM images of internal oxidation in CR samples oxidized in 0°C DPT atmosphere for 1 800 s A) with and B) without a reaction tube.

pic interfacial energy between the oxide and surrounding matrix and/or variation in the ease with which atoms can adhere to various crystallographic planes.³¹⁾ The orientation and growth of dendrites are typically an expression of the underlying crystal structure of the oxide that is forming. Oxide orientation relative to the grain (observable in Fig. 11) is related to coherency between the oxide and matrix crystal structures. Upon nucleation, the oxide particles will align in an orientation of least misfit between the two lattice structures³⁰⁾ to minimize interfacial energy. Though typically reported as amorphous, SiO₂ is thought to be briefly crystalline upon nucleation.³⁰⁾ A temperature-pressure phase diagram of the SiO₂ system predicts β -quartz to be the stable crystal structure at 850°C, which has a hexagonal crystal structure. This would explain the dendritic appearance of many of the intragranular oxides and also why many appear to be oriented relative to the grain. The initial coherence between the crystalline oxide and the surrounding matrix would allow them to align in such a way so as to minimize the misfit between the two lattices.³⁰⁾ While the SiO₂ remains crystalline, growth would be guided/restricted to the directions of least misfit. When the SiO₂ becomes amorphous, however, growth would likely become determined by concentration gradients within the IOZ. It is not clear what factors lead to the transition to amorphous SiO₂. The amorphization of α -quartz, the lower temperature polymorph of SiO₂ with similar crystal structure, suggests the process can occur with the application of pressure (15–40 GPa) sufficient to break bonds and cause small atomic displacement within the crystal.³²⁾ Rudimentary calculations to estimate elastic compressive stresses imposed on a growing SiO₂ particle based on differences in density between iron (7.87 g/cm³) and SiO₂ (2.65 g/cm³) indicate the particle was subjected to ~11 GPa.

Strain was estimated using the volumetric difference between a constrained and unconstrained sphere of SiO₂. An unyielding iron matrix was assumed and a Young's modulus of 16.3 GPa (α -quartz, at 550°C) was used in this estimate.³³⁾ The actual stresses will be lower since the temperature is higher and the iron matrix deforms. Stresses generated during oxidation may play a role in the transition, but more work must be performed to investigate this possibility.

Regarding internal oxidation behavior, there were no significant differences in oxidation behavior with the different

microstructures after 120 s oxidation. After 1 800 s, the CR sample oxidized at 0°C DPT appeared to differ in behavior from the other samples. This was the only sample consistent with the results reported in gettered argon,²³⁾ where shallow internal oxidation was observed in CR samples after oxidation for times up to 5 400 s. Also similar to the gettered argon results, intragranular internal oxides were absent. Absence of intragranular oxides from the CR sample oxidized in 0°C DPT atmosphere for 1 800 s suggests decarburization may have influenced oxidation behavior. Previous studies have suggested decarburization does not influence oxidation^{8,34)} but in this current experimental setup it was possible that the reaction tube restricted gas supply. The gas near the specimen surface would then become starved of oxidant due to decarburization.

To test this theory, an additional CR sample was oxidized in 0°C DPT atmosphere for 1 800 s without a reaction tube. **Figure 12** below shows SE SEM images of cross sections from each CR sample, oxidized with and without a reaction tube.

The images above clearly show that without the reaction tube, intragranular oxidation occurred, whereas only intergranular oxidation was observed with the tube. This suggested a higher oxidant partial pressure at the specimen surface without the reaction tube. Extensive intragranular oxidation was observed in samples decarburized prior to the oxidation experiments, even with the reaction tube. Since they were already decarburized, the oxidant concentration in the atmosphere was higher for these samples and more oxidation was observed. Decarburization and selective oxidation occur simultaneously, and it appears that decarburization can influence selective oxidation when supply of gas is restricted.

5. Conclusions

The following conclusions from this set of experiments were made:

- External and intergranular internal oxidation was observed under all conditions examined; all samples oxidized at –30°C DPT and the CR sample oxidized for 1 800 s at 0°C DPT displayed particularly small and sparse (or absent) intragranular oxidation localized near grain boundary oxides. Internal oxidation in general was, as expected,

not as deep in -30°C DPT samples.

- Near-surface microstructures did not have as significant an effect under industrially-relevant controlled DPT $\text{N}_2 + 5\%\text{H}_2$ atmospheres and shorter times compared to conditions described in Story *et al.*²³⁾ (longer time and argon with low oxygen atmosphere). At longer times in $\text{N}_2 + 5\%\text{H}_2$ with 0°C DPT, a microstructural effect was observed, but was ultimately attributed to effects of carbon competing for oxygen under restricted gas conditions in CR samples during simultaneous decarburization and oxidation.

- Many of the grain-interior surface features found on samples oxidized in a 0°C DPT atmosphere were iron nodules that formed due to stresses generated by oxide formation. Similar nodules were observed on 1 200 A and 850 A samples oxidized at -30°C DPT. This was attributed to the apparent formation of larger and more prevalent intra-granular oxides.

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