Effect of Surface Microstructure on Oxidation of a CMnSi Advanced High Strength Steel

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The work presented here demonstrated that changes to the near-surface microstructure could promote internal oxidation in a CMnSi advanced high strength steel (AHSS) grade. The starting material was industrially-supplied cold-rolled sheet. Samples with this microstructure were compared against two other conditions: annealed at 1 200°C and 850°C prior to oxidation. The surface regions of both annealed samples were decarburized. All samples were then oxidized at 850°C in an argon atmosphere with approximately 10−20 atm oxygen for 5–90 minutes. The oxidation treatments were performed in a high-temperature confocal scanning laser microscope (CSLM) setup that enabled in-situ visualization of surface oxide formation. Analysis of CSLM and scanning electron microscopy (SEM) images of sample surfaces indicated there were differences in oxide morphology and coverage between samples with different starting microstructures. Cold-rolled samples showed little internal oxidation but extensive external oxidation. Samples annealed prior to oxidation exhibited both internal and external oxidation. The differences in behavior were attributed to the formation of a decarburized surface layer during the pre-anneal, which led to ferritic iron near the surface. Another result of the pre-anneal was a reduction in dislocation density, which potentially led to fewer preferential nucleation sites for oxides very close to the sample surface.

KEY WORDS: AHSS; CMnSi steel; dew point; selective oxidation; internal oxidation; external oxidation; FIB; TEM.

1. Introduction

Since the beginnings of the automotive industry in the late 19th century, steel has been an essential material for cars due to its low cost, high strength, and wide availability. Growing demand for lighter, more fuel-efficient vehicles has led the steel industry to develop multiple generations of AHSS grades1,2) to meet ever increasing requirements for strength and ductility. 3) The unique properties of AHSS grades are frequently enabled by the alloying elements manganese and silicon. These elements have a higher affinity for oxygen than iron and selectively oxidize during the continuous annealing process prior to hot-dip galvanizing.4,5) Traditional conditions in the annealing furnace (800 to 900°C, N2−H2 atmosphere with dew points of −30 to −20°C) typically cause silicon- and manganese-rich oxides to grow on the steel surface,6−8) reducing molten zinc coating adherence and the steels corrosion resistance.9,10) In addition to oxide chemistry, it has been shown that surface oxide morphology is equally important for determining zinc wettability.11) For these reasons, understanding the selective oxidation behavior of these alloys and finding a way to prevent detrimental external oxides from forming is of interest to steel producers.

There are several proposed techniques for controlling oxidation and improving zinc adherence to grades of AHSS containing manganese and silicon.4,10,12−17) The method most relevant to this study is the promotion of internal oxidation over external oxidation. This transition can be induced by raising the dewpoint of the annealing furnace atmosphere.16,18−20) Raising the atmospheric dewpoint increases the surface oxygen concentration and the flux of oxygen into the steel, promoting internal oxidation over external oxidation. The classic analytical model of this transition phenomenon was formulated by Wagner.20) The quantitative internal/external transition criterion from Wagner’s model was developed under the assumption that oxidation occurs in a binary, single phase, solid solution alloy with no grain boundaries or dislocations. While there has been work to relax these assumptions,6,21−26) quantitative predictions of the oxidation behavior in AHSS grades are still challenging.

Many of the challenges in predicting oxidation behavior stem from the variety of microstructural variables that affect oxidation. These include, but are not limited to: (1) the phase of iron present, ferrite or austenite, (2) the presence of dislocations, and (3) the presence of grain boundaries and grain size. These variables will affect the diffusion of manganese, silicon, and oxygen. The effects of annealing temperature and near-surface microstructure on oxide development have been studied previously in CMnSi AHSS.12,27) Similar external oxidation behavior was observed between...
fully austenitic and intercritically annealed samples, but the behavior was different for fully ferritic samples. For austenitic and intercritical samples, two distinct layers were reported to have formed: a mixed oxide, crystalline, outer layer and an amorphous, SiO$_2$, inner layer. The fully ferritic sample formed a crystalline oxide film on the surface decorated with amorphous lens shaped oxides. For all sample types, amorphous oxides were either pure SiO$_2$ or SiO$_2$-rich and mixed oxides had a xMnO · SiO$_2$ composition. Both deformation and annealing affect the surface distribution of alloying elements, which in turn influences oxide chemistry and morphology.

Glow discharge optical emission spectroscopy (GDOES) and EDS results indicated manganese enrichment at the surface was greatest at low temperatures or when the matrix was entirely ferritic. Grain size has also been shown to impact oxidation behavior, influencing overall coverage as well as surface oxide chemistry and morphology. Coarse-grained samples from the study by Thorning et al. tended to form a continuous network of manganese-rich oxides along the grain boundary, but sparse oxidation on grain interiors. Oxidation of the fine-grained samples was more uniform across the entire surface. Fine-grained samples also formed some oxides along grain boundaries, but not to the same extent as the coarse-grained samples.

The stable phase of iron is determined not only by annealing temperature, but by decarburization that can occur during annealing. Figure 1 below is an Fe–C pseudobinary phase diagram generated using ThermoCalc (version 2015b, TCFE8 database) illustrating that decarburization can lead to the formation of ferrite during annealing in the single-phase austenite field. There is very little information in the literature regarding direct effects of decarburization on oxidation. Studies based around thermogravimetric data on simultaneous oxidation and decarburization in AHSSs have noted that decarburization depths are greater than internal oxidation depths, indicating they are independent processes. It is also noted that increasing external oxidation thickness seems to slightly hinder decarburization, indicating oxidation may influence decarburization kinetics.

The work presented in this report further demonstrates the effect of near-surface microstructure on oxidation and also qualitatively examines the role of grain boundaries and dislocations as fast diffusion paths. CMnSi AHSS grade samples with the same chemistry but three different microstructures were oxidized at 850°C in a low oxygen atmosphere for times ranging from 5 to 90 minutes in a CSLM. Longer hold times were performed to collect a more complete set of kinetic data via internal oxidation depths. Two sample types were pre-annealed to ensure the surface was ferritic at the start of oxidation, and a third was left in the cold-rolled state to ensure an austenitic surface at the start of oxidation. Pre-annealing in an argon atmosphere containing sufficient oxygen impurities to cause iron oxidation results in a reaction with the carbon in the metal at the metal-oxide interface to form carbon monoxide. Assuming a sufficiently porous scale, the carbon monoxide can escape and cause decarburization. This differs from prior experiments seen in the literature because a pre-anneal step was used to control the surface microstructure as opposed to oxidation temperature. Post-oxidation, all sample surfaces and cross sections were examined with a SEM. For select shorter time experiments, transmission electron microscope (TEM) sample were prepared with a NOVA 600 gallium focused ion beam (FIB) instrument for better characterization of oxides too small to characterize with an SEM.

2. Materials and Experimental Methods

The material of interest in this study is an industrial AHSS grade with chemistry shown below in Table 1.

A circular punch was used to create 8 mm diameter disc samples from 1.5 mm thick cold-rolled sheets. Two different pre-oxidation annealing treatments were performed: (1) in an open-air box furnace at 850°C for two hours (samples were placed in the pre-heated furnace and cooled in still air) and (2) in a horizontal alumina tube furnace under flowing argon (0.25 L/min) at 1200°C for two hours (ramp up and cool down rate of 2°C/min).

The pre-oxidation anneals were intended to recrystallize the cold-rolled samples and cause grain growth and decarburization. An argon atmosphere was used at 1200°C to avoid excessive oxidation, but the amount of oxygen impurities ($\sim 10^{-5}$ atm $P_O$) was sufficient to cause bulk iron oxidation to occur. Cold-rolled samples underwent no additional heat treatment prior to the experiment. Prior to CSLM experi-

| Table 1. Chemistry of AHSS grade investigated in this study. |
|---------------------|-------|-------|-------|-------|
| Element | C    | Si    | Mn    | Al    |
| wt%     | 0.090| 0.91  | 2.02  | 0.038 |
ments, both sides of all samples were then polished flat through 1 μm diamond with a Struers automatic polisher. The microstructures of all as-received samples were examined by light optical microscopy (LOM) after etching in 2% nital. The Vickers microhardness of all three conditions was also measured.

All oxidation experiments were conducted in a high-temperature CSLM setup (see Fig. 2 below). The CSLM furnace allowed for in-situ observation of high temperature processes such as melting, solidification, solid state phase transformations, and oxidation.28,32) Infrared heating via a halogen lamp allowed for rapid heating and cooling. Confocal optics combined with a red He–Ne laser (wavelength 632.8 nm) enabled sample viewing at high temperatures. The image contrast in CSLM images was due to height differences, i.e. a polished steel surface appeared uniform while growing oxides appeared dark on the images. Surface relief due to the ferrite/austenite transformation and thermal grooving at grain boundaries also lead to contrast in the images. Samples were contained in alumina crucibles for all CSLM experiments.

Twenty-three oxidation treatments were all conducted at 850°C for times ranging from 5 to 90 minutes. Separate samples and experiments were conducted for each time point. The gas used for all experiments was 99.9999% pure argon at a flowrate of 0.25 L/min. Prior to reaching the chamber, the gas was passed over pure copper and magnesium shavings at ~400°C to decrease oxygen pressure from ~10⁻⁵ to ~10⁻²⁰ atm $P_{O_2}$. The oxygen partial pressure of the gas in the chamber was monitored and collected with an electrochemical oxygen sensor. The minimum, maximum, and average oxygen pressure during each experiment can be found below in Fig. 3.

After oxidation, the surface oxides on CSLM samples were examined with either a FEI Quanta 200 field emission gun SEM or an FEI/Phillips XL-30 SEM. The latter SEM was equipped with energy dispersive x-ray spectroscopy (EDS) for chemical analysis. For internal oxidation characterization, samples were cross-sectioned with a Buehler low speed saw and mounted on edge in diallyl phthalate compression mounting compound. All samples were polished in the same manner as the original CSLM samples and examined in the SEM. Depth measurements were collected from a minimum of five locations on each SEM sample, spanning the entire cross section. An FEI Nova Nanolab 600 focused ion beam (FIB) system was used to create transmission electron microscope (TEM) samples by the lift-out technique from specimens oxidized for 5 minutes. These samples were examined in a 200 kV FEI Tecnai F20 TEM/STEM in STEM mode. Fewer than five depth measurements were collected from samples prepared with the FIB.

3. Results

3.1. Starting Microstructure and Vickers Hardness Measurements

Figure 4 shows LOM images of the microstructure for each sample type after pre-annealing but before the oxidation experiments. Enlarged equiaxed grains in the pre-anneal samples indicated the surfaces were decarburized.

To make sure the correct surface microstructure had been achieved, Vickers hardness tests were conducted. For each microstructure, twenty microhardness measurements were conducted between two different samples. The results of the Vickers measurements are shown in Fig. 5.
3.2. Chemistry, Coverage, and Morphology of External Oxides

Figure 6 shows CSLM still frames of each sample type at the beginning and end of a 30 minute 850°C oxidation treatment. The image contrast resulted from thermal grooving at grain boundaries and from surface relief due to the ferrite/austenite phase transformation. As time progresses, the growth of external oxides on the surface cause the images to darken.

SEM images revealed a wide variety of oxide morphologies and sizes. Representative images are shown below in Fig. 7 for samples oxidized a total of five minutes. EDS revealed that the rounded oxides were predominantly silicon-rich with varying levels of manganese. Individual cold-rolled samples displayed a wide range of oxide sizes, morphologies, and chemistries. Samples with higher average oxygen partial pressure, and also those held for shorter times, tended to exhibit smaller lens shaped oxides. Samples exposed to lower oxygen partial pressures and/or held for longer times (30+ minutes) tended to have larger oxides and also displayed a wider range of oxide morphologies. Rounded oxides are commonly found growing along grain boundaries, while faceted oxides are typically found growing in clusters at grain interiors.

For pre-annealed samples, a thin crust comprised of small, irregularly shaped oxides was common to all samples. External grain boundary oxides were also common, forming a continuous ridge along exposed grain boundaries intersecting the surface. Select samples displayed faceted oxides growing in clusters on grain interiors, but this was not common to all samples.

3.3. Depth and Morphology of Internal Oxides

Internal oxidation was observed in SEM images after 15 minutes in the pre-annealed samples and after 30 minutes in the cold-rolled samples. Preferential internal oxidation at grain boundaries was observed in all samples, but dispersions of small, intragranular oxides (referred to as bulk internal oxidation) were observed only in the pre-annealed samples. Figure 8 shows comparative SEM images of internal oxidation from each sample type.

Though not visible in SEM images, TEM imaging confirmed internal oxidation occurred in both 1 200°C pre-annealed samples as well as the cold-rolled sample. STEM images can be found below in Fig. 9, showing both intra and intergranular oxidation in the 1 200°C pre-annealed sample (Figs. 9(a), 9(c), and 9(e)) and intragranular oxidation in the cold-rolled sample (Figs. 9(d) and 9(f)). EDS collected from the pre-anneal samples indicated both inter and intragranular oxides were primarily silicon rich. EDS from the cold-rolled sample showed elevated manganese in the intragranular oxides.

4. Discussion

The main goal of this study was to observe the impacts of grain size and surface phase on oxidation behavior and to compare the results to literature as well as existing predictive models. As mentioned previously in the Introduction, it has been shown in other studies that ferrite and austenite
exhibit different oxidation behavior.\textsuperscript{7)} Their results indicate ferrite does not form a pure, amorphous, SiO\textsubscript{2} layer at the surface during oxidation\textsuperscript{7)} a feature known to inhibit galvanization.\textsuperscript{10,14,15,17)} Galvanization simulations were not performed on the materials discussed in this report,\textsuperscript{7)} making improvements on zinc adherence indeterminate at this time. Regardless of ferritic oxidation behavior observed by Gong et al., the mechanical properties of AHSS grades cannot be obtained if the steel is annealed at temperatures where it remains fully ferritic. In this study, a decarburization step was performed to create a ferrite layer at the surface of a CMnSi AHSS during oxidation at 850°C. The pseudobinary Fe–C phase diagram above in Fig. 1 indicated that at 850°C, the alloy for this experiment should be completely austenitic. If that same material were sufficiently decarburized (\textit{i.e.} wt\% C below $\sim$0.055), the microstructure (specifically at the surface) would be at least partially ferritic.

Samples pre-annealed at 850°C were in the furnace for two hours to form a decarburized layer thick enough to remain intact during CSLM sample prep. The time and temperature were selected to accomplish this while minimizing grain growth.\textsuperscript{33)} The influence of grain size was also of interest for this study, so a set of samples were pre-annealed at 1 200°C for two hours with a heating and cooling rate of 2°C/min to promote grain growth as well as decarburization. A third set of samples, described as having a cold-rolled microstructure, received no pre-anneal and functioned as a control against which the other samples could be compared. These cold-rolled samples were expected to decarburize somewhat during oxidation at 850°C in the CSLM, but to a very small extent given the low oxygen pressures.\textsuperscript{29)} Accurate predictions were not possible due to a lack of atmospheric carbon monoxide and carbon dioxide analysis equipment. Physical depth measurements using LOM were not possible because samples etched with 2\% nital after oxidation at 850°C bore no signs of a large-grained single-phase region characteristic of decarburization.

To ensure decarburization was achieved, Vickers hardness tests were carried out and reported in Fig. 5. Hardness values of the pre-annealed samples were similar to those published for ferrite,\textsuperscript{34)} and LOM images of etched samples showed a single-phase region near the surface, so a decarburized surface microstructure was likely achieved for both pre-annealed samples. The 850°C pre-anneal type samples had a slightly higher average hardness, but this was expected because the grains were smaller.

Oxygen, silicon, and manganese diffusivity values differ between ferrite and austenite,\textsuperscript{26)} so the selective oxidation behaviors were expected to be different. As a starting point for discussion regarding the comparison between experimental results to existing analytical models, Eq. (1) is a
variation\textsuperscript{22}) of the original model developed by Wagner to predict the transition point between internal and external oxidation.\textsuperscript{29,35}

\[
\sum_{\beta} N_{\beta}^{(o)} [nD_{\beta}V_{\beta O}]^{1/2} = \left[ \frac{g \pi V}{2} \right]^{1/2} \left[ N_{O}^{(s)} D_{O} \right]^{1/2} \quad \text{...... (1)}
\]

In Eq. (1), \( N_{\beta}^{(o)} \) is the bulk solute content at which the transition occurs between internal and external oxidation. For this alloy, “B” represents either silicon or manganese. \( N_{O}^{(s)} \) is the surface oxygen concentration in the metal. The equilibrium between oxygen gas and dissolved oxygen in iron has been extensively investigated in several works.\textsuperscript{36–40} This study used equilibrium constants from\textsuperscript{25,38} to calculate dissolved oxygen in ferrite and austenite with the average measured \( p_{o} \) from all experiments. The results of this calculation and the values used are shown in Table 2.

- \( D_{O} \) is the oxygen diffusivity. Calculations were phase specific (austenite or ferrite).
- \( D_{\beta} \) is the alloying element diffusivity for either silicon or manganese.
- \( N_{\beta} \) is the molar fraction of dissolved oxygen at the surface of the metal.
- \( V \) is the molar volume of the base metal. Calculations were phase specific (austenite or ferrite).
- \( V_{\beta O} \) is the molar volume of the oxide of interest, either MnO or SiO\(_{2}\).
- \( g \) is the critical volume fraction of internal oxide at which the transition occurs from internal to external oxidation.
- \( n \) represents the stoichiometric ratio of oxygen to alloying element required to form the oxide of interest (i.e. for SiO\(_{2}\), \( n = 2 \)).

The calculation results in Table 2. suggested internal oxidation would occur in the pre-annealed samples, while external oxidation would occur in the cold-rolled samples. This was attributed to the difference in oxygen diffusivity in austenite at 850°C.\textsuperscript{36} While there were many simplifications in the above transition model, experimental results were qualitatively consistent with the predictions. More internal oxidation occurred in samples that were expected to be predominately ferrite at the surface, though all samples externally oxidized to some degree (see Fig. 8). The presence of external oxidation was also expected as all literature concerning the subject indicated some amount of external oxidation occurring during annealing. Though most of the external oxides were too small to analyze by EDS, their morphology could be observed. The pre-annealed samples had smaller, more well dispersed external oxides. External oxides on the cold-rolled samples tended to be large and often appeared to have merged into one another, forming patchy crusts and continuous networks of branching oxides. Internal oxidation was visible in SEM images for all but the 1 200°C annealed sample held for 5 minutes. No internal oxidation was visible in cold-rolled samples held for less than 30 minutes. TEM images of the short-time 1 200°C pre-anneal sample and cold-rolled sample showed evidence of internal oxidation, but the extent of internal oxidation was still greater in the pre-annealed sample.

Figure 10 shows plots of bulk and grain boundary internal oxidation depth over time. Each plot compared experimental results to depths predicted by Wagner’s internal oxidation model (Eq. (2)).\textsuperscript{20,35}

\[
X = \frac{2D_{O}N_{O}^{(s)}}{N_{B}^{(o)}} t \quad \text{.......................... (2)}
\]

In the above equation, \( X \) represents internal oxidation depth, \( t \) is the reaction time, and additional variables carry the same meaning as in the previous equation (Eq. (1)). For grain boundary calculations, the diffusivity was estimated by dividing the activation energy for lattice diffusion by two.\textsuperscript{23} For these comparative calculations, only SiO\(_{2}\) was considered because in the literature it is noted that below one micron in depth, only amorphous SiO\(_{2}\) forms.\textsuperscript{8}

There was some correlation between the internal oxidation depth predictions calculated using Eq. (2) and the experimental results for both pre-annealed type samples, but no correlation for cold-rolled samples (see Fig. 10 above). Experimental results for all pre-annal sample types are to be compared to trends calculated using ferrite parameters. Results for cold-rolled samples are to be compared to trends calculated using austenite parameters. Bulk internal oxidation depths were generally greater than the predicted for longer hold times (Fig. 10(a)), but the lines in Figs. 10(a) and 10(b) were calculated based on a single, average oxygen pressure and there was some variability in actual experiments. Lateral diffusion of oxygen from grain boundaries in the subsurface region may also have contributed to this observation.

The occurrence of shallow internal intergranular oxidation and an absence of intragranular oxidation in the cold-rolled
sample was attributed to two factors: the nucleation of oxides close to the surface during heating enabled by high dislocation densities from cold-rolling, and the austenitic microstructure which limited oxygen diffusion into the steel at the 850°C hold temperature. Slower diffusion into the metal would lead to formation of oxides closer to the surface. The formation of an internal oxide barrier blocking diffusion of oxygen was discussed by Rapp and could be playing a role in a highly cold-worked system. With the current results the relative importance of behavior on heating vs. near-surface microstructure cannot be separated. In the pre-annealed samples, there should have been less external oxidation on heating, and the near-surface ferritic structure at the hold temperature enabled more rapid oxygen diffusion, which promoted internal oxidation. In all samples, there was preferential internal oxidation at the grain boundaries, but in the case of the pre-annealed samples the grain size did not change the observed depth of intergranular oxidation.

It should be noted that during industrial production, these AHSS grades are annealed for times of approximately two minutes in N₂–H₂ gas mixtures (so the oxidant is H₂O). The conditions in this study included low \( p_o \) environments (main oxidant O₂) and longer soak times. In addition, the gas flow patterns in the CSLM furnace chamber are complex which could potentially affect supply of oxygen to the sample surface. Even when oxidizing with H₂O, the validity of assuming a constant surface oxygen concentration \( (N_0) \) has been challenged. Despite these differences, the results of this study suggested that modifying the near-surface microstructure could potentially be exploited to promote internal oxidation and improve zinc wettability of AHSS grades.

5. Summary

This study examined the effect of near-surface microstructure on the oxidation of AHSS grades. Samples pre-annealed at 1 200°C and 850°C (ferritic at the surface due to decarburization) were compared to a cold-rolled sample (austenitic at the surface) after oxidation at 850°C. Based on the results presented and discussed above, the following can be concluded regarding the influence of grain size and near-surface phase on oxidation behavior of Cmnsi AHSS grade:

- External oxidation behavior was approximately the same for both 1 200°C and 850°C pre-annealed samples. The coverage, chemistry, and oxide morphologies were similar despite some variation in oxygen partial pressure from sample-to-sample.
- There were clear differences in external oxidation behavior between the cold-rolled and pre-annealed samples. Overall oxide size was greater for austenite samples and a much broader range of oxide morphologies was observed.
- Both intra- and intergranular internal oxidation occurred to a similar extent in both 1 200°C and 850°C pre-annealed samples. The depth of internal oxidation for both samples was comparable to an oxygen diffusion-controlled model. This was attributed to the presence of a ferrite layer and reduced dislocation content near the sample surface.
- Internal oxidation of cold-rolled samples occurred as grain boundary oxidation after times greater than 30 minutes. Intragranular internal oxidation depths were very shallow (visible via TEM only) and oxides were approximately ~50 to 75 nm. This was attributed to the preferential nucleation of oxides at dislocations during heating in the CSLM, and to the austenitic structure near the surface at temperature (850°C).

Overall, grain size appeared to have less of an effect on oxidation behavior compared to the presence of austenite vs. ferrite and the dislocation content at the surface.

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