Residual copper contents in low carbon steels lead to a cracking phenomenon known as surface hot shortness. This phenomenon is caused by a copper-rich liquid layer that forms due to copper enrichment as iron oxidizes during casting, reheating and/or hot rolling. Evolution of the copper-rich liquid layer is dependent on the competing processes of enrichment due to iron oxidation and diffusion of copper back into the metal. This paper presents comparisons between experiments and calculations of a fixed grid finite difference model that predicts the evolution of the copper-rich region. Experiments involved oxidizing an iron–0.3 wt% copper alloy in a gold-image furnace equipped with thermogravimetric balance. Samples were oxidized at 1150°C in three atmospheres, dry air, wet air (15 vol% H₂O), and argon–15 vol% H₂O. Model predictions agree with measured data for dry air oxidation at 1150°C for 60, 300, 420, 600, 900, and 1200 s. Agreement was also obtained for iron oxidized for 1800 and 2700 s in argon–15 vol% water vapor. However, model predictions deviated for samples oxidized 3600 s in dry air, 3600 s in water vapor, and 600 s in wet air. The deviations arise due to grain boundary penetration and diffusion of copper. Results suggest a critical amount of separated copper is necessary for substantial grain boundary penetration to occur and the required amount decreases when the gas contains H₂O. The model was also used to estimate the evolution behavior of the liquid copper phase under industrially relevant conditions.

KEY WORDS: high-residual containing steels; copper; finite difference model; surface hot shortness.
Unfortunately proprietary and do not appear in published literature, although it appears to fit experimental results under a variety of conditions.\(^9\) Darken\(^6\) and Bergman and West’s\(^7\) models are analytical and restricted to only parabolic oxidation kinetics. O’Neill\(^8\) did not find a solution with their analytical model. O’Neill’s\(^8\) numerical model accounts for initially linear oxidation kinetics that transition to parabolic behavior. However, its ability to predict the evolution of the copper-rich liquid was validated only for limited oxidation times in air.\(^8\) In addition, this model relies on an iterative procedure that involves changing the liquid/solid interface position to achieve mass balance.

This work was undertaken to validate a model that incorporates a variety of input conditions and predicts the evolution of the separated copper-rich liquid. The model predicts the copper-rich layer thickness directly from diffusion and mass balance equations, details were described in a previous publication.\(^10\) This work discusses the model’s validity to various oxidation times and atmospheres.

2. Problem Formulation

The evolution of the copper-rich liquid layer is determined by a balance between enrichment of copper due to iron oxidation and diffusion of copper back into the steel. The transport processes that must be considered are: those determining the iron oxidation rate (gas phase convection/diffusion of oxidant to the solid surface, dissociation of the oxidant, ionic diffusion in the oxide), liquid phase convection/diffusion in the copper-rich layer, and metallic diffusion in the solid iron-rich phase. A schematic of the processes that determine the evolution of the separated liquid copper phase is shown in Fig. 2.

Consideration of moving phase boundaries is also necessary. The oxide/gas interface grows out from the metal as new oxide is formed, the oxide/metal interface moves towards the bulk metal due to differences in molar volume between the oxides and the metal. Finally, motion of the liquid copper/\(\gamma\)-iron interface is determined by the balance between copper enrichment and back-diffusion rates.

3. Model Development

The goal of the model is to predict the evolution of the copper-rich liquid layer given information about the oxidation behavior, solubilities, and diffusivities. All concentrations and diffusivities refer to copper since we are primarily concerned only with its distribution. Figure 3 shows a sketch of the arrangement of phases, concentration gradients, and relevant quantities. A summary of the quantities shown in Fig. 3 is given in Table 1.

The following quantities are taken as inputs to the model:
1) Initial copper content, \(N_0\)
2) Interface concentrations, \(N_{\text{L/FeO}}\), \(N_{\text{L/\gamma}}\), and \(N_{\gamma/L}\)
3) The oxidation behavior as a function of time, \((\Delta m/A)(t)\)

The main quantity of interest in this model is the liquid phase thickness, \(L_{\text{Liq}}\). This is determined by an equation describing the global mass balance of copper in the system

\[
\frac{1}{2} (N_{\text{L/FeO}} + N_{\text{L/\gamma}}) L_{\text{Liq}} + \int_{\text{All } \gamma\text{-Fe}} N_{\gamma}(x,t) dx = L_0 N_0 \quad \ldots (1)
\]

To solve Eq. (1), the concentration profile of copper in the \(\gamma\)-phase, \(N_{\gamma}(x,t)\) must be calculated. This is accomplished by solving Fick’s Second Law in the \(\gamma\)-phase with a fixed-grid, finite difference technique following Crank,\(^11\) Lee and Oh,\(^12\) and Zhou and North.\(^13\) The global mass balance equation (Eq. (1)) was used to calculate the copper-rich layer thickness for each time step. This model was implemented using the computer program Mathematica\textsuperscript{TM} (a trademark of Wolfram Research).

The following assumptions are necessary to obtain input quantities and to simplify calculation.
1) Transport in the liquid, by either diffusion or convection, establishes a steady-state copper concentration profile in the liquid copper-rich phase.
2) The difference in molar volume between solid iron and liquid copper are negligible and therefore mole fraction is used as the concentration variable. The molar volume of austenite is 7.1 cm\(^3\)/mol that for liquid copper is 8 cm\(^3\)/mol. Thus, this approximation should not lead to significant errors.
3) Local equilibrium is maintained at interfaces so concentration profiles are constant.

![Fig. 2. Schematic of the problem showing arrangement of phases and direction of diffusing species.](image)

![Fig. 3. Sketch showing arrangement of phases, and examples of copper concentration gradients in the liquid and \(\gamma\) phases.](image)

| \begin{tabular}{|c|}
| N_0 |
| \hline
| Initial copper concentration |
| N_{\text{L/FeO}} |
| \text{Copper concentration in the liquid phase at the L/FeO interface} |
| N_{\gamma/L} |
| \text{Copper concentration in liquid phase at the L/\gamma interface} |
| N_{\gamma/g} |
| \text{Copper concentration in the } \gamma \text{ phase at the } \gamma/L \text{ interface} |
| \(\Delta m/A)(t)\) |
| Mass gain per unit area with time due to oxidation |
| L_{\text{Liq}}(t) |
| Copper-rich liquid phase thickness |
| \end{tabular} |
Diffusion is the only mechanism by which copper is re-entered as a table of concentrations. The system of interest has three components, iron, copper and oxygen, a sketch of the relevant phase diagram at 1200°C (after Ref. 14) is shown in Fig. 4. The sketch shows that the interface between γ-iron and the copper-rich liquid is virtually identical to that in the two component iron-copper system. Thus, this concentration can be determined by the binary iron–copper phase diagram at 1150°C (shown in Fig. 1). At the interface between wüstit and the copper-rich liquid, the diagram shows that the copper concentration can vary between 0.94 and 0.98 (mole fraction copper) at 1200°C. At 1010°C (diagram not shown), the range over which wüstit and liquid copper are in equilibrium decreases to 0.97–0.98 (mole fraction copper). For the temperature of simulations, 1150°C, an intermediate value of 0.97 was chosen.

4) Diffusion occurs only in the dimension normal to the plane of the interfaces. Although it is possible for non-planar oxide/metal interfaces to form during oxidation of binary alloys, they should not occur in the presence of a liquid phase. In addition, grain boundary penetration and lateral diffusion of copper from penetrated areas are not considered by this model.

5) The diffusivity of copper in γ-iron is independent of concentration.

6) Diffusion is the only mechanism by which copper is removed from the near-interface region. In steels containing nickel, copper-rich material can become engulfed by the oxide layer, a phenomenon known as occlusion. Since the current work considers only binary iron–copper alloys, no occlusion is expected. Kondo found small (≤500 nm) particles of copper-rich liquid in the wüstit layer even in steels containing very low amount of nickel. The mechanism by which these liquid drops enter into wüstit has not yet been adequately explained, but they are assumed so small that they do not appreciably contribute to copper removal.

The final input to the model, oxidation behavior, is entered as a table of $\Delta m / A$ vs. $t$ values, usually from direct experimentally measured data. This method was chosen instead of using kinetic rate constants as an input to give the model greater flexibility. Iron oxidation in atmospheres relevant to steel production often involves multiple rate-determining steps (see results below and work by Lee et al.) so the use of a table eliminates the need to model any transition regions where the kinetics are not well-described by a single rate constant. If only kinetic constants are available, they can be used to generate a table of $\Delta m / A$ vs. $t$ values for input into the model. The $\Delta m / A$ data are converted to values representing the amount of metal consumed by the relations given by O’Neill. A function in the computer program Mathematica (a trademark of Wolfram Research) is used to interpolate between the points when necessary.

4. Experimental Verification—Materials and Methods

4.1. Materials

An alloy of iron with 0.3 wt% copper was used to investigate the ability of the model to predict experimental results. The sample chemistry is listed in Table 2. The alloy was obtained as plate samples from the Materials Production Center at the US Department of Energy’s Ames Laboratory located in Ames, Iowa, USA. The alloy was arc-melted in an inert atmosphere, cold-rolled, and cyclically heat treated between 850°C and 950°C in an inert atmosphere for 1 h. The heat treatment produced equiaxed ferrite grains of approximately 500 μm (measured from nital-etched samples, not shown). Even with the grain size decrease due to the ferrite/austenite transformation, the number of grain boundaries is sufficiently small that the amount of copper diffusing laterally into the grains due to fast-path grain boundary diffusion can be neglected. It is important to note that this assumption does not apply if the copper-rich liquid penetrated down austenite grain boundaries. In this case however, copper would likely diffuse laterally along the entire length of the penetrated region and would not follow the typical distribution expected from grain boundary diffusion theory (see, for example, Kaur and Gust).

4.2. Methods

Oxidation kinetics were measured by thermogravimetric (TG) analysis in three atmospheres, air, wet air (15% water vapor) and argon–15vol%H2O at 1150°C. 1150°C was chosen because it ensures the copper-rich phase will be liquid during the experiments and is close to the temperature of maximum hot shortness severity, as discussed in the
Introduction. A schematic of the apparatus used is shown in Fig. 5.

Samples were heated in an infrared gold image furnace. This furnace uses four high energy density halogen lamps to heat samples by radiative heat transfer. The lamps are placed at one focus of gold-plated ellipsoidal furnace walls; the sample is placed at the other focus. Due to the geometric properties of ellipsoids, light from the lamps is reflected by the gold-plated walls to the other focus, i.e. the sample. A schematic of the radiative heating mechanism is shown in Fig. 6.

The halogen lamps permit heating rates of $\sim$40°C/s and rapid cooling rates. The furnace has a constant temperature hot zone 14 cm in length by 1 cm in diameter (temperature range was measured to be $\pm 1^\circ$C). Hot zone temperature was measured with a K-type thermocouple inserted into the bottom of the tube. The samples were attached to a balance by a platinum chain, and sample weight was recorded every second. The results are reported as mass change per unit surface area. The individual experimental parameters are listed below in Table 3.

Air, encountered during cooling after casting and prior to hot rolling, was chosen as one atmosphere. For these experiments, the air used had a measured partial pressure of water vapor of $1.4 \times 10^{-4} \text{ atm}$ at 23°C. The second atmosphere was air containing 15 vol% water vapor (wet air). This gas was produced by bubbling air through flasks heated to 55°C (establishing a water vapor partial pressure of 0.15 atm$^{21}$) and passed through heated lines to prevent condensation. Prior to each experiment, the system was purged for 3 h with dry argon.

Gas flow rate is an important experimental parameter because mass transfer of the oxidant, if too slow, can affect oxidation rates. Experiments in both gases were conducted at a flow rate of 3.1 standard liters per minute (sL/min), corresponding to a linear velocity of 2.8 cm/s. Flowrate was measured with a variable-area flow meter. Previous work on iron oxidation in water vapor under similar flowrates, temperatures, and water vapor partial pressures has shown that the oxidation rate is controlled solely by dissociation of water molecules.$^{22}$ In air, the gas velocity was chosen high enough to minimize effects of mass transfer on oxidation rate$^{23}$ but low enough to prevent cooling of the sample.

Oxidized sample microstructures were investigated in a scanning electron microscope (SEM). To preserve the interface structure, the samples were mounted in a cold-curing epoxy resin with the following vacuum-impregnation procedure: (i) samples were placed in a chamber that was subsequently evacuated, (ii) the epoxy was added under vacuum, and (iii) air was slowly introduced to force the epoxy into pores and gaps in the oxide. The samples were then sectioned with a low-speed diamond saw and polished to a 1 μm diamond finish. All samples were coated with 2.5 nm of platinum to prevent charging in the SEM.

The SEM used was a Philips XL-30 scanning electron microscope with a field emission gun source operating at 25 kV and a solid-state backscattered detector installed. The working distance was 10 mm. All images were taken in backscattered electron (BSE) mode. Energy dispersive X-ray spectroscopy (EDS) was used to obtain qualitative compositional information.

From the BSE images, areas of separated copper-rich phase in the metal were quantified; these areas appear brighter than the surrounding iron. EDS was used to confirm the presence of copper. The open source software ImageJ$^{20}$ was used to measure the above quantities. For all measurements, conversion factors were established between number of pixels and actual lengths using the scale bar on the SEM micrograph. The areas of separated material were isolated by manually thresholding the images and measured using ImageJ’s “Wand” function (an automatic area trace). These area measurements were then normalized to the length of the field of view, 63.2 μm in all cases. This procedure amounts to considering the separated area as layers of uniform thickness over a length of 63.2 μm. Several measurements were repeated and error due to reproducibility

| Experiment Number | Oxidation Time | Temperature | Gas Velocity | Atmosphere |
|-------------------|----------------|-------------|--------------|------------|
| 1                 | 60 s           | 1150°C      | 10 cm/s      | Dry Air    |
| 2                 | 300 s          | 1150°C      | 10 cm/s      | Dry Air    |
| 3                 | 420 s          | 1150°C      | 10 cm/s      | Dry Air    |
| 4                 | 600 s          | 1150°C      | 10 cm/s      | Dry Air    |
| 5                 | 900 s          | 1150°C      | 10 cm/s      | Dry Air    |
| 6                 | 1200 s         | 1150°C      | 10 cm/s      | Dry Air    |
| 7                 | 3600 s         | 1150°C      | 10 cm/s      | Dry Air    |
| 8                 | 600 s          | 1150°C      | 10 cm/s      | Wet Air (15 vol% H$_2$O) |
| 9                 | 1800 s         | 1150°C      | 10 cm/s      | Ar - 15 vol% H$_2$O |
| 10                | 2700 s         | 1150°C      | 10 cm/s      | Ar - 15 vol% H$_2$O |
| 11                | 3600 s         | 1150°C      | 10 cm/s      | Ar - 15 vol% H$_2$O |
was found to be negligible.

4.3. Input Data to the Model for Experimental Verification

To produce model calculations for comparison to the experimental results, the values listed in Table 4, were used as inputs.

5. Results

The following sections present the experimentally measured oxidation behavior, oxide/metal interface microstructures, and measured copper-rich layer thicknesses. They also describe how the experimentally measured oxidation behavior was incorporated into the model. Finally, comparisons are presented of the measured and calculated copper-rich layer thicknesses.

5.1. Dry Air Oxidation

5.1.1. Oxidation Behavior

The TG measurements for oxidation in dry air are shown in Fig. 7. These results correspond to experiments 1–7 listed in Table 3. Oxidation times were varied to produce various amounts of separated copper-rich phase.

As expected, oxidation in dry air exhibits linear kinetics initially and then transitions to parabolic behavior. During the initial linear stage, the rate-controlling process for oxidation is oxygen diffusion through a gas phase boundary layer.23,25) After the transition, the rate controlling step is diffusion of iron ions through the wüstite layer.26) The measured rate constants are tabulated and compared with literature values in Table 5. Measured data correlates well to values from the literature.

The measured oxidation behavior was used to produce tables of $\Delta m/A$ vs. $t$ values for input to the model. Due to the linear/parabolic transition region during air oxidation, a procedure averaging the measured data was adopted. For the first 60 s, data for all experiments was averaged. After 60 s, data for 300, 420, 600, 900, 1200, and 3600 s experiments were averaged. After 300 s, data for the 420, 600, 900, 1200, and 3600 s experiments were averaged. This scheme was continued to generate a table of averaged $\Delta m/A$ vs. $t$ values which were then used as inputs to the model.

5.1.2. Oxide/Metal Interface Microstructure

Figure 8 shows representative micrographs of the oxide/metal interface for 60, 600, and 3600 s oxidation in air. For the oxidation times up to 1200 s (experiments 1–6), the separated copper was found to exist as a layer at the oxide/metal interface as shown in Figs. 8(a) and 8(b). The thickness of this layer increased with oxidation time. For experiment 7, significant grain boundary penetration was found as shown in Fig. 8(c).

Table 4. Values for model simulations used to compare with experimental results.

| $D = 2 \times 10^{-15}$ cm$^2$/s | Lattice diffusivity, taken from Majima and Mitani25) |
| $N_{Cu} = 0.003$ | Initial copper concentration |
| $N_{Cu}^1 = 0.06$ | Copper concentration at the $L/\gamma$ interface |
| $N_{Cu}^1/2 = 0.97$ | Copper concentration at the $L/FeO$ interface |
| $N_{Cu} = 0.08$ | Copper concentration at the $L/\gamma$ interface |
| $L_\gamma = 0.03$ cm | Initial $\gamma$ phase thickness |
| $\Delta (m/A)/\Delta t$ | Amount of oxide formed, taken from experimental data |

Table 5. Comparison of measured rate constants (linear-averaged over all samples, parabolic-averaged over 420 s, 600 s, 900 s, 1200 s, and 3600 s) with values obtained from literature.

| Measured | Literature Value |
|-----------|------------------|
| Dry Air $k_1$ | $0.25 \pm 0.02$ mg/cm$^2$/s | $0.21$ mg/cm$^2$/s - Equations and data from Abulwafa et al.25) |
| Dry Air $k_2$ | $3.70 \pm 0.51$ mg/cm$^2$/s | $5.02$ mg/cm$^2$/s - Regression of literature data by Chen & Yuen 37) |

Fig. 7. TG measurements for oxidation in dry air.

Fig. 8. Example micrographs of copper-rich liquid formed after oxidation in air for (a) 60 s, (b) 600 s, and (c) 3600 s. There is a significant amount of copper at grain boundaries after 3600 s.
5.1.3. Copper-rich Layer Thickness

Figure 9 shows a comparison of the measured and calculated copper-rich liquid layer thicknesses for oxidation in dry air. The curve labeled “Calculated” was generated using the average measured oxidation data as discussed above. Agreement between the measured and computed thicknesses is reasonable for all the points except experiment 7 were the oxidation time was 3 600 s and significant grain boundary penetration occurred. Grain boundary penetration appears to occur after approximately 0.8 µm of copper accumulates at the oxide/metal interface.

5.2. Effect of Water Vapor

5.2.1. Oxidation Behavior

Two water vapor-containing atmospheres were used in this work, wet air and argon–15vol%water vapor. Figure 10(a) shows the mass change per unit area with time for air–15vol%water vapor compared to dry air, while Fig. 10(b) shows the mass change per unit area for argon–15vol%water vapor. According to Fig. 10(a), the presence of water vapor does not affect the TG-measured oxidation behavior and therefore the rate constants listed in Table 5 are valid for wet air oxidation. Oxidation in argon–water vapor is controlled by the dissociation of H₂O molecules on the wüstite surface, leading to linear kinetics for all oxidation times. The measured linear rate constant is 0.015 mg/cm² s, which compares well to a value of 0.011 mg/cm² s calculated using equations and data from Abuluwefa et al.

Incorporating the oxidation rate in argon–water vapor into the model was straightforward, with the table generated by Eq. (2).

\[
\frac{\Delta m}{A} = k_{l_{av}} t
\]

with \(k_{l_{av}}\) the average measured linear rate constant for oxidation in argon–water vapor.

5.2.2. Oxide/Metal Interface Microstructure

The oxide/metal interface microstructure for the sample oxidized 600 s in wet air is shown below in Fig. 11(a). The interface microstructure for the sample oxidized in dry air is shown in Fig. 11(b) for comparison.

Interface microstructures for the samples oxidized in argon–15vol%water vapor are shown below in Fig. 12.

5.2.3. Copper-rich Layer Thickness

For oxidation in wet air, the amount of copper-rich liquid formed is tabulated and compared to the calculated value in Table 6. Increased grain boundary penetration of copper in wet air (see Fig. 11(a)) is not accounted for by the model. Therefore, it overpredicts the thickness of the separated copper-rich layer at the oxide/metal interface. Comparison of the measured and calculated copper-rich layer thicknesses for oxidation in argon–15vol%water vapor is shown in Fig. 13. Significant grain boundary penetration was observed in experiment 11 (oxidation for 3 600 s, see Fig. 12(c)) and as in previous cases, the model overpredicts the copper-rich layer thickness. Grain boundary penetration ap-
pears to occur after approximately 0.4 µm of copper accumulates at the oxide/metal interface in the water–vapor containing gases.

6. Discussion

The results above show that the thin, copper-rich layer forming at the oxide metal interface can be adequately modeled under a variety of conditions. However, extended times and the presence of water vapor in the gas atmosphere cause the model to overpredict the amount of separated copper-rich liquid.

Experimentally, the copper-rich material is often present as a layer of approximately uniform thickness (see Fig. 8 and Fig. 12). When this occurs, the problem can be adequately treated as one-dimensional as assumed in the model (see assumption 4 above). The copper-rich liquid does not form as a layer of uniform thickness after long oxidation times or if water vapor is present in air according to Fig. 8(c), Fig. 11(a), and Fig. 12(c). Instead, a significant amount of copper is found at austenite grain boundaries. Figure 9, Fig. 13, and Table 6 show that the experimentally measured amounts of copper-rich phase differs from the model predictions only when a large amount of copper-rich material is present at grain boundaries. Thus, it appears that the model no longer simulates copper behavior after the occurrence of grain boundary penetration.

It should be noted that the difference between the predicted and measured separated liquid copper-rich layer thickness is not accounted for solely by the amount of liquid copper in the grain boundaries. Once the copper-rich liquid penetrates, copper begins to diffuse out along the length of the penetration into the austenite grains. Since the penetrations can be long, approximately 10 µm or more, a large amount of copper will diffuse into the iron grains, while the liquid at the grain boundary is likely replenished by liquid that is continuously forming at the oxide/metal interface. Thus, grain boundary penetrations effectively increase the area for back diffusion, allowing more copper to diffuse back into the steel and leading to less separated copper-rich liquid. Figure 14 shows schematically how this could occur. Since diffusion from the area of copper along grain boundaries is not considered, it is expected and observed that the model would overpredict the amount of copper present at the oxide/metal interface (see Fig. 9 and Fig. 13).

Incorporating the effects of grain boundary penetration into the model is not straightforward. Close to the oxide/metal interface, accurate simulations of the copper concentration require solution of the two-dimensional diffusion equation. Solutions for this behavior exist from grain boundary diffusion theory.20) It should be noted that the problem of grain boundary penetration is not completely analogous to grain boundary diffusion because the copper-rich liquid has approximately constant thickness and constant copper concentration down the length of the penetration. Thus, far from the oxide/metal interface, the lateral diffusion of copper from the boundary can be simulated by a simple, constant-surface concentration solution to the diffusion equation. This implies that the copper in the penetra-
tion is continually replenished by copper from the layer at the oxide/metal interface.

It is also necessary to consider why grain boundary penetration of copper occurs at certain times as shown in Fig. 12 and why these times are shortened by the presence of water vapor in the gas as suggested by Fig. 11. As mentioned in the Introduction, grain boundary penetration by liquids is not a well-understood phenomenon. However, it is apparent that a certain amount of copper is necessary for grain boundary penetration to occur (see Fig. 9 and Fig. 13). Although their experiments were very different than those of this work, Hough and Rolls found that grain boundary embrittlement of iron was dependent on the amount of copper. Fredriksson et al. immersed iron in a bath of liquid copper (a nearly infinite supply), finding nearly 70 μm deep penetrations after only 1800 s exposure. These penetration depths are much deeper than the penetration depths found in this work, suggesting again a correlation between amount of copper-rich liquid and penetration depth.

The results above also suggest that water vapor decreases the amount of copper necessary to cause penetration. In wet air, boundary penetration was observed after only 600 s oxidation, compared to 3600 s oxidation in dry air. Boundary penetration was also observed after 3600 s oxidation in water vapor, though there is much less copper present than 3600 s oxidation in dry air.

The effect of water vapor on boundary penetration cannot be due to a change in oxidation kinetics, since the kinetics of dry and wet air oxidation are nearly identical (see Fig. 10(a)). It is well known, however, that oxidation in water vapor produces oxides that are compact, adherent, and relatively pore-free. In addition, the presence of water vapor has been theorized to increase the plasticity of oxides, again causing the oxide layer to better adhere to the metal. It could be possible that the lack of pores and gaps in the oxide changes the stress state at the oxide/metal interface. It appears reasonable that a change in the stress state at the oxide/metal interface could essentially push copper into austenite grain boundaries.

With the above results showing that the model effectively simulates copper behavior up to a certain time (depending on oxidation conditions), the final section of this work demonstrates the applicability of the current model to steel processing. Specifically, the model and experimental results above are used to determine at what point copper penetrates down grain boundaries. The atmosphere was assumed products of methane combustion with an air-to-fuel ratio of 1.12. The chemistry of this atmosphere is shown in Table 7. The oxidation behavior was taken from a study by Lee et al. They found parabolic oxidation rates for high temperatures (>1200°C) and an extended initial linear regime followed by a transition to parabolic behavior at lower temperatures (~1100°C). As above, the model input was a table of Δm/Δ vs. t values based on the rate constant measured by Lee et al. Since these furnace atmospheres contain water vapor, a significant amount of grain boundary penetration is expected.

Two reheating time/temperature profiles were employed, one for steels undergoing conventional processing (where slabs are cast and stored before reheating), the other for steels undergoing a direct hot charge into the reheat furnaces. Schematics of the two processes along with representative times and temperatures are shown in Fig. 15. Under each schematic is a plot of the copper-rich liquid layer thickness evolution as a function of time assuming that no copper has penetrated down grain boundaries. The point at which boundary penetration is expected is based on the experimental results for wet gas oxidation from this work.

Table 7. Atmosphere chemistry (in atm) for products of methane combusted in air with a 1.12 air/fuel ratio. Values are from Lee et al.

| Air/Fuel Ratio | CO₂ | CO | N₂ | O₂ | H₂O | H₂ |
|---------------|-----|----|----|----|-----|----|
| 112%          | 0.6857 | 3.5*10⁻³ | 0.72 | 0.021 | 0.171 | 3.5*10⁻³ |

Fig. 15. Schematic of (a) conventional processing and (b) direct hot charge processing schemes. Nominal times and temperatures for the furnace zones are indicated. Below is a plot of the evolution of the copper-rich layer thickness during reheating. The lines represent the approximate points at which the copper-rich liquid should penetrate down austenite grain boundaries.
work. The plot in Fig. 13 suggests that the copper-rich layer must be approximately 0.4 μm thick before grain boundary penetration occurs. This is supported by the wet air experiment (see Table 6), in which grain boundary penetration was observed. Due to the longer oxidation times in Fig. 15(a), more grain boundary penetration of copper is expected. Thus, steel produced under conventional processing conditions may be more susceptible to hot shortness cracking due to deeper grain boundary penetration of copper. The model could therefore be used to estimate the time at which copper penetrates down grain boundaries under different reheating furnace atmospheres. However, more experiments are necessary to justify fully the model's validity under industrially relevant conditions.

7. Conclusions

1. Finite difference model results were found to correlate extremely well with experimental results from an iron–0.3wt%copper alloy oxidized at 1 150°C in air for 60, 300, 420, 600, 900, and 1 200 s and in and H2O for 1 800 and 2 700 s. Under these conditions, the copper-rich liquid is present as a layer at the oxide/metal interface.

2. Model results deviated after 3 600 s oxidation in dry air, 3 600 s oxidation in H2O, and 600 s oxidation in wet air. Under these conditions, the copper-rich liquid had penetrated down austenite grain boundaries.

3. The results suggest there is a critical amount of copper that must build up at the oxide/metal interface before it penetrates into austenite grain boundaries. This amount corresponds to a layer approximately 0.8 μm thick in air. The critical amount decreases to a layer about 0.4 μm thick when the gas atmosphere contains water vapor.

4. Significant copper-rich liquid penetration should be expected under industrial processing conditions due to water vapor in the oxidizing gas.

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