Beneficial effects of molten silicates on the oxidation of Type 304 stainless steel under slab reheating conditions

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Abstract: Type 304 (austenitic) stainless steel tends to form a subscale during reheating before hot rolling. The subscale is difficult to remove, is typically several hundred microns thick, and may cause surface defects during hot rolling; the subscale mainly consists of chromite (spinel) and metallic remnants (containing mainly iron and nickel). Mold flux residues, which are present on the slab before reheating, have been found to suppress formation of the subscale. The effect has been found not to be specific to mold flux, and occurs with other molten silicates too. The beneficial effect of the molten silicates on surface quality is the opposite of what would be expected from a simple hot corrosion mechanism. This paper gives an overview of the likely mechanisms of the beneficial effect; these are related to the low solubility of chromium oxide in molten silicates, and suppression of volatilization of chromium oxide. The low solubility of chromium oxide in molten silicate, compared with the high solubility of iron and nickel oxides, may cause iron and nickel oxides to be preferentially removed from the scale/metal interface, giving enrichment in chromium oxide which may promote formation of a protective chromium oxide layer. Chromium oxide is known to volatilize readily from the oxidized steel surface at reheating temperatures, with increased volatilization rates in atmospheres which contain water vapor. Molten silicates (and borates), with their low solubility for chromium oxide, may simply form a physical barrier to chromium loss by volatilization, and so promote formation of a more protective oxide.

Key words: Mold flux; Hot corrosion; High temperature oxidation; Internal oxidation

1. Background

It has recently been shown that mold flux residues – of the order of tens to hundreds of microns thick – substantially change the morphology of primary (reheating) scale on Type 304 stainless steel slabs [1][2]. The effect is illustrated in Figure 1: the deep subscale (consisting mainly of chromite internal oxide and metallic remnants) which forms under reheating conditions is eliminated by the presence of mold flux. Also, a continuous layer of eskolaite (Cr_2O_3) forms at the steel-scale interface. For slabs with mold flux residues, the observed sequence of oxides follows the predicted equilibrium sequence, which is given in Figure 2: the spinel manganese chromite (approximate composition $MnCr_2O_4$) is predicted to be the first oxidation product, followed by Cr_2O_3, then more iron-rich spinel (composition approximately $FeCr_2O_4$ at the stage when all Cr has been oxidized from the metal), molten silicate ("slag" in the figure, approximately Fe_2SiO_4 in composition), and finally wüstite. Manganese chromite spinels are observed as internal oxides for reheated steels with or without mold flux (Figure 1), and spinels with varying composition are common oxidation products. However, for steel reheated in moist air and in typical reheating atmospheres (4% O_2, 15% H_2O, balance CO_2 and N_2) Cr_2O_3 is only observed if mold flux residues are present; in the absence of mold flux, protective Cr_2O_3 does not form, and a deep subscale grows.

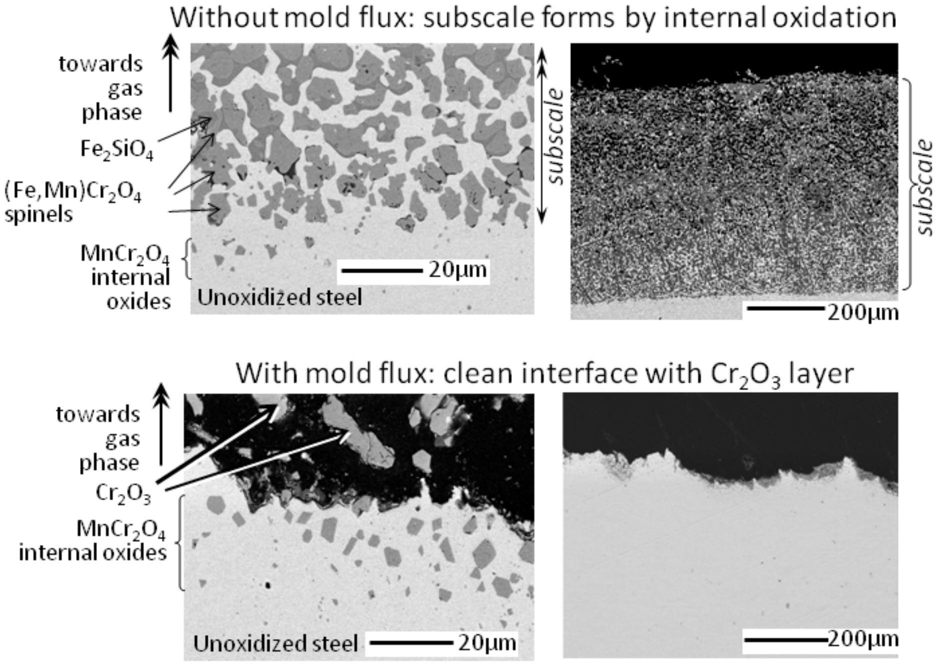

Fig. 1 Micrographs (backscattered electron images of polished cross-sections) illustrating the effect of mold flux on the primary scale morphology on reheated Type 304 stainless steel. The images at the right are at lower magnification.

The absence of protective eskolaite (Cr_2O_3) in the absence of mold flux may result from loss of chromium from the slab surface by vaporization: chromium oxides and hydroxides have a significant vapor pressure under reheating conditions, and the resulting loss of chromium is enhanced by the presence of water vapor.[4] A thin layer of mold flux may lower the rate of chromium vaporization sufficiently to allow a protective Cr_2O_3 layer to form.

Part of the effect of mold flux may depend on the low solubility of chromium oxide in mold flux. Cr_2O_3 is poorly soluble in molten silicates generally, and similarly in molten borates [5]. The poor solubility of chromium oxide (relative to the iron and nickel oxides) would tend to trap chromium oxide at the scale-steel interface, which can promote formation of a protective Cr_2O_3 layer.

These two proposed (and interrelated) effects of mold flux – reduced chromium vaporization, and hindered chromium oxide transport through the molten flux – are the subjects of ongoing experimental work. This paper presents some fundamental tests of the feasibility of the two effects, based on equilibrium calculations.

2. Chromium oxide solubility in molten mold flux

It is not only solubility (of chromium, iron and nickel oxides) in the mold flux which affects transport of these oxides through the flux (as oxidation proceeds), but also the change of solubility with oxygen activity. As pointed out by Rapp [6], hot corrosion is promoted by a gradient of solubility of the oxidation products through the molten layer, specifically if the solubility decreases from the metal side of the melt (lower oxygen activity) to the gas side of the melt (higher oxygen activity). In the absence of such a gradient, there would be no driving force for transport of the oxidation product through the melt from the metal side. Here, the effect of oxygen activity on solubility was tested by calculating the compositions when equal masses of steel (70%Fe, 18%Cr and 10%Ni) and mold flux (approximated as 45% CaO, 45% SiO_2 and 10% Na_2O) equilibrated with a N_2-O_2 atmosphere with different oxygen activities (Figure 3).

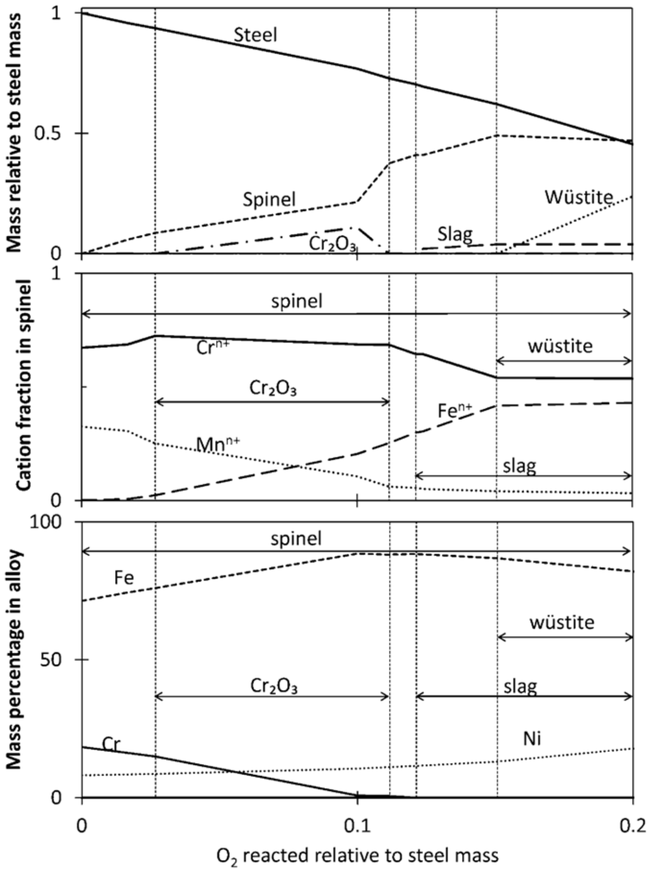

Fig. 2 Predicted phases, spinel composition, and composition of remaining metal, for oxidation of Type 304 stainless steel (18.4% Cr, 8.2% Ni, 0.37% Si, 1.7% Mn, balance Fe) at 1250°C; calculated with FactSage [3].

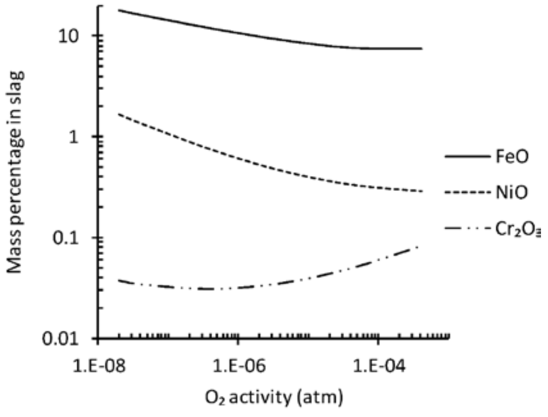

Fig. 3 Equilibrium concentrations of iron oxide (expressed as FeO), nickel oxide and chromium oxide in the molten silicate, when equal masses of steel (70%Fe, 18%Cr and 10%Ni) and mold flux (45% CaO, 45% SiO_2 and 10% Na_2O) equilibrate at different oxygen activities, at 1280°C. Spinel is the stable solid oxide in all cases; metal is stable only at the lowest oxygen activity shown. (Calculated with FactSage [3].)

The results in Figure 3 confirm the low solubility of chromium oxide compared with iron oxide ("FeO" in the figure refers to the total ferrous and ferric iron, expressed as FeO) and nickel oxide. The curves for nickel oxide and the iron oxides show lower solubility in the melt at higher oxygen activities, which is in line with the Rapp criterion (negative solubility gradient) for transport of these oxides away from the metal surface. In contrast, the solubility of chromium oxide is weakly dependent on oxygen activity, and after reaching a minimum *increases* slightly with increased oxygen activity. Both the low solubility of chromium oxide and its positive solubility gradient would tend to trap chromium oxide at the metal-mold flux interface, promoting formation of a protective layer.

3. Vaporization of chromium oxide

Water vapor in the gas atmosphere promotes volatilization of chromium. Equilibrium vapor pressures for Cr_2O_3 in contact with dry and wet oxidizing gases are shown in Figure 5. The figure confirms the large increase in chromium oxide / hydroxide vapor pressure in wet furnace atmospheres. Experimental results (not shown here) confirmed that in dry oxidizing atmospheres the deep subscale of Figure 1 does not form on reheated Type 304, whether mold flux is present or not; in the dry atmosphere a continuous (apparently protective) Cr_2O_3 layer formed.

This experimental observation suggests that in wet reheating atmospheres the beneficial effect of mold flux is to limit chromium volatilization (likely through the low solubility of chromium oxide in the molten flux, as shown in the previous section). This implies that in wet atmospheres, Type 304 stainless steel without the protection of mold flux might not form a protective Cr_2O_3 layer simply because the chromium content at the surface of the steel is too low. To test this suggestion, the stable phases for oxidation of chromium-depleted steel was calculated; these calculations used the same conditions as those relevant to Figure 2, with the single difference that half the chromium was removed from the steel. (The choice of half was arbitrary, and served simply to test the idea.)

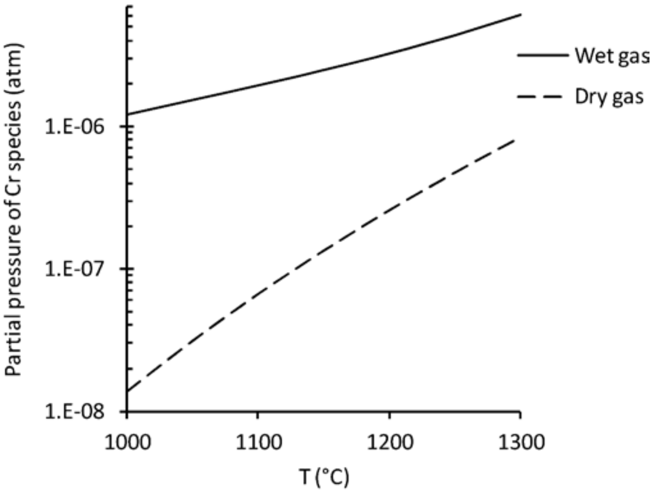

Fig. 5 Total vapor pressure of volatile chromium oxides and hydroxides in equilibrium with pure Cr_2O_3 and $4\%O_2$-$96\%N_2$ gas (dry) or $4\%O_2$-$15\%H_2O$-$81\%N_2$ gas (wet); calculated with FactSage [3].

Upon oxidation of the chromium-depleted steel (Figure 6), Cr_2O_3 is indeed suppressed. The sequence of phases for equilibrium oxidation is similar to that practically observed during oxidation of Type 304 in wet gas (Figure 1).

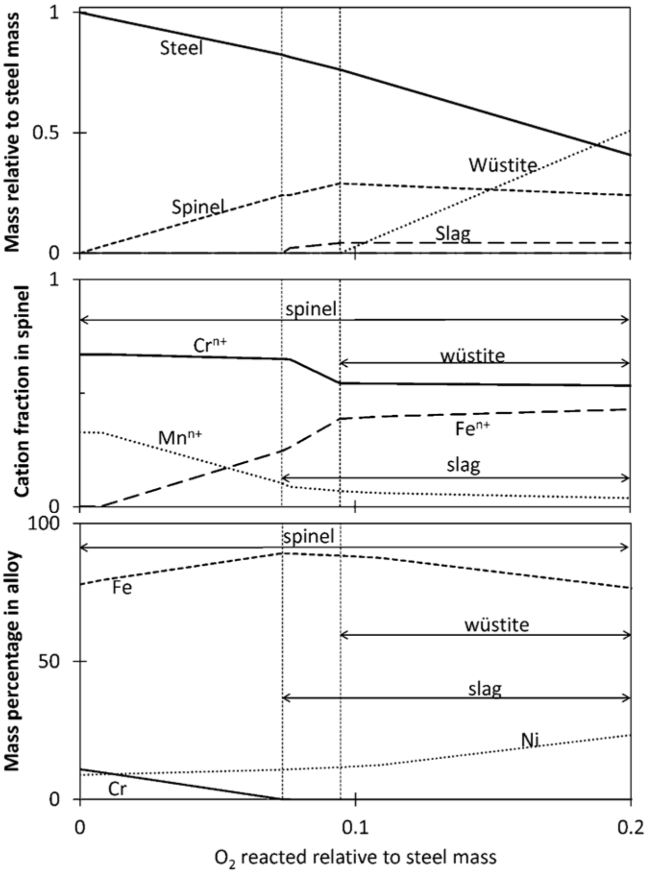

Fig. 6 Predicted phases, spinel composition, and composition of remaining metal, for oxidation at 1250°C of steel with the same composition as in Fig.2, but with half the chromium removed; calculated with FactSage [3]. Cr_2O_3 does not form as a separate phase.

4. Conclusion

The beneficial effect of mold flux residues to suppress subscale formation and promote formation of a protective Cr_2O_3 layer appears to be a rare example of a favorable effect of hot corrosion. Because of its low solubility and positive solubility gradient, chromium oxide would tend not to be transported through the molten flux. The chromium oxide would be trapped at the metal surface, which may also result in decreased loss of chromium by volatilization, which also promotes formation of a protective Cr_2O_3 layer.

Acknowledgment

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References

[1] J-.J.N. Mukadi, P.C. Pistorius. Mould flux residues aid descaling of reheated austenitic stainless steel. *Ironmaking and Steelmaking*, 2010, 37, p57-62.

[2] K.H. Cheung and P.C. Pistorius. Effect of mold flux on reheating scale – austenitic stainless steel slabs. *AISTech2011 conference proceedings*, vol. I, p1319-1326.

[3] C.W. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R.B. Mahfoud, J. Melançon, A.D. Pelton and S. Petersen. FactSage thermochemical software and databases. *Calphad*, 2002, 26, p189-228.

[4] C.T. Fujii and R.A. Meussner. The mechanism of the high-temperature oxidation of iron-chromium alloys in water vapor. *Journal of the Electrochemical Society*, 1964, 111, p1215-1221.

[5] R.K.W. Merkle, M. Loubser and P.P.H. Gräser. Incongruent dissolution of chromite in lithium tetraborate flux. *X-ray spectrometry*, 2004, 33, p222-224.

[6] R.A. Rapp. Chemistry and electrochemistry of the hot corrosion of metals. *Corrosion*, 1986, 42, p568-577.