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Thermodynamic consideration on selective surface oxidation of high strength steels prior to hot-dip galvanizing

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Abstract The galvanizability of high strength steel is dependent on the surface selective oxidation of alloy elements during intercritical annealing. First, this study reviewed the selective oxidation of Mn, Si, Al, Cr, and their possible products. Then we applied three sets of elemental activity data, i.e., calculated from Thermo-Calc, molar fraction, and a_M (M = Mn, Si, Al, Cr) = 1 to calculate the equilibrium oxygen partial pressure of each oxidation reaction. It was found that there is a significant deviation among the results calculated from different data. Finally, this study established the stabilities and precipitation sequences of Mn–Si, Mn–Al and Mn–Cr mixed oxides, and proposed a new Mn–Cr rule to predict the oxides formed on the surface of Mn–Cr steel.

Keywords Hot-dip galvanizing, Selective oxidation, Thermodynamics

Introduction

To reduce the body weight of modern cars, advanced high strength steel has been developed, such as Dual Phase steel and TRIP-aided steel. When applied to automotives, these steel sheets can be thinner without losing their mechanical performance. The promising performance is always achieved by well-designed heat treatment routines and appropriate addition of alloy elements, such as C, Si, Mn, Cr, or Al. Though these elements are favorable for the strength and ductility, they are adverse to the continuous hot-dip galvanizing because of their preferential oxidation over iron during intercritical annealing. In general, the annealing atmosphere employed in industry is 5%H_2+N_2 with a dew point of −30°C and termed as galvanizing atmosphere. The atmosphere can reduce the iron oxides, but fails to prevent the oxidation of alloy elements mentioned above because of the trace amounts of water vapor and oxygen. This is the selective oxidation. The oxides cover the steel surface, resulting in poor wetting of the zinc.

Already there have been many experimental investigations on the selective surface oxidation of alloy elements and their influences on the galvanizing properties.[1,2] Some theoretical investigations also have been conducted. Wagner promoted a model describing the selective oxidation of alloy system containing a noble matrix element and oxytropic alloy element at low oxygen partial pressure and high temperature environment.[3] According to Wagner, the oxidation can either be external on the steel surface or internal under the surface, depending on the partial pressure of oxygen above the alloy surface, besides the annealing temperature and the solute content of alloy. Aiming to find out the necessary conditions to avoid bare spot defects, Suzuki calculated the chemical potential diagram of Fe–Si-Mn–O and isothermal pseudo ternary phase diagram of FeO–SiO_2–MnO by thermodynamic software Factsage.[4] They predicted the oxide phases and explained the reaction path of the selective oxidation behavior in Si–Mn steel. Using Thermo-Calc thermodynamic software, Liu studied the influence of the dew point and hydrogen content of the atmosphere on the selective oxidation behavior of dual phase steel.[5]

Although there has been a lot of researches on selective oxidation, some basic issues still need to be addressed.

One is the equilibrium oxygen partial pressure over an oxide. As shown in the Ellingham diagram in Fig. 1, the equilibrium oxygen partial pressure over each

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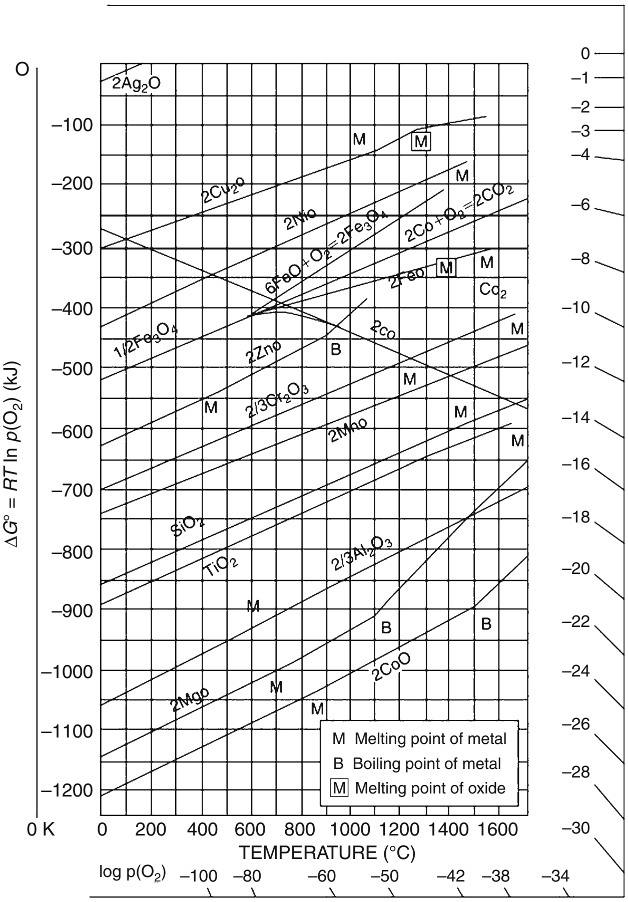

Fig. 1: Ellingham diagram for several oxides[6]

oxide is different. Please note that this value of oxygen partial pressure is calculated by setting the activity of the element concerned equal to unity, i.e., over the pure substance. However, for a multicomponent steel system, Si, Mn, Cr, and Al are all present as alloy elements and their activities can never reach unity; instead their values should be related to their molar fractions. It is natural to notice that the oxygen partial pressure over an oxide on the steel surface, termed the real equilibrium oxygen partial pressure in this study, will be much higher than the values shown in the Ellingham diagram. This means a low oxygen potential atmosphere oxidizable for a pure substance may not oxidize the same substance present in a solid solution. Hence, this real oxygen partial pressure over an oxide on the steel surface is important for determining the oxidation-or-reduction state when annealing the steel under a certain low oxygen potential atmosphere.

Another issue is the possible formation of the oxide phases on the steel surface. There are two reasons for its importance.

The first reason is that the morphology of oxides is different; for example, SiO_2 always forms as a film on the steel surface, while others always precipitate as nodular or granular particles. The film-like SiO_2 will cause the worst wetting problems, whereas others, if present as fine, homogeneously distributed particles, will cause fewer problems.[7,8]

The second reason is that the influence of each oxide on the wetting behavior is different. There are many experimental studies on this issue and the different influence will be reviewed in "Possible oxide phases precipitating during annealing" section.

However, there are few theoretical studies on the stabilities of oxide phases and their precipitation orders under the real low oxygen potential atmosphere, especially for the complex oxides, such as Mn_2SiO_4, $MnSiO_3$, $MnAl_2O_4$, and $MnCr_2O_4$.

Therefore, first this study calculated the real equilibrium oxygen partial pressure at the surface of two steels (0.15 wt%C–1.5 wt%Mn–1 wt%Si–0.5 wt%Al (steel 1) and 0.2 wt%C–1.5 wt%Mn–1 wt%Si–0.5 wt%Cr (steel 2)) using the activity data from Thermo-Calc's calculation. For comparison, we also conducted calculations by setting the activity as "1" and molar fraction separately. Then, this study calculated the real Gibbs energy of each oxidation reaction. By comparing the Gibbs energy values, this study estimated the stabilities of all possible oxides and their precipitation order.

Selective oxidation during intercritical annealing

Selective oxidation is defined as the preferential oxidation of less noble elements in an alloy system.[3] The basic process can be described thermodynamically as follows:

For an oxidation reaction,

$$xM(s)+\frac{y}{2}O_2(g)=M_xO_y(s), \qquad (1)$$

The Gibbs energy of the reaction is,

$$\Delta G=\Delta G^\circ+RT\cdot\ln\frac{a_{M_xO_y}}{a_M^x\cdot P_{O_2}^{y/2}}, \qquad (2)$$

where ΔG° is the standard free energy of formation for M_xO_y, and a is the thermodynamic activity.[9] The activity of oxygen is written as its partial pressure P_{O_2}.

At equilibrium, the Gibbs energy of the reaction is equal to zero, and the activity of the condensed phase M_xO_y is unity; then equation (2) is written as

$$\Delta G^\circ=RT\cdot\ln\left(a_M^x\cdot P_{O_2}^{y/2}\right)_{\text{equilibrium}} \qquad (3)$$

and the equilibrium partial pressure of oxygen over oxide M_xO_y is

$$P_{O_2,\text{equilibrium}}=\left[\frac{\exp\left(\frac{\Delta G^\circ}{RT}\right)}{a_M^x}\right]^{2/y} \qquad (4)$$

Some studies treat equation (4) by setting the a_M as unity even if M is just an alloy element in a solid solution.[10,11] In fact, a_M is far less than unity; thus, the real equilibrium partial pressure $P_{O_{2,\text{equilibrium}}}$ is much higher than the pressure over pure M and M_xO_y.

Possible oxide phases precipitating during annealing

During intercritical annealing under galvanizing atmosphere, many products of selective oxidation will form at the steel surface. This section reviews possible oxide phases precipitating during annealing.

Simple oxides

Mn oxide

MnO forms on the surface of various steels.[12,13] This oxide can be reduced by dissolved Al in the zinc bath and will not cause a wetting problem. However, after the aluminothermic reduction, the dissolved Al will be locally consumed, leading to the formation of brittle Fe–Zn phase rather than Fe–Al compound.[5,13–15] Oren also pointed out that manganese oxides tend to form at grain boundaries and the wetting problem is not severe.[15]

Si oxide

Under low oxygen potential atmosphere, SiO_2 forms on the surface of Si-contained steel. It is commonly agreed that this oxide is very harmful to galvanizing, especially for the case of the film-like SiO_2 formation.[4,16] Although from a thermodynamic view SiO_2 can be reduced by dissolved Al from zinc bath, there is no experimental evidence for it.[5]

Al oxide

Al_2O_3 forms under low potential oxygen atmosphere on the surface of Al-containing steel. Under low oxygen potential atmosphere, Al_2O_3 can form on the external steel surface. When the oxygen potential increases, this oxide tends to form under the steel surface, i.e., transforms to internal oxidation, because of its strongest affinity for oxygen.[17] Al_2O_3 will not cause a wetting problem, even if it is present as an external scale on the steel surface.[8]

Cr oxide

Cr is the noblest among the above four elements; the formation of Cr_2O_3 needs high oxygen partial pressure. It is reported in the literature that Cr in steel can also cause a wetting problem, but there is no direct evidence for the bad wetting behavior of Cr_2O_3.[15,18]

Complex oxides

Mn–Si combination

Two different Mn–Si mixed oxide phases are reported and the possible chemical reactions are as follows:

$$2MnO(s) + SiO_2(s) = Mn_2SiO_4(s) \tag{5}$$

or

$$MnO(s) + SiO_2(s) = MnSiO_3(s) \tag{6}$$

Both Putte and Gong pointed out that the Mn_2SiO_4 is the most likely oxide to form on CMnSi TRIP steel.[19,20] However, Cvijovic claimed the Mn–Si mixed oxide formed on the surface of low-carbon steels is $MnSiO_3$.[21] No matter which of Mn–Si mixed oxides formed on the surface, both of them have been reported as a cause of the bad wetting behavior.[21–24] However, Gong found that Mn–Si mixed oxides can be reduced by dissolved Al during dipping so that the stable oxide, $MnAl_2O_4$ forms.[25] However, because there are no other similar findings, it still needs an in-depth investigation.

Mn–Al combination

The Mn–Al mixed oxide formed on the Al containing steel surface is $MnAl_2O_4$ by the following reaction[2,13,26]:

$$MnO(s) + Al_2O_3(s) = MnAl_2O_4(s) \tag{7}$$

From thermodynamics, this oxide is more stable than Mn–Si mixed oxide and seems to be the first phase to precipitate on the steel surface.[27,28] It is believed that $MnAl_2O_4$ may not worsen the wettability.[2]

Mn–Cr combination

$MnCr_2O_4$ is the Mn–Cr mixed oxide that forms on the surface of Cr-containing steel. This oxide is commonly on the surface of stainless steel when exposed to oxidizing atmosphere.[29] By TEM, Wilson found, for the first time, that $MnCr_2O_4$ precipitates on the surface of low carbon, low alloy steel, and this oxide is responsible for the "edge defect" during tin plating.[30] Wilson proposed that the $MnCr_2O_4$ forms by the solid-state reaction of MnO and Cr_2O_3,

$$MnO(s) + Cr_2O_3(s) = MnCr_2O_4(s) \tag{8}$$

Swaminathan also reported that this mixed Mn–Cr oxide forms on surface of Fe–Mn–Cr model an alloy for high strength steel under a general galvanizing atmosphere.[31]

Thermodynamics analysis of the reactions for simple oxides' formation

Because of their different influences on the wetting behavior of liquid Zn, this study classifies oxides into two types: the bad influencing type, such as SiO_2, and the less-influencing type, such as Al_2O_3, MnO, etc. It is therefore advisable to avoid the formation of the bad influencing oxides or minimize the quantity of their presence on the steel surface, by controlling the steel chemistry and the annealing atmosphere. Therefore, the stability of each oxide under different atmospheric conditions becomes quite interesting. This study calculated the real equilibrium oxygen partial pressure and Gibbs energy values of each oxidation reaction over two steels according to equations (4) and (2). The standard Gibbs energy of oxidation reactions are listed in Table 1.

By defining an equilibrium system with steel composition, the standard air pressure, and temperature, we calculated the activity of each element in α-Fe and γ-Fe using Thermo-Calc software (with database TCFE5). According to the calculations, the stable temperature range for ferrite is below 910°C for steel 1, and below 822°C for steel 2; while the stable temperature for austenite is 709–1450°C for steel 1, and 705–1475°C for steel 2. As shown in Fig. 2, Si and Al have the greatest difference between activity and molar fraction; while Cr has a smaller difference, and Mn has the smallest difference.

According to equation (2), the real Gibbs energy of oxidation reactions can be calculated, and results are shown in Fig. 3. Due to the same trend as α-Fe, the results of γ-Fe are not present in this article. For both steels, iron cannot be oxidized and iron oxide can be reduced under the galvanizing atmosphere because the Gibbs energy for its oxidation is positive. Al is the easiest to be oxidized, and the Cr is the noblest. In this study, the Gibbs energy of Mn oxidation is more negative than Si, which is different from the case shown in Ellingham diagram. This difference is due to the higher content of Mn than Si.

Furthermore, the real Gibbs energy of alloy element oxidation is more negative than that of iron oxidation, indicating the preferential oxidation of Mn, Si, Al, and Cr. This is the thermodynamics explanation for selective oxidation. Among the alloy elements, the precipitation sequence in present steels, from easy to difficult, is Al_2O_3, MnO, SiO_2 and Cr_2O_3.

Figure 4 shows the calculated equilibrium oxygen partial pressures in atm. It can be noted that there is much deviation between the results calculated using three sets of data, i.e., the calculated activity a_M, $a_M = 1$ and $a_M = X_M$ (M = Mn, Si, Al, Cr, X is molar fraction). Once more, we can see that the element easiest for oxidation is Al, the noblest is Cr. The real oxygen partial pressure is about two orders of magnitude higher than the value calculated by setting $a_M = 1$. From Fig. 4, it is reasonable to calculate the oxygen partial pressure using molar fraction instead of activity for Mn and Cr, but not appropriate for Si and Al since there is a great deviation between molar fraction and activity shown in Fig. 2.

Though the Gibbs energy of Mn oxidation is more negative than Si, the real oxygen partial pressure is higher than Si; that is, at 800°C, Si can be oxidized at the dew point below −60°C, while Mn will not be oxidized until dew point is higher than −60°C. Cr requires a higher dew point than Mn.

Furthermore, there is a small difference of real oxygen partial pressure between the bcc and fcc phases for each steel.

Thermodynamics comparisons of the reactions for mixed oxides' formation

As mentioned in "Possible oxide phases precipitating during annealing" section, the mixed oxides generally form by solid-state reaction of two simple oxides, which means the formation of mixed oxide consumes its constitutive simple oxides. Suppose that the bad

Table 1: Standard Gibbs energy of oxidation reactions[32–34]

Reaction equation	Standard Gibbs energy ΔG° (J), T in K
$\frac{4}{3}Al(s) + O_2(g) = \frac{2}{3}Al_2O_3(s)$	$\frac{2}{3}(-1688046 + 327T)$
$\frac{4}{3}Cr(s) + O_2(g) = \frac{4}{3}Cr_2O_3(s)$	$\frac{2}{3}(-1110671.4 + 247.4T)$
$2Mn(s) + O_2(g) = 2MnO(s)$	$-778093.6 + 152.8T$
$Si(s) + O_2(g) = SiO_2(s)$	$-907524.8 + 175.8T$
$\frac{4}{3}Fe(s) + O_2(g) = \frac{2}{3}Fe_2O_3(s)$	$\frac{2}{3}(-814511.9 + 250.8T)$
$2Fe(s) + O_2(g) = 2FeO(s)$	$-530031.4 + 130.8T$
$MnO(s) + Al_2O_3(s) = MnAl_2O_4(s)$	$-48139 + 7.3T$
$MnO(s) + Cr_2O_3(s) = MnCr_2O_4(s)$	$-77.985 + 0.0136T$
$2MnO(s) + SiO_2(s) = Mn_2SiO_4(s)$	$-53580.8 + 24.7T$
$MnO(s) + SiO_2(s) = MnSiO_3(s)$	$-28046.2 + 2.8T$

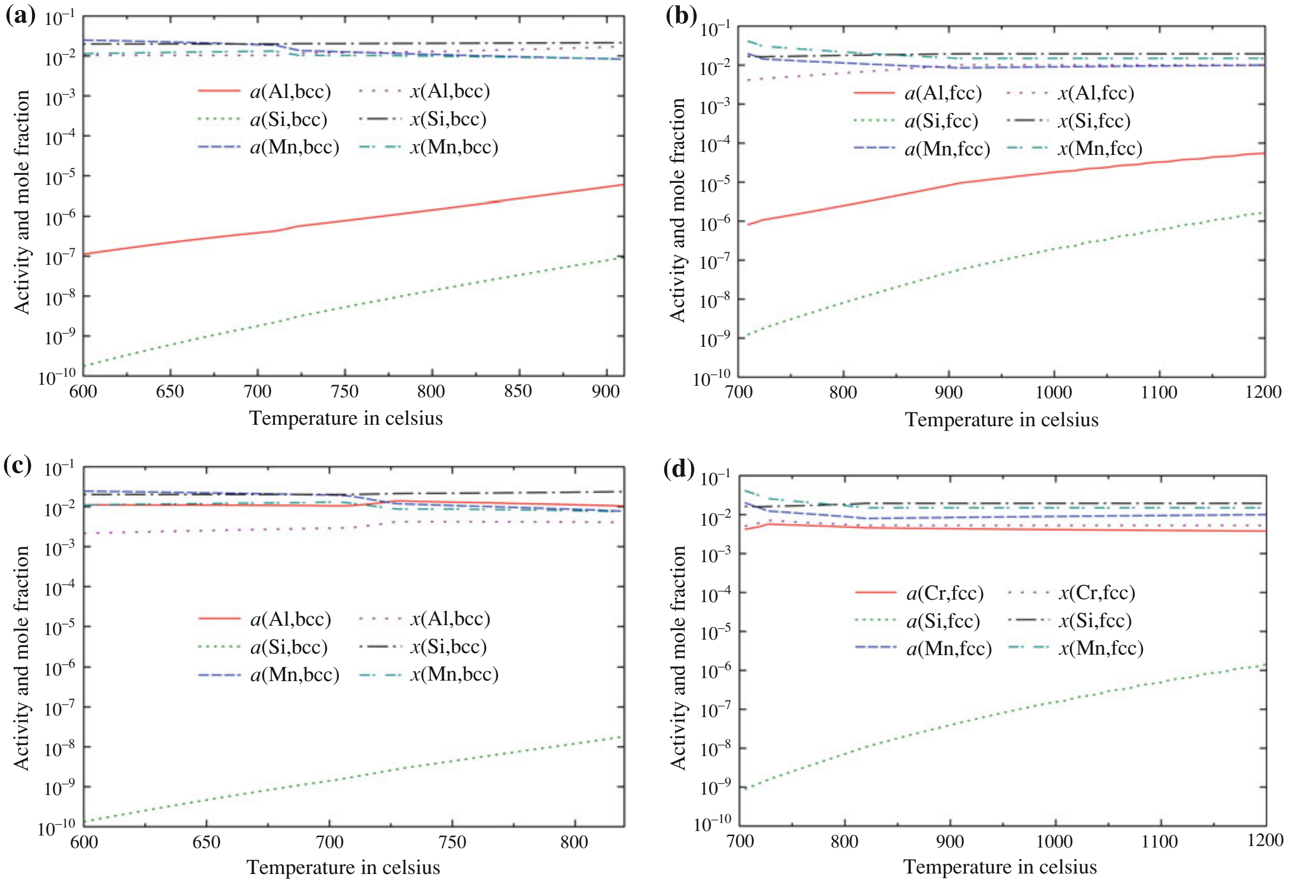

Fig. 2: Calculated activity and molar fraction data for (a) bcc iron for steel 1, (b) fcc iron for steel 1, (c) bcc iron for steel 2, (d) fcc iron for steel 2

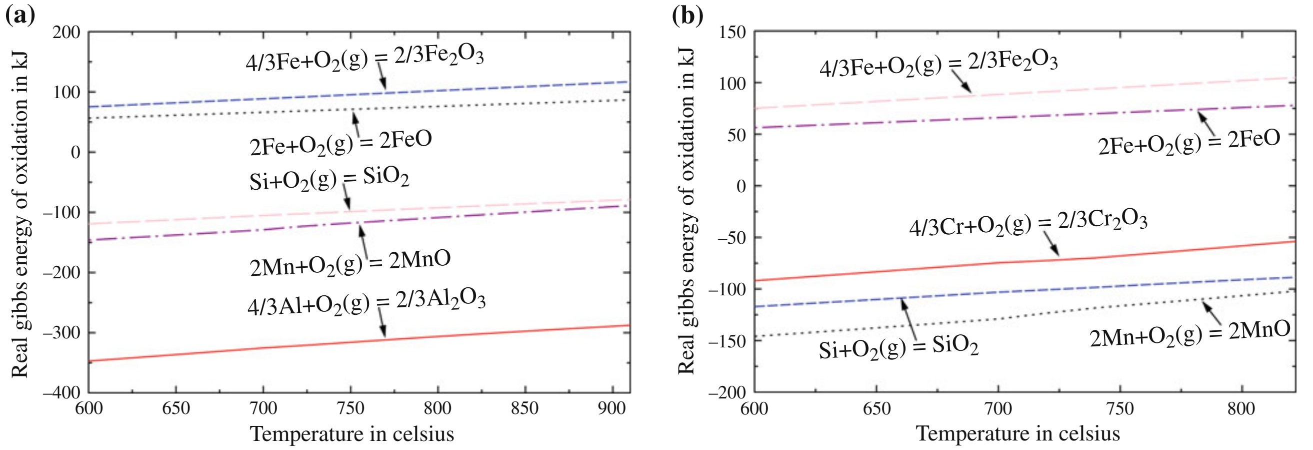

Fig. 3: Real Gibbs energy of different oxidation reactions under galvanizing atmosphere: (a) bcc iron for steel 1, (b) bcc iron for steel 2

influencing simple oxide will be consumed by the formation of complex oxides, the wetting problem might be improved. For Al–Mn–Si, Mn–Si–Cr, or Al–Mn–Cr steel annealed under galvanizing atmosphere, it is very likely that Al, Cr, or Si combines with Mn to form their corresponding mixed oxide. Please note that Mn_2SiO_4 or $MnSiO_3$ will cause harm to wetting, while $MnAl_2O_4$ will cause less harm. Again the stability of each mixed oxide becomes interesting. The Gibbs energy of their formation was also calculated according to equation (9),[35]

$$\Delta G = \Delta G^{\circ} + RT \cdot \ln \frac{P_{H_2}}{P_{H_2O}} \tag{9}$$

Figure 5 shows the calculation results for the galvanizing atmosphere. The most negative Gibbs energy is for $MnCr_2O_4$, followed by $MnAl_2O_4$, and Mn–Si oxides.

Discussions

Formation of simple oxides

From Fig. 4, the real oxygen partial pressure over each oxide on the steel surface is about two orders of magnitude higher than the values calculated by setting the activity of alloy element as unity. In fact, the solute element is more difficult to be oxidized than its pure state. Hence, we cannot simply use unity instead of

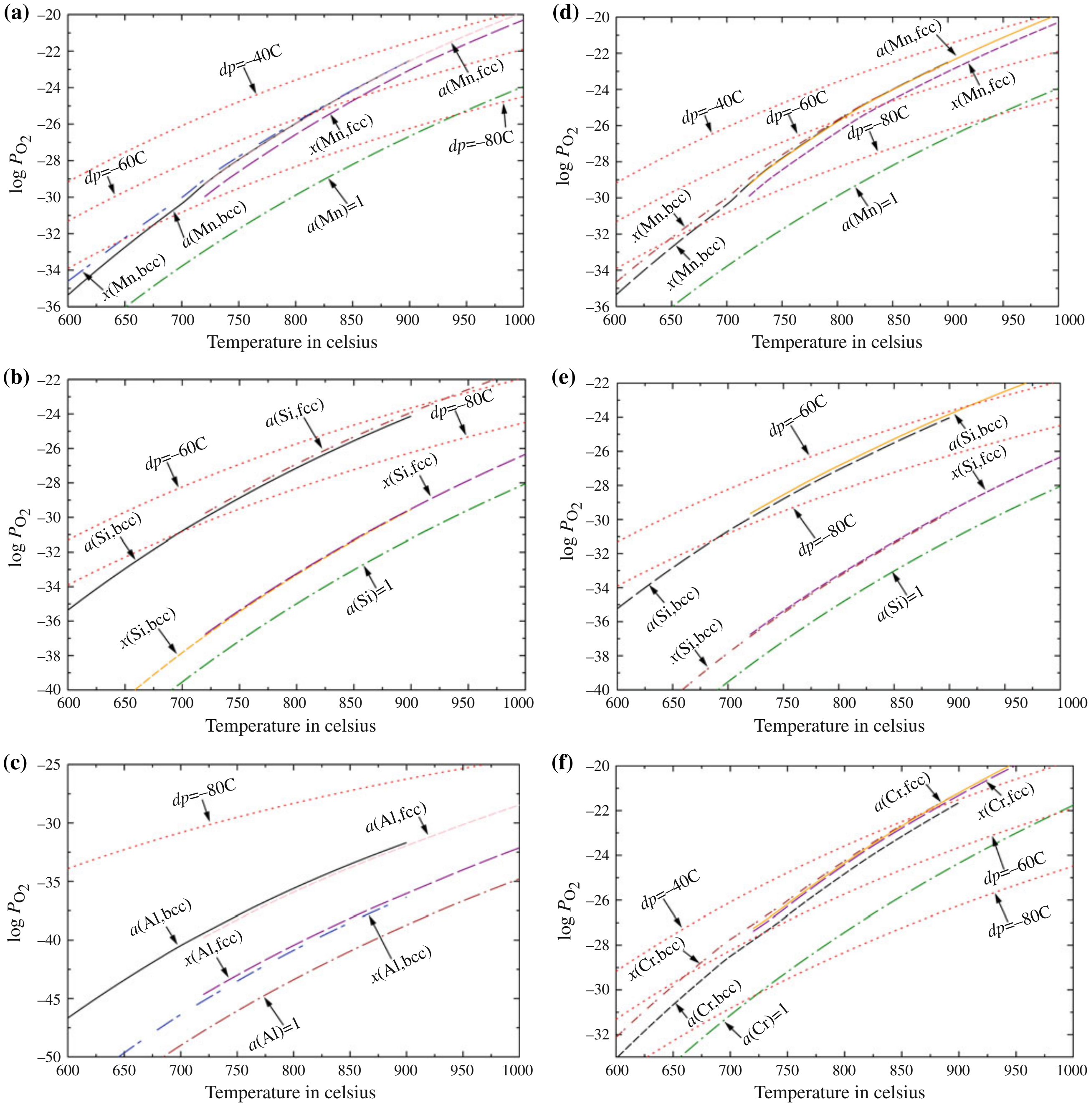

Fig. 4: Equilibrium oxygen partial pressure (in atm) calculated with different data: (a) for Mn in steel 1, (b) for Si in steel 1, (c) for Al in steel 1, (d) for Mn in steel 2, (e) for Si in steel 2, (f) for Cr in steel 2

activity when the element is present as an alloy element. Using molar fraction instead of activity is suitable for Mn and Cr, but it is not appropriate for Si and Al.

Besides, different elements contribute to different oxidation modes. Aluminum tends to cause internal oxidation, while the noblest element—Cr, whose oxidation depends on the partial pressure of oxygen, tends to cause external oxidation. The tendencies of Si and Mn are between Al and Cr.

Then, it becomes important to get a critical dew point from the calculation results, e.g., −80°C, under which many elements will not be oxidized, improving the surface wettability. However, it is nearly impossible for an industrial operation to set the annealing dew point as low as −80°C, but it is always possible to do so within the range of −50°C to −30°C. Hence, it seems that these simple oxides mentioned above can hardly be avoidable under industrial annealing conditions.

The calculation results also show that the equilibrium oxygen partial pressure increased significantly when the element activity decreased from unity to a limited content. Then it is natural to deduce that if the element bulk concentration is reduced to a certain value, the selective oxidation might be suppressed under industrial conditions. However, these elements are added to the steel to develop suitable properties given the capabilities of the continuous galvanizing line. Their removal is not optional if the desired properties are to be achieved. Hence, the oxidation cannot be avoided for the current generation of AHSS using the current generation of continuous galvanizing lines.

Precipitation of mixed oxides

The formation order

As shown in Fig. 5, among the complex oxides mentioned above that occur below 900°C, $MnCr_2O_4$ is the most stable, followed by $MnAl_2O_4$, Mn_2SiO_4, and $MnSiO_3$ in sequence. According to this stability order, $MnCr_2O_4$ may be the foremost mixed oxide formed, then, $MnAl_2O_4$, Mn_2SiO_4, and $MnSiO_3$ followed depending on the Mn/Me (Me = Cr, Al, Si) weight percent ratio.

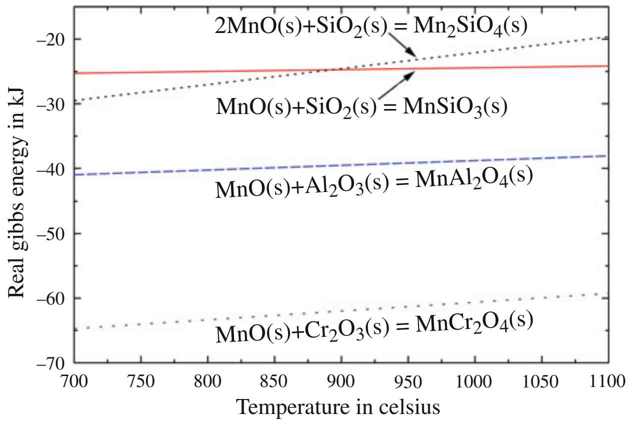

Fig. 5: Real Gibbs energy of mixed oxidation formation under galvanizing atmosphere

Since $MnAl_2O_4$ does less harm to zinc wettability, it is not difficult to substitute Al for Si in high-strength steel, replacing Mn_2SiO_4 or $MnSiO_3$ with $MnAl_2O_4$. Meanwhile, Cr might be considered analogously, but there is no experimental evidence for its influence on wetting.

The effect of alloy elements on the formation of mixed oxides

While investigating the selective oxidation behavior of Mn–Si steel, Drillet suggested that the Mn/Si ratio in weight percent can predict the oxides ready to form on the steel surface during intercritical annealing prior to galvanizing.[36] Similarly, Liu also proposed an Al/Mn ratio to predict the oxides to form on the surface of Mn–Al–Si steel.[28] These rules are termed the Mn–Si rule and the Al–Mn rule, respectively.

Considering the stability of $MnCr_2O_4$ over $MnAl_2O_4$ and $Mn_2SiO_4/MnSiO_3$, a similar Mn/Cr ratio is proposed on the surface of Mn–Cr steel, and is termed the Mn–Cr rule. When annealed under the galvanizing atmosphere, Mn–Cr steel will be selectively oxidized. Similar to Drillet and Liu's study, it can be estimated that the first oxide growing on the Mn–Cr steel surface is $MnCr_2O_4$ because of its sufficient stability. In the chemical formula, the Mn/Cr weight ratio is,

$$\mathrm{Mn/Cr} = \frac{54.938}{51.996 \times 2} = 0.53 \qquad (10)$$

Therefore, the critical value is 0.53. If the ratio is greater than 0.53, then $MnCr_2O_4$ will consume all the Cr, and extra Mn will form other mixed or simple oxides. If the ratio is less than 0.53, the oxides will be $MnCr_2O_4$ and Cr_2O_3 due to the full consumption of Mn.

However, at 800°C, the diffusion coefficient ranking of Al, Mn, Si, and Cr in α-Fe is $D_{\mathrm{Mn}} > D_{\mathrm{Si}} > D_{\mathrm{Al}} \approx D_{\mathrm{Cr}}$, and in γ-Fe, the order is $D_{\mathrm{Al}} > D_{\mathrm{Si}} > D_{\mathrm{Mn}} \approx D_{\mathrm{Cr}}$. In bcc iron, Mn and Si can diffuse much faster than Cr; in fcc iron, though Mn has the similar diffusivity with Cr, but Cr prefers to enrich in bcc iron while Mn prefers to enrich in fcc iron. These two factors may hinder the formation of Mn–Cr mixed oxide.

Kinetics considerations

Although this study is focusing on the thermodynamics analysis of selective oxidation, we should also consider another important aspect, kinetics. The process of selective oxidation depends on the diffusion of oxygen and alloy elements.

According to the thermodynamic stability, the first oxide to precipitate is the most stable one, such as Mn_2SiO_4 in C–Mn–Si TRIP steel. However, in most literatures, the surface oxides are not always the expected ones according to the Mn–Si, Mn–Al, or Mn–Cr rules. This would seem to indicate that these rules are wrong. However, most of the oxide characterization results are from XPS or SIMS analysis. These micro-analysis techniques usually give an average oxide layer composition at the macro scale.[20,37]

By high resolution-TEM, Gong conducted a direct observation of the external and internal oxides, including the morphology, size, distribution, and the precise determination of the composition of oxides on a C–Mn–Si TRIP steel.[20,37] Gong further reported that the first oxide formed on the surface is $2MnO{\cdot}SiO_2$, and then due to the local depletion of Mn and its slow diffusivity, the oxide becomes xMnO·SiO_2 ($x < 2$). Owing to a local lack of Mn or Si, the SiO_2 or MnO will form. Although the Al content in the steel is only 0.028 wt%, MnO·Al_2O_3 still formed.

From Gong's study, it is believed that the first oxide should always be the most stable Mn–Si or Mn–Al mixed oxide due to thermodynamic reasons. The formation of other oxides not only depends on thermodynamics, but also depends on kinetics. Owing to the consumption of alloy elements and their differences in diffusivity, a local depletion will cause different oxide precipitation, changing the Mn–Si or Mn–Al rule.

Conclusions

This study analyzed the selective oxidation behaviors of Al and Cr-added high strength steel sheets during intercritical annealing based on thermodynamics. The results are summarized as follows.

(1) The real equilibrium oxygen partial pressure of oxidation reactions over steel surface is much larger than those over the pure substance. When calculating the real equilibrium oxygen partial pressure, we cannot simply use unity instead of activity when element is present as alloy element; using molar fraction instead of activity for Mn and Cr may work, but it is not appropriate for Si and Al.

(2) The industrial galvanizing atmosphere reduces iron oxides, while it oxidizes Mn, Cr, Si, and Al, even if they are just present as alloy elements with limited concentration.

(3) The most stable mixed oxide is $MnCr_2O_4$, followed by $MnAl_2O_4$, Mn_2SiO_4, and $MnSiO_3$ in sequence. This stability order may tell which of the mixed oxide will be the first precipitation on the steel surface.

(4) Similar to the Mn–Si rule and the Al–Mn rule, this study proposed a Mn–Cr rule to predict the oxides formed on the surface of Mn–Cr steel in this article.

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