



The change of steel surface chemistry regarding oxygen partial pressure and dew point

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ABSTRACT

By investigating the surface state of a Ti-IF, TiNb-IF and a MnCr-DP after several series of intercritical annealing, the impact of the annealing gas composition on the selective oxidation process is discussed. On behalf of the presented results, it can be concluded that not the general oxygen partial pressure in the annealing furnace, which is a result of the equilibrium reaction of water and hydrogen, is the main driving force for the selective oxidation process. It is shown that the amounts of adsorbed gases at the strip surface and the effective oxygen partial pressure resulting from the adsorbed gases, which is mainly dependent on the water content of the annealing furnace, is driving the selective oxidation processes occurring during intercritical annealing. Thus it is concluded, that for industrial applications the dew point must be the key parameter value for process control.

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1. Introduction

The necessity of reducing carbon dioxide emission is the driving force of the increased use of Advanced High Strength Steels (AHSS) in the body in white (BIW) as well as in outer part panels of modern automobiles. During annealing of AHSS in continuous annealing as well as continuous galvanizing lines, oxides of the alloying elements can occur. Although a reductive gas mixture of approximately 5% H₂ and N₂ is used to protect the steel strip surface from becoming oxidized, only Fe could be reduced at typical industrial conditions. Due to the selective oxidation process, alloying elements are enriched and oxidized at the steel strip surface during, annealing temperature and alloying concept interact in a complex way [1–4]. Many approaches annealing and prior to hot dipping. It is well known that the dew point (DP) of the annealing gases, the gas composition were created to predict the mode of selective oxidation and the occurring oxide species segregating at the surface of binary and ternary model alloys as well as already available steels by computer simulations, thermodynamical calculations and laboratory trials [5–9]. As the oxides of the alloying elements causes surface defects as bare spots as well as bad zinc adhesion, the influence of DP during intercritical annealing on the surface chemistry of steel strips and the impact of selective oxidation on zinc wetting

is widely discussed in many research works, especially regarding Si and Mn alloyed Transformation Induced Plasticity (TRIP) aided steels [10–21].

There are several approaches to modify the selective oxidation process at industrial scale. One is the costly, electrochemically deposited pre-coatings – so called flash-coating – of Fe or Ni, which are used to prevent the enrichment of alloying elements at the steel strip surface during intercritical annealing [22,23]. Another is the reactive annealing procedure with NH₃, CO and CO₂ which are known to improve the surface quality of AHSS [24]. By controlling the DP in the annealing furnace and thus the oxygen partial pressure of the furnace, surface chemistry could be altered in a positive manner by promoting internal oxidation. But the improvement is limited because at high DP conditions de-carburization is significantly encouraged [25–29]. Additionally, enhancement of the surface reactivity of Si containing AHSS is limited due to its high oxygen affinity. Alternatively, an oxidation/reduction procedure – so called pre-oxidation – is a well-known tool used to improve the surface quality of hot dip galvanized (GI) or galvanized (GA) coated AHSS [30–32]. Furthermore, bright annealing at high annealing temperatures has been discussed, but this approach is far removed from the ordinary industrial practice [33].

There are already several approaches discussed in a broad manner, but it is still essential to understand the reaction mechanisms taken place at the interface of gas and metal in detail. A lack of knowledge to be discussed is whether the oxygen partial pressure of the annealing furnace, resulting from the equilibrium reaction

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of hydrogen and water vapor, or the oxygen partial pressure of the adsorbed gases is the driving force for selective oxidation processes.

2. Theoretical background

In regards to the so-called oxygen partial pressure, it has to be distinguished the oxygen partial pressure of the annealing atmosphere from the oxygen partial pressure of the adsorbed oxygen at the steel surface. The oxygen partial pressure of the annealing atmosphere is a result of the equilibrium reaction of hydrogen and water vapor in the annealing furnace as shown in Eqs. (I) and (II).



$$K_f = \frac{p_{\text{atm}}(\text{H}_2\text{O})}{p_{\text{atm}}(\text{H}_2) \cdot p_{\text{atm}}(\text{O}_2)^{1/2}} \rightleftharpoons p_{\text{atm}}(\text{O}_2) = \left(\frac{p_{\text{atm}}(\text{H}_2\text{O})}{p_{\text{atm}}(\text{H}_2) \cdot K_f} \right)^2 \quad (\text{II})$$

where K_f is the reaction constant (isotherm), $p_{\text{atm}}(\text{H}_2\text{O})$ the partial pressure of water vapor in the annealing furnace [bar], $p_{\text{atm}}(\text{O}_2)$ the partial pressure of oxygen in the annealing furnace [bar], and $p_{\text{atm}}(\text{H}_2)$ is the partial pressure of hydrogen in the annealing furnace [bar].

This specific oxygen partial pressure in the annealing atmosphere is often referred to be the dominating oxygen partial pressure when defining the metal/metal oxide equilibrium conditions in an annealing furnace according to the Ellingham diagram [34,35]. But with Wagner's model of the selective oxidation process (Eq. (III)), it could be concluded, that the mode of selective oxidation (approximately given as: Eq. (IV) (external oxidation) and Eq. (V) (internal oxidation)) depends on the amount of the selectively oxidizing alloying element and especially the amount of adsorbed oxygen at the steel surface [5].

$$N_{X,\text{critical}}^0 = \left(\frac{\pi \cdot g^* \cdot V \cdot N_{\text{O}}^S \cdot D_{\text{O}}}{2 \cdot n \cdot V_{X\text{O}_n} \cdot D_X} \right)^{1/2} \quad (\text{III})$$

where $N_{X,\text{critical}}^0$ is the critical molar fraction of alloying element X, D_{O} the diffusion coefficient of oxygen in the metal matrix [$\text{cm}^2 \text{s}^{-1}$], D_X the diffusion coefficient of X in the metal matrix [$\text{cm}^2 \text{s}^{-1}$], g^* the critical volume fraction of formed oxide blocking of all inwards diffusion ($g^* \approx 0.3$), N_{O}^S the molar fraction of free adsorbed oxygen, V the molar volume of alloy, $V_{X\text{O}_n}$ the molar volume of oxide, and n is the stoichiometric coefficient.

$$N_{X,\text{critical}}^0 \cdot D_X > N_{\text{O}}^S \cdot D_{\text{O}} \Rightarrow \text{external oxidation} \quad (\text{IV})$$

$$N_{X,\text{critical}}^0 \cdot D_X < N_{\text{O}}^S \cdot D_{\text{O}} \Rightarrow \text{internal oxidation} \quad (\text{V})$$

N_{O}^S can be calculated by Eq. (VI) [36] or as presented by Huin et al. as a concentration according to Eq. (VIII) [7].

$$N_{\text{O}}^S = \left(\frac{1}{K[T]} \right) \cdot \left(\frac{56}{1600} \right) \cdot \left(\frac{p_{\text{atm}}(\text{H}_2\text{O})}{p_{\text{atm}}(\text{H}_2)} \right) \quad (\text{VI})$$

with

$$K[T] = 0.162 \cdot e^{22.876/R \cdot T} \quad (\text{VII})$$

$$\Leftrightarrow c_{\text{surf}}(\text{O}_2) = 10^{4 - (3690/T) + \log_{10}(p_{\text{ads}}(\text{H}_2\text{O})/p_{\text{ads}}(\text{H}_2))} \quad (\text{VIII})$$

where $K[T]$ is the reaction coefficient (dependent of temperature), T is the annealing temperature [K], R is the universal gas constant [$\text{m}^3 \text{bar K}^{-1} \text{mol}^{-1}$] ($R \approx 8.3144621 \times 10^{-5}$), and $c_{\text{surf}}(\text{O}_2)$ is the concentration of adsorbed oxygen at the steel surface [ppm].

Furthermore the amount of adsorbed oxygen is dependent on the adsorbed amount of the oxygen at the steel strip surface. Due to this, not only should the oxygen adsorption of the annealing atmosphere equilibrium (Eq. (I)) be taking into account as a source of oxygen for the selective oxidation process, but more importantly,

the impact of the adsorbed water vapor has to be considered, as following equilibrium reaction takes place at the surface as well:



$$K_{f(\text{ads})} = \frac{p_{\text{ads}}(\text{H}_2\text{O})}{p_{\text{ads}}(\text{H})^2 \cdot p_{\text{ads}}(\text{O})} \quad (\text{X})$$

where $K_{f(\text{ads})}$ is the reaction constant (isotherm), $p_{\text{ads}}(\text{H}_2\text{O})$ the partial pressure of water vapor adsorbed at surface [bar], $p_{\text{ads}}(\text{O})$ the partial pressure of oxygen adsorbed at surface [bar] and $p_{\text{ads}}(\text{H})$ is the partial pressure of hydrogen adsorbed at surface [bar].

Up to this point the heterogeneous gas/metal reactions are discussed without considering the reaction partners in different state of aggregation. H_2 , O_2 and H_2O are at typical annealing conditions gaseous, but metals are solid and diffusion takes place in solid state. The place of reaction (here: the steel surface) is the interface between gas and metal. Therefore, the heterogeneous gas/metal reaction can be divided in following steps.

1. Transport of the gases via convection toward the metal surface (Fig. 1).
2. Diffusion through the gaseous laminar boundary layer (Fig. 1).
3. Adsorption and dissociation of the reactants at the surface (Fig. 1).
4. Absorption of the reactants into the matrix (Fig. 2).
5. Diffusion of the reactants in the sub-surface (Fig. 2).
6. Oxide formation (Fig. 3).
7. Desorption of the gaseous reaction products (Fig. 3).
8. Back-transport through the gaseous laminar boundary layer (Fig. 3).

For this work, sub-surface diffusion of the reactants (step 5) is supposed to be constant and homogeneous, as an idealization. Nevertheless, it should keep in mind that diffusibility of the reactants within the sub-surface is influenced by crystal defects and can considerably differ between inside the grains and on grain/phase boundary and between austenite and ferrite (\rightarrow intercritical annealing), as well.

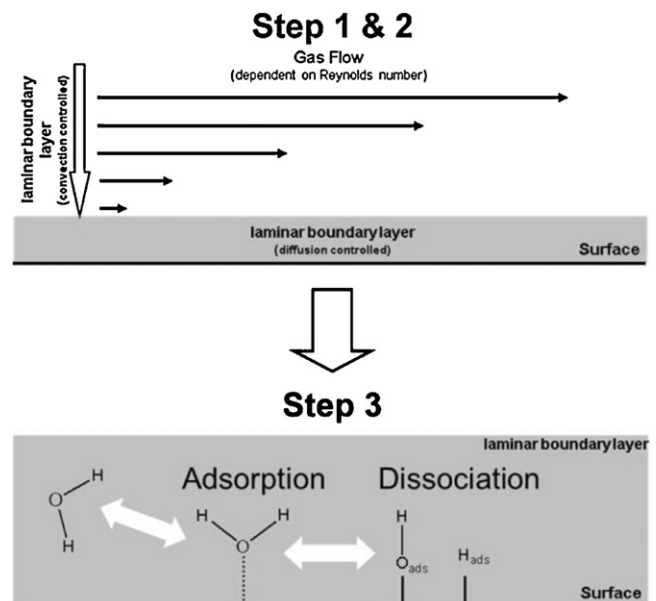


Fig. 1. Schematic diagram of the reaction steps 1–3.

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