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Time and temperature dependence of the adhesion of oxide scales formed on phosphorus-containing steels during short term oxidation

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ABSTRACT

The influence of phosphorus (0.15 wt.%) on iron oxide scale adhesion is studied for short time oxidation of carbon steel in air at 800 and 1000 °C. Adhesion is measured after cooling to room temperature by Vickers indentation. It is shown to increase with increasing oxidation time as the result of the formation of a phosphorus-containing phase at the steel–scale interface. It also exhibits much higher values after oxidation at 1000 °C than after oxidation at 800 °C. This is suggested to be due to molten oxide infiltrating the metal grain boundaries during oxidation at the highest temperature. The FeO–$Fe_3(PO_4)_2$ eutectic temperature of 940 °C appears therefore as a critical parameter in the steel descaling process on the production line.

1. Introduction and literature survey

Phosphorus is generally a residual element in low carbon steels, with a concentration kept at a maximum of ~0.01 wt.% to avoid embrittlement problems, particularly at low temperatures. However, higher concentrations of this element sometimes are used for special applications as cold-forming or machining. In these cases, the P-concentration may be increased to a maximum of ~0.15%, a concentration within the solubility domain of substitutional P in ferrite or austenite [1]. This results in a high strength increase balanced by a strong decrease in ductility. Such high phosphorus steels exhibit better annealing textures [2] but they were shown to be subject to phosphorus enrichment at grain boundaries [3]. A sensible increase in atmospheric corrosion was also reported for rephosphorized steels.

For the steelmaking industry, it is of importance to know the modifications induced by the presence of high levels of phosphorus during processing in the hot rolling mill, particularly on scaling rate, oxide morphology and scale adhesion, the main parameters contributing to the final quality of the strip.

Phosphorus is an element more oxidizable than iron. According to the literature, phosphorus (V) and iron (II) can form ternary oxides [4,5] (Fig. 1); the best known have the compositions "~18 FeO.P_2O_5" ("Q oxide") and "3 FeO.P_2O_5" (iron (II) phosphate, more correctly written $Fe_3(PO_4)_2$). Q oxide is a peritectic-decomposing oxide, existing below 960 °C only. $Fe_3(PO_4)_2$ is probably melting congruently near 1020 °C. A eutectic between FeO and $Fe_3(PO_4)_2$ appears when cooling the liquid, with the composition 65.5%FeO-34.5%P_2O_5 and a melting point of 940 °C.

Other ternary ferrous oxides were reported, with various compositions (4 FeO·P_2O_5, 2 FeO·P_2O_5 and FeO·P_2O_5), but their thermodynamic stability is not established. Several iron (III) phosphates are also known, but they were not considered in the present study, as short term oxidation of steel at high temperatures does not allow iron to oxidise to the (+III) state near the metal-oxide interface where phosphorus oxide is stable, due to its highly negative Gibbs energy of formation.

Due to the presence of the low-melting eutectic, the oxidation of P-containing steels was reported to be different at low or high temperatures. When P-containing steels are heated in oxidizing atmospheres at temperatures below 940 °C – the eutectic

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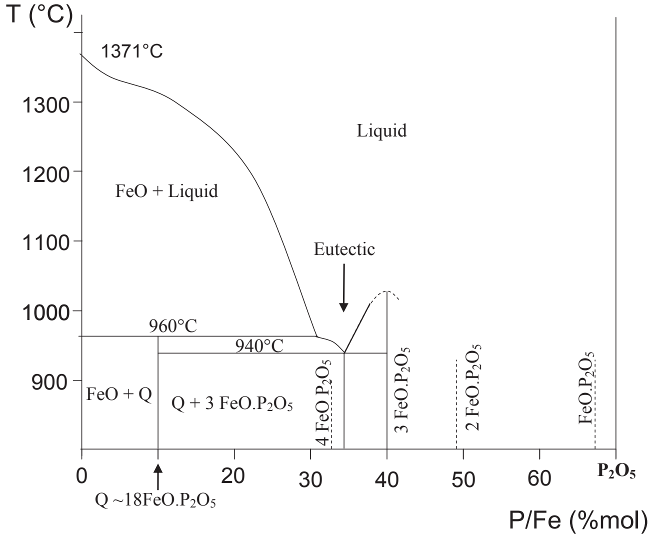

Fig. 1. FeO–P_2O_5 pseudo-binary phase diagram according to Slag Atlas.[5].

temperature – phosphorus oxidizes to solid phase(s), mostly at the interface between the metal and the growing wüstite, where a continuous or discontinuous oxide layer is formed, mainly containing iron (II) phosphate [7,8]. The morphology of this layer depends on the phosphorus content of the steel. The iron phosphate particles appearing at the metal-scale interface are reported to inhibit vacancy injection and/or diffusion within the steel matrix, i.e. the metal vacancies formed from the iron atoms flowing into wüstite condense onto the steel–particle interfaces, forming voids [6,7]. Consequently the scale adhesion was reported to decrease with increasing time. It must be noted that internal oxidation of phosphorus to diphosphorus pentoxide P_2O_5 was also observed [4].

At temperatures higher than 940 °C, a molten eutectic forms at the metal-scale interface during oxidation and infiltrates the grain boundaries of FeO [4]. According to Svedung et al. [9,10], a high vapour pressure of phosphorus pentoxide is generated above 950 °C, leading to scale buckling and complete loss of adhesion after extended times.

As no quantitative values of scale adhesion could be found in the literature, the objective of the present work was to determine the mechanical adhesion of the scale grown at high temperatures during short times (minutes) on a P-containing steel, in order to assess the influence of this element on the descaling ability in the production line. Indeed, mechanical and/or hydraulic removal of the scale formed after hot rolling is a key parameter controlling the quality of the final strip.

2. Experimental procedure

2.1. Sample preparation and oxidation

A laboratory-made steel containing 0.15%wt. P was prepared by adding elementary phosphorus to an industrial low carbon steel containing 109 ppm residual P. The complete composition of this steel, without the additional P, is shown in Table 1.

A specially designed vacuum furnace was used for this purpose, with the metal to be alloyed contained in a refractory crucible securely placed in a protective second one. The assembly presents four airtight gates, used for various additions, temperature measurements and extraction of samples. They prevent any air leakage into the furnace. Temperature was measured by a thermocouple placed at the bottom in the first crucible. Experiments were carried out under secondary vacuum. The furnace design is presented in Fig. 2.

The operating procedure was as follows: 1 kg of base material was introduced in the crucible and induction-heated to melt at 1600 °C. Deoxidation of the charge was performed by adding the calculated necessary amount of carbon. A reference sample was then taken out by suction into a silica tube introduced into the molten bath through one of the airtight gates. A metal rod was thus obtained, with dimensions 10 cm in length and 5 mm in diameter. On-site immediate analysis by Optical Emission Laser Spectroscopy was performed to control the non-metallic element (O, N, C and S) contents. If acceptable, red phosphorus was added to the melt to obtain the targeted grade composition. After equilibration time, several rods of the Fe–P alloy were extracted by suction and their chemical composition was immediately verified. In the present study, the obtained composition was 0.15wt.% P, similar to the projected one.

The rods of the obtained steel containing 0.15%wt P were cut into slices 2 mm thick which were mechanically polished to 1 μm diamond paste surface finish. They were rapidly introduced in a laboratory air furnace set at 800 or 1000 °C and exposed for 2, 5 or 10 min; they were subsequently withdrawn from the furnace and allowed to cool down in air. Although the thermal shock was very strong, no scale spallation was observed, except for the samples oxidised 2 min at 1000 °C. The same experiments were performed with several base steel samples (without phosphorus addition). Scale thicknesses obtained from the mass gain assuming only FeO in the scale and checked by optical microscopy are reported in Table 2.

2.2. Adhesion tests

Due to the special shape of the specimens – 2 mm thick disks, 5 mm in diameter – the methods commonly used for forcing oxide spallation on metal foils (Blister Test [11]) or strips (Tensile Test [12]) could not be used. Oxidised specimens were therefore submitted to Vickers indentation perpendicularly to the oxide scale surface in order to induce scale-metal delamination. A series of increasing loads (10 gf, 25 gf, 50 gf, 100 gf, 500 gf, 1 kgf, 2 kgf, 3 kgf, 5 kgf, 10 kgf, 20 kgf) were applied during 10 s onto the scale at different locations of the surface to force oxide spallation. After removing the indenter, both the diagonal of the diamond imprint in the metal ($2a$) and the radius of the disk-shaped delamination area (R) were measured under the optical microscope. It was noted at this stage that all samples showed the metal surface within the delamination area, indicating the fracture path followed the metal-scale interface.

From the measured values of $2a$ and R, the scale delamination critical energy release rate G_c (mechanical adhesion energy) was calculated using the method developed by Drory and Hutchinson [13] and recently used by Vasinonta and Beuth [14]. Following these authors, G_c can be measured using any Vickers load, and is a function of only the radial (ε_r) and circumferential (ε_θ) strains generated in the oxide at the distance R from the imprint centre where delamination ends, according to equation (1):

$$\frac{2\cdot G_c\cdot(1-\nu^2)}{E\cdot t} = (\varepsilon_r+\varepsilon_\theta)^2 \qquad (1)$$

In this equation, the Young's modulus E and the Poisson's ratio ν refer to the oxide and t is the thickness of the oxide scale. Both ε_r and ε_θ were calculated by adding the strains due to indentation (ε_r^I andε_θ^I) to the strains due to oxidation and cooling (biaxial residual strain$\varepsilon_0^{\mathrm{res}}$):