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.%) in steel is studied during oxidation at 800 and 1000°C in air. Oxide scale adhesion is measured at room temperature by Vickers indentation. Adhesion between the scale and the steel is much higher after oxidation at 1000°C than after oxidation at 800°C. This is suggested to be due to a liquid phase infiltrating metal grain boundaries during oxidation at the higher temperature. The FeO-$Fe_3(PO_4)_2$ eutectic temperature of 940°C appears therefore as a critical parameter in the steel descaling processes.

Keywords

Phosphorus steels; oxidation; hardness test; scale adhesion

Phosphorus is a residual element in low carbon steels, more oxidizable than iron. For the steelmaking industry, it is of importance to know the modifications induced by the presence of this element during processing in the hot rolling mill, particularly on scaling rate, oxide morphology and scale adhesion, the main parameters contributing to the quality of the strip.

According to the literature, phosphorus (V) and iron (II) can form ternary oxides [1,2] (Fig. 1); the best known have the composition "~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

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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. 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.

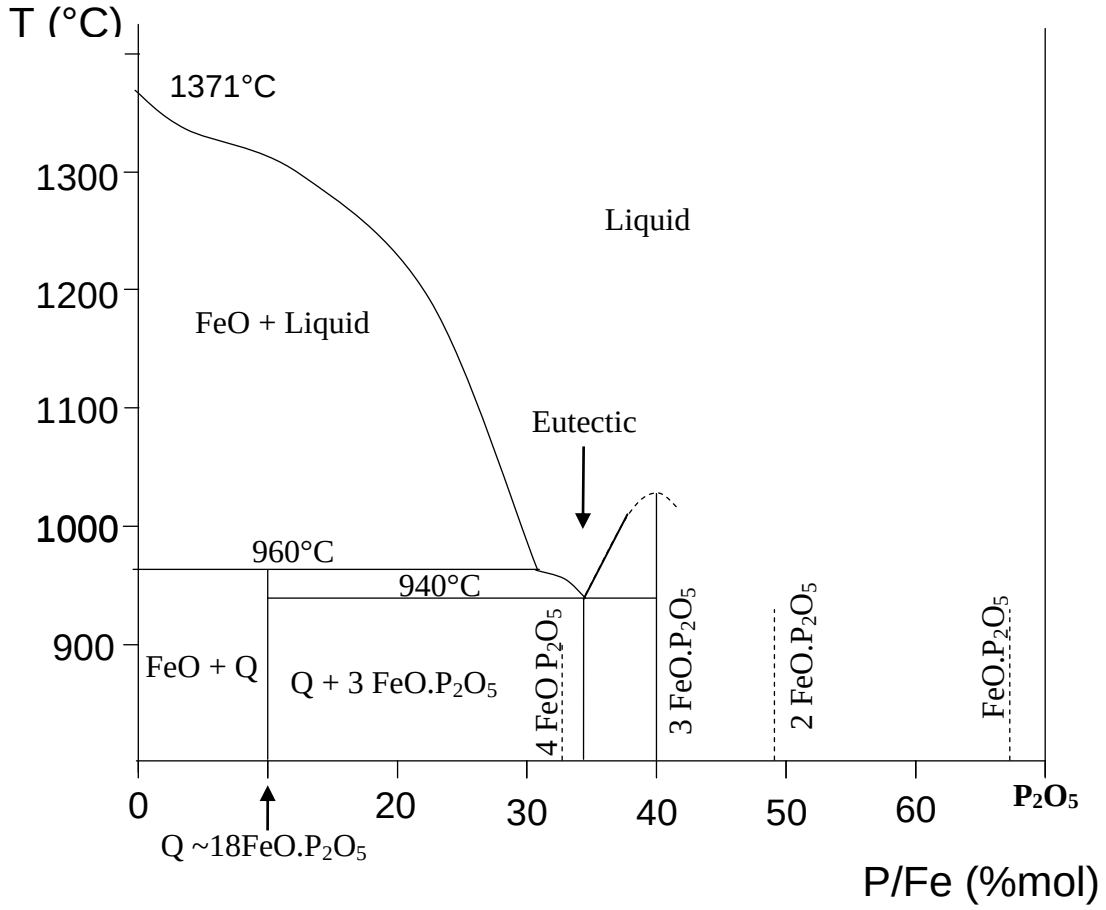


Fig. 1. FeO-P_2O_5 pseudo-binary phase diagram according to the Slag Atlas [2].

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 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 [4,5]. 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 [3,4]. 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 [1].

At temperatures higher than 940°C, a molten eutectic forms at the metal-scale interface during oxidation and infiltrates the grain boundaries of FeO [1]. According to Svedung *et al* [6,7], a high vapour pressure of phosphorus pentoxide is generated above 950°C, leading to scale buckling and complete loss of adhesion after extended times [5].

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.

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.

Table 1. Composition of the low carbon steel used as the base material (all values in weight fraction, bal: Fe).

Mn (%)	Cr (ppm)	Si (ppm)	Cu (ppm)	Ni (ppm)	P (ppm)	S (ppm)	N (ppm)	C (ppm)	Al (ppm)
0.229	238	228	226	165	109	74	23	15	14

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 phosphorus additions, sampling and temperature measurements, preventing 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 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.

Table 2. Average thickness of the scales grown on the 0.15% P steel in function of oxidation temperature and time. Sp: spalled.

	2 min	5 min	10 min
800°C	4.3	9.3	17.5
1000°C	Sp	139.0	164.0

Oxidised specimens were submitted to Vickers indentation perpendicularly to the oxide scale surface in order to force scale spallation. 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 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 (mechanical adhesion energy) was calculated using the method developed by Drory and

Hutchinson [9] and recently used by Vasinonta and Beuth [10]. Following these authors, *G* 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):

$$\frac{2 \cdot G \cdot \left(1-\nu^2\right)}{E \cdot t} = \left(\varepsilon_r + \varepsilon_\theta\right)^2 \qquad \text{Eq. (1)}$$

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 and ε_θ^I) to the strains due to oxidation and cooling (biaxial residual strain ε_0^{res}):

$$\varepsilon_r = \varepsilon_0^{res} + \varepsilon_r^I \qquad \text{(Total radial strain)} \qquad \text{Eq. (2)}$$

$$\varepsilon_\theta = \varepsilon_0^{res} + \varepsilon_\theta^I \qquad \text{(Total circumferential strain)} \qquad \text{Eq. (3)}$$

The radial and circumferential strains due to indentation were obtained from the value of *U*, the radial surface displacement of the metal due to the penetration of the indenter. This parameter *U* was predicted by Vasinonta and Beuth [10] using a finite element method indentation model, assuming (*i*) the wüstite scale is homogeneous and (*ii*) the indenter tip reaches the metallic substrate, assumptions which were observed to be reasonable in the present case. The results of the calculations by these authors appear as several curves describing the evolution of *U/a* as a function of *R/a*, depending on the values of two parameters related to the metal: *(i)* the ratio σ_y/E (tensile yield stress/Young's modulus) and *(ii)* the strain hardening exponent *N*. Using the appropriate curve, the values of *U* were determined for all loads used. From *U*, the strains due to indentation: ε_θ^I (radial) and ε_r^I (circumferential), were obtained using the following relations:

$$\varepsilon_\theta^I = \frac{U}{R} \qquad \text{Eq. (4)}$$

$$\varepsilon_r^I = \frac{dU}{dR} \qquad \text{Eq. (5)}$$

For determining the biaxial residual strain ε_0^{res}, the biaxial compressive residual stress in the oxide scale (σ_0^{res}) was used as shown by Eq. (6):

$$\varepsilon_0^{res} = \sigma_0^{res} \times \frac{1-\nu_{ox}}{E_{ox}} \qquad \text{Eq. (6)}$$

with E_{ox} = 128 GPa and ν_{ox} = 0.36, being values previously reported for wüstite [12].

The biaxial residual stress σ_0^{res} is a function of both growth stresses appearing at the oxidation temperature, due to oxide-metal volume difference, and thermal stresses generated at cooling, due to oxide-metal Coefficients of Thermal Expansion (CTE) mismatch. Contrary to what is currently observed for chromia- or alumina-forming alloys, where growth stresses are an important part of room temperature residual stresses, the FeO-Fe system is thought to develop very few growth stresses, and the main part of the residual stresses is due to CTE mismatch, as proposed by Corkovic and Pyzalla [11]. To calculate the thermal stresses, Eq. (7) was used. This equation is a reasonable simplification of the relations first proposed by Oxx [12] and Tien and Davidson [13] in the case where the oxide scale is much thinner than the metal substrate, which is the case here.

$$\sigma_0^{res} = E_{ox}\,\Delta T\left(\alpha_{ox} - \alpha_{met}\right) \qquad \text{Eq. (7)}$$

with E_{ox}, the Young's modulus of wustite (128 GPa)

a_{ox}, the coefficient of thermal expansion of wüstite (12.1×10^{-6} K^{-1})

a_{met}, the coefficient of thermal expansion of the steel (15.3×10^{-6} K^{-1})

ΔT, the temperature drop to room temperature at the end of the oxidation (K).

With the above values, the thermal compressive stresses at room temperature were determined:

Oxidation at 800°C: $\sigma_0^{res}(800) = 320\ MPa$

Oxidation at 1000°C: $\sigma_0^{res}(800) = 400\ MPa$

Good agreement is observed between these calculated values and the residual stresses measured by Buscail *et al.* [14] using X-Ray Diffraction.

From these values and from the thickness of the scale (t), the energy release rate (adhesion energy) G ($J.m^{-2}$) was determined using Eq. (1) for each sample at all values of load used.

After Vickers indentation, the samples were mounted in resin and cross sections were prepared with a 1 µm diamond paste finish. The cross-sections were observed by optical microscopy

(OM) and scanning electron microscopy (SEM). The nature of oxidation products was determined by EDX, FTIR and Raman spectroscopy using the green line (514 nm) of an argon laser.

It must first be reported that all oxide scales formed by oxidation of samples containing no added phosphorus (only 109 ppm residual P) spontaneously spalled to various extents at cooling; this was observed for all oxidation durations, at both 800 and 1000°C and reflects the very small adhesion energy of the wüstite scales. This explains why these samples were not submitted to Vickers indentation. On the contrary, almost all scales grown on the P-containing steel were adherent enough to be tested by indentation. This shows that the presence of phosphorus increases scale adhesion for short time oxidation, contrary to what has been previously reported for longer oxidation times [3,6,8]. These specimens were tested by Vickers indentation at different loads and the adhesion energy was calculated in each case. The results showed that the load used did not influence the adhesion energy value to within experimental error. This result is in agreement with the model presented above and confirmed that this model could be used in the present study. Scale adhesion values calculated from the delamination measurements are reported in Table 3.

Table 3. Adhesion values of scales grown on the P-containing steel.

T (°C)	800			1000		
Time (min)	2	5	10	2	5	10
Scale adhesion ($J.m^{-2}$)	8	18	28	~ 0	215	350

As observed in Fig. 2, the adhesion of scales on the phosphorus-containing steel increases with increasing oxidation time, with much higher values at 1000°C compared to 800°C. The repeatability of the measurements lies in the ± 12 to ± 28% range. These energies (particularly for the specimens oxidised at 1000ºC) are much higher than normally reported for oxide/steel adhesion. The Young's modulus of the scale was assumed to be 128 GPa; in reality, this can be much smaller due to defects (pores, microcracks, vacancies) in the scale. This could indicate also that there are probably other processes absorbing energy (such as plastic deformation and local scale fracture) in addition to brittle interfacial delamination. Nevertheless, the important point is

that there is a clear increase in the adhesion energy for specimens oxidised at 1000ºC compared to 800°C.

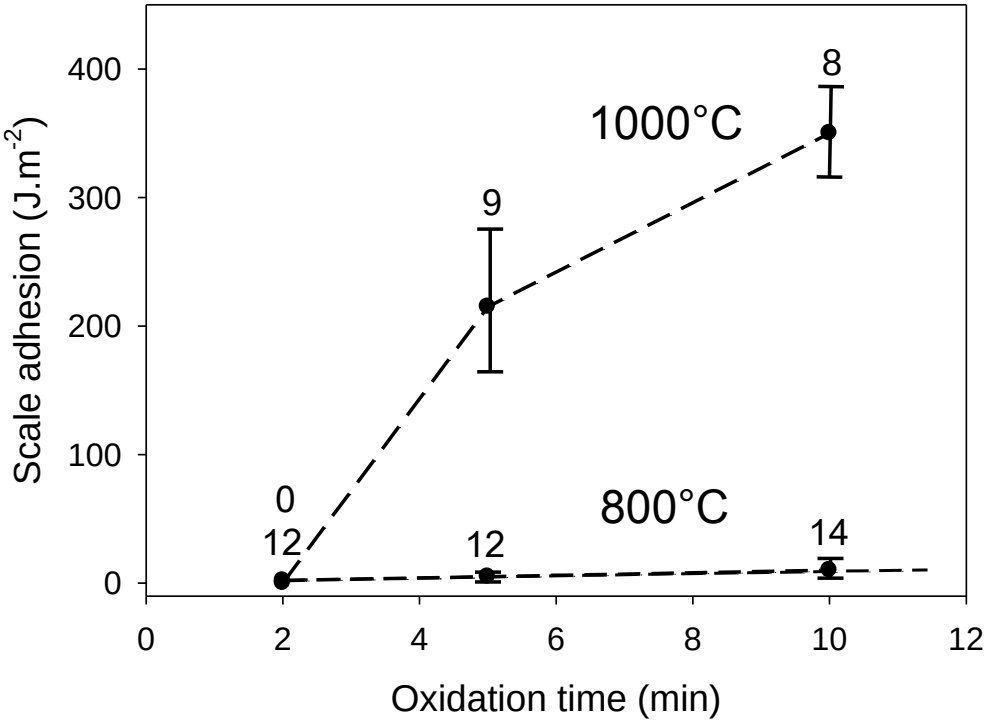


Fig. 2. Adhesion energy measured as a function of oxidation time on scales grown on the P-containing steel at 800 and 1000°C. The number of measurements is presented above each error bar.

In all conditions, FeO wüstite constituted the main part of the oxide scale. Some magnetite Fe_3O_4 also appeared on top of it, with its amount increasing with time and temperature. Microscopic observations of cross-sections always showed detectable phosphorus enrichment at the metal-scale interface. For oxidation experiments at 800°C – below the eutectic temperature – the interfacial zone between wüstite and steel was a few microns thick, with internal oxide penetrations generating metal protrusions and sometimes isolated metal islands (Fig. 3). Small pores were also observed above the interfacial oxide. EDX analysis revealed that this region is phosphorus-rich, containing also some silicon and iron to a lesser extent (Fig. 4). The amount of interfacial phosphorus was shown to increase with increasing oxidation duration.

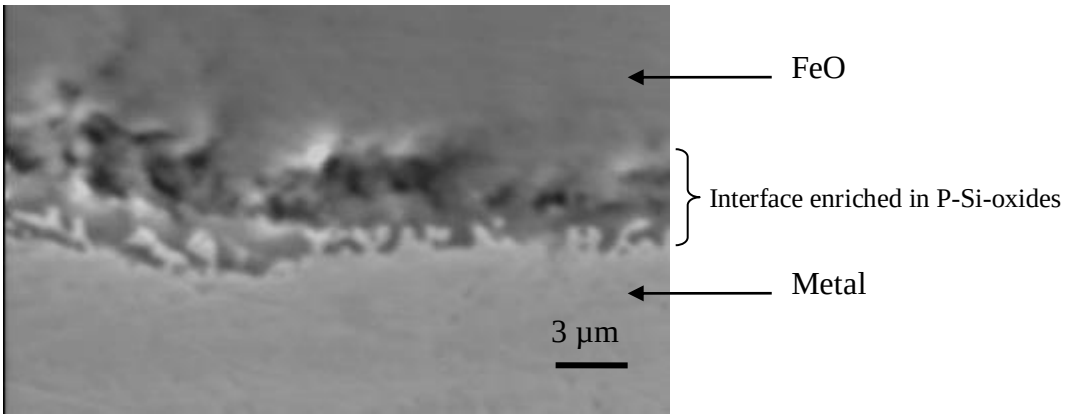


Fig. 3. Cross-section of a sample containing 0.15%P oxidized at 800°C during 15 minutes.

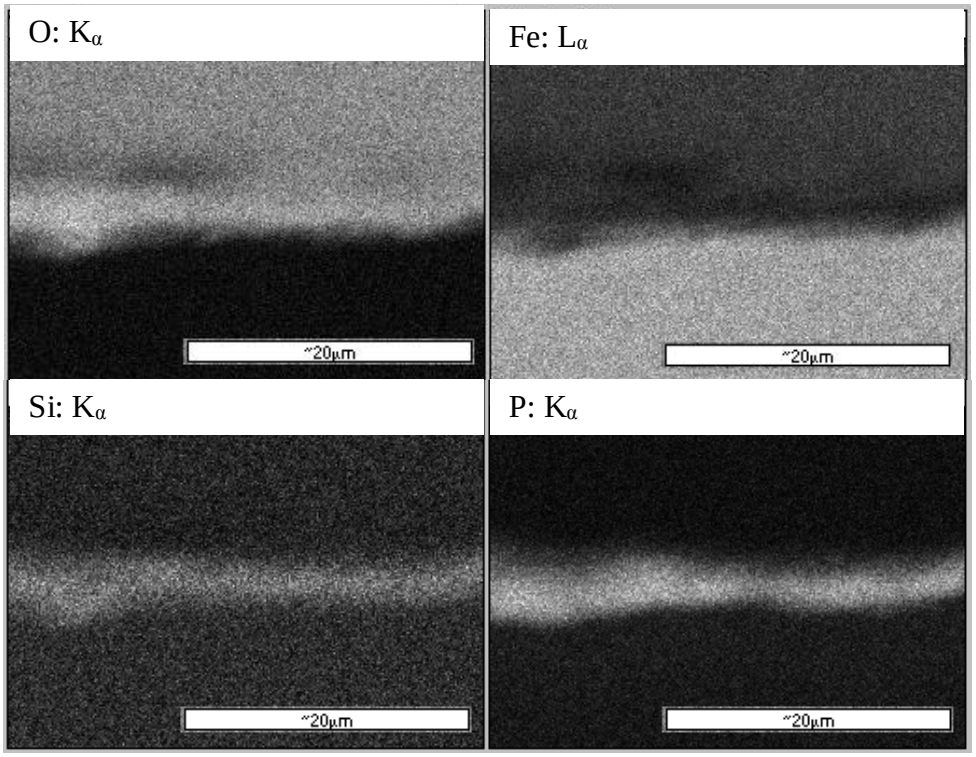


Fig. 4. EDX mapping of the same region of the sample in Fig. 3.

For samples oxidised at 1000°C – above the eutectic temperature – the interface morphology was similar, with much thicker interfacial oxide (up to 40 µm after 15 min), often detached by places from the substrate and from the main wüstite scale as a result of cooling and/or sample mounting in resin. Clear internal penetrations were also observed (Fig. 5). Both the interfacial oxide and the penetrations were analysed using Raman spectroscopy and were concluded to contain iron phosphate as they revealed the same typical strong doublet at 960-980 cm^{-1} as calcium phosphate (Fig. 6).

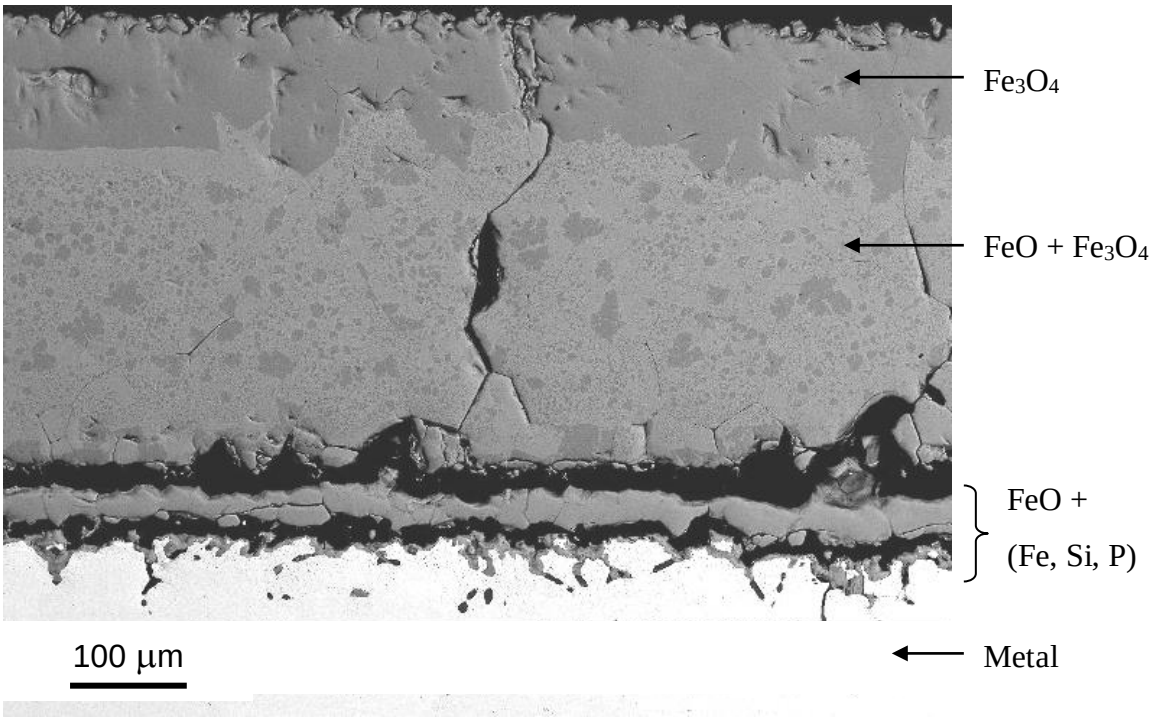


Fig. 5. Cross-section of a sample containing 0.15%P oxidized at 1000°C during 15 mn.

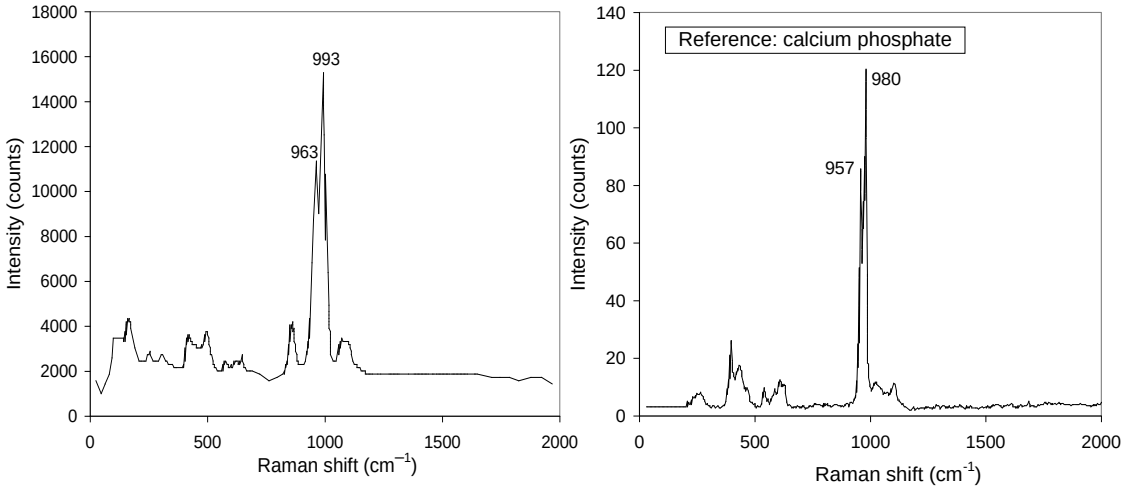


Fig. 6. (a) Typical Raman analysis within the interfacial oxide and at the grain boundaries of the metal (sample containing 0.15%P oxidized at 1000°C during 15 mn); (b) Raman spectrum of calcium phosphate [15].

The results described above show that the metal-oxide interface of the P-containing steel is enriched in phosphate even after only minutes of oxidation. Comparing to the steel containing no added phosphorus, it appears that this enrichment provides a large increase in the scale adhesion. This could be due to the P-containing oxide(s) nodule growth in the interface region of the steel,

where vacancies condense as the result of external iron transport. Such oxide nodules can hinder delamination propagation. This effect is amplified at temperatures above the $FeO\text{-}Fe_2(PO_4)_3$ eutectic temperature, where the molten nature of the formed products allows grain boundary penetration, providing excellent scale anchoring during Vickers testing.

As a result of this work, it is concluded that the adhesion of the oxide scales grown on steels during steelmaking processes is increased by the presence of phosphorus. For high phosphorus steels, increasing the time at high temperatures makes the adhesion larger. Also oxidation above the wustite-iron phosphate eutectic temperature makes the scales one order of magnitude more adherent. To retain a good descaling ability of high phosphorus steels, it is therefore recommended to limit the time at high temperatures, without going above 940°C.

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