A review of published models to predict the extent of surface oxidation

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Rapid Alloy Prototyping
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1. Background

- Advanced High Strength Steels (AHSS) are widely used in the automotive industry to reduce vehicle CO_2 emissions.
- This is owing to their excellent strength and formability properties, which allow the material to be rolled thinly (reducing weight) yet remain strong.
- Typically, AHSS are annealed for greater formability and surface finish, then directly coated with zinc for corrosion protection, **however issues arise if the AHSS alloying elements oxidised externally during annealing...**

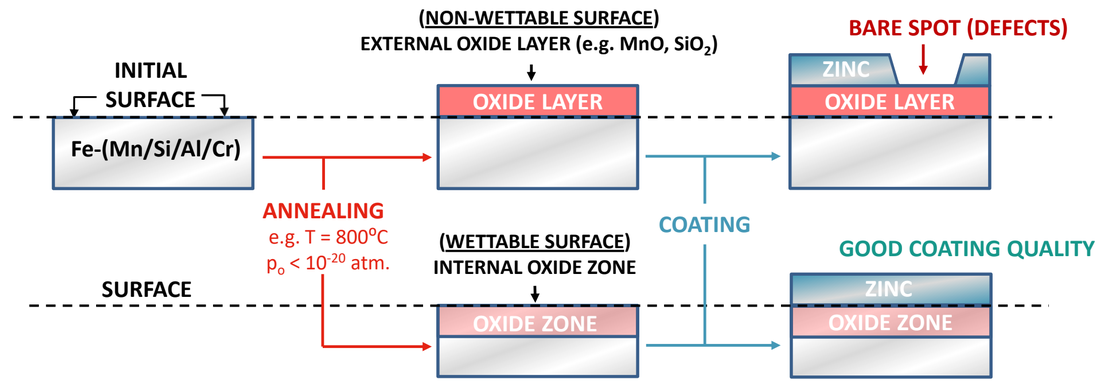

Fig 1. A comparison of steel surface conditions along the annealing and galvanising lines.

It is essential to know if/when internal oxidation will occur!

2. Review Scope

This review highlights several key modelling contributions, written here as responses to questions that relate to predicting the extent of surface oxidation.
Common methods that also reach these conclusions are given in red.

3. Review of Existing Models

WILL OXIDATION BE INTERNAL OR EXTERNAL?

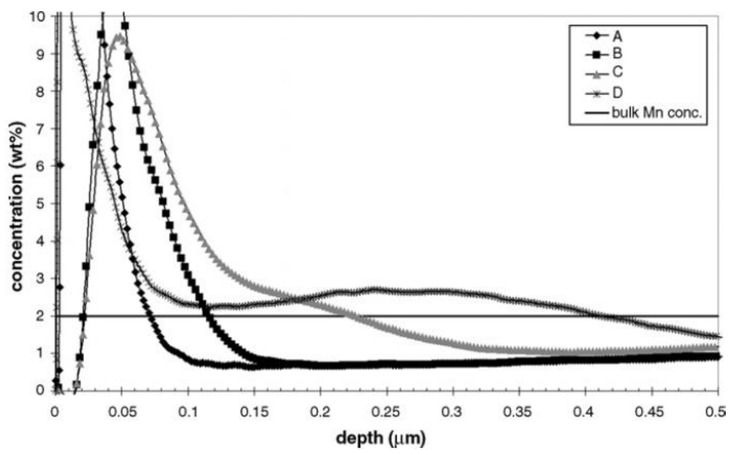

Fig 2. GDOES concentration profiles of DP steels oxidised at differing oxygen partial pressures, referred to as A, B, C, D [1].

- The conditions resulting in the external oxidation of a sample could be deduced by use of Glow-Discharge Optical Emission Spectrometry (GDOES).
- In addition, Wagner [2] provided an analytical solution:

$$N_B \cdot D_B = N_o \cdot D_o$$

Where: N_B, N_O = *Concentration flux of element, oxide*
D_B, D_O = *Diffusion coefficient of element, oxide*

- Which means that a flux equilibrium exists. The alloying element's critical concentration leading to external oxidation is calculable.
- There are a number of extensions to Wagner's work such as the incorporation of temperature changes on the diffusion of atomic oxygen [3].

WHICH STABLE OXIDE PHASES WILL FORM?

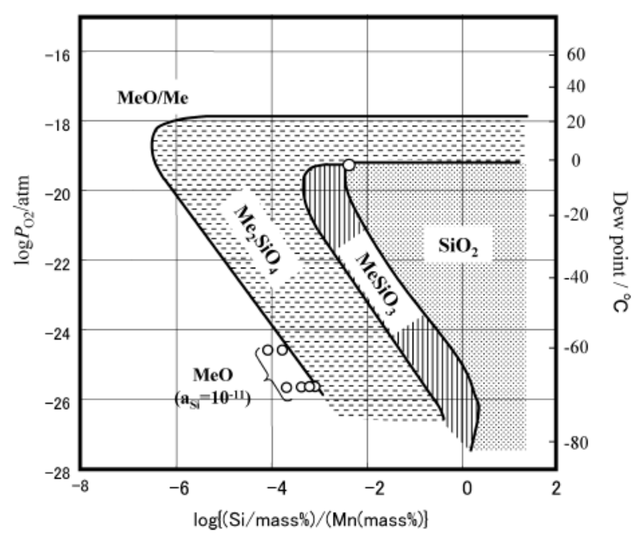

Fig 3. Chemical potential diagram, produced in FactSage [4].

- The oxide phases formed at the surface of an oxidised sample could be identified by X-Ray Diffractometry (XRD).
- Alternatively, the stable phases can be thermodynamically calculated.
- In literature, thermodynamic modelling software has been used to produce oxide phase diagrams in good agreement with experimental results.
- This was true of the thermodynamic analysis by Suzuki *et al.* [4], which assumed that a local equilibrium was reached between the oxides and the outermost surface region of the steel.

AT WHAT RATE WILL OXIDATION OCCUR?

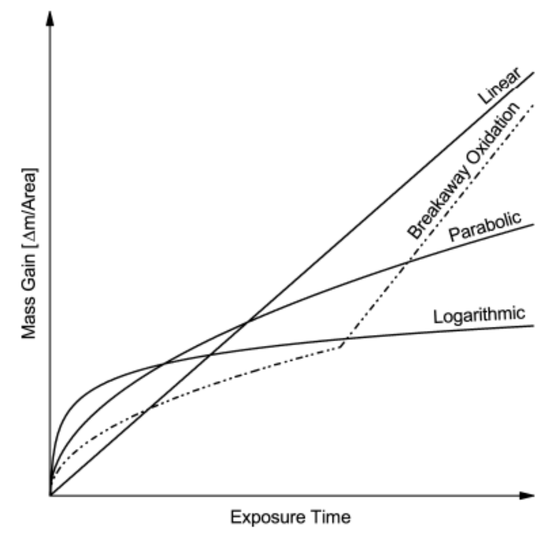

Fig 4. Example weight gain curves [5].

- It is common practice to determine oxidation rate from thermogravimetric weight gain measurements over time.
- In most cases, the weight gain follows a parabolic law:

$$\left(\frac{W}{A}\right)^2 = K_P \cdot t + C$$

Where: *W = Weight* *A = Area* *t = Time*
K_P = Parabolic weight coefficient *C = Constant*

- K_P is then found through fitting a line to the curve.
- Reasonable predictions of K_P have also been made by machine learning [6] – a method not yet applied to Fe-alloys, but will form an integral part of this PhD.

4. Summary

- Wagner's criterion allows for the calculation of critical alloying element concentrations, above which oxidation will be external.
- Assuming a local equilibrium exists at the alloys surface, a stable oxide phase diagram can be calculated and will be developed as part of this PhD.
- A novel machine learning model to predict K_P of Fe-alloys will also form part of this PhD.

5. Future Work

Oxidation models for Fe-Mn-Si alloys will be developed using the Wagner criteria (MATLAB), thermodynamic calculations (FactSage) and machine learning.

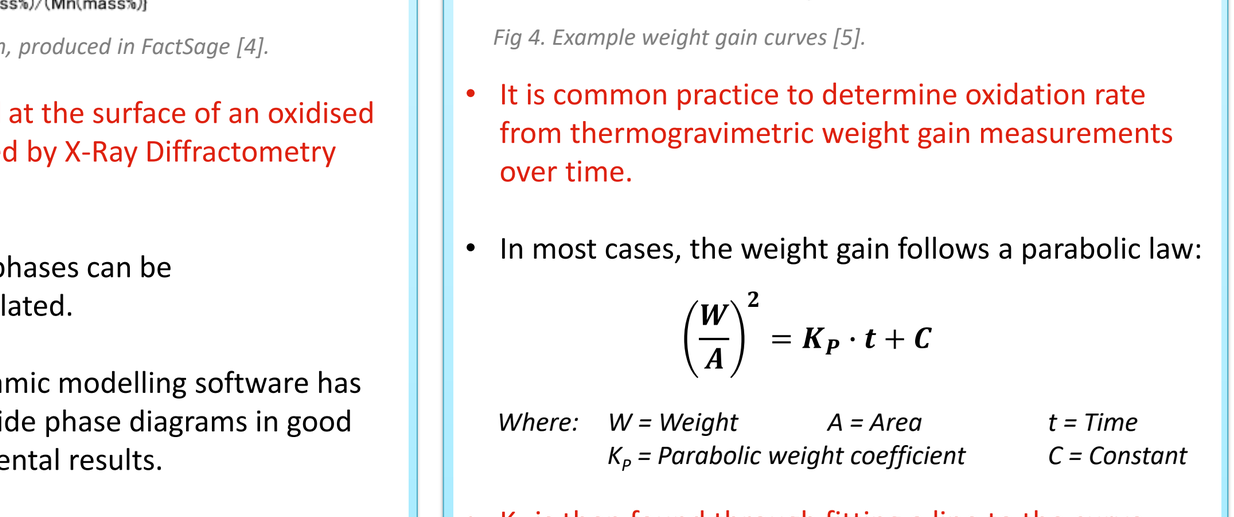

Fig 5. Transition between internal and external oxidation in Fe-Mn-Si alloys (left), and thermodynamic stability of formed phases (right) oxidised at 800°C with 10^{-28} atm.

References

1. *Khondker, R., Mertens, A. and McDermaid, J.R. Effects of annealing atmosphere on the galvanizing behaviour of dual-phase steel. Mat. Sci. Eng. A. 2006;463: 157-165.*
2. *Wagner, C. Theoretical Analysis of the Diffusion Processes Determining the Oxidation Rate of Alloys. J. Electrochem. Soc. 1952;99(10): 369-380.*
3. *Rapp, R. A. The transition from internal to external oxidation and the formation of interruption bands in silver-indium alloys. Acta. Met. 1961;9(8): 730-741*
4. *Suzuki, Y. Yamashita, T., Sugimoto, Y., Fujita, S., Yamaguchi, S. Thermodynamic Analysis of Selective Oxidation Behaviour of Si and Mn-added Steel during Recrystallization Annealing. ISIJ Int. 2009;49(4): 564-573.*
5. Göbel, C. Corrosion of Ferritic Stainless Steels Used in Solid Oxide Fuel Cells. Licentiate of Engineering. Chalmers University of Technology. Göteborg. 2018.
6. Battacharya, S. K., Sahara, R., Narushima, T. Predicting the Parabolic Rate Constant of High-Temperature Oxidation of Ti Alloys Using Machine Learning. Oxid. Met. 2020;94(3-4): 205-218.