Modelling internal oxidation in Fe-Cr alloys

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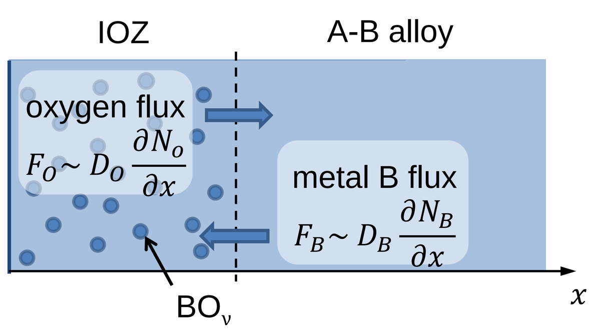
Introduction

Motivation

- Iron-chromium alloys play a crucial role in various applications when resistance to corrosion at high temperatures is important
- Corrosion in water containing atmospheres (e.g. on the anode side of SOC interconnects) can be more pronounced than in air and thus requires additional investigation
- At temperatures above 830°C Fe-Cr alloys undergo phase transformations when Cr is depleted due to oxide formation, so analytical description of oxidation (e.g. using Wagner model) can be problematic
- CALPHAD-based 1D model was developed to describe internal oxidation in model Fe-Cr alloys and compared with experimental observations and Wagner solution

Wagner model for internal oxidation

Let us consider A-B metal system, where only B metal can be oxidized to BO_ν



The depth of IOZ depends on the time parabolically:

$$X^2 = 2k_p t$$

Oxygen and metal flux must satisfy the following equation on the IOZ boundary:

$$\nu F_O = -F_B$$

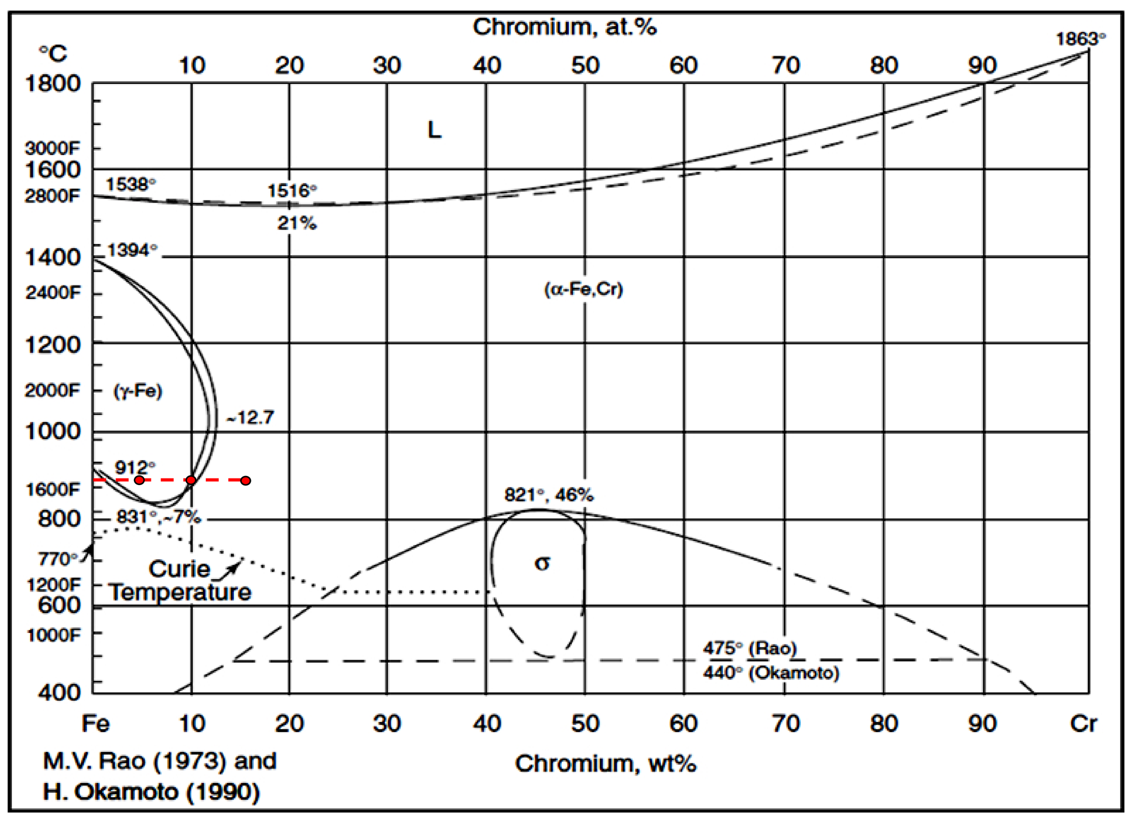
Diffusion equations and condition on the fluxes give the following solution for the parabolic constant:

$$k_p = \frac{D_O N_O^{(s)}}{\nu N_B^{(0)}}, \text{ if } D_B N_B \ll D_O N_O^{(s)}$$

$$k_p = \frac{\pi}{2D_B}\left(\frac{D_O N_O^{(s)}}{2\nu N_B^{(0)}}\right)^2, \text{ if } D_B N_B \gg D_O N_O^{(s)}$$

Wagner model:
- phase information required
- information about oxide type required
- hard to apply when several phase transformations during oxidation are present

Fe-Cr phase diagram



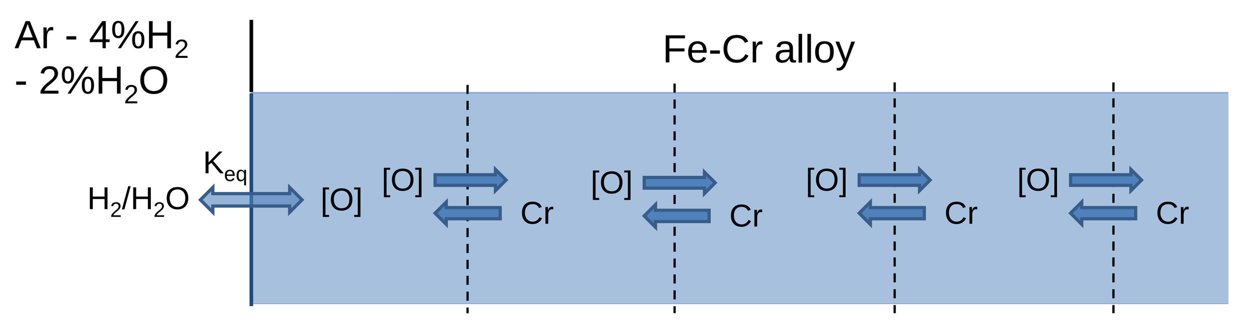
Experimental

- Binary wrought model alloys Fe-5Cr, Fe-10Cr, Fe-16Cr, Fe-17Cr (wt.%)
- Specimens ground to 1200 grit surface finish
- Exposures in tube furnaces under flowing Ar-4%H_2-2%H_2O (2l/h) at 900°C for 24h or 72h
- Analysis of exposed specimens in cross-section by optical metallography and SEM / EDX
- Image analysis to determine depth of IOZ and volume fraction of oxides using tools implemented in OpenCV Python library

Modelling procedure

Coupled kinetic-thermodynamic model *

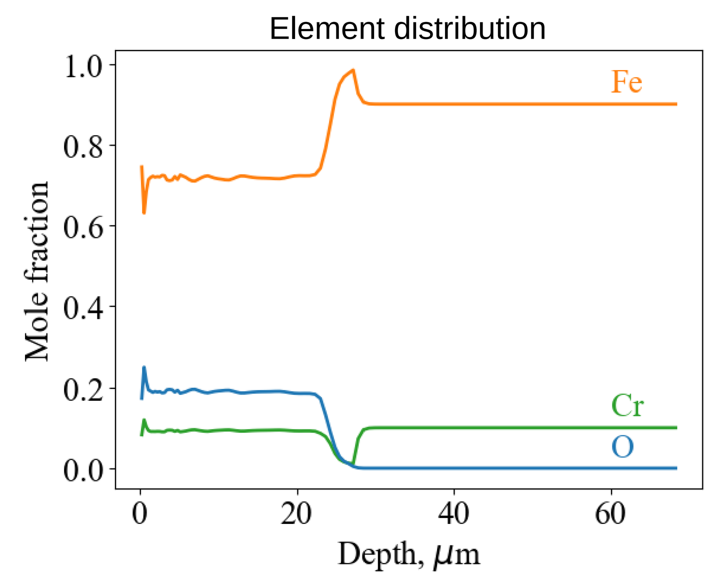
- Two steps: kinetic & thermodynamic
- Thermodynamic: coupling with ThermoCalc API
- Kinetic: in-house developed Fortran code, diffusion equation use chromium and oxygen content in metal phase
- Boundary condition: no flux of Cr, fixed concentration of dissolved oxygen on the surface
- Layer thicknesses: recalculated based on inward and outward fluxes in the layer

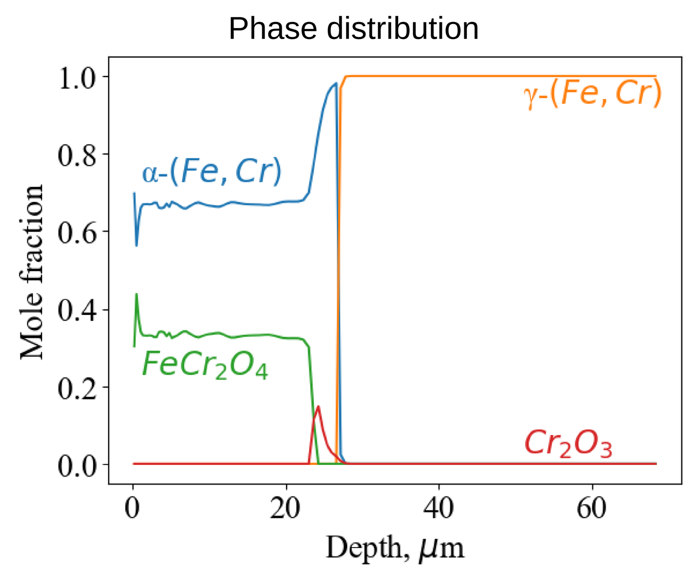


* R. Pillai et al., Materials at High Temperatures Vol. 32 No 1-1 (2015) 57-67

Model output

Fe-10Cr, 900°C, 24 hours

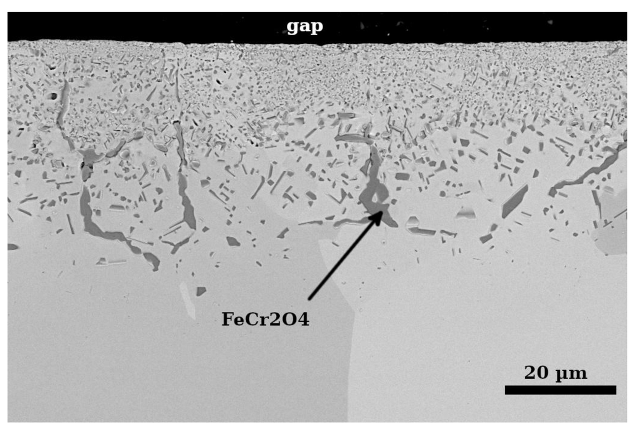


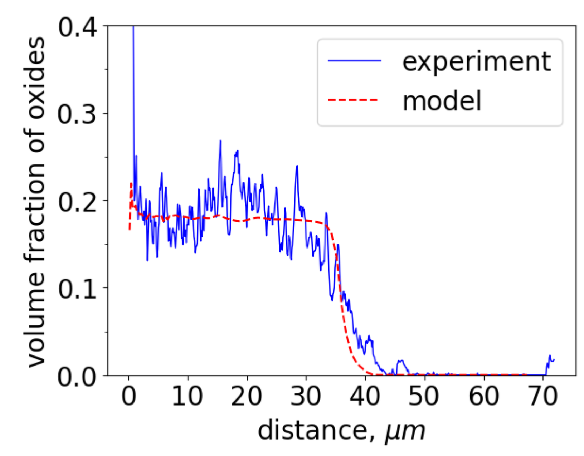


- Constant oxide fraction in all IOZ
- Chromium oxide formation on the boundary of IOZ

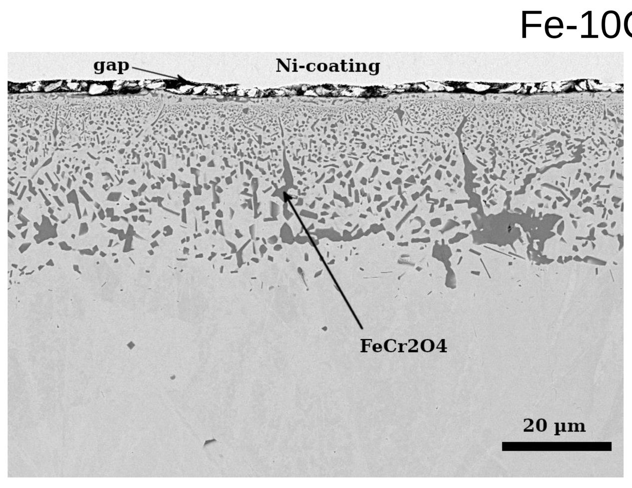
Oxidation test results

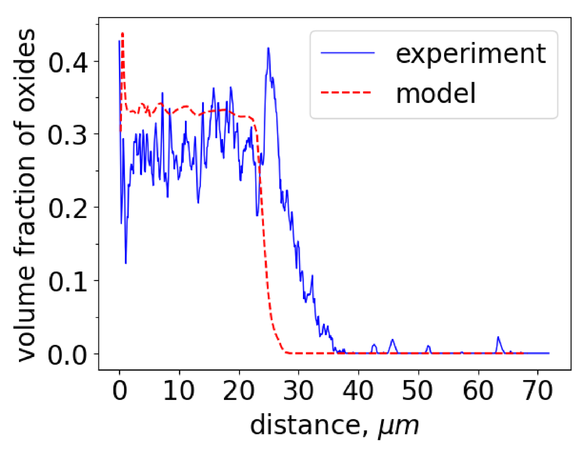
Fe-5Cr, 900°C, 24 hours





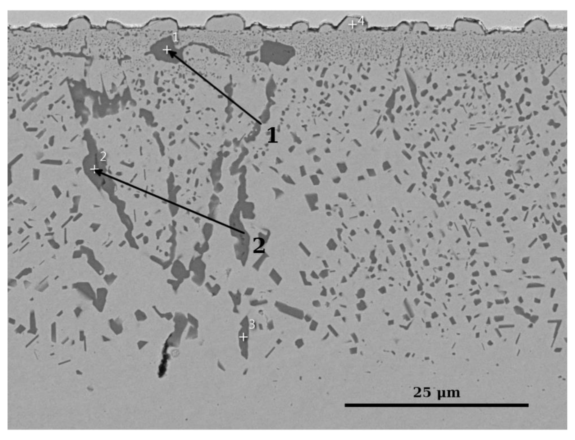
Fe-10Cr, 900°C, 24 hours





Good agreement between experimental and modelled depths of IOZ as well as volume fraction of oxides

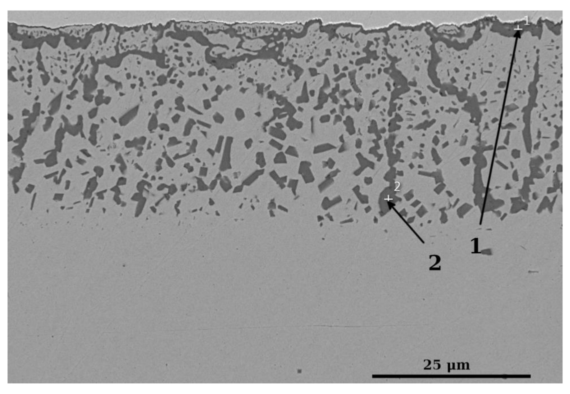
Fe-5Cr, 900°C, 24 hours



EDX analysis

Point	O, at.%	Cr, at.%	Fe, at.%
1	59.7	25.5	14.6
2	58.8	25.9	15.3

Fe-10Cr, 900°C, 24 hours

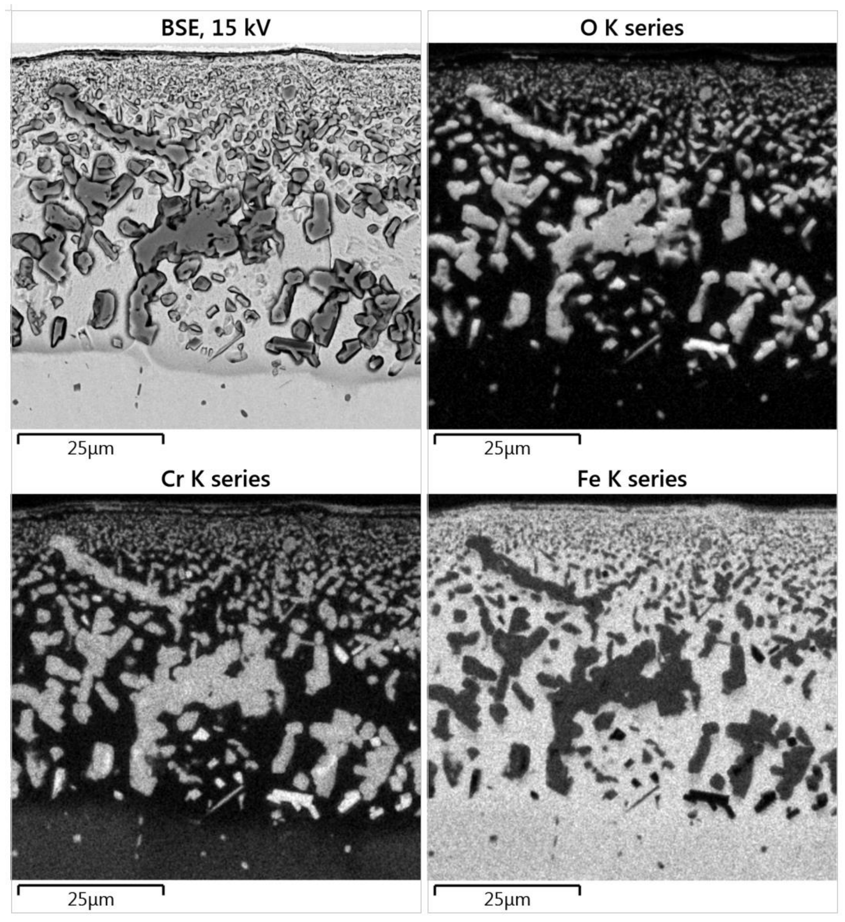


EDX analysis

Point	O, at.%	Cr, at.%	Fe, at.%
1	59.8	23.0	17.1
2	58.5	26.8	14.7

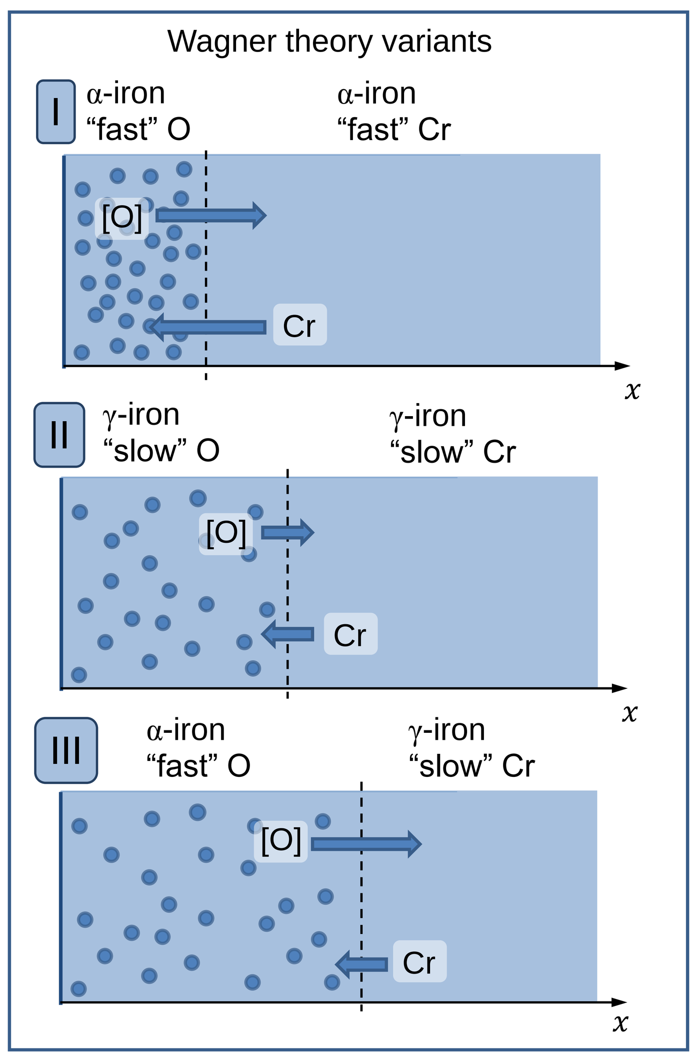
Spinel $FeCr_2O_4$ are main precipitates formed during internal oxidation process

Fe-10Cr, 900°C, 72 hours

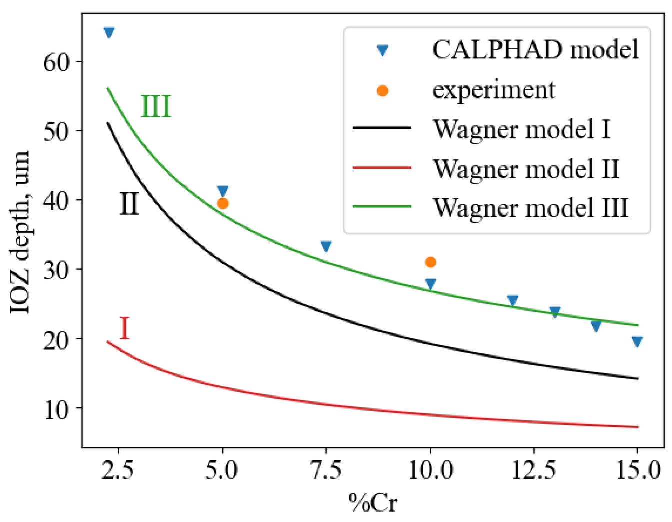


Chromia precipitates can be found near the boundary of IOZ as predicted by the model

Comparison to Wagner model

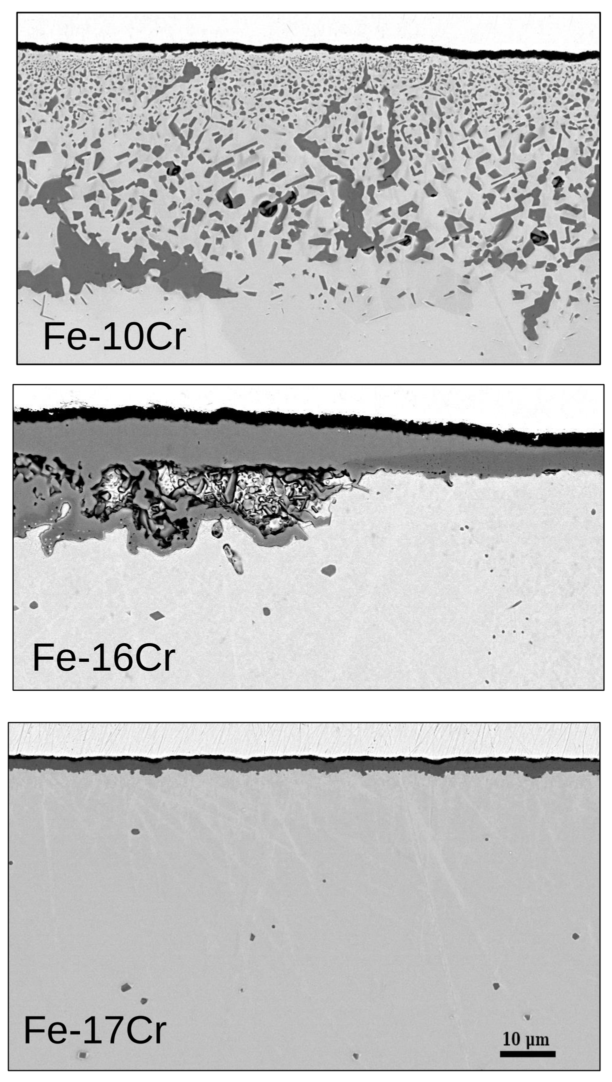


900°C, 24 hours



- Good agreement between experimental and CALPHAD-modelled depths of IOZ
- Good agreement between Wagner model type III and CALPHAD-model
- Linear approximation to zero IOZ depth gives 19-21 wt. %Cr content for transition to external oxidation, while continuous oxide layer formation experimentally observed at about 16-17 wt. %Cr

900°C, 72 hours



Conclusions & perspectives

- Thermodynamic-kinetic model describing inward diffusion of oxygen and inner oxidation in Fe-Cr alloys was developed considering oxide and metal phase transformations
- The model shows satisfactory agreement with experimental results and analytical Wagner solution assuming transformation of austenite to ferrite in internal oxidation zone
- Approximation of model predicts higher critical Cr content for transition from internal to external oxidation than observed in experiments, thus the model needs further reviewing and improvement for high Cr contents > 10%
- The model can be further updated for use for Fe-Cr alloys with additions of alloying elements (Mo, W,…) and lead to better understanding of oxidation behavior of commercial chromia-forming stainless steels
- 2D-model describing the growth of oxide precipitates as well as their size and number can be developed based on this model. This 2D-model may shed light on the mechanisms for continuous oxide layer formation from growing internal oxide precipitates and describe the transition between internal and external oxidation with higher accuracy

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