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OXIDATION OF ALLOYS

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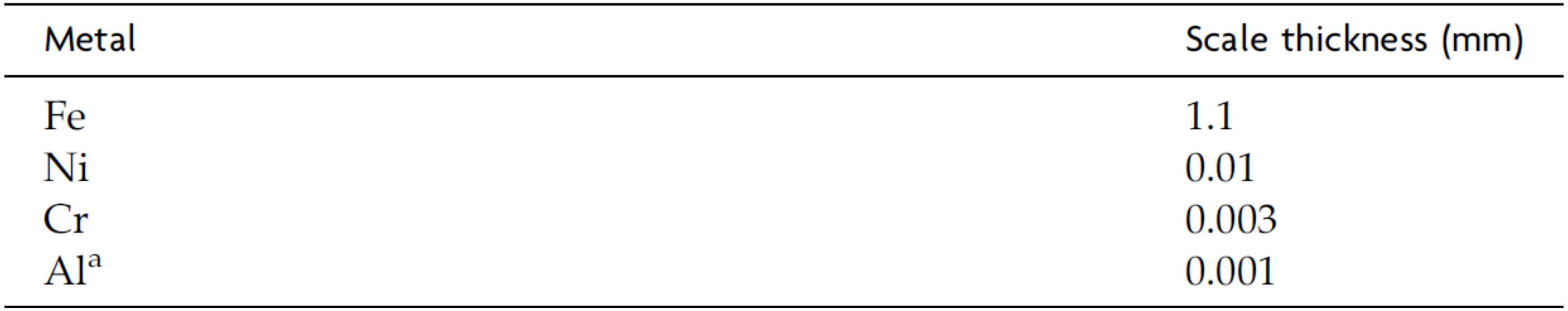
Literature

1. P. Kofstad, „High-Temperature Oxidation of Metals”, John Wiley & Sons, Inc, New York-London-Sydney, 1978.
2. S. Mrowec, Kinetyka i mechanizm utleniania metali, 1980.
3. S. Mrowec, „An Introduction to the Theory of Metal Oxidation”, National Bureau of Standards and the National Science Foundation, Washington, D.C., 1982.
4. A.S. Khanna, „Introduction to High Temperature Oxidation and Corrosion”, ASM International, Materials Park, 2002.
5. Wei Gao and Zhengwei Li ”Developments in high-temperature corrosion and protection of metals”, Ed, Woodhead Publishing Limited, Cambridge, England, 2008.
6. N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.
7. R. Cottis, M. Graham, R. Lindsay, S. Lyon, J. Richardson, J. Scantlebury, F. Stott, „Basic Concepts, High Temperature Corrosion, tom I” w „Shreir’s Corrosion”, Elsevier, Amsterdam, 2010.
8. D. J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2016.

Problems

1. Oxidation of alloys containing noble metals
2. Internal oxidation
3. Oxidation of two-component alloys
4. Oxidation of multi-component alloys

Thicknesses of scales formed on selected metals during their oxidation for 100 h at 800 °C in oxygen



Metal	Scale thickness (mm)
Fe	1.1
Ni	0.01
Cr	0.003
Al[a]	0.001

a – measured on Al-50%Ni

David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008

Oxidation process of the Ni-Pt alloys

- nickel with platinum create a substitutional solid solution in the entire concentration range (>800 K)
- during nickel oxidation only one oxide (NiO) is formed with low defect concentration

Basic assumptions of Wagner’s oxidation theory of two-component alloys containing a noble metal:

- mutual diffusion coefficients in the alloy are not dependent on component concentrations
- throughout the entire oxidation process there is a thermodynamic equilibrium state at the alloy-scale interface

Model characteristics of the Ni-Pt alloy oxidation process

Wagner derived an analytical equation that enables the calculation of nickel concentration in the alloy, above which the rate limiting step of the oxidation reaction is outward nickel diffusion in NiO. In these conditions, the alloy oxidation rate practically does not depend on the alloy composition and is the same as the nickel oxidation rate.
In the case of nickel concentration lower than the critical value, the oxidation process is determined by nickel diffusion in the alloy, and the oxidation rate is lower than that of pure nickel and decreases along with nickel concentration.

$$N_{Ni}^{alloy} = \frac{V_m}{V_{NiO}} \left(\frac{\pi k_p}{2\tilde{D}} \right)^{1/2}$$

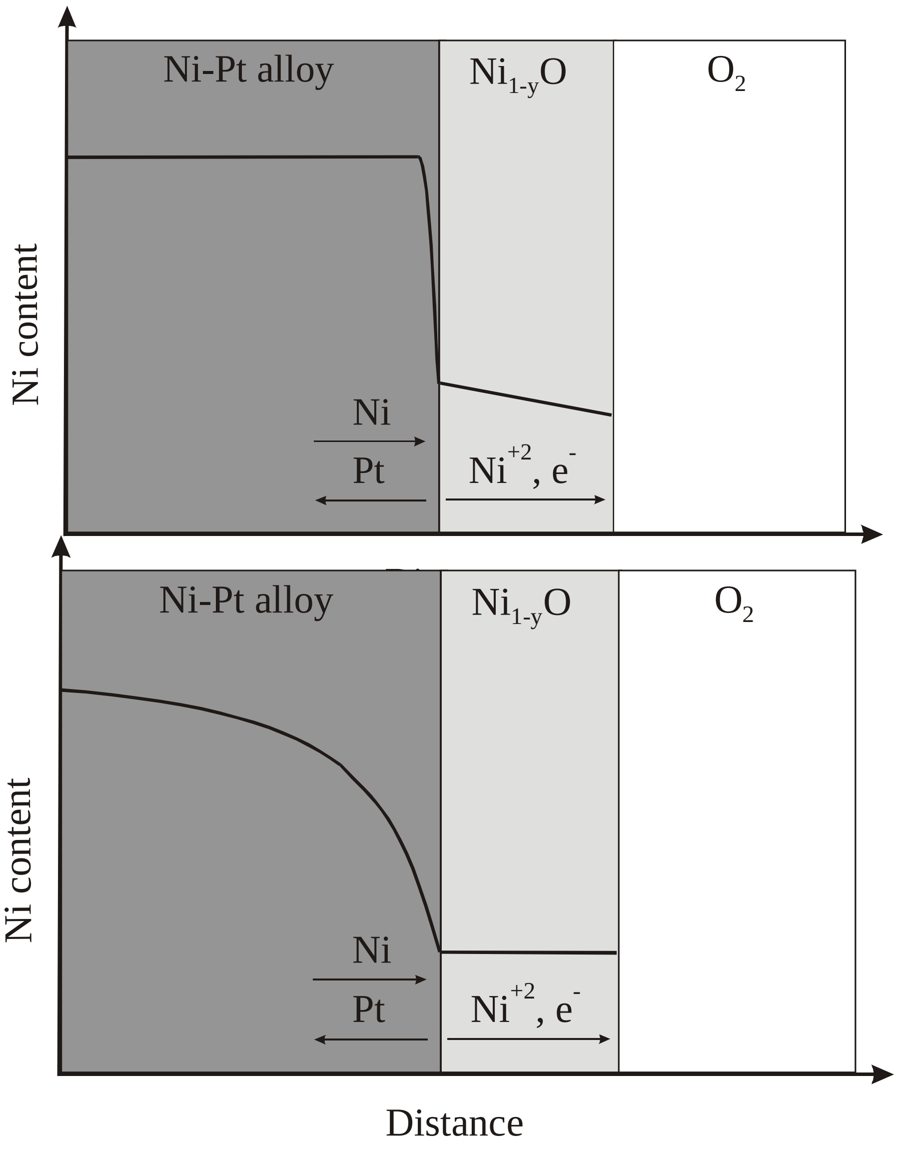
N_{Ni}^{alloy} – nickel concentration in the alloy, V_m – molar volume of the alloy,

k_p – parabolic oxidation rate constant,

$\tilde{D}$ – diffusion coefficient of nickel in the alloy

David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2016

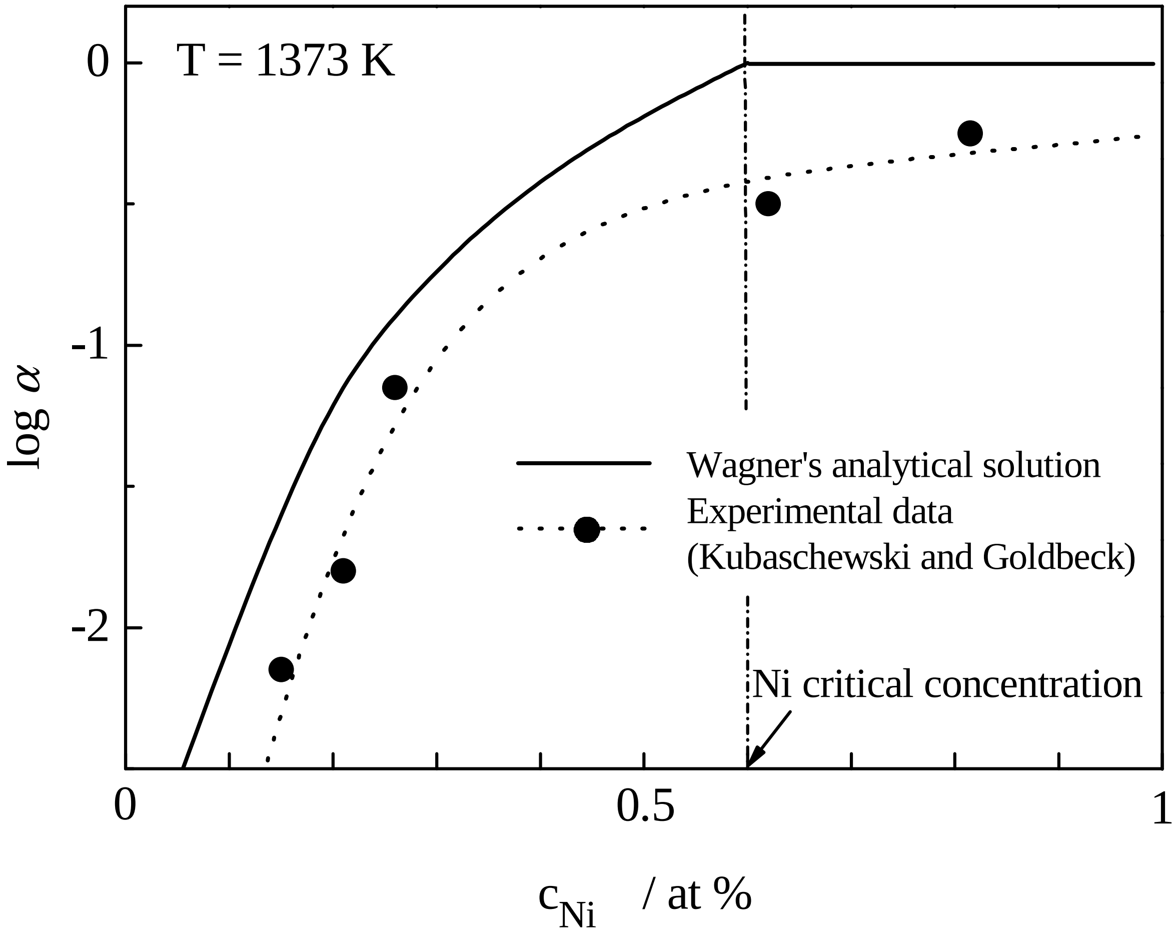
Schematic illustration of diffusion processes present during oxidation of Ni-Pt alloys



Case I:
The oxidation process is determined by nickel diffusion in NiO.

Case II:
The oxidation process is determined by mutual diffusion of the alloying components inside the Ni-Pt alloy.

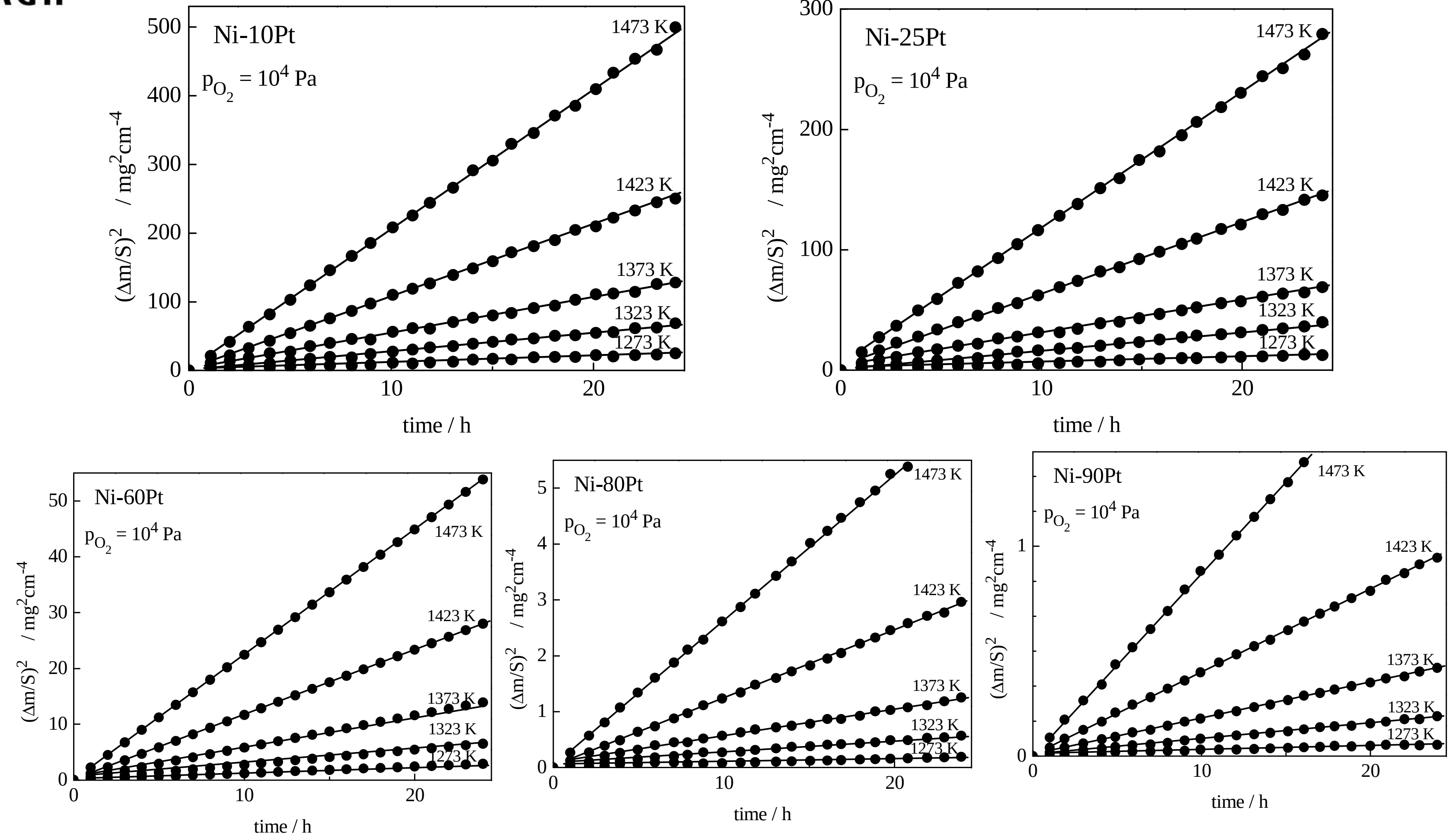
Comparison between calculated oxidation rates of Ni-Pt alloys with experimental data



α - ratio between the parabolic oxidation rate constant of the alloy and pure nickel

O. Kubaschewski and von Goldbeck, J. Inst. Metals 76 (1949) 255

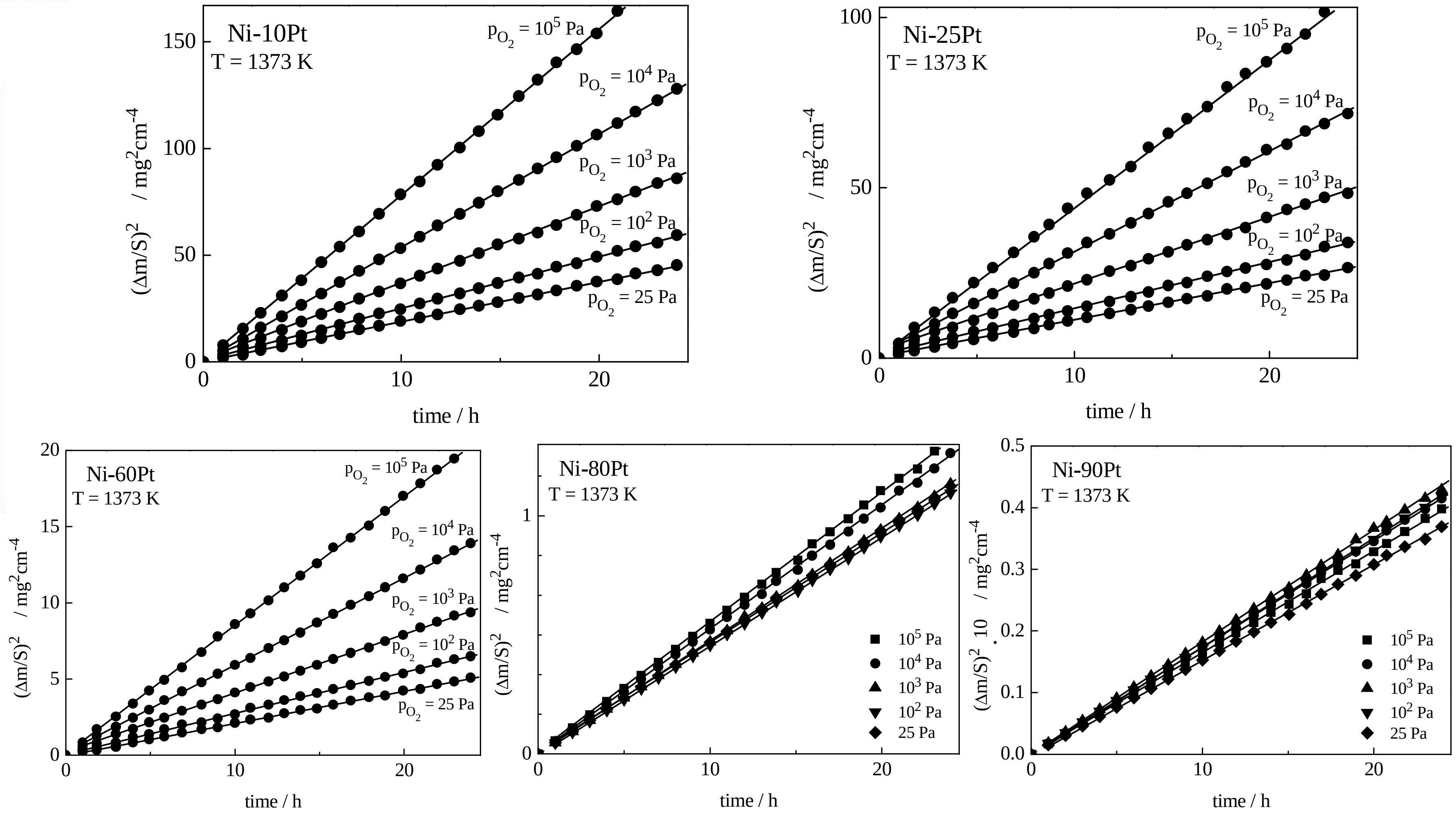
Oxidation kinetics of Ni-Pt alloys



Conclusion: Ni-Pt alloys oxidize according to the parabolic rate law

M. Danielewski, Z. Grzesik, S. Mrowec, Corrosion Science, 53, 2785-2792 (2011)

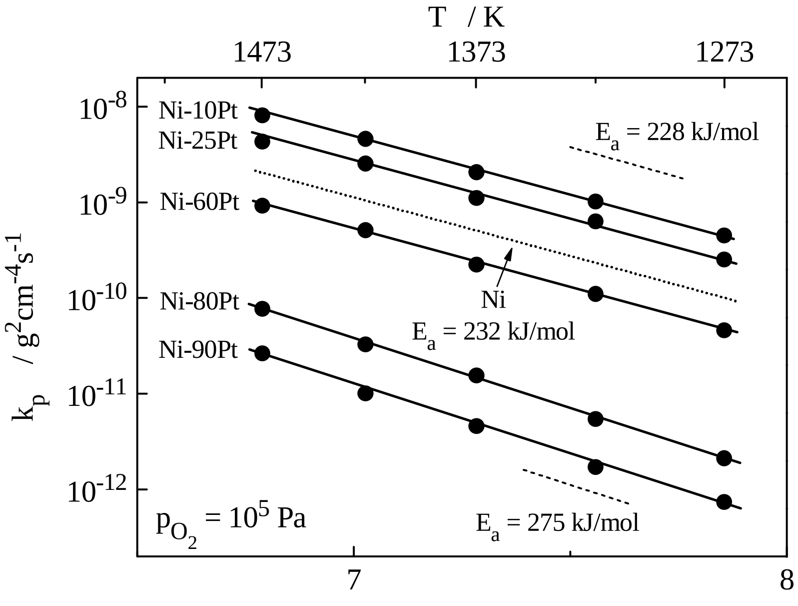
Oxidation kinetics of Ni-Pt alloys

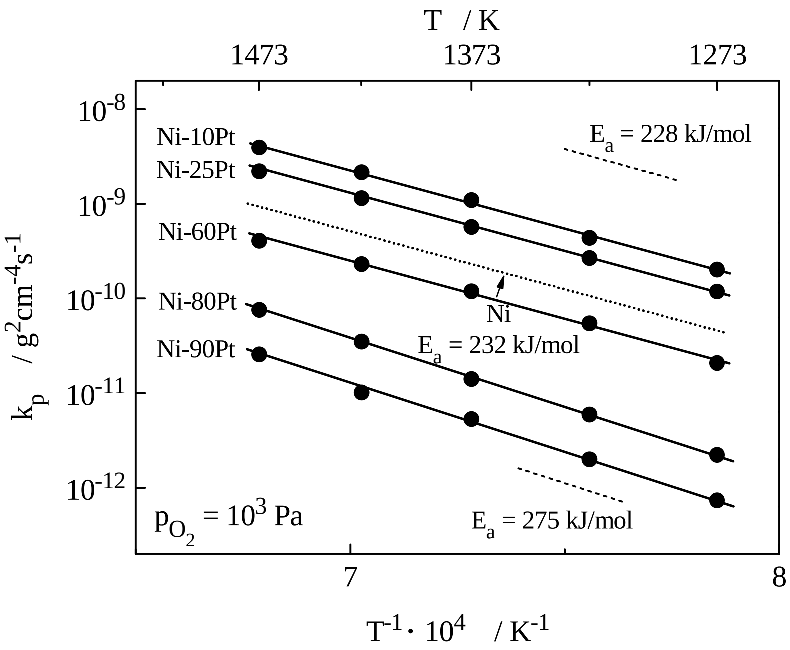


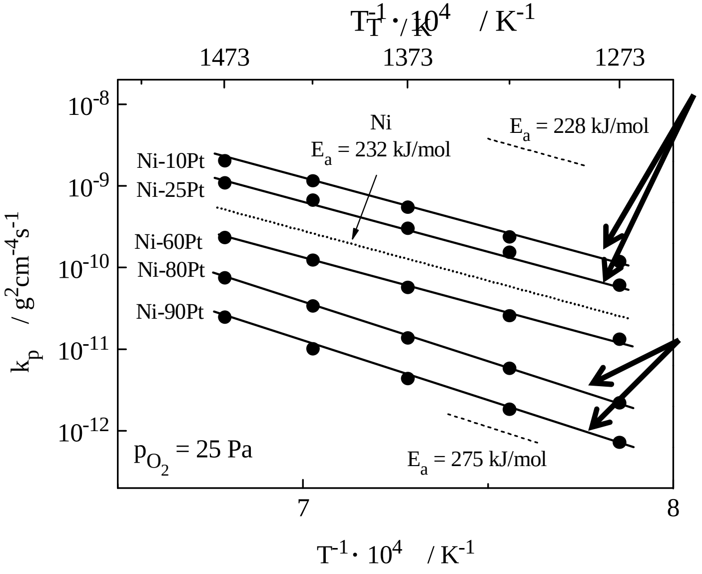
Conclusion: the oxidation process of Ni-Pt alloys exhibits a complex pressure dependence

M. Danielewski, Z. Grzesik, S. Mrowec, Corrosion Science, 53, 2785-2792 (2011)

Temperature dependence of Ni-Pt alloy oxidation rates







E_a (Pt-Ni) = 228 kJ/mol

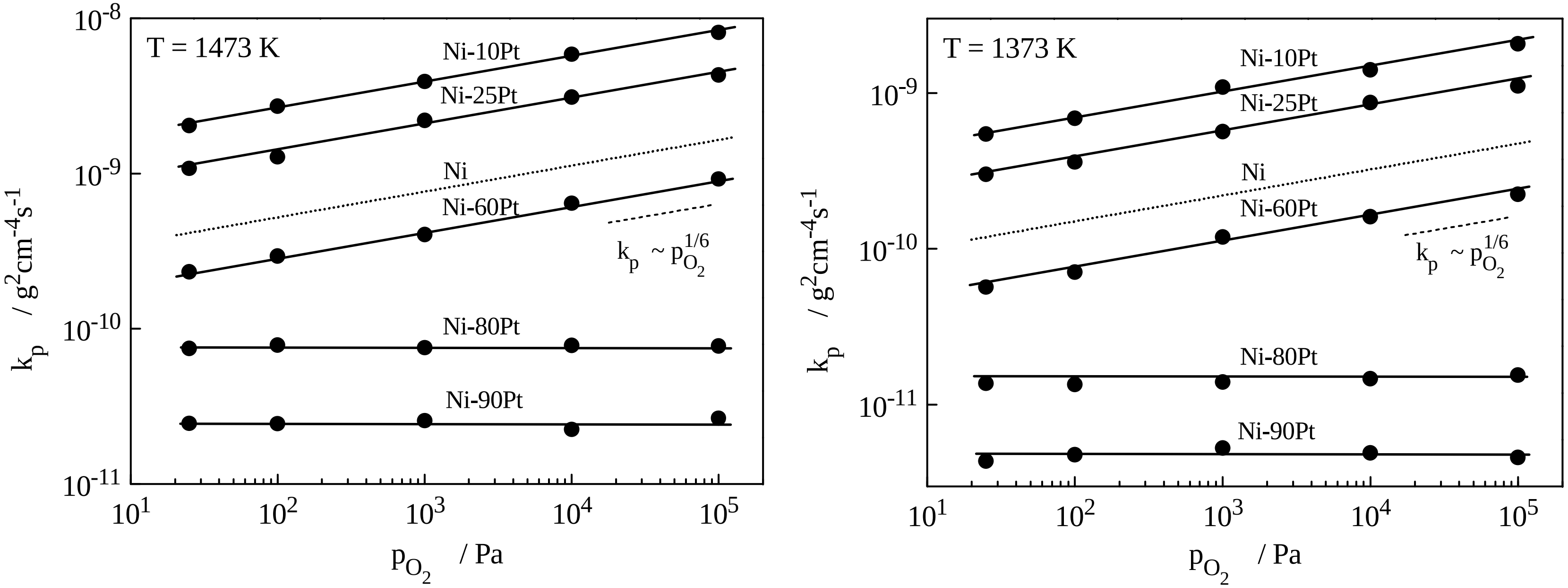
E_a (Ni) = 232 kJ/mol

E_a (Pt-Ni) = 275 kJ/mol

E_a (D_{inter}, Pt-Ni) = 280 kJ/mol

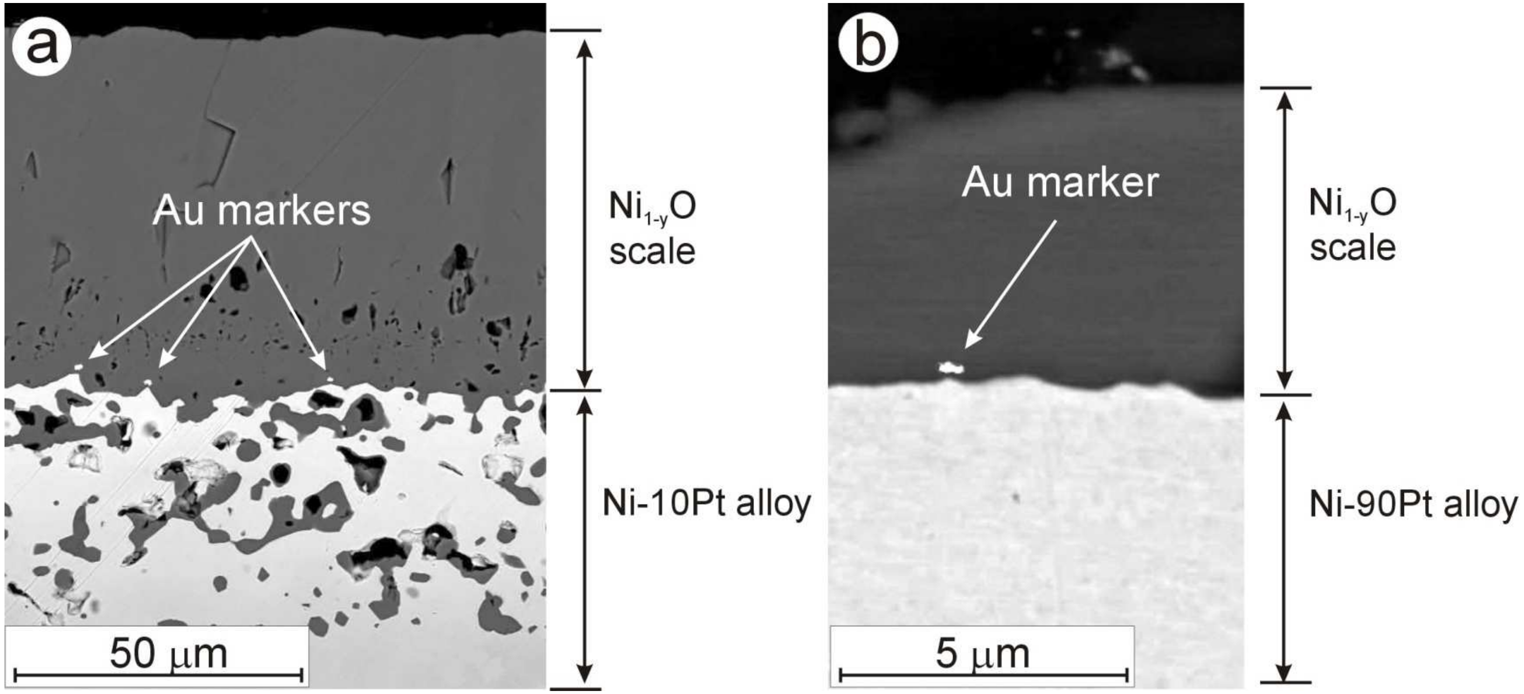
M. Danielewski, Z. Grzesik, S. Mrowec, Corrosion Science, 53, 2785-2792 (2011)

Pressure dependence of Ni-Pt alloy oxidation rates



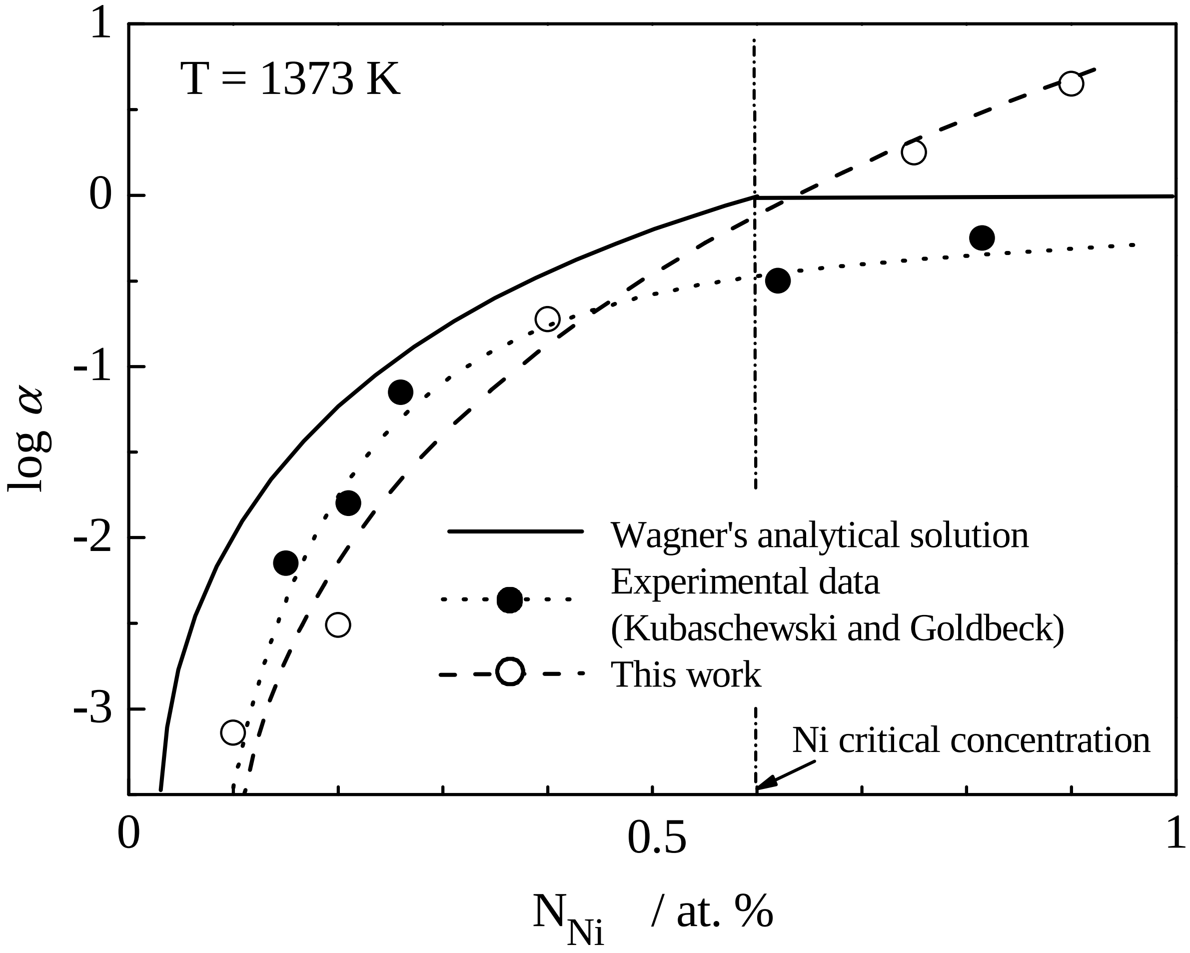
M. Danielewski, Z. Grzesik, S. Mrowec, Corrosion Science, 53, 2785-2792 (2011)

Cross-section of the oxide scale on Ni-Pt alloys with an indicated marker location (1273 K)



M. Danielewski, Z. Grzesik, S. Mrowec, Corrosion Science, 53, 2785-2792 (2011)

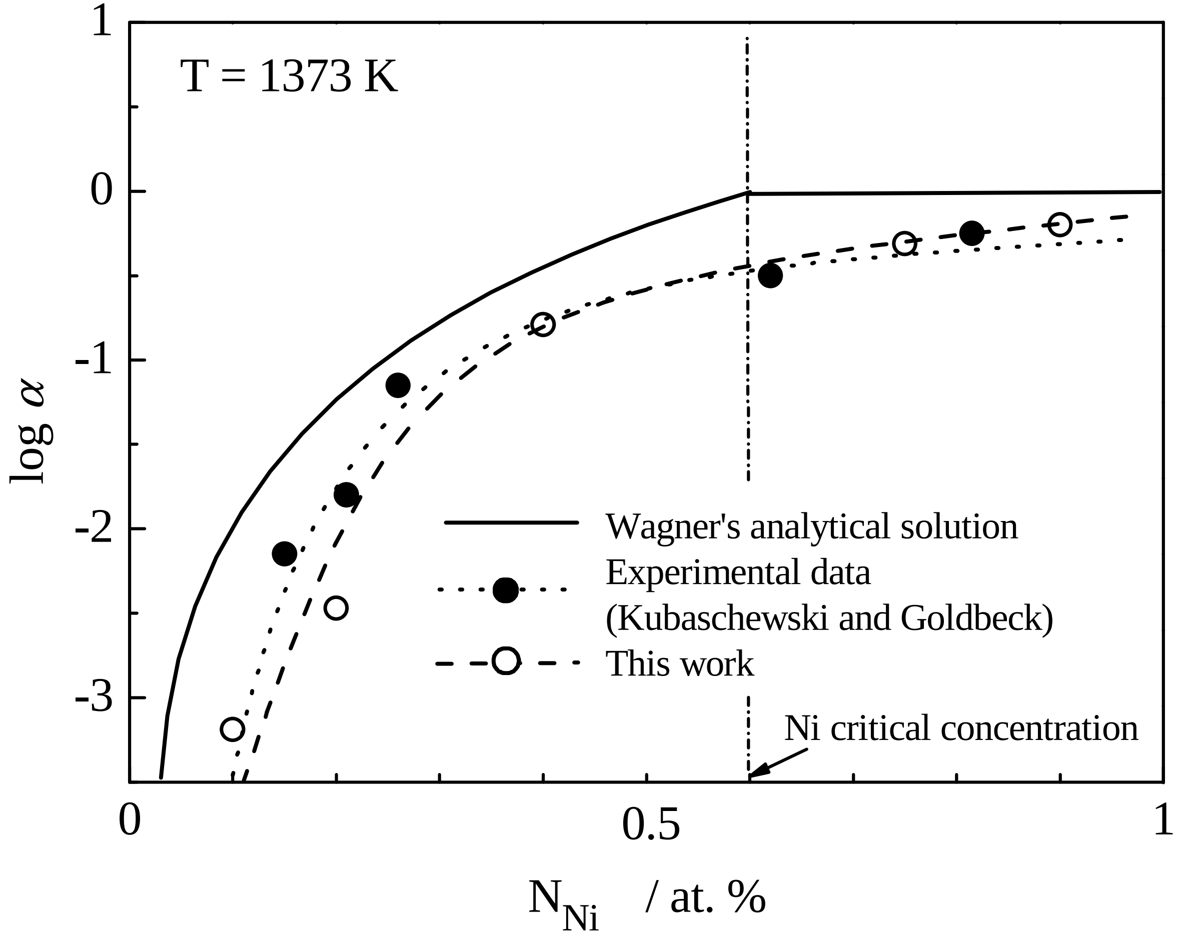
Comparison between calculated oxidation rates of Ni-Pt alloys and experimental data



NOTE: White indicators pertain to thermogravimetric results, which encompasses the internal oxidation zone.

M. Danielewski, Z. Grzesik, S. Mrowec, Corrosion Science, 53, 2785-2792 (2011)

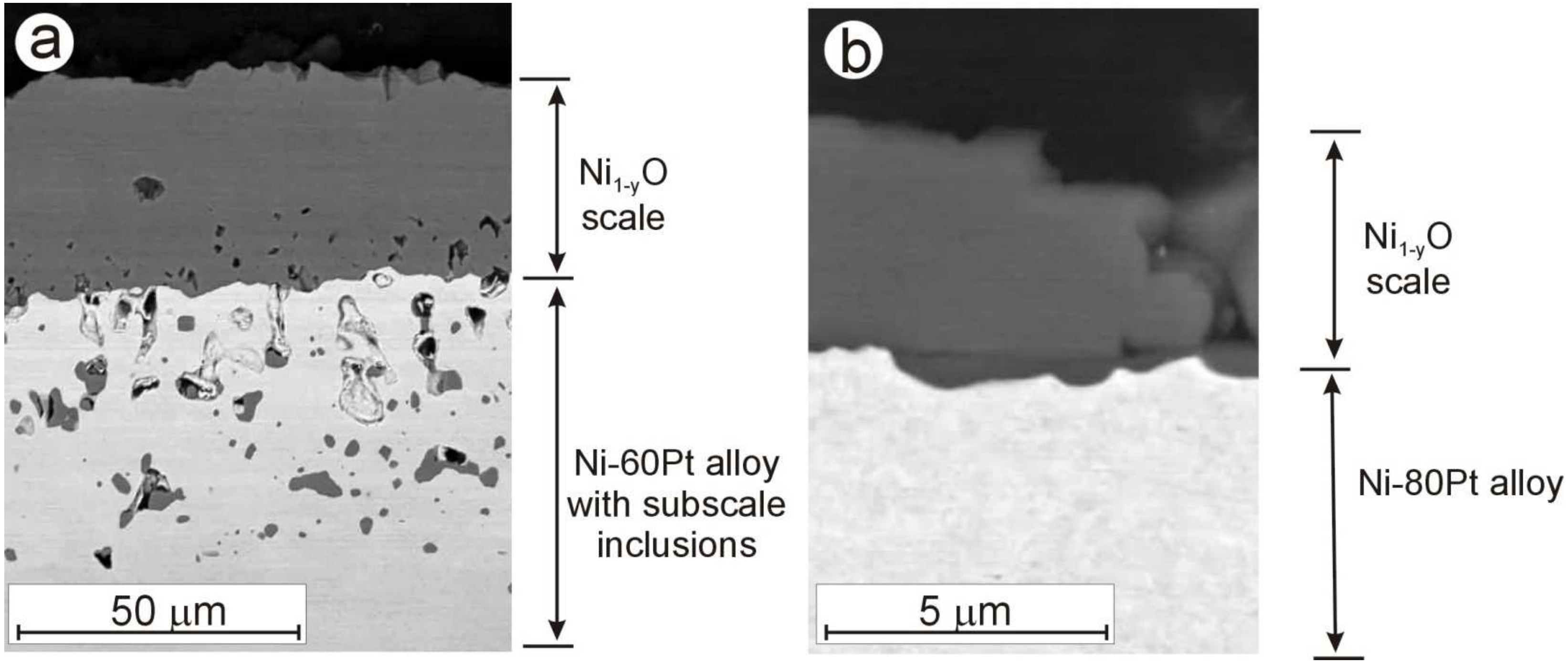
Comparison between calculated oxidation rates of Ni-Pt alloys and experimental data



NOTE: White indicators pertain to scale thickness measurements, and thus do not encompass the internal oxidation zone.

M. Danielewski, Z. Grzesik, S. Mrowec, Corrosion Science, 53, 2785-2792 (2011)

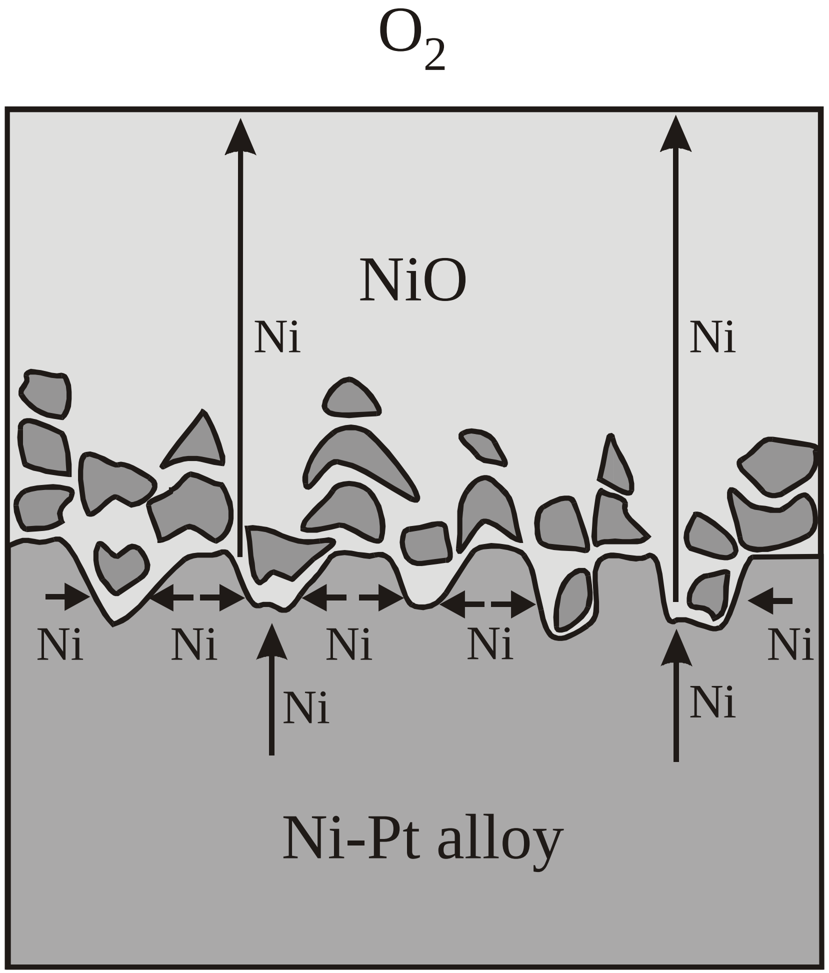
Cross-section of the oxide scale on Ni-Pt alloys obtained at 1373 K



The lack of an internal oxidaiton zone for Ni-Pt alloys with low nickel content is due to the low nickel concentration gradient both in the scale and in the alloy.

M. Danielewski, Z. Grzesik, S. Mrowec, Corrosion Science, 53, 2785-2792 (2011)

Schematic illustration of the morphology of a heterophase scale grown on Ni-Pt alloys in the case of an unstable alloy-scale interface



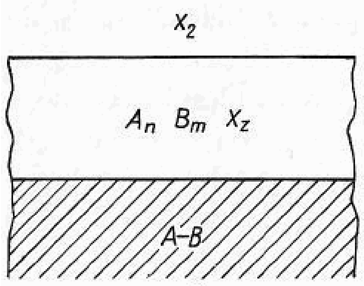
Necessary condition for predicting oxide scale morphology on two-component alloys with a noble metal

$$f = \frac{n_{Ni}^{o}}{1 - n_{Ni}^{o}} \cdot \frac{\dfrac{D}{V_{alloy}}}{\dfrac{D_{Ni}}{V_{NiO}}}$$

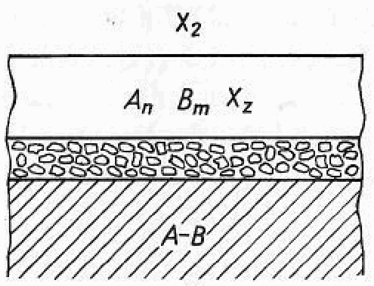
f – parameter decribing the homogeneity of the scale,
n_{Ni}^{o} – molar fraction of nickel on the alloy-scale interface,
D – coefficient of mutual diffusion in the alloy,
D_{Ni} – self-diffusion coefficient of cations in NiO,
V_{alloy} and V_{NiO} – molar volumes of nickel in the alloy and NiO, respectively.

f > 1 means the formation of a single phase scale with a flat alloy-scale interface. f < 1 means the formation of a dual phase scale with an unstable alloy-scale interface.

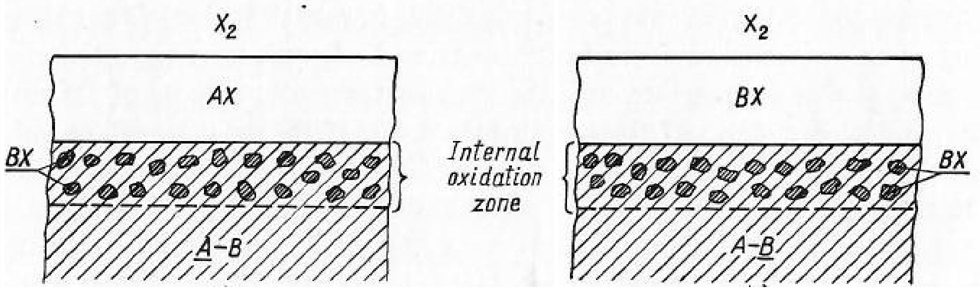
Types of scales formed on alloys

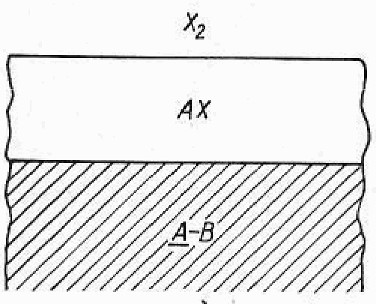


initial stage

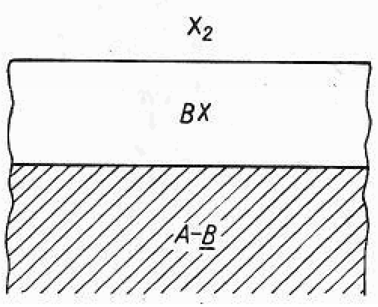


stacionary stage

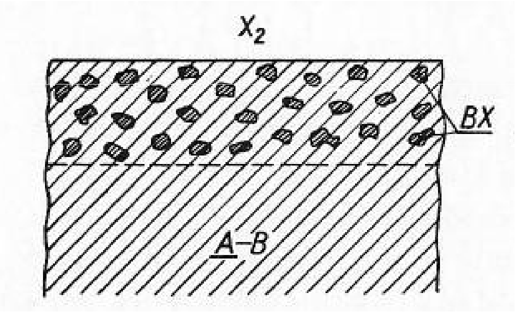


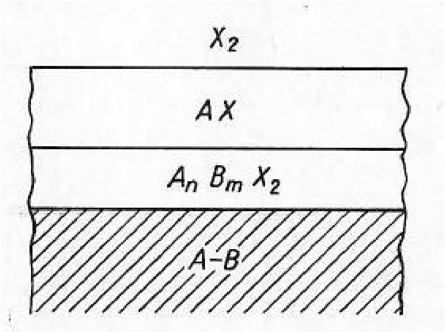


alloy rich in A



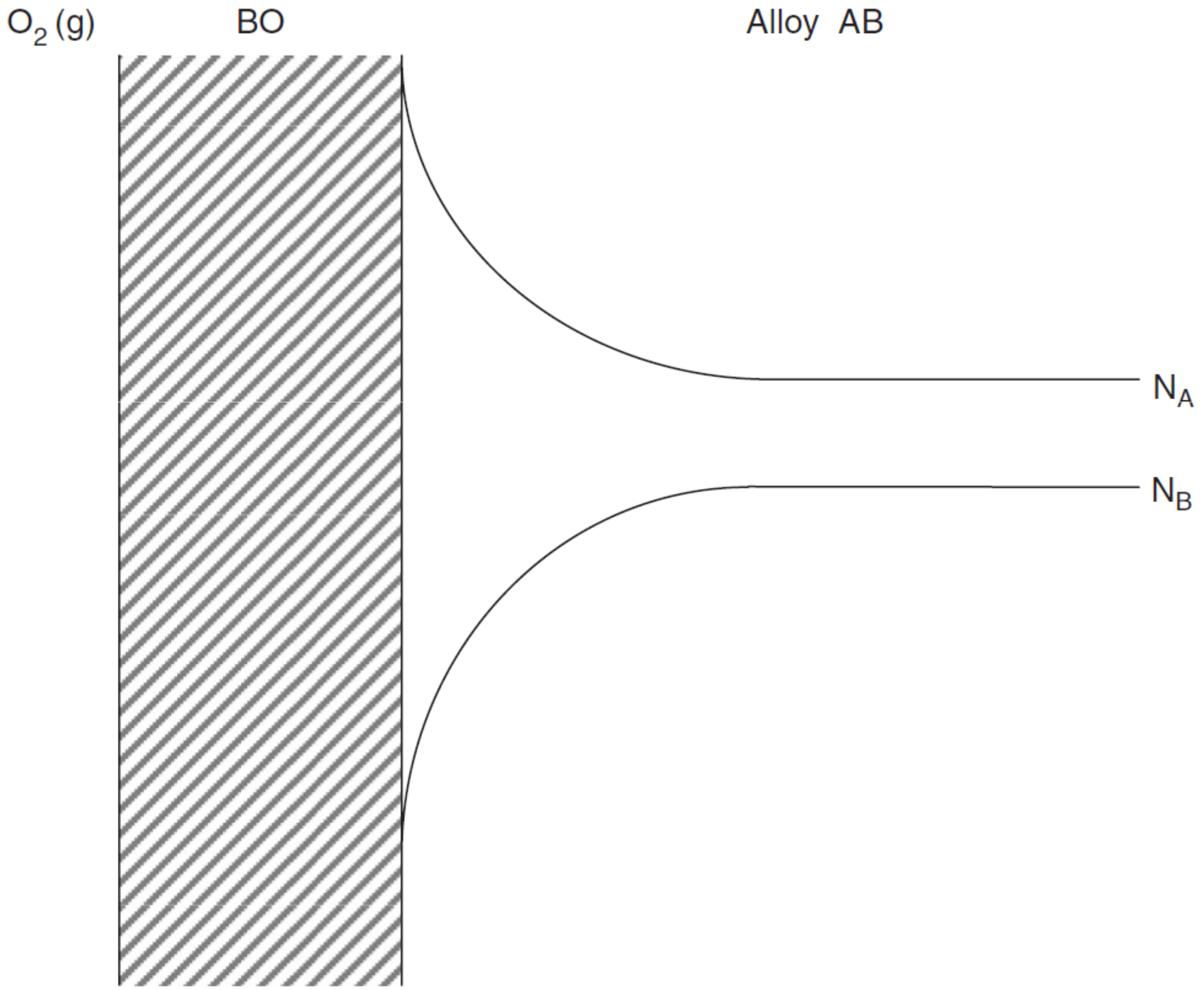
alloy rich in B





S. Mrowec, „An Introduction to the Theory of Metal Oxidation”, Washington, D.C., 1982

Concentration distribution of components of AB alloy during selective oxidation of component B



David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008.

Internal oxidation

Internal oxidation – process of oxidation product formation in the alloy as a result of inward oxygen diffusion and its reaction with a certain component/components of the alloy.

The internal oxidation zone can be in direct contact with the reaction atmosphere (no scale) or isolated from the gas environment by a scale.

Due to the neglibile solubility of most oxidants (e.g. sulfur and chlorine) in a metallic phase, the internal oxidation process mostly proceeds due to reactions with oxygen.

Necessary conditions for internal oxidation to take place in single phase two-component alloys, according to Rapp

1. ΔG of alloying element oxide formation should be lower than that for a base metal, where the metal is on the lowest oxidation state.
2. ΔG of the reaction between oxygen dissolved in the metallic phase and the alloying element B located inside the phase must have a negative value.
3. Concentration of the alloying element dissolved in the base metal should be lower than the limit concentration necessary for formation of a continuous layer of the alloying element oxide on the alloy surface.
4. The surface layer of an alloy, which due to thermal or chemical treatment has different properties than the interior of the material, should be inhibit oxygen dissolution.

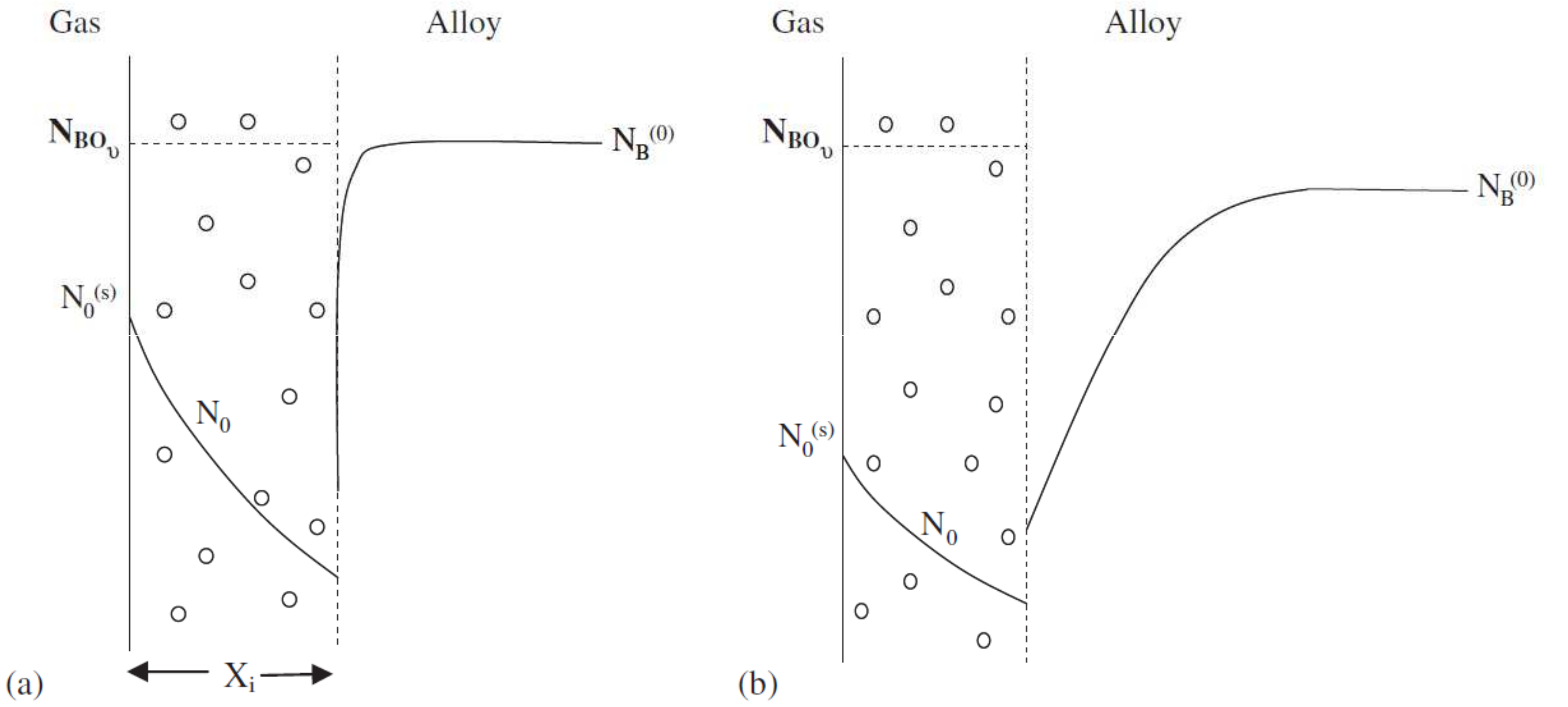
Thickness of the internal oxidation zone and the rate of its formation

$$x = k_p \cdot t = \left(\frac{2\, N_O\, D_O\, t}{m\, N_B^o} \right)^{1/2}$$

$$\frac{dx}{dt} = \left(\frac{N_O\, D_O}{2\, m\, N_B^o} \right)^{1/2}$$

x – thickness of the internal oxidation zone
D_O – oxygen diffusion coefficient in the base metal A
t – reaction time
N_O – oxygen concentration in the subsurface layer of the alloy
N_B^o – initial concentration of metal B in the alloy
m – ratio of oxygen to metal atoms in the internal oxide, BO_m

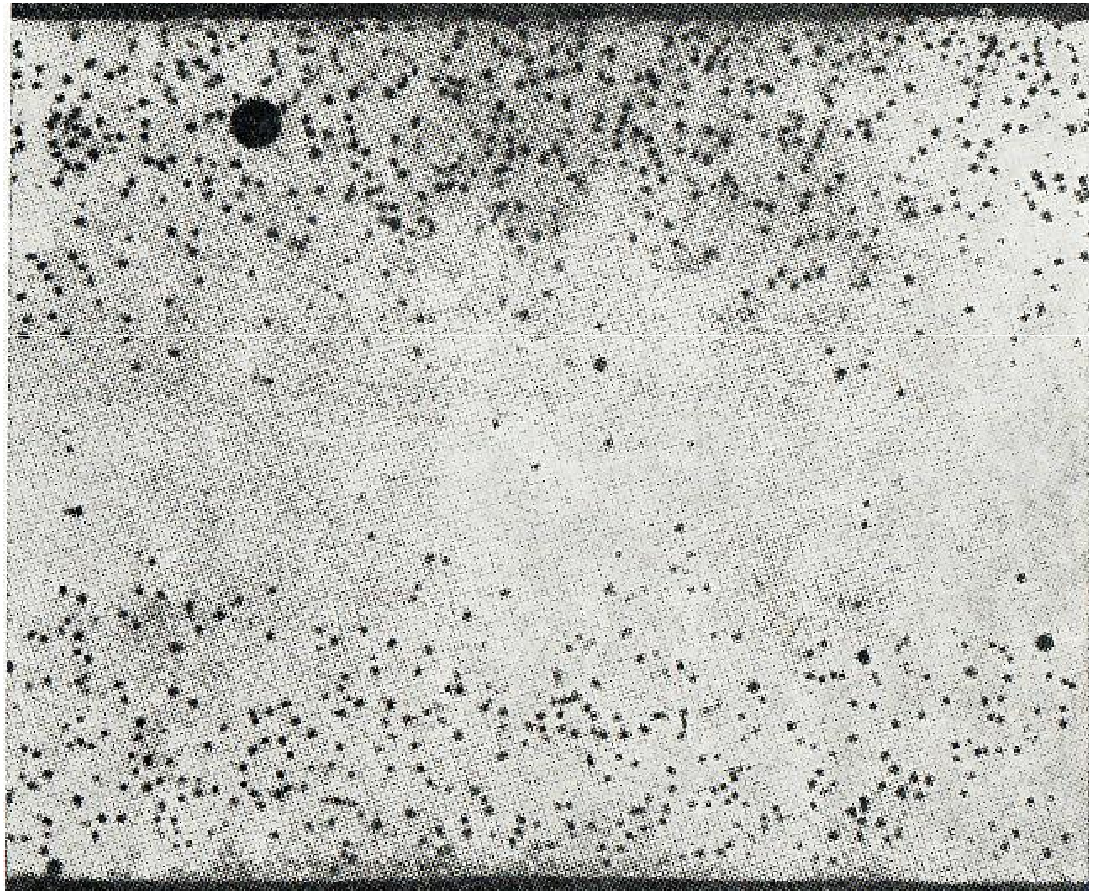
Concentration distribution of alloying element B inside a non-oxidized alloy and in the internal oxidation zone, when there is no scale



a) oxygen diffusion in the alloy is much faster than metal B diffusion in the alloy
b) oxygen diffusion and metal B diffusion rates in the alloy are comparable

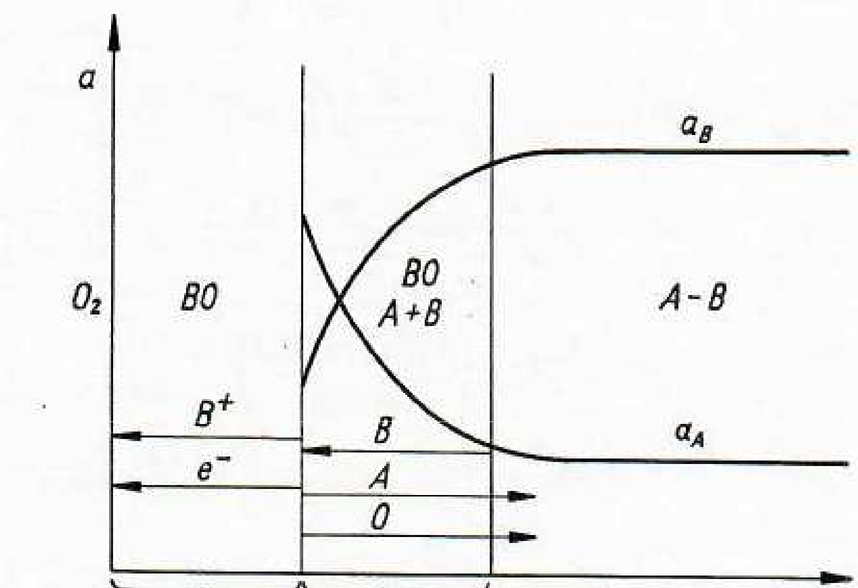
David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008.

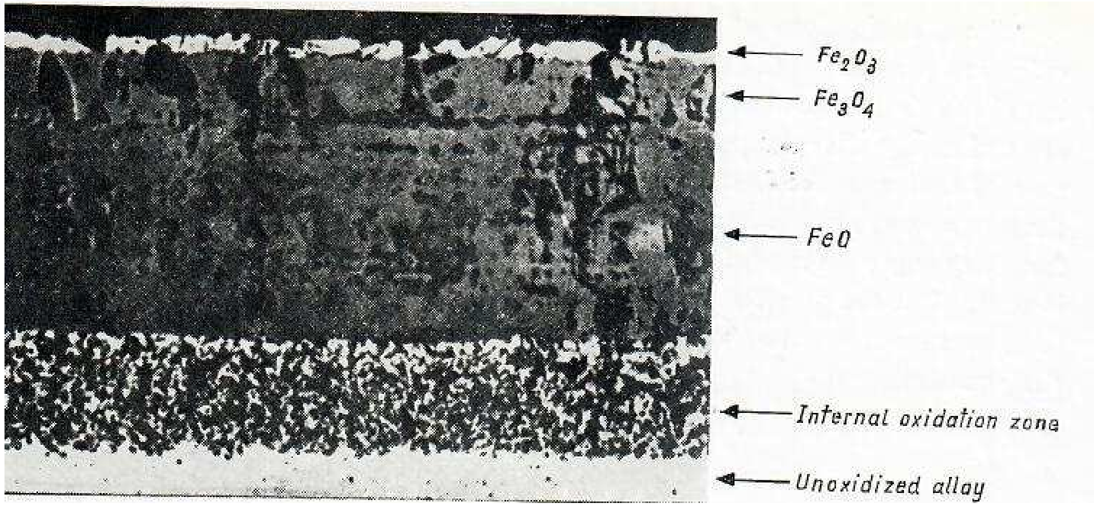
Picture of the morphology of oxidized Fe-0,235%Si alloy in conditions that make FeO formation impossible



S. Mrowec, „An Introduction to the Theory of Metal Oxidation”, Washington, D.C., 1982

Scheme of diffusion processes in the scale and alloy AB, based on metal B and the cross-section of an oxided Fe-3%Ni alloy sample





S. Mrowec, „An Introduction to the Theory of Metal Oxidation”, Washington, D.C., 1982

Oxidation of two-component alloys based on nickel, iron and cobalt

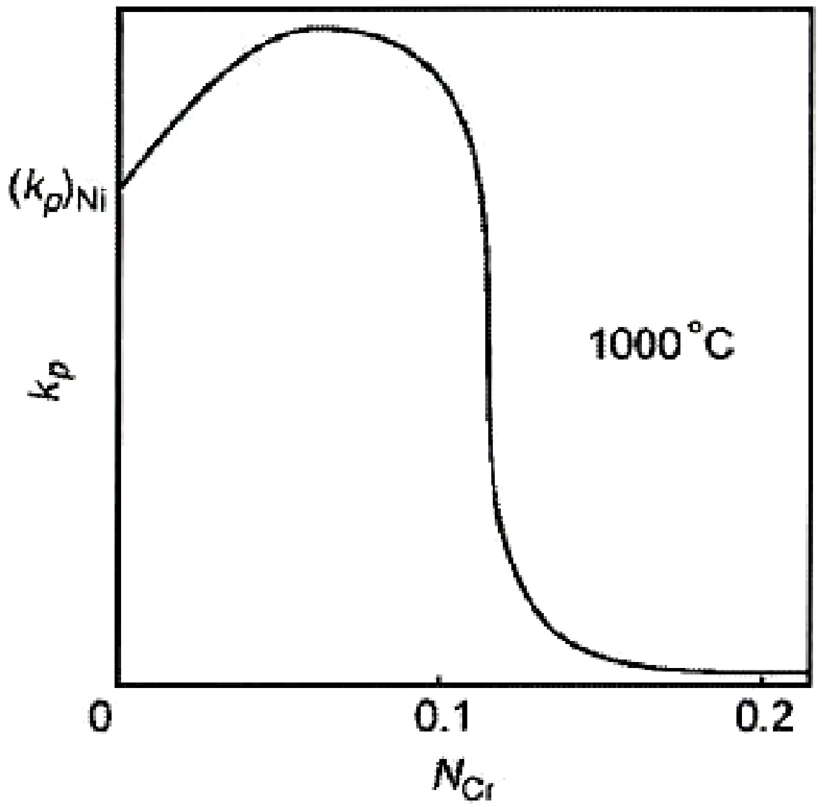
Two-component alloys containng nickel, iron and cobalt constitute the basis for several multiphase commercial alloys that cover themselves during oxidation with stable oxides exhibiting good and excellent protective properties. From the point of view of high scaling-resistance of these materials, the main alloying elements are: chromium, aluminum and silicon, responsible for forming: Cr_2O_3, Al_2O_3 and SiO_2. Alloys, on the surface of which these oxides grow, are called: *chromia formers*, *alumina formers* and *silica formers*, respectively.

The content of each alloying element, required for forming and ensuring a stable growth of a protective oxide layer, is:

Cr_2O_3 – 20 % wt. Cr
Al_2O_3 – 5 % wt., with simultaneous 20 % wt. Cr content
SiO_2 – from 1 % wt.

Ni-Cr alloy oxidation

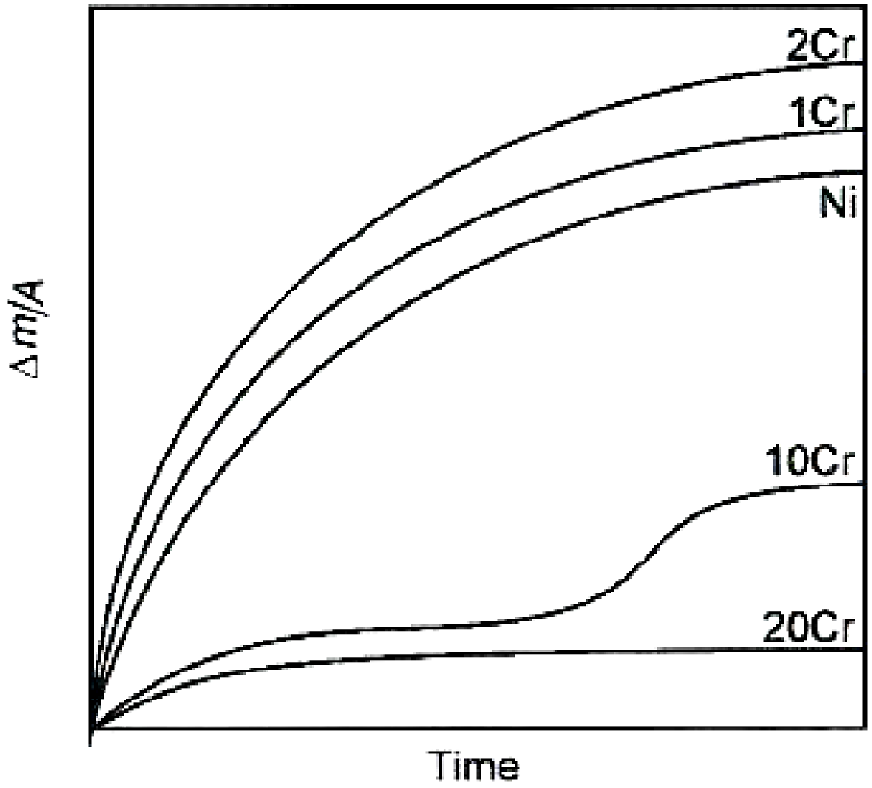
Schematic dependence of the oxidation rate of Ni-Cr alloys on chromium content



N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

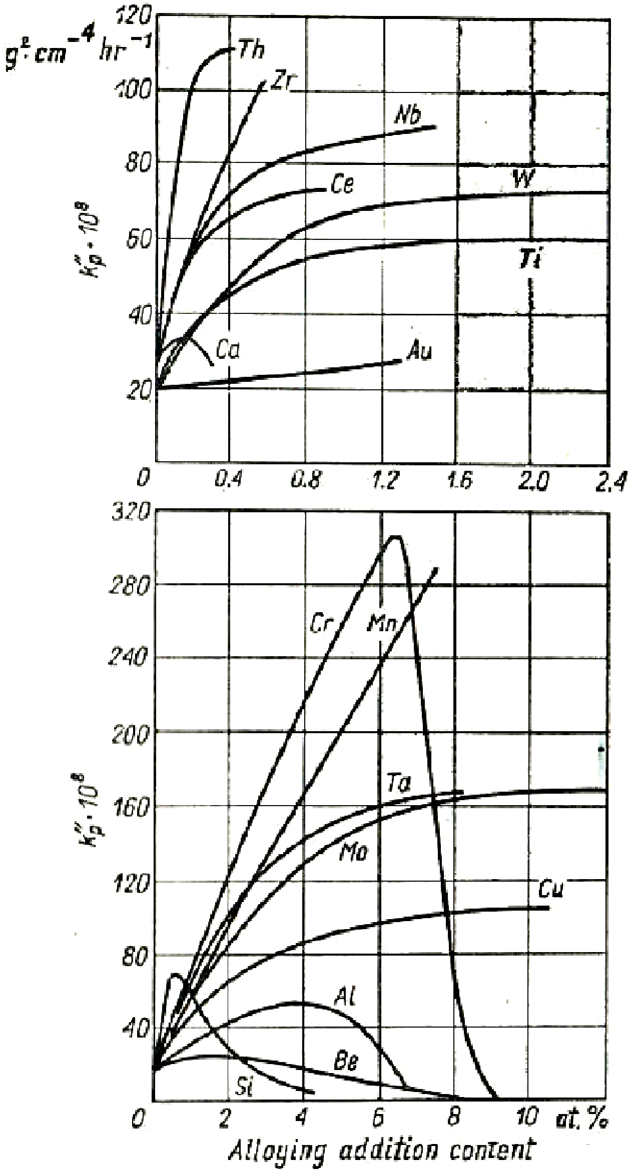
Ni-Cr alloy oxidation

Schematic procedure of the oxidation kinetics of Ni-Cr alloys with different chromium contents



N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

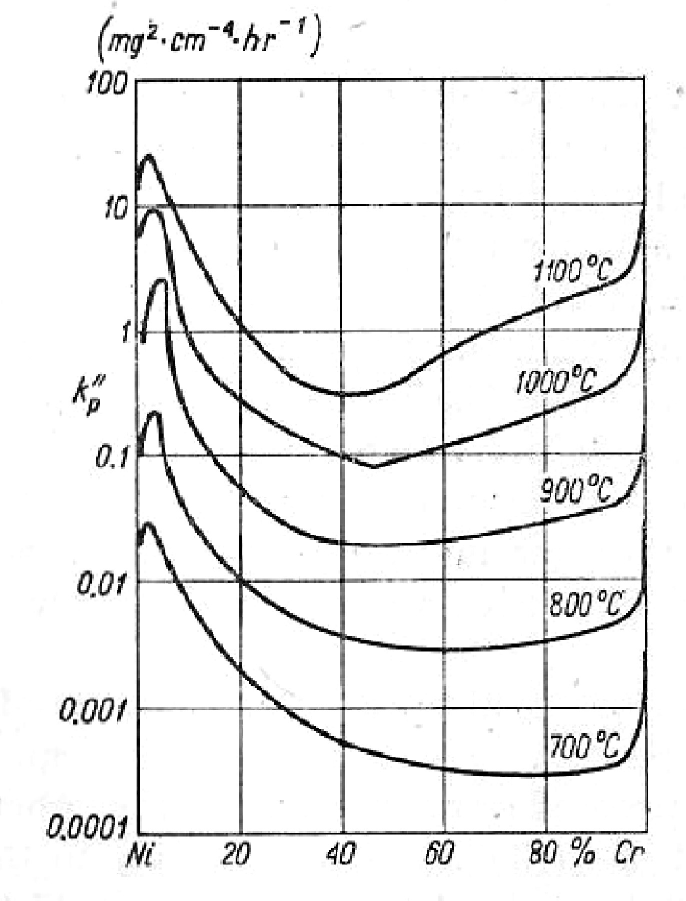
Influence of alloying elements on nickel oxidation kinetics



S. Mrowec and T. Werber, Modern Scaling-Resistant Materials, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.

Ni-Cr alloy oxidation

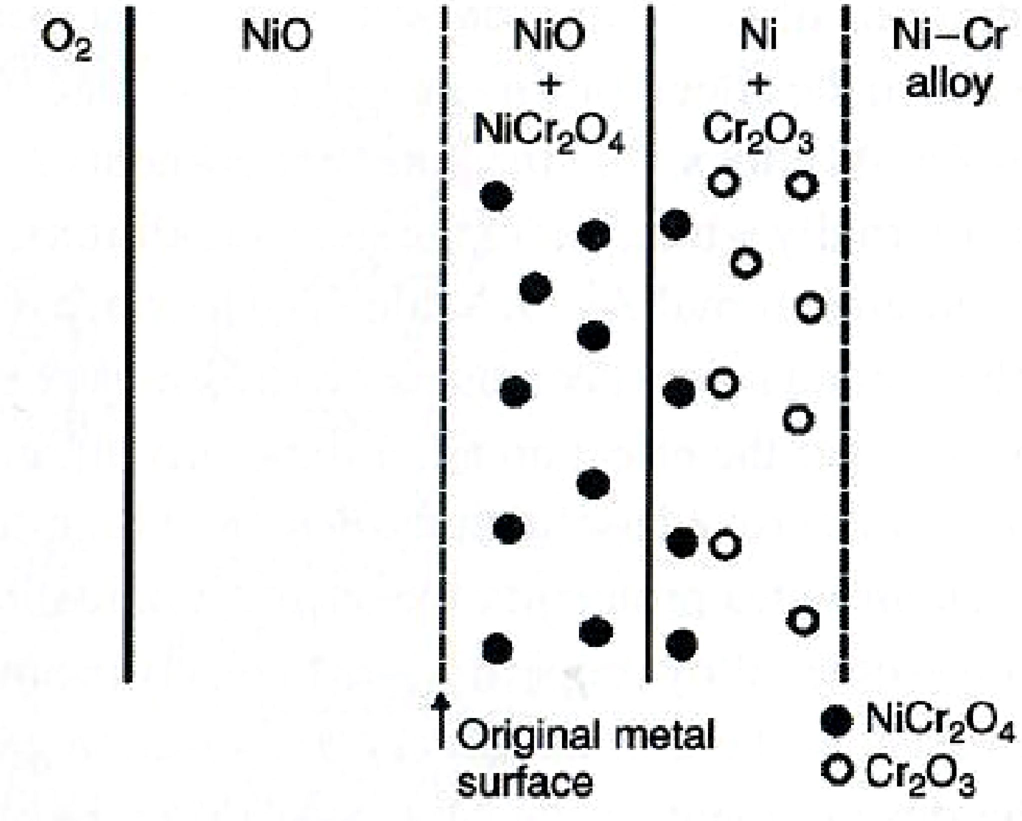
Influence of chromium on the oxidation kinetics of Ni-Cr alloys at several different temperatures



S. Mrowec and T. Werber, Modern Scaling-Resistant Materials, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.

Ni-Cr alloy oxidation

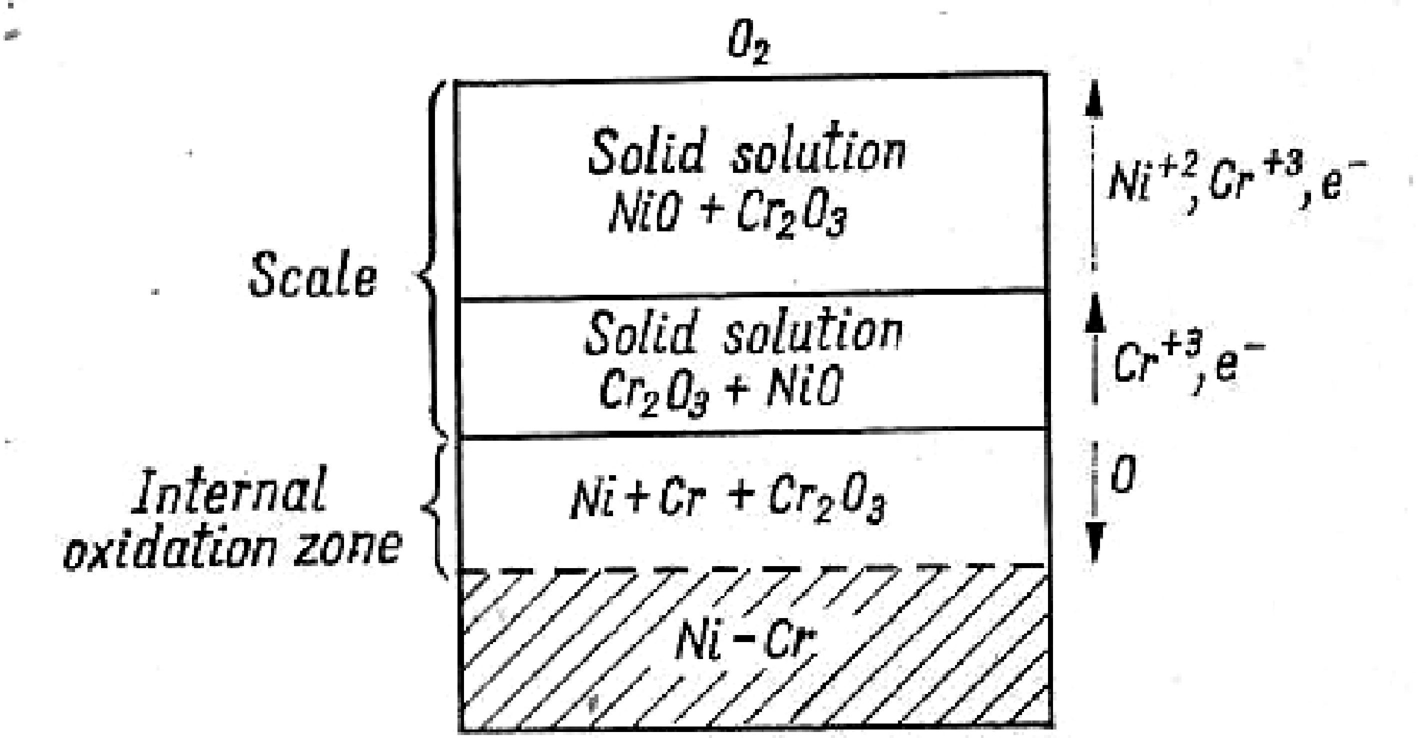
Schematic illustration of the morphology of the oxide scale formed on diluted Ni-Cr alloys



N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

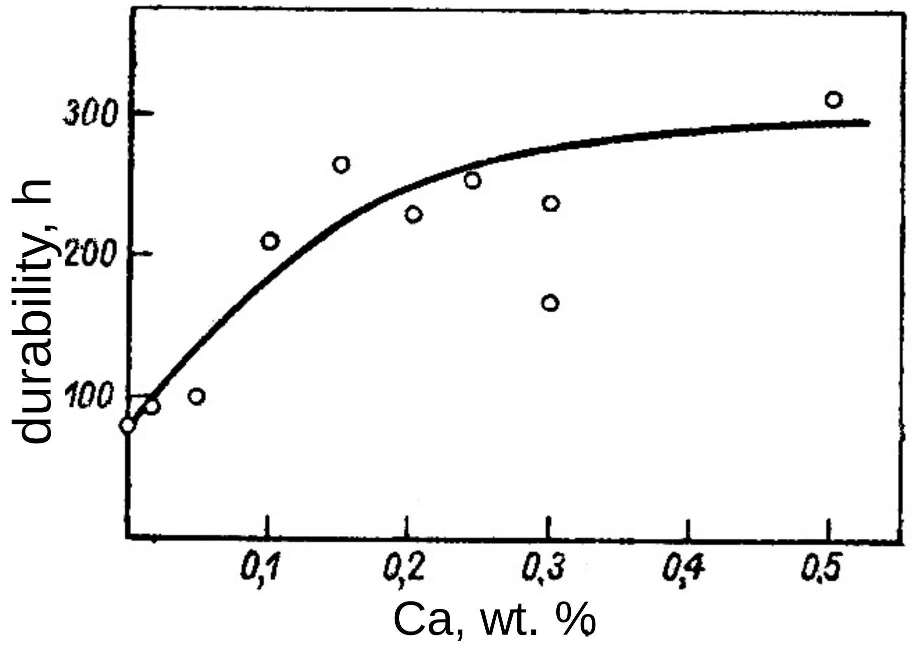
Ni-Cr alloy oxidation

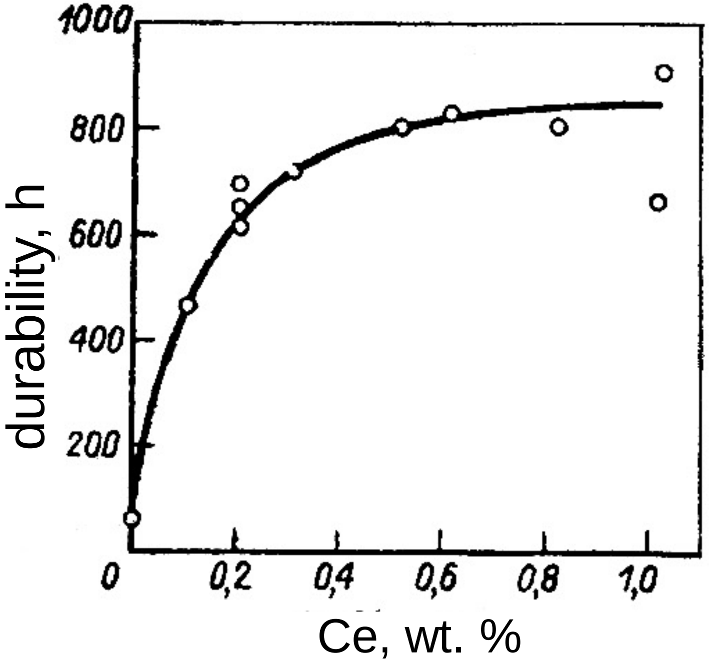
Schematic illustration of the morphology of the oxide scale formed on Ni-Cr alloys



S. Mrowec and T. Werber, Modern Scaling-Resistant Materials, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.

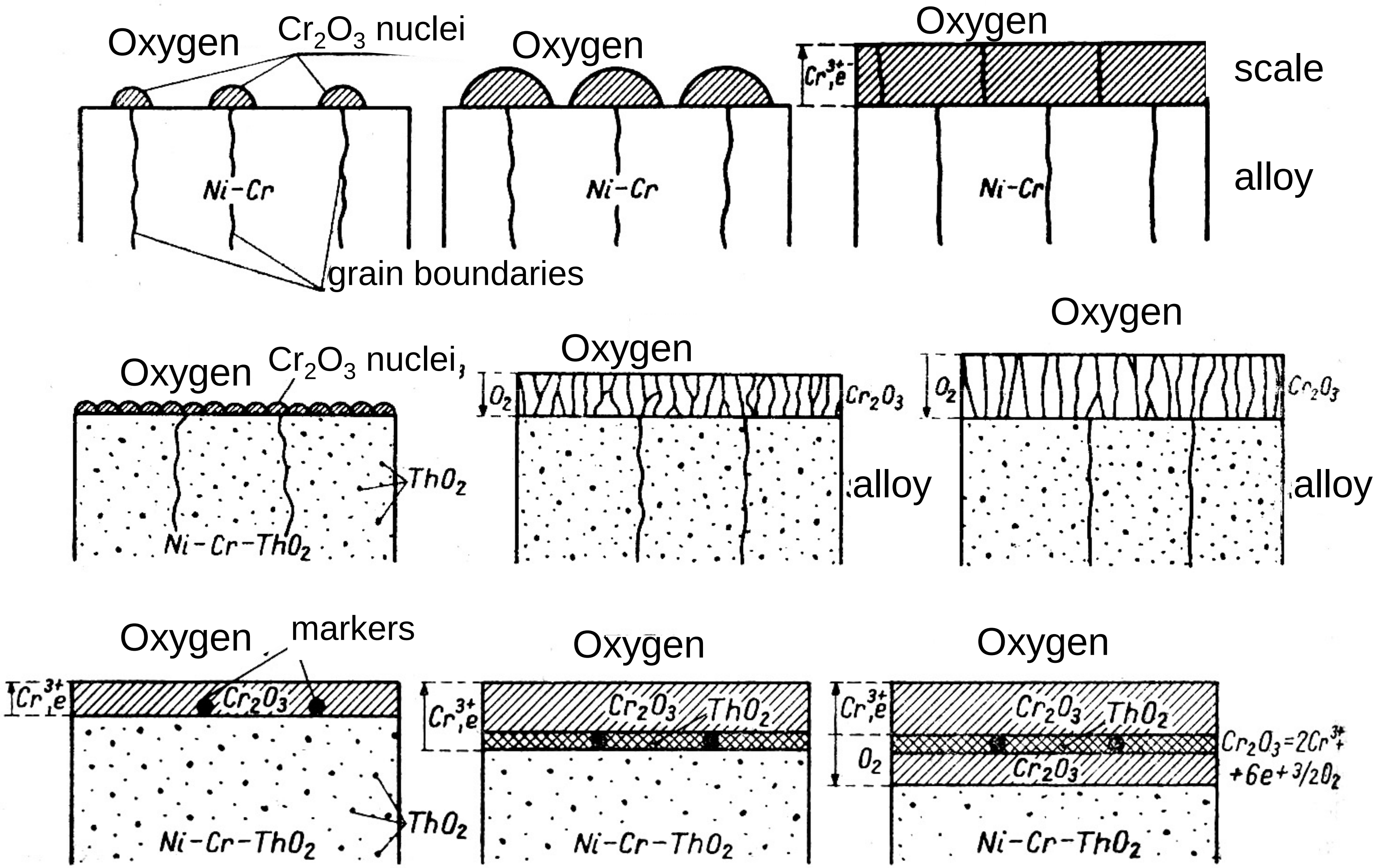
Influence of Ca and Ce on the lifetime of Ni-20Cr alloy at 1050 ^{o}C





S. Mrowec and T. Werber, Modern Scaling-Resistant Materials, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.

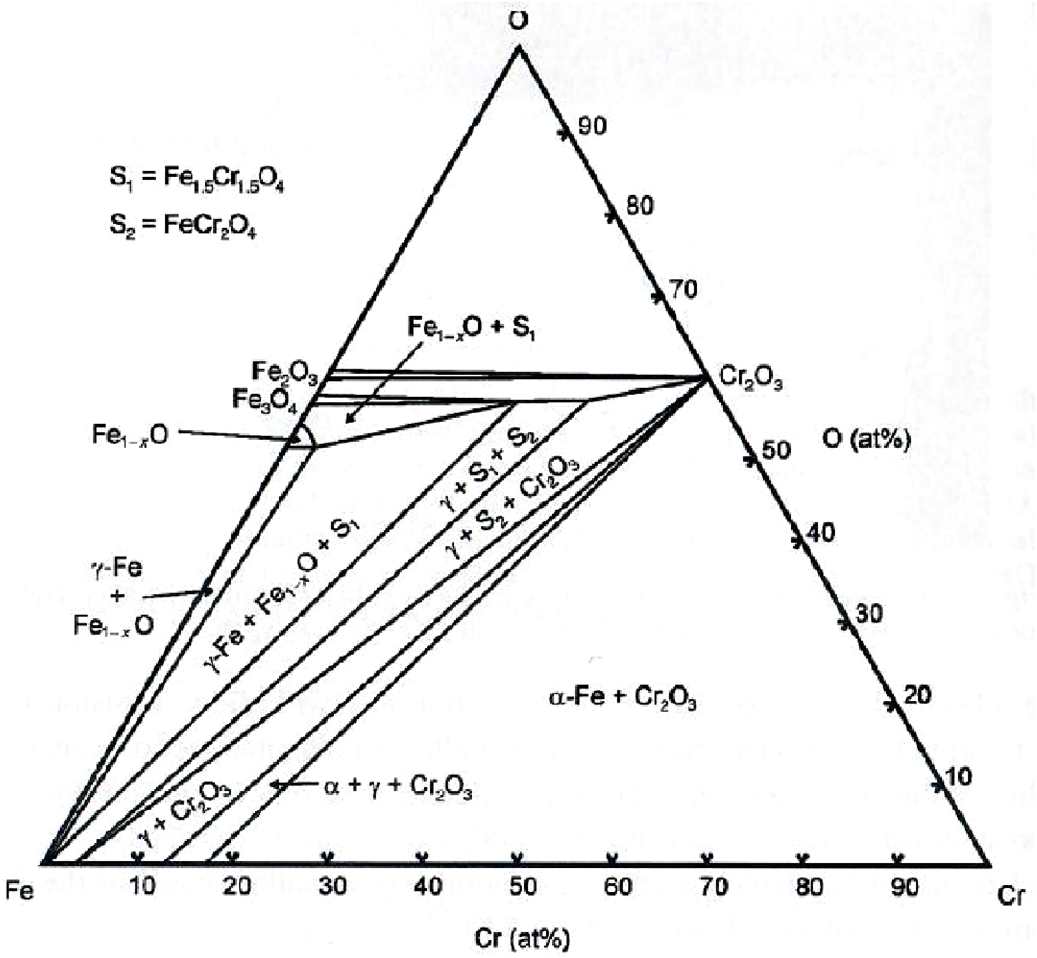
Scheme of Cr_2O_3 scale formation on high-percent Ni-Cr alloys



S. Mrowec, „An Introduction to the Theory of Metal Oxidation”, Washington, D.C., 1982

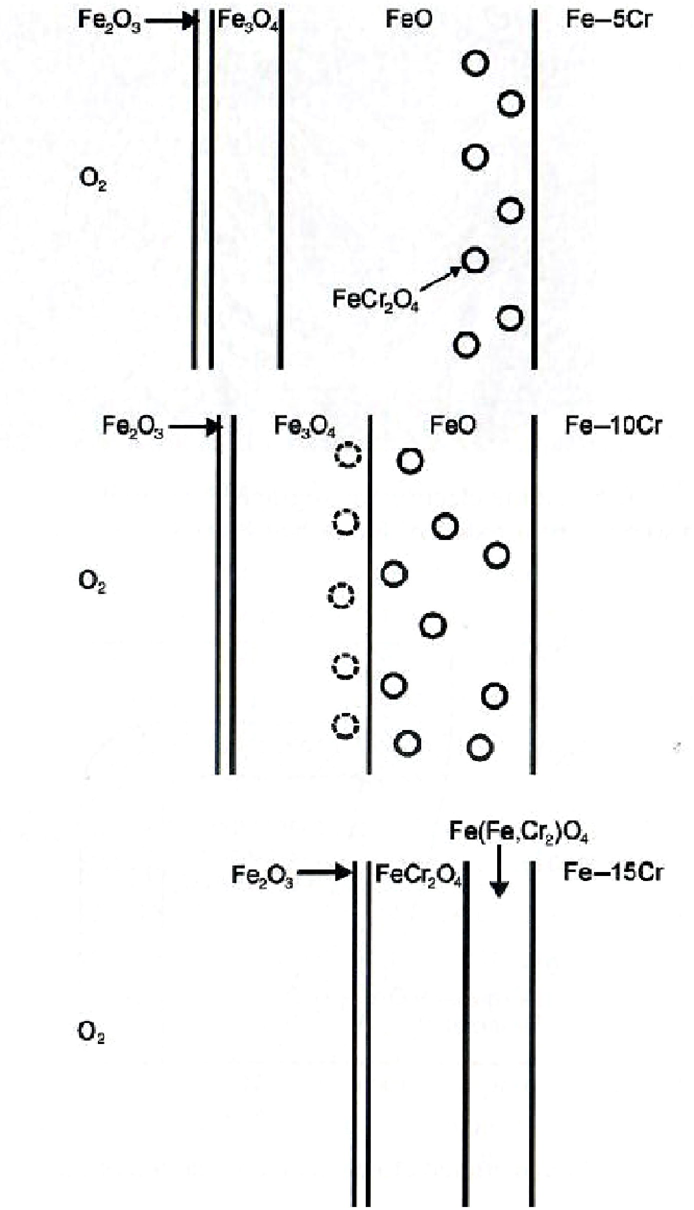
Fe-Cr alloy oxidation

Phase diagram of the Fe-Cr-O system



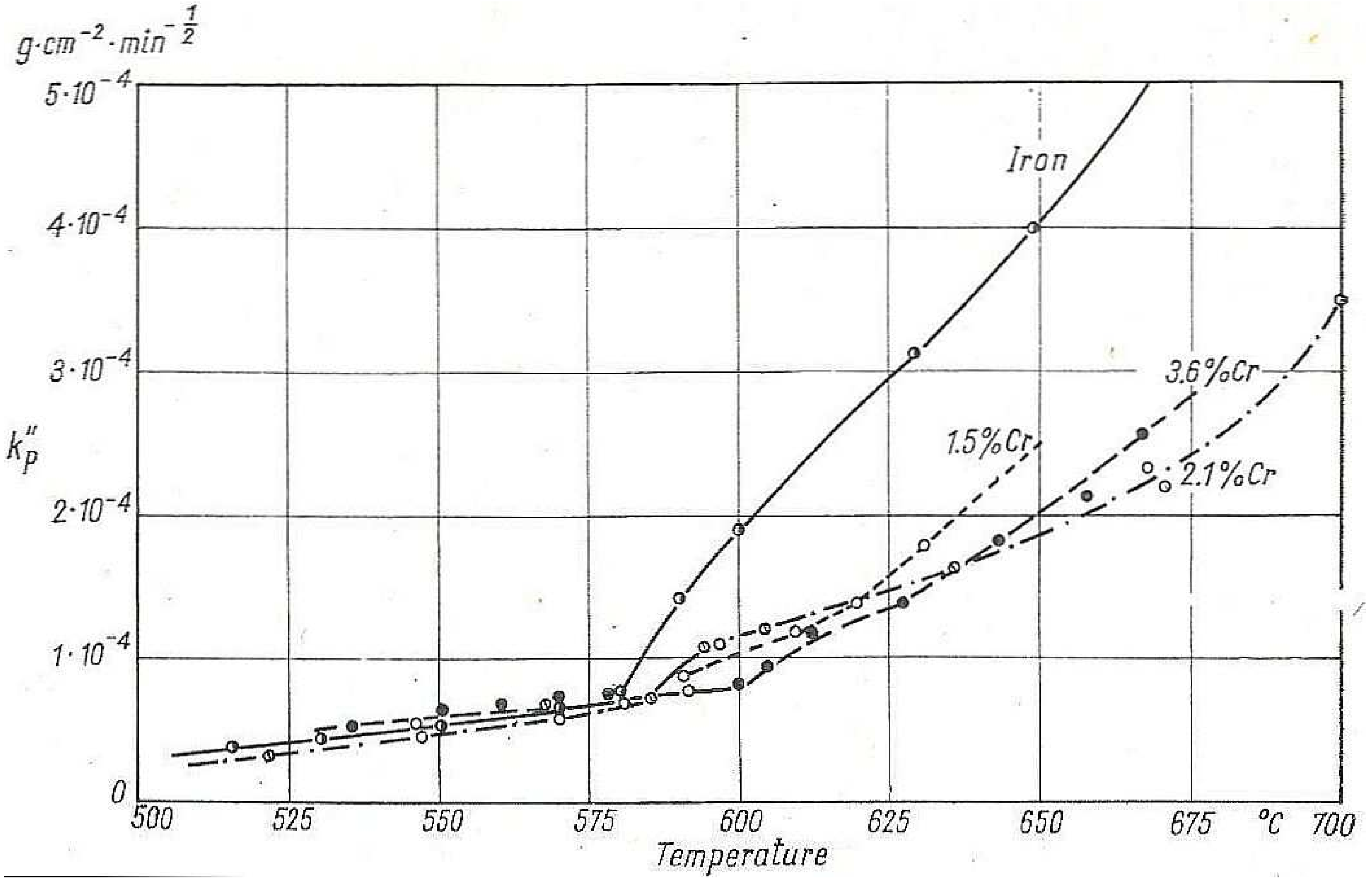
N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

Schematic illustration of the morphology of the oxide scale that grows on Fe-Cr alloys



N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

Chromium influence on iron oxidation kinetics



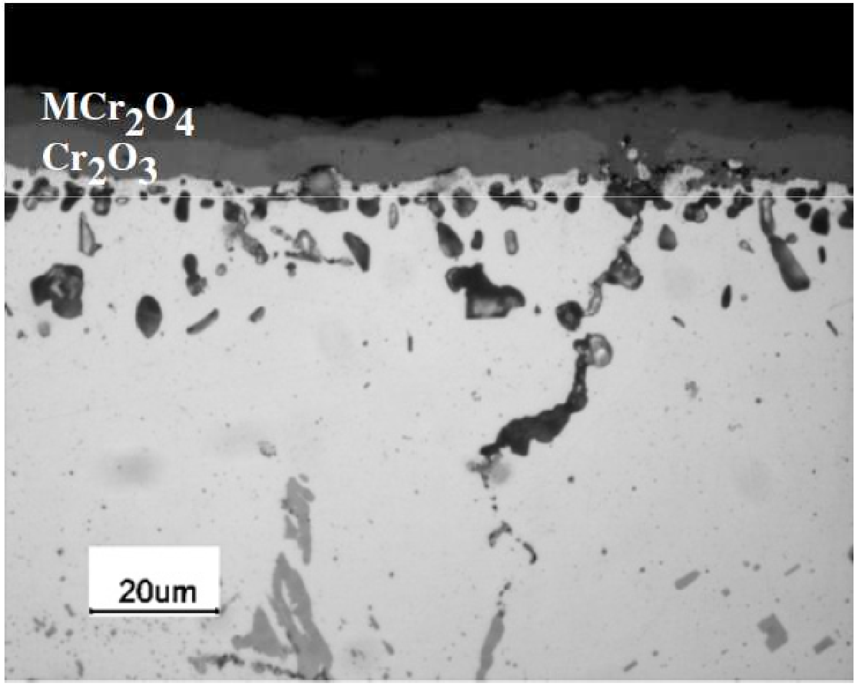
S. Mrowec, T. Werber, Modern scalling-resistant materials, National Bureau of Standards, 1982

Influence of manganese on the oxidation of chromia-former materials

Expectations:

$$\Delta G_{(MnO)} < \Delta G_{(Cr2O3)} \longrightarrow \text{alloy}/MnO/Cr_2O_3$$

Reality: alloy/Cr_2O_3/$MnCr_2O_4$



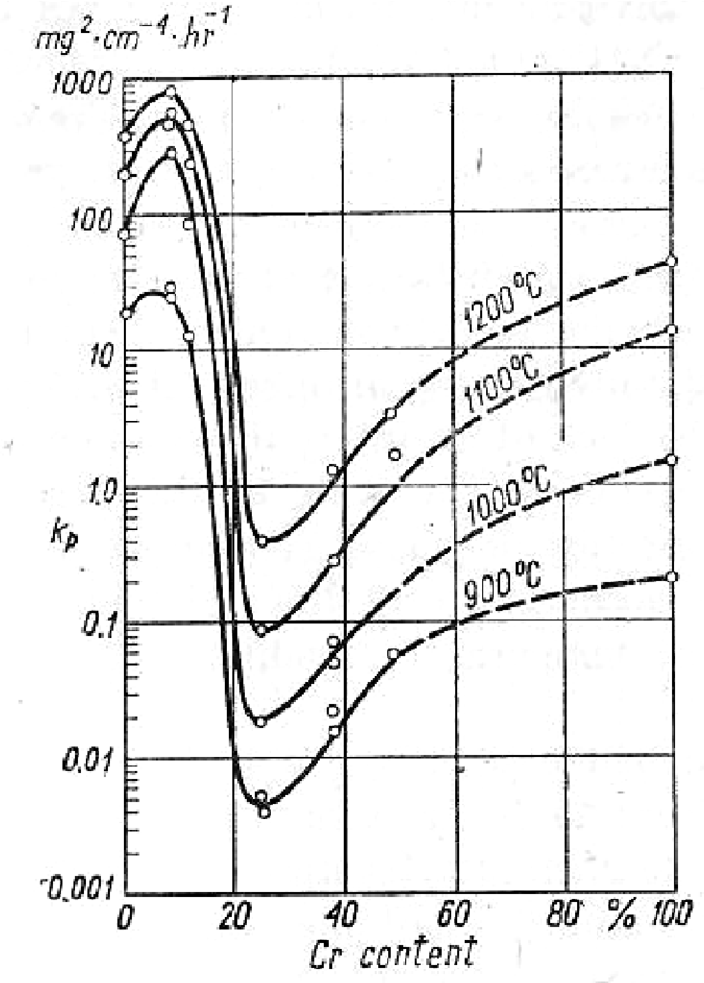
Reasons:

- presence of stable $MnCr_2O_4$
- as a rule low Mn concentration in the alloy
- solubility limt of Mn in Cr_2O_3: 1.6%
- $D_{Mn}(Cr_2O_3) \gg D_{Mn}(alloy)$

David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008

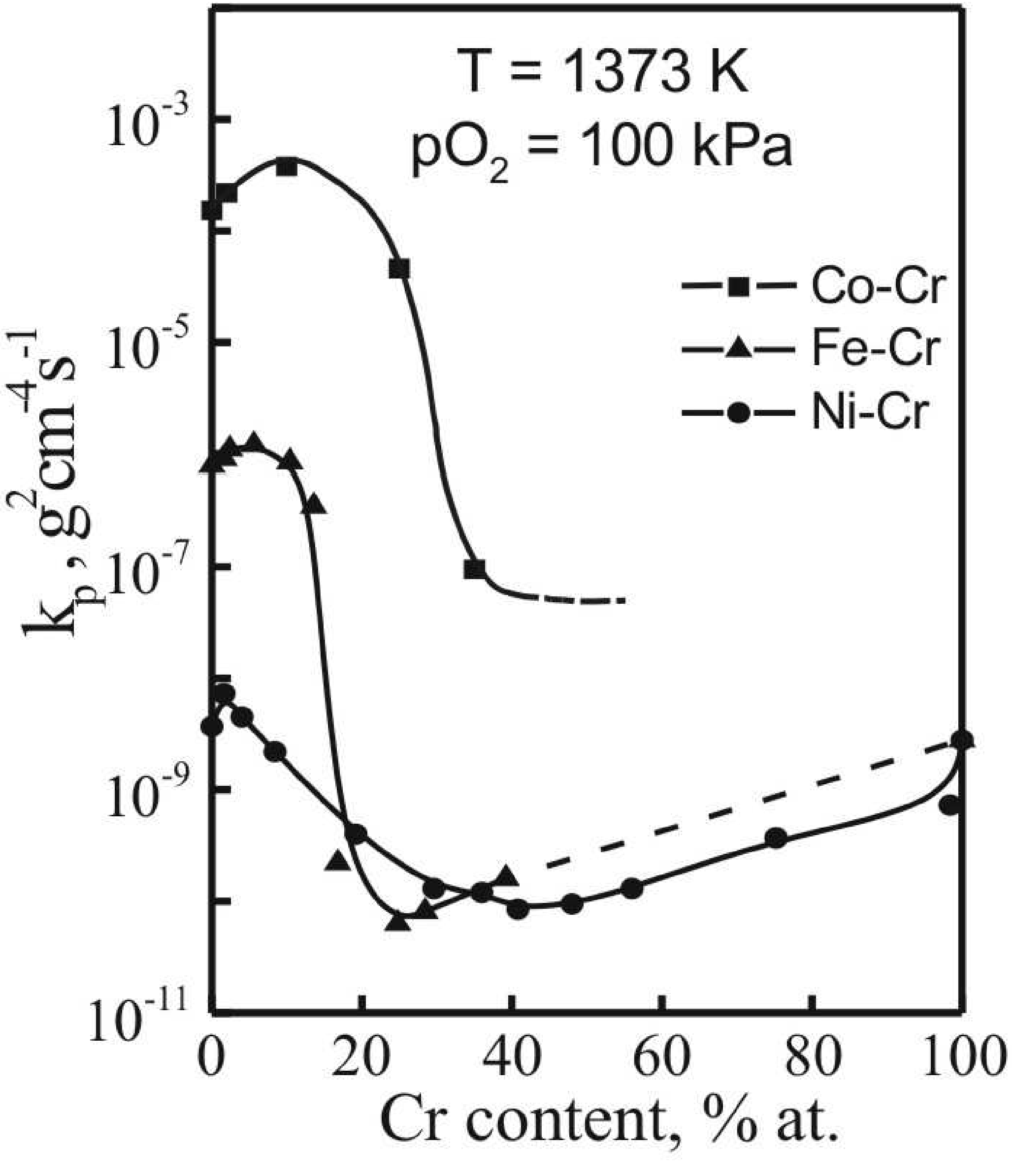
Co-Cr alloy oxidation

Influence of chromium on oxidation kinetics
of Co-Cr alloys at several different temperatures



S. Mrowec, T. Werber, Modern scalling-resistant materials, National Bureau of Standards, 1982

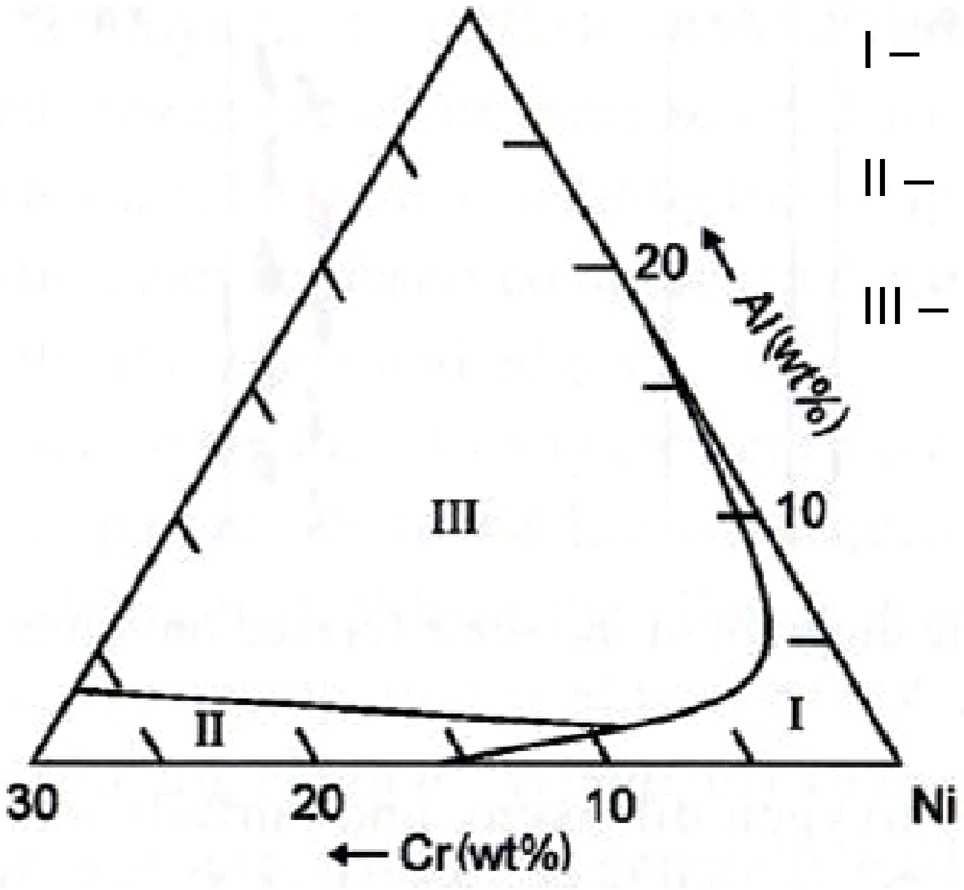
Comparison between oxidation rates of two-component alloys: chromium with cobalt, iron and nickel



Oxidation of alumina-formers

In two-component alloys from the alumina-forming group, aluminum concentration ensuring the formation of an Al_2O_3 protective layer (> 20 %) is so high that it results in the alloy being brittle. Therefore, only alumina-formers that are multi-component alloys with aluminum concentration on the level of 5% have practical use, or an intermetallic compound (e.g. from the Ni-Al system) can be applied as a coating material.

Dependence of oxide scale phase composition and morphology on the composition of Ni-Cr-Al alloys



I – NiO (external)

$Cr_2O_3/Al_2O_3/Ni(Al,Cr)_2O_4$ (internal)

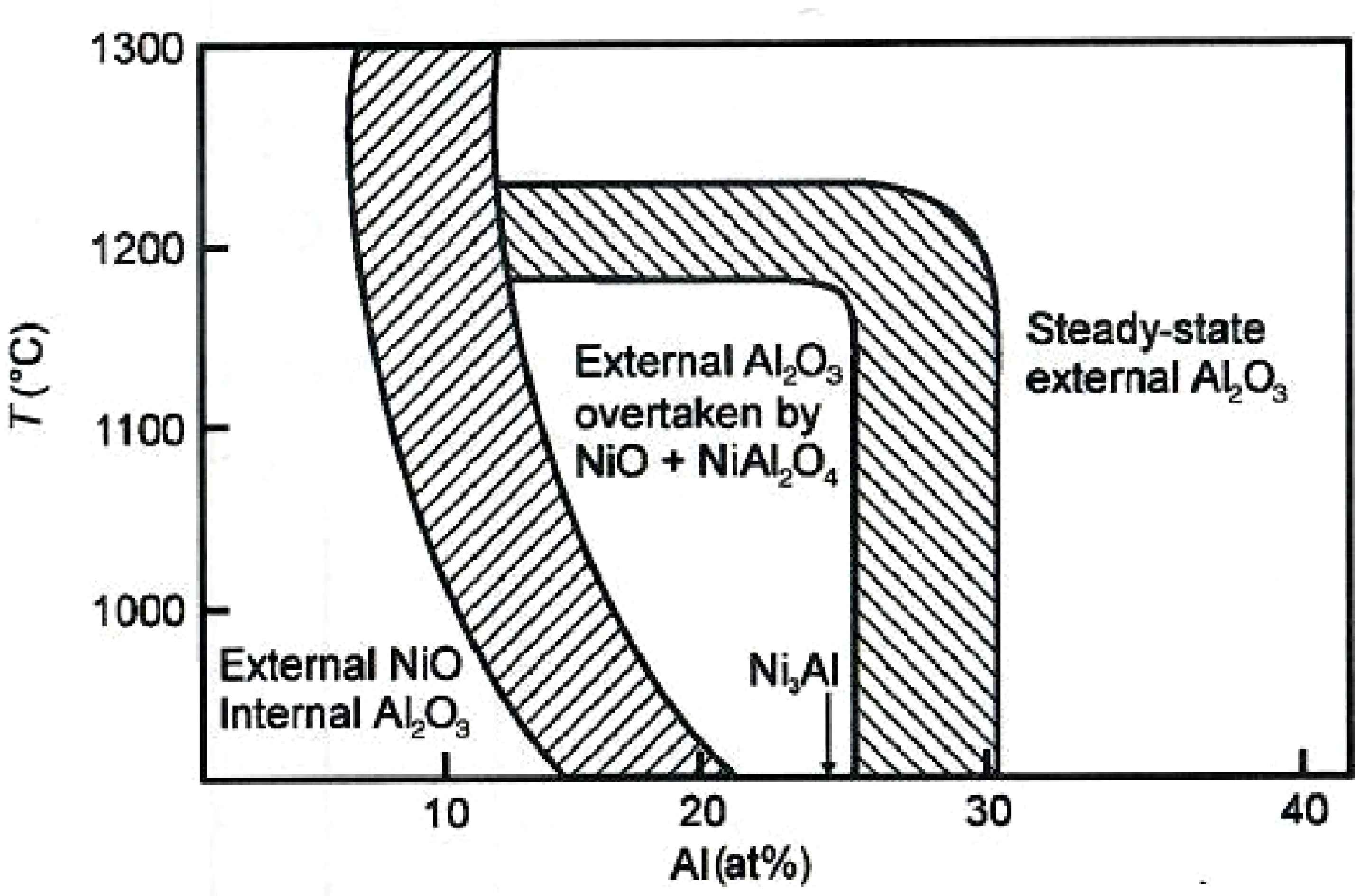
II – Cr_2O_3 (external)

Al_2O_3 (internal)

III – Al_2O_3 (external)

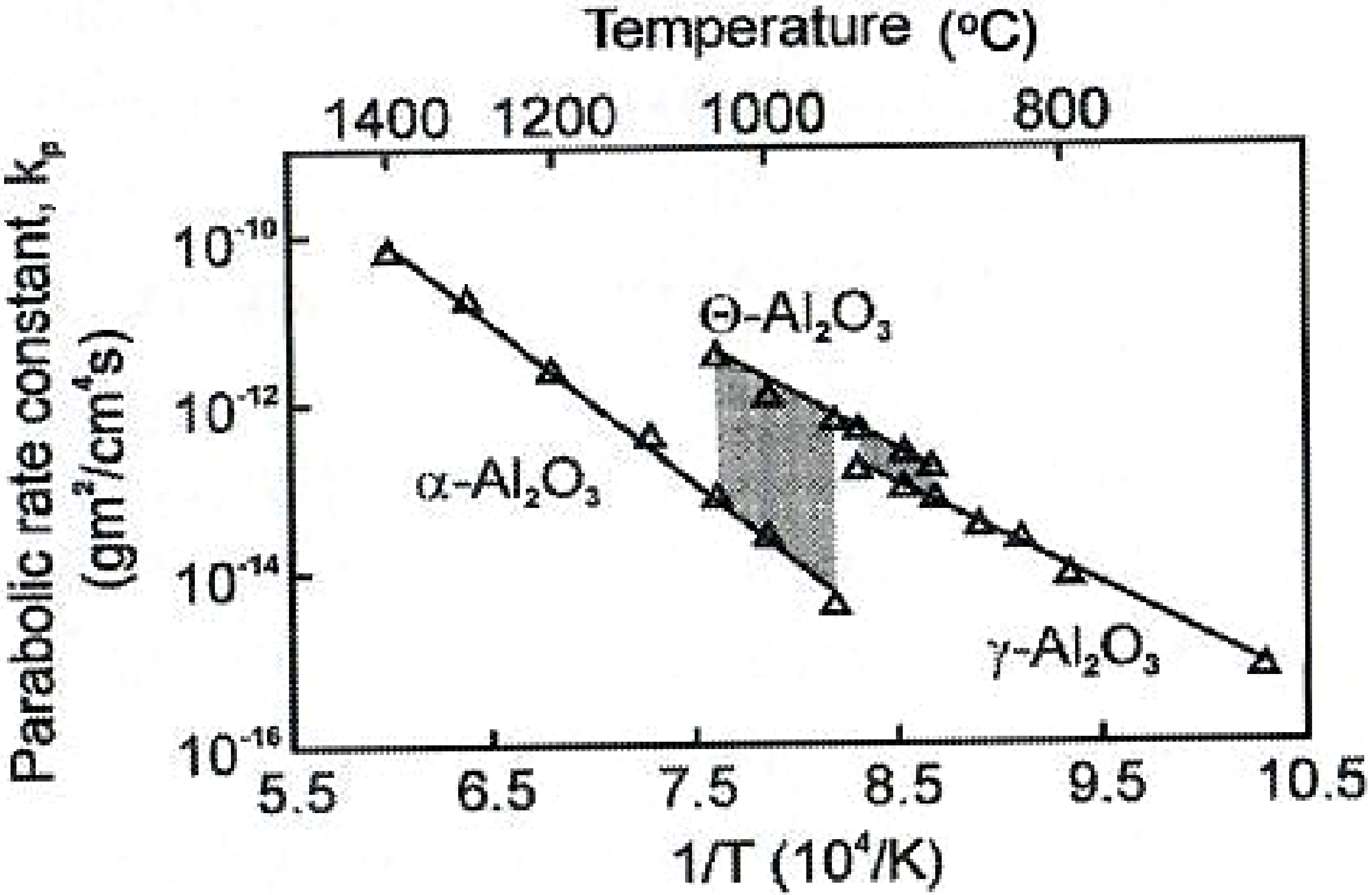
N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

Dependence of oxide scale phase composition and morphology on the composition of Ni-Al alloys



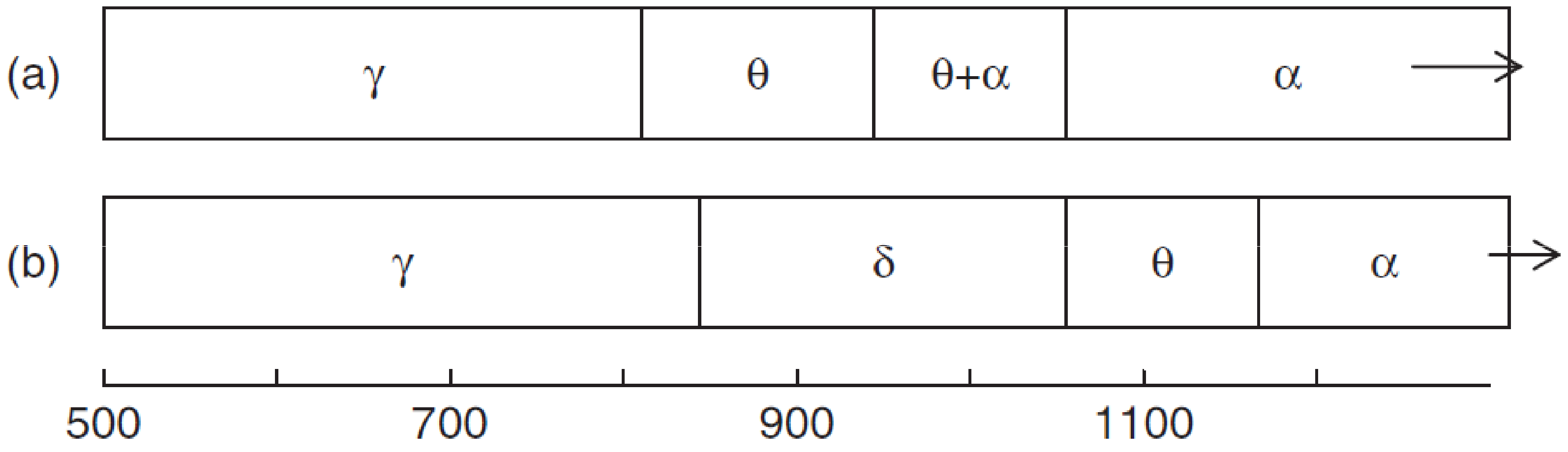
N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

Temperature dependence of the oxidation rate of NiAl with specified oxides constituting the scale



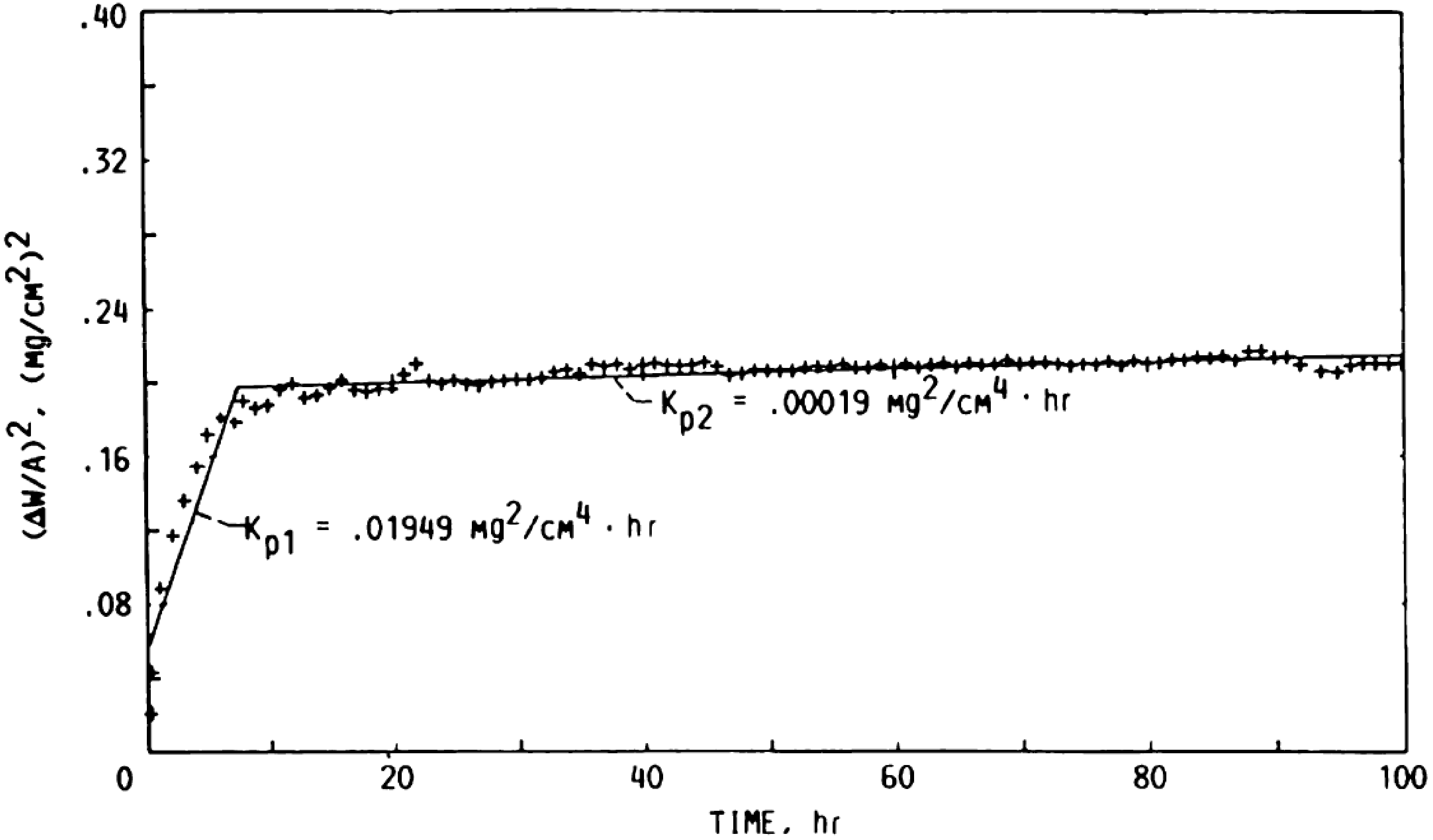
N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

Transformation temperature of Al_2O_3 placed on a γ-Al_2O_3 +3% Pt catalizer (a) and γ-Al_2O_3 (b)



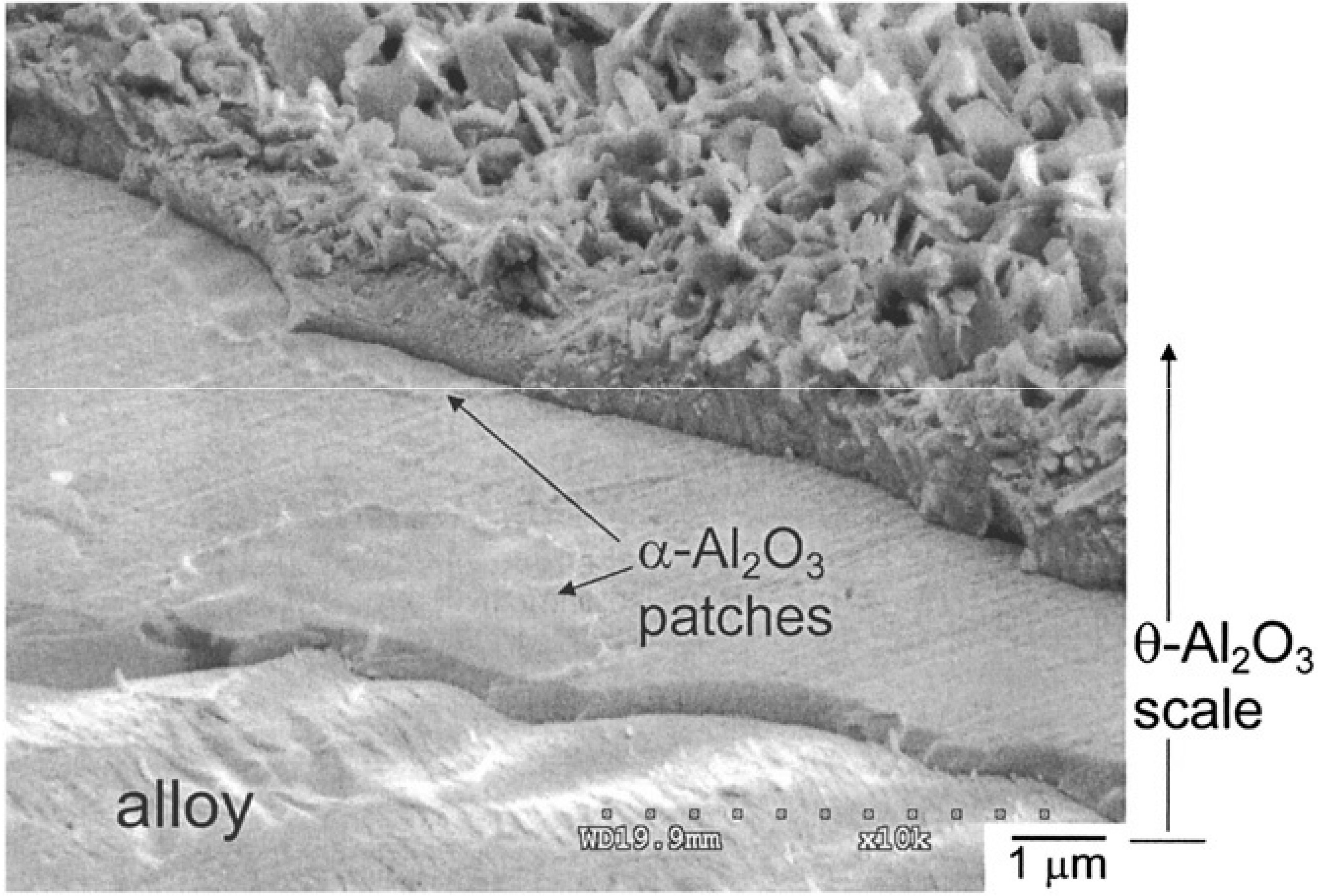
David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008

Oxidation kinetics of β-NiAl+Zr involving γ-Al_2O_3 to α-Al_2O_3 transformations



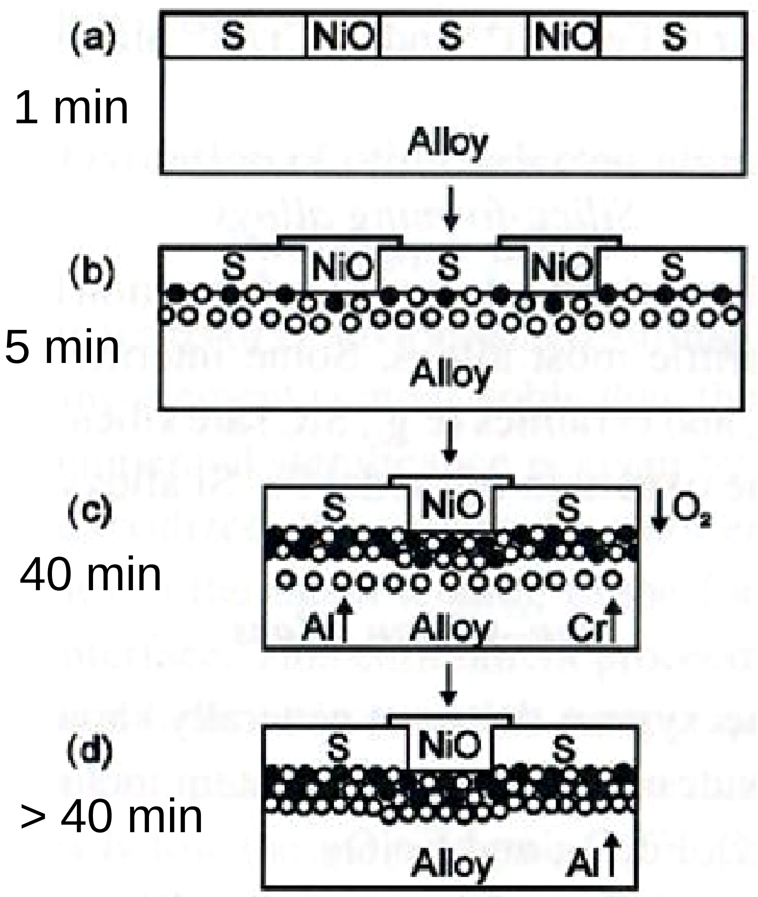
David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008

SEM picture of an oxide scale grown on β-NiAl at 1100 °C, demonstrating an α-Al_2O_3 layer on the substrate-scale interface



David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008

Chromium influence on Al_2O_3 scale on a Ni-15Cr-6Al (mass %) alloy at 1000°C



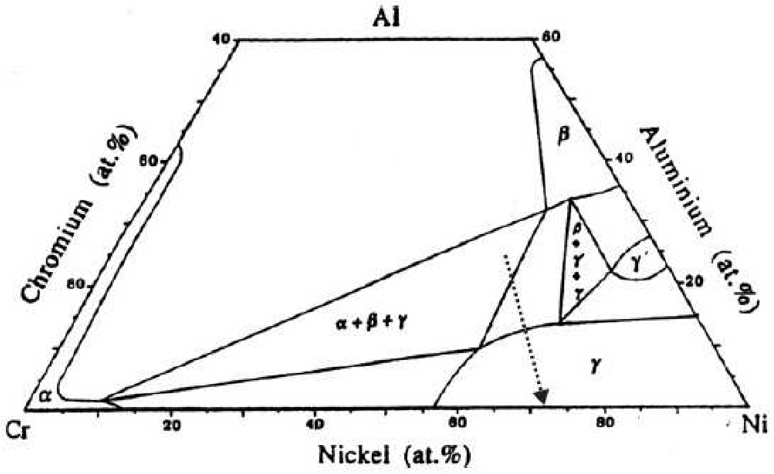
S – $Ni(Cr,Al)_2O_4$

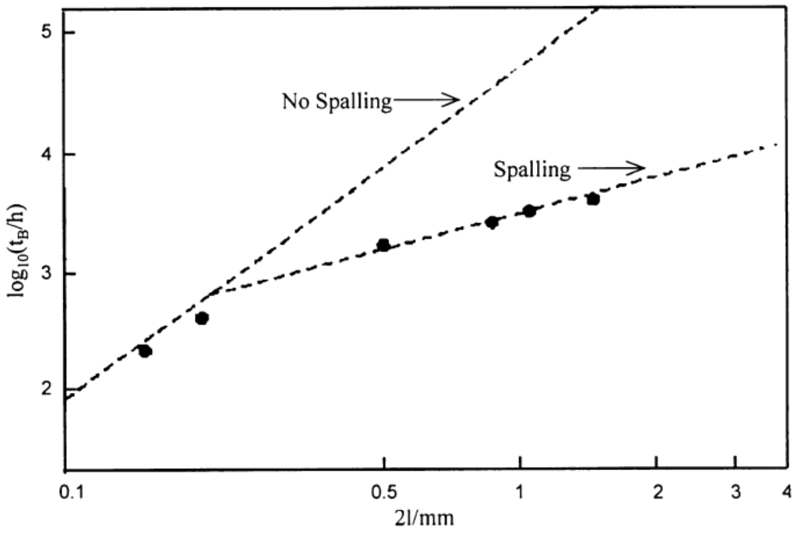
● – Cr_2O_3

○ – Al_2O_3

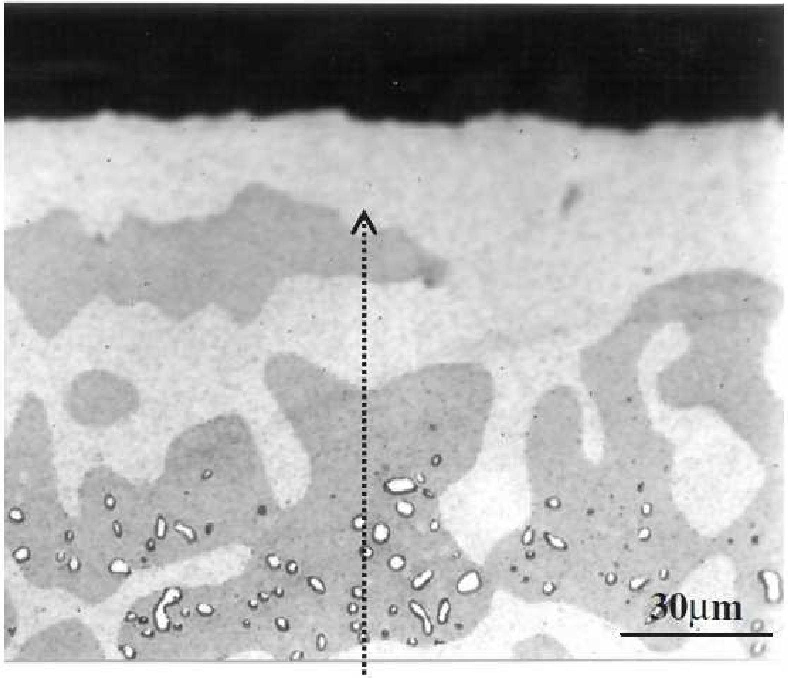
N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

Distribtution of an α-Al_2O_3 protective layer



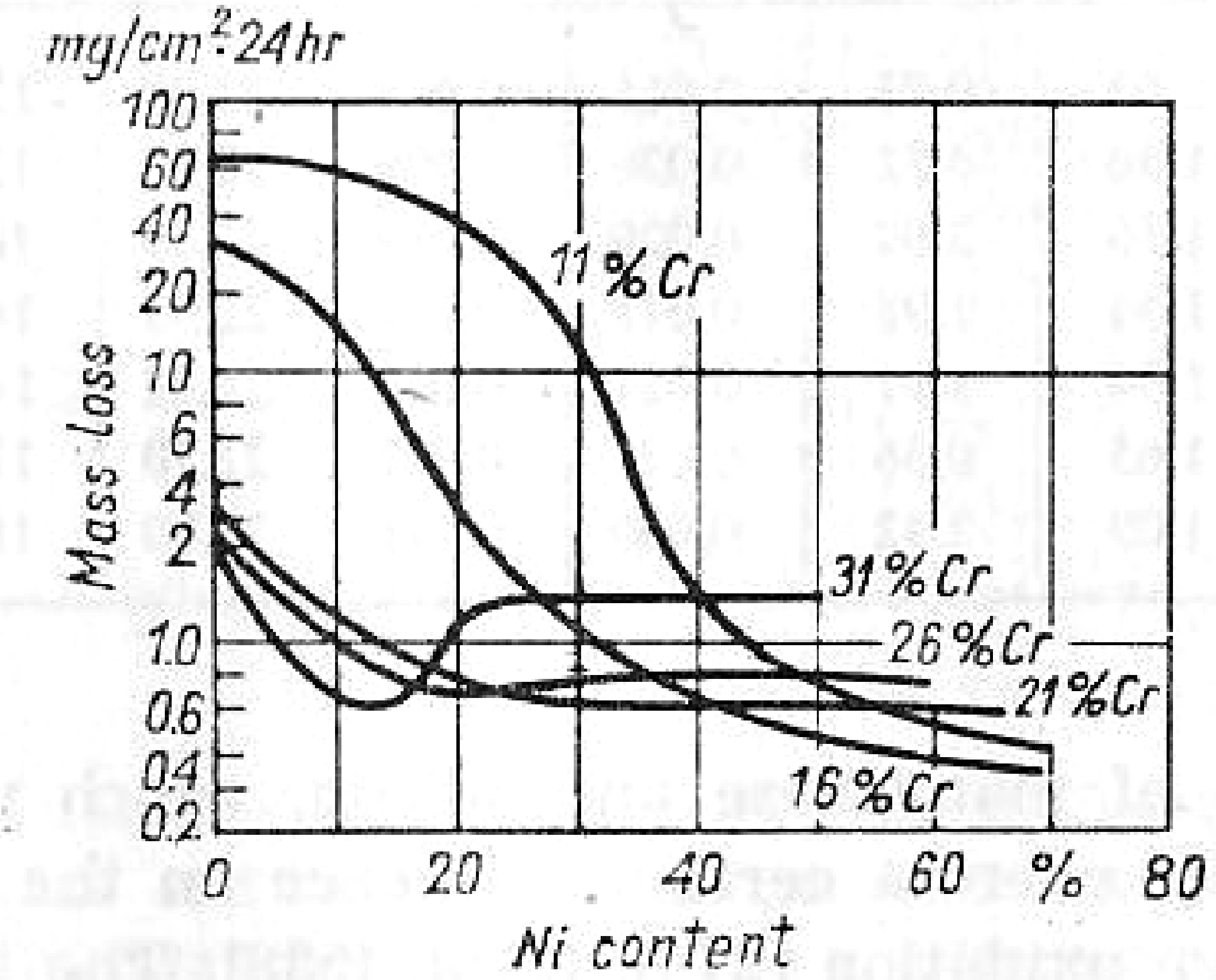


2l – sample thickness



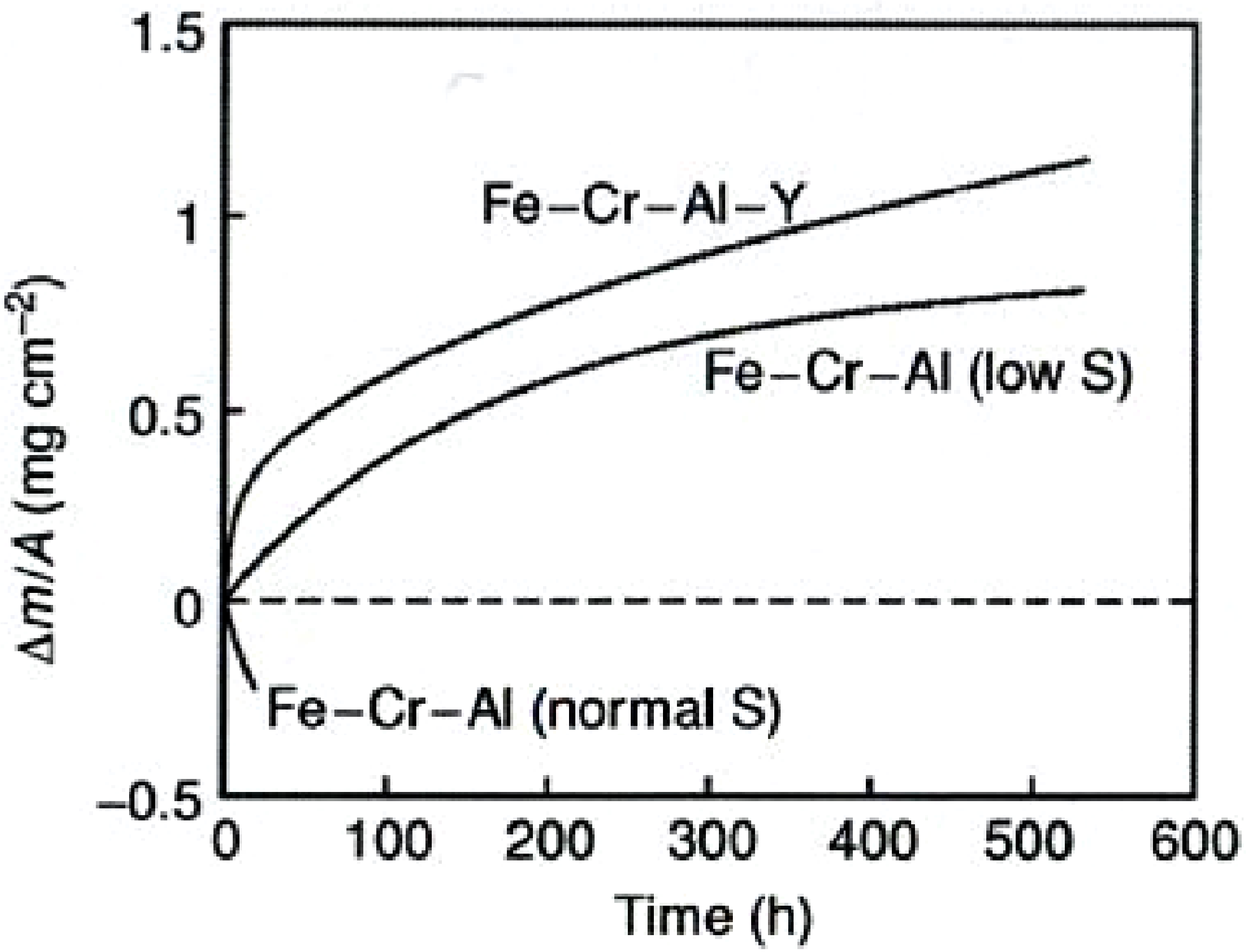
David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008

Influence of nickel on chromium steel oxidation rate



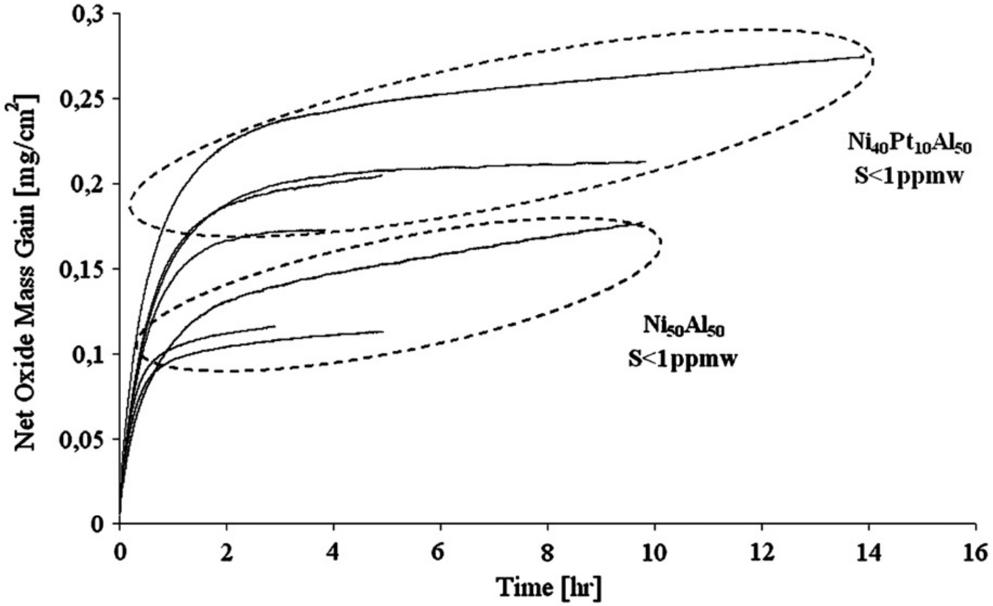
S. Mrowec, T. Werber, Modern scalling-resistant materials, National Bureau of Standards, 1982

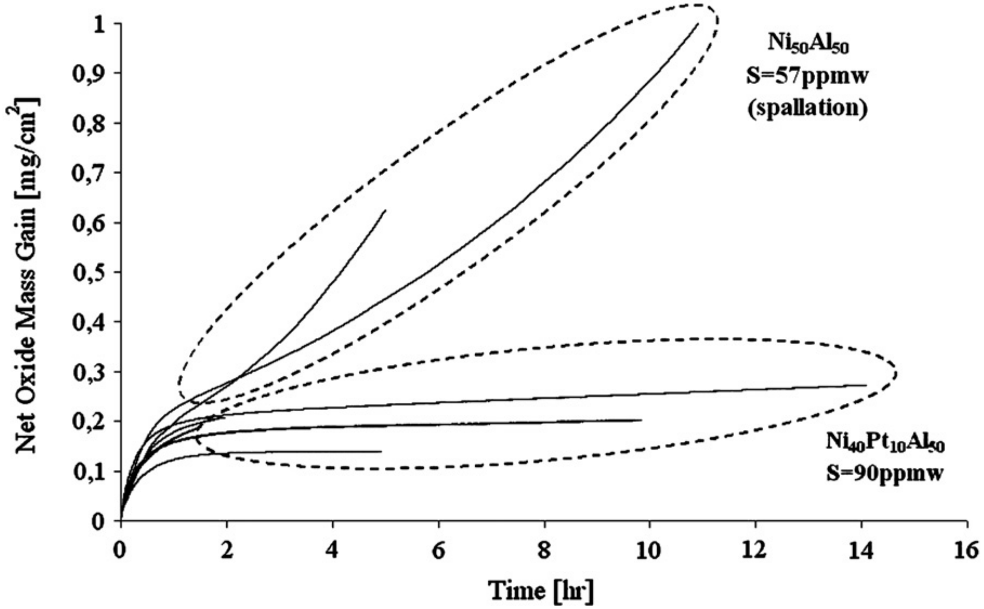
Results of cyclic oxidation of Fe-Cr-Al alloys with different sulfur contents (sulfur effect)



N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

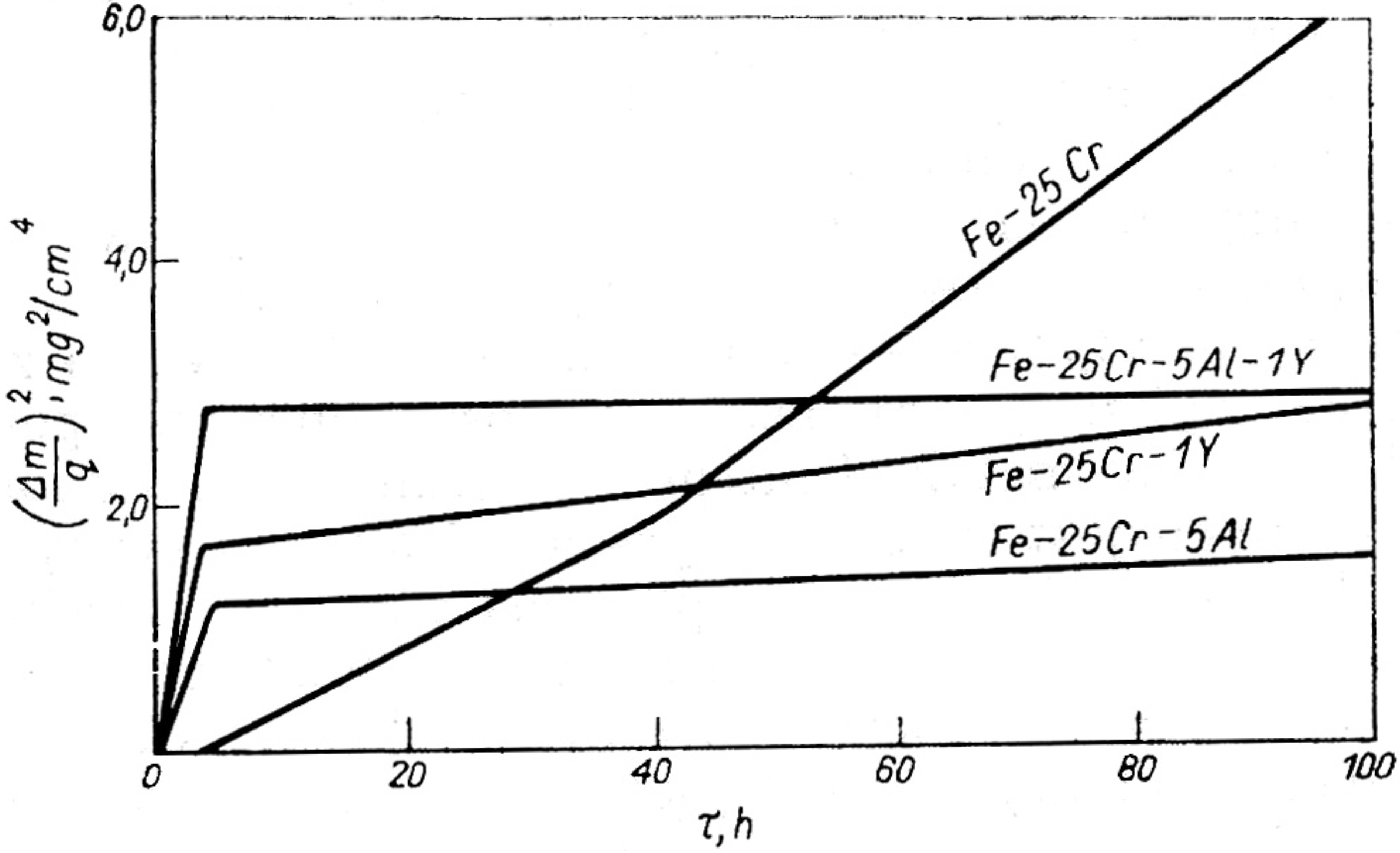
Influence of platinum on oxidation of alloys with different sulfur contents (platinum effect)





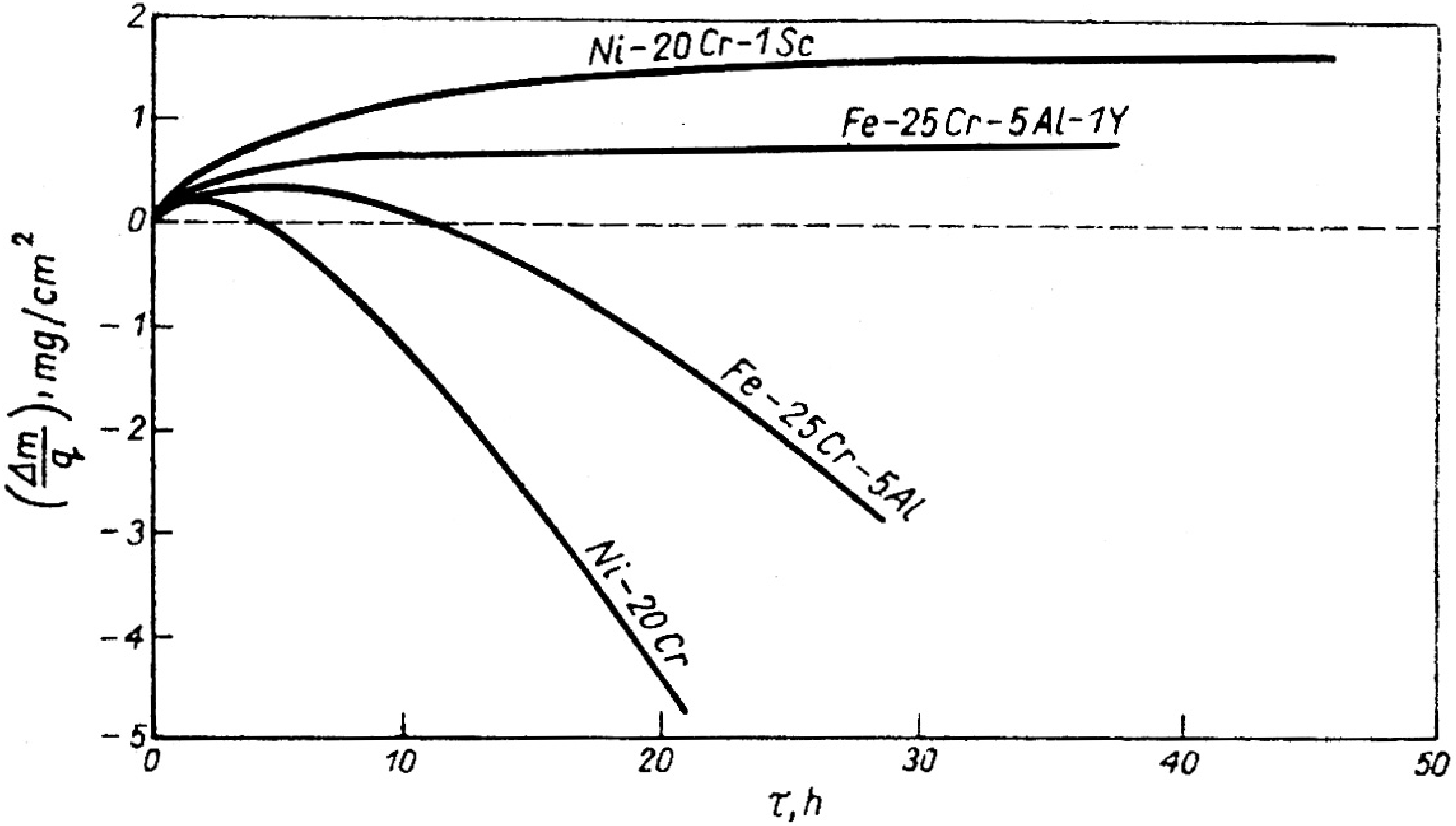
David J. Young, „High temperature oxidation and corrosion of metals”, Elsevier, Sydney 2008

Influence of Y on Fe-25Cr-5Al alloy oxidation rate



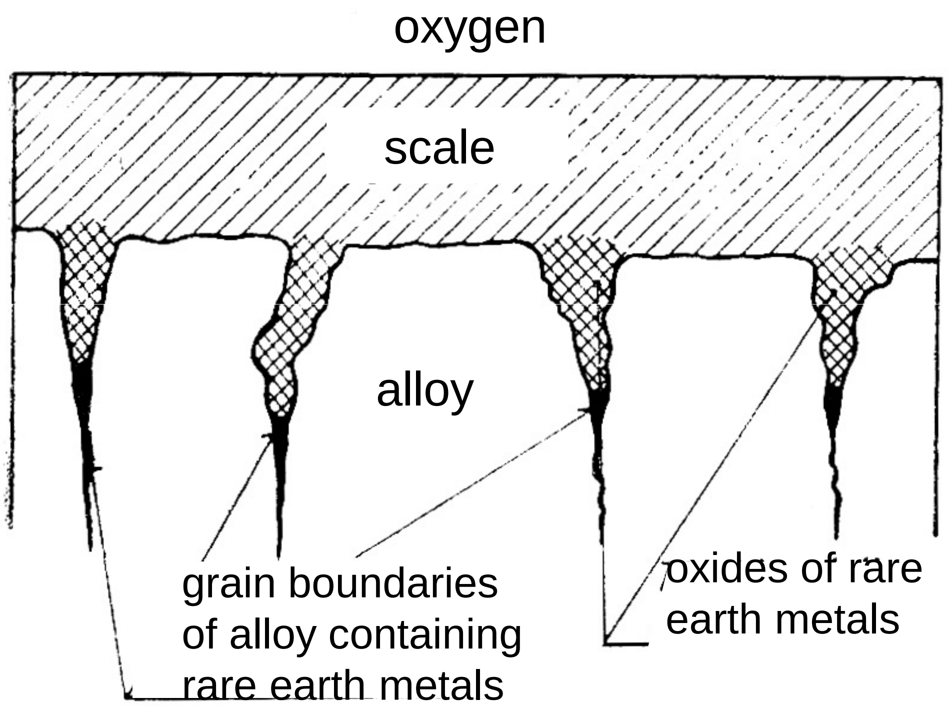
S. Mrowec, „An Introduction to the Theory of Metal Oxidation", Washington, D.C., 1982

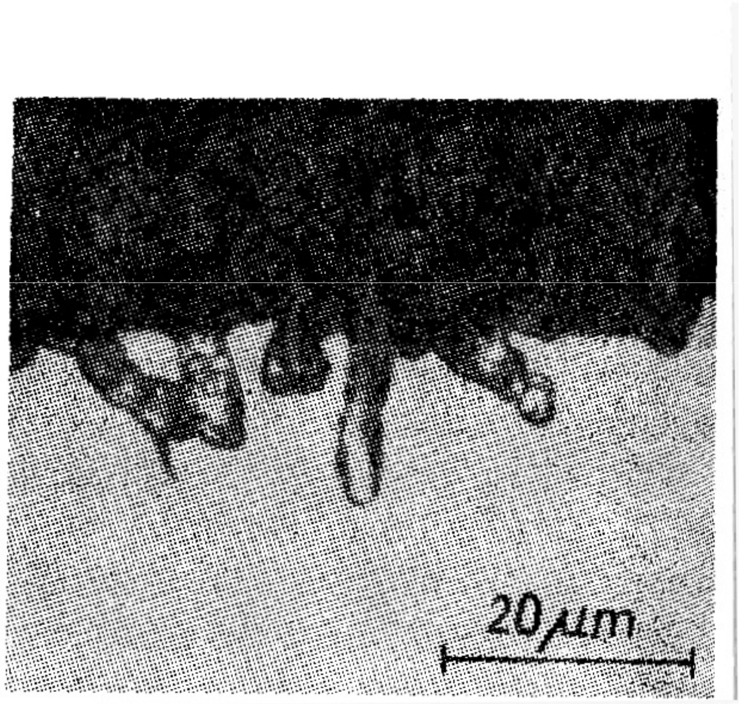
Influence of Y and Sc on the degradation rate of Fe-25Cr-5Al and Ni-20Cr alloys in cyclic oxidation conditions



S. Mrowec, „An Introduction to the Theory of Metal Oxidation”, Washington, D.C., 1982

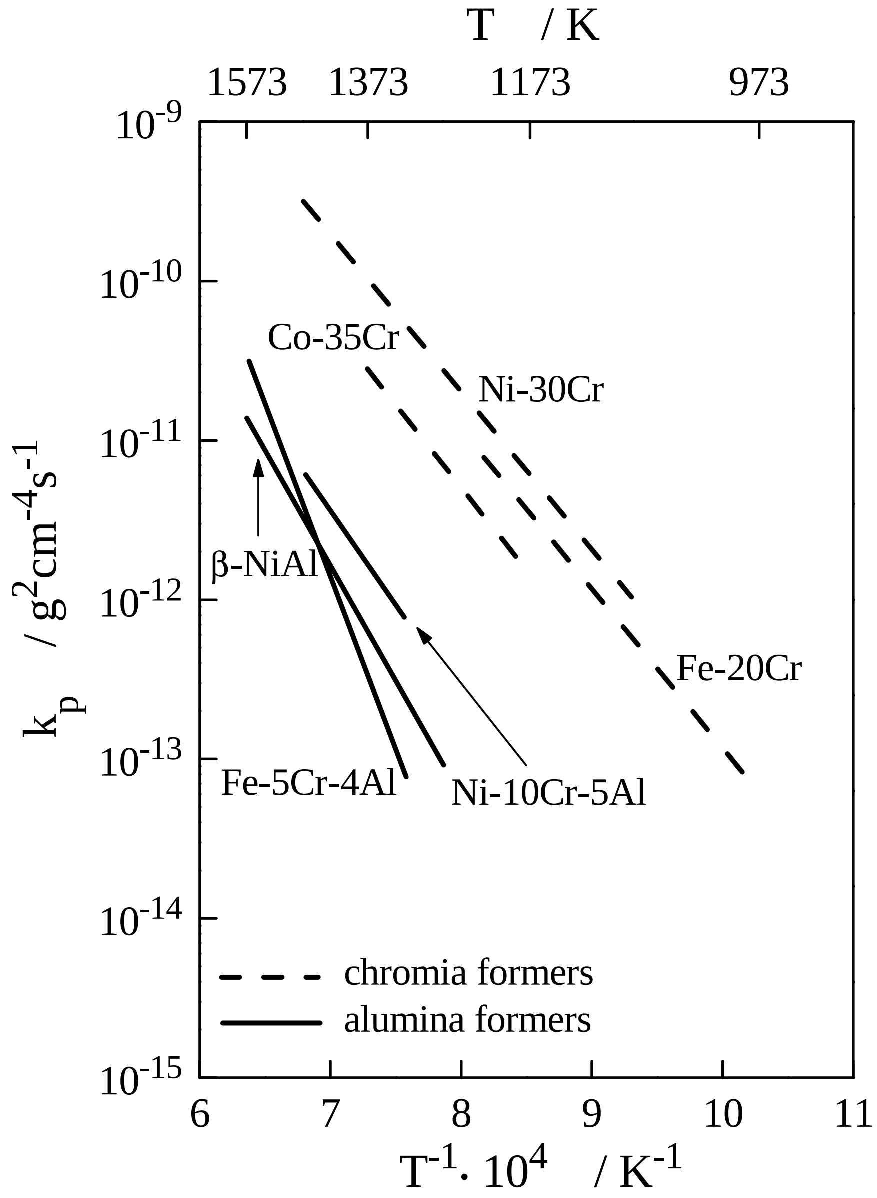
Scheme of mechanical binding of the scale to the substrate by the internally oxidized rare earth metals, assembled at the alloy grain boundaries (keying effect)





S. Mrowec, „An Introduction to the Theory of Metal Oxidation", Washington, D.C., 1982

Oxidation rates of selected alloys



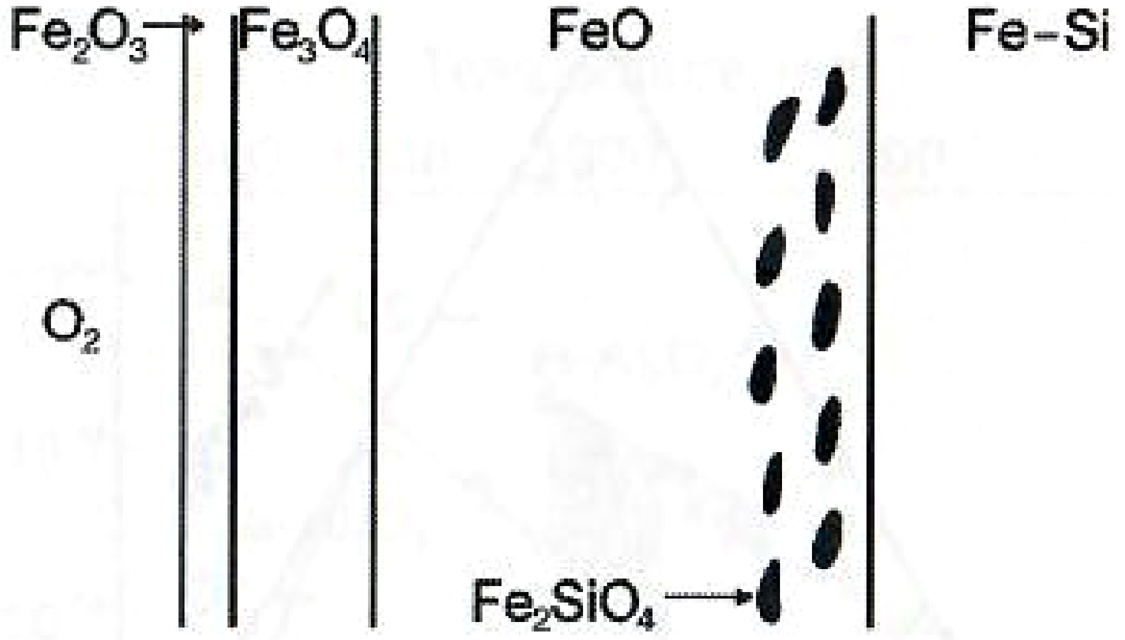
Silica-former materials oxidation

The presence of silicon in alloys even at relatively low concentrations makes the materials brittle. Thus, there are no multicomponent alloys with silicon used as construction materials. This type of alloy, similar to intermetallic compounds or silicon-containing ceramics (e.g. $MoSi_2$, SiC, SiN), can however be used as coatings.

N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

Oxidation of model Fe-Si alloys

Schematic diagram of the cross-section of the scale formed on diluted Fe-Si alloys



N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.

THE END