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AND TECHNOLOGY

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HIGH TEMPERATURE CORROSION

IN MULTICOMPONENT

AGGRESIVE ENVIRONMENTS

http://home.agh.edu.pl/~grzesik

Literature

1. P. Kofstad, „High-Temperature Corrosion", John Wiley & Sons, Inc, New York-London-Sydney, 1988.
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. S. Mrowec and T. Werber, Modern Scaling-Resistant Materials, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.
5. A.S. Khanna, „Introduction to High Temperature Oxidation and Corrosion", ASM International, Materials Park, 2002.
6. Wei Gao and Zhengwei Li "Developments in high-temperature corrosion and protection of metals", Ed, Woodhead Publishing Limited, Cambridge, England, 2008.
7. N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009.
8. D. J. Young, „High temperature oxidation and corrosion of metals", Elsevier, Sydney 2016.

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Oxidation in different oxidizing atmospheres

The same aggresive element can be present in the form of different molecules or form aggresive chemical compounds. The most common agressive element (oxygen) is usually found as molecular oxygen O_2, but can also be present as atomic oxygen, O, or form compounds with other elements, e.g. H_2O, CO, CO_2, SO_2, etc.

Depending on its form, an aggresive component can influence the rate and mechanism of high temperature corrosion.

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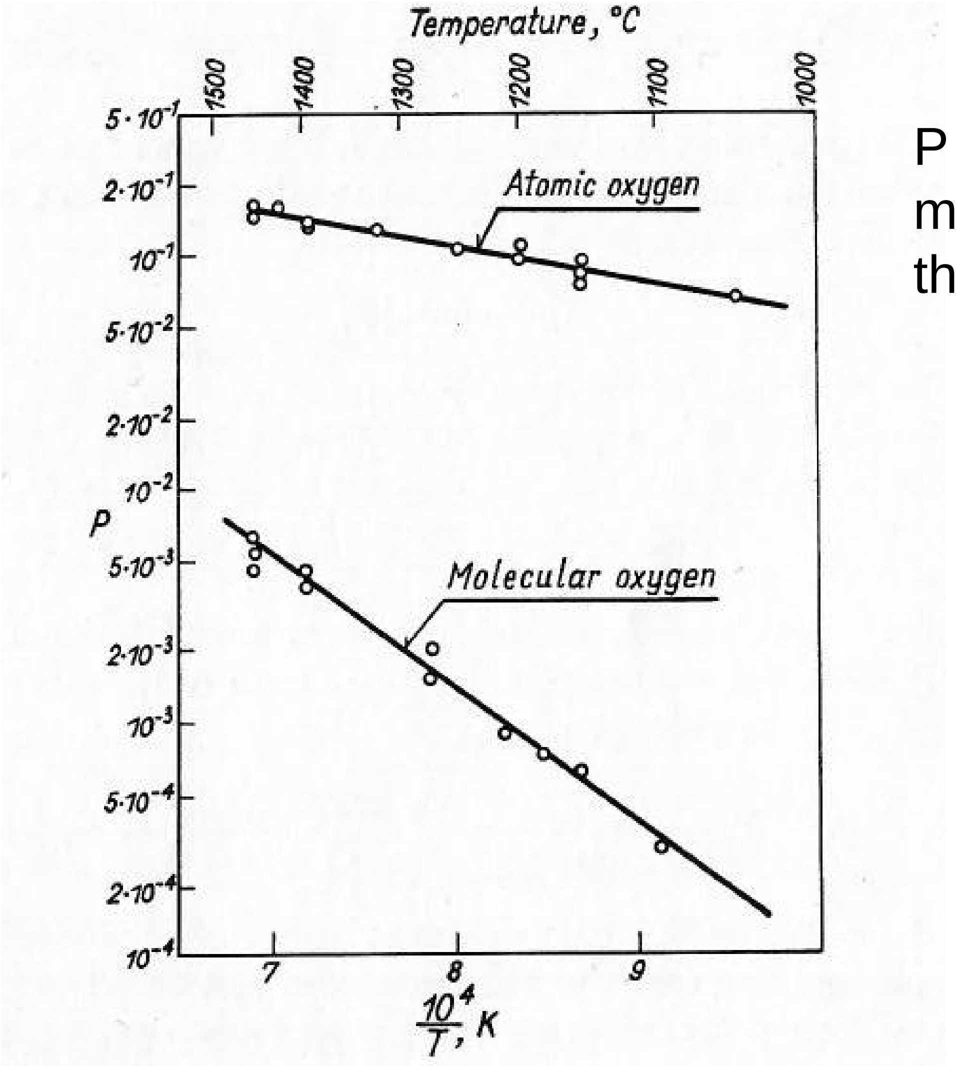
Mo oxidation in two oxidizing atmospheres



P – parameter being the measure of oxidation rate at the same oxidant pressure

S. Mrowec, „An Introduction to the Theory of Metal Oxidation", National Bureau of Standards and the National Science Foundation, Washington, D.C., 1982.

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Oxidation in air atmosphere (21% O_2 and 79% N_2)

The role of nitrogen in high temperature metal corrosion processes in air:

- enables nitride formation
- influences intrinsic defect concentration by doping the anion sublattice of the oxide, e.g. increases anion vacancy concentration in TiO_2:

$$TiO_2 + N_2 \Leftrightarrow Ti_{Ti}^{x} + 2N_O' + V_O^{\bullet\bullet} - O_O^{x} + \frac{3}{2} O_2$$

- influences corrosion process kinetics

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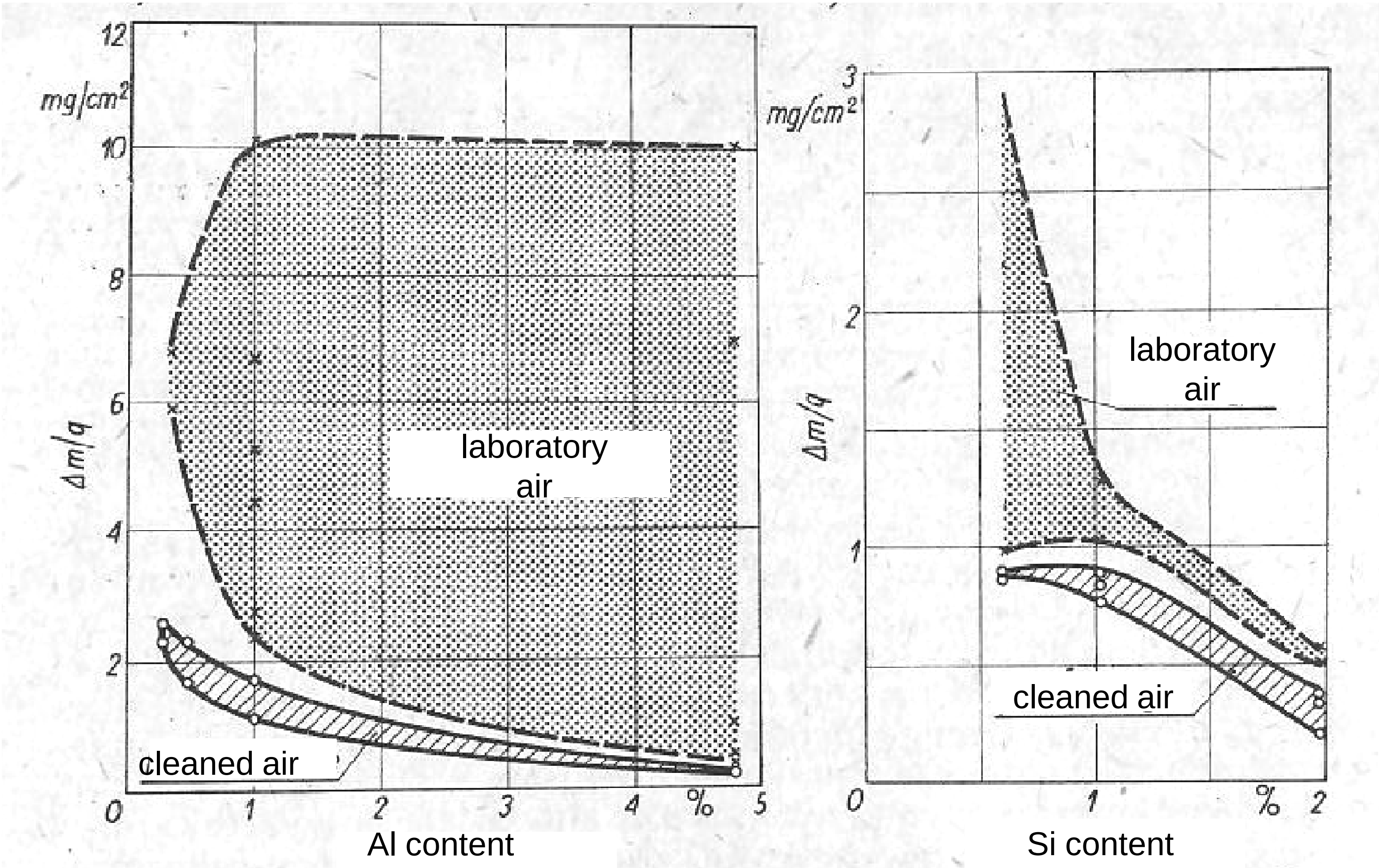
Mass gains of oxidized Fe-Al and Fe-Si alloys in laboratory and specially cleaned air (700 ^{o}C, 24 h)



S. Mrowec i T. Werber, Nowoczesne materiały żaroodporne, PWN, Warszawa1982

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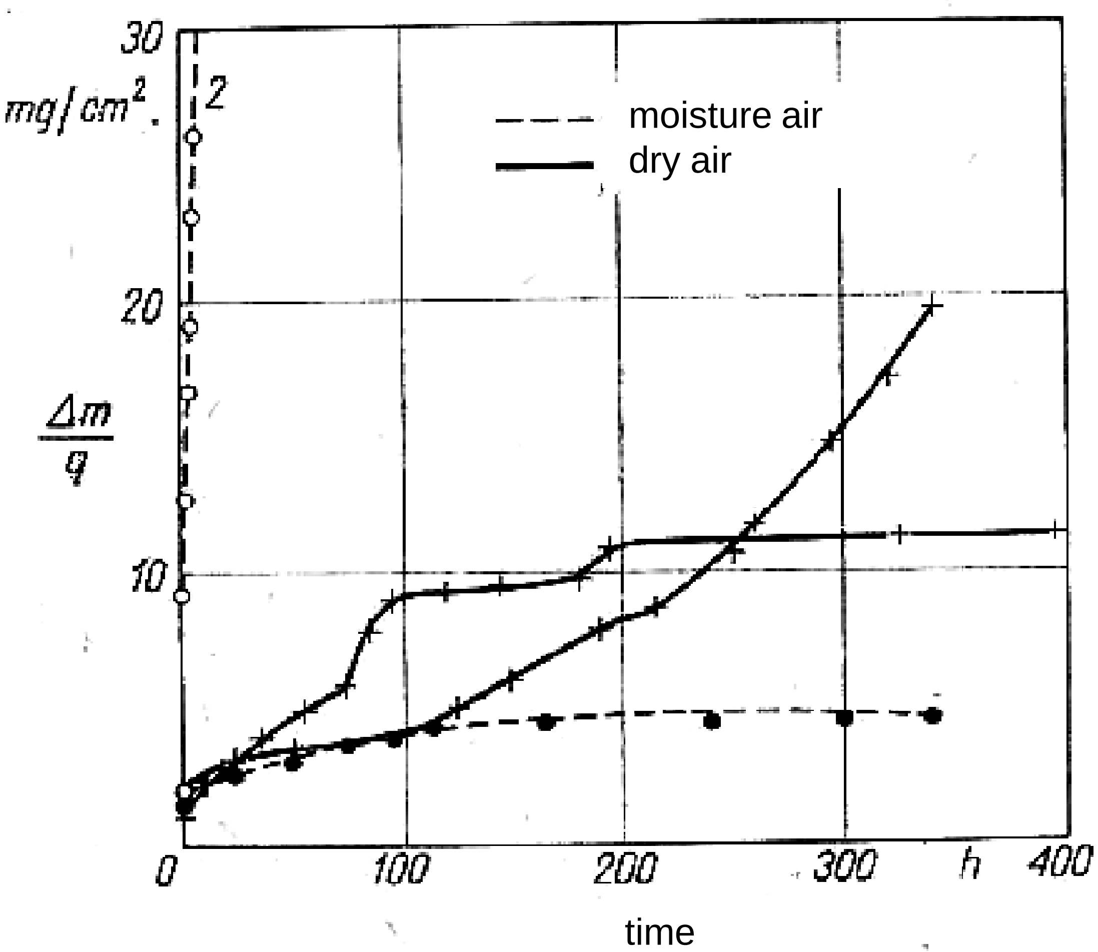
Influence of moisture in air on oxidation kinetics of chromium-nickel steels at different temperatures



S. Mrowec i T. Werber, Nowoczesne materiały żaroodporne, PWN, Warszawa1982

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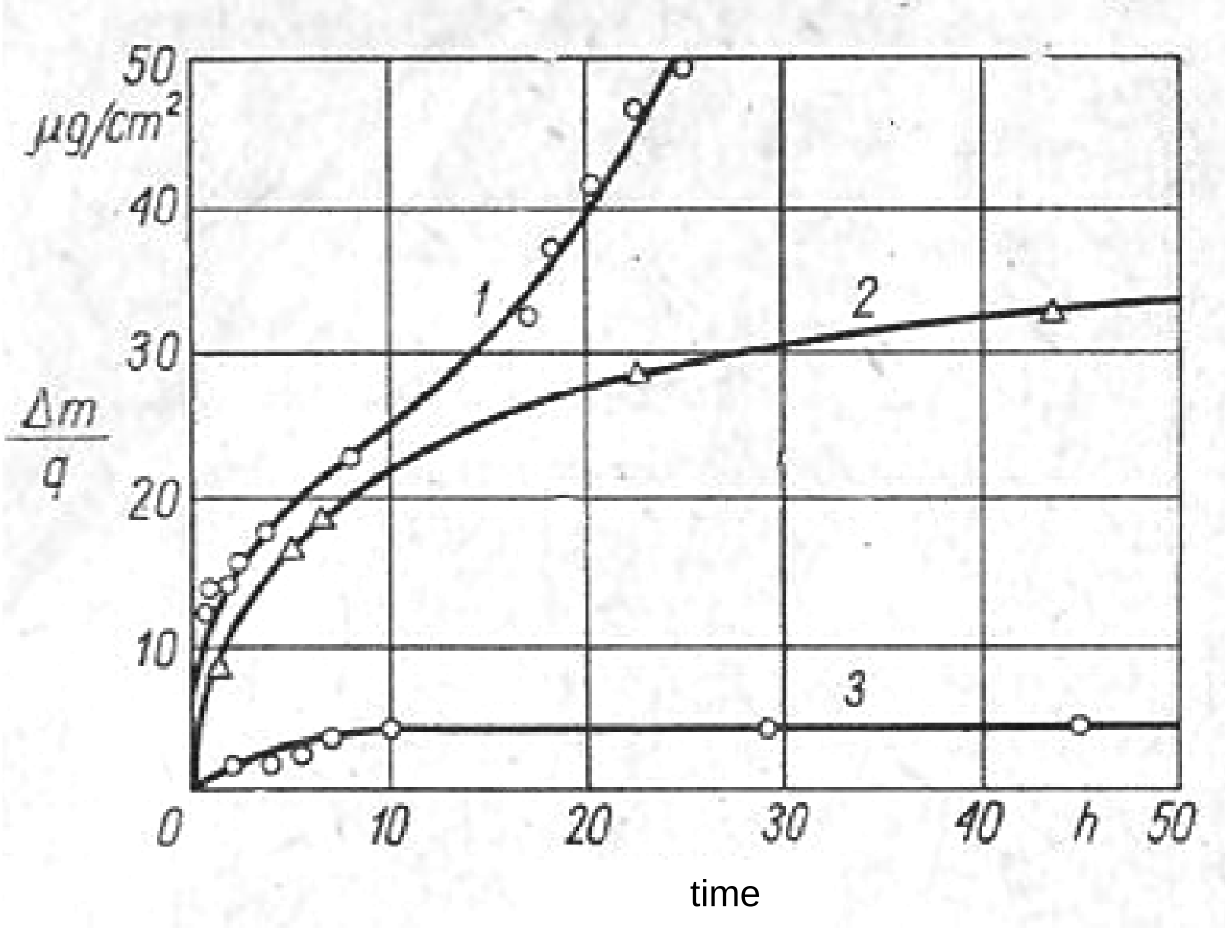
Influence of organic impurities in air on Mg oxidation kinetics at 525 ^oC



time

1 – oxygen + 0,5% n-nonane
2 – unclean oxygen from grease vapors
3 – specially cleaned oxygen

S. Mrowec i T. Werber, Nowoczesne materiały żaroodporne, PWN, Warszawa1982

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Role of water vapor in oxidation

- decarburization of alloys due to hydrogen
- worsening of material physical properties
- at high water vapor temperatures and pressures the corrosion mechanism is similar to the electrochemical corrosion mechanism
- as a rule, selective oxidation of alloys
- change in corrosion mechanism and rate
- enabling the formation of volatile metal hydroxides
- most steels oxidize in water vapor or air, or exhaust gases containing water vapor faster than in “dry” air.

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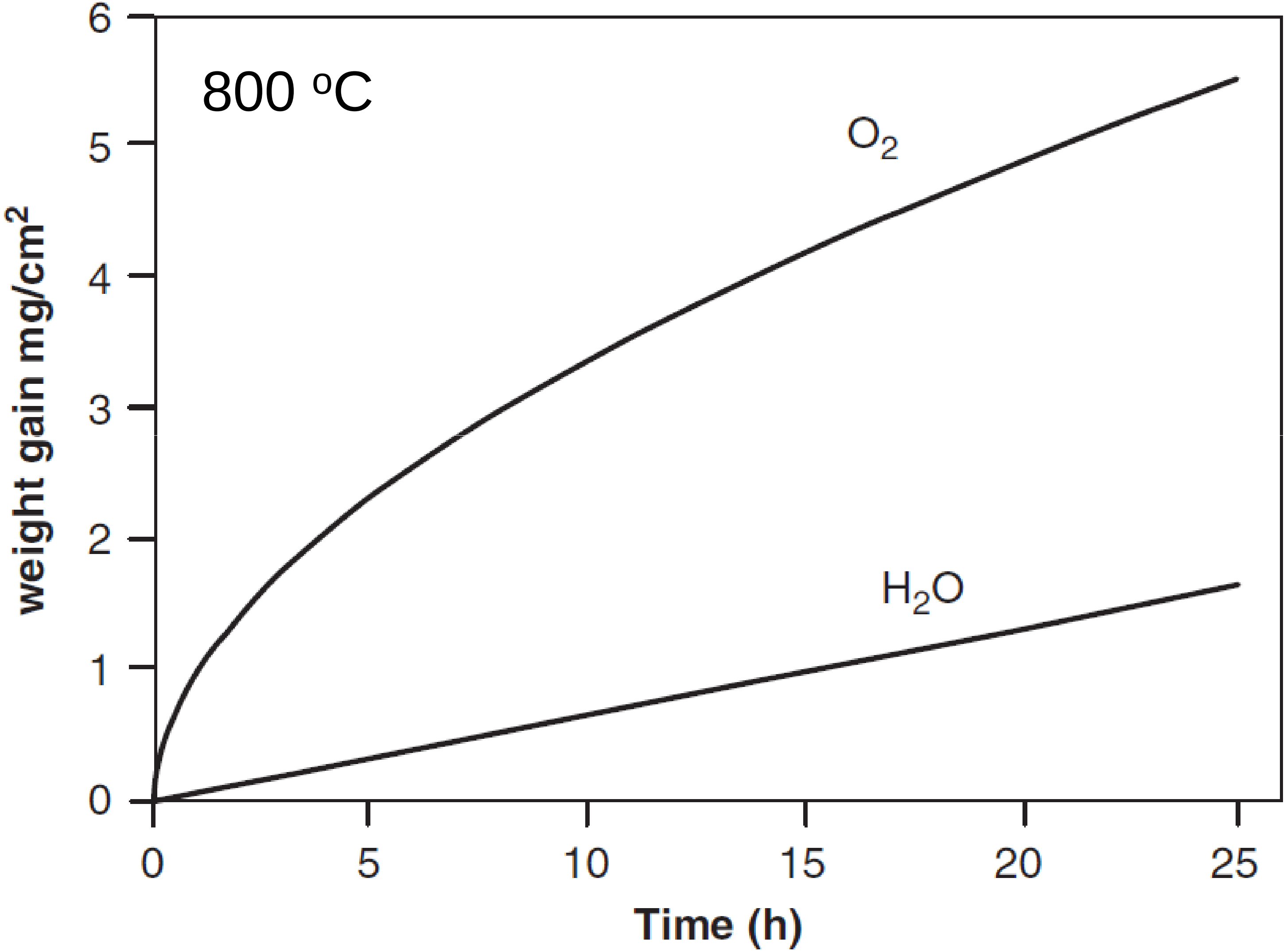
Nickel oxidation kinetics in oxygen and water vapor



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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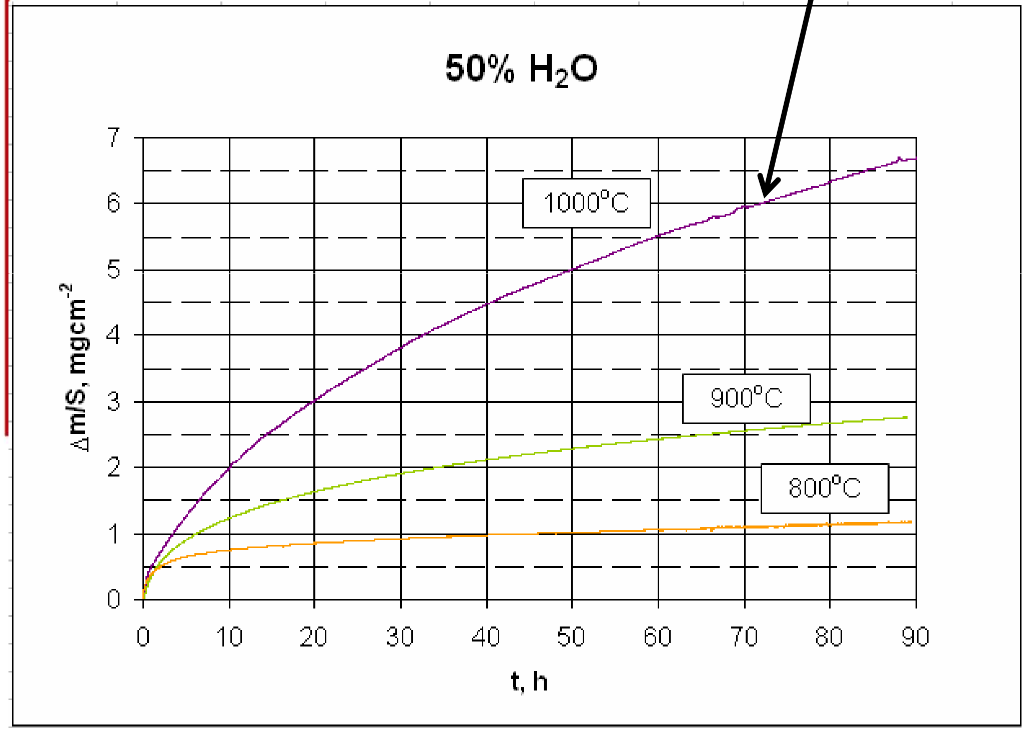
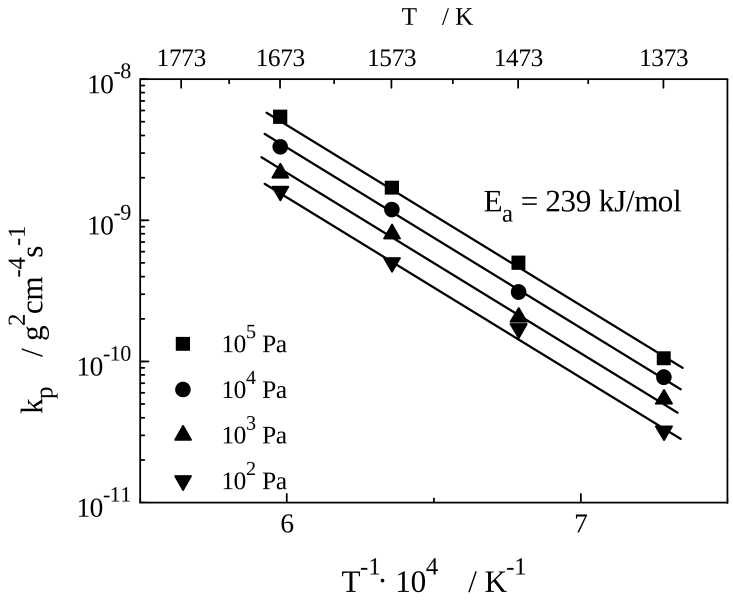
Nickel oxidation kinetics in O_2-50%H_2O atmosphere

$k_p = 1{,}4 \cdot 10^{-10}\ g^2cm^{-4}s^{-1}$



Klaudia Wrona, Master Thesis „Utlenianie niklu w atmosferach zawierających parę wodną", AGH, Kraków, 2009



S. Mrowec, Z. Grzesik, Journal of Physics and Chemistry of Solids, 65, 1651-1657 (2004).

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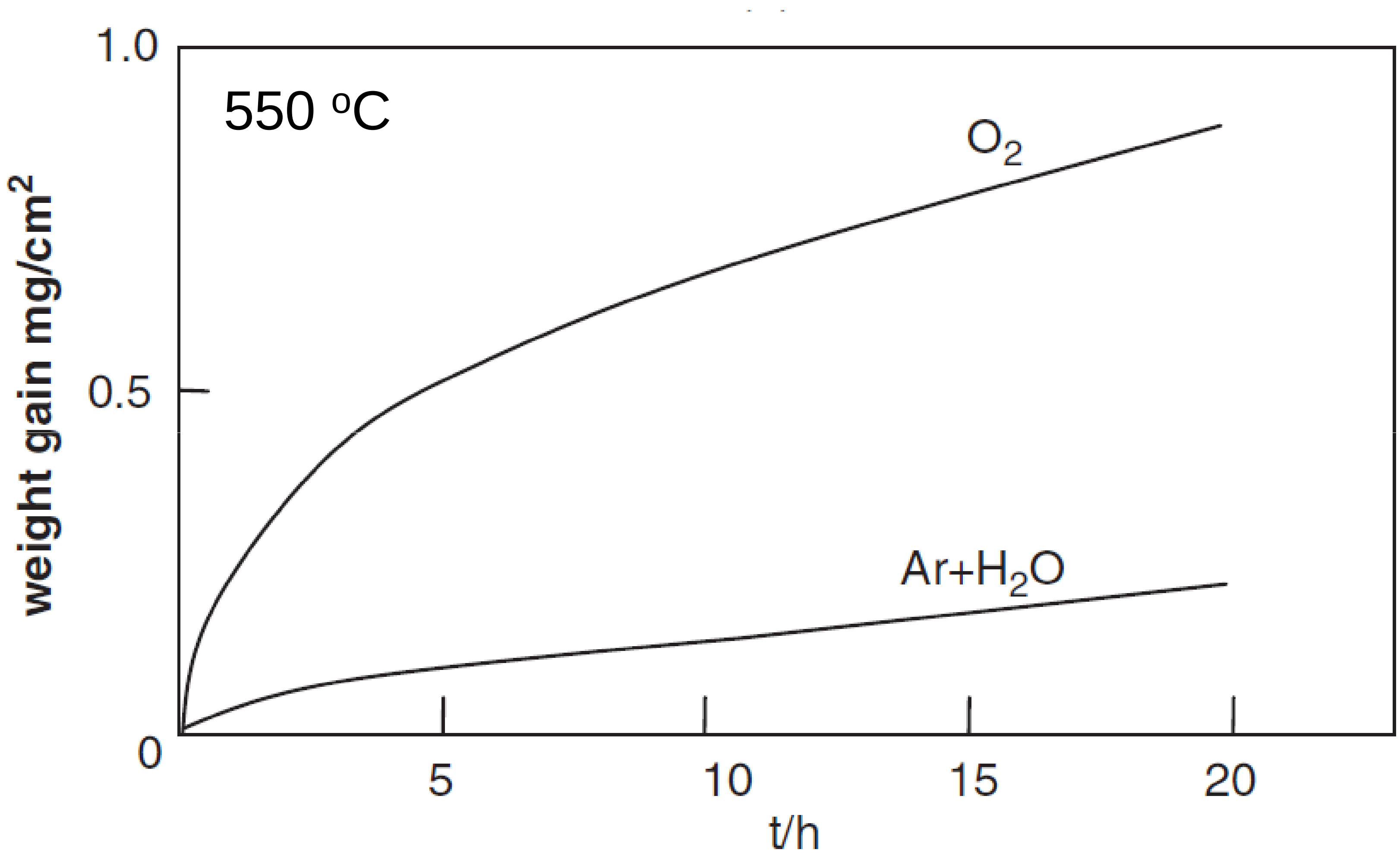
Oxidation kinetics of iron in oxygen and an argon-water vapor mixture



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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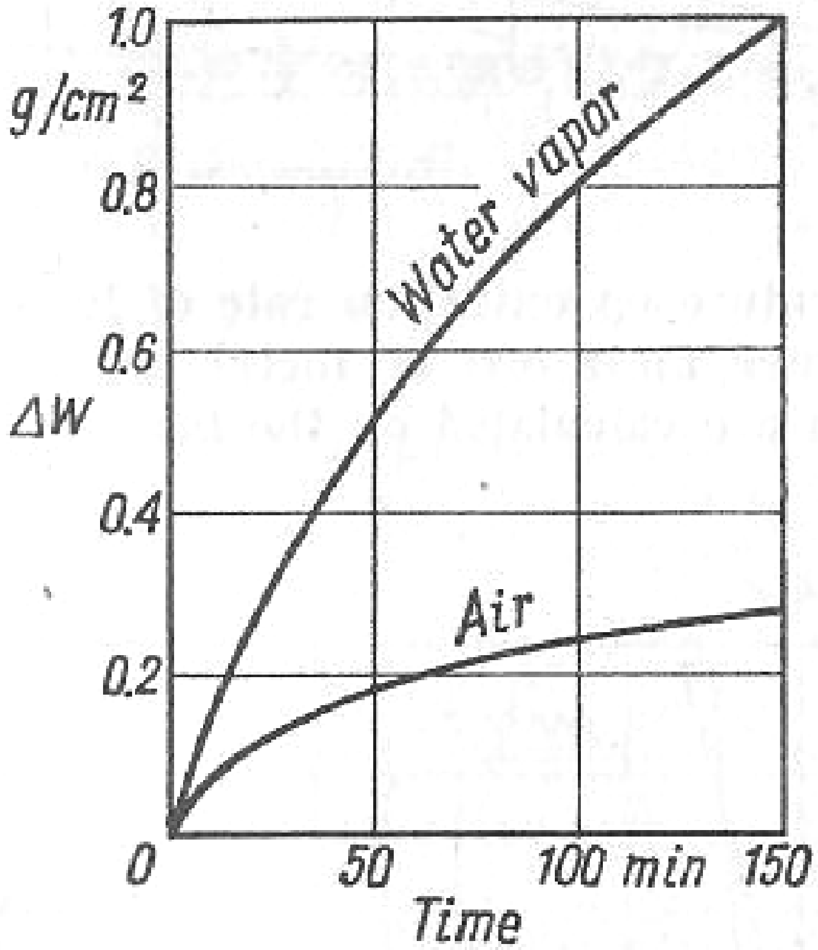
Influence of water vapor on the oxidation rate of carbon steels



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

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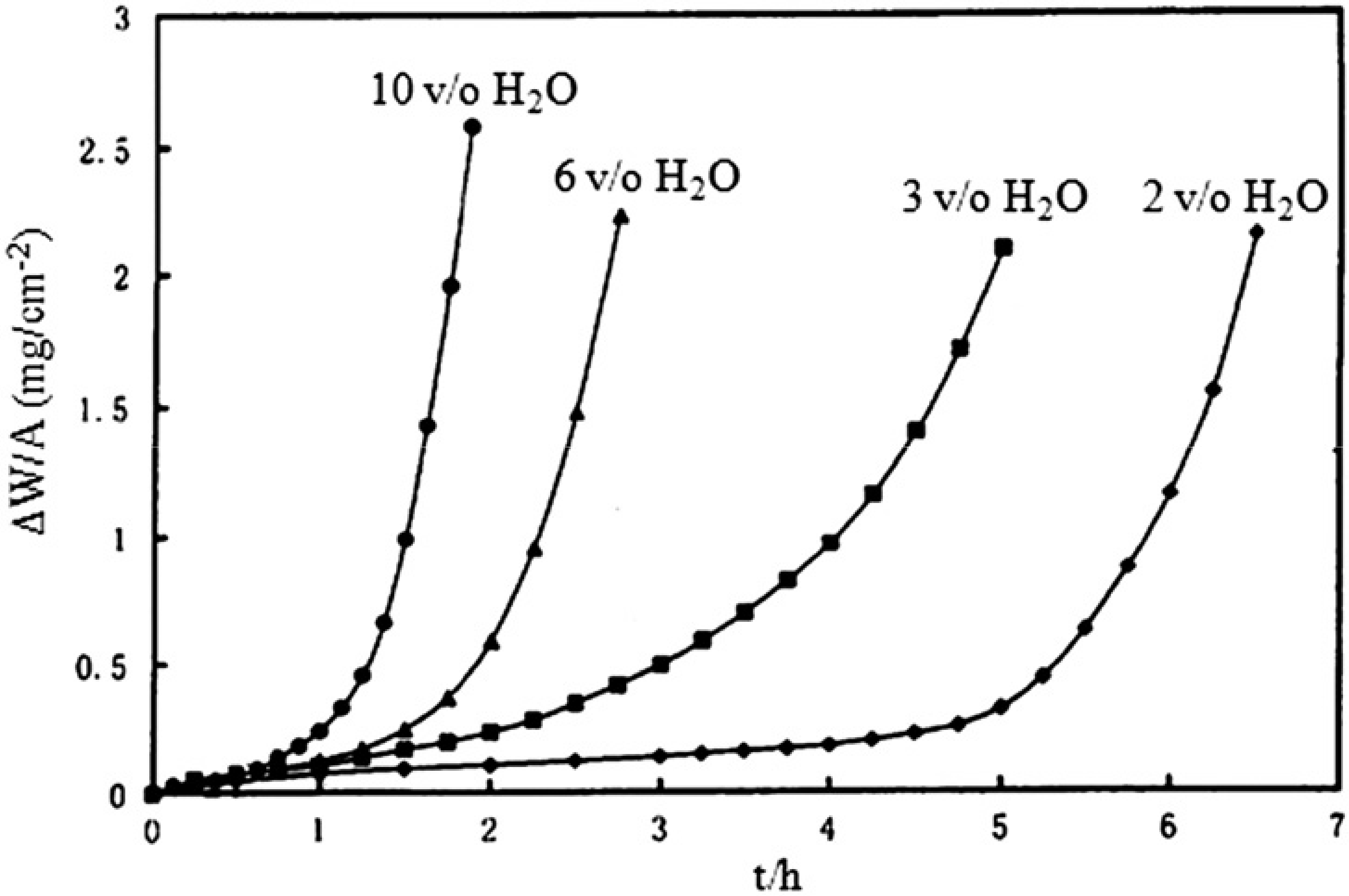
Influence of water vapor on the oxidation rate of Fe-15Cr steel in oxygen at 900 ^oC



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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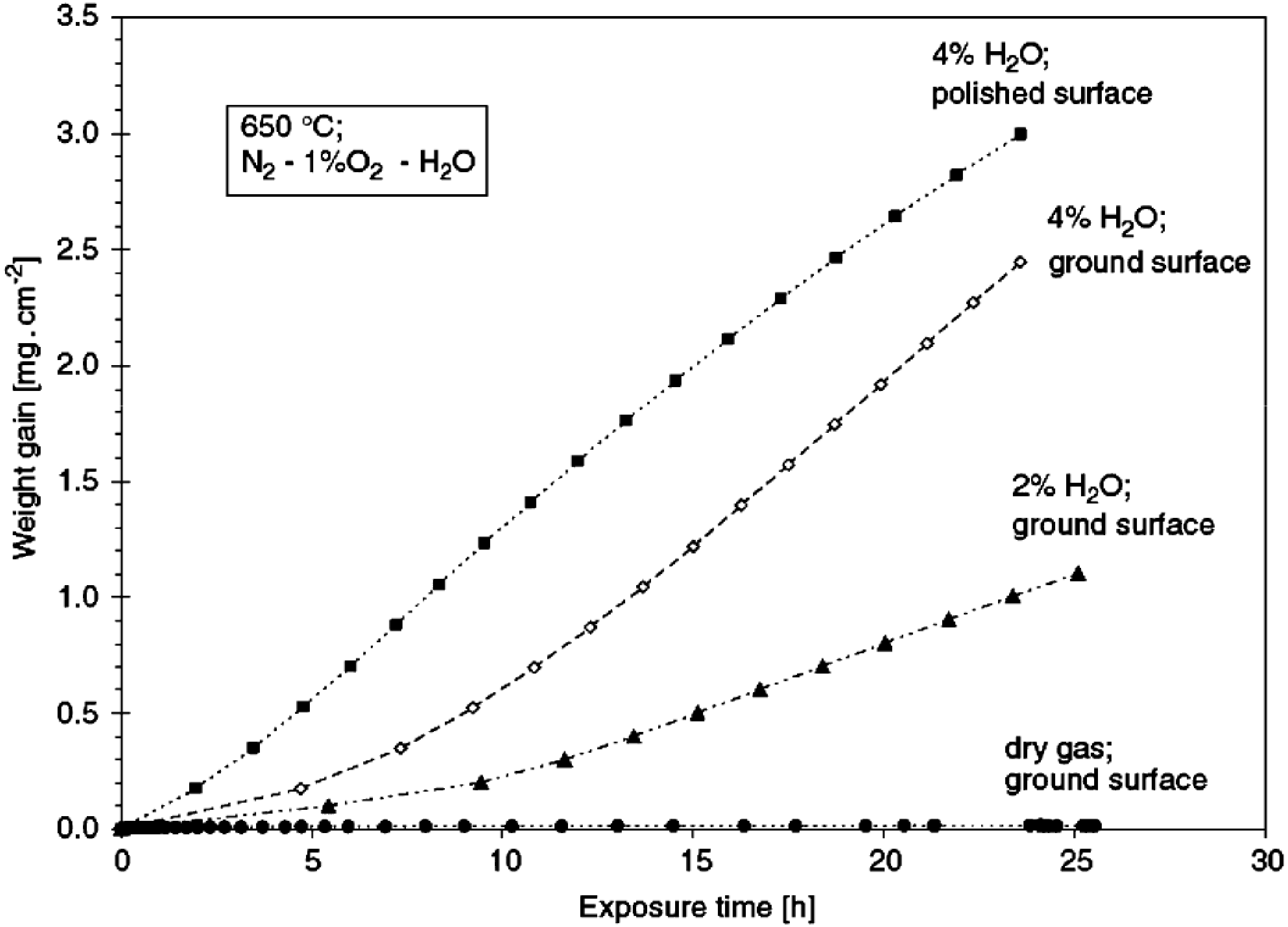
Influence of water vapor on the oxidation rate of boiler steel P91



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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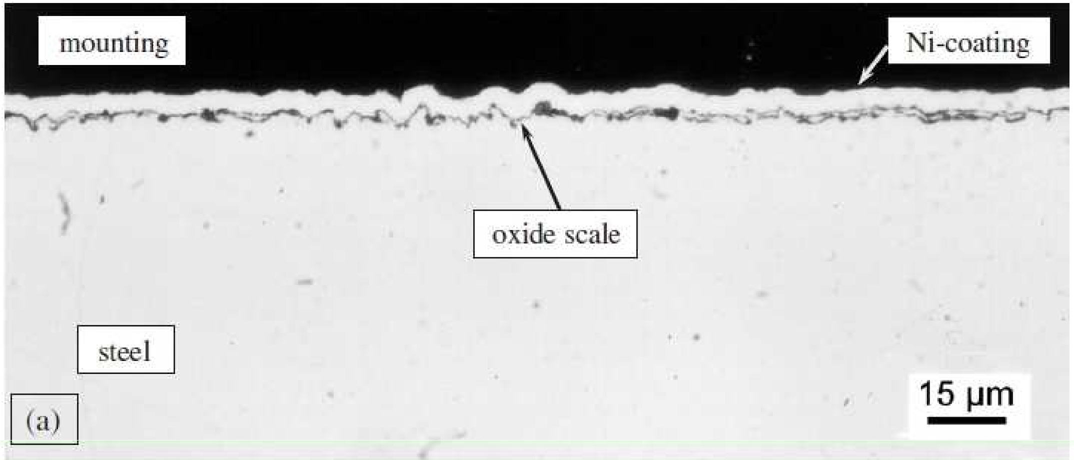
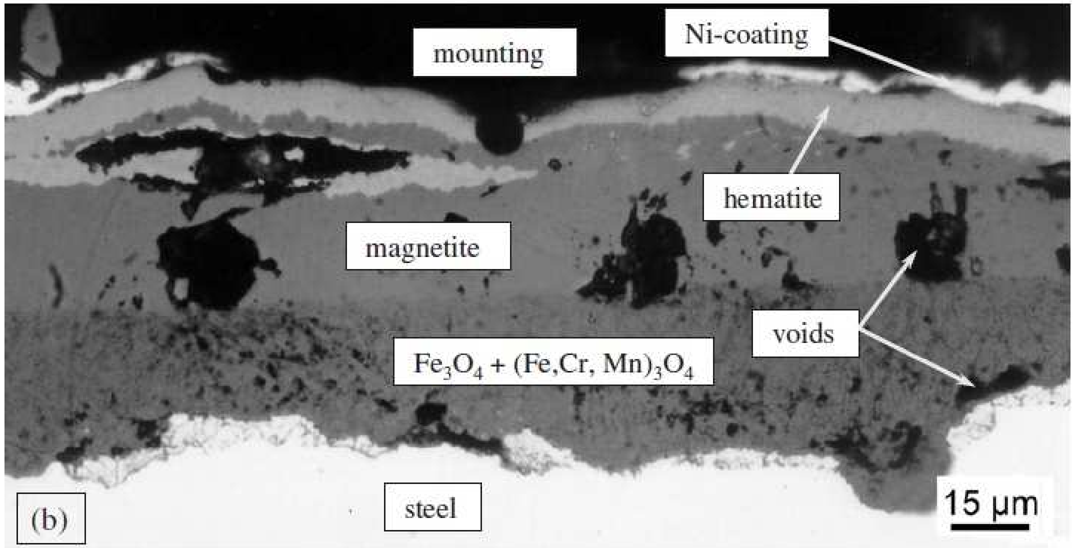
Influence of water vapor on the morphology of the scale formed on a P91 boiler steel sample oxidized for 100 h at 650 °C



N_2-1%O_2



N_2-1%O_2-2% H_2O

D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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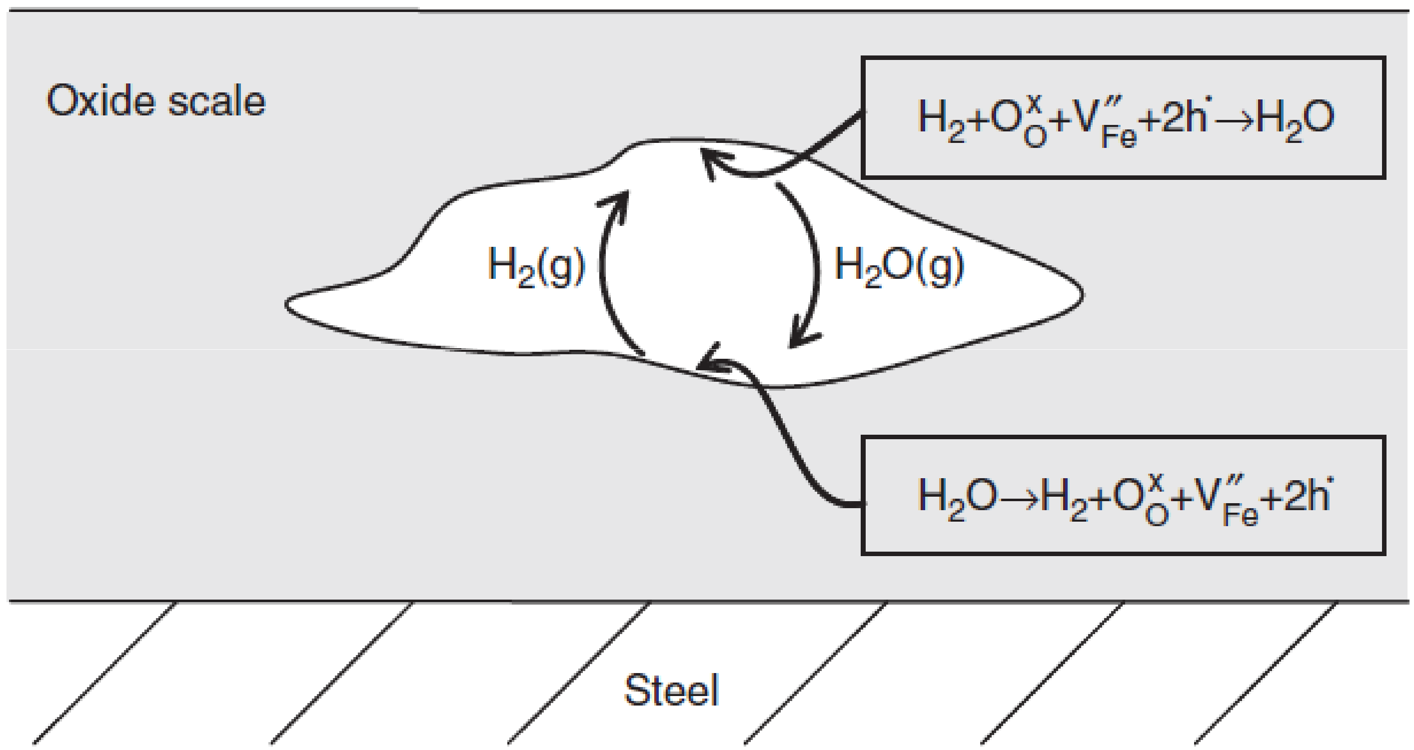
Schematic illustration of oxygen transport through water vapor in a porous scale formed on diluted Fe-Cr alloys



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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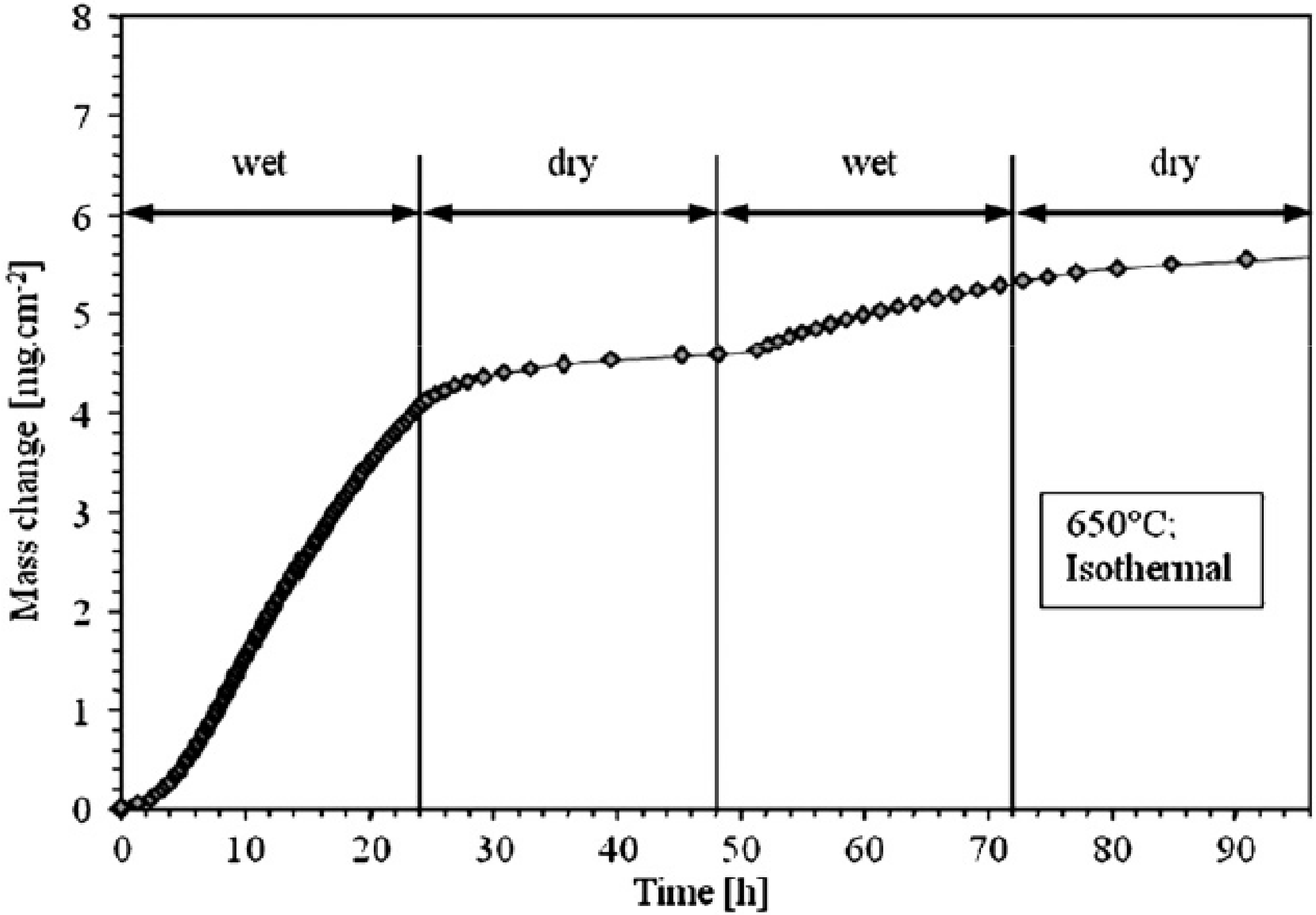
Oxidation kinetics of P91 steel at 650 ^oC in an atmosphere with an alternating composition of N_2-1%O_2-4%H_2O (wet) and N_2-1%O_2 (dry)



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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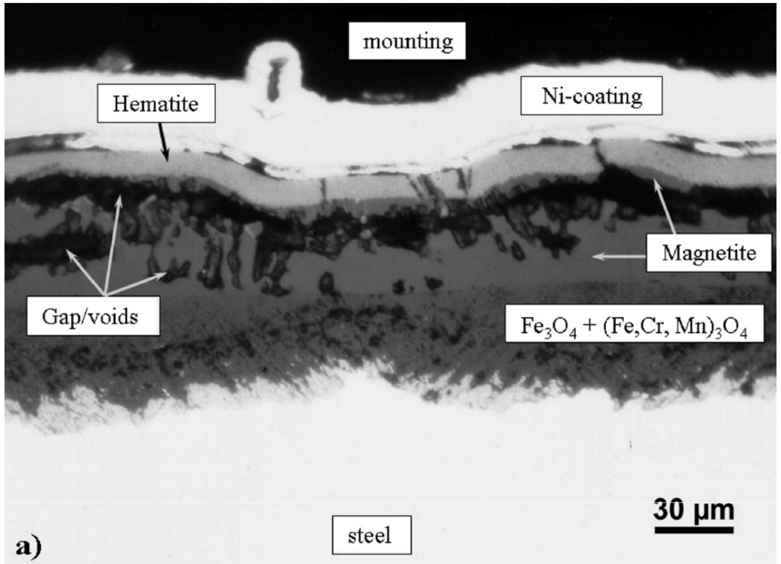
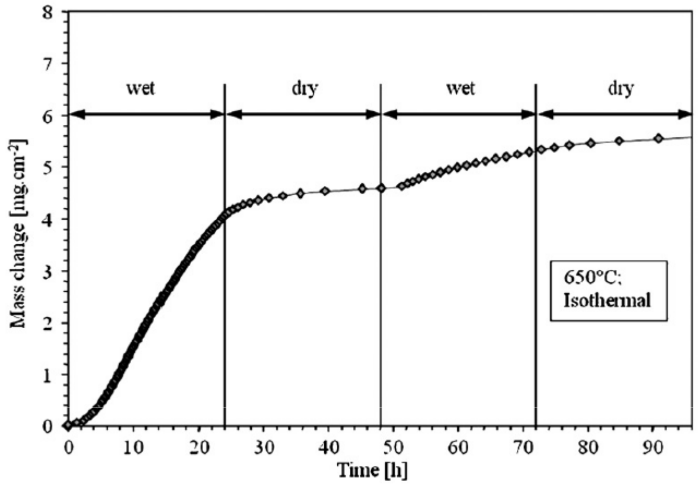
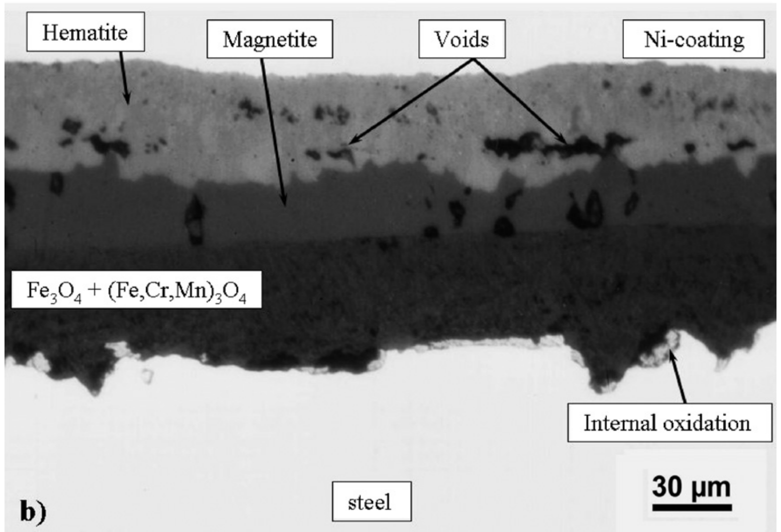
Cross-sections of scales formed on P91 steel at 650 °C in N_2-1%O_2-4%H_2O (a) and N_2-1%O_2 (b)



t = 24 h





t = 48 h

⇨ decrease in porosity

⇨ conversion of Fe_3O_4 to Fe_2O_3

⇨ improvement in scale protective properties

D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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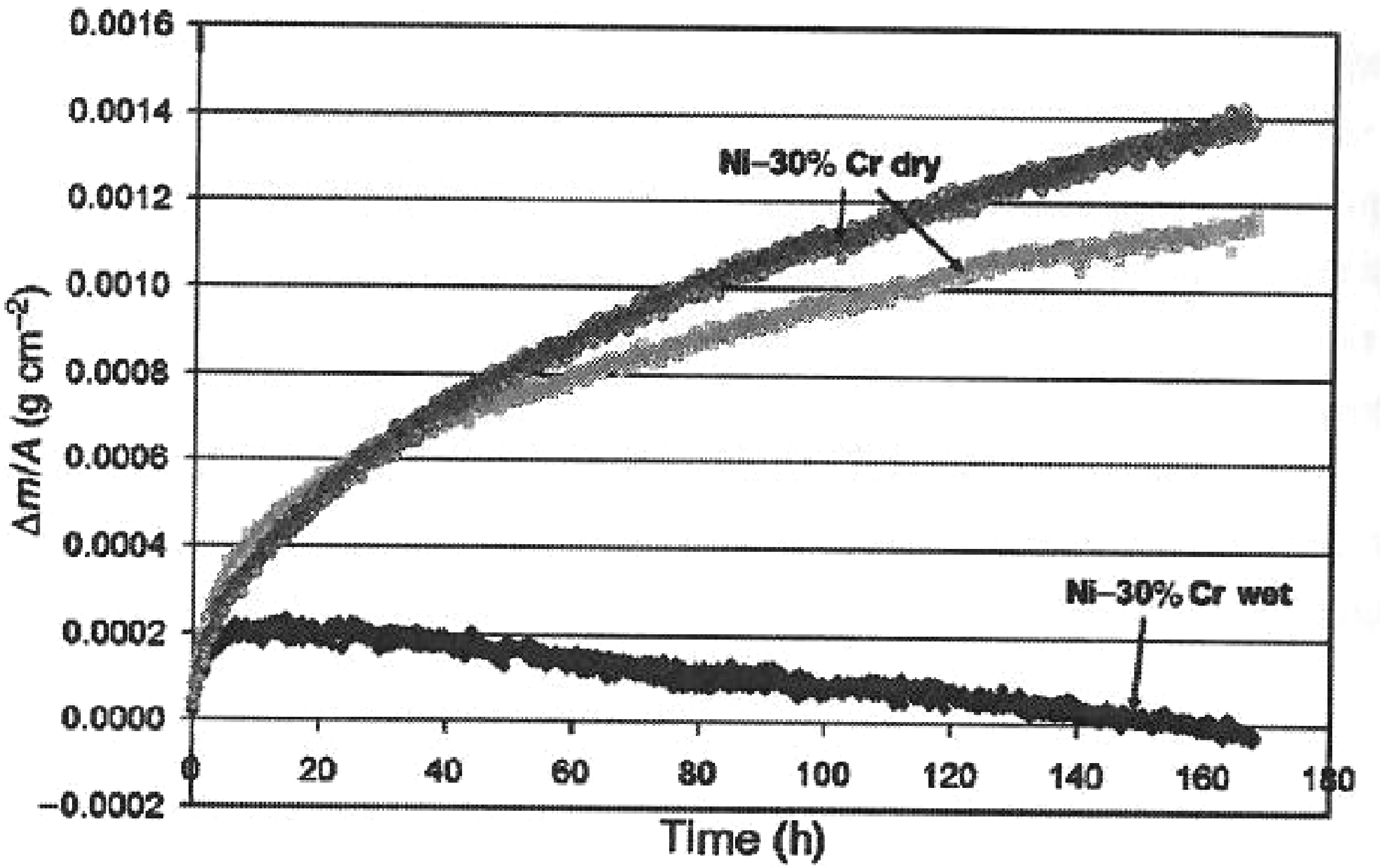
Influence of water vapor on the oxidation rate of Ni-30 %wt. Cr steel at 900 °C



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

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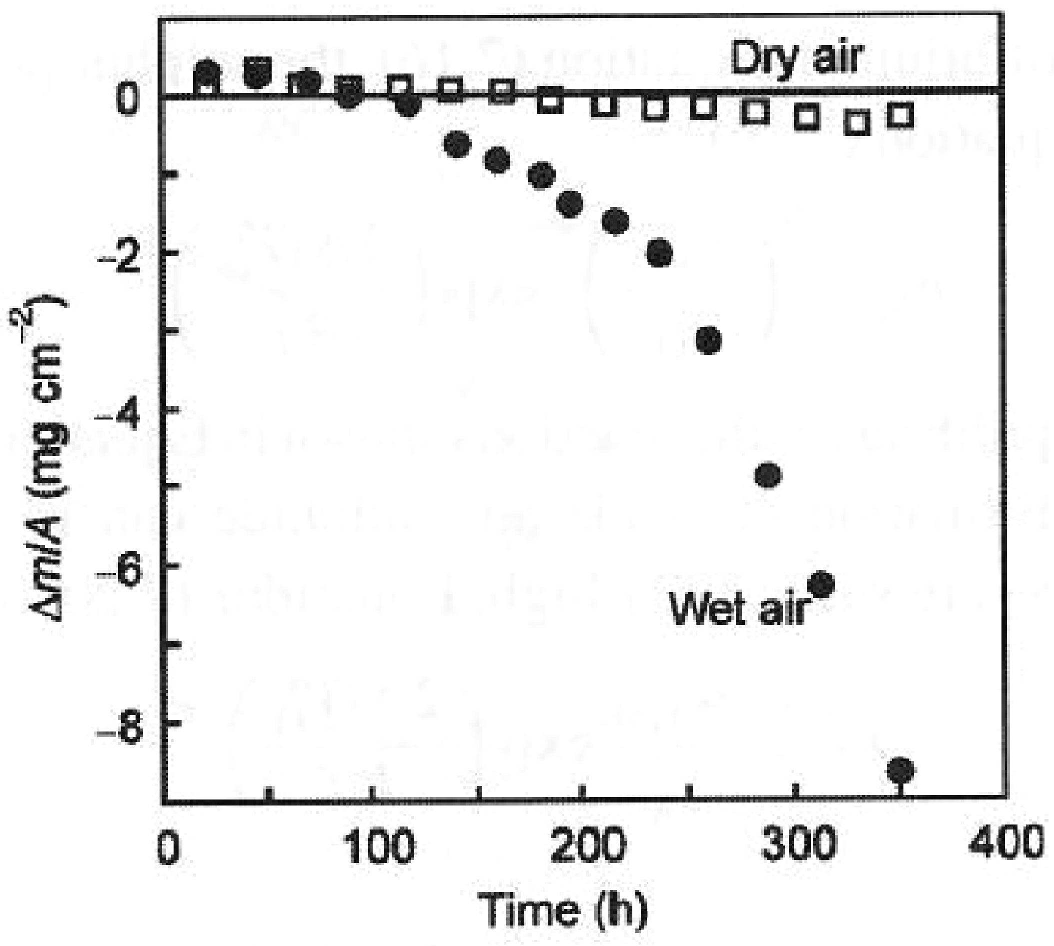
Influence of water vapor on the oxidation rate of CMSX-4 alloy in cyclic conditions (25 - 1100 ^{o}C)



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

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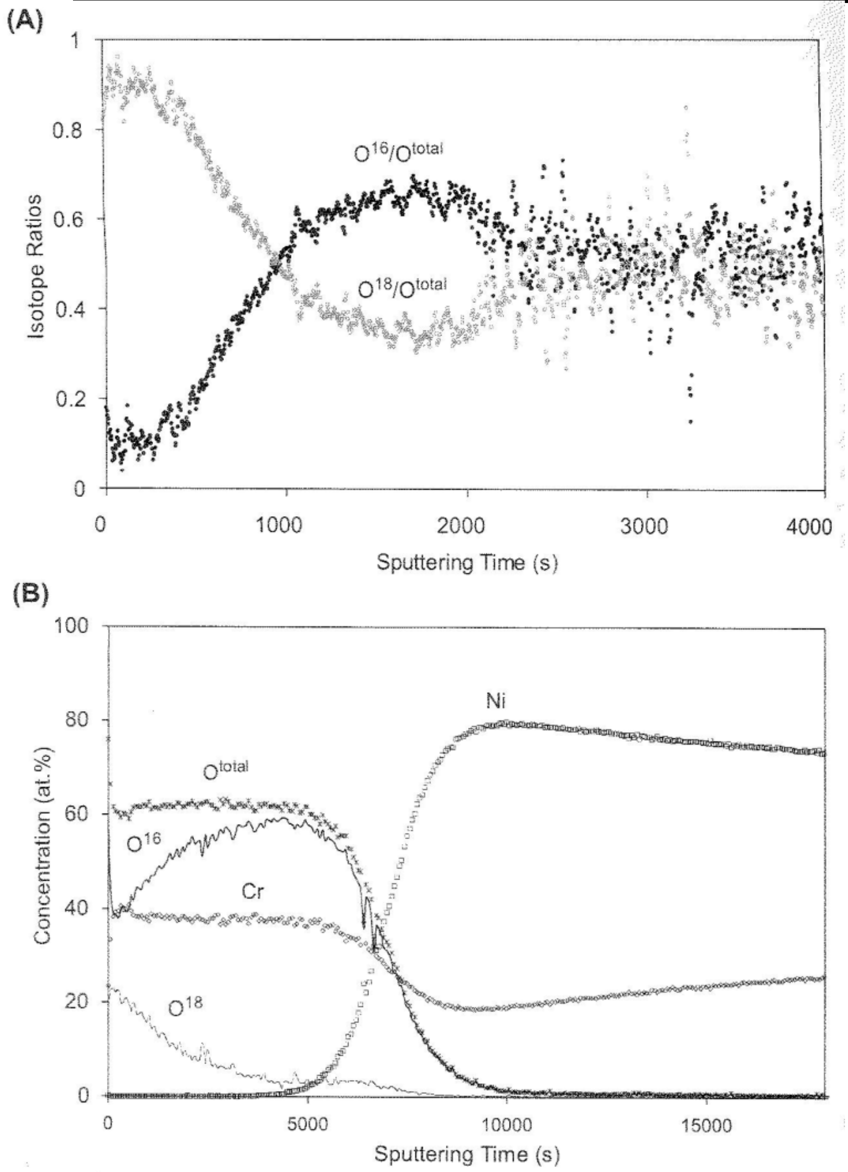
Concentration profiles of O^{16} and O^{18} in a Ni-Cr sample after two-stage oxidation at 1323 K, illustrating the change in oxidation mechanism



I stage: Ar-20%$^{16}O_2$; 0,5 h
II stage: Ar-20%$^{18}O_2$; 2 h

I stage: Ar-4%H_2-2%$H_2{}^{16}O_2$; 0,5 h
II stage: Ar-4%H_2-2%$H_2{}^{18}O_2$; 2 h

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

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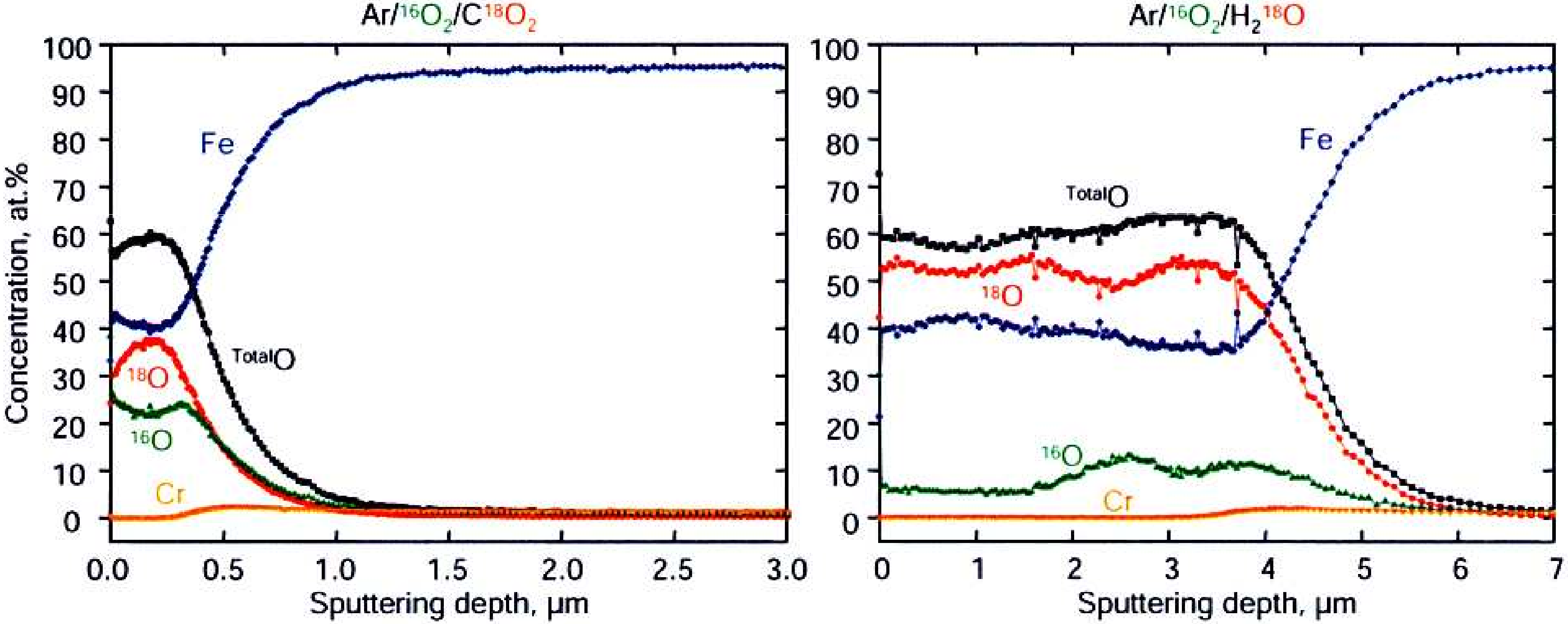
Concentration profiles of Cr, Fe, O^{16} and O^{18} in a 13CrMo4-4 steel sample after oxidation at 823 K, explaning the influence of water vapor on the oxidation process

Ar / 1% $^{16}O_2$ / 1% $C^{18}O_2$; 2 h — Ar / 1% $^{16}O_2$ / 2% $H_2{}^{18}O$; 2 h



T. Olszewski, „Oxidation mechanisms of materials for heat exchanging components in CO_2/H_2O-containing gases relevant to oxy-fuel environments", Forschungszentrum Jülich GmbH, Jülich, 2012

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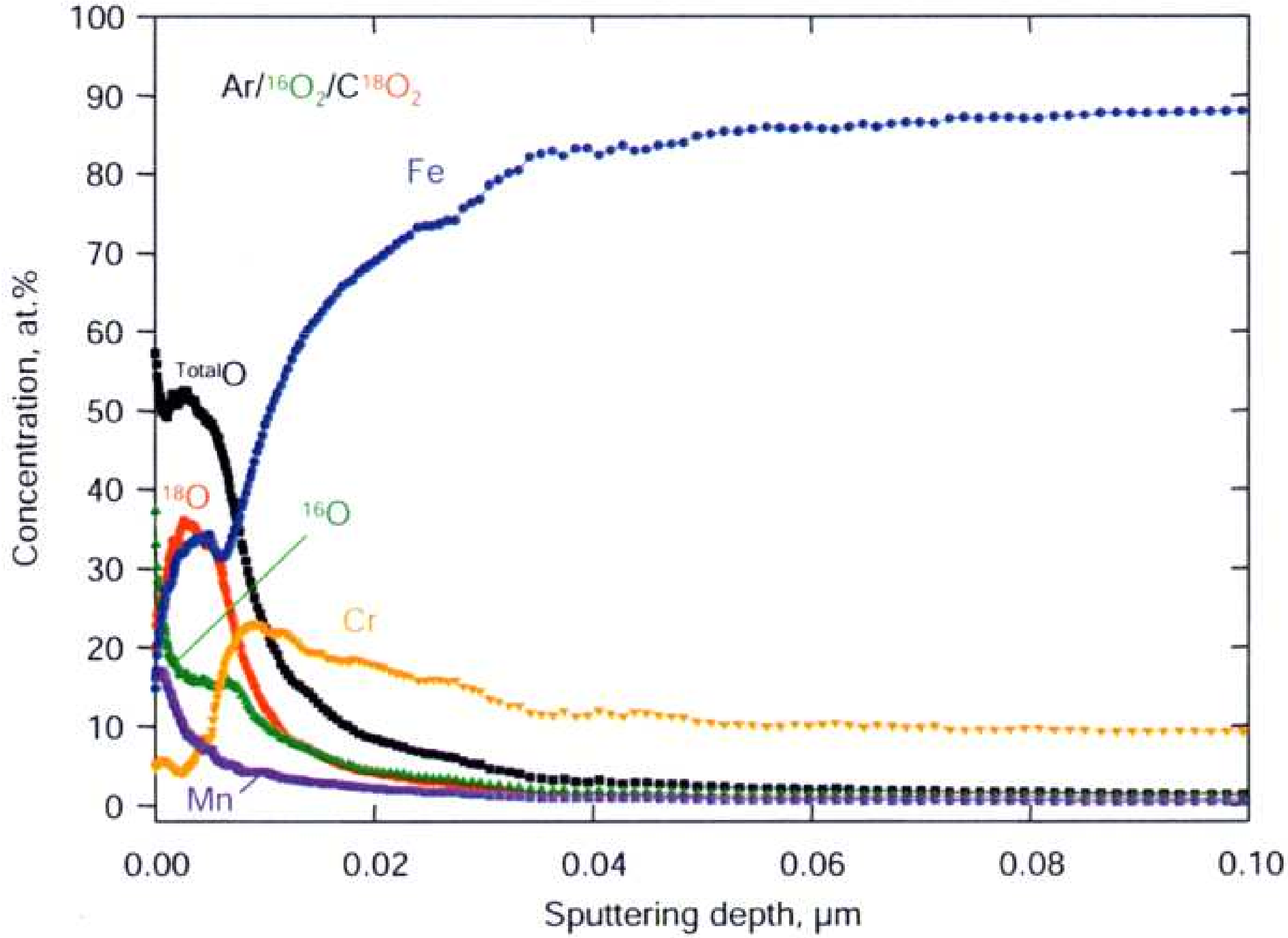
Element concentration profiles in an INCONEL 617 sample after oxidation, explaning the influence of water vapor on the oxidation process

Ar / 1% $^{16}O_2$ / 2% $H_2{}^{18}O$ T = 1173 K



T. Olszewski, „Oxidation mechanisms of materials for heat exchanging components in CO_2/H_2O-containing gases relevant to oxy-fuel environments", Forschungszentrum Jülich GmbH, Jülich, 2012

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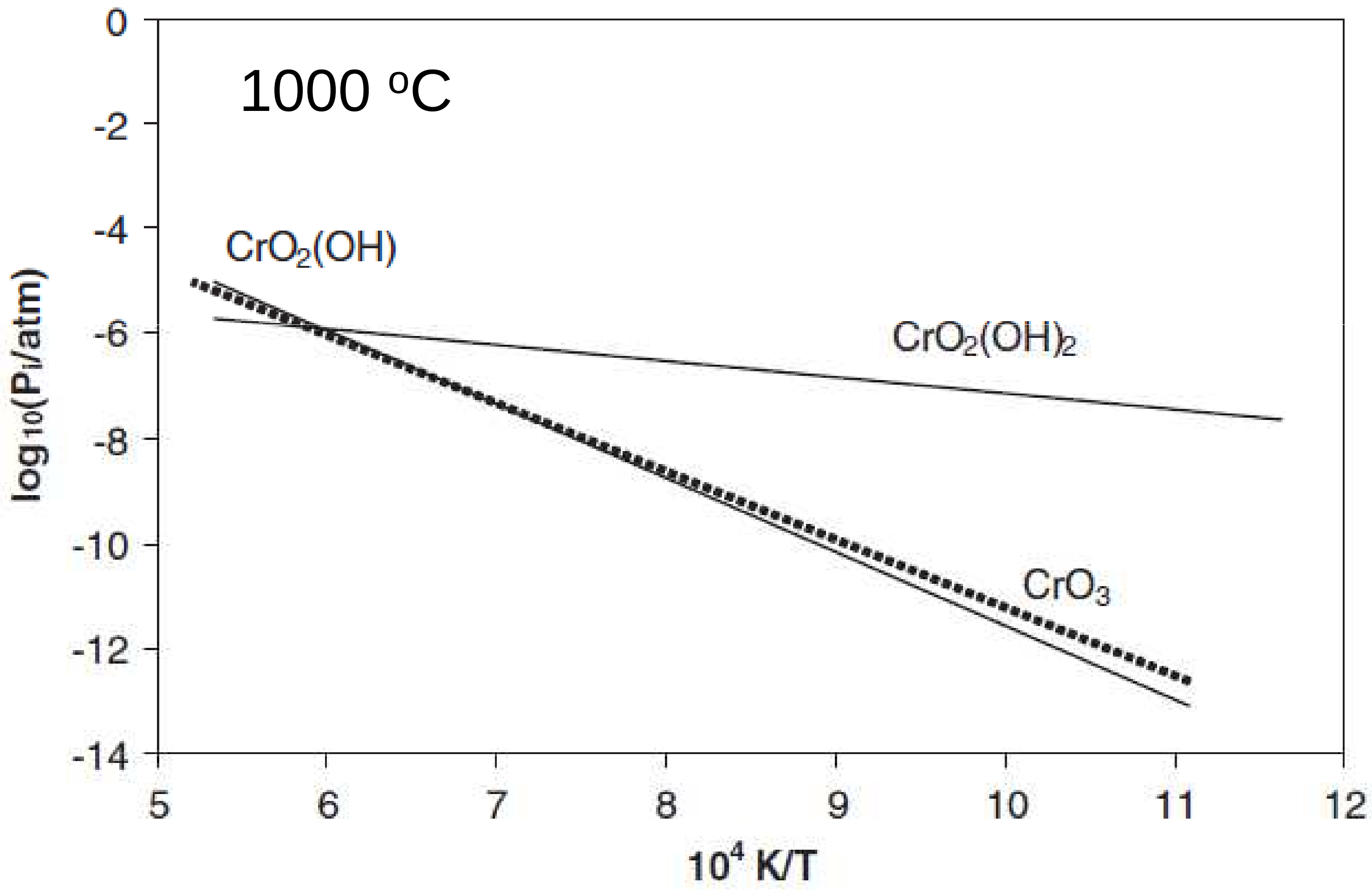
Temperature dependence of the pressures of selected volatile chromium oxides and hydroxides at oxygen pressure 0.21 atm and water vapor pressure 0.04 atm



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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Standard free enthalpy of formation reactions for several metal hydroxides

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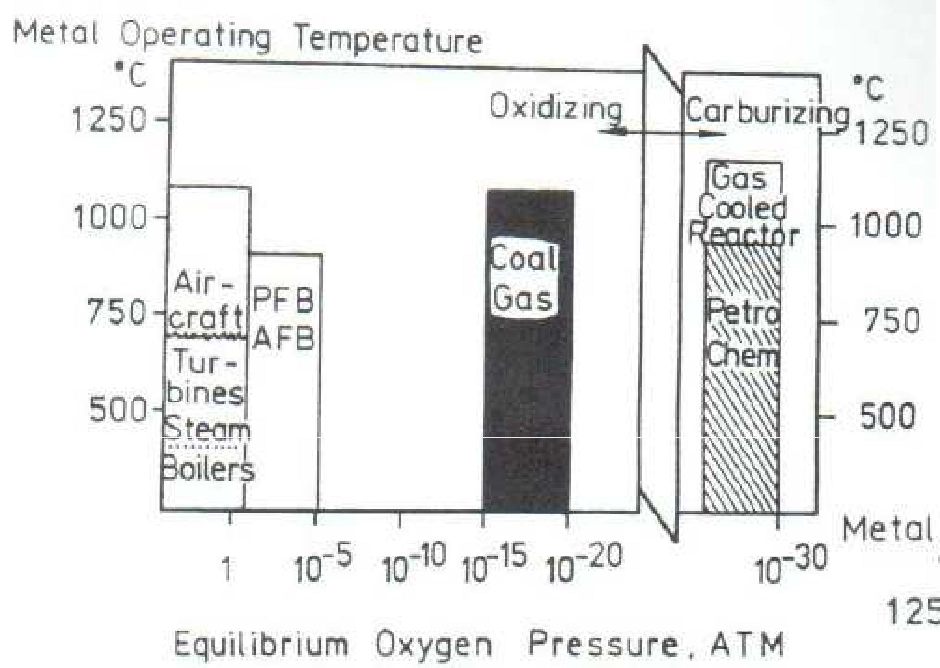
Table 10.1 Standard free energies of metal hydroxide formation reactions[a]

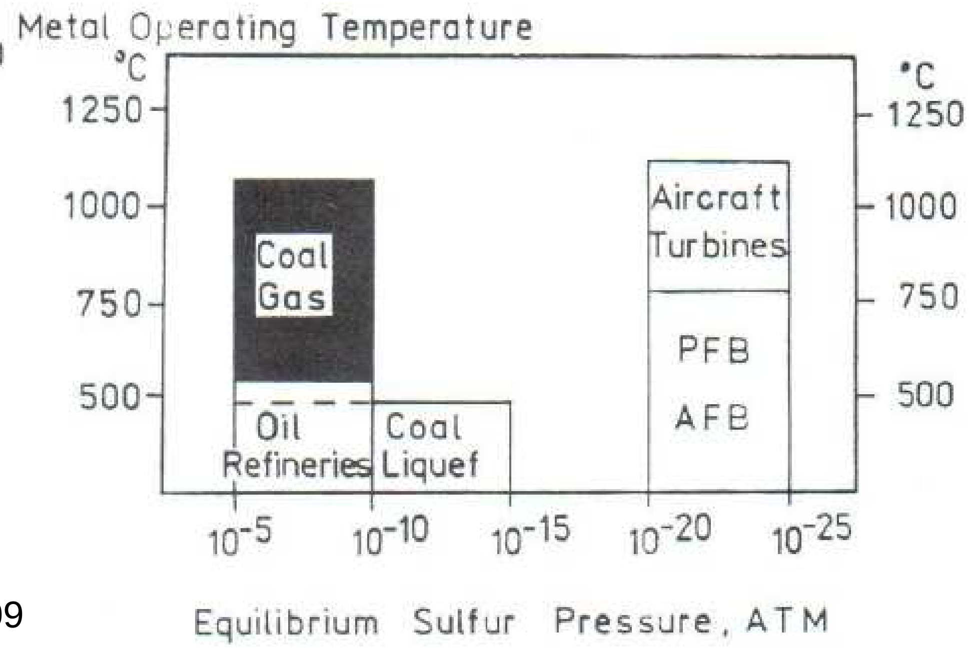
Reaction	$\Delta G^\circ = A + BT$ (J)		Ref.
	A	*B*	
$FeO(s) + H_2O(g) = Fe(OH)_2(g)$	175,700	−31.4	[5]
$Fe_3O_4(s) + 3H_2O(g) = 3Fe(OH)_2(g) + \frac{1}{2}O_2(g)$	818,400	−193	[6]
$Fe_2O_3(s) + 2H_2O(g) = 2Fe(OH)_2(g) + \frac{1}{2}O_2(g)$	663,300	−200	[7]
$NiO(s) + H_2O(g) = Ni(OH)_2(g)$	219,000	−50.7	[6]
$Cr_2O_3(s) + 2H_2O(g) + \frac{3}{2}O_2(g) = 2CrO_2(OH)_2(g)$	53,500	45.5	[8]
$Al_2O_3(s) + 3H_2O(g) = 2Al(OH)_3(g)$	220,000	−14.7	[9]
$SiO_2(s) + 2H_2O(g) = Si(OH)_4(g)$	47,900	72.3	[10–12]

[a]For mole numbers of reactions as written.

D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

Schematic illustration of sulphidizing-oxidizing atmospheres present in selected branches of modern industry





S. Mrowec, Oxidation of Metals, 44 (1995) 177-209

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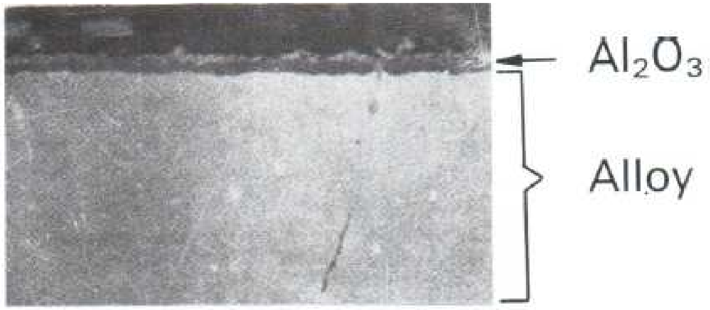
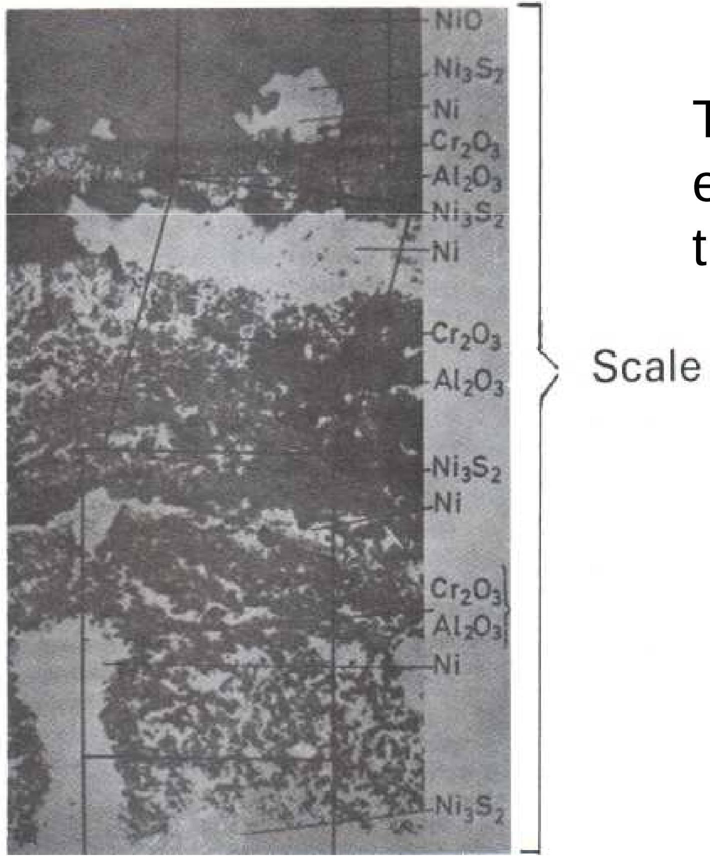
Cross-sections of scales formed on Ni-9Cr-6Al-0.1Y in two different aggresive atmospheres



T = 1000 ^oC
air
t = 40 h



T = 950 ^oC
exhaust gases with 550 ppm sulphur
t = 96 h

S. Mrowec, Oxidation of Metals, 44 (1995) 177-209

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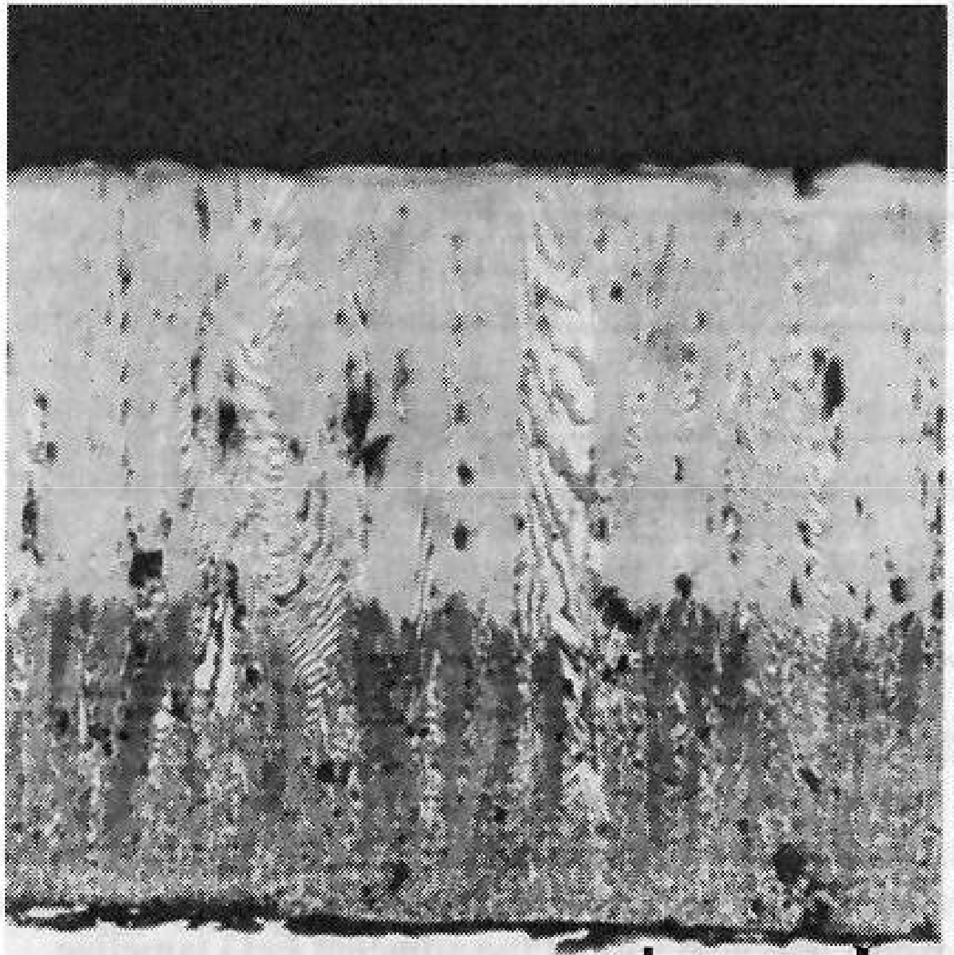
Cross-section of a sulphide-oxide scale, grown on iron at 900 ^oC in Ar-1%SO_2 atmosphere



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

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Formation of metastable sulfides in SO_2 atmosphere

Thermodynamic and kinetic aspects of the formation of complex duplex-type scales in SO_2-containing atmospheres

$$2\,M + SO_2 \leftrightarrow 2\,MO + \tfrac{1}{2}\,S_2$$

$$M + SO_2 \leftrightarrow MS + O_2$$

$$3\,M + SO_2 \leftrightarrow 2\,MO + MS$$

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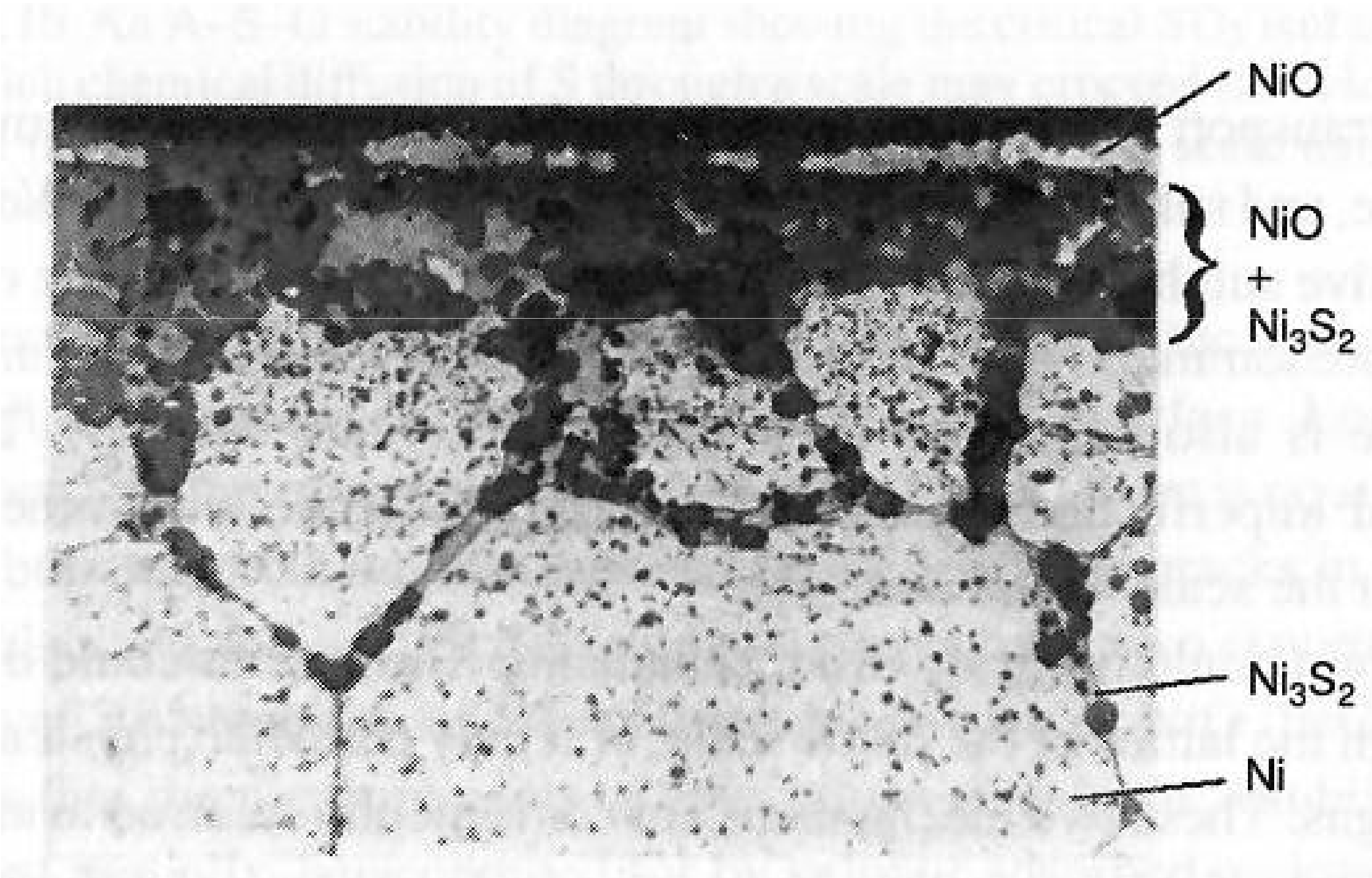
Cross-section of a sulphide-oxide scale, grown on nickel at 1000 ºC in SO_2 atmosphere, illustrating substrate penetration along grain boundaries by a liquid eutectic from the Ni-S-O system



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

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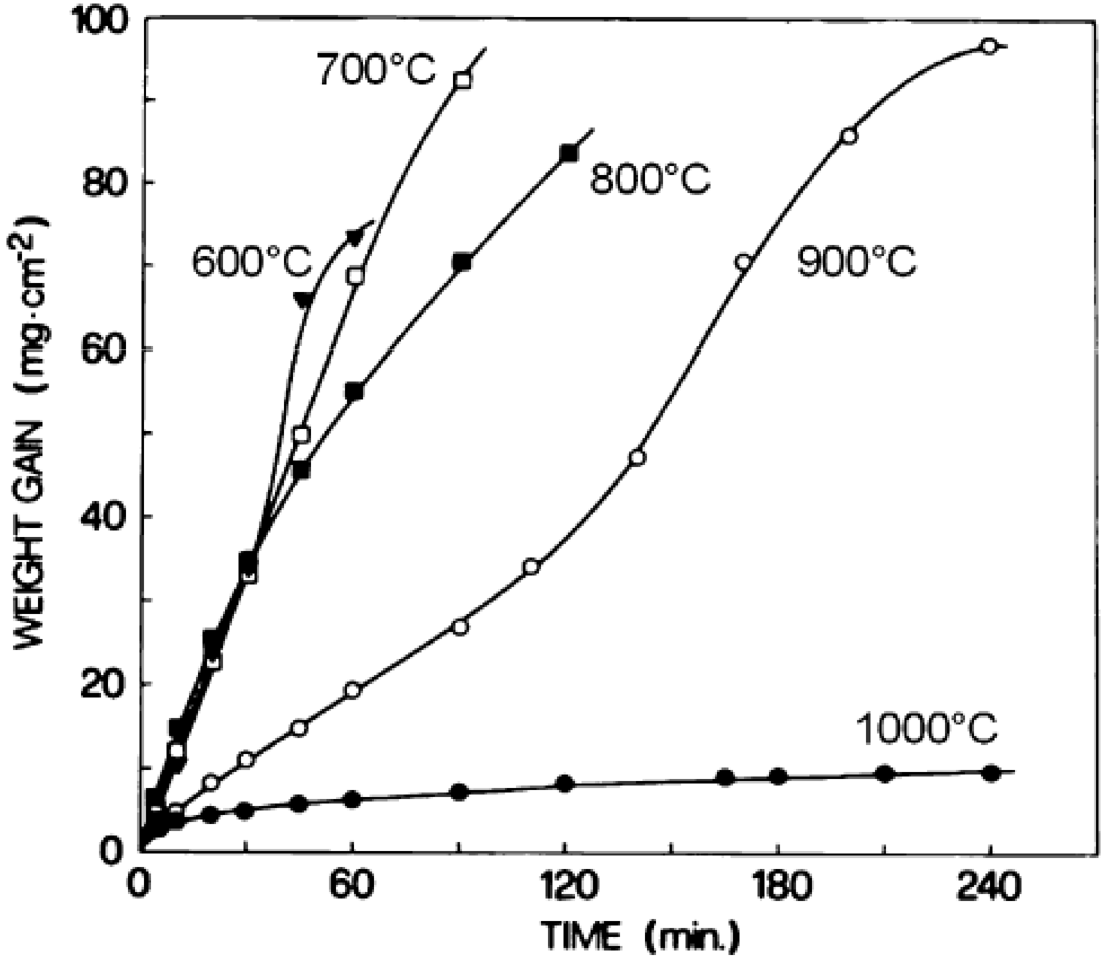
Oxidation kinetics of nickel in SO_2 at selected temperatures



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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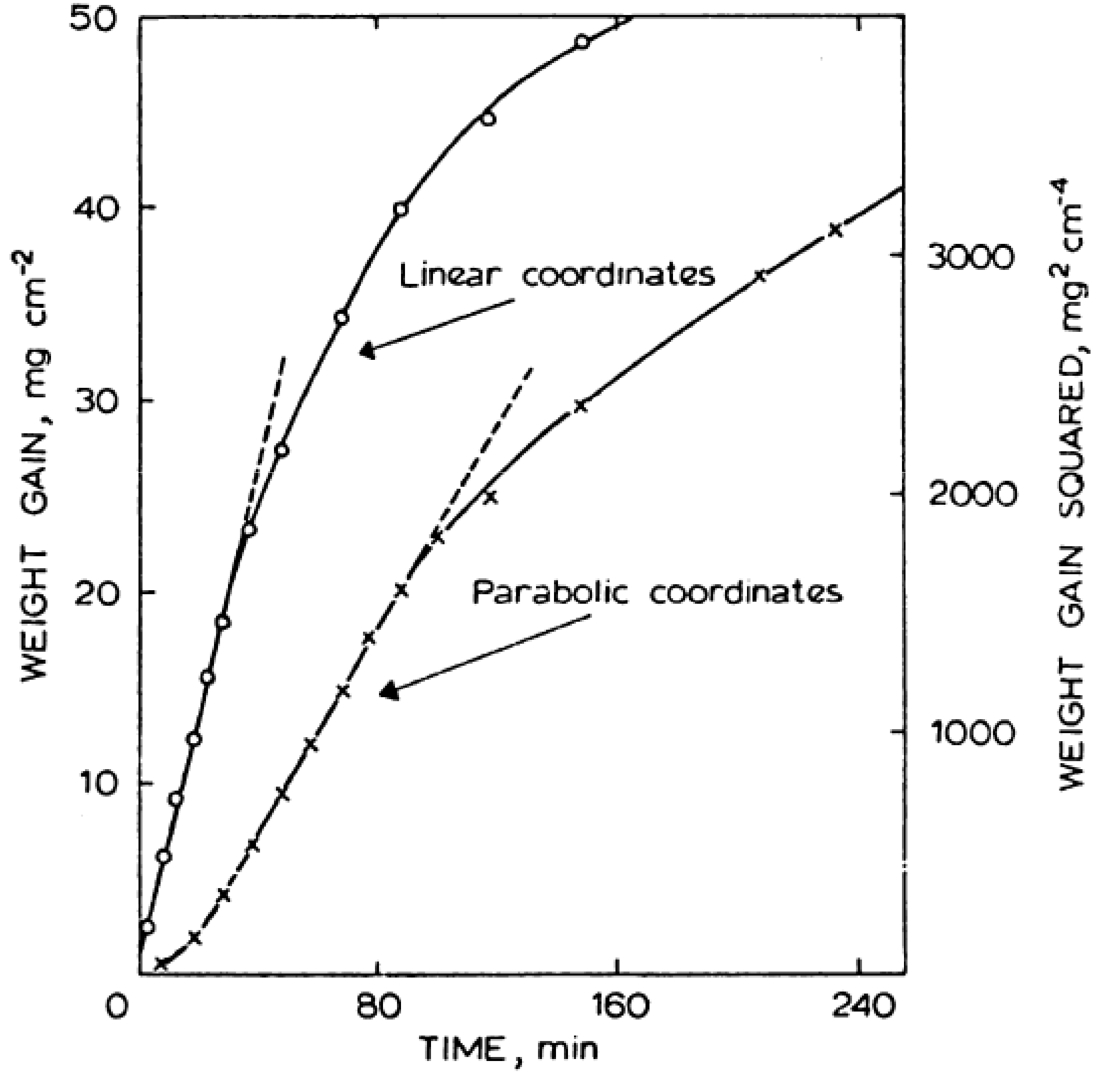
Complex oxidation kinetics of iron in Ar-SO_2 atmosphere (800 ^oC)



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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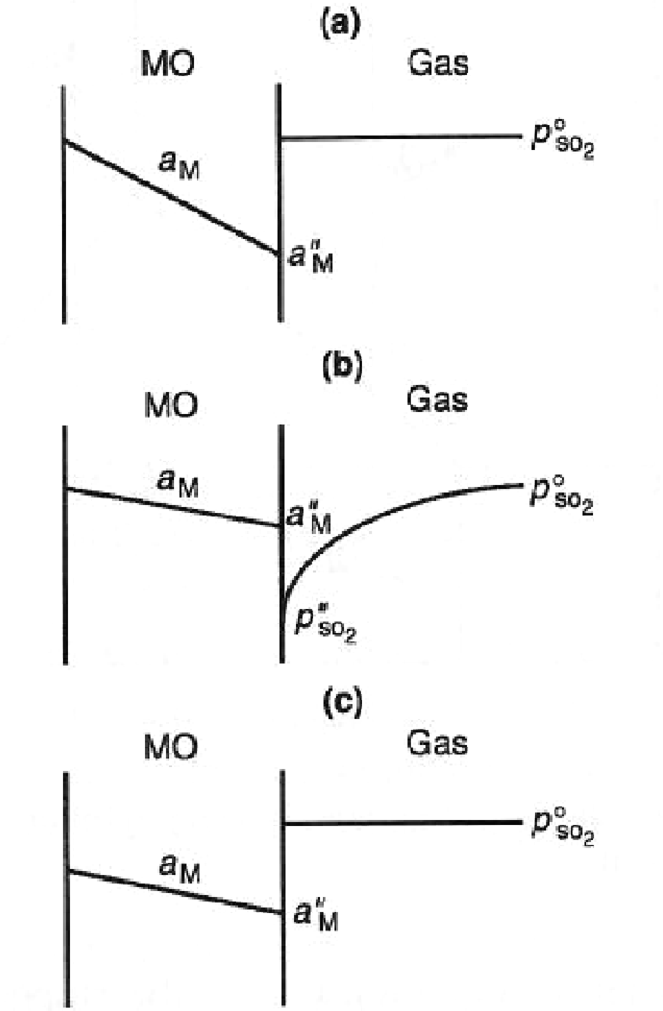
Partial processes that determine the corrosion rate in SO_2 atmosphere



diffusion in the scale

diffusion in the gas

MO/SO_2 interface reactions

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

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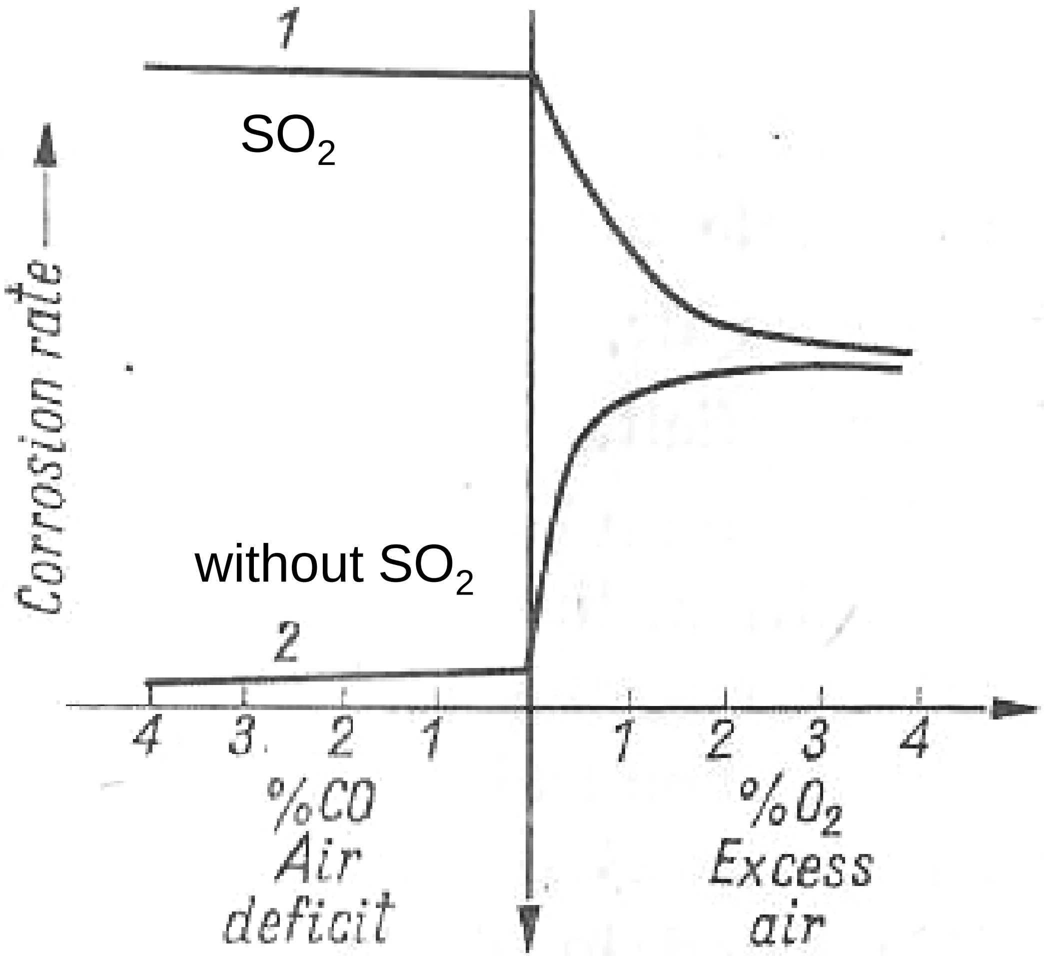
Dependence of the corrosion rate of low-carbon steels in exhaust gases on the presence of SO_2



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

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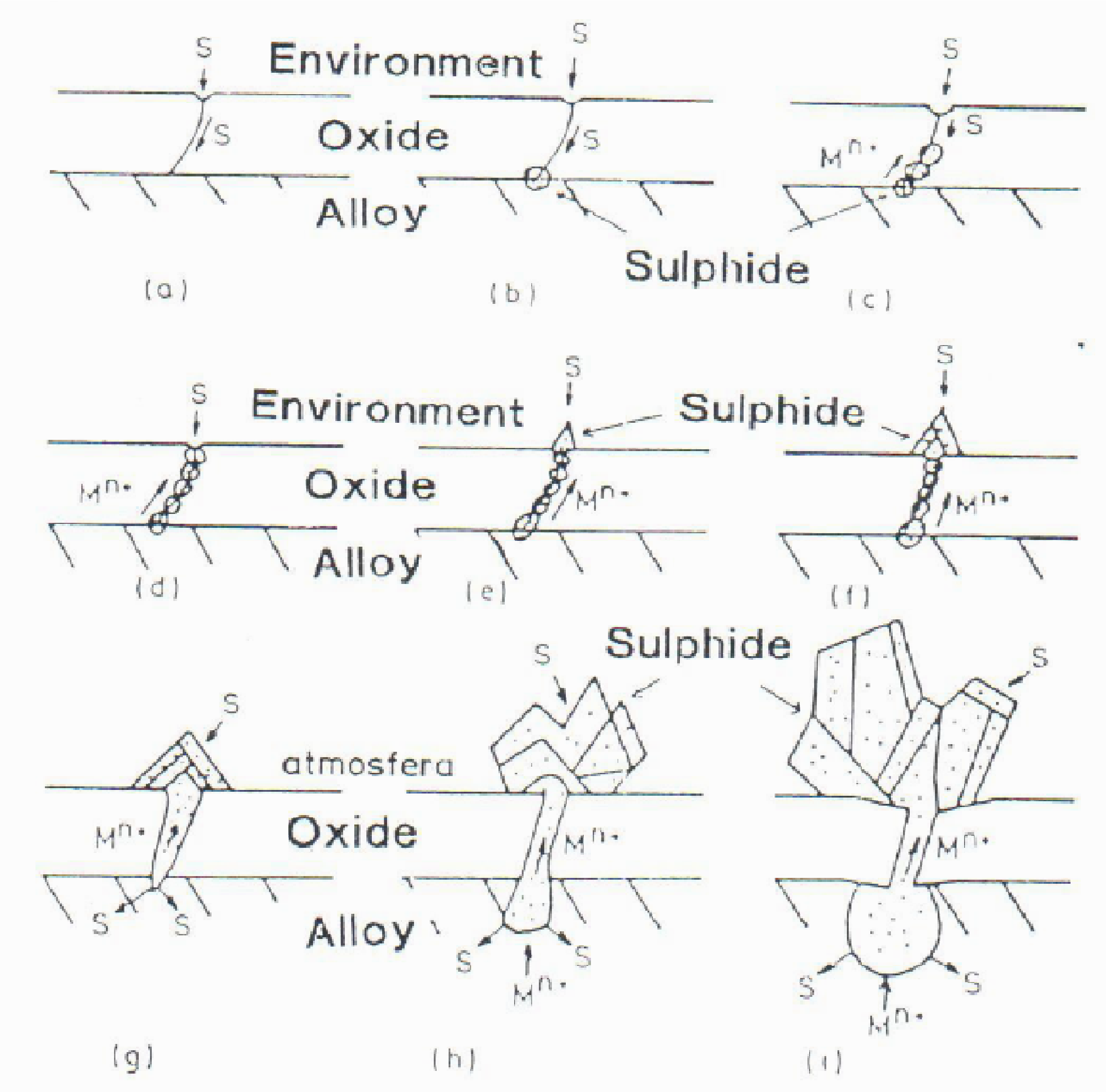
Schematic illustration of the sulphidation of previously oxidized Fe-Cr-Al and Fe-Cr alloys



S. Mrowec, Oxidation of Metals, 44 (1995) 177-209

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Influence of H_2S on the corrosion rate of Fe-Cr alloys

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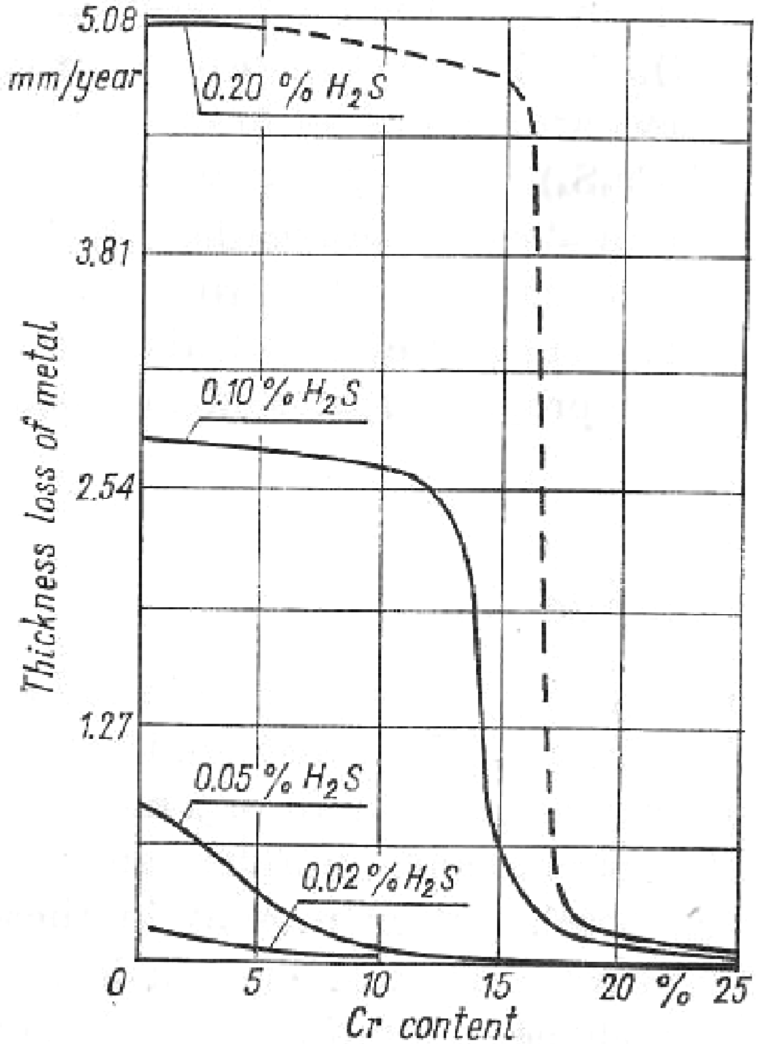

S. Mrowec and T. Werber, Modern Scaling-Resistant Materials, National Bureau of Standards and National Science Foundation, Washington D.C., 1982

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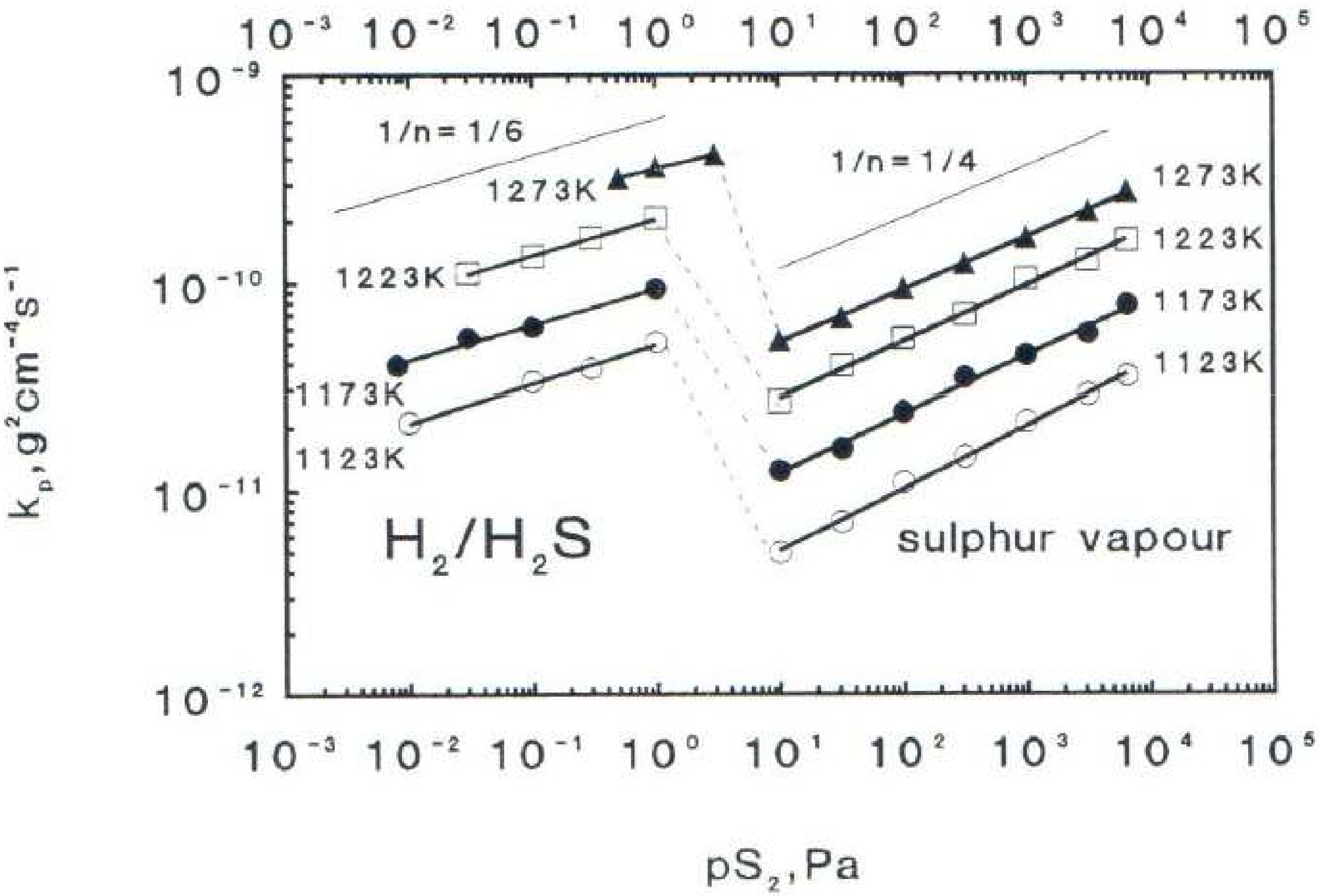
Comparison between the molybdenium sulphidation rate in H_2-H_2S atmosphere and in sulfur vapors



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

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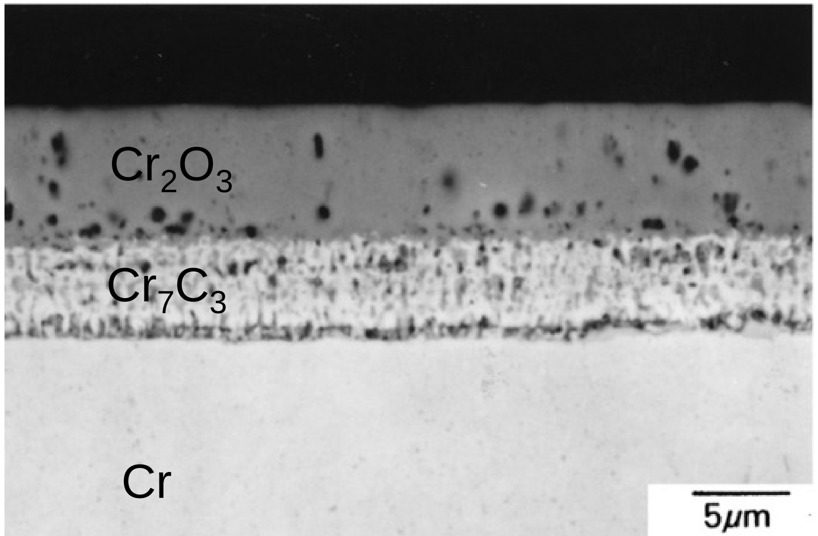
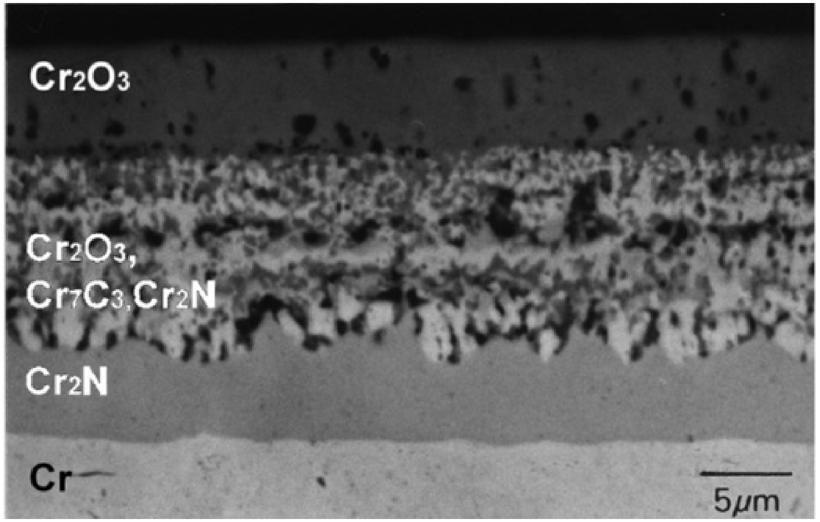
Chromium corrosion in CO-CO_2-containing atmosphere

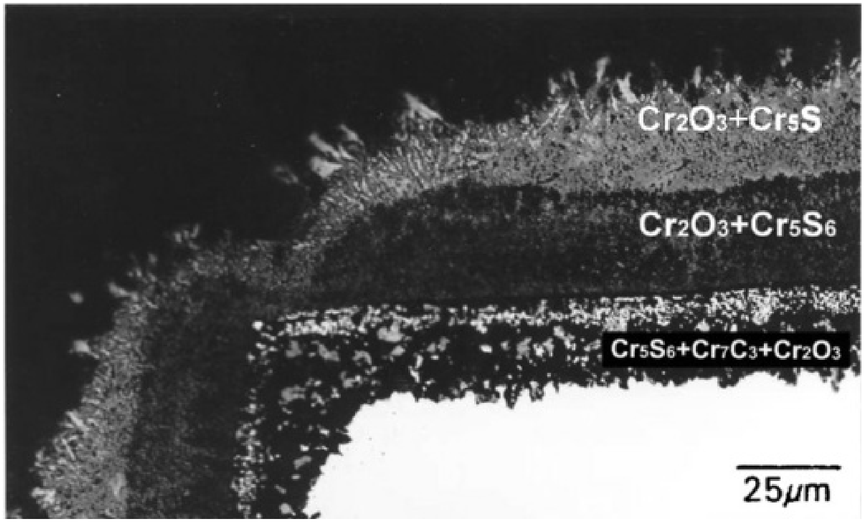


CO-CO_2

CO-CO_2-N_2



CO-CO_2-SO_2-N_2



D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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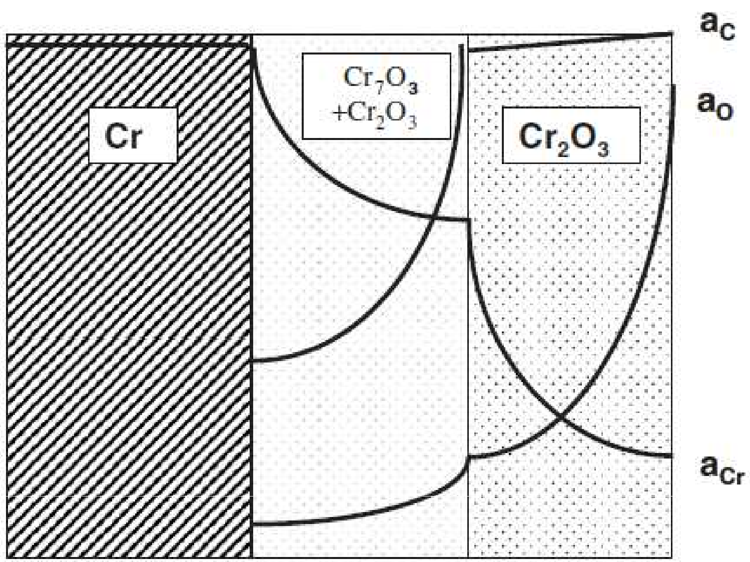
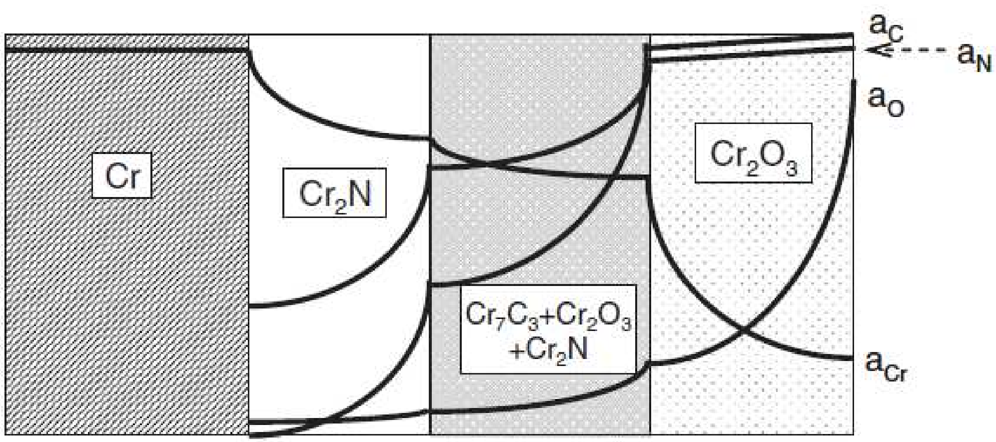
Schematic illustration of element concentration distribution in a scale formed due to chromium corrosion



(a)

$CO\text{-}CO_2$



(b)

$CO\text{-}CO_2\text{-}N_2$

D. J. Young, High temperature oxidation and corrosion of metals, Elsevier, Sydney 2008

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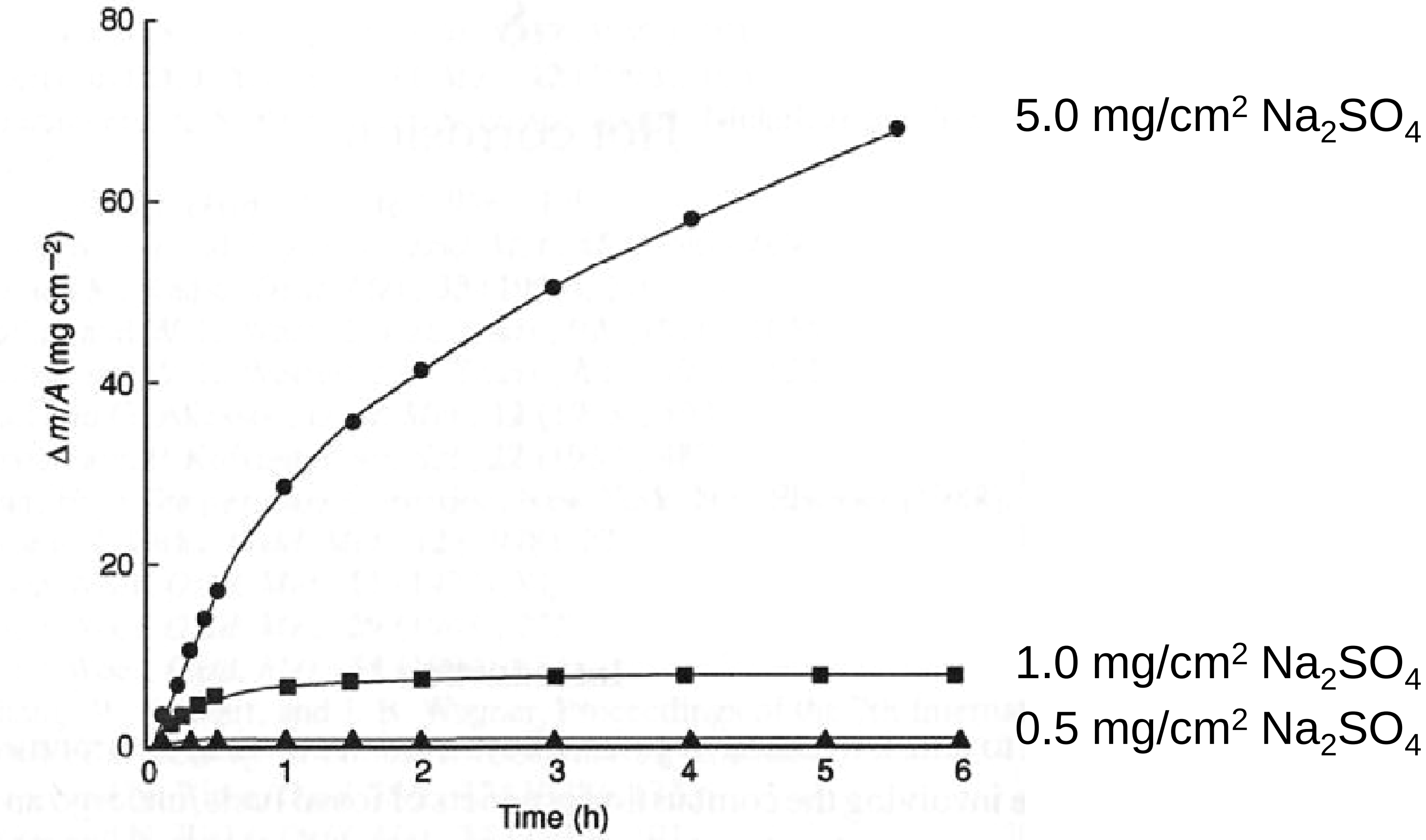
Influence of Na_2SO_4 additive on Ni-8Cr-6Al alloy oxidation kinetics at 1000 ^oC (hot corrosion)



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

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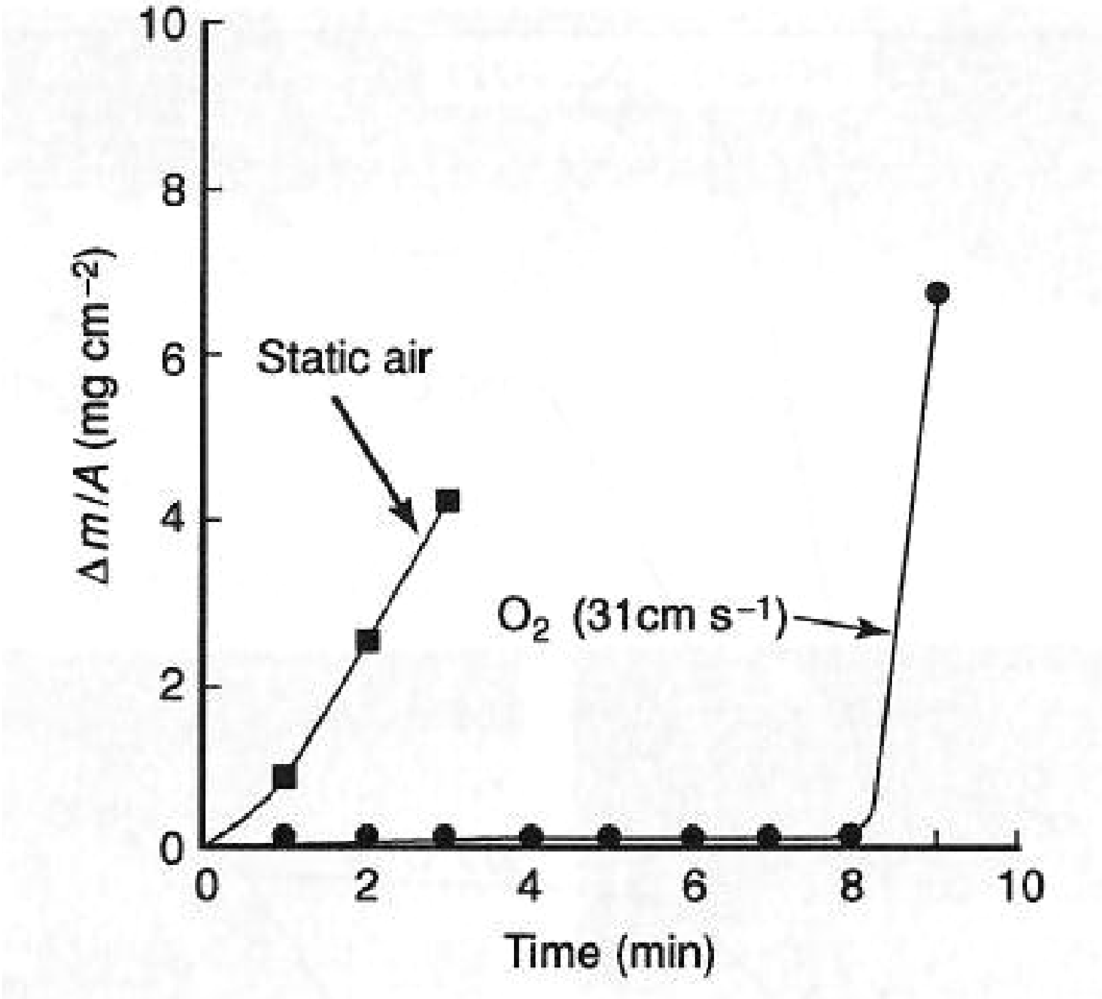
Oxidation kinetics of Ni-8Cr-6Al alloy in the presence of Na_2SO_4 in static and dynamic conditions (1000 ^oC)



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

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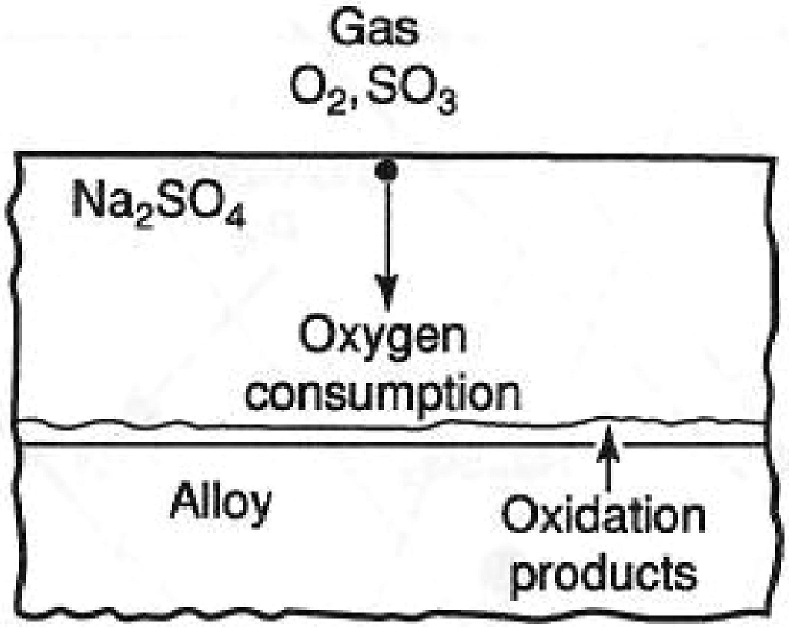
Diagram of the oxygen consumption process during the early stage of corrosion in the presence of Na_2SO_4



Melting temperature of Na_2SO_4: 884 ^oC

$$Na_2SO_4 \rightarrow Na_2O + SO_3$$

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

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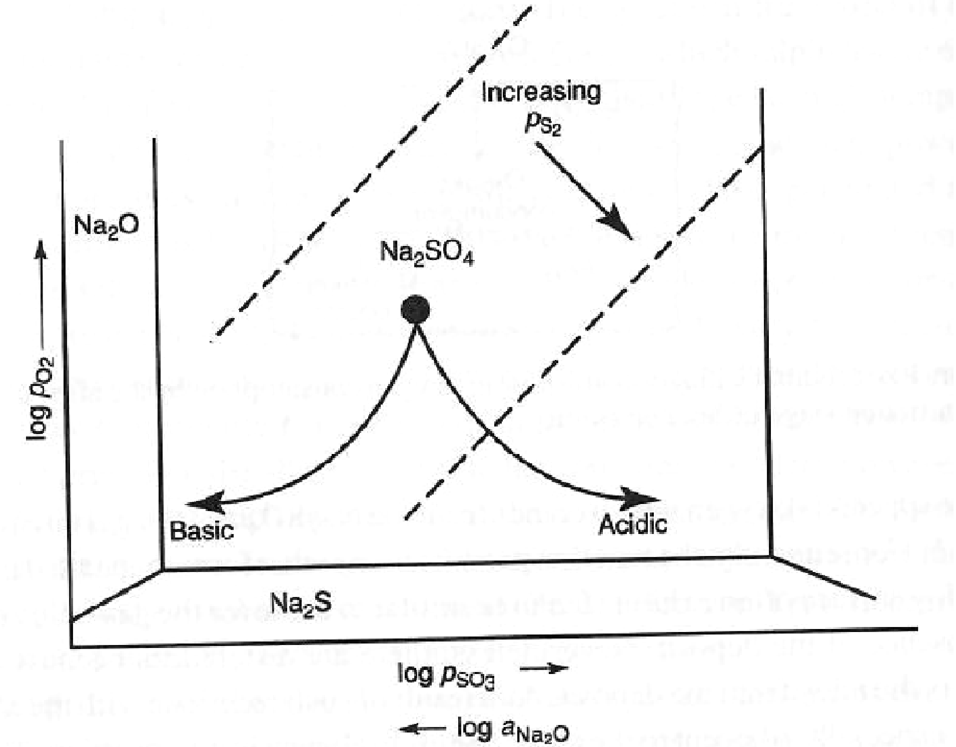
Schematic diagram of Na-O-S system stability



alkaline mode:

$$NiO + Na_2O \rightarrow 2Na^+ + NiO_2^{2-}$$

$$NiO + O^{2-} \rightarrow NiO_2^{2-}$$

$$NiO + Na_2SO_4 \rightarrow 2Na^+ + NiO_2^{2-} + SO_3$$

acidic mode:

$$NiO + SO_3 \rightarrow Ni^{2+} + SO_4^{2-}$$

$$NiO \rightarrow Ni^{2+} + O^{2-}$$

$$NiO + Na_2SO_4 \rightarrow Ni^{2+} + SO_4^{2-} + Na_2O$$

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

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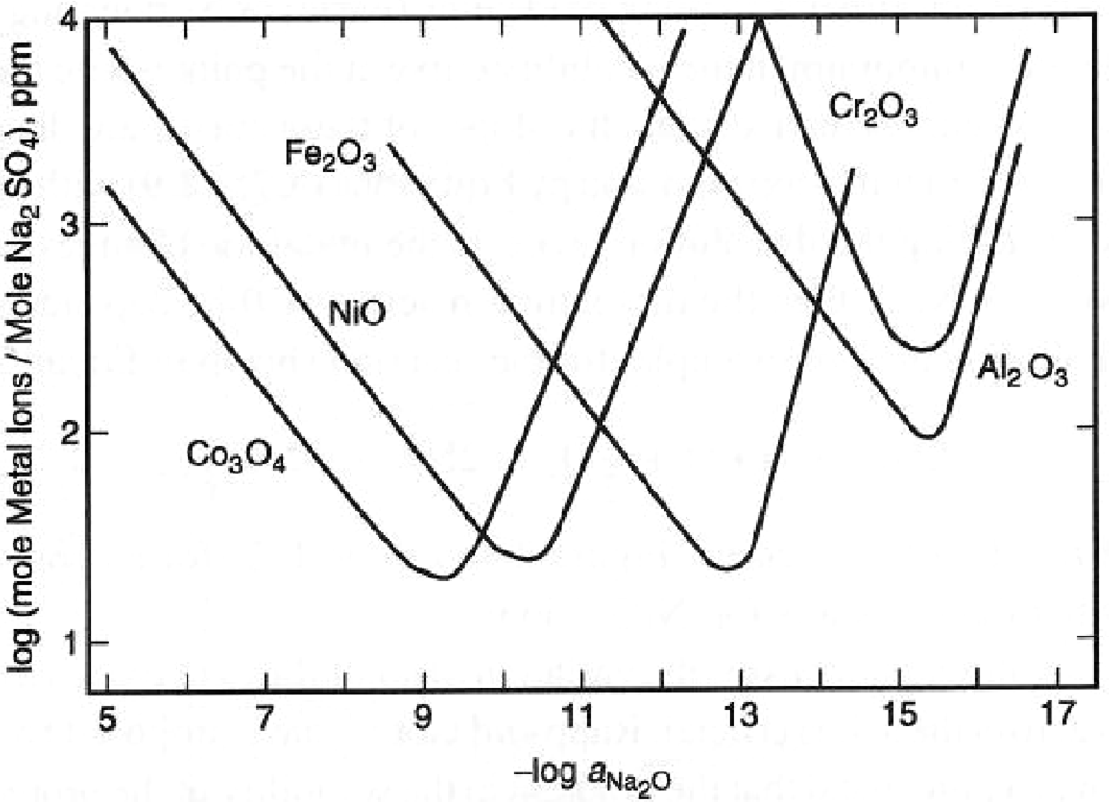
Solubility of selected oxides in Na_2SO_4 at 1200 K, at oxygen pressure equal to 1 atm



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

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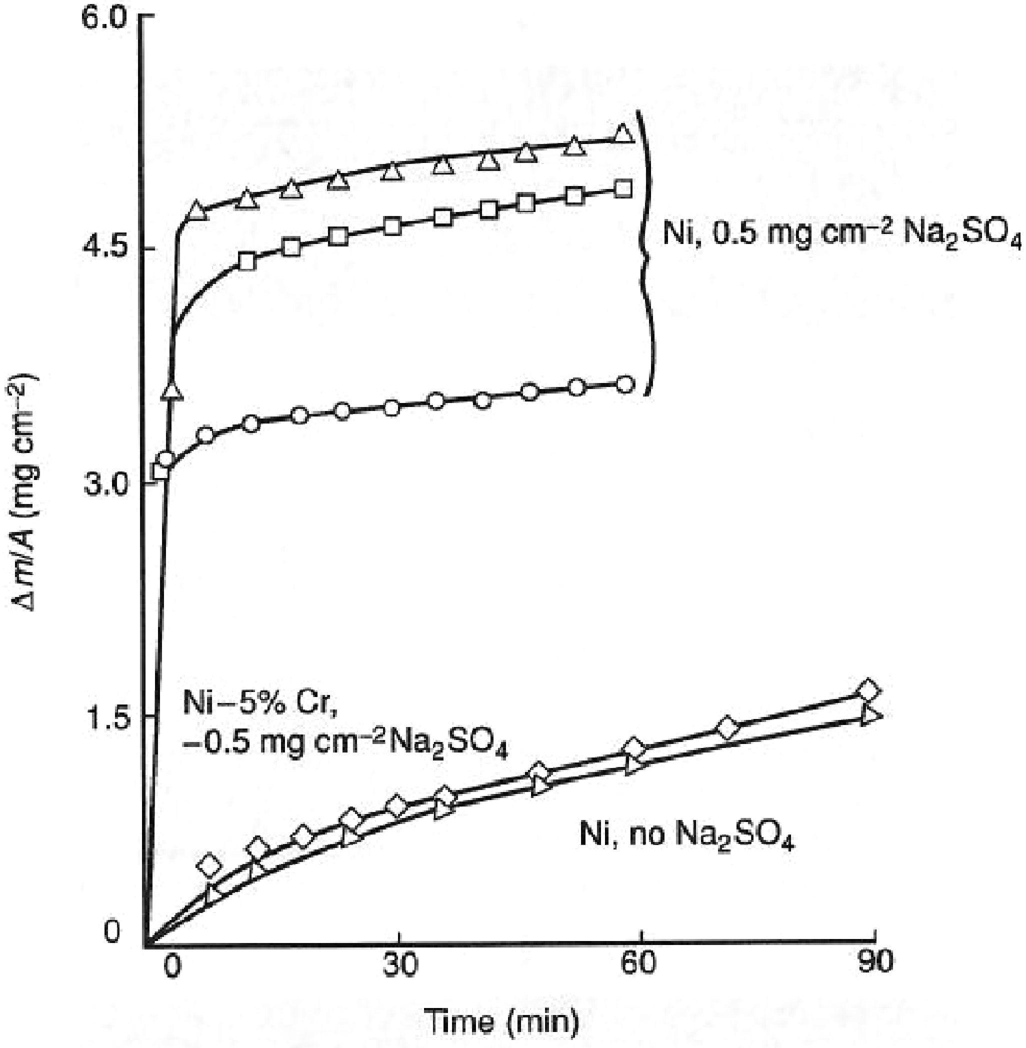
Influence of Na_2SO_4 additive on oxidation kinetics of nickel and Ni-5%Cr alloy



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

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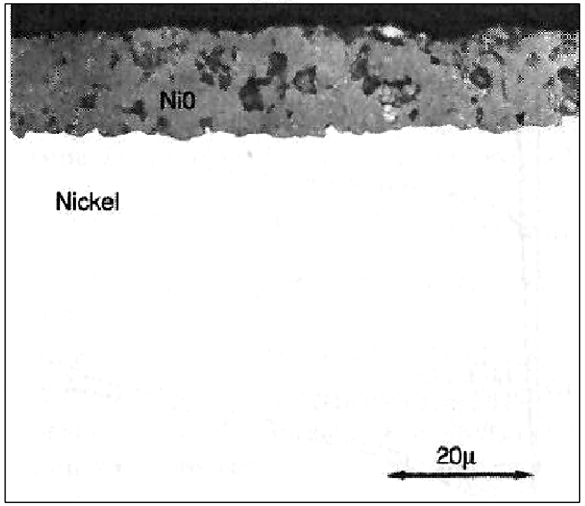
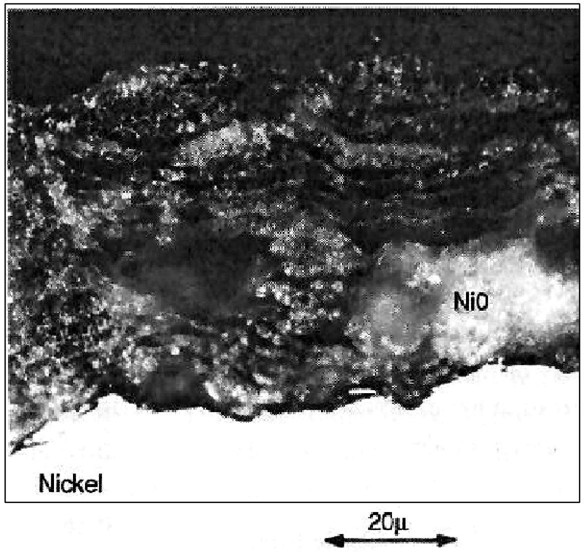
Cross-section of a scale grown on nickel oxidized in different conditions (1000 ^oC)

(a)



air
t = 3 h

(b)



air + 0.5 mg/cm^2 Na_2SO_4
t = 1 min

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

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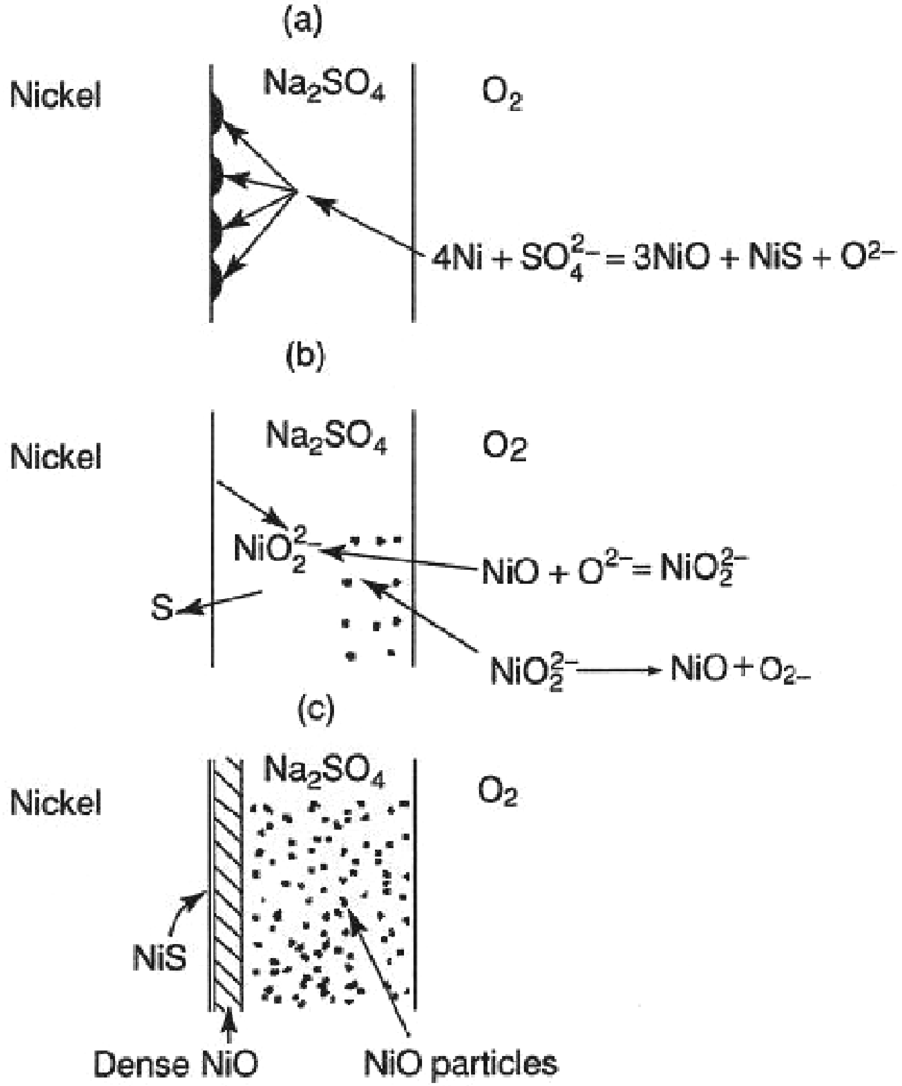
Model of nickel corrosion in the presence of Na_2SO_4



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

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Salts present in gas turbines

Salt Constituent	Deposit Chemistry (mole %)	
External Airfoil Surface	First Stage	Second Stage
Na_2SO_4	40	28
K_2SO_4	4	3
$CaSO_4$	40	59
$MgSO_4$	13	8
Internal Cooling Passages		
Na_2SO_4	45	37
K_2SO_4	3.2	4.4
$CaSO_4$	41	46
$MgSO_4$	9.5	11.5

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Salts present in sea water

Salt Constituents	Concentration, g/L (%)
NaCl	23 (52)
$MgCl_2\,6H_2O$	11 (25)
KCl, KBr	1.1 (2)
$CaCl_2\,2H_2O$	1.4 (3)
$Na_2SO_4\,10H_2O$	8 (18)
Total	44.5 (100)

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THE END

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