AKADEMIA GÓRNICZO-HUTNICZA
IM. STANISŁAWA STASZICA W KRAKOWIE
AGH UNIVERSITY OF SCIENCE
AND TECHNOLOGY

AGH

OXIDATION OF PURE METALS

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

Fundamental 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.

Partial reactions of the oxidation process

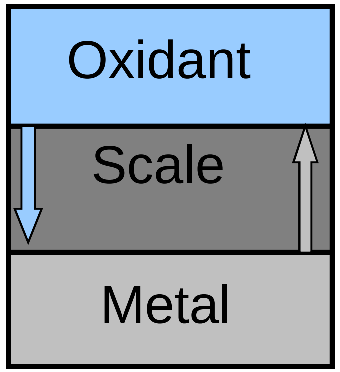
Initial stages of oxidation:

- adsorption of molecular oxygen on the sample surface
- dissociation of oxygen molecules on the sample surface
- chemisorption of atomic oxygen on the sample surface
- oxygen ionization and embedment into the crystal lattice

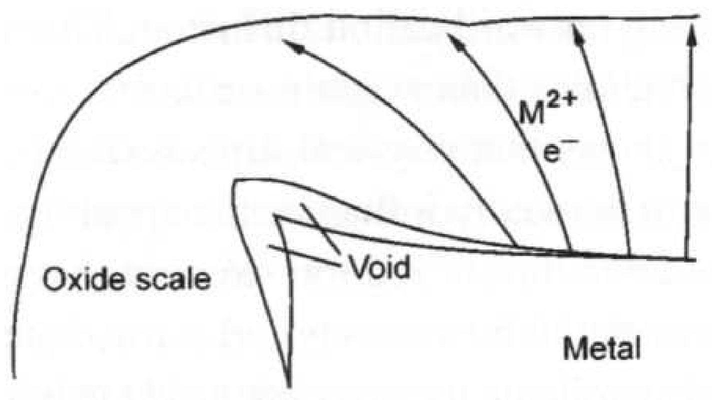
$$O_2(g) \rightarrow O_2(ad) \rightarrow 2O(ad) \rightarrow 2O^-(chem) + 2h^\bullet \rightarrow 2O^{2-}(latt) + 4h^\bullet$$

Schematic illustration of reagent diffusion through the scale

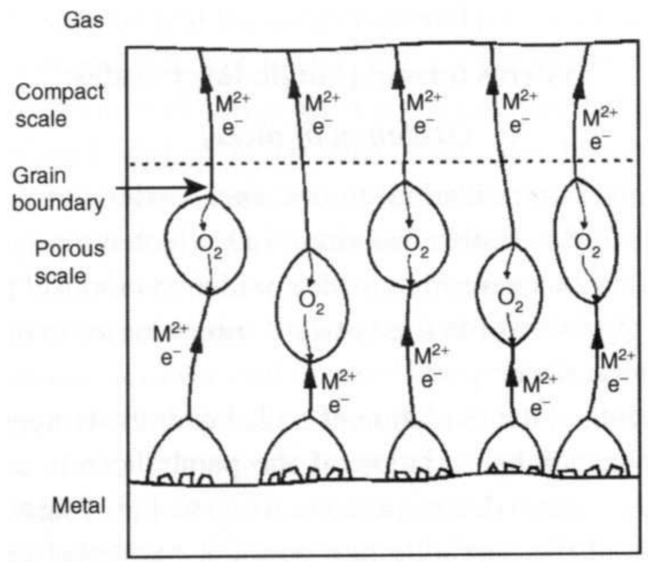
compact scale



presence of pores on the metal-scale interface



porous scale



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

Selected properties of chosen metal oxides

Oxide	*Structure*	*Melting point, °C*	*Boiling point, °C*	*Molar volume, cm^3*	*Volume ratio (oxide/metal)*
α-Al_2O_3	$D5_1$(corundum)	2015	2980	25.7	1.28
γ-Al_2O_3	(defect spinal)	$\gamma \rightarrow \alpha$	. . .	26.1	1.31
BaO	Bl (NaCl)	1923	~2000	26.8	0.69
BaO_2	Tetragonal (CaC_2)	450	d.800	34.1	0.87
BeO	Br (ZnS)	2530	~3900	8.3	1.70
CaO	Bl (NaCl)	2580	2850	16.6	0.64
CaO_2	Cll (CaC_2)	. . .	d.275	24.7	0.95
CdO	B1 (NaCl)	~1400	d.900	18.5	1.42
Ce_2O_3	$D5_2$ (La_2O_3)	1692	. . .	47.8	1.15
CeO_2	Cl (CaF_2)	~2600	. . .	24.1	1.17
CoO	Bl (NaCl)	1935	. . .	11.6	1.74
Co_2O_3	Hexagonal	. . .	d.895	32.0	2.40
Co_3O_4	Hl_1 (spinal)	$\rightarrow$ CoO	. . .	39.7	1.98
Cr_2O_3	$D5_1$ (αAl_2O_3)	2435	4000	29.2	2.02
Cs_2O	Hexagonal ($CdCl_2$)	. . .	d.400	66.3	0.47
Cs_2O_3	Cubic (Th_3P_4)	400	650	70.1	0.50
CuO	B26 monoclinic	1326	. . .	12.3	1.72
Cu_2O	C3 cubic	1235	d.1800	23.8	1.67
FeO	Bl (NaCl)	!420	. . .	12.6	1.78 on α-iron
α-Fe_2O_3	$D5_1$ (Haematite)	1565	. . .	30.5	2.15 on α-iron
γ-Fe_2O_3	$D5_7$ cubic	1457	. . .	31.5	2.22 on α-iron
Fe_3O_4	Hl_1 (spinel)	. . .	d. 1538	44.7	2.10 on α-iron
Ga_2O_3	Monoclinic	1900	. . .	31.9	1.35
HfO_2	Cubic	2812	~5400	21.7	1.62

Selected properties of chosen metal oxides

Oxide	*Structure*	*Melting point, °C*	*Boiling point, °C*	*Molar volume, cm³*	*Volume ratio (oxide/metal)*
In_2O_3	$D5_3(Sc_2O_3)$	. . .	d.850	38.7	1.23
IrO_2	C4 (TiO_2)	. . .	d.1100	19.1	2.23
La_2O_3	D53 (Sc_2O_3)	. . .	d.850	38.7	1.23
Li_2O	Cl (CaF_2)	~1700	1200	14.8	0.57
MgO	Bl (NaCl)	2800	3600	11.3	0.80
MnO	Bl (NaCl)	. . .	. . .	13.0	1.77
MnO_2	C4 (TiO_2)	. . .	d.535	17.3	2.37
Mn_2O_3	D53 (Sc_2O_3)	. . .	d.1080	35.1	2.40
Mn_3O_4	Hl_1 (spinel)	1705	. . .	47.1	2.14
MoO_3	Orthorhombic	795	. . .	30.7	3.27
Na_2O	Cl (CaF_2)	Subl. 1275	. . .	27.3	0.57
Nb_2O_5	Monoclinic	1460	. . .	59.5	2.74
Nd_2O_3	Hexagonal	~1900	. . .	46.5	1.13
NiO	Bl (NaCl)	1990	. . .	11.2	1.70
PbO	B10 tetragonal	888	. . .	23.4	1.28
Pb_3O_4	Tetragonal	. . .	d.500	75.3	1.37
PdO	B17 tetragonal	870	. . .	14.1	1.59
PtO	B17 (PdO)	. . .	d.550	14.2	1.56
Rb_2O_3	(Th_3P_4)	489	. . .	62.0	0.56
ReO_2	Monoclinic	. . .	d.1000	19.1	2.16
Rh_2O_3	D51 (α-Al_2O_3)	. . .	d.1100	31.0	1.87
SiO	Cubic	~1700	1880	20.7	1.72

Selected properties of chosen metal oxides

Oxide	*Structure*	*Melting point, °C*	*Boiling point, °C*	*Molar volume, cm³*	*Volume ratio (oxide/metal)*
SiO_2	β cristobalite C9	1713	2230	25.9	2.15
SnO	B10 (PbO)	. . .	d.1080	20.9	1.26
SnO_2	C_4 (TiO_2)	1127	. . .	20.9	1.26
SrO	Bl (NaCl)	2430	~3000	22.0	0.65
Ta_2O_5	Triclinic	1800	. . .	53.9	2.47
TeO_2	C_4 (TiO_2)	733	1245	28.1	1.38
ThO_2	Cl (CaF_2)	3050	4400	26.8	1.35
TiO	Bl (NaCl)	1750	~3000	13.0	1.22
TiO_2	C4 (Rutile)	1830	~2700	18.8	1.76
Ti_2O_3	$D5_1$ (α-Al_2O_3)	. . .	d.2130	31.3	1.47
Tl_2O_3	$D5_3$ (Sc_2O_3)	717	d.875	44.8	1.30
UO_2	Cl (CaF_2)	2500	. . .	24.6	1.97
U_3O_8	Hexagonal	. . .	d.1300	101.5	2.71
VO_2	C4 (TiO_2)	1967	. . .	19.1	2.29
V_2O_3	$D5_1$ (α-Al_2O_3)	1970	. . .	30.8	1.85
V_2O_5	$D8_7$ Orthorhombic	690	d.1750	54.2	3.25
WO_2	C4 (TiO_2)	~1550	~1430	17.8	1.87
B-WO_3	Orthorhombic	1473	. . .	32.4	3.39
W_2O_5	Triclinic	Sub.~850	~1530	29.8	3.12
Y_2O_3	$D5_3$ (Sc_2O_3)	2410	. . .	45.1	1.13
ZnO	B3 (wurtzite)	1975	. . .	14.5	1.58
ZrO_2	$C4_3$ monoclinic	2715	. . .	22.0	1.57

Pilling-Bedworth rule

If metal oxidation takes place due to inward oxidant diffusion, then the ratio of the molar volume between the oxide and metal (V_{ox}/V_m) being greater than one means expansion of the metal-scale system, which generates stresses that compress the oxide. However, if this ratio is below 1, then a porous oxide is formed. A compact scale without stresses should grow for a molar volume oxide to metal ratio equal to 1.

In the case of outward metal diffusion, $V_{ox}/V_m > 1$ does not mean that stresses are generated.

The Pilling-Bedworth rule, while conceptually correct, does not allow for a reliable quantitative description of stresses in most metal-scale systems, due to the presence of several additional factors that influence the stress formation mechanism, not taking into account e.g. process temperature, pressure, reaction time, oxide grain size, surface preparation method, mutual reagent diffusion.

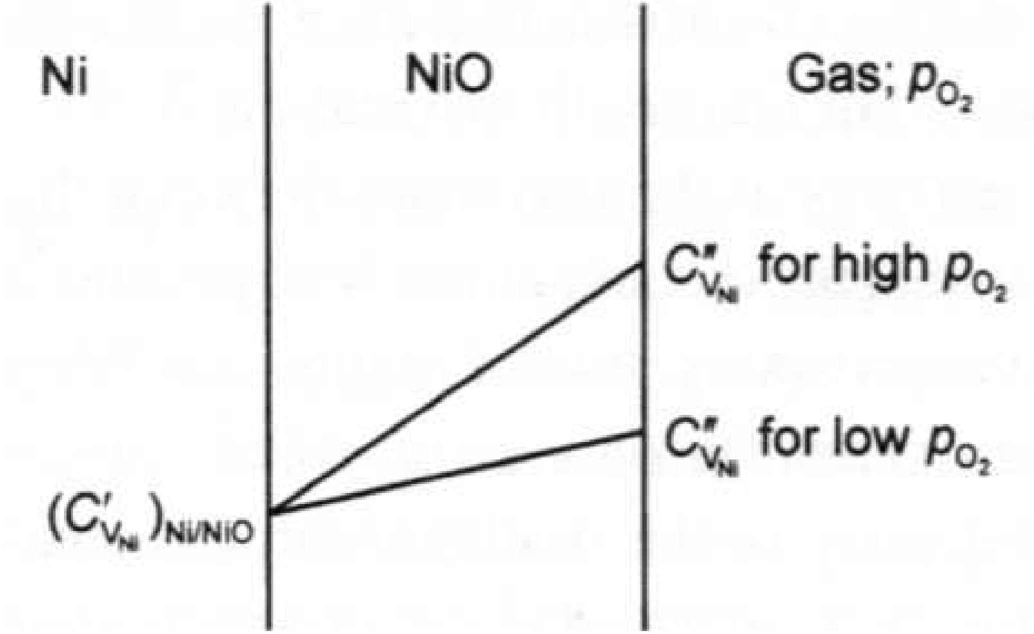
Nickel oxidation

$$\frac{1}{2}O_2 = V''_{Ni} + 2h^{\bullet} + O_O$$

$$y = \left[V''_{Ni}\right] = \frac{1}{2}\left[h^{\bullet}\right] = \left(\frac{1}{4}K_{V''}\right)^{1/3} p_{O_2}^{1/6} = 0.63 p_{O_2}^{1/6} \exp\left(\frac{\frac{1}{3}\Delta S_f}{R}\right) \exp\left(-\frac{\frac{1}{3}\Delta H_f}{RT}\right)$$

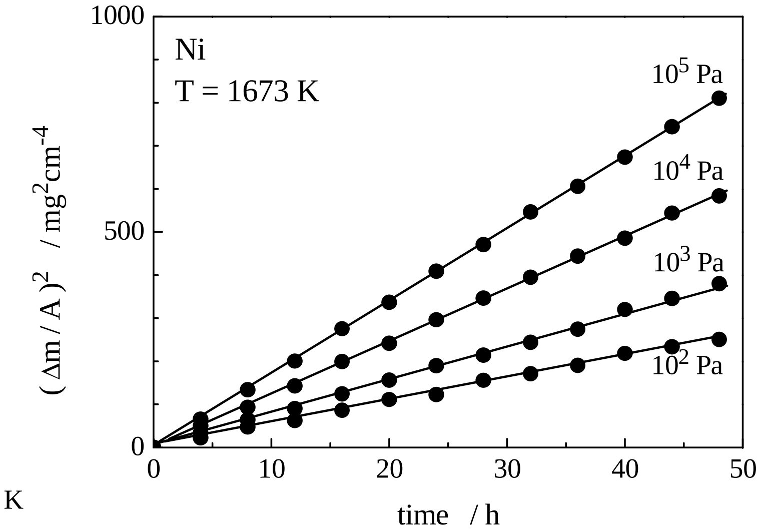
$$y = 0.153 \cdot p_{O_2}^{1/6} \cdot \exp\left(-\frac{80\ kJ/mol}{RT}\right)$$

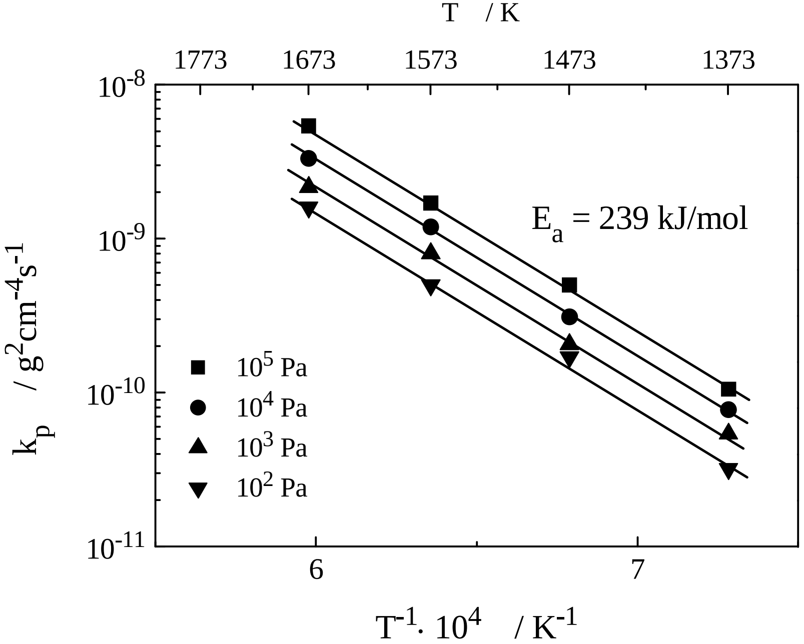
Z. Grzesik and S. Mrowec, Polish Journal of Chemistry, 79, 907-917 (2005)

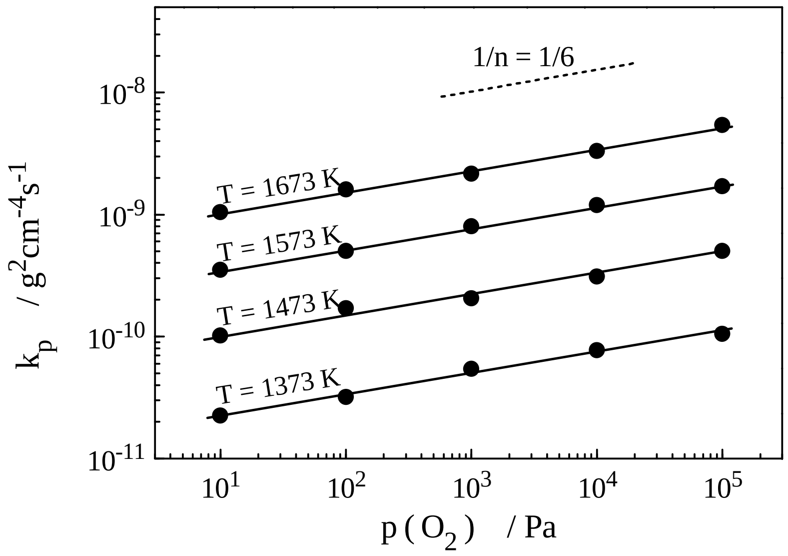


N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009

Nickel oxidation





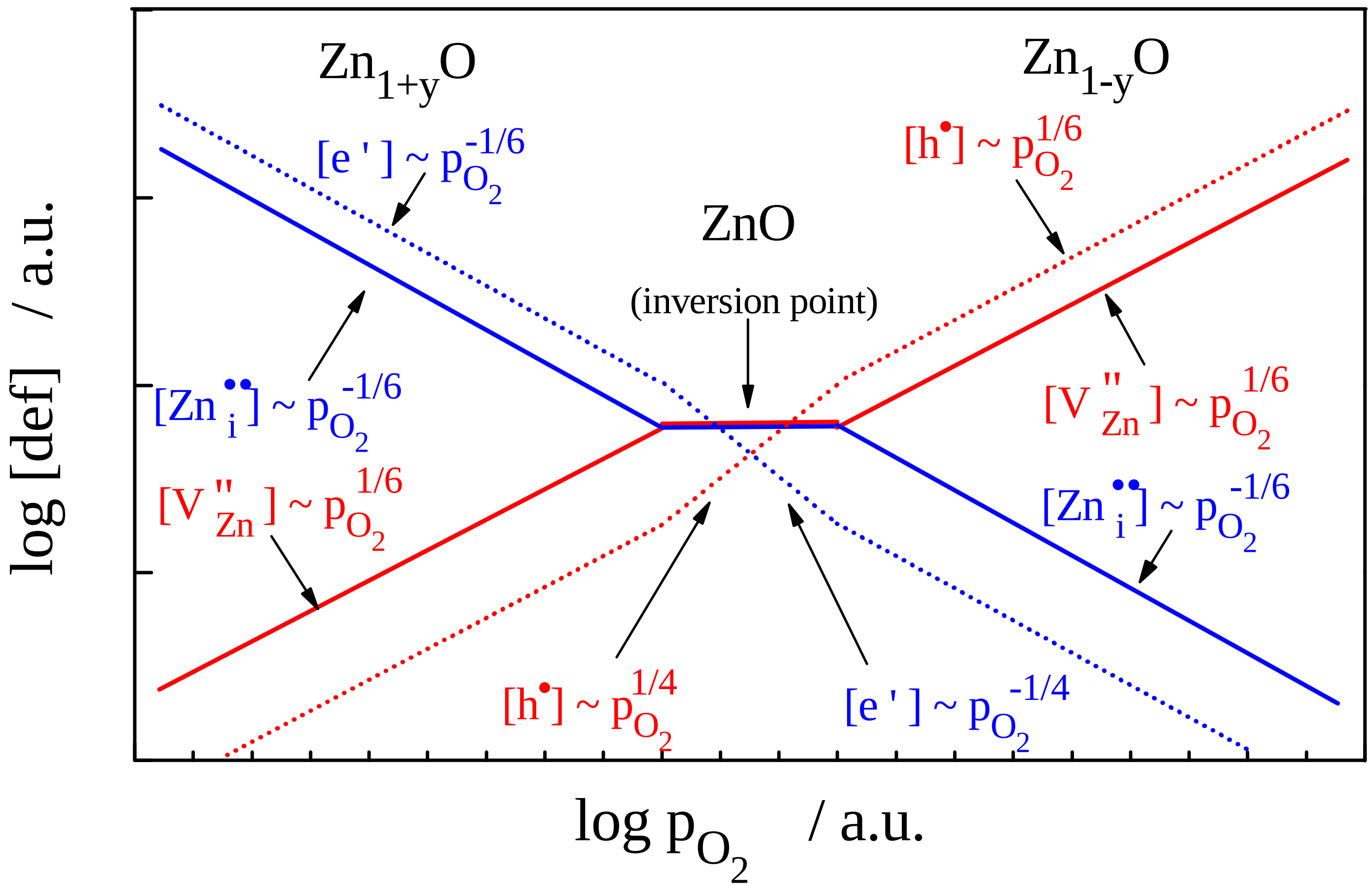


S. Mrowec, Z. Grzesik , Journal of Physics and Chemistry of Solids 65 (2004) 1651–1657

Zinc oxidation

$$ZnO = Zn_i^{\bullet\bullet} + 2e' + \frac{1}{2}O_2$$

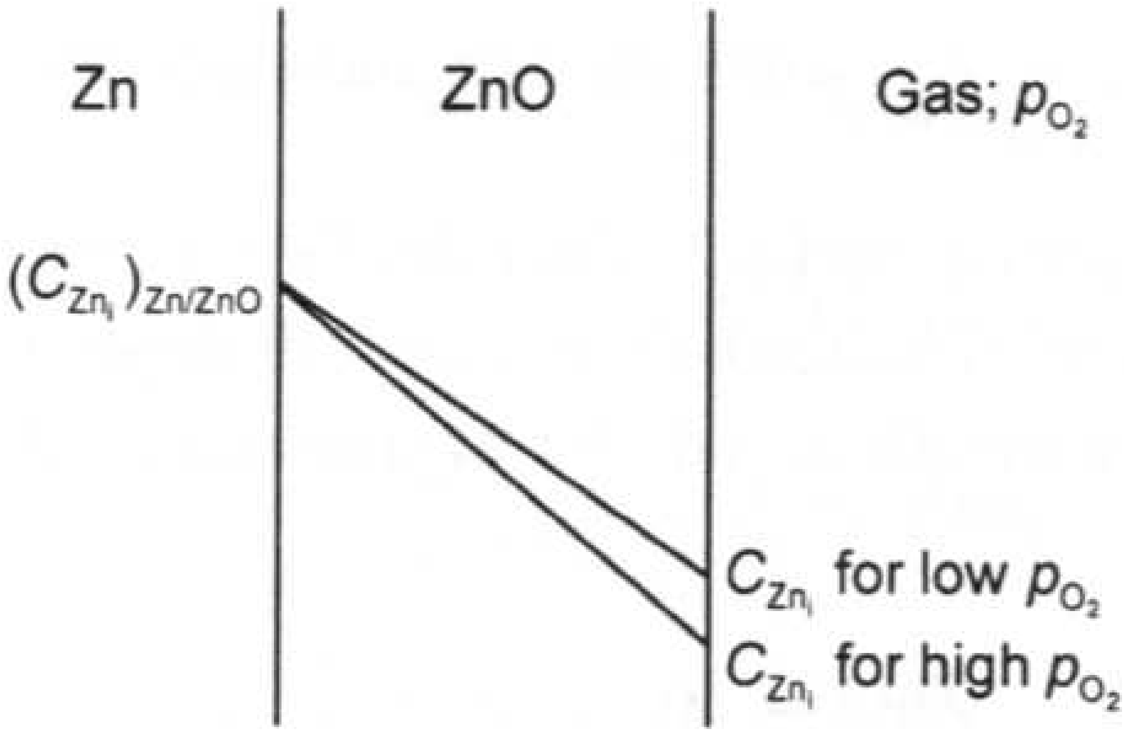
$$\frac{1}{2}O_2 = V_{Zn}'' + 2h^{\bullet} + O_O$$



M. Drożdż, B. Wierzba, Z. Grzesik, High Temperature Materials and Processes, 37(1), 17-23 (2018)

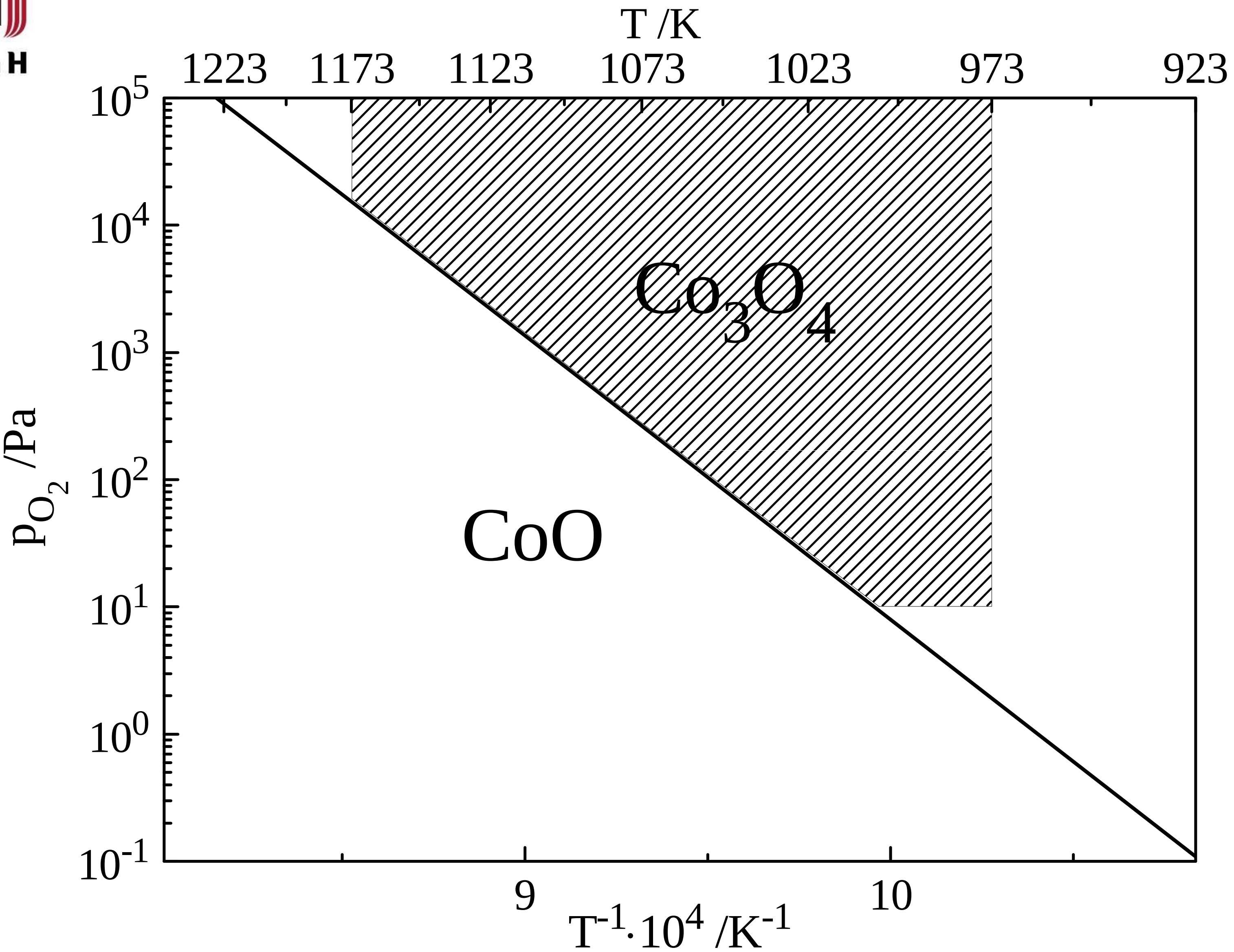
Zinc oxidation

$$ZnO = Zn_i^{\bullet\bullet} + 2e' + \frac{1}{2} O_2$$

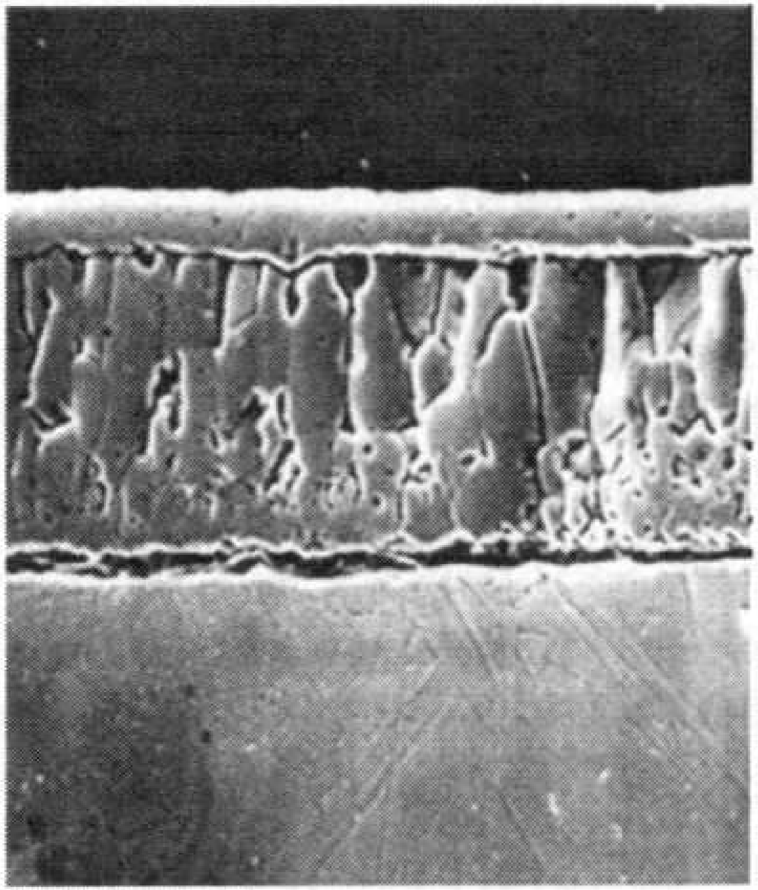


N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009

Cobalt oxidation, fragment of the Co-O_2 diagram

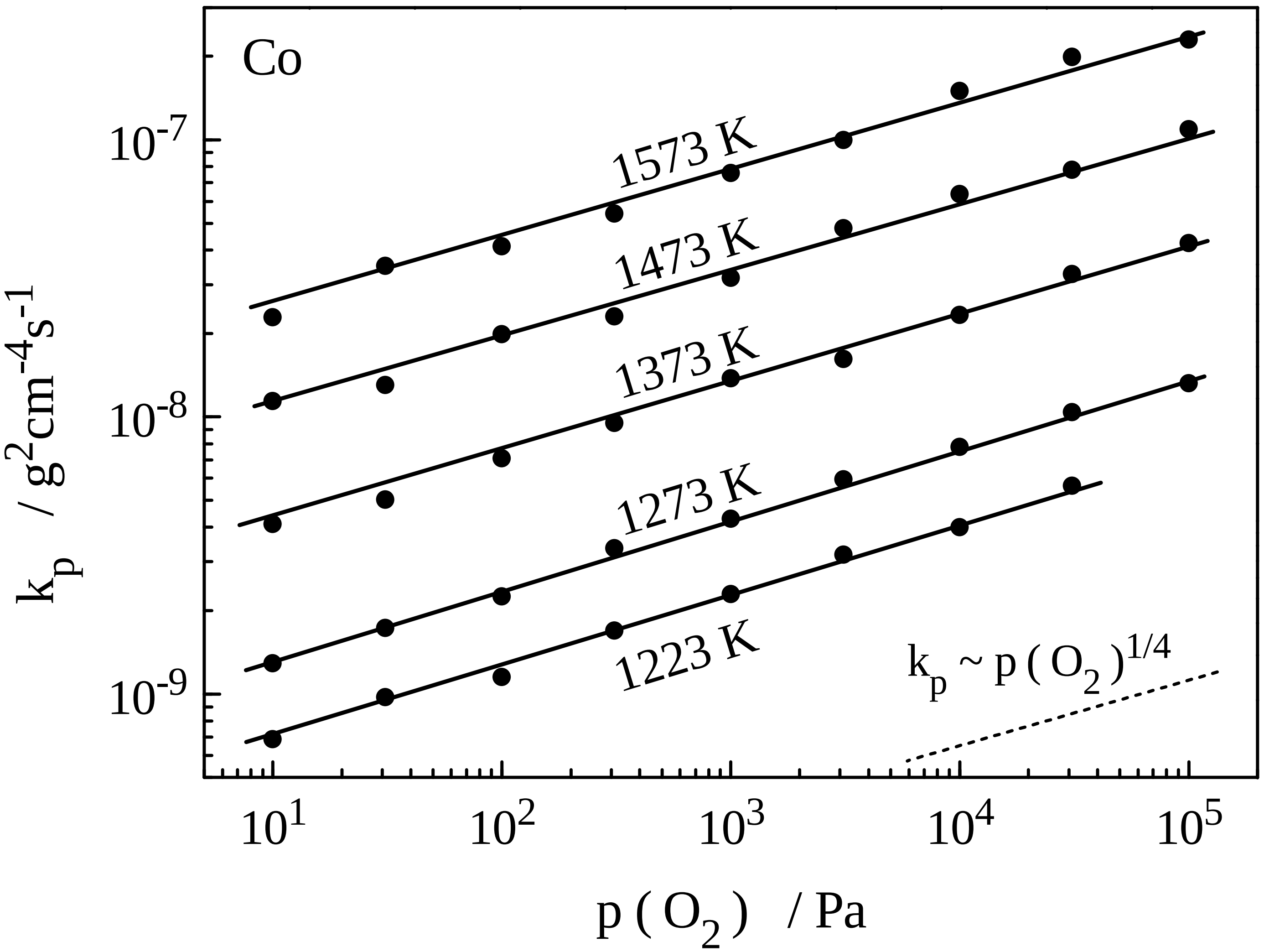


Picture of the cross-section of cobalt oxidized to Co_3O_4



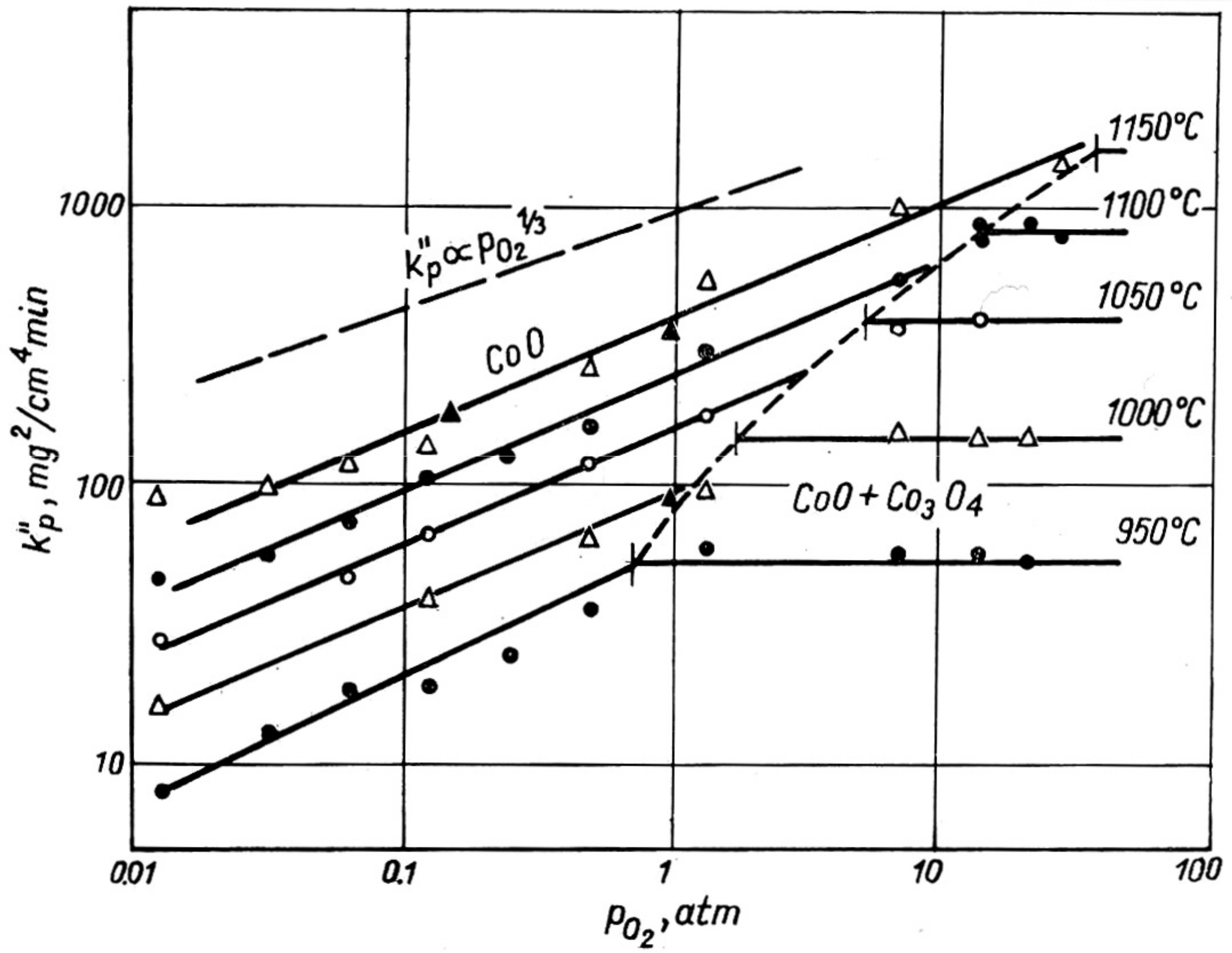
N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009

Pressure dependence of the parabolic rate constant of cobalt oxidation at T > 1200 K



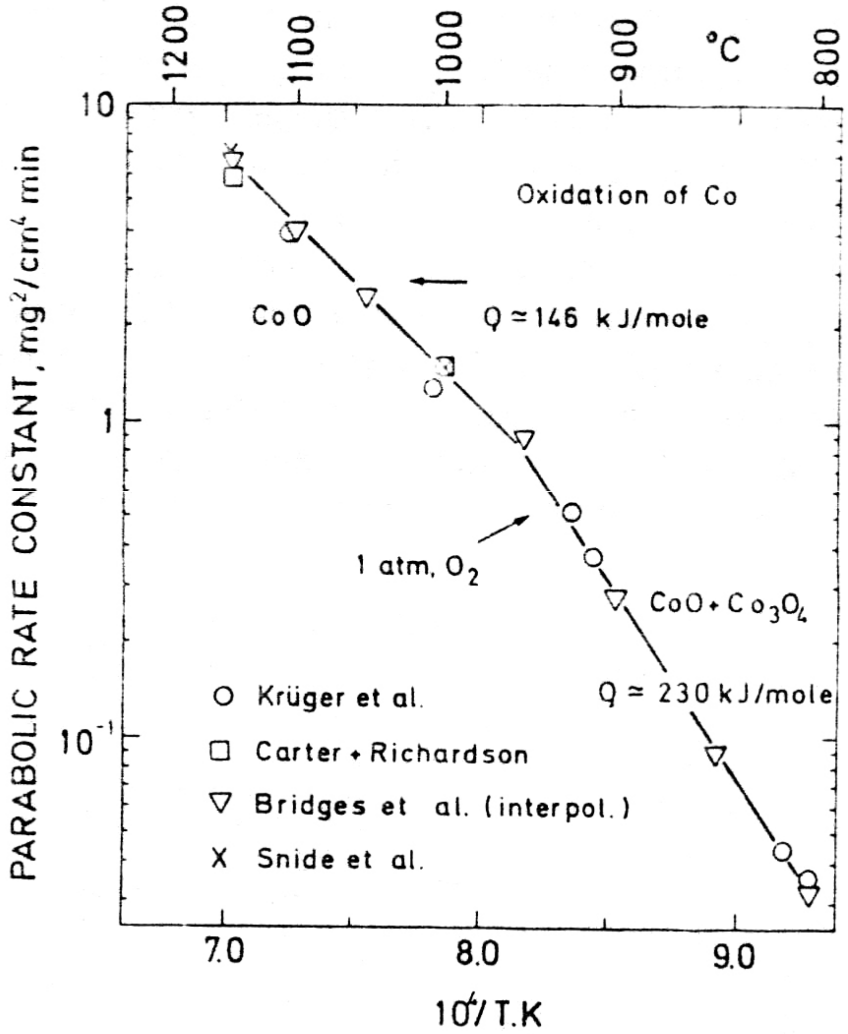
S. Mrowec and Z. Grzesik, Journal of Physics and Chemistry of Solids, 64, 1387-1394 (2003)

Pressure dependence of the parabolic rate constant of cobalt oxidation at T < 1450 K



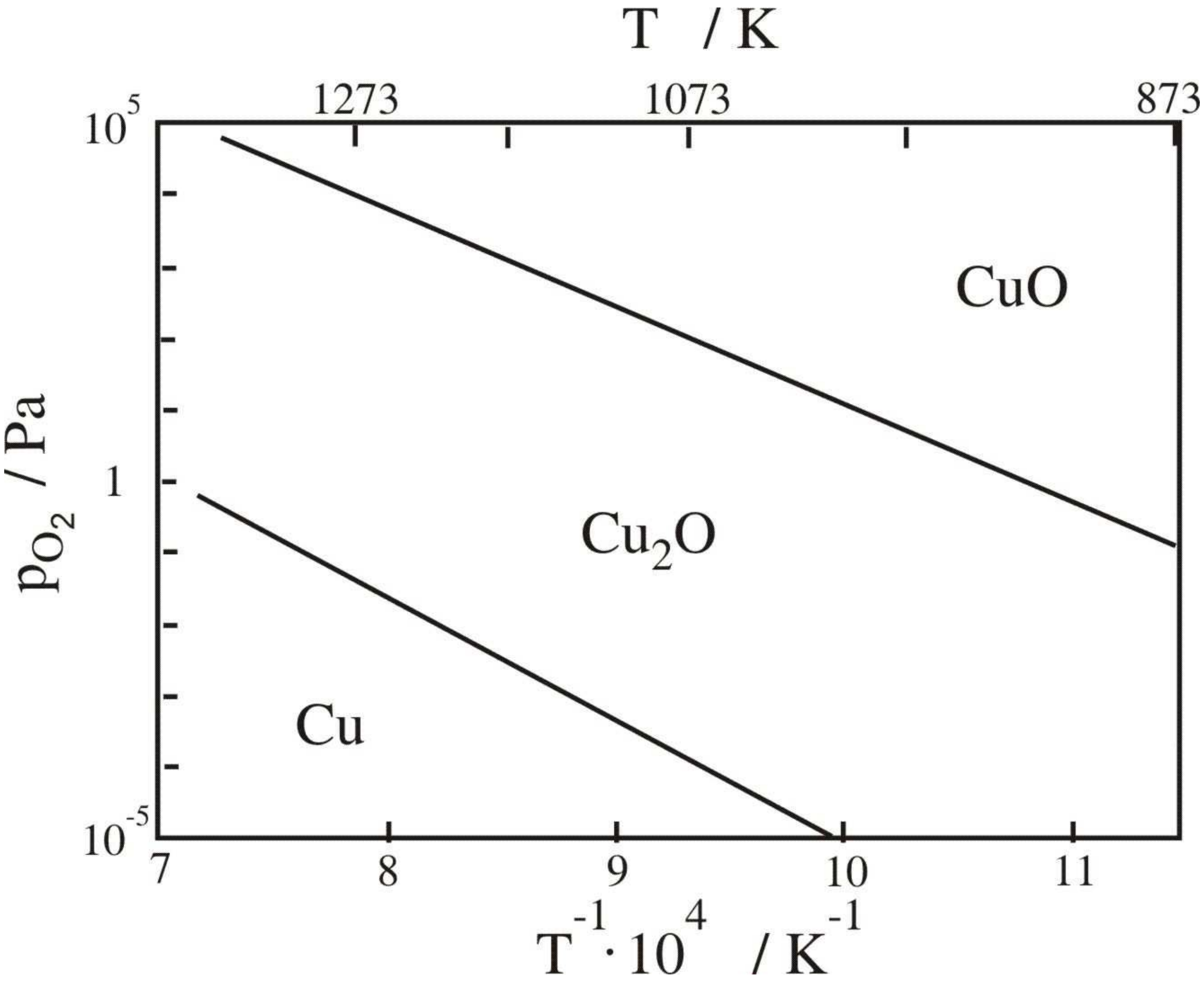
S. Mrowec, *An Introduction to the Theory of Metal Oxidation*, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.

Dependence of the cobalt oxidation rate on temperature

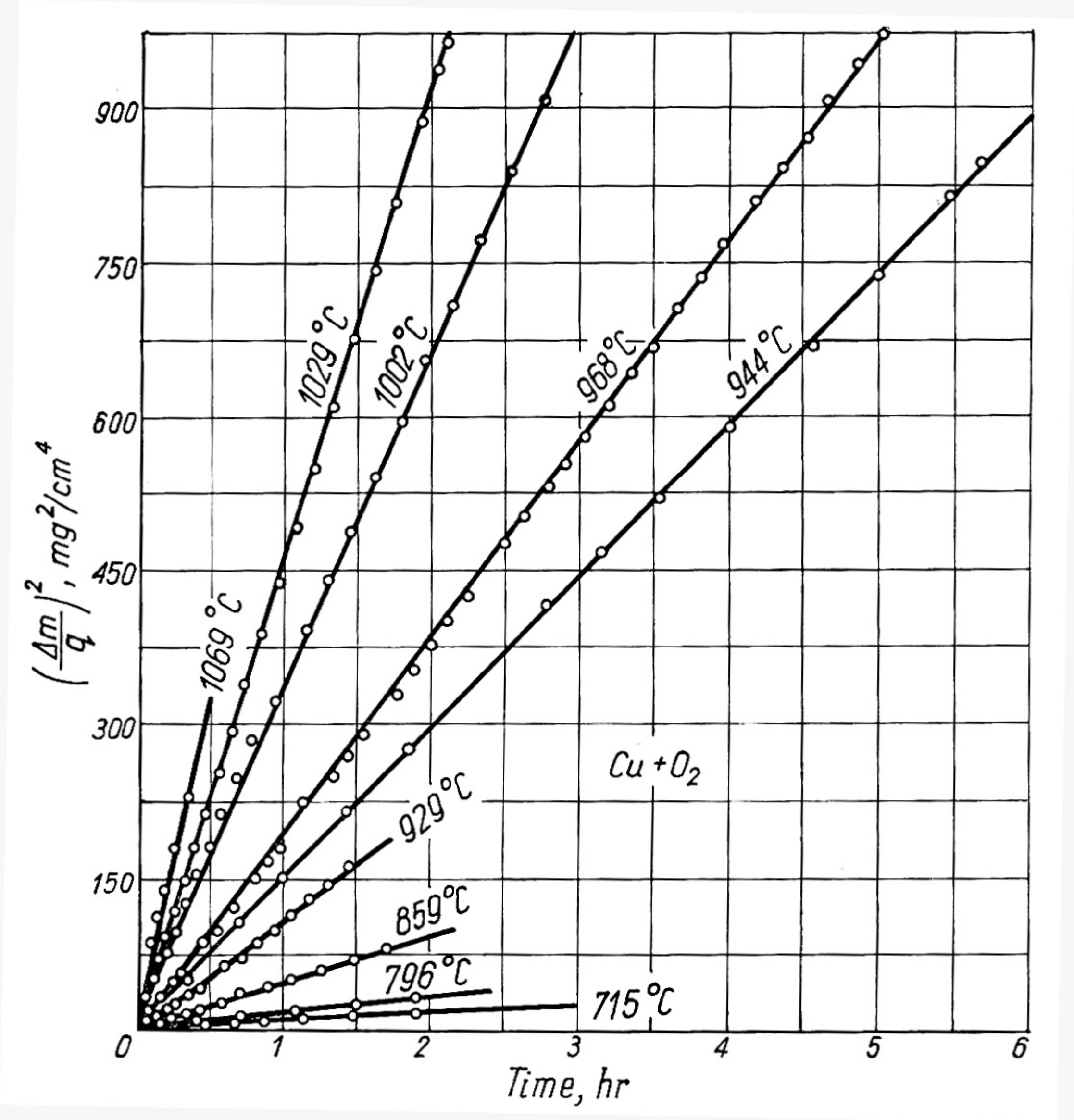


S. Mrowec, *An Introduction to the Theory of Metal Oxidation*, National Bureau of Standards and National Science Foundation, Washington D.C., 1982.

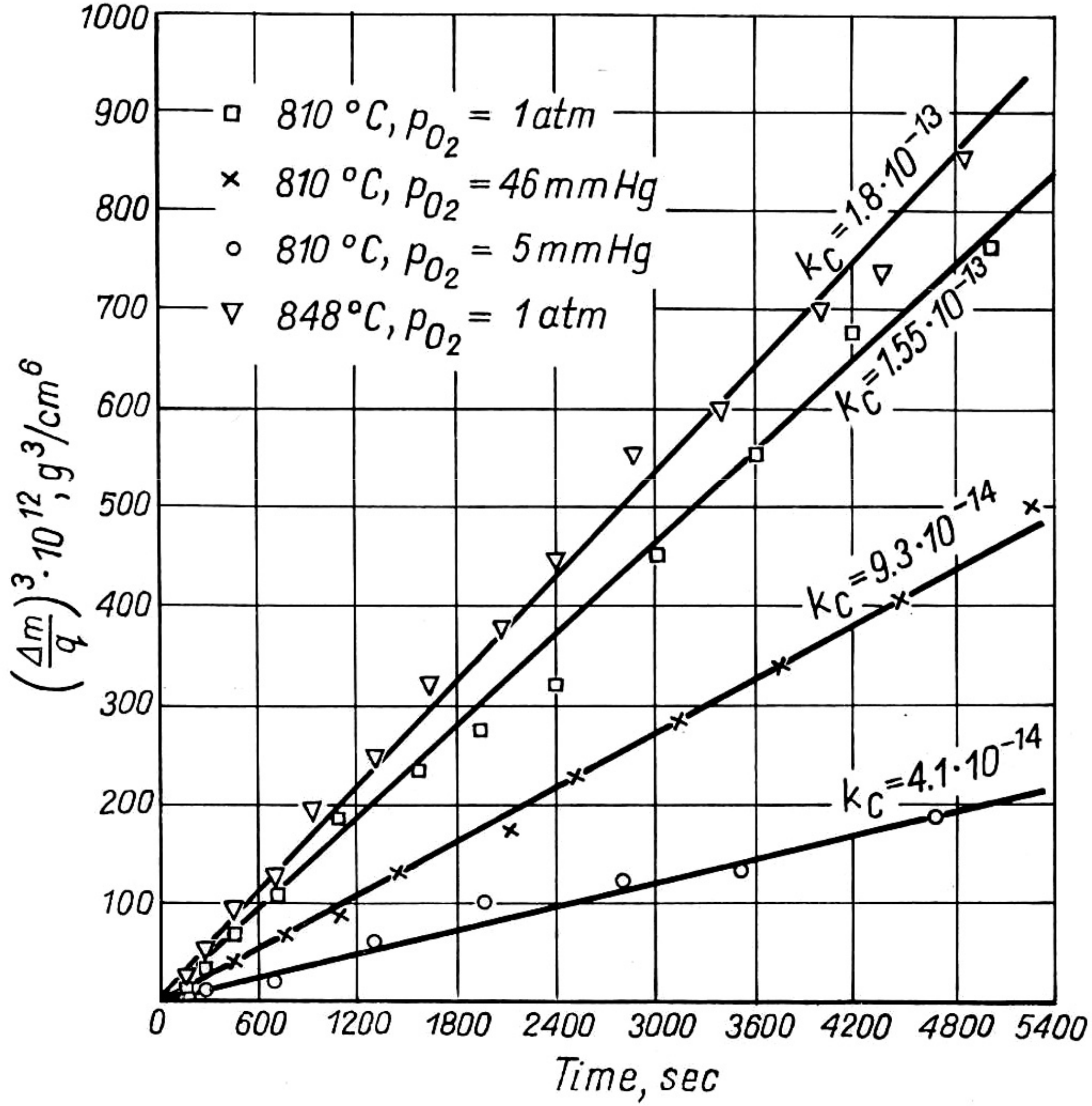
Copper oxidation



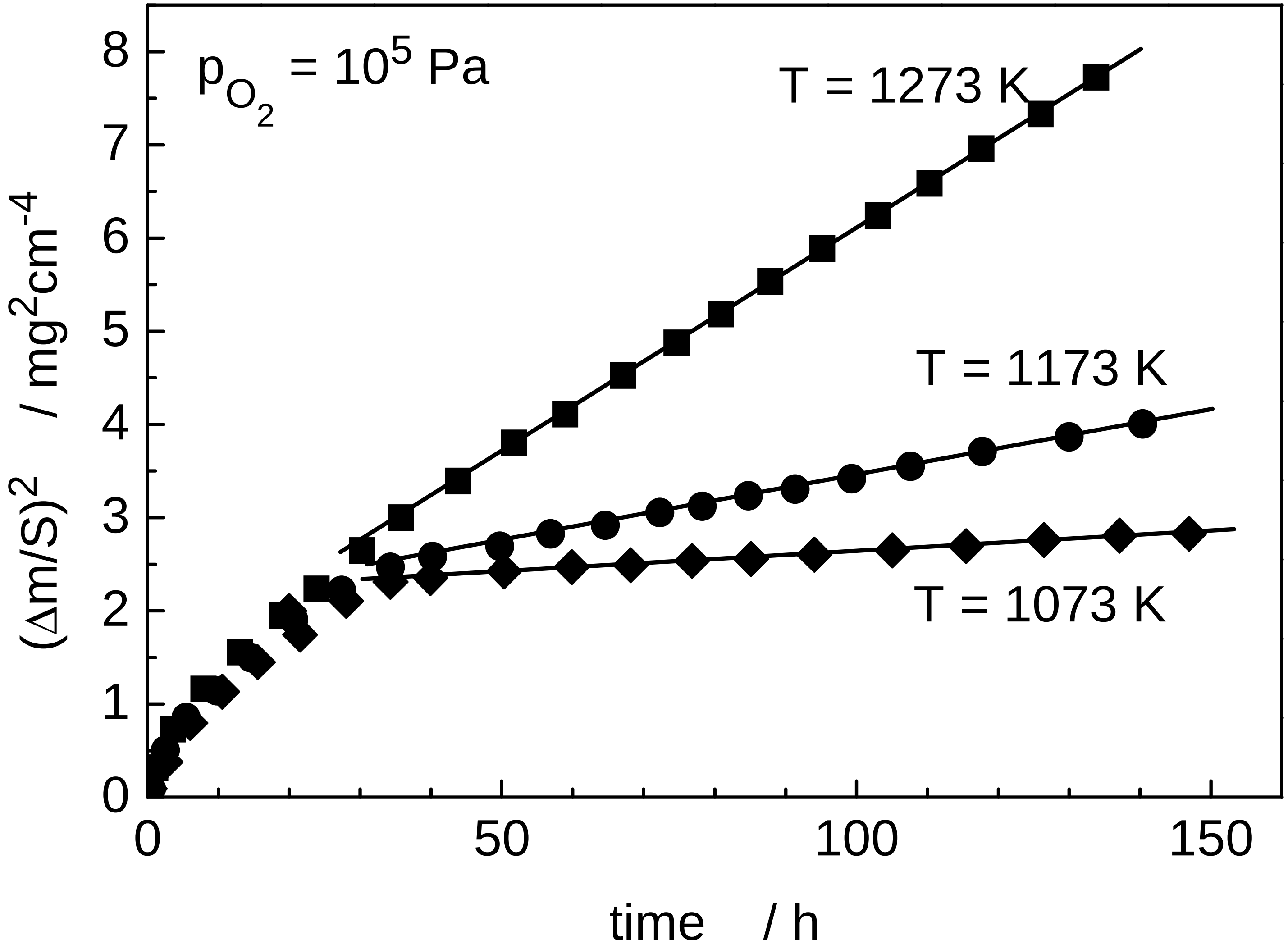
Copper oxidation kinetics



Cu_2O oxidation kinetics – initial stage

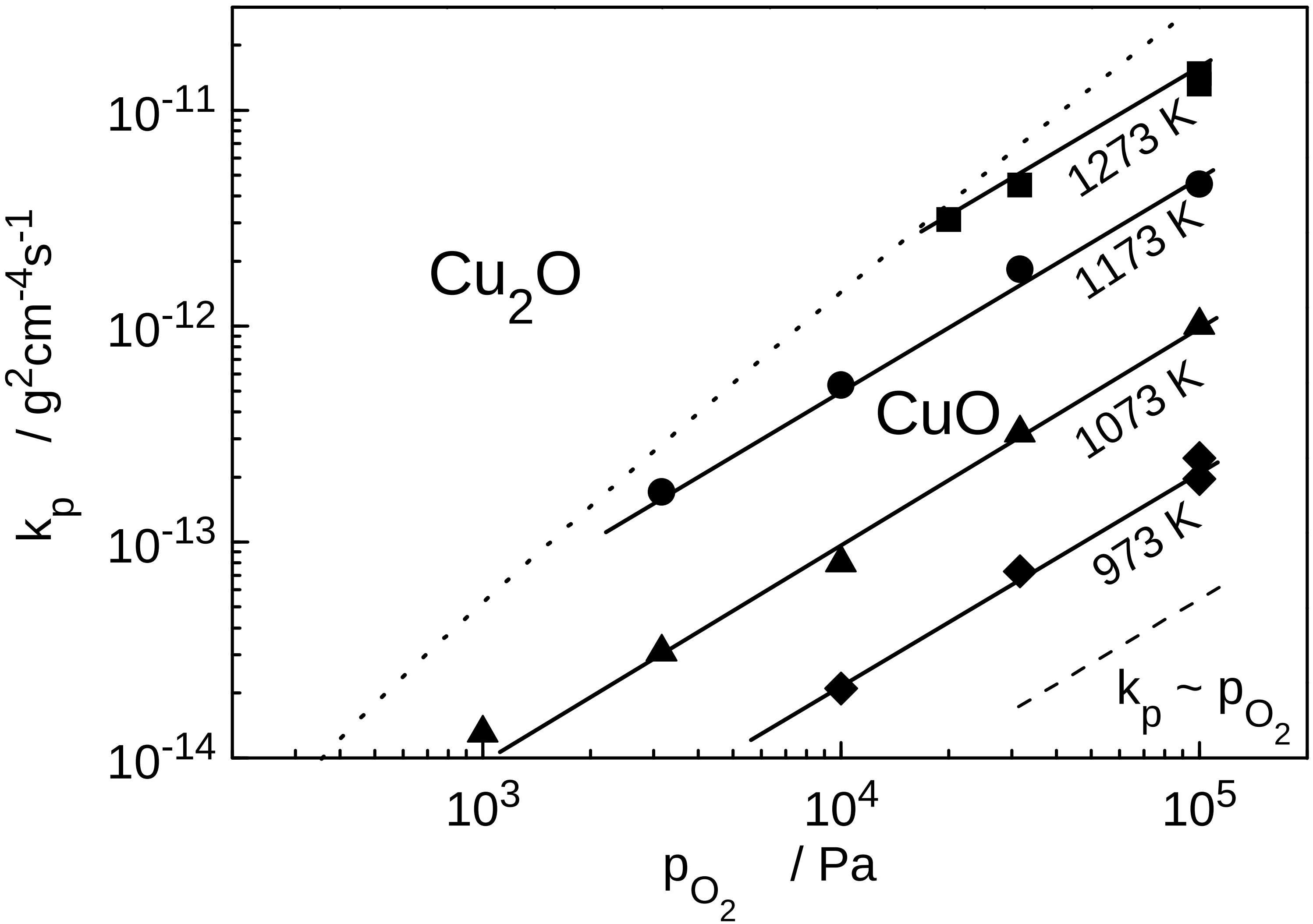


Kinetics of long-term Cu_2O oxidation



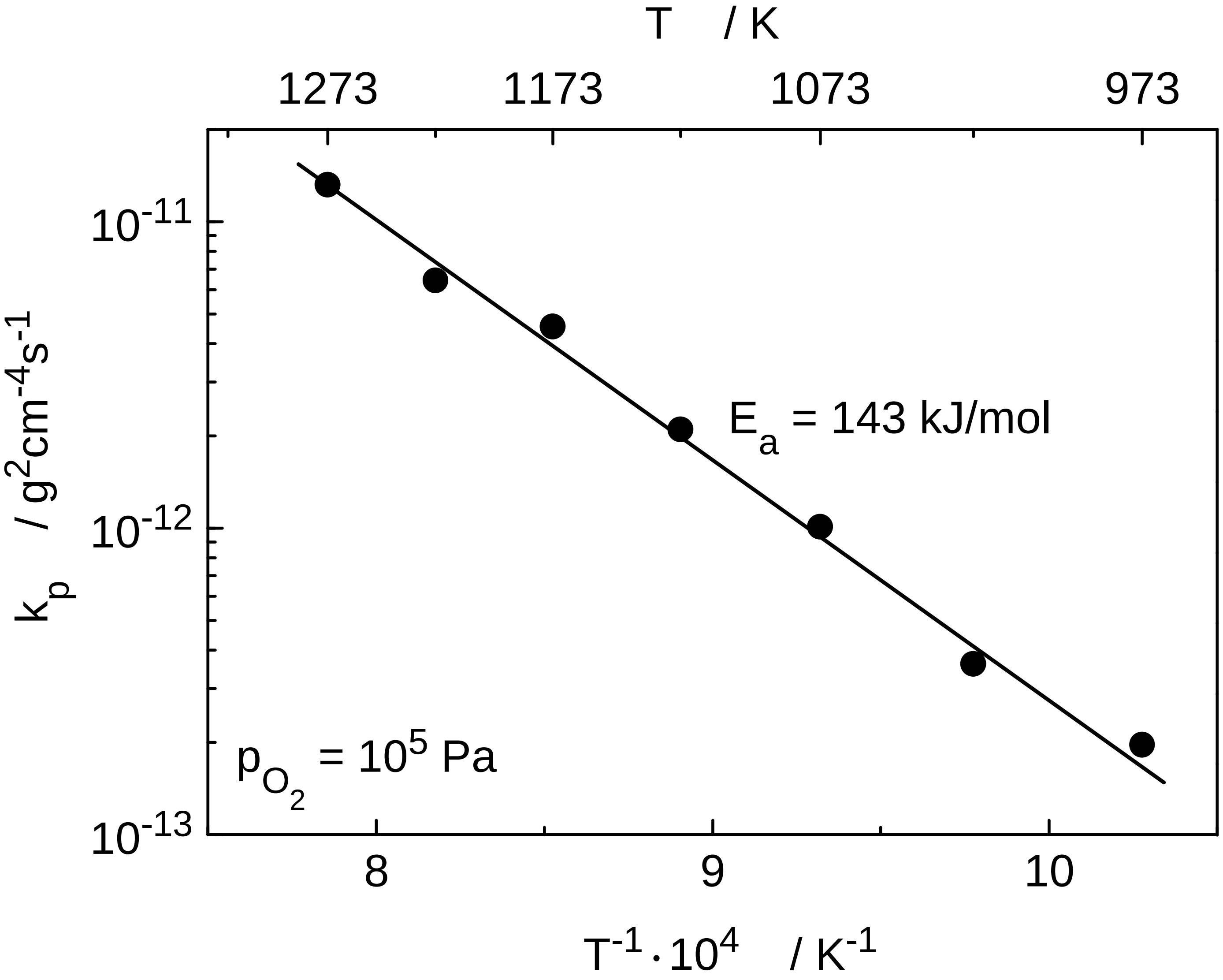
Z. Grzesik, M. Migdalska and S. Mrowec, High Temperature Materials and Processes, 30, 277-287 (2011)

Pressure dependence of the Cu_2O oxidation parabolic rate constant



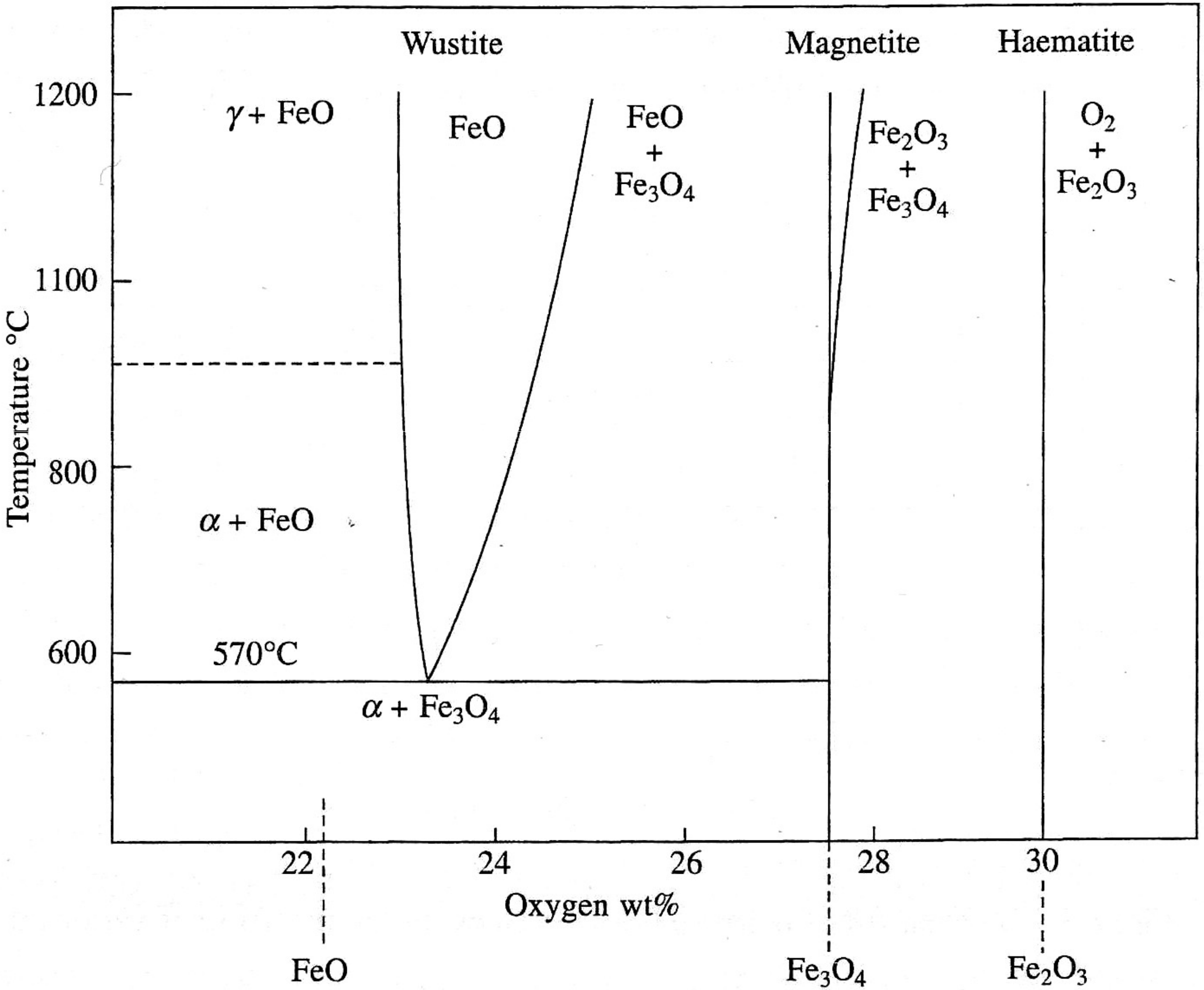
Z. Grzesik, M. Migdalska and S. Mrowec, High Temperature Materials and Processes, 30, 277-287 (2011)

Temperature dependence of the Cu_2O oxidation parabolic rate constant

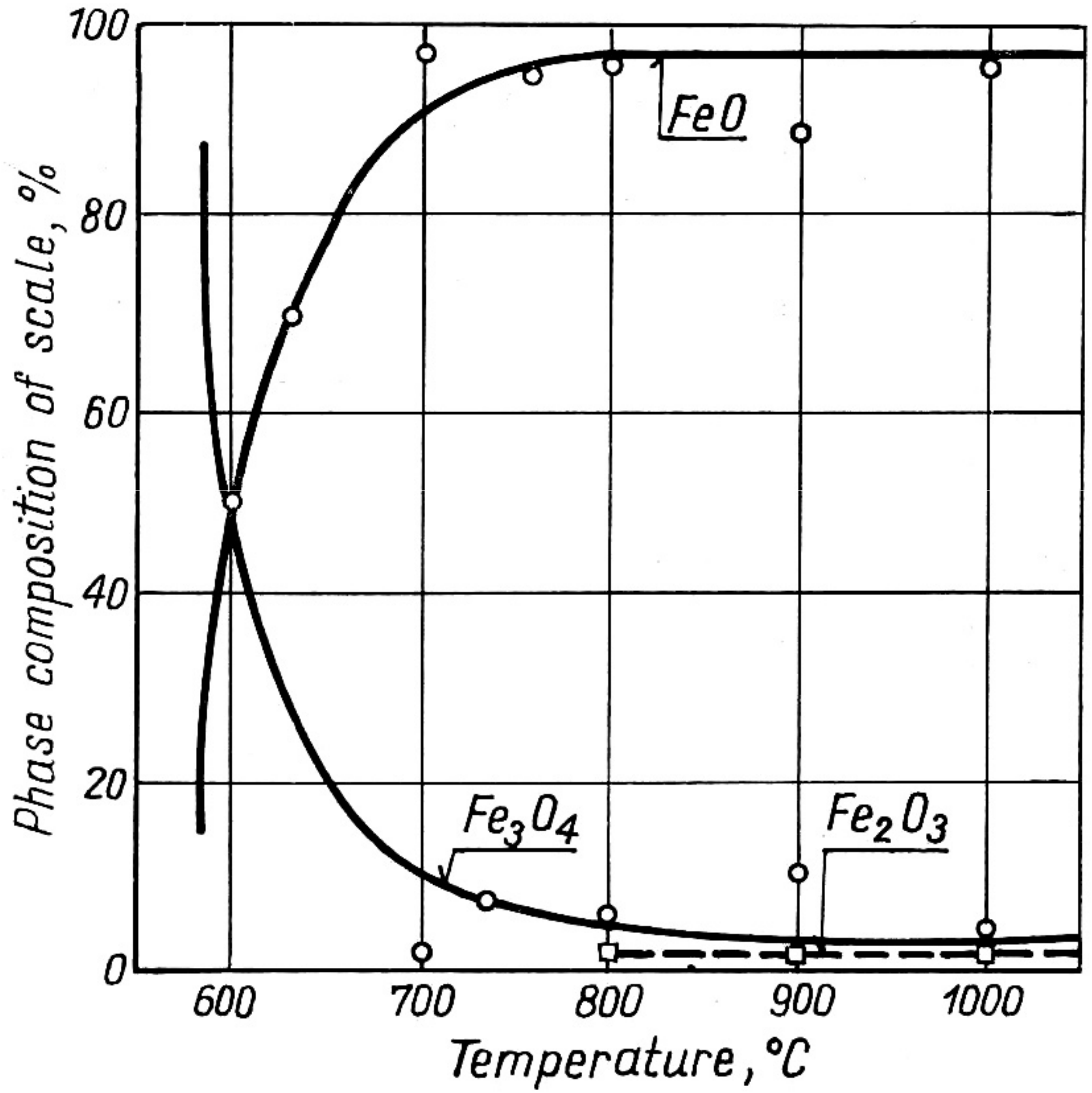


Z. Grzesik, M. Migdalska and S. Mrowec, High Temperature Materials and Processes, 30, 277-287 (2011)

Phase diagram of the Fe-O_2 system

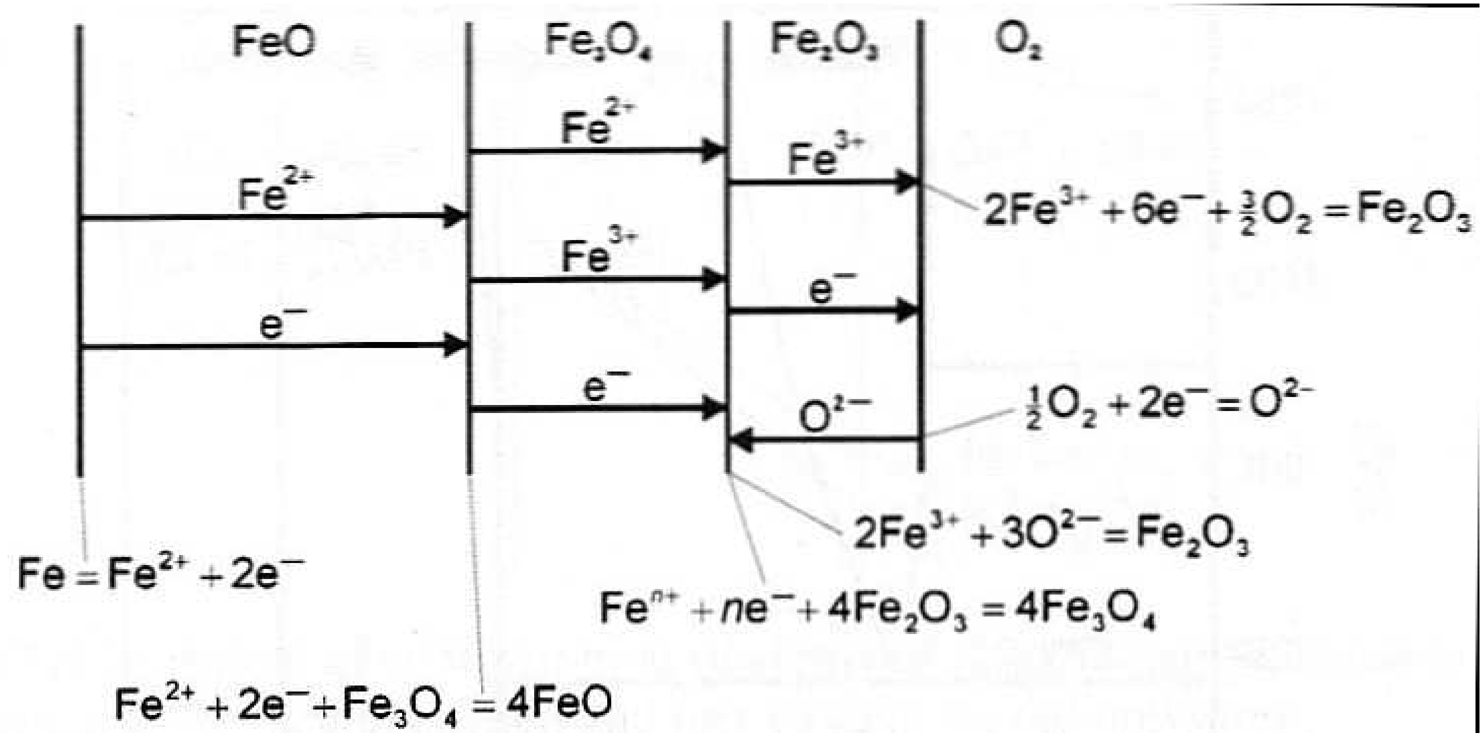


Temperature influence on the composition of the oxide scale growing on iron

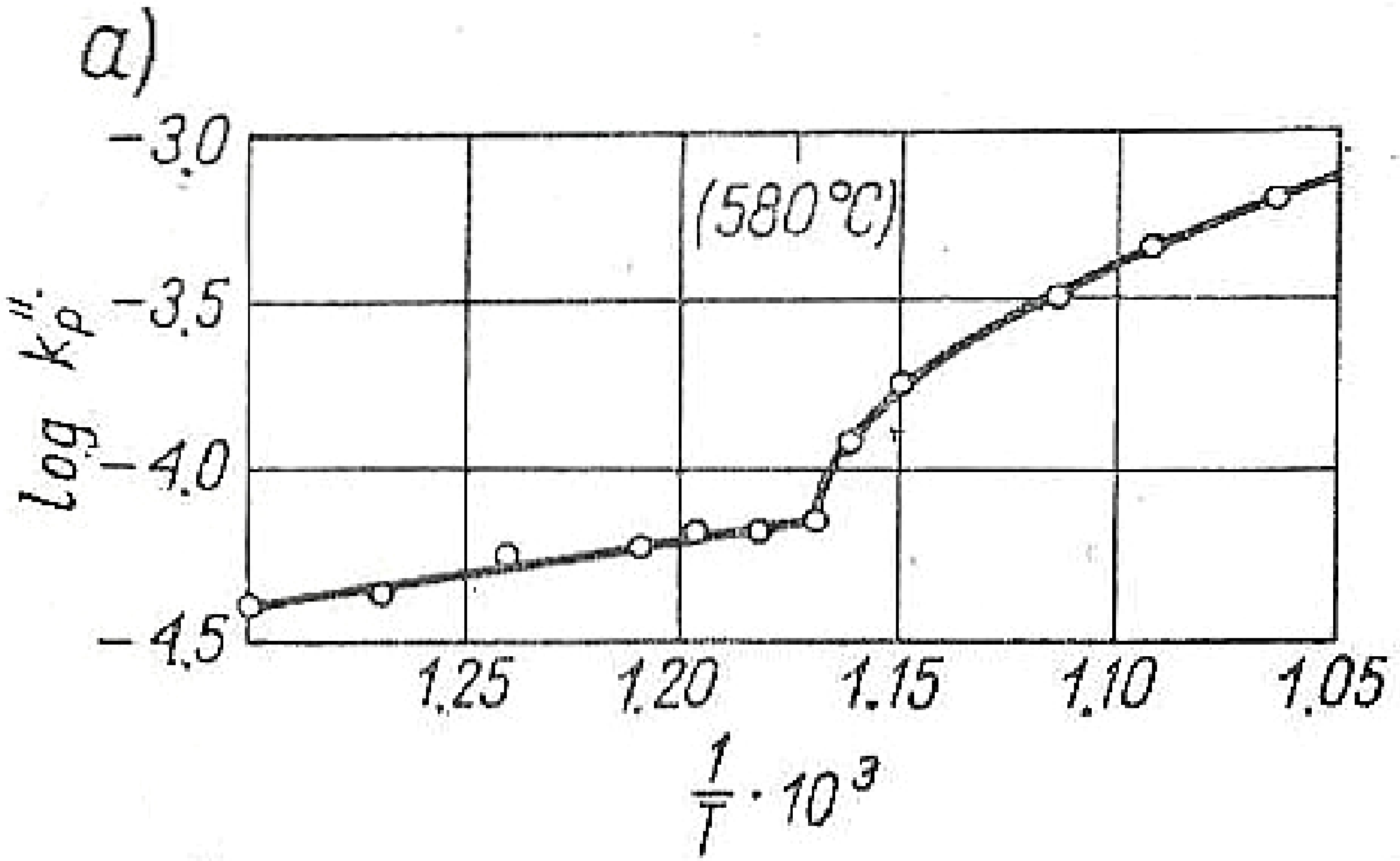


S. Mrowec, „An Introduction to the Theory of Metal Oxidation", National Bureau of Standards and the National Science Foundation, Washington, D.C., 1982.

Schematic illustration of the mechanism of triple layer scale formation on iron



Temperature dependence of the parabolic rate constant of iron oxidation



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

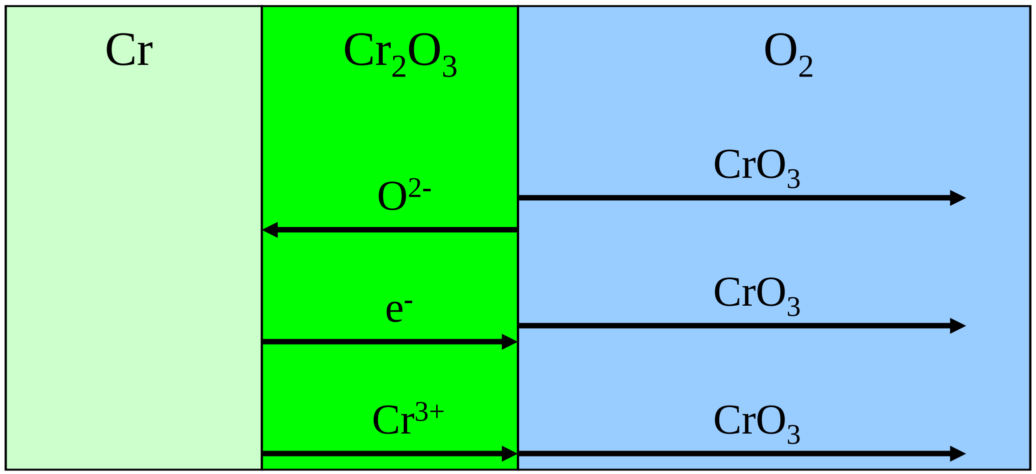
Metal oxidation leading to the formation of volatile reaction products – chromium oxidation

$$\frac{dx}{dt} = \frac{k_p}{x} - k_v$$

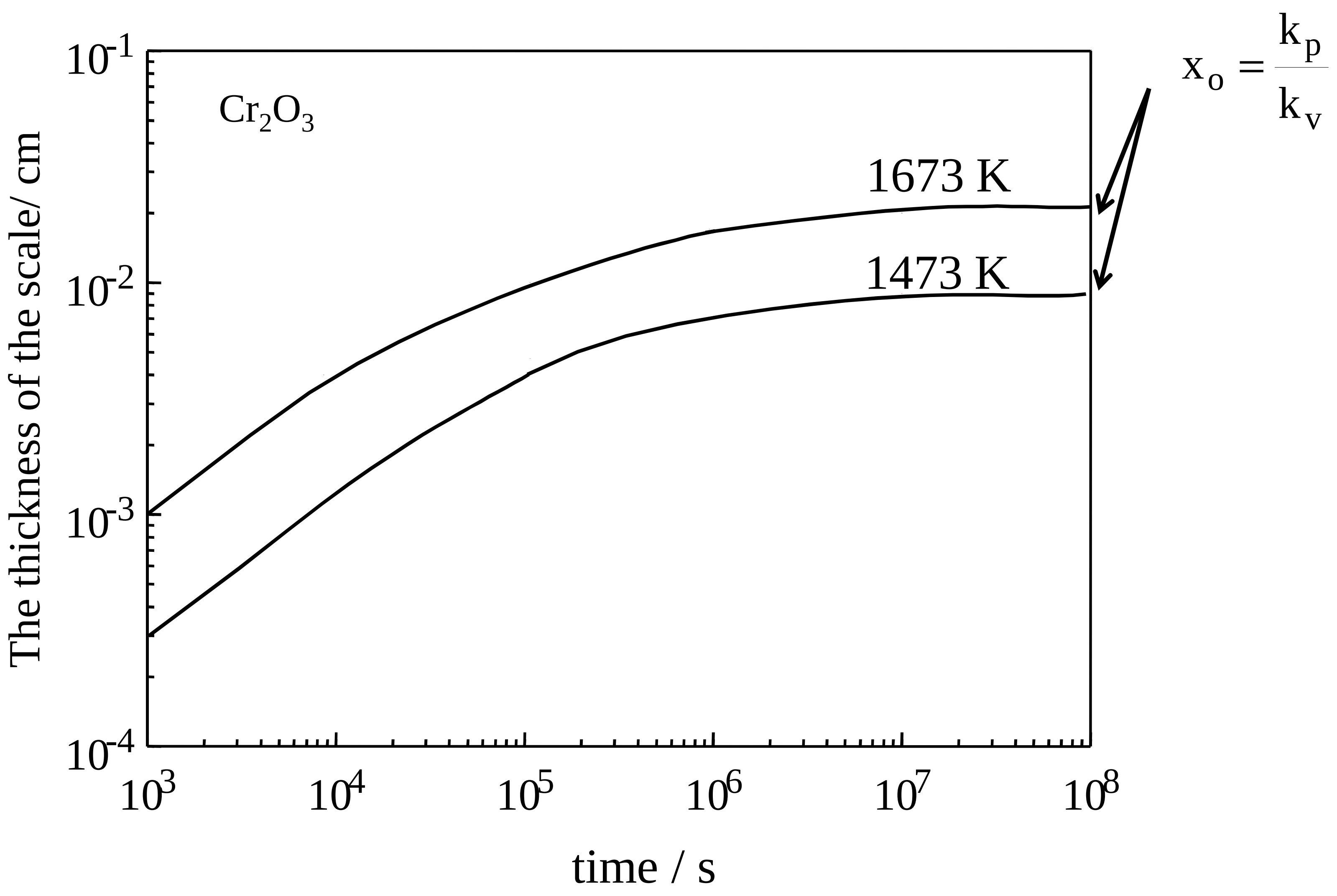
$$t = \frac{k_p}{k_v^2} \cdot \left[-\frac{k_v \cdot x}{k_p} - \ln\left(1 - \frac{k_v \cdot x}{k_p} \right) \right]$$

k_v – linear evaporation rate constant

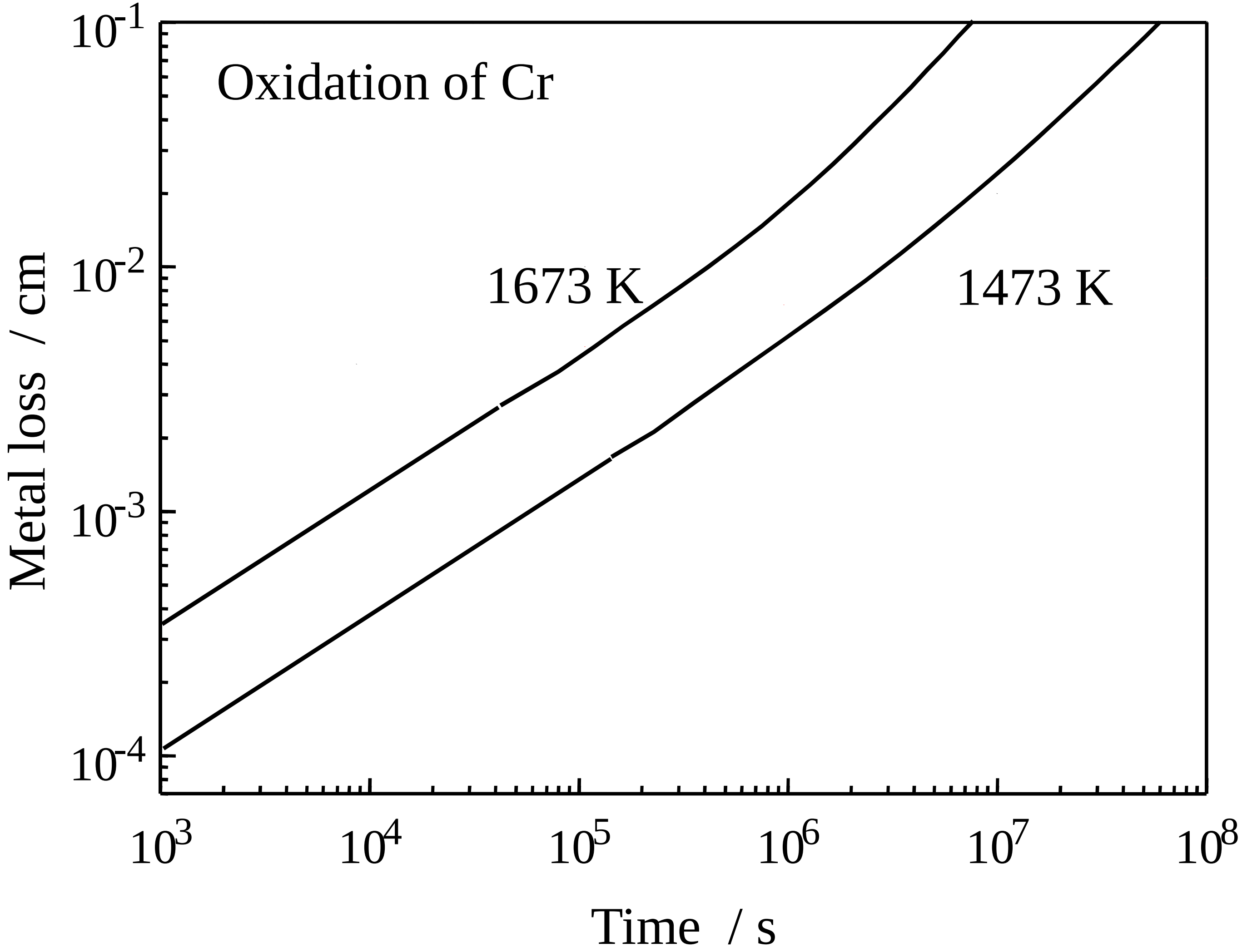
$$x_o = \frac{k_p}{k_v}$$



Kinetics of the Cr_2O_3 scale thickness growing during chromium oxidation

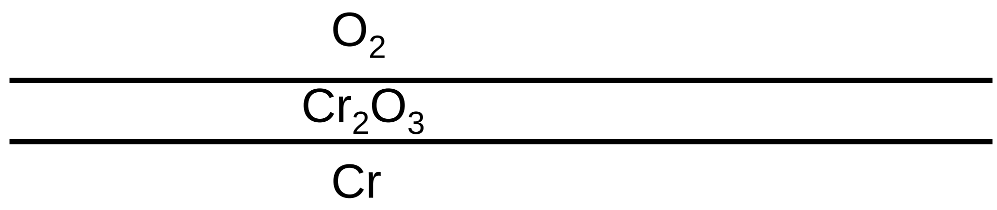


Kinetics of metal thickness loss during oxidation of pure chromium

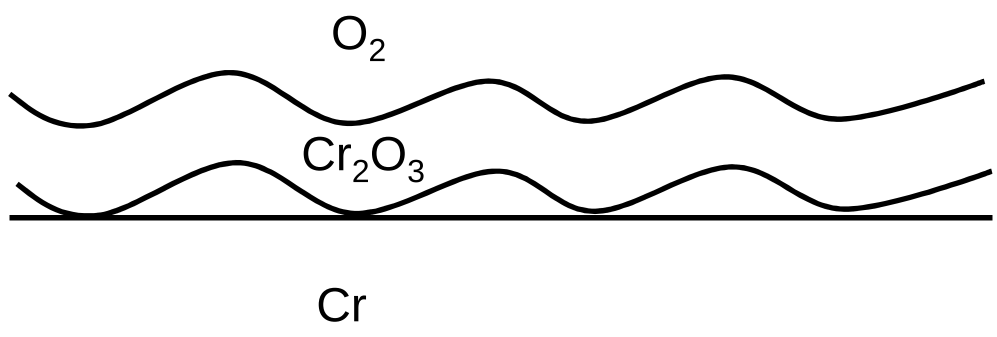


Influence of stresses on the scale shape (Cr_2O_3, Al_2O_3)

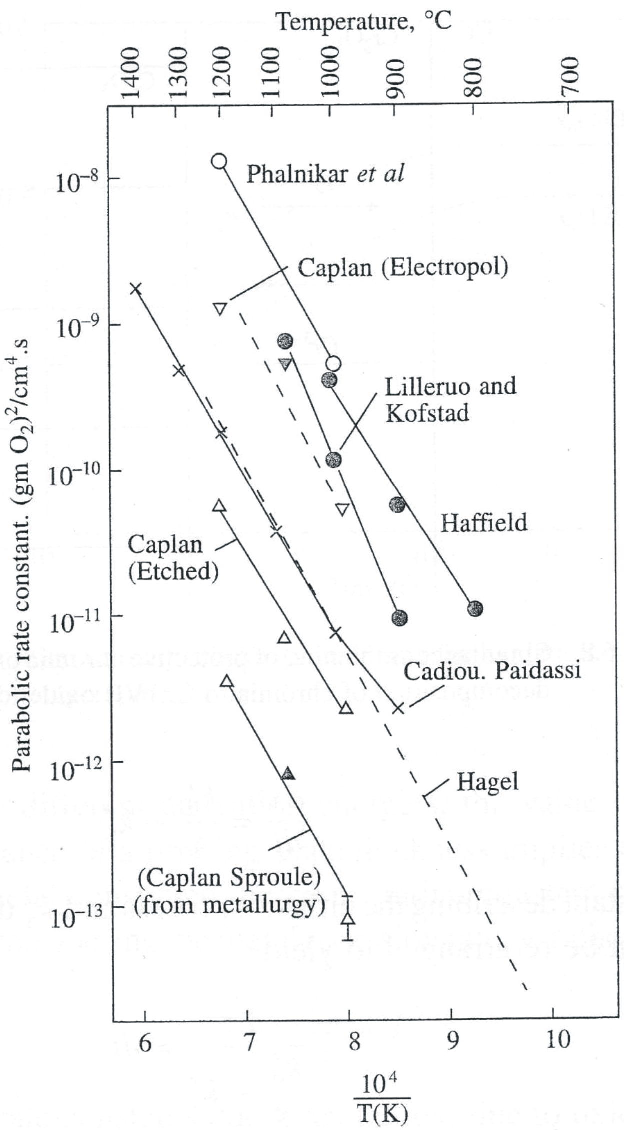
Initial oxidation stage



Later oxidation stages



Influence of the type of chromium surface treatment on its oxidation rate

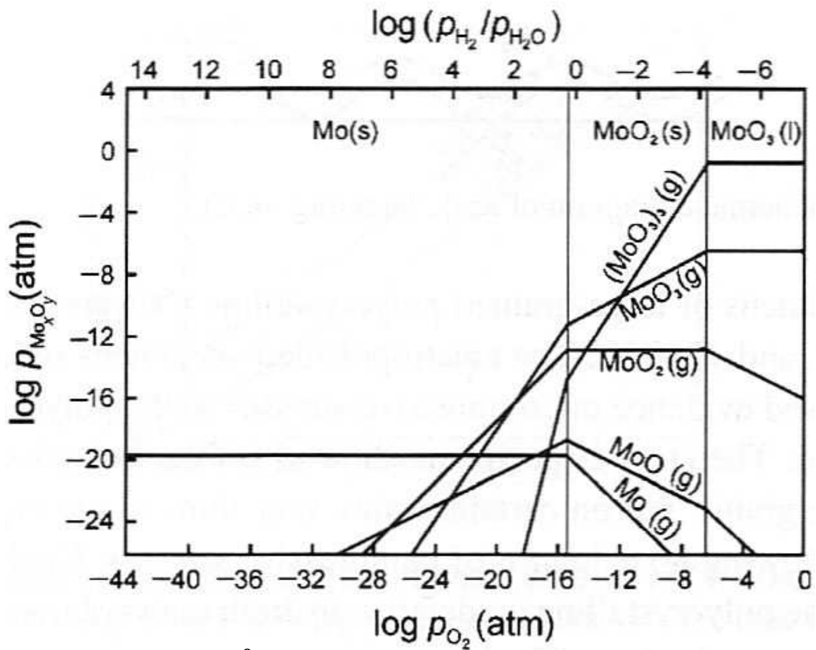


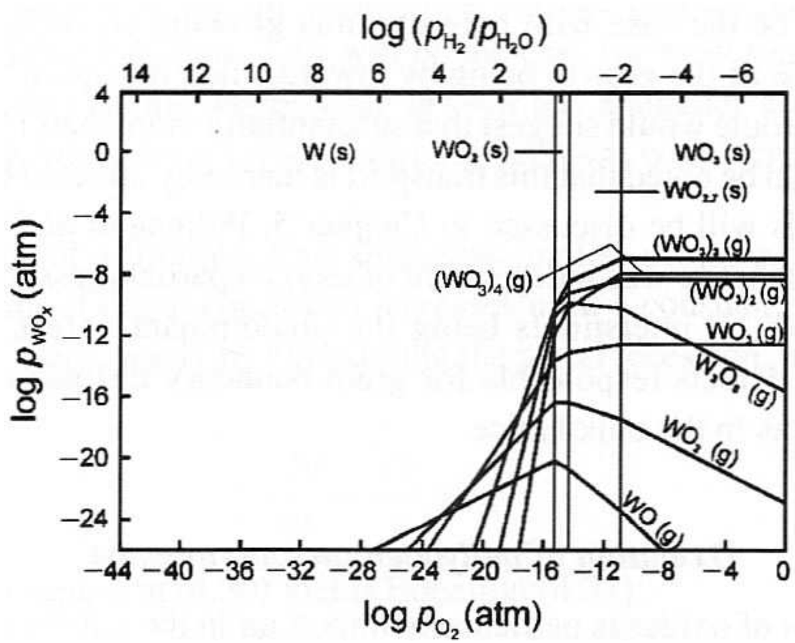
The chromium oxidation rate depends on grain size and crystallographic orientation, which can be controlled, to a certain extent, by the choice of surface treatment (grinding and polishing, electropolishing, etching). Electropolished chromium oxidizes very fast, however on etched chromium certain grains oxidize very quickly and others significantly slower.

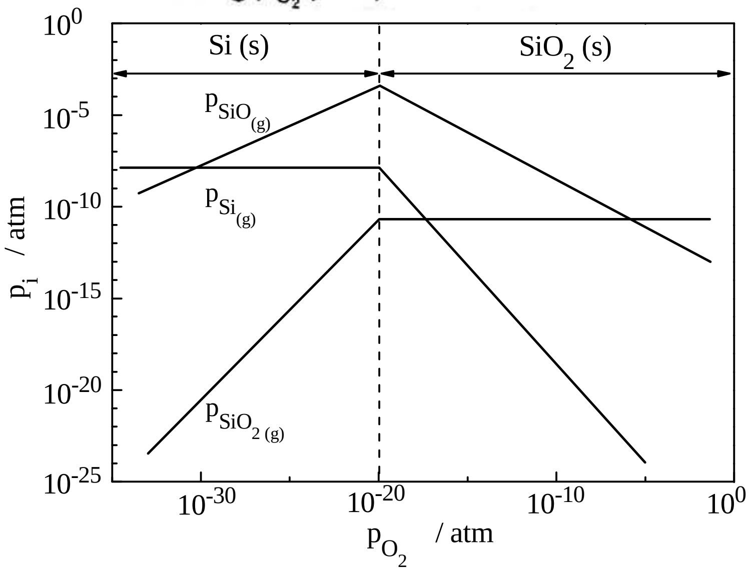
<u>CONCLUSION:</u>
An oxide formed in the initial oxidation stage determines to a large degree the oxidation rate in the later stages of the process.

P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science, London and New York, 1988.

Oxidation of metals (Mo, Nb) and Si leading to the formation of volatile reaction products

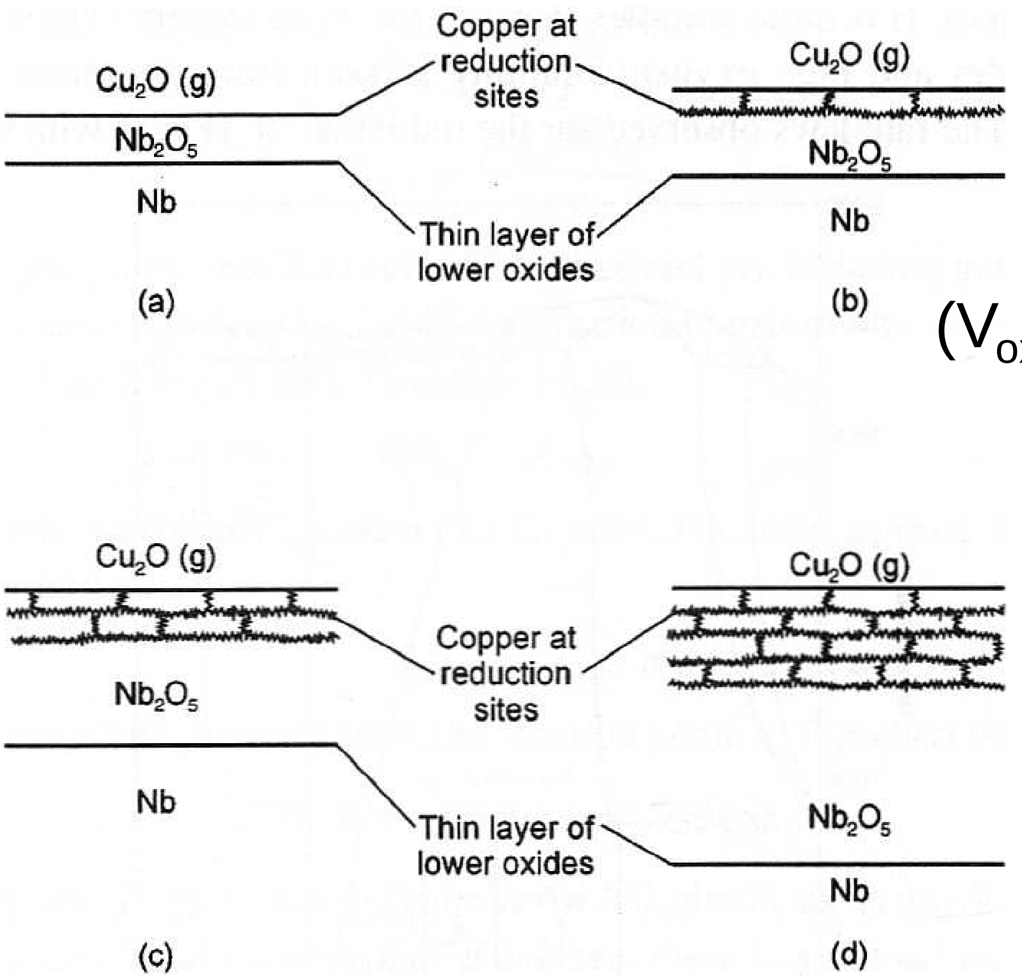






N. Birks, G.H. Meier and F.S Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press, 2009

Cracking of an oxide scale on Nb due to stresses accompanying inward oxygen diffusion

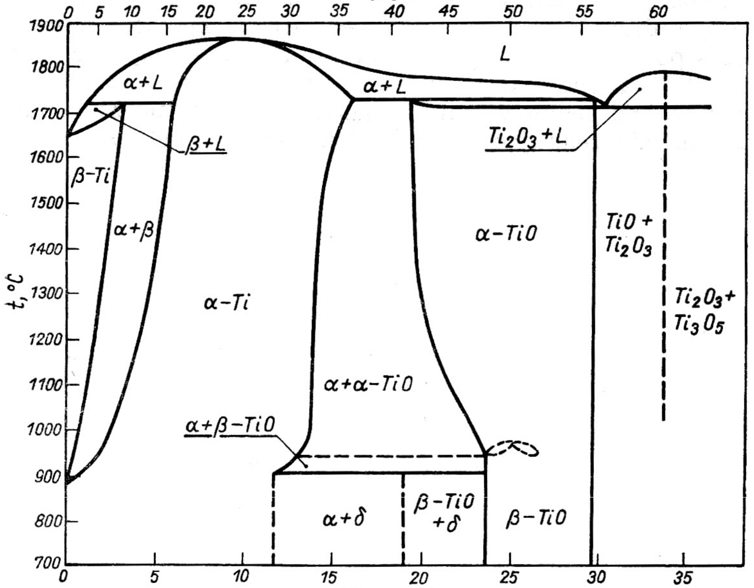


$(V_{ox}/V_m) = 2{,}74$

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

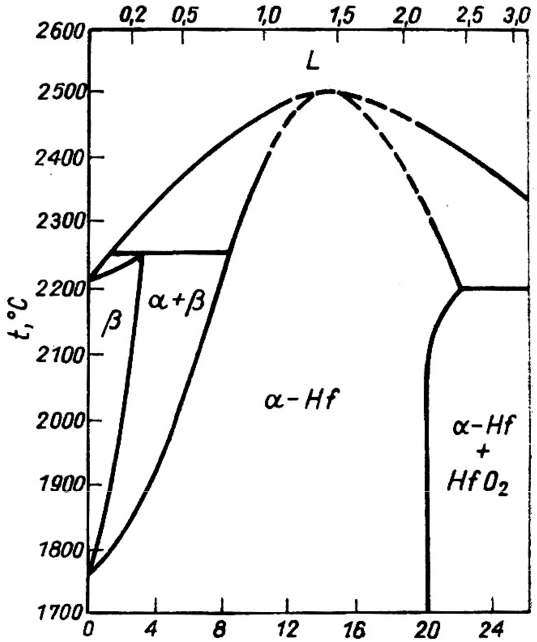
Oxidation of metals exhibiting large oxygen solubility (Ti, Hf, Zr)

oxygen, at. %



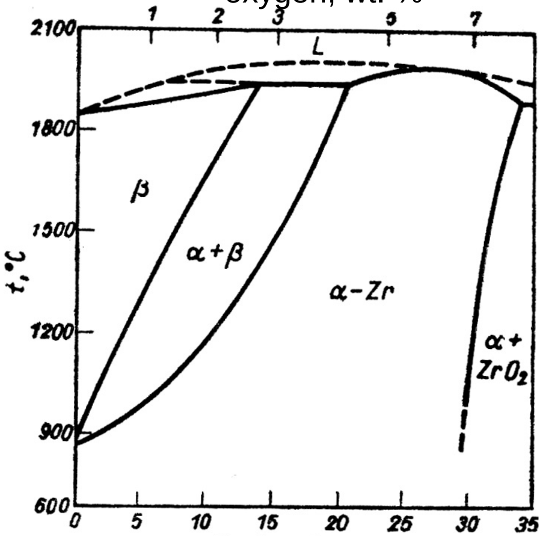
oxygen, wt. %

oxygen, wt. %



oxygen, at. %

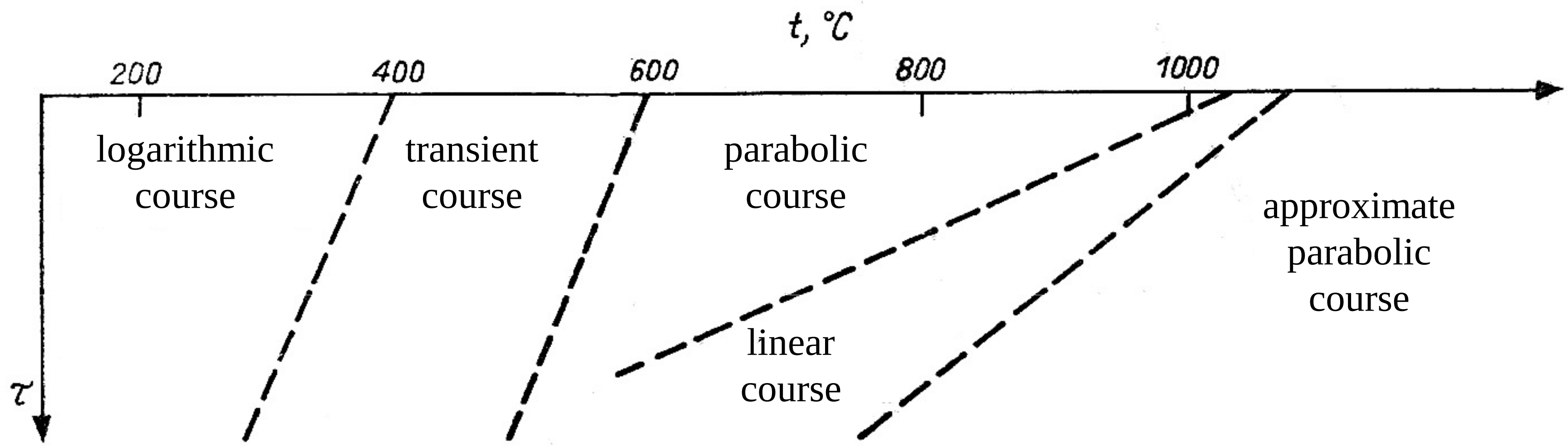
oxygen, wt. %



oxygen, at. %

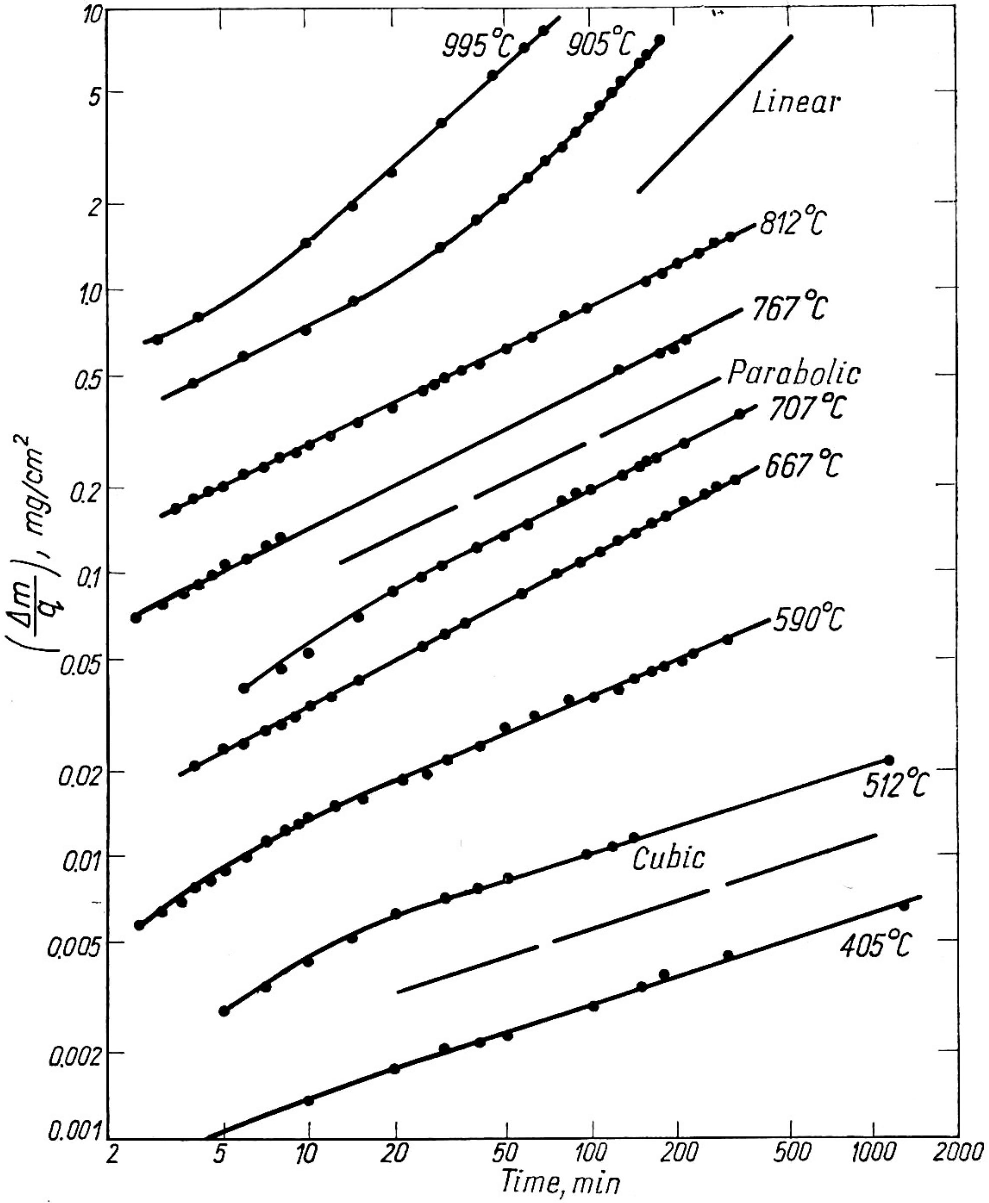
$$\frac{\Delta m}{S} = k_p\ (\text{scale growth}) \cdot t^{1/2} + k_p\ (\text{O solubility}) \cdot t^{1/2}$$

Schematic illustration of the influence of temperature and time on titanium oxidation kinetics



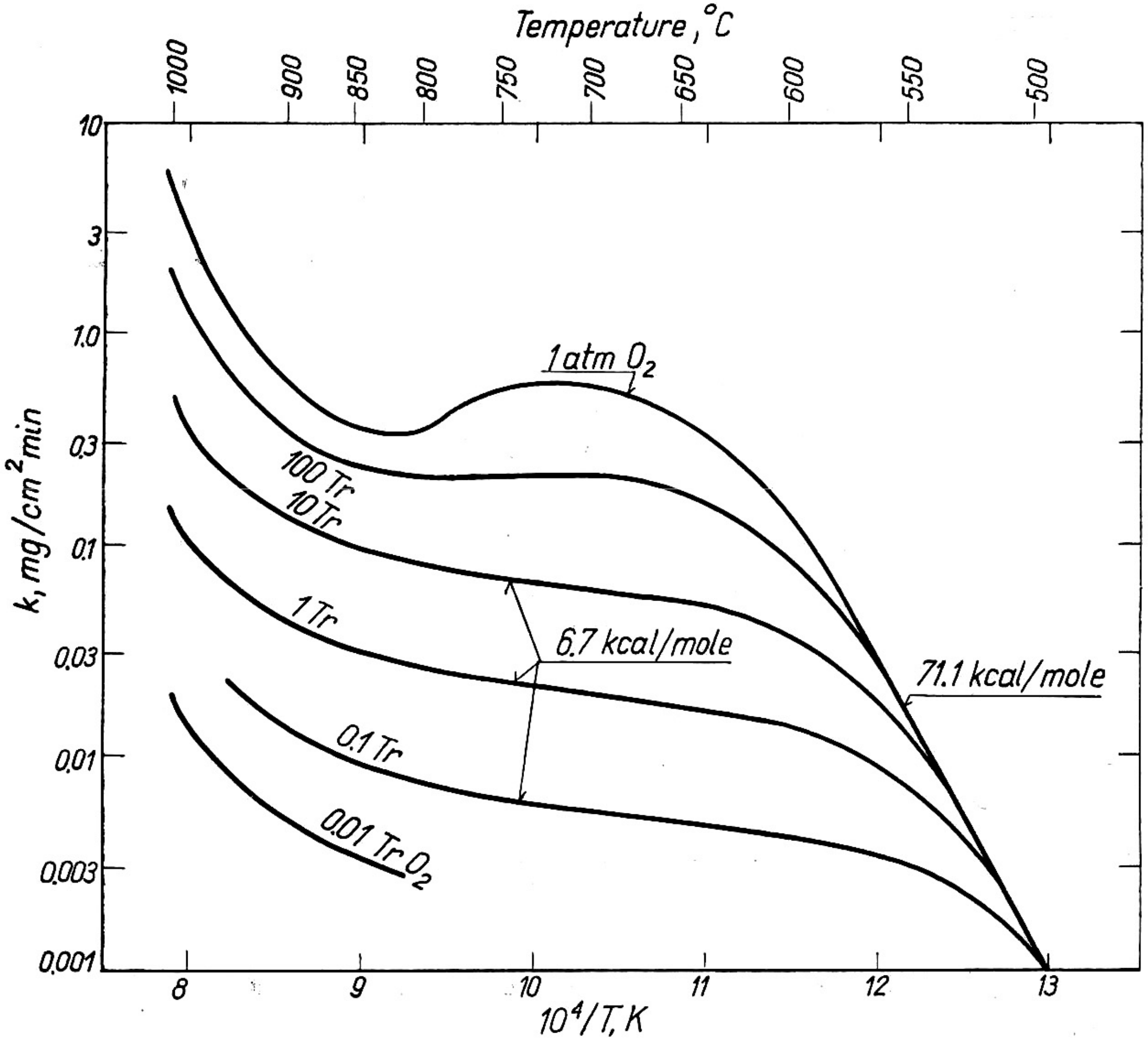
S. Mrowec, „An Introduction to the Theory of Metal Oxidation", National Bureau of Standards and the National Science Foundation, Washington, D.C., 1982.

Influence of temperature on titanium oxidation kinetics



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

Influence of temperature and oxygen pressure on titanium oxidation kinetics



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

Oxidation process kinetics of selected metals

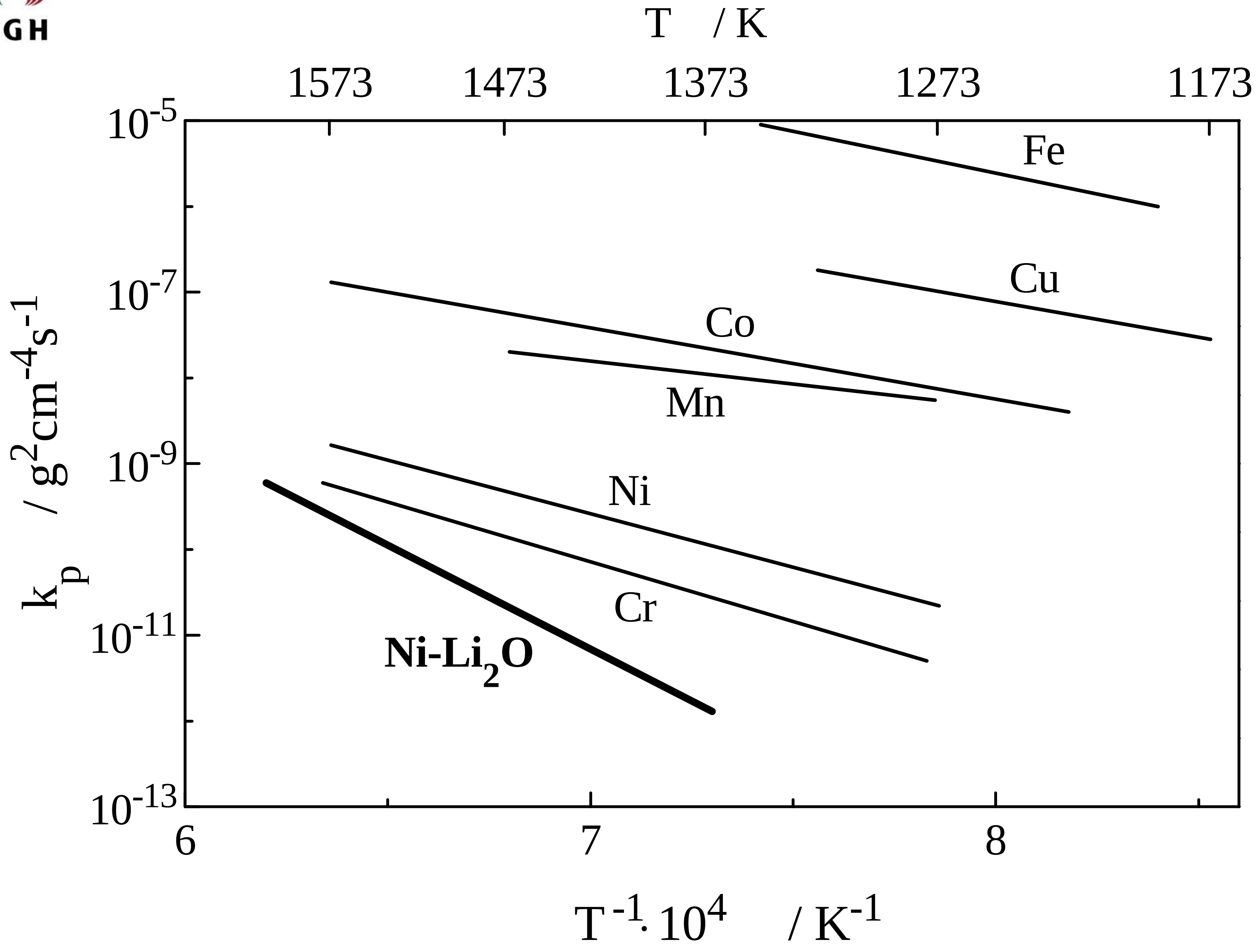
Metal	< 100	100–200	200–300	300–400	400–500	500–600	600–700	700–800	800–900	900–1000	1000–1100	> 1100
Mg	log.		par.	paralin.		lin.						
Ca	log.			par.	lin.	lin.						
Ce	log.	lin.	incr.									
Th			par.		lin.	lin.						
U	par.	paralin.	lin.	incr.								
Ti			log.		cu.	cu.	paralin.			paralin.		
Zn			log.	cu		cu.			cu.	cu.	lin.	
Nb			par.	par.	paralin.			lin.	lin.		incr.	
Ta	log.	inv. log.		par.	paralin.			lin.		lin.		
Mo			par.	paralin.		paralin.		lin.		lin.		
W				par.		par.		paralin.		paralin.	paralin.	
Fe	log.	log.	par.	par.	par.			par.		par.		par.
Ni		log.	log.	cu.	par.					par.		par.
Cu	log.	cu.	cu.		par.		par.	par.				
Zn		log	log.	par.								
Al	log.	inv. log.	log.	par.		lin.						
Ge				par.		paralin.						

Temperature, °C

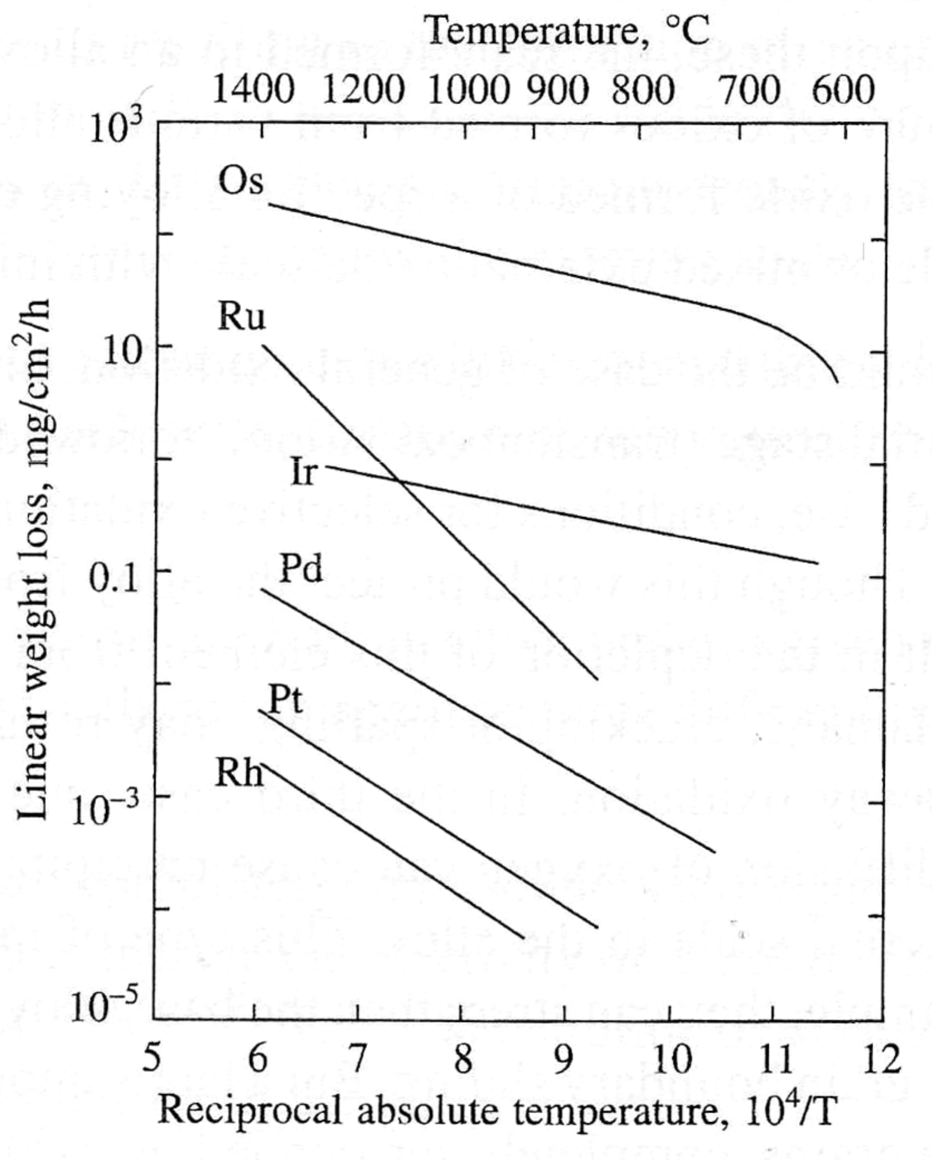
Denotations: log. — logarithmic law; inv. log. — inversely logarithmic law; cu — cubic law; par. — parabolic law; paralin. — paralinear law; lin. — linear law; incr. — increased oxidation rate.

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

Comparison of the oxidation rates of selected metals



Influence of temperature on the degradation rate of noble metals



THE END