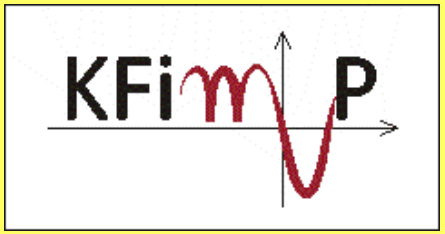
SULPHIDATION - RESISTANT HIGH TEMPERATURE COATINGS

Zbigniew Grzesik

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



Department of Physical Chemistry and Modelling

Z. Grzesik and K. Przybylski, „Sulfidation of metallic materials” w „Developments in high temperature corrosion and protection of materials”, Eds. Wei Gao and Zhengwei Li, Woodhead Publishing Limited, Cambridge England, 2008, str. 599-638.

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.

Properties of selected metal sulfides and oxides

Sulfide	ΔG^0_{1273K} [kJ/mol S]	p_{S_2} [Pa]	Oxide	ΔG^0_{1273K} [kJ/mol O]	p_{O_2} [Pa]
Al_2S_3	-191	$2.4 \cdot 10^{-11}$	Al_2O_3	-424	$1.8 \cdot 10^{-30}$
CoS	-43.8	26	CoO	-145	$1.2 \cdot 10^{-7}$
Cu_2S	-95.7	$1.4 \cdot 10^{-3}$	Cu_2O	-77.7	$4.3 \cdot 10^{-2}$
CuS	63.6	$1.6 \cdot 10^{10}$	CuO	-11.6	$1.1 \cdot 10^{4}$
FeS	-78.9	$2.9 \cdot 10^{-2}$	FeO	-179	$2.3 \cdot 10^{-10}$
MnS	-196.9	$7.3 \cdot 10^{-12}$	MnO	-292	$1.2 \cdot 10^{-19}$
MoS_2	-78.3	$3.8 \cdot 10^{-2}$	MoO_2	-182	$1.3 \cdot 10^{-10}$
NiS	-50.4	7.5	NiO	-127	$3.8 \cdot 10^{-6}$
TiS	-228	$2.1 \cdot 10^{-14}$	TiO	-420	$3.9 \cdot 10^{-30}$

Properties of selected metal sulfides and oxides

Sulfide	Melting point [K]	Oxide	Melting point [K]
Al_2S_3	1373	Al_2O_3	2288
CoS	1389	CoO	2068
Co_3S_4	?	Co_3O_4	1223
Cr_2S_3	1623	Cr_2O_3	2539
Cu_2S	1373	Cu_2O	1508
CuS	376	CuO	1599
FeS	1472	FeO	1642
MnS	1598	MnO	2058
MoS_2	1458	MoO_2	2200
NiS	1083	NiO	2230
TiS	2373	TiO	2023
TiS_2	?	TiO_2	2123
La_2S_3	2423	La_2O_3	2490
Ce_2S_3	2373	Ce_2O_3	1965
ThS_2	2198	ThO_2	3593

Sulfide	Melting point [K]	Oxide	Melting point [K]
US_2	1373	UO_2	3151
Y_2S_3	1873	Y_2O_3	2683
InS	965	InO	1325
In_2S_3	1323	In_2O_3	2273

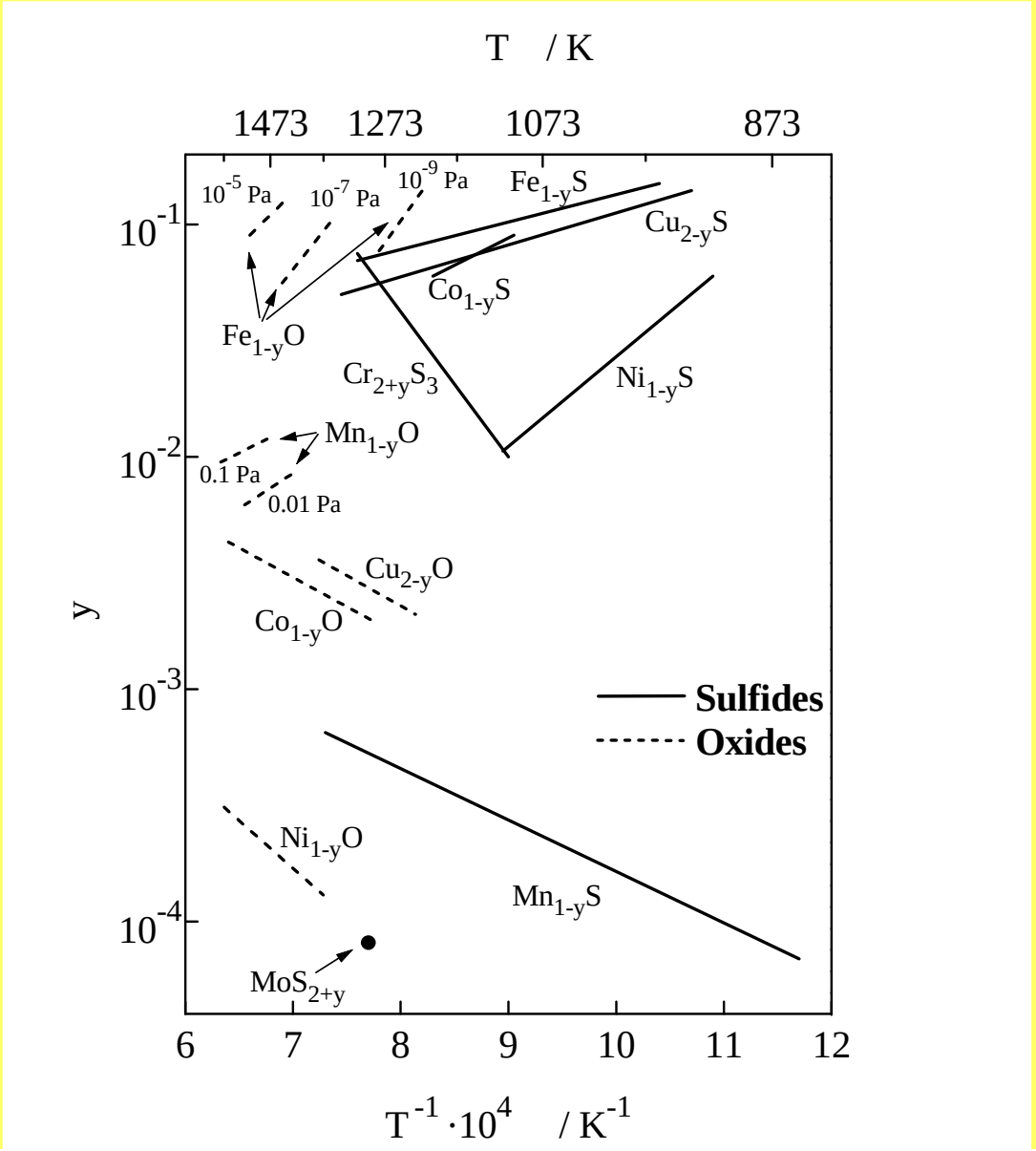
Properties of selected metal sulfides and oxides

Metal	Sulfides	Oxides
Co	Co_4S_3	CoO
	Co_9S_8	Co_3O_4
	CoS	
	Co_3S_4	
	CoS_2	
Cr	CrS	Cr_2O_3
	Cr_7S_8	
	Cr_5S_6	
	Cr_3S_4	
	Cr_2S_3	
Ni	Ni_3S_2	NiO
	Ni_7S_6	
	NiS	
	Ni_3S_4	
	NiS_2	

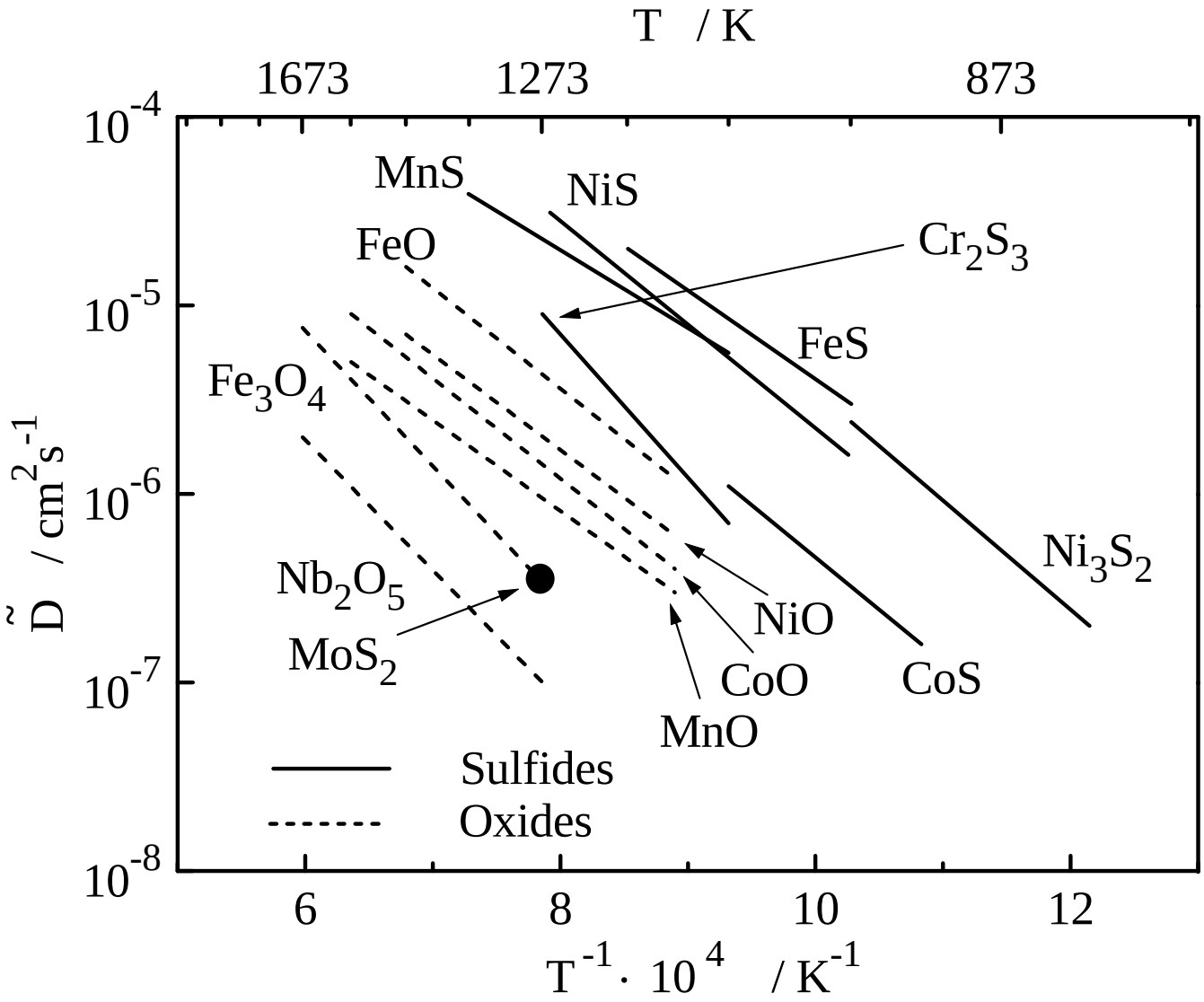
Maximum deviation from stechiometry of selected metal sulfides and oxides

Sulfide	y	Oxide	y
$Co_{1-y}S$	0.16	$Co_{1-y}O$	0.009
$Cr_{2+y}S_3$	0.18	$Cr_{2-y}O_3$	0.00009
$Cu_{2-y}S$	0.17	$Cu_{2-y}O$	0.004
$Fe_{1-y}S$	0.24	$Fe_{1-y}O$	0.12
$Mn_{1-y}S$	0.002	$Mn_{1-y}O$	0.016
$Ni_{1-y}S$	0.17	$Ni_{1-y}O$	0.0006

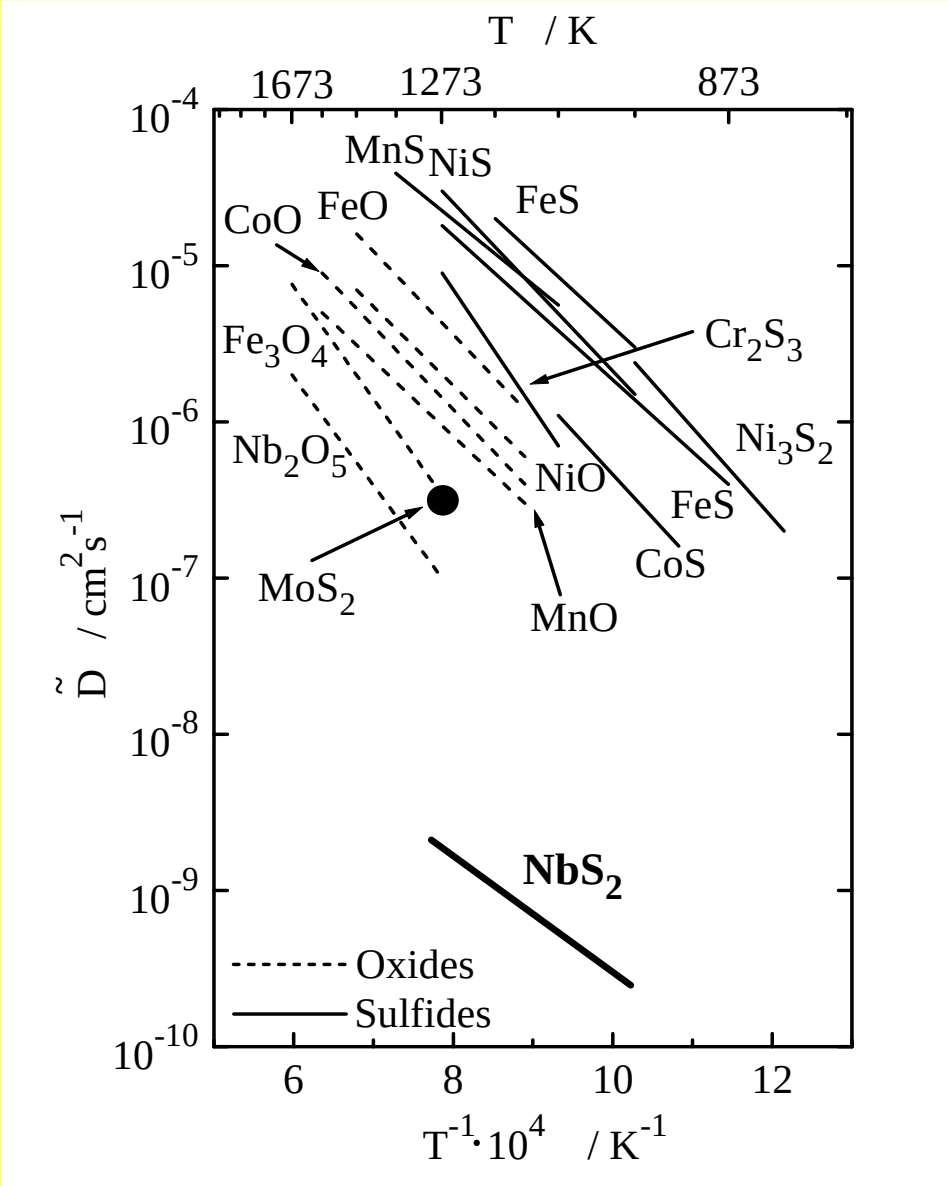
Deviation from stechiometry of selected metal sulfides and oxides



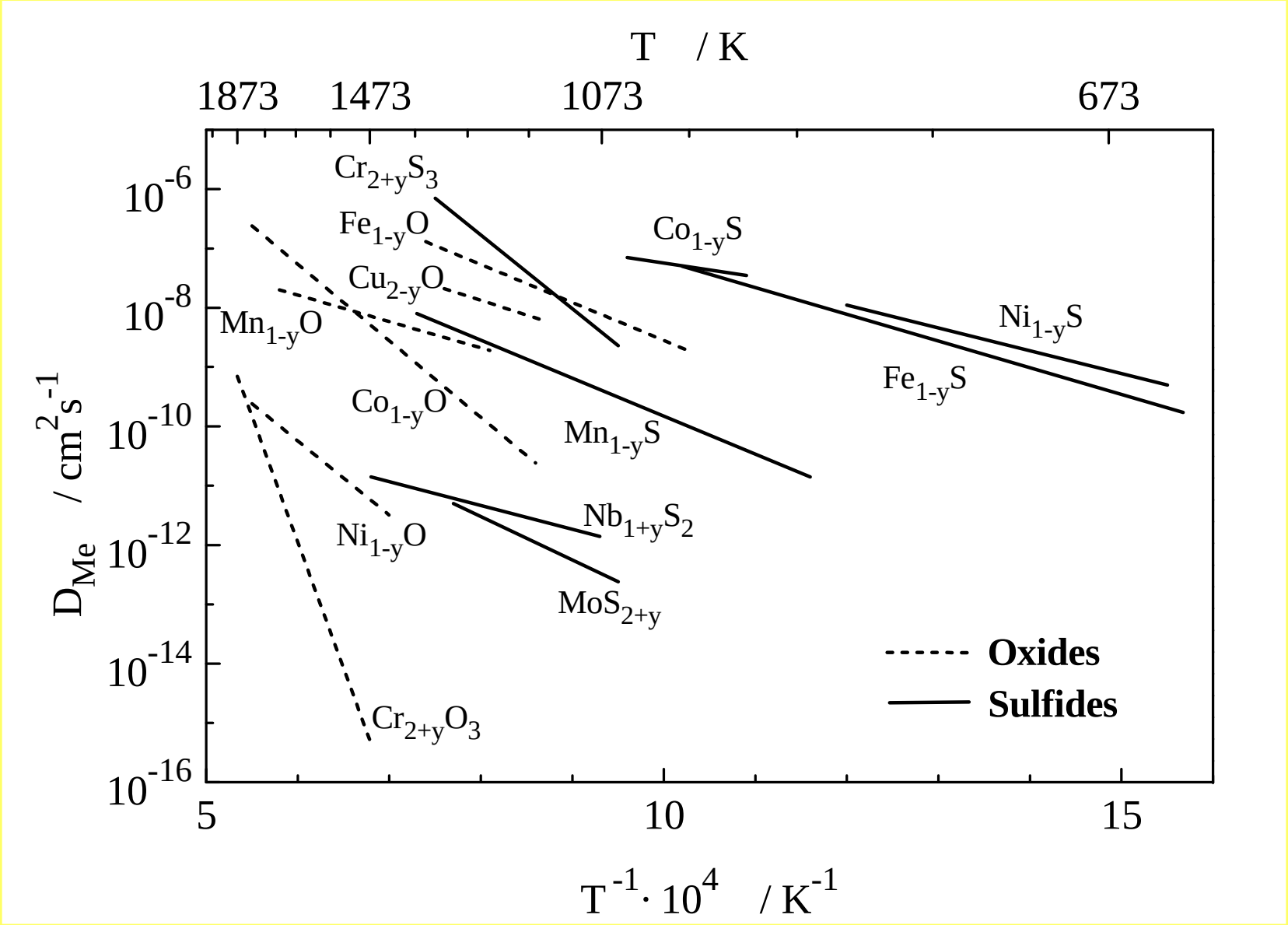
The chemical diffusion coefficient in a number of metal sulphides and oxides



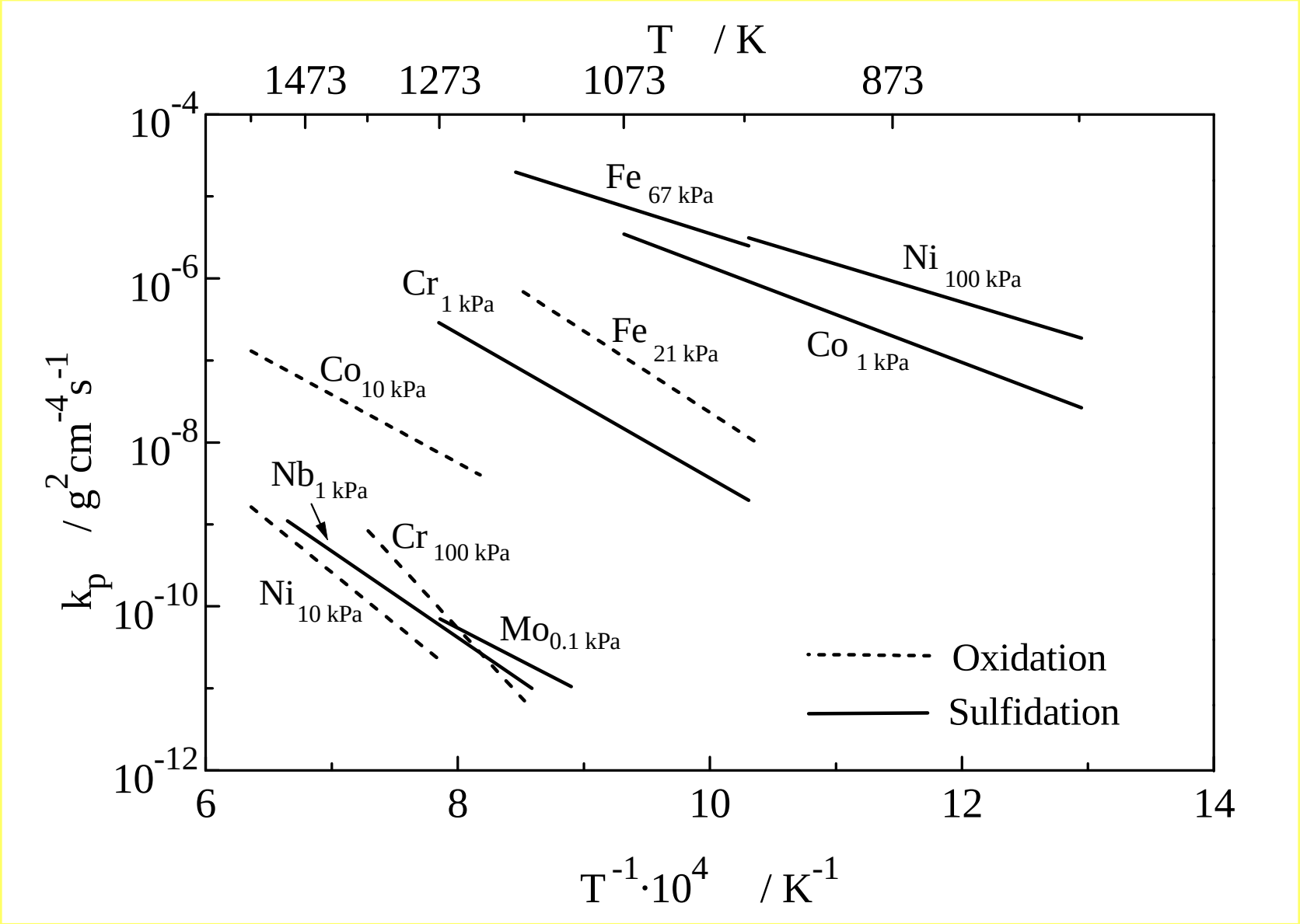
The chemical diffusion coefficient in a number of metal sulphides and oxides



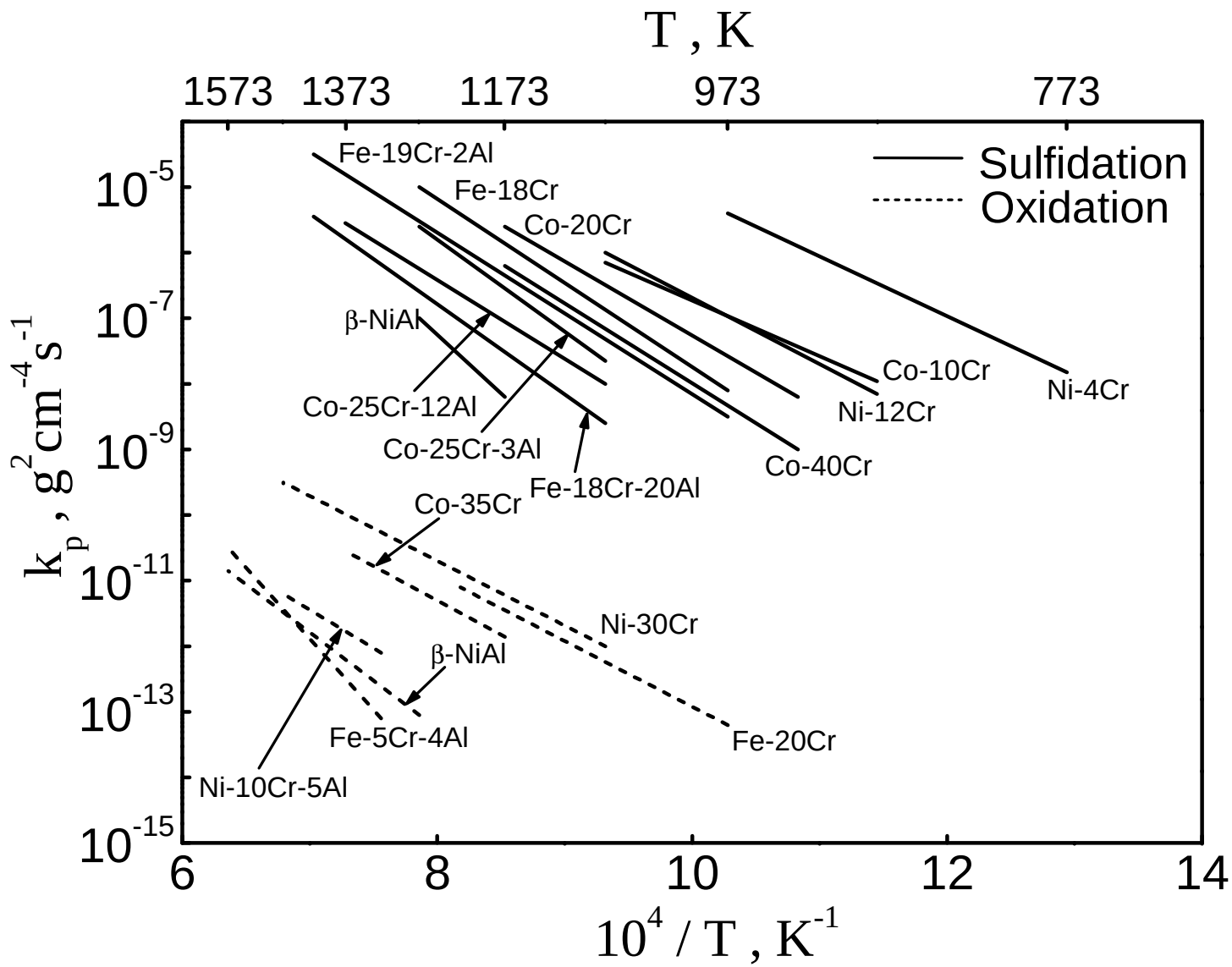
Temperature dependence of self-diffusion coefficient for selected metal sulphides and oxides



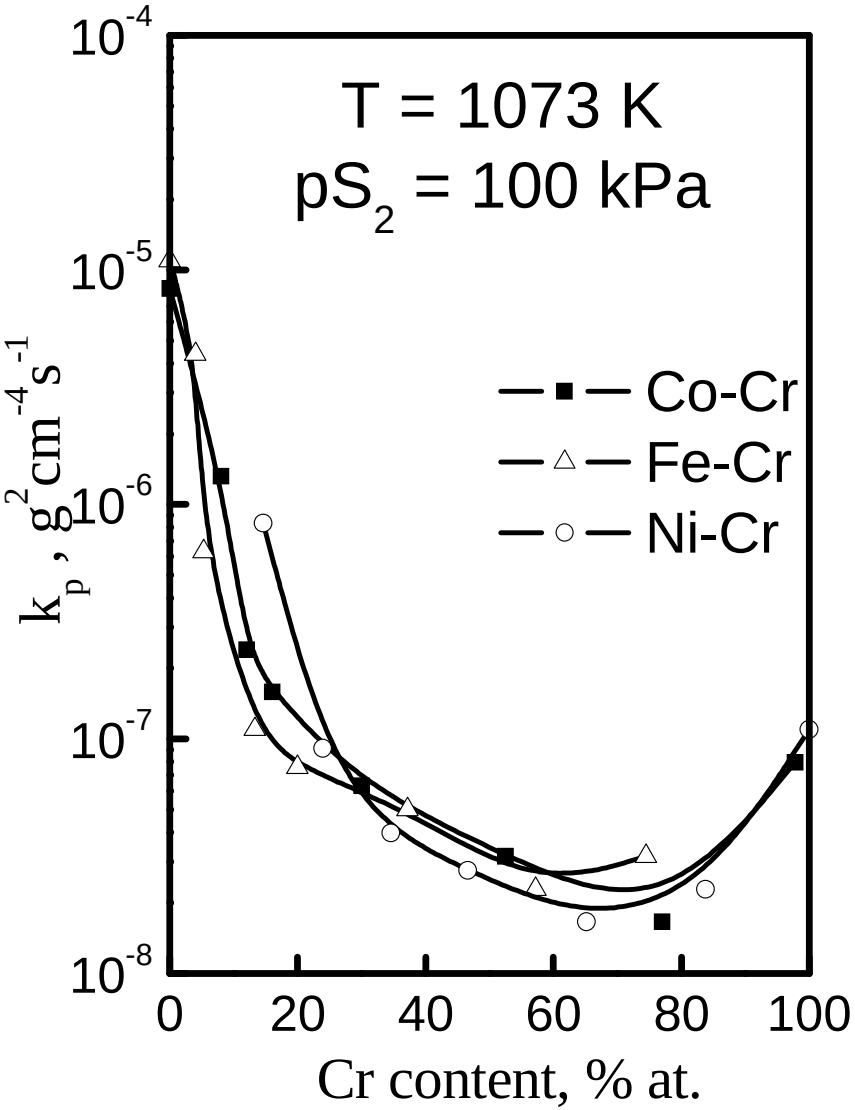
Comparison of sulphidation and oxidation rate of metals

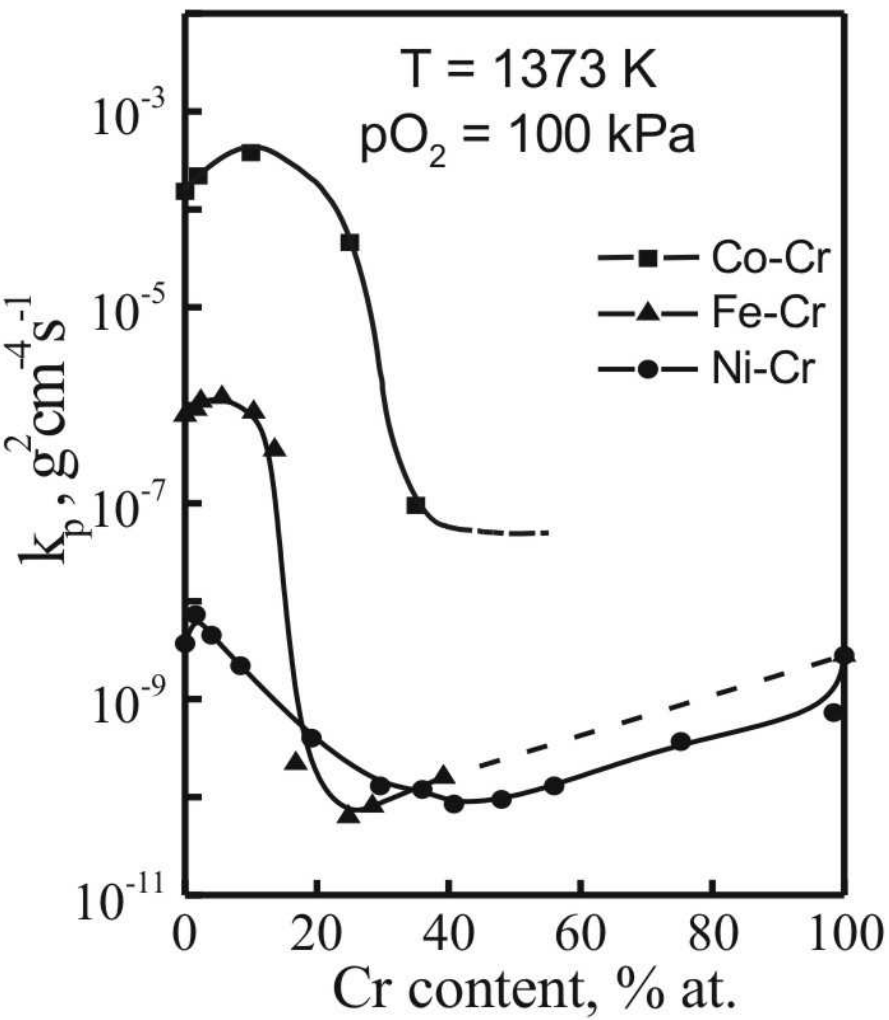


Comparison of sulphidation and oxidation rate of alloys

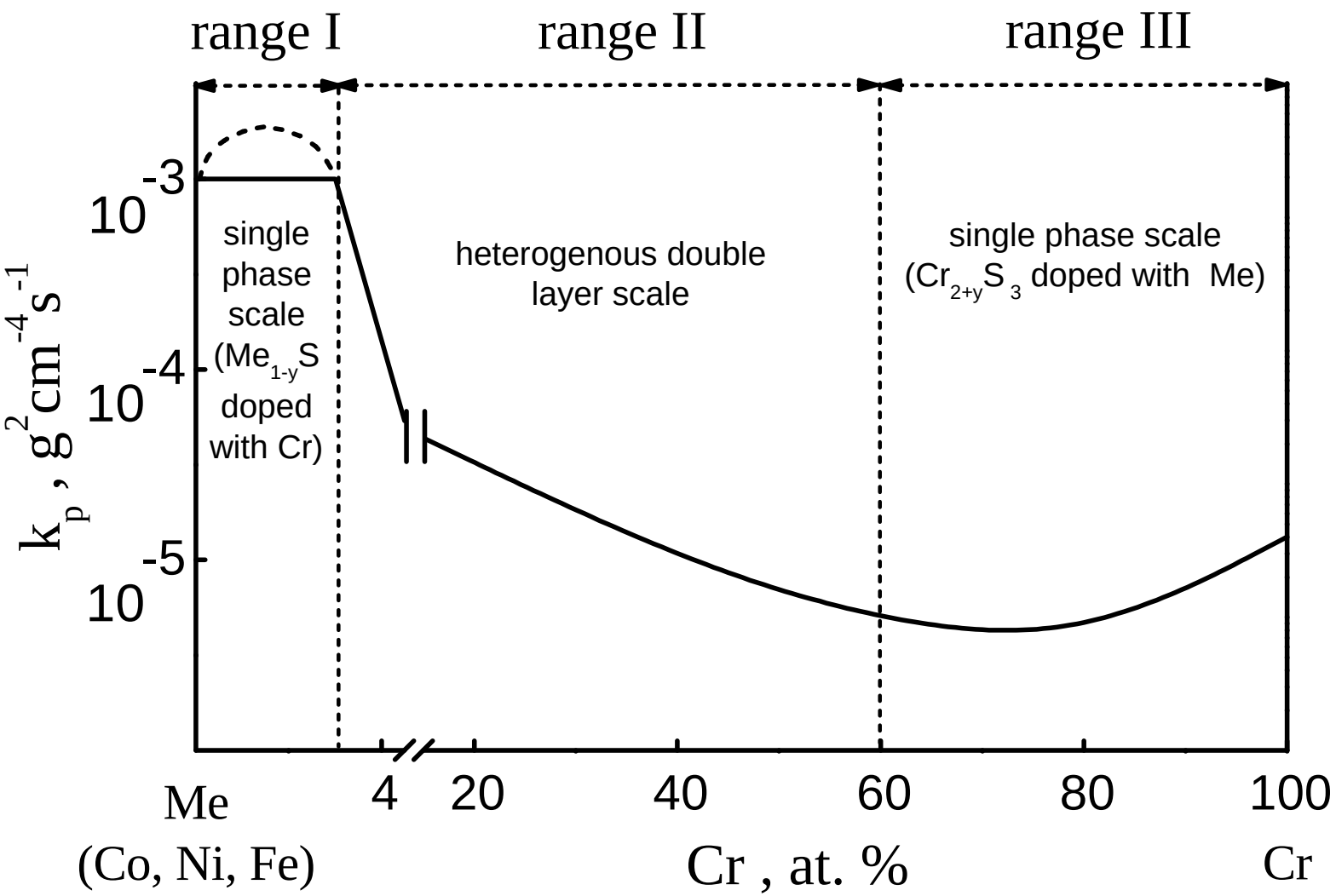


The influence of chromium on the sulphidation and oxidation rate of selected metals

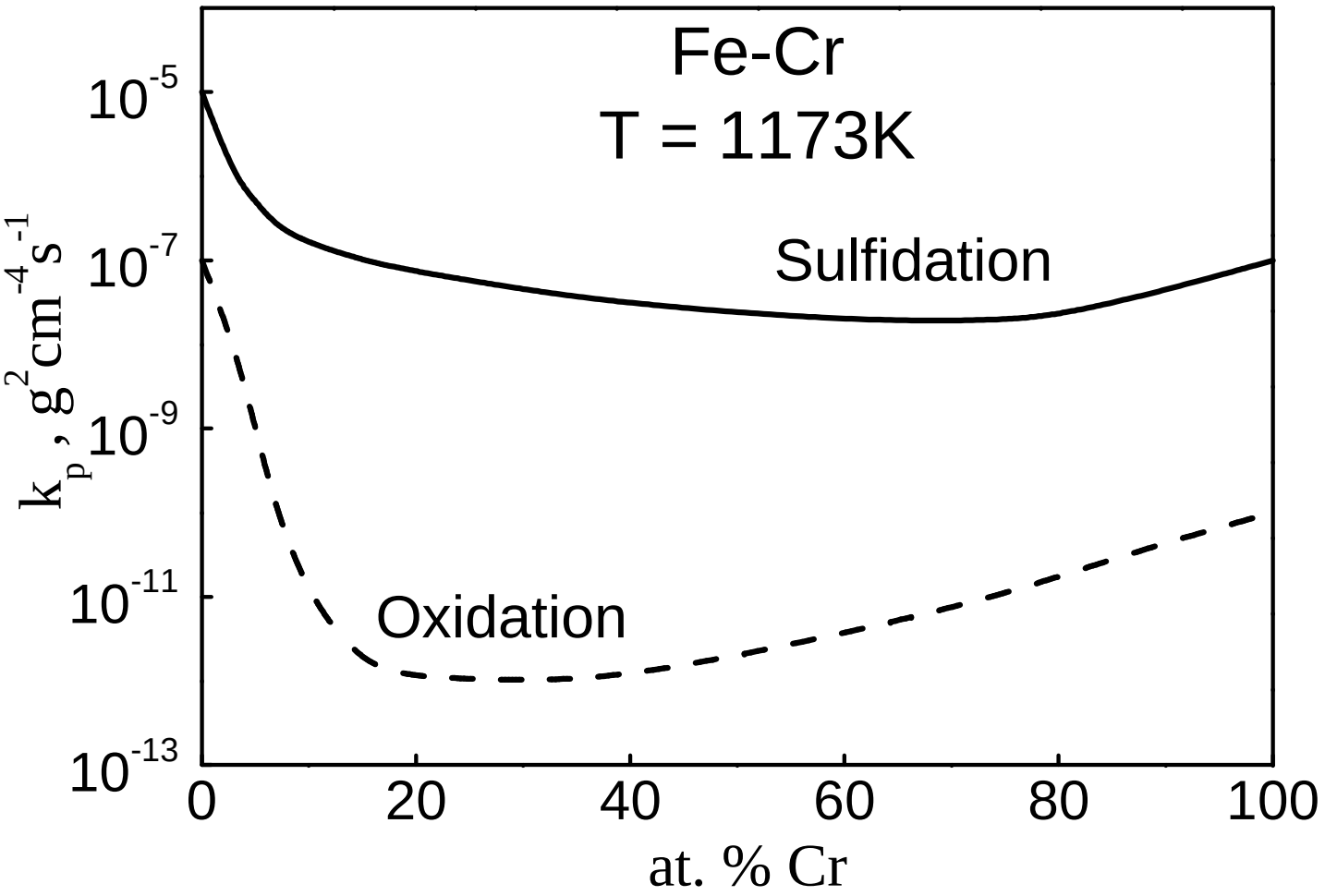




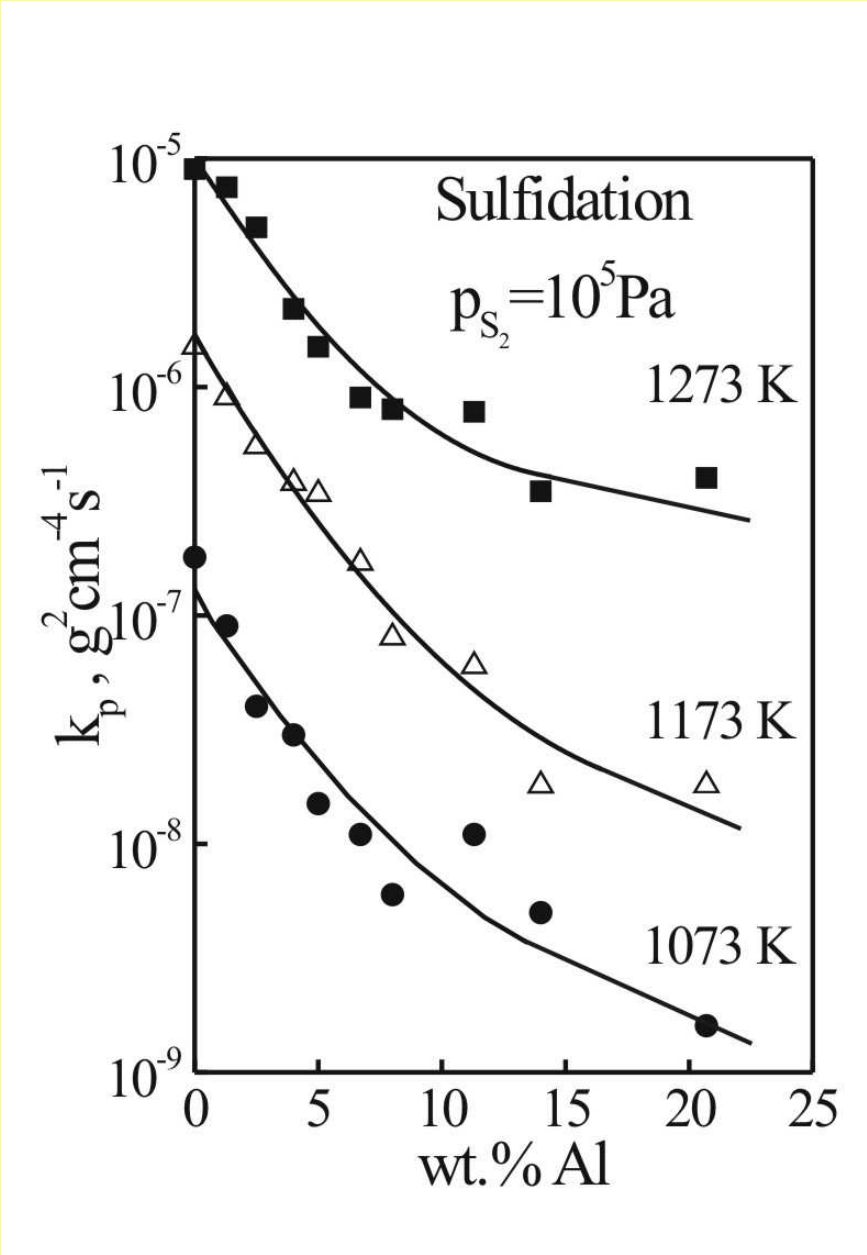
The influence of chromium on the sulphidation and oxidation rate of selected metals



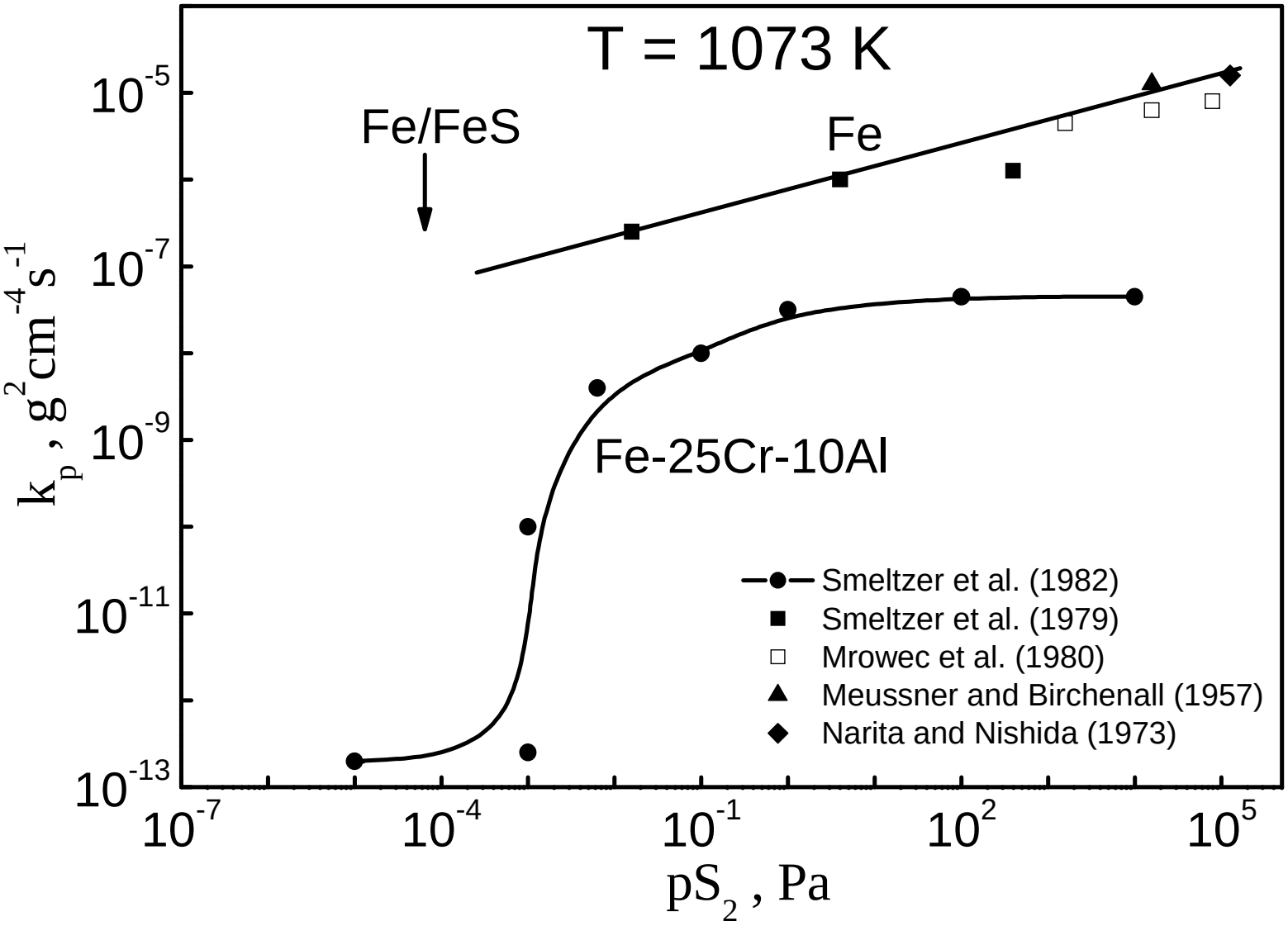
The influence of chromium on the sulphidation and oxidation rate of iron



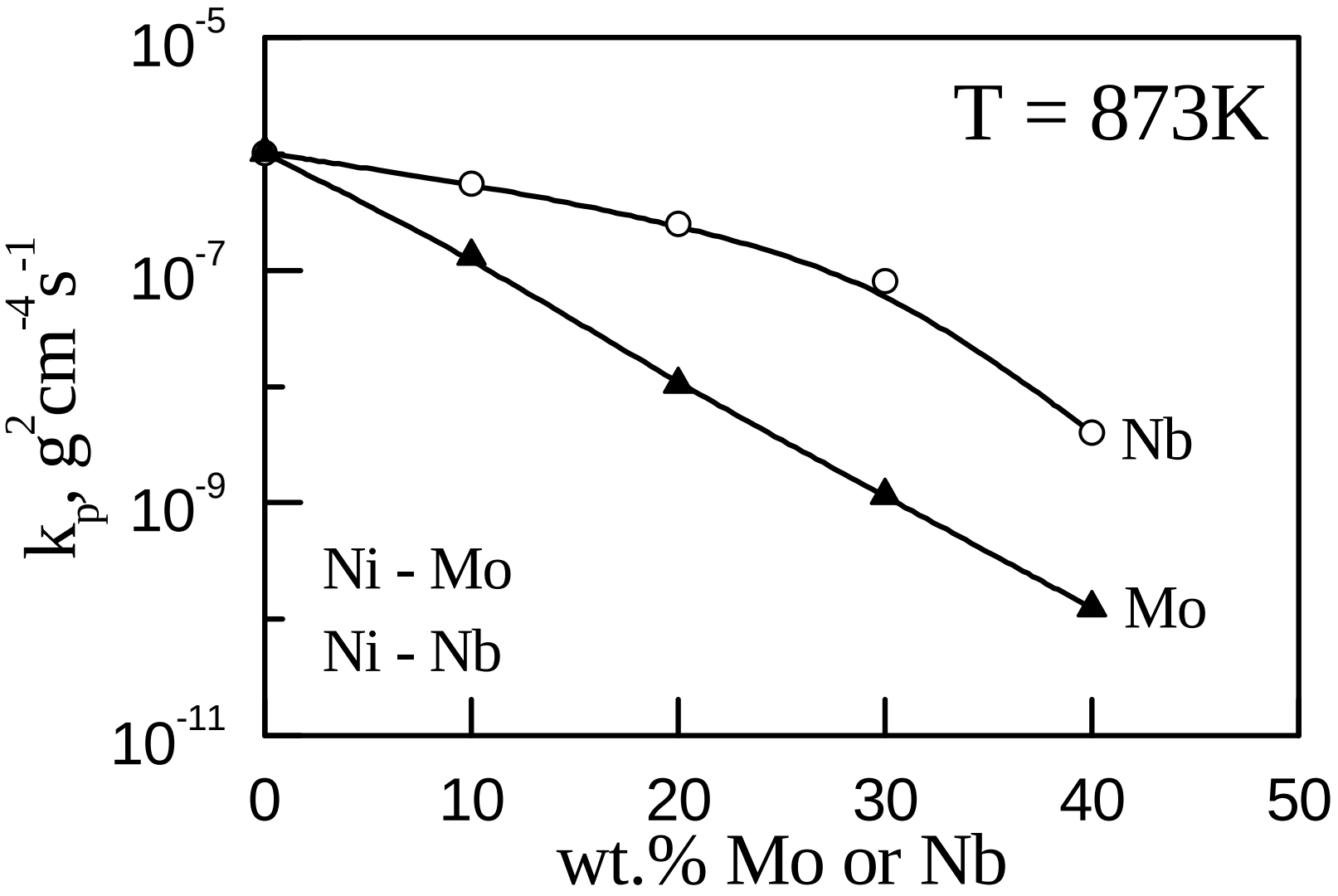
The influence of aluminum on the sulphidation rate of iron



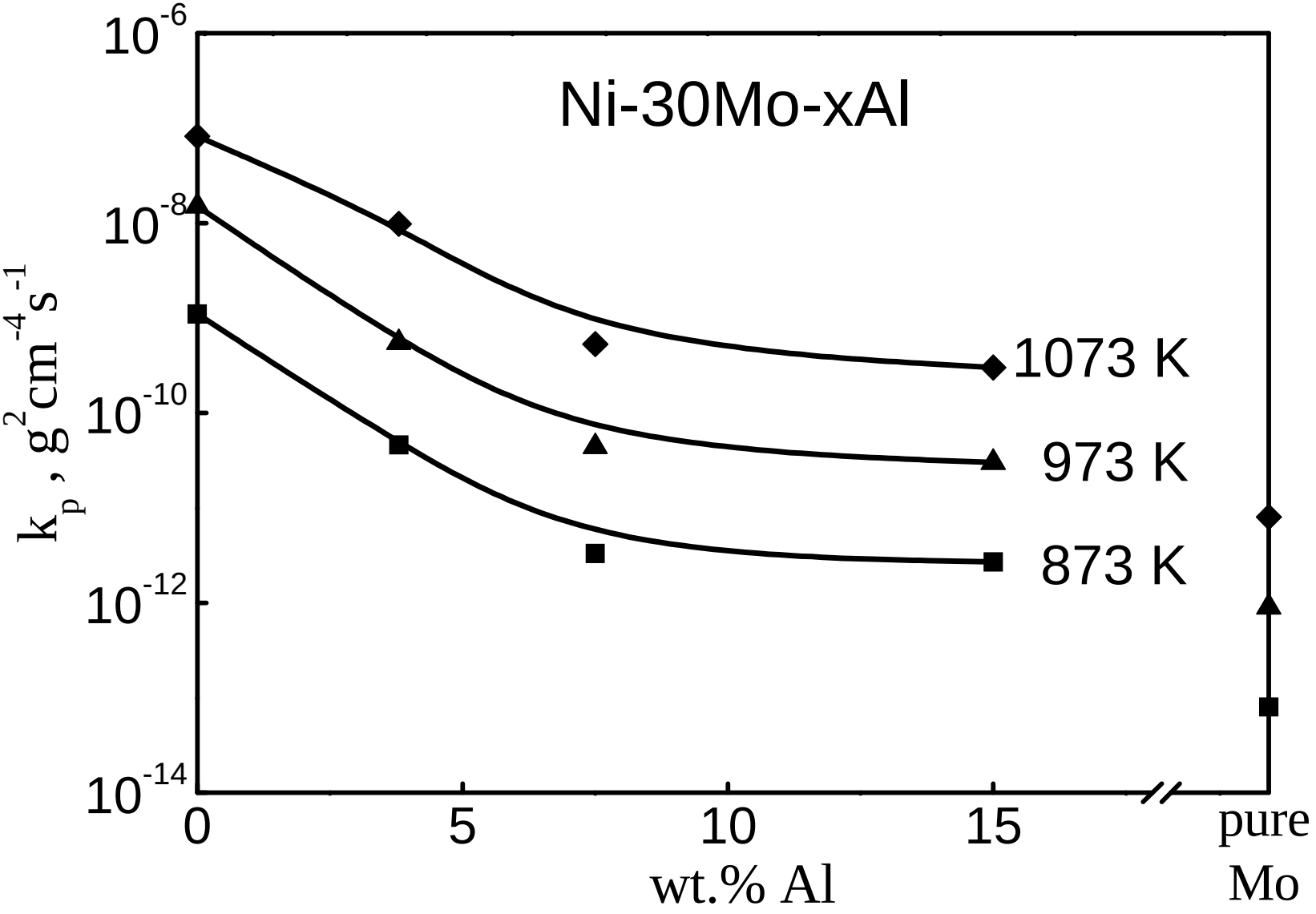
The influence of chromium and aluminum on the sulphidation rate of iron



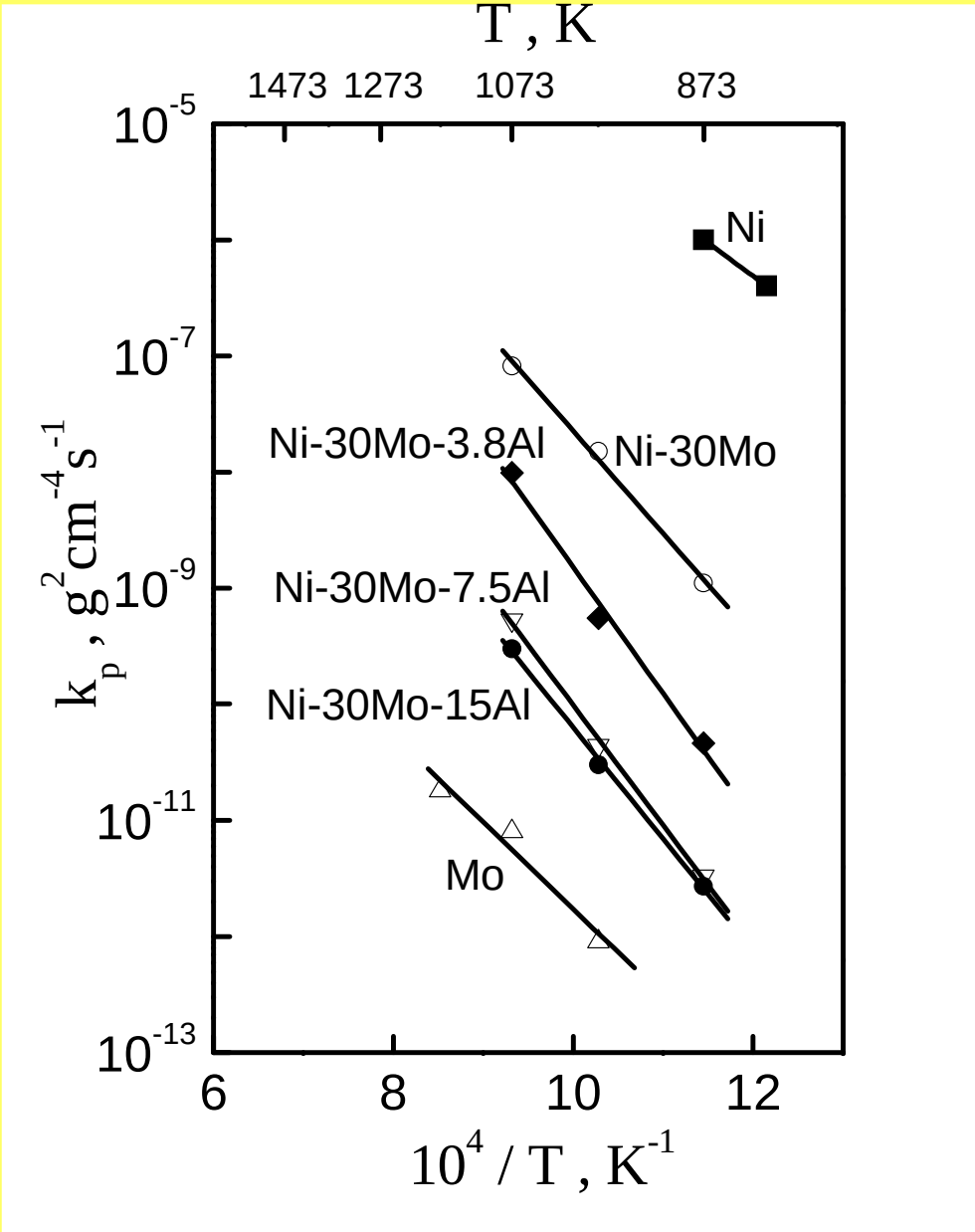
The influence of Mo and Nb on the sulphidation rate of nickel



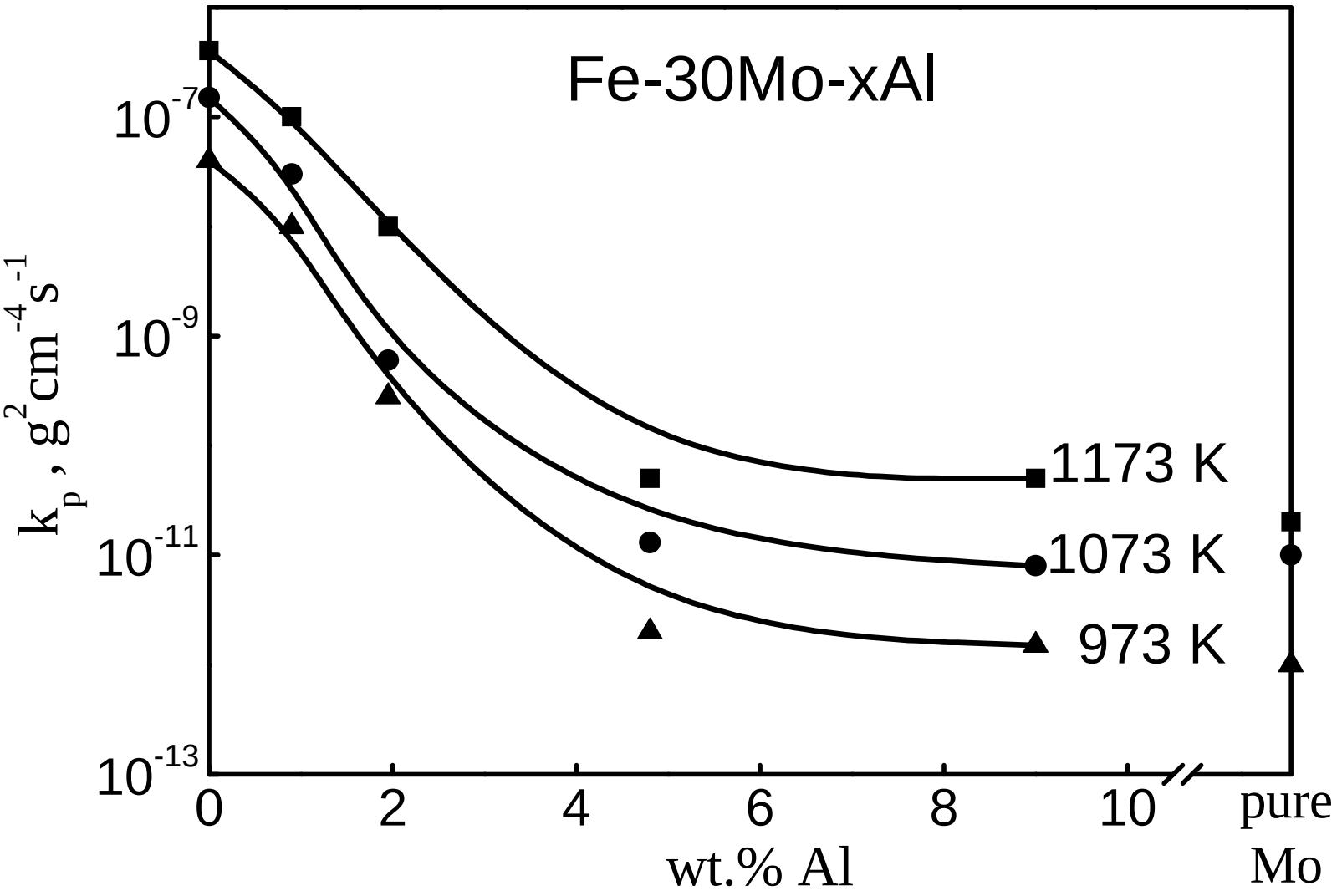
The influence of Al and Mo on the sulphidation rate of nickel



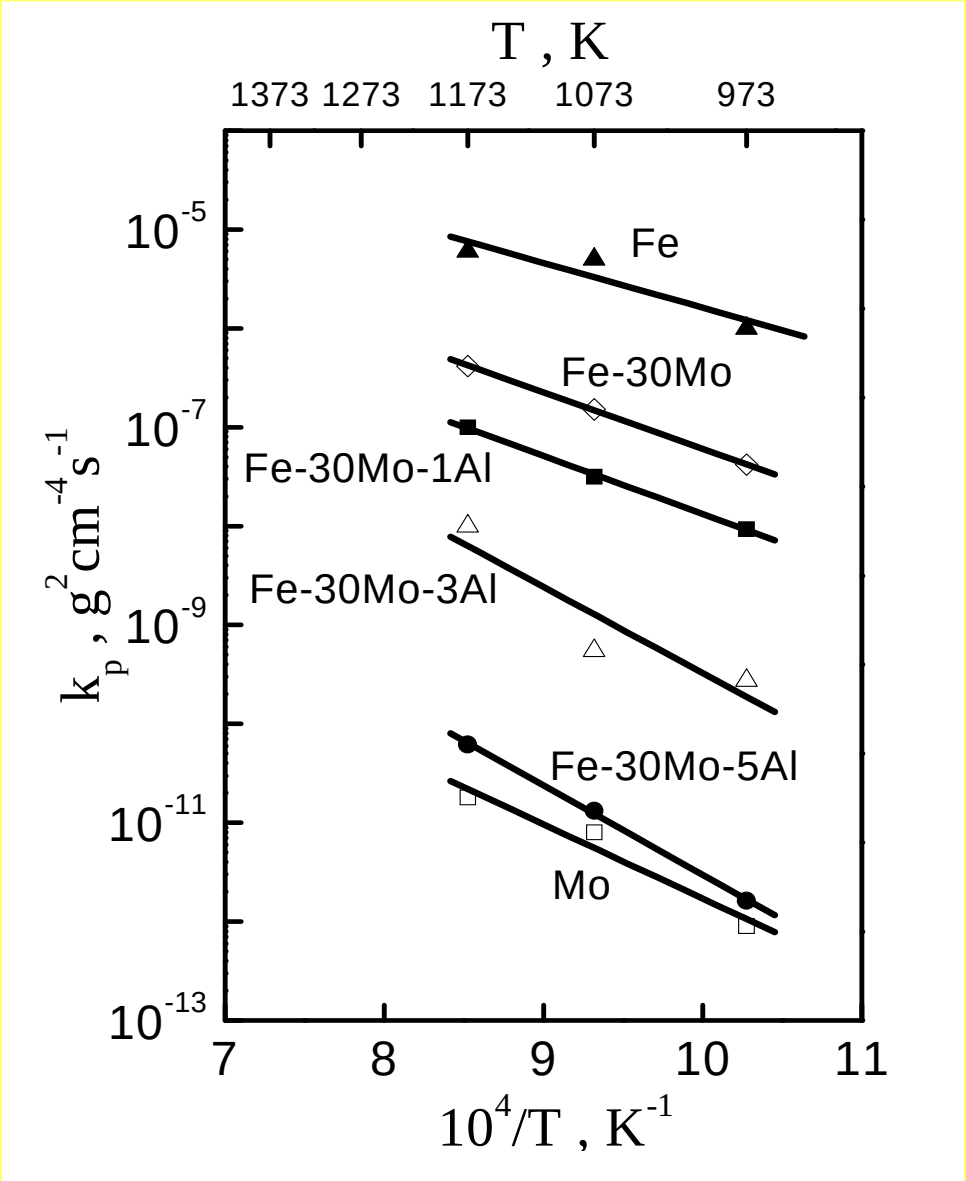
Comparison of sulphidation rate of a number of Ni alloys with Mo and Al



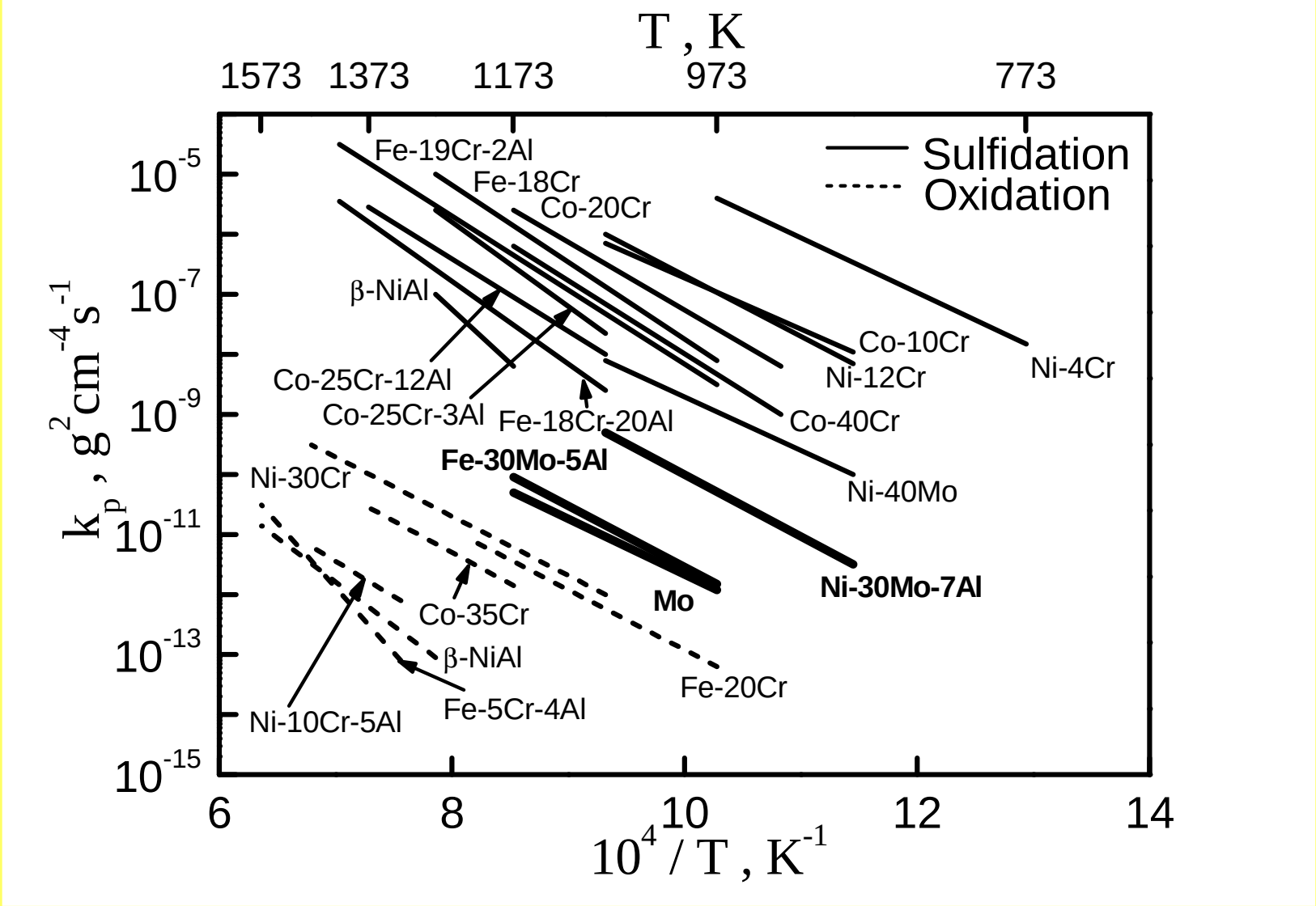
The influence of Al. And Mo on the sulphidation rate of iron



Comparison of sulphidation rate of a number of Fe alloys with Mo and Al



Sulphidation rates of several Ni and Fe alloys containing Mo and Al



PROTECTIVE COATINGS APPLIED IN CORROSION OCCURRING IN SULPHIDIZING ATMOSPHERES

Mn – MnS

Ti – TiS_2

Mo – MoS_2

Nb – NbS_2

Ta – TaS_2

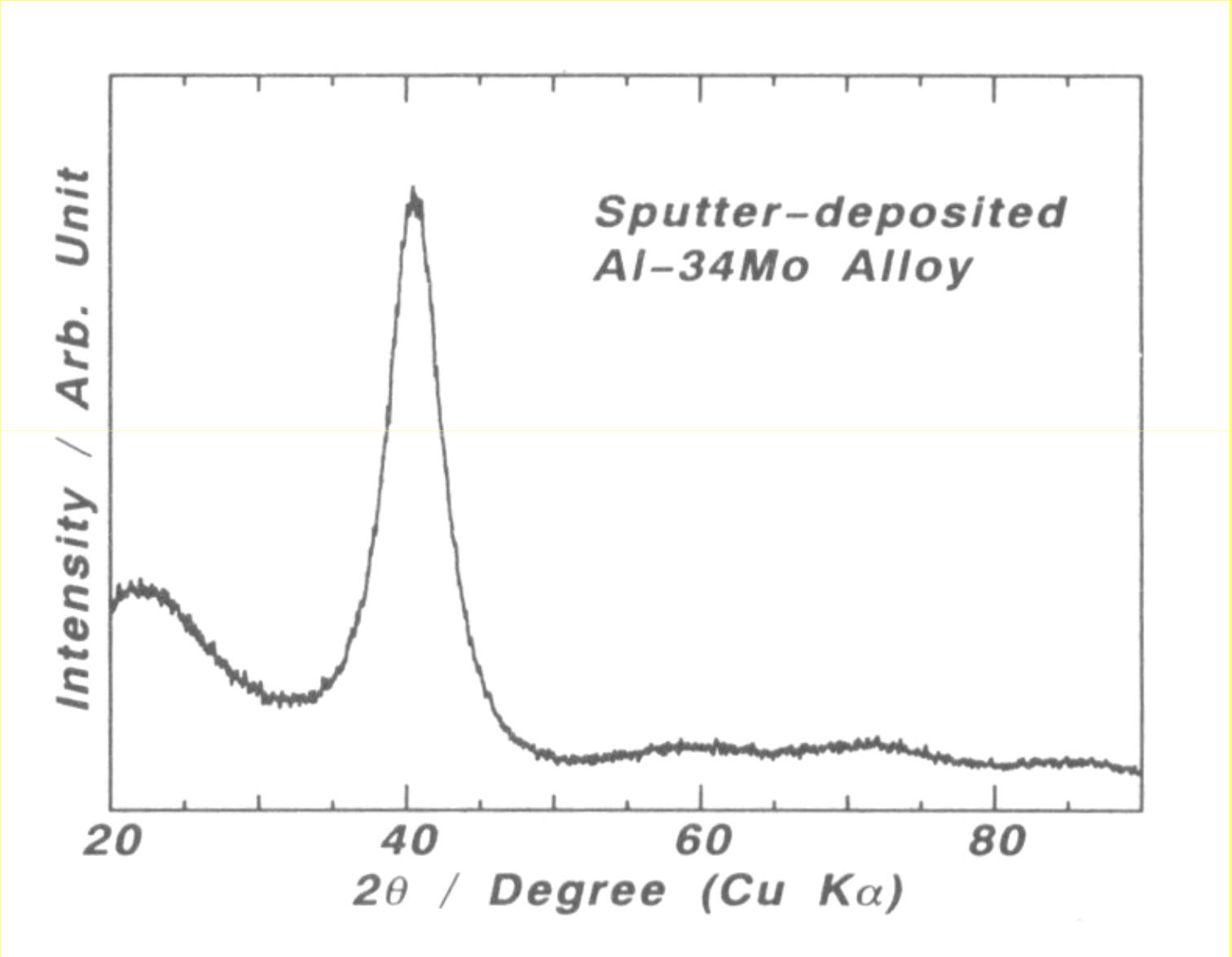
Ni-Mo, Fe-Mo, Co-Mo

Fe-Mo-Al

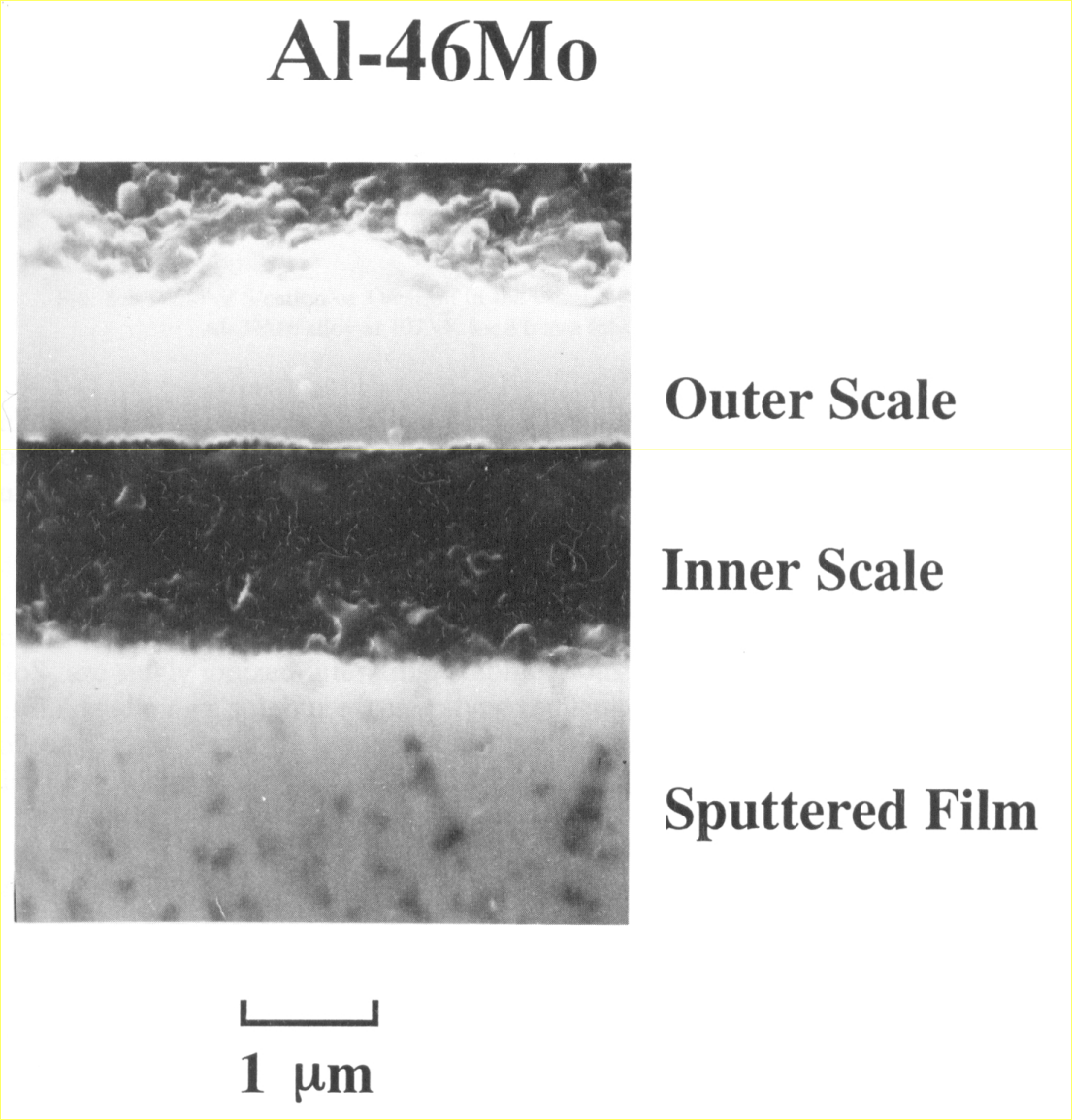
Melting and boiling points of several metals

	Melting point, K	**Boiling point, K**
Al	933.52	2740.15
Mo	2890.15	4885.15
Ta	3269. 15	5698.15
Mn	1518.15	2235.15
Nb	2468	4927
Co	1495	2870

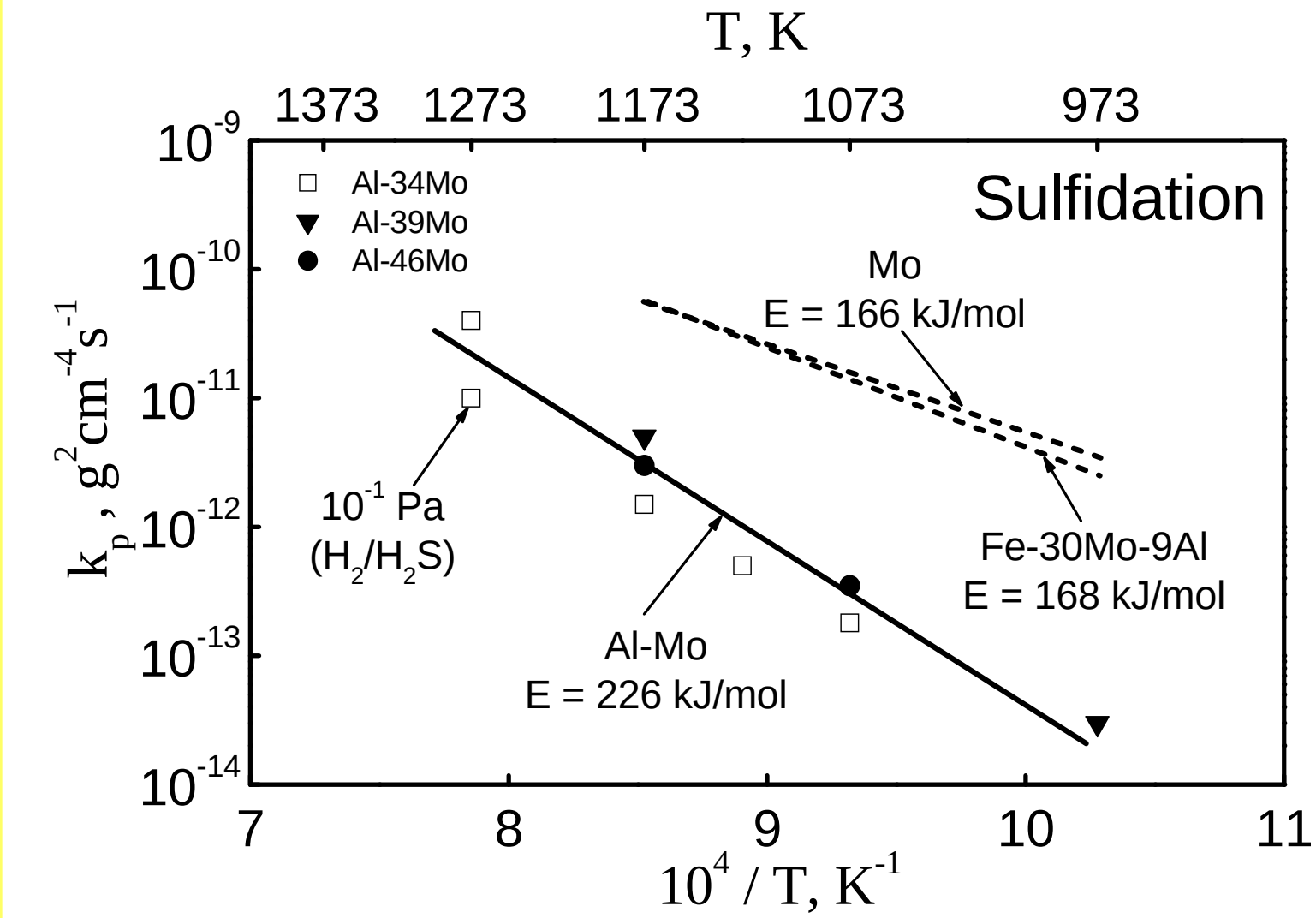
X-ray data of the Al-34Mo alloy



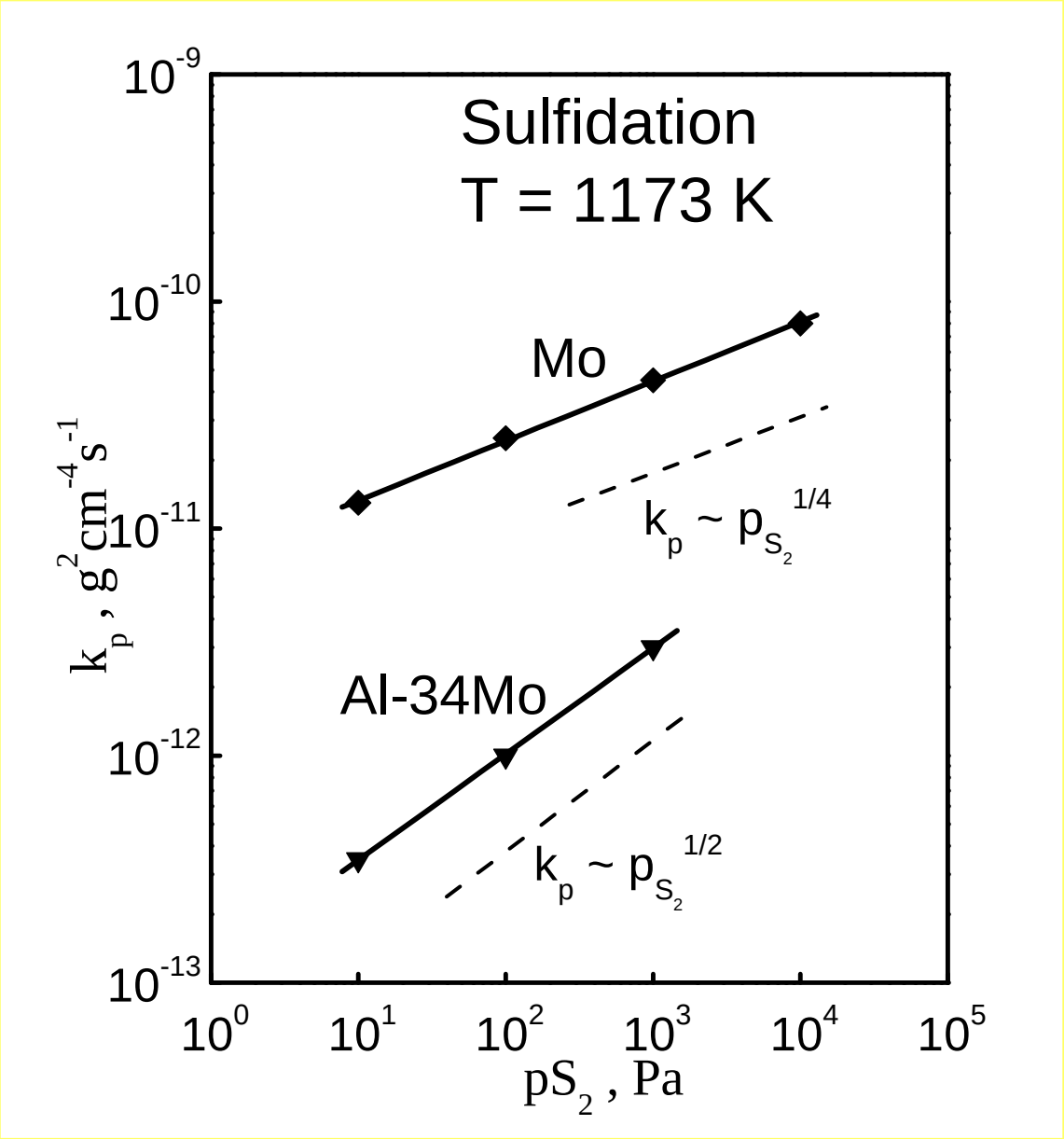
Cross-section of sulphide scale growing on the Al-46Mo alloy



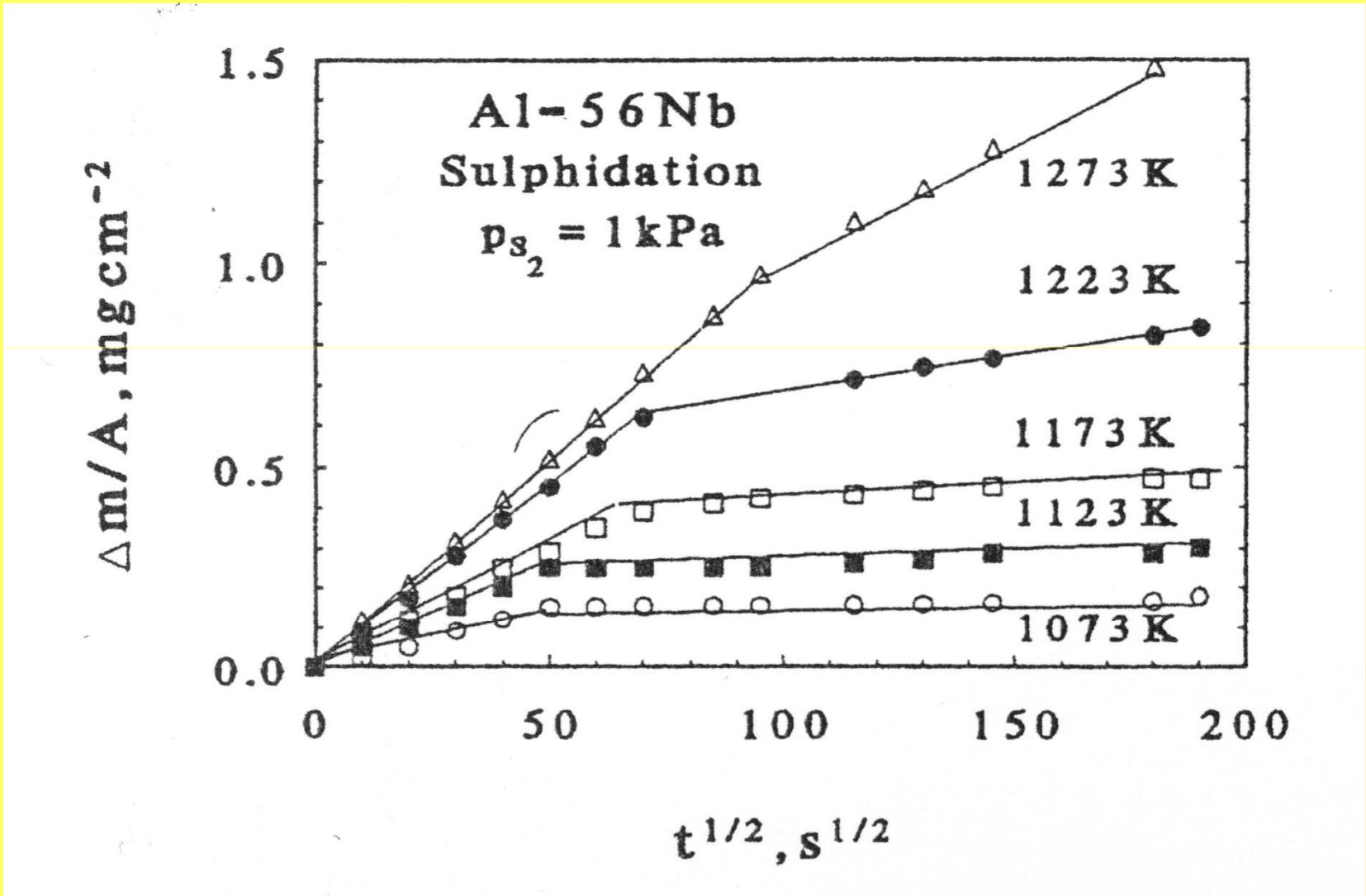
Sulphidizing rates of Mo-Al alloys



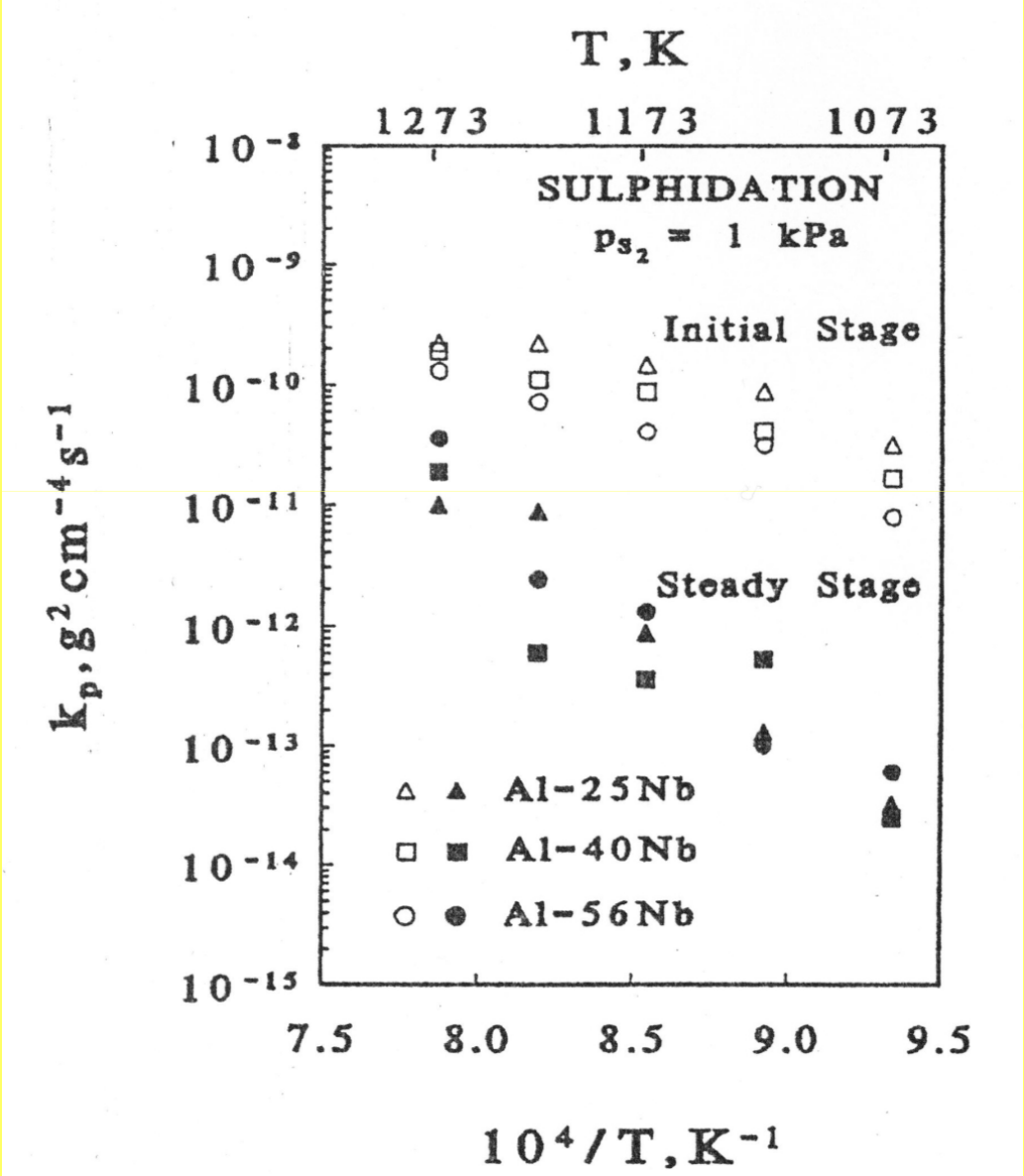
Szybkości siarkowania stopów molibdenu z glinem



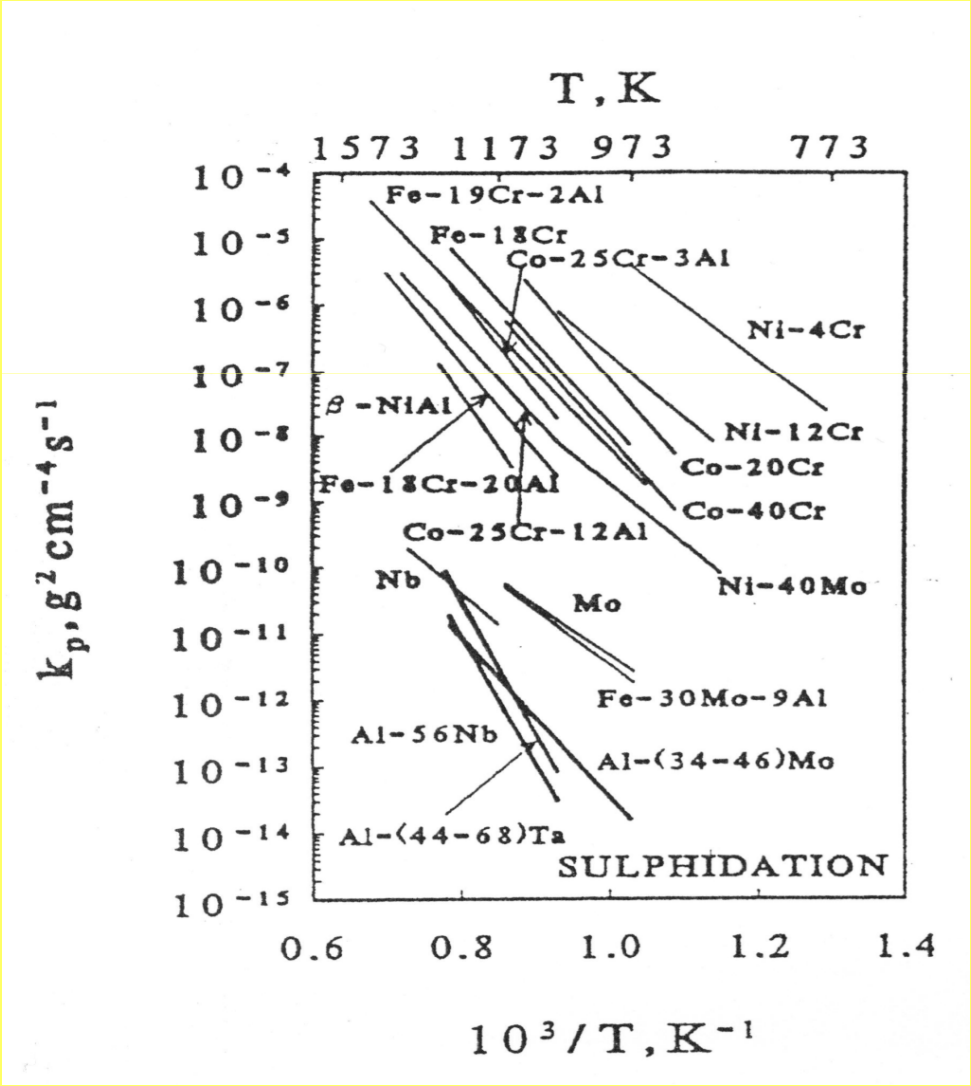
Sulphidation kinetics for sputter-deposited Al-56 Nb alloy



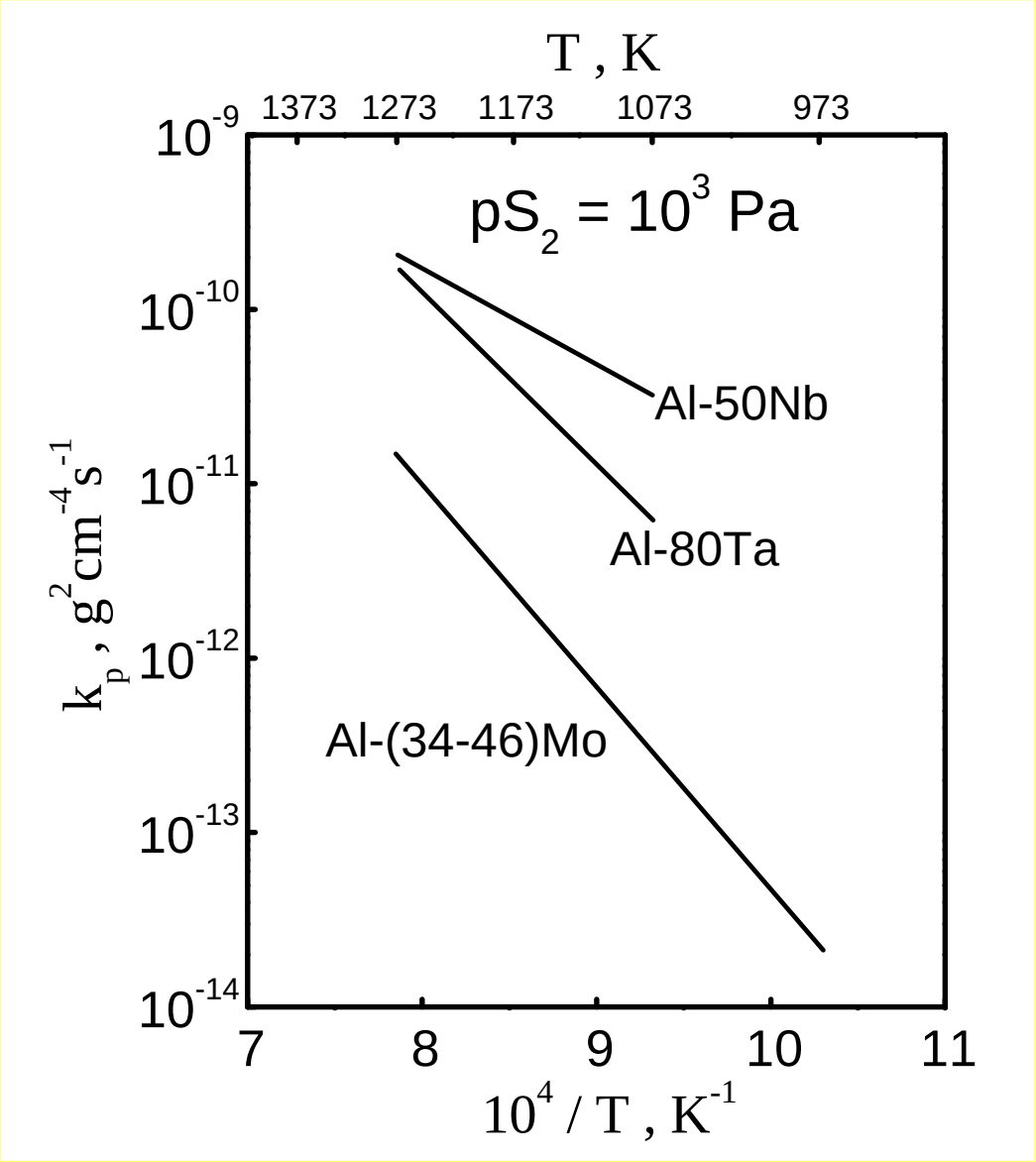
The temperature dependence of the sulphidation rate of Al-56Nb alloy



Temperature dependence of the sulphidation rate of Al-Mo, Al-Nb and Al-Ta alloys on the background of analogous dependence for several high tepmperature alloys and refractory metals



Sulphidizing rates of high-temperature alloys containing aluminum



Point defect situation in pure MoS_2

$$k_p = const\ p_{s_2}^{1/4}$$

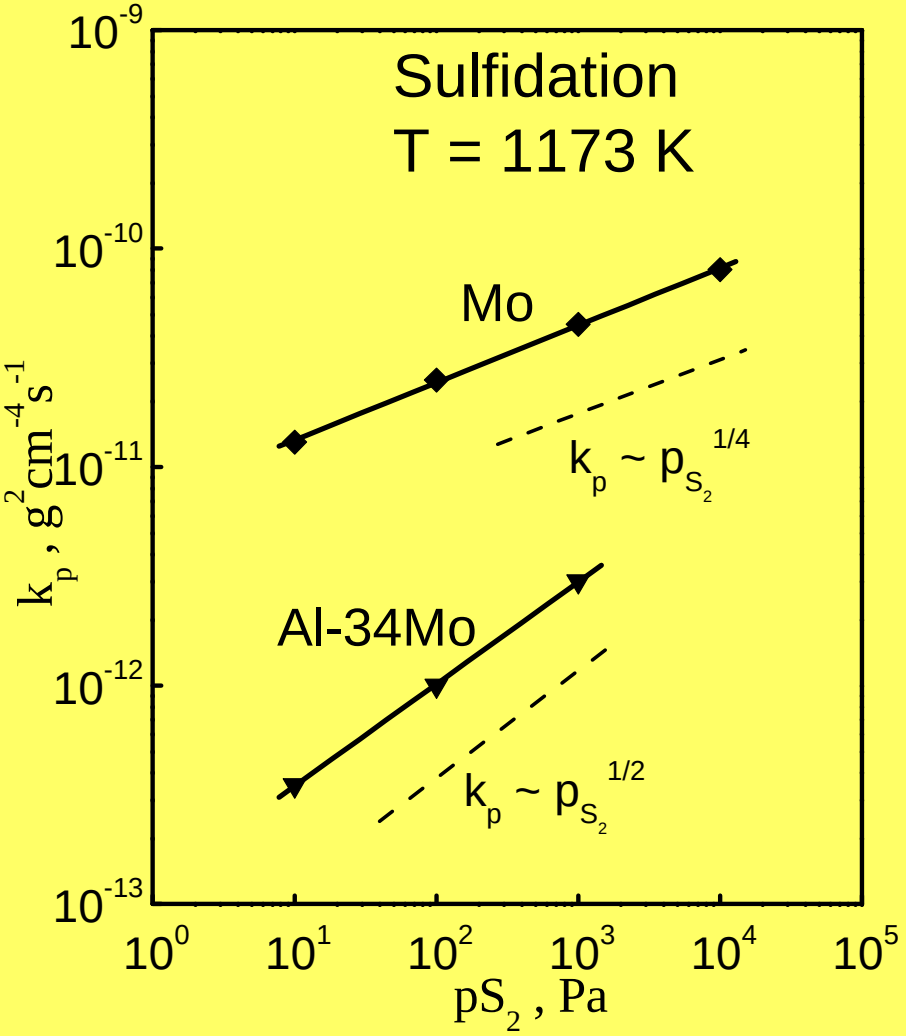
$$\frac{1}{2} S_2 = S_i' + h^{\cdot}$$

$$K_i = [S_i'][h^{\cdot}] p_{(s_2)}^{-1/2}$$

$$[S_i'] = [h^{\cdot}]$$

$$[S_i'] = K_i^{1/2} p_{(s_2)}^{1/4}$$

$$k_p = const\ p_{(s_2)}^{1/4}$$



Point defect situation in Al-doped MoS_2

$$Al_2S_3 + 1/2\,S_2 = 2Al'_{Mo} + 2h^{\cdot} + 4S_S$$

$$Al_2S_3 + S'_i = 2Al'_{Mo} + h^{\cdot} + 4S_S$$

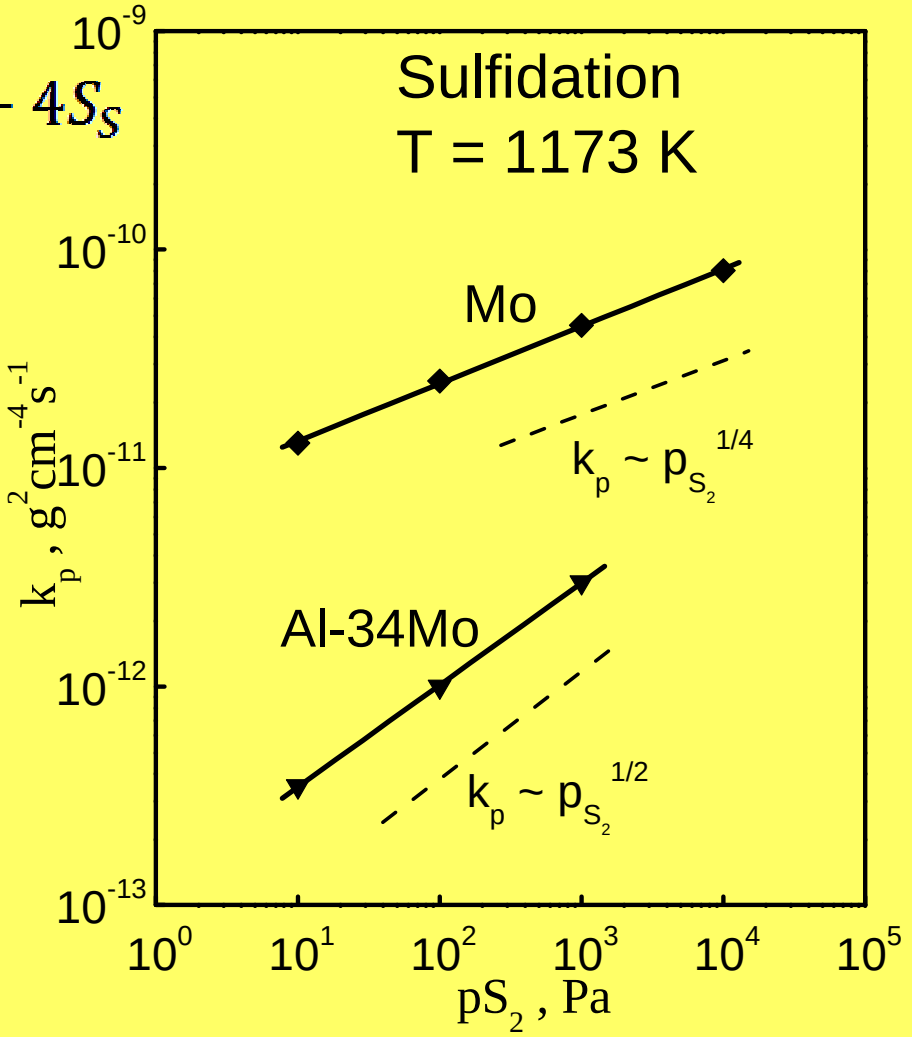
$$[h^{\cdot}] = [S'_i] + [Al'_{Mo}]$$

$$[S'_i] \ll [Al'_{Mo}]$$

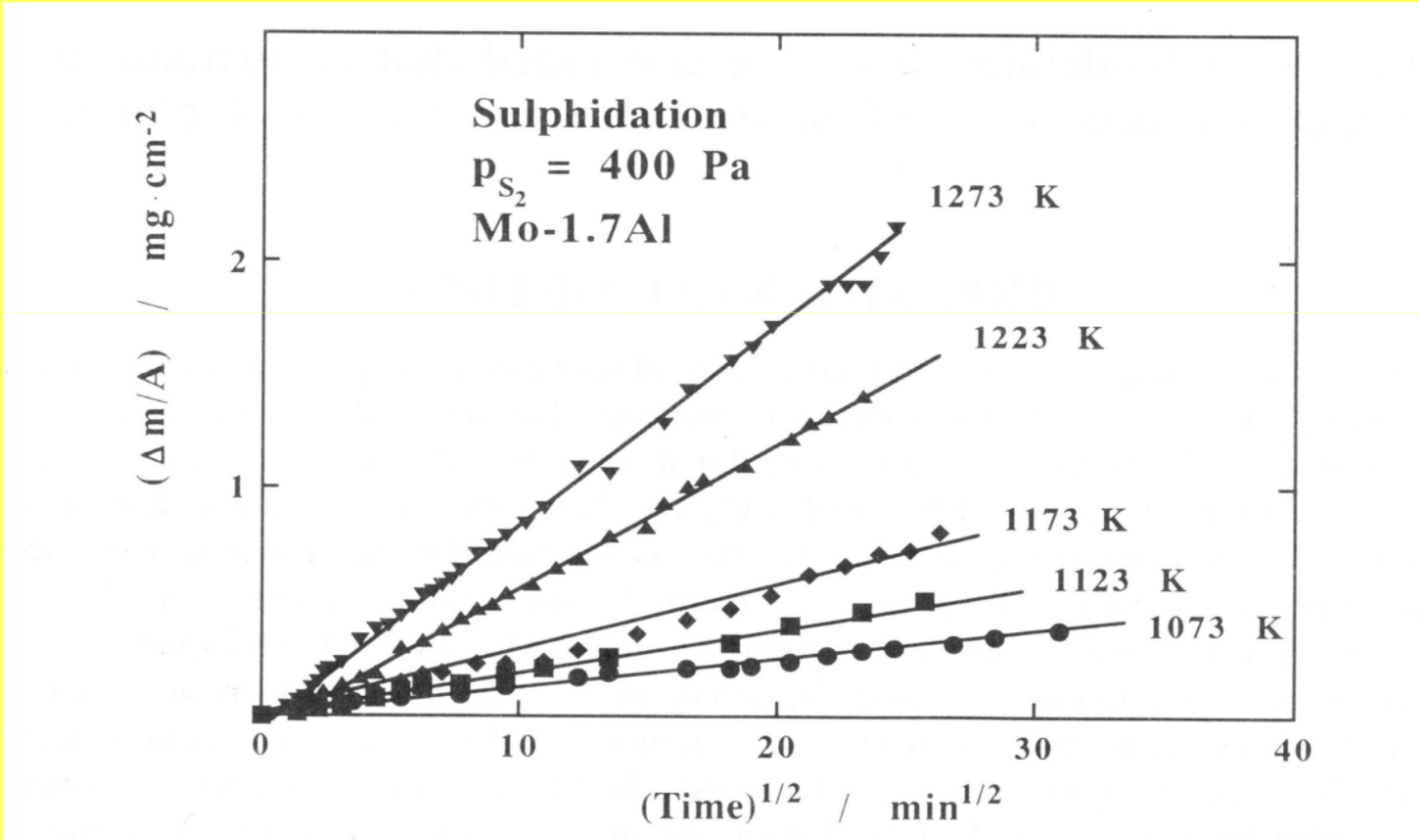
$$[h^{\cdot}] \approx [Al'_{Mo}]$$

$$[S'_i] \approx (K_i/[Al'_{Mo}])p_{(S_2)}^{1/2}$$

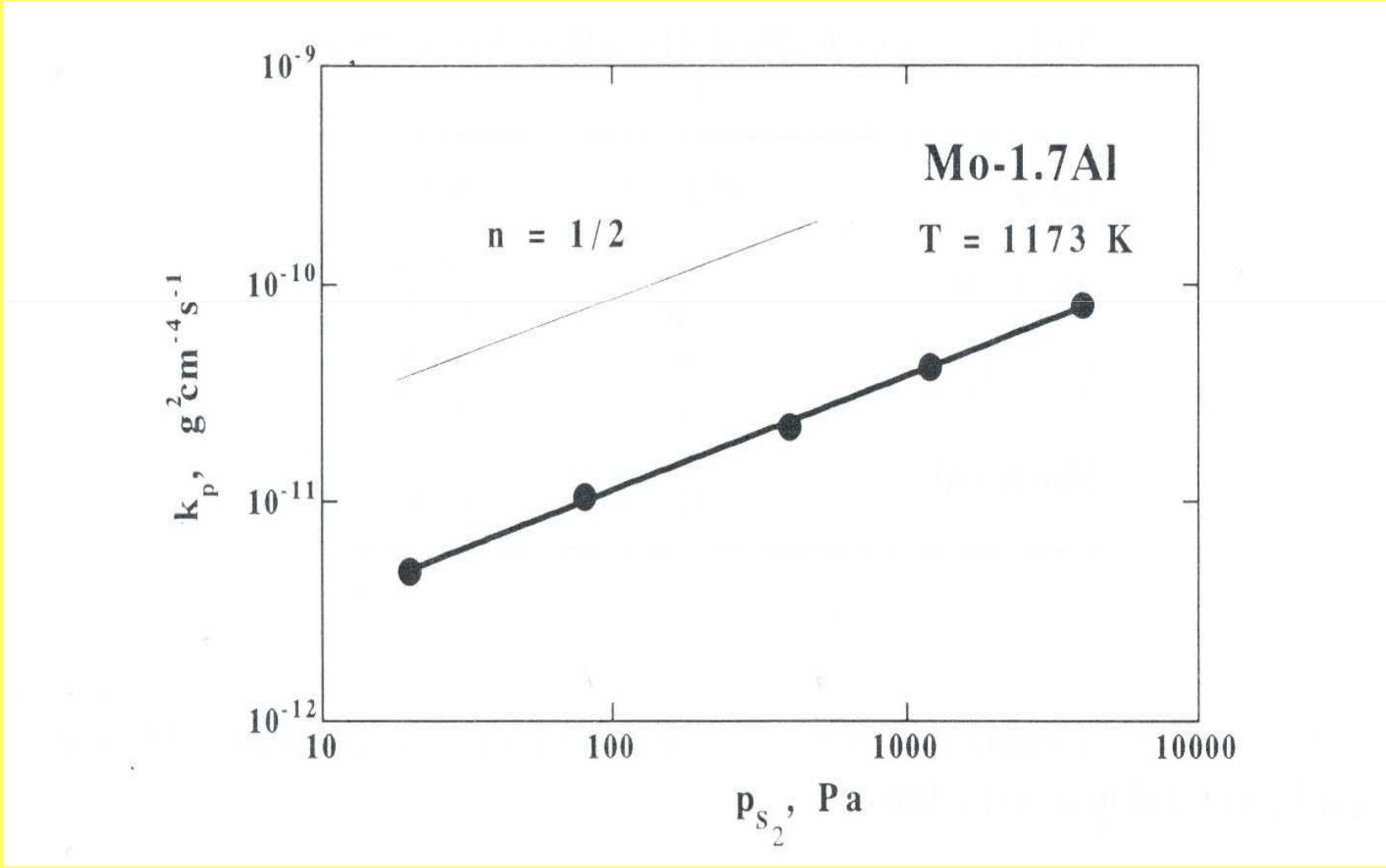
$$k_p \approx const\; p_{(s_2)}^{1/2}$$



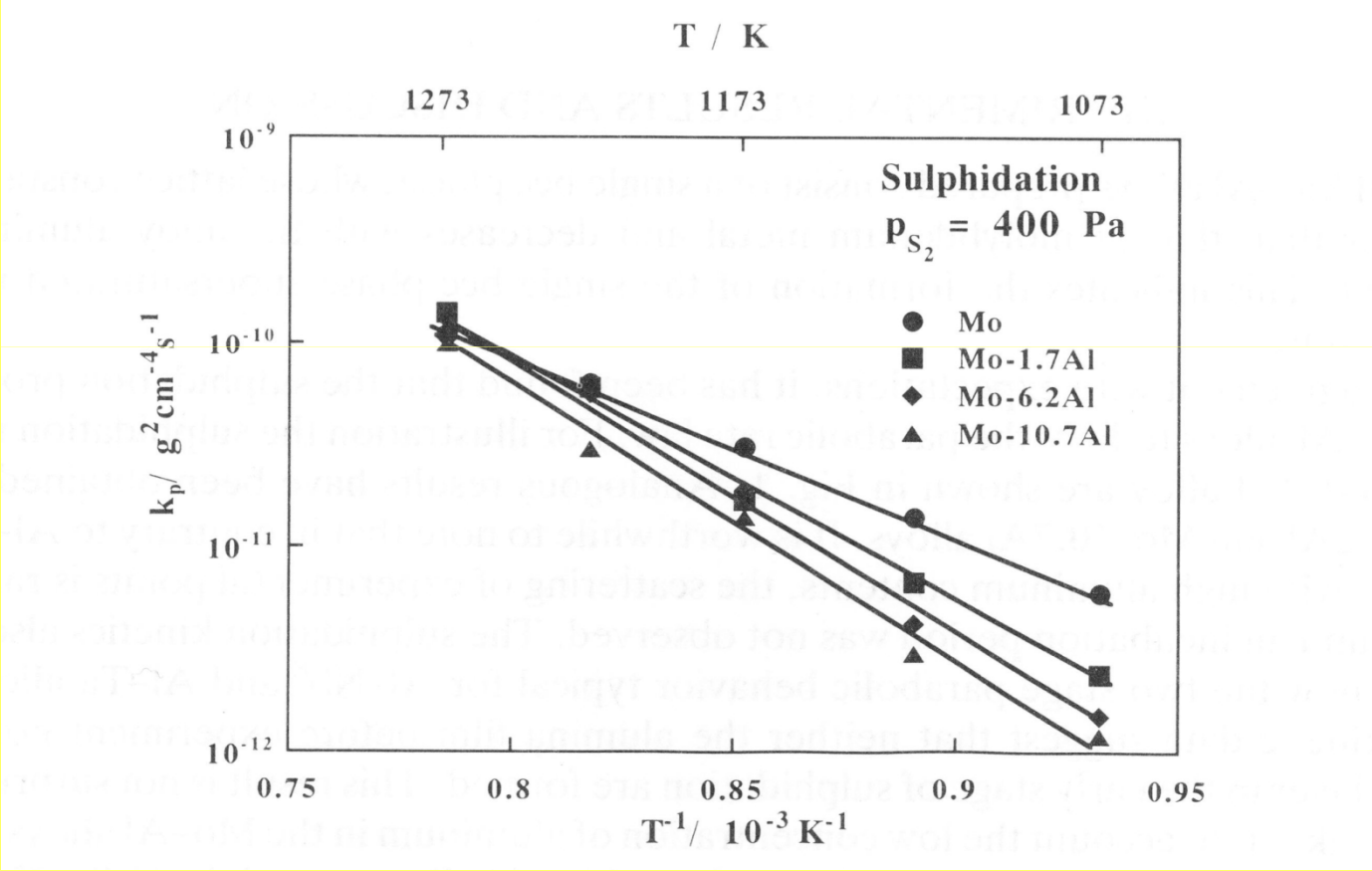
Sulfidation kinetics of Mo-1.7 Al alloy at several temperatures



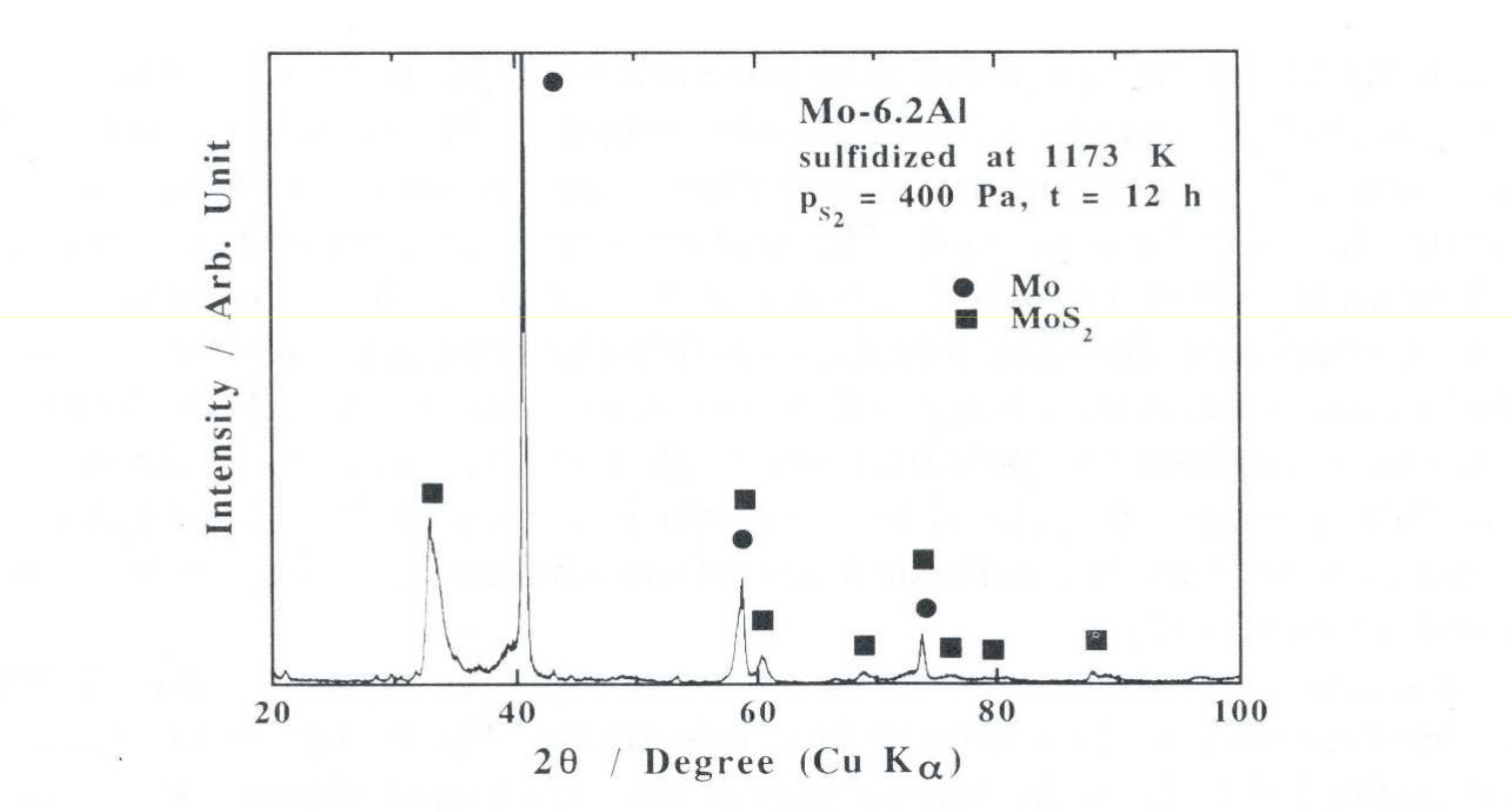
The dependence of the sulphidation rate for Mo-1.7 Al alloy on the sulphur pressure at 1173 K



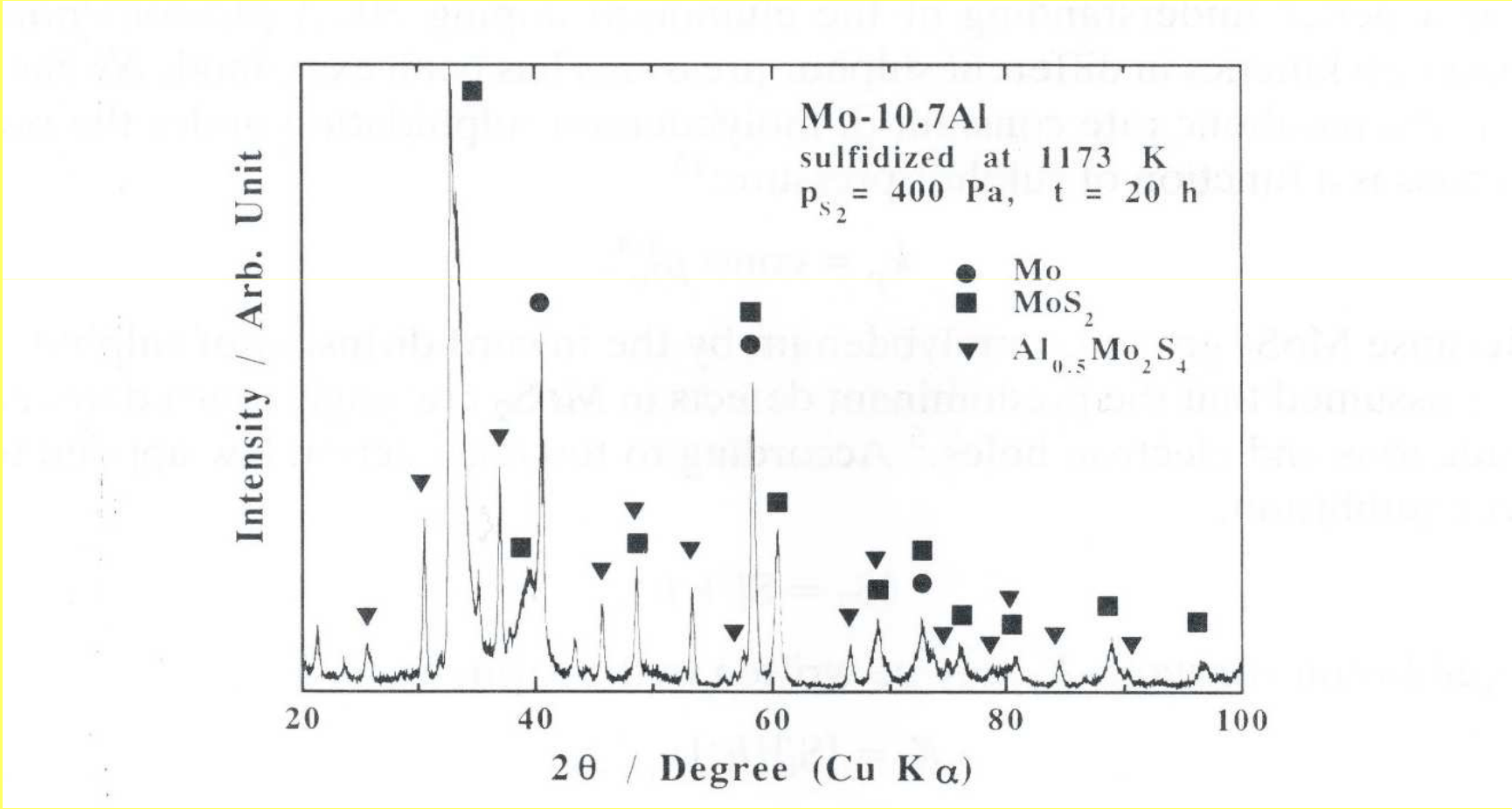
Temperature dependence of the sulphidation rate for Mo-Al alloys and molybdenum



X–ray diffraction pattern for Mo-6.2 Al alloy after 12 h sulphidation at 1173 K



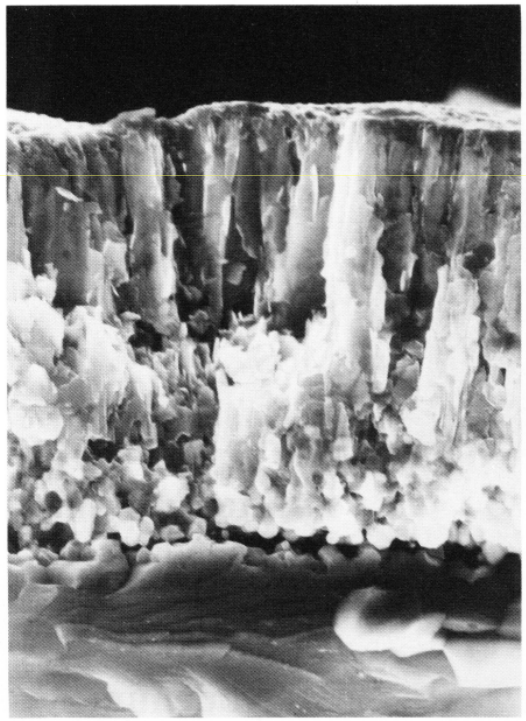
X–ray diffraction pattern for Mo-10.7 Al alloy after 20 h sulphidation at 1173 K



Microphotographs of cross-sections of Mo-Al alloys after sulphidation

Mo–1.7Al

T = 1173 K, p_{S_2} = 400 Pa, t = 24 h,



Scale
MoS_2

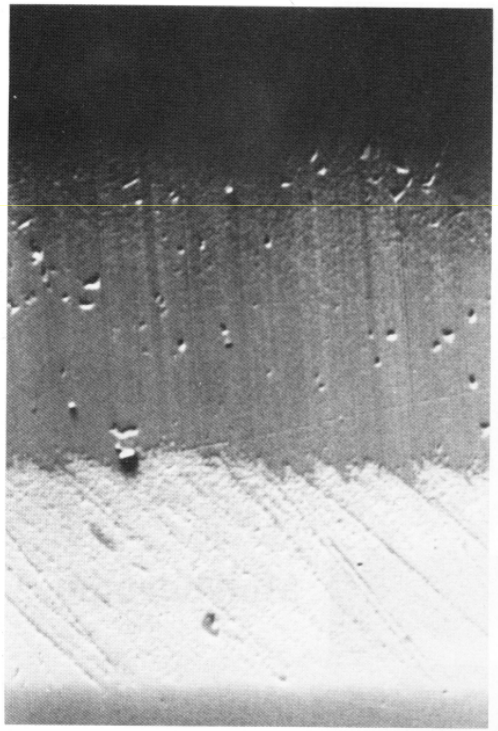
Sputtered Film
Mo–Al alloy

Molybdenum

1 μm

Mo–6.2Al

T = 1173 K, p_{S_2} = 400 Pa, t = 24 h,



Scale
MoS_2

Sputtered Film
Mo–Al alloy

Molybdenum

20 μm

PROTECTIVE COATINGS UTILIZED IN THE CASE OF OXIDIZING-SULPHIDIZING ATMOSPHERES

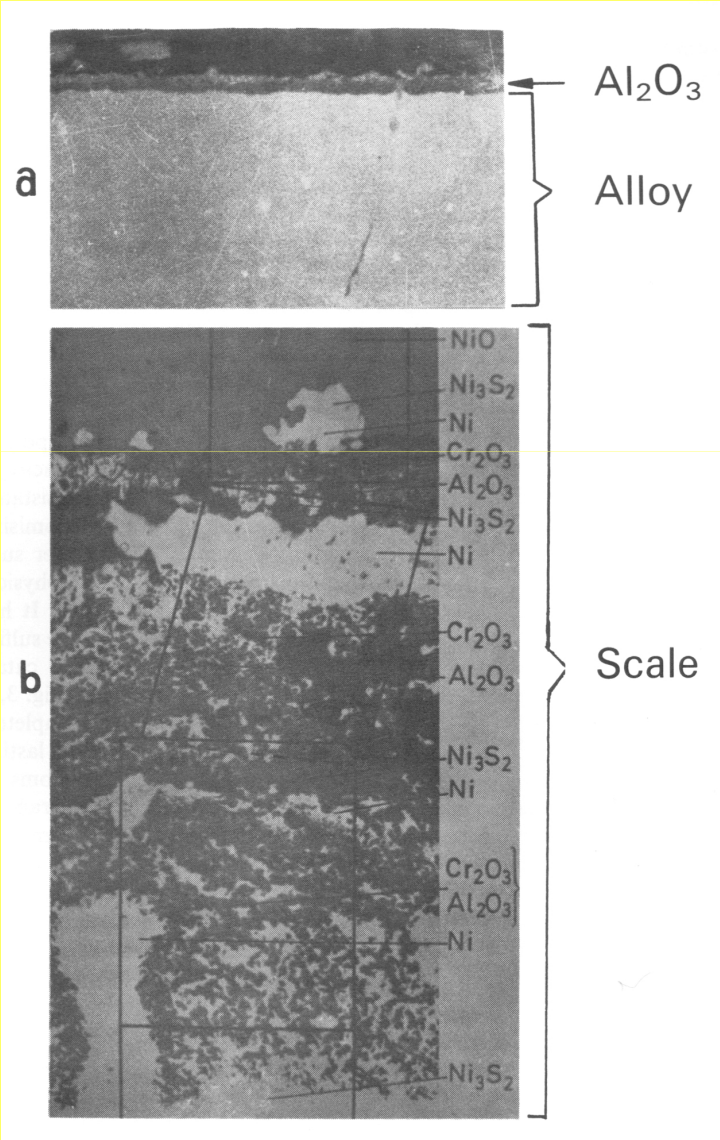
Fe-Mo-Al

Mo-Al

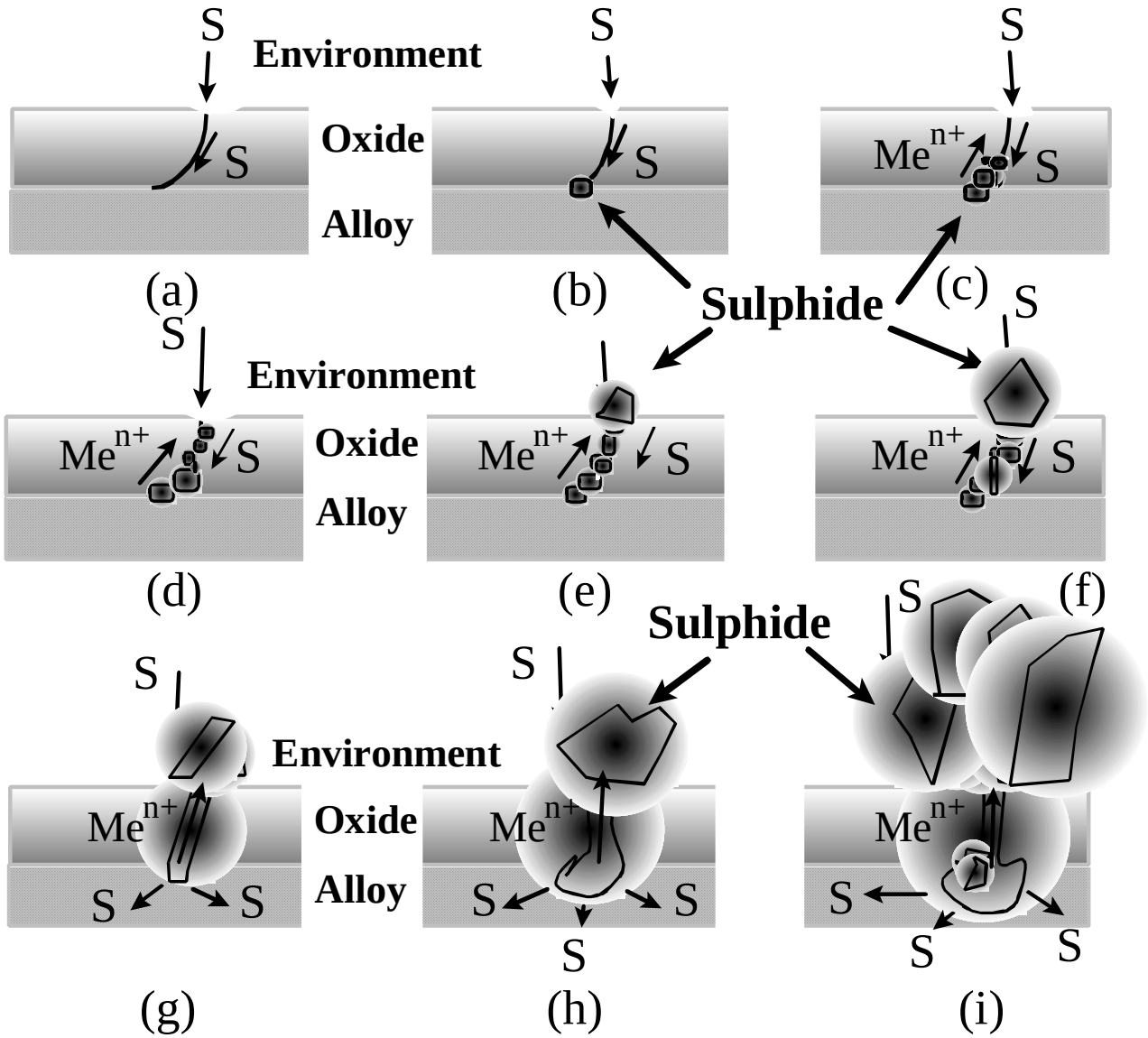
Mo-Al-Si

Nb-Al

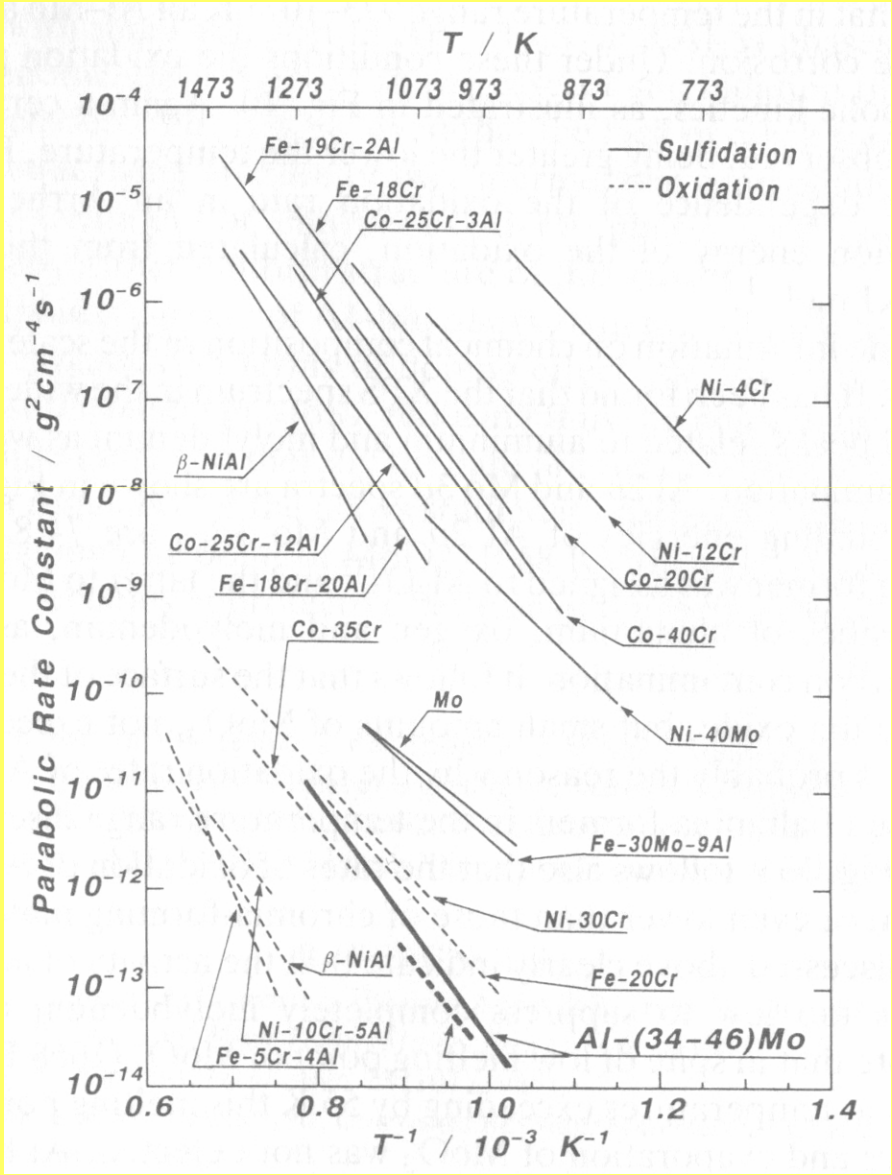
Cross-section of scales formed on a superalloy in oxidizing and oxidizing-sulphidizing atmospheres



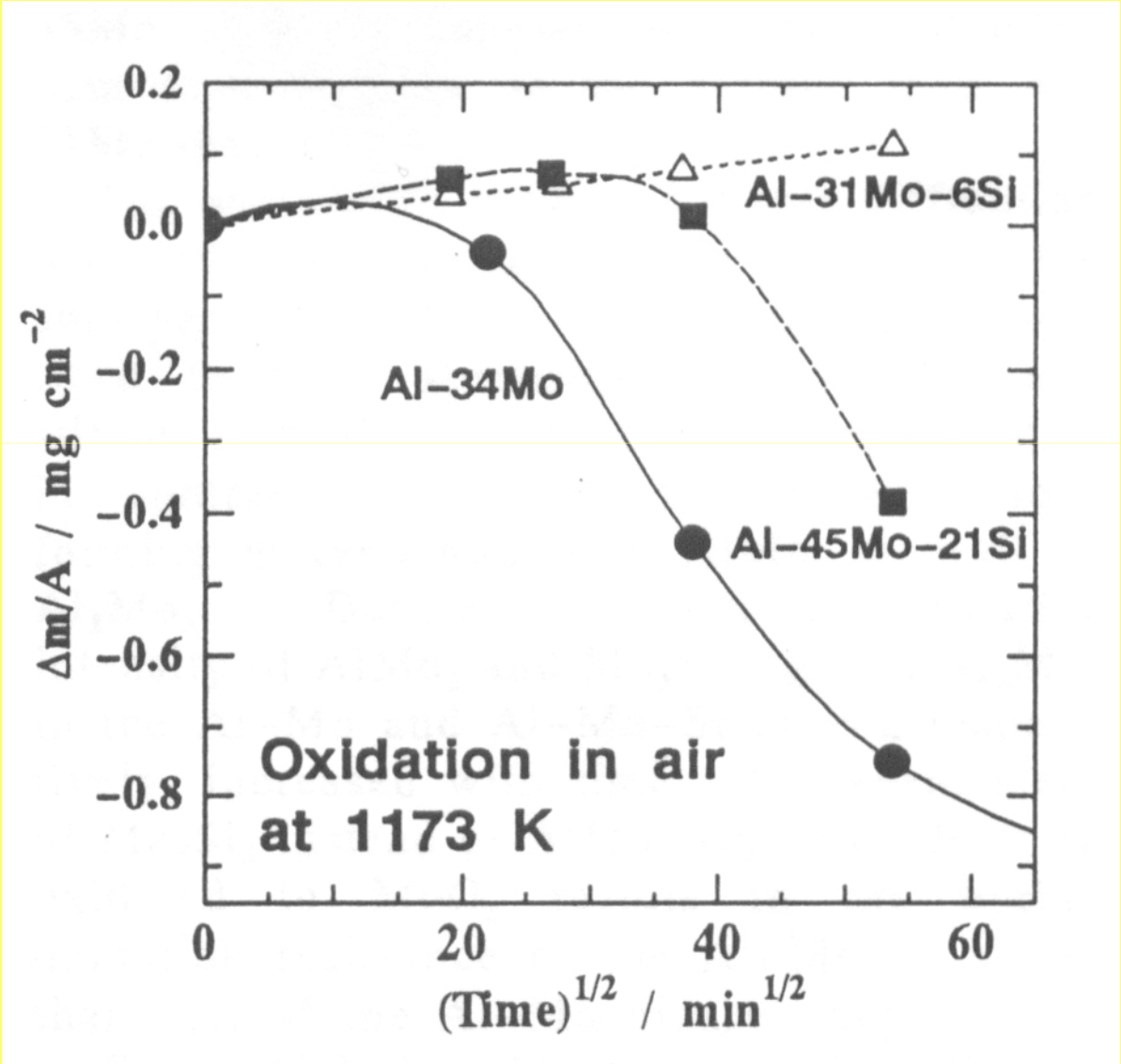
Scheme of degradation of materials in the oxidizing-sulphidizing atmospheres



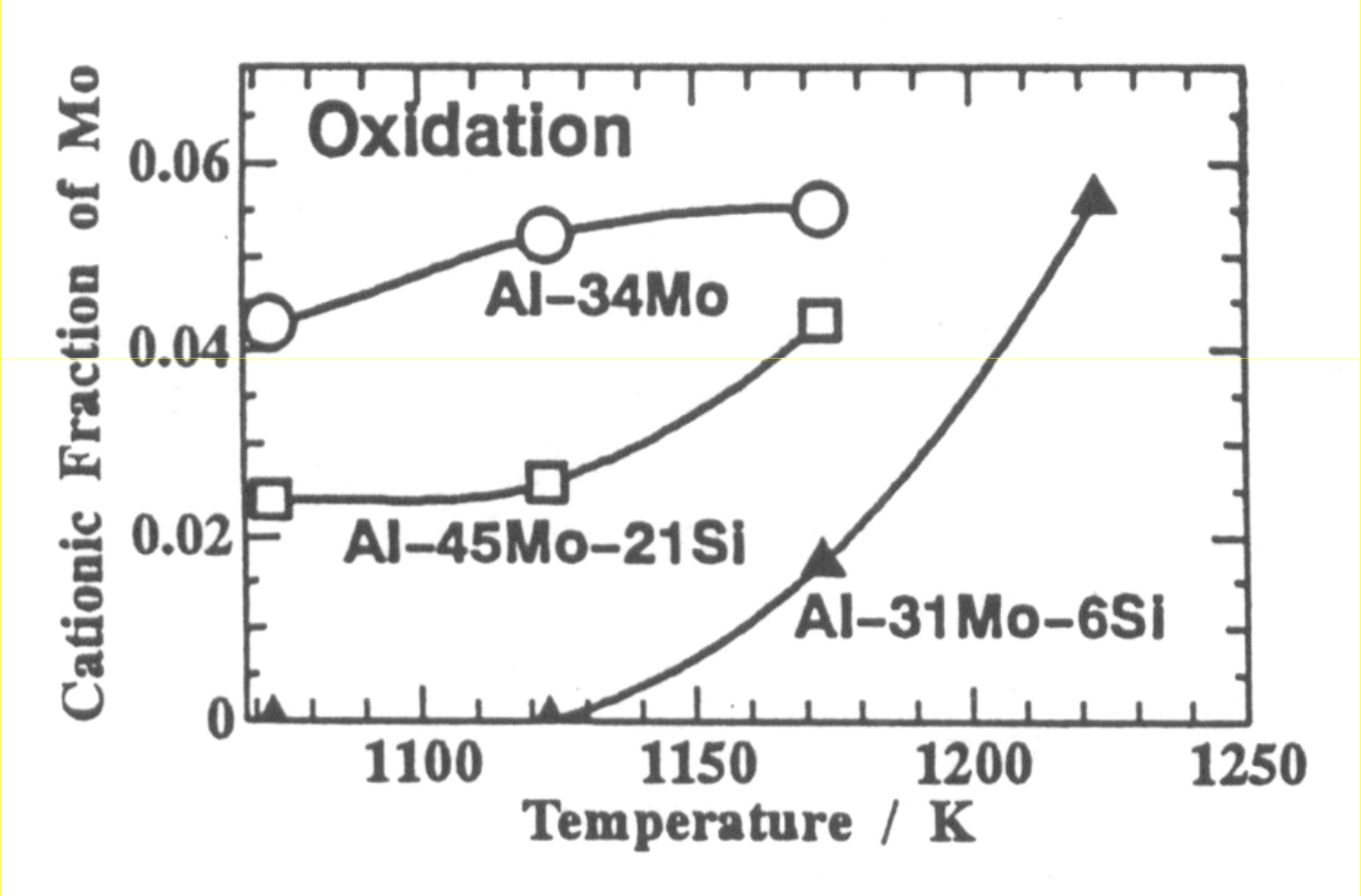
Comparison of the sulphidizing and oxidizing rates of several alloys



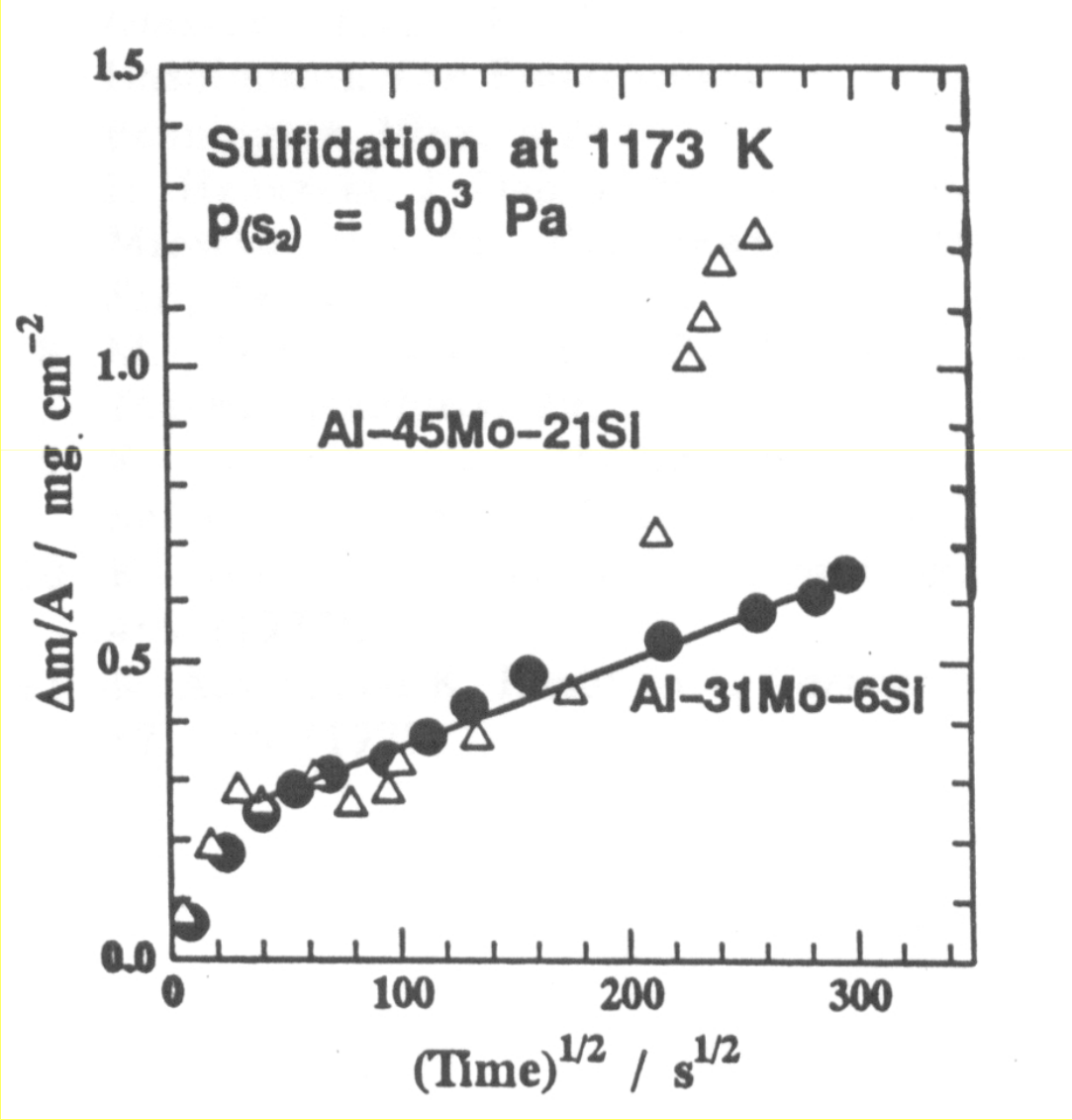
Comparison of the oxidizing rates of several Al-Mo-Si alloys



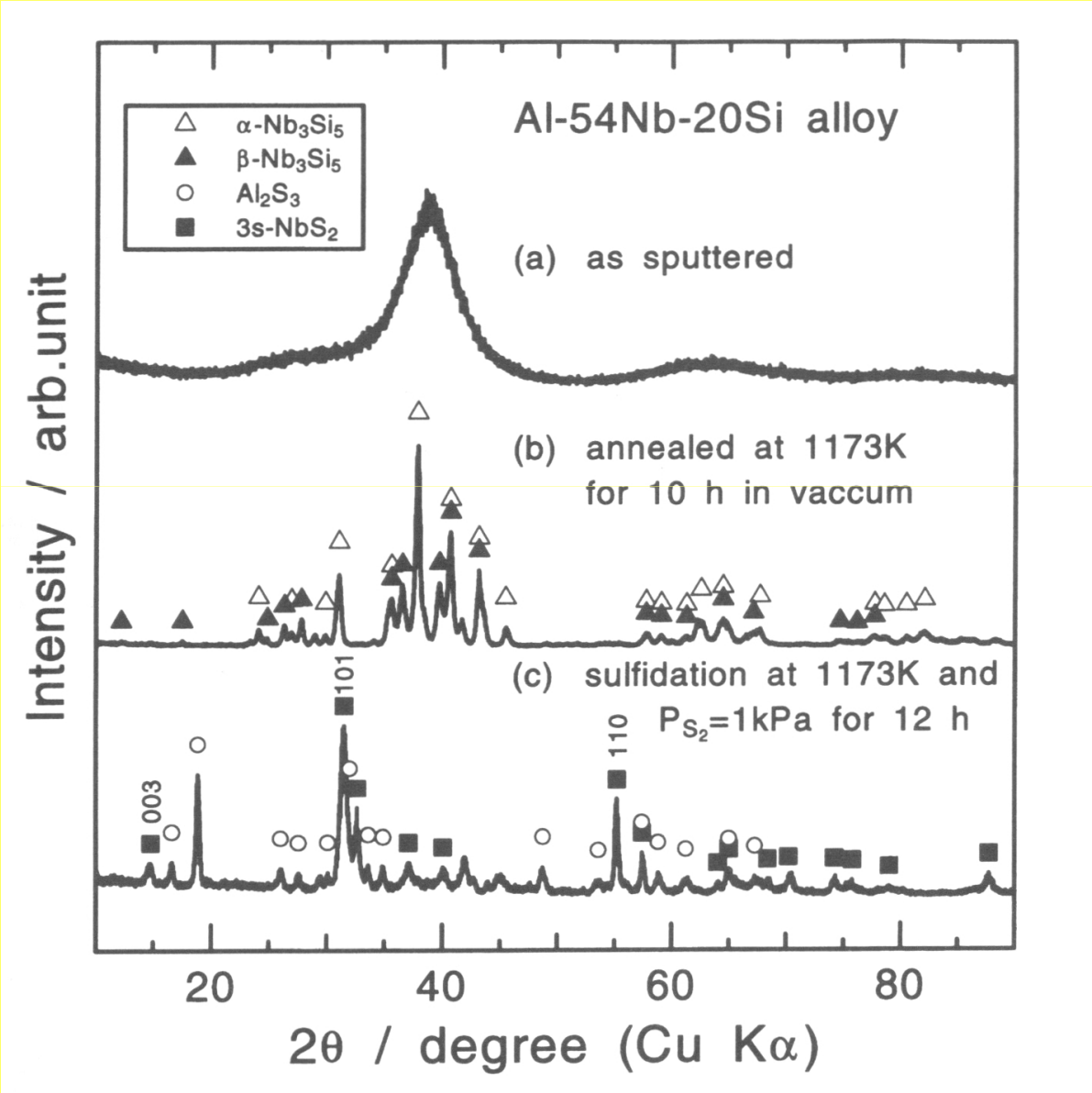
The molybdenum content in scales growing on several Al-Si-Mo alloys



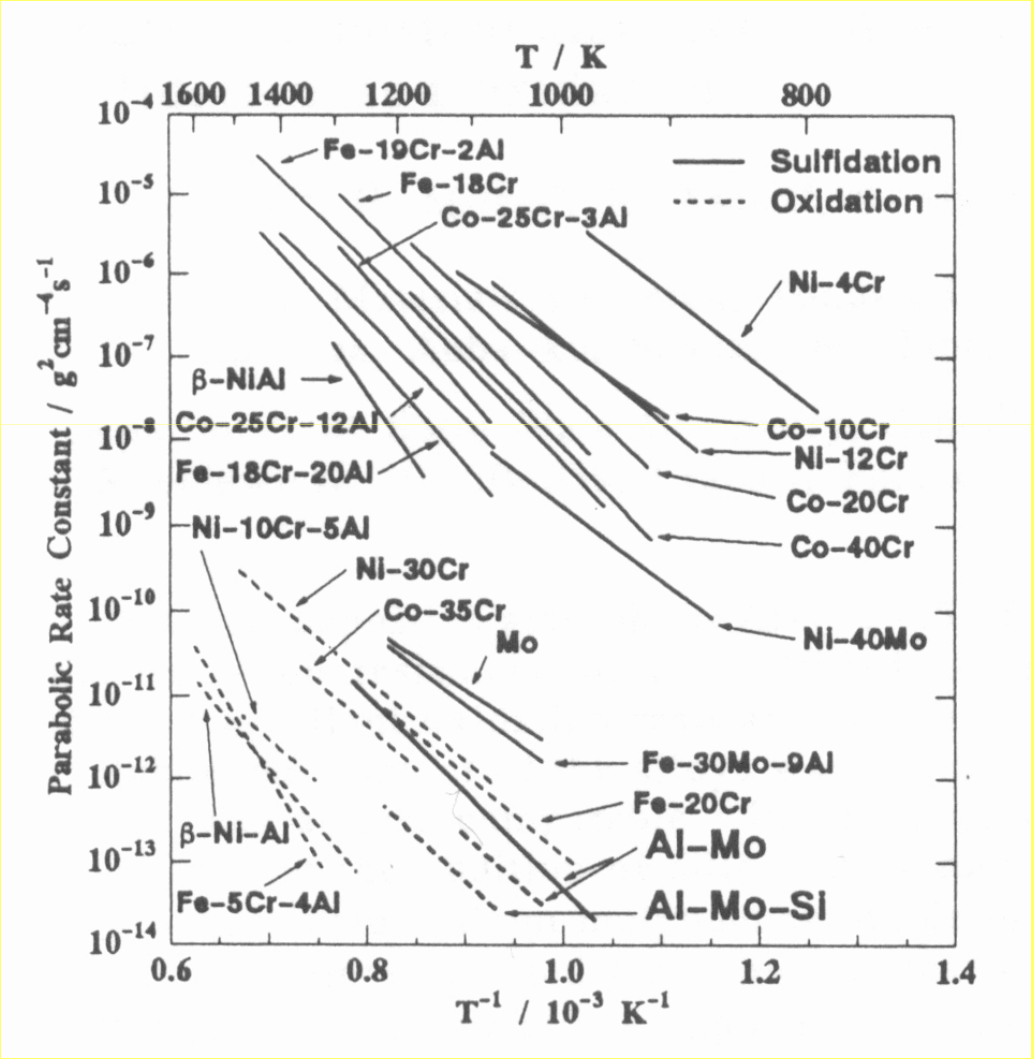
Comparison of the sulphidizing kinetics of two Al-Mo alloys with different Si contents



The result of X-ray analysis of Al-54Nb-20Si alloy



Comparison of the sulphidizing and oxidizing rates of several alloys



CONCLUSION

Protective coatings against high temperature corrosion in oxidizing-sulphidizing environments have not been elaborated.

THE END