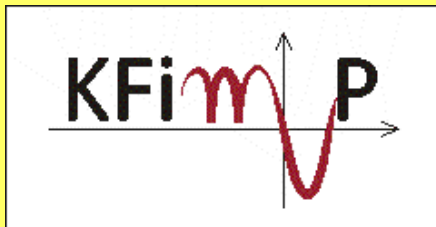


# HIGH TEMPERATURE COATINGS

Zbigniew Grzesik

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



Department of Physical Chemistry and Modelling

# Plan of presentation

- 1) Fundamental definitions
- 2) Fabrication of coatings
- 3) High temperature coatings in corrosion processes:
  - oxidizing atmosphere
  - sulphidizing atmosphere
  - oxidation-sulphidizing atmosphere
  - strongly carburizing atmosphere
- 4) Thermal barrier coatings (TBC)
- 5) Summary

# DEFINITIONS

The coating is the thin outer layer of the object, which physiochemical properties and/or structure are different from those of the coated material.

The high temperature coating is the outer layer of a material that provides the protection against corrosion.

# REFERENCES

1. Developments in high-temperature corrosion and protection of materials. Ed. Wei Gao, Zhengwei Li. Woodhead Publishing Ltd. Cambridge, England, 2008.
2. High-temperature oxidation of metals. N. Birks, G.H. Meier, F.S. Pettit. Cambridge University Press. New York, USA 2008.
3. Corrosion: Fundamentals, Testing and Protection. ASM Handbook, vol. 13A. ASM International. Ohio Park, USA, 2003.

# METHODS OF COATINGS FABRICATION

1. Electrolytic method
2. Chemical methods
3. Immersion method
4. Thermal spraying
5. Diffusion methods
6. Plating
7. Vacuum deposition of electroless method

# THE SURFACE PREPARATION METHODS OF STEEL FOR COATINGS

1. Mechanical methods:
  - abrasing and/or polishing,
  - brushing
2. Physico-chemical methods:
  - degreasing in solvents
  - emulsion degreasing,
  - alkaline degreasing,
  - etching in acids and bases (removing of oxides and hydroxides)
  - electrolytic degreasing,
  - degreasing using ultrasounds
3. Thermal methods – flame desurfacing.

# ELECTROLYTIC COATINGS (GALVANIC)

Electrolytic metal coatings produced on the conductive substrate are obtained by deposition of metals from a solution of their salts or anodes made from appropriate metal, using electric current. The coated object is the cathode and the anode constitutes the plating material.

Coatings are obtained in the first stage by the formation of crystallization centers, which subsequently grow to form a continuous layer with required thickness.

Factors affecting the properties of the coatings: the type of metal substrate, type and concentration of additives (eg, increasing the electrical conductivity of the bath, causing the formation of finely coating or brightening shell), current density, bath temperature, time of the process and methods of mixing the bath (mechanical, compressed air, etc.).

# CHEMICAL COATINGS

Chemical (electroless) imposition of metals involves the reduction of metal compounds from solutions of their salts by using reducers (hypophosphoric acid salts, or other). Until now chemical methods are developed, consisting in chemical vapor deposition of nickel, cobalt, tin, copper, silver, gold, palladium or platinum. The contact coating method consists in displacement of the metal ions from solution by the metal substrate.

Metallic coatings deposited by chemical methods are rarely used for protection against high temperature corrosion.



# HOT-DIP COATINGS (IMMERSION)

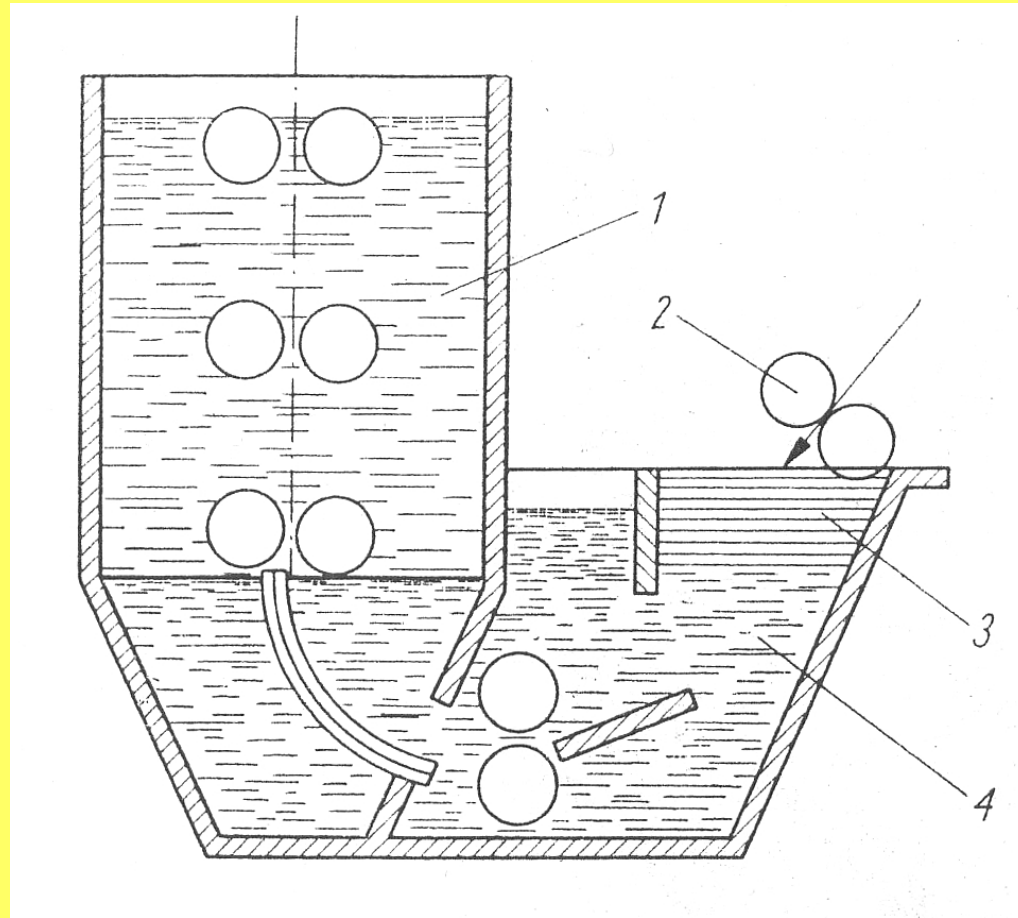
Hot-dip coatings are obtained by immersion of a given material in a molten metal bath. This method is the oldest and cheapest one, currently utilized in obtaining metallic coatings, well adherent to the substrate.

This method is mainly used in those cases when the material shows considerable length (tapes, wires).

This method can be applied only when the melting point of a given material is higher than that of the coating. In practice, this method is used for coating tin (232°C), lead (327°C), zinc (419°C) and aluminum (660°C).

# HOT-DIP COATING (DIP COATING)

- scheme of device for hot-dip tinning



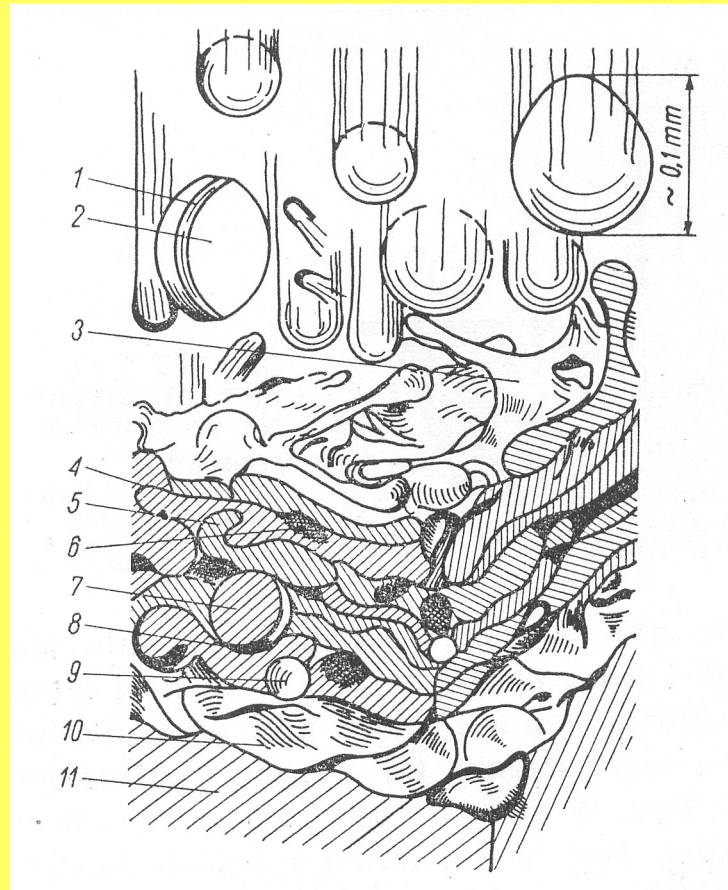
1 – oil, 2 - cylinder head, 3 – fluxing agent, 4 - molten tin

# THERMAL SPRAY COATINGS

Thermal metal spraying involves melting, using different heat sources (flame, electric arc, plasma arc or high-frequency current). The metal for coating production is used in the form of wire or powder, which after melting is directed to the substrate in a stream of compressed gas (usually air). In the high temperature flame or arc, metal particles are partially oxidized, and after hitting the ground are flattened. During hitting of the ground the oxide thin film is cracking and consequently the coating constitutes a shell of sprayed metal, its oxide and pores. The total pore volume generally does not exceed 15%.

# THERMALLY SPRAYED COATING

## Scheme formation of the sprayed metal layer



- 1 - oxide on particle film, 2 - the liquid inside the particle, 3 - particle splash during impact, 4 - rest of the oxide film between sprayed particles, 5 - jamming the particles, 6 - particles coupled by mutual welding, 7 - particle at low temperature (not plastic), 8 - the gap between the particles (not plastic), 9 - micropores (developed due to trapped exhaust gas between particles), 10 - surface of the substrate, 11 - substrate

# DIFFUSION COATINGS

Diffusion coatings are produced by changing the chemical composition of the surface layer of a given material as a result of the introduction of alien elements. Diffusion coating is a part of the substrate material saturated with alien elements, which cannot be separated from it. Metals plated on the substrate surface diffuse into the crystal lattice, not influencing the apparent changes of its dimensions.

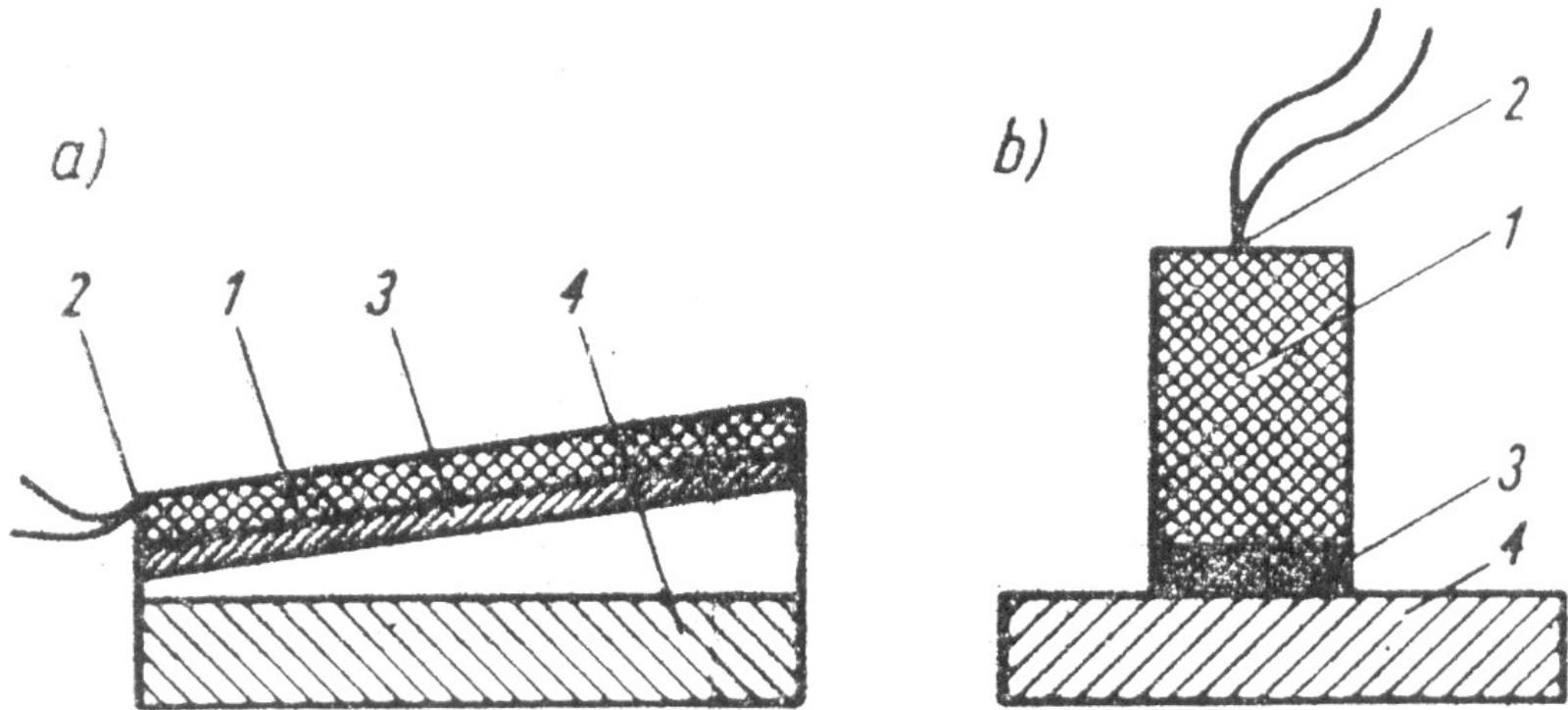
Typical diffusion processes:

- Aluminizing
- Chrome plating
- Chrome aluminizing
- Galvanizing
- Chrome siliconizing

# PLATING

Plating method consists in mechanical coating of a relatively thick layers of a given metal on protected substrate, being in the form of tape or wire. Metal coating (more noble or more decorative) can be obtained by casting, welding, soldering, rolling or explosive plating. The penetration of the coating metal into the substrate proceeds under the influence of pressure and temperature, providing the welding. Carbon steels are usually plating by copper, nickel, aluminum and acid resistant steels.

# METHOD OF EXPLOSIVE PLATING



a) planar system, b) cylindrical system; 1 – explosive material  
2 – detonator, 3 – material applied as a coating,  
4 – substrate

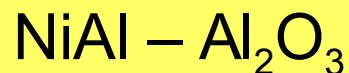
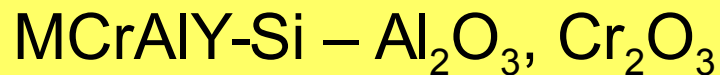
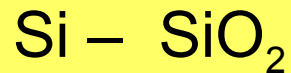
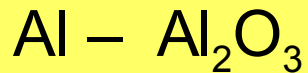
# VACUUM DEPOSITION COATINGS

Methods of vacuum deposition of metals:

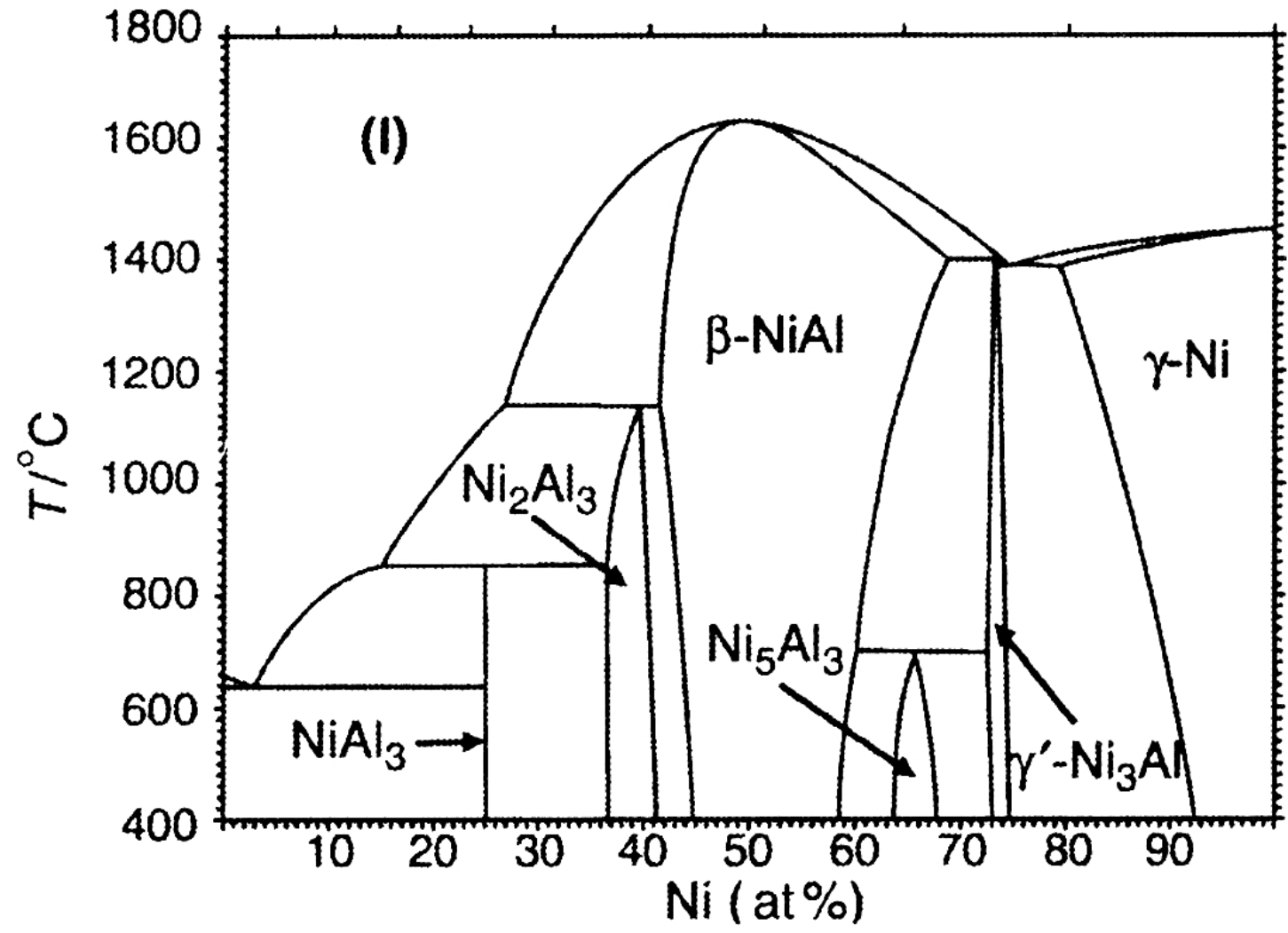
- Electroless vacuum deposition
- Cathodic sputtering
- Ionic metallization



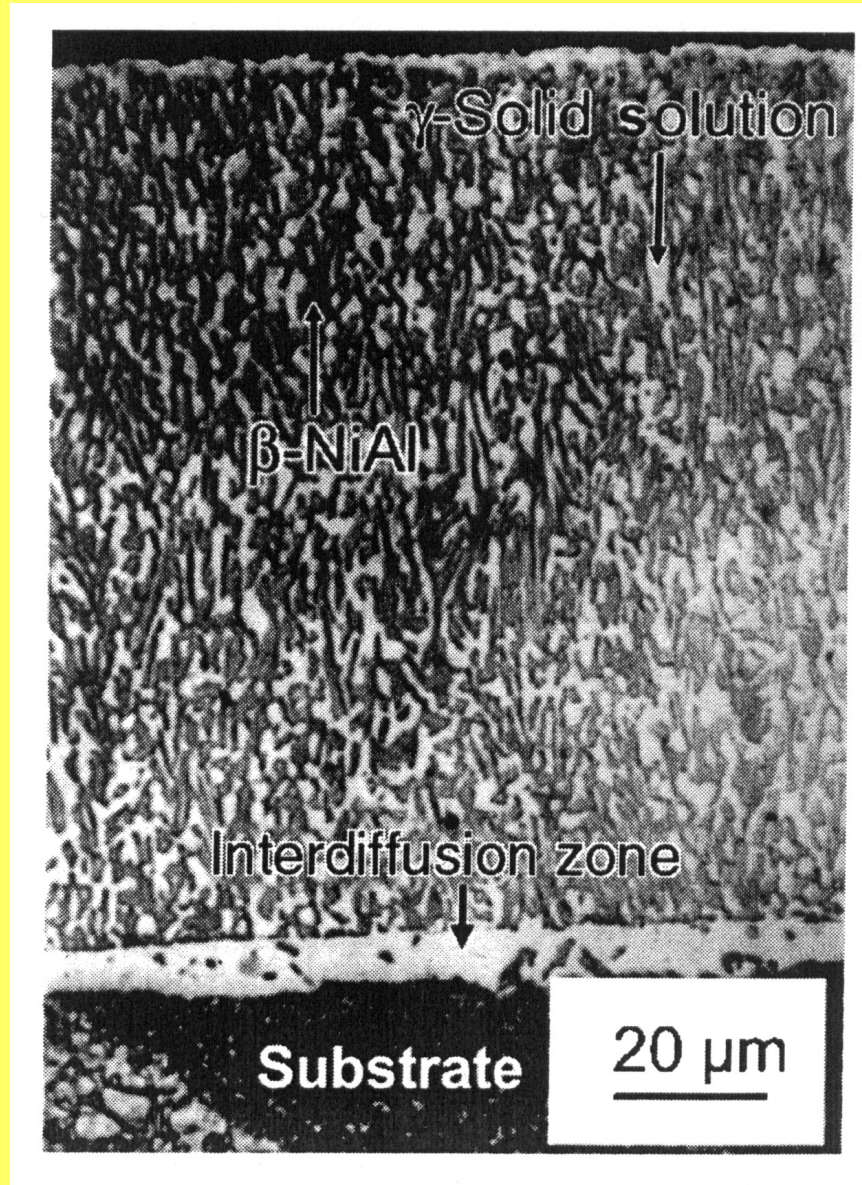
# PROTECTIVE COATINGS APPLIED IN THE CASE OF CORROSION OCCURRING IN OXIDIZING ATMOSPHERES



# Ni-Al phase diagram

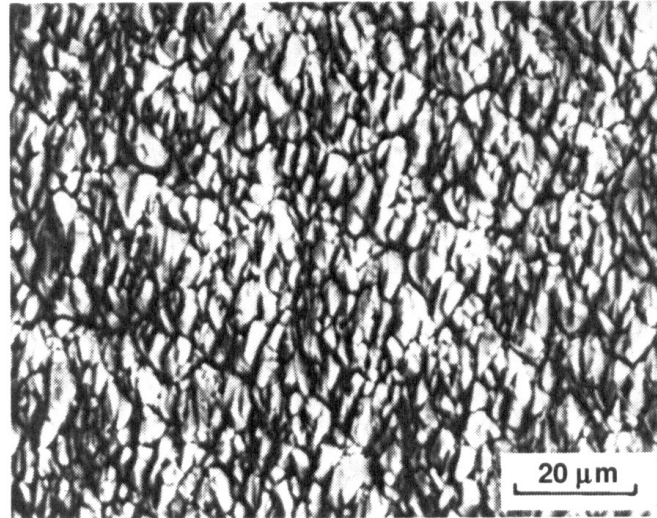


# Cross-section of the Ni-Cr-Al-Y coating obtained by the EB-PVD method

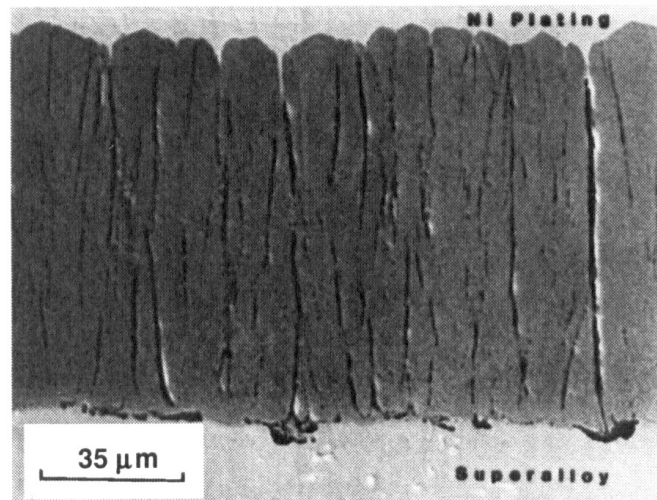


# Surface and cross-section of the Co-Cr-Al-Y coating obtained by the EB-PVD method on the IN-738 alloy

(a)



(b)



# PROTECTIVE COATINGS APPLIED IN CORROSION OCCURRING IN SULPHIDIZING ATMOSPHERES

Mn – MnS

Ti – TiS<sub>2</sub>

Mo – MoS<sub>2</sub>

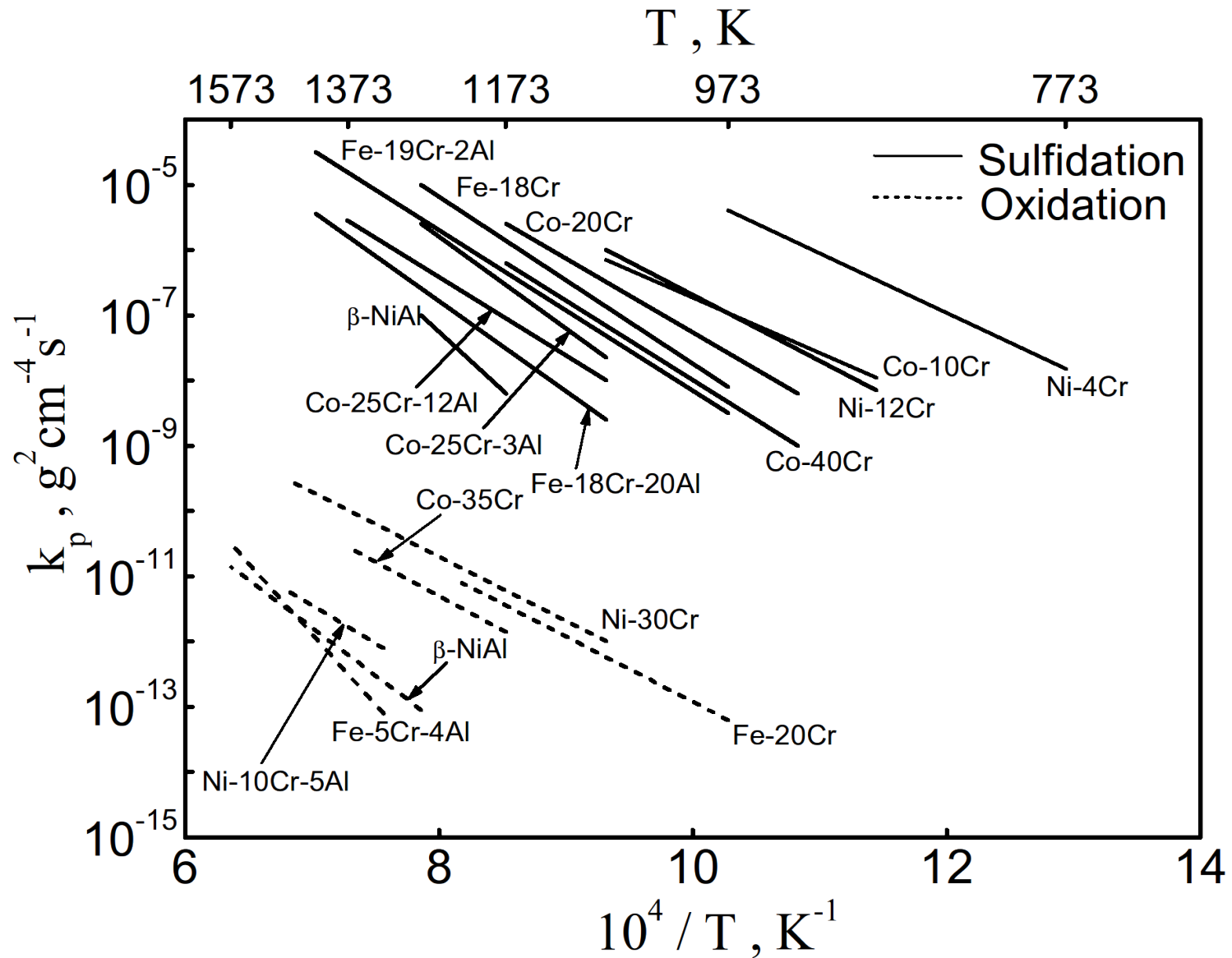
Nb – NbS<sub>2</sub>

Ta – TaS<sub>2</sub>

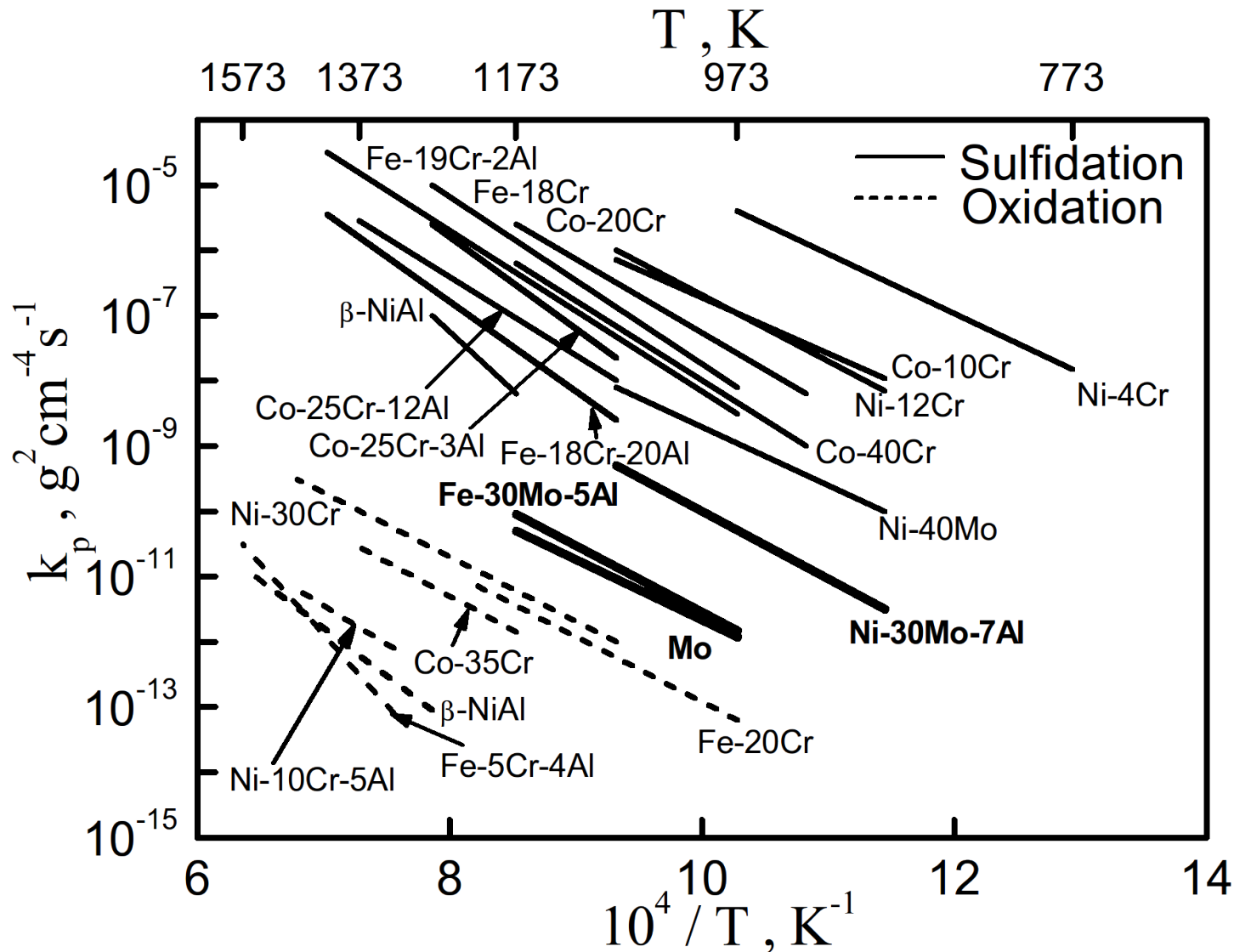
Ni-Mo, Fe-Mo, Co-Mo

Fe-Mo-Al

# Comparison of sulphidation and oxidation rates of several alloys



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



# PROTECTIVE COATINGS UTILIZED IN THE CASE OF OXIDIZING-SULPHIDIZING ATMOSPHERES

Fe-Mo-Al

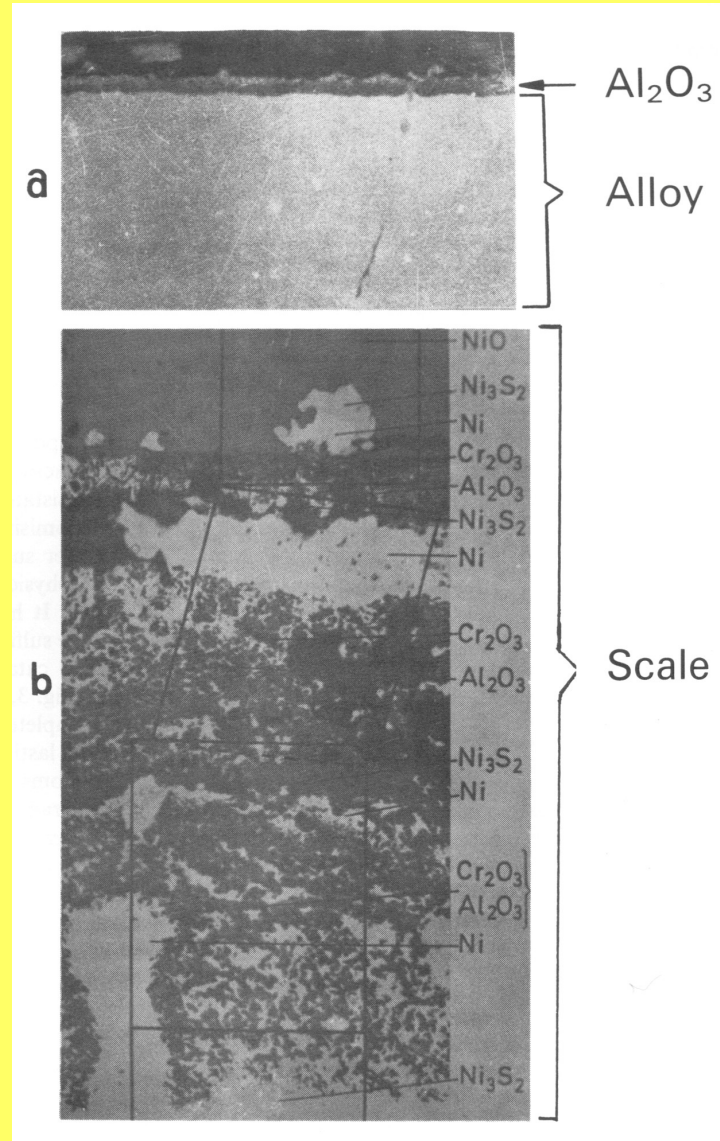
Mo-Al

Mo-Al-Si

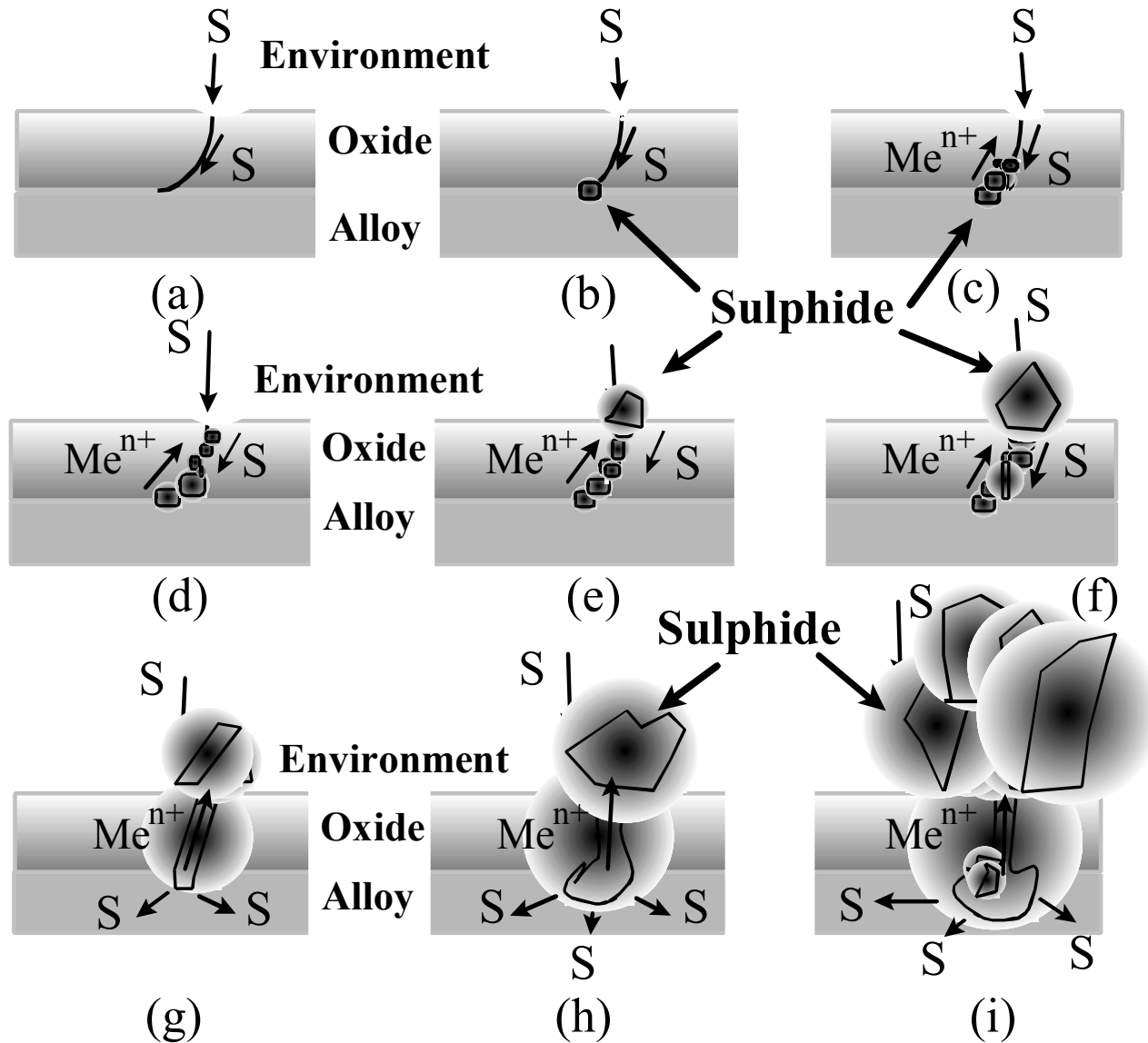
Nb-Al



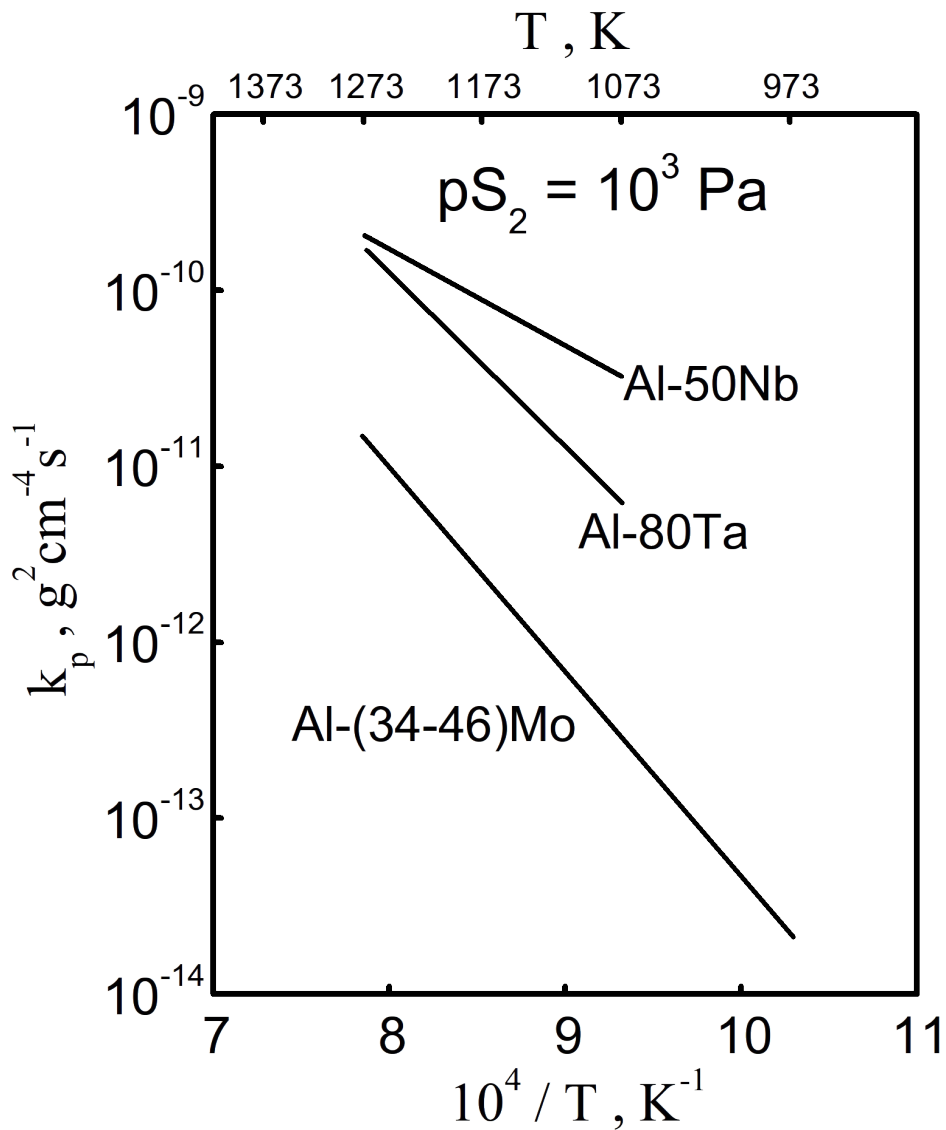
# Cross-section of scales formed on a superalloy in oxidizing and oxidizing-sulphidizing atmospheres



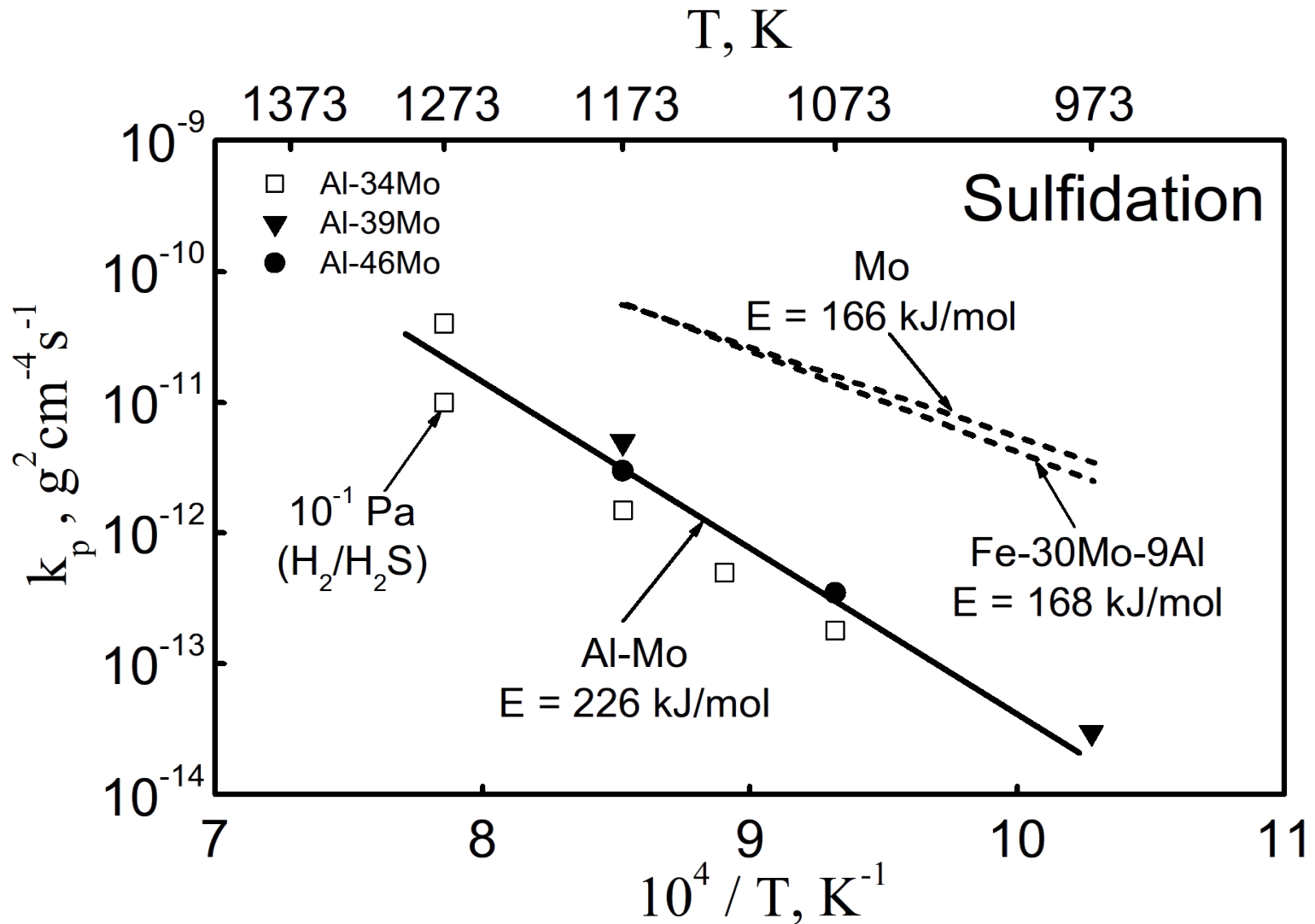
# Scheme of degradation of materials in the oxidizing-sulphidizing atmospheres



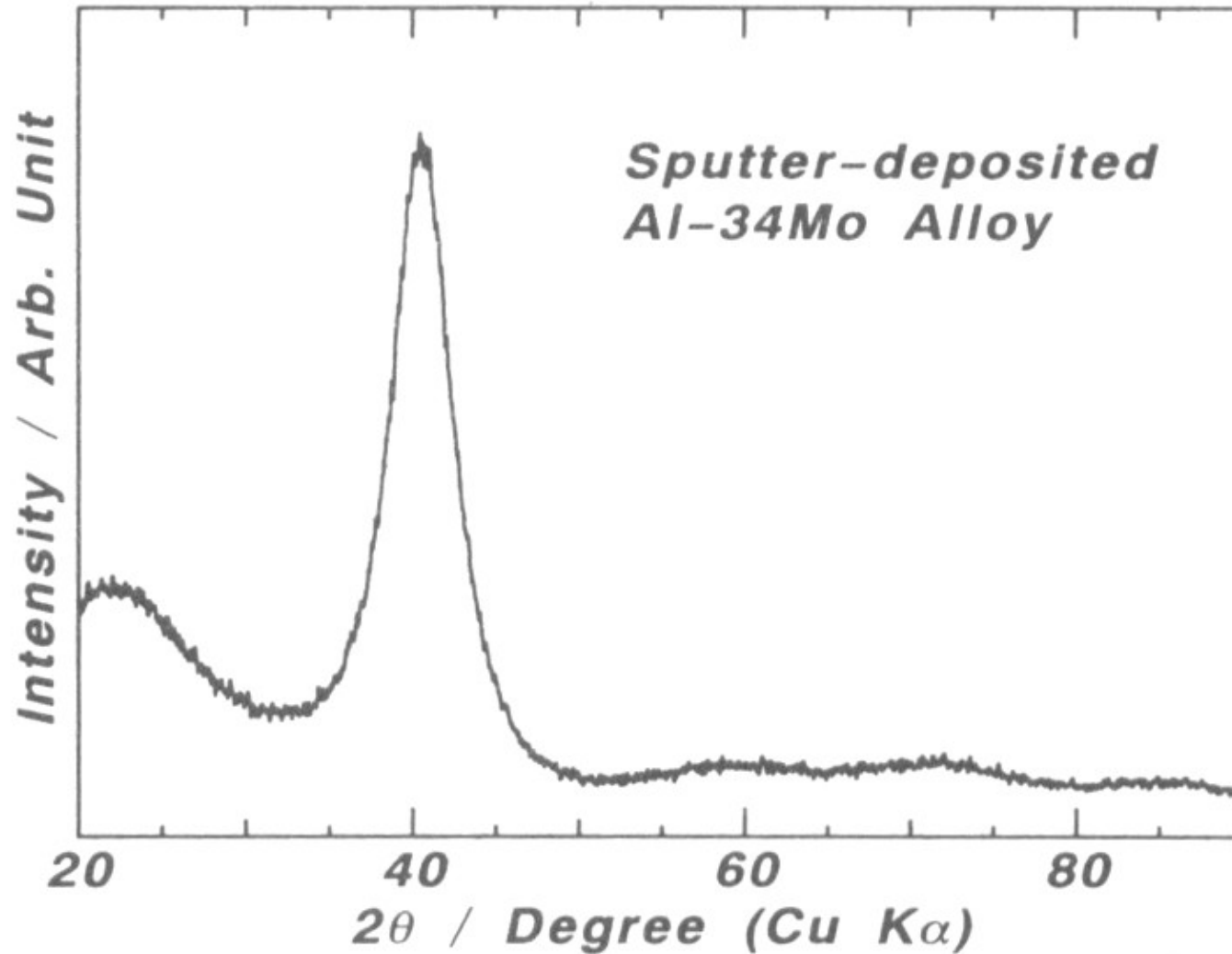
# Sulphidizing rates of high-temperature alloys containing aluminum



# Sulphidizing rates of Mo-Al alloys

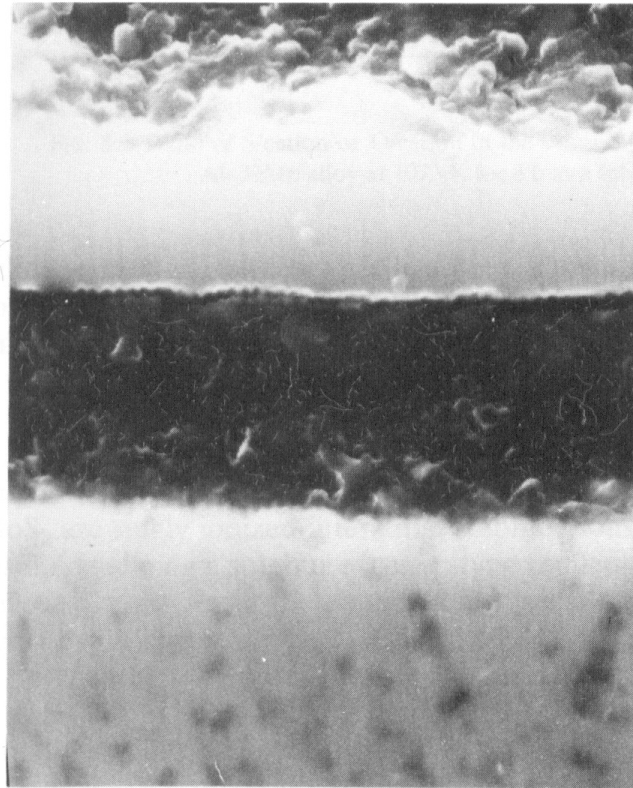


# X-ray data of the Al-34Mo alloy



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

**Al-46Mo**



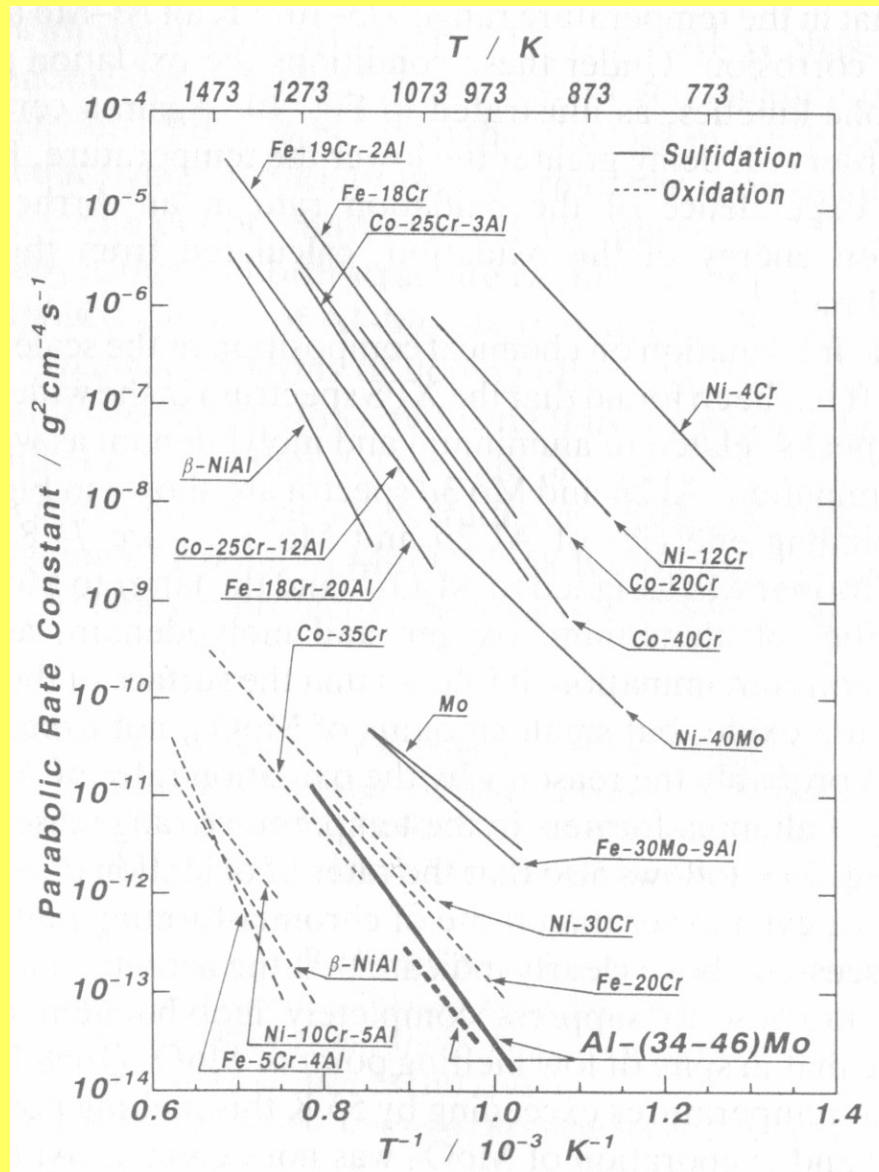
**Outer Scale**

**Inner Scale**

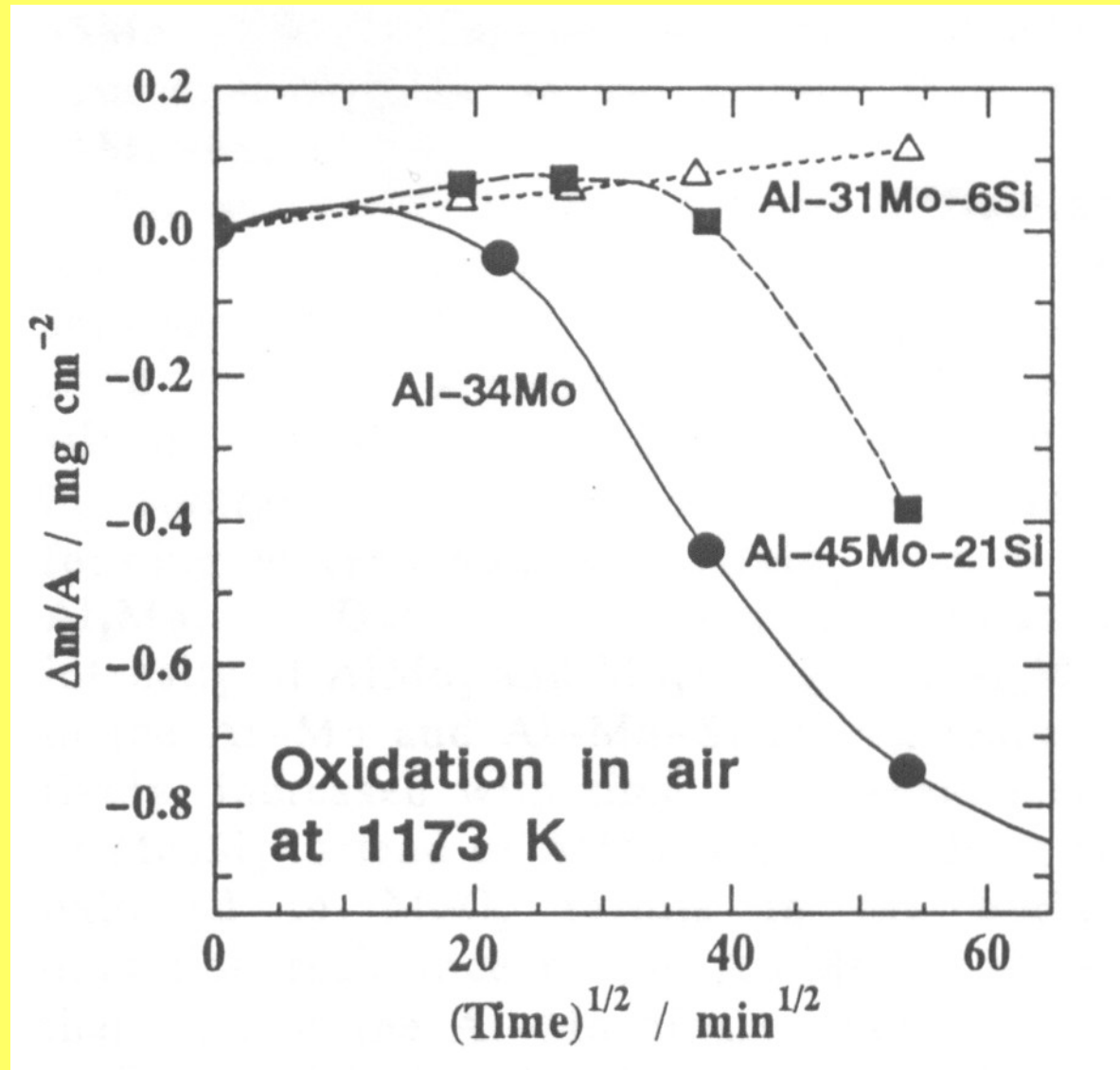
**Sputtered Film**

  
1  $\mu\text{m}$

# Comparison of the sulphidizing and oxidizing rates of several alloys

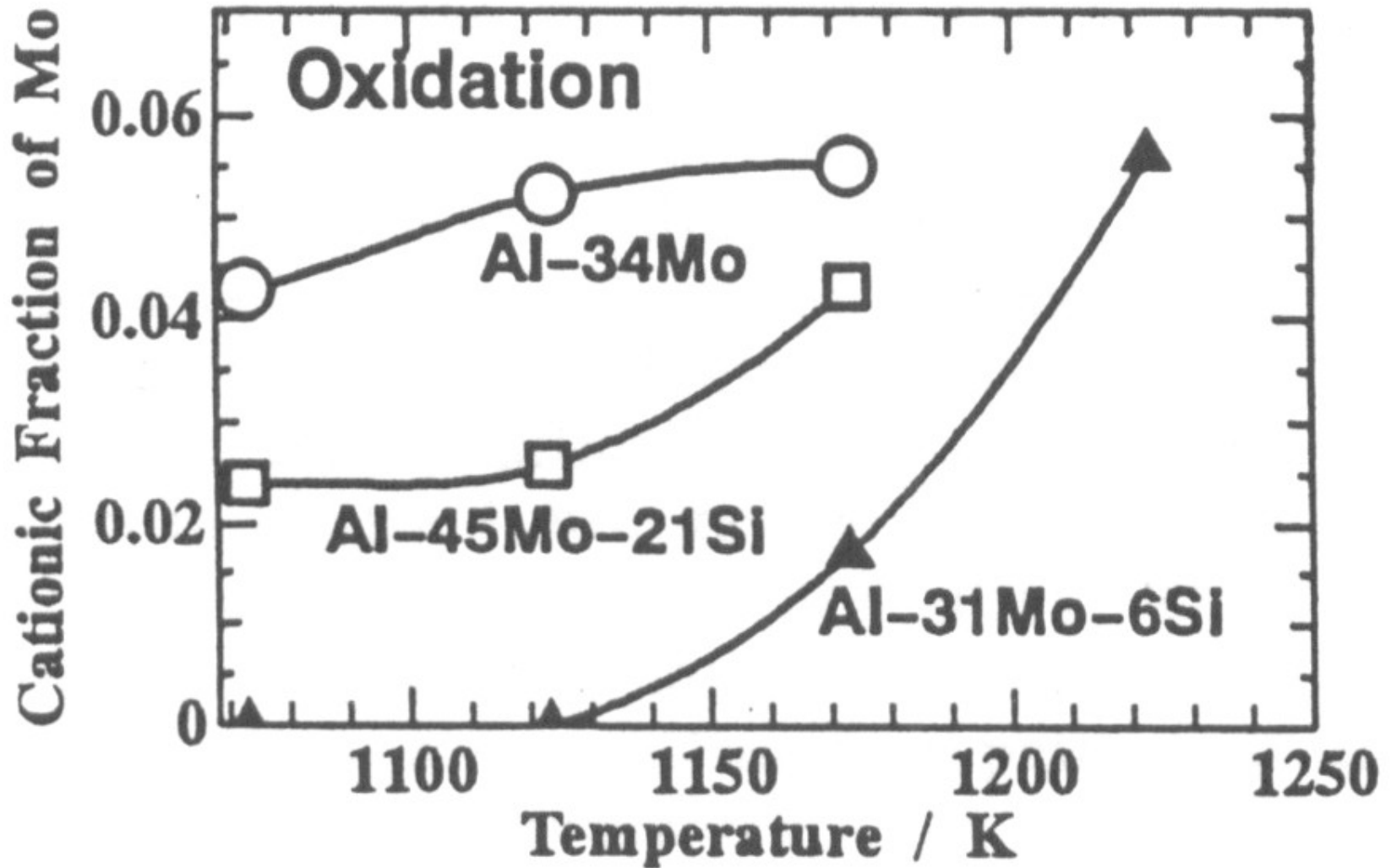


# Comparison of the oxidizing rates of several Al-Mo-Si alloys

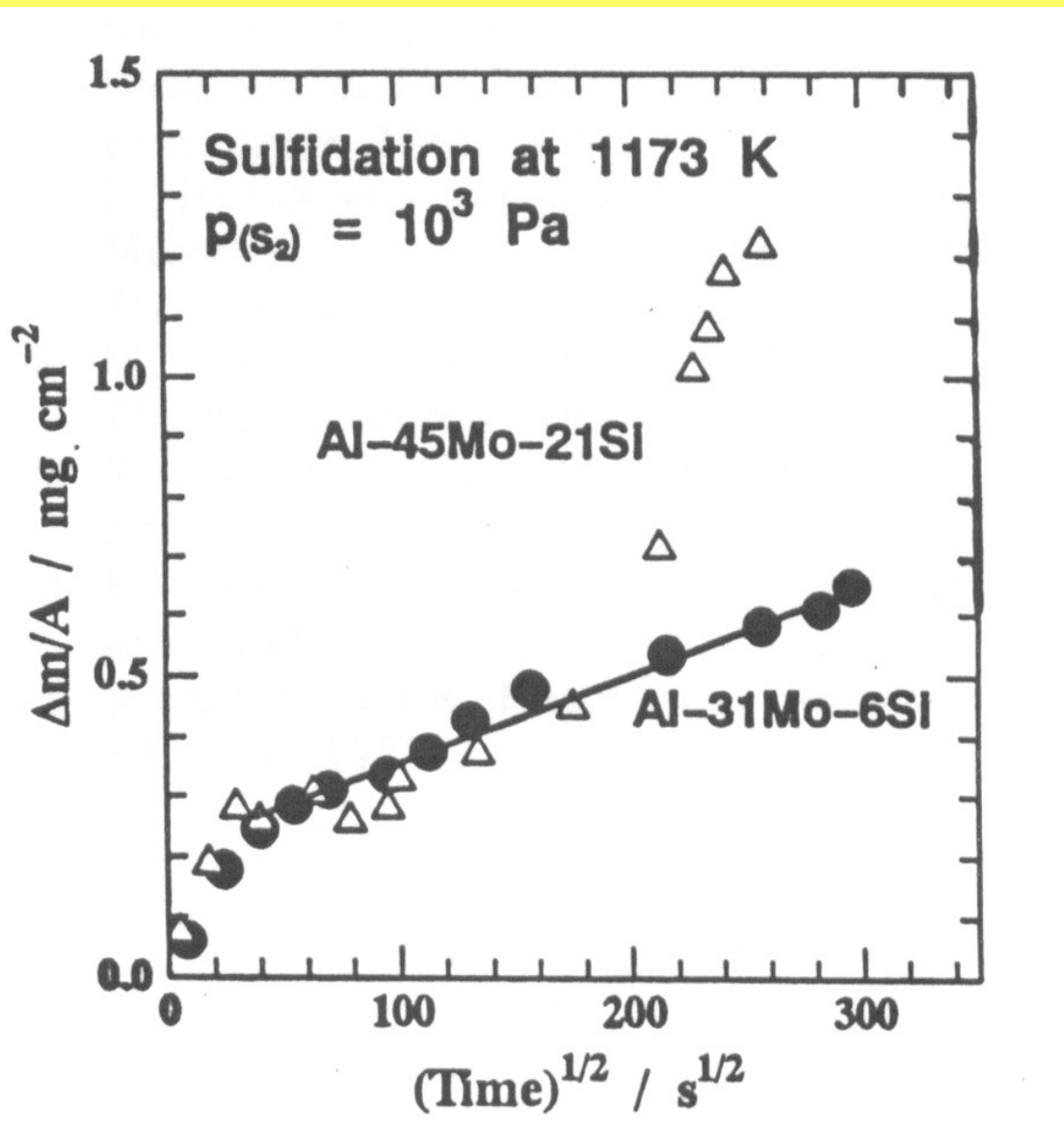




The molybdenum content in scales growing on several Al-Si-Mo alloys

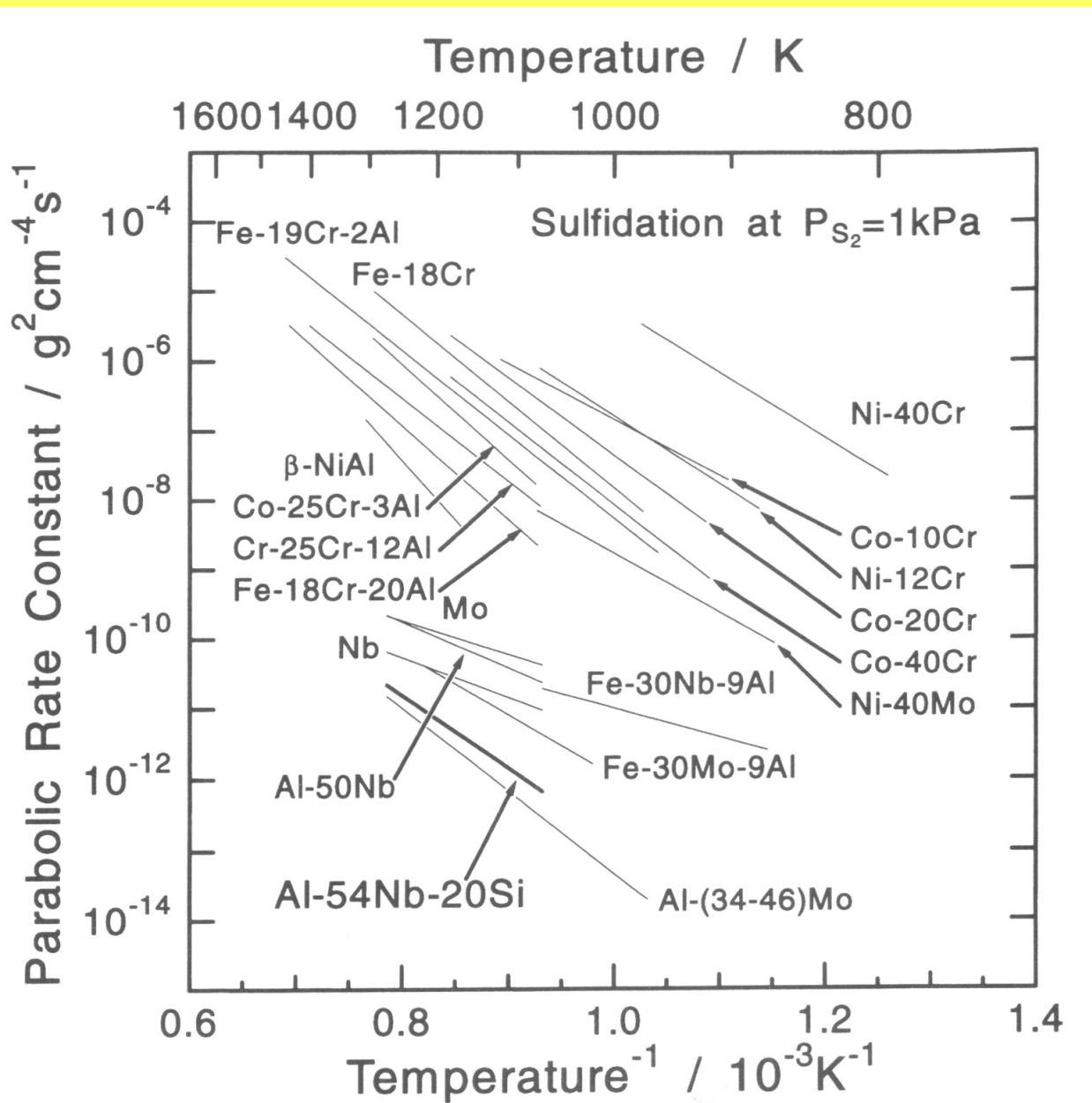


# Comparison of the sulphidizing kinetics of two Al-Mo alloys with different Si contents

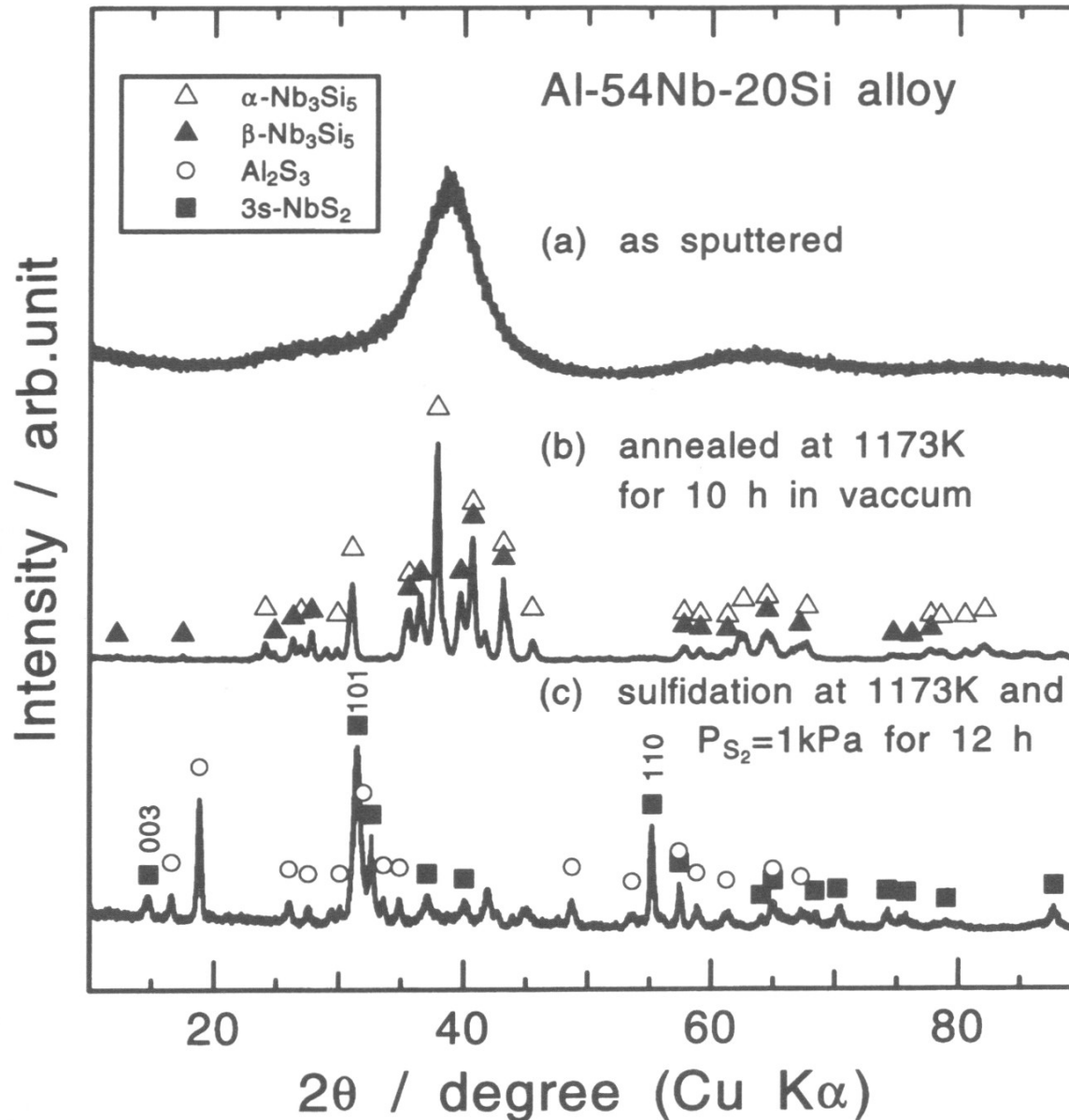




# Comparison of the sulphidizing rates of several alloys



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

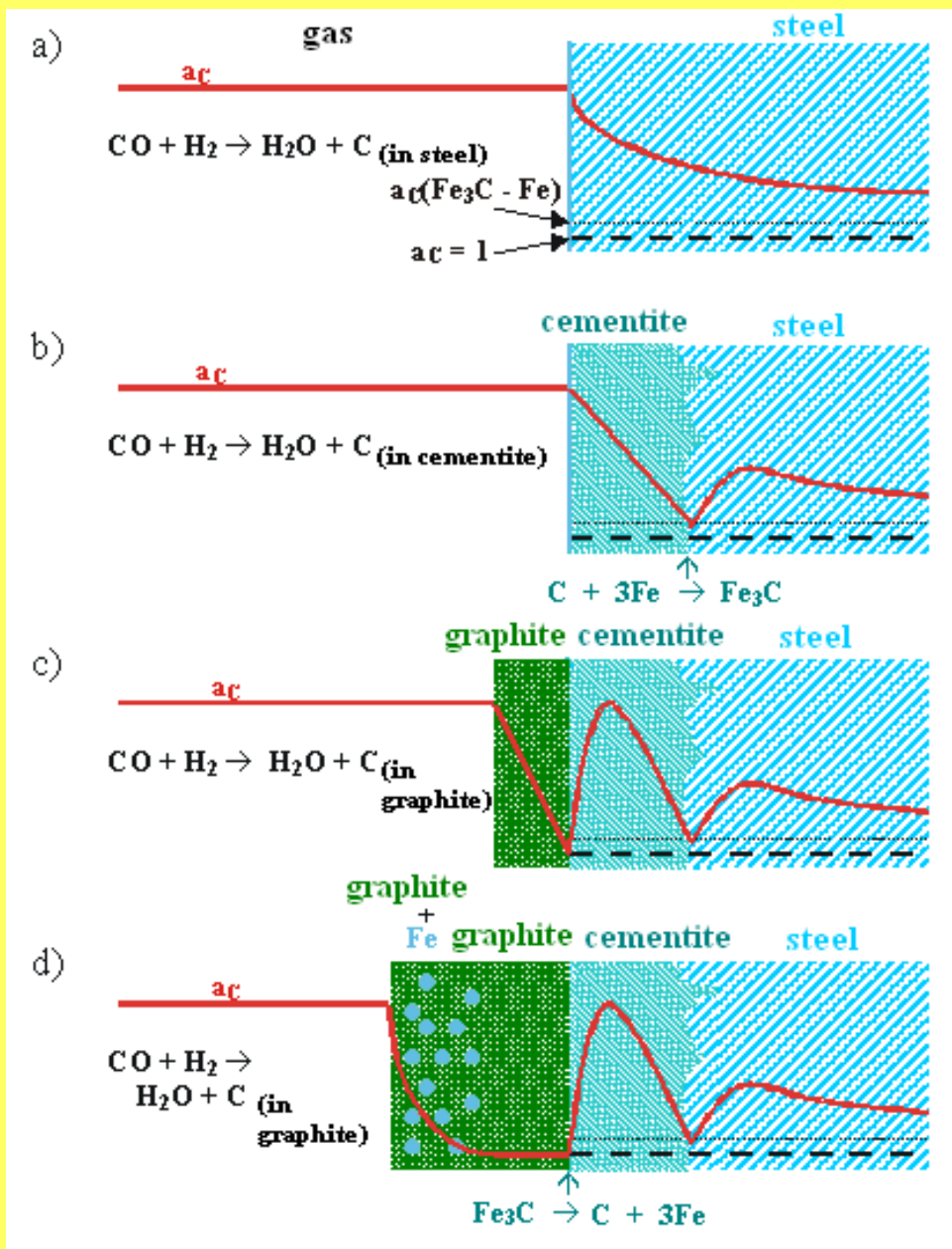


# CONCLUSION

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

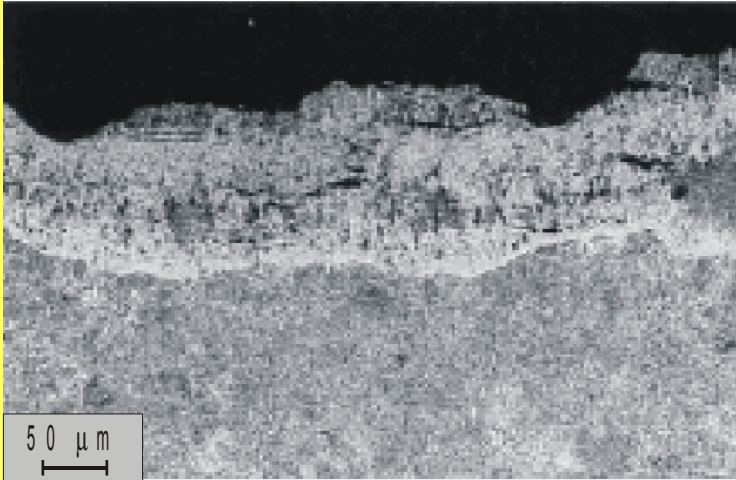
# Coatings in the protection against corrosion at highly carburizing atmospheres

# The mechanism of a metal-dusting corrosion of iron and low-alloy steels

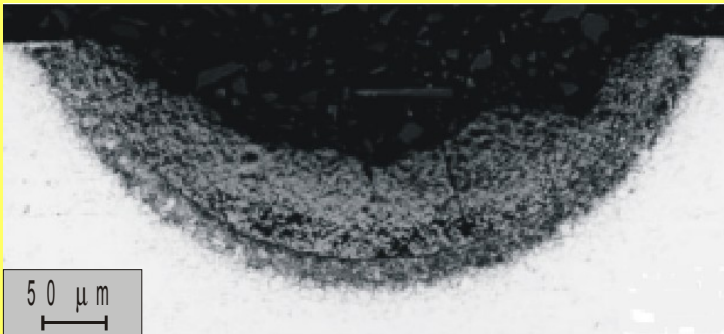




# Typical corrosive destructions

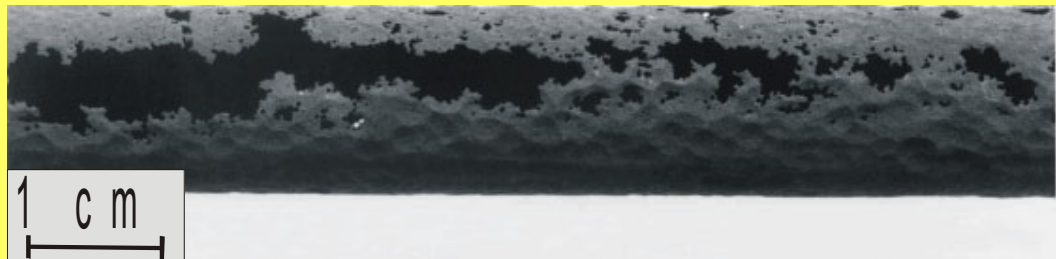
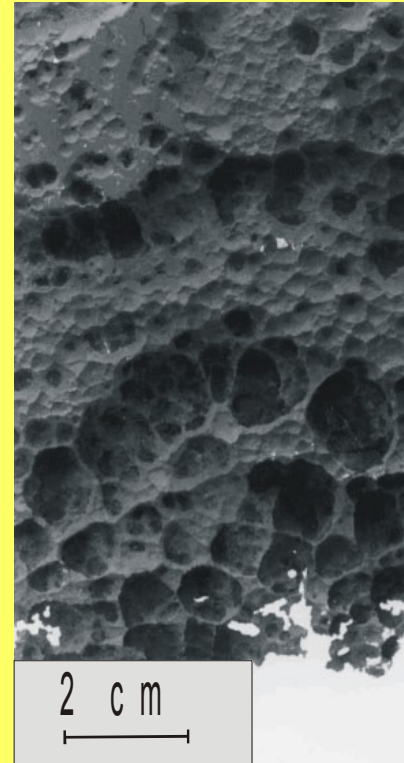
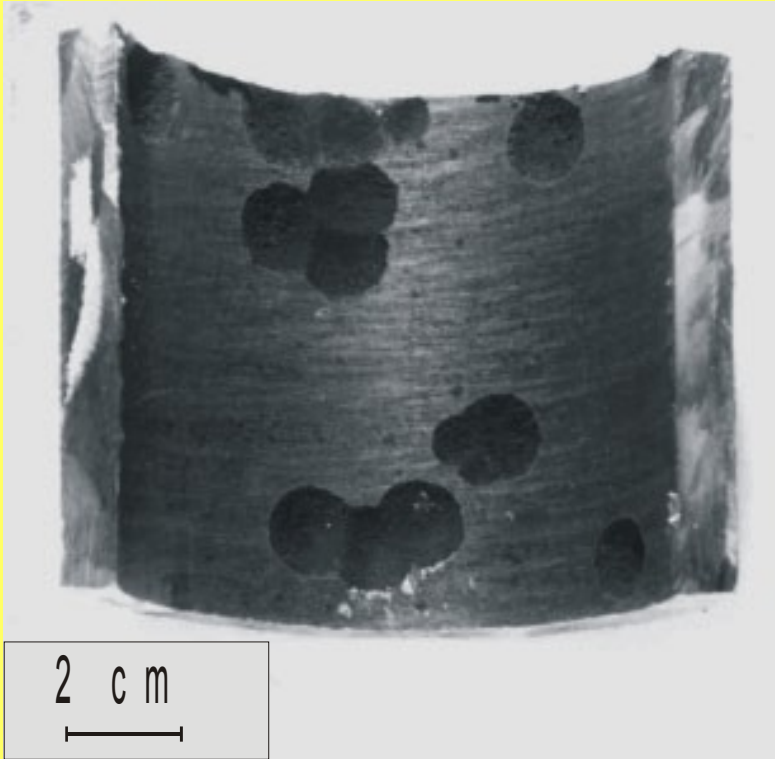


low-alloy steel



alloyed steel

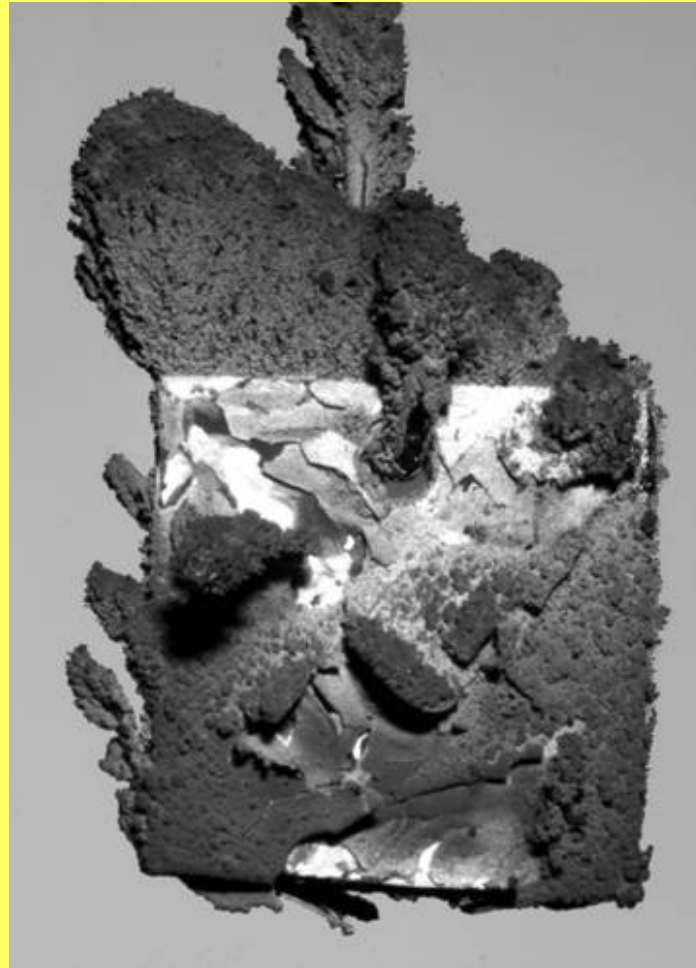
# Typical corrosive destructions



# Typical corrosive destructions

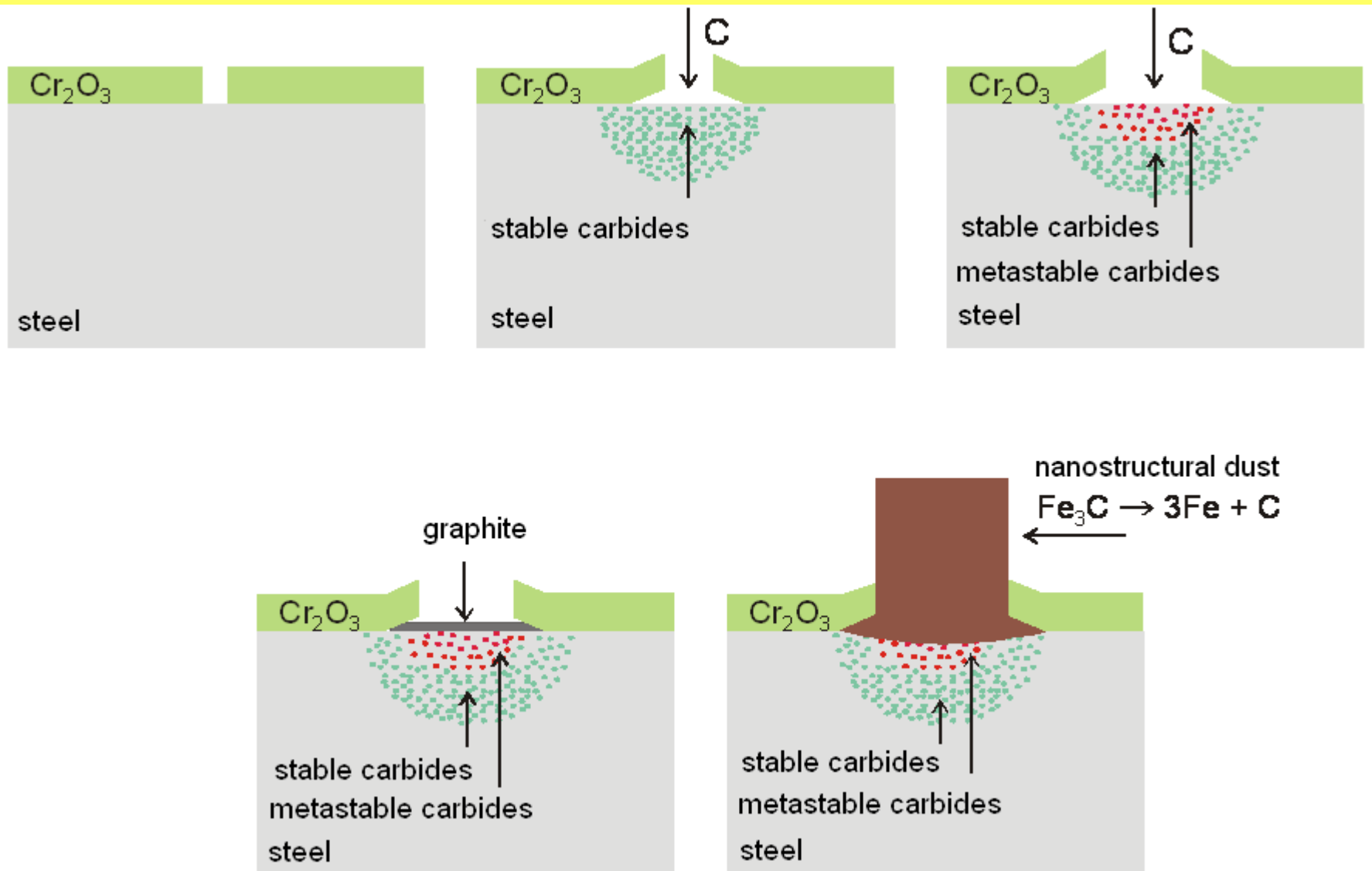


The 9Cr-1Mo steel sample after 3 hours reaction in propane-butane atmosphere at a temperature of 1173 K



10 mm

# The mechanism of a metal-dusting corrosion of high alloyed steels

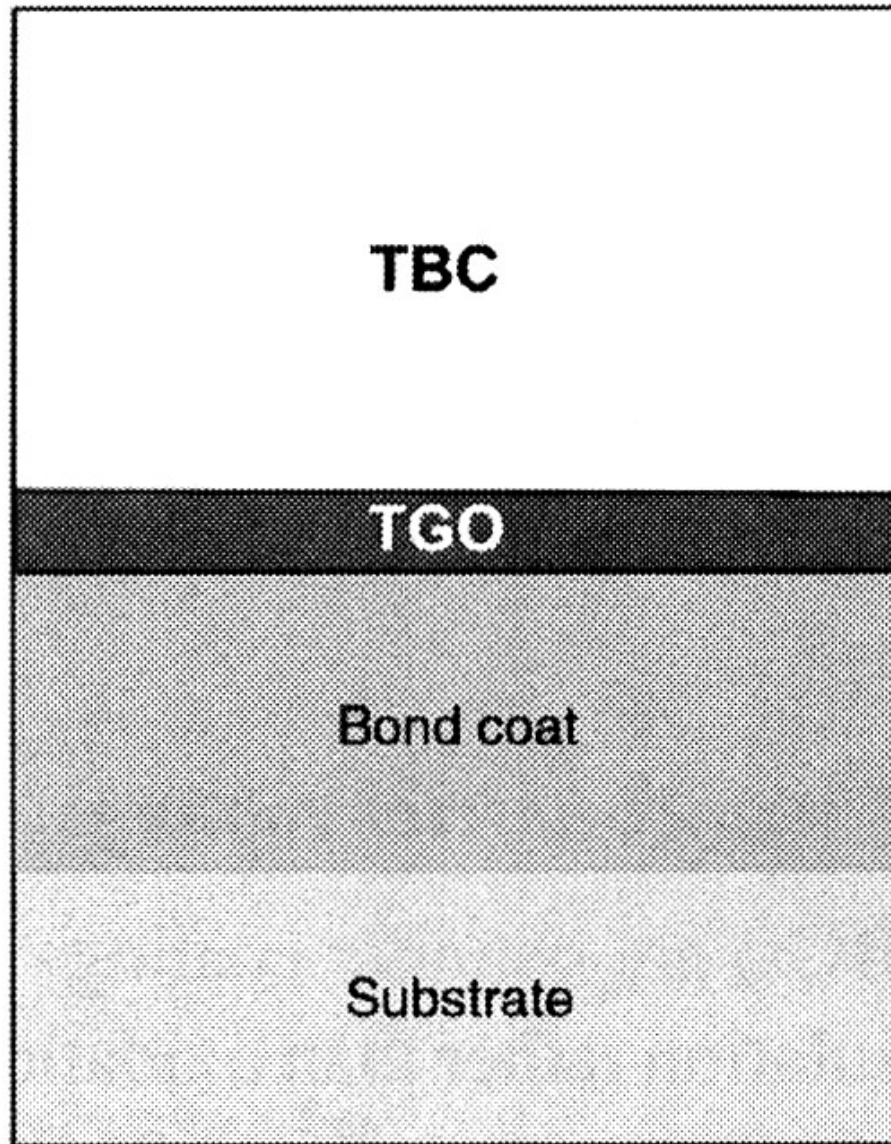


# CONCLUSION

In spite of long-term studies of metal dusting corrosion, no rational basis has been created for decreasing the rate of this form of high temperature corrosion. Further studies are required to control this detrimental phenomenon.

# Thermal barrier coatings (TBC)

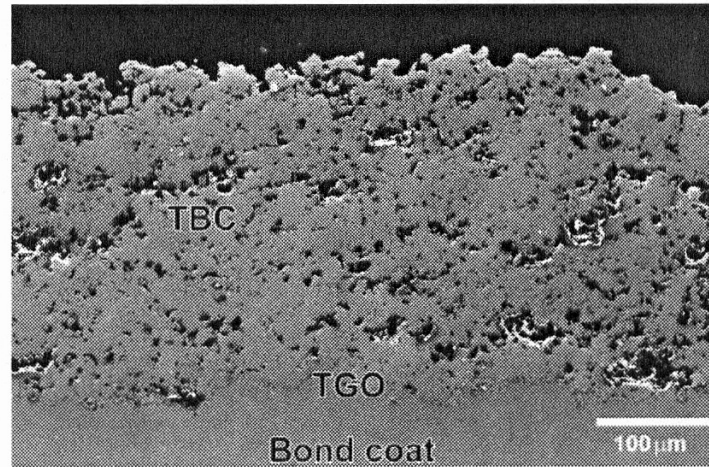
# Scheme of a typical TBC system



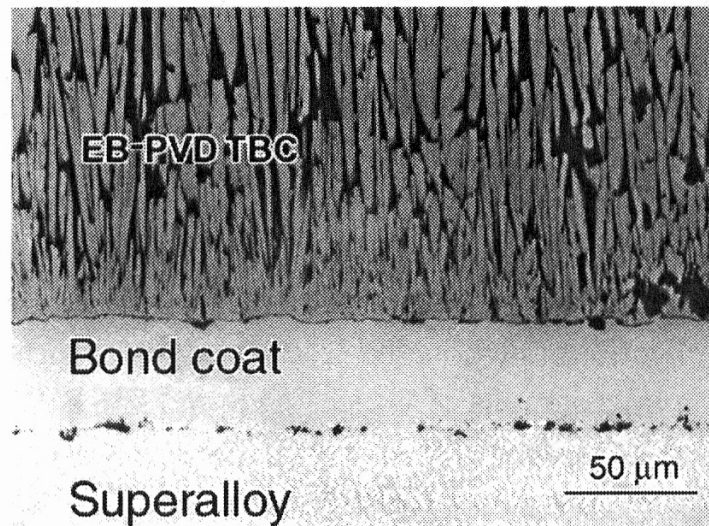


# Cross-sections of TBC coatings

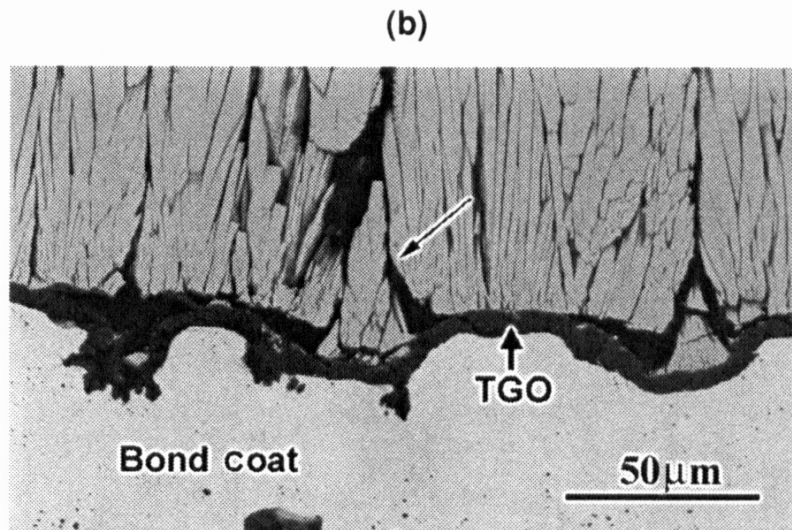
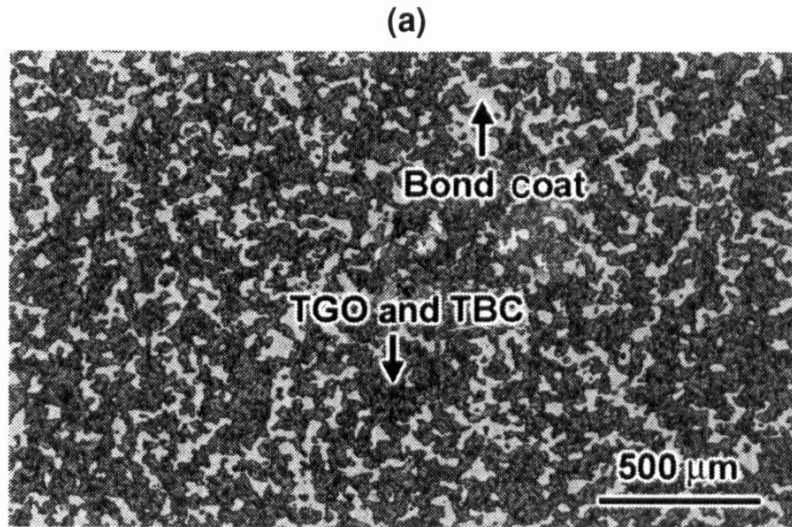
(a)



(b)



# Surface and cross-sections of a layer of TBC protective coating after oxidation

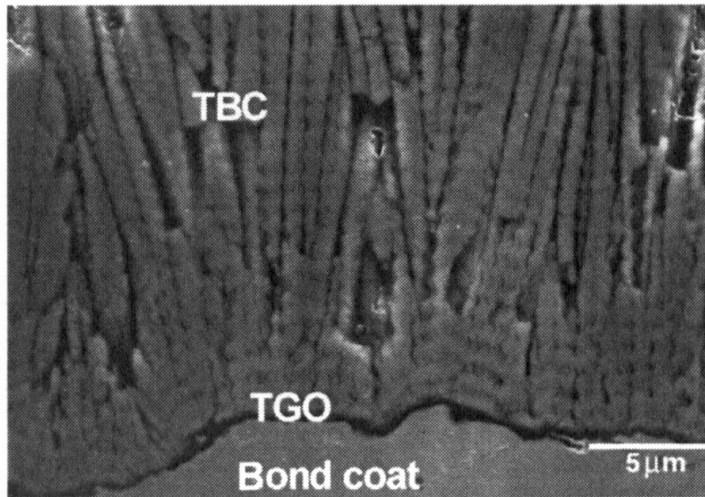


EB-PVD YSZ TBC

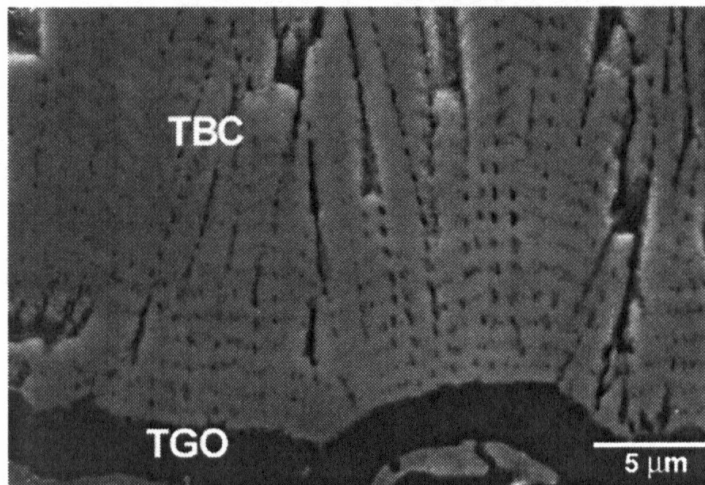
Pt-modified bond coat

# Cross sections of a layer of TBC protective coating after oxidation

(a)

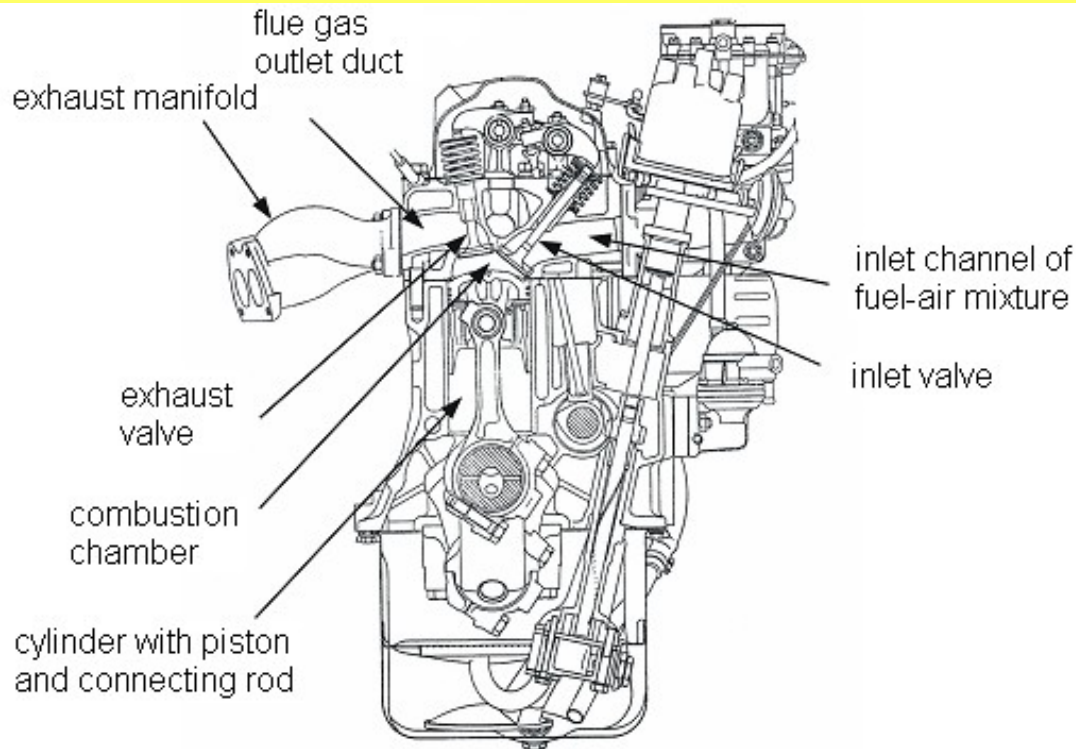


(b)



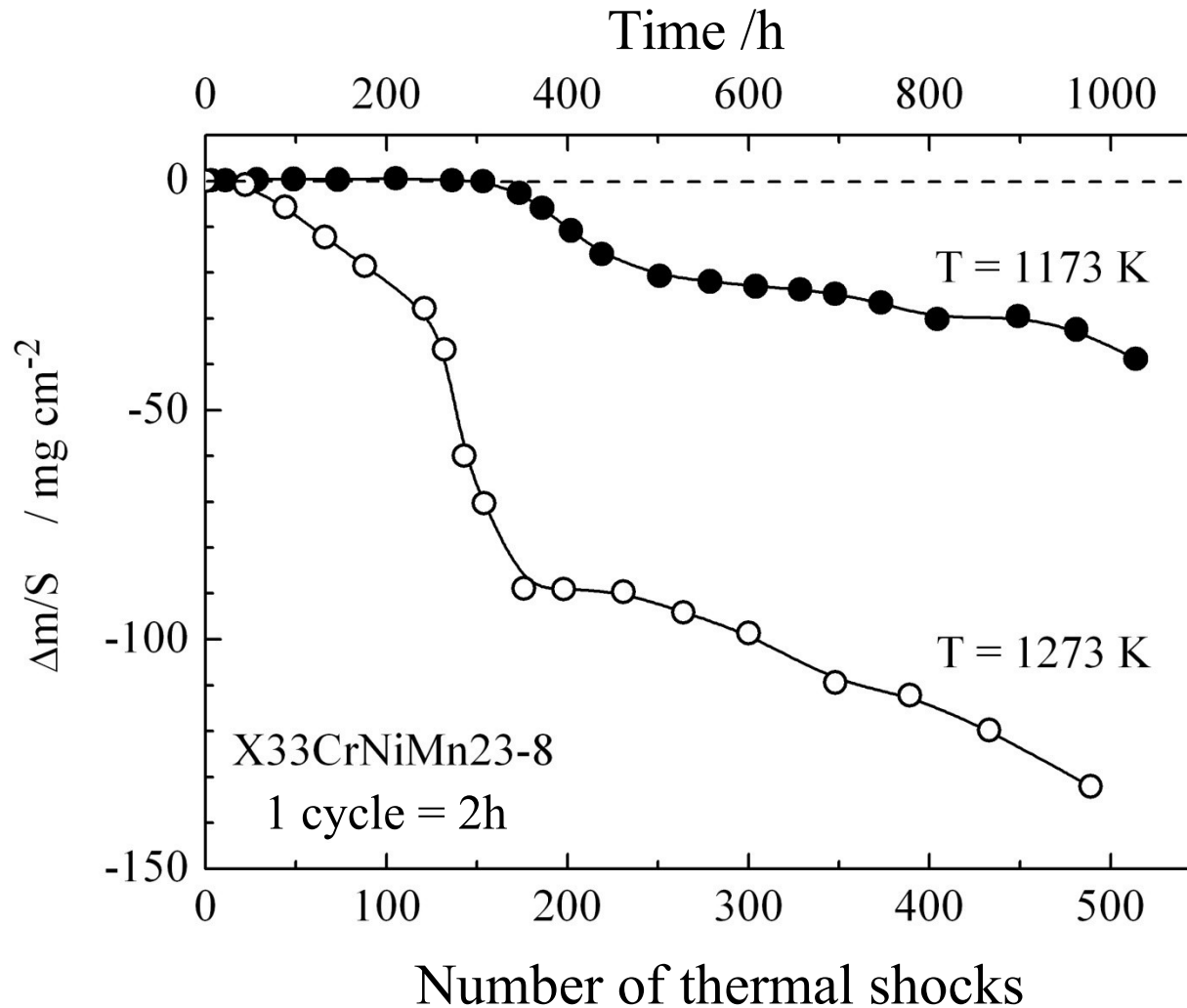
EB-PVD YSZ TBC

# Cross section of four-cylinder in-line engine with spark ignition, Fiat

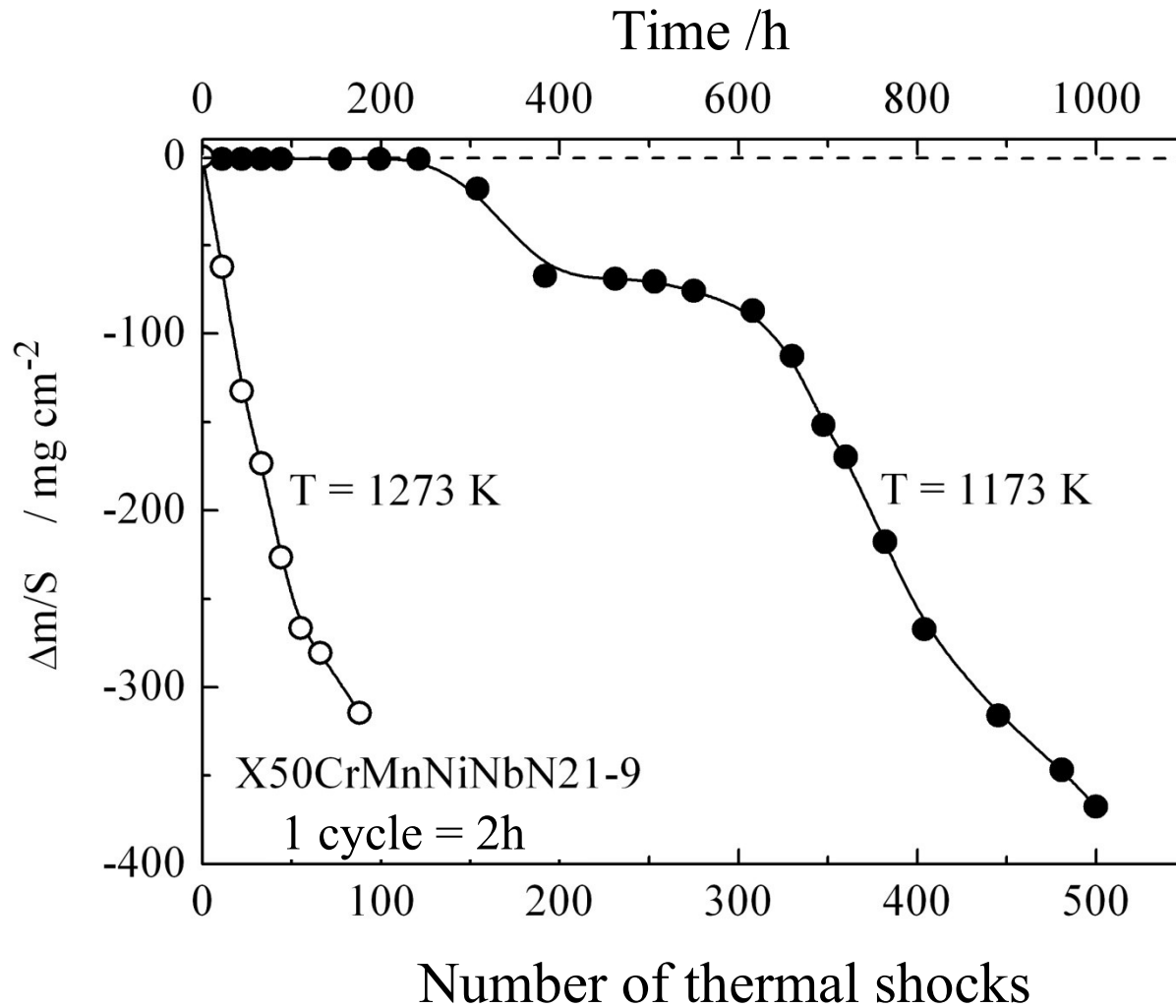


M. Bernhardt, S. Dobrzyński, E. Loth, *Silniki samochodowe*,  
Wydawnictwo Komunikacji i Łączności, Warszawa, 1988, s.327

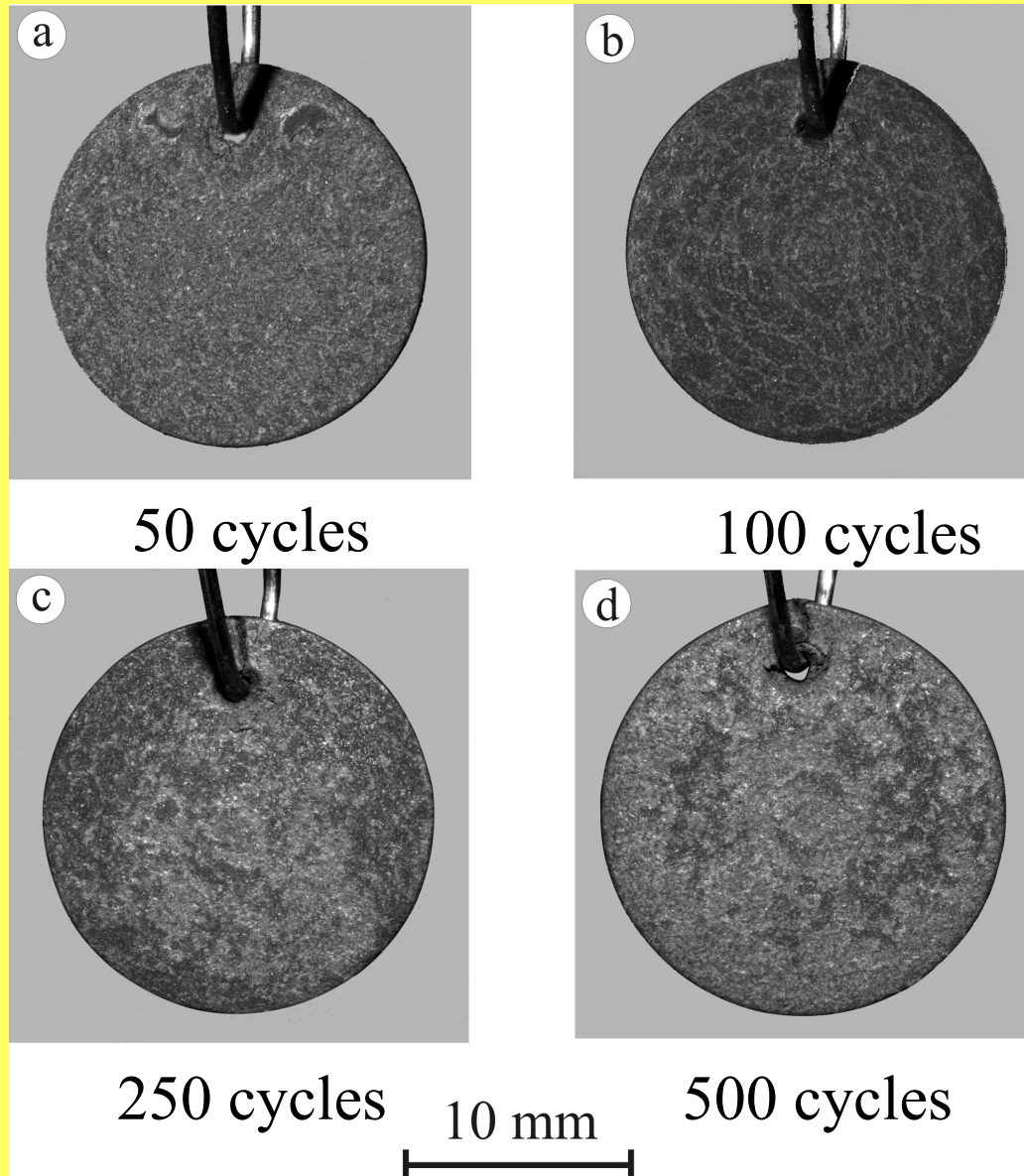
# The results of oxidation of X33CrNiMn23-8 steel under thermal shock conditions



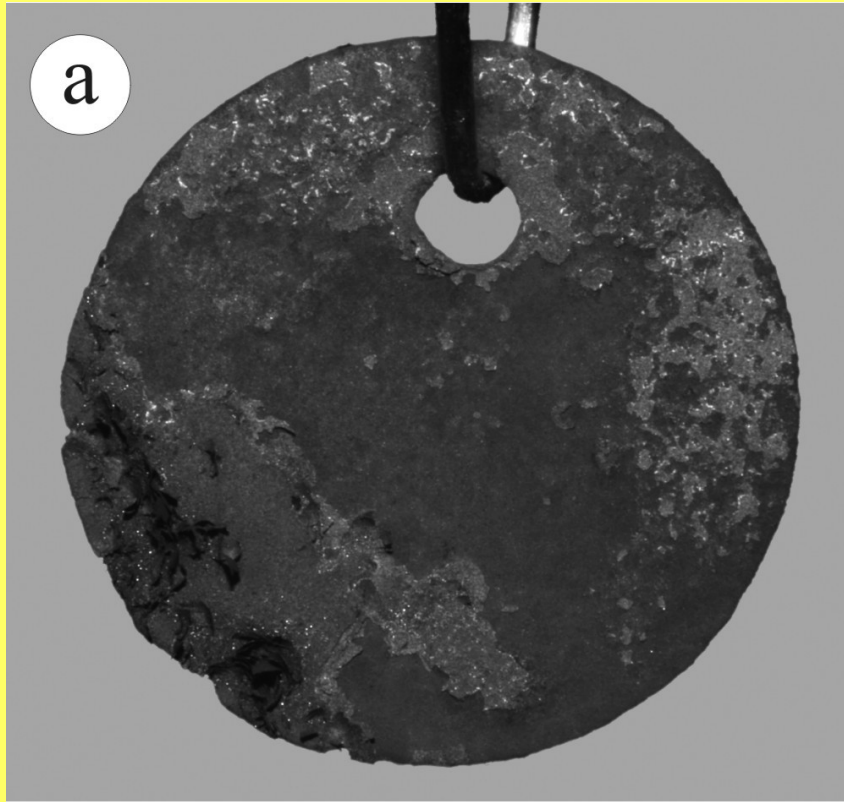
# The results of oxidation of X50CrMnNiNbN21-9 steel under thermal shock conditions



# Images of sample surfaces of X33CrNiMn23-8 steels under thermal shock conditions at 1173 K



The photographs of surfaces of uncovered  
X50CrMnNiNbN21-9 steel sample  
after different thermal shock numbers



300 cycles

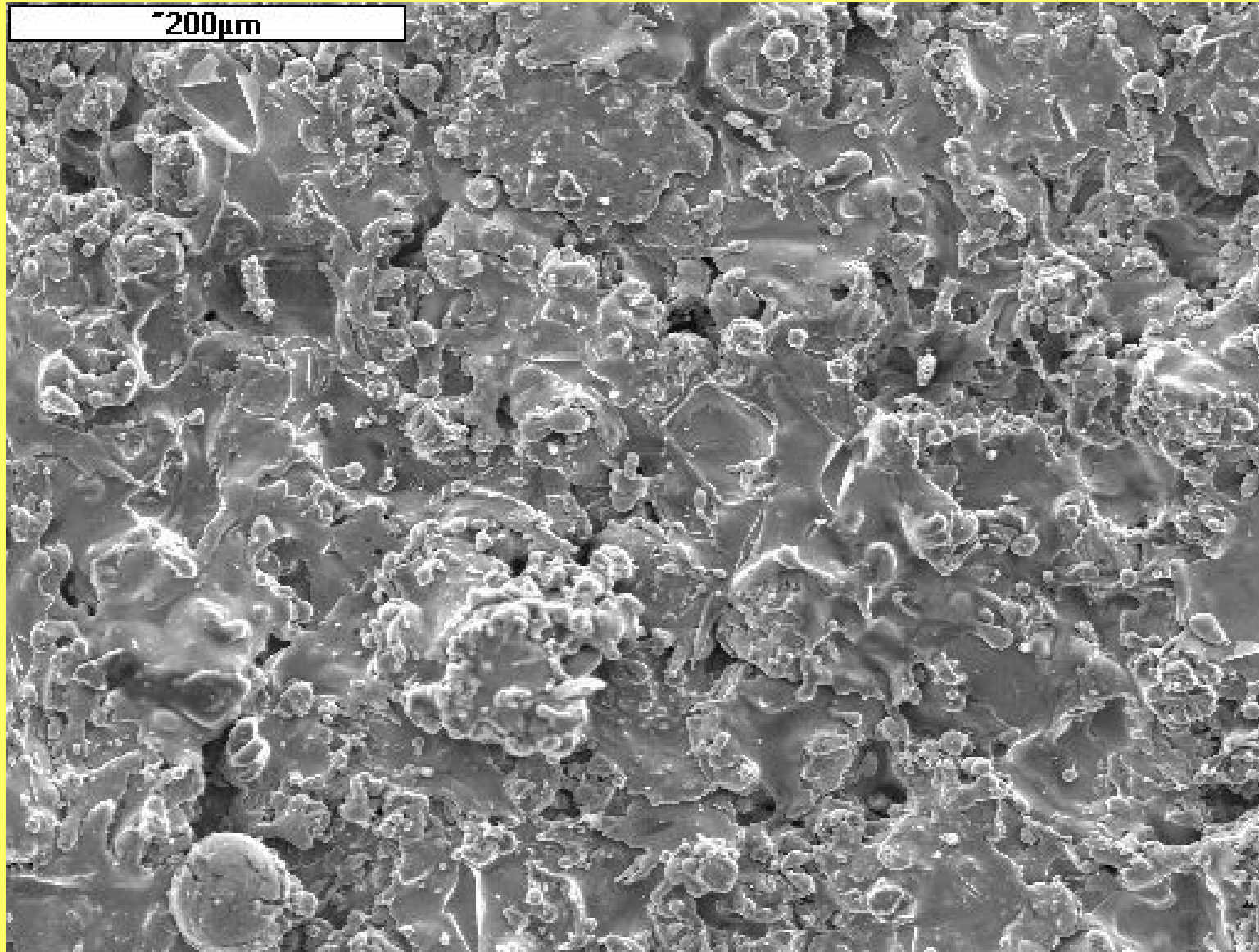


500 cycles

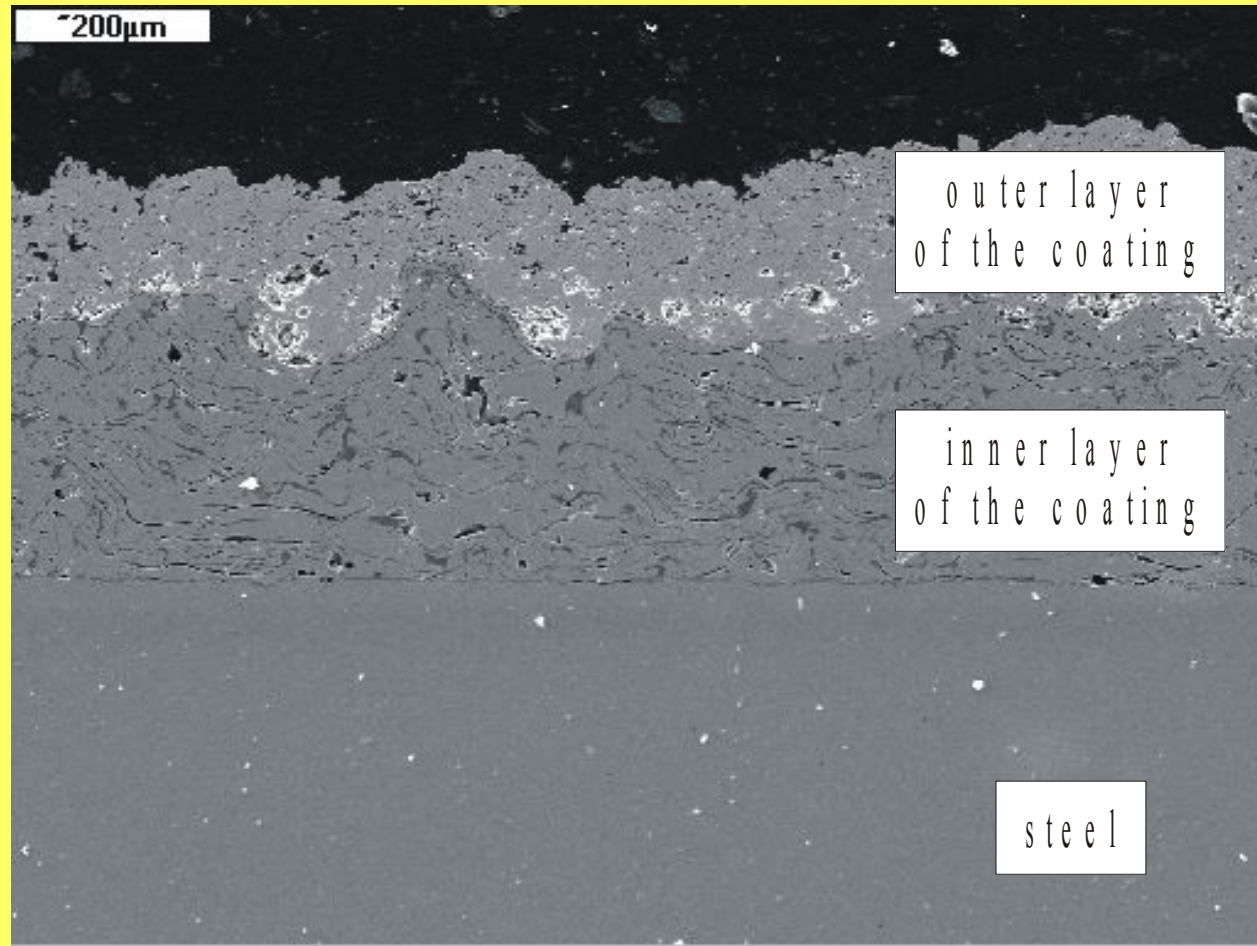
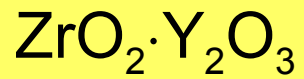
10 mm



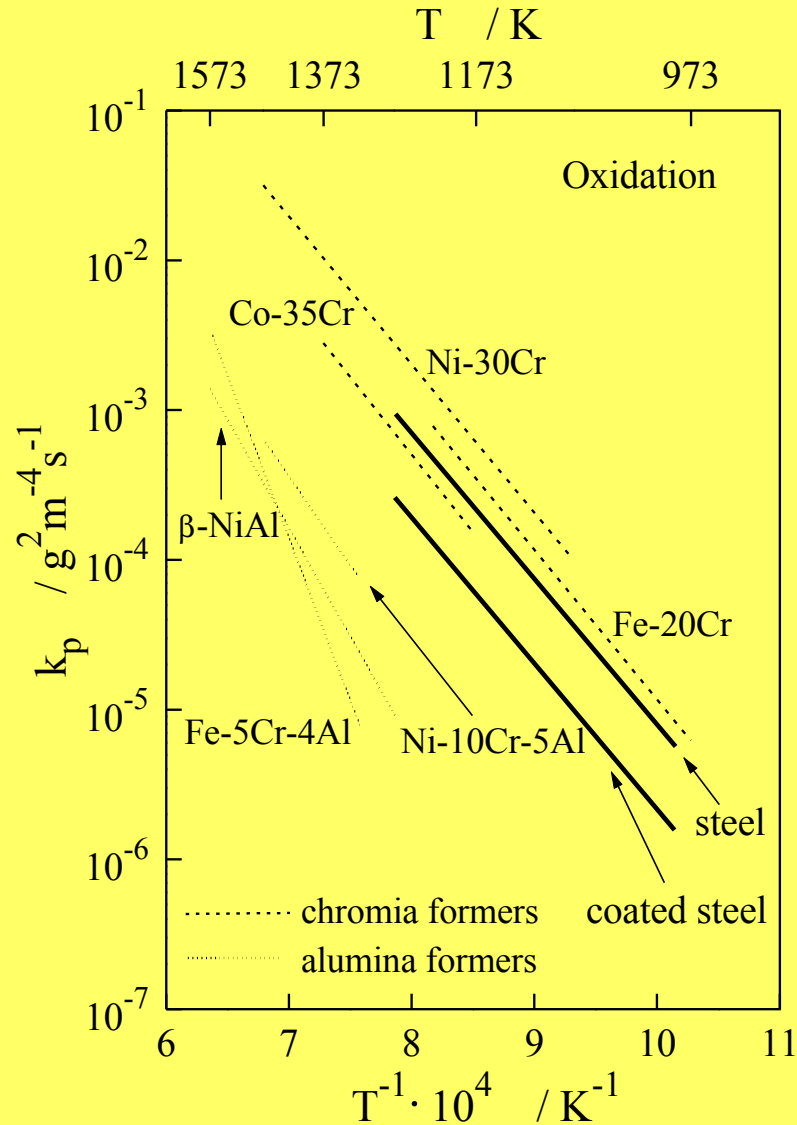
# Surface layer of the TBC



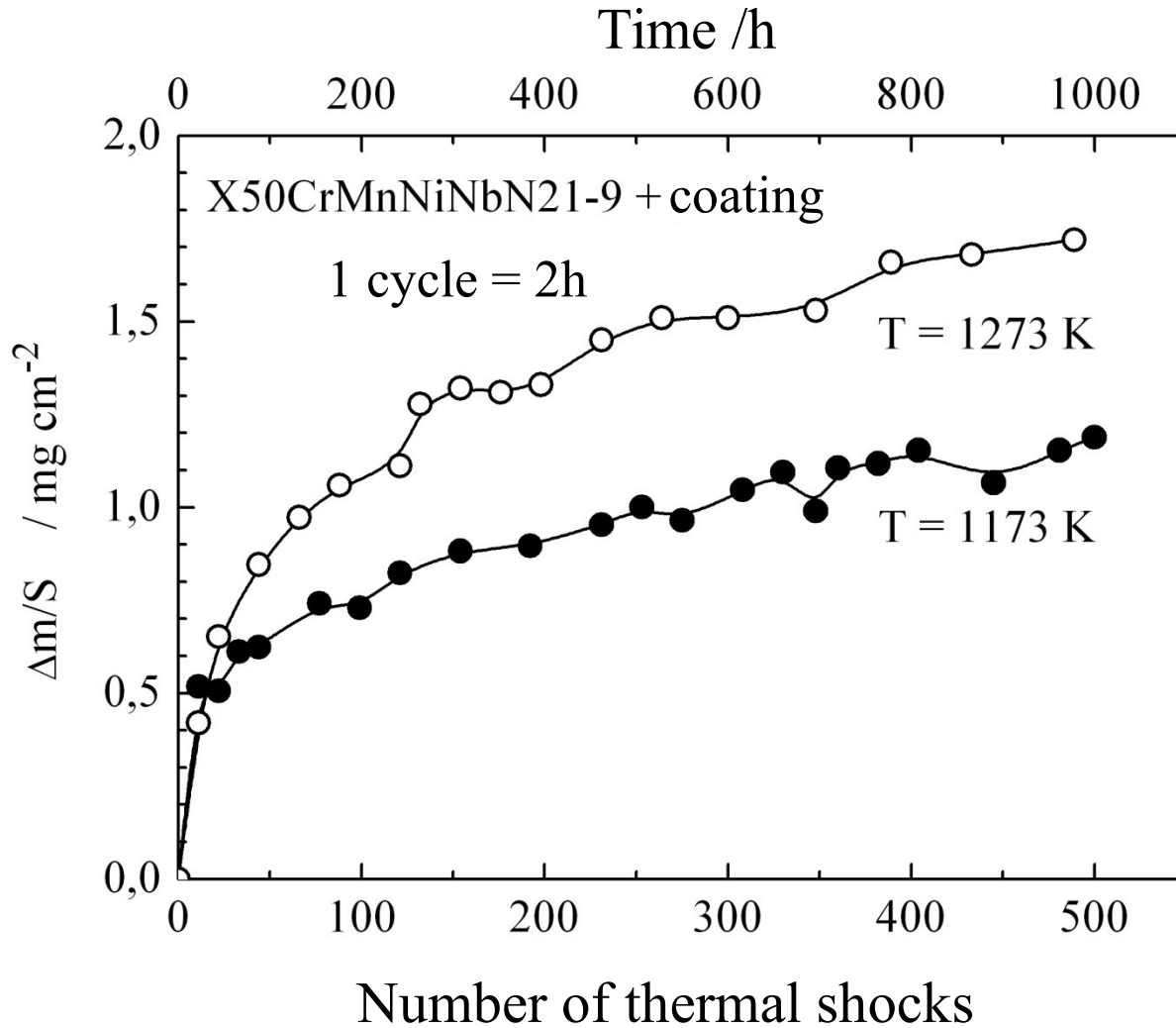
# Cross-section of a layer of TBC coating deposited on steel



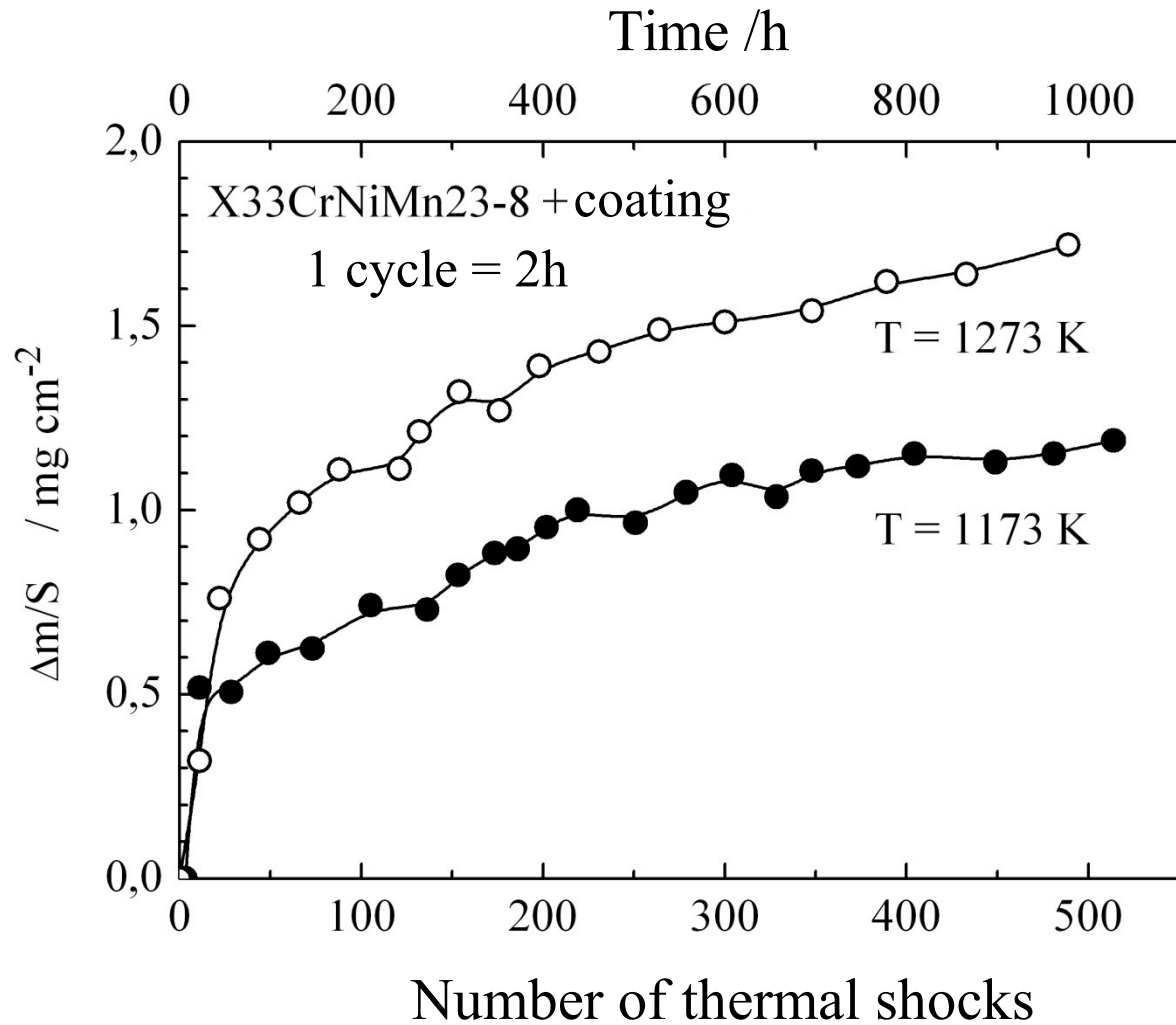
# Temperature dependence of the oxidation rate of steel coated with a protective coating



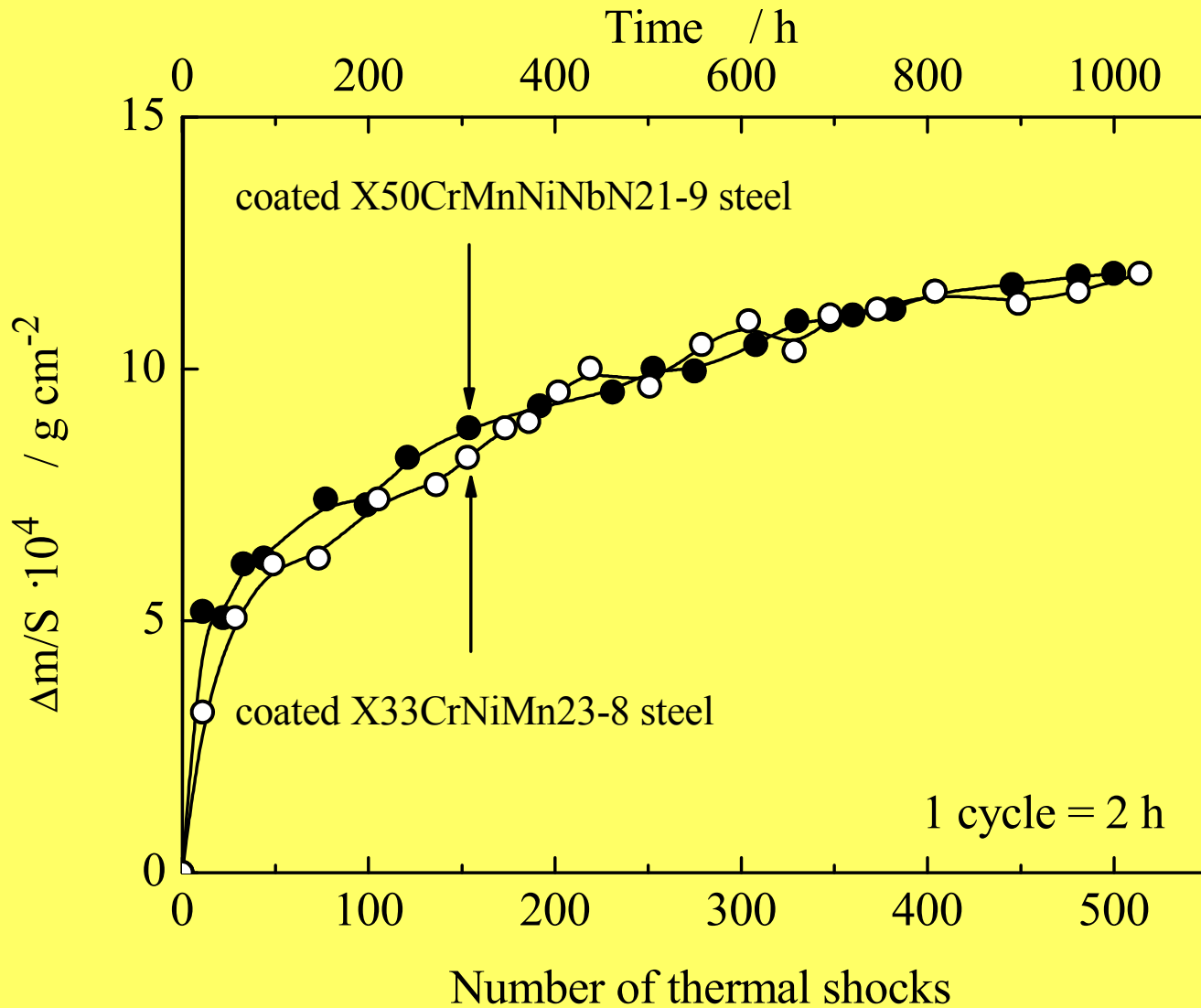
# The results of oxidation of X50CrMnNiNbN21-9 steel coated with a protective coating under thermal shock conditions



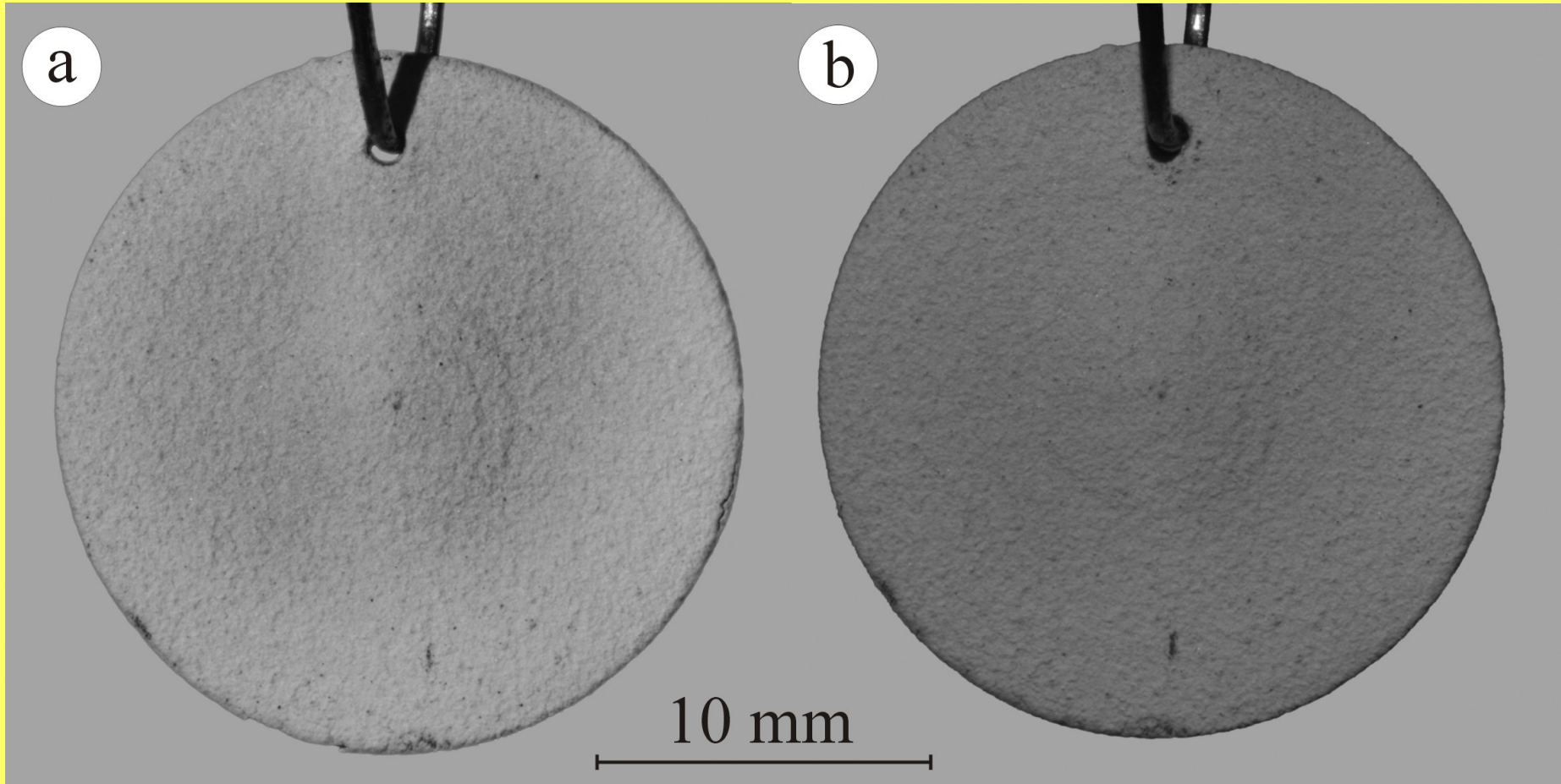
# The results of oxidation of X33CrNiMn23-8 steel coated with a protective coating under thermal shock conditions



# The results of oxidation of two valve steels coated with a protective coating under thermal shock conditions



The photographs of the surface sample of X33CrNiMn23-8 steel covered with hybrid coating in 1173 K



before oxidation

after 500 cycles

The influence of yttrium on kinetics of chromia scale growth on Fe-Cr-Ni base steels



# EXPERIMENTAL

## **Materials:**

X33CrNiMn23-8, X50CrMnNiNbN21-9, X53CrMnNiN20-8,  
X55CrMnNiN20-8

## **Specimens:**

- discs: diameter 20 mm, thickness 1 mm
- weight: 1 g

## **Yttrium deposition:**

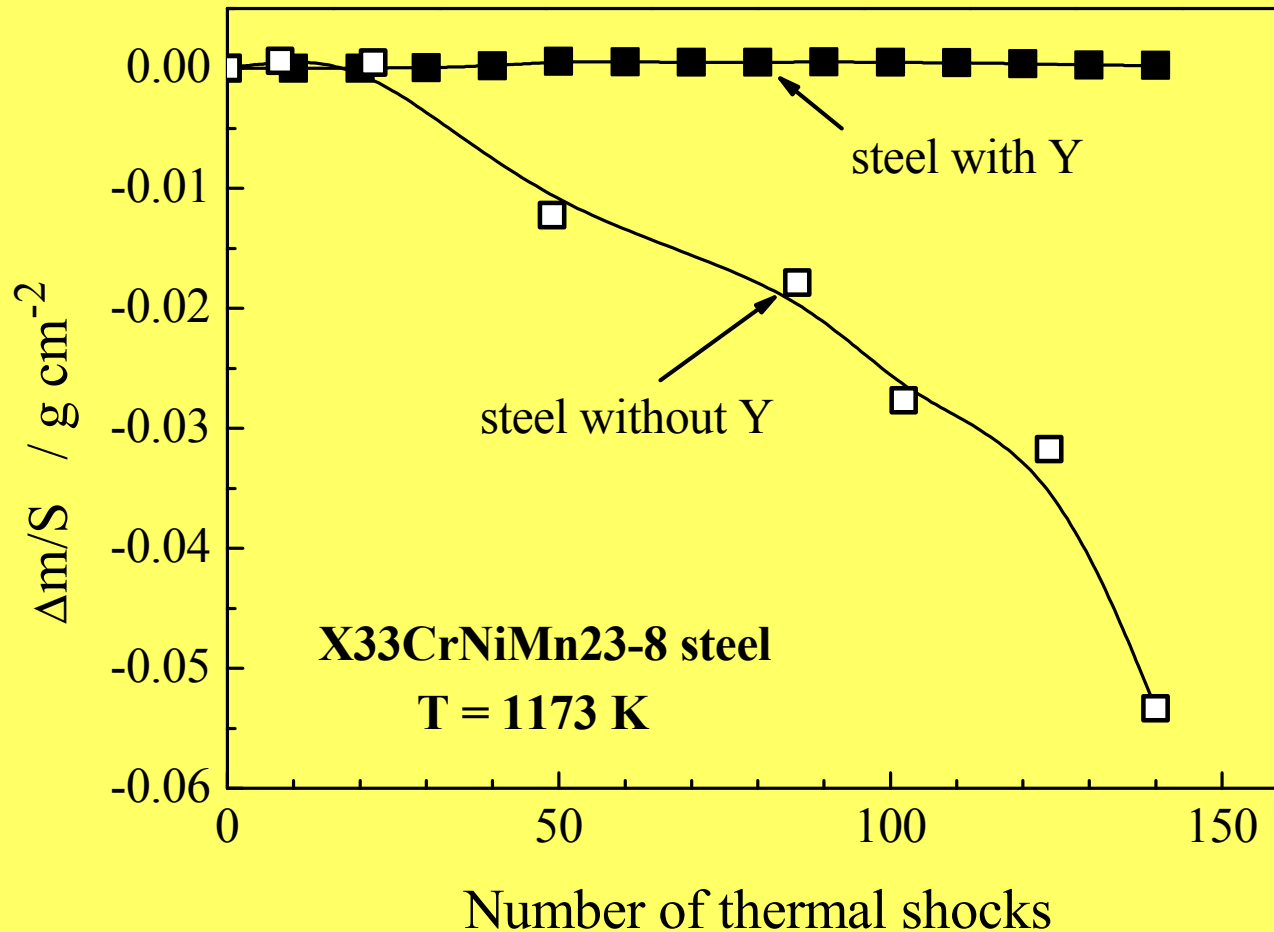
- degreasing
- electrochemical treatment:  
0.01 m  $Y(NO_3)_3$  solution in  $C_2H_5OH$   
 $U = 10V$ ;  $I = 10 \text{ mA}$ ;  $t = 45 \text{ s}$
- drying:  $T = 50 \text{ }^\circ\text{C}$ ;  $t = 10 \text{ min.}$
- annealing:  $T = 400 \text{ }^\circ\text{C}$ ;  $t = 30 \text{ min.}$

## **Corrosion tests under thermal shock conditions:**

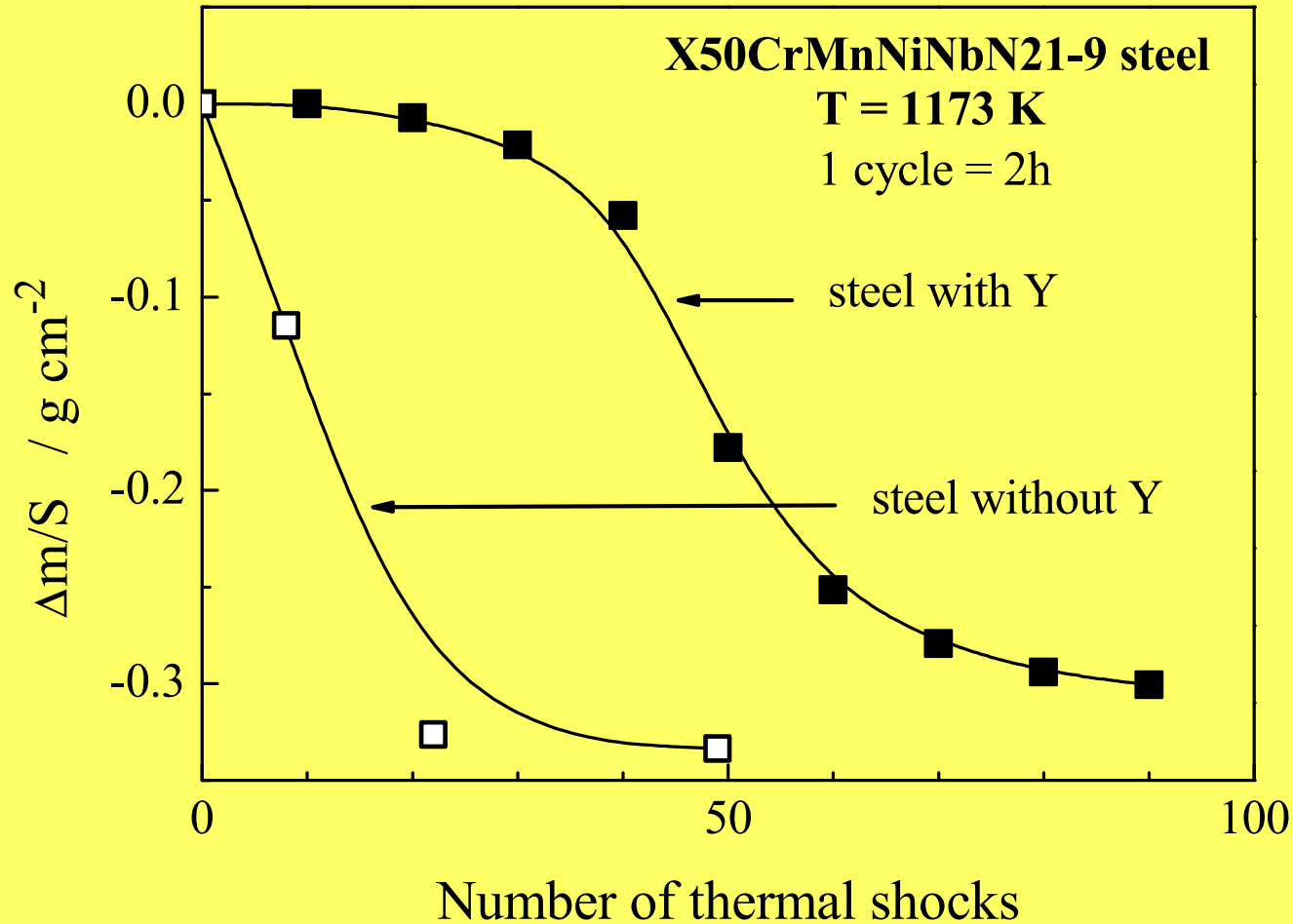
- reactive atmosphere: combustion gases of diesel oil with 10 wt. % addition of FAME (B10)
- temperature range: 295 - 1173 K
- time of experiments: 150 shocks x 2 h, quenching cycle: 15 min.

## **SEM, EDX, XRD EXAMINATION**

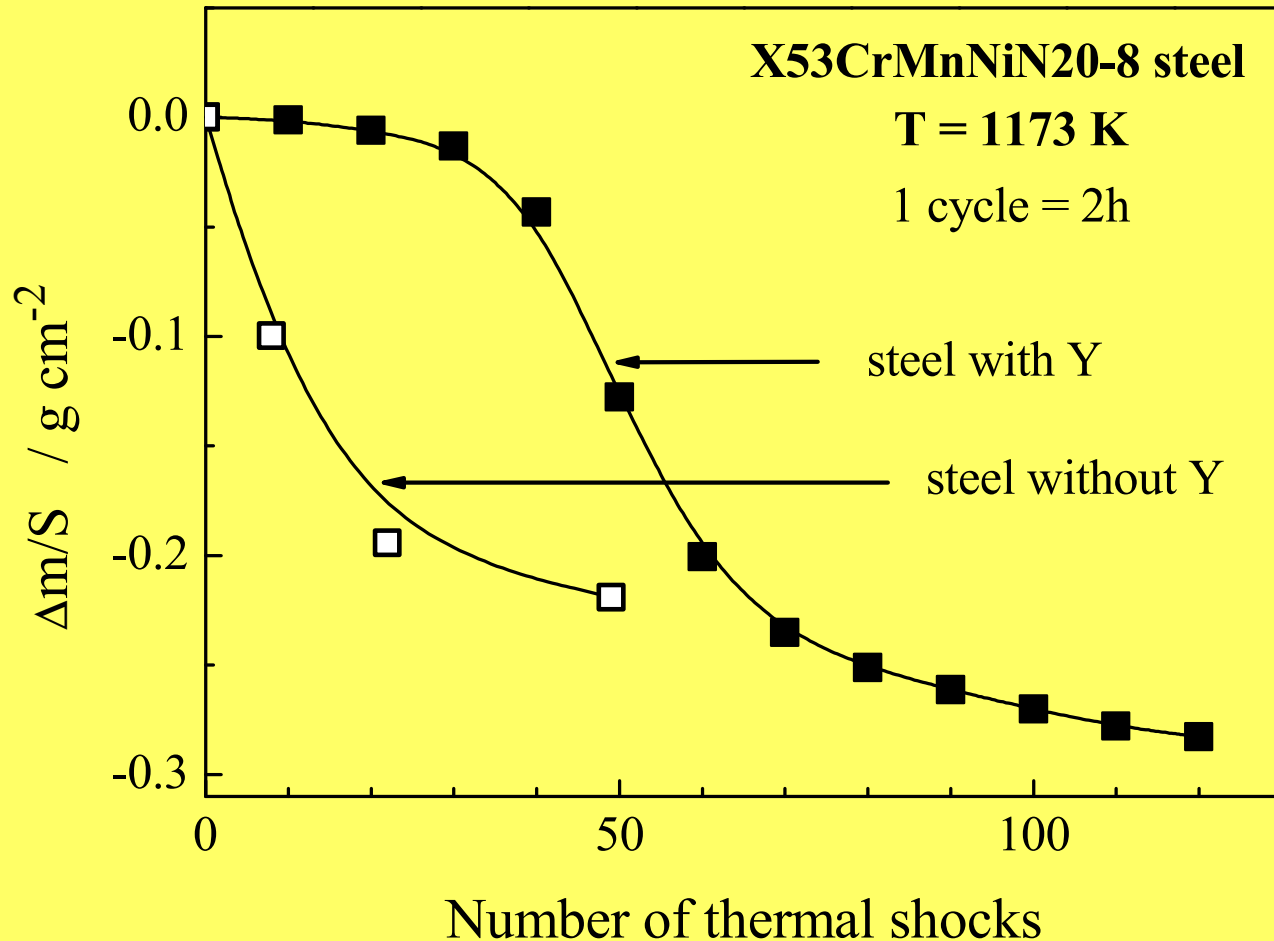
# Corrosion behaviour of the X33CrNiMn23-8 steel uncovered and covered with yttrium under thermal shock conditions



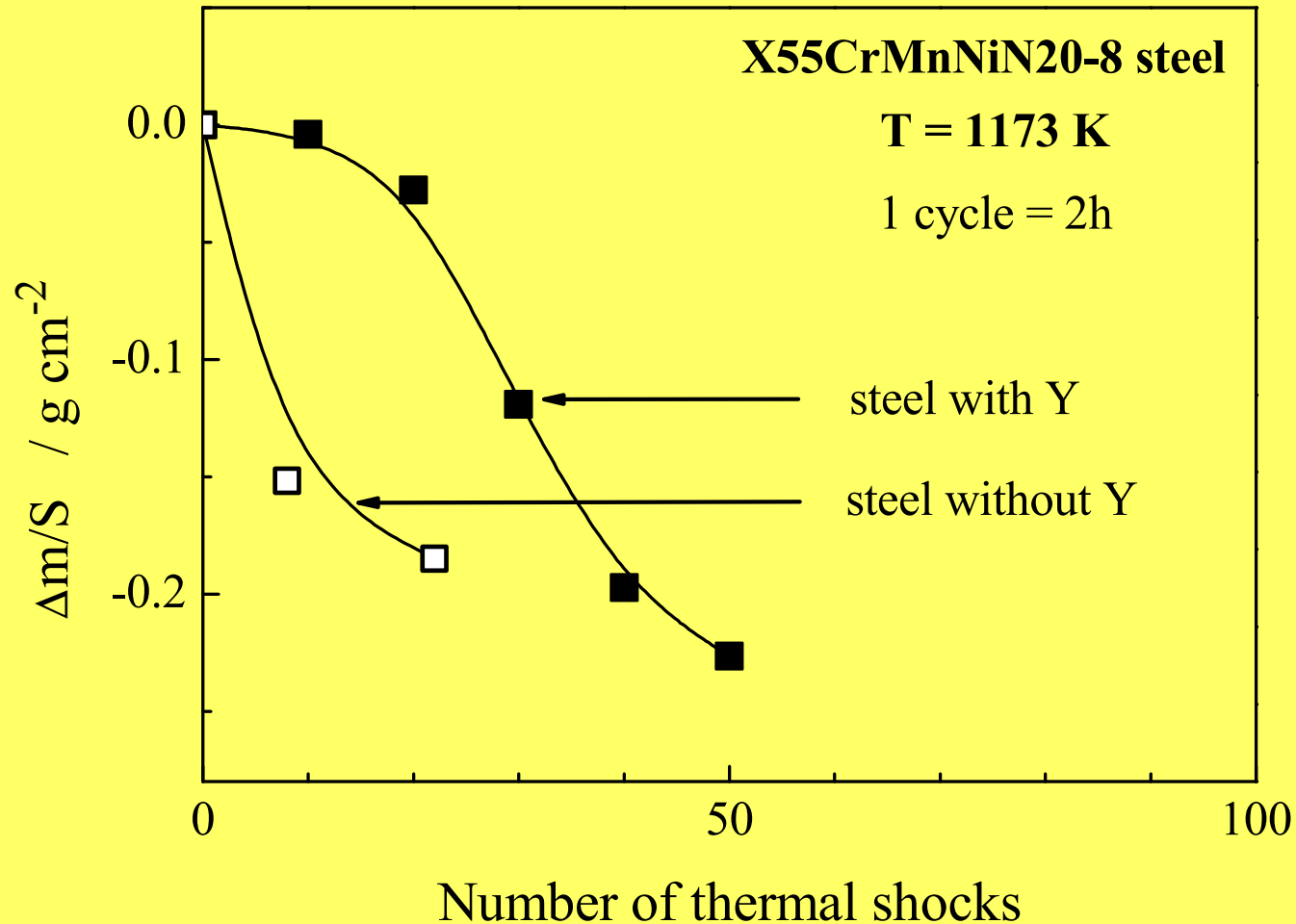
# Corrosion behaviour of the X50CrMnNiNbN21-9 steel uncovered and covered with yttrium under thermal shock conditions



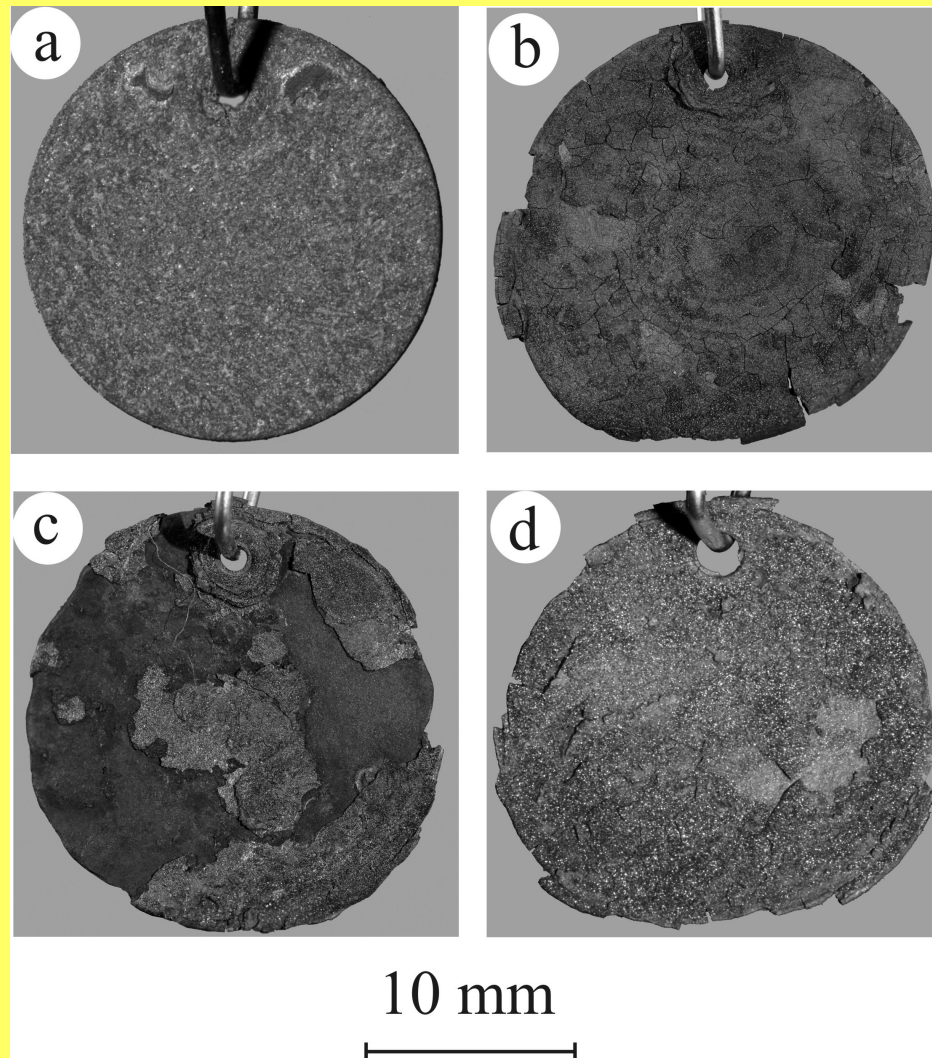
# Corrosion behaviour of the X53CrMnNiN20-8 steel uncovered and covered with yttrium under thermal shock conditions



# Corrosion behaviour of the X55CrMnNiN20-8 steel uncovered and covered with yttrium under thermal shock conditions



# The photographs of surfaces of steel samples coated with yttrium after 100 thermal shocks



a) X33CrNiMn23-8; b) X50CrMnNiNbN21-9; c) X53CrMnNiN20-8; d) X55CrMnNiN20-8

# Conclusion

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The results of thermal shock experiments have demonstrated that small amounts of yttrium electrochemically deposited on the surface of the X33CrNiMn23-8 steel, containing highest chromium concentration ( $> 23$  wt. %), dramatically improves the chromia scale adherence to the surface of this steel, due to selective oxidation of chromium and formation of  $\text{Cr}_2\text{O}_3$  oxide. This effect is not observed in the case of three remaining steels with lower chromium concentration, because of heterogeneous scale formation. From practical point of view, it may be then concluded that engine valves should be produced in the future only from X33CrNiMn23-8 steel covered by yttrium.

# SUMMARY

Up to now, no universal coatings for high temperature applications have been elaborated.



**THE END**