PROSPECTS IN DESIGNING NEW GENERATION OF FUNCTIONAL COATINGS

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MATERIALS USED AS PROTECTIVE COATINGS IN OXIDIZING ATMOSPHERES

Cr – Cr_2O_3

Al – Al_2O_3

Si – SiO_2

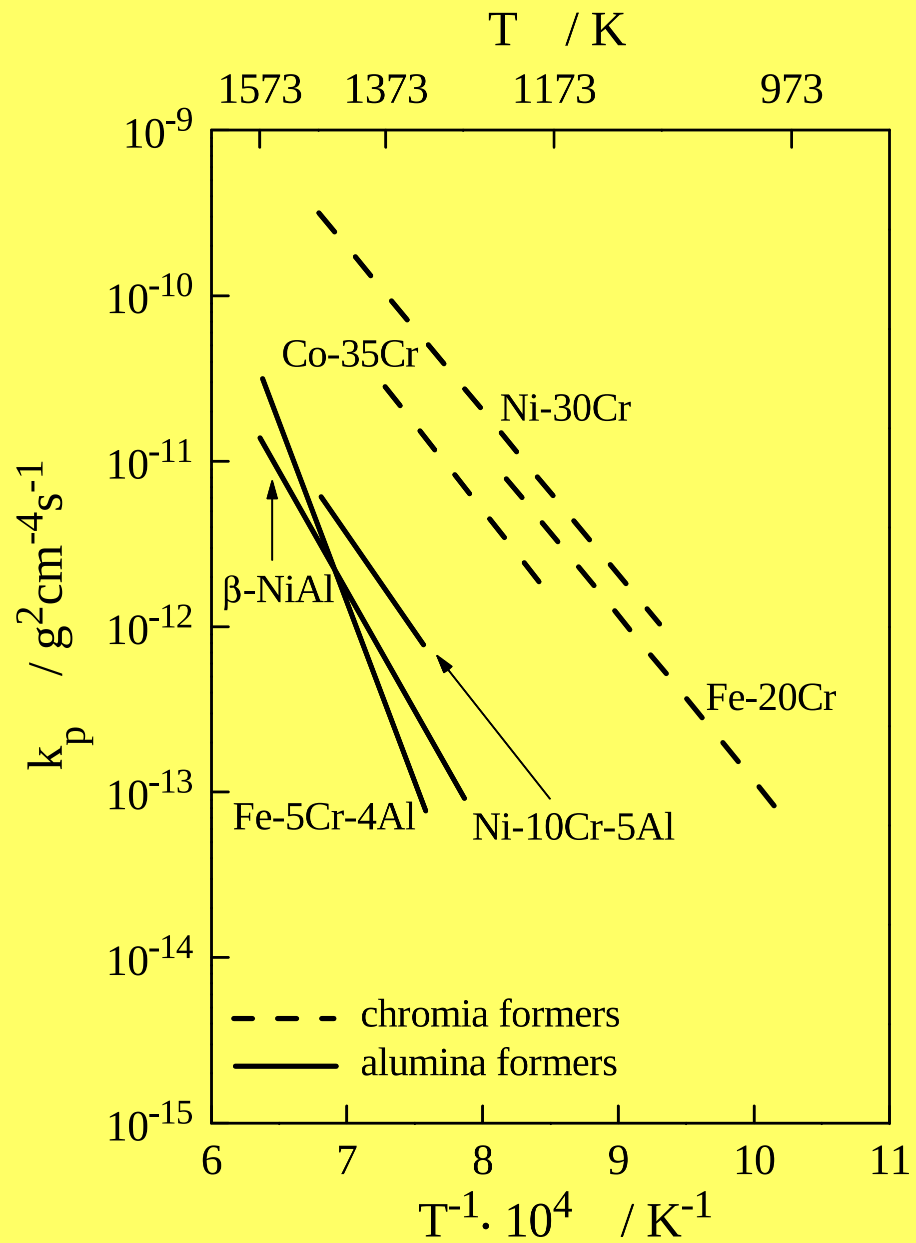
MCrAlY (where M = Co, Ni, Co/Ni) – Al_2O_3, Cr_2O_3

MCrAlY-Si – Al_2O_3, Cr_2O_3

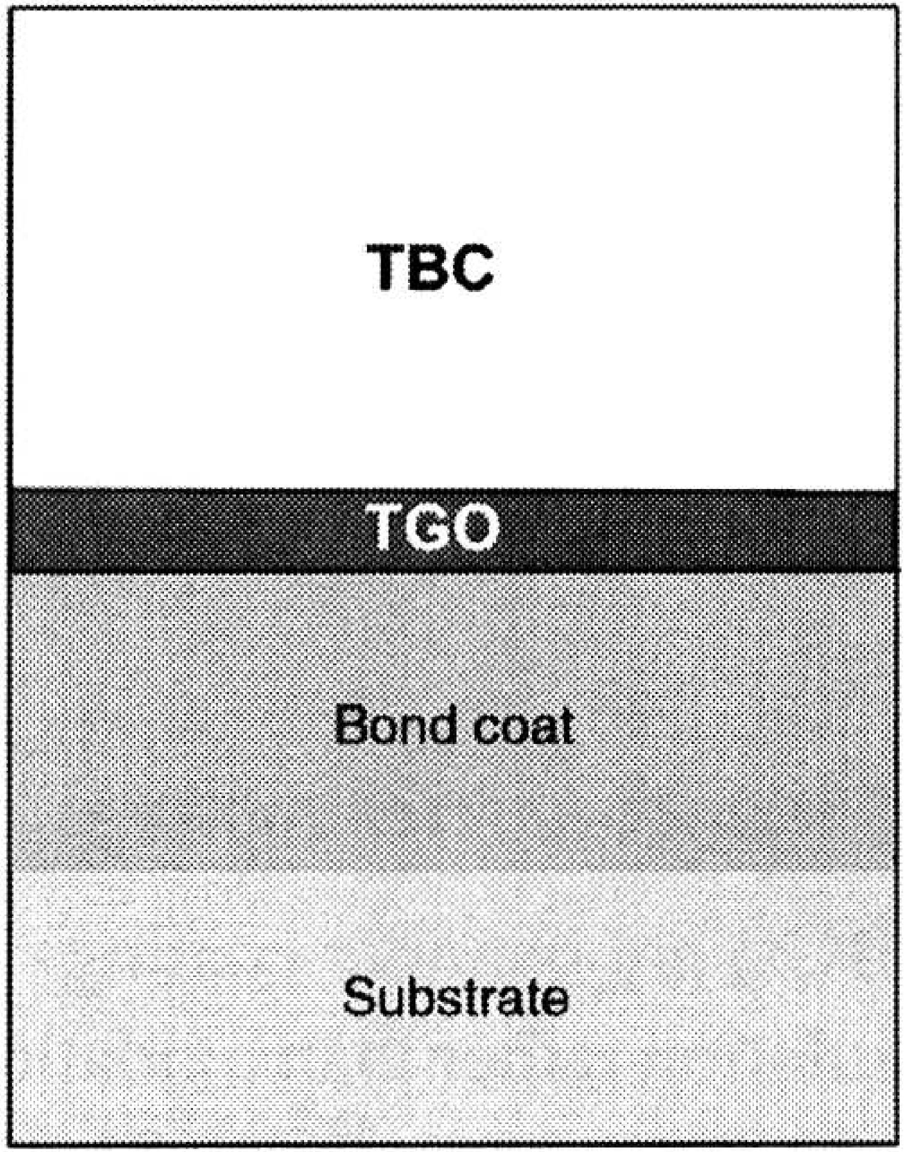
MCrAlY-RE (where RE = Y, Hf, Zr) – Al_2O_3

NiAl – Al_2O_3

Oxidation resistance of selected alloys



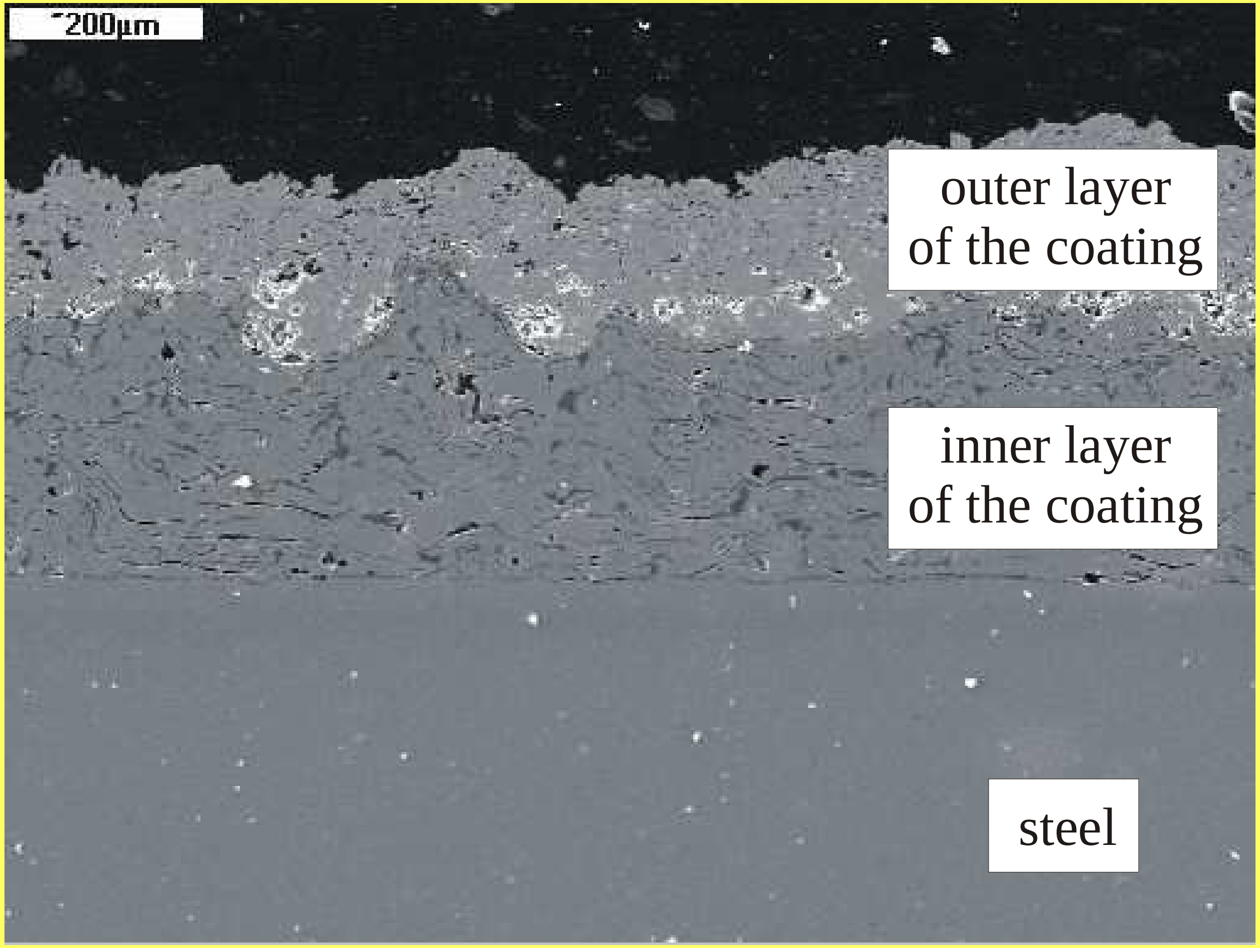
Scheme of a typical TBC system



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

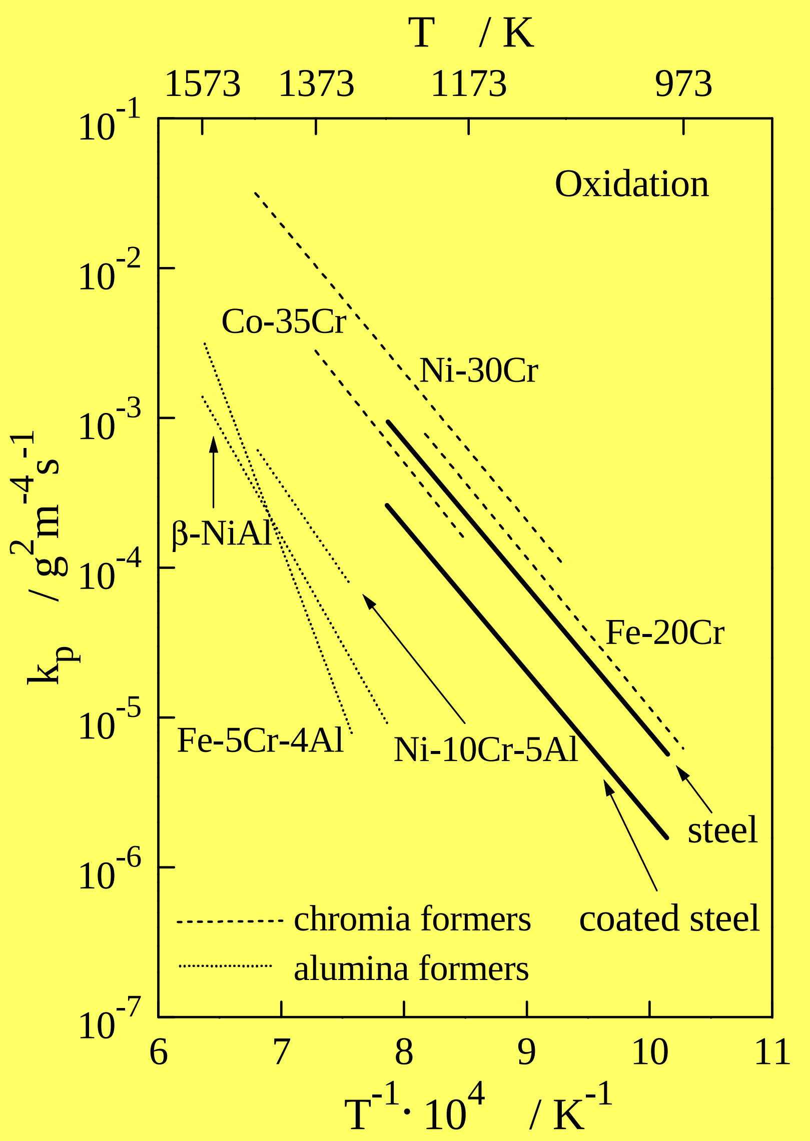
$ZrO_2{\cdot}Y_2O_3$

Ni22Cr10AlY

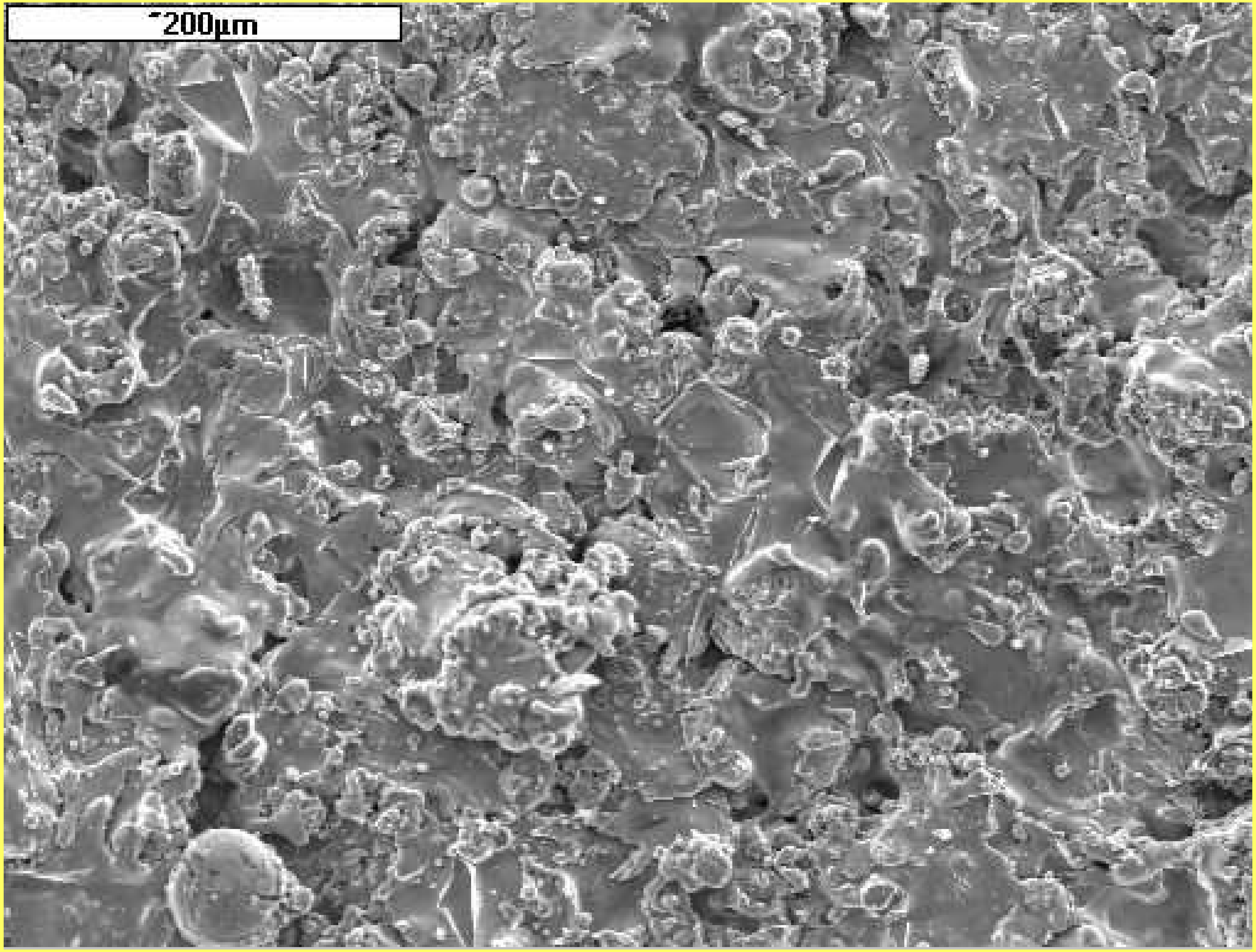


K. Adamaszek, Z. Jurasz, L. Swadzba, Z. Grzesik, S. Mrowec, High Temp. Mater. Proc. **26**, 2007, 115-122.

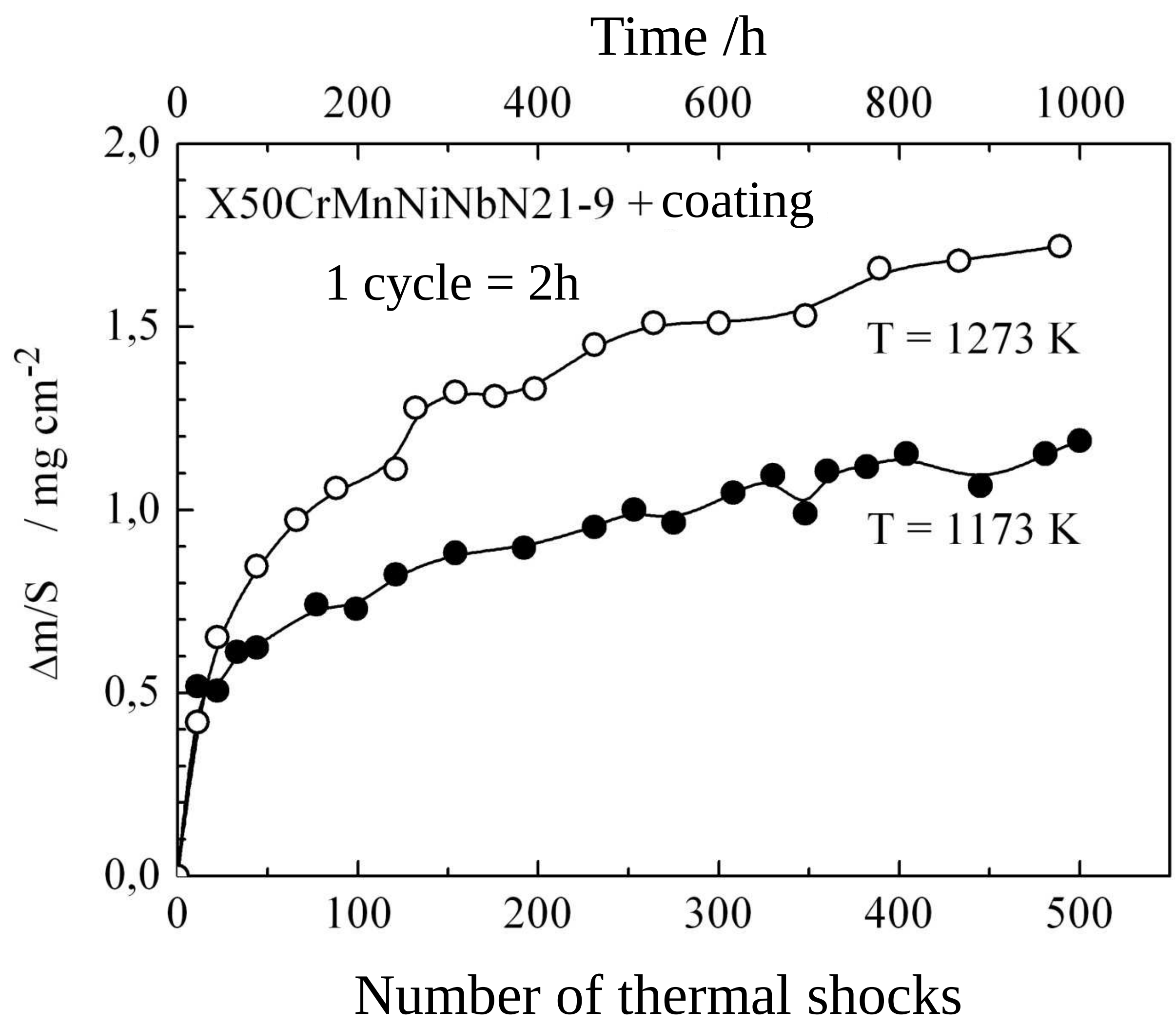
Temperature dependence of the oxidation rate of steel coated with a protective coating



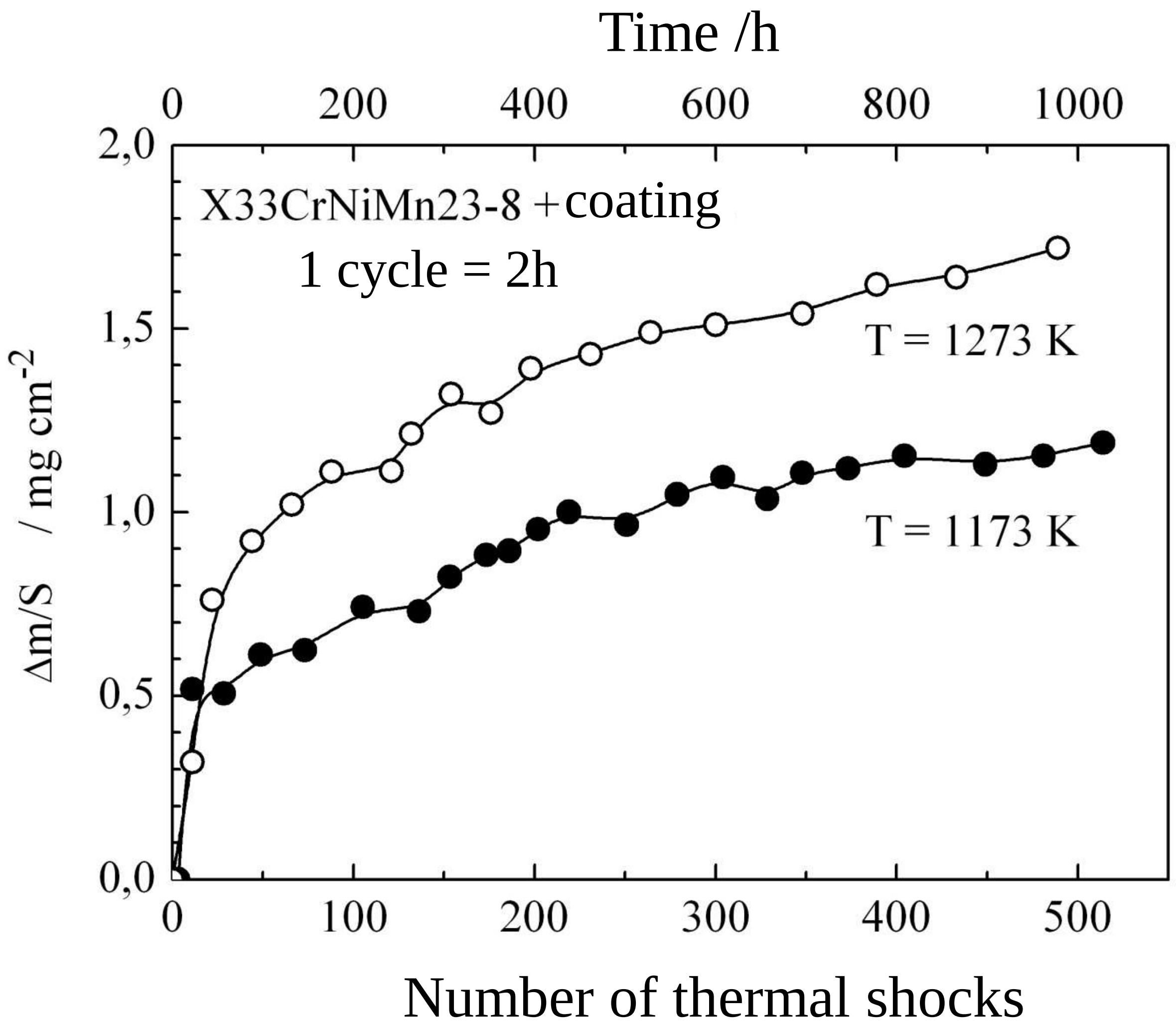
Surface layer of the TBC



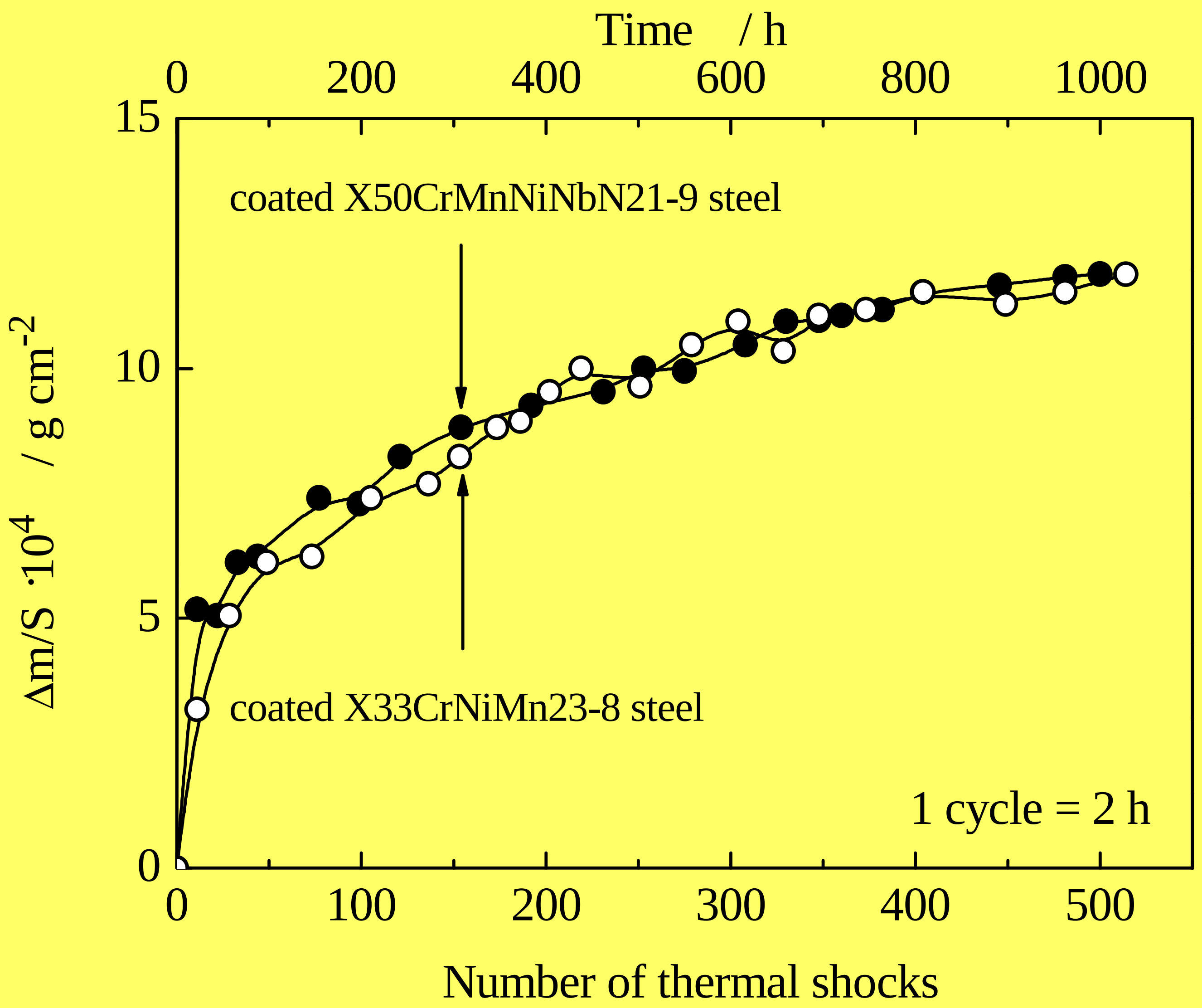
The results of oxidation of X50CrMnNiNbN21-9 steel coated with a protective coating under thermal shock conditions



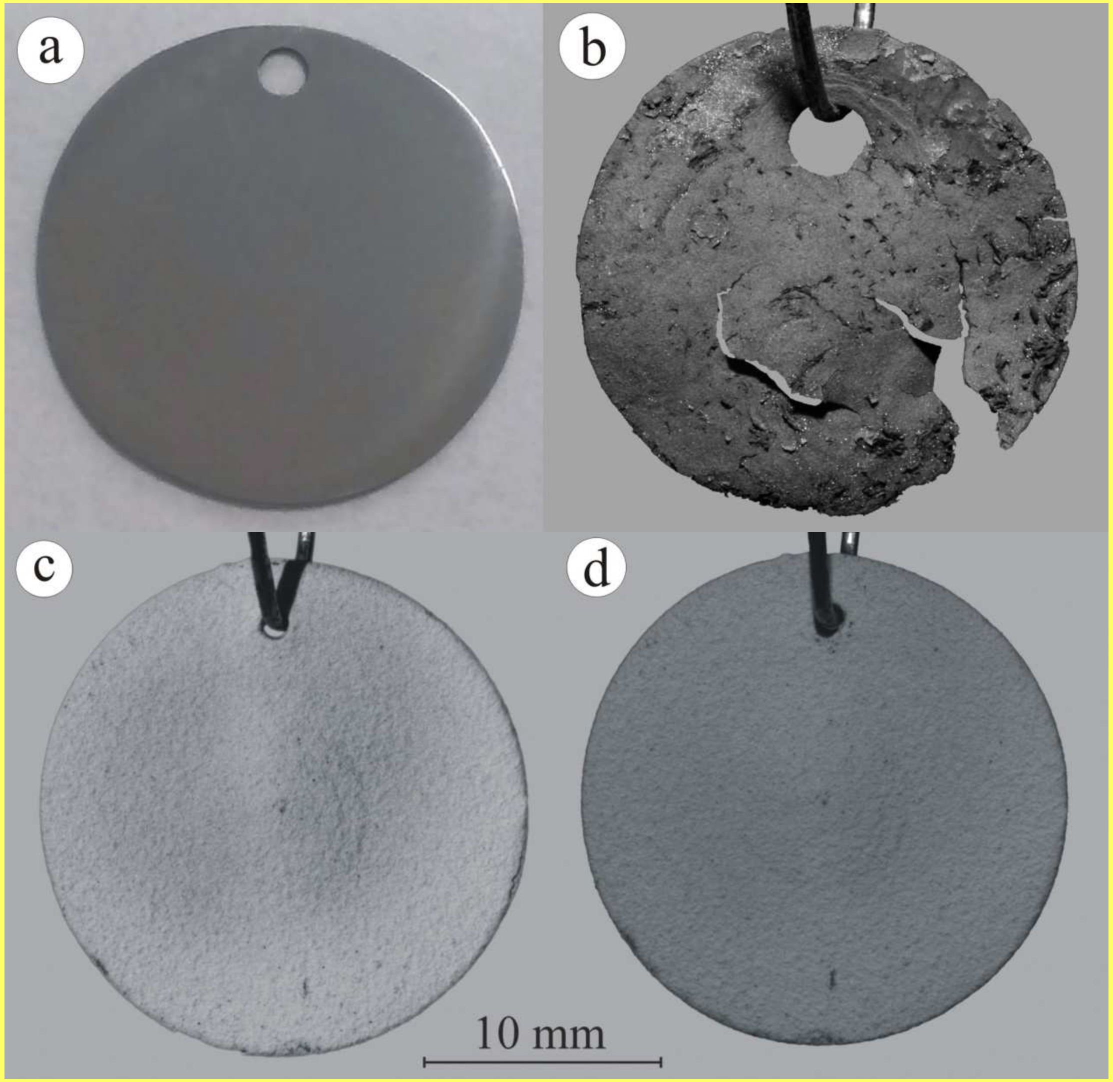
The results of oxidation of X33CrNiMn23-8 steel coated with a protective coating under thermal shock conditions



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



The photographs of the X50CrMnNiNbN21-9 surface steel sample, uncovered and covered with hybrid coating



before oxidation after 500 cycles

X50CrMnNiNbN21-9

X50CrMnNiNbN21-9
+ TBC coating

RESULT

In spite of excellent protective properties of proposed hybrid coatings, they were never applied for protection of engine valves in automobile industry from economic reasons.

AIM OF INVESTIGATIONS

The aim of presented investigations consists in elaboration of new generation of inexpensive, corrosion-resistant coatings, which could be applied in protection of low percentage chromium steels against high temperature corrosion in modern technologies.

IDEA OF INVESTIGATIONS

In contrast to rather thick and expensive actually being utilized corrosion-resistant coatings, constituting large chromium reservoir necessary for developing of protective Cr_2O_3 layer, the new generation of coatings proposed in these studies will consists very small amount of chromium, because the thickness of the coating will be about 1 micrometer. Such a low chromium concentration will be possible to be utilized because the coating will play only the role of initiator for formation of Cr_2O_3 layer, later annihilating. The stability of further growth rate of chromium oxide layer will result from outward diffusion of chromium from the protected substrate.

RESEARCH OBJECTIVES

Long-term reduction of corrosion rate of low percentage chromium steels obtained using new generation of coatings will be possible after solution of a number of problems:

- First of all, the optimal chemical composition and the structure of the coatings will be determined in order to get the maximum corrosion resistance of steels in a given reaction conditions.
- In addition, the parameters determining the protected material (chemical composition, crystal structure, grain size, a.s.o.) will be defined to assure the effective utilization of coatings.
- Subsequently, the scale adherence will considerably be increased by incorporation of trace amounts of selected rare earth elements to the coatings materials.
- Effective time of protecting effect of coatings, being much longer than the life-time of coatings will be also determined.
- The final step in the development of proposed coatings will consists in elaboration of the most economic method of their fabrication, enabling its application in industry.

EXPERIMENTAL

Materials:

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

Steel specimens:

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

Sputter-deposition process:

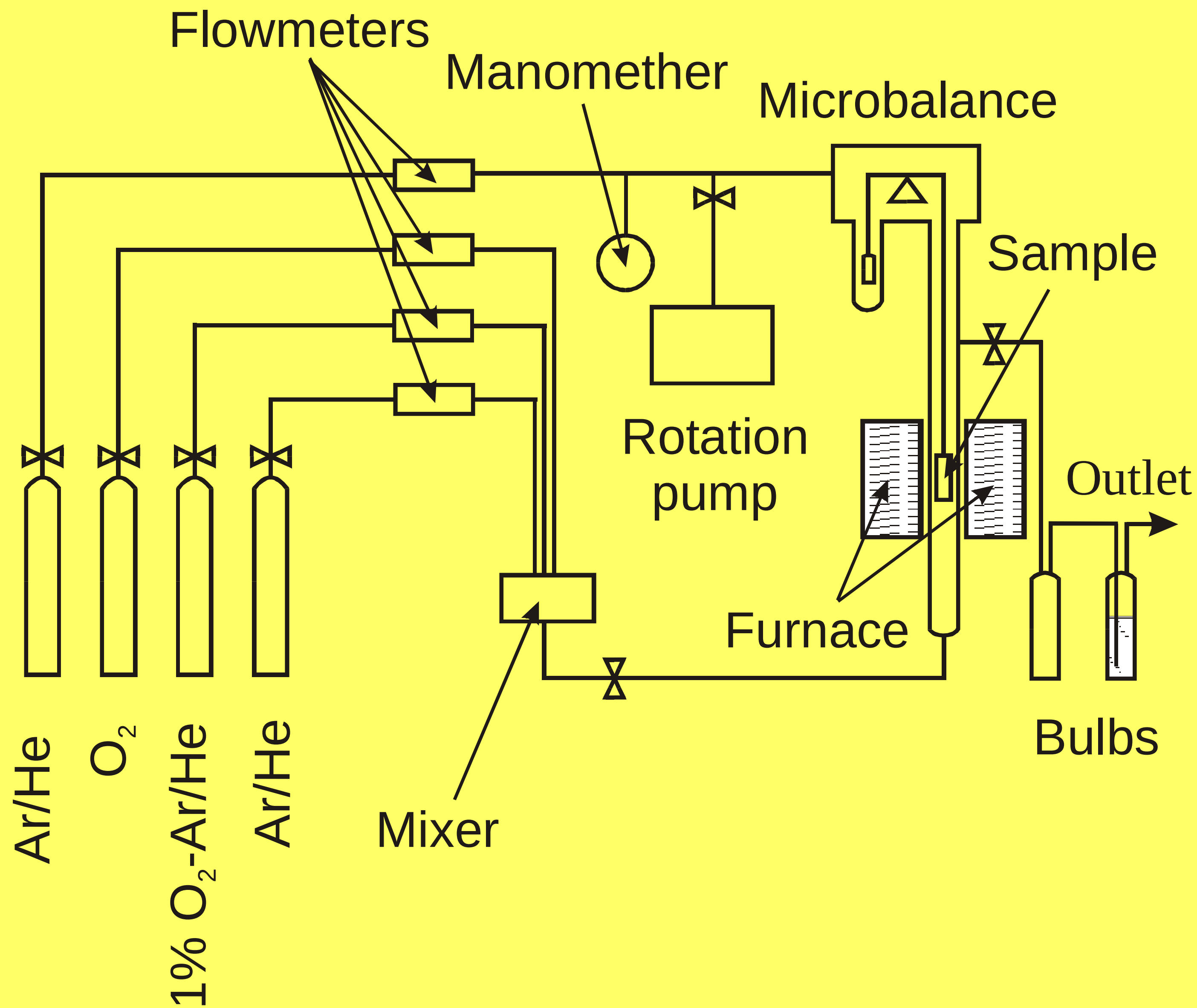
- chromium layer, thickness: 1 micrometer
- evacuation: 10^{-3} Pa
- Ar ions energy: 4 KeV
- sputtering time: 40 min.

Oxidation tests under isothermal conditions:

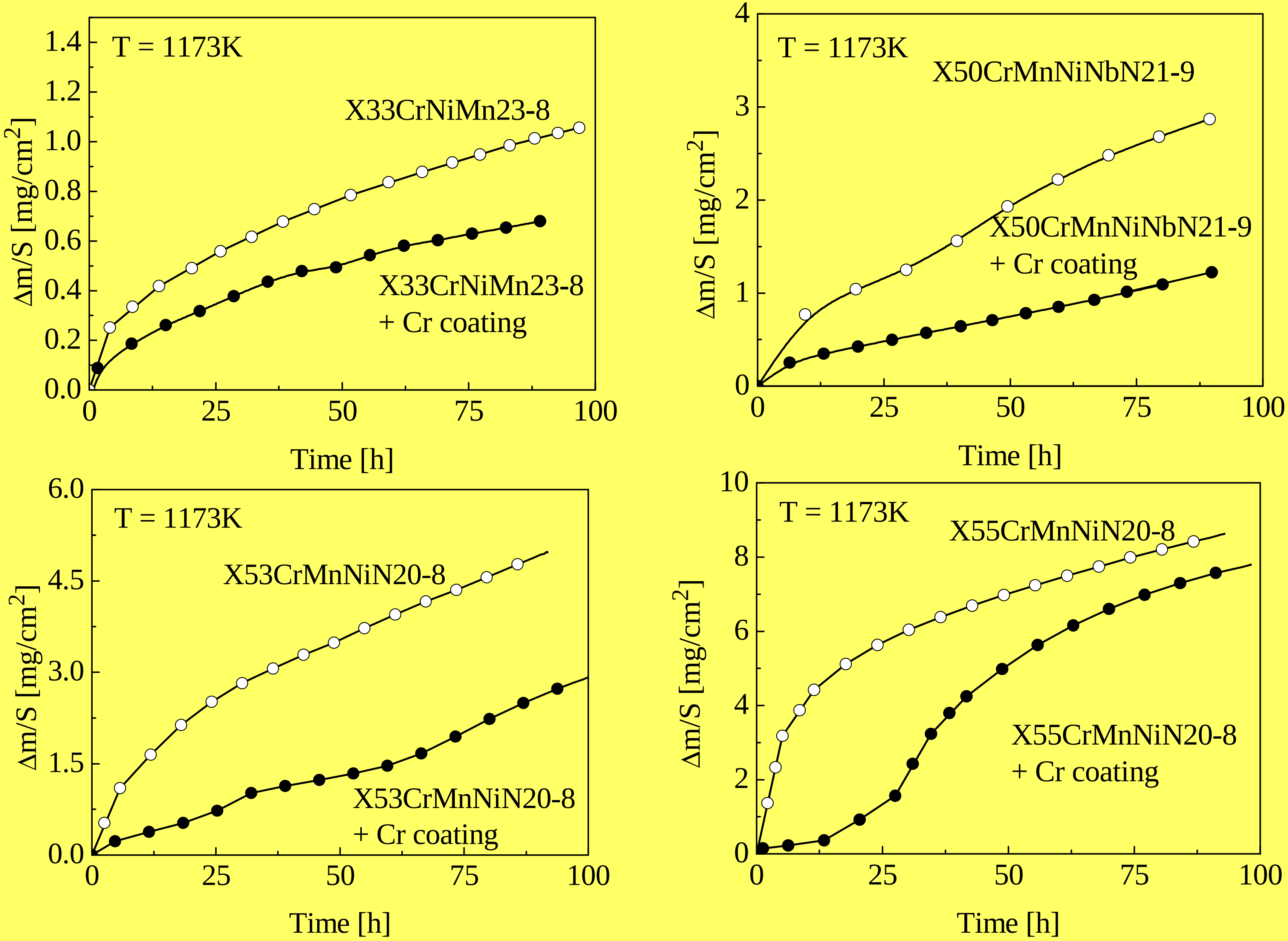
- reactive atmosphere: air
- temperature: 1173 K
- time of experiments: 100 h.

SEM, EDX, XRD EXAMINATION

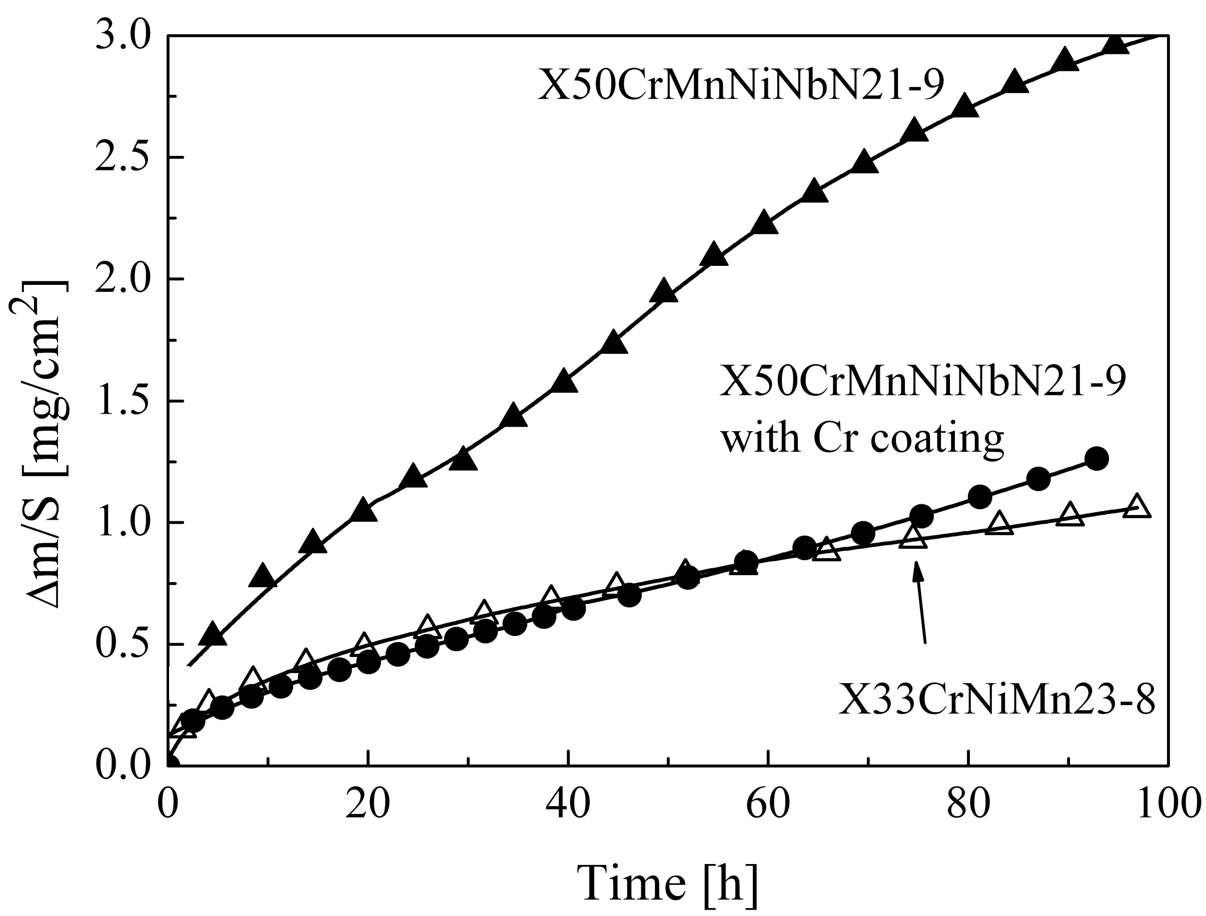
Microthermogravimetric apparatus for studying the kinetics of solid-oxygen interactions at high temperatures



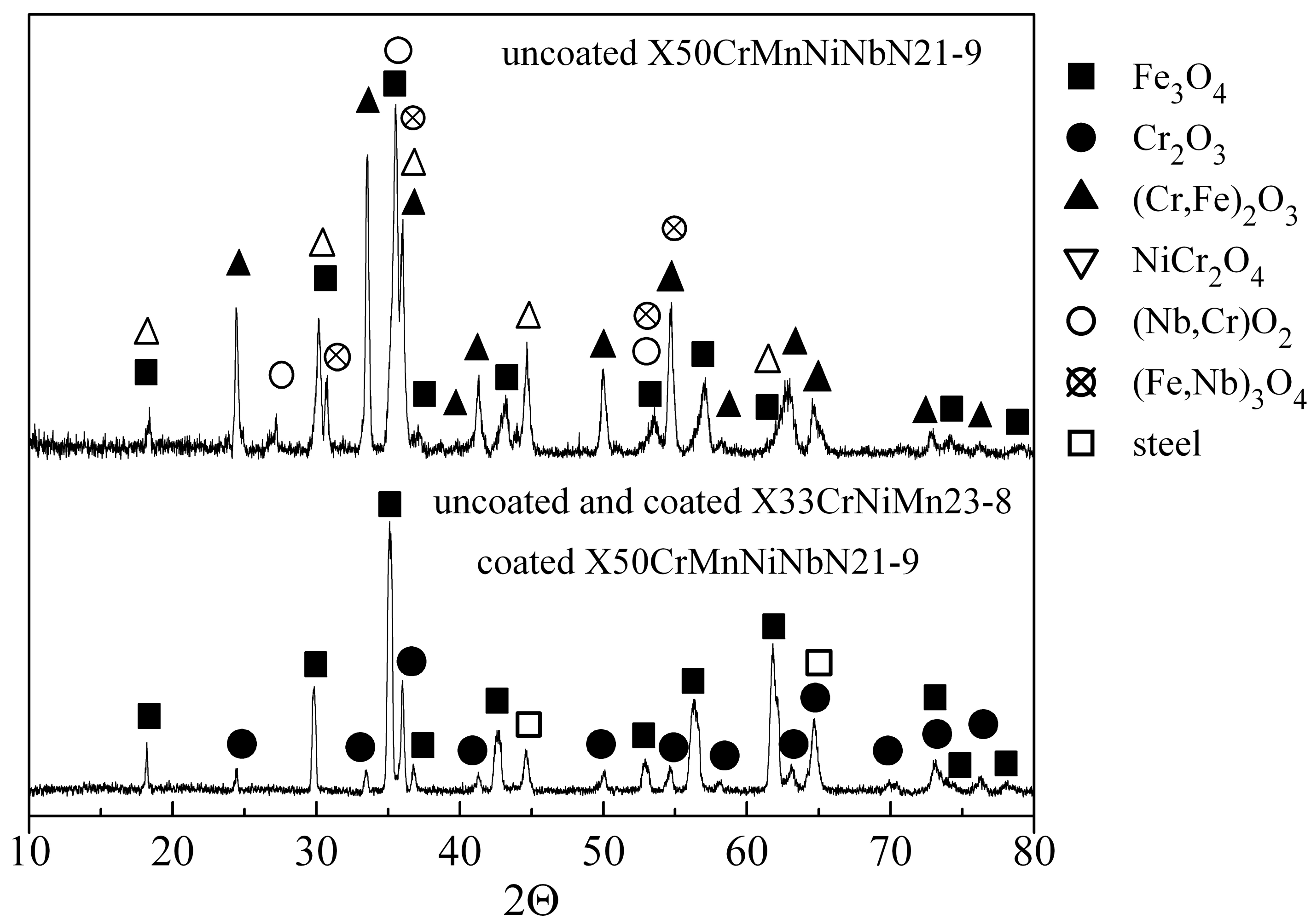
Oxidation kinetics of coated and uncoated valve steels

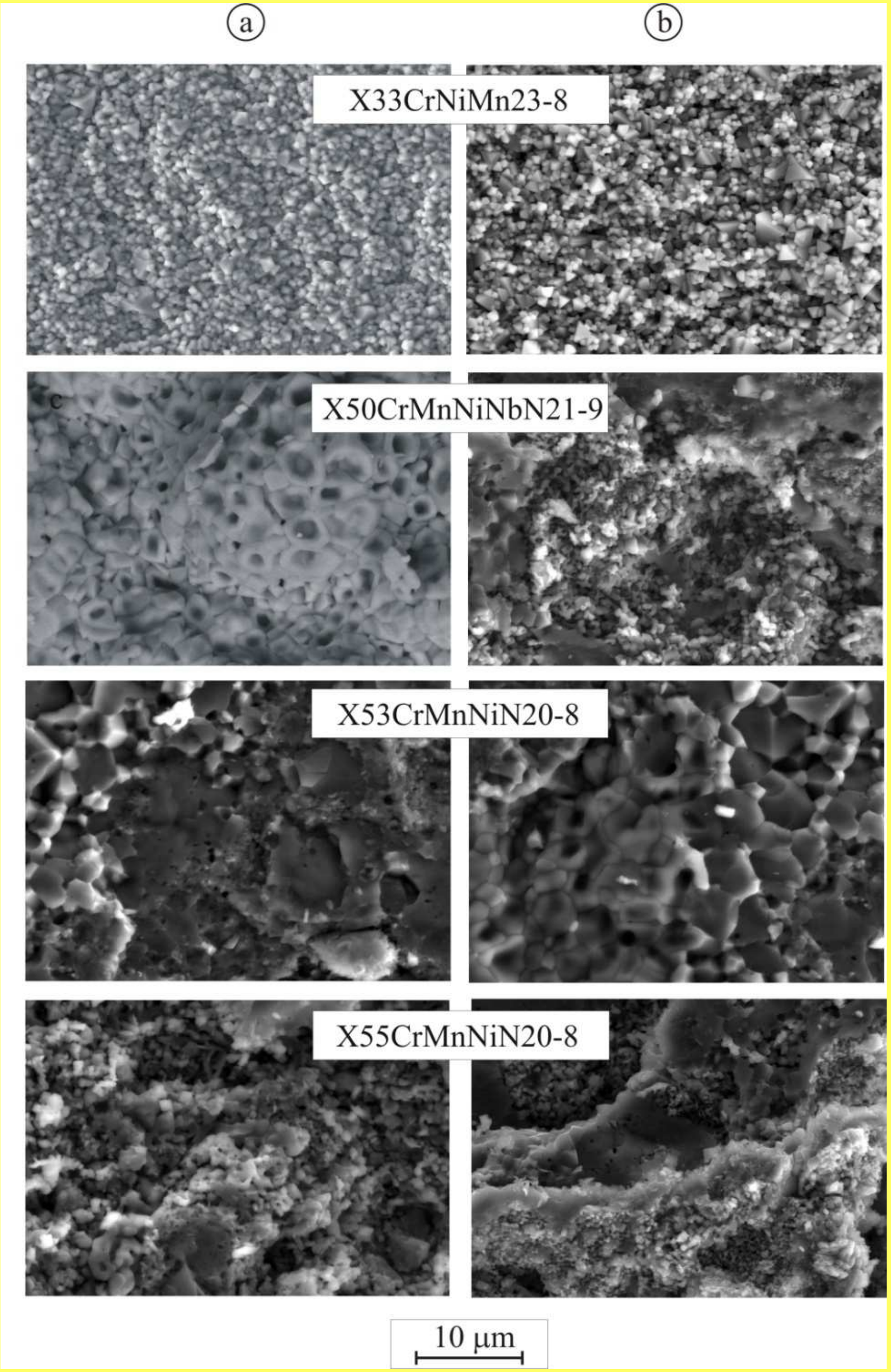


The comparison of oxidation rate of the uncoated and coated X50CrMnNiNbN21-9 steel on the background of the analogous results for the uncoated X33CrNiMn23-8 steel



X-ray diffraction patterns of studied valve steels, oxidized at 1173 K in air





SEM images of the surfaces of studied steel samples:

a) uncoated steels
b) coated steels

CONCLUSIONS

The application of thin chromium coatings for protection of valve steels increases the resistance of these steels against high temperature oxidation. This effect is a result of the formation of the scale built mainly from highly protective chromium oxide. The positive effect of chromium on the oxidation resistance of investigated steels is observed during <u>much longer period of time than the life-time of the chromium coating</u>, what strongly support the idea of tailoring of new generation of high temperature inexpensive coatings for automobile industry.

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:

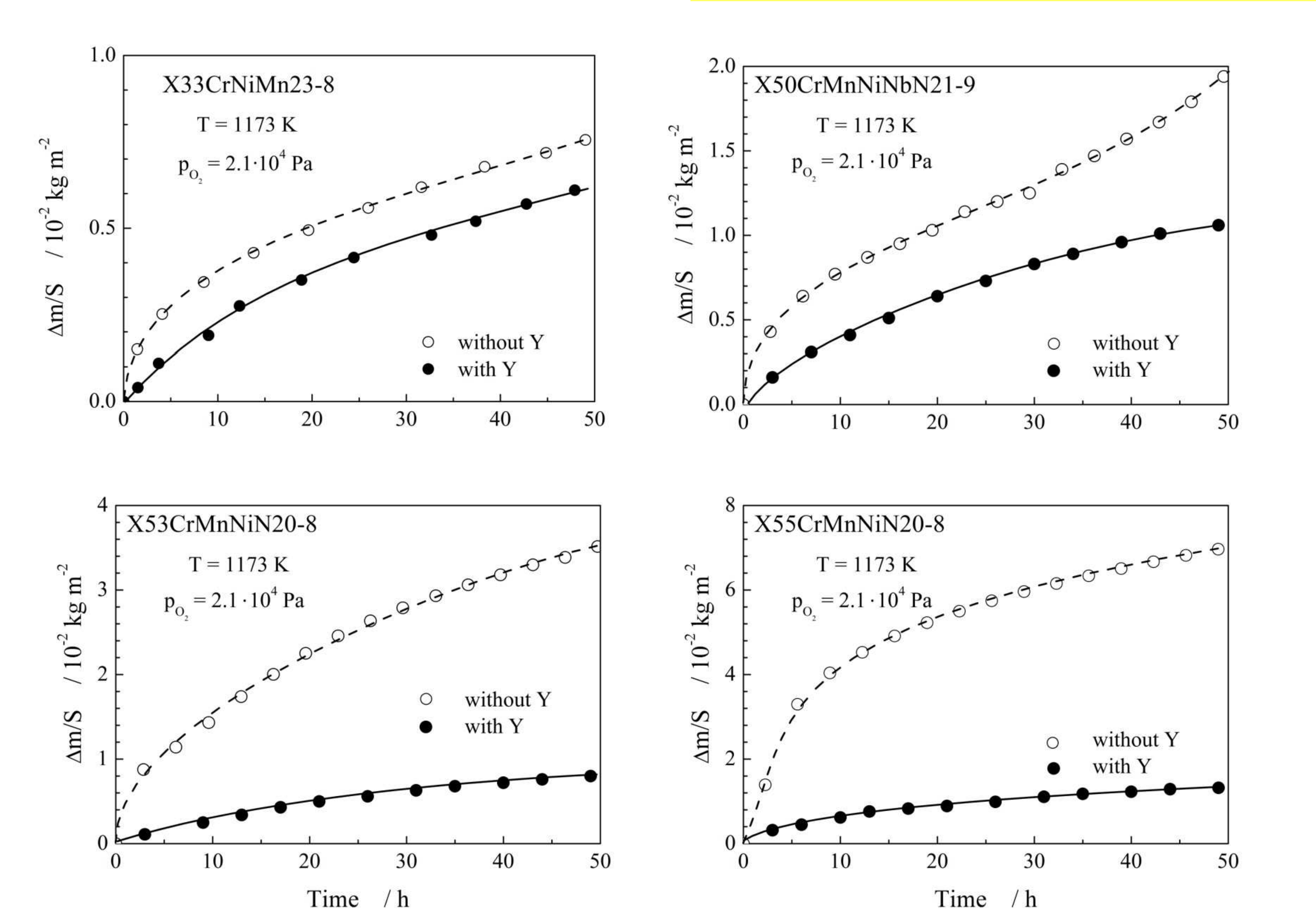
- degreasing
- electrochemical treatment:
  0.01 m $Y(NO_3)_3$ solution in C_2H_5OH
  U = 10V; I = 10 mA; t = 45 s
- drying: T = 50 ^oC; t = 10 min.
- annealing: T = 400 ^oC; t = 30 min.

Corrosion tests under thermal shock conditions:

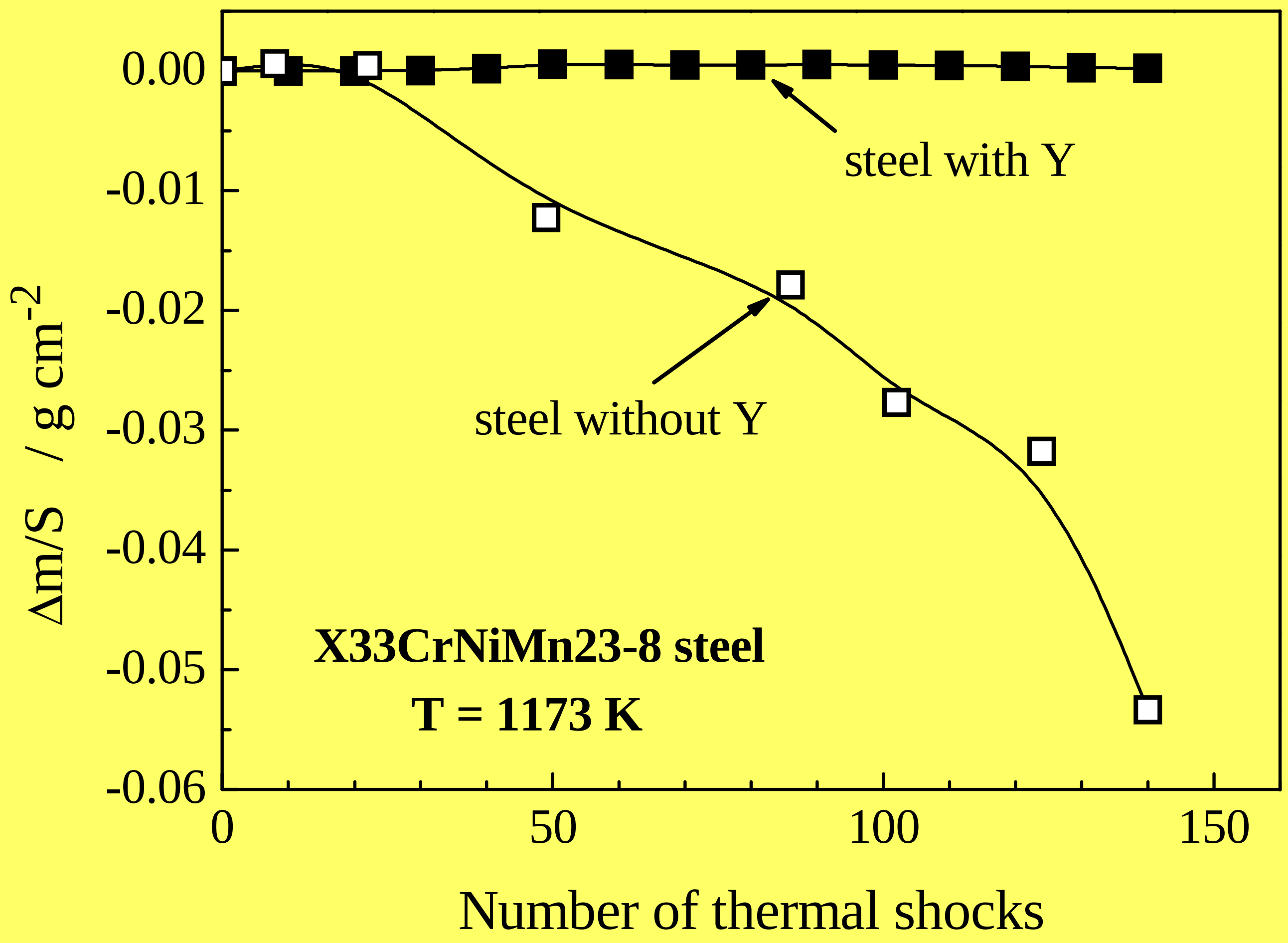
- reactive atmosphere: combustion gases of diesel oil with 10 wt. % addition of FAME (B10)
- temperature range: 295 – 1173 K
- time of experiments: 150 shocks x 2 h, quenching cycle: 15 min.

SEM, EDX, XRD EXAMINATION

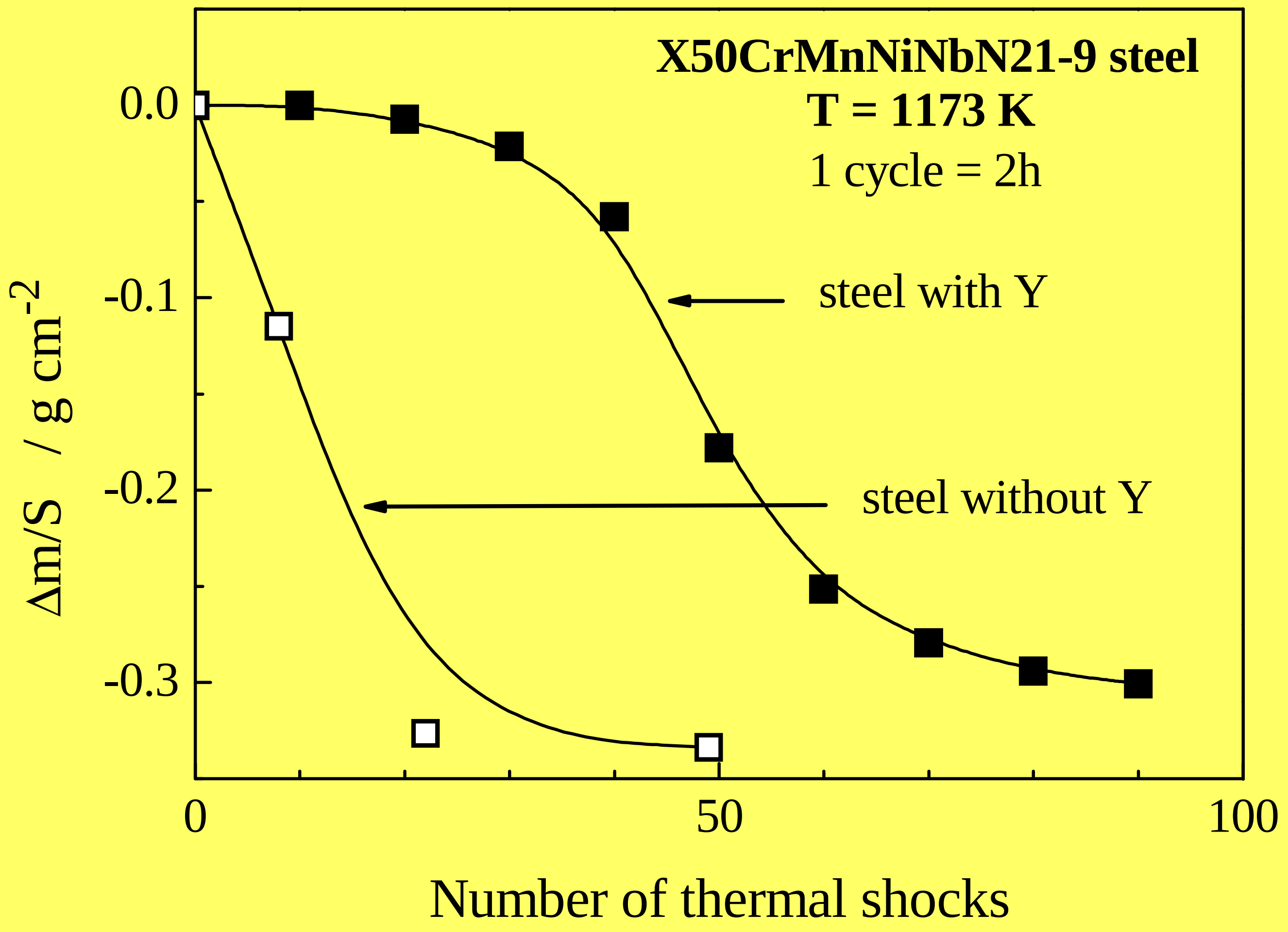
Kinetics of the isothermal oxidation of valve steels covered electrochemically with yttrium on the background of analogous results obtained without yttrium addition



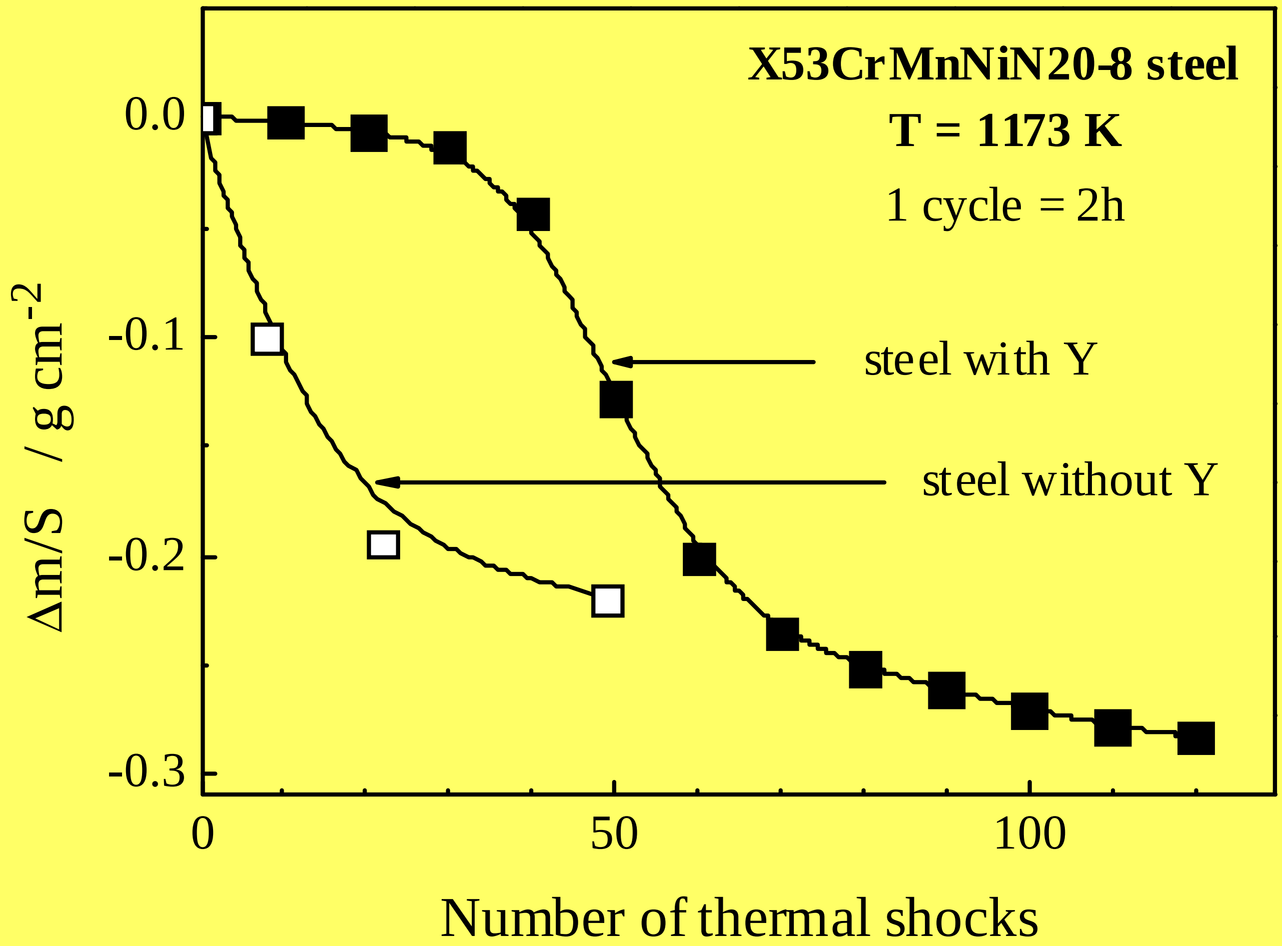
Corrosion behaviour of the X33CrNiMn23-8 steel uncovered and covered with yttrium under thermal shock conditions



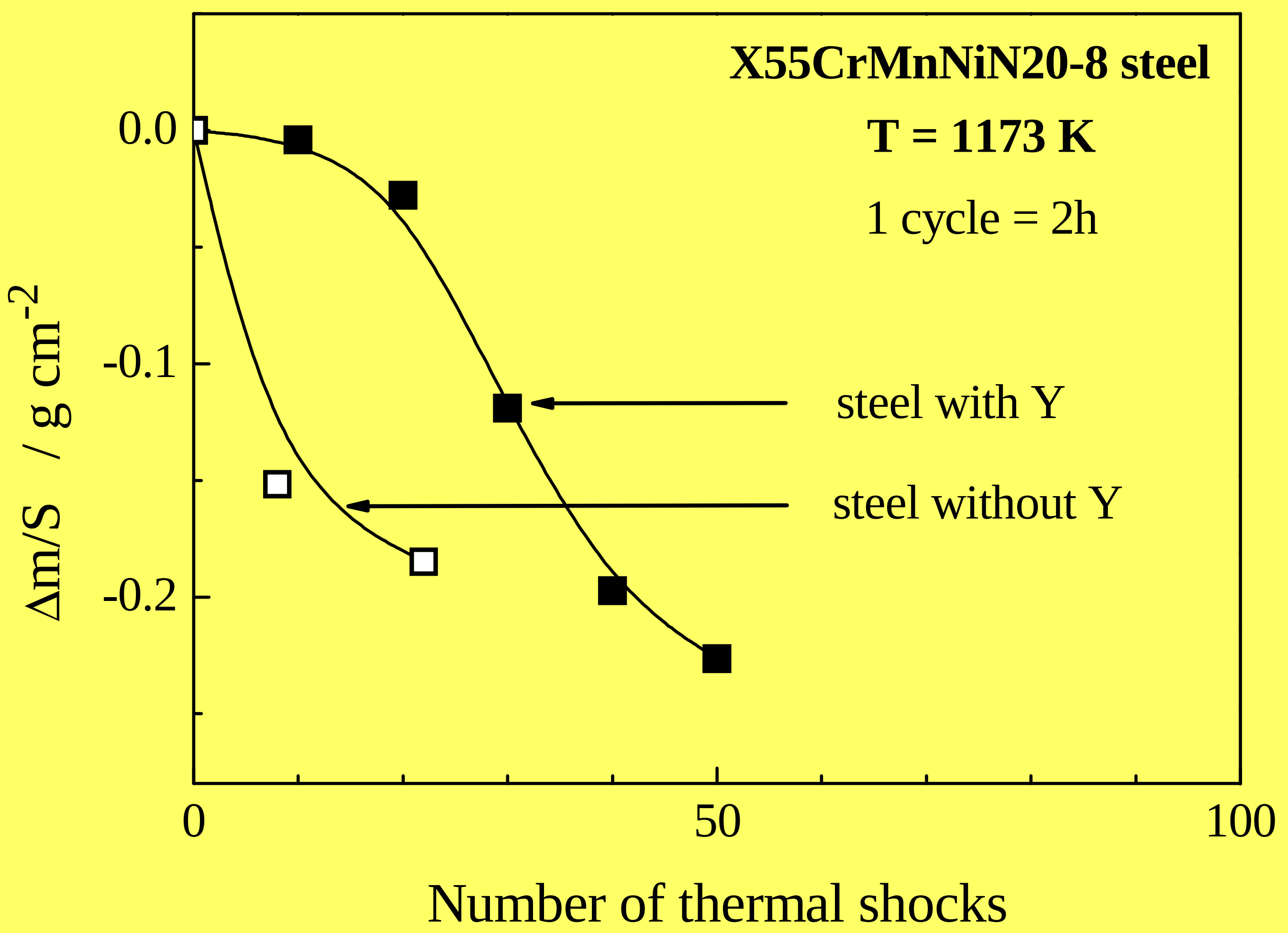
Corrosion behaviour of the X50CrMnNiNbN21-9 steel uncovered and covered with yttrium under thermal shock conditions



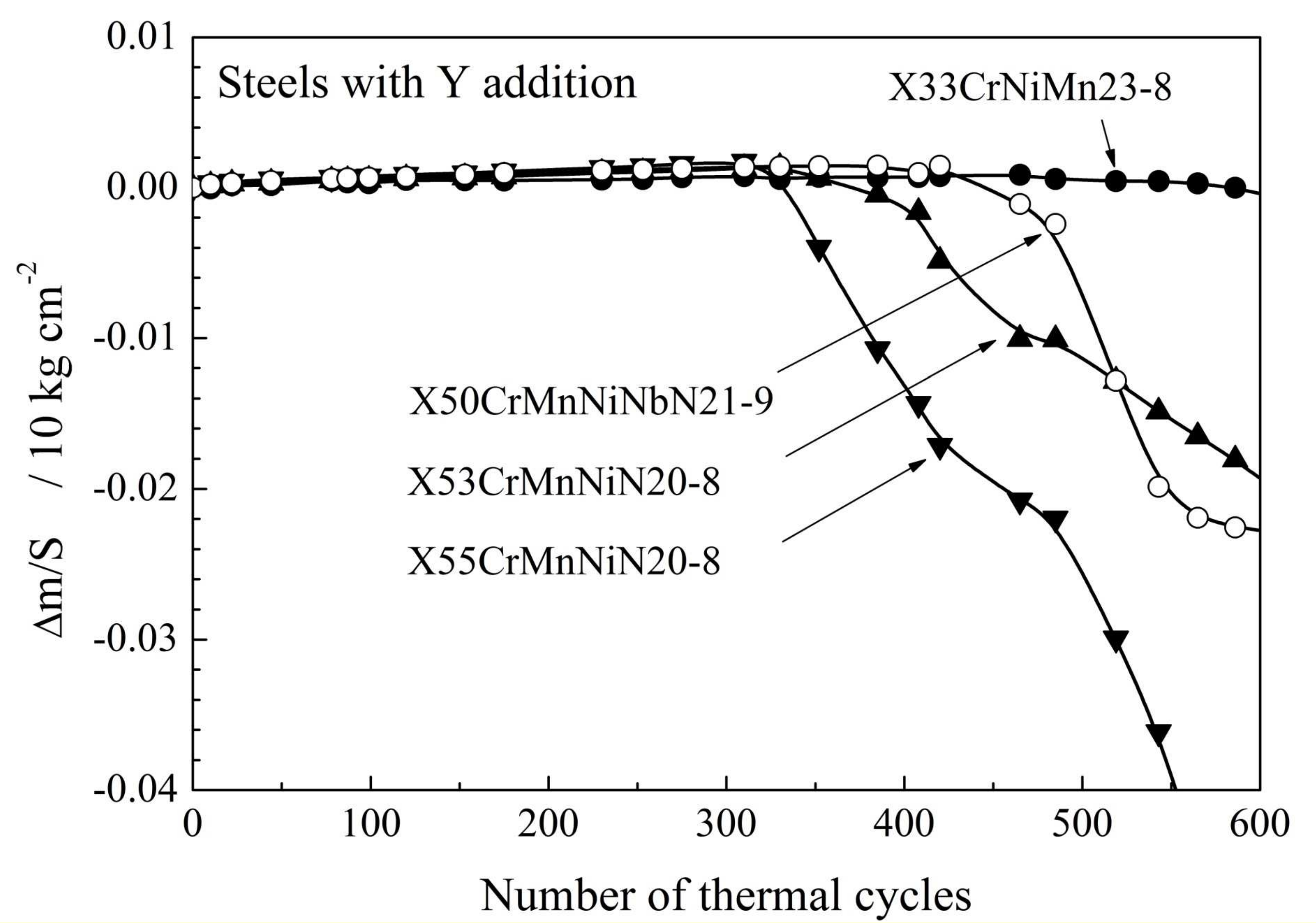
Corrosion behaviour of the X53CrMnNiN20-8 steel uncovered and covered with yttrium under thermal shock conditions



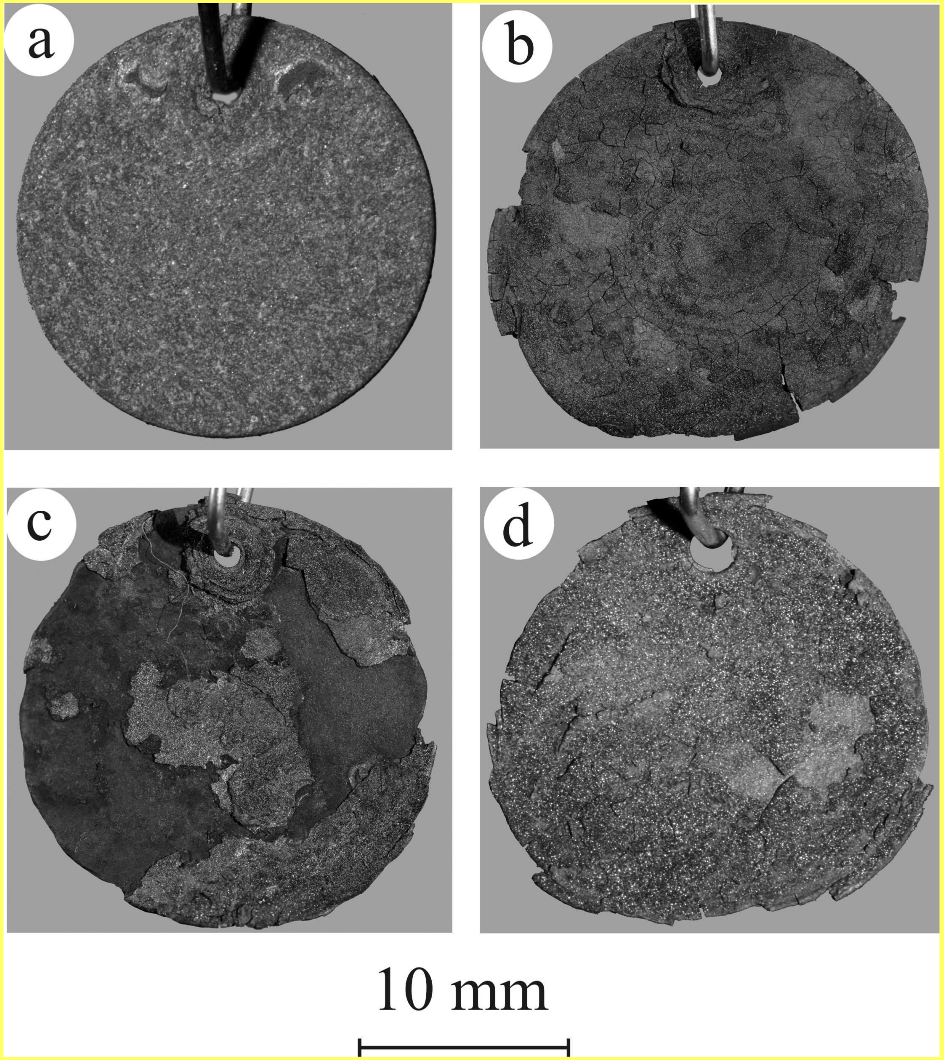
Corrosion behaviour of the X55CrMnNiN20-8 steel uncovered and covered with yttrium under thermal shock conditions



The collective plot, summarizing the results of thermal cycles of four studied steels covered electrochemically with yttrium



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

Conclusions

The presence of small amounts of yttrium in all studied steels improves protective properties of scales as well as the scale adherence to the surface of investigated materials. This positive influence of yttrium is particularly high in the case of steels with low chromium content. However, in spite of this effect, the highest resistance against oxidation during long period of reaction was observed only for the X33CrNiMn23-8 steel with the highest chromium concentration, covered by yttrium. This situation is a result of the formation of highly protective and well adherent to the substrate chromium oxide. In the case of three remaining steels with lower chromium concentration, after long period of oxidation heterogeneous scales start to be formed, build mainly from iron Fe_3O_4 and Fe_2O_3 oxides, which protective properties and adherence to the surface of steels is much worse than that observed in the case of chromium oxide. The final conclusion is that engine valves should be produced in the future only from X33CrNiMn23-8 steel, covered with chromium coating, containing small amount of yttrium.

THE END