



AKADEMIA GÓRNICZO-HUTNICZA
IM. STANISŁAWA STASZICA W KRAKOWIE

AGH UNIVERSITY OF SCIENCE
AND TECHNOLOGY

New generation of thin coatings for protection against high-temperature corrosion

Zbigniew Grzesik

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

Background

Creep and oxidation resistance in high-temperature environments are the most important deciding factors when considering the appropriate materials for future commercial application. Unfortunately, alloys with high creep resistance do not always exhibit good heat resistance.

One of the most popular methods of correcting this problem is the application of protective coatings on the surface of such a material. The most effective coatings include thermal barrier coatings (TBC), which demonstrate very good heat resistant properties.

However, this type of comparatively thick coating has a fundamental disadvantage, namely its thickness results in the inability to deposit this layer on well-matched machine parts. In this case, before coating deposition it is necessary to design the parts in order to give them the appropriate reduced size. This procedure is difficult from a technical point of view and its costs can be disproportionately high. Therefore, these coatings cannot be universally applied due to economic or technical reasons.

New generation of protective coatings

Candidates for the corrosion-resistant thin coatings ($1 \mu\text{m}$):

- Cr
- Cr-Ni
- SiC

New generation of protective coatings

Being active in this area of research since years, we proposed to apply, as an alternative to thick and expensive TBC coatings, much more inexpensive layers with around 1 micrometer thickness. We demonstrated that such thin SiC coatings or chromium layers can be widely used without the necessity of redesigning individual engine elements. Among these solutions, chromium layer application seems to be very interesting due to their better adherence to the metallic substrate compared to ceramic coatings.

Such coatings, unlike expensive TBCs, do not contain large amounts of a scale-forming element, in this case chromium. Nevertheless, they have proven to be sufficient for facilitating the formation of a continuous Cr_2O_3 oxide layer with highly protective properties during the first stage of oxidation. Then, outward chromium diffusion from the protected steel substrate leads to the aforementioned layer becoming stable and increasing in thickness. After initiating Cr_2O_3 growth, the novel coatings quickly disappear. However, it has been determined that application of the thin Cr layers enhances the oxidation behaviour of valve steels under isothermal conditions for a much longer period of time than the lifetime of the coatings.



AGH

New generation of protective coatings - potential directions of developments

It should be emphasized that chromium content in the 1 micrometer thick coating is very minor. Therefore, if such a layer is deposited on steel with relatively low amounts of chromium (< 20 wt.% Cr), then Cr can diffuse from the coating to the substrate interior. In that case, the remaining amount of chromium in the deposited layer may be insufficient for the formation of a continuous protective Cr_2O_3 oxide layer in the initial oxidation stage. Consequently, the thin coating will not have met its requirements. This problem is especially important in the case of steels with low chromium content that simultaneously contain low amounts of nickel, which facilitates outward chromium diffusion, thereby increasing chromium oxide growth, or large amounts of manganese that have the opposite effect. In order to widen the potential number of applications for these thin metallic coating, it is necessary to perform investigations on increasing their protective influence on steel substrates. An obvious method of increasing the chromium content in the layer is to increase the thickness of the coating. However, if the deposited layers are to remain thin, then the coating thickness cannot be significantly increased. Another possibility is to incorporate an active element, such as yttrium, the influence of which on the heat-resistant properties of chromia-formers is well known.

Current views pertaining to thin protective coating usage at high temperatures

Up to now it has been believed that coatings with thickness the order of 1 micrometer used for protection against high-temperature corrosion are completely ineffective, because:

- the chromium content in the coating is insufficient for generating a protective chromium oxide layer
- the coating will disappear very quickly due to inward chromium diffusion
- the coating will undergo oxidation after a brief period of time

Concept of using thin chromium coatings

The main role of thin coatings is to immediately initiate in the first oxidation stage the growth of a protective chromium oxide, Cr_2O_3 , layer. The amount of chromium necessary to enrich the surface layer of the steel in that element is not large, because it is only used to ensure the formation of a continuous chromium oxide layer, the further growth of which should be sustained by chromium originating from inside the protected material.

Concept of using thin Cr-Ni coatings

During the above-described studies, the following question was asked: Are thin chromium coatings the optimal solution from the point of view of protection against corrosion, or should the chromium layers be enriched with another element that positively affects heat resistance by means of synergy?

When analyzing this aspect, it should be noted that greater nickel content in chromium-containing valve steels has a beneficial influence on improving their heat resistance. Thus, we should determine whether an analogous phenomenon can be observed in the case of thin coatings containing both chromium and nickel. It should be noted that such an effect was reported in reference to the oxidation of the Ni–Cr binary alloys. However, in the case of the very thin coatings used in this work, this influence is not obvious due to relatively small Ni content and its possible inward diffusion into the steel.

Concept of using thin SiC coatings

The role of new generation of corrosion-resistant coating can be fulfilled by a thin silicon carbide layer due to the oxidation resistance of the material at high temperatures.

However, it should be noted that the oxidation kinetics and mechanism of only solid SiC samples or metallic materials covered with thick (order of several dozen to several hundred micrometers) SiC layers have been studied up to now. On the other hand, systematic studies on the oxidation rate of valve steels covered by a thin (order of a few micrometers) SiC coating have not yet been carried out.

Fabrication and tests of thin coatings

Studied materials:

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

Samples:

discs: 18 mm diameter, 1 mm thickness, weight: 1 g

Coatings:

Cr, Cr-10% wt. Ni, Cr-50% wt. Ni, SiC

PVD process:

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

RF CVD process, assisted by plasma generated using electromagnetic waves with radio frequency (13.56 MHz)

Corrosion rate studies in isothermal conditions:

synthetic air, temperature: 1173 K, reaction time: 100 h

Corrosion rate studies in thermal shock conditions:

temperature range: 298-1173 K, heating: 2 h, cooling: 15 min.

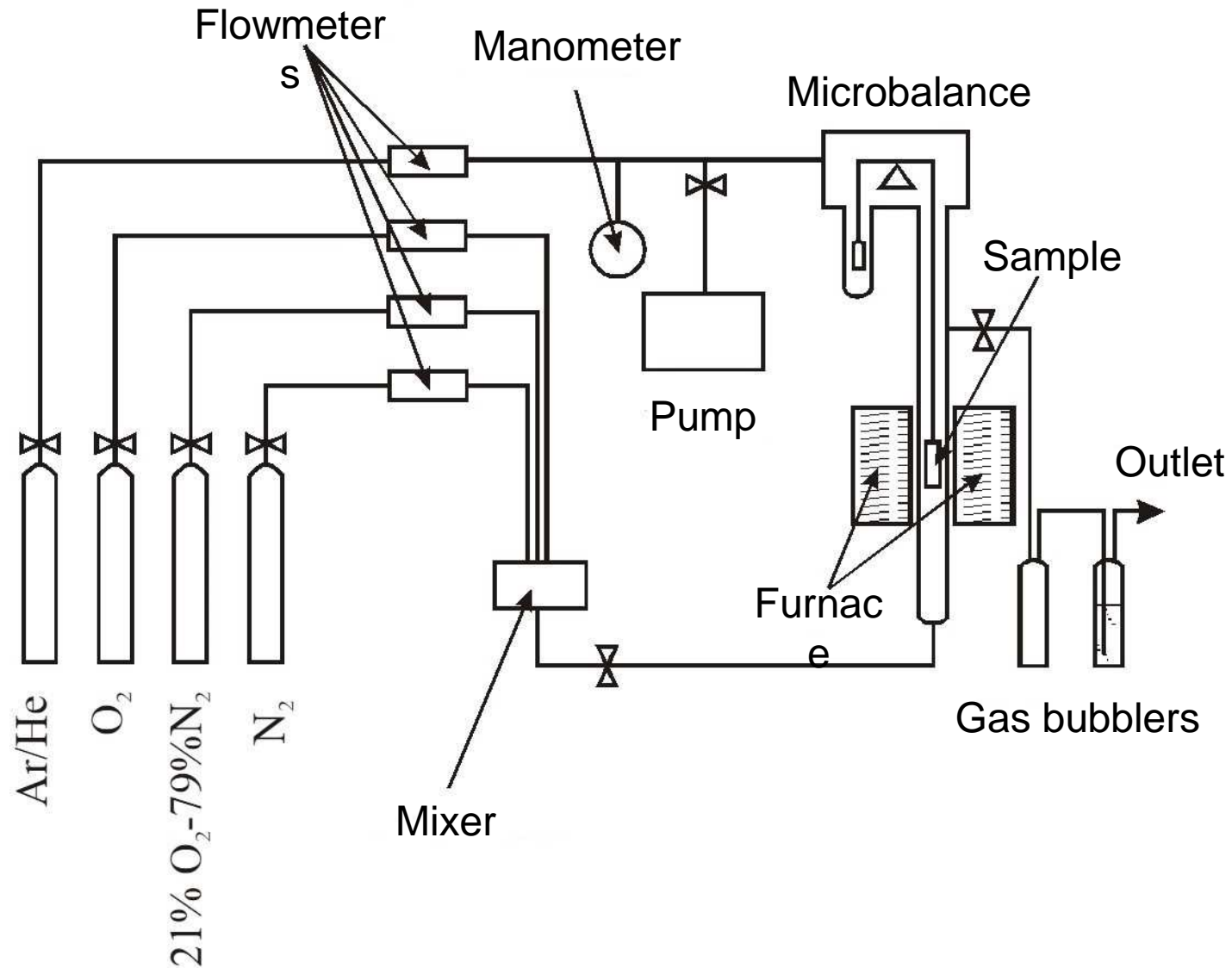
Corrosion studies on valve steels covered by a Cr or SiC coating

200 h durability tests carried out on a 0.9 SGE TC80 CNG engine powered by natural gas

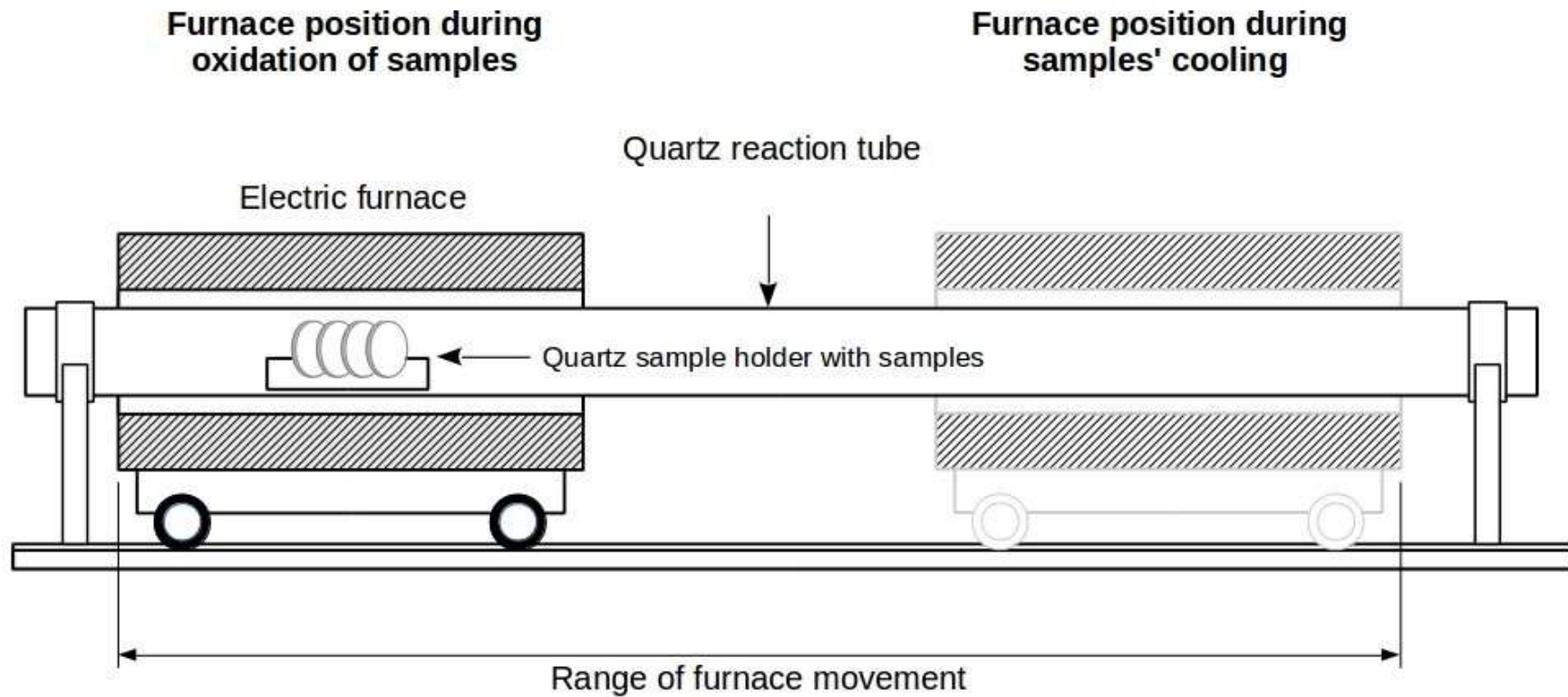
Valve steel chemical compositions (wt.%)

Grade of steel	C	Mn	Si	Cr	Ni	N	W	Nb	S	P	Mo	Fe
X33CrNiMn23-8	0.35	3.3	0.63	23.4	7.8	0.28	0.02	-	<0.005	0.014	0.11	bal.
X50CrMnNiNbN21-9	0.50	7.61	0.30	19.88	3.64	0.44	0.86	2.05	0.001	0.031	-	bal.
X53CrMnNiN20-8	0.53	10.3	0.30	20.5	4.1	0.41	-	-	<0.005	0.04	0.12	bal.
X55CrMnNiN20-8	0.55	8.18	0.17	20.0	2.3	0.38	-	-	<0.005	0.03	0.11	bal.

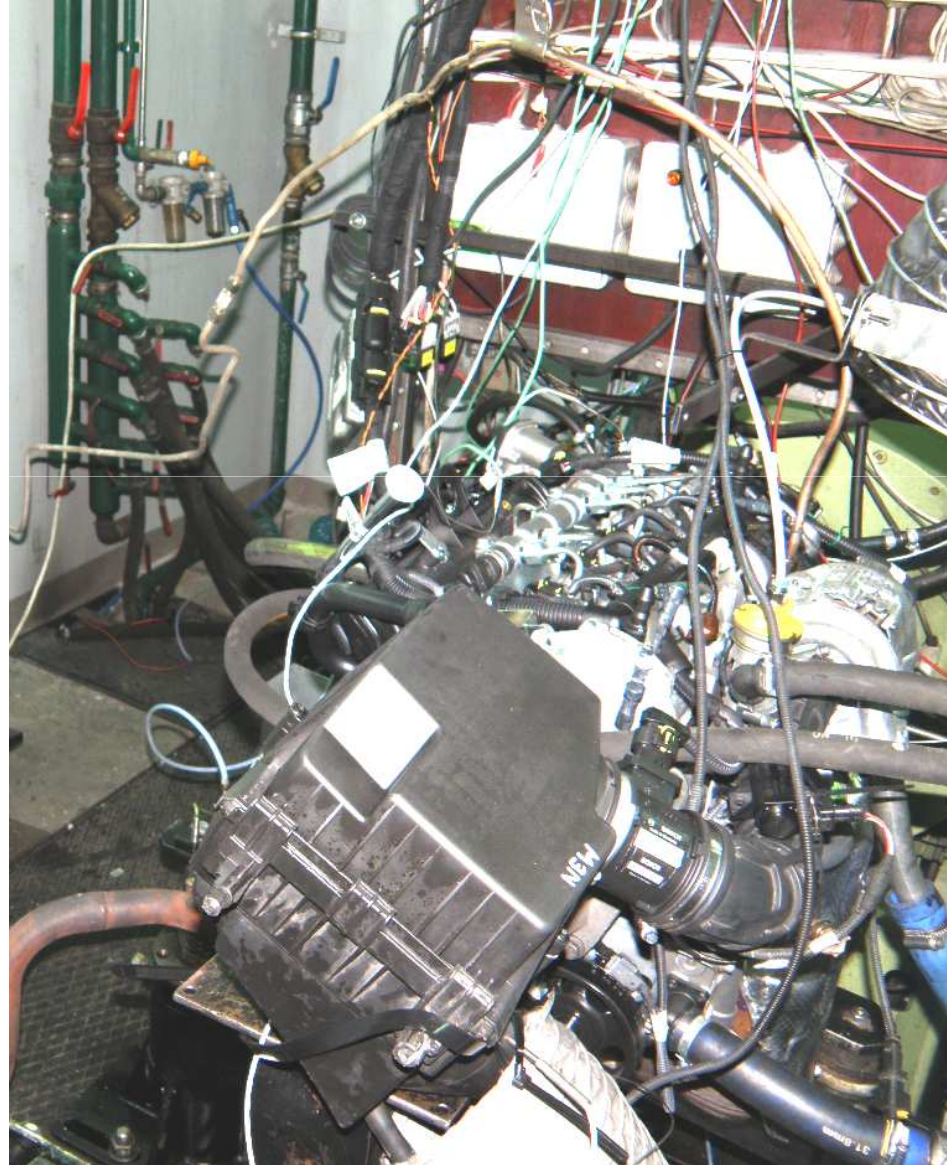
Scheme of apparatus used for oxidation in isothermal conditions



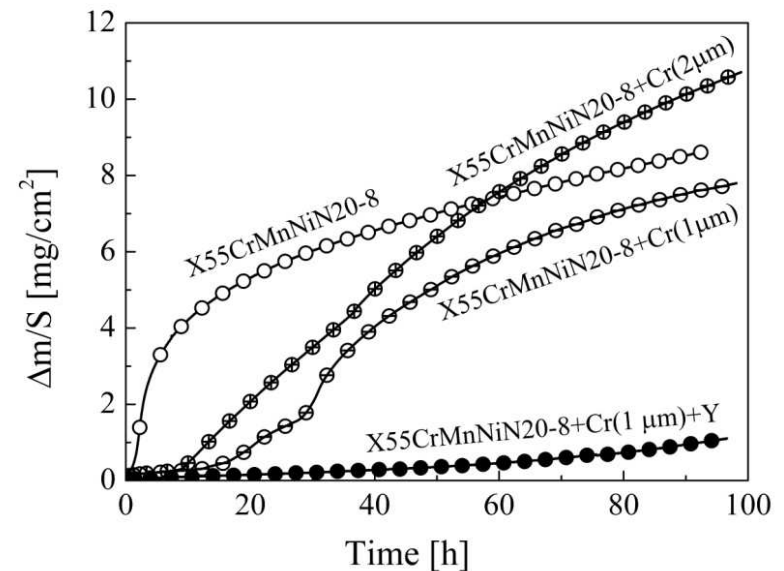
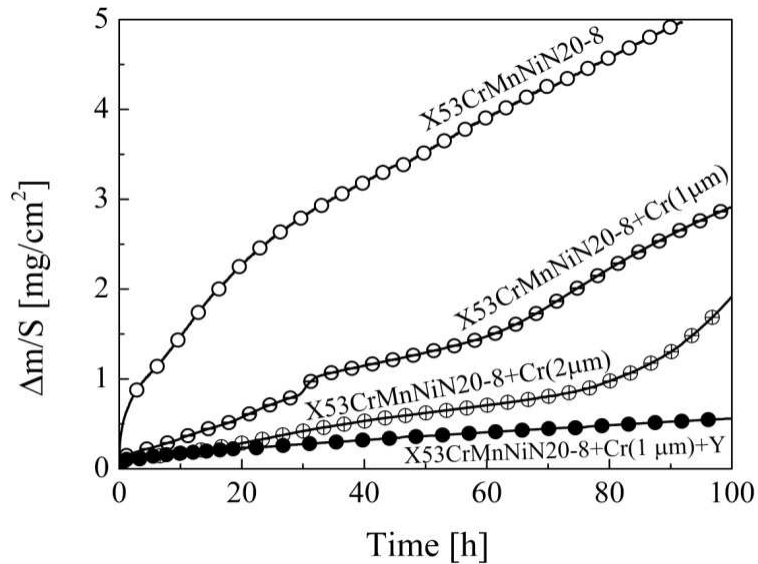
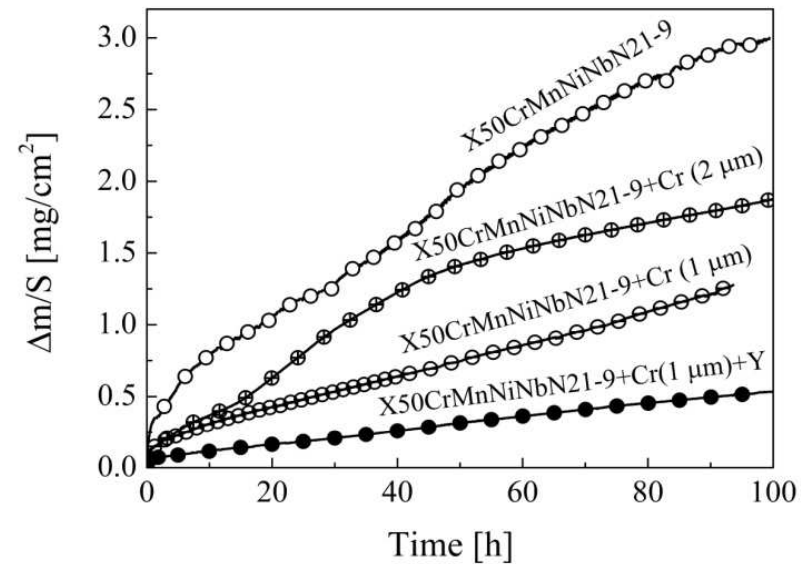
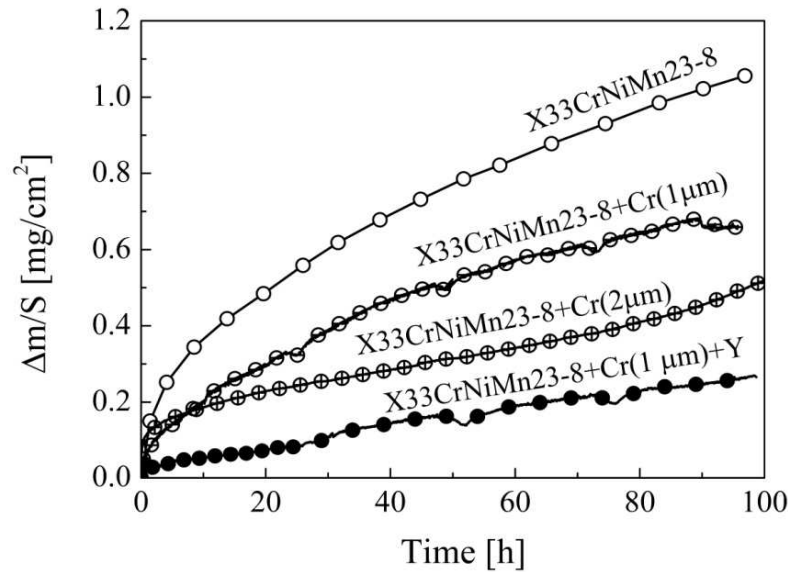
Scheme of the apparatus used for oxidation in thermal shock conditions



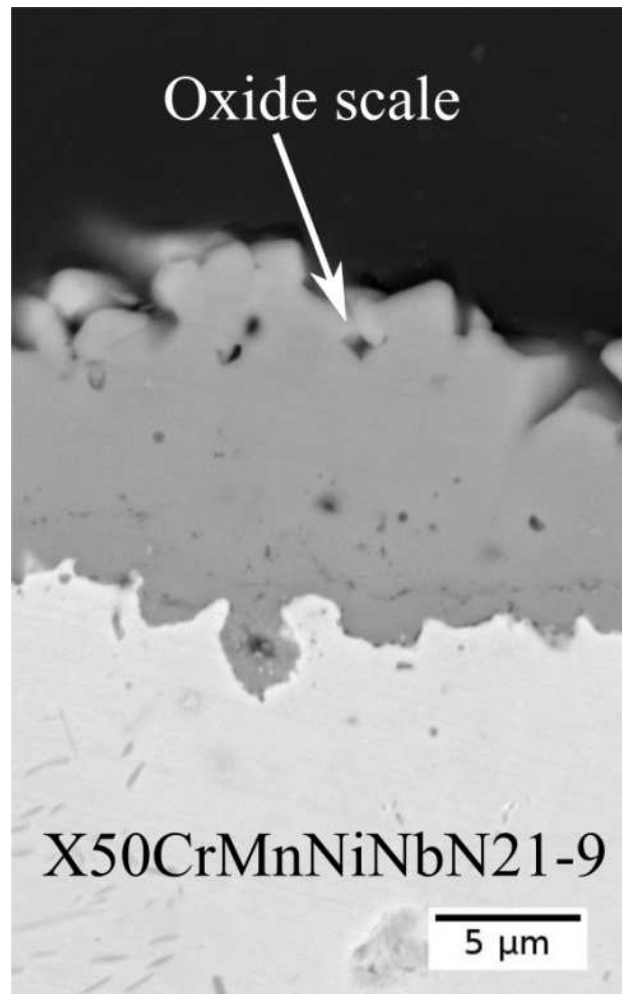
Engine testing house in Bosmal Automotive Research and Development Institute Ltd



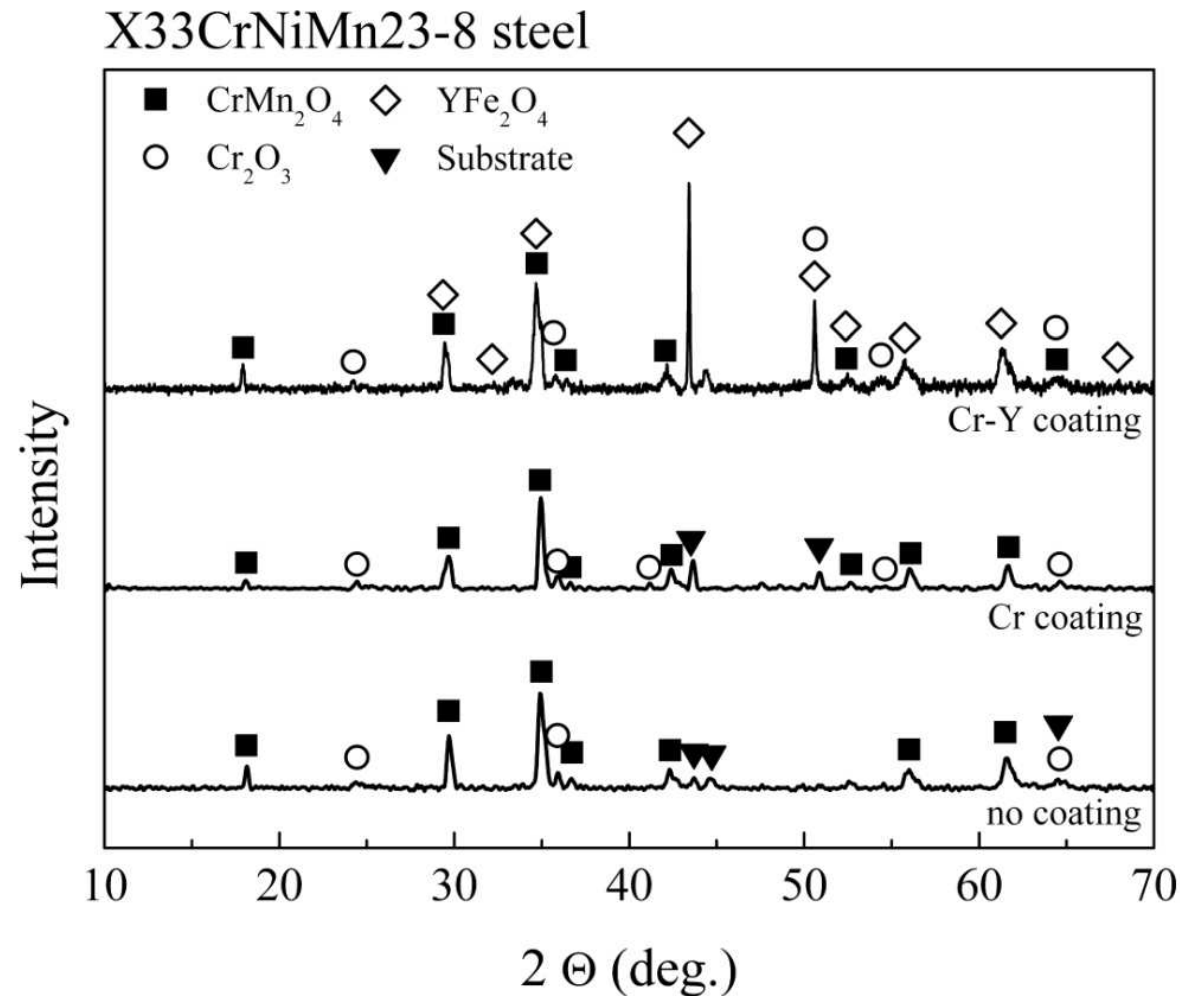
Comparison of the oxidation kinetics of coated and uncoated valve steels, studied at 900°C in air



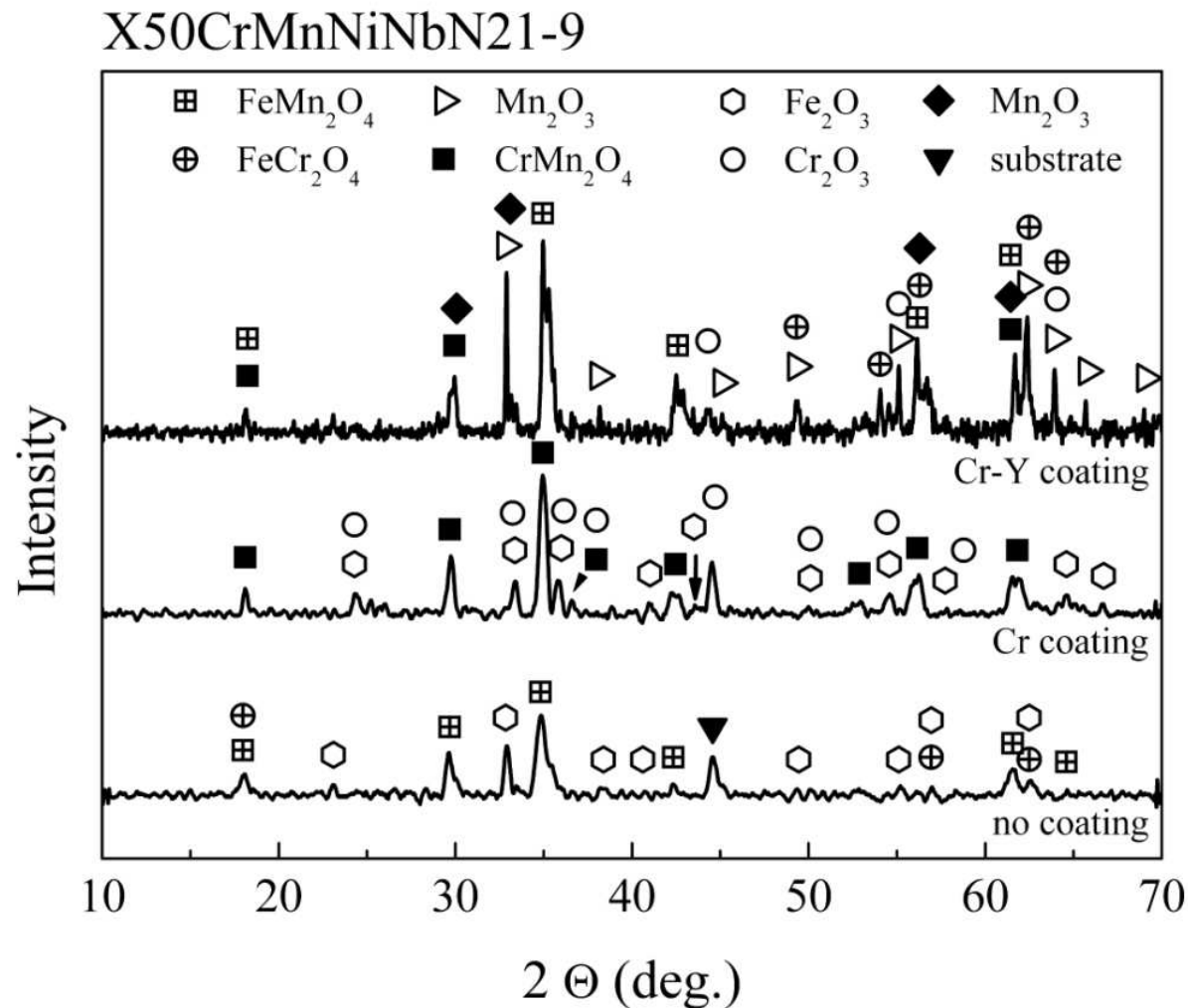
Cross-section image of the oxide scale grown on the X50CrMnNiNbN21-9 steel covered by a chromium coating with 2 μm thickness after isothermal oxidation at 900°C



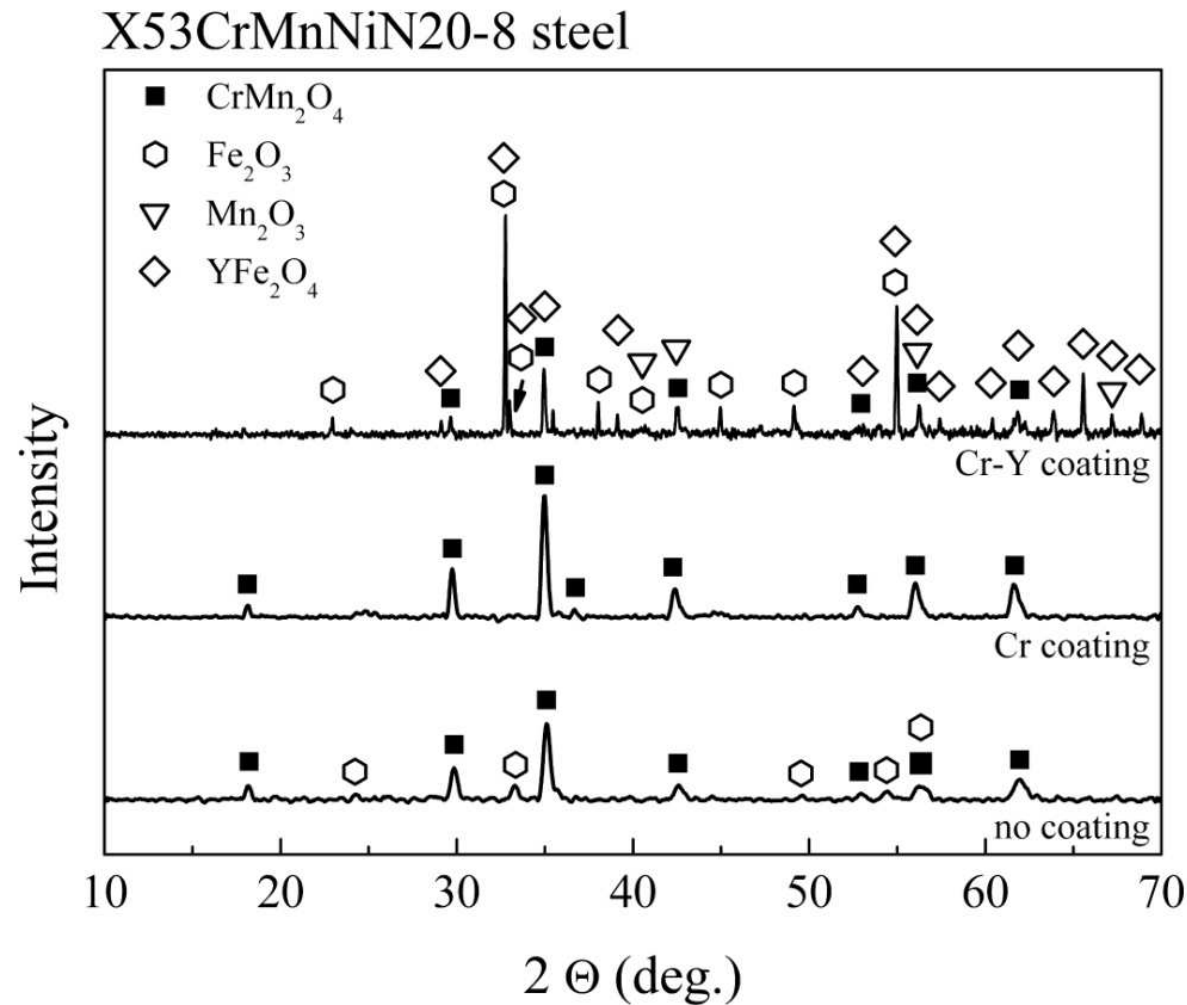
Phase composition of the oxide scales formed on uncoated and coated X33CrNiMn23-8 steel after 100 h isothermal oxidation in air at 900°C



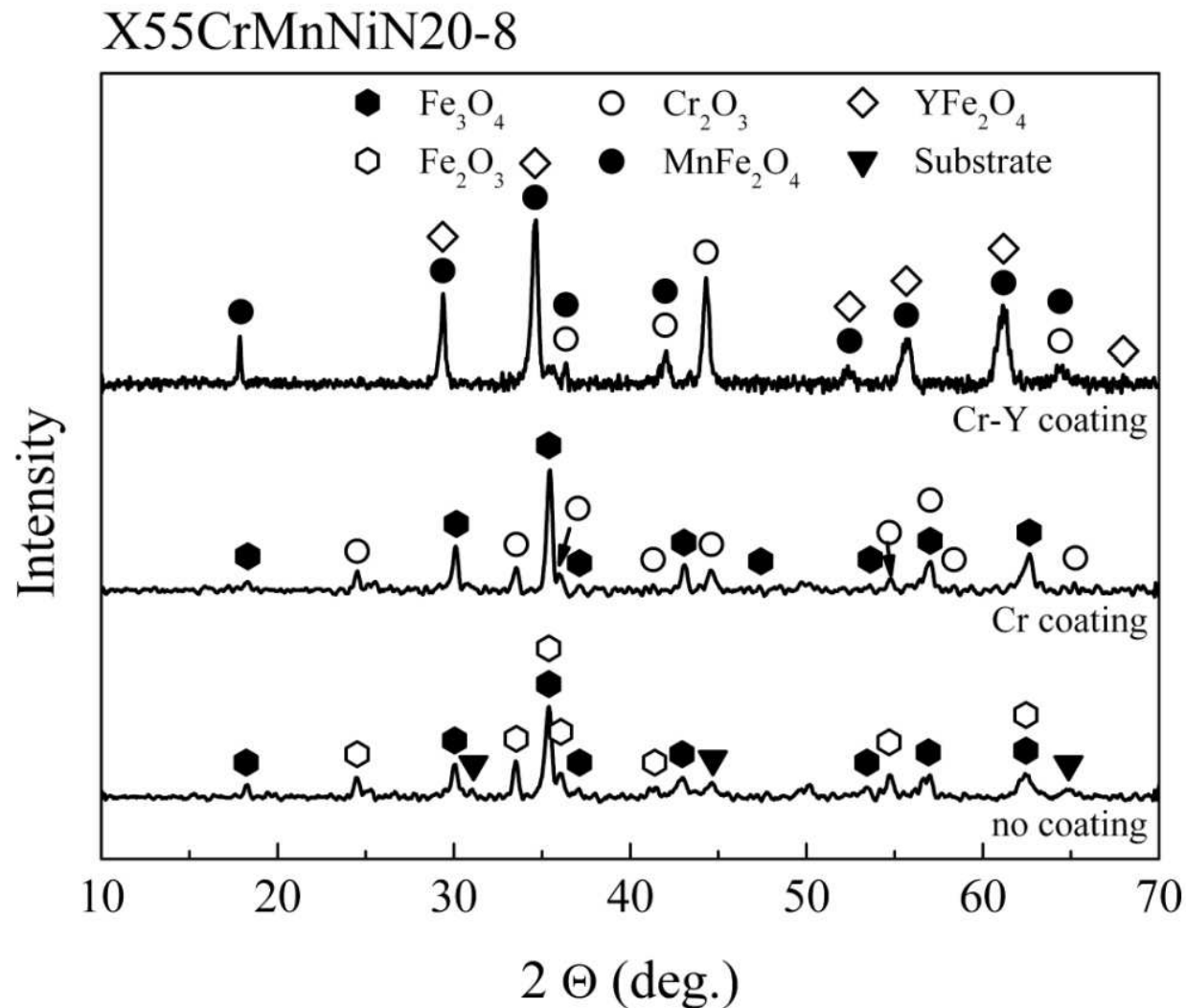
Phase composition of the oxide scales formed on uncoated and coated X50CrMnNiNbN21-9 steel after 100 h oxidation in air at 900°C



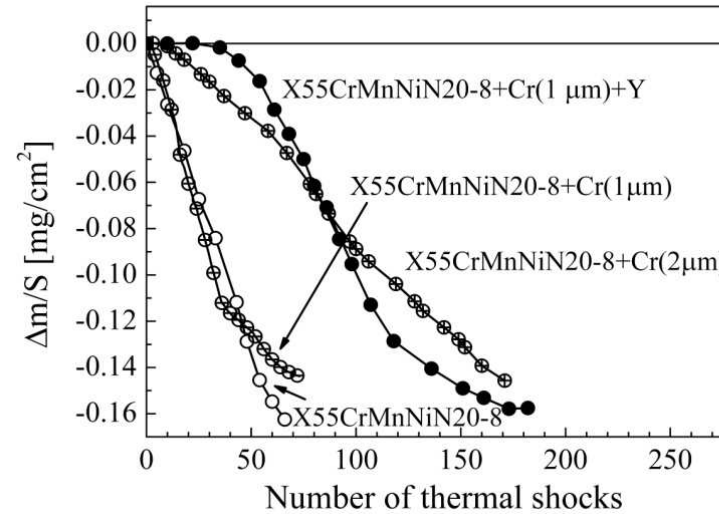
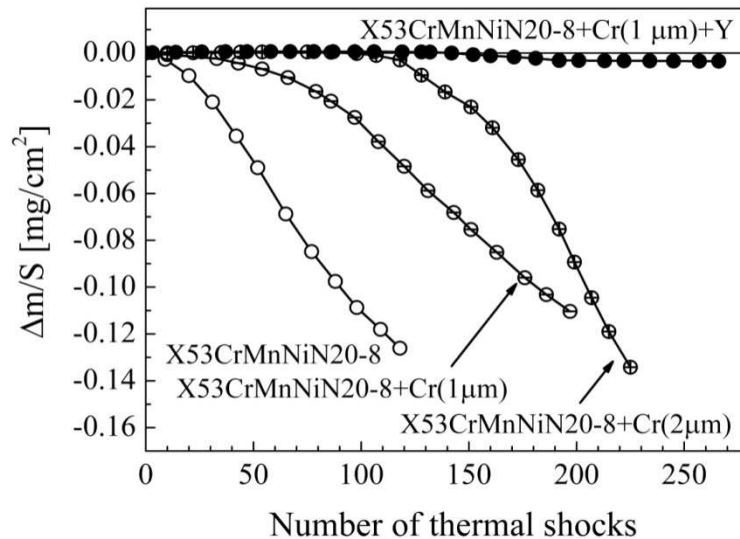
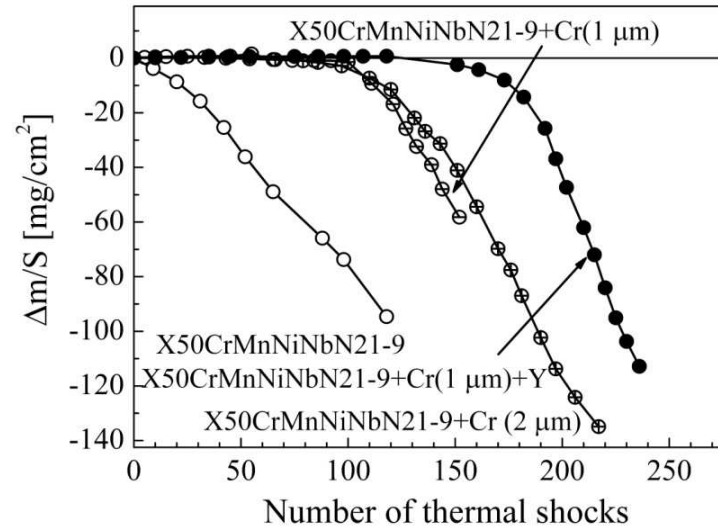
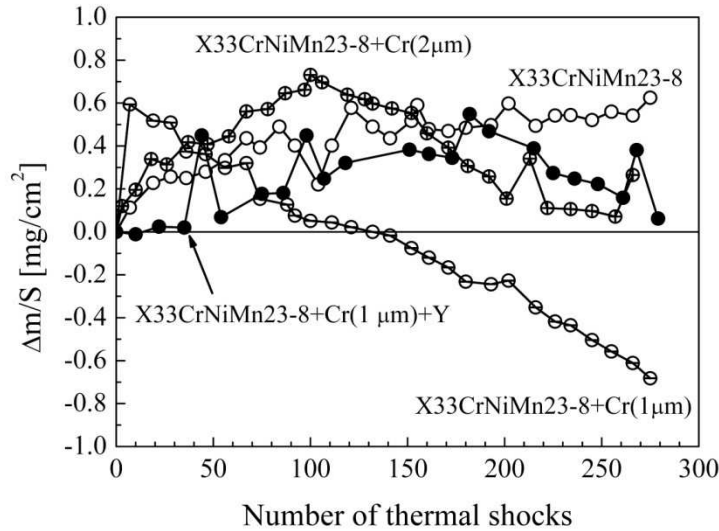
Phase composition of the oxide scales formed on uncoated and coated X53CrMnNiN20-8 steel after 100 h oxidation in air at 900°C



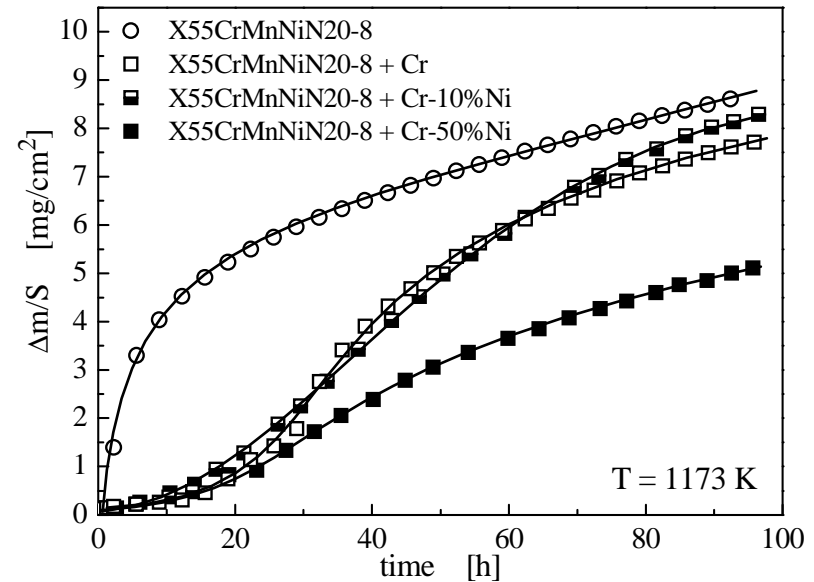
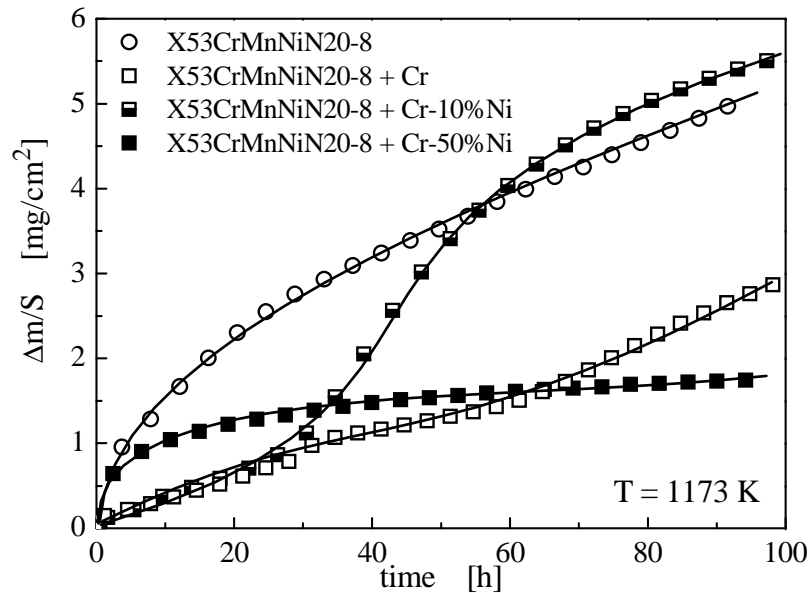
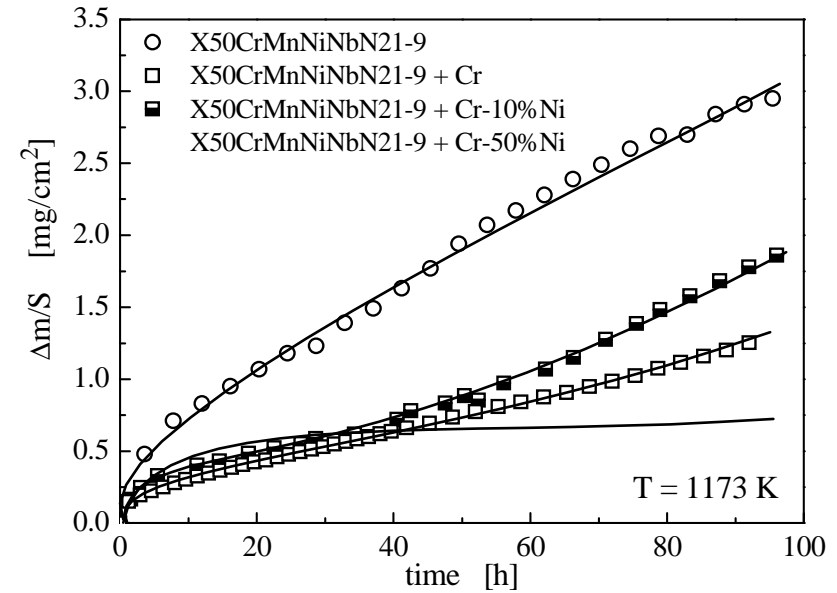
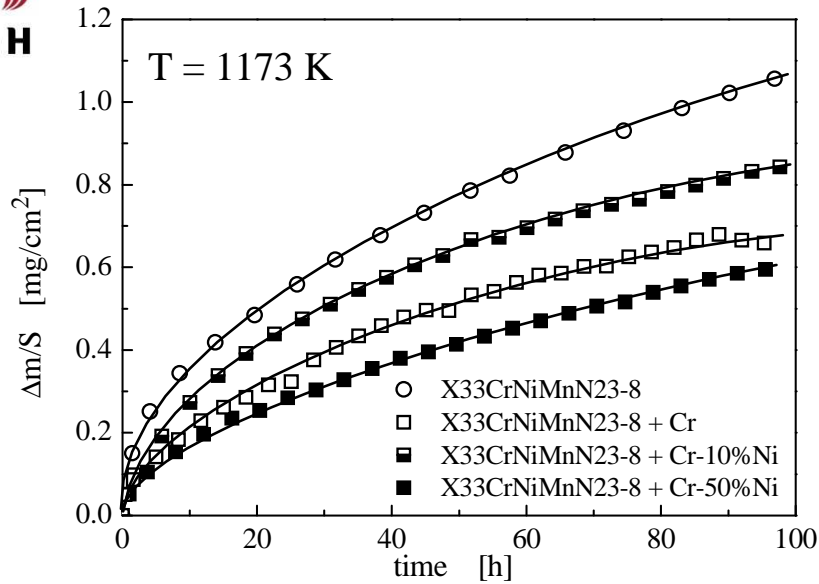
Phase composition of the oxide scales formed on uncoated and coated X55CrMnNiN20-8 steel after 100 h oxidation in air at 900°C



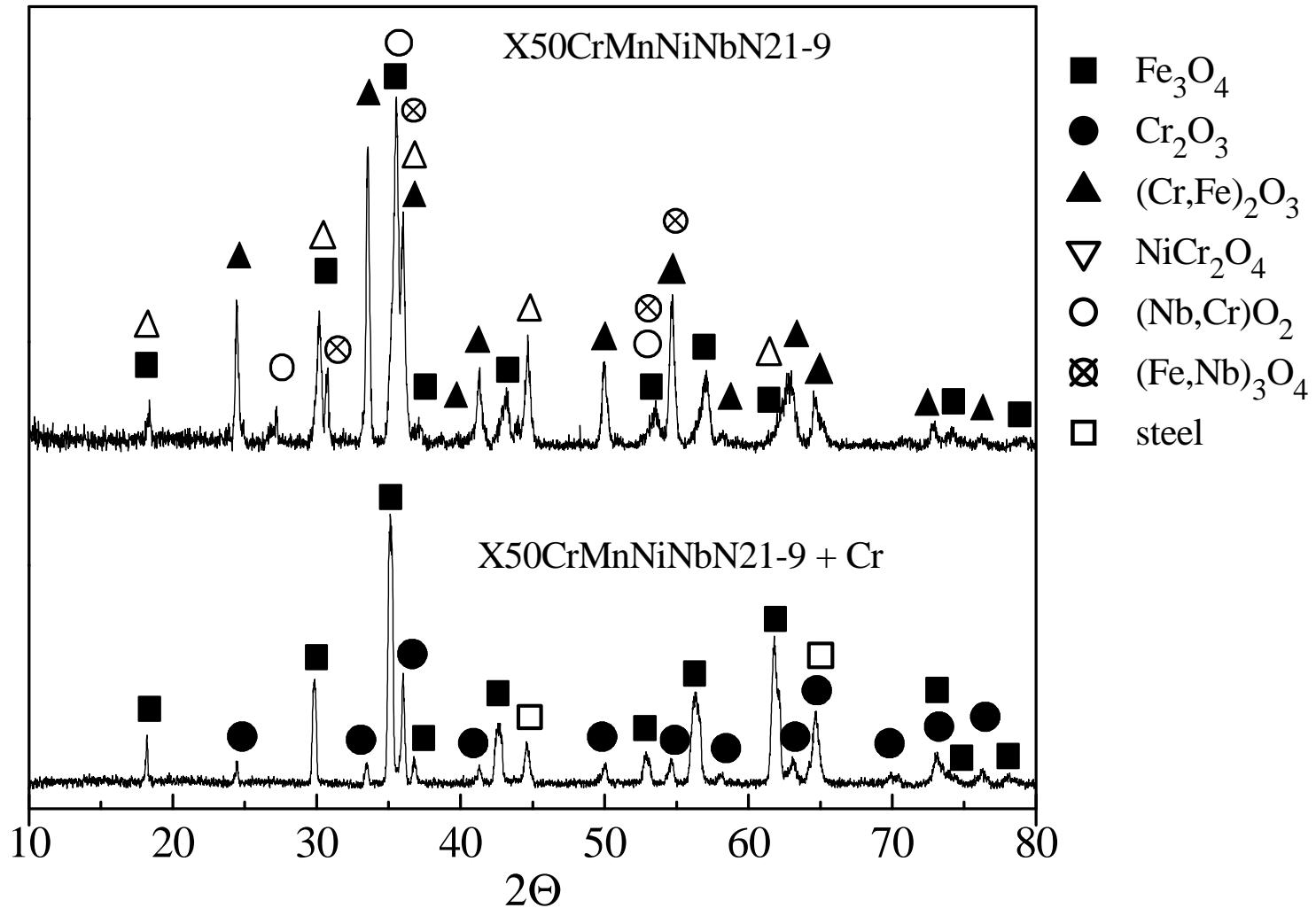
Results of oxidation studies in the thermal shock conditions of coated and uncoated valve steels



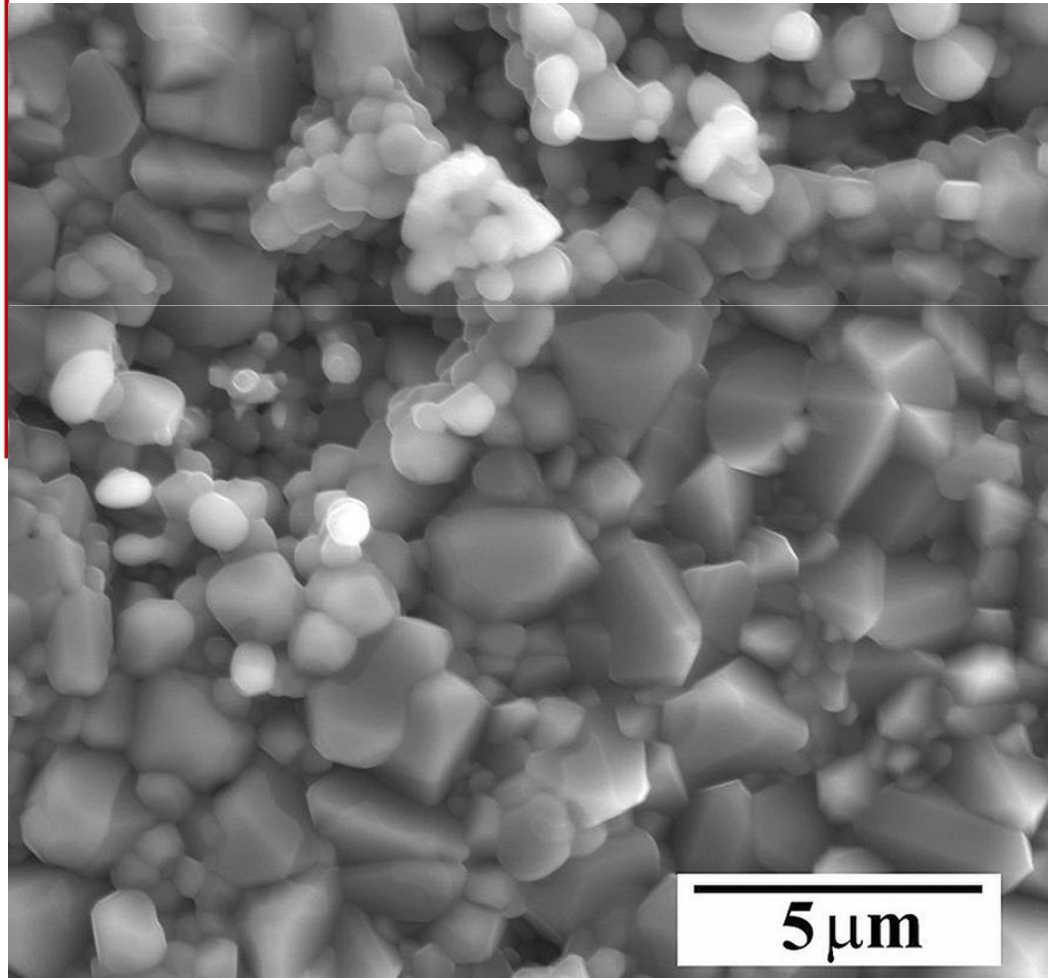
Oxidation kinetics of valve steels covered with chromium-nickel coatings



Phase compositions of the scales formed on X50CrMnNiNbN21-9 steel with and without chromium coating

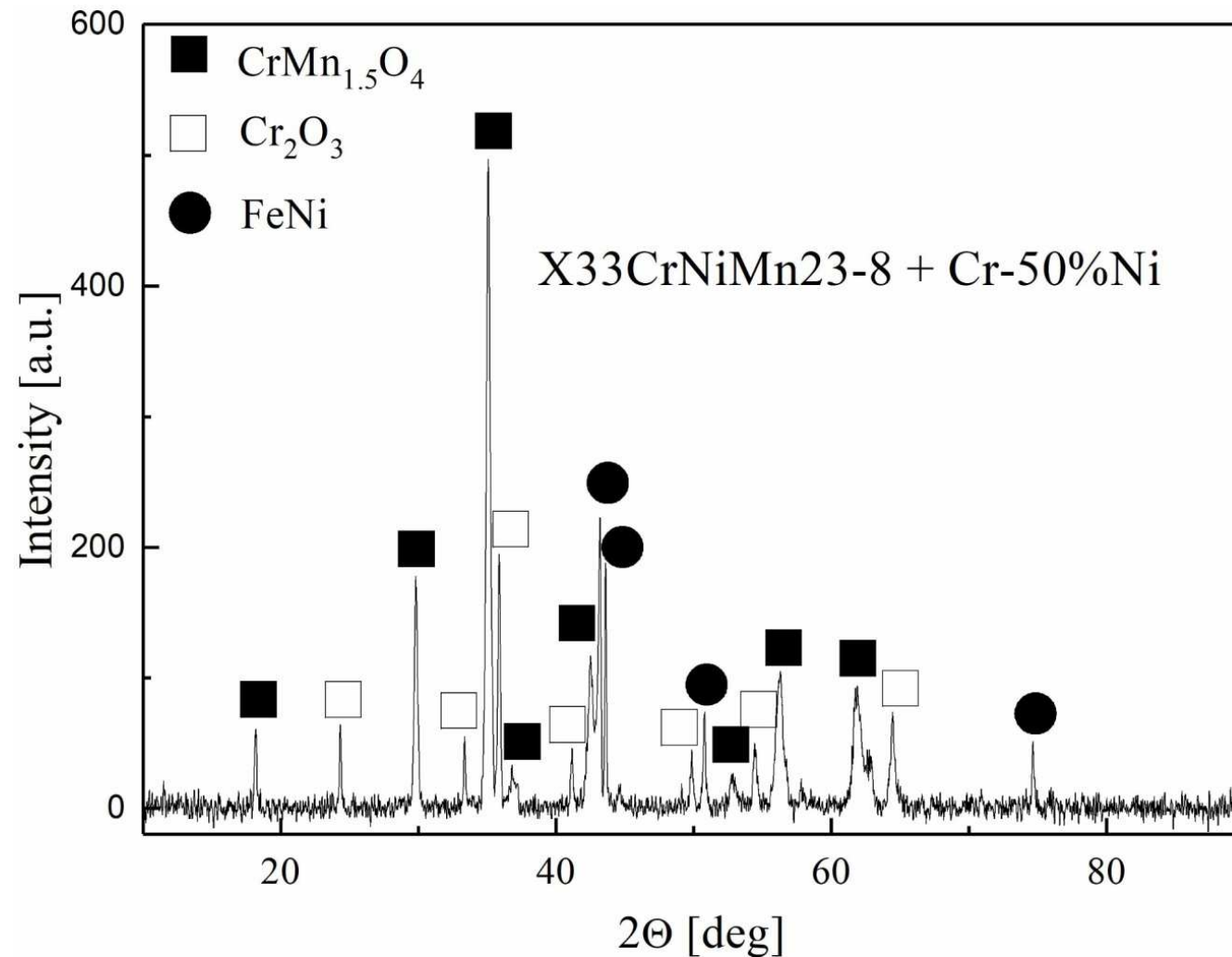


Surface of the oxide scale grown on X33CrNiMn23-8 steel covered with a Cr–50%Ni coating with visible small grains characteristic for Cr_2O_3

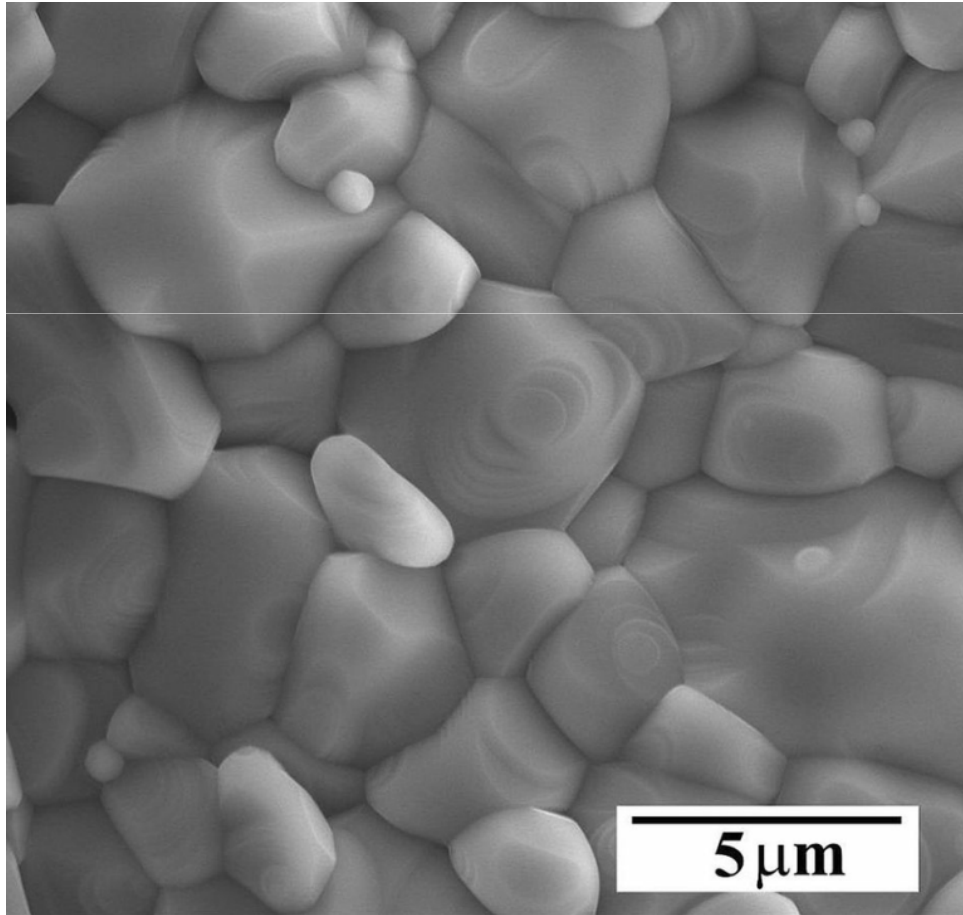


Element	Atomic percent [%]
O	39.32
Cr	8.96
Mn	24.70
Ni	27.02

XRD analysis of the oxide scale formed on X33CrNiMn23-8 steel covered with a Cr-50%Ni coating

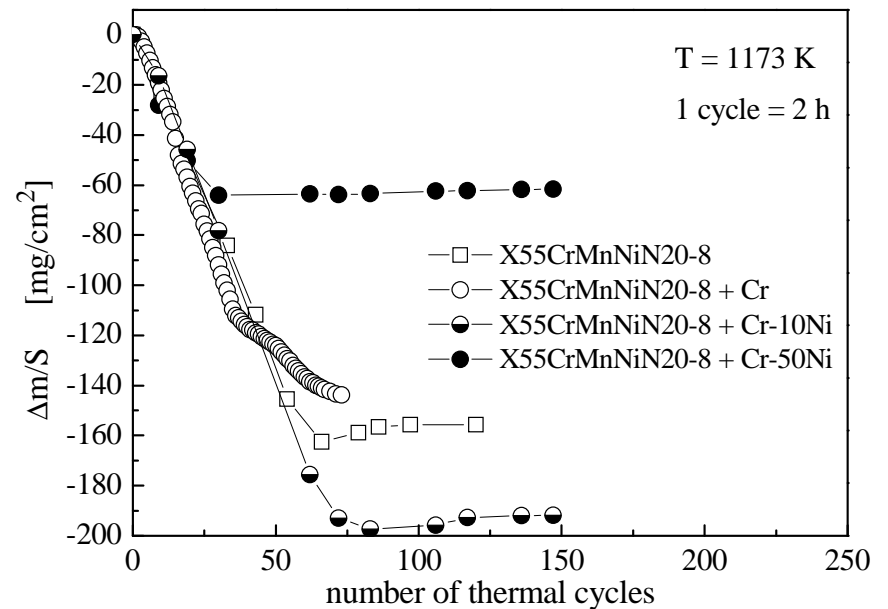
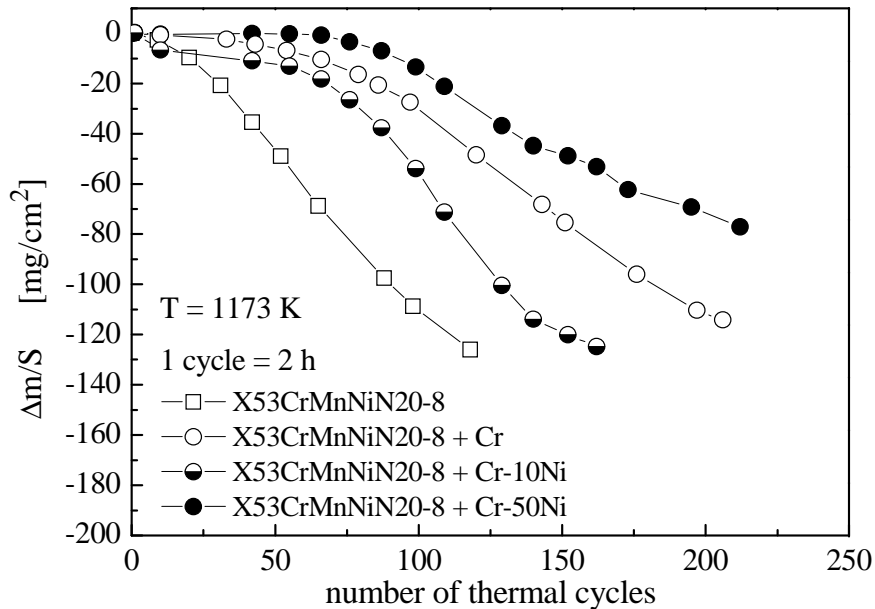
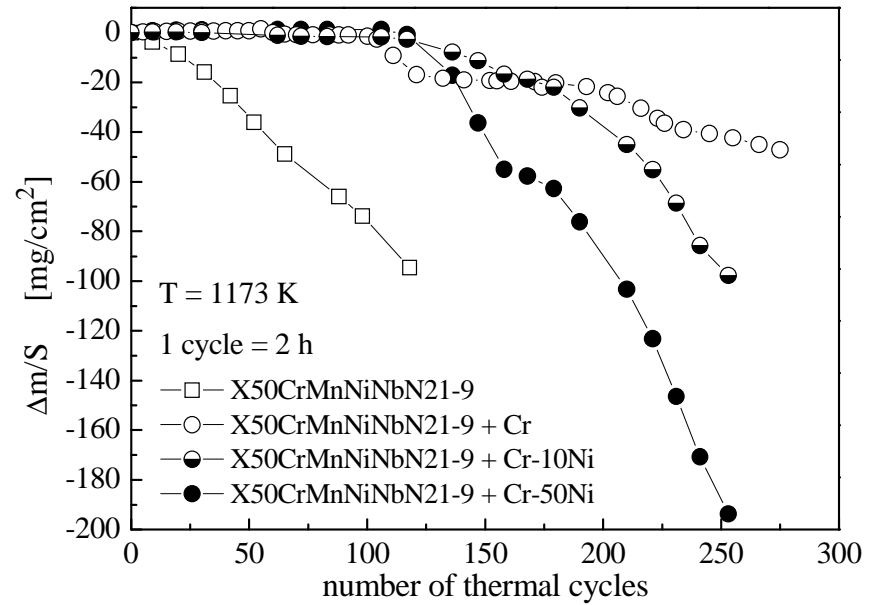
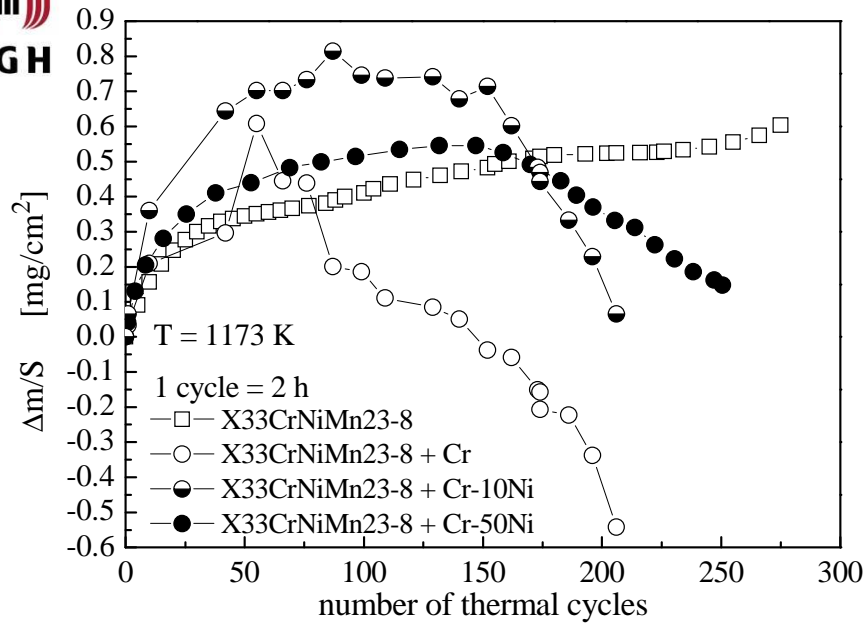


Surface of the oxide scale formed on X53CrMnNiN20-8 steel covered with a Cr–10%Ni coating



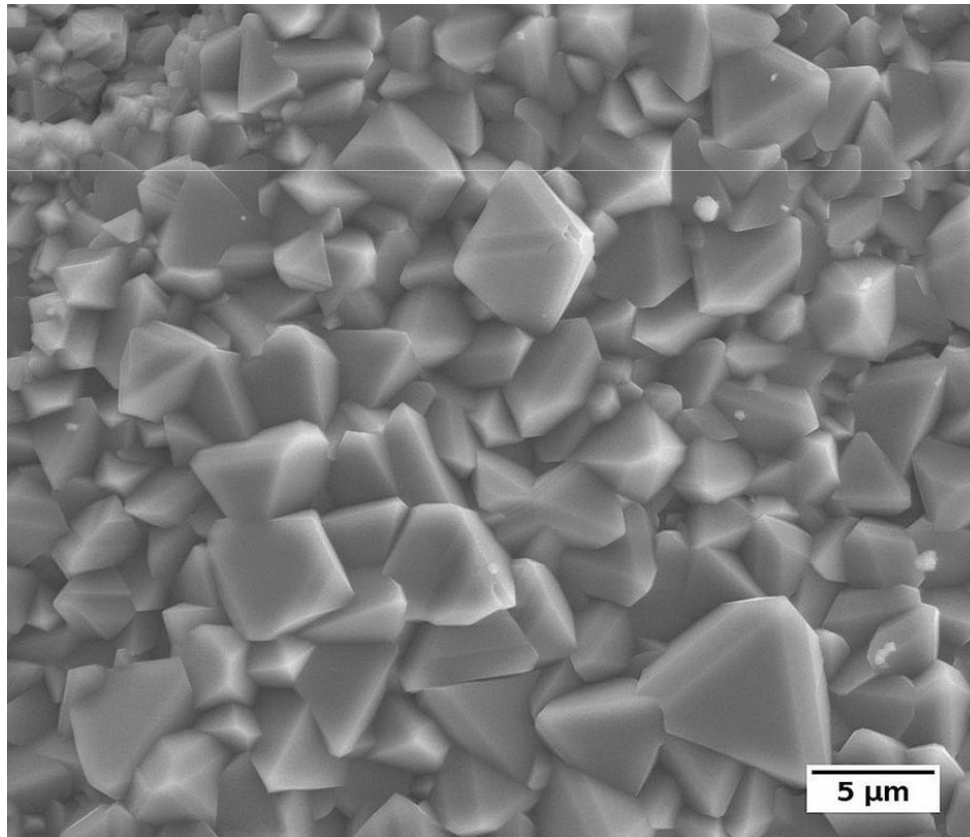
Element	Atomic percent [%]
O	42.04
Cr	19.85
Mn	26.76
Fe	9.96
Ni	1.39

Results obtained in thermal shock conditions



Oxidation behavior of valve steels covered by Cr–Ni coatings in thermal shock conditions

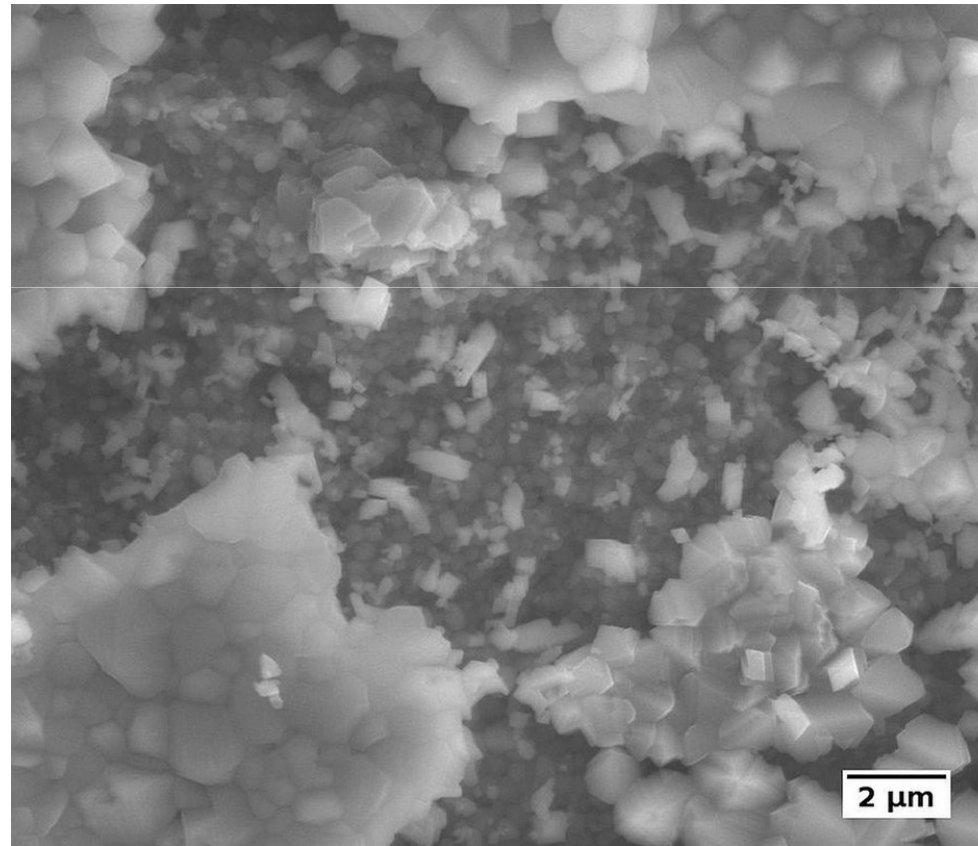
Surface of the oxide scale grown on X33CrNiMn23-8 steel covered with a Cr–50%Ni coating with visible small grains characteristic for Cr_2O_3



Element	Atomic percent [%]
O	46.11
Cr	26.78
Mn	18.93
Fe	1.95
Ni	6.23

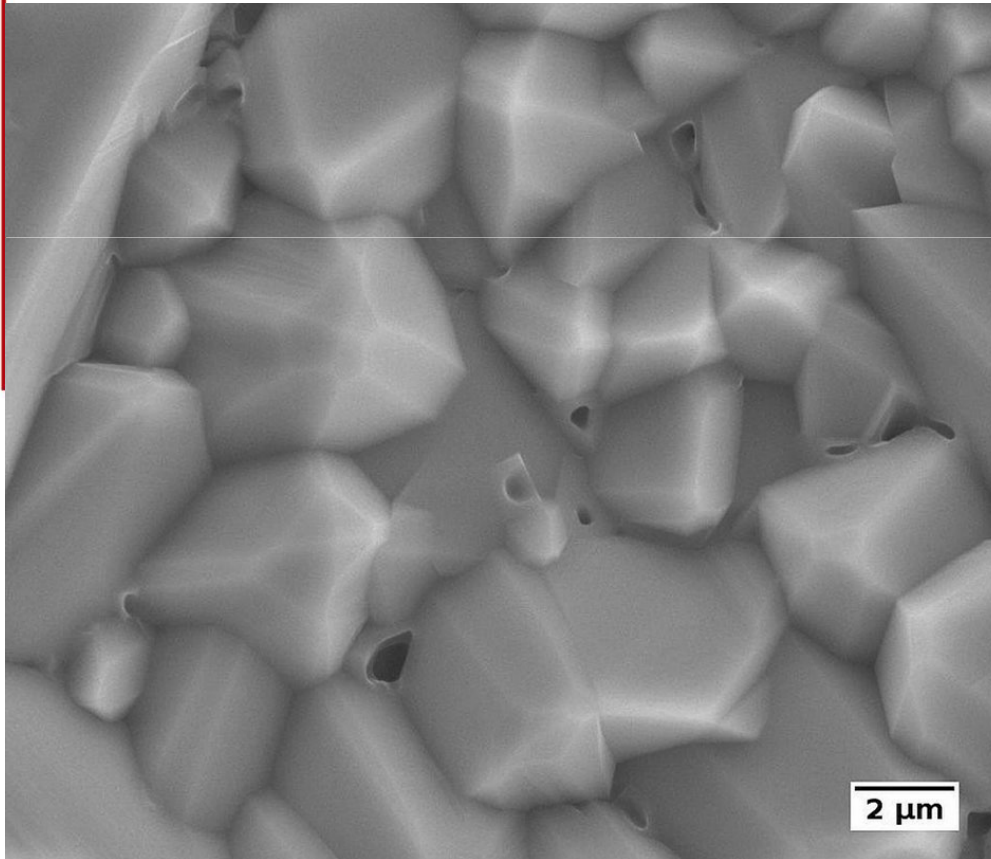
Oxidation behavior of valve steels covered by Cr–Ni coatings in thermal shock conditions

Oxide scale surface on X50CrMnNiNbN21-9 steel covered with a Cr–50%Ni coating



Oxidation behavior of valve steels covered by Cr–Ni coatings in thermal shock conditions

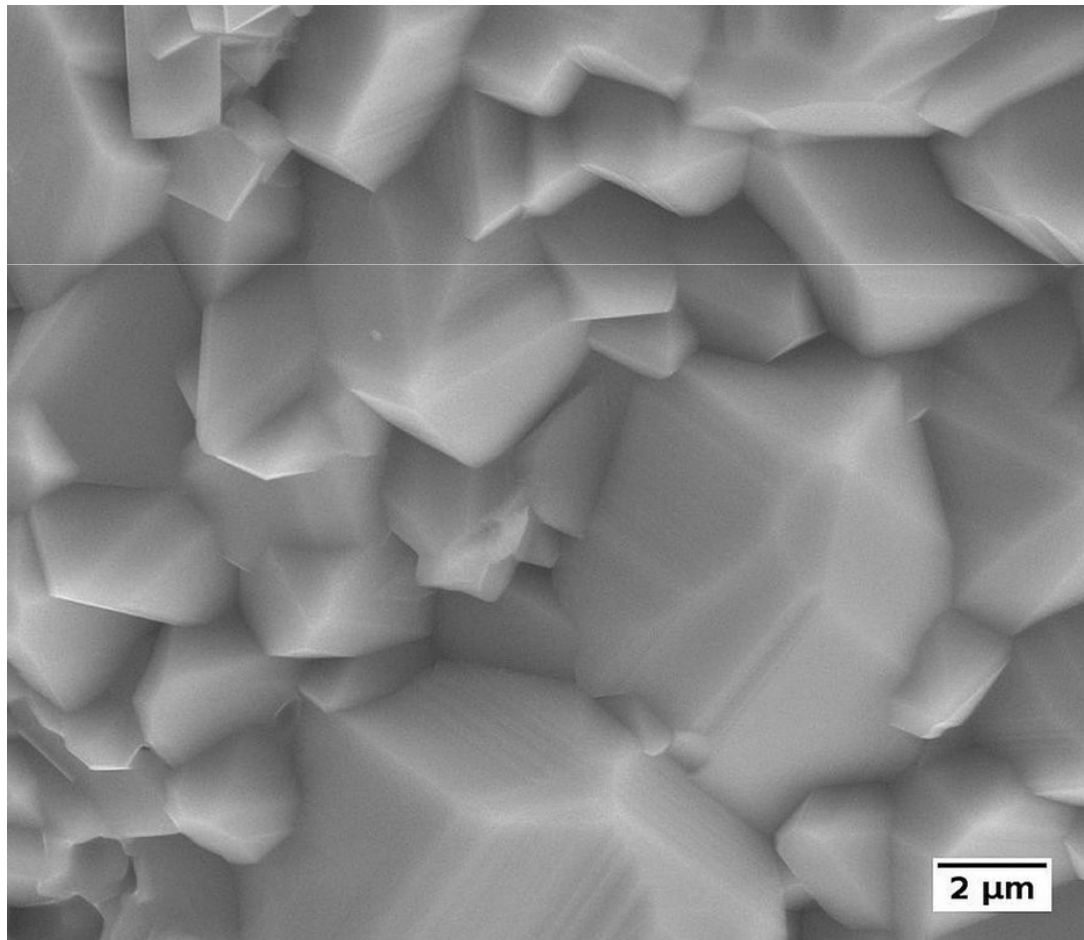
Oxide scale surface on X53CrMnNiN20-8 steel covered with a Cr–50%Ni coating



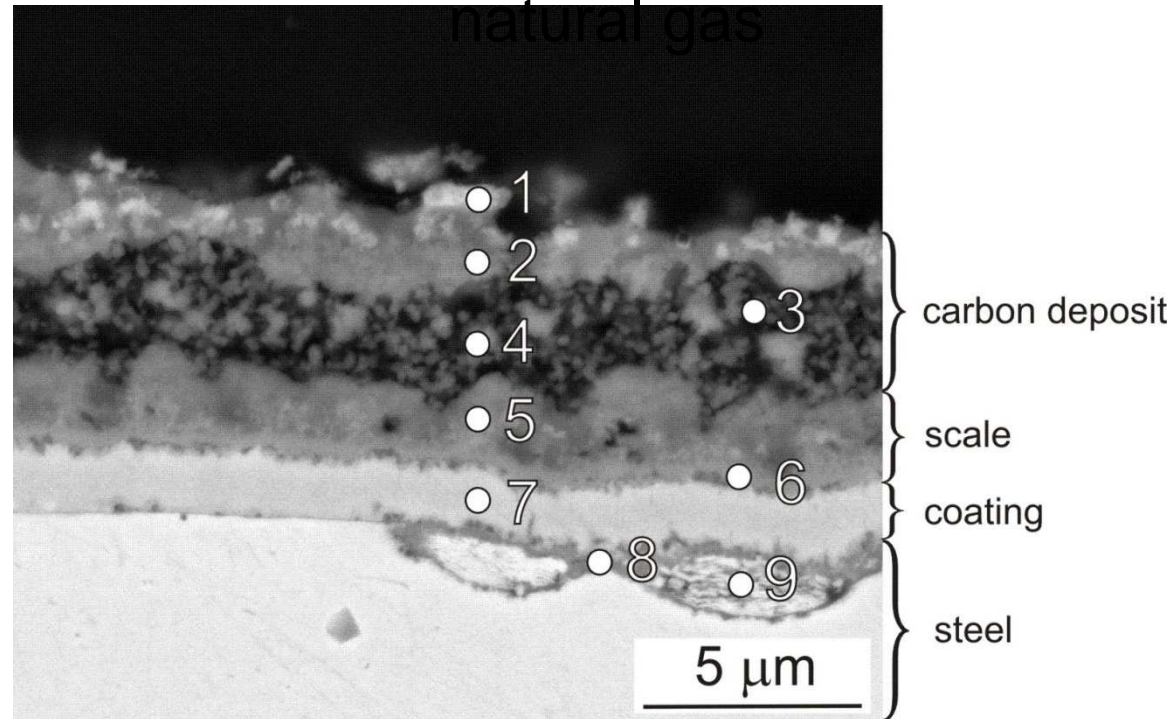
Element	Atomic percent [%]
O	41.73
Cr	3.01
Mn	23.33
Fe	28.68
Ni	3.25

Oxidation behavior of valve steels covered by Cr–Ni coatings in thermal shock conditions

Oxide scale surface on X55CrMnNiN20-8 steel covered with a Cr–50%Ni coating

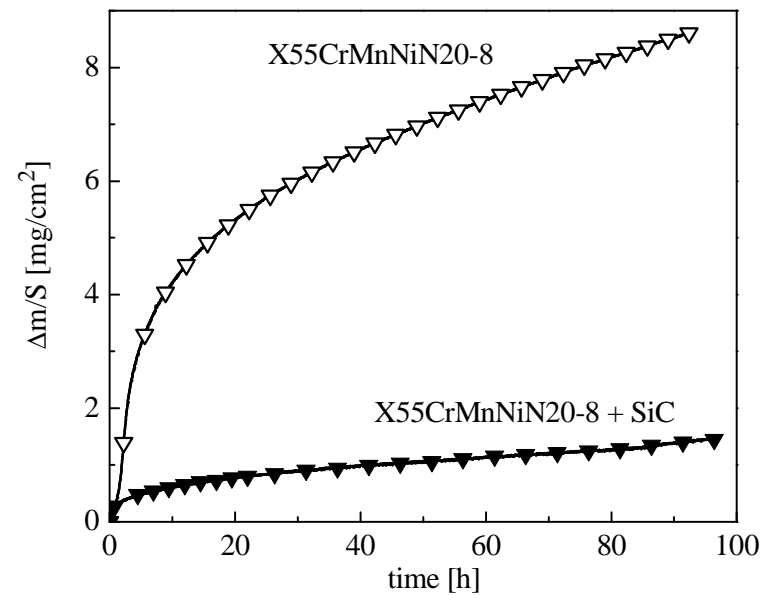
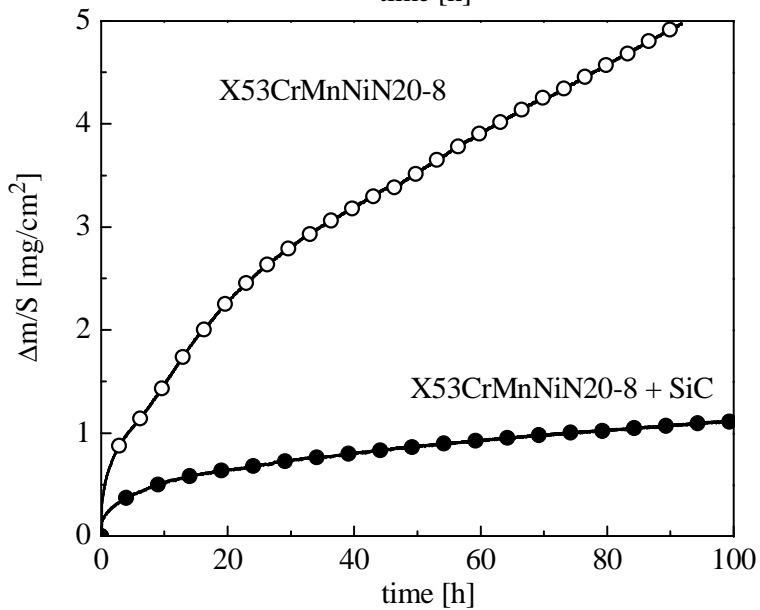
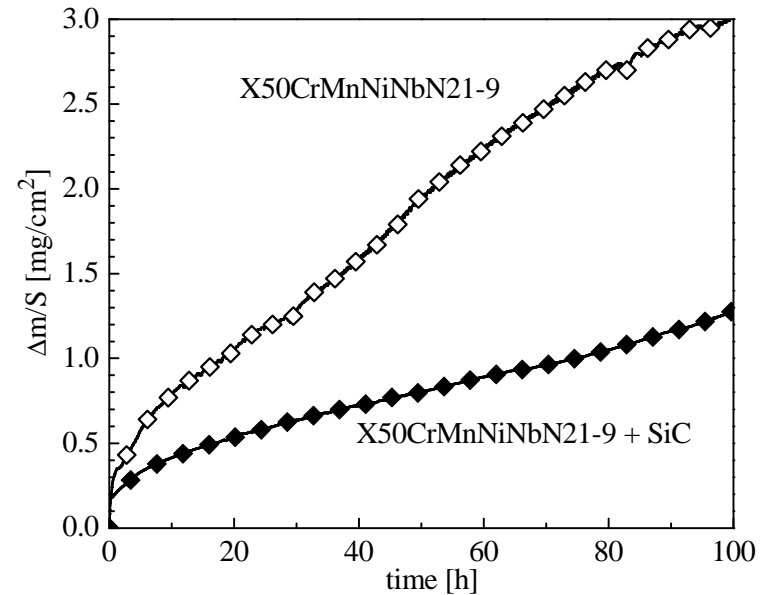
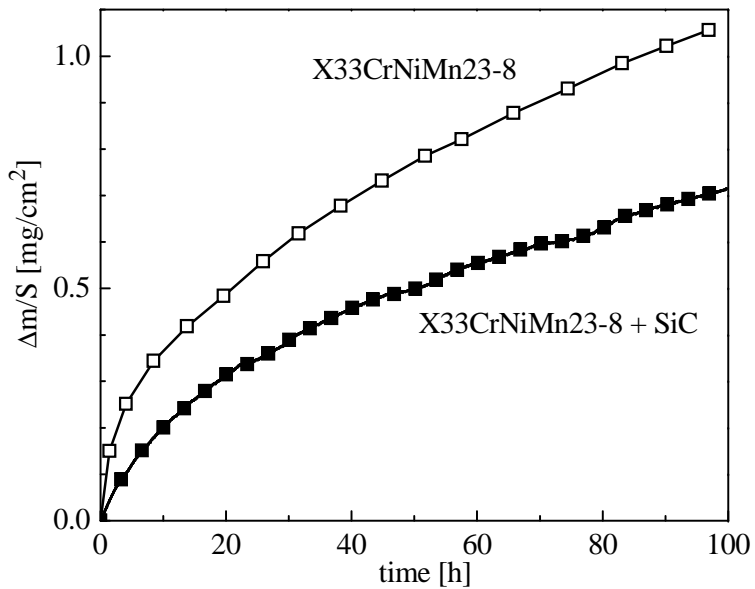


Cross-section of a Cr coated mushroom valve after testing a 0.9 SGE TC80 CNG engine powered by natural gas

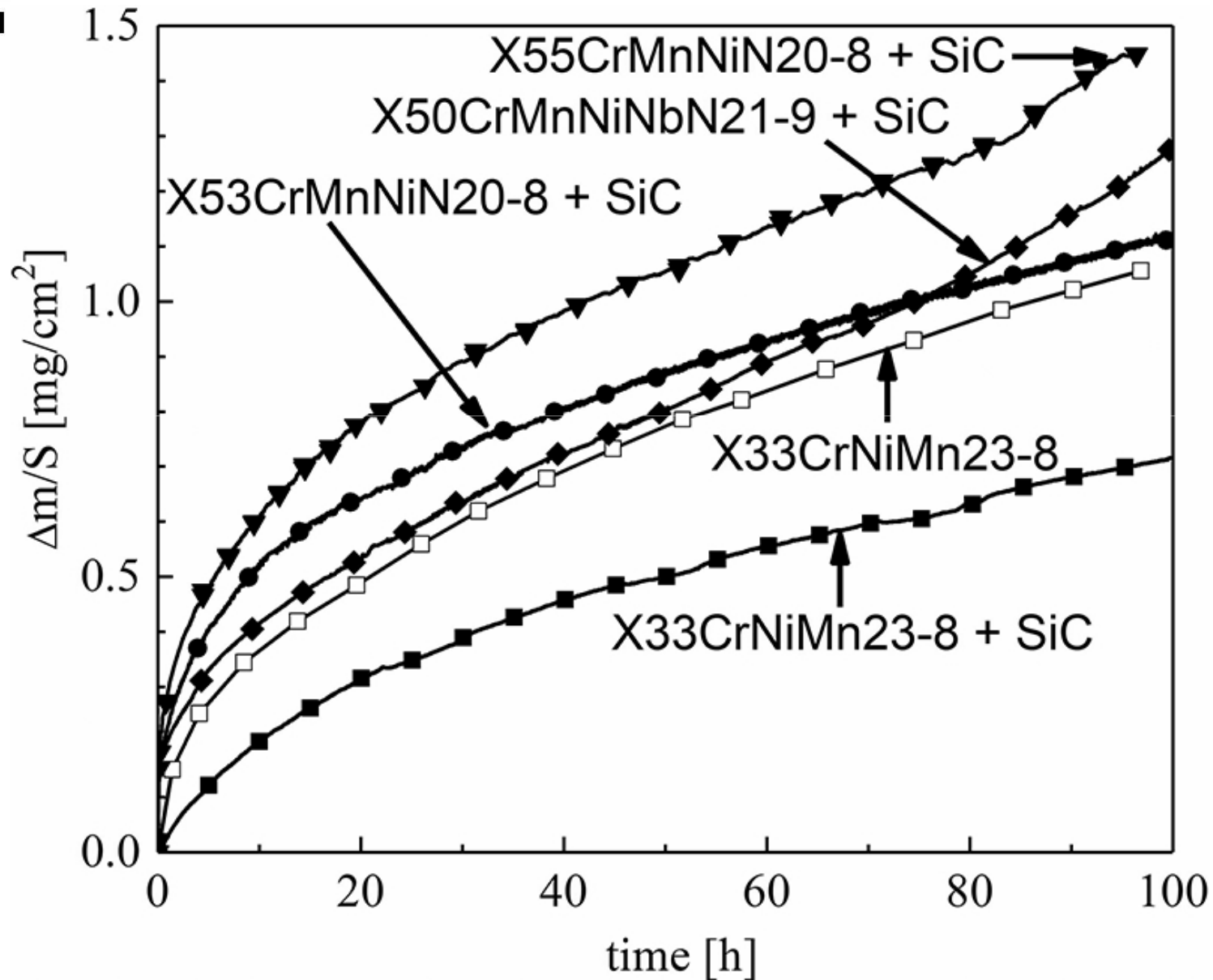


Element	Chemical composition (% at.)								
	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7	Point 8	Point 9
O	67.3	62.8	46.4	46.2	63.7	26.2	8.8	8.2	7.8
Cr	4.7	1.6	1.0	0.9	5.9	67.2	20.3	19.0	19.5
Ni	0.8	0.7	0.8	1.2	0.7	1.4	60.0	61.3	63.0
Mn	2.1	1.6	1.4	3.8	3.4	0.0	0.5	0.3	0.5
Fe	5.3	0.5	0.4	0.3	0.6	0.4	2.0	2.2	2.0
P	7.7	7.5	4.0	5.8	4.5	0.8	0.3	0.2	0.2
S	0.0	0.2	0.6	0.6	0.3	0.6	0.3	0.5	0.3
Al	0.8	1.8	1.2	0.9	2.4	1.1	2.8	3.4	2.9
Ca	4.2	6.5	1.8	1.4	1.0	0.4	0.6	0.3	0.7
Ti	1.1	14.5	41.5	36.7	13.4	1.1	3.6	3.7	2.0
Zn	6.1	2.3	1.0	2.3	4.1	0.7	0.8	0.8	1.0

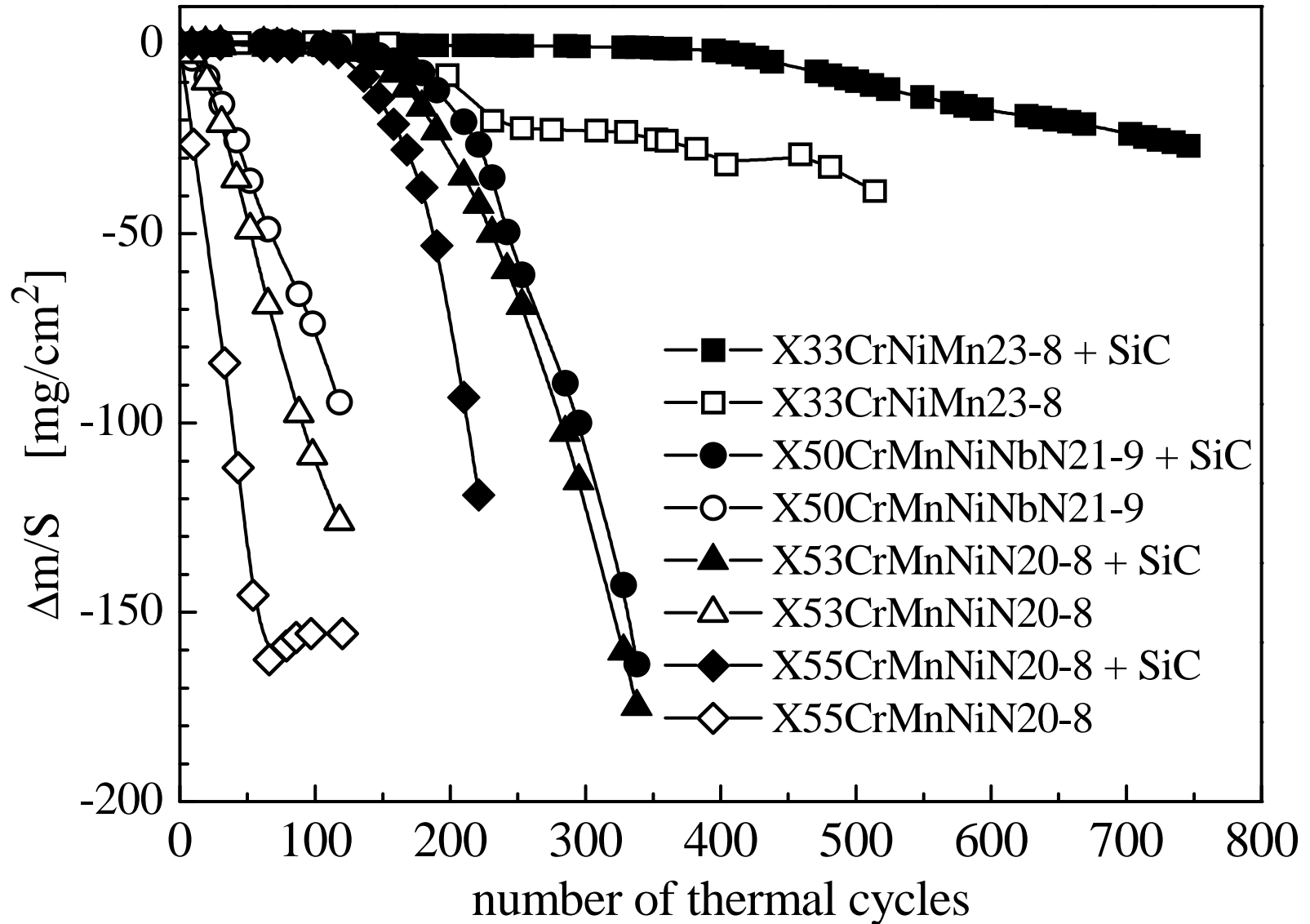
Influence of SiC coating with 1 μm thickness on oxidation kinetics at 1173 K of the studied valve steels



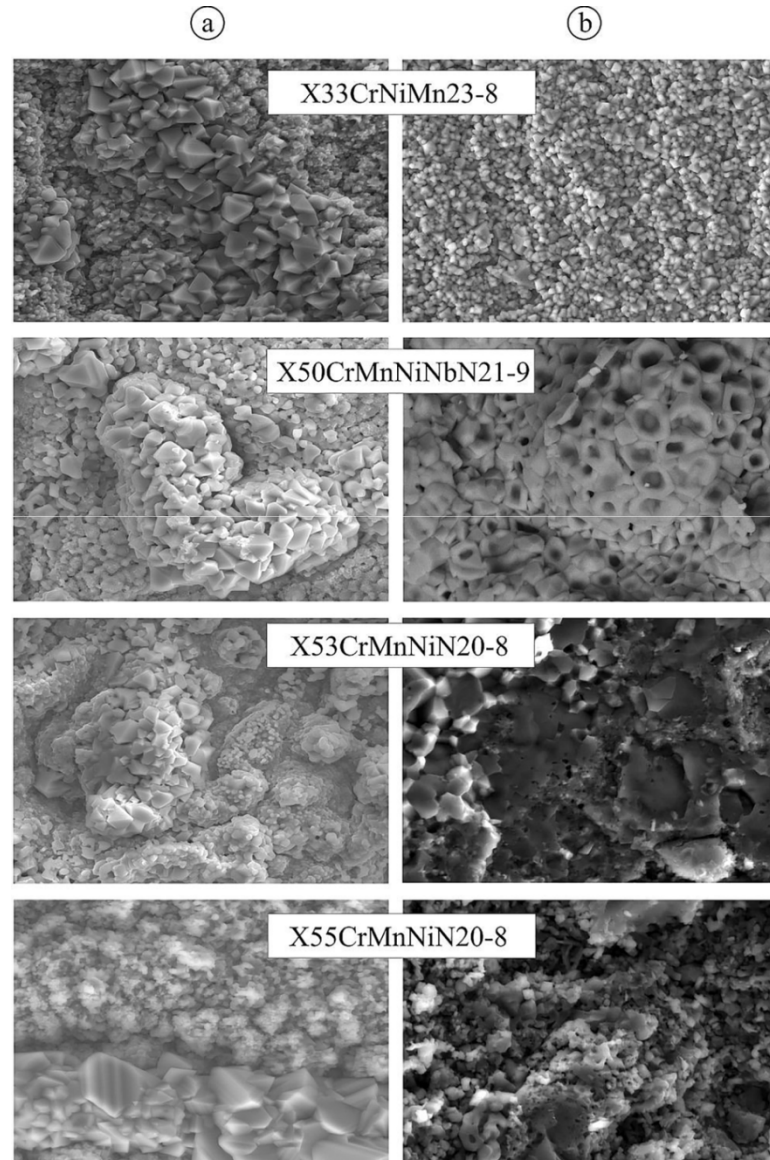
Influence of SiC coating with 1 μm thickness on oxidation kinetics at 1173 K of the studied valve steels



Influence of the SiC coating on oxidation kinetics of the valve steels in thermal shock conditions

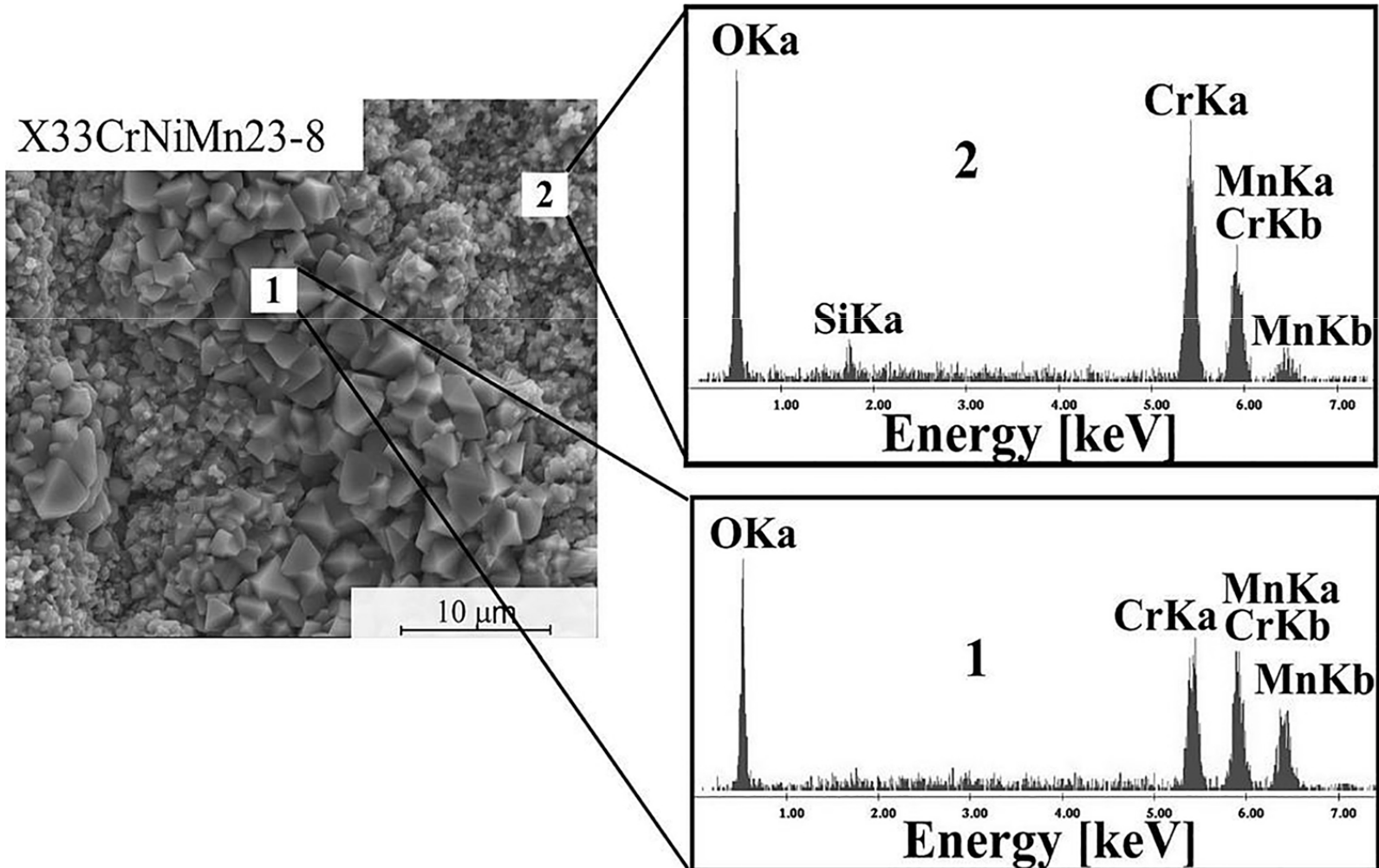


SEM images of the studied steels after oxidation in air: a) coated steel, b) uncoated steel

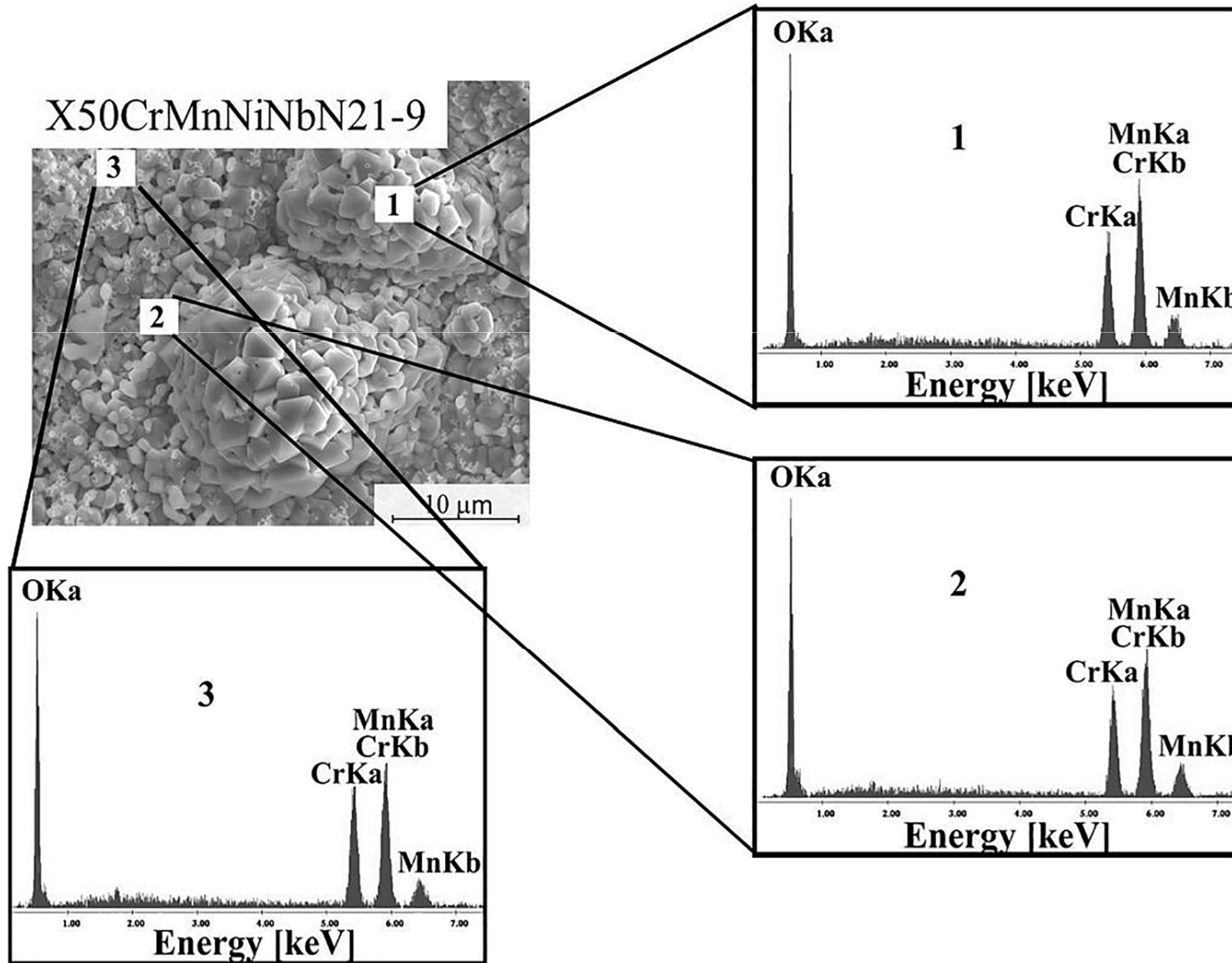


10 μm

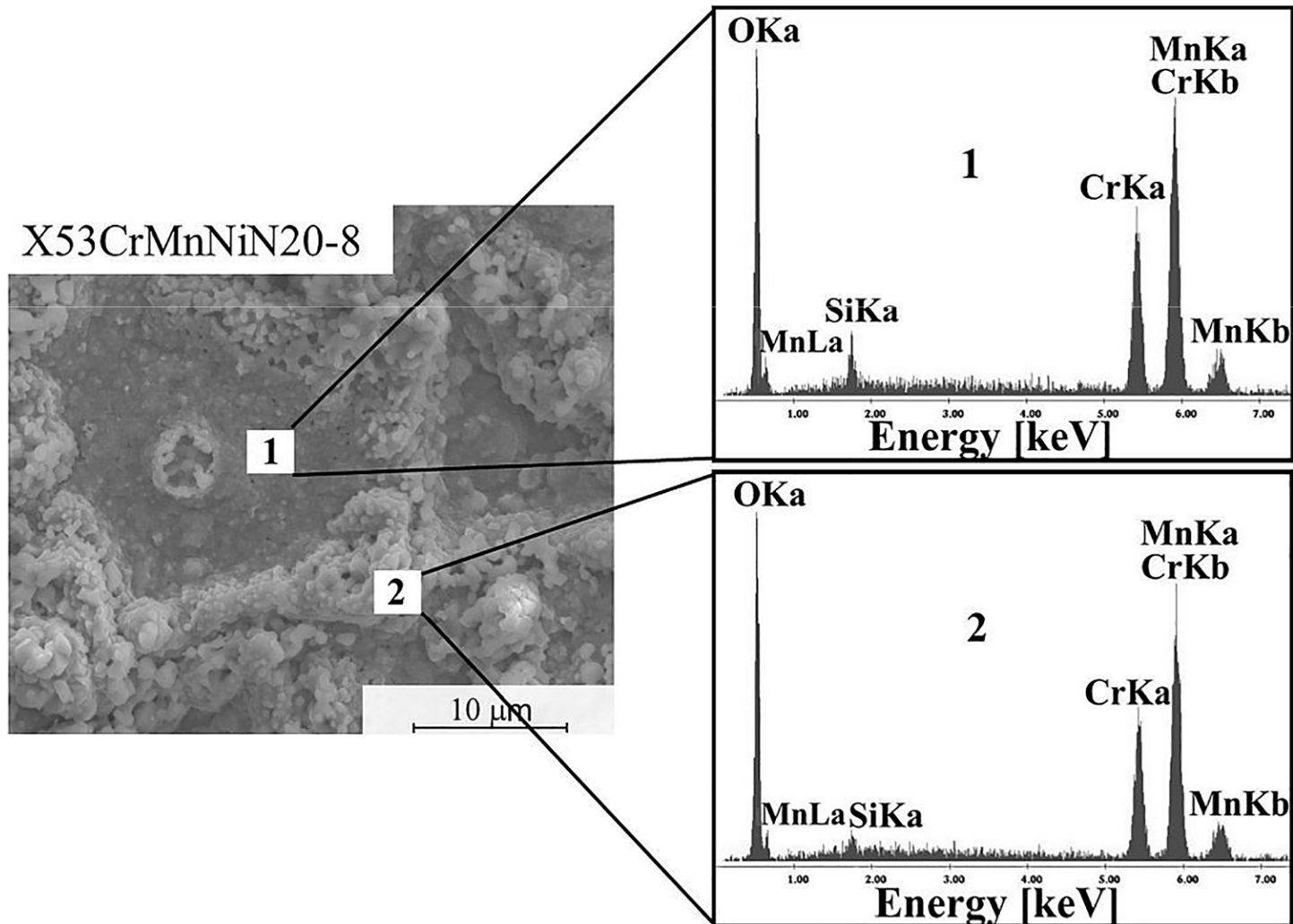
SEM surface microphotograph of the scale grown on X33CrNiMn23-8 steel with SiC coating after 100-hr oxidation at 1173 K in air and EDS analysis of selected points



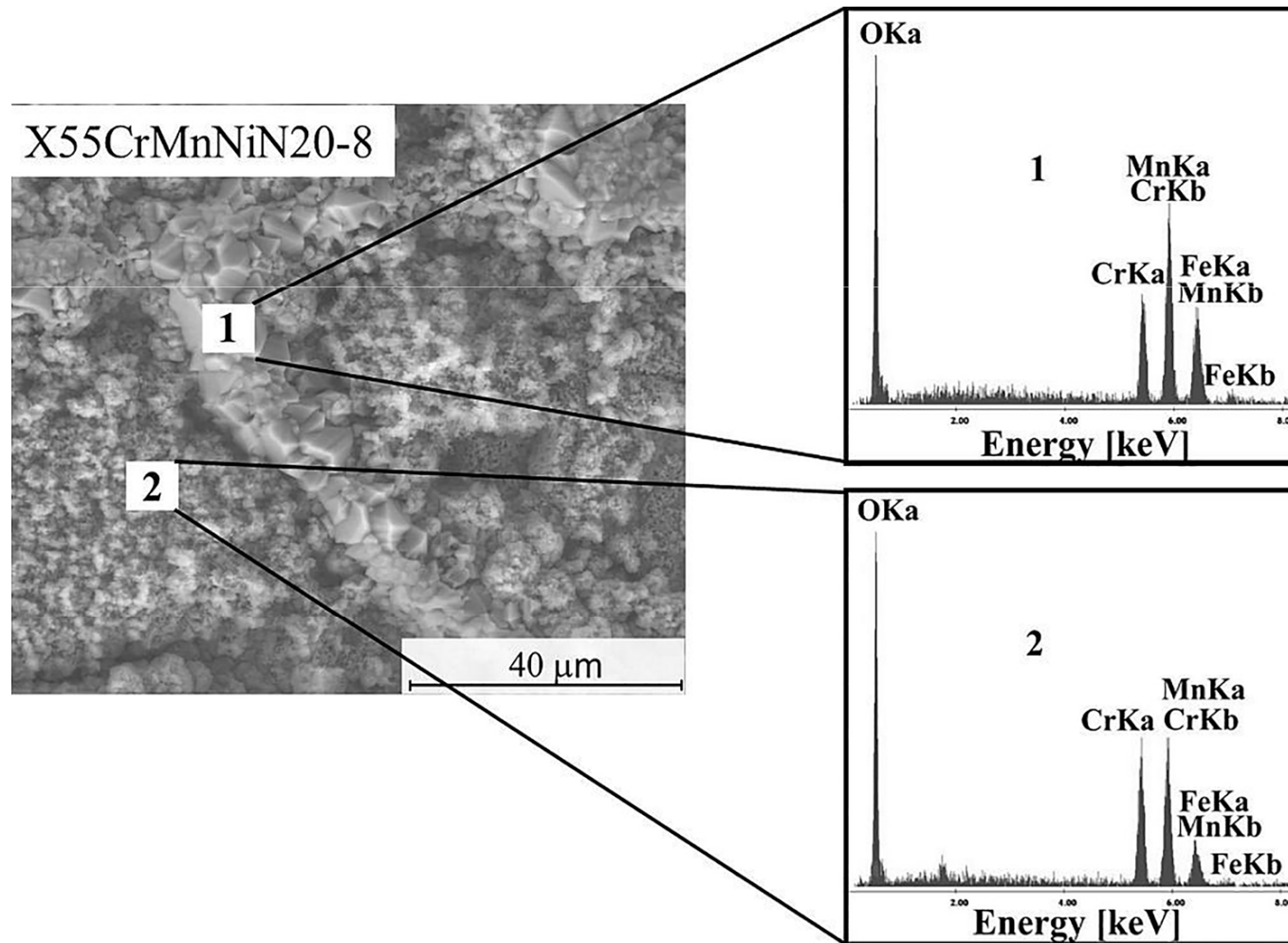
SEM microphotograph of the scale grown on X50CrMnNiNbN21-9 steel with SiC coating after 100-hr oxidation at 1173 K in air and EDS analysis of selected points



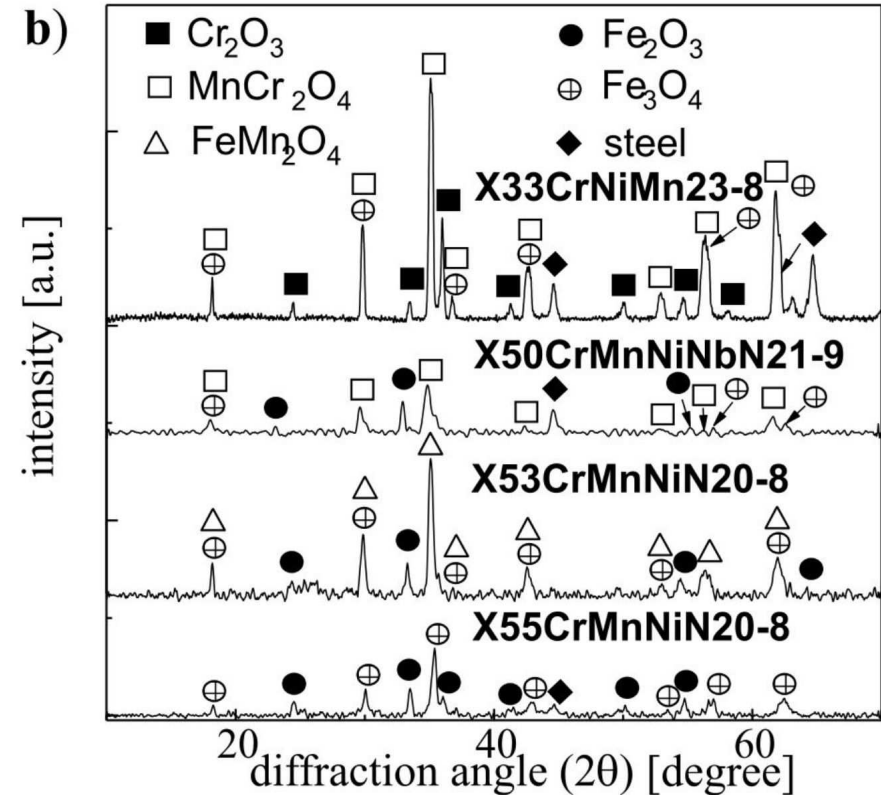
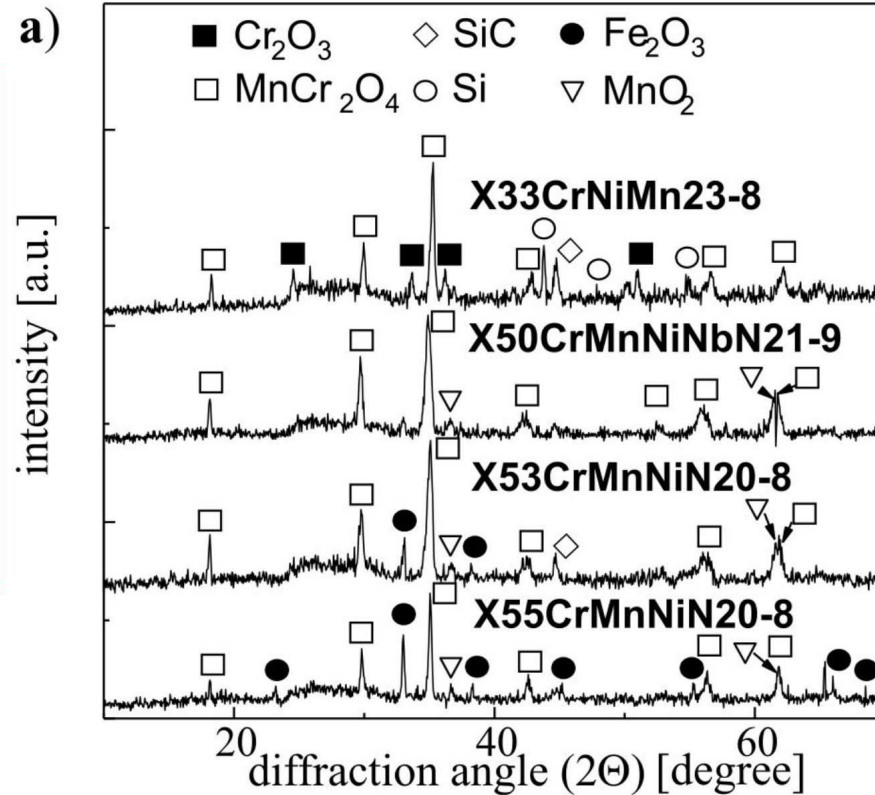
SEM microphotograph of the scale grown on X53CrMnNiN20-8 steel with SiC coating after 100-hr oxidation at 1173 K in air and EDS analysis of selected points



SEM microphotograph of the scale grown on X55CrMnNiN20-8 steel with SiC coating after 100-hr oxidation at 1173 K in air and EDS analysis of selected points



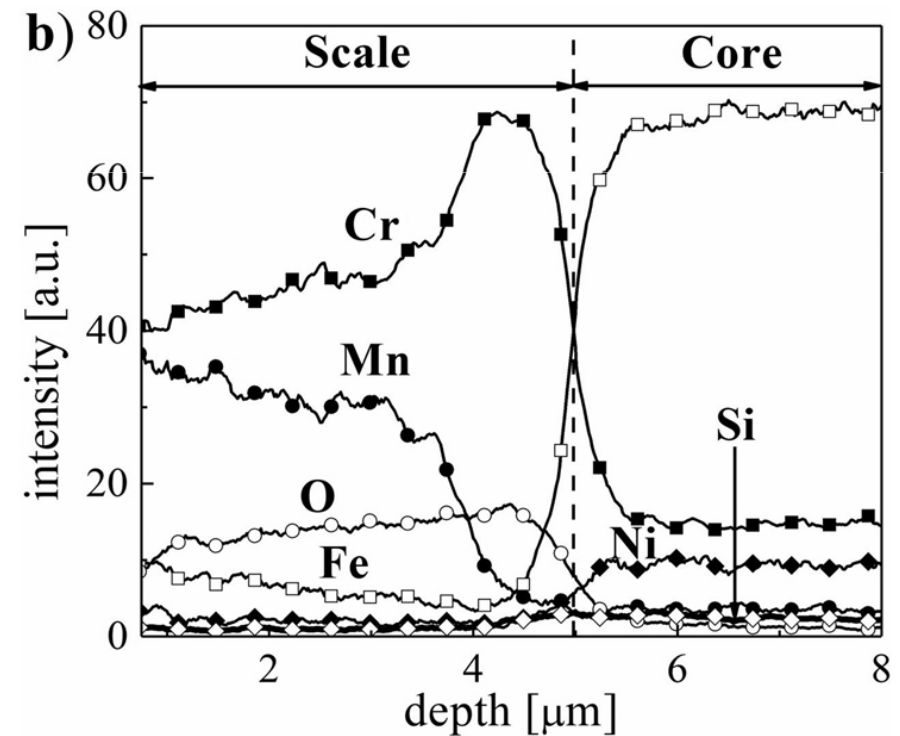
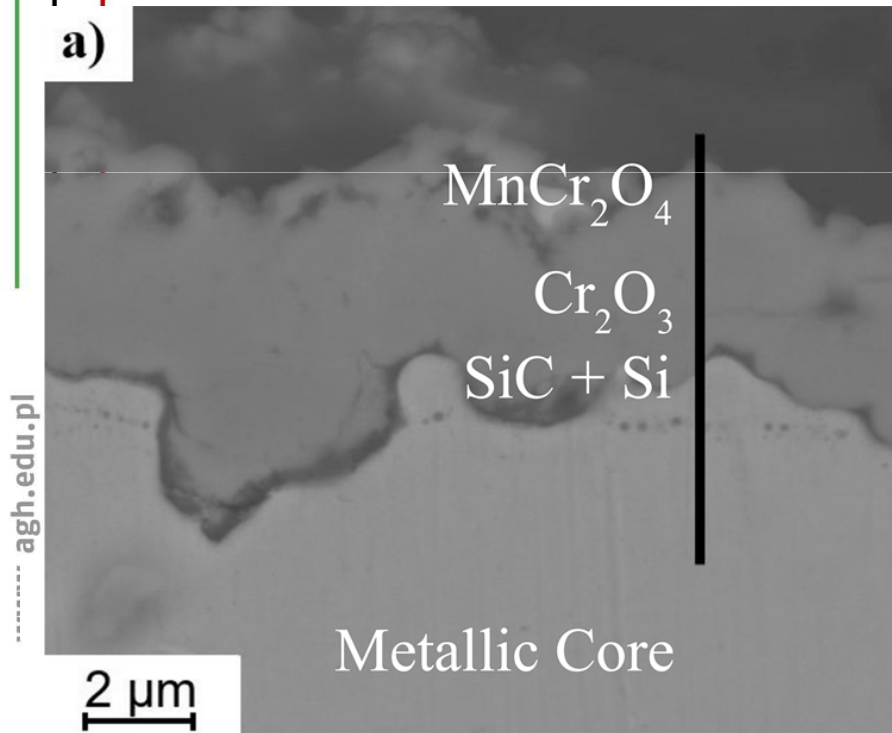
Influence of SiC coating on phase composition of the scales formed during oxidation at 1173 K



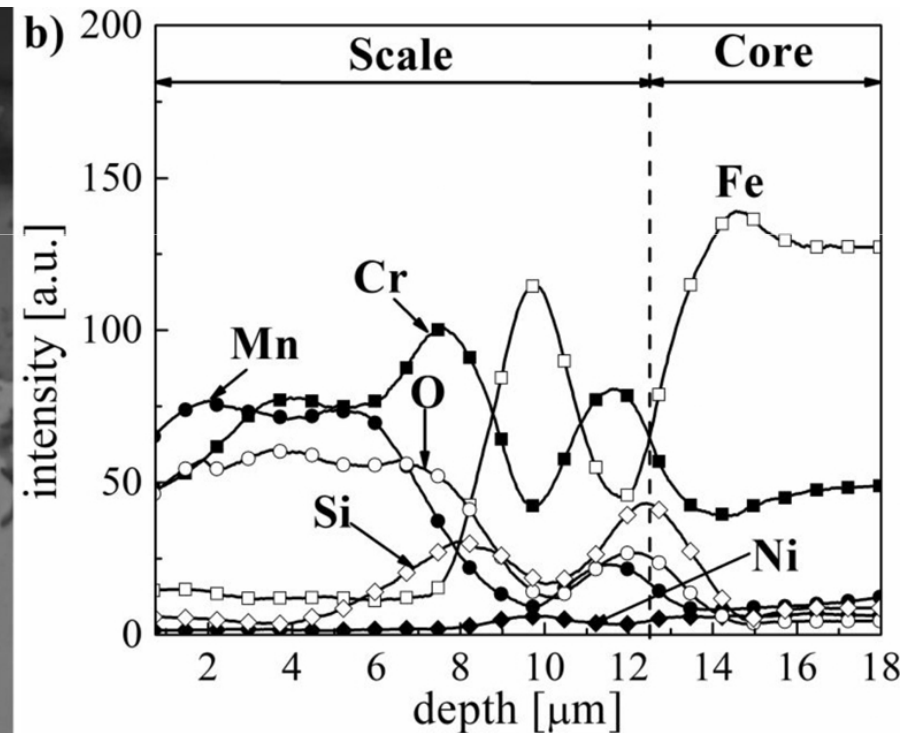
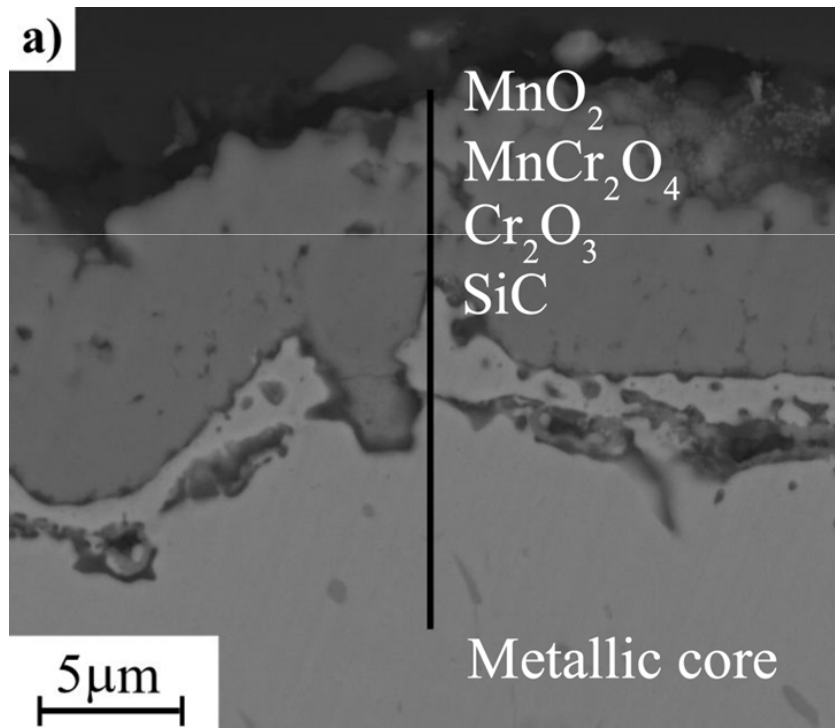
Linear thermal expansion coefficient:

steel: $1.6 \times 10^{-5} \text{ K}^{-1}$ Cr_2O_3 : $3.0 \times 10^{-5} \text{ K}^{-1}$ SiO_2 : $5.5 \times 10^{-7} \text{ K}^{-1}$

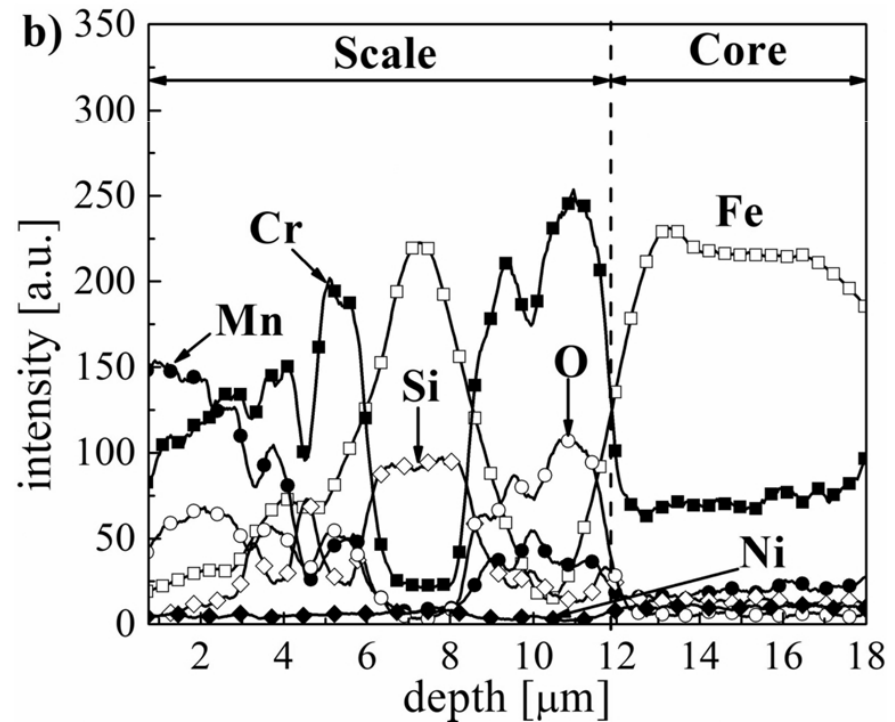
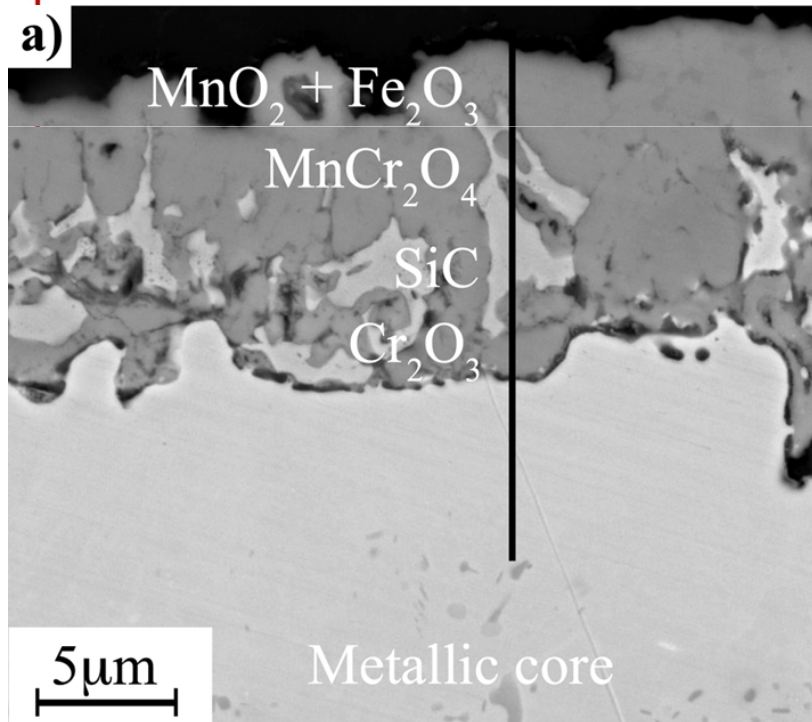
SEM cross-section microphotograph of X33CrNiMn23-8 steel covered by SiC coating (a) and the element distribution in the scale grown due to isothermal oxidation performed at 1173 K for 100 h in air atmosphere (b)



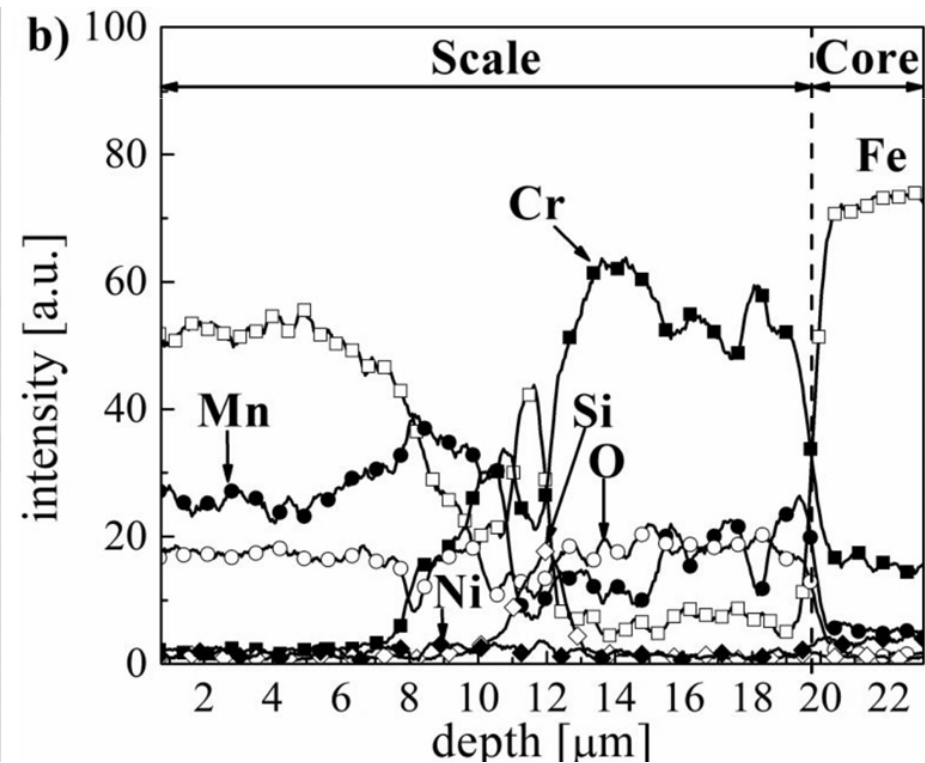
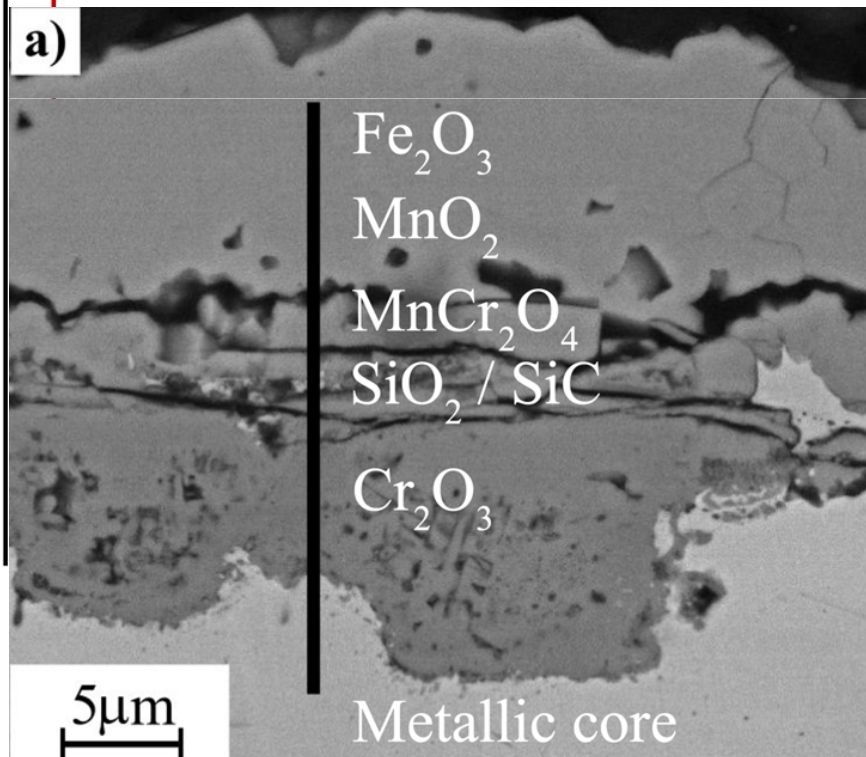
SEM cross-section microphotograph of X50CrMnNiNbN21-9 steel covered by SiC coating (a) and the element distribution in the scale grown due to isothermal oxidation performed at 1173 K for 100 h in air (b)



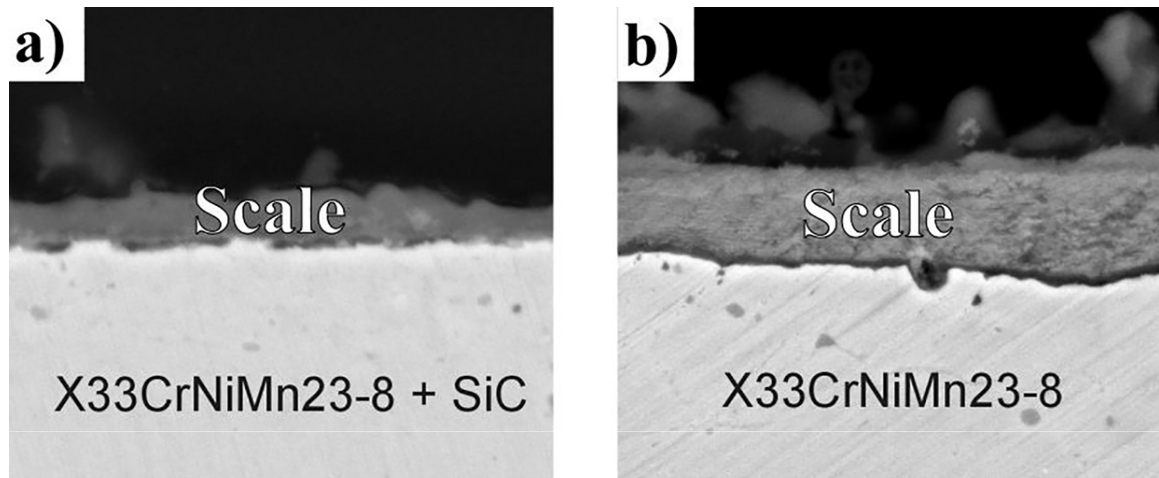
SEM cross-section microphotograph of X53CrMnNiN20-8 steel covered by SiC coating (a) and the element distribution in the scale grown due to isothermal oxidation performed at 1173 K for 100 h in air (b)



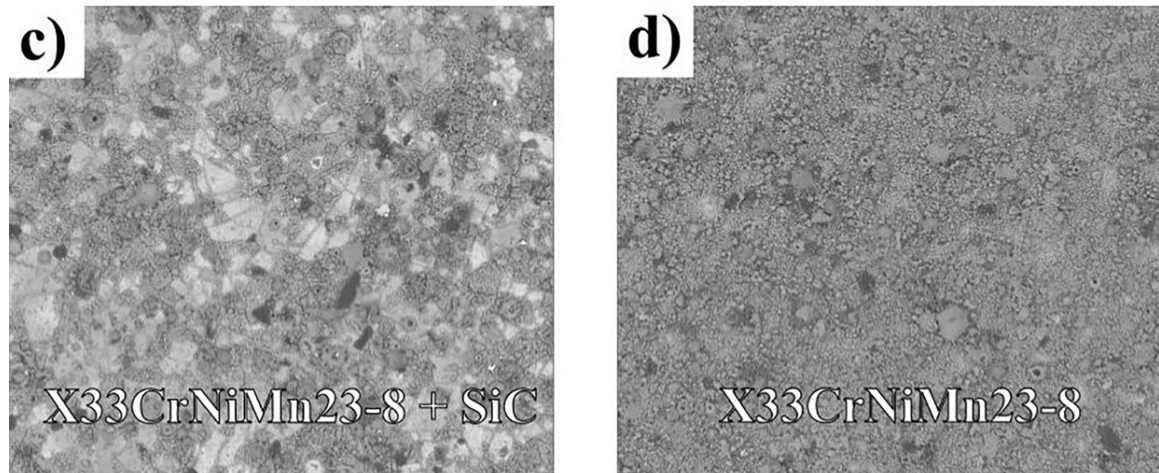
SEM cross-section microphotograph of X55CrMnNiN20-8 steel covered by SiC coating (a) and the element distribution in the scale grown due to isothermal oxidation performed at 1173 K for 100 h in air (b)



Cross-section microstructure and surface morphology of a valve mushroom covered by SiC coating (a, c) and uncovered (b, d), after tests performed on a two-cylinder 0.9 SGE TC80 CNG type engine fueled by compressed natural gas (CNG)



5 μ m



400 μ m

SUMMARY

Valve steels covered by a thin Cr-containing or consisting of silicon carbide coatings with around 1 micrometer thickness exhibit greater resistance against oxidation both in isothermal and thermal shock conditions compared to the respective steels with unmodified surfaces. This phenomenon is attributed to the formation of chromium-rich oxides (e.g. Cr_2O_3 , NiCr_2O_4 , MnCr_2O_4) during oxidation, which exhibit better protective properties than iron oxides (Fe_3O_4 and Fe_2O_3) grown on unmodified steels under analogous conditions. The positive effect of thin coatings is observed for a much longer time than the lifetime of the coatings. Consequently, the obtained results indicate the previously unnoticed potential of thin metallic and nonmetallic coatings, enabling their application as a means of protection against high-temperature corrosion in several branches of modern industry.