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HIGH TEMPERATURE CORROSION
OF ENGINE VALVES

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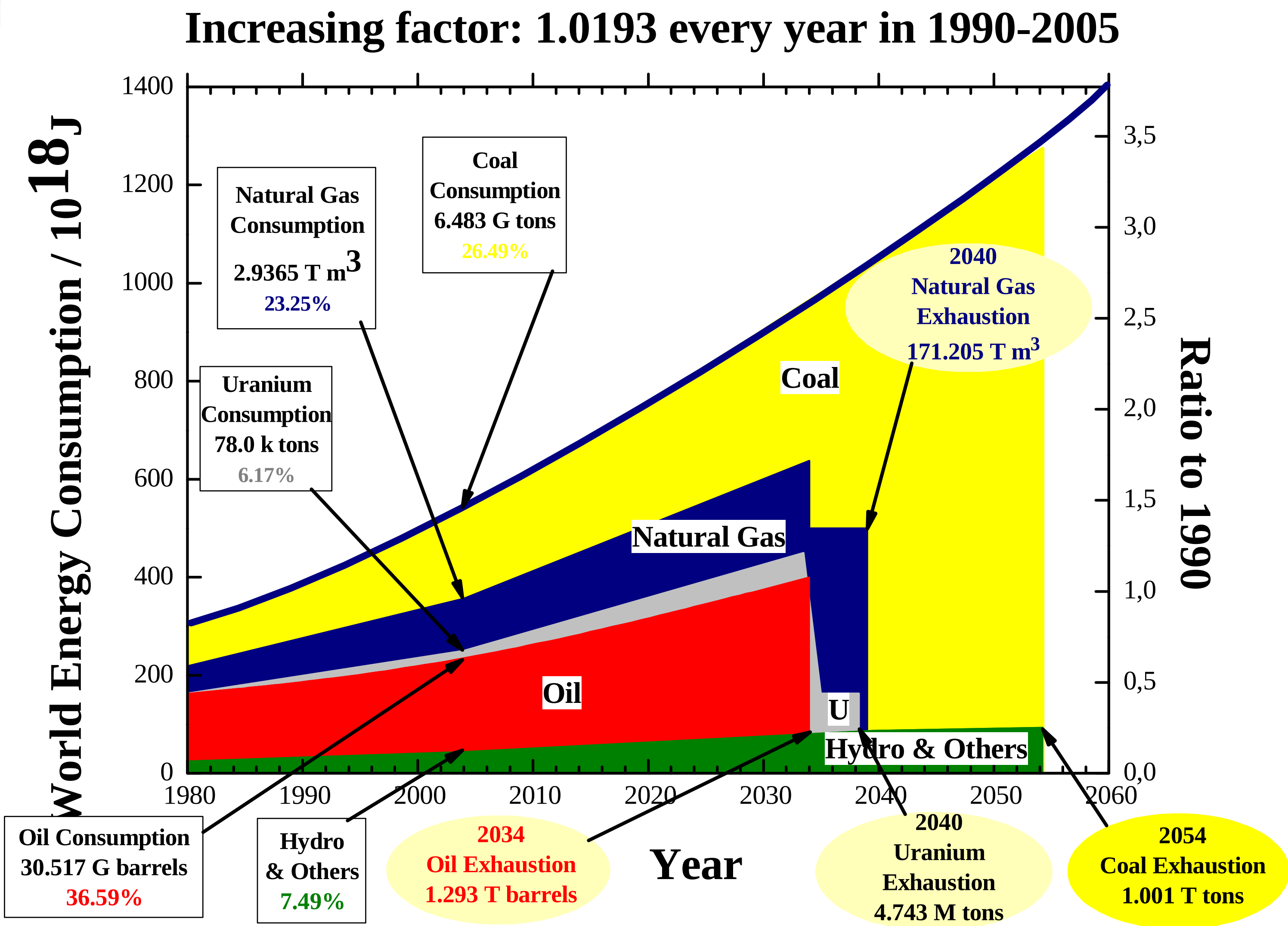
Fuels using in motorization

- Classic liquid fuels (benzene and fuel oil)
- Natural gas (propane-butane)
- Biofuels
- Electrical current
- Hydrogen
- Other (compressed air, methane, etc.)

Predictions of the energy consumption level up to 2054

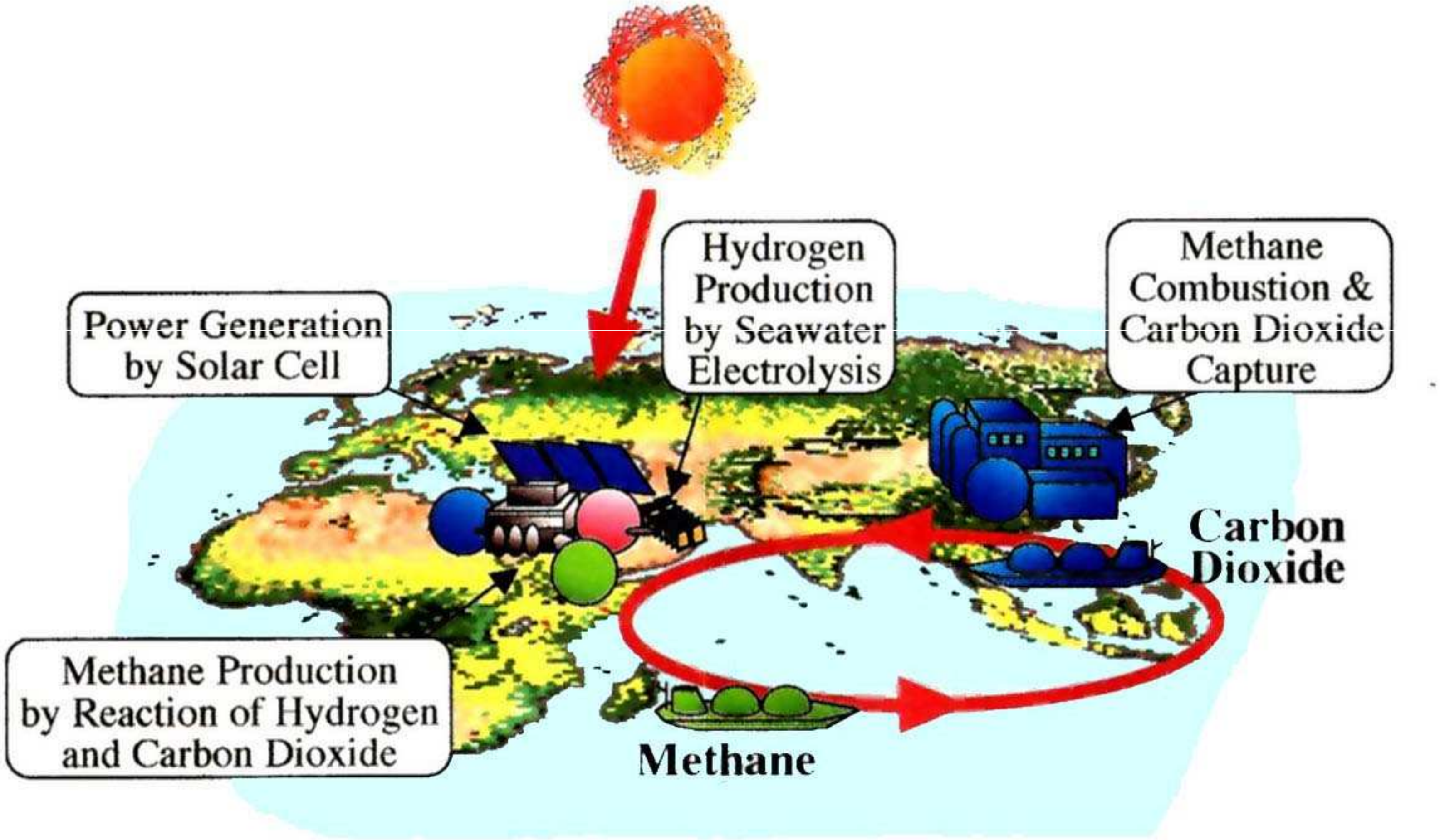


K. Hashimoto, Global carbon dioxide recycling, Springer, 2019

Consequences of exploiting fossil fuels

- exhausting fossil fuel resources
- lowering the energy safety of certain regions of the world
- increase in fossil fuel prices
- degradation of the natural environment
- climate destabilization
- worsening of peoples health due to pollution increase.

Schematic representation of prof. K. Hashimoto's concept of using methane as an energy carrier



K. Hashimoto, Global carbon dioxide recycling, Springer, 2019

Alternative energy sources

- solar energy (solar cells and collectors)
- nuclear energy
- hot and cold fusion
- geothermal energy
- wind energy
- water energy
- wave energy
- biofuels – optimal solution in this transitional period

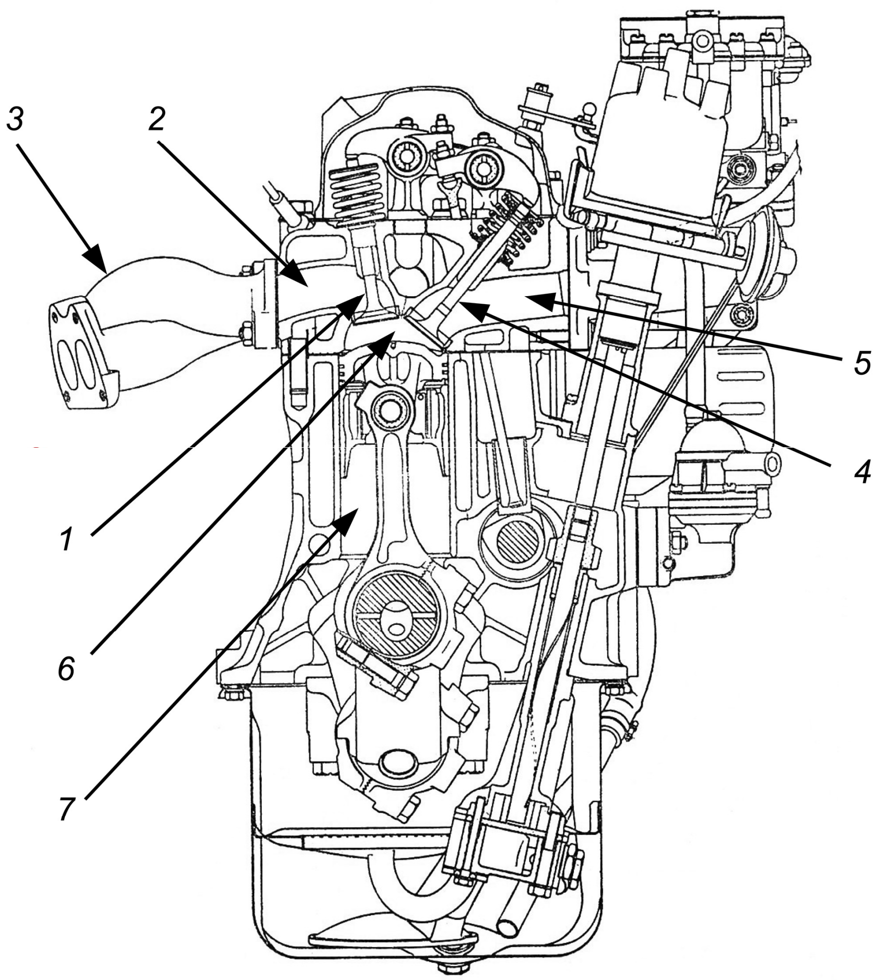
Legal regulations

Directive 2003/30/EC of the European Parliament and European Council of 8 May 2003 “Promotion of the use of biofuels or other renewable fuels for transport”, Official Journal of the European Union, 2003, L 123/43-46.

Currently used bio-additives to liquid fuels

- Ethyl alcohol (additive to benzene)
- Fatty acid methyl esters, FAME (additive to fuel oil)

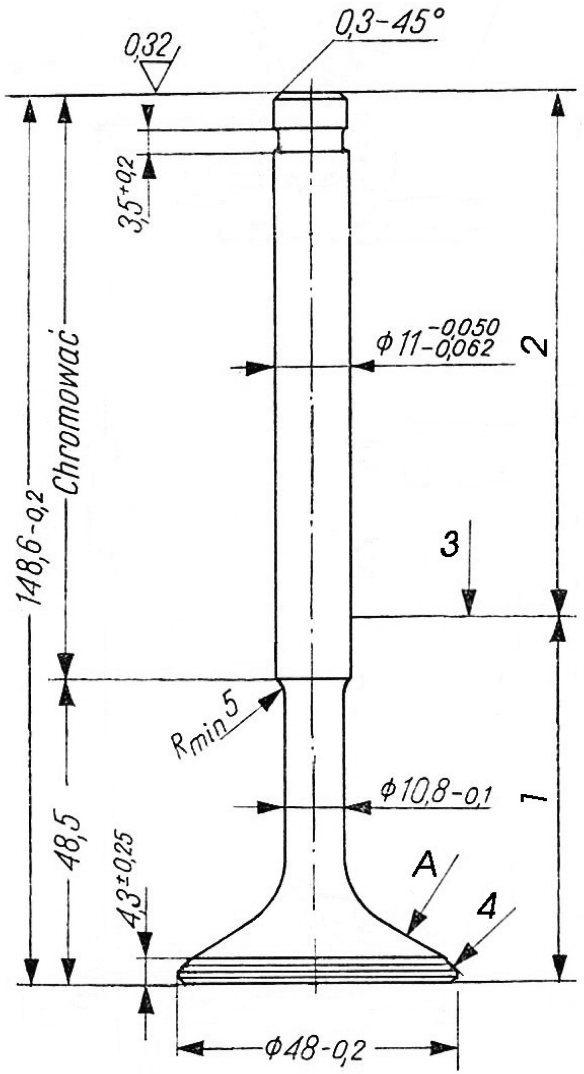
Cross-section of a four-cycle engine with a spark ignition, Fiat



1 – outlet valve,
2 – exhaust outlet channel,
3 – exhaust collector,
4 – inlet valve,
5 – fuel-air mixture inlet channel,
6 – combustion chamber
7 – cylinder with a press and crankshaft

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

Schematic illustration of an outlet valve



1 – mushroom valve – austenitic Cr-Ni-W-Mo steel in a supersaturated and worn out state,
2 – valve stem - Cr-Si-Mo steel in a thermally improved state,
3 – friction welding location,
4 – valve face filled with napawana Co-Cr-W stellite

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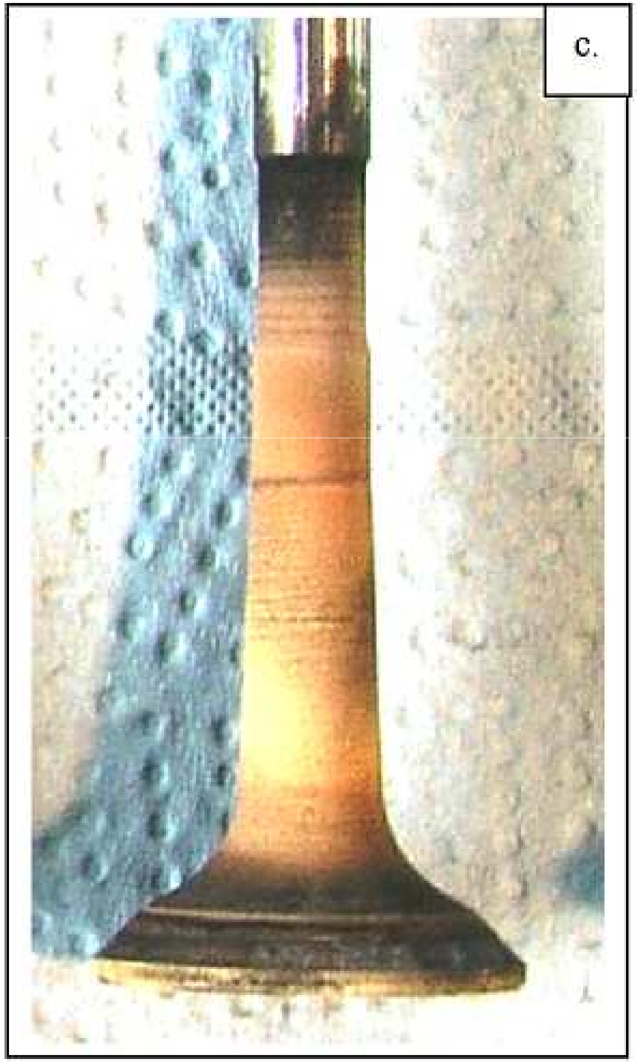
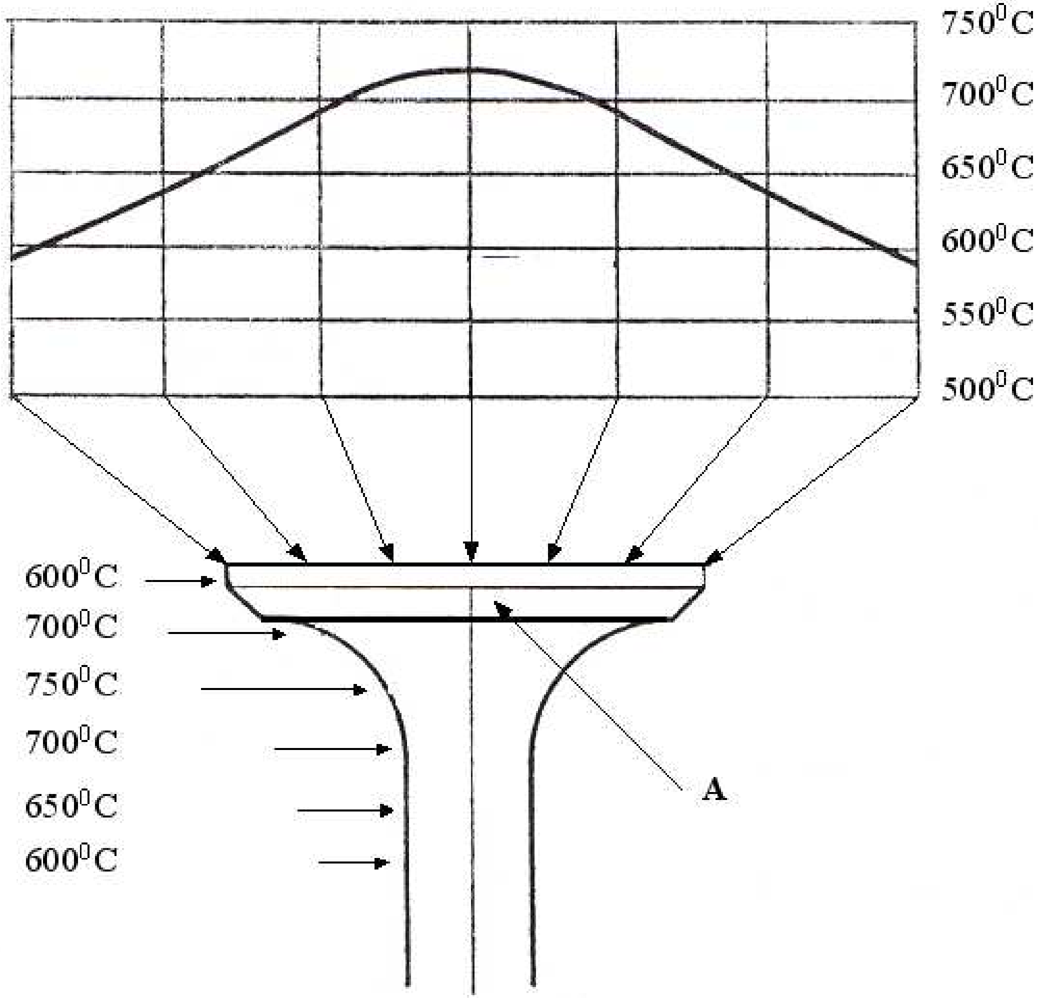
Outlet valves after a 1000-hr test of an engine with a spontaneous ignition



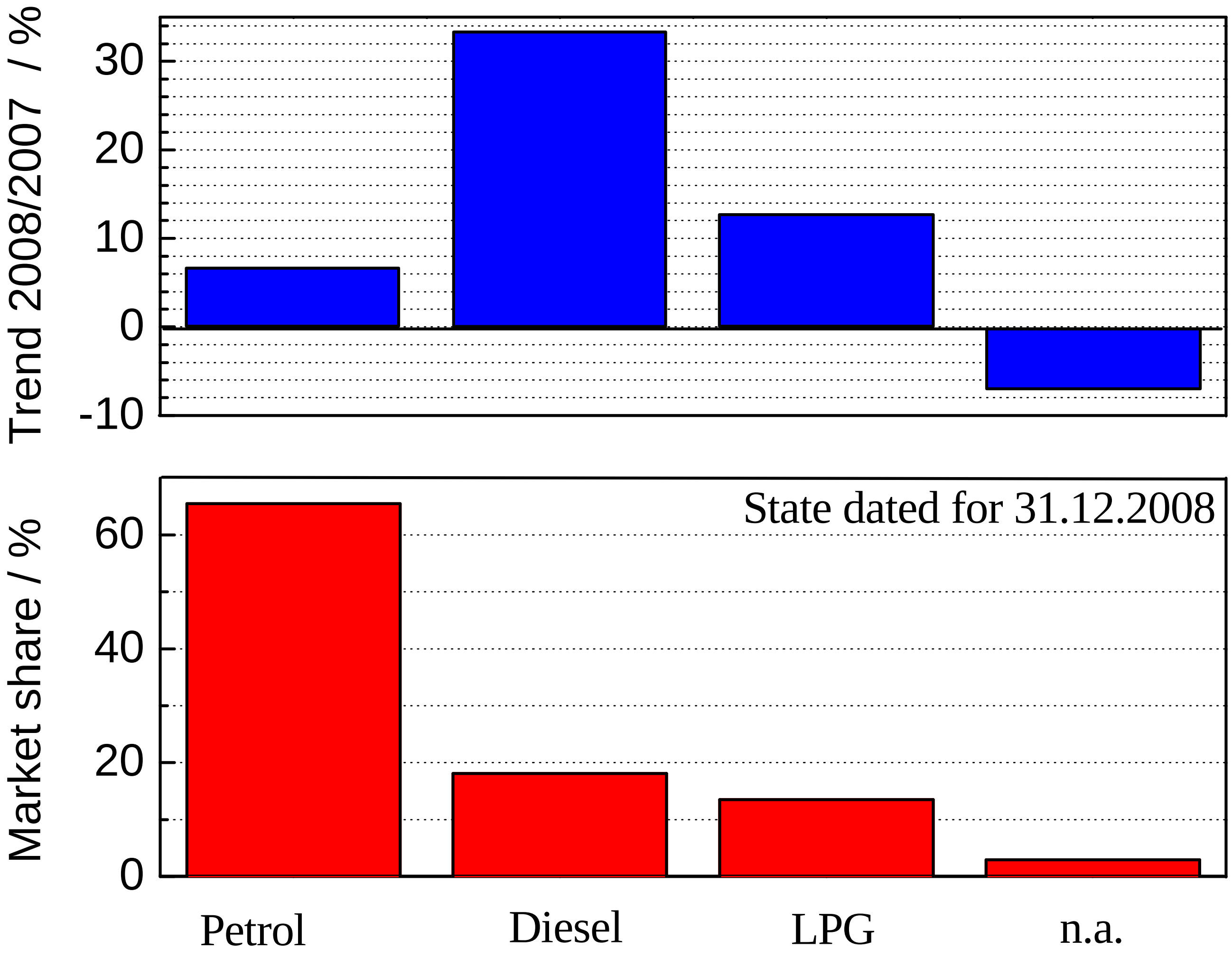
Temperature distribution of outlet valve work - petrol engine with a spark ignition



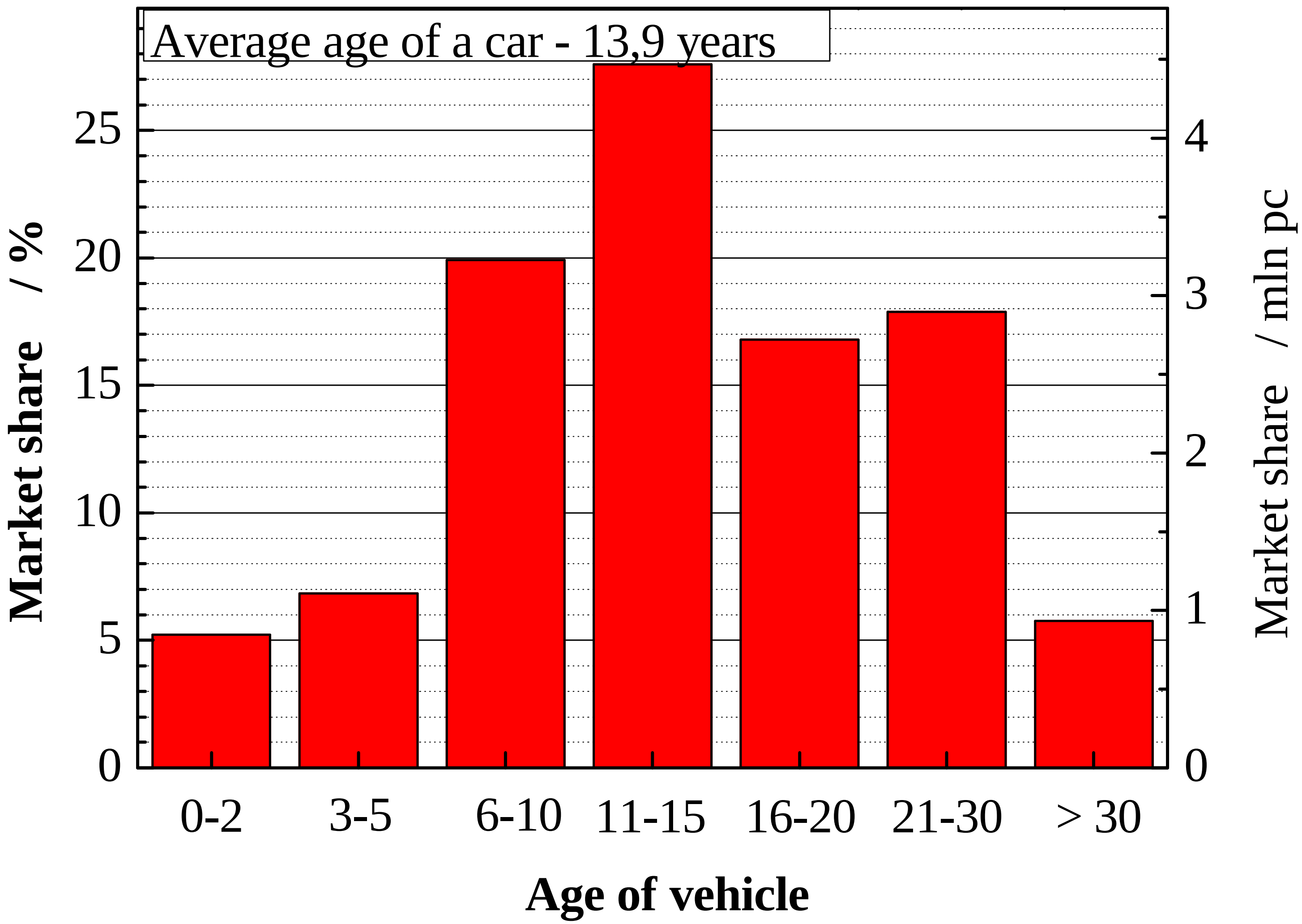
Typical engine valve operating conditions

- presence of aggresive exhaust gas atmosphere
- high maximum temperature (T ≈ 1173 K)
- rapid temperature changes (thermal shocks)

Fuels using in the automotive industry in Poland



Age of personal vehicles in Poland



Chemical composition of exhausts from engines with a spark and spontaneous ignition (% wt.)

Exhaust gas components	Measuring unit	Engines with ignitions		Toxicity grade
		spark	compression	
Nitrogen	% vol.	74-77	76-78	Neutral
Oxygen	**% vol.**	0,3-8,0	2,0-18,0	see above
Water vapor	**% vol.**	3,0-5,5	0,4-5,0	see above
Carbon dioxide	**% vol.**	5,0-12,0	1,0-10,0	see above
Carbon monoxide	% vol.	5,0-10,0	0,01-0,5	Toxic
Nitrogen oxides	% vol.	0,0-0,8	0,002-0,5	see above
Carbohydrates	% vol.	0,2-3,0	0,009-3,0	see above
Aldehydes	% vol.	0,0-0,2	0,001-0,009	see above
Soot	g/m^3	0,0-0,04	0,01-1,1	see above
3,4 benzopyrene	g/m^3	do 15,0	do 10,0	Cancerous

Merkisz J., *Ekologiczne problemy silników spalinowych Tom I i II.* Wydawnictwo Politechniki Poznańskiej, Poznań 1999

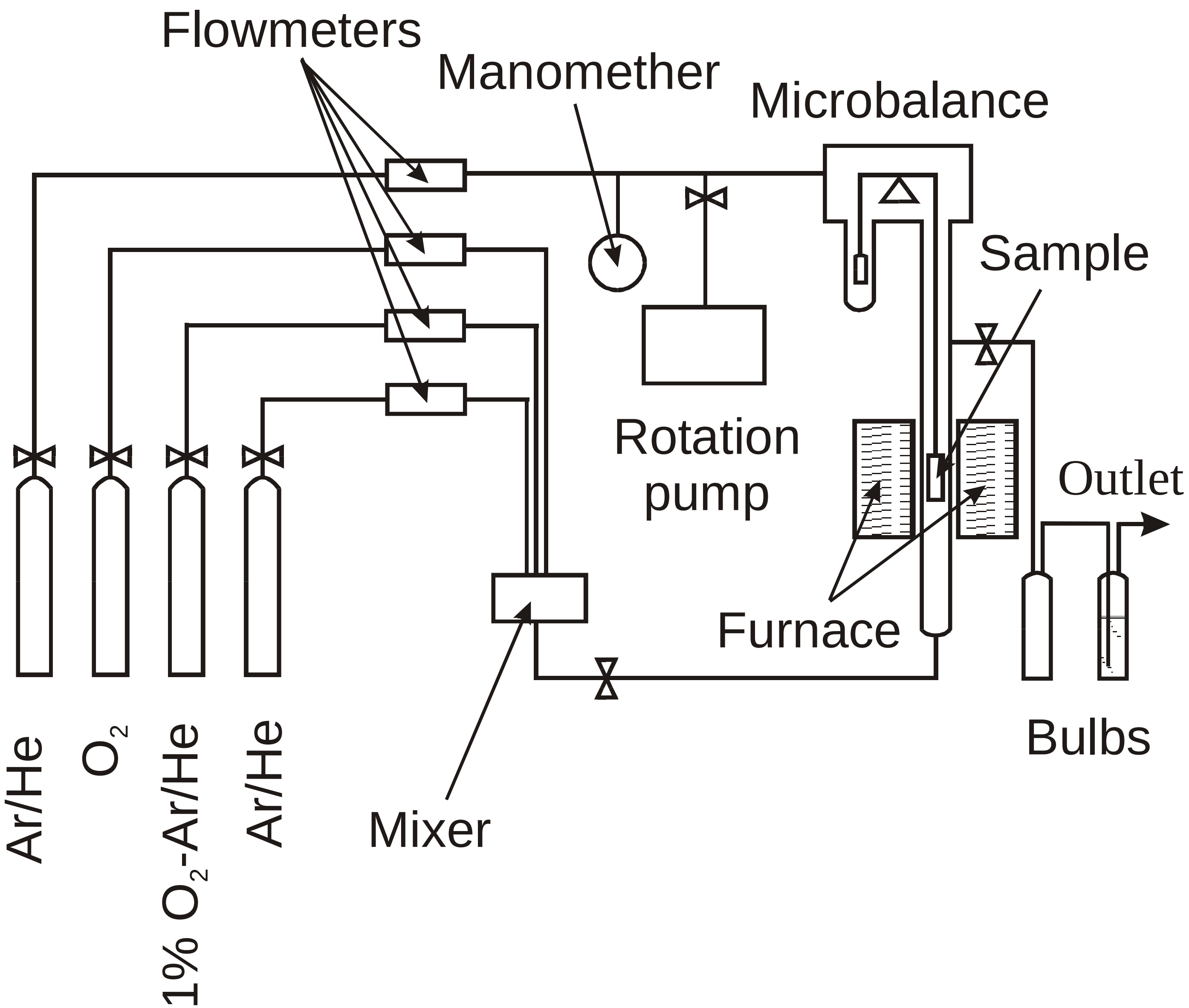
Chemical composition of steels used for production of engine valves (% wt.)

Steel grade	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	0.54	**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.

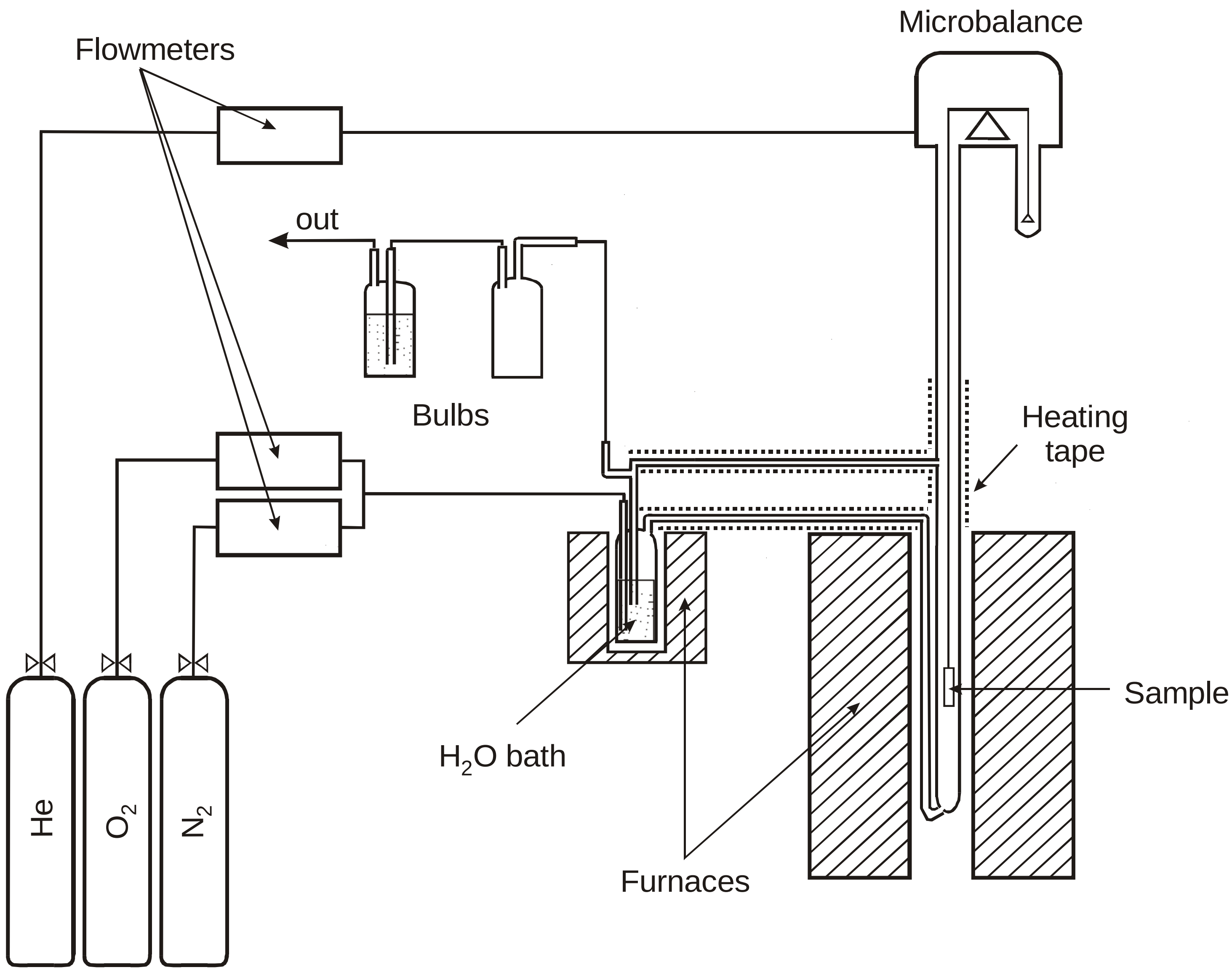
Literature on valve steel corrosion

- K. Adamaszek, Z. Jurasz, L. Swadzba, Z. Grzesik, S. Mrowec, "The Influence of Hybrid Coatings on Scaling-resistant Properties of X33CrNiMn23-8 Steel", High Temperature Materials and Processes, 26, 115-122 (2007).
- Z. Jurasz, K. Adamaszek, R. Janik, Z. Grzesik, S. Mrowec, „High temperature corrosion of valve steels in atmosphere containing water vapor", Journal of Solid State Electrochemistry, 13, 1709-1714 (2009).
- Z. Grzesik, S. Mrowec, Z. Jurasz, K. Adamaszek, „The behavior of valve materials utilized in Diesel engines under thermal shock conditions", High Temperature Materials and Processes, 29, 35-45 (2010).
- Z. Grzesik, M. Migdalska, S. Mrowec, „Corrosion behavior of valve steels in oxidizing atmosphere containing acetic acid", High Temperature Materials and Processes, 29, 203-214 (2010).
- Z. Grzesik, Z. Jurasz, K. Adamaszek, S. Mrowec, „Oxidation Kinetics of Steels Utilized in the Production of Valves in Automobile Industry", High Temperature Materials and Processes, 31, 775-779 (2012).
- Z. Grzesik, K. Adamaszek, Z. Jurasz, S. Mrowec „The influence of yttrium on kinetics and mechanism of chromia scale growth on Fe-Cr-Ni base steels", Defect and Diffusion Forum, 333, 91-100 (2013).
- Z. Grzesik, G. Smola, K. Adamaszek, Z. Jurasz, S. Mrowec, „Thermal shock corrosion of valve steels utilized in automobile industry", Oxidation of Metals, 80, 147-159 (2013).
- Z. Grzesik, G. Smola, K. Adamaszek, Z. Jurasz, S. Mrowec, „High Temperature corrosion of valve steels in combustion gases of petrol containing ethanol addition", Corrosion Science, 77, 369-374 (2013).

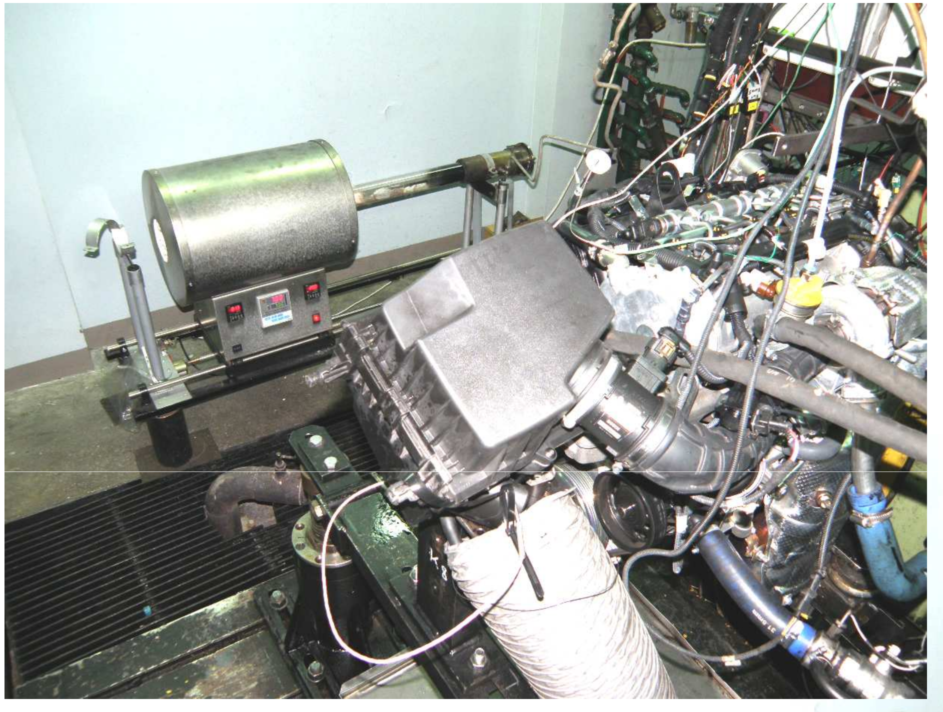
Schematic illustration of a microthermogravimetric apparatus for studying valve steel oxidation kinetics

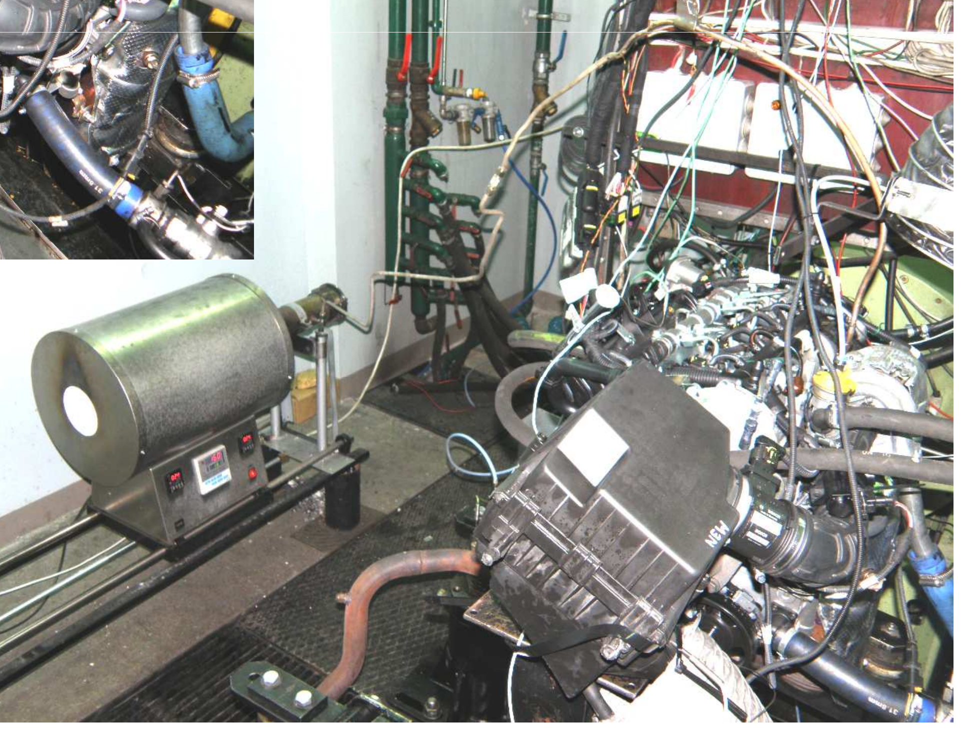


Schematic illustration of a microthermogravimetric apparatus for studying corrosion rate in the presence of water vapor

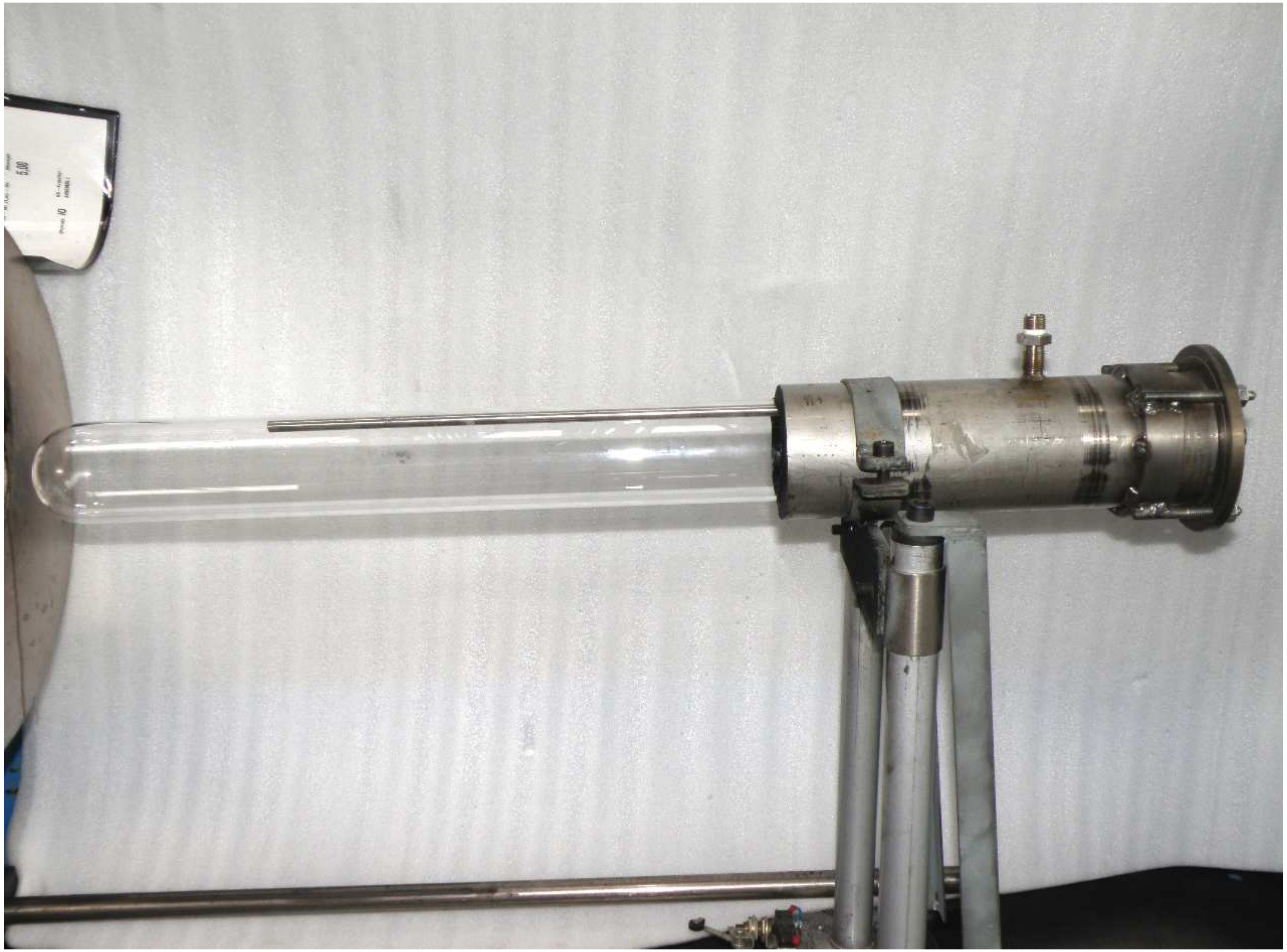


Test stand for studying corrosion in thermal shock conditions on an engine test bench

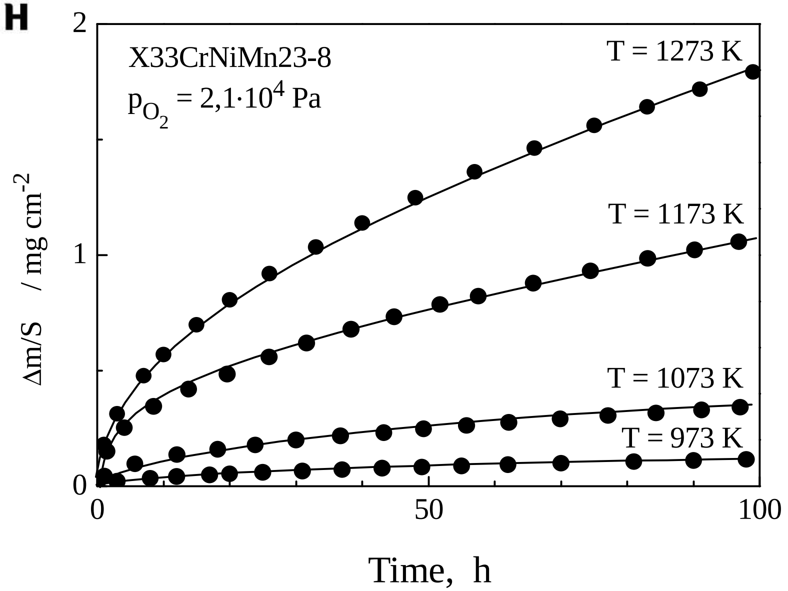


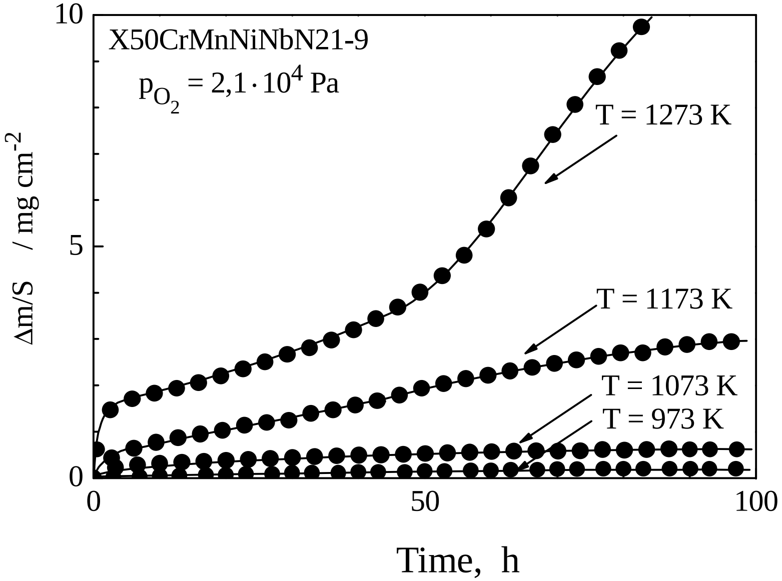


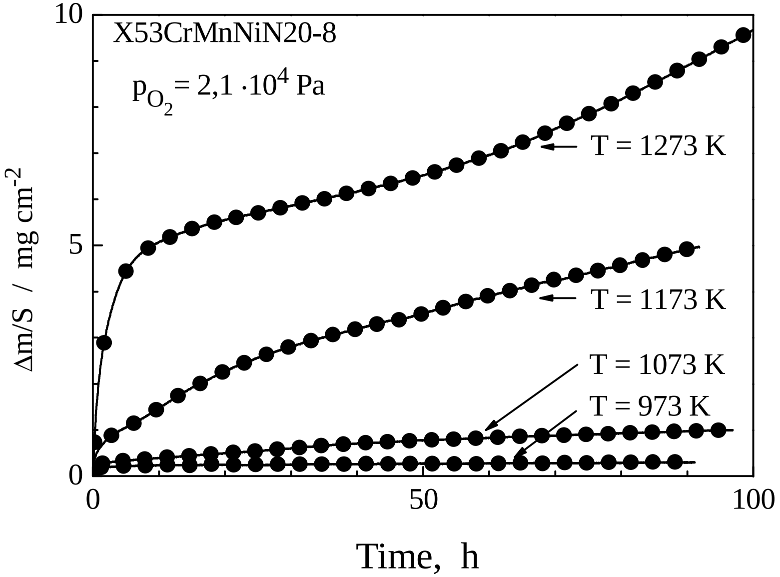
Hybrid reaction head

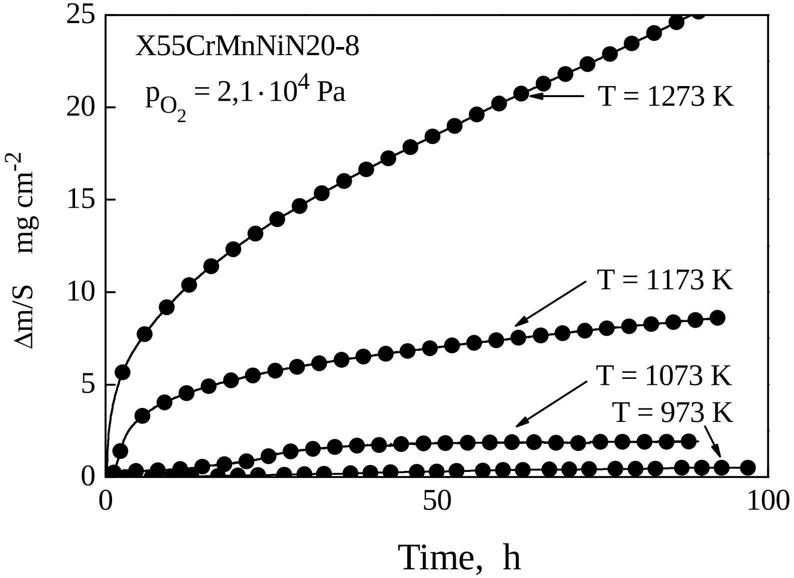


Valve steel oxidation kinetics
– linear coordinate system

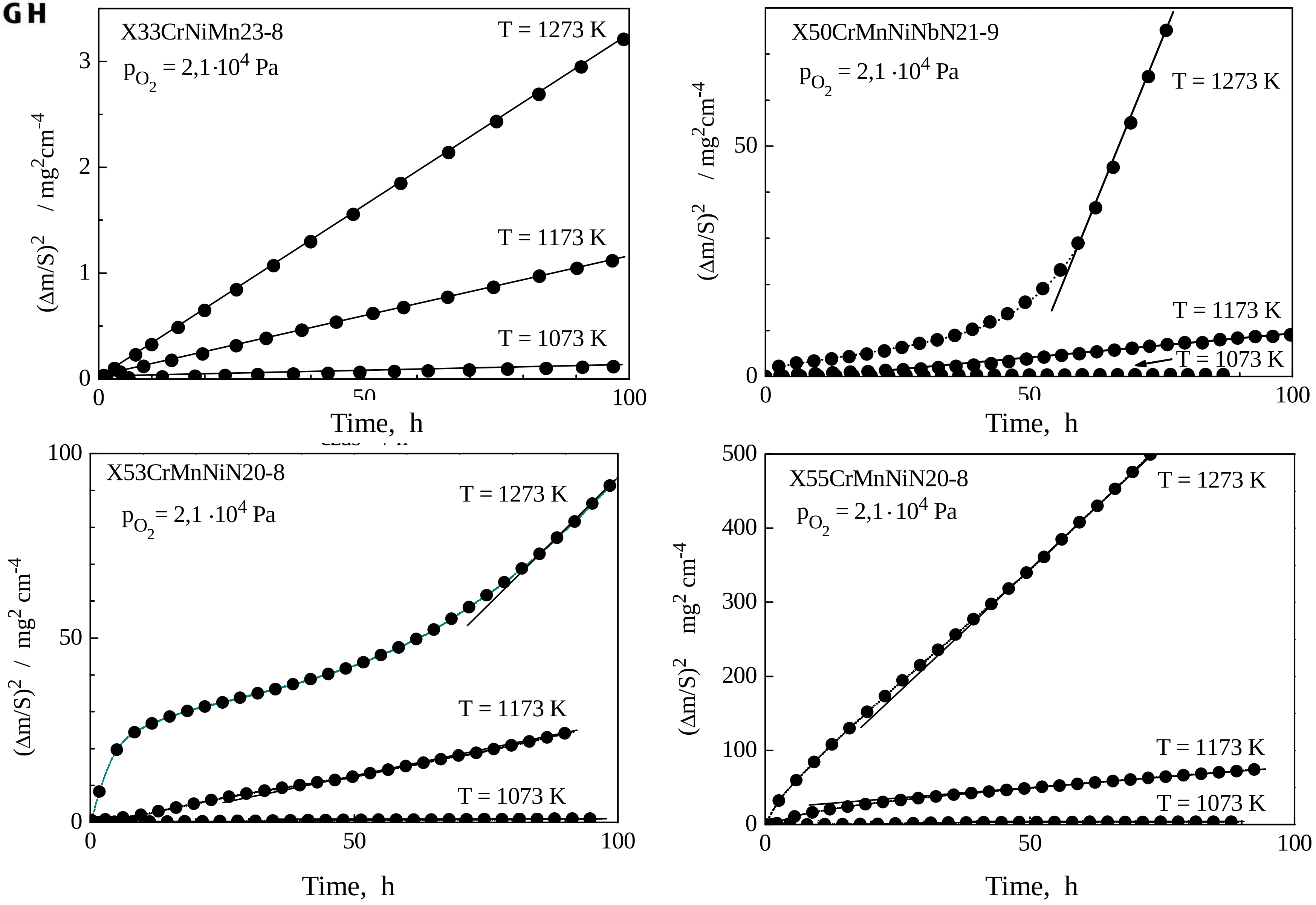




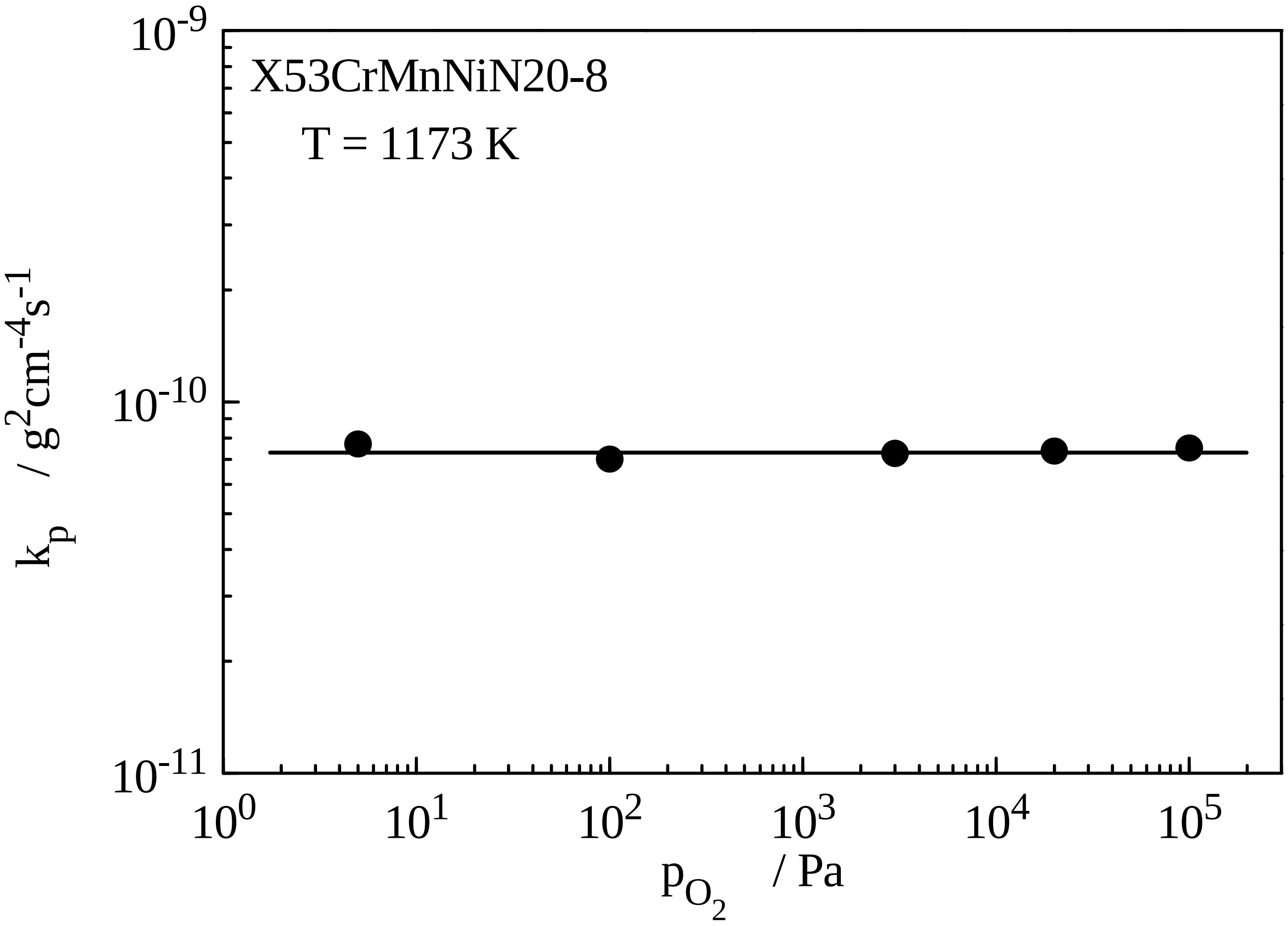




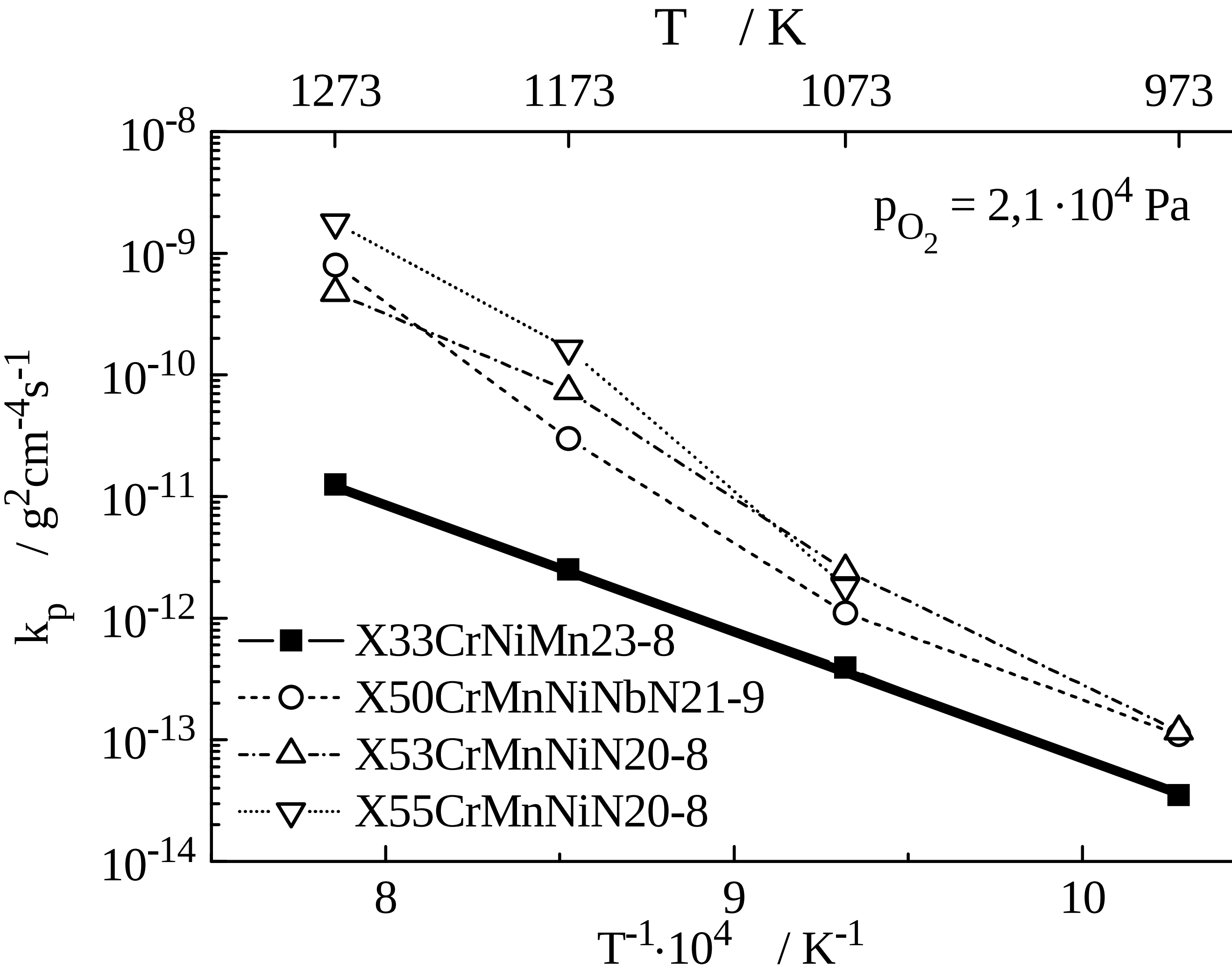
Valve steel oxidation kinetics – parabolic coordinate system



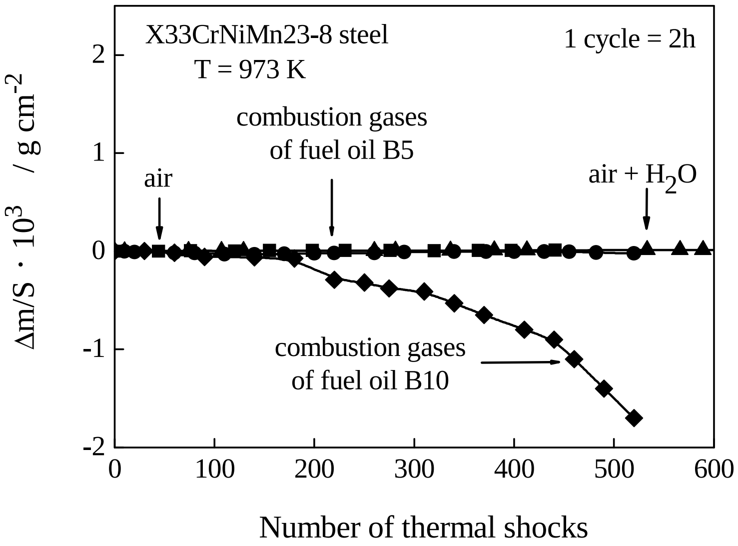
Pressure dependence of X53CrMnNiN20-8 valve steel oxidation rate, obtained at 1173 K

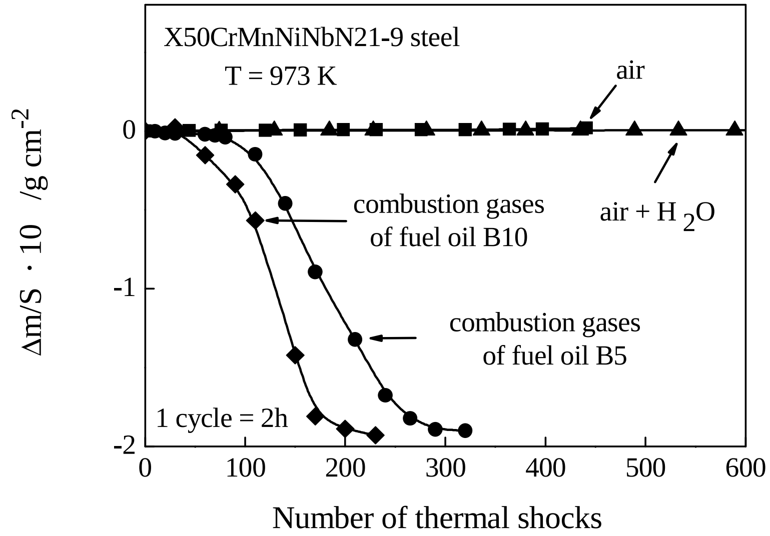


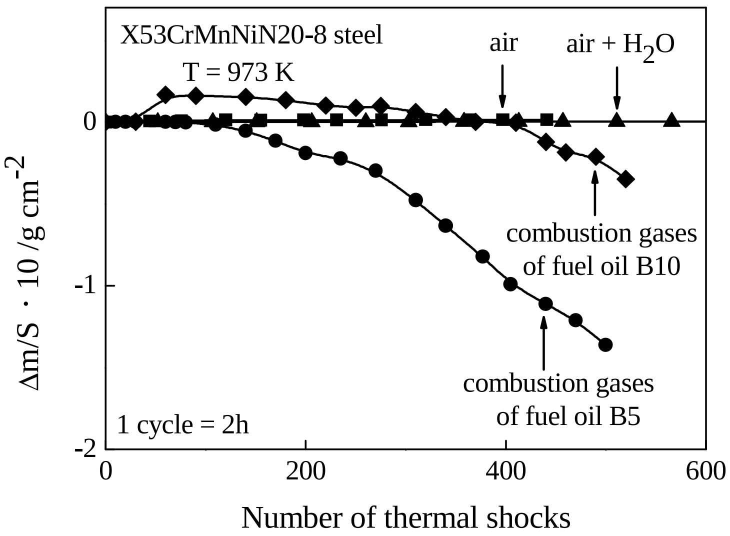
Temperature dependence of different valve steel oxidation rates

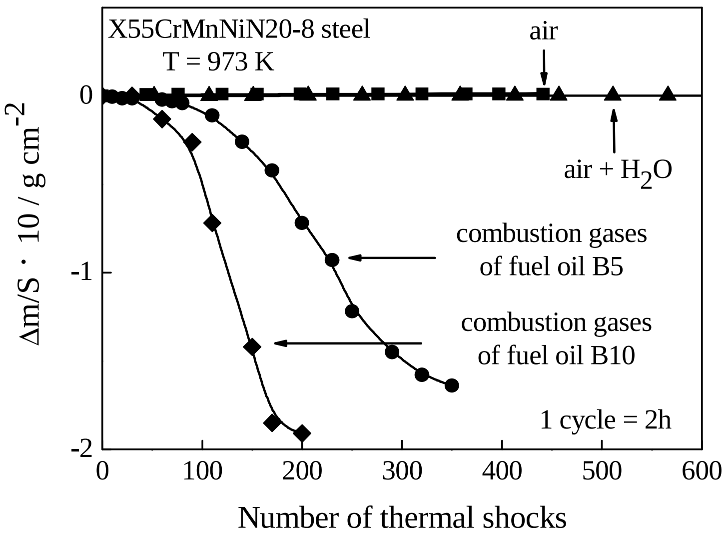


Kinetics of valve steel corrosion in combustion gases of fuel oil with a bio-additive

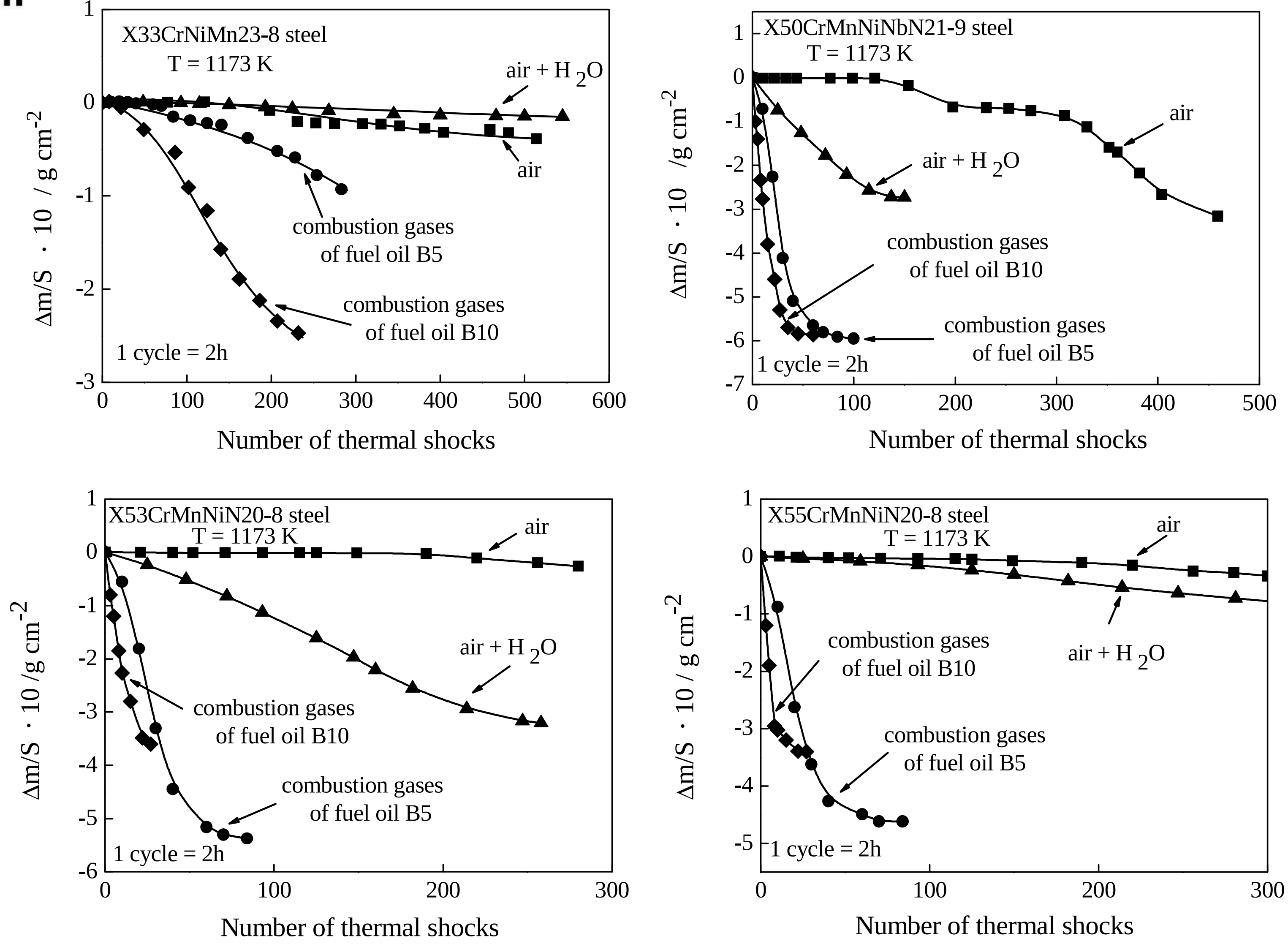




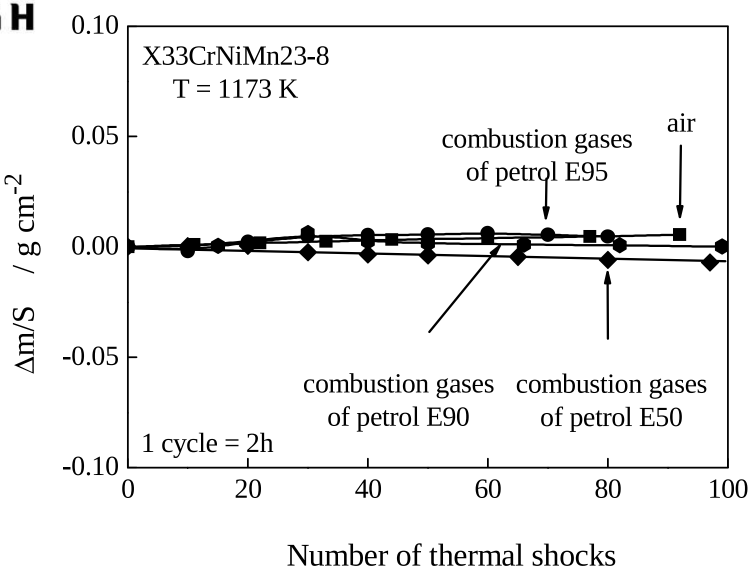


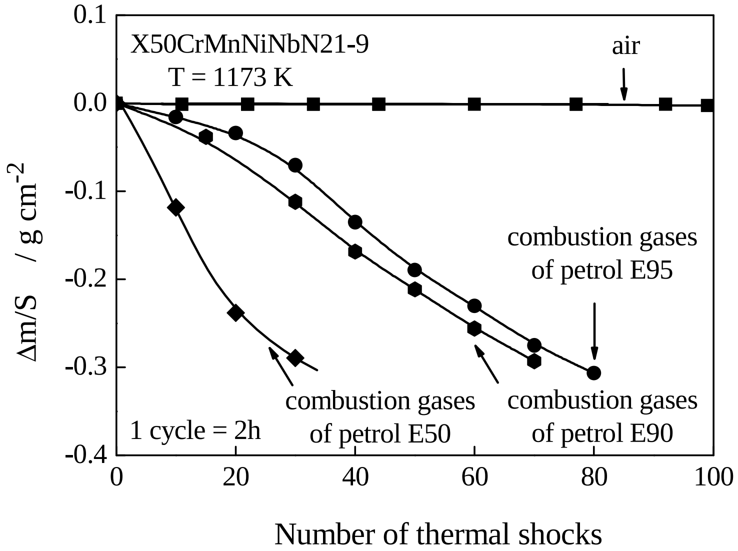


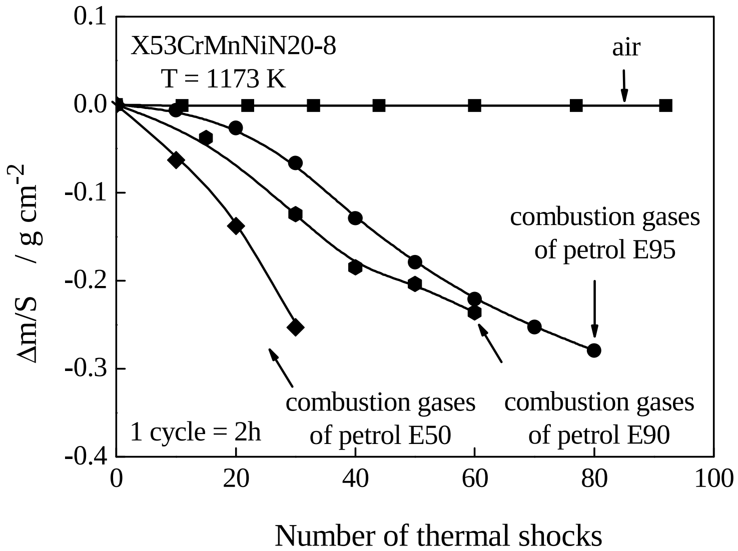
Kinetics of valve steel corrosion in combustion gases of fuel oil with a bio-additive

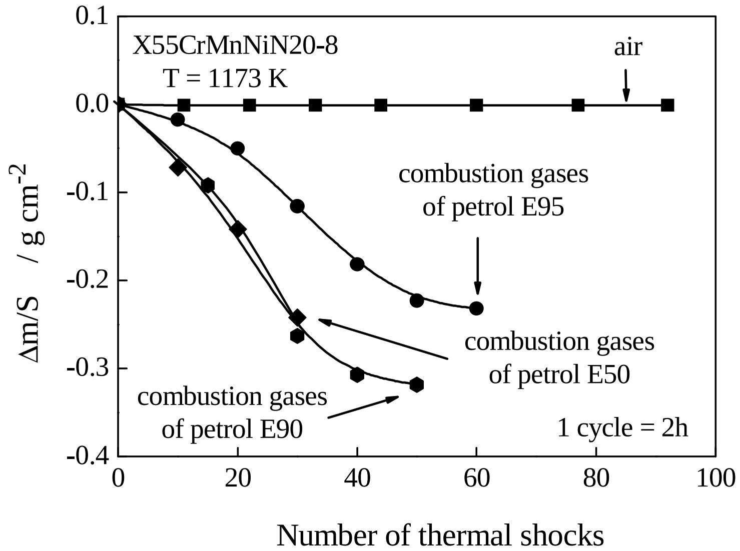


Kinetics of valve steel corrosion in combustion gases of petrol with a bio-additive

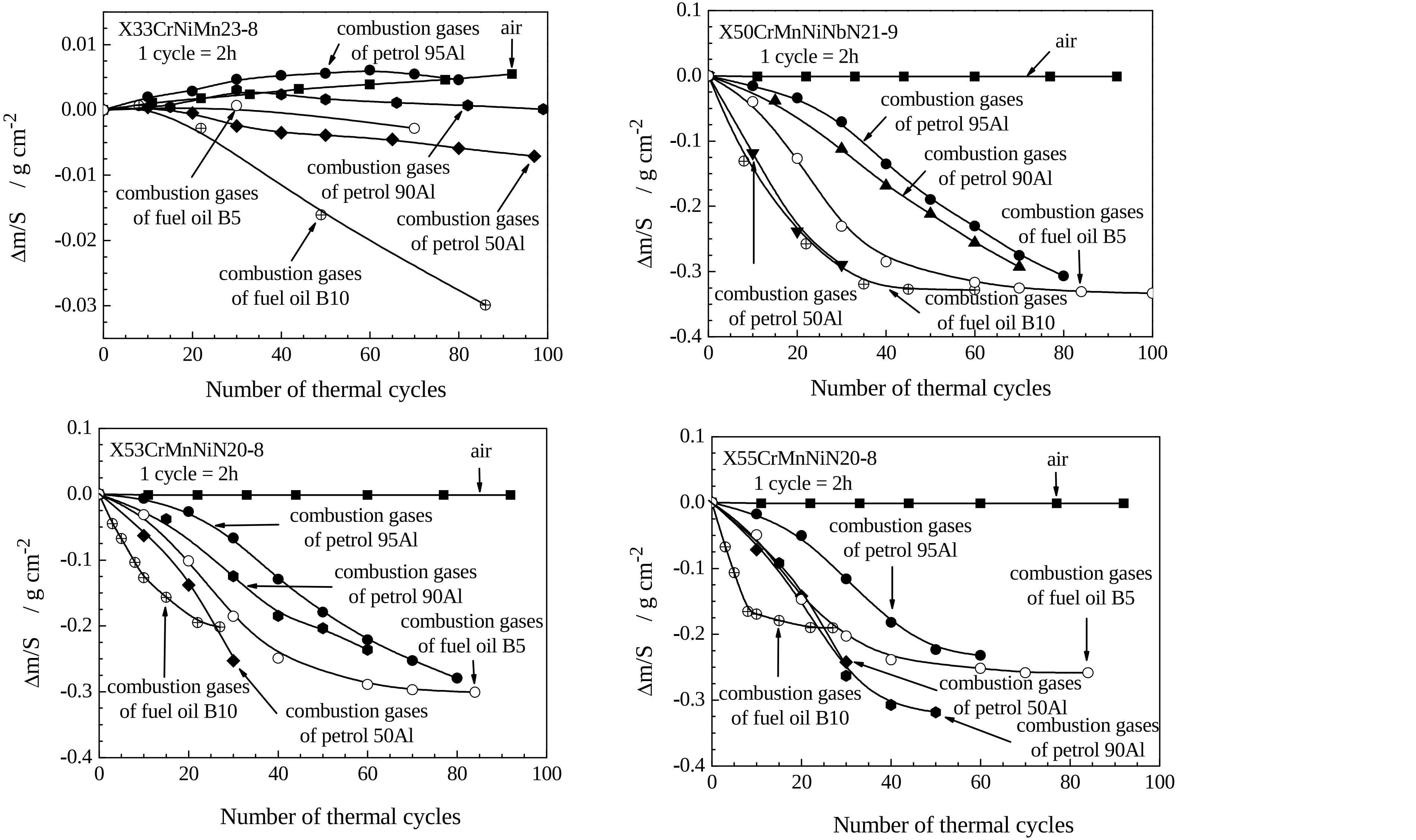








Comparison between valve steel corrosion in exhaust fumes of different fuels with bio-additives



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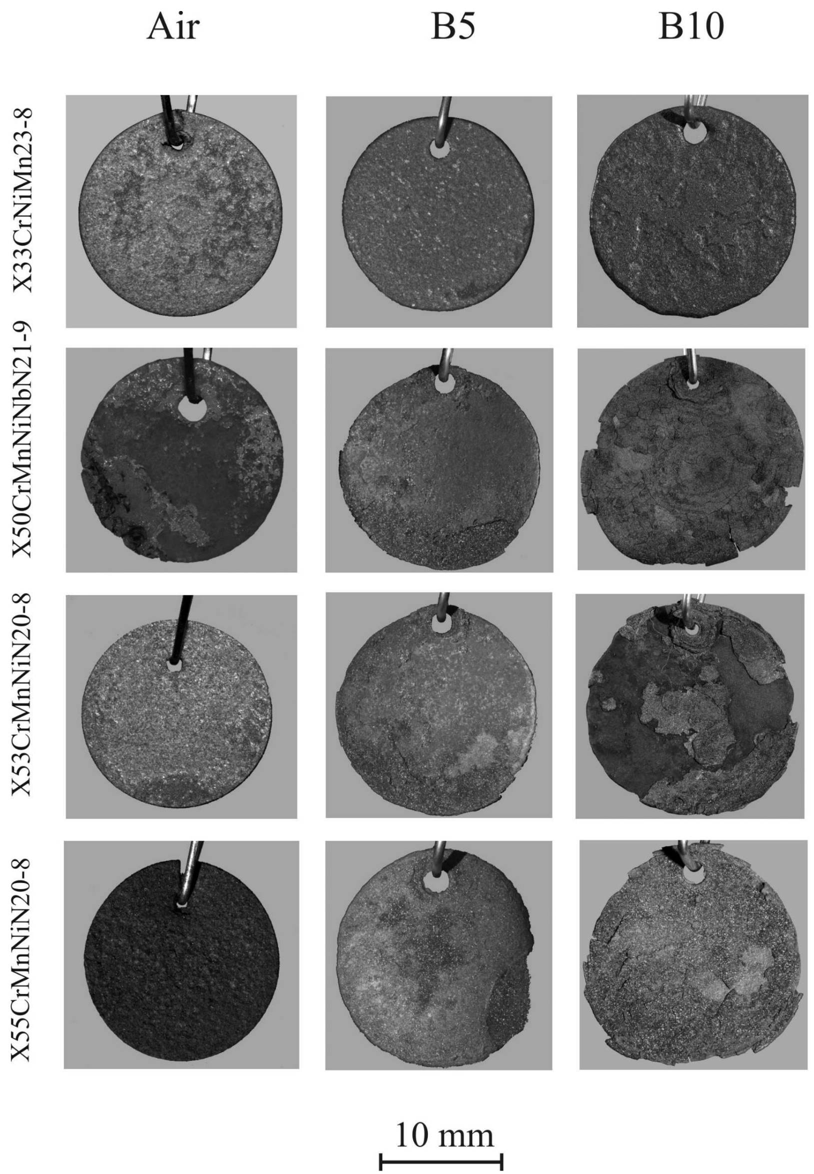
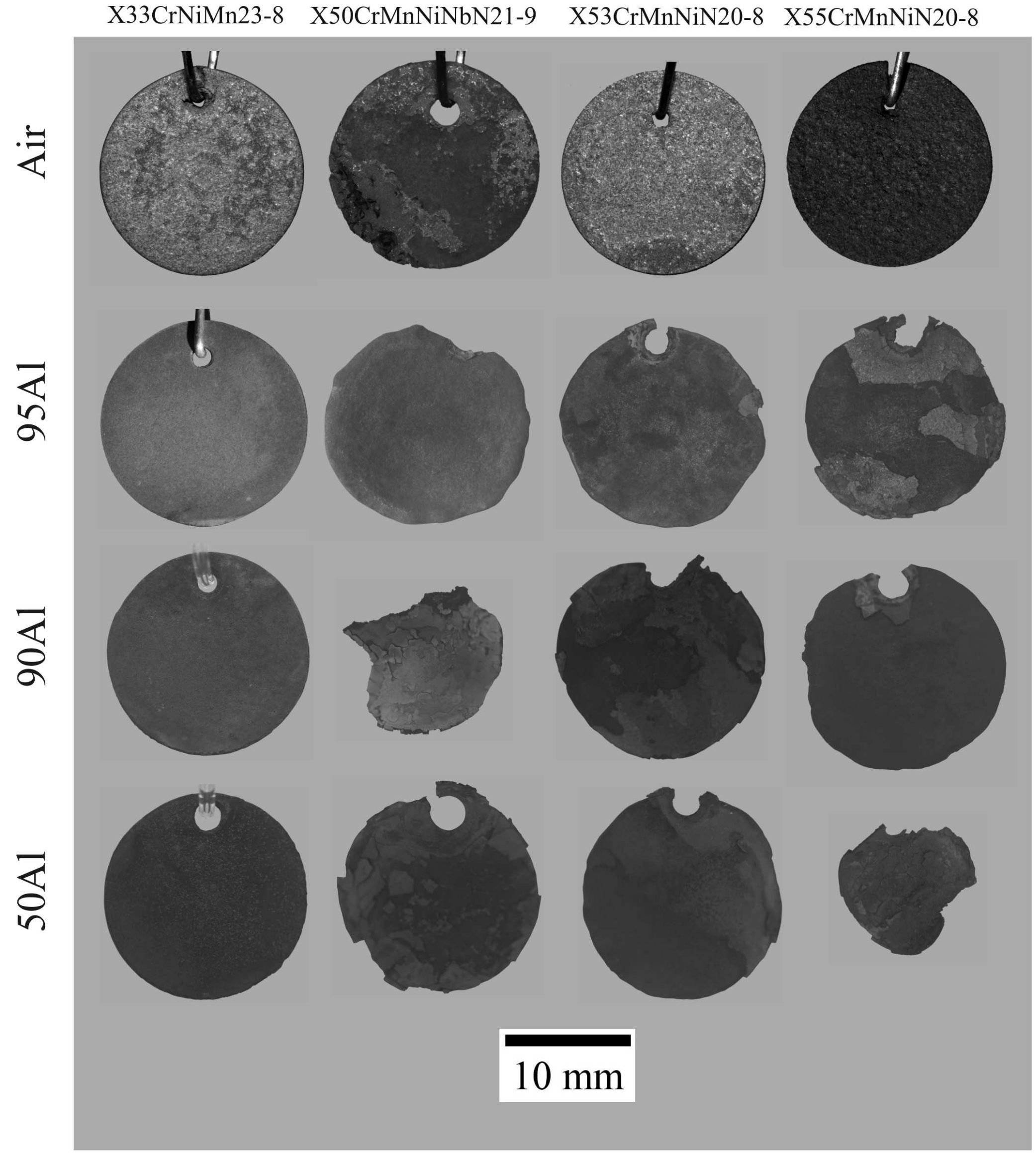
Surface images of valve steel samples after corrosion in air and diesel oil exhaust with bio-additives



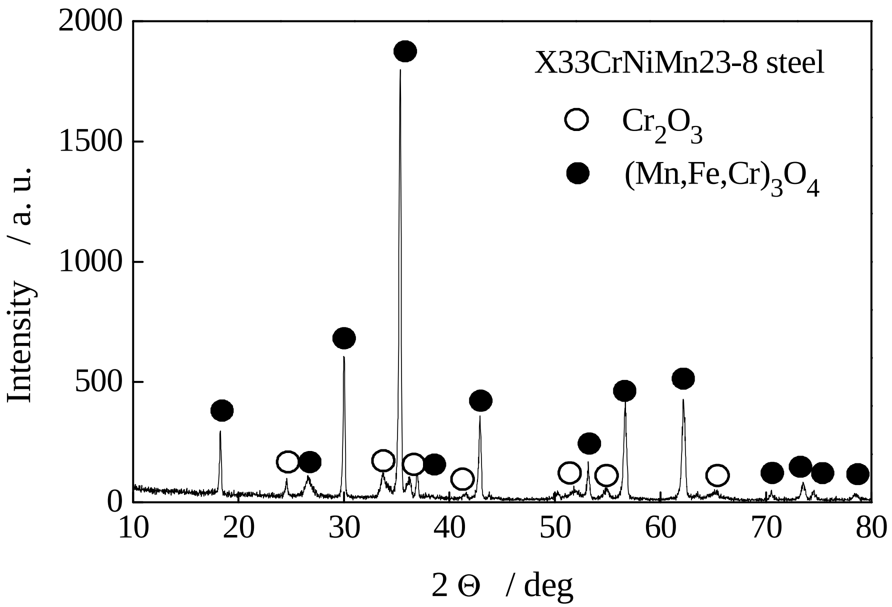
T = 1173K

Surface images of valve steel samples after corrosion in air and combustion gases of petrol with bio-additives

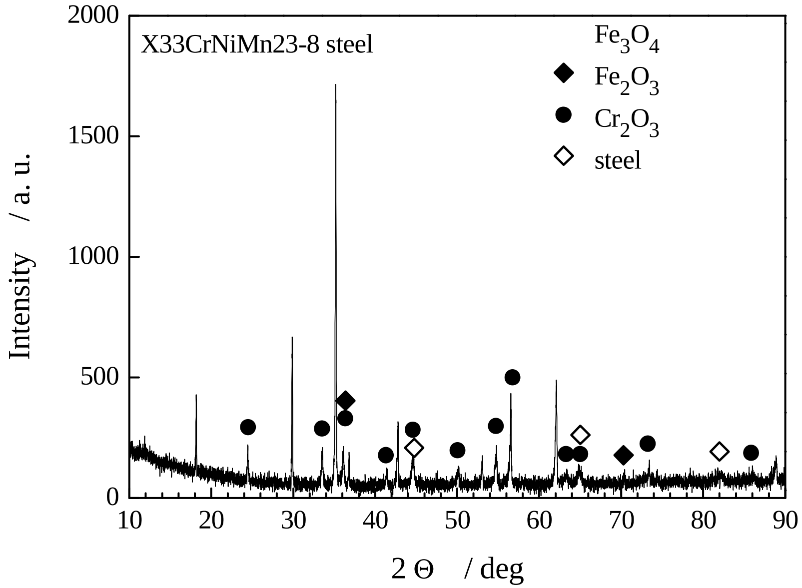


Phase composition of scales formed on X33CrNiMn23-8 steel in thermal shock conditions (T = 1173 K)

a) after 50 cycles

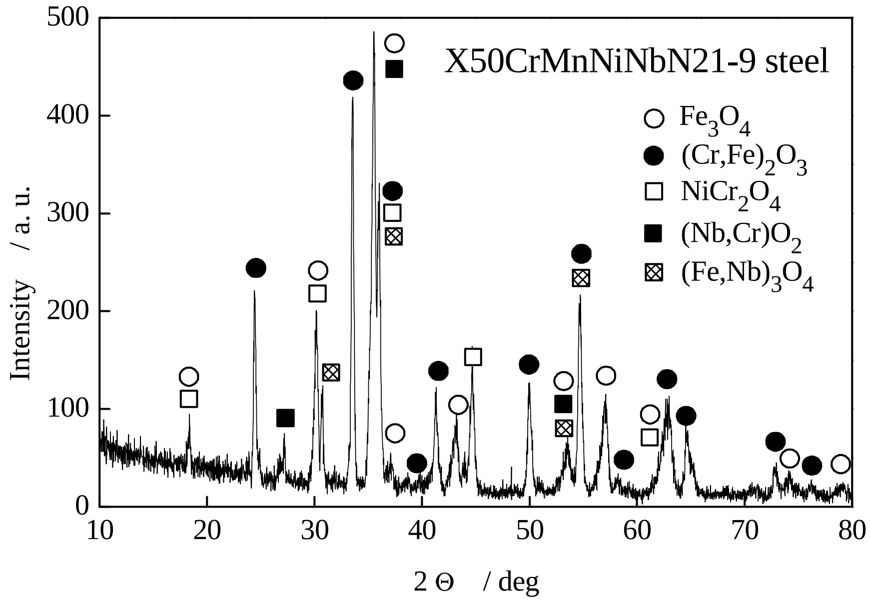


b) after 500 cycles

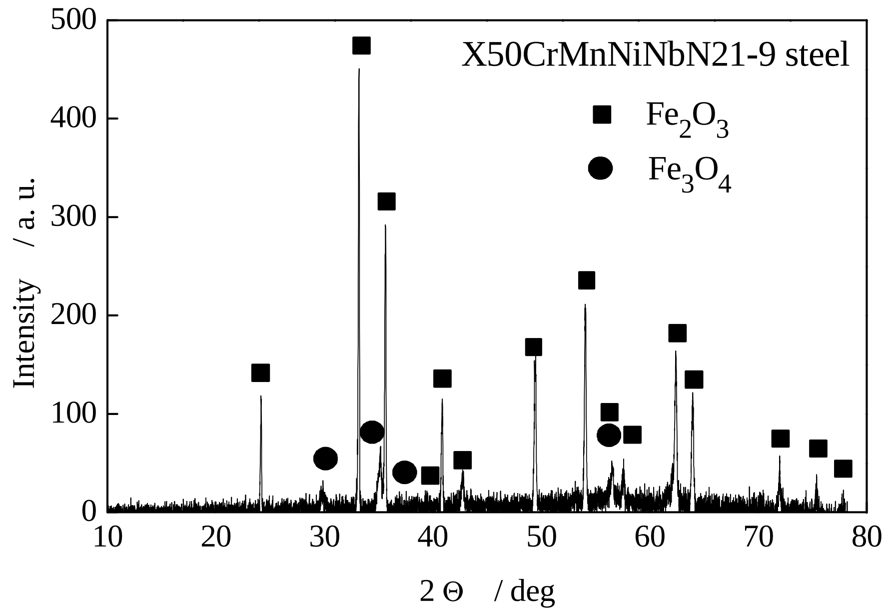


Phase composition of scales formed on X50CrMnNiNbN21-9 steel in thermal shock conditions (T = 1173 K)

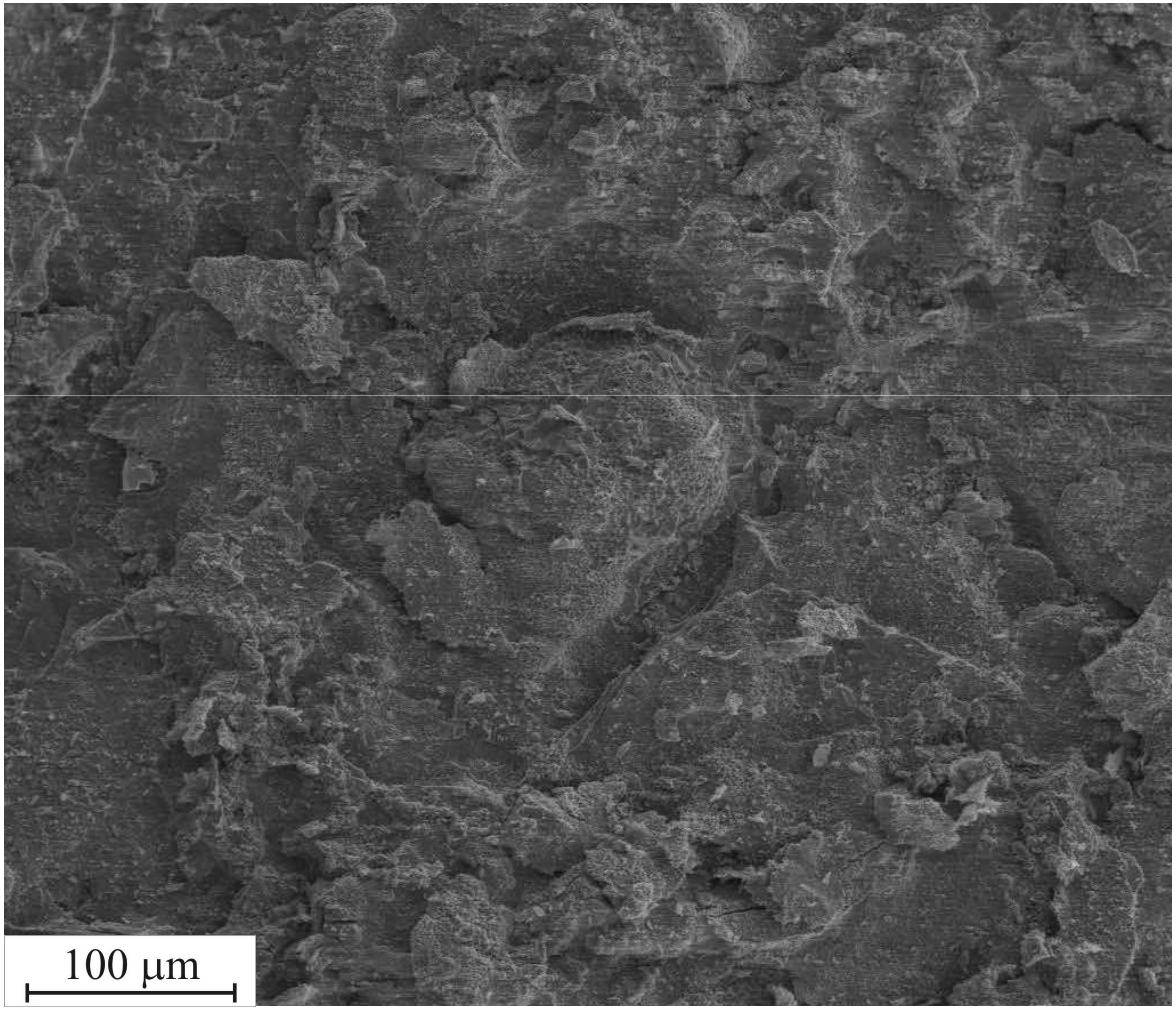
a) after 20 cycles



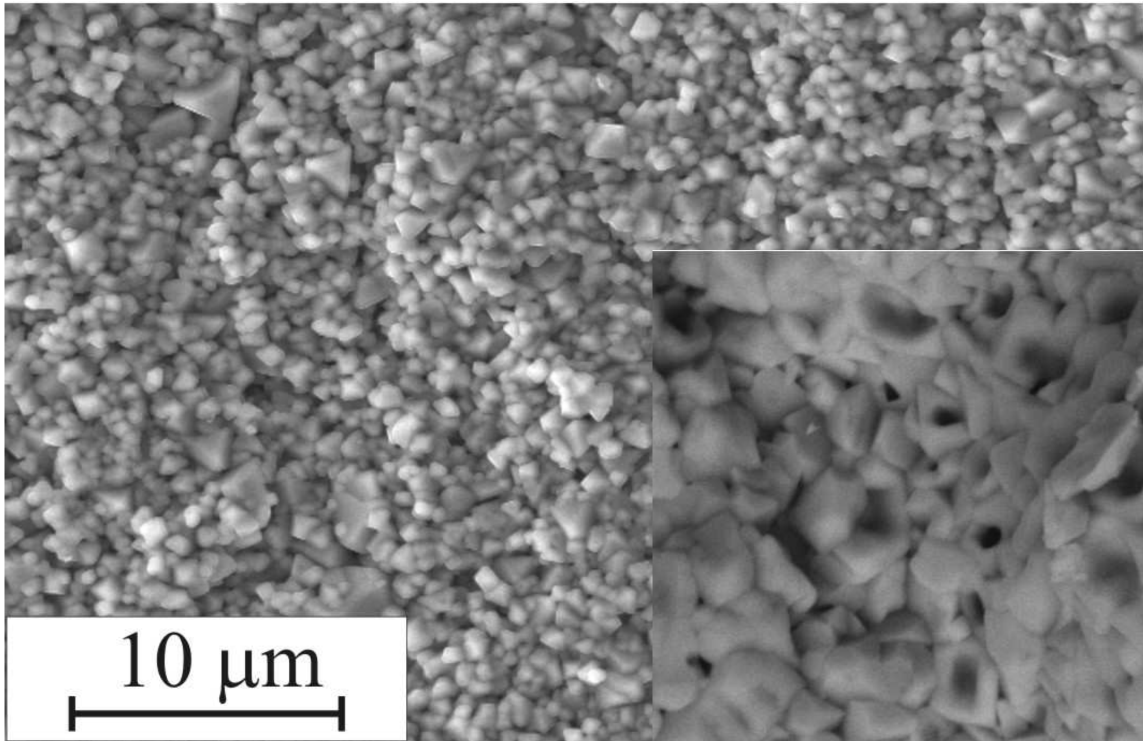
b) after 150 cycles



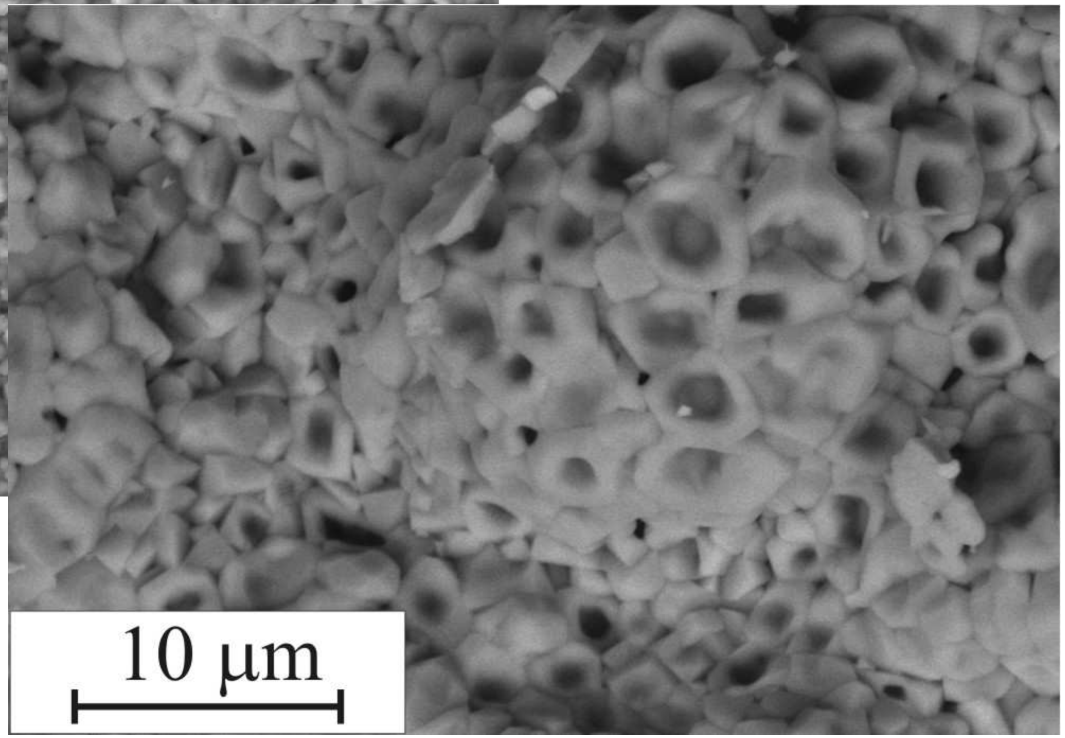
SEI picture of a scale grown on X50CrMnNiNbN21-9 steel in thermal shock conditions (T = 1173 K) in B10 combustion gases



SEI pictures of scales grown on selected valve steels in thermal shock conditions (T = 1173 K) in B10 combustion gases



X33CrNiMn23-8



X50CrMnNiNbN21-9

Summary

Experimental results confirmed the assuptions that addition of a bio-component into fuel oil worsens the resistance of steels, currently used for engine valve production, against the aggresive effects of exhaust fumes. Thus, it can be concluded that increasing the biocomponent content in fuel oil from 5 do 10 wt. % would make it practically impossible to use steels with less than 23 % chromium content for valve production. X33CrNiMn23-8 steel could be used for that purpose, however, the application of appropriate protective coatings should be taken into consideration.

THE END