

## **INFLUENCE OF ETHANOL PERCENTAGE IN PETROL ON CORROSION RESISTANCE OF VALVE STEELS IN COMBUSTION ENGINE GASES**

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### **Abstract**

The corrosion behavior of four grades of valves steels i.e. X33CrNiMn23-8, X50CrMnNiNbN21-9, X33CrNiMnN23-8, X50CrMnNiNbN21-8, X53CrMnNiN20-8 and X55CrMnNiN20-8 in combustion gases of petrol with different of ethanol volume percentage has been studied. In this work, the results of kinetic oxidation of above mentioned valve steels in combustion gases of petrol-ethanol mix with 5, 10, 50% [v/v] of ethanol are presented. It has been found that increase of ethanol in a petrol-ethanol mix up to 50% ethanol volume percentage decreases corrosion resistance of examined steels.

The corrosion tests have been performed gravimetrically under thermal shock conditions by heating of specimens from room temperature up to 1173 K. After heating at 1173 K for two hours, specimens were quenching at room temperature for 20 minutes and again heated. This experiment simulated the working conditions of a highly thermal loaded exhaust valves in spark or self-ignited combustion engines. The analysis performed shows that the corrosion resistance of X50CrMnNiNbN21-9, X53CrMnNiN20-8 and X55CrMnNiN20-8 valve steels in an environment of combustion gases from petrol with 50% ethanol additive (v/v) is significantly worse than in an environment of combustion gases of petrol-ethanol mix with 5 and 10% [v/v] of ethanol.

**Keywords:** valve steels, combustion gases, petrol-ethanol mix, kinetic of oxidation

### **1. INTRODUCTION**

The exhaust valves of four-stroke, spark and self-ignited combustion engines belong to the heavier loaded thermally and mechanically components, operating in extremely corrosive environment of hot exhaust gases. Among numerous structural components, To assure high-temperature creep resistance of highly-loaded thermally and mechanically exhaust valves, i.e. high resistance of valve steels to low, and especially high temperature creeping [1], and high heat resistance in exhaust gases of petrol, where to the main oxidizing agents belong: oxygen from 0.3 to about 8.0%, carbon dioxide from about 5.0 to about 12.0% and overheated steam from about 3.0 to about 5.5% [2, 3]. The objective of the present work was to investigate an effect of alloying additions, especially Cr, Ni, Mn and Si, on corrosion resistance of highly alloyed austenitic valve steels in exhaust gases of petrol with 5, 10 and 50% [v/v] ethanol additives (v/v) [4]. Oxidation of the specimens was carried out at temperature 1173 K, in conditions of cyclic thermal shocks, simulating operation of the exhaust valves in self-ignited combustion engine. Performed investigations have shown considerable effect of simultaneous increase of ethanol contents in petrol and Cr, Si and Ni alloy additive contents on corrosion resistance of the valve steels in an environment of combustion gases.

### **2. OWN REASERCH**

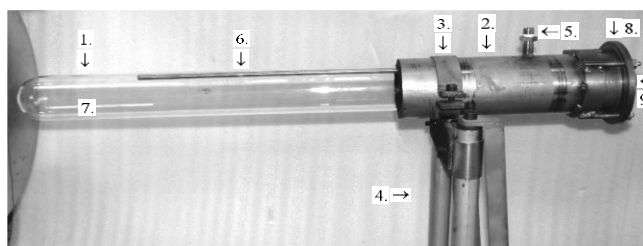
The investigations into the corrosion resistance of valve steel were conducted on samples in the form of discs of the thickness of approximately 1 mm and a diameter 16 and 19 mm obtained through machining process of the drawn bars (of the diameters of 17 and 20 mm respectively) of an industrial high-alloy valve

steel X33CrNiMnN23-8, X50CrMnNiNbN21-8, X53CrMnNiN20-8 and X55CrMnNiN20-8 with composition given in Table 1.

**Table 1** Chemical compositions of steel valves

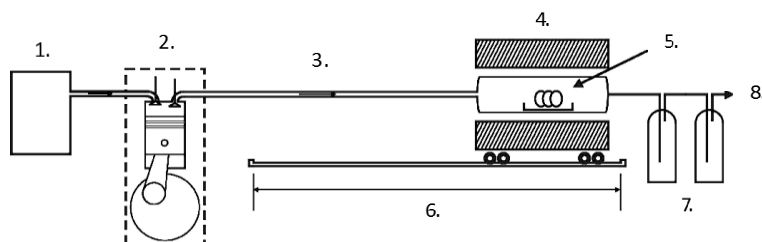
Steel	Chemical composition, % wt.										
	C	Cr	Ni	Mn	Si	Mo	W	Nb	S	P	N
X33CrNiMnN23-8	0.35	23.40	7.80	3.30	0.63	0.11	0.02	-	<0.005	0.014	0.28
X50CrMnNiNbN21-8	0.54	19.88	3.64	7.61	0.30	-	0.86	2.05	0.001	0.031	0.44
X53CrMnNiN20-8	0.53	20.50	4.10	10.30	0.30	0.12	-	-	<0.005	0.040	0.41
X55CrMnNiN20-8	0.55	20.00	2.30	8.18	0.17	0.11	-	-	<0.005	0.040	0.38

The samples to the tests of corrosion resistance, after machining and drilling  $\varnothing 2$  [mm] holes in distance of about 2 mm from the edge of specimens, underwent operation of grinding and polishing with use abrasive compounds and then cleaned with methanol and dried under a stream of compressed air. Next, the samples were weighed with use of an analytical balance with the accuracy of  $10^{-4}$ g in an air-conditioned room. Then the samples were hung on kanthal hooks and in a glass hanger they were put inside the pipe of the oxidation reactor. The specimens oxidized in determined time interval were taken from the working chamber of the reactor tube and next cooled down at room temperature, and then cleaned mechanically and with the use of compressed air (Fig.1).



**Fig.1** Reactor used in corrosion resistance tests of valve steels in hot flux of exhaust gases from a combustion engine: 1 – the glass tube of the reactor, 2 - steel housing, 3 - grip, 4 - pedestal, 5 - connector pipe, 6 - pipe delivering the combustion gases to reactor, 7 - oxidation area of samples, 8 - collar, 9 - combustion outlet

The examinations of corrosion resistance of valve steels in combustion gases of petrol with 5, 10 and 50% ethanol additives (v/v) were conducted at 1173 K under the conditions simulating work of valves in self-ignited combustion engine i.e. continuous flow of gas through the oxidation reactor under cycling of thermal shock condition i.e. heating the samples at temperature of 1173 K for 2 hours and subsequently cooled at room temperature and keeping them at room temperature for 25 minutes (Fig.2) [5]:



**Fig.2** The scheme of setup used in corrosion tests: 1- fuel tank, 2 – combustion engine, 3 – delivering pipe of combustion gas, 4 – furnace, 5 – reactor with samples, 6 – range of funeral movement, 7 – combustion bulbs, 8 – combustion outlet

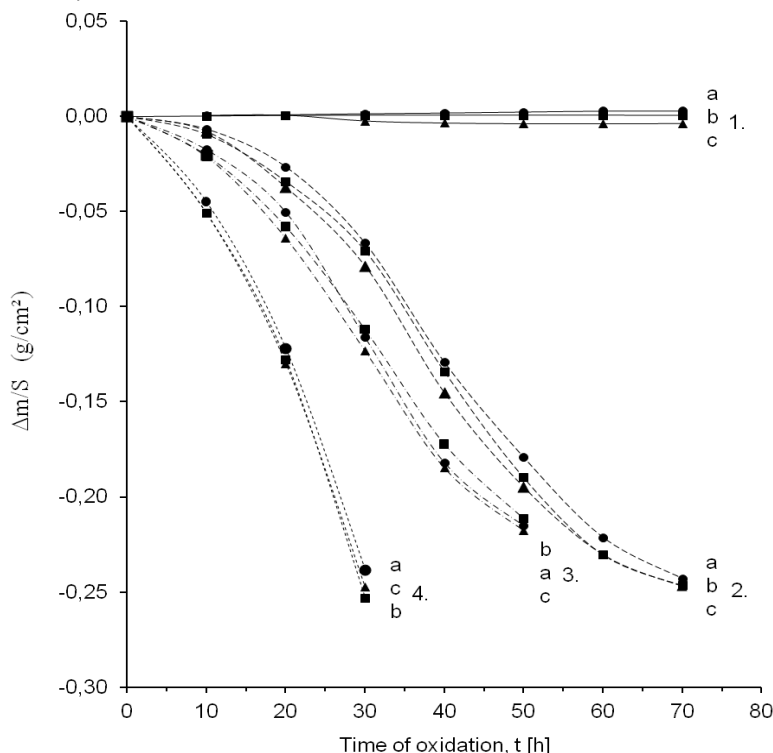
The oxidation rate was investigated by measurement of mass loss in the oxidized specimens with reference to the initial surface area of the specimens  $S$  [ $\text{g}/\text{cm}^2$ ] and time of oxidation  $t$  [hours], and in the following step, results of the measurements were again related to the duration of the oxidation step as a function of the number of thermal shocks and oxidation times [6, 7].

### 3. TEST RESULTS AND DISCUSSION

The obtained results shows that among examined steels the highest corrosion resistance in combustion gases of petrol-ethanol mix with 5% ethanol [v/v] reveals X33CrNiMnN23-8 steel, which contains the followed highest alloy additives Cr (23.40%), Ni (7.82%) and Si (0.63%), and the lowest Mn additive (3.30%) - (Fig.3, curve 1a). The other examined steels i.e. X50CrMnNiNbN21-9, X53CrMnNiN20-8 and X55CrMnNiN20-8 in the same conditions show significantly lower corrosion resistance with increasing of time oxidation up to 70 hrs (Fig.3, curves 2a, 3a and 4a). Behavior of above mentioned steels can be explained by lower Cr, Ni and Si content.

The corrosion resistance of X33CrNiMnN23-8 in combustion gases of petrol-ethanol mix with 10% ethanol [v/v] was similar as with 5% [v/v] ethanol (Fig.3, curve 1b), whereas for X50CrMnNiNbN21-9, X53CrMnNiN20-8 and X55CrMnNiN20-8 steel decrease of corrosion resistance were observed (Fig.3 curve 2b, 3b and 4b).

The growth of ethanol in petrol-ethanol mix up to 50% [v/v] in steel X33CrNiMnN23-8 did not influence on significant decreases its corrosion resistance in combustion gases (Fig.3 curve 1c). Also the similar corrosion resistance were observed for other examined steels i.e. X50CrMnNiNbN21-9, X53CrMnNiN20-8 and X55CrMnNiN20-8 oxidized at the same temperature respectively for 70, 50, 30 hrs and combustion gases (Fig.3 curves 2c, 3c and 4c).



**Fig.3** Corrosion resistance of the valve steels 1 - X33CrNiMnN23-8, 2 - X50CrMnNiNbN21-9, 3 - X53CrMnNiN20-8 and 4 - X55CrMnNiN20-8 in combustion gases of petrol with: a - 5%, b - 10% and c - 50% ethanol additive [v/v]. The samples were oxidized under the conditions of cyclic thermal shocks at the temperature of 1173 K

## CONCLUSION

The analysis performed shows that corrosion resistance of X33CrNiMnN23-8 steel in an environment of combustion gases from petrol-ethanol mix up to 50% of ethanol [v/v] is better than for other examined steels i.e. X50CrMnNiNbN21-9, X53CrMnNiN20-8 and X55CrMnNiN20-8 (Fig. 3). Moreover it was concluded that all examined steels in combustion gases from petrol-ethanol mix with increase of ethanol up to 50% ethanol [v/v] have slightly worse corrosion resistance properties (Fig.3). The differences on corrosion resistance between X33CrNiMnN23-8 steel and other examined steels in combustion hot exhaust gases from petrol-ethanol mix with the same ethanol percentage can be explained by alloy additives contents in examined steels such as Cr, Ni, Si (Tab.1). The higher Cr, Ni, and Si contents cause better corrosion resistance properties of valve steels.

## REFERENCES

- [1] Mrowec S., Werber T. Modern Sc-Resistant Materials / Eds. National Bureau of Standards and National Science Foundation, Washington D.C., 1982, p. 277.
- [2] Newkirk J.B. High Temperature Materials Coatings and Surface Interactions / Eds. Freund P.H. Tel Aviv, 1980, p.56.
- [3] Kofstad P. High Temperature Corrosion / Eds. Elsevier Applied Science, London and New York, 1988, p.389.
- [4] Agarwal A. K. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines // Progress in Energy and Combustion Science. 2007, Vol. 33, p. 233-271.
- [5] Naumienko D., Singheiser L., Guadakkars W.J. Oxidation Limited of FeCrAl Based Alloys during Thermal Cyclic, by /Eds. M. Schutze and W.J. Quadakkars // Proceedings of an EFC Workshop, Frankfurt/Main, Germany, 1999. p. 287- 306.
- [6] Grzesik Z., Adamaszek K., Jurasz Z., Mrowec S. Corrosion of Valve Steels in Combustion Gases of Diesel Engines under Thermal Shock Conditions // Defect and Diffusion Forum. Trans Tech Publications, Switzerland, 2012, Vol. 323-325, p. 327- 332.
- [7] Grzesik Z., Mrowec S. and Jurasz Z., Adamaszek K. The behavior of valve materials utilized in diesel engines under thermal shock conditions // High Temperature Materials and Processes, Freund Publishing House Ltd. Tel Aviv, Israel, 2010. Vol. 29, № 1-2, p.35-46.

