

# INFLUENCE OF FATTY ACID METHYL ESTERS QUANTITIES IN FUEL OIL ON CORROSION RESISTANCE OF VALVE STEELS IN COMBUSTION GASES

## Krzysztof ADAMASZEK, Jan NOWAK, Zbigniew JURASZ

BOSMAL Automotive Research & Development Institute, Bielsko-Biala, Poland, EU <u>krzysztof.adamaszek@bosmal.com.pl</u>, jan.nowak@bosmal.com.pl, zbigniew.jurasz@bosmal.com.pl

### Abstract

The corrosion behaviour 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 fuel oil with different quantities of FAME (Fatty Acid Methyl Esters) has been studied. In this work, the results of kinetic oxidation of above mentioned valve steels in combustion gases from diesel engine with 5, 10, 20% [v/v] of FAME are presented. It has been found that increase of FAME up to 20% volume percentage to the fuel oil decreases corrosion resistance of tested 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 valves work conditions of highly thermal loaded combustion engines.

Keywords: Valve steels, combustion gases, fuel oil, FAME, kinetic of oxidation

### 1. INTRODUCTION

In recent years, fuel oil with different FAME additive has been increasingly used in spark-ignited Diesel engines. Exhaust valves belong to the most thermally and mechanically heavily loaded components working in the extremely corrosion aggressive environment of hot exhaust gases. The durability of exhaust valves mainly depends on the high-temperature creep resistance of the steels used; i.e. simultaneously high resistance to mechanical deformation and corrosion resistance to combustion gases at high temperature [1-3].

The temperature of exhaust gases reaches high temperatures of up to 1200 K. To ensure high heat resistance of the exhaust valves, i.e. high heat resistance in the strongly oxidizing environment of hot exhaust gases from combustion of fuel oil, as well as high resistance to mechanical deformations at high and increased temperatures, i.e. resistance to low - and high-temperature creep valve heads of modern bimetallic exhaust valves are usually produced from grades of high temperature resistant austenitic valve steels having the chemical constitution specified in **Table 1**. Investigations were performed at a temperature of 1173 K under thermal shock conditions, simulating operation of the exhaust valves of spark-ignited Diesel engines.

The objective of the present study was to determine the corrosion resistance of commonly used valve steels in combustion gases from fuel oil with 5, 10, and 20 % of FAME (v/v) additive [4].

### 2. OWN RESEARCH

Investigations of an effect of FAME quantities on corrosion resistance of valve steels in exhaust gases of fuel oil having various contents of FAME were performed on a specimens in form of discs with thickness of about 1mm and diameter of 16 and 19 mm, produced in turning operation from a drawn bars having diameters of 17 and 20mm respectively, from industrial heat of highly alloyed austenitic valve steels of X33CrNiMnN23-8 and X55CrMnNiN20-8 grades, as well as X50CrMnNiNbN21-9 and X53CrMnNiN20-8 grades respectively, having chemical analysis given in the **Table 1**.



Grade of steel	Chemical composition.										
	С	Cr	Ni	Mn	Si	Мо	W	Nb	S	Р	Ν
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	2.08	7.57	0.17	0.11	-	-	< 0.005	0.040	0.38

 Table 1 Chemical compositions of examined valve steels (wt. %)

Specimens to the tests of corrosion resistance, after machining and drilling  $\emptyset$  2 [mm] holes in distance of about 2 mm from the edge of specimens, underwent operation of grinding and polishing with use of a suitable abrasive paper and abrasive compounds. In the next stage the specimens were washed in methyl alcohol and dried in stream of compressed air. After performing of mechanical treatments as mentioned above, the specimens were weighted with accuracy of up to  $10^{-4}$  [g] in air conditioned room, in the next step the specimens were hanged on kanthal pendants, and next, the specimens located in ceramic vessel were inserted into quartz tube of the reactor (**Fig. 1** and **2**).



**Fig. 1** Specimens to the tests of corrosion resistance of valve steels in exhaust gases from fuel oil with FAME additive engine hanged on glass transportation "boat"

The rapid heating of the tested specimens in combustion gases from fuel oil with 5, 10 and 20 % FAME [v/v] to a temperature of 1173 K, and next, being held at the above mentioned temperature for 2 hours and finally cooling down at room temperature for about 25 min (**Fig. 1, 2**) [5].

The specimens oxidized in determined time interval, every 25 hours up to 100 hours were taken from the working chamber of the reactor tube and next cooled down to room temperature, and then cleaned mechanically and with the use of compressed air. After cleaning, the specimens were weighed in an air-conditioned room with use of an analytical balance of accuracy 10<sup>-4</sup>g. 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 [g/cm<sup>2</sup>] and time of oxidation [h], and in the following step, results of the measurements were again related to the duration of the oxidation step [6, 7]. After 100 h process oxidation at 25 h intervals was increased up to 50 h intervals.





Fig. 2 Reactor used in corrosion resistance tests of valve steels in hot flux of exhaust gases from a combustion engine: 1 - samples in the glass tube of the reactor, 2 steel pipe used to deliver exhaust gases, 3 connector pipe delivering the combustion gases to reactor, 4 - combustion outlet, 5 - furnace used to increase the temperature of the combustion

### 3. TEST RESULTS AND DISCUSSION

The obtained results shows that among tested steels the highest corrosion resistance in combustion gases from fuel-oil with 5 and 10 %, additive of FAME [v/v] reveals the best corrosion resistance of X33CrNiMnN23-8 steel, which contains the followed highest alloy additives Cr (23.40 %), Ni (7.82%) and Si (0.63 %), and the lowest Mn alloy additive (3.30%) - (**Fig. 3**, curve 1). Other tested 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 75 h (**Fig. 3**, curve 2, 3 and 4 and **Table 2**).



**Fig. 3** The comparison of oxidation rate of austenitic valve steels: 1 and 1' - X33CrNiMnN23-8, 2 and 2' - X50CrMnNiNbN21-9, 3 and 3' - X53CrMnNiN20-8, 4 and 4' - X55CrMnNiN20-8 in combustion gases from fuel oil with 5% and 10 % additive of FAME [v/v]. Time of oxidation of tested steels is given in **Table 2** 



 Table 2 Data connected with Fig. 3

Steel	Time (h)	5% FAME	Time,	10% FAME	
		Point in Fig. 3	(h)	Point in Fig. 3	
X33CrNiMnN23-8	350	1	300	1'	
X50CrMnNiNbN21-9	75	2	50	2'	
X53CrMnNiN20-8	75	3	50	3'	
X55CrMnNiN20-8	75	4	50	4'	

The growth of FAME additive in fuel oil up to 20 % [v/v] in steel X33CrNiMnN23-8 did not influence on decreases its corrosion resistance in combustion gases (**Fig. 4** curve 1, **Table 3**), whereas significant influence on corrosion resistance at the same experimental condition for other steels i.e. X50CrMnNiNbN21-9, X53CrMnNiN20-8 and X55CrMnNiN20-8 were observed after oxidation for 75 h. (**Fig. 5** curve 2", 3" and 4", **Table 4**). It was observed that specimens from these steels were completely destructed (**Fig. 6**).



Fig. 4 The rate of oxidation of X33CrNiMnN23-8 austenitic valve steel in combustion gases from fuel oil with 5, 10 and 20% additive of FAME [v/v]. Time of oxidation of tested steels is given in **Table 3**.

Steel	Time (h)	5% FAME Point in <b>Fig. 5</b>	Time (h)	10% FAME Point in <b>Fig. 5</b>	Time (h)	20% FAME Point in Fig. 5
X33CrNiMnN23-8	350	1	300	1'	300	1"





Fig. 5 The comparison of oxidation rate of austenitic valve steels: 2, 2' and 2" - X50CrMnNiNbN21-9,
3, 3' and 3"- X53CrMnNiN20-8, 4, 4', 4" - X55CrMnNiN20-8 in combustion gases from fuel oil with 5, 10, 20% additive of FAME [v/v]. Time of oxidation of tested steels is given in Table 4

Steel	Time, (h)	5% FAME Point in <b>Fig. 5</b>	Time, (h)	10% FAME Point in <b>Fig. 5</b>	Time, (h)	20% FAME Point in <b>Fig. 5</b>
X50CrMnNiNbN21-9	75	2	50	2'	25	2"
X53CrMnNiN20-8	75	3	50	3'	25	3"
X55CrMnNiN20-8	75	4	50	4'	25	4"

Table 4 Soma data connected v	with	Fig. 5
-------------------------------	------	--------

### 4. CONCLUSION

The obtained results for X33CrNiMnN23-8 steel did not show significant lower corrosion resistance with increasing of additive FAME additive up to 20 % [v/v]. The other tested steels i.e. X50CrMnNiNbN21-9, X53CrMnNiN20-8 and X55CrMnNiN20-8 in the same experimental conditions show significantly lower corrosion resistance in combustion gases from fuel-oil with 5, 10 and 20 % FAME additive [v/v]. These steels were completely destructed, respectively after c.a. 75, 50 and 25 h. The respectively points 2, 2', 2", 3, 3' 3" and 4, 4', 4" are shown in **Fig. 5**. The different behaviour of above mentioned steels can be explained by lower content of alloy additives such as Cr, Ni and Si in relation to X33CrNiMnN23-8 steel.





Fig. 6 The macrographs of austenitic valve steels: 1 - X33CrNiMnN23-8, 2 - X50CrMnNiNbN21-9,
3 - X53CrMnNiN20-8 and 4 - X55CrMnNiN20-8 in combustion gases from fuel oil with 5, 10, 20% additive of FAME [v/v]. Time of oxidation of tested steels is given in Tables 2 - 4 and in Figs. 3 - 5

#### REFERENCES

- [1] MROWEC S., WERBER T. Modern Sc.-Resistant Materials / Eds. National Bureau of Standards and National Science Foundation, Washington D.C., 1982, 277 p.
- [2] KOFSTAD P. High Temperature Corrosion / Eds. Elsevier Applied Science, London and New York, 1988, 389p.
- [3] PN-EN 10098 1:2001 Standard, Steels and valve alloys in combustion engine.
- [4] PN-EN 14214:2012 standard, Fuels for vehicles. Fatty Acid Methyl Esters (FAME) for self-ignited Diesel engines Requirements and Examinations.
- [5] 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, Vol. 323-325, 2012, pp. 327-332.
- [6] GRZESIK Z., MROWEC S. AND JURASZ Z., ADAMASZEK K. The behaviour of valve materials utilized ion diesel engines under it thermal shock conditions. High Temperature Materials and Processes, Vol. 29, No. 1-2, 2010, pp. 35-46.
- [7] 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, Vol. 323-325, 2012, pp. 235-243.