D. DULIŃSKA*, W. PAWLAK**, Z. GRZESIK*,♯

THE PROSPECTS IN DESIGNING NEW GENERATION OF HIGH TEMPERATURE COATINGS IN AUTOMOBILE ENGINES

PERSPEKTYWY PROJEKTOWANIA NOWEJ GENERACJI WYSOKOTEMPERATUROWYCH POWŁOK OCHRONNYCH W SILNIKACH SAMOCHODOWYCH

The influence of the chromium layer with the thickness of 1 micrometer sputter-deposited on the X33CrNiMn23-8 and X50CrMnNiNbN21-9 steel surfaces on the oxidation behavior of these steels has been studied at 1173 K in air, using the microthermogravimetric technique. It has been found that coated materials show very good oxidation resistance under isothermal conditions, comparable with that of chromia formers, due to the formation of Cr_2O_3 scales on their surfaces. It has been also demonstrated that the positive effect of chromium addition on the oxidation resistance of investigated steels is observed during a much longer period of time than the life-time of the chromium coating.

Keywords: valve steels, coatings, oxidation

W pracy zbadano metodą grawimetryczną wpływ warstwy chromu o grubości 1 mikrometra, nałożonej metodą magnetronową na powierzchnie stali X33CrNiMn23-8 i X50CrMnNiNbN21-9, na kinetykę utleniania tych stali w temperaturze 1173 K w powietrzu. Przeprowadzone badania wykazały, że stale pokryte powłoką wykazują bardzo dobrą odporność na utlenianie w warunkach izotermicznych, porównywalną do tej, jaką charakteryzują się stopy z grupy *chromia formers*, w wyniku powstawania na ich powierzchni zgorzeliny zbudowanej z Cr_2O_3. Wykazano również, że korzystny wpływ dodatku chromu na odporność na utlenianie badanych stali obserwowany jest przez znacznie dłuższy czas od czasu stabilności samej powłoki.

1. Introduction

Austenitic chromium-nickel steels are being generally utilized nowadays in the production of valves in automobile engines. These materials are working in very sever conditions due to rather high temperatures (873-1173 K) and aggressive atmosphere of combustion gases. In the last dozen years, the problem of corrosion resistance of automobile engine valves started to be more and more important [1-7]. This situation is mainly a result of application in automobile industry of alternative fuels, like biofuels, liquid petroleum gas (LPG), compressed natural gas (CNG), etc., the combustion products of which are very aggressive [8,9]. Such alternative fuels are very attractive especially for automotive transport, because they could replace petroleum and its secondary products [10-12] but unfortunately, they cause the enhanced corrosion of exhaust engine valves. In addition, new generations of car engines are characterized by increased working temperature with the simultaneous decrease in fuel consumption. It should be noted that according to the present experience in this area, the engine temperature growth as well as the application of alternative fuels, creates serious danger of enhanced corrosion of engine valves [7,8,13].

Considering this situation, it can be concluded that new methods of engine valve protection against high temperature corrosion should be applied. Among these methods the most promising one seems to be the application of protective coatings [14-16]. In this case, the main idea is the creation of such conditions, under which selective oxidation of chromium or aluminum takes place [17-20], because oxides of both these metals (Cr_2O_3 and Al_2O_3) show excellent corrosion protection. The most frequently utilized protective coatings are those, called thermal barrier coatings (TBC) in literature [15]. Such coatings are generally composed of two layers. The inner layer is built of scaling resistant MCrAlY alloy (where M = Fe, Ni or Co) and the outer ceramic layer playing the role of thermal barrier. This layer is composed of zirconium dioxide, stabilized by calcium, magnesium or yttrium. The stability of TBC coatings depends mainly on the inner, scaling resistant layer of MCrAlY alloy, due to the formation of a highly protective Al_2O_3 scale on its surface. The high effectiveness of TBC coatings in protection of valve steels against high temperature corrosion has been proved experimentally [21]. Unfortunately, TBC coatings were never used in mass-production in the automobile industry due to considerably increased costs of engine valves production.

Being active in this area of research for many years, we started rather long-term investigations, aimed at the development of a new generation of high temperature inexpensive coatings, which could be used in automobile industry

*   AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

** TECHNICAL UNIVERSITY OF LODZ, LODZ, POLAND

♯ Corresponding author: grzesik@agh.edu.pl

TABLE 1

The chemical compositions (wt. %) of studied valve steels

Type 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	0.54	7.61	0.30	19.88	3.64	0.44	0.86	2.05	0.001	0.031	-	bal.

for protection of engine valves. The main idea for the solution to this problem consists in the substitution of alumina formers with chromia formers, which means that high concentration of aluminum is replaced by chromium, resulting in the formation of a Cr_2O_3 layer during high temperature selective oxidation. In contrast to rather thick and thereby expensive corrosion-resistant coatings, constituting large chromium reservoir, the proposed novel coatings contain a very small amount of chromium, because the thickness of the coating is on the level of 1 micrometer. Consequently, these coatings play only the role of initiator for the formation of Cr_2O_3 layer and then they disappear. The stability of further growth of the chromium oxide layer should result from outward diffusion of chromium from the protected chromium steel. The development of new corrosion-protective coatings needs long-term investigations under isothermal and thermal shock conditions, carried out at different aggressive atmospheres. In first step, the oxidation behavior of new coatings under isothermal conditions in air has been tested and the obtained results are reported in the present paper.

2. Materials and experimental procedure

From all steels utilized for engine valve production, two valve steels with the highest and lowest chromium content have been selected for investigations in this work. Chemical compositions of these steels are summarized in Table 1.

The samples for corrosion experiments have been obtained from rods of steels with diameters of about 20 mm and thickness of approximately 1 mm. These disc-shaped samples were grinded with emery papers (up 800 SiC) and finally polished using diamond pastes to obtain mirror-like surfaces. The size of diamond particles in the paste was 0.25 μm. Some of these samples were covered by a chromium layer with the thickness of 1 micrometer. In this case, the substrates were mounted onto a two-fold rotary holder using a nickel-chromium wire. After evacuation of air to a pressure below 10^{-3} Pa, the argon ion cleaning was conducted with the use of three ion guns. Argon ions energy was about 4keV, sample bias was changed from 0 to 2kV and the cleaning time was 1.8ks. Magnetron sputtering of the pure chromium target was started immediately after argon ion cleaning. Argon pressure during deposition was equal to 0.39Pa. The magnetron sputtering process was carried out under 640V and 1A. Sample bias of modulated DC current during deposition was 50V/0.03A. Time of sputtering was 40min.

The oxidation kinetics of both types of specimens (uncoated and coated ones) have been studied thermogravimetrically in a microthermogravimetric apparatus described elsewhere [7]. This apparatus has been equipped with electronic microbalance enabling the determination of weight gains

of the oxidizing steel samples with accuracy of the order of 10^{-6} g. The oxidation rate measurements have been carried out in air at 1173 K. The test temperature (1173 K) was chosen in relation to the highest temperature of valves in diesel and modern petrol engines. The phase composition of the oxidation products (scale) has been studied by X-ray diffraction (XRD), and the morphology and chemical composition of reaction products by electron probe micro analysis (EPMA) and scanning electron microscopy (SEM) with an energy disperse X-ray analyzer (EDX).

3. Results and discussion

Figure 1 illustrates the oxidation kinetic of the X33CrNiMn23-8 steel sample covered with chromium coating, on the background of analogous result obtained using the same steel sample without surface modification.
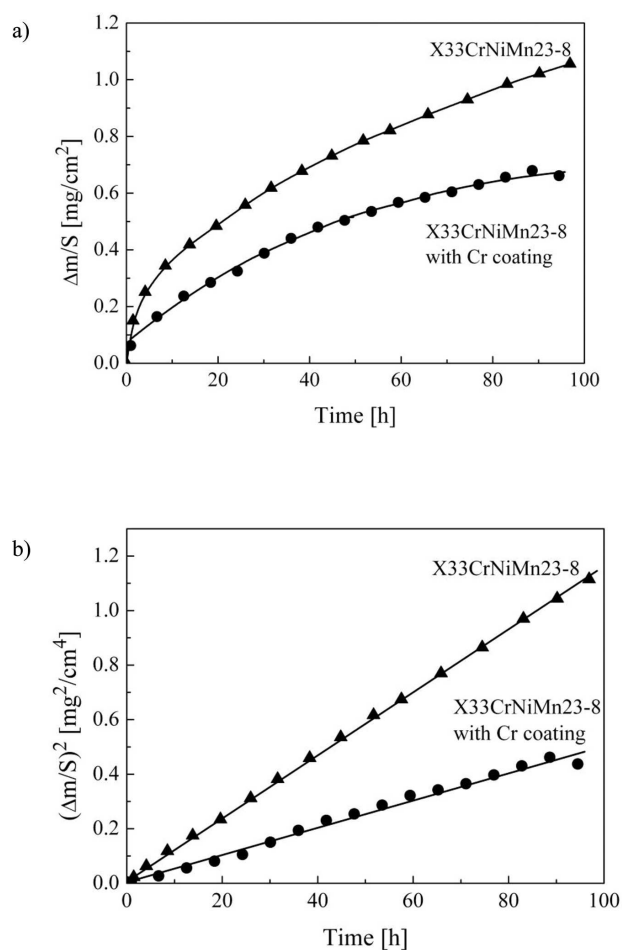

Fig. 1. Comparison of the oxidation kinetics of coated and uncoated X33CrNiMn23-8 steel at T = 1173 K in air (Δm/S – weight changes of the oxidized sample per unit surface area): a) linear plot of coordinates, b) parabolic plot of coordinates

As can be seen, the oxidation rate of the X33CrNiMn23-8 steel sample covered by chromium coating is lower than that observed in the case of the same steel without coating (Fig. 1a). In both cases the oxidation process follows strictly parabolic kinetics (Fig. 1b), indicating that it is diffusion controlled. Fig. 2, in turn, presents the analogous data obtained during oxidation of the coated and uncoated X50CrMnNiNbN21-9 steel.
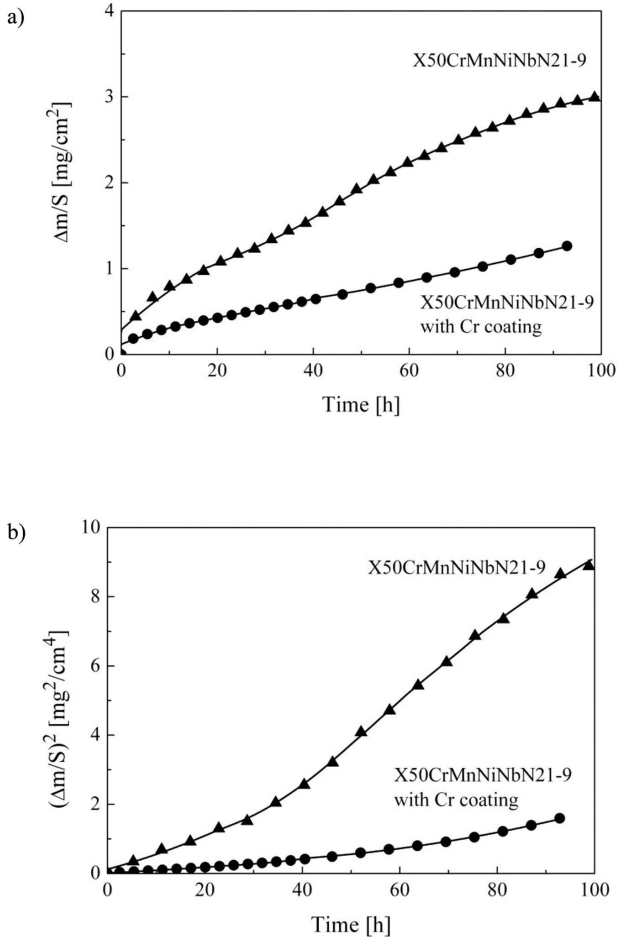

a)

Fig. 2. Comparison of the oxidation kinetics of coated and uncoated X50CrMnNiNbN21-9 steel at T = 1173 K in air ($\Delta m/S$ – weight changes of the oxidized sample per unit surface area): a) linear plot of coordinates, b) parabolic plot of coordinates

Again, the oxidation rate of the coated steel sample is lower than that observed for the uncoated material (Fig. 2a). In spite of the oxidation behavior of the uncoated X50CrMnNiNbN21-9 steel, in the case of the sample covered by chromium, the oxidation kinetics follows the parabolic rate law for about 50 hours, with the rate slightly increasing in later oxidation stages (Fig. 2b). It should be noted that the oxidation rate of the chromium coated sample of the X50CrMnNiNbN21-9 steel is virtually the same, as that observed in the case of the uncoated X33CrNiMn23-8 steel sample, the resistance of which against high temperature oxidation – as already mentioned – is very good. This fact is well illustrated in Fig. 3, which compares the oxidation rate of the uncoated and coated X50CrMnNiNbN21-9 steel on the background of the analogous result obtained during oxidation of the uncoated X33CrNiMn23-8 steel.
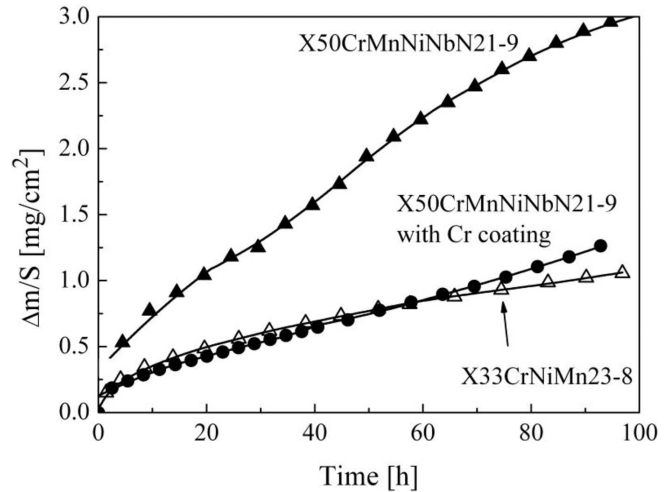

Fig. 3. The comparison of oxidation rate of the uncoated and coated X50CrMnNiNbN21-9 steel on the background of the analogous results obtained during oxidation of the uncoated X33CrNiMn23-8 steel

It is very interesting that the positive effect of chromium on the oxidation resistance of investigated steels is observed during a much longer period of time than the life-time of the chromium coatings. In the case of coated X33CrNiMn23-8 and X50CrMnNiNbN21-9 steels, the chromium layer disappears after about 20 and 15 hours, respectively. However, in spite of the lack of the metallic chromium layer on the surface of investigated steels, the oxidation resistance of both steels remains on the same level, because the character of the kinetic curve virtually does not change. Thus, the obtained results strongly support the main thesis of this work, leading to the statement that it is possible to develop a new generation of high temperature inexpensive coatings for protection of valve steels against high temperature oxidation.

The observed behavior of investigated materials can be explained in terms of scale chemical composition. It has been found, namely, that during oxidation of the uncoated and coated X33CrNiMn23-8 steel as well as the coated X50CrMnNiNbN21-9 steel, the oxidation product forming the scale is built mainly from highly protective Cr_2O_3 oxide, as determined in Fig. 4.
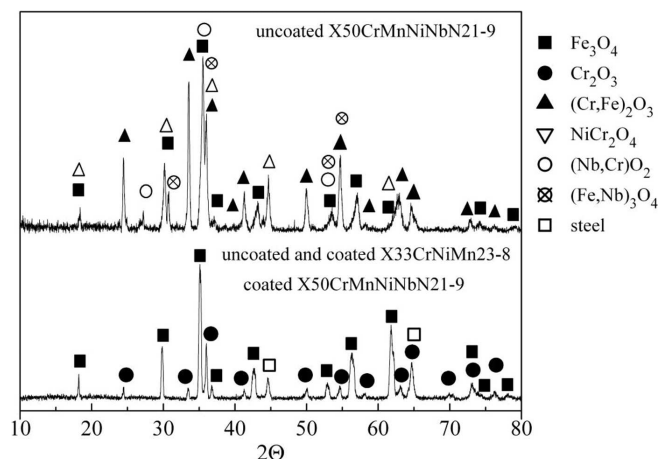

Fig. 4. X-ray diffraction patterns for all steels under discussion, oxidized at 1173 K in air for 100 hours

906

In all these cases, the concentration of chromium at the surface of the steel is high enough to form in early stages of Cr$_2$O$_3$ layer oxidation, characterized by very good protective properties. On the other hand, in later stages of oxidation, the chromium supply from the metallic core to the scale is sufficiently high for assuring the stability of this chromium oxide layer. In the case of the X33CrNiMn23-8 steel, which contains high enough chromium content for the formation of a continuous layer of chromium oxide, chromium coating can only slightly improve the protective properties of the scale and consequently, the oxidation resistance of the X33CrNiMn23-8 steel sample covered by chromium layer is only slightly better than that of uncovered material. In the case of the uncoated X50CrMnNiNbN21-9 steel, the chromium concentration, being on the level of 20 wt. %, is not high enough for selective oxidation of chromium and the formation of the continuous Cr$_2$O$_3$ oxide layer [13,18]. Thus, a heterogeneous scale is formed, the protective properties of which are much worse than that assured by chromium oxide. Consequently, the chromium layer, sputter-deposited on the surface of this steel, assures the formation of a continuous chromium oxide layer in the early stage of oxidation instead of heterogeneous spinel scales, considerably increasing the oxidation resistance of the X50CrMnNiNbN21-9 steel. It should be mentioned that the results obtained using XRD analysis are in full agreement with the morphological observations of the scale surfaces forming on investigated materials, presented in Fig. 5.
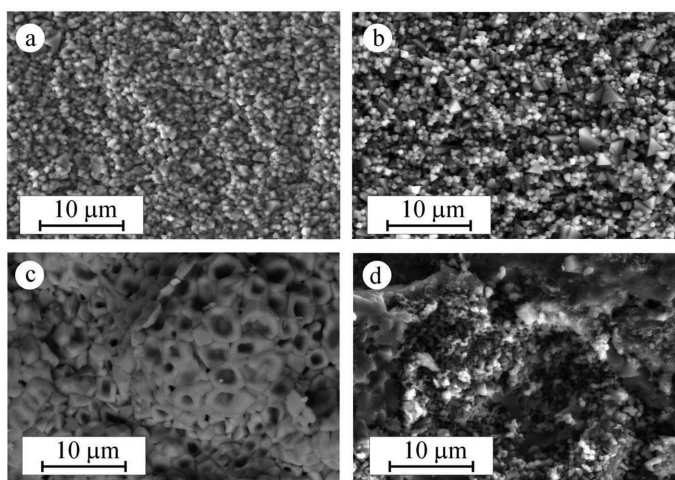

Fig. 5. SEM images of the surface of studied steel samples a) uncoated X33CrNiMn23-8 steel, b) coated X33CrNiMn23-8 steel, c) uncoated X50CrMnNiNbN21-9, d) coated X50CrMnNiNbN21-9

It has been found, namely, that scales formed on coated and uncoated X33CrNiMn23-8 steel samples virtually do not differ (Fig. 5a,b), because in both these cases chromium oxide is mainly present in the scale. On the other hand, a large difference is observed in the case of oxidized coated and uncoated X50CrMnNiNbN21-9 steel samples (Fig. 5 c,d). This difference is a result of the chemical composition of growing scales. On the uncoated X50CrMnNiNbN21-9 steel, an unprotective heterogeneous scale is formed, while the scale formed on the coated X50CrMnNiNbN21-9 steel contain chromium oxide. As a consequence, the surface of the scale formed on the coated X50CrMnNiNbN21-9 steel looks similar to that observed in the case of the X33CrNiMn23-8 steels, being dis-

similar to the heterogeneous scale growing on the uncoated X50CrMnNiNbN21-9 steel samples.

4. 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 a much longer period of time than the life-time of the chromium coating, which strongly supports the idea of tailoring a new generation of high temperature inexpensive coatings for the automobile industry.

REFERENCES

[1] C.G. Scott, A.T. Riga, H. Hong, Wear **181-183**, 485 (1995).
[2] A.S.M.A. Haseeb, M.A. Fazal, M.I. JahIrul, H.H. Masjuki, Fuel **90**, 922 (2011).
[3] Z.W. Yu, X.L. Xu, Eng. Fail. Anal. **13**, 673 (2006).
[4] D. Schlager, C. Theiler, H. Kohn, Mater. Corros. **53**, 103 (2002).
[5] M. Velliangiri, A.S. Krishnan, J. Energ. Technol. Policy **2**, 42 (2012).
[6] P. Lawrence, P.K. Mathews, B. Deepanraj, J. Sci. Ind. Res. **70**, 789 (2011).
[7] T. Hejwowski, Vacuum **80**, 1386 (2006).
[8] Z. Grzesik, G. Smola, K. Adamaszek, Z. Jurasz, S. Mrowec, Corros. Sci. **77**, 369 (2013).
[9] Z. Grzesik, G. Smola, K. Adamaszek, Z. Jurasz, S. Mrowec, Oxid. Met. **80**, 147 (2013).
[10] R. Gilbert, A. Perl, Energy And Transport Futures. A report prepared for national round table on the environment and the economy, Calgary 2005.
[11] D.G. Kesse, J. Pet. Sci. Eng. **26**, 157 (2000).
[12] C.N. Hamelinck, A.P.C. Faaij, Energ. Policy **34**, 3268 (2006).
[13] Z. Grzesik, Z. Jurasz, K. Adamaszek, S. Mrowec, High Temp. Mater. Proc. **31**, 775 (2012).
[14] B. Gleeson, High-Temperature Corrosion of Metallic Alloys and Coatings, in: R.W. Cahn, P. Haasen, E.J. Kramer (Ed.), Materials Science and Technology, Wiley-VCH, Weinheim-New York-Chichester-Brisbane-Singapore-Toronto **2**, (2000).
[15] H. Xu, H. Guo, S. Gong, Thermal barrier coatings in Developments in High-temperature Corrosion and Protection of Materials, Woodhead Publishing in Materials, Cambridge, England (2008).
[16] H. Evans, High Temperature Coatings: Protection and Breakdown in Shreir's Corrosion, 4th Edition, vol. 1, Elsevier Ltd., Amsterdam, The Netherland (2010).
[17] S.N. Birks, G.H. Meier, F.S. Pettit, Introduction to the high temperature oxidation of metals, Cambridge, University Press (2009).
[18] S. Mrowec, T. Werber, Modern Scaling-Resistant Materials, National Bureau of Standards and National Science Foundation, Washington D. C. (1982).

[19] B.A. Pint, Design strategies for new oxidation-resistant high temperature alloys, in Developments in High-temperature Corrosion and Protection of Materials, Woodhead Publishing in Materials, Cambridge, England, (2008).

[20] S. Chevalier, Formation and growth of protective alumina scales in Developments in High-temperature Corrosion and Protection of Materials, Woodhead Publishing in Materials, Cambridge, England, (2008).

[21] K. Adamaszek, Z. Jurasz, L. Swadzba, Z. Grzesik, S. Mrowec, High Temp. Mater. Proc. **26**, 115 (2007).