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High temperature corrosion of valve steels in atmosphere containing water vapor

Z. Jurasz · K. Adamaszek · R. Janik ·
Z. Grzesik · S. Mrowec

Abstract The kinetics and mechanism of high temperature corrosion of two valve materials (X33CrNiMn23-8 and X50CrMnNiNbN21-9 steels) in water-vapor-containing atmosphere have been studied as a function of temperature (973–1,273 K) and gas composition, being the mixture of nitrogen, oxygen, and water vapor. In all experiments this atmosphere contained 50 vol.% of water vapor and the concentration of oxygen was changed from 0.001 to 50 vol.%. The oxidation kinetics have been studied thermogravimetrically in microthermogravimetric equipment, enabling the registration of weight changes of the oxidizing samples as a function of time with the accuracy of the order of 10^{-6} g. It has been found that the corrosion process of both steels is rather complex and can not be described by one kinetic rate law. X33CrNiMn23-8 steel, containing higher chromium concentration, shows better corrosion resistance than the X50CrMnNiNbN21-9 steel, but both these materials undergo more rapid corrosion in water vapor than in oxygen atmospheres. This phenomenon results from non-protective, heterogeneous scales, formed in water vapor, as compared to protective Cr_2O_3 scales, developing in oxygen atmosphere. It may be then concluded that the presence of water vapor in corrosive atmosphere plays a definitely negative role in corrosion processes.

Keywords Oxidation kinetics · Water vapor · Steel

Introduction

Most frequently utilized materials for the production of valves in diesel engines are X33CrNiMn23-8 and X50CrMn-NiNbN21-9 steels. These materials are working in very severe conditions because of relatively high temperatures (≈1,173 K) and highly aggressive combustion gases. In addition to oxygen, these atmospheres contain water vapor and carbon oxides, as well as nitrogen oxides and sulphur traces. The mechanism of corrosion of valve materials under such conditions is very complex and still not satisfactorily understood. Most dangerous components of these atmospheres constitute oxygen and water vapor [1–5]. Some information on the role of oxygen in corrosion process has already been obtained [6, 7] but virtually no data are available concerning water vapor participation in degradation of valve materials. Thus, the present work is an attempt to make the next step in explaining the corrosion mechanism of valve materials in water-vapor-containing environments, modeling in some way the combustion gases in diesel engines.

Materials and experimental procedure

Chemical composition of two steels under investigation is summarized in Table 1. As can be seen, the concentration of chromium in the first X33CrNiMn23-8 steel is higher than that in the second one. It will be shown later that the higher concentration of chromium in the first steel

Z. Jurasz · K. Adamaszek · R. Janik
BOSMAL Automotive Research and Development Center,
ul. Sarni Stok 93,
43-300 Bielsko-Biala, Poland

Z. Grzesik (✉) · S. Mrowec
Department of Solid State Chemistry,
Faculty of Materials Science and Ceramics,
AGH University of Science and Technology,
al. A. Mickiewicza 30,
30-059 Krakow, Poland
e-mail: grzesik@uci.agh.edu.pl

Table 1 The chemical composition of X33CrNiMn23-8 and X50CrMnNiNbN21-9 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.

constitutes the main reason why this material show better corrosion resistance.

The rate of corrosion has been studied as a function of temperature (973–1,273 K) and gas composition, being the mixture of nitrogen, oxygen, and water vapor. In all experiments these atmospheres, contained 50 vol.% of water vapor, but the concentration of oxygen was changed from 0.001 up to 50 vol.%, in order to explain the possible role of different oxygen concentrations in corrosion process. The kinetics of corrosion have been studied thermogravimetrically in microthermogravimetric apparatus, enabling continuous registration of mass changes of oxidized samples as a function of time with the accuracy of the order of 10^{-6} g. The scheme of this equipment is shown in Fig. 1. The most important detail, distinguishing this apparatus from all conventional microthermogravimetric equipments, utilized in studying the kinetics of high temperature corrosion in water vapor containing environments, consists in closed system of water vapor circulation, as depicted in Fig. 1. Due to continuous circulation of water vapor between water bath and reaction chamber, long-term oxidation experiments, lasting hundreds of hours, could continuously be followed without breaking the reaction in order to refill the water bath with water. In addition, volatile oxidation products, if any, due to continuous water vapor

circulation, dissolve in water and after terminating experiments they may be identified by chemical analysis. Detailed description of this equipment and the experimental procedure have been published elsewhere [8]. Phase composition of oxidation products (scales) have been studied by X-ray diffraction techniques and the morphology and chemical composition of scales by electron probe microanalysis and scanning electron microscopy (SEM) with energy disperse X-ray analyzer.

Results and discussion

Some results of oxidation rate measurements, obtained in water vapor are shown in Figs. 2 and 3, in linear plot, for two steels under investigation. These results are shown once again in Figs. 4 and 5 in parabolic plot. Considerable differences in corrosion behavior of two steels, presented in both, linear and parabolic plots, are clearly visible. The first important conclusion following from these results is that the X33CrNiMn23-8 steel, containing higher chromium concentration is much more corrosion resistant than the second one. This is even better visualized in Fig. 6. From these diagrams it follows also that the oxidation behavior of both steels in water-vapor-containing atmospheres and in

Fig. 1 The schematic representation of new thermogravimetric apparatus for studying the kinetics of corrosion in water vapor containing atmospheres
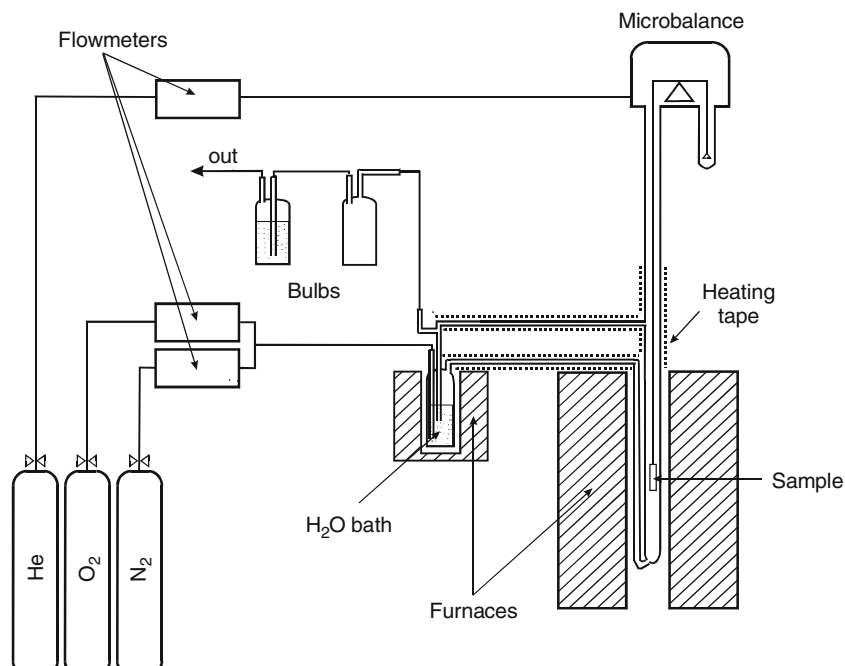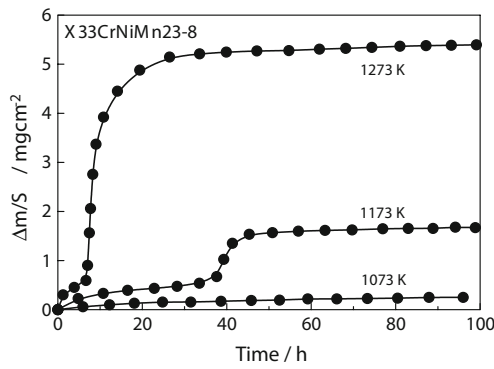
Fig. 2 The kinetics of corrosion of X33CrNiMn23-8 steel in air, containing 50 vol.% of water vapor, for several temperatures (*linear plot*)
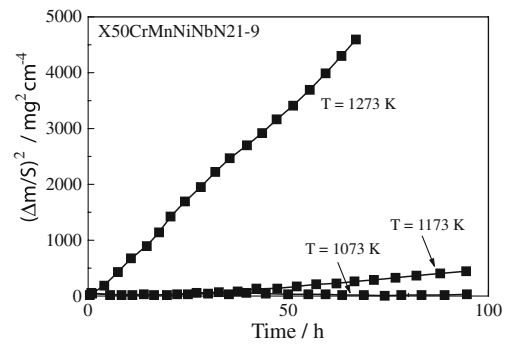

Fig. 5 The kinetics of corrosion of X50CrMnNiNbN21-9 steel in air, containing 50 vol.% of water vapor, for several temperatures (*parabolic plot*)
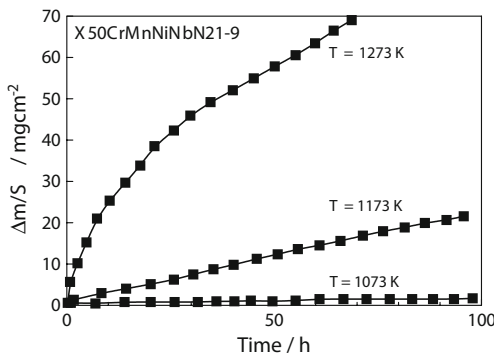

Fig. 3 The kinetics of corrosion of X50CrMnNiNbN21-9 steel in air, containing 50 vol.% of water vapor, for several temperatures (*linear plot*)
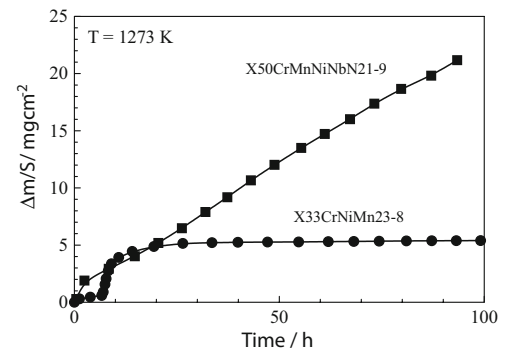

Fig. 6 Comparison of corrosion kinetics of two steels under investigation in water vapor containing atmosphere
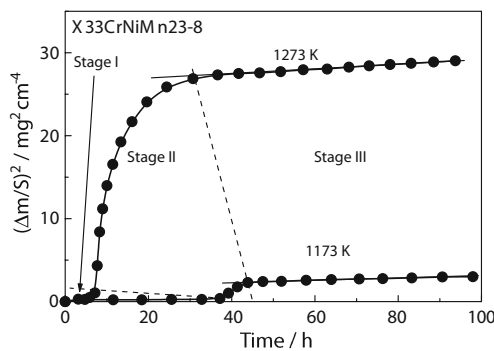

Fig. 4 The kinetics of corrosion of X33CrNiMn23-8 steel in air, containing 50 vol.% of water vapor, for several temperatures (*parabolic plot*)
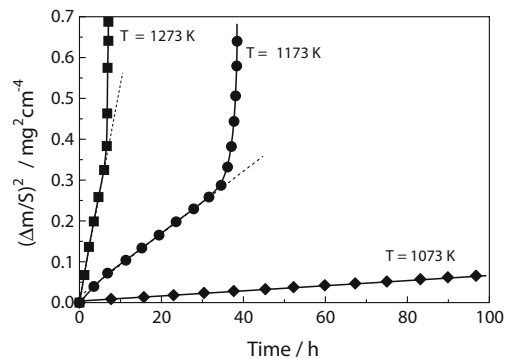

Fig. 7 Early stages of corrosion of X33CrNiMn23-8 steel in air, containing 50 vol.% of water vapor, for several temperatures (*parabolic plot*)
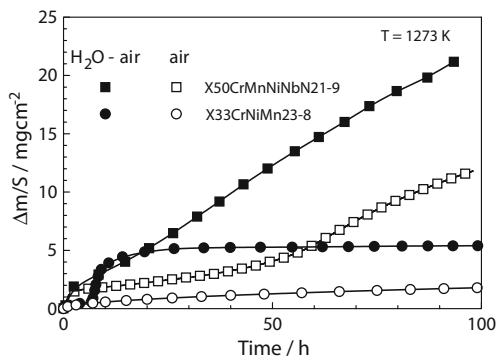
Fig. 8 Comparison of the oxidation behavior of both steels in air and in water vapor containing atmospheres

air is rather complex and can not be described by one kinetic law. In the case of the first steel (X33CrNiMn23-8), three stages of the reaction may be distinguished (Figs. 2 and 4). In the first stage, reaction proceeds rather slowly in agreement with parabolic rate law (Figs. 4 and 7). In the second stage dramatic increase of corrosion rate is observed, which gradually decreases and in third stage, lasting hundreds of hours, the process follows again the parabolic kinetics with rather low rate (Fig. 4). In the case of the second steel (X50CrMnNiNbN21-9), again complicated kinetic results have been observed, but no definite stages could be distinguished. At the highest temperature, the process follows approximately parabolic rate law (Figs. 3 and 5), but at lower temperatures the corrosion behavior may rather be described by linear rate law. It should be stressed, however, that the first steel (X33CrNiMn23-8) shows much better corrosion resistance not only in air, but also in water-vapor-containing atmospheres, than the second one (X50CrMnNiNbN21-9). This conclusion follows directly from Fig. 8. It should be mentioned that the rate of corrosion of both steels does not change virtually with gas composition, as shown for illustration in Fig. 9.

Different oxidation behavior of the two steels under discussion results mainly from various phase composition of scales. In oxygen atmosphere, the scale on X33CrNiMn23-
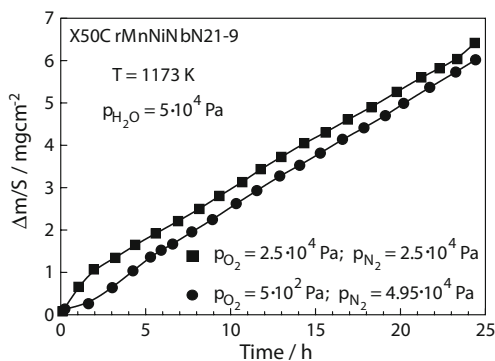

Fig. 9 The kinetics of corrosion of X33CrNiMn23-8 steel in air, containing 50 vol.% of water vapor, for several oxygen pressures (*linear plot*)
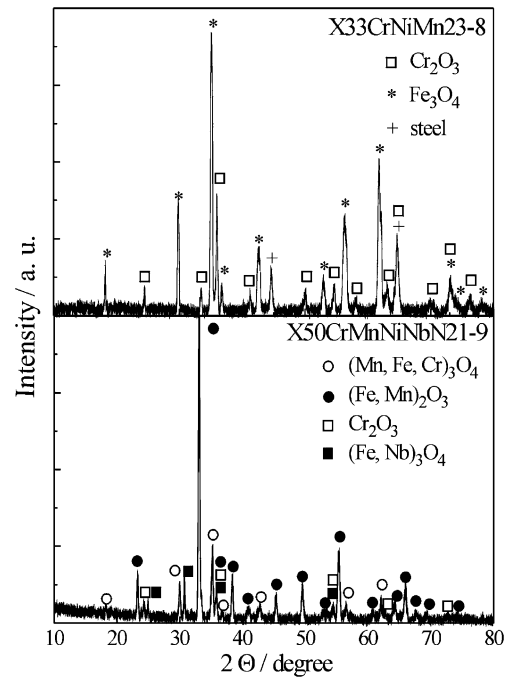

Fig. 10 X-ray diffraction patterns of investigated steels, after 100 h oxidation in air at 1173 K

8 steel was composed virtually only of protective Cr_2O_3 scale layer, while on the second one (X50CrMnNiNbN21-9) spinel phases were observed (Fig. 10). Highly protective Cr_2O_3 scale on X33CrNiMn23-8 steel results from higher chromium concentration in this material, as compared to the second X50CrMnNiNbN21-9 steel, enabling thus selective oxidation of chromium. The concentration of chromium in the second steel (X50CrMnNiNb21-9) was too low for its
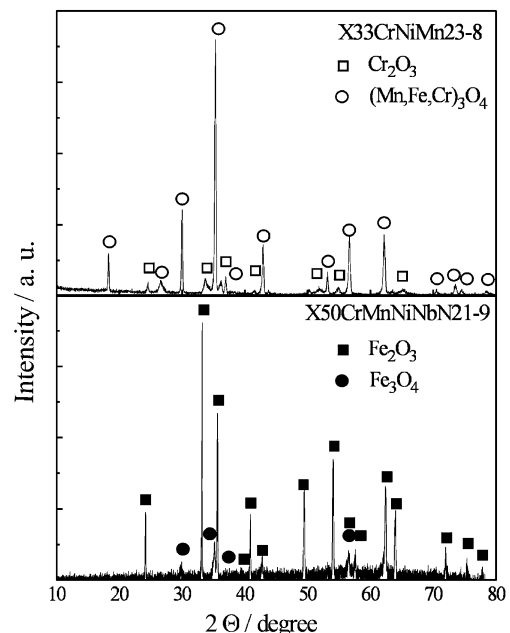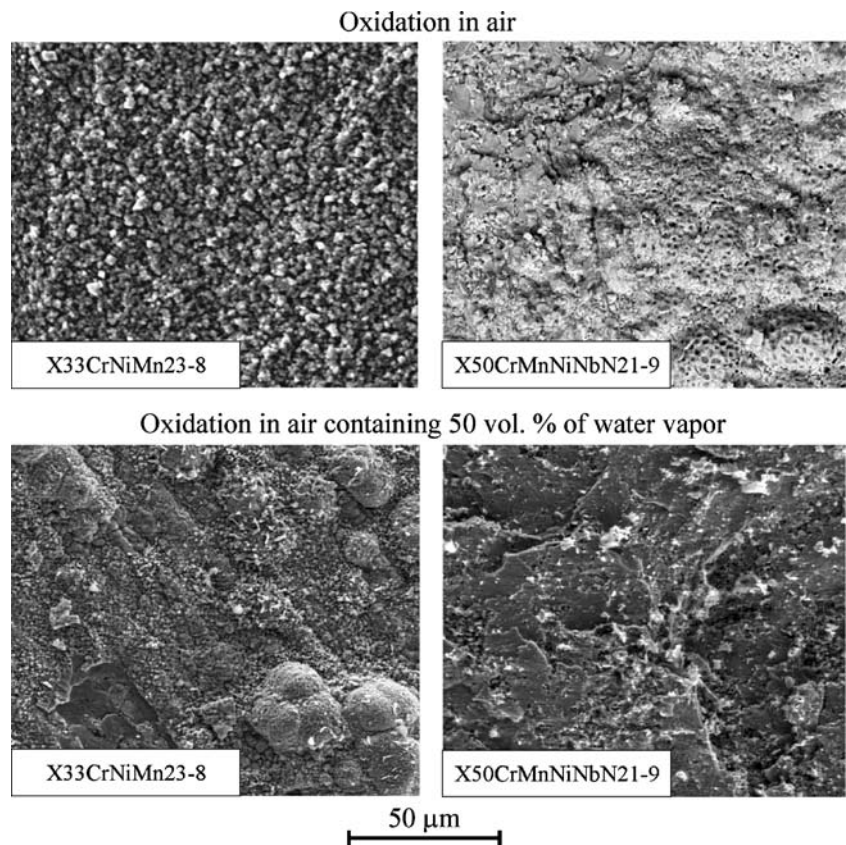

Fig. 11 X-ray diffraction patterns of investigated steels, after 100 h oxidation in water vapor containing atmosphere at 1173 K

Fig. 12 SEM images of the surface of scales formed on investigated steels, oxidized in air as well as in water vapor containing atmosphere at 1173 K

selective oxidation and consequently, the heterogeneous scale has been found, build mainly from spinel phases. On the other hand, in water-vapor-containing environments, the scale on X33CrNiMn23-8 steel was built of Cr_2O_3 and (Mn, Fe,Cr)$_3$O$_4$ spinel. The scale on X50CrMnNiNbN21-9 steel was also heterogeneous but contained only iron oxides, Fe_3O_4 and Fe_2O_3 (Fig. 11). In addition, the protective Cr_2O_3 scale formed in oxygen show better adherence to the substrate than that containing spinel phases (Figs. 12 and 13). This conclusion follows directly from the kinetics of mass changes of both steels, observed during quenching to room temperature, after a 100 h of oxidation at 1,273 K. As can be seen, in oxygen atmosphere virtually no mass changes are observed during cooling, indicating that virtually no scale spallation did occur. On the other hand, the scales formed in water-vapor-containing atmospheres break off from the surface of the steel, which is visualized by dramatic mass losses of the sample, observed during cooling (Fig. 13). These spallations result from mechanical stresses, generated by different thermal expansion coefficients of scale and steel materials [2]. Finally, it is important to note that due to the close system of water vapor circulation in microthermogravimetric apparatus utilized in this study, possible evaporation of scale components could have been proven. Actually, chemical analysis of this water have shown traces of chromium.

Conclusions

The results described in the present paper allow the following conclusions to be formulated.

The corrosion behavior of two valve steels in water-vapor-containing atmospheres is rather complex and can not be described by one kinetic rate law. The concentration of chromium in these materials plays the most important role with respect to corrosion resistance. It has been found, namely, that the X33CrNiMn23-8 steel containing higher
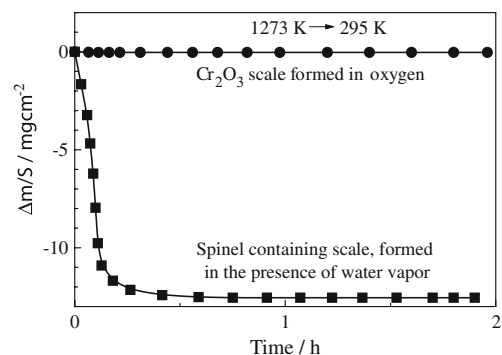

Fig. 13 The kinetics of mass changes of X33CrNiMn23-8 steel samples, observed during rapid cooling, after a 100 h of oxidation in pure oxygen or in water vapor containing atmosphere

chromium concentration than the X50CrMnNiNbN21-9 steel (Table 1) shows much better corrosion resistance in both, pure air, and water-vapor-containing atmospheres. However, the presence of water vapor accelerates considerably the corrosion rate of both steels (Fig. 8). This accelerating effect of water vapor results from more complicated phase and chemical compositions of scales, as compared to those formed in oxygen or air. In oxygen atmosphere the scale is composed virtually only of protective Cr_2O_3 layer, while in water-vapor-containing environments the scale is highly heterogeneous, containing mainly spinel phases and only small amounts of chromium oxide. In addition, the protective Cr_2O_3 scale formed in oxygen shows better adherence to the substrate, than that containing spinel phases. It may be then concluded that the presence of water vapor in corrosive atmospheres plays definitely negative role in corrosion processes.

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