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Behavior of Selected Martensitic Steels in Supercritical Water

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***Abstract*—In order to increase the effectiveness of fossil-fueled power plants the parameters of the cooling medium are increased nowadays up to 600 °C and 25 MPa (supercritical water). Currently even higher parameters (ultra supercritical water) are planned to be employed in the future. In this paper the unique supercritical water research infrastructure in Research Centre Řež is presented. The newly designed ultra supercritical water research loop is described in detail.**

The corrosion resistance of ferritic-martensitic steels P91, P92 and VM12-SHC was investigated under the conditions of supercritical water at 600 °C and 25 MPa. The high-temperature structural stability of these steels was evaluated and the oxides formed during the supercritical water exposure were analyzed and described. As expected the higher chromium containing steel VM12-SHC showed the best corrosion behavior among the examined steels.

***Keywords*—supercritical water, martensitic steels, ultra supercritical water, corrosion behaviour, structural stability**

I. Introduction

In order to increase effectiveness and to reduce the harmful gas emission of fossil-fueled power plants the working parameters of cooling medium, water, are gradually increased. Nowadays the power plants working at parameters of supercritical water (SCW) are employed. Water reaches its supercritical point at 374 °C and 22.1 MPa. The working parameters in newly constructed power plants go often up to 600 °C and 27 MPa. Supercritical water properties significantly differ from that of ordinary water. Due to its high thermal capacity and conductivity it is beneficial for the effectiveness of the power plants thermal cycle. On the other hand the high corrosiveness of supercritical water together with high temperature and pressure applied place high demands on constructional materials and therefore impose a great engineering challenge.

Among various steel types the ferritic-martensitic stainless steels (commercial labels P91, P92 and VM12-SHC) are used as steam pipes, superheater pipes and turbine parts (blades etc.). The P91 steel alloyed with 9 wt. % of Cr and V, Mo, Nb, N and C has exceptional creep properties. The P92 steel was invented in Japan in 1990's in order to even increase the creep resistance of P91 steel [1]. Because some Mo content in P91 steel is replaced by W, the P92 steel possesses higher strength. In addition the P92 contains borides which stabilize $Cr_{23}C_6$ carbides and limit their coarsening [2,3]. The intention to create more corrosion resistant material while preserving the creep properties of the 9% Cr steels (P91 and P92) lead to the development of the VM12-SHC steel containing up to 13 wt. % of Cr [4].

The aim of this paper was to confirm the corrosion behavior of the P91, P92 and VM12-SHC steels under the supercritical water conditions. This behavior was evaluated by electrochemical measurements and suitable surface analyses.

II. SCW Research in RC Řež

The Research Centre Řež possesses unique research infrastructure to carry out the experiments under the supercritical water conditions. Nowadays there is a supercritical water loop (see Fig. 1) operational with water parameters of 25 MPa and 600 °C. The loop consists of several circuits enabling the on-line water physics and chemistry surveillance, water filtering and purifying, sampling, dosing etc. To be able to carry on additional experiments the simple supercritical water autoclave is under operation as well. This device enables to perform experiments at parameters of 25 MPa and 600 °C. The water chemistry is monitored off-line. To be able to evaluate both the influence of supercritical water and irradiation on constructional materials the supercritical water loop for fuel qualification test will be constructed in RC Řež in 2015. The active channel is planned to be positioned in the grid of the research reactor LVR-15. Apart of the material testing the construction of this loop will allow evaluation of the suitability of the security systems used in nuclear power plants for application in SCW conditions.

A. *Ultra Supercritical Water Loop*

In order to even increase the efficiency of Clausius-Rankine cycle of fossil-fueled power plants, which would lead to the higher savings of fuel and less production of the harmful emissions, the ultra-supercritical parameters of water are considered worldwide [5–8]. Such parameters (25 MPa and higher and the temperature around 700 °C) are a huge challenge for material scientist all over the world as they impose great requirements on the constructional material

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properties. Nowadays the USCWL is being designed in Research Centre Řež in order to provide sufficient experimental support to the USCW power plants research effort.

Figure 1. Supercritical water loop in Research Centre Řež. Active channel (vertical pipe in the very left is still in out-of-pile operation)

III. Experimental

Three steels were studied in this work: the 1.4903 hereafter denoted as P91, the 1.4901 hereafter denoted as P92 and 1.4915 hereafter denoted as VM12-SHC. The chemical composition (see Table 1.) of these steels was verified by the optical emission spectrometry (ARCMET 8000 SL Mobil Lab).

TABLE I. CHEMICAL COMPOSITION OF EXAMINED STEELS

	C	Mo	Cr	Ni	Nb	W	V	Co
P91	0.11	0.77	8.6	0.2	0.1	-	0.25	-
P92	0.12	0.24	8.7	0.33	0.1	1.7	0.24	-
VM12-SHC	0.13	0.17	11.6	0.25	0.06	1.4	0.27	1.25

The microstructure of the steels was observed by light microscope Nikon Epiphot 300. Prior to the observation the samples were ground and polished up to OPS solution by Struers. Finally the samples were electrolytically etched by 10 % solution of oxalic acid. The microhardness of the steels was measured by Anton Paar MHT 4 device before and after the supercritical water exposure. The microhardness loading was 100 g for 10 s.

The steel samples were exposed in supercritical water environment at 600 °C and 25 MPa for 1000 hours. Prior to the exposure the water was demineralized and deaerated. The water conductivity was below 0.1 μS.cm^{-1} and pH was adjusted to 9.2 by borate buffer. Such exposed samples were then cut and the cross-sections of the formed oxide layers were observed and analyzed by scanning electron microscopy (Tescan Vega TS 5130 XM). The oxides were also analyzed by photoelectron spectroscopy (XPS, ESCA Probe P) with Al anode and monochromator. Their chemical composition was analyzed by Raman spectroscopy (Labram HR) and the results were confirmed by X-Ray diffraction (XRD, PANanalytical X'PertPRO).

IV. Results and discussion

A. *Structural Stability*

As-received samples of all steels possessed tempered martensitic structure (not shown). During exposure in supercritical water this structure has not undergone any significant changes as can be seen from the microhardness development (see Table 2.) as well. This structural stability of the examined steels was verified also by X-Ray diffraction analyses (not shown) before and after the exposure in SCW.

TABLE II. MICROHARDNESS DEVELOPMENT OF EXAMINED STEELS DURING EXPOSURE IN SCW

	As-received	Exposed at SCW
P91	224 ± 3	221± 5
P92	250± 5	246± 6
VM12-SHC	260± 5	255± 6

B. *Corrosion Behavior*

In order to evaluate the corrosion kinetics the weight gain of the exposed samples was observed. To do so the samples

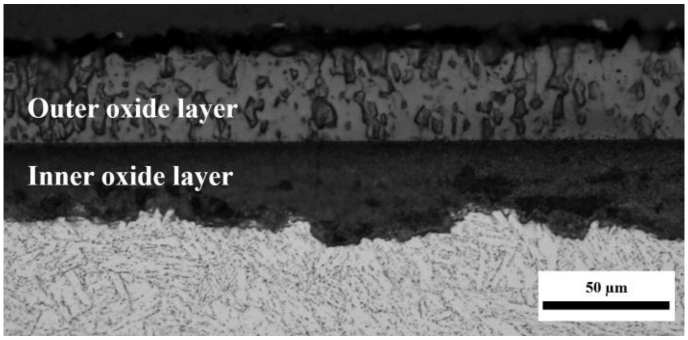

Figure 2. Oxide layer formed on P91 steel during exposure at 600 °C and 25 MPa for 1000 h.

were weighed before and after the exposure. The weight gain expressing the mass of oxides formed on the steels surface is presented in Table 3. Apparently the highest weight gain was observed for the P92 steel and the lowest for the VM12-SHC steel. This shows the important role of chromium in the high-temperature corrosion as the VM12-SHC steel (12% Cr) shows two or three time slower oxidation rate then its two 9% Cr counterparts. As mentioned previously in the paper the P92 was developed from the P91 steel in order to enhance its mechanical properties. Some of the elements beneficial for the corrosion behavior (Mo, Nb) were replaced by those beneficial for mechanical properties (W, B). This fact lead to the lower corrosion resistance and higher oxidation rate of the P92 steel in comparison with its precursor, P91 steel.

TABLE III. WEIGHT GAIN OF EXAMINED SAMPLES DURING EXPOSURE IN SCW

Steel	P91	P92	VM12-SHC
Weight gain [mg.cm^{-2}]	6.87	11.68	3.26

The oxide layers formed on the samples during the exposure in supercritical water were observed by SEM. Their cross-sections can be seen in Figs 2-4. In the case of all three steels the oxide layers were formed by two sublayers. The inner layer is so-called topotactic layer, highly adhesive layer with structure coherent with the bulk material. The outer layer is so-called epitactic layer without any coherence with the bulk metal, lower adhesivity and often separated by pores and cracks from the inner layer. The formation of thick epitactic layer is often detrimental in relation to the power plants service as it can exfoliate easily due to its lower adhesivity. In accordance with the weight gain results, the thickest oxide layer was formed on the surface of P92 steel meanwhile the thinnest on the surface of the VM12-SHC steel.

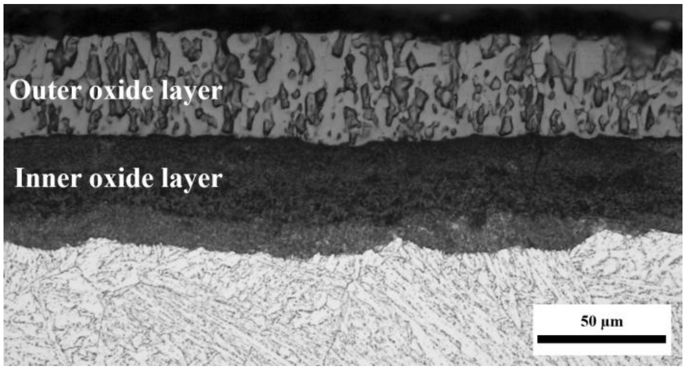

Figure 3. Oxide layer formed on P92 steel during exposure at 600 °C and 25 MPa for 1000 h.

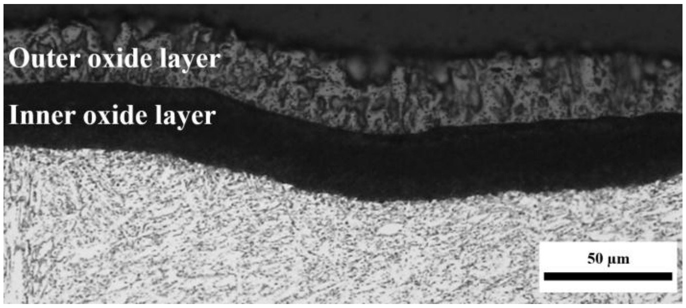

Figure 4. Oxide layer formed on VM12-SHC steel during exposure at 600 °C and 25 MPa for 1000 h.

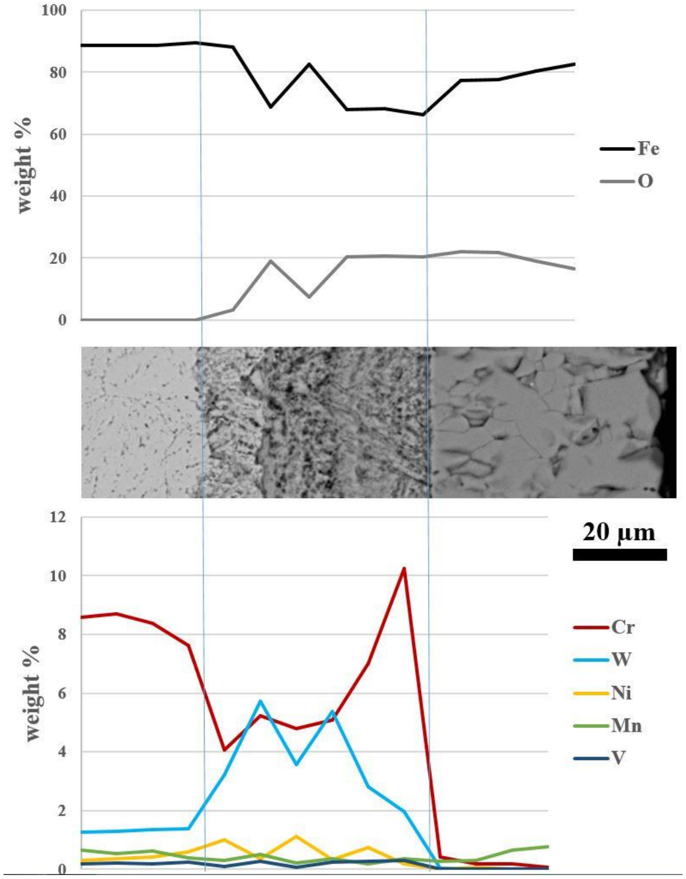

Figure 5. Distribution of elements in a cross-section of the oxide layer formed on P92 steel during exposure at 600 °C and 25 MPa for 1000 h

The distribution of elements in the cross-section of the oxide layers was analyzed by SEM equipped with WDS detector. Since P91 and P92 steels showed similar chemical behavior, only the results concerning the P92 steel are showed (see Fig. 5). These results are in agreement with the works published on the topic of high-temperature oxidation of stainless steels. The inner oxide is usually formed by spinel with some amount of hematite ($FeCr_2O_4.2Fe_3O_4$) which explains the higher content of chromium in the inner oxide layer. Chromium is enriched in the inner oxide layer near the inner/outer layer interface which is given by its very high reactivity with oxygen at this (600 °C) temperature. The clearly observable higher content of tungsten is probably caused by the depletion of the inner oxide by chromium and iron which react with oxygen and therefore diffuse towards the inner/outer layer interface or directly to the outer layer. Apparently the outer layer is formed only by iron and oxygen in order to form the less protective magnetite (Fe_3O_4) layer.

The cross-sectional elements distribution in oxide formed on VM12-SHC steel is showed in Fig. 6. The situation is similar to the previous one. The inner layer is formed mainly by iron, oxygen and chromium which points out to the presence of mixture of $FeCr_2O_4$ and Fe_3O_4 oxides. Again, the inner layer is enriched by tungsten as it is depleted by chromium and iron since these two elements diffuse to react with oxygen in outer oxide layer or at the oxides interface (see higher chromium concentration at the interfaces). The cross-sectional analyses of oxide scales formed on all P91, P92 and VM12-SHC steels were in one hand confirmed by the results of XPS, XRD and Raman analyses (not shown).

It has been published elsewhere that the oxide layer formed during the exposure in supercritical water contains two sublayers where iron is enriched in the outer sublayer and other alloying elements such as Cr, W or Mo are found enriched preferentially in the inner sublayer [9]. The different distribution of alloying elements in the oxide layers is above all attributed to their different affinities to oxygen and different outward diffusivities in the oxide scale itself. During the oxidation firstly Fe and Cr are oxidized due to their high affinity to oxygen. As a result a mixed chromium iron oxide, spinel, is formed which hinders further inward diffusion of oxygen. Due to the low activity of oxygen the iron oxide becomes less stable and iron starts to diffuse onto the surface forming and outer Fe-rich oxide layer. The inner oxide layer acts as a barrier against the diffusion of metals and oxygen, therefore the alloying elements become enriched there due to their relative immobility in this inner oxide layer [2].

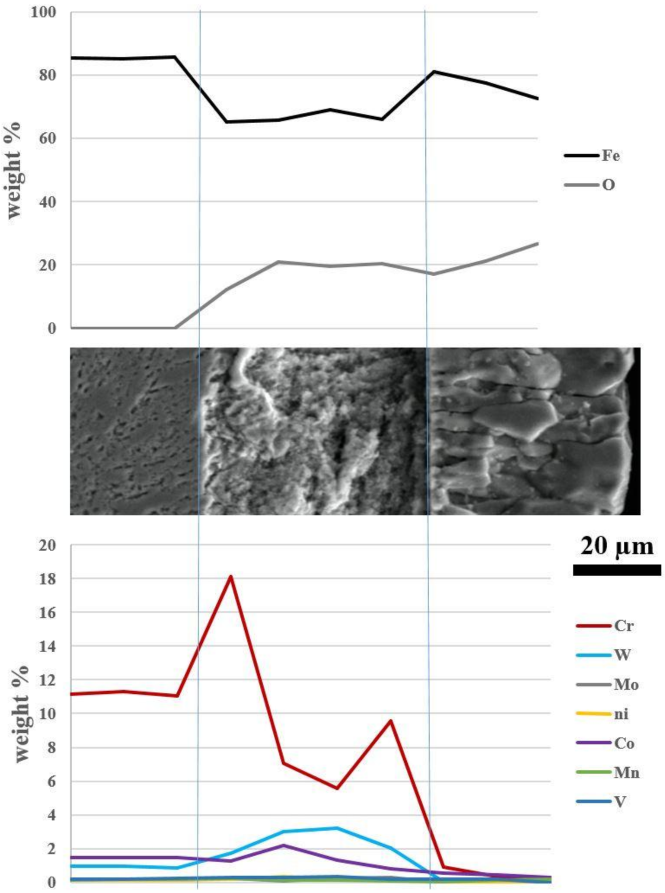

Figure 6. Distribution of elements in a cross-section of the oxide layer formed on VM12-SHC steel during exposure at 600 °C and 25 MPa for 1000 h

The observed behavior of examined steels verifies the corrosion resistance superiority of VM12-SHC since it contains significantly higher content of chromium than the P91 and P92 steels. Chromium is generally beneficial for corrosion resistance either at room or elevated temperature [10]. In addition the difference in corrosion behavior of two 9% Cr steels was registered. The fact that the P91 steel is more corrosion resistant than the P92 steel could be explained above all by the lower content of molybdenum in the latter steel. Molybdenum significantly decreases the oxidation rate of iron in the temperature range 500 – 1000 °C. It also promotes the formation of protective duplex spinel-magnetite scale [11].

The overall behavior of examined steels in supercritical water observed elsewhere implies that the mechanism of corrosion is similar to that in gaseous environment where only solid growth/oxidation takes place without any metallic dissolution. The kinetics show in other papers generally parabolic trend, therefore the dominant mechanism in supercritical mechanism is oxidation over standard electrochemical corrosion [2,12].

V. Conclusion

The unique research infrastructure focused on supercritical water research in Research Centre Řež was presented. Together the designed ultra supercritical research loop was described.

The structural stability and corrosion resistance of selected martensitic steels (P91, P92 and VM12-SHC) in the environment of supercritical water at parameters of 600 °C and 25 MPa were evaluated in this study. Structural stability was evaluated by comparing microstructures and microhardness of the examined steels before and after exposure to SCW. To understand the corrosion behavior the structure and composition of oxide scales were observed and qualitative analyses were performed. On the surface of all examined steels the outer and inner oxide scales were formed. The outer oxide scales were composed preferentially by magnetite and the inner oxide scales were formed by duplex spinel-magnetite oxide.

It was confirmed the corrosion resistance given by the content of chromium and other important role playing alloying element such as Mo and Nb. The highest corrosion resistance showed the 12% Cr containing VM12-SHC steel meanwhile the worst corrosion resistance was evaluated for P92 steel. As published in other papers, the mechanism of oxide forming complies with the theory of oxidation taking place in supercritical water preferentially over the standard electrochemical corrosion mechanism.

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