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Microstructural Evaluation of HR6W and T92 after Supercritical CO2 Exposure

Lucia Rozumová
Centrum vyzkumu Rez
Hlavní 130
250 68, Husinec-Rez, Czech Republic
lucia.rozumova@cvrez.cz

Jan Berka[1, 2], Ladislav Velebil[1], Tomáš Melichar[1]
[1]Centrum vyzkumu Rez
Hlavní 130
250 68, Husinec-Rez, Czech Republic

[2]University of Chemistry and Technology Prague
Technicka 1905
166 28 Prague 6, Czech Republic
jan.berka@cvrez.cz, ladislav.velebil@cvrez.cz, tomas.melichar@cvrez.cz

ABSTRACT

The supercritical carbon dioxide Brayton cycle is being considered as an innovative technology with potential for replacement of conventional steam cycles. Increased efficiency and operational flexibility at specific operational parameters are expected that can be beneficial for various power sources including nuclear, fossil or renewable. The optimization of the design of supercritical CO2 (sCO2) Brayton cycle and of its main components is essential to achieve requested parameters of the thermal cycle. The optimization requires not only the cycle layout and the components design studies but also selection of the materials. The materials research is critical in the field of the sCO2 technology development due to the fact that the main benefits of the sCO2 cycles are gained at extreme operational conditions such as temperatures above 550°C and pressures up to 25 MPa.

This work addresses the testing of the resistance HR6W and T92 materials before and after exposure. The corrosion behaviour of the materials selected for the high temperature components in the sCO2 environment was investigated. The corrosion behaviour was evaluated by observation of the surface and cross-section of the samples after exposure in sCO2 by microscopy methods - SEM and LOM. The results summarise the experimental campaign characterized by 1000 hours of exposure of the selected steels in the sCO2 at 550°C and 25 MPa. The materials compatibility testing was conducted for materials that were identified as potential candidates for high temperature components of the sCO2 cycles such as boiler, heat exchangers or pipes. Testing was completed for samples in the unstressed conditions. The samples exposed to sCO2 showed the oxidation of the surface, the extent of which varied considerably between the materials tested. Examination of cross sections of the samples showed perceptible differences of the formation of oxide layers on the surface caused by the sCO2 exposure.

INTRODUCTION

The thermal cycles with supercritical CO2 (sCO2) as a working fluid are considered as the innovative technology for thermal to power energy conversion. The sCO2 power cycles are characterized by increased electric power conversion (the efficiency may exceed 50 %) and significantly reduced size of some components (e.g. turbines) [1,2]. This may result in an improved return on investment. The sCO2 power cycles can be applied in both nuclear and non-nuclear power industry. To ensure high thermodynamic efficiency of a cycle, high operational parameters must be achieved (pressures up to 30 MPa, temperatures up to 600°C or even higher). For this reason, proper selection of structural materials is essential to ensure long-term safe and reliable operation. Dozens of cycles with various components layout and corresponding suitable operational parameters were proposed. The list of possible utilizations and basic parameters is listed in cit. [3]. The investigation and utilization of these power cycles is being extensively studied worldwide and Czech research organisations and industrial companies are involved in the R&D activities. For this research, the unique infrastructure originated. Among others, the sCO2 experimental loop was constructed at Centrum vyzkumu Rez s.r.o. (CVR) organisation. The research activities concerning sCO2 are aimed (among others) to sCO2 coolant chemistry, purification and purity control and candidate structural materials resistivity and degradation in sCO2 medium. The samples of more than 10 types of metallic alloys were exposed in the sCO2 experimental loop during the first long-term experimental campaign focused on the corrosion tests in this device (1000 hours of operation at the relevant parameters). T92 is a ferritic-martensitic steel with strong corrosion resistance, steam oxidation resistance, and good creep rupture strength, used typically for applications up to approx. 600 °C [4]. HR6W is nickel-base alloy (23Cr-45Ni-6IN-Nb-Ti-B) with a high creep resistance alloy designed for components operating at 700 – 800 °C [5]. Due to these properties both alloys are suitable candidate alloys for sCO2 cycle components, especially to the ones that are exposed to the extreme conditions in the cycles. In this paper, the results of the materials degradation in the sCO2 relevant environment will be described along with the experimental setup and conditions. The weight gain, surface and microstructural observation were carried out using Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDS) methods.

1 EXPERIMENTAL CONDITIONS

In this section, the experimental conditions including the materials description, experimental setup and operational parameters is described. Moreover, the methodology for the sample's assessment is also mentioned.

1.1 Materials and pretreatment

The materials examined in this study are HR6W and T92. Their chemical composition is shown in Table 1. The test samples with the dimensions of 40 mm × 10 mm × 2 mm were made of tubes delivered by RINA (project partner of the sCO2-FLEX project). Prior to the test, the samples were ground up to 600 grit SiC paper, which is more representative of industrial surfaces, rather than fine polishing, then rinsed with deionized water, alcohol, and dried. The weight of each sample was measured before and after the corrosion test using a Radwag AS

82/220.R2 Plus Analytical Balance. All the samples were weighed on an electronic balance with an accuracy of 0.00001 g.

Table 1: Chemical composition of steels (wt.%)

	C	Mn	P	Cr	Mo	V	Al	S	Si	Nb	W	N	Ni	B	Ti	Fe
T92	0.07 - 0.13	0.3-0.6	0.01 max	8.5-9.5	0.3-0.6	0.15-0.25	0.04 max	0.01 max	0.5 max	0.04-0.09	1.5-2.0	0.03-0.07	0.4 max	0.001-0.006	-	Bal.
HR6W	0.1	1.5	0.03	21.5-24.5	-	-	-	0.015	1.0	0.1-0.35	6.0-8.0	0.02 max	Bal.	-	0.05-0.20	20-30

1.2 Experimental loop sCO2 and corrosion experiment

The sCO2 loop has been built to enable the study of the key aspects of the cycle (heat transfer, erosion, corrosion etc.) with wide range of operational parameters. The main nominal operational parameters are in Table 2. Schematic diagram of sCO2 loop is shown in Fig. 1. The whole sCO2 loop was designed not only to meet the highest standards, but also with focus on high modular conception. Such a design allows easy way to fit the loop to wide variety of temperature, pressures and still meet whatever needs of the experimental conditions they may have. The main configuration is shown at simplified diagram Fig.1. The samples holder must be placed inside the test section, which is located in the high-pressure part and the highest temperatures in the loop are reached in this section. The test section has 2 m length and 58 mm internal diameter. The section is made of Inconel 625 alloy. Both ends are flanged for easy assembly and disassembly. Holder itself consist of two main body parts; the corrosion and erosion part, where the flow is accelerated by three narrow channels up to 100 $m.s^{-1}$ at given parameters 20 MPa, 550 °C and mass flow 0,1 $kg.m^{-1}$ and possibly even to higher stats.

The corrosion and erosion testing of the materials preselected for the individual components of the cycle (turbine and heat exchangers) was carried out. The corrosion experiment was carried out in the sCO2 loop. The test was performed for exposure duration of 1000 h with the pre-selected samples. The samples for such a testing had to be placed in the predesigned test section. The samples were fixed in the test section using a dedicated samples holder. The experimental conditions are listed in Table 3.

Table 2: The main operational parameters of the sCO2 loop

Max. operating temperature:	550 °C
Max pressure at high pressure site:	30 MPa
Max. pressure at low pressure site:	15 MPa
Max. flow rate:	0.35 kg/s
Total heating power:	110 kW

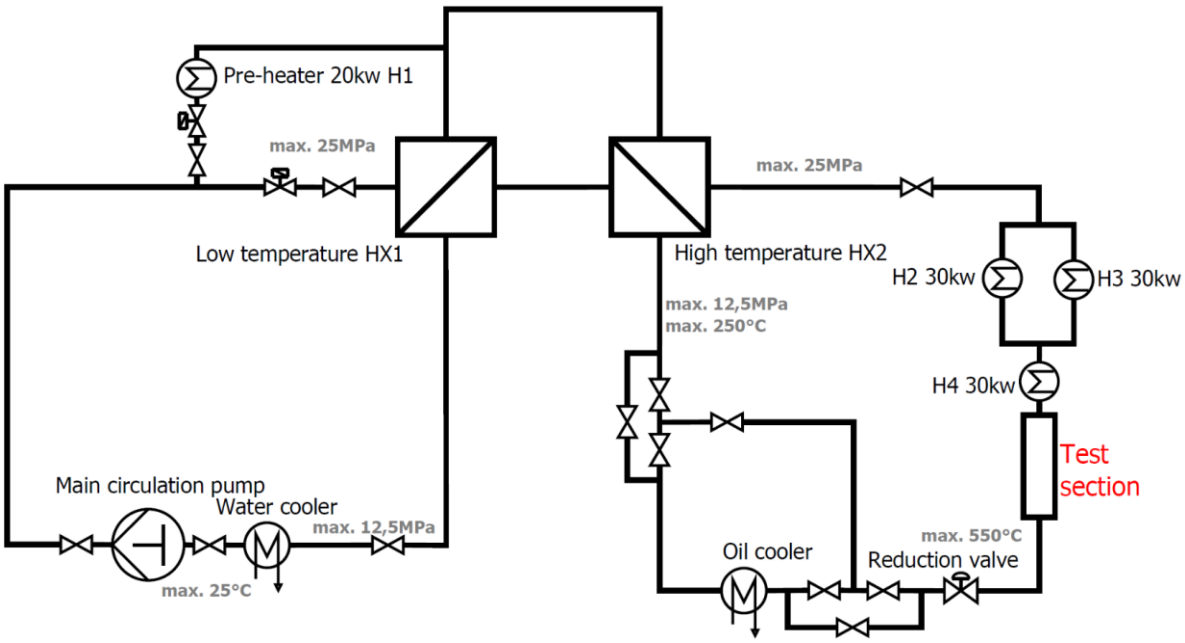


Figure 1: Scheme of the supercritical CO2 loop

Table 3: The experimental conditions of the exposure

Operating temperature:	550 °C
Pressure at high pressure site:	20 MPa
Mass-flow rate:	0.1 $kg.s^{-1}$
Flow velocity:	<10 $m.s^{-1}$
CO2 purity:	99.995 %

1.3 Morphology and composition characterization

Structural analysis of the surface corrosion product layer was performed using by Light Optical Microscope (LOM) and by Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS). An Olympus BX51P was used for characterization of the surface observation. A LYRA3 Tescan SEM integrated with EDS system was used for characterizing the morphology and compositions of the surface oxide corrosion product layer in both plan and cross-sectional views of the samples.

2 RESULTS

2.1 Weight gain analysis and oxide thickness analysis

Table 4 shows the weight gain of the two materials after the exposure. The T92 samples exhibited the high weight gain (hence the least corrosion resistance), while HR6W material exhibited small weight gain (hence better corrosion resistance). Three parallel samples from each material were exposed and the weight gains were nearly identical for all three parallel samples of each materials.

Table 4: The weight gain of the tested samples

Sample	Mass before EXP [g]	Mass after EXP [g]	Mass change [%]
T92_1	5.52948	5.56850	0.70600
T92_2	5.40140	5.44133	0.73900
T92_3	5.37648	5.41630	0.74000
HR6W_1	5.80885	5.80941	0.00964
HR6W_2	6.13758	6.13818	0.00978
HR6W_3	6.18344	6.18397	0.00857

Fig. 2 and 3 shows the surface of the tested materials before and after the exposure. The weight gain analysis indicated the oxidation of the T92 sample hence the formation of oxide layer on the surface as can we seen in Fig. 2. The weight gain of the HR6W sample was significantly lower and Fig. 3 shows the almost the same surface before and after the exposure which indicates very thin oxidation on the surface.

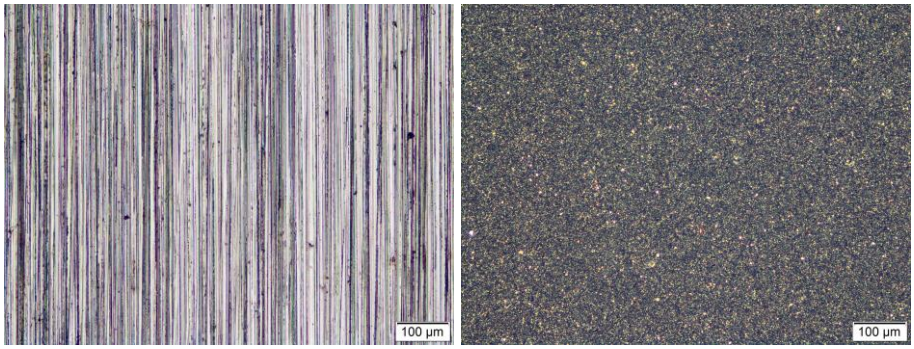


Figure 2: LOM photographs of the T92 sample before experiment (left) and after (right) the exposure in sCO2 loop

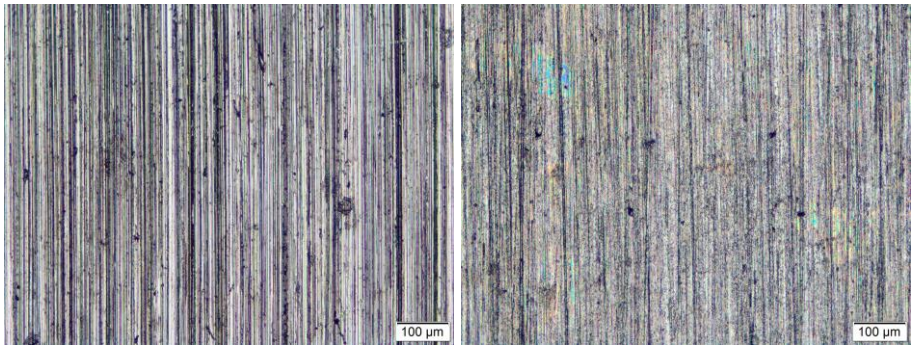
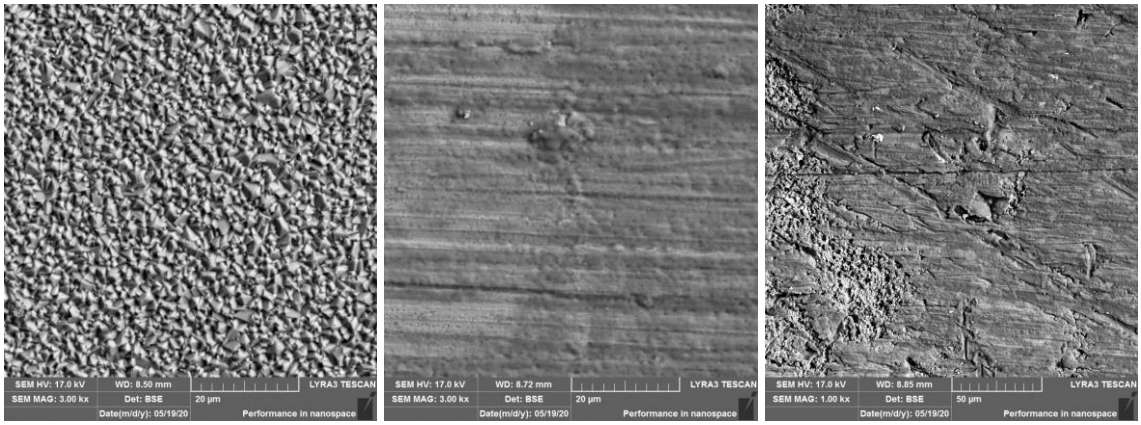


Figure 3: LOM photographs of the HR6W sample before experiment (left) and after (right) the exposure in sCO2 loop

2.2 Microstructural analysis of the oxide layers

Fig. 4 shows surface morphology of the tested materials. The SEM analysis confirmed the obtained weight gain data and the LOM observation. T92 has the homogeneous and thick oxide layer on the surface, without defects and damages (Fig. 4 a). On the sample surface of T92, the oxide layer consisting of Fe oxide which was formed all over the surface. HR6W material have very thin oxide layer on the surface, which is not homogeneous and uniform over the entire surface. Lighter and darker spots show different oxide thicknesses (Fig. 4 b). Some

places are without oxide with another structure and these places could indicate the local corrosion attack, pits, holes or the lack of the time for the growth of the oxide layer on the surface (Fig. 4 c).



a) b) c)

Figure 4: SEM surface photographs of the T92 (a) and HR6W (b, c) samples after the exposure in sCO2 loop

The cross-section of T92 steel is shown in Fig. 5. The EDS analysis indicated that the corrosion layer mainly consisted of Fe, O and the typical alloy element Cr (Fig. 5), and the contents of Fe were much lower than those in the steel matrix, as listed in the EDS linescan (Fig. 5). The oxide layer on the T92 steel surface is covered with three types of layers. The oxide layer is about 25 µm thick and is composed by two Fe oxides: outer layer – Fe-O at the surface, probably magnetite (about 15 µm) and inner layer on base of Fe-Cr oxide (about 10 µm) and an internal oxidation zone (IOZ) consists from Fe-Cr-O with different composition of elements than inner layer. IOZ is layer enriched of Fe and Cr compared with steel matrix.

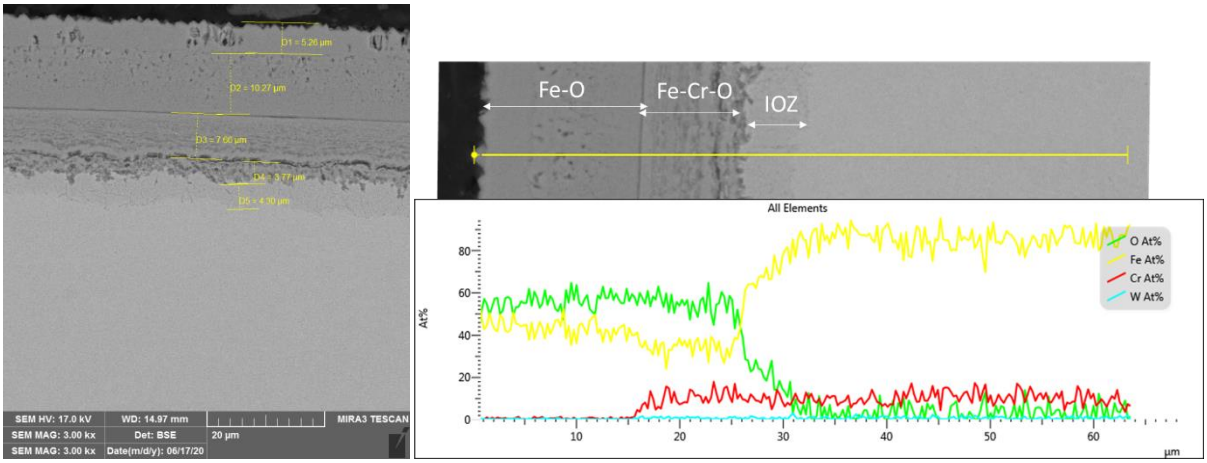


Figure 5: SEM cross-section and EDS linescan of the T92 sample after the exposure

Fig. 6 shows the cross-section of HR6W after the 1000 h exposure to sCO2, imaged by SEM. The SEM observation confirmed very thin outer Cr-rich layer. The oxide layer thickness reaches up to ~ 0.5 µm (the widest place). There does not appear to be a good bonding between this oxide layer and the steel substrate given its propensity to spall from the alloy surface. Inner layer was consisted of mixed oxides, Cr diffuse to the surface where Cr-O layer is created. Few areas on the surface were corroded and it seems to be pitting corrosion, probably the growth and dissolution of the mixed layer and localized corrosion areas or pits (Fig. 7).

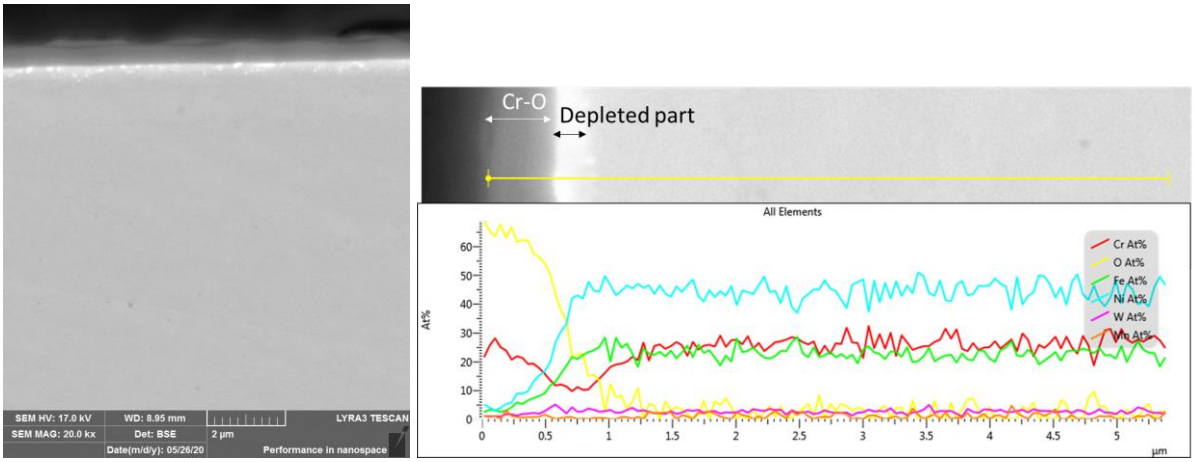


Figure 6: SEM cross-section of the HR6W and EDS linescan of the oxide layer

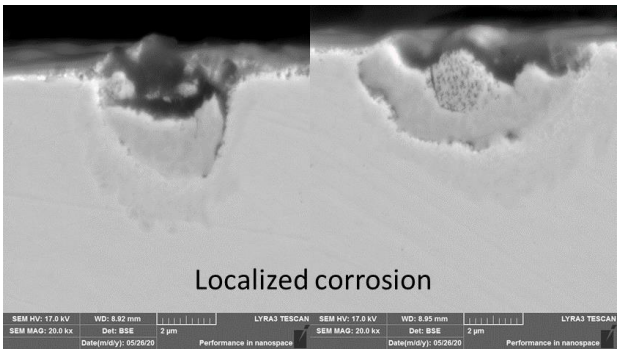


Figure 7: SEM cross-section of the HR6W detail of pitting corrosion

3 DISCUSSION AND CONCLUSIONS

T92 sample has greater weight gain compared to other steels selected for sCO2 power cycle components. This sample has thick and compact duplex layer on the surface, which could with time increase the thickness of outer layer with subsequent spalling. This can be reason of circuit pollution with the corrosion layers.

The material HR6W reported the very different behaviour in comparison to T92, but the formation of oxide layer was very slow compared with T92. The thin oxide layer was formed on the surface, which could be passivation effect, and also depleted part under the outer layer was created. The weight gain was very small. Localized corrosion attack was observed on this sample.

Based on the tests carried out in dynamic condition of loop for 1000 h, better corrosion resistance for boiler component in the supercritical CO2 was found for HR6W material.

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REFERENCES

[1] K. Brun, P. Friedman, R. Dennis, “Fundamentals and Applications of Supercritical Carbon Dioxide (sCO_2) Bases Power Cycles, Woodhead Publishing, Duxford, 2017.

[2] M. Li, H. Zhu, J. Guo, K. Wang, W. Tao, *Applied Thermal Engineering* 126, 2017, pp. 255-261

[3] K. Brun, P. Friedman a R. Dennis, “Fundamentals and Applications of Supercritical Carbon Dioxide (sCO_2) Based Power Cycles”, 2017.

[4] Y- Lia, J. Du, L. Li, K. Gao, X. Pang, A. A. Volinsky, Mechanical properties and phases evolution in T91 steel duringlong-term high-temperature exposure, Engineering Failure Analysis (111), 2020, pp. 104451

[5] G. Golański, A. Merda, A. Zieliński, P. Urbańczyk, J. Słania, M. Kierat, Microstructure and mechanical properties of HR6W alloy dedicated for manufacturing of pressure elements in supercritical and ultrasupercritical power units, E3S Web of Conferences 82, 01005, ICBT Poland 2018, 2019