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Corrosion Behavior of Materials in SCW Environment

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ABSTRACT

The use of supercritical water (SCW) in energy technologies is limited by the lifetime of the structural materials. Therefore, it is crucial to obtain specific data on the behaviour of suitable materials in this corrosively aggressive environment. In this work, the exposure of several selected materials (T24, 316L, and 800H) under supercritical conditions (450°C, 22.1MPa) in an experimental loop for 500h is described. After the experiment, the surface state and composition were evaluated by XPS (X-ray photoelectron spectroscopy) and SEM (scanning electron microscopy)/EDS (energy dispersive spectroscopy) methods.

1 INTRODUCTION

A current problem in the development of the contemporary energy industry is increasing the efficiency of thermal power plants. This can be achieved by increasing the steam parameters to supercritical values, which is a temperature above 374°C and a pressure higher than 22.1MPa. Above these values, water changes its properties significantly, and its corrosion behaviour is very problematic for the selection of suitable construction materials. In addition to increasing the efficiency of current power plants, supercritical water is a potential coolant for IV generation nuclear reactors - SCWR (Supercritical Water Cooled Reactor) and an economical and safe coolant of the future [1].

One of the available candidate materials for supercritical water environments is Ni-Fe-Cr alloy 800H, which has good mechanical properties at high temperatures and good resistance to oxidation and carburization up to temperatures of approximately 1000°C [2]. This paper presents the behaviour of 800H in comparison with low-chromium steels T24 and 316L. Ferritic steel T24 is a low-alloy, refractory steel T24 developed for membrane walls of boilers with supercritical parameters. Cr-Ni-Mo austenitic stainless steel 316L is characterized by increased resistance to intergranular corrosion at high temperatures, high strength, and corrosion resistance. The composition of the tested materials is shown in Table 1.

Table 1: Composition of tested materials in wt.% [3-5]

Material	Fe	Ni	Cr	Ti	Al	Mo	Mn	V	Si	Other
800H	39.5-51.0	30.0-35.0	19.0-23.0	0.15-0.60	0.15-0.60	-	0.0-1.5	-	0-1	C,Cu,S

316L	62-67	10-14	16-18	-	-	2-3	0-2	-	0-1	P,S,C
T24	95-96	-	2.2-2.6	0.05-0.1	0.00-0.02	0.9-1.1	0.3-0.7	0.2-0.3	0.15-0.45	C,B,P,N,S

2 DESCRIPTION OF EXPERIMENT

The aim of this experiment was to compare the corrosion behaviour of the materials from Table 1 under SCW conditions and to evaluate the surface condition of the tested samples. This work is part of a larger project connecting several research institutes in the Czech Republic, studying materials for high temperature applications. In addition to the part focused on materials for SCW environments, the project also deals with materials for gaseous energy environments, especially N_2, CO_2, and flue gas environments.

2.1 Experimental setup

The material samples were polished (sandpaper grit 2500) and degreased in acetone in an ultrasonic cleaner, and placed in a metal holder in a high-temperature autoclave (Fig. 1). The experimental apparatus includes a storage tank with demineralized water, which was continuously degassed by argon. The experiment was carried out at a temperature of 450°C and a pressure of 22.1MPa for 500h.

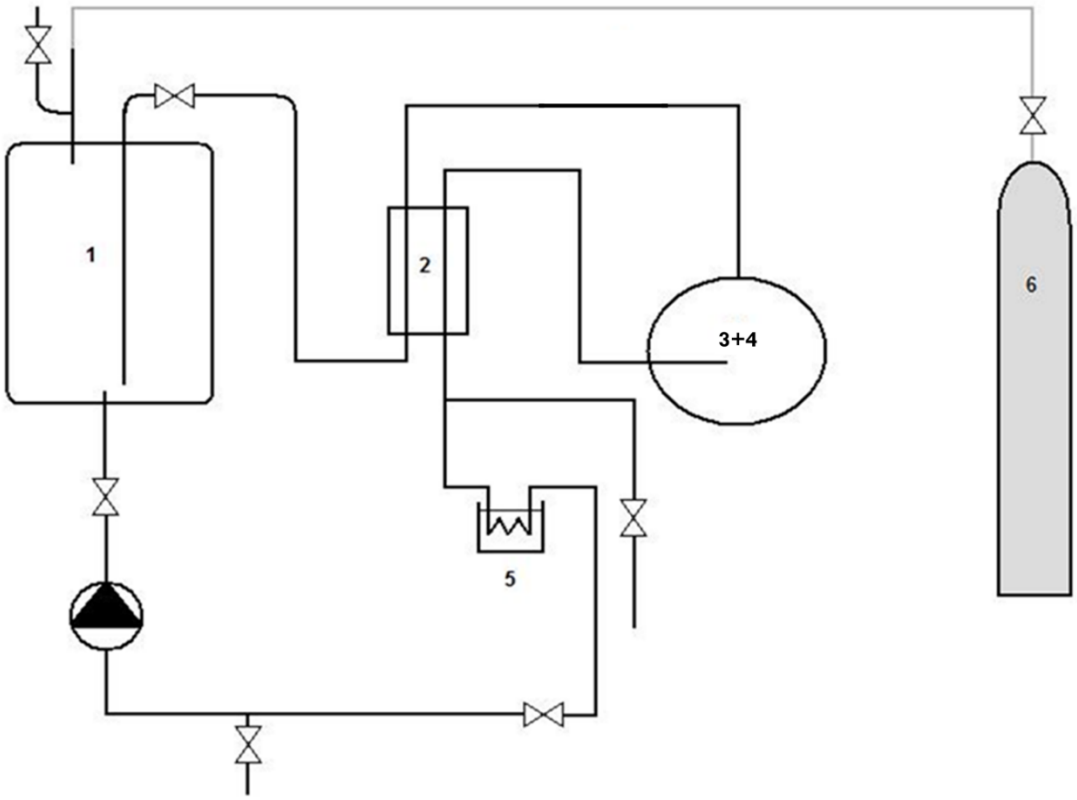

Figure 1: Scheme of an experimental device for SCW environment. 1) demineralized water tank 2) heat exchanger 3+4) high-temperature autoclave with heating and internal sample space 5) water cooling 6) argon pressure vessel [6].

After exposure, the chemical composition of the oxides on the surfaces was studied by XPS, and then the surface layers in the cross-sectional cut were analyzed by point analysis by EDS on SEM.

2.2 Results

The table of results of XPS spectra (Table 2) shows the formation of thin oxides layers on the surface of exposed materials. After the exposure, the surfaces of materials were composed of chromium and iron oxides. With increasing Fe content in the composition of the base materials, the Fe content in the surface oxide layer also increased. Carbon monolayer (adventitious carbon) is usually found on the top layer of the alloy surface. This film is produced during air exposure of the samples and is also deposited from the residual atmosphere in vacuum chamber. Example XPS spectrum of exposed sample 800H is shown in Figure 2.

Table 2: Result of the composition of the sample surfaces by the XPS method (BS – base state, ES – exposed state) in atomic percentages.

Material		Ni	Cr	C	Fe	Mo	O	Other
800H	BS	20.9	14.7	15.1	27.5	-	21.6	Ti 0.1
	ES	2.5	21.9	7.8	15.0	-	52.8	-
316L	BS	1.5	11.9	28.4	53.4	1.5	3.4	-
	ES	1.6	14.0	7.0	26.3	-	50.5	Mn 1.6
T24	BS	-	1.8	12 .2	82.1	0.5	3.4	-
	ES	-	8.3	17.0	36.0	-	38.7	-

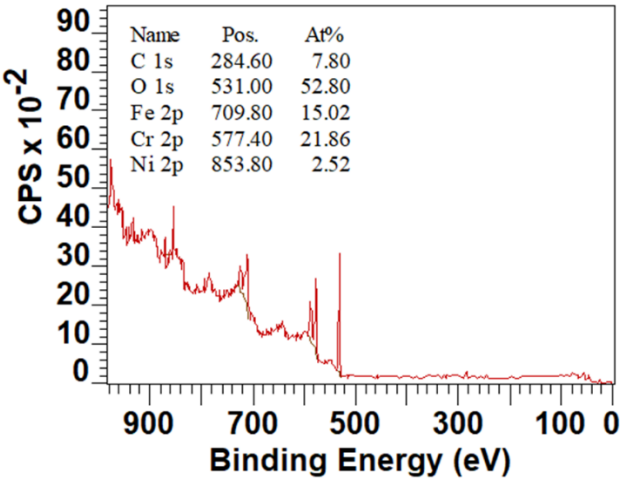

Figure 2: Example XPS spectrum of exposed sample 800H (CPS – photoemission intensity in counts per second)

Analysis of the surfaces and cross-sections of the samples 800H and 316L was performed using SEM. Unfortunately, sample T24 was contaminated and degraded during transport. SEM and EDS analyses will be performed on a new sample after repeated exposure. Surface analysis of 800H samples showed a local increase in Cr (and slightly also Ni) concentrations. The contamination grains on the surface of 316L material contained elevated concentrations of Mo (approx. 12% wt.), W (approx. 17% wt.), and Ca (approx. 7% wt.) see Figure 3.

EDS analysis showed that in the cross-sections of sample 800H, inhomogeneities composed of Ti (88% wt.) were found below the surface of the material (at a depth of approximately 1 μm) see elemental maps in Figure 4.

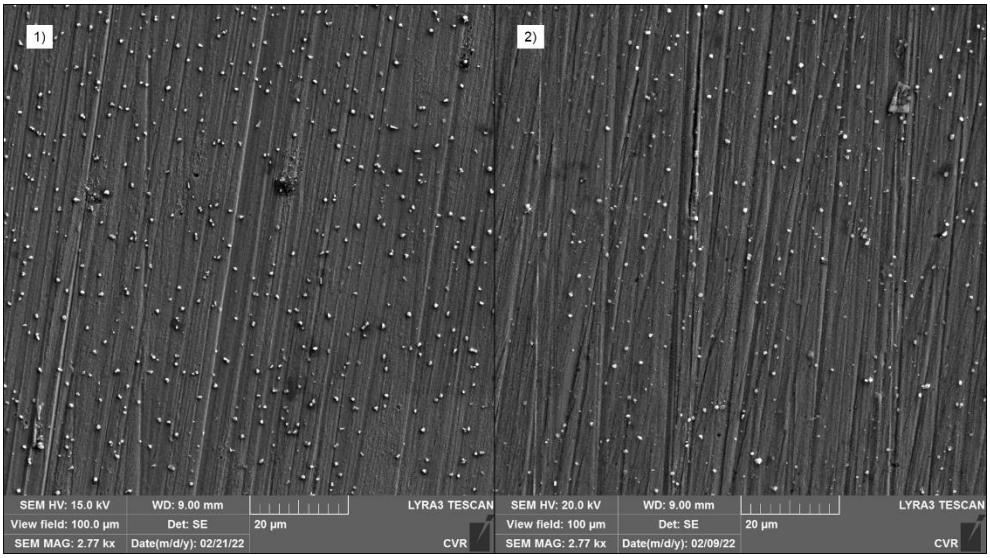

Figure 3: Surface of 1) 800H, and 2) 316L after exposure (by SEM, SE, MAG 2.77 kx)

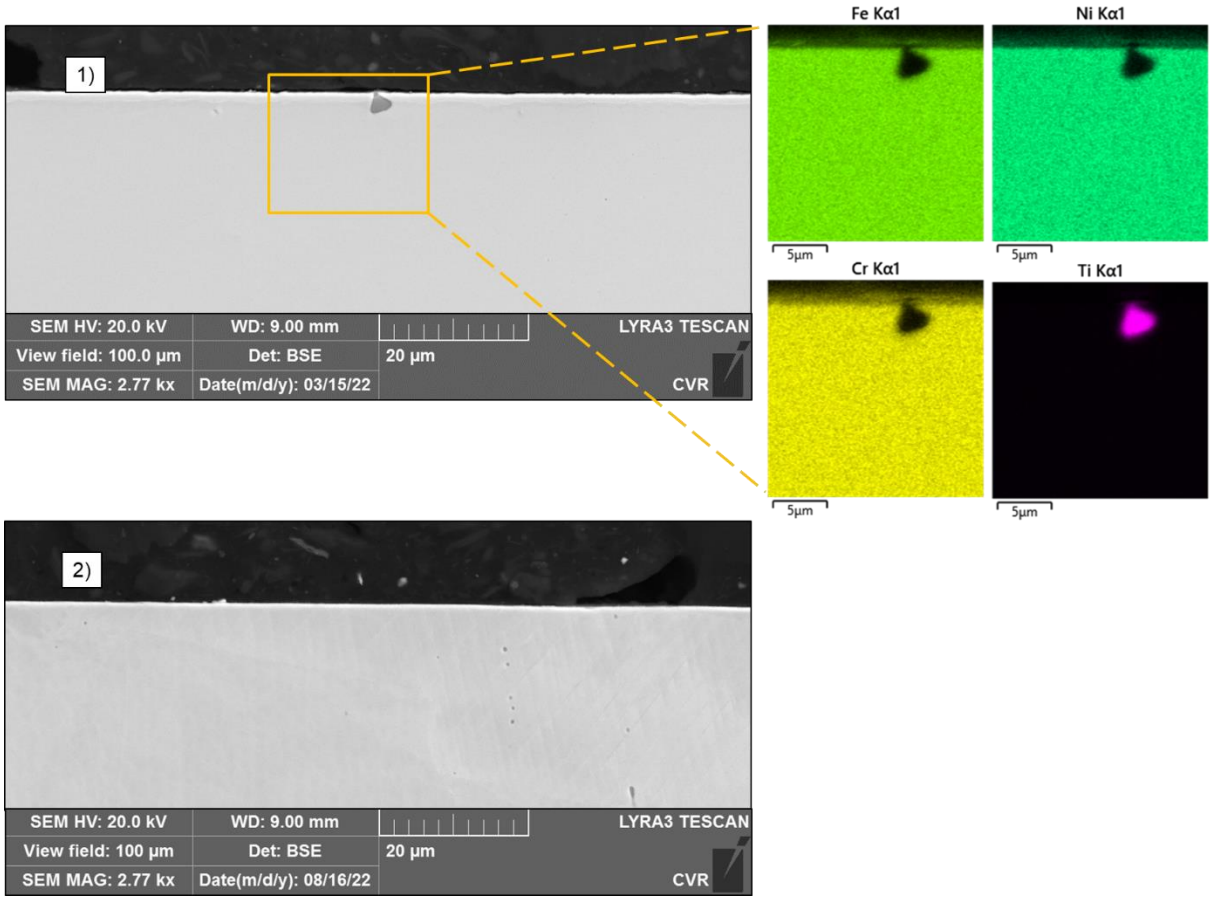

Figure 4: Cross-section of 1) 800H with elemental maps 2) 316L after exposure (by SEM, BSE, MAG 2.77 kx)

3 CONCLUSION

XPS analyses of the exposed materials showed the formation of a very thin oxide protective layer for all materials. SEM analysis revealed inhomogeneities in the base material 800H, which may cause mechanical and chemical resistance problems when the material is

used in industrial applications. An issue with post-exposure sample handling was contamination of samples between analyses, and corrective measurements will be taken. According to the results, both 800H and 316L materials analysed by XPS and SEM methods resisted the demanding SCW environment, the surface layers were very thin, and the materials did not show local corrosion damage. The detailed composition of the oxide layers will be further studied.

ACKNOWLEDGMENTS

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