

MATERIAL RESEARCH FOR SMALL MODULAR REACTOR COOLED BY SUPERCRITICAL WATER – ECC-SMART^{1,2}Daniela MARUŠÁKOVÁ, ¹Monika ŠÍPOVÁ¹Research Centre Řež s.r.o., Husinec-Řež, Czech Republic, EU,
daniela.marusakova@cvrez.cz, monika.sipova@cvrez.cz²University of Chemistry and Technology Prague, Prague, Czech Republic, EU<https://doi.org/10.37904/metal.2022.4480>**Abstract**

The main objectives of the project are to define the design requirements for the future SCW-SMR technology, to develop the pre-licensing study and guidelines for the demonstration of the safety in the further development stages of the SCW-SMR concept including the methodologies and tools to be used and to identify the key obstacles for the future SMR licencing and propose strategy for this process. The project consortium consists of laboratories from Europe, Canada and China. Beside the thermo-hydraulics, safety, neutronics, and reactor physics, assessment of the corrosion behaviour of cladding candidate materials (alloy 800H, stainless steel 310S, alumina forming austenitic alloy - AFA) in supercritical water (SCW) at 380/500 °C and 25 MPa is one of the key activities. For this purpose, experiments such as long-term (1000-8000 hours) exposure tests in autoclaves, neutron irradiation, electrochemistry, and radiolysis are involved. The paper describes the progress made on the ECC-SMART project with focus on microstructural characterization of candidate cladding materials. In addition, the description of the setup of corresponding experiments is included.

Keywords: Cladding material, supercritical water, scanning electron microscopy, tensile testing, alloy 800H, stainless steel 310S

1. INTRODUCTION

As a result of concerns about fossil fuel resources availability and environmental issues, interest in nuclear power technologies is growing over the last decades. After a period in which large units were developed and privileged, there is currently a revival of interest concerning the small and simpler reactors for electricity generation, heat production, cogeneration and desalination, the so-called small modular reactors (SMRs). SMR technologies using various concepts are being developed worldwide. It is believed that the most promising concept of SMR is the water-cooled one since they inherit experience gained by most of the power reactors operating worldwide. In this frame, the supercritical water (SCW) with temperature above 374 °C and pressure 22.1 MPa technology can play an important role, representing a natural evolution of current advanced water-cooled nuclear reactor technologies, while integrating much of the advances in SCW technology used in modern conventional fossil power plants. It is expected that SCW-SMR will improve the standard of living and technological development not only in cities but also in remote areas and small towns [1]. Based on the scientific results [2-3] and previous projects, the stainless steel 310S and alloy 800H has been selected as the most promising commercially produced materials for application as the cladding in SCW-SMR. The investigation of given materials will be accompanied by experimental steel such as Alumina-Forming Austenitic (AFA) alloy [4]. Alloy 310 (UNS S31000) is an austenitic stainless steel developed for use in high-temperature corrosion resistant applications. The alloy resists oxidation up to 1100 °C under mildly cyclic conditions. At a higher temperature, the alloy is subjected to sigma phase precipitation. The σ -phase is a tetragonal crystal structure, and its precipitation temperature is between 600 and 1000 °C [5,6]. Fe-Ni-Cr alloy 800 has been

widely used for its strength at high temperatures and its ability to resist oxidation, carburization, and other types of high-temperature corrosion. 800H (UNS N08810) with the carbon range of 0.05-0.10 wt.%, content of Al + Ti between 0.30 and 1.20 wt.%, is certified for usage in nuclear systems for temperatures up to 760 °C [3,7,8]. Alloy 800H is austenitic with FCC structure, solid solution alloys. TiN, TiC and chromium carbides normally appear in the alloys' microstructure. The nitrides are stable at all temperatures below the melting point (1357-1385 °C) and are therefore unaffected by heat treatment. Chromium carbides precipitate in these alloys at temperatures between 400 and 900 °C. Such precipitates can be dissolved in the temperature range of 900-1000 °C [9]. Consequently, alloys 800H and 800HT are similar to other austenitic alloys, in that they can be rendered susceptible to intergranular corrosion (sensitized) in certain aggressive environments by exposure to temperatures of 540-760 °C [7].

As a promising cladding candidate material, Al-forming austenitic (AFA) stainless steel was first developed at Oak Ridge National Laboratory (ORNL). The AFA steels not only show good corrosion resistance at high temperature due to the formation of Al₂O₃ scale but also exhibit improved strength due to precipitation hardening. The typical strengthening phase reported in AFA steels includes NbC, Laves phase and B₂-NiAl [10]. In addition, these alloys require a significant quantity of Cr (also a ferrite stabilizer) to help promote protective Al₂O₃ scale formation. Thus, large addition of Ni is needed to achieve an austenitic matrix structure which significantly influences the cost of these alloys. AFA alloys show a promising combination of oxidation resistance, creep resistance, tensile properties, and potential for good welding behaviour [4].

2. ABOUT ECC-SMART

One of the main challenges of the ECC-SMART project, which is supported by Horizon 2020 EURATOM is to demonstrate the feasibility of the supercritical water-cooled reactor (SCWR) concept as one of the six advanced nuclear reactors of the future Generation IV. The project aims to support and help to solve the issues such as materials, heat transfer, physics and safety. The project consortium has 20 partners and consists of 15 European institutions from 12 member states and is supplemented by an important international collaboration with the Canadian, Chinese, and Ukraine supercritical water research programs. The project consortium and project scope were created according to the joint research activities under the International Atomic Energy Agency, Generation-IV International Forum, SNETP and NUGENIA umbrella. Hence, ECC-SMART maximizes international synergy between the national programs of the European member states on the one hand and the international programs on the other hand. The biggest work package is focused on material testing (WP2). For this purpose, the test matrix was established including more than 700 specimens. The focus is devoted to stainless steel 310S and alloy 800H, which have been selected as the most perspective material for fuel cladding for SCWR. In addition, experimental material such as AFA (alumina forming austenitic alloy) was supplied by colleagues from China (USTB). Most of the tested specimens have been manufactured from the tubes to get closer to the real conditions and to support the progress in the SCWR and SCW-SMR field. The SCC behavior and oxidation behavior of these alloys will be studied in SCW at 380 °C and 500 °C that were defined by Canadian Nuclear Laboratories (CNL) based on previous calculations as the average temperature and maximum cladding temperature for the SMR-SCW, respectively. To complete these studies, materials will be studied at simulated accident conditions. It is expected that results from these tests will be useful not only for the SMR-SCW but for the LWR too.

Another important task is the study of the effect of neutron radiation on pre-irradiated specimens exposed to SCW at the maximum estimated cladding temperature for the SCW-SMR (500 °C). The irradiation and subsequent oxidation tests are carried out at CVR facilities. On the other hand, CNL will work on the study of radiolysis processes in SCW and VSCHT and JRC will perform electrochemical measurements from liquid water to SCW in order to provide valuable results on the corrosion behavior of water in the SCW region. It is expected that results from these studies will help to understand results from corrosion tests. The first planned experiments have been started and the results are being evaluated at each laboratory.

3. EXPERIMENTAL AT CVR

The tubes and rods from 310S and 800H were purchased from Czech company UNIONOCEL. The AFA material was manufactured as plate by one of the partners of the project, the University of Science Technology of Beijing (USTB) and is under the basic characterization, not included in this paper. In addition, Pt foil was purchased from the company SAFINA a.s. to study the contribution of each autoclave to the oxide layers that are formed during the test. Based on the results of previous Round Robin tests [11] large variations in weight gains were observed depending on the autoclave in which the tests were carried out. The composition of the tubes from 310S and 800H is summarised in **Table 1**.

Table 1 The chemical composition (in %wt) of 310S and 800H

Elements	C	Si	Mn	P	S	Ni	Cr	Cu	Ti	Al	Mo	Co	Fe
310S	0.060	0.39	1.190	0.024	0.0006	21.45	25.27	-	-	-	0.250	-	Bal.
800H	0.08	0.2	0.7	≤0.03	0.0005	30.7	19.7	0.45	0.58	0.40	0.18	0.11	Bal.

Tensile specimens, circumferential specimens and oxidation coupons were machined at CVR and distributed along the consortium. After that, roughness measurement, microhardness, nanoindentation (NI), Scanning Electron Microscopy (SEM), equipped with Energy Dispersive Spectrometry (EDS) and Electron Back-Scattered Diffraction (EBSD), and Transmission Electron Microscopy (TEM) were used to evaluate the microstructure of as-received materials. Tensile tests were performed at room temperature, 380 °C and 500 °C before the exposure to the supercritical water (SCW).

The irradiation of the materials is carried out in reactor – LVR15, that is a light water tank-type research reactor placed in a stainless-steel vessel under a shielding cover. It has forced cooling, IRT-4M fuel and an operational power level of 10 MWt. Reactor operations run in campaigns (cycles) which last for 3 weeks, followed by an outage lasting for 10-14 days for maintenance and fuel reloading. As a moderator and a coolant, demineralised water is used. A reflector is composed of a water, or beryllium block, depending on the operation configuration. Expected average value of the neutron fluence after this experiment is $3.60E+20$ n/cm² with 0.37 dpa. The samples are placed in the special holder inside the rig, which is filled with pure He to keep the inert atmosphere. The temperature of irradiation (within the rig) is kept under 100 °C. The low temperature of irradiation will lead to slightly higher radiation damage as the microstructure changes like Frankel loops, pair etc. (caused by the irradiation) will not be able to easily annihilate or the recovery process will be limited in comparison with higher temperature. Nevertheless, the neutron flux, fluence and dpa are not influenced by the temperature of irradiation. The irradiated samples will be exposed to the supercritical water in SCW autoclave manufactured from 316L stainless steel and placed in the hot cell. The inner dimensions of autoclave are about 300 x Ø 60 mm with volume about 1 dm³. The flow rate is 2.5 dm³ per hour. Dissolved oxygen and conductivity can be controlled on-line. The exposure in SCWAc will last 1000h and carried out at 500 °C and 25 MPa.

Table 2 Roughness of 310S and 800H inside and outside of the tube and on the rods.

Material	310S tube	800H tube	310S rod	800H rod
Ra (µm) outside	0.2	0.5	0.8	0.4
Ra (µm) inside	0.9	0.3	-	-

4. RESULTS

Only part of the microstructural analysis is presented here. Results of roughness measurements in longitudinal direction inside and outside of the tube and on the rods, **Table 2**, showed differences between surfaces. The surfaces of the as-received tubes were also observed via SEM, **Figures 1, 2**. The EDS analysis revealed that

there are dark secondary phases enriched in chromium and the light one enriched in molybdenum and niobium in case of outer surface of 310S. The light elongated particles present on the inner surface are probably the oxides of chromium based on the EDS analysis.

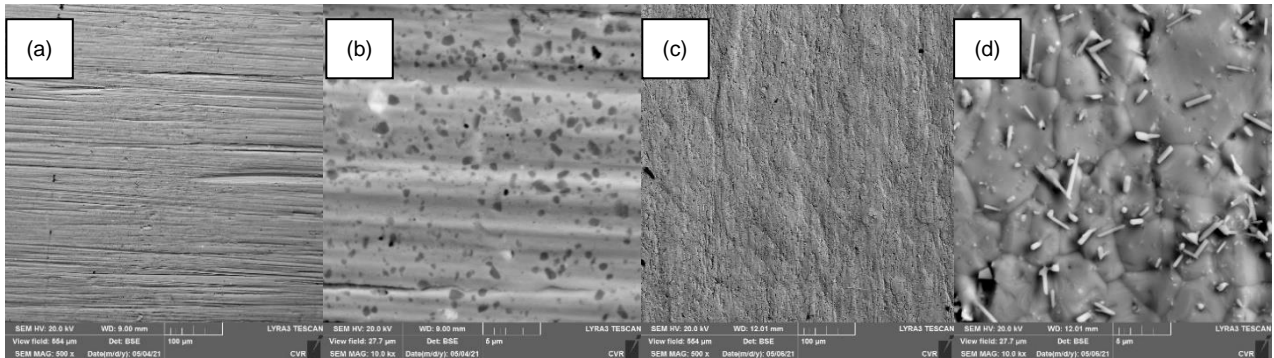


Figure 1 The SEM/BSE of the outer (a, b) and inner (c, d) surface of as-received tube of 310S

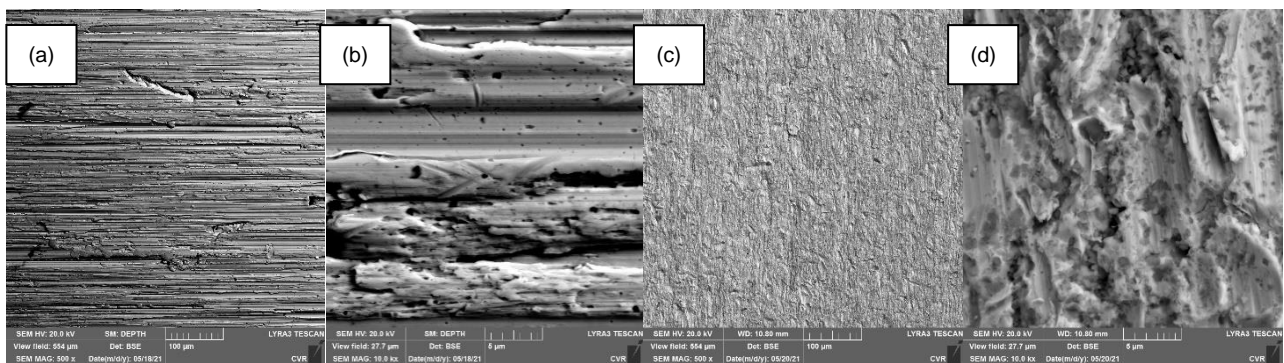


Figure 2 The SEM/BSE of the outer (a, b) and inner (c, d) surface of as-received tube of 800H

The EDS analysis of the outer surface shows homogeneous distribution of the alloying elements and the presence of a small secondary phase enriched in Ti and Al, the presence of oxide on the inner surface of 800H-tube was revealed. The characterization of the as-received microstructure of 310S and 800H-tube was completed by EBSD. The crystallographic analyses were determined on the cross-section, **Figures 3, 4**, and on the longitudinal cut. As can be seen in the overview of IPF map, **Figure 3 (a)**, the microstructure of 310S-tube is composed of the homogeneous equiaxed grains with the average size of 8 μm (calculated from ~ 500 grains). In case of higher magnification and detailed EBSD analysis close to the inner and outer surface, the presence of twins and the secondary phase (in black colour) is observed. The misorientation map, **Figure 3 (b, left)**, reveals the thin deformed layer close to the outer surface. By comparison of both cuts, it can be concluded that the microstructure of the 310S-tube is homogeneous. As can be seen in the overview of IPF maps, **Figure 4 (a)**, the microstructure of 800H-tube is not as homogeneous as in case of 310S-tube, **Figure 3** as the dominant coarser grains can be found in the as-received microstructure of 800H. The average size of the grains is decreased close to the surface. In case of inner surface, fine grains are present. In detailed maps, there are well-defined grains which contain parallel sets of long straight twinning boundaries. The thin deformation layer can be found close to both surfaces inside and outside (highlighted by green colour in misorientation maps, **Figures 4 (b, c)**). However, the average grains size was determined as 45 μm (calculated from ~ 350 grains) in cross-section and 35 μm (calculated from ~ 900 grains) in longcut. It should be noted that the high angle ($>15^\circ$) grain boundaries are marked by the black colour in all maps.

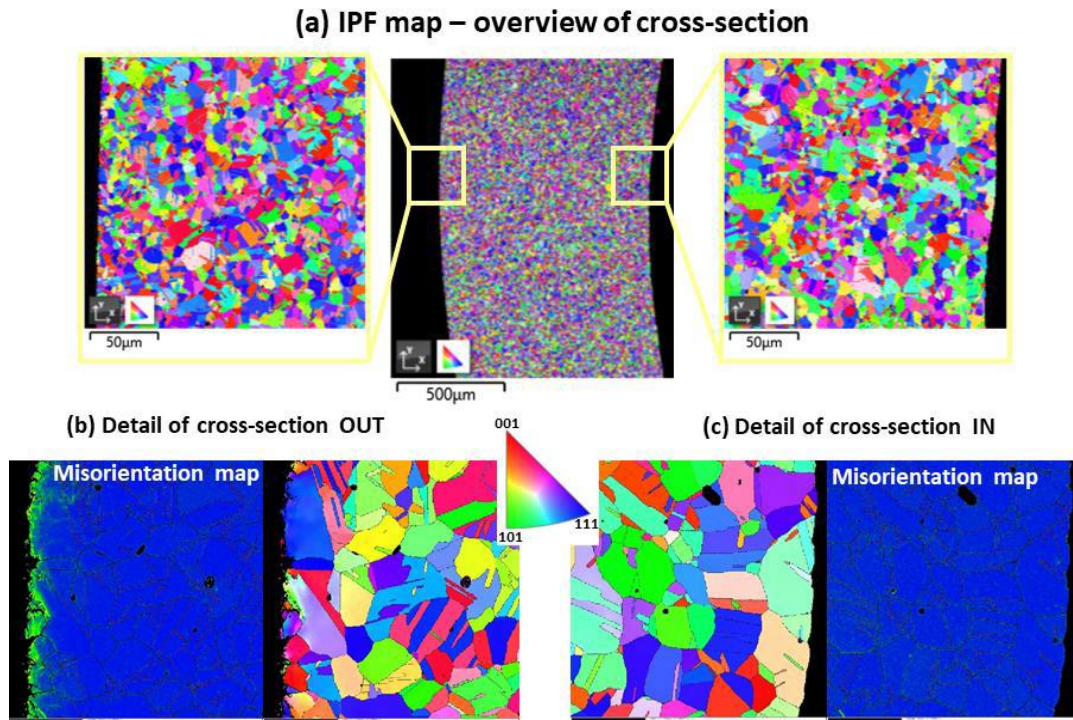


Figure 3 (a) Inverse pole figure (IPF) map with a step size of 2.5 µm shows the initial microstructure in cross-section of 310S tube at MG 140x (on left and right, there are IPF maps at MG 1000x with a step size of 0.6 µm). The two detailed IPF maps are at MG 6000x, with a step size of 0.1 µm and they are accompanied with the highlighting of the misorientation (b) close to outside and (c) close to inside of the tube.

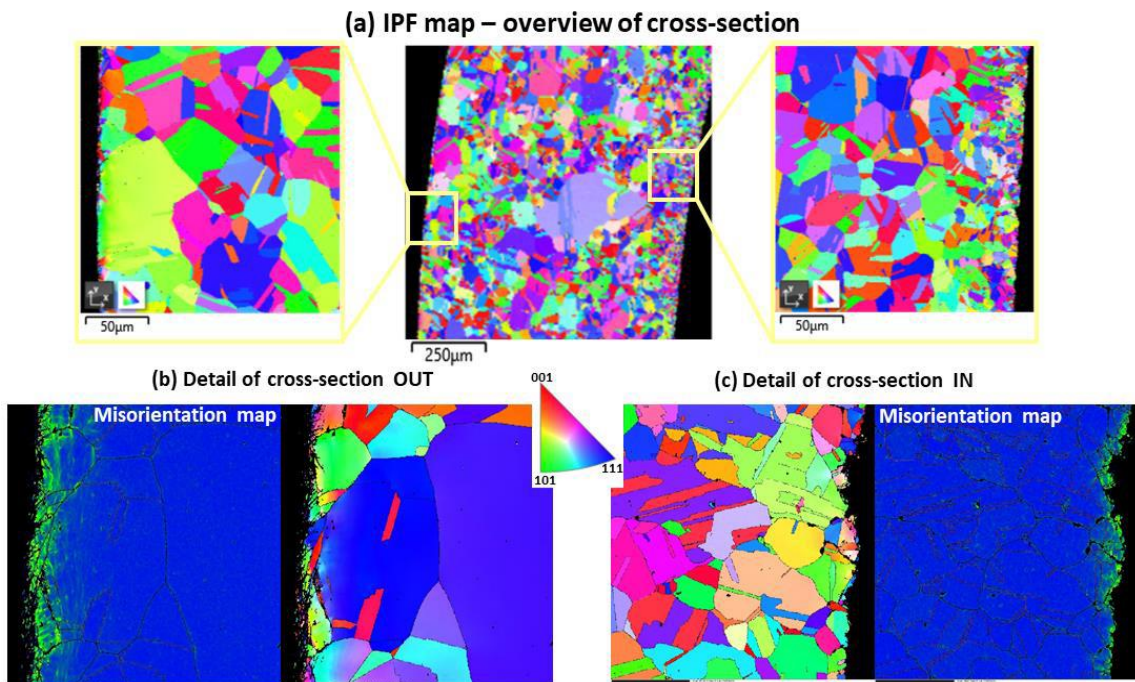


Figure 4 (a) Inverse pole figure (IPF) map with a step size of 2.5 µm shows the initial microstructure in cross-section of 800H at MG 140x (on left and right, there are IPF maps at MG 1000x with a step size of 0.6 µm). The two detailed IPF maps are at MG 6000x, with a step size of 0.1 µm and they are accompanied with the highlighting of the misorientation (b) close to outside and (c) close to inside of the tube.

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5. CONCLUSION

Stainless steel 310S and alloy 800H have been selected as the most perspective for the application in the concept of the SCWR and its small modular version based on the previous scientific results. The microstructure of materials was analysed via SEM (and accompanied analyses). In addition, the surface roughness was characterized via measurement of Ra and SEM.

The results revealed that 310S-tube possesses the most homogeneous microstructure with the presence of secondary phase enriched in Nb and Mo. The average grain size is about 8 μm . In contrast, the microstructure of 800H-tube contained a mixture of coarse and fine grains with a higher presence close to the inner surface. The average grain size is about 40 μm . The presence of TiN, TiC and chromium carbides was confirmed by EDS. The outer surface roughness characterized by the parameter of Ra was kept at the level of tenths of micrometres (in the interval of 0.2 up to 0.8) in case of all materials.

The presented data will be used as the reference for the planned experiments. The project reached the first third of its duration, thus, most activities and corresponding results are expected in the next months.

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