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INVESTIGATION OF MATERIAL DEGRADATION AND COOLANT CHEMISTRY FOR SCO_2 POWER CYCLES

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ABSTRACT

sCO_2 power cycles are characterized by the enhanced efficiency of thermal to electric power conversion and more compact turbine size compared with the steam power cycle. The organizations from Czech Republic take part the extensive research activities in this field. The research infrastructure including sCO_2 experimental loop was constructed. The sCO_2 coolant chemistry and material degradation are among the solved topics. The objectives are to identify impurities in sCO_2 medium and propose the purification and purity control system. Another objective is to gain data of structural material degradation in sCO_2 medium. First results concerning impurities and materials were obtained during laboratory tests and the 1000 h operation of the sCO_2 loop. The most important of them are presented in the paper and also conference presentation.

INTRODUCTION

The increasing electric power consumption and the CO_2 emissions reduction requirements demands new, effective energy sources. One way of increasing the conversion of mechanical power to electric power is by using carbon dioxide as a working medium in the power cycle. Currently, the power cycles that are based on supercritical CO_2 (sCO_2) have been investigated [1, 2]. Carbon dioxide becomes supercritical above a critical temperature of 30.98 °C (304.13 K) and above a pressure of 7.32 MPa [2]. The sCO_2 power cycle efficiency of the conversion of mechanical power to electric power may exceed 50% compared to the conventional steam power cycle, which has a maximum efficiency of approximately 40% [3, 4]. The efficiency of sCO_2 increases within the temperature range of 500–950 °C. Therefore, this technology is suitable for power conversions in both high temperature non-nuclear and nuclear technologies, including the generation IV nuclear reactors [5]. Another advantage of the sCO_2 cycles is that they use more compact turbines compared to the turbines for the steam power cycle [6].

The sCO2 cycles are subject of worldwide research and development program, in which organizations from Czech Republic are also involved. One of the topics of the extensive research program is the sCO_2 coolant chemistry (i.e. purity, purification and purity control of CO_2 medium) and resistivity of structural materials in sCO_2 medium.

SUPERCRITICAL CARBON DIOXIDE LOOP IN REZ

The research activities are related (also) to the Supercritical carbon dioxide loop (sCO_2 loop; see the scheme on Figure 1). The purpose of the loop is to measure the thermohydraulic performance and physical parameters of the sCO_2 circuits, the loop also enables the exposure of material samples in sCO_2 environment.

For the main parameters of the loop, see Table 1. The function of the loop could be described as follows: after the passage through the heat exchanger in the high-pressure section (7), CO_2 flows to two parallel (8) and one serial (9) heater branches. After heating, the medium flows to the test section (10). Behind the test section, the reduction valve (11) is placed, which reduces the medium pressure to 12.5 MPa. Due to the accurate temperature reduction, part of the flow is passed through the oil cooler (12), and the second part flows through the bypass. Following that, the medium reaches the low-pressure part of the high temperature heat exchanger (7), which

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has a maximum allowed temperature of 450 °C. It then flows to the low temperature heat exchanger (1). Next, it flows through the cooler (4), which is situated before the entrance to the main circulator (3).

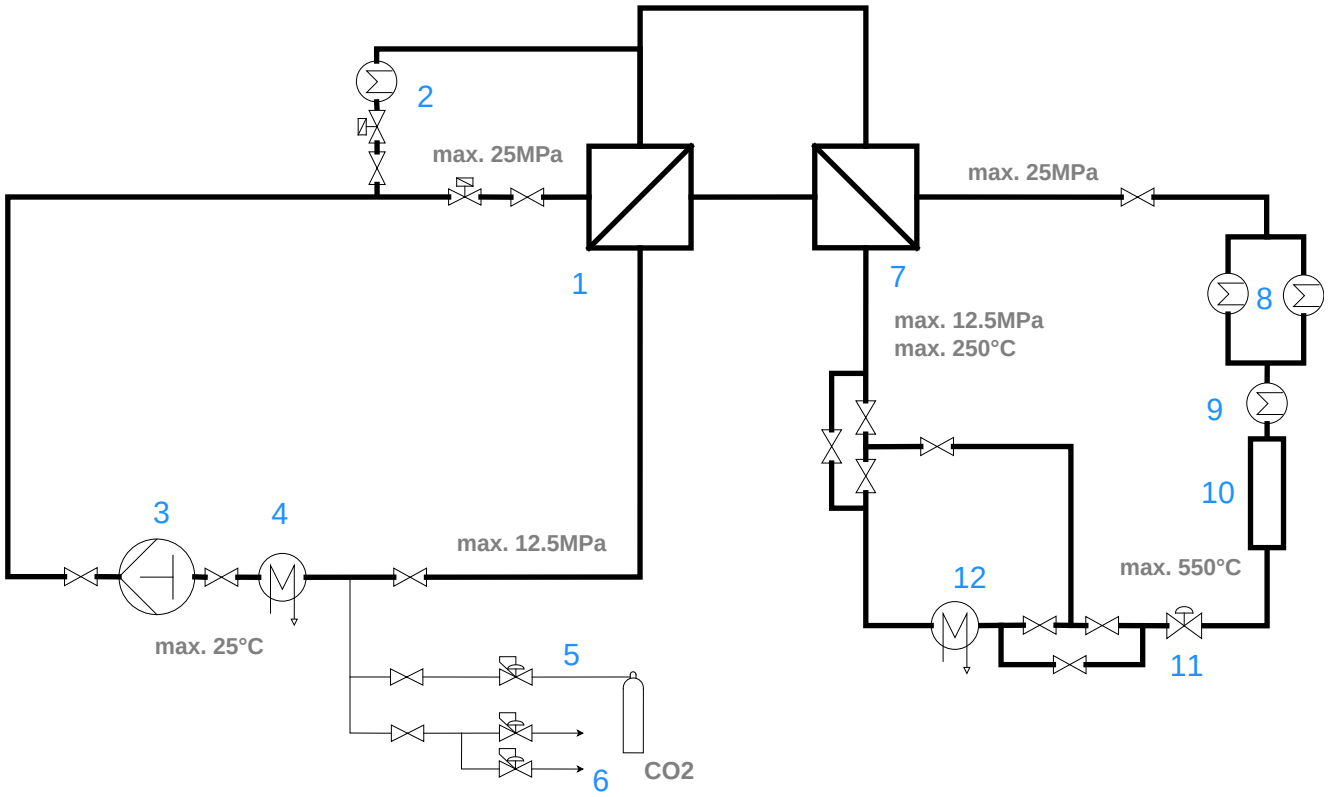

Figure 1: Scheme of the Supercritical carbon dioxide experimental loop. 1: low temperature heat exchanger, 2: preheater, 3: main circulation pump, 4: cooler, 5: CO_2 dosing system, 6: sampling system, 7: high temperature heat exchanger, 8: parallel heaters, 9: heater, 10: test section, 11: reduction valve, 12: cooler

Table 1: The main parameters of the Supercritical carbon dioxide experimental loop

Maximum medium temperature	550 °C
Maximum pressure in the high-pressure section	25 MPa
Maximum pressure in the low-pressure section	12.5 MPa
Maximum flow rate	0.4 $kg.s^{-1}$
The loop volume	0.08 m^3

SCO_2 POWER CYCLES CHEMISTRY

Contrary of the water or helium cooled power systems there is not much information about sCO_2 power cycle medium chemical composition, typical impurities content, purification and purity control systems. Some knowledge can be transferred from the operation's experience with the nuclear reactors, which use carbon dioxide (not in a supercritical state) as a primary coolant. These reactors have been operated in Great Britain (MAGNOX and Advanced Gas Cooled Reactors) [7], and the first nuclear power plant in former Czechoslovakia, which is A1, also used carbon dioxide as a primary coolant [8].

Impurities can get into the CO_2 (or sCO_2) medium by several ways. Some impurities can be contained in the source CO_2 gas stored in pressure vessels. Within the research program composition of several different CO_2 gases available on the market was verified and compared. The results are summarized in Table 2. As a source gas for sCO_2 power stations the CO_2 with purity 3.0 or 4.5 will be used for economical reason.

Table 2: CO2 purity available on the market in Czech Republic

CO_2 type	Purity	Impurities (vppm)					
	% vol.	H_2O	O_2	CO	C_nH_m	N_2	Oil
SFC/SFE	99.9993	1	2	0,5	1	3	-
CO_2 for food industry (E290)	99.5	52	-	10	-	-	5
4.8	99.998	5	2	1	2	10	-
4.5	99.995	5	15	1	2	30	-
R-744	99.9	10	15	1	2	30	-
3.0	99.9	120	500	-	50	500	-
5.3	99.9993	1	2	0,5	1	3	-

Another sources of impurities in CO_2 in power cycles can be also the leakage of air or moisture from surrounding environment, lubricants from devices connected to the circuits, residual organics on internal surfaces from production and (not least) as products of chemical reactions in the circuit. In case of sCO_2 cycle with direct combustion the sCO_2 may contain also combustion products [5]. Typical admixtures in the CO_2 medium are as follows: O_2, H_2O, H_2, CO, CH_4, N_2 [5, 9]. In the direct combustion cycles that use synthesis gas as a fuel, SO_2, SO_3, NO, NO_2, and halogen compounds may be present in the medium. . Examples of the medium composition in the direct combustion power cycles are listed in Table 3.

Table 3: Examples of the medium composition in the turbine inlet for the direct combustion cycle, according to the used fuel [10, 11]

Component	**Natural gas (vol. %)**	**Synthesis gas (vol. %)**
CO_2	91.80	95.61
H_2O	6.36	2.68
O_2	0.20	0.57
N_2	1.11	0.66
Ar	0.53	0.47

The higher content of impurities (units of % by vol. or more) can influence the thermodynamic properties of the medium. For example, the power consumption of the compressor when working with a medium that is near the critical point increases by six percent, whereas the medium purity decreases by 4.4%. With a medium of 90.9% purity, the compressor power consumption increases by 34% compared to 100% with pure CO_2. This increase in power consumption is caused by a decrease in the medium density, which is due to the impurities [9].

In cycles with indirect heating the content of impurities is expected to be lower – probably below 1 % by vol. The medium composition may be similar to primary CO_2 coolant in nuclear power plants, e.g. the most significant admixtures in A1 power plant primary coolant were H_2O (about 1000 $mg.kg^{-1}$) and oil (1 – 5 $mg.kg^{-1}$) [8].

The admixtures in the CO_2 medium even in lower contents may enhance corrosion and degradation of components. Higher content of oil (1 % by weigh and more) in the medium may negatively affect the heat transfer properties caused by deposition of oil an internal surfaces [3, 12].

SCO_2 PURIFIACATION METHODS

Data concerning CO_2 purification in power engineering are relatively rare. In some experimental devices, oil separators are used. For example, in the SCARLETT loop, the oil separator is located behind the compressor. The separator separates 99% of the oil that is contained in the medium in the loop [13]. To limit the damage to the turbines and other parts of the devices, the particle separators are inserted into the circuit. For lower flow rates, the "Y filters" (Figure 2) can be used, through which the medium passes.

Some gaseous impurities are expected to be effectively separated by adsorption methods. The experimental verification of these methods for CO_2 purification is in the experimental program for next years.

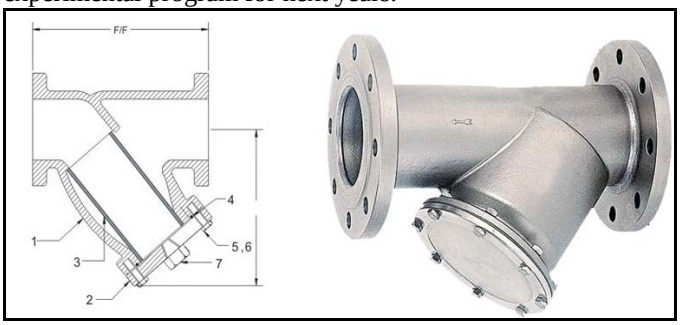

Figure 2: The Y-filter [14]

METHODS OF ANALYTICAL PURITY CONTROL

For CO_2 purity control several analytical methods can be assumed, e.g. gas chromatography with thermal conductivity detector (GC-TCD), mass spectroscopy detector (GC-MS) or helium ionization detector (GC-HID), analyzers based on infra red spectroscopy, etc. Every method is suitable for specific compounds detection. The method selection and verification for CO_2 purity control in sCO_2 loop is also in experimental program for next years.

Currently, the combination of the gas chromatography with the helium ionization detector (GC-HID) directly connected with sampling site of the loop and the moisture analyzer is based on changes to the infrared light wavelength. Experience with these technologies was gained in connection with another technology: the high temperature helium experimental loop. The details were published in cit. [15]. The GC-HID method is sensitive when determining the content of H_2, CO, CH_4, O_2, and N_2. Detection limit for some of these compounds is below 0.1 vppm. Gas chromatography methods are not suitable H_2O content determination. The disadvantage of methods based on gas chromatography is that this method is relatively slow. The analysis of one sample lasts approximately 20 minutes.

The moisture (H_2O) analyzer with probe placed directly to the CO_2 circuit enables continuous moisture content monitoring. The detection limit is about 1 vppm of H_2O, pressure and temperature limits for the probe are 20 MPa and 70 °C respectively. During operation approx. 40 kg per day of CO_2 was continuously replaced by "new" one (by dosing and blowing off).

SCO_2 PURITY CONTROL DURING SCO_2 OPERATION CAMPAIGN

During the last 1 000 hours operation campaign (in 2019/2020) the monitoring of CO_2 medium purity was performed. The monitoring was aimed to the organic impurities. The source organics in the circulating medium could be the residual oil, degreasers and dissolvents from production and also the leakage of oil e.g. from circulator. During operation of the loop the organics take the chemical reaction by which another compounds may be formed. The topic with more details is commented in citation [16], which deals with reactions of residual organic compounds during High Temperature Helium Loop operation.

Before operation the loop was filled with high-purity CO_2 (4.8), therefore the minimum impurity level from source gas was expected. The sCO_2 loop was operated at a temperature of 550 °C in the test section and a pressure of 20 MPa in the high-pressure section of the loop.

The purity was monitored by sampling of medium during operation. The first sample was taken after 170 operation hours, the sampling was repeated after 360 and 820 operation hours. The samples were taken by passing the gas through the sampling tubes with the active carbon. The volume of the samples was 10 – 170 l , with a pressure of 100 kPa and temperature of 25 °C. In the next step, the compounds that were adsorbed by the active carbon were desorbed by carbon disulfide, which was subsequently determined by the GC-MS technique.

The amount of the organic compounds in the loop's medium that were determined in the samples has been recorded in the chart in Figure 3. The contents of the organic impurities in the medium decreased from ca. 1800 to 5 $ng.l^{-1}$ (at 25°C and 1 bar). In the sample after 170 operation hours several organic compounds contained a large amount of benzene. The relative distribution of the organic compounds in this sample is shown in Figure 4. In the samples after 360 and 820 operation hours, only benzene was detected. The source of the organic compounds in the loop medium could be the residual organics from the loop production, and subsequent conversion by chemical reactions. The amount of organic impurities significantly decreased during the loop operation, which is likely to be due to the continuous new CO_2 dosing in the loop. The amount of undesired organic compounds was significantly lower compared to that during operation of another experimental device (see cit. [16]). Though the compounds were able to be detected by sensitive analytic method based on GC-MS.

Table 4: Chemical composition of alloys exposed in sCO_2 loop (% by weigh)

	C	Mn	Cr	Mo	V	Al	Si	Nb	W	Ni	Ti	Cu	Fe
T92	0.07-0.13	0.3-0.6	8.5-9.5	0.3-0.6	0.15-0.25	0.04 max	0.5max	0.04-0.09	1.5-2.0	0.4 max			Bal.
HR6W	0.1	1.5	21.5-24.5				1.0	0.1-0.35	6.0-8.0	Bal.	0.05-0.20		20-30
HR235	0.06 max	0.65 max	31	5.6		0.4 max	0.6 max	1.0 max		Bal.	0.5 max	3.8	1.5 max
SS 316L	0.21	0.36	16.5	2	<0.001	<0.001	0.34	<0.001	<0.001	10	<0.001	<0.001	Bal.
800 H	0.06	0.7	20.5	<0.001	<0.001	0.28	0.5	0.01	<0.001	30.5	0.34	0.1	46.7
Inconel 738	0.11	-	16	2	-	3.4	-	0.9	2.6	Bal.	-	-	-
Inconel 617	0.05-0.15	1	20-24	8-10	-	0.8-1.5	Max. 1	-	-	Bal.	Max. 0.6	Max. 0.5	Max. 3

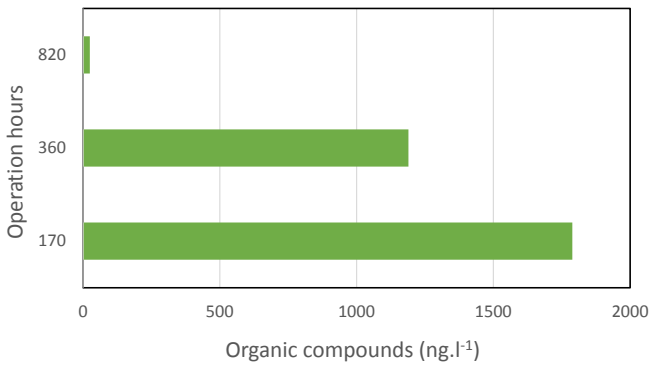

Figure 3: The sum of the organic compounds in the CO_2 medium during sCO_2 loop operation

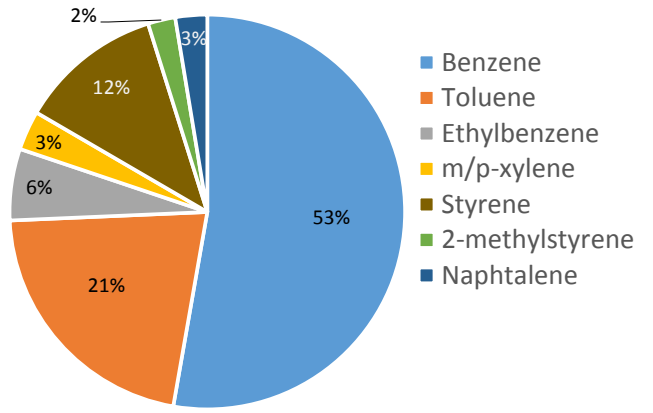

Figure 4: The relative distribution of organic compounds in sCO_2 medium after 170 operation hours

TEST OF MATERIAL DEGRADATION IN SCO_2 LOOP

During 1000 h. sCO_2 loop operation (550 °C@20 MPa) the samples of metallic alloys were exposed in the test section of the loop. In sum about 20 types of alloys were exposed. Some samples were provided with special coating for resistivity enhance. The ferritic (e.g. T92) and austenitic steels (e.g. 316L) and also nickel based alloys (e.g. Inconel 738 and 617) were among tested alloys. The chemical composition of selected alloys is listed in Table 4. The high resistance of some of these alloys was already verified in other environments, mentioned nickel based proved high corrosion resistance and mechanical stability even at temperatures near 900 °C.

After exposure the differences in weigh of samples were recorded and the corrosion and changes of the samples were investigated by using the optical and electron microscopy (Scanning Electron Microscopy with Energy-dispersive X-ray spectroscopy – SEM-EDX). The investigation has been in progress and not all data have not been evaluated in the time of finishing this paper.

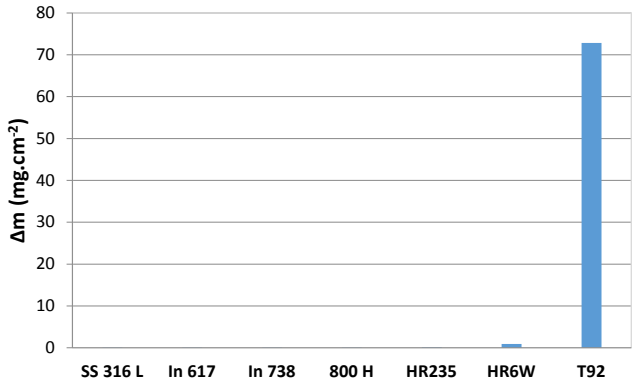

Figure 5: Mass gains of metallic alloys samples after 1000 h exposure in sCO_2 loop **(**550 °C@20 MPa)

On the chart in Figure 5 the mass gains of (selected) alloys samples are compared. The significant differences among particular alloys are evident. The highest mass gain (almost 100 mg per cm^2 of sample surface) was stated in case of ferritic steel T92. On the other hand the mass gains of austenitic steels and nickel based alloys were much lower, generally below 1 $mg.cm^{-2}$.

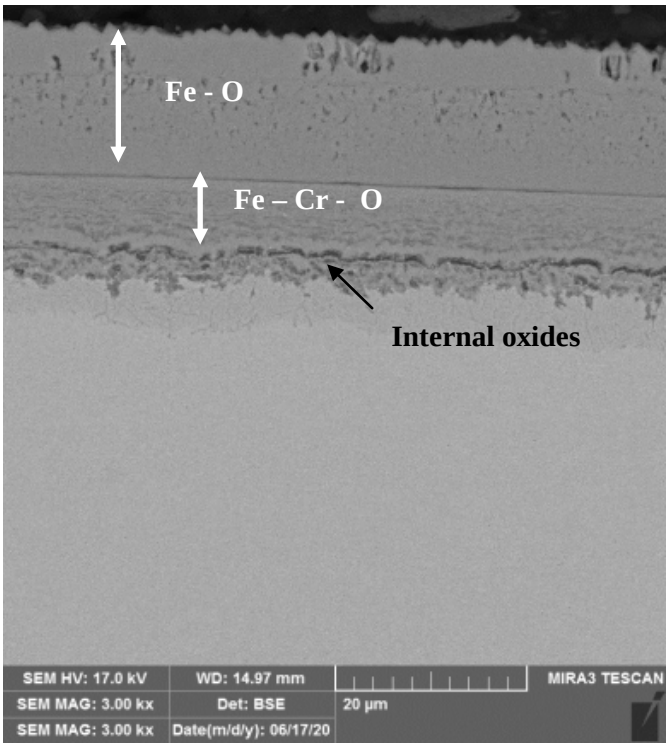

Figure 6: SEM image of sample cross section of ferritic steel T92

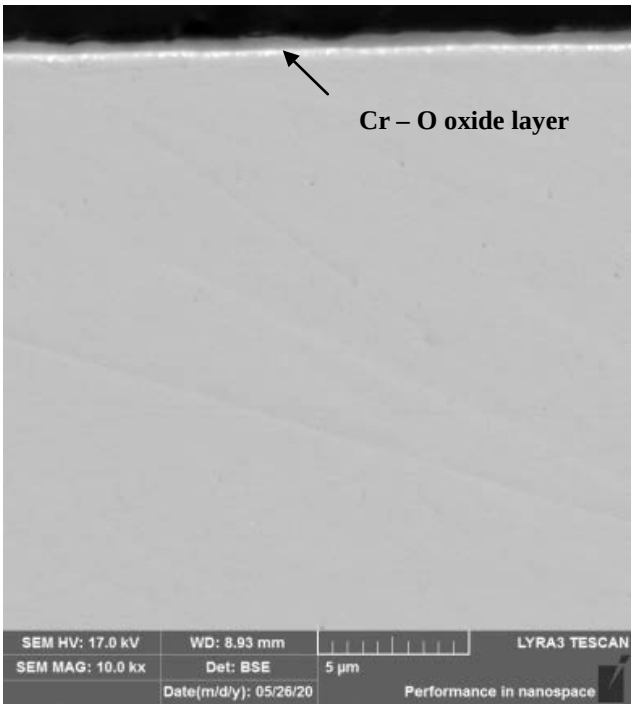

Figure 7: SEM image of sample cross section of nicke based alloy HR6W

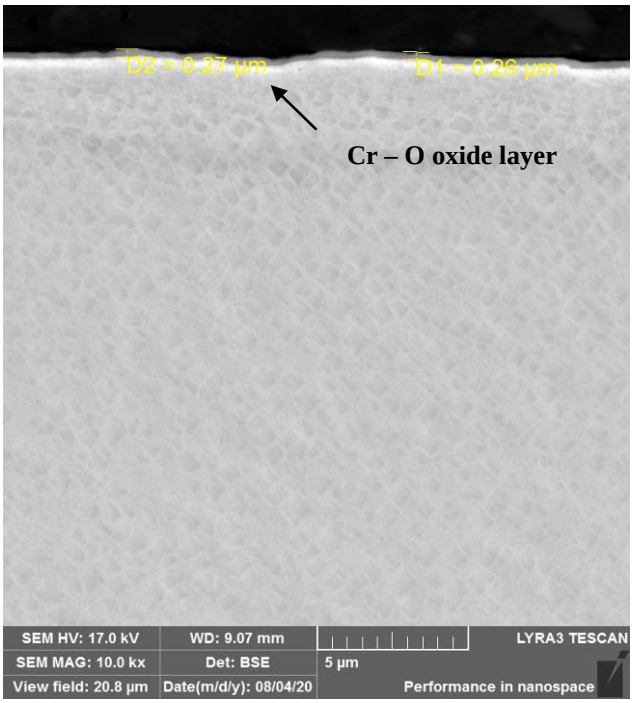

Figure 8: SEM image of sample cross section of nicke based alloy Inconel 738

The differences in mass gains correspond with microscopic observation of sample cross sections. On the surface of ferritic steel P91 the more than 20 µm thick double oxide layer was observed. The outer layer was formed of iron oxides, the inner layer was formed of iron and chromium oxides (see Figure 6). Under the oxide layer internal oxides were observed. On the surfaces of nickel based alloys only thin chromium layers (thickness about 0.2 – 0.3 µm) were observed. As examples the SEM images of the sample cross section of alloy HR6W (Figure 7) and Inconel 738 (Figure 8) are shown. More results will be available after finalization of samples investigation and evaluation.

CONCLUSION

The organizations from Czech Republic take part of extensive research program of power system using supercritical carbon dioxide. The sCO_2 power cycle chemistry and resistance of materials in sCO_2 are among the research topics. As typical impurities in sCO_2 cycles with indirect heating O_2, H_2O, H_2, CO, CH_4, N_2 and in some case also organic compounds (oil, etc.) were identified. As analytical methods suitable for CO_2 purity control Gas Chromatography with Helium Ionization Detector (GC-HID) connected directly with sampling point of the circuit and optical hygrometer with probe placed directly to the sCO_2 circuit were proposed. The methods will be tested. For trace concentrations of organic compounds determination the Gas Chromatography with Mass Spectrometry detector (GC-MS) can be used. This method was verified by analysis of real samples from sCO_2 loop operation. For separation of impurities from CO_2 the processes based on adsorption will be tested within the continuation of research program.

During the 1000 hours operation of sCO_2 experimental loop (with 550 °C and 20 MPa in test section) the test of material resistance was performed. Samples of about 20 kinds of alloys (ferritic and austenitic steels and nickel based alloys) were exposed in the test section of the loop. The investigation and evaluation of samples corrosion and degradation is not finished yet. However according to the preliminary results the significant corrosion was observed on ferritic steels. The thickness of corrosion layer on T92 was about 20 µm and the internal oxidation under surface layer was also observed. The austenitic steels and nickel base alloys proved high corrosion resistance in sCO_2 at 550 °C. On the samples of these materials only very thin oxide layers after exposure were observed.

The activities will continue in the next years of experimental program.

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