

Evaluation of Materials and Media Resistance in Waste Heat Recovery Systems

Great potential for reducing GHG emissions and increasing the efficiency of internal combustion engines lies in the use of exhaust heat. In waste heat recovery systems, the exhaust heat is at least partially returned into mechanically useable energy via rankine process. Working fluids and materials are subjected to high thermal and corrosive levels in such systems. At the Institute for Materials Technology of the Technische Universität (TU) Darmstadt, relevant media and materials were evaluated in the FVV project No. 1184 in terms of their chemical and thermal resistance.

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1 MOTIVATION

The sustainable reduction of Greenhouse Gas (GHG) emissions in the transport sector requires both new drive concepts and a further development of existing technologies. Great potential for reducing GHG emissions and increasing the efficiency of internal combustion engines lies in the use of waste gas heat. The waste gas heat is intended to be at least partially fed back into mechanically usable energy using the Rankine process in what are known as Waste Heat Recovery (WHR) systems. **FIGURE 1** shows a schematic representation of the key functional elements in the WHR process. A heat exchanger feeds the waste gas heat into an evaporator, which evaporates the moving fluid. The steam is expanded in a downstream expansion machine. With the aid of the over-

heated medium, the thermal energy is thus converted into mechanical work. The working fluid is then condensed. A key aspect in designing such systems is the selection of thermodynamically suitable media [1, 2] and materials as well as knowledge of their resistance (ageing) and possible interactions (material degradation). A further scientific challenge lies in developing a testing method for the valid transferability of the results.

2 EXPERIMENTAL SETUP

2.1 INVESTIGATED MEDIA AND MATERIALS

A total of three media groups were investigated [3, 4]. These are ethanol (ethanol blend), cyclopentane and acetone (technically pure). To depict a field-relevant worst-case formulation, it was decided not to use ethanol as a purified substance but rather to mix it with corrosion-stimulating components, **TABLE 1**. Cyclohexane was used as a denaturant. Steels with corresponding strength properties are relevant for the high-pressure side of the expansion machine under a high thermal load. A high-alloyed martensitic chromium steel X20Cr13 (material number: 1.4021) was exemplarily investigated. The samples exist as round specimens (diameter: 8 mm, length: 100 mm). In the area of the condenser with relatively moderate temperatures, aluminum materials are generally an option due to their lightweight construction potential and high thermal conductivity. The investigated aluminum material is the aluminum-manganese wrought alloy AlMn1Cu (EN AW-3003), which is braze-clad on both sides with AlSi7.5 (EN AW-4343). The material exists as rolled flat samples (length × width × sheet metal thickness: 100 mm × 12 mm × approximately 2 mm).

2.2 STATIC EXPOSURE TESTS IN HIGH-PRESSURE REACTORS

To assess the thermal resistance of the media and material resistance, exposure tests initially took place in a static medium in pressure-tight reactors. The reactors consist of CrNi steel X6CrNi-

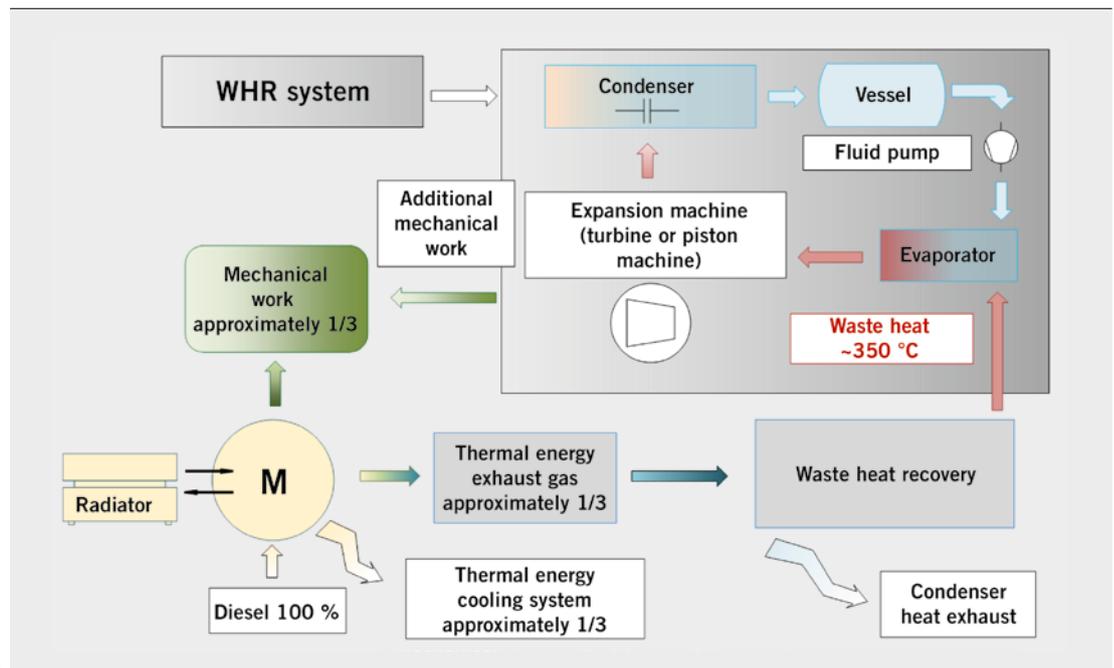


FIGURE 1 Schematic drawing of the WHR process (© TU Darmstadt)

Component	Unit	Concentration
Cyclohexane	% V/V	2
Water	% m/m	5
Chloride (as NaCl)	mg/kg	10
Sulfate (as Na ₂ SO ₄)	mg/kg	4
Formiate (as formic acid)	mg/kg	10
Acetate (as acetic acid)	mg/kg	40

TABLE 1 Composition of the ethanol blend (© TU Darmstadt)

MoTi17-12-2 (1.4571), **FIGURE 2** (left). Seals and inlays are made of PTFE. During the test, the internal pressure and medium temperature are recorded. This makes it possible, for instance, to document gases created as a result of corrosion processes. It is also possible to introduce nitrogen into the reactors in order to investigate the influence of oxygen partial pressure on the corrosion behavior.

2.3 IMMERSION TESTS UNDER CONDITIONS CORRESPONDING TO THOSE IN A WHR SYSTEM

The examination of media ageing and material resistance with a superimposed flow took place in a Rankine testing facility (made inert with nitrogen). This facility makes it possible to show the parameters relevant to the WHR system. The material samples were exposed in the flow direction before expansion (200 °C, 20 bar) as well as before condensation (approximately 150 °C, 0.6 bar) for a total of 1008 h, **FIGURE 2** (right). The maximum medium temperature in the condenser was 250 °C with a flow rate of 250 ml/min.

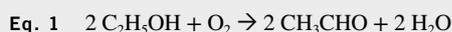
2.4 MATERIAL CHARACTERIZATION AND WET-CHEMICAL ANALYZES

The visual appraisal is based on high-resolution sample photos and on a confocal-microscopic assessment of the material surface to characterise corrosion morphology. Corrosion products, layer thicknesses and progressive selective metal dissolution were assessed metallographically. To identify a fundamental chemical change in the medium, the proportion of water (volumetric Karl Fischer titration) and electrical conductivity [5] were recorded. Oxidation and decomposition products were determined wet-chemically using gas chromatography (GC-MS). Ions were determined using ion chromatography (IC) [6].

3 RESULTS

3.1 THERMAL RESISTANCE OF THE ETHANOL BLEND

The investigations showed that a change in chemical composition can occur in the medium ethanol – based on the temperature and the available proportion of oxygen. The following reaction mechanisms can generally be found. Ethanol (C₂H₅OH) initially reacts with oxygen (O₂) to form ethanal (acetaldehyde, CH₃CHO) with the separation of water (H₂O):



Ethanal, in turn, is a starting product for subsequent reactions. An interaction also occurs with ethanol with the formation of 1,1-Diethoxyethane (C₆H₁₄O₂) and water:

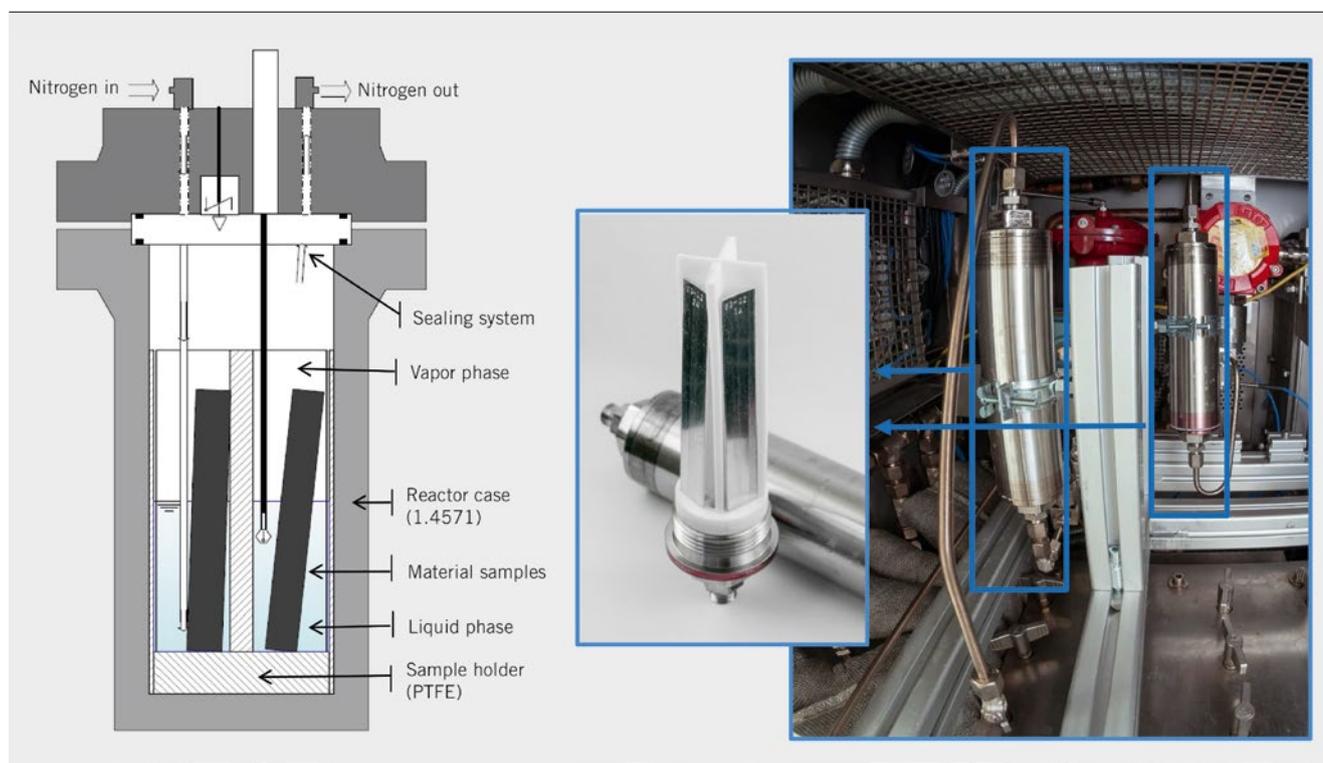


FIGURE 2 Schematic drawing of the reactor (left) and samples position in the WHR test bench (right) (© TU Darmstadt)

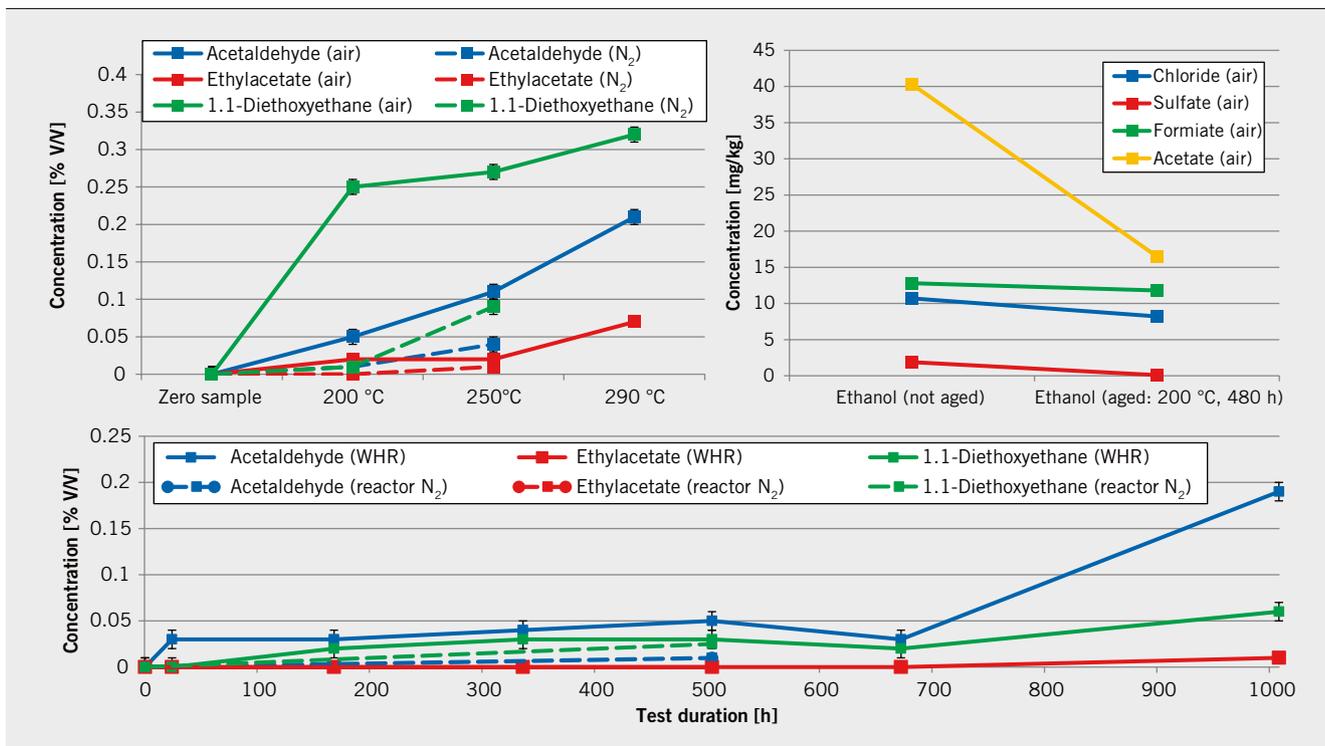


FIGURE 3 Oxidation products of ethanol (upper left) and ion concentration (upper right) as well as oxidation products of ethanol during immersion test in the WHR test facility (below) (© TU Darmstadt)

Direct oxidation of the ethanol with oxygen is also possible, resulting in acetic acid (CH_3COOH) as a reaction product:



Acetic acid, in turn, reacts with ethanol in an esterification reaction with the formation of ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$) and separation of water:



No oxidation products of ethanol can be verified using GC-MS up to a temperature of 60 °C. The formation of acetaldehyde (0.05 % V/V), ethyl acetate (0.02 % V/V) and 1,1-Diethoxyethane (0.25 % V/V) can be recorded following 480 h of exposure at 200 °C in air, **FIGURE 3** (upper left). The comparatively high concentration of 1,1-Diethoxyethane indicates a high acetaldehyde conversion rate. The balance in the reaction path clearly lies on the side of the 1,1-Diethoxyethane at this temperature. In a nitrogen atmosphere, all three products are in the order of 0.02 % V/V and are thus significantly lower than in air due to the lower oxygen partial pressure.

As the temperature increases to 250 °C in air, a further increase in 1,1-Diethoxyethane (0.27 % V/V) and acetaldehyde (0.11 % V/V) can be identified. There is no further increase of ethyl acetate. The constant production rate of ethyl acetate should be viewed in connection with the consumption of the acetate ion, which, in turn, is in equilibrium with the autoprotolysis of the dissociated acetic acid. Following exposure, a reduction in the concentration of acetate from 40 to 17 mg/kg can be documented, **FIGURE 3** (upper

right). Acetaldehyde increases disproportionately in comparison with 1,1-Diethoxyethane as this oxidation product is no longer consumed for the formation of further ethyl acetate. With a further temperature increase to 290 °C, a significant increase in all three oxidation products occurs once again.

Compared with the static exposure in the reactor in an oxygen atmosphere, there is less formation of oxidation products following exposure in the WHR testing facility, **FIGURE 3** (below). A reduced formation of acetaldehyde (0.03 % V/V) takes place after just 24 h. This value increases slightly to 0.05 % V/V up to 504 h. However, the value is around 2.5 times higher in comparison with static reactor exposure at 200 °C in an oxygen atmosphere after 480 h (dashed line), whereby the locally superheated medium temperature of 250 °C in the evaporator should be taken into account. A further increase in acetaldehyde to 0.19 % V/V can be recorded by the end of the investigation after 1008 h.

3.2 MATERIAL RESISTANCE OF SELECTED MATERIALS

A local electrochemical corrosive attack was shown for the aluminum material EN AW-3003/4343 after 480 h of exposure in the ethanol blend at Environmental Temperature (ET) and at 60 °C, particularly in the liquid phase, **FIGURE 4**. The corrosion-morphological structure already corresponds to the behavior known from the field of fuel corrosion [7, 8]. The corrosion depressions are up to 20 µm. The electrochemical attack can above all be attributed to the inorganic ions chloride and sulphate, which destroy the passive layer of the aluminum and accelerate the metal-dissolving process as an unstable intermediate corrosion product. The organic ions are also significantly involved in the cathodic sub-processes and the formation of corrosion products.

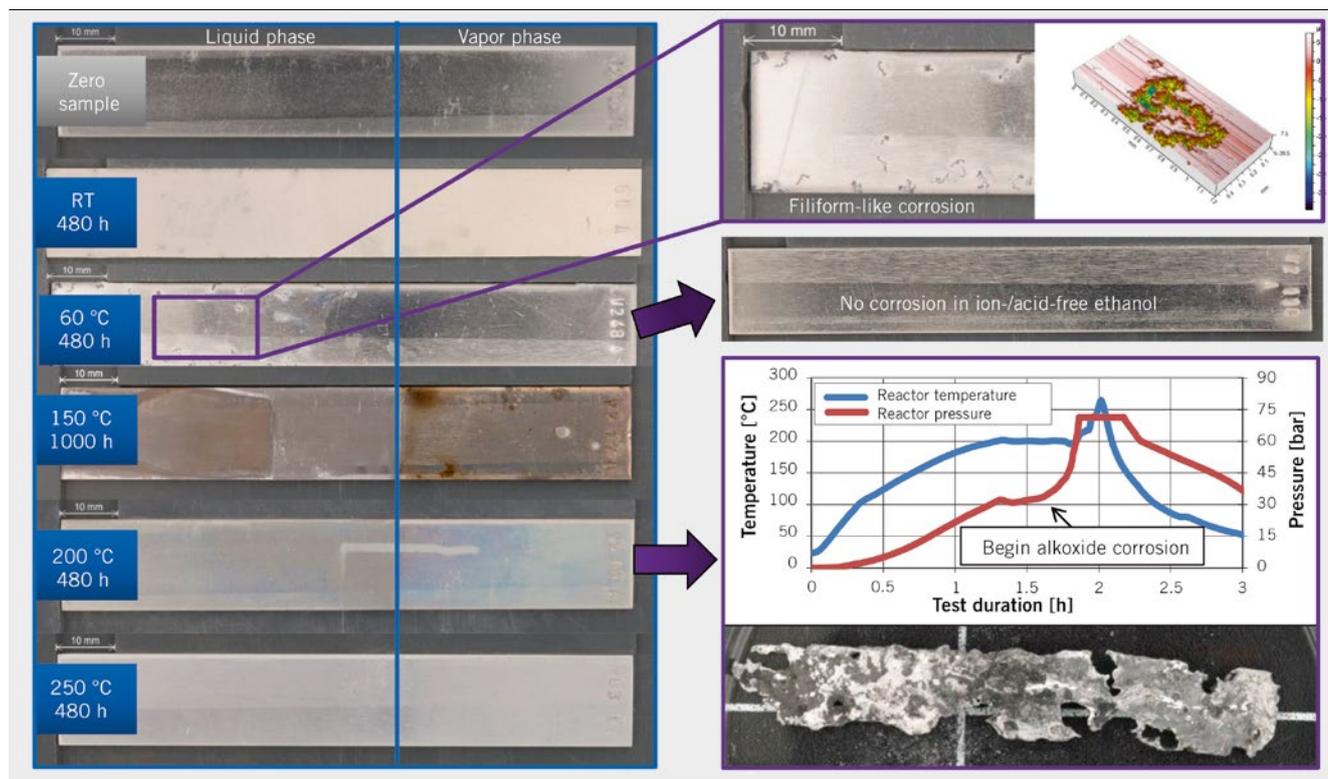


FIGURE 4 Sample documentation of the material EN AW-3003/4343 (© TU Darmstadt)

After an immersion test at a temperature of 150 °C, the material displays a discoloration of the surface, which indicates the formation of an additional passivating hydroxide layer. The hydroxide layers formed due to the proportion of water present due to the ethanol blend (5 % V/V) also lead to a significant increase in resistance towards alcoholate corrosion, whereby further test replications are required in order to make reliable statements [9, 10]. A valid assessment of the results is thus only possible using statistical methods [11].

For the immersion tests at 200 and 250 °C, a more differentiated corrosion pattern is shown – based on the oxygen partial pressure. A hydroxide layer is formed once again following exposure at 200 and 250 °C in the ethanol blend in air. There is no corrosion in terms of metal-dissolving material erosion, even if the formation of such hydroxide layers also fundamentally involves a surface change. However, at 200 °C in the reactor with a nitrogen atmosphere, significant material degradation is shown as a result of alcoholate corrosion after exposure duration of just approximately 1.5 h, **FIGURE 4**. Aluminum ethanolate ((C₂H₅O)₃Al) and hydrogen (H₂) are formed during the reaction of aluminum (Al) and ethanol (C₂H₅OH):



The hydrogen created would lead to a significant pressure increase of 79 bar in a closed reactor. The enthalpy of reaction for alcoholate corrosion is negative and thus exothermic, which results in an additional temperature increase following the initiation of corrosion.

The martensitic steel X20Cr13 exposed in the ethanol blend displays local corrosion attacks with the depositing of iron oxides

(corrosion products) at ET and at 60 °C, **FIGURE 5**. At 200 °C, a brown discoloration and isolated local corrosion in places (primarily originating at Si deposits as the local element) can be identified in the samples exposed in air. Such areas of corrosion cannot be found in the samples exposed in the nitrogen atmosphere at 150 and 200 °C, neither after exposure in the reactor nor in the WHR testing facility. This may be due to the passivating character of the oxidic reaction layers formed. The wet-chemical analysis using GC-MS also showed that the concentration of acetate at 200 °C is significantly reduced, which leads to an increase in the pH value in the environment. Susceptibility to corrosion is thus also reduced.

4 SUMMARY

As part of the research project, it was possible to develop and validate a suitable testing method to investigate the resistance of media and materials for use in WHR systems. As a rule, reactor immersion is suitable as medium/material screening with comparatively reliable results along with small expenditures (with regard to costs, test duration, testing apparatus). However, investigations under conditions corresponding to those in a WHR system are essential for a quantitative and temporal description using the Rankine process. Both material groups display electrochemical corrosion at temperatures of up to 60 °C, which is attributed to the ions contained in the medium. Passivating oxidic layers, which significantly reduce the reaction kinetics, are formed at 200 °C. Overlapping effects due to alcoholate corrosion with significant material degradation are to be noted with aluminum.

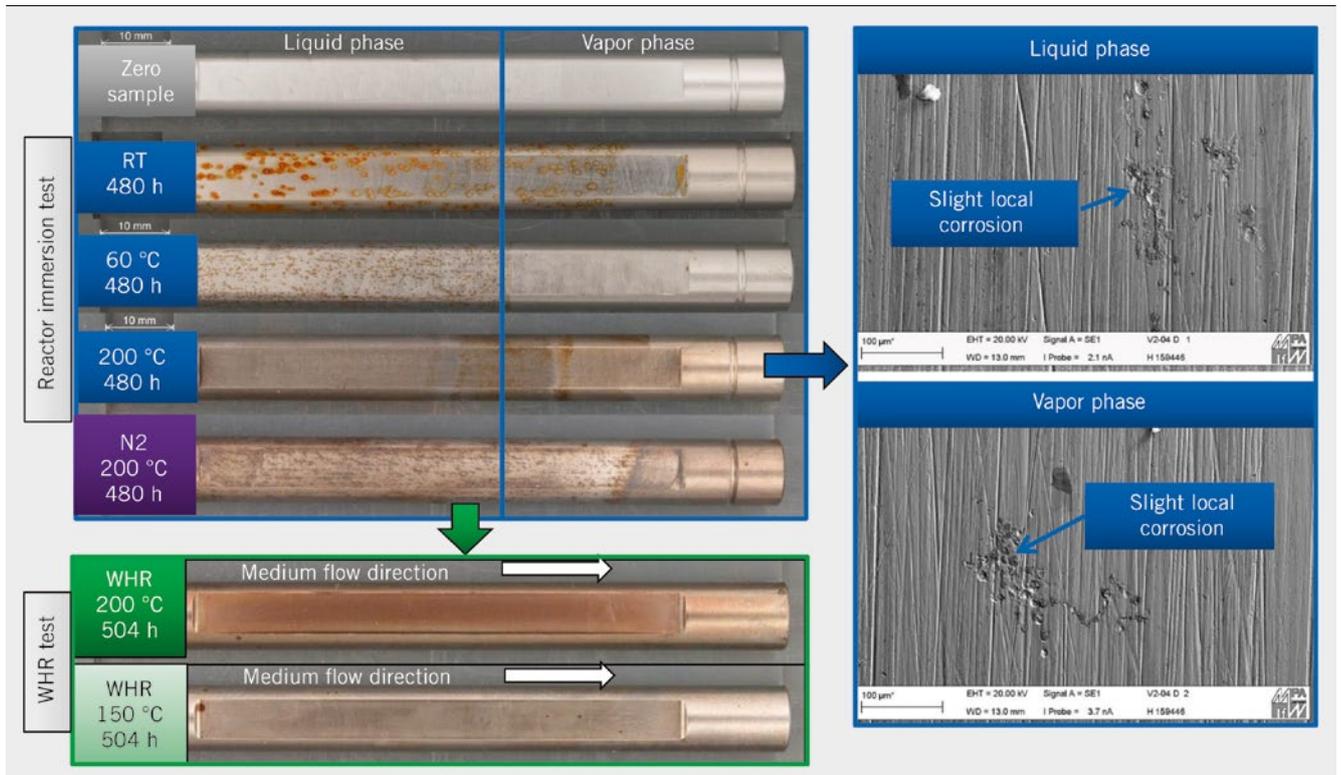


FIGURE 5 Sample documentation of the material X20Cr13 (© TU Darmstadt)

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