

INVESTIGATION OF CORROSION AND HIGH TEMPERATURE OXIDATION OF PROMISING ATF CLADDING MATERIALS IN THE FRAMEWORK OF THE IL TROVATORE PROJECT

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The aim of the IL TROVATORE project is the development, characterization and testing of potential materials for nuclear fuel rod claddings with enhanced accident tolerance. One main task of the ongoing investigations are testing of the cladding/coolant interactions under operational as well as accident conditions. A wide range of materials was already tested: oxides, MAX phases, SiC and iron based alloys. The paper gives a rough overview about the results of autoclave tests simulating operational conditions and steam oxidation tests at 1200°C covering transient design basis accident conditions.

The results of corrosion tests demonstrates the excellent performance of protective zirconia layers under operational conditions. Whereas chromia shows a low corrosion rate too, the water corrosion of alumina is problematic. The reaction rates obtained for Cr₂AlC MAX phase depends strongly on the porosity of the material. Dense material behaves well whereas the corrosion of porous material is fast. The best performance in the steam oxidation tests at 1200°C shows SiC followed by dense Cr₂AlC MAX phase, FeCrAl and high entropy alloys. Additional information concerning the reaction rates were obtained by measuring the hydrogen release. For several materials it could be shown that not only processes occur resulting in mass gain but simultaneous reactions take place resulting in a mass loss,

I. INTRODUCTION

The objective of the IL TROVATORE project, sponsored by the EU research and innovation program Horizon 2020, is the development and characterization of selected materials promising for accident tolerant fuel claddings (Ref(1)). The project comprises the fabrication and joining of the materials as well as the investigation of the mechanical properties, the irradiation behavior and the

coolant/cladding/pellet interactions. Four groups of materials were examined:

- oxides and silicates,
- MAX phases,
- silicon carbide and
- iron based alloys (FeCrAl).

Whereas the materials of the first two groups are candidates for coatings on zirconium alloys², the SiC and the iron based alloys can be also applied as bulk materials. Additionally to the aspect of possible oxidic and silicatic coatings, the characterization of the corrosion behavior of the oxides and silicates provides information about the performance of materials forming protective layers of alumina, chromia or silica. This passivation layers can be dissolved under operational and transient conditions.

This paper gives a rough overview on selected results of the ongoing corrosion tests in stagnant and flowing autoclaves as well as high temperature oxidation tests at 1200°C in steam. The aim of these studies was the preselection of materials for further investigations like irradiation tests in the BR2 material test reactor at SCK-CEN, long-term corrosion tests and oxidation tests at temperatures above 1200°C.

II. MATERIALS AND TEST CONDITIONS

II.A Materials

The investigations comprise the following materials divided into four groups:

II.A.1. Oxides

Oxides were investigated by two reasons: Firstly, they are candidate materials for coatings on zirconium alloys, FeCrAl or SiC. Secondly, the tests give hints on the performance of the ATF claddings, for instance

forming passivation oxide scales or undergoing rapid dissolution, under operational conditions. Both binary oxides (e.g., Al_2O_3 , Cr_2O_3 , etc.) and rare earth silicates (Y_2SiO_5 , $\text{Y}_2\text{Si}_2\text{O}_7$), were investigated in terms of their compatibility with the coolant (water, steam). The first batch of tested simple oxides and rare earth silicates included:

- pure alumina (99.99% Al_2O_3)
- lanthanum-doped alumina (La-doped Al_2O_3)
- yttrium-doped alumina (Y-doped Al_2O_3)
- pure titania (TiO_2)
- pure chromia (Cr_2O_3)
- ceria-stabilized zirconia (ZrO_2 - 12 mol% CeO_2)
- yttria-stabilized zirconia (ZrO_2 - 8 mol% Y_2O_3)
- yttrium orthosilicate (Y_2SiO_5)
- yttrium disilicate ($\text{Y}_2\text{Si}_2\text{O}_7$)

II.A.2- MAX phases

The MAX phases are nano-laminated ternary carbides and nitrides described by the $\text{M}_{n+1}\text{AX}_n$ general stoichiometry, where M is an early transition metal, A is an A-group element in the periodic table of elements, X is C or N, and n typically equals 1, 2 or 3 (Ref. 3). The tests comprised the following MAX phases:

- Ti_2AlC (two different grades)
- Cr_2AlC (three different grades: one porous & two dense)
- Ti_3SiC_2 (two different grades: one in both as-produced & pre-oxidized states)
- $(\text{Ti},\text{Nb})_2\text{AlC}$ solid solution
- $(\text{Zr}_{0.5},\text{Ti}_{0.5})_2(\text{Al}_{0.5},\text{Sn}_{0.5})\text{C}$ double solid solution

II.A.3. FeCrAl and iron based high entropy alloys

The first batch of tested FeCrAl iron containing alloys included:

- PM2000 ($\text{Fe-19Cr-5.5Al-0.5Ti-0.5Y}_2\text{O}_3$) –an ODS-FeCrAl alloy
- SH64 ($\text{Fe-16Cr-4Al-24Ni-1.5Nb-0.5Y}$)
- HEA40 ($\text{Fe-Ni}_{37}\text{Cr}_{22.5}\text{Al}_{4.5}$) a high entropy alloy

II.A.4. SiC_f/SiC composites & joining materials

The first batch of SiC-based materials included: SiC_f/SiC composites, and different SiC joining materials. Possible joining materials like rare earth silicates were investigated too.

II.B. Testing Methodology

II.B.1. Static autoclave tests at IIT

The material screening tests at Italian Institute of Technology (POLITO, Milan) were performed at a temperature of 360°C and a pressure of 18.7 MPa (equilibrium steam pressure), using a static autoclave. The tests were repeated three times subsequently in order to obtain an estimate of the scatter of the results. The

autoclave and the sample holders were made of 304 or 316L stainless steels to minimize effects associated with the aqueous corrosion of the equipment. Ion exchanged water was used for the tests. The water was replaced with fresh water after each test run. The duration of the test runs was 10, 5 and 5 days for the 1st, 2nd and 3rd test, respectively. The samples were fully immersed in water for the whole duration of the performed tests.

II.B.2. Static autoclave tests at SCK/CEN

These tests were performed at a temperature of 330°C and a pressure of 13 MPa in the PARR facility of SCK/CEN Mol, Belgium. A prototypic water chemistry was applied by adding 2 ppm Li as LiOH and 1000 ppm B as $\text{B}(\text{OH})_3$. The test duration was 14 days. No additional hydrogen was induced into the test water.

Before and after testing, the samples were cleaned ultrasonically in ethanol, followed by drying at 100°C in an oven for 30 min.

II.B.3. Loop tests at SCK/CEN

The tests using the CORTELINI loop of SCK/CEN were performed under similar conditions as the tests performed in the PARR facility but with flowing coolant. The pressure was 17 MPa. Additional to the water chemistry of the PARR tests, hydrogen (H_2) was added to the CORTELINI loop at a rate of 35 cm³ H_2 /kg water (possible range: 25-50 cm³ H_2 /kg water).

Technical difficulties were encountered during the 1st CORTELINI loop test, which were the reason that this test was shorter than the planned exposure of 30 days at 330°C. These difficulties were caused by the corrosion processes in the alumina-rich or alumina-forming materials. Spalled or dissolved and re-precipitated Al_2O_3 particles blocked the loop filters in more than one case resulting in the steep increase of the loop pressure. The SEM/EDS investigation of the filters confirmed the presence of Al_2O_3 particles suggesting that the alumina-rich materials were responsible for the filter blockage; this has led to the decision to remove these materials from the loop. The hydrothermal decomposition of alumina ceramics has been previously documented in the open literature² and is herein confirmed by their poor performance during the first CORTELINI loop test.

II.B.4. Steam oxidation tests at KIT

Steam oxidation tests were performed in the BOX furnace at KIT, in order to investigate the design-basis accident (LOCA) behavior of the candidate materials. These first screening tests were performed isothermally at 1200°C for 1 h. Heating and cooling at 10 K/min occurred in an argon (Ar) flow of 20 l/h through the furnace. Steam was supplied at a flow rate of 20 g/h after the test temperature has been reached and after holding for some minutes for temperature normalization. The argon gas and steam flow rates were controlled by a BRONKHORST

CEM system. The furnace outlet gas composition was measured by a quadrupole mass spectrometer BALZERS GAM300. This allowed quantitative determining the hydrogen release as a direct product of the reaction of the tested materials with steam. It is particularly important if the high temperature oxidation of the material results in both, weight gain and loss simultaneously for instance by the formation of a metal oxide scale on the surface (weight gain) and of volatile species like carbon oxides or silicon hydroxides (weight loss).

II.C. Post-Test Examinations

The corrosion behavior of the exposed materials was determined using the following range of characterization techniques:

- The samples were weighed to determine mass gain or loss, and the expected corrosion rate was calculated as an average of the corrosion rates measured for each one of the test runs.
- The sample dimensions were measured using a caliper, allowing calculation of total surface area and volume.
- The samples were visually inspected to detect possible color changes, macroscopic dissolution or loss of integrity, such as cracking or spalling.
- Scanning electron microscopy (SEM) was used to detect any corrosion-induced changes below the specimen surface.
- Raman spectroscopy was applied to detect the crystalline phases present on the corroded parts of the specimen surface.
- Grazing angle and classical X-ray diffraction (XRD) measurements were performed to verify the Raman spectroscopy results, regarding the crystalline phases present close to the sample surface.

III. RESULTS AND DISCUSSION

III.A. Tests under Operation-like Conditions

Table 1 provides an example of the data acquired from the first screening tests, after 20 days of exposure in water at 360°C at IIT. These data give an estimate of the corrosion rates, calculated as an average of the three tests conducted.

Figs.1 and 2 compare the corrosion rates of the oxides investigated in the tests performed at IIT and at SCK•CEN, respectively. For samples tested in both facilities, their corrosion rates are comparable except the relative high mass gain of the yttria-stabilized zirconia TZ8Y ZrO₂. The small quantitative differences could be expected due to the slightly different temperatures and the different water chemistry.

The results obtained after 24 day in the loop tests performed at SCK/CEN are summarized in Fig. 3.

Tab. 1. Summary of the IIT static autoclave test data, and average material corrosion rate after 20 days exposure.

Sample	Mass change	Mass change per unit area (mg/dm ²)	Average corrosion rate (µm/year)
Pure Al ₂ O ₃	-0,76	-353,0	-208,8 ± 34,4
La-doped Al ₂ O ₃	-0,21	-96,8	-53,9 ± 6,8
Y-doped Al ₂ O ₃	-0,44	-207,7	-95,6 ± 4,7
TZ8Y ZrO ₂	-0,010	-7,1	-1,9 ± 0,3
CEZ12 ZrO ₂	-0,014	-9,7	-2,2 ± 1,0
TiO ₂	-0,24	-97,9	-47,4 ± 29,3
Cr ₂ O ₃	-0,15	-91,4	-45,2 ± 13,7
Y ₂ SiO ₅	0,17	86,2	51,9 ± 16,9
Y ₂ Si ₂ O ₇	-0,353	-160,5	-84,0 ± 4,2

The excellent corrosion behavior of zirconia is visible in particular in the results of the tests performed at IIT. For the materials, possibly substituting the currently used zirconium alloys it is hard to reach the low reaction rates of zirconium based cladding tubes after formation of a dense and protective oxide scale. In particular, for the alumina forming materials, dissolution of the alumina scale is an issue⁴ at least as long as no other more protective oxide scales like chromia are formed. Low corrosion rates show TiO₂ and Cr₂O₃ too.

Also the relative high mass loss of two of the MAX phases investigated is remarkable: the Sandvik Cr₂AlC and the (Zr_{0.5},Ti_{0.5})₂(Al_{0.5},Sn_{0.5})C. The worse behavior of the Sandvik Cr₂AlC can also be seen in the results of the loop tests given in Fig. 3.

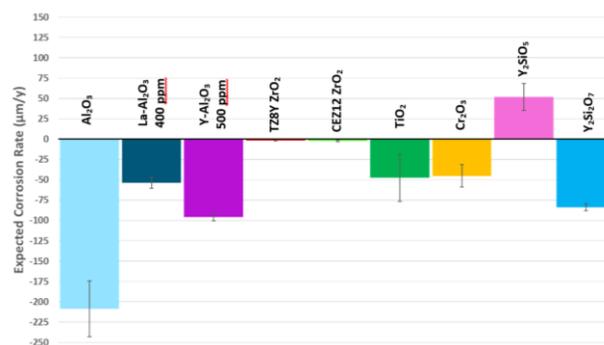


Fig. 1. The average corrosion rate of oxides (simple oxides and rare earth silicates) exposed to water at 360°C. Error bars correspond to the standard deviation.

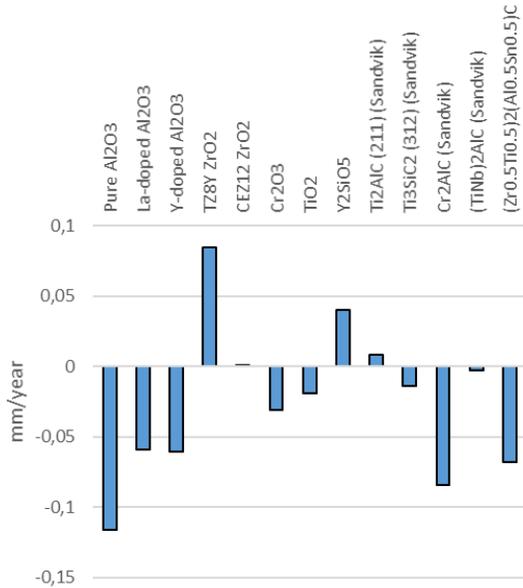


Fig. 2. Comparison of the material-specific corrosion rates, determined from the screening test in the PARR static autoclave at 330°C.

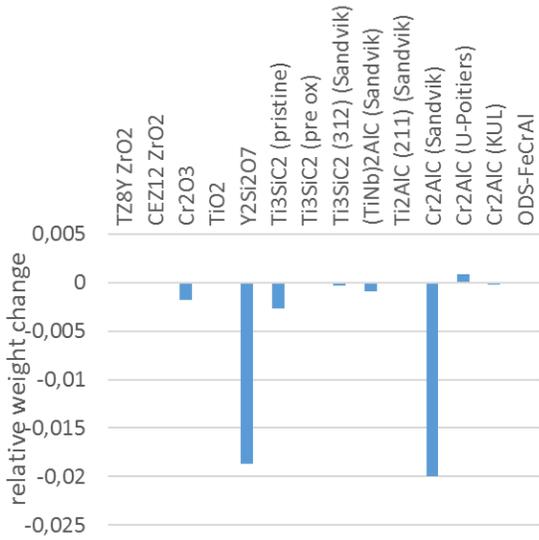


Fig. 3. Comparison of material corrosion rates after exposure in the CORTELINI loop for 24 days (no bar: weight change close to zero).

The reason for the high corrosion rate of this material differing significantly from the performance of the other Cr₂AlC investigated is the high porosity of this samples as can be seen in Fig. 4. This increases the reacting surface by orders of magnitude.

The oxide layer of the (Zr_{0.5}Ti_{0.5})₂(Al_{0.5}Sn_{0.5})C MAX phase consists of ZrTiO₄ and SnO₂ grains. The microstructure of this superficial oxide is shown in Fig. 5: The small nodular grains have a high surface roughness. The extensive formation of this oxide explains the large weight change in Fig. 2. Based on these findings,

(Zr_{0.5}Ti_{0.5})₂(Al_{0.5}Sn_{0.5})C was the least stable MAX phase ceramic.

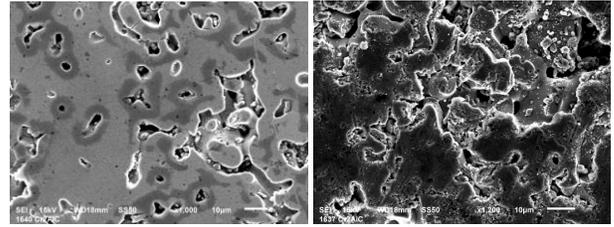


Fig. 4. SE detector images of Cr₂AlC: left pristine, and right after testing in the static PARR autoclave.

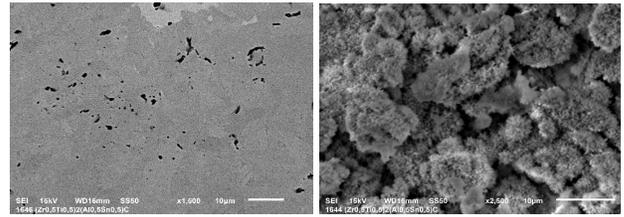


Fig. 5. SE detector images of the (Zr_{0.5}Ti_{0.5})₂(Al_{0.5}Sn_{0.5})C MAX phase before and after testing in the PARR autoclave.

Remarkably high mass loss of Y₂Si₂O₇, which is a joining material for silicon carbide, is confirmed from the loop test results. The reasons are the well-known high solubility of silica in water and/or the porosity formed during processing of the material.

III.B. Tests under Design Basis Loss of Coolant Conditions (1200°C)

Tab. 2 gives the results of the oxidation tests for 1 h at 1200°C in steam performed at KIT. The oxide samples were tested together. Therefore, no individual hydrogen release values are available.

The mass of most of the oxide samples slightly decreases except the two zirconia samples. The reason for the mass increase of the zirconia sample seems to be filling of oxygen vacancies of sub-stoichiometric ZrO_{2-x} as the shift of the zirconia XRD peak to lower angles confirmed. However, the effects for all oxide samples are small. The oxides are as expected stable under these conditions.

More relevant are the mass gain and the hydrogen release for the other materials.

In the group of the MAX phases, the porous Cr₂AlC and the (Zr_{0.5}Ti_{0.5})₂(Al_{0.5}Sn_{0.5})C show the highest reaction rates, similar to the corrosion tests given above. The high surface area of the porous Cr₂AlC also resulted in the high reaction rate calculated based on the geometric surface under these conditions.

The $(Zr_{0.5},Ti_{0.5})_2(Al_{0.5},Sn_{0.5})C$ sample has been completely oxidized. Fig. 6 shows a white thick layer on the sample, which was analyzed by XRD to be $ZrTiO_4$, which is a porous and non-protective oxide scale. This scale failed at the sample edges due to the high local stress concentration. The poor steam oxidation resistance of $(Zr_{0.5},Ti_{0.5})_2(Al_{0.5},Sn_{0.5})C$ indicates that this MAX phase compound is not suitable for the ATF application. Ti_3SiC_2 forms a double-layered oxide scale with high oxidation rate. Cr_2AlC , Ti_2AlC and $(Ti,Nb)_2AlC$ form protective alumina passivation layer.

The FeCrAl and the high entropy alloy HEA40 (both confirmed as alumina formers) show high resistance against high temperature oxidation.

Tab. 2 Results of steam oxidation tests at 1200°C for 1 h

Category	Sample	Mass change (g/m ²)	H ₂ release (g/m ²)
reference	Zircaloy-4 (Zry-4)	431.520	54.78
Oxide-based materials	Al ₂ O ₃ (SM8)	-0.925	-
	La-doped Al ₂ O ₃	-0.403	-
	Y-doped Al ₂ O ₃	-0.203	-
	ZrO ₂ CEZ12	2.364	-
	ZrO ₂ TZ8Y	4.728	-
	Cr ₂ O ₃	-5.704	-
	TiO ₂	-6.105	-
	Y ₂ SiO ₅	-4.932	-
Y ₂ Si ₂ O ₇	-0.839	-	
MAX phase-based materials	Maxthal® 211	8.201	4.26
	Ti ₂ AlC	3.431	2.57
	Maxthal® 312	70.292	21.79
	Ti ₃ SiC ₂	37.975	14.66
	Pre-oxid. Ti ₃ SiC ₂	44.211	12.52
	Cr ₂ AlC	2.834	3.97
	Porous Cr ₂ AlC	126.324	25.39
	(Ti,Nb) ₂ AlC	3.987	4.59
$(Zr_{0.5},Ti_{0.5})_2(Al_{0.5},Sn_{0.5})C$	532.178	124.31	
SiC/SiC	SiC/SiC	0.167	2.57
FeCrAl-based alloys	PM2000	1.668	2.80
	HEA40	2.368	4.36
	SH64	34.837	10.42

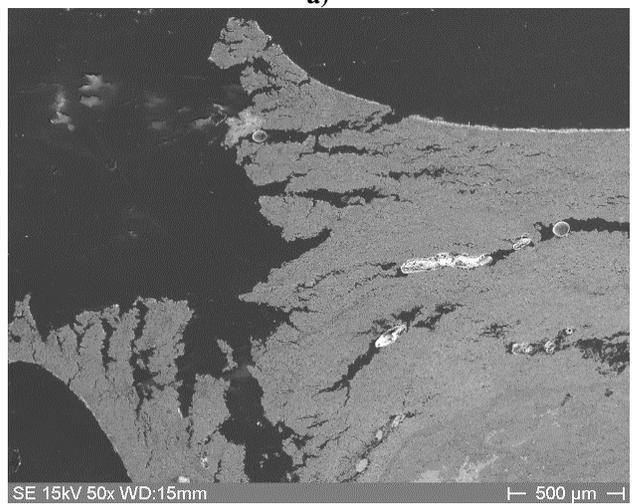
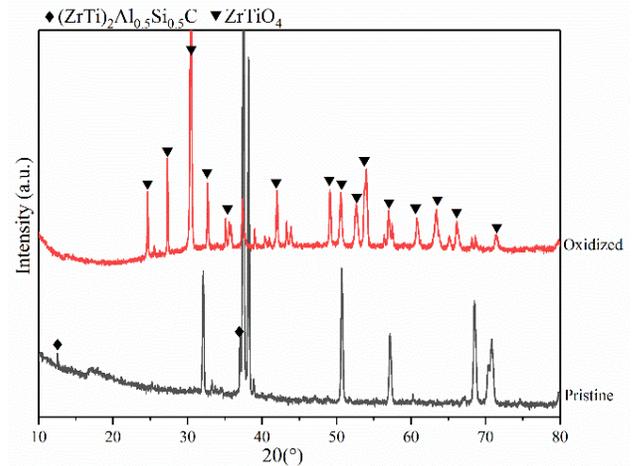


Fig. 6. XRD pattern of the $(Zr_{0.5},Ti_{0.5})_2(Al_{0.5},Sn_{0.5})C$ before and after testing (a); and SE detector image of a sample cross-section close to one of the edges (b).

As expected, the silicon carbide shows the lowest mass gain and hydrogen release at 1200°C. This demonstrates the excellent performance of SiC as possible cladding material under accident conditions.

Fig. 7 compares the ratios between sample mass gain and the mass of the released hydrogen. If the processes occurring during oxidation results only in mass gain and not in mass loss and no significant hydrogen uptake occurs, the ratio between sample mass gain and mass of the released hydrogen should be 7.94 (mass ratio between O and H₂ in H₂O). This value was measured only for the Zircaloy-4 reference sample. For the other ones, the ratio is significantly lower. This demonstrates that in all the other samples processes occur resulting in a mass loss like the formation of the volatile carbon oxide or SiO gases or spallation of oxide parts. This shows that the mass change alone give not the complete information about the oxidation behavior at least at high temperatures.

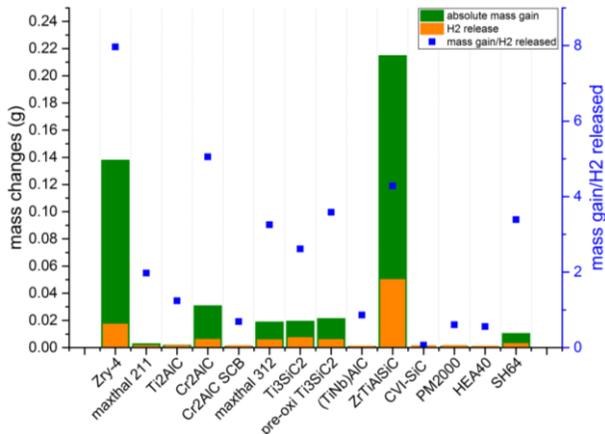


Fig. 7. Comparison of the sample mass gain and the mass of released hydrogen.

IV. SUMMARY AND CONCLUSIONS

In the framework of the IL TROVATORE project a wide range of potential ATF cladding materials are investigated and tested. In order to study the cladding/coolant interactions under operational and design basis LOCA conditions, autoclave tests at 330°C and 360°C as well as steam oxidation tests at 1200°C were performed.

Hydrothermal corrosion tests of various oxides demonstrated the excellent behavior of the currently used zirconium alloys. It is a challenge producing a material with such an excellent corrosion performance. Chromia showed the lowest corrosion rate after zirconia. Therefore, chromia forming coatings represent one of the most promising ones under operational conditions. On the other hand, alumina corrodes strongest among the oxides tested. In addition, the blockage of the loop filters by spalled alumina particles showed that alumina is not suitable as surface layer directly in contact to the coolant.

The results of the corrosion tests of the MAX phases are consistent with the results determined for the oxides. The chromia forming materials show low corrosion rates as long as the material is not porous.

The steam oxidation tests at 1200°C reproduce the low reaction rates of alumina and silica forming materials except for $(Zr_{0.5}, Ti_{0.5})_2(Al_{0.5}, Sn_{0.5})C$. No protective oxide scale is formed on this material. As expected, silicon carbide showed the best performance.

The comparison between the sample mass gain and the mass of released hydrogen indicate that at least for steam oxidation the sample mass change does not give the complete information. For example, during oxidation of MAX phases and silicon carbide, processes take place resulting in mass gain owing to the formation of the metal oxides layer as well as in mass loss due to the formation of volatile reaction products like hydroxides, SiO and

carbon oxides. Therefore, the measurement of mass change is not sufficient to analyse the reaction behaviour of these materials.

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