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Development of new cladding types for nuclear fuel

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Abstract. Three different cladding types were tested for nuclear fuel in traditional light water reactors and generation IV gas-cooled fast reactors. Cr coated Zr cladding was tested in steam atmosphere up to 1200 °C to demonstrate moderate oxidation and hydrogen production in accident conditions. 15-15Ti stainless steel alloy and SiC_f/SiC cladding tube samples were treated in helium atmosphere with different impurities for several hours at 1000 °C. Additional mechanical testing and microstructure examinations were carried out with as-received samples and with specimens after high temperature treatments. The experiments results indicated the applicability of the tested materials for reactor conditions in the investigated range of parameters.

1. Introduction

The cladding of the nuclear fuel elements serves as an important barrier against radioactive fission product release from the fuel rod. Furthermore, the cladding tube stabilizes the geometrical arrangement of fissionable materials in the reactor core. Most of current nuclear power plants operates with zirconium cladding tubes. The Zr alloys have low neutron capture cross section, good corrosion and irradiation resistance and high mechanical strength. However, at high temperature the creep of the Zr alloys become significant and in case of incidents or accidents, the steam-zirconium reaction may result in severe degradation of cladding capabilities.

After the Fukushima accident, it was recognized that a hydrogen explosion is one of the major risks of reactor safety during a loss of coolant accident (LOCA) in a light water reactor. The development of accident tolerant fuel (ATF) became a major concern in the nuclear industry. Several ATF cladding concepts are considered [1, 2, 3, 4] and one of the promising technology is to coat zirconium cladding with chromium.

The development of gas-cooled fast reactor technology includes the selection and qualification of fuel components capable to withstand very high temperatures The first core of ALLEGRO will be composed of UOX/MOX pellets in stainless steel 15-15Ti cladding, which was already tested in several sodium-cooled fast reactors for many years. There are very limited data available on the behavior of 15-15Ti cladding in high temperature helium atmosphere [5]. For this reason, a modest experimental program was launched at the Centre for Energy Research (EK).

The second core of ALEGRO could be built using ceramic fuel components. The 850 °C core outlet temperature will need the introduction of new pellets and cladding materials. The candidates are carbide pellets in SiC cladding. The applicability of SiC cladding in gas cooled reactor was addressed in several experimental programmes in the past [6, 7, 8] An important step of this work was the testing of SiC_f/SiC (silicon-carbide fibre reinforced silicon carbide composite) claddings in high temperature helium with the investigation of the effect of different impurities.

2. Coated Zr cladding for light water reactors

The International Atomic Energy Agency (IAEA) launched a Coordinated Research Project (CRP) on the Analysis of Options and Experimental Examination of Fuels with Increased Accident Tolerance (ACTOF) for the period 2015-2019. The CRP objectives included both corrosion and high-temperature oxidation tests. The aim of our studies was to investigate the consequences of high temperature oxidation on the chromium coated E110 type cladding material. (The E110 alloy contains 1% niobium and very low amount of hafnium. This alloy is produced in Russia for structural elements of nuclear fuel assemblies.) The samples were shared between the participating organizations. EK received chromium coated zirconium samples from the Czech Republic for testing at 1100 °C and 1200 °C. The test specimens were Cr-coated samples with about 25 μm coating and reference samples had no coating on the Zr surface (Figure 1.) [4]. The tube specimens were closed by two plugs, so one-side oxidation took place.

Figure 1. Cr coated (top) and reference Zr (bottom) specimens with 9.1 mm external diameter

The specimens were oxidised in steam mixed with 12 vol.% argon or in pure air atmosphere under isothermal conditions, at 1200 °C and 1100 °C. A high temperature tube furnace with a quartz tube was used for the oxidation of the samples. The experimental setup consisted of a steam generator, a three-zone horizontal furnace with temperature control system and a condensing system. A large vessel (approx. 6 dm^3) filled with cold water was placed under the outlet part of the furnace to quench the oxidised samples. The inlet of the furnace was maintained at 200 °C via a pre-heater to avoid condensation of steam. The outlet gas flow rate was measured by a calibrated bubble gas flow meter. The steam flow rate was about 2 $mg/cm^2/s$. It was determined by measuring the mass of the condensed water collected during the test period, divided by the oxidation time and the cross-sectional area of the quartz tube. After stabilization of the temperature and the steam flow, the quartz boat with the sample was pushed into the heated zone of the furnace. At the end of oxidation, the sample was quenched. The steam oxidation experiments were successfully completed. Table 1 contains the conditions and results of the high temperature oxidation.

Table 1. Results and conditions of the high temperature oxidation

Sample	Type	Atm.	Ox. temp. (°C)	Ox. time (s)	Initial mass (g)	Mass gain (g)	A (cm^2)	$\Delta m/A$ (g/m^2)
IAEA-02	Zr ref.	steam	1100	3600	11.02454	0.35719	18.64	191.6
IAEA-03	Cr coated	steam	1100	3600	9.96257	0.01582	17.96	8.8
IAEA-04	Cr coated	steam	1100	10800	10.26797	0.02497	18.25	13.7
IAEA-05	Zr ref.	steam	1200	1800	10.98722	0.43748	18.75	233.3
IAEA-06	Cr coated	steam	1200	1800	10.34523	0.02312	18.29	12.6
IAEA-07	Cr coated	steam	1200	2700	9.83425	0.02837	17.88	15.9
IAEA-08	Cr coated	steam	1200	3600	10.37083	0.03443	18.33	18.8

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The mass gain of Cr coated samples was very low compared to the reference Zr samples oxidised under similar conditions. The mass gain for Zr samples was 0.3-0.4 g, while the Cr coated samples showed only 0.01-0.04 g increase in steam atmosphere.

After the oxidation tests the tube samples were cut into five pieces. Three 8 mm long rings and two 14 mm long plugs were produced for further testing. From each sample two rings were used for ring compression tests.

Radial ring compression tests were carried out with a standard INSTRON 1195 type tensile test machine at 135 °C. The tensile test machine was equipped with a special furnace in order to keep the high temperature during the test. Each measurement started with a heat-up period (10 min) to establish uniform temperature distribution in the test section. The applied crosshead velocity was 2 mm/min. During the tests, the load-displacement curves were recorded. The results of the ring compression tests showed significant differences between the reference Zr cladding and the Cr coated tubes.

- The Cr coated IAEA-03 sample oxidised at 1100 °C for 3600 s indicated ductile behaviour. The ductile plateau continued after the plastic deformation for a long displacement. The Zr reference sample IAEA-02 reached 450 N maximum load. After that less and less load was enough to cause further deformation, but no clear breakdown was observed for this sample (Figure 2., left)).
- The oxidation at 1200 °C for 1800 s resulted in brittle Zr IAEA-05 samples with maximum force of ≈300 N. The large breakdown at 1.5 mm displacement indicated brittle fracture of the specimen. The Cr coated IAEA-06 rings could withstand loads above 500 N and remained ductile (Figure 2, right).

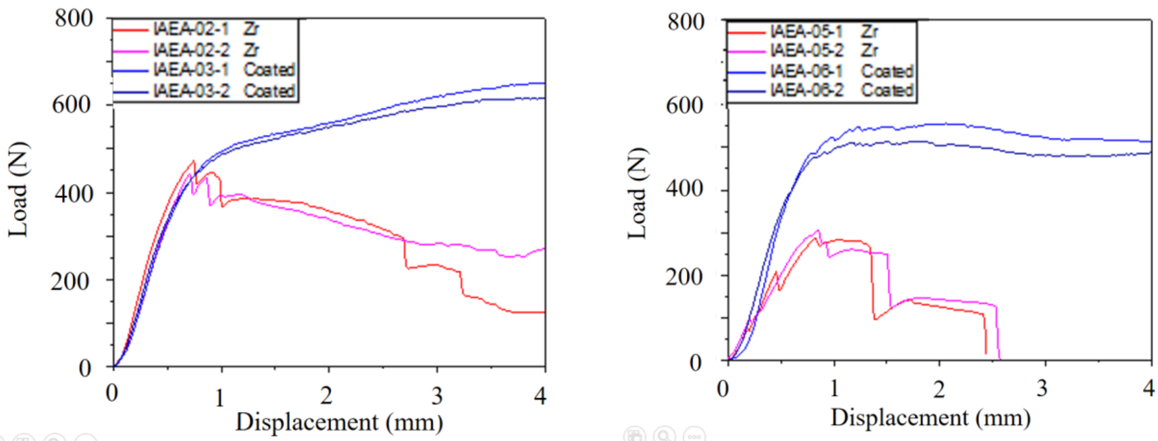

Figure 2. Load-displacement curves of ring compression tests with Zr and coated samples after oxidation at 1100 °C for 3600 s (left) and after oxidation at 1200 °C for 1800 s (right)

SEM examinations were performed to analyse the microstructure of a selected oxidised Cr coated sample. The studied sample was labelled as IAEA-08, oxidised at 1200 °C in steam atmosphere. The oxidation period was 3600 s. It was investigated both in as-received state and after grinding and polishing its cross sectional surface.

A scanning electron microscope (ThermoScientific Scios 2 type) was used for morphological studies. The elemental composition and the distribution of the most interesting elements were investigated with an Oxford energy dispersive X-ray microanalyser (EDX) with a silicon drift detector.

Figure 3 shows a typical Secondary Electrons (SE) image from the outer oxide layer and the neighbouring metal of the as received sample. Also, Backscattered Electrons (BSE) image of the ground and polished sample is represented.

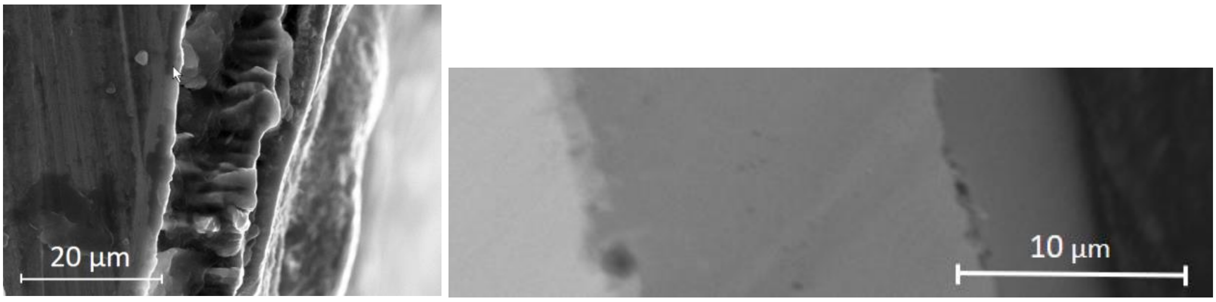

Figure 3. SE and BSE images of IAEA-08 cladding sample taken at 2000 (left) and 3500 (right) times of magnification

On the left hand side part of the SE image the surface of the E110G ring sample can be seen, which has remnants of the cutting process during sample preparation. At the edge of the sample two layers can be distinguished:

- a chromium layer, consisting of columnar crystallites, with thickness between 12 and 16 µm and
- a rather smooth layer of chromium oxide with thickness varying between 2.1 and about 5 µm, which is in good agreement with the data estimated on the basis of mass gain measurements.

On the backscattered electron images (BSE) image shown at right hand side of Figure 3., besides the above mentioned two layers, a third layer between the zirconium and the chromium layer can be recognized. It is brittle intermetallic Cr-Zr layer caused by interdiffusion of Cr and Zr composed of Cr_2Zr phase or $Zr(Fe, Cr)_2$ intermetallic Laves phases with the thickness of about 1 µm.

3. 15-15Ti alloy for the first core of ALLEGRO gas cooled fast reactor

The main objective of the planned experiments was the investigation of the behaviour of titanium stabilized DIN 1.4970 stainless steel claddings under conditions, which are similar to those expected in the ALLEGRO reactor. Furthermore, the high temperature testing in helium was focused on the effect of impurities, which may be present in the atmosphere of the reactor.

The cladding material DIN 1.4970 (15-15Ti) austenitic stainless steel was provided by Studiecentrum voor Kernenergie / Centre d'Étude de l'énergie Nucléaire (SCK·CEN), as support by the MYRRHA project for ALLEGRO. This cladding material was developed as part of the MYRRHA-project. The Ti-stabilized DIN 1.4970 (15-15Ti) austenitic stainless steel cladding tubes were manufactured in 2013 by Sandvik according to specifications from SCK•CEN [5].

The experiments were carried out in a laboratory at EK, in which several high temperature oxidation tests were performed earlier with traditional zirconium claddings [9, 10, 11, 12]. The test conditions were selected taking into account the parameters of GFR reactors and considering the available data on DIN 1.4970 alloy oxidation from other laboratories.

Table 2. Results and conditions of high temperature treatment of 15-15Ti samples

Sample	Atmosphere	Temp. (°C)	Time (s)	Initial mass (g)	Final mass (g)	Mass gain (g)	Mass gain (%)
Allegro–1	100% Helium 6.0	1000	25200	0.56777	0.56873	0.00096	0.3
Allegro–2	90% Helium 6.0 + 10% Hydrogen 6.0	1000	25200	0.56765	0.56768	0.00003	0.0
Allegro–3	90% Helium 6.0 + 10% Methane 4.5	1000	25200	0.56629	0.59128	0.02499	7.7
Allegro–4	90% Helium 6.0 + 10% Nitrogen 6.0	1000	25200	0.56586	0.56696	0.00110	0.3
Allegro-5	as received						

The review of potential impurities for the helium cooled HTR-10 reactor indicated that during normal operation H_2O, CO, N_2, O_2, H_2 and CH_4 components may be present in the atmosphere of the reactor [13]. It was decided to focus on the separate effect of different impurities. Hydrogen, nitrogen and methane were selected for further studies. High content (10%) of impurities were chosen in order to enhance the potential chemical reactions. Testing in pure helium was also a main item in the test programme. The selected test atmospheres are summarised in Table 2.

Treatment at 1000 °C temperature was selected in order to have higher than typical for ALLEGRO reactor temperature in the experimental facility. The treatment time was 7 hours (25200 s) for each test to have comparable conditions in different atmospheres. Furthermore, this period seemed long enough to indicate the potential effects of gases on DIN 1.4970 alloy. The high temperature treatment of DIN 1.4970 steel samples was carried out in a horizontal resistance furnace. The gas mixtures were injected at the inlet of the furnace. The gas flowrate was measured in the outlet section. The cladding samples were placed into a quartz sample holder, which could be moved in and out of the furnace inside a hermetically closed tube.

At the beginning of the tests the furnace was heated up to 1000 °C. When the stabilized temperature profile was reached the samples were moved into the furnace and the treatment was initiated. The gas flow rate was 5.9 $cm^3/(cm^2\ s)$ in the gas flow meter after the quartz tube. At the end of the treatment time (25200 s) the samples were removed from the tube and were cooled down in the external tube. Finally, the samples were taken from the sample holder and the mass changes were determined by weighing.

The change of the masses showed the followings results:

- The pure helium atmosphere resulted in small (0.3%) mass gain.
- The hydrogen content in the atmosphere seemed to have no effect on the mass change of samples compared to pure helium.
- The presence of nitrogen in helium showed 0.3% mass gain for the sample.
- The highest mass gain was measured in the case of methane impurity: the mass of the sample increased by 7.7%. The carbon deposition observed on the investigated samples caused the mass gain. The mass gain in methane atmosphere could be associated to the decomposition of methane at high temperature, which can produce carbon deposit: $CH_4 \rightarrow C + 2\ H_2$.

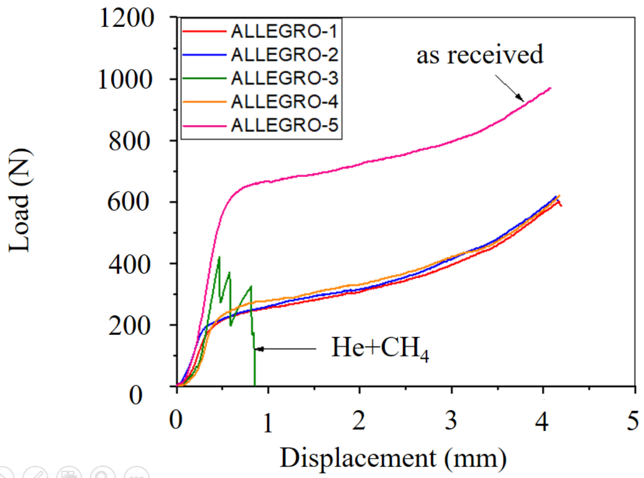

Figure 4. Load-displacement curves of ring compression tests with 15-15Ti samples after thermal treatments in different atmospheres

Ring compression tests were applied to characterize the compression resistance of the samples The as-received and pre-treated 15-15Ti ring specimens were examined in radial compression tests using an Instron 1195 universal test machine. The velocity of the crosshead movement was fixed at 2 mm/min, and the tests were performed at room temperature. In the mechanical tests the samples were loaded until

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failure or until maximum possible displacement. The high temperature treatment obviously softened the cladding material.

The ring compression tests showed ductile behavior for most of the samples. On the basis of load-displacement curves (Fig. 4.) the following conclusions could be drawn:

- Brittle failure was observed only for the Allegro-3 ring, which was treated in helium+methane atmosphere. It cannot be explained by the simple carbon deposition on the surface of the samples. However, due to the long (7 h) oxidation time and the high temperature (1000 °C) the carbon could interact with the steel and the microstructural changes could cause the brittle behavior.
- The elastic behavior ended at about 600 N force for the as-received sample (Allegro-5), the sample showed ductile behavior up to 4 mm displacement.
- The samples after treatment in pure helium (Allegro-1), in helium+hydrogen (Allegro-2) and in helium+nitrogen mixture (Allegro-4) ended the elastic deformation at about 200 N force. There were practically no differences between these samples in the mechanical behavior.

It was an important observation that the pure helium content did not result in brittle failure. So the suspected helium uptake and its embrittlement effect did not take place.

The failure of 15-15Ti cladding tubes in accident conditions was investigated in burst tests. An electrically heated, three-zone steel tube furnace was constructed and built to keep the steel samples at a constant high temperature. The high pressure argon gas was fed into the cladding samples by a needle valve, in order to maintain a certain rate of internal pressure increment. In the case of very small pressure increments, a 1 dm^3 buffer was put between the needle valve and the sample via a 0.7 mm inner diameter capillary to better regulate the argon flow.

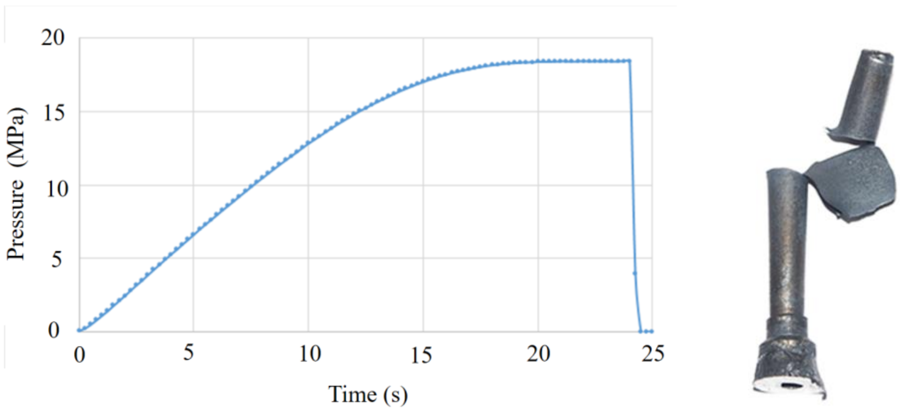

Figure 5. Pressure history and view of the 15-15Ti sample after burst at 1000 °C

The pressure was measured by two Suco 0720 type, linear mechanical– inductive transducers and two MAI-250 type Bourdon-tube manometers to read the pressure of the buffer and the sample during operation. The measurements were performed on 80 mm long stainless steel cladding samples. The pressure of the argon gas in the cylinder used as argon source was around 19 MPa at the beginning of the experiment and therefore this was the highest achievable pressure in the samples. This value has continuously decreased during the experiment as the argon gas has been used up. Burst of the samples with this pressure condition could be reached at 1000 °C temperature. Figure 5. shows the pressure history and the view of the sample after burst.

4. SiC_f/SiC cladding for the second core of ALLEGRO gas cooled fast reactor

SiCf/SiC cladding tubes were produced at Korea Atomic Energy Research Institute (KAERI) and their behavior was tested in the framework of extensive experimental series [6, 7, 8]. The work performed at KAERI with SiC_f/SiC composites for nuclear applications includes the development of light water reactor (LWR) fuel cladding and in-core components for very high temperature reactors (VHTR). One series of KAERI tests focused on the investigation of behaviour CVD (Chemical Vapour Deposition) SiC and SiC_f/SiC composite in the oxygen containing He and air. In air atmosphere positive mass gains were observed above 1100 °C [6].

Important step of qualification for gas-cooled fast reactor conditions was the testing of SiC_f/SiC claddings in high temperature helium with different impurities. Four Duplex (two-layer composite, cross section shown in the left hand side picture of Figure 6.) and four Triplex (three layer composite with polished external surface, cross section shown in the right hand side picture of Figure 6.) type specimens were treated in following atmospheres: 10% H_2 + 90% He, 10% N_2 + 90% He, 10% CH_4 + 90% He and 100% He. 1000 °C oxidation temperature was selected and the oxidation time was 7 hours. The change of masses showed the followings results:

- The pure helium atmosphere resulted insmall (0.02-0.04%) mass reduction for both Duplex and Triplex samples.
- The hydrogen content in the atmosphere seemed to have no effect on the mass change of samples compared to pure helium. Small mass reduction (0.02%) was detected in both sample types.
- In case of methane impurities the mass gain was measured. The mass of Duplex sample increased with 1.7%, while the Triplex with 0.3%.
- The presence of nitrogen in helium showed 0.03% mass reduction for the Triplex sample and no mass change for the Duplex one.

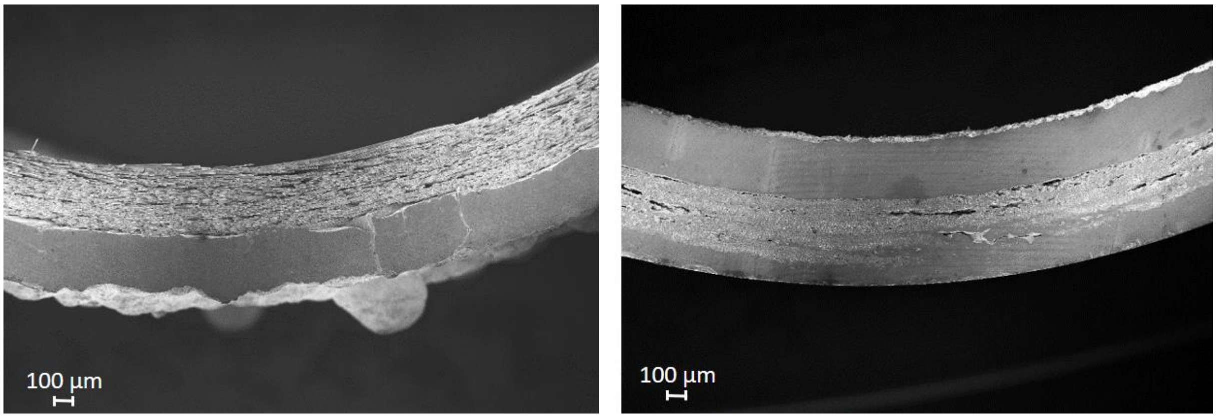

Figure 6. SEM images of Duplex (left) and Triplex (right) SiC_f/SiC tube cross sections

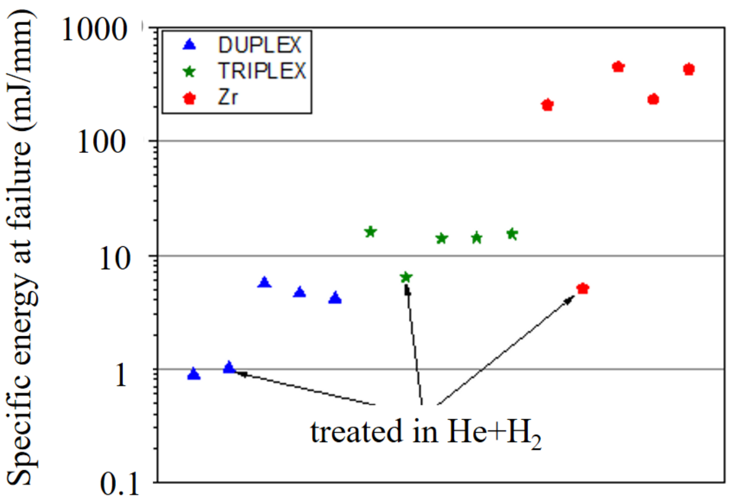

Figure 7. Specific energy at failure for Duplex, Triplex and Zr samples (the order of samples for all three series corresponds to treatments in He, He+H_2, He+CH_4, He+N_2 and as-received condition)

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Ring compression tests were applied to characterize the compression resistance of the sample. The as-received and pre-treated Duplex and Triplex ring specimens were examined in radial compression tests using an Instron 1195 universal testing machine. The velocity of the crosshead movement was fixed at 2 mm/min, and the tests were performed at room temperature. The rings were compressed until fracture of the samples. The comparison of Duplex and Triplex samples shows that the Triplex tubes have much higher compression resistance capability.

On the basis of load-displacement curves the specific energy to failure (related to unit length of the ring) was calculated. There were parallel zirconium (E110 type) cladding specimens tested in the high temperature helium environment under the same conditions as the SiC samples. The comparison of calculated specific energies at failure showed that for the SiC_f/SiC samples much less energy was needed to cause failure compared to Zr samples. Figure 7. shows these energy values for Duplex, Triplex and Zr samples in logarithmic scale. The last point of each series is the as-received sample. Figure 7. indicates that the treatment in hydrogen rich helium caused dramatic changes for all three types of samples, while the Duplex sample after treatment in pure He suffered the most impact.

5. Summary and conclusions

Three different new cladding types were tested in high temperature facilities. The investigations included mechanical testing and microstructure examinations, too. As general conclusion, the performed testing confirmed the applicability of all three cladding for reactor conditions in the investigated range of parameters:

- The comparison of Cr coated Zr tubes with the non-coated Zr specimens after oxidation in steam at 1100-1200 °C proved that the coated samples could withstand the high temperature conditions without severe degradation. Only modest oxide scale was formed on the Cr coating and the tube samples remained ductile. The internal metallic phase of coated tube did not suffer such changes, which are typical for uncoated Zr cladding.
- The thermal treatment at 1000 °C softened the 15-15Ti samples. The detrimental effect of methane resulted in brittle failure of the sample at low load. The burst tests proved that the DIN 1.4970 (15-15Ti) cladding tubes can keep their integrity at high temperature even with very high internal pressure. The failure pressure of samples tested at 960-1000 °C was above 18 MPa.
- The ring compression tests in SiC_f/SiC indicated that the compression resistance capability of Triplex type cladding is much better compared to Duplex ones. The comparison with traditionally used Zr claddings showed much less energy to failure for SiC_f/SiC samples.

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