

# CORROSION RESISTANCE AND HIGH-TEMPERATURE BEHAVIOUR OF ZR-BASED CLADDING MATERIALS WITH CHROMIUM-BASED PVD COATINGS

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Following the Fukushima Daiichi accident, new nuclear fuel cladding designs improving the performance and enhancing nuclear power plants' safety have been extensively investigated. The chromium-based accident tolerant fuel cladding coating designs were developed by ALVEL in the frame of the project sponsored by the Ministry of Industry and Trade and UJP PRAHA in collaboration with CTU in Prague. This study introduces a set of experiments determining a wide range of coated cladding material properties. Metallic Cr, CrAl and multicomponent CrN + Cr were tested, focusing on long-term corrosion resistance during normal operating conditions, high-temperature oxidation in the steam environment and mechanical properties during an accidental transient. All coatings revealed enhancement in corrosion resistance when compared to Zr alloy. However, diffusion of chromium into the zirconium substrate was observed for the metallic chromium coatings at temperatures above Cr-Zr eutectic. Coating deposition is further beneficial for claddings' mechanical properties. Overall, all tested coatings may be attractive candidates as possible ATF claddings.

## 1 Introduction

Zirconium-based alloy claddings used for current light water reactors possess various beneficial features during normal operating conditions. However, in accident scenarios, these cladding materials experience fast degradation and rapid exothermic reaction with high-temperature steam associated with hydrogen generation. The events in Three Miles Island (1979) and more recently in Fukushima Dai-ichi (2011) revealed the importance of developing enhanced accident tolerant fuel (ATF) claddings. [1][2][3]

The general demands for the before-mentioned ATF concepts are reducing oxidation kinetics in a high-temperature steam environment, minimalization of combustible hydrogen

generation, and overall improvement on cladding physical and mechanical properties. The increased coping time for severe accident management is likewise required. [4] A reasonable solution to improve the accidental tolerance of the zirconium alloy cladding in accidental conditions while preserving its behaviour under normal operating conditions is external surface modification via thin coating deposition.

When developing and licensing a new fuel cladding concept, it is essential to understand the damage mechanisms, i.e., the oxidation behaviour and mechanical properties under normal operating conditions and during the loss of coolant scenarios high-temperature steam environment.

The main objective of the experimental study conducted in UJP PRAHA in collaboration with CTU in Prague is to evaluate chromium-based coatings deposited by the physical vapour deposition technique. The ongoing long-term autoclave tests reveal its corrosion behaviour. Additional analyses focus on large break LOCA and design extension conditions. [5][6]

## **1.1 Materials and coatings**

### **1.1.1 Materials**

All the experiments were performed using Zirconium-based alloy as reference material. The as-received fully recrystallized Zr-1Nb cladding rods (OD = 9.1 mm, and thickness 0.57 mm) were cut and deburred according to specific experiment requirements. The longitudinally cut 30 mm tubular segments coated from all sides were used for long-term corrosion experiments. The 30 mm tubular segments with outer coated surface were used for high-temperature steam oxidation, and 95 mm segments were used for burst-tests. All specimens were ultrasonically cleaned in acetone, ethanol and demineralised water in 10-minute intervals. Afterwards, they were dried up in a furnace at 90 degrees Celsius. Additionally, the specimens' surface was treated by ion etching in the argon plasma for approximately 20 minutes to remove the thin Zr-oxide and other impurities before coating deposition.

### **1.1.2 PVD Deposition**

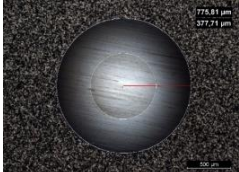
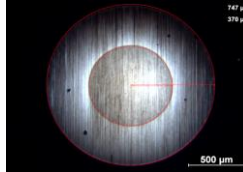
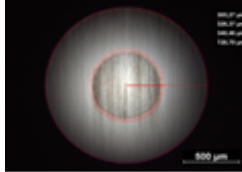
A variety of coatings and their combinations were chosen to be deposited. The metallic chromium (Cr) and chromium-aluminium (CrAl) were chosen to investigate due to their superb oxidation resistance, high thermal conductivity and increase in surface hardness. [7][8][9] The multi-layer CrN + Cr coating, was selected in order to enhance the adherence and to prevent the diffusion of chromium into the substrate under very high temperatures.

Zirconium specimens were coated using Hauzer Flexicoat 850 industrial system. Depending on the type of coating, the device may utilise a combination of different deposition techniques, such as sputtering, HIPIMS, PACVD and others. In this work, Unbalanced Magnetron sputtering has been used. During the process, the coating material is vaporised and transported through a low-pressure plasma environment to the Zirconium specimen, where it condensates onto the surface while forming a thin film. The sputtering was performed in DC mode using two cathodes with chromium targets. Negative DC bias was applied to the specimens. The working pressure was 0.2 Pa and deposition temperature 250°C.

The coatings were deposited on the outer surfaces of tubular samples. The thicknesses of the as-deposited coatings were measured using a Calotest (CSM, Switzerland),

as summarized in Table 1. The resulting coating layer dimensions varied from 14 to 20  $\mu\text{m}$  depending on the particular batch.

Table 1: Deposited coatings with corresponding thicknesses.

Coating	Cr	CrAl	Multicomponent CrN+Cr
Thickness [ $\mu\text{m}$ ]	18.6	14.4	15.4/18.6
Calotest			

Additionally, for the purpose of the investigation of coating layer cracking through the high-temperature transient, few specimens with the chromium coatings were artificially pre-damaged. Several scratches through the chromium layer were performed using the CSM Instruments Revetest Xpress device.

## 1.2 Experimental methods

Several experiments were performed to study the performance of accident tolerant concepts. The ongoing long term autoclave test were performed to study corrosion resistance compared to uncoated cladding material under simulated WWER normal operating conditions. High-temperature oxidation in steam was focused on a diffusive process of Cr into the Zr substrate. Thermomechanical tests were designed to understand the cladding deformation and the burst conditions during the LOCA phenomena.

### 1.2.1 Long-term corrosion

Long-term corrosion tests were done in a static autoclave with the WWER chemistry environment (Boron: 1050 ppm; Potassium: 15.9 ppm; Lithium: 1 ppm) for both - reference and coated specimens. The active volume of the autoclave is 4  $\text{dm}^3$ . The experimental temperature is 360  $^{\circ}\text{C}$ , and the pressure is 18.6 MPa.

The tests have been performed for 841 days with a predefined period of 21 days. After every period, the specimens were visually evaluated, i.e., the change of colour and spallation of the surface were described. Then, the specimens were weighed and measured. The results of weight gain have been used to determine the oxidation kinetics. Some of the specimens were removed for destructive testing, including hydrogen content analysis and metallography analysis.

### 1.2.2 High-temperature steam oxidation

Oxidation in steam occurs during DBAs such as LOCA. Based on the standard DBA fuel safety criteria, such as the 17% ECR limit, the high-temperature oxidation tests were performed in steam at 1200  $^{\circ}\text{C}$ . The experimental facility consists of a resistance furnace performing tests up to 1450  $^{\circ}\text{C}$ , temperature regulator, steam generator, piston pump, and ice-water container for fast quenching.

First, the retort was pre-heated and cleaned with Argon to remove the atmospheric gases. Consequently, it was conditioned with a mixture of Argon and Steam. Each specimen was held by a platinum wire. Following the conditioning, the specimen was inserted into the resistance furnace within a predefined temperature zone. The flow of the Argon and Steam mixture remained constant. Once the specimen reached the desired temperature, the timer was launched. The temperature was recorded throughout the experiment using the Platinum thermocouple installed near the specimen's surface. Just as prototypically presumed for LOCA, the specimen was eventually rapidly quenched into the ice-water at the end of the transient.

All specimens were characterised before and after testing. The characterisation techniques involved visual inspection, SEM, metallography, weight gain, and hydrogen content measurements. Detailed elemental composition was identified by performing the wavelength-dispersive spectroscopy (WDS) analysis. Three specimens (Cr-coated, Cr-coated (artificially pre-damaged), CrN/Cr coated multi-layer) were characterized using the Tescan Lyra3 GMU scanning electron microscope (SEM) with Field Emission Gun at an accelerating voltage of 15 kV. To conduct the WDS analysis, Fe, Cr, Nb, and ZrO<sub>2</sub> standards were used. To obtain the distribution profiles of Fe, Cr, Zr, Nb, and O, point analyses with a 2- $\mu$ m interval were conducted at the area below the outer wall in both directions – parallel and perpendicular to the specimen surface. The spectra were processed automatically by software IncaWave.

### **1.2.3 Burst test**

The burst test facility consists of the resistance furnace, temperature regulator and Argon containing reservoir to pressurise the specimen. Moreover, a constant flow of Argon is induced to the retort to prevent high-temperature oxidation. Before the experiment, both the reference and the coated tubular specimens were sealed using end-plugs and connected to the Argon reservoir. Each specimen was equipped with two K-thermocouples - enclosed and welded. Both pressure and temperature were measured online by pair of sensors.

Two different experimental methods of burst test were implemented. During the first one, the specimen was inserted into the pre-heated resistance furnace at 750 °C into a predefined temperature zone. After a while, when the Zirconium alloy was surely heated at the temperature stabilized, the specimen was pressurised. The experiment was terminated after cladding failure and consequent pressure decrease. A different method, called RAMP, was initiated at 360 °C. Subsequently, the pressurised specimen was heated with the given heating rate (1 - 6 °C/s) until its failure.

After the burst test, the specimens were visually analysed and photographed. The cladding diameter was measured in the position of the maximal deformation and the position of 20 mm from burst-opening, where uniform deformation occurs. The measurements were carried out both using tape and micrometre. The diameter measured with tape reflects the creep phenomena, whereas the diameter measured by micrometre has its relevance in water flow blockage in an assembly.

## **2 Results**

### **2.1.1 Long-term corrosion**

As shown in *Fig 1*, the results show meagre weight gains for coated specimens throughout the long-term corrosion test. Enclosed photos present a typical microstructure of coated

and uncoated materials after corrosion test in WWER chemistry. While uncoated specimens reveal the top Zr oxide layer, no change in microstructure occurs at coated specimens.

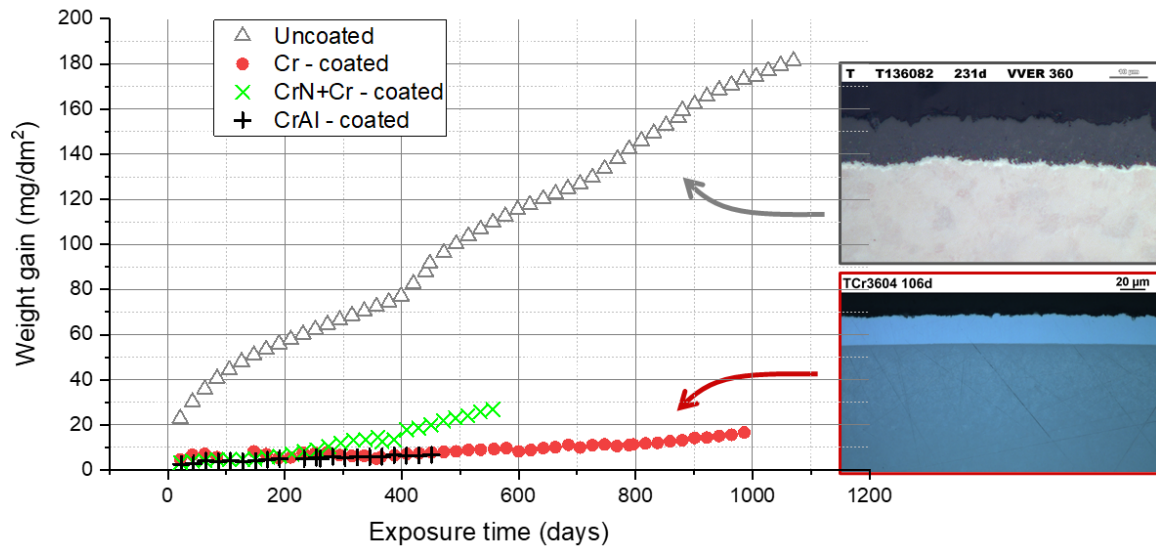


Fig 1: Weight gain of the coated and uncoated Zr alloy during the long-term corrosion test.

Fig 2 shows the results of hydrogen pickup and its concentration in the cladding after the corrosion test. The coated specimens exhibit a very low hydrogen pickup.

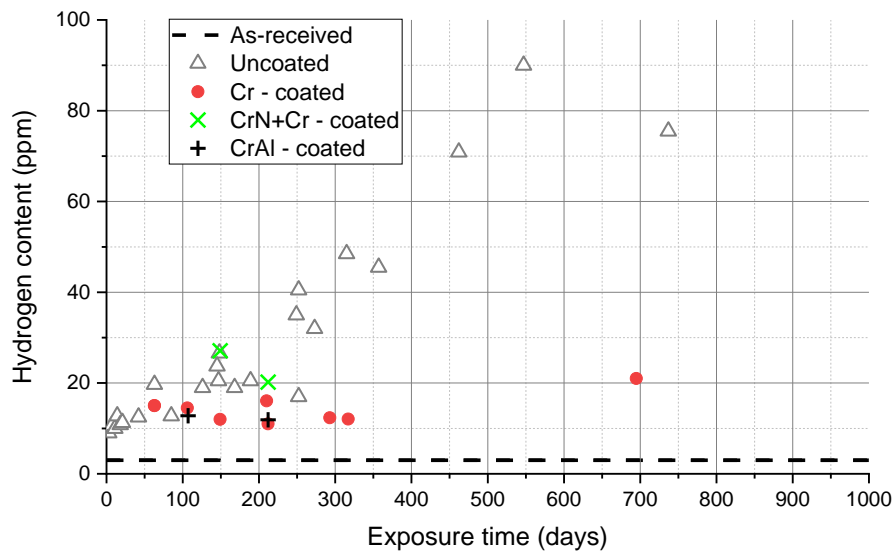


Fig 2: Hydrogen pickup of the coated and uncoated Zr alloy during the long-term corrosion test.

### 2.1.2 High-temperature steam oxidation

The weight gain was observed for all tested specimens. Results of tests at 1200 °C are summarized in Fig 3. Due to the oxidation from the inner uncoated side the weight gain is higher than for welded specimen exposed only from the outer side [6]. Nevertheless, the benefit of the coating (including the one with scratch) is for weight gain significant and the values for all coatings are very close.

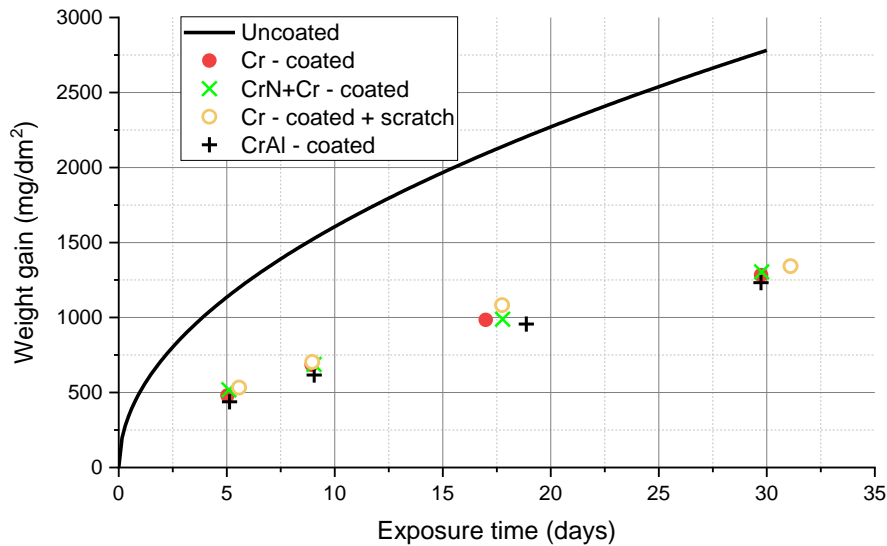


Fig 3: Weight gain of the coated and uncoated Zr alloy after high-temperature steam oxidation at 1200 °C.

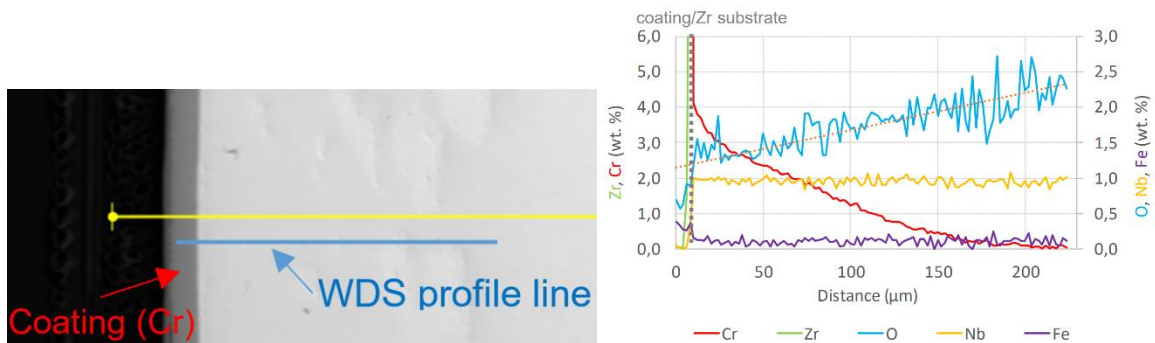


Fig 4: WDS profile, Cr-coated specimen, 9 min oxidation, metallography (left), detailed composition (right)

As it can be seen in the Fig 4, the Cr clearly diffused into the Zr substrate. After a 9-minute exposition to 1200 °C the Cr concentration dropped to zero at the distance of approx. 200 µm from the specimen's surface. Since the O diffuses only from the inner uncoated surface, its concentration constantly increases in that direction. In the Fig 5, there is a line scan of a 4,5-minute exposed specimen at the area close to the defect, not right below it, therefore the profile is not directly affected by the defect. After 4,5 minutes the Cr diffused approx. 150 µm far from the specimens' outer surface. In comparison with the single-sided diffusion of O shown in the Fig 4, the concentration of O is increased with any non-zero amount of Cr diffused. The cause is the accelerated diffusion of O through the area of coating defect leading to O dissolving rapidly in the Cr enriched substrate. The Cr stabilizes beta-Zr phase, where the diffusion coefficient is significantly higher than in alpha-Zr(O). The concentration of O rapidly drops when the Cr concentration reaches zero.

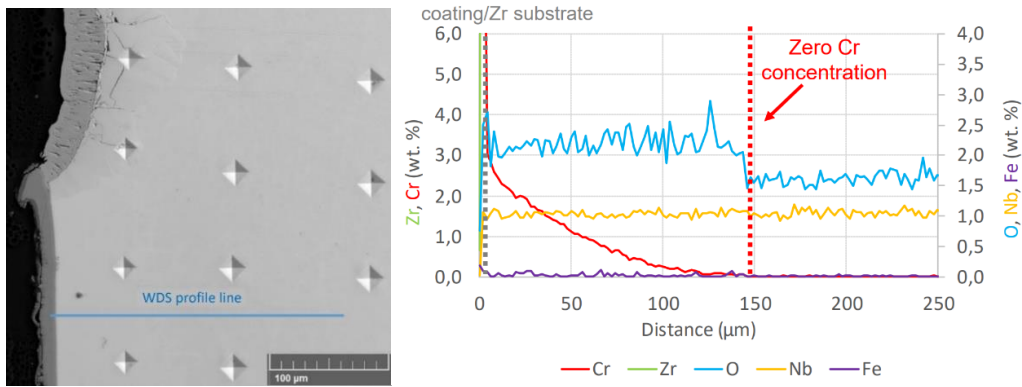


Fig 5: WDS profile, Cr-coated (damaged) specimen, 4,5 min oxidation, metallography (left), detailed composition (right)

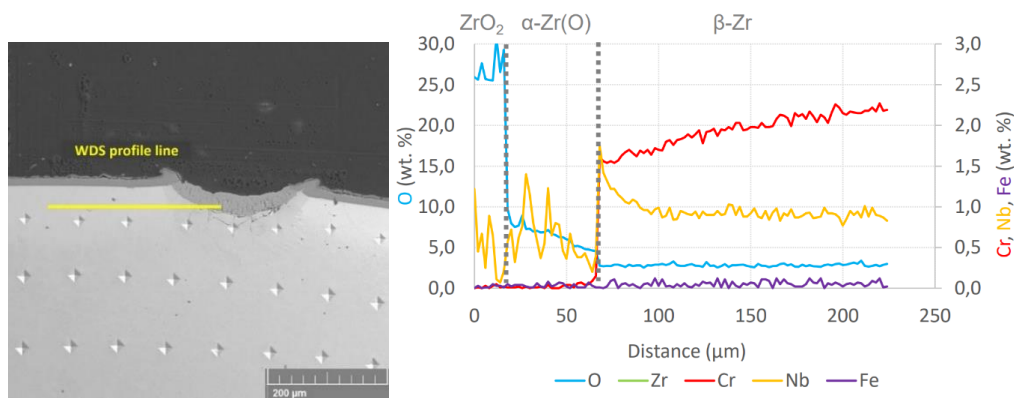


Fig 6: WDS profile, Cr-coated (damaged) specimen, 9 min oxidation, the parallel line to the coated surface at the distance of 25 μm, metallography (left), detailed composition starting from defect position (right)

The process diffusive process of Cr into substrate was measured also in a longitudinal direction, particularly in the parallel line to the coated surface at the distance of 25 μm (Fig 6). The graph demonstrates the fact that the Cr enriched substrate contains an increased amount of O, particularly the concentration of O is approx. 3 %. From those Figures, it can be confirmed that the presence of Cr dissolved in the substrate accelerates the diffusion of O. In the result, under the coating, there is an area with very rapid oxygen diffusion and significantly higher O dissolved than beta-Zr, which can have the major influence the mechanical properties.

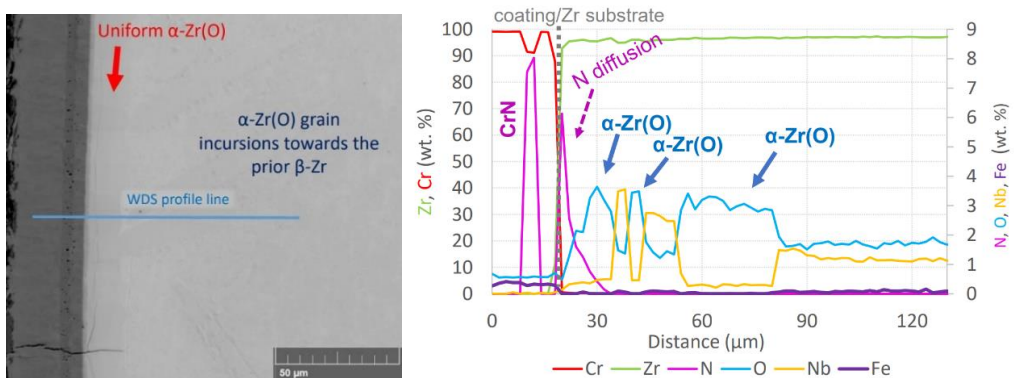


Fig 7: WDS profile, CrN-coated specimen, 9 min oxidation, metallography (left), detailed composition (right)

The diffusive process of Cr into the Zr substrate was not observed in the specimen coated with the CrN/Cr multi-layer. The reason behind this is a diffusion of N; therefore, the thin layer of ZrN is formed directly below the coating, and thus the diffusion of Cr into the substrate is impeded. Both N and O stabilize the  $\alpha$ -Zr(O) phase. The difference is, that the N remains equally distributed in a layer parallel to the coating surface and does not affect the inner substrate, and thus we can see the uniform  $\alpha$ -Zr(O) layer next to the coating. On the other hand, the O diffused in the substrate concentrates in  $\alpha$ -Zr(O) grains including the incursions towards the prior  $\beta$ -Zr phase, therefore several peaks and valleys in the O concentration can be seen in Figure 7.

### 2.1.3 Burst tests

Presented results of burst tests extend previous study [10] focused on thermomechanical properties of metallic Cr, multicomponent CrN + Cr and multi-layer CrN/Cr coatings. Recent experiments confirm the high resistance of coated specimens. As shown in Fig 8, coating usage prolongs time to burst compared to reference specimens.

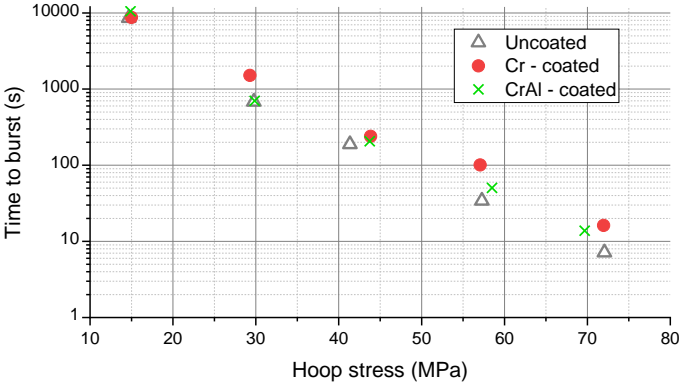


Fig 8: Time to burst at temperature 750 °C in relation to hoop stress for Cr and CrAl coatings and uncoated specimens

Fig 9 presents maximal deformation (left) and creep rate (right) for Cr and CrAl - coated and uncoated specimens. The maximal deformation has particular relevance in water flow blockage in assembly. The deformation was reduced for all tested coatings. The creep rate was determined from uniform deformation. Since the experiment was performed at 750 °C, the alloy stays in the  $\alpha$ -Zr phase with a low creep rate. It can be assumed that coatings decrease the creep rate.

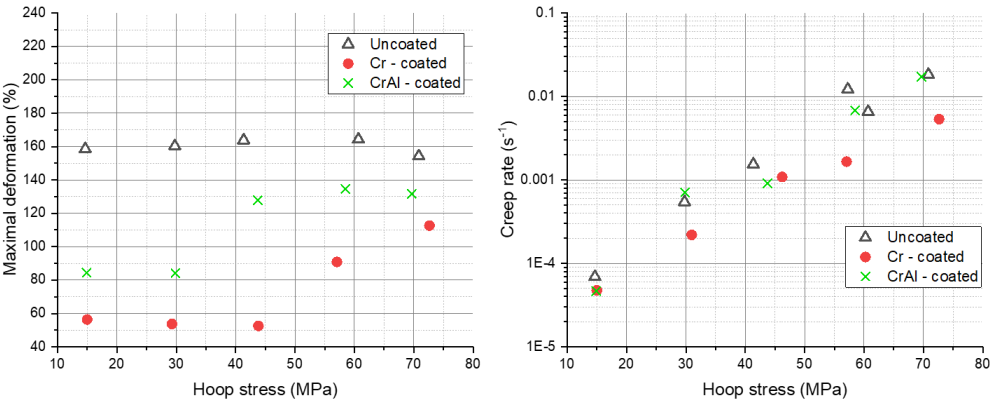


Fig 9: Maximal deformation (left) and creep rate (right) at temperature 750 °C in relation to hoop stress for Cr and CrAl coatings and uncoated specimens



### 3 Discussion

Cr-based coated cladding reveals apparent enhancement of corrosion resistance when compared to Zr alloy. The results show almost negligible weight gains for Cr, CrAl, and CrN+Cr coated specimens and minimal hydrogen pickup, connected to hydrides formation and cladding embrittlement. Nevertheless, the test needs to be continued to confirm the coated claddings behaviour up to the whole operation period.

The tests simulating high-temperature oxidation in the steam environment, typical for accidental scenarios, have shown Cr diffusion into the Zr substrate in case of Cr-coated specimens. Chromium enrichment leads to rapid oxygen dissolution in  $\beta$ -Zr, and the process results in embrittlement. The recently introduced multi-component CrN + Cr coating prevents Cr diffusion into the Zr substrate while maintaining its excellent performance.

A few specimens were artificially pre-damaged to simulate the coating layer cracking throughout the temperature transient and its influence on high-temperature oxidation. The experiments extend research in [11]. The chromium and oxygen diffusion in pre-damaged areas has been observed; although the impact of the scratches appears to be local considering the  $\alpha$ -Zr(O) formation, the enhanced oxygen dissolution under coating was observed. Therefore, a suitable methodology to perform mechanical tests is demanded.

Presented results of burst tests extend previous study [10] focused on thermomechanical properties of metallic Cr, multicomponent CrN + Cr and multi-layer CrN/Cr coatings. Continuous study confirms enhanced thermomechanical properties of coated cladding materials. Coatings efficiently prolong the time to burst, reduce maximal deformation and slow down creep phenomena. The whole range of temperatures relevant for the LOCA conditions needs to be investigated in the future.

### 4 Conclusion

New cladding materials with enhanced accidental tolerance for WWER reactors have been developed. The experimental study carried by UJP PRAHA in collaboration with CTU in Prague and ALVEL specializes in protective coating application on traditional Zr alloys. The continuous testing and optimization present an extensive project before the commercial implementation.

Tests simulating normal operation, including corrosion testing, were performed with very satisfactory results. However, some challenges, especially during DBA conditions, have come out. The Cr diffusion into the Zr substrate and its influence on oxygen diffusion has been confirmed. In response, ceramic multicomponent and multi-layer coatings were presented. Still, before the ultimate implementation, the ATF cladding should be further optimized and tested.

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