DEVELOPMENT OF CHROMIUM AND CHROMIUM NITRIDE COATED CLADDING FOR VVER REACTORS

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ABSTRACT: *Development of nuclear fuels with enhanced accident tolerance is one of the main current objectives of researchers around the world. The paper focuses on multi-layer cladding concepts developed in cooperation of CTU in Prague, UJP Praha a.s. and CEZ a.s. utility. Two coating materials - Chromium Nitride and Chromium metal were chosen as promising candidates for future applications based on the evaluation of metrics developed specifically for VVER reactor* [1]. *Coating materials were deposited on the E110 alloy currently utilized in VVER reactors by magnetron sputtering. The thicknesses of the coating vary from 5 microns to 20 microns. Fabricated samples were characterized before the testing to determine the exact thickness of the coating and other basic material properties as hardness and wear resistance. High-temperature tests were performed in conventional resistance furnace with various exposition times. Weight gains, thicknesses of the oxygen-rich zirconium alpha phase and hydrogen content were determined. Both types of coatings proved to be very protective at high temperatures. However, cracks appeared in the CrN coating during the oxidation, which led to an increase in hydrogen and oxygen absorption in the E110 substrate. The biggest cracks observed originate most likely from faults in the fabrication process. The chromium coating is very protective even above 1200°C. However, with longer expositions above 30 minutes, the oxygen diffused through the protective layer and created the layer of Zr-alpha phase homogeneously. This suggests that oxygen can diffuse through the layer rather than that crack appeared in the coating material. Burst tests for CrN-coated cladding showed a drastic reduction of displacement and decrease of the size of a balloon. Total deformation is considerably lower in the case of coated sample. Time to burst remains similar as in the case of the uncoated cladding.*

KEYWORDS: *ATF, coatings, chromium nitride, chromium, LOCA, high-temperature oxidation, burst test*

I. INTRODUCTION

The research of Accident Tolerant Fuels (ATF) accelerated due to the Fukushima accident in 2011 and various concepts have been developed around the world. The ultimate objective of the ATF development is to increase the coping time in case of an incident or accident and provide the operating staff more time to react and handle the event [2]. There are different options and concepts being developed around the world with various levels of benefits and required development time. The near-term options include mainly multi-layer claddings where traditional Zr-based alloys serve as a substrate and different layers are applied as protective coatings on various substrate materials.

This paper presents preliminary results of accident tolerant fuel cladding development for VVER reactors. The design of VVER cores differ from traditional PWR reactors in several characteristics, namely: the hexagonal geometry of fuel assemblies, material compositions (E110, E635), coolant chemistry, neutron spectrum etc. To include the specifics of VVER reactors, projects developing ATF fuels started in the Czech Republic and will continue for several years. The near-term concepts are based on the E110 alloy with different layers deposited by various techniques. Previous results of high-temperature testing of chromium coated cladding materials were studied by [3–5] and others, chromium nitride coatings are also considered as a potential ATF candidate but results are in comparison with pure chromium limited [6]. Further testing simulating accident and also normal operating conditions is needed for all ATF concepts before their potential insertion into commercial reactors. Testing of fuel performance in beyond design basis accident conditions (e.g. above 1200°C) is also planned to determine values of coping time for particular accident scenario.

II. METHODS
II.A. Materials and coatings

Due to the focus of the development on the VVER reactors, all the tests presented in this study were performed using the E110 cladding alloy, which is a binary Zr-Nb alloy used mainly in VVER reactors. The chemical composition of the alloy is shown in TABLE I. The tested tubular non-irradiated segments had the following dimensions: outer diameter 9.1 mm, length 30 mm for double-sided high-temperature oxidation, or 75 mm for a burst test. For burst test, the specimens were closed by end-plugs manufactured from a zirconium rod. The tubular samples were welded with the end-plugs using electron beam welding.

TABLE I. The chemical composition of the E110 cladding material.

wt. %	Nb	Hf	O	Zr
Zr1Nb	1.7 ± 0.1	0.05	0.04 ± 0.01	balance

The chromium and chromium nitride coatings were deposited on outer walls of zirconium alloy tubes by magnetron sputtering using the Hauzer Flexicoat 850 industrial system. Before deposition, the tubes were ultrasonically cleaned in acetone, ethanol, DI water and dried with a blower. The tubes were placed into a vacuum chamber on rotating holders where the tube surfaces were cleaned by ion etching in the argon plasma. This process removes the thin Zr-oxide on the substrate's surface and other impurities. The thicknesses of the coatings after the deposition was measured with an optical microscope and LUCIA G image analyzer and were found to be 10.6 +/-0.6 μm for Cr layer and 12.8 +/-0.3 μm for CrN layer.

First, magnetron sputtering was modified to reduce the maximal temperature and therefore to prevent re-annealing of the substrate alloy which is annealed at 600°C. Moreover, the residual stresses that build up in the coating are mainly resulting from differences between the coefficient of thermal expansion in coating and substrate. Reducing the deposition temperature leads also to the reduction of intrinsic stress in the coating.

II.B. High-temperature oxidation

Coated tubular segments were cleaned, degreased, and then weighted. The specimens were then exposed for variable time intervals to high-temperature steam at low pressure (0.1 MPa). The test was performed in a resistance furnace at a constant temperature. Since the steam oxidation samples were not welded, the oxidation was double-sided. The sample temperature was measured by a thermocouple placed inside the quartz tube just above a sample.

After the high-temperature oxidation, the samples were quenched in ice water, dried out, and then weighted. Then the segments of a fuel cladding were visually evaluated and cut into several rings for further investigation. The metallographic cross sections were prepared with the standard polishing procedure and metallographic evaluation followed.

Thicknesses of the chromium oxide layer, ZrO_2 layer and the α-Zr(O) layer (including the grains extended towards the β-phase region) were measured in more directions at both inner and outer cladding edges. An optical microscope and LUCIA G image analyzer were used for the metallographic analysis.

Parts of the samples intended for hydrogen content measurements were analyzed using the Analyzer G8 GALILEO (Bruker), which works on the inert gas fusion principle.

II.C. Burst test

First, the cladding segments were cleaned, degreased, and weighted. After that, the samples were filled with an inert gas (argon) at required inner pressure (corresponding to 120 bar at 600°C), and welded in a special pressure chamber using TIG method.

The cleaned and welded samples were then coated by the same procedure as described in the previous paragraph. Then, the specimens were exposed to an inert argon atmosphere at the constant temperature in a resistance furnace. The furnace is equipped with a window allowing to shot a video. The camera can precisely record ballooning of a sample. An image (video) analysis is then used to evaluate deformation of a sample during the experiment.

After ballooning and burst of the specimens, the samples were cooled using argon gas. The specimens were then visually inspected and evaluated. Later, the size of the opening gap and outer diameter in several positions were measured.

III. RESULTS
III.A. High-temperature oxidation

The visual evaluation showed very compact black or black-green surface for all Cr-coated samples. Nodular corrosion was observed in the case of CrN-coated samples: prior grey color was changing into black and local swelling was observed.

The coated samples were compared to the uncoated E-110 samples oxidized at the same conditions. A black oxide formed in this case as shown in Fig. 1. For longer time exposures (above 30 min at 1200°C which corresponds to 22% ECR for one-sided oxidation calculated using the Cathcart-Pawel correlation [7]) cracking, oxide spallation or decomposition of samples after quenching was observed.
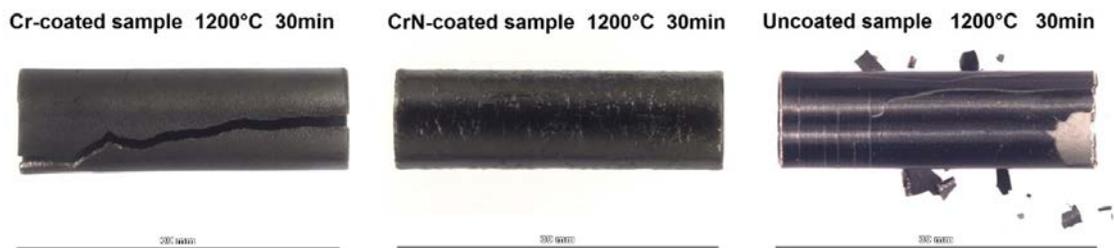

Fig. 1. Samples after steam oxidation at 1200°C for 30 minutes. Comparison of Cr, CrN coated and uncoated samples after oxidation and subsequent quenching.

After testing, significantly lower mass gains were measured for all coated samples. However, there were local coating failures observed after testing of CrN-coated samples which makes it difficult to clearly interpret the weight increase. In contrast, the results of mass gain measurements for Cr-coated specimens can be clearly interpreted and used for other purposes, because there were no local failures observed.

The metallographic observations were performed and results for coated samples are shown in Fig 2. The influence of coating is obvious from the comparison of outer (coated) side and inner (uncoated) side. Excellent behavior was observed for Cr-coating, where first α-Zr(O) grains under the coating were observed after 30 minutes and first ZrO_2 after 60 minutes. On the other hand, for CrN-coated samples were observed local cladding failures and nodular corrosion already for the shortest time of exposure (3 min).
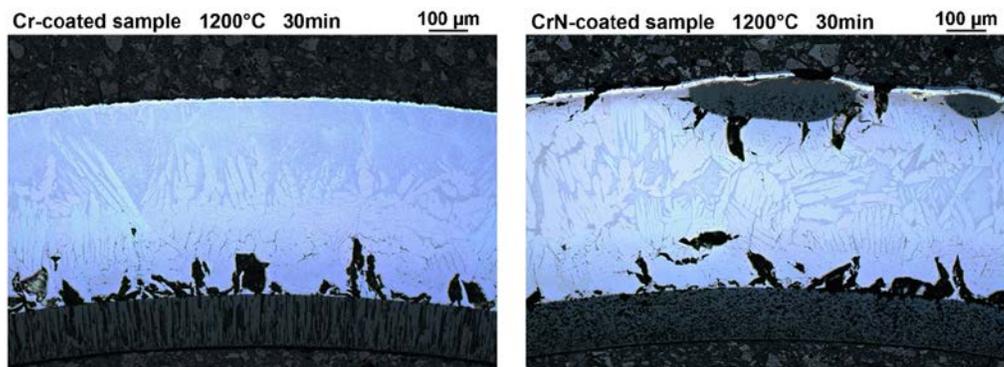

Fig. 2: Microstructure of Chromium and Chromium nitride coated samples after high-temperature steam oxidation. Both inner and outer surfaces were exposed to the same experimental conditions. The outer surface was coated by Cr or CrN (up) and the inner surface is uncoated (down).

Hydrogen content analysis showed that hydrogen absorption is directly connected to the behavior of coating. When coating failure appeared or oxygen diffused through a coating, the hydrogen absorption started. Due to the local defects, the detected hydrogen concentration was higher for all CrN coated samples (e.g.: 3 min ~ 21 ppm, 15 min ~ 76 ppm, 30min ~ 173 ppm). For Cr-coated samples, the hydrogen concentration increased slowly and at longer exposition times (45 min ~ 21 ppm, 60 min ~ 378 ppm).

III.B. Burst test

The burst tests performed with the CrN-coated sample and uncoated E110 samples showed a drastic reduction of displacement and considerable decrease of the size of a balloon. Total deformation is considerably lower in the case of coated sample, as is shown in Fig 3. Both tests showed similar characteristics in time to burst, deformation kinetics, and size of rupture. Surface observation of CrN coated sample showed cracks along the whole length of the sample. Metallography evaluation in six cross-sections along the specimen showed thinning of Zr-cladding, caused by plasticity during creep. No thickness changes for CrN-coating were observed.

Figure 3: Left: development of deformation during burst test; Center: image of CrN-coated (down) and uncoated sample (up); Right: diameter of CrN-coated and uncoated sample after burst test in several positions.

IV. CONCLUSIONS

Strongly protective behavior in high-temperature steam oxidation environment for the Cr-coating deposited on the E110 alloy by magnetron sputtering was shown. Similar behavior of the Cr coating was previously published [5] and results shown in this study confirm that chromium is protective also in combination with the E110 alloy and magnetron sputtering technique. No local failures were observed for Cr-coating. The corresponding value of ECR = 17% (limiting value for oxidation criteria) for one-sided oxidation was reached in between 45 and 60 minutes of time exposure (~ 55 minutes). In comparison with uncoated E110 samples, this difference provides about 37 minutes at temperature 1200°C before reaching the ECR criteria.

After testing of CrN-coated samples in high-temperature steam, local failures of coating for all tested samples at temperature 1200°C were observed. Observed cracking and failures of CrN-coating are related to transformation in microstructure (from CrN to $Cr_2N + N_2$). This decomposition occurs at temperatures below 850°C [8] causing cracking of the coating due to density differences between CrN and Cr_2N. For that reason, dichromium nitride coating will be tested in the near future to avoid phase changes and corresponding density changes.

Burst tests for CrN-coated samples showed a significant decrease of deformation (displacement and balloon size). On the other hand, time to burst has not increased by using coated sample and no plasticity or thinning of the coating was observed. This leads to a conclusion, that cracks in the CrN coating probably appeared at the very beginning of burst test.

Further investigation will be focused on chromium-coated samples during burst test and during normal-operating conditions. An autoclave test in VVER water chemistry will be also performed.

ACKNOWLEDGMENTS

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