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Study on the production of Cr-coated Zr-1%Nb tubes as an ATF evolutionary cladding candidate

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HIGHLIGHTS

- Advanced Technology and Accident Tolerant Fuels.
- Arc-PVD Coating condition.
- Coating defects (macro-particles and pin-holes).
- Fuel design evaluation tests.

ABSTRACT

After some accidents like TMI and Fukushima Daiichi, the belief that nuclear fuels can safely and reliably be used up to 65 MW.d/kgU was revised, and many efforts have been devoted to develope different Accident Tolerant Fuel (ATF) concepts. In this study, an optimized cathodic arc PVD (ARC-PVD) coating condition, from the coating layer homogeneity and defect density point of views, have been obtained. Two coating material (i.e. pure Chromium and Chromium Nitride) with thicknesses up to 10 microns on typical VVER-1000 cladding tubes (Zr-1%Nb alloy) are developed. Presented SEM results approved improvements in coatings visual properties, and further modifications have been postponed until finalizing the performance examinations in normal operational as well as accidental conditions (LB LOCA). Eventyally, the general list of planned tests, from characterizations to mechanical and performance viewpoints, which are currently being carried out, is reported.

KEYWORDS

Accident Tolerant Fuels (ATFs)
Coated cladding tubes
Zr-1%Nb
ARC-PVD

HISTORY

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1 Introduction

Nuclear fuels have been under continuous enhancement during the last decades, and it was believed that they could be used safely and reliably up to 65 MW.d.kg^{-1}U^{-1}. However, after a sequence of events in the Three Mile Island and Fukushima Daiichi, the research of ATFs accelerated, and various concepts started to be examined more seriously. Recognizing that the current fuel designs are vulnerable to severe accident conditions, renewed interest in alternative fuel designs that would be more resistant to fuel failure and hydrogen production (IAEA-TECDOC-1797, 2014). Different concepts, from modifications and improvements of existing technologies to the introduction of revolutionary materials have been considered, as illustrated in Fig. 1 (Krejčí et al., 2020).

Among different alternatives concerning the increase of cladding accident tolerance, Cr-coated cladding is common to various fuel manufacturing companies as a short-term resolution (Shirvan, 2020); The reason is that the kinetics for oxidation of Cr-coated samples is several orders of magnitude slower than that for Zr alloys at LOCA conditions (Terrani, 2018).

AREVA has tested Cr-coated Zircaloy-4 samples in the 1000 to 1200 °C temperature range (typical of LOCA conditions) under steam, and then water quenched down to Room Temperature (RT). In Fig. 2, the weight gain as a function of the steam oxidation time at 1200 °C is illustrated. As it can be seen, coated materials display a much slower high-temperature (HT) steam oxidation kinetics, up to 1500 s at 1200 °C (Schuster et al., 2015).

In addition to Cr-coated Zr claddings as an ATF promising candidate, Chromium Nitride-coated cladding materials are considered, and results have been compared with Cr-coated samples in different publications (Krejčí et al., 2017; Daub et al., 2015; Van Nieuwenhove et al., 2018; Meng et al., 2019). To compare CrN with Cr coatings, the main drawbacks are summarized as follows

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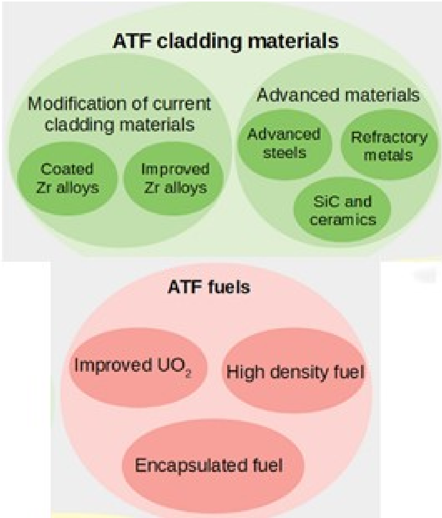

Figure 1: Classification of different ATF concepts around the world (Krejčí et al., 2020).

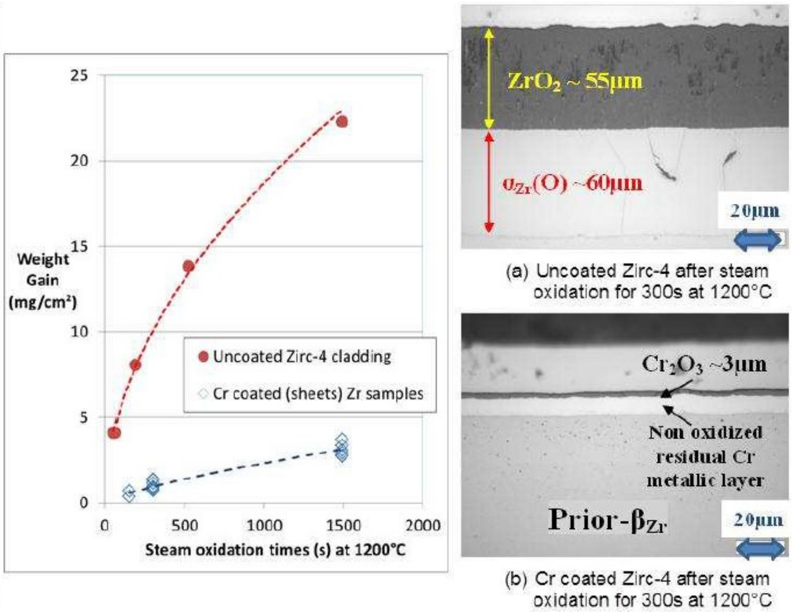

Figure 2: Comparison between the respective HT steam oxidation behaviors at 1200 °C of uncoated vs. Cr coated Zircaloy-4 samples (Schuster et al., 2015).

(Krejčí et al., 2020, 2017; Krejci et al., 2017):

- Cr + Zr eutectic formation at about 1330 °C.
- Cr enhanced embrittlement of Zr substrate at accidental conditions.
- Hydrogen permeability through coatings and their oxides and/or potentially increased H-pickup fraction.
- CrN cracking at high temperature due to phase changes.
- Limited ductility of ceramic materials such as CrN.

Studies on Cr and CrN coatings are still under accomplishment, and researchers are working on possible remedies to enhance the aformentioned drawbacks. For instance, Nitrogens in CrN can migrate towards the Zr substrate at relatively lower temperatures and form ZrN layer, which prevents the formation of eutectic Zr-Cr at 1330 °C. So, double-layer Cr/CrN coating has been considered as a promising alternative as well.

However, another concern from the coating perspective itself is the coating methodology. There are a wide range of coating techniques, such as chemical vapor deposition (CVD), laser coating, physical vapor deposition (PVD), and cold spray (CS) techniques. However, the PVD technique has been frequently used to produce Cr-coated cladding samples, and its applicability has been checked in different studies. Among diverse PVD techniques (some are shown in Fig. 3), cathodic arc evaporation is a method that is commonly used for the same goal as this study, and will be discussed later on.

Defects are inevitable in every deposition method and

Table 1: Coating condition.

Coating method	Cathodic Arc Evaporation or Arc-PVD
Evaporation current	130 A
Bias voltage on the sample	100 V
Sample rotation speed	4 RPM
Sample temperature during coating	About 300 °C
Coating thickness	6 to 10 microns
Atmosphere Pressure during coating:	1×10^{-5} torr
reactive gas control method	by MFC
Coating duration (hours):	
Cr (pure)	10
CrN	7
Atmosphere Reactive gas:	
Cr (pure)	-
CrN	N_2

can not be removed entirely but must be reduced as low as possible. In PVD arc evaporation, the size distribution of particles migrating from the target towards the substrate is a crucial factor controlling the coating layer homogeneity. Two commonly observed defects in PVD arc evaporation coatings are pin-holes and macro-particles. Unfortunately, there are no significant studies on the dependensy of corrosion rate in Cr or CrN coated Zr tubes available, and since it can affect the manufacturing costs, furthur experiments on this issue seem to be essential.

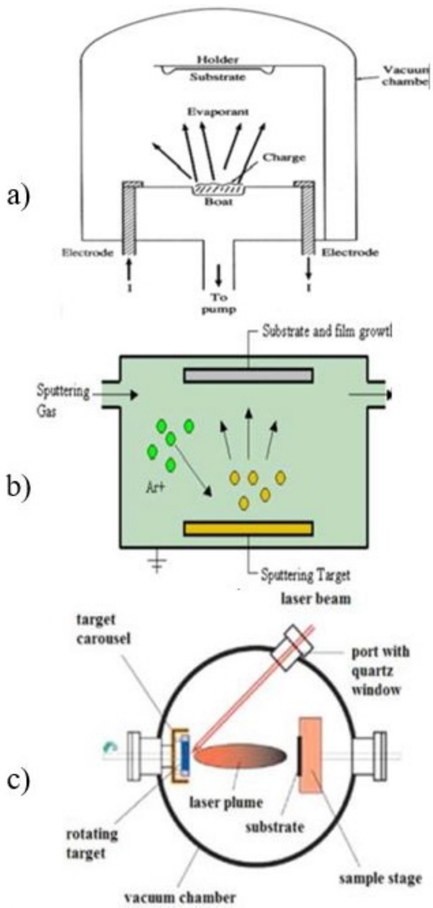

Figure 3: a) Vacuum evaporation system, b) Sputtering deposition system, c) Pulsed laser deposition (PLD) system (Shahidi et al., 2015).

This article focuses on the production of Cr- and CrN-coated Zr-1%Nb cladding tubes as a near-term solution to 1) improve cladding performance during normal operating conditions, and 2) increase cladding tolerance on a design basis accidents (such as large break loss of coolant condition). Eventually, the preliminary results concerning the production of such cladding tubes, and the planned/on-going tests, have been reviewed in the following sections.

2 Experimental

2.1 Materials and Methods

The coatings were applied using a semi-industrial PVD machine with four cathodic arc evaporators. The chromium targets used has a purity of 99.9%. Before deposition, samples were cleaned by Alkaline degreasing, as well as by Aston and Ethanol in the ultrasonic bath for 15 min, and finally, rinsed with distilled water. After putting samples inside the chamber, pulse Argon ions sputtered for 20 min with 700 bias voltage. A schematic diagram of the PVD machine is shown in Fig. 4, whereas a detailed coating condition is presented in Table 1.

The lower deposition rate belongs to Cr since, in the case of CrN, the reactive nitrogen gas was injected into the chamber atmosphere, which enhances the coating rate. It should be noted that as a restriction enforced by the cladding manufacturer to control the phase exchange in the Zr-1%Nb tubes, the temperature of the substrates was kept below 300 °C during the deposition procedure. Also, nitrogen gas flow (concentration in the chamber) was controled using a mass flow controller (MFC) in a condition that stoichiometric CrN to be achieved.

3 Results and Discussion

3.1 Production of optimized coated samples

First, coated samples were produced and then characterized using SEM tests. Results are shown in Fig. 5. Detected non-homogeneities in the particle sizes confirmed the necessity of changing the coating condition. After performing modifications to the coating condition and introducing magnetic filters in the way of evaporated particles

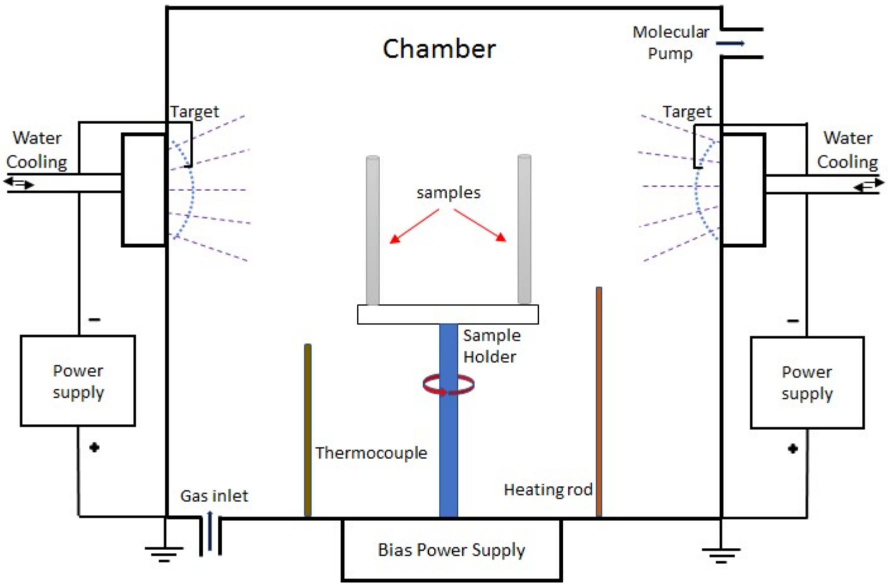

Figure 4: Schematic of the PVD machine for arc ion platting.

towards the cladding tubes, samples illustrated in Fig. 6 were achieved. As can be seen, some pin-holes and macro-particles are still noticeable in the micrographs. However, based on the relatively minor density of these defects (i.e., pin-holes and macro-particles), it was decided to examine coated samples under a series of mechanical and performance experiments and evaluate the influence of such defect densities and sizes on the expected cladding behavior.

A close-up view of the defects detected in final samples is illustrated in Fig. 7. Based on the preliminary evaluations, the affected depth of the defects are expected to be negligible in comparison with the coating thickness. However, since studies on such ATF concepts in different research and manufacturing organizations around the world are not finalized yet, it is needed to wait for further experimnetal data in order to discuss the influence of noticed defects more rigorously.

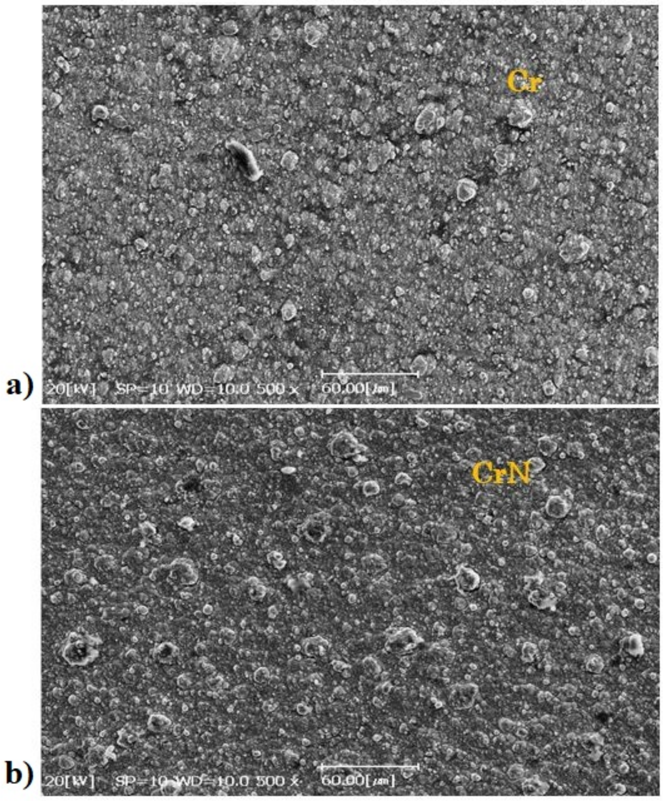

Figure 5: SEM photomicrographs from the top surface of the coated tubes (initial samples).

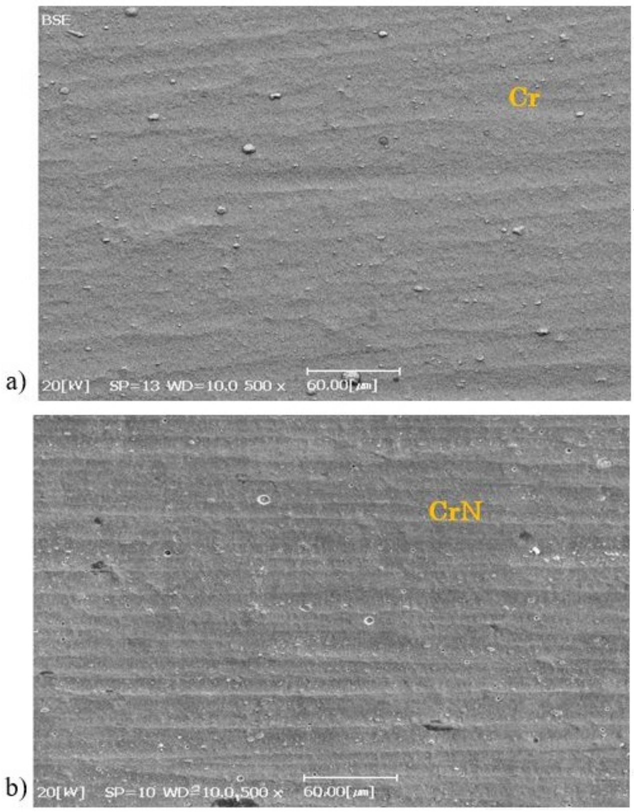

Figure 6: SEM photomicrographs from the top surface of the coated tubes (final samples).

Table 2: On-going tests.

Microstructural analysis:
- Metallography
- SEM
- EDS (line, spot) XRD
Mechanical tests:
- Nano-indentation test
- Nano scratch or scratch adhesion test
- Bulge test
- Ring compression test
- Thermal properties (thermal conductivity, heat capacity, diffusivity, and emissivity)
- Tensile test
- Mandrel test hydrogen charging (cathodic charging); Hydrogen content measurement, Hydride reorientation treatments
Performance tests:
- Ballooning a burst
- High-temperature oxidation (air and steam)
- Long-term corrosion in VVER chemistry

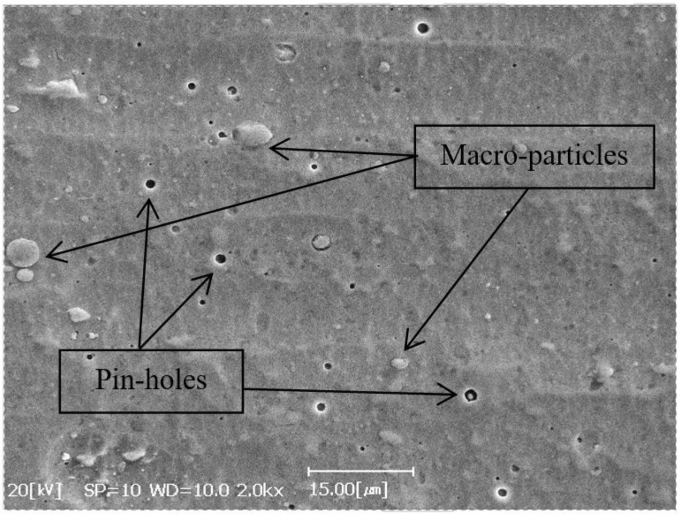

Figure 7: Close-up SEM photomicrograph of the top surface to emphasize defects.

3.2 On-going and future activities

In order to analyze the impact of coated material on Zr-1%Nb tubes under normal and accidental conditions, a series of experimental tests have been considered as listed in Tabel 2. The same tests are to be performed on the reference (uncoated) tubes, and the results will be compared. These tests are categorized into three main topics, including 1) microstructural, 2) mechanical, and 3) performance analyses.

Based on some manufacturing characteristics and results obtained from the quality control tests (including Hydride orientation fraction tests, transverse tensile test, and corrosion behavior in 400 °C/100 bars/3 days (ASTM G2M)), different uncoated tubes were selected and coated in order to analyze a wide range of substrates with various manufacturing properties. Further results are not finalized yet, and they will be released in future publications.

4 Conclusions

Breakaway oxidation of Zr-base cladding tubes under high-temperature accidental conditions (typical to LOCA temperature ranges), and consequently, accelerated Hydrogen release, renewed interests for more tolerant nuclear fuel concepts. Among these concepts, coated claddings are approved as a promising short-term remedy and are being under preliminary, and in some cases, LTR (lead test rod) testings by different fuel manufacturing companies around the world.

NRF company, as the only fuel manufacturer organization in IRAN, planned to carry out a wide variety of efforts, from choosing and optimizing the efficient coating technique to performing performance examinations. This work presents the final results in production of Cr- and CrN-coated samples. Initial results show acceptable coating characteristics, so produced samples are sent to test institutes and organizations through an international collaboration with the IAEA and the project dedicated to testing and simulating ATF concepts (CRP ATF-TS).

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