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BEHAVIOR OF CHROMIUM COATED M5™ CLADDINGS UNDER LOCA CONDITIONS

J.C. Brachet¹, M. Dumerval¹, V. Lezaud-Chaillieux¹, M. Le Saux¹, E. Rouesne¹, D. Hamon¹, S. Urvoy¹, T. Guilbert¹, Q. Houmaire¹, C. Cobac¹, G. Nony¹, J. Rousselot¹, F. Lomello², F. Schuster³, H. Palancher⁴, J. Bischoff⁵, E. Pouillier⁶

¹ DEN, Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

² DEN, Service d'Etudes Analytiques et de Réactivité des Surfaces, CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France

³ DEN, DP, CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France

⁴ DEN-DEC, CEA, F-13108 Saint-Paul-lez-Durance, France

⁵ AREVA NP, 10 rue Juliette Récamier, F-69456 Lyon, Cedex 06, France

⁶ EDF R&D, MMC Department, avenue des Renardières, F-77818 Moret-Sur-Loing, France

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ABSTRACT: The present paper will report some results recently obtained on Cr-coated M5™ claddings under loss-of-coolant accident conditions. Internal pressure creep and temperature ramp tests were done in steam environment using the CEA “EDGAR” testing facility. These thermal-mechanical tests were performed on 50 cm long M5™ cladding samples with a 10 to 15 μm thick outer chromium coating. Cladding burst temperatures ranging from the α_{Zr} phase temperature range (< 850°C) up to the β_{Zr} phase domain (> 950°C) were investigated. As already observed during preliminary tests performed on

Cr-coated cladding samples with a Zircaloy-4 substrate, the results showed generally a strengthening effect of the Cr coating, associated with smaller cladding ballooning. Excellent Cr coating adhesion was also confirmed, even at the balloon location where high cladding deformation is observed. Additionally, one-sided steam oxidation tests were performed on Cr-coated M5™ in steam at 1200°C, thanks to the CEA “DEZIROX” facility. Then, microstructural observations as well as elemental analyses were performed on the coated materials oxidized at High Temperature (HT) and quenched. They confirmed that, for design based accident and beyond conditions, the resistance to HT oxidation was enhanced with a Cr coating, which prevented oxygen diffusion into the metallic zirconium-based substrate. Post-Quenching (PQ) mechanical tests were performed to confirm the enhanced PQ behavior of Cr-coated M5™ compared to the uncoated cladding materials.

KEYWORDS: Enhanced Accident Tolerant Fuels (EATF), chromium coating, M5™, LOCA, high temperature steam oxidation, oxygen diffusion, mechanical behavior

I. INTRODUCTION, MATERIALS AND EXPERIMENTAL

Chromium coated zirconium based nuclear fuel claddings are developed with CEA, AREVA NP and EDF as “Enhanced Accident Tolerant Fuel” (EATF) cladding concept for light water reactors, and studied at CEA. It has previously been shown that Cr-coated Zircaloy-4 claddings have an enhanced tolerance to Loss-of-Coolant Accident (LOCA) in comparison with the current standard Zircaloy-4 claddings (Refs 1-3). The objective of the present work is to briefly present the results obtained more recently in LOCA conditions on the last generation of Cr coated M5™ claddings. For that purpose, two types of tests were performed on coated M5™ claddings:

- High Temperature (HT) internal pressure creep and thermal ramp tests (“EDGAR” tests, Ref. 4);
- HT steam oxidation and direct water quenching from the oxidation temperature tests (“DEZIROX” tests, Ref. 5).

Additionally, some Post-Quenching (PQ) impact tests and metallurgical analysis were done and the first results obtained will be described. All results presented in this article were obtained on M5™ alloy coated with 10-15 μm of Cr.

For the chromium deposition, PVD (Physical Vapor Deposition) type process has been applied. Figure 1 shows an illustration of the typical microstructure of the as-received 10-15 μm Cr thick coating on M5TM substrate. It has to be mentioned that the Cr coating is dense and very homogenous in thickness, with a very good bonding on the M5TM substrate. Moreover the as-received M5TM microstructure is not affected by the coating process. Thus, the overall nominal mechanical properties of coated M5TM claddings is expected to be similar to those of the reference uncoated material, as already discussed in Ref. 6.

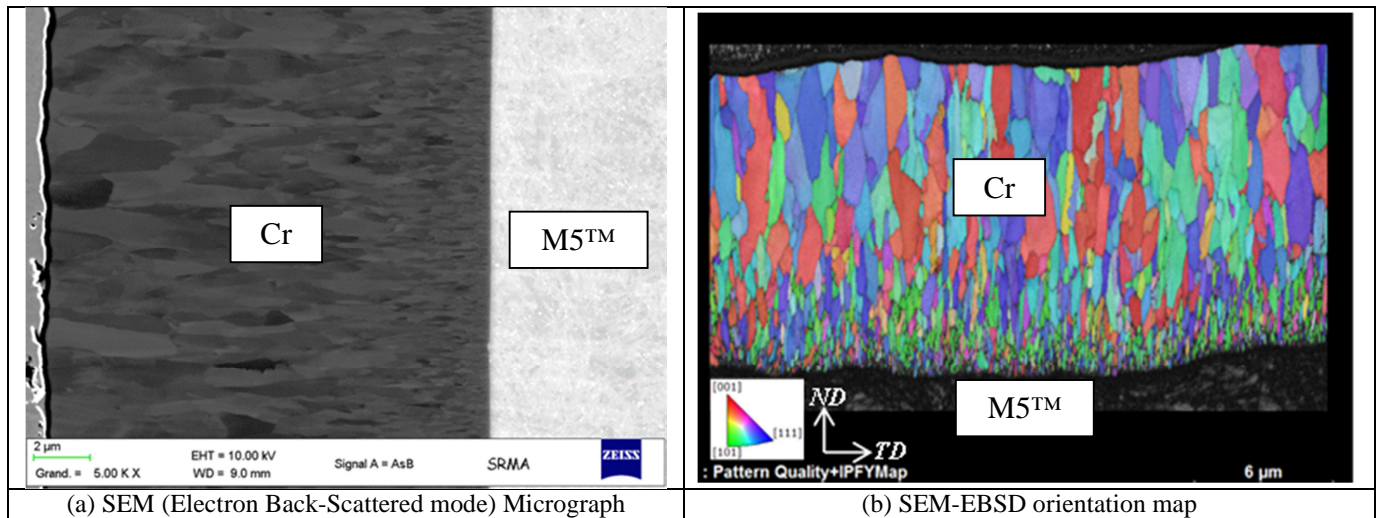


Fig. 1. Typical microstructure of a 10-15 μm Cr thick chromium coating on a M5TM clad substrate

II. INTERNAL PRESSURE CREEP & THERMAL RAMP TESTS AT HT UNDER STEAM ENVIRONMENT

Both isothermal creep and thermal ramp tests were done on 50 cm long coated clad segments. The internal pressures applied range from ~ 10 up to 120 bar and the creep or rupture temperatures (in case of thermal ramp tests) range from 600 $^{\circ}\text{C}$ (α_{Zr} temperature range) up to 1000-1100 $^{\circ}\text{C}$ (β_{Zr} temperature range).

II.A. Isothermal creep tests

Figure 2 illustrates some typical creep curves obtained on uncoated reference materials and on Cr coated M5TM upon creep tests at 750 $^{\circ}\text{C}$, with the same applied internal pressure. As already observed on Zircaloy-4 substrate (Ref. 3), a strengthening effect of the Cr coating at HT is observed on the overall thermal-mechanical response of the coated clad segments under internal pressure, especially in the 600-800 $^{\circ}\text{C}$ temperature range (α_{Zr} temperature range). This induces an increase of the time to rupture, for any given applied internal pressure (*as discussed in Ref. 3, the slightly higher thickness of the coated claddings compared to the uncoated ones is not sufficient to explain the reduction of the creep rate observed on the coated materials*). Fig. 3 gives an overview of the relative increase of the creep rupture time for Cr coated materials compared to the uncoated reference ones, for both Zircaloy-4 and M5TM substrates.

Additionally, as illustrated in Figure 4, Cr-coating may induce a significant reduction of the balloon size, especially in the “low-temperature” range (α_{Zr}). For the higher creep temperature range, even if significant ballooning occurs, the rupture opening is very small (less than 1mm²) as illustrated on Figure 5. This last trend has been already observed on Cr-coated Zircaloy-4 (Ref. 3). One may anticipate that such a small rupture opening could have a positive effect on the potential fuel relocation and dispersal (*as already observed for some Studsvik or Halden LOCA tests performed on high Burn-Up fuel, Refs 12-13*); moreover, this would induce some benefits by reducing the steam ingress inside the clad segment (within the clad - fuel pellet gap) and then would limit the extent of the inner clad surface oxidation and the associated secondary hydriding phenomena following clad burst occurrence. Finally, it can also be observed in Figure 5 that the chromium coating is still fully adherent to the substrate with very limited oxidation and/or damage/cracking, including at the vicinity of the burst

location, where significant creep deformation has occurred (*i.e.*, up to potentially a few tenths of % of clad circumferential elongation), thus preserving the oxidation protection capacity of the Cr coating after the clad burst occurrence.

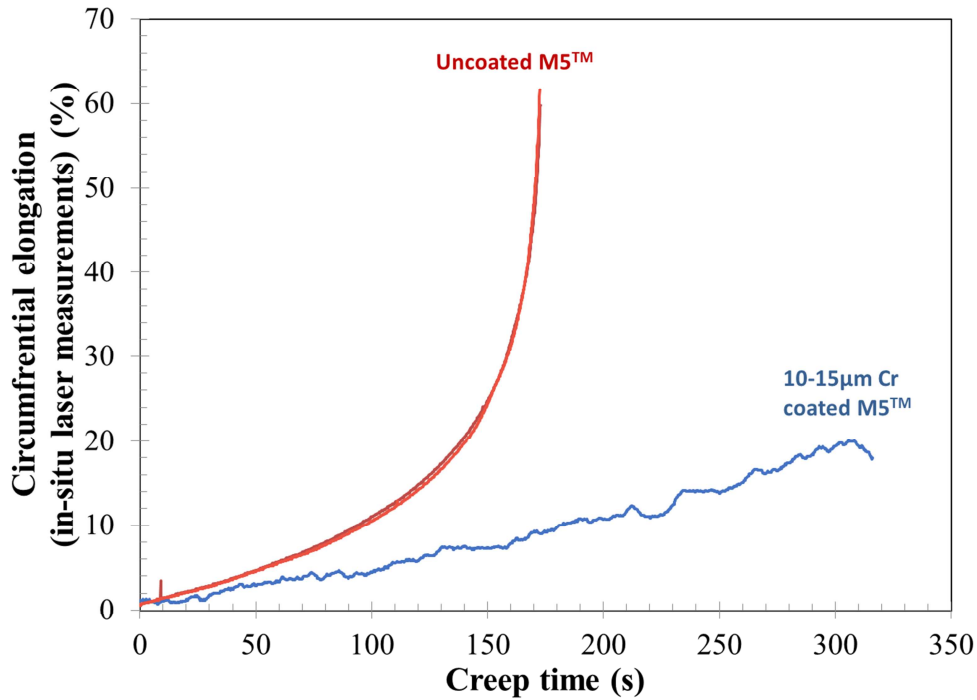


Fig. 2 Creep curves obtained on coated/uncoated M5TM claddings upon isothermal creep tests at 750°C, with the same applied internal pressure: two uncoated reference ones superposed, in red, and one standing for 10-15µm Cr coated (in blue)

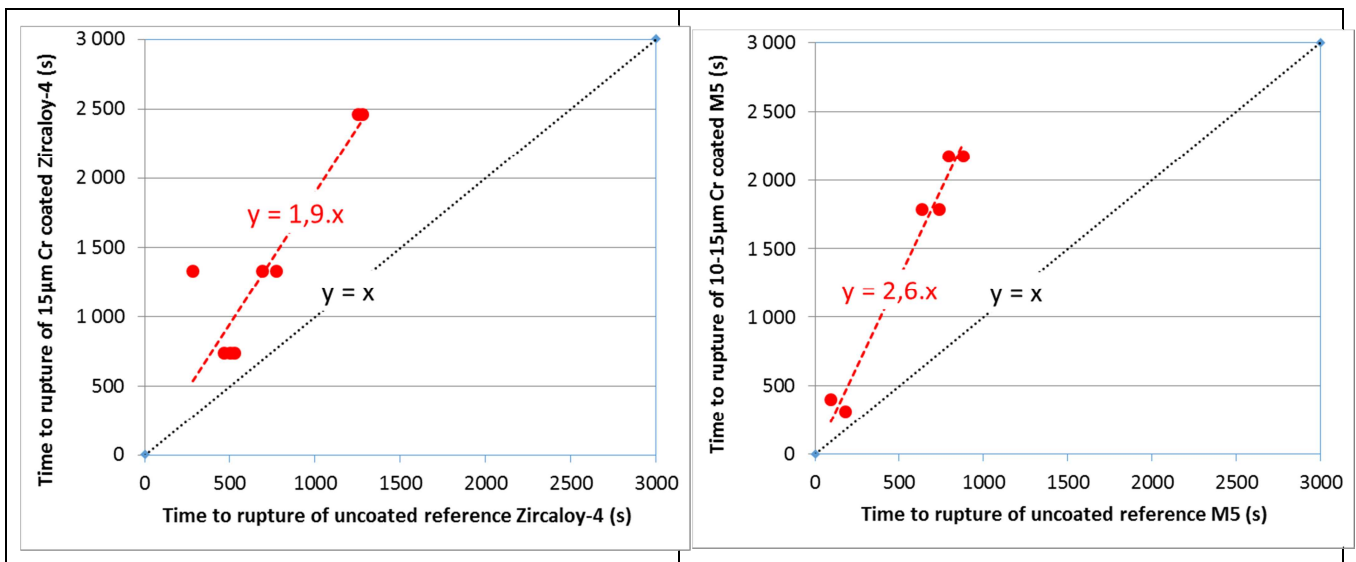


Fig. 3 Creep rupture times for Cr coated materials compared to those measured for uncoated reference ones (Zircaloy-4 – left and M5TM - right)

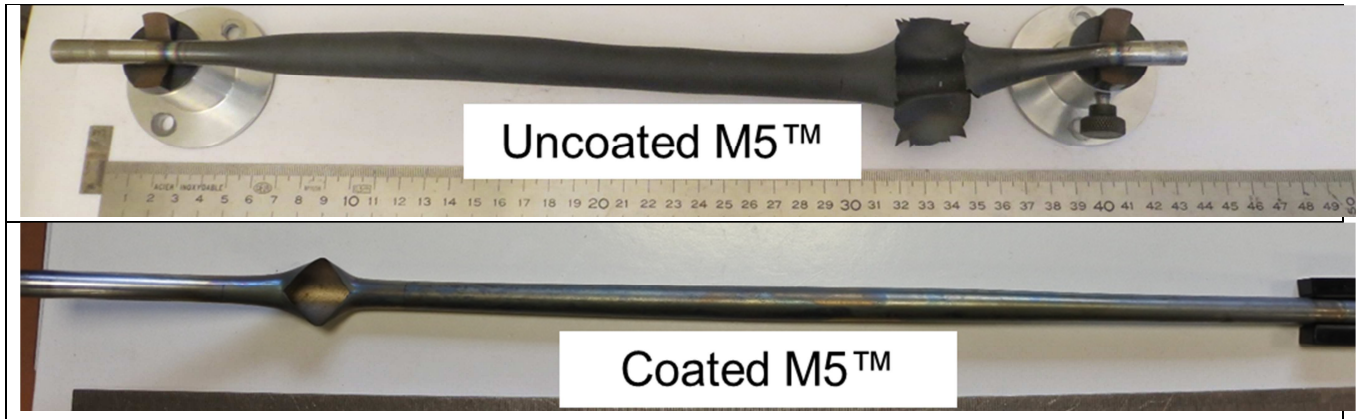


Fig. 4 Visual examinations of two tested clad segments after “EDGAR” creep tests performed at 600°C

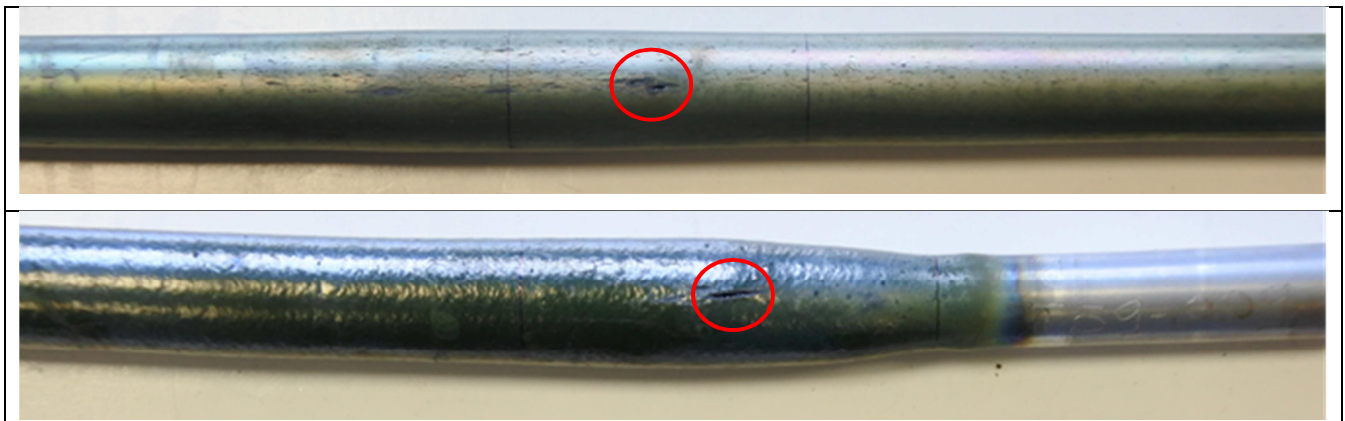


Fig. 5 Visual examinations of two tested 10-15µm Cr coated M5™ clad segments after “EDGAR” creep tests, performed at 850°C (top) and at 1000°C (bottom), respectively

II.B. On-going thermal ramp tests

Thermal ramp tests are on-going under constant internal pressure ranging from 10 up to 100 bar, for heating rates ranging from 1°C/s up to 25°C/s. From the preliminary results obtained it can be observed that, for any given internal pressure and heating rates tested so far:

- balloon sizes of Cr coated M5™ claddings are generally lower than those of the uncoated ones, thus confirming the tendency observed upon isothermal creep tests;
- burst temperatures of Cr coated M5™ claddings are comparable or slightly above those of the uncoated ones;
- in one particular case (i.e., 10 bar and 25°C/s), the 10-15µm Cr coated M5™ clad segment did not fail before reaching 1100°C (*then the ramp test was stopped before burst occurrence*) while, in the same conditions, burst occurs at temperatures lower than 1100°C for the uncoated reference materials, indicating that the HT strengthening effect of Cr coating can be operant upon dynamic thermal ramp tests, which are more prototypical of LOCA transients than isothermal creep tests.

To summarize the above results, it can be concluded that, as already observed on zircaloy-4 substrate and especially upon internal pressure isothermal creep in the 600-800°C α_{Zr} temperature range, the 10-15 μ m Cr coating induces a HT strengthening of more of a factor of two on the creep rupture time for the coated M5™ cladding.

Discussion - The scarce creep data available in the literature for pure chromium (Ref. 16) suggest that the Cr coating has a significantly higher creep resistance than the Zr-based substrate at high temperature (Ref. 17), such that the global creep behavior of the cladding is strengthened. More data on the mechanical behavior of chromium are needed to further investigate this effect. Such an effect was also observed in oxidized Zr-based alloys in the presence of oxygen-rich layers (Ref. 18). On the contrary, at lower temperature, the mechanical strength of pure chromium (Ref. 19) is expected to be close to the ones of Zircaloy-4 or M5™. Then, one does not expect a significant effect of the Cr coating on the overall creep behavior of the coated cladding at normal operation temperatures, as shown by creep tests performed at AREVA (Ref. 20).

However, more ramp tests are planned in the near future to confirm this effect in more representative LOCA transient conditions. The ultimate goal is to derive a thermal-mechanical creep-rupture model, as already done on reference uncoated cladding materials, to be able to take advantage of the benefits gained by using the Cr-coated M5™ cladding (Ref. 4).

III. HT STEAM OXIDATION AND POST-QUENCHING BEHAVIOR

One-sided oxidation tests were performed on cladding segments with plugs welded at the ends, to be more representative of the overall HT oxidation of the nuclear fuel rod far from (potential) local burst occurrence. HT steam oxidation tests were done at 1200°C thanks to the “DEZIROX” facility (Ref. 5) for Design-Based-Accident (DBA) and for Design-Extension-Conditions (DEC) oxidation times, that is, from a few minutes up to a few hours. At the end of the isothermal oxidation step, direct water quenching was applied down to Room Temperature (RT). Thus, such final cooling conditions are likely to be conservative with respect to the two-sided oxidation with a two-steps final cooling scenario generally applied by other R&D institutes/teams (*i.e.*, cooling first at an intermediate cooling rate (1-10°C/s) down to an intermediate temperature (700-800°C) from which the final water quenching is applied down to RT (Refs 14-15)), this last two-steps cooling scenario being likely more prototypical of “real” LOCA transients.

Figure 6 shows the weight gain measured as a function of the one-sided steam oxidation time at 1200°C. On this figure we have also indicated the typical oxidation time (~600s) corresponding to the historical LOCA regulatory limit based on an Equivalent Cladding Reacted (ECR) = 17%, calculated using the “Baker-Just” (BJ) correlation (Ref. 7).

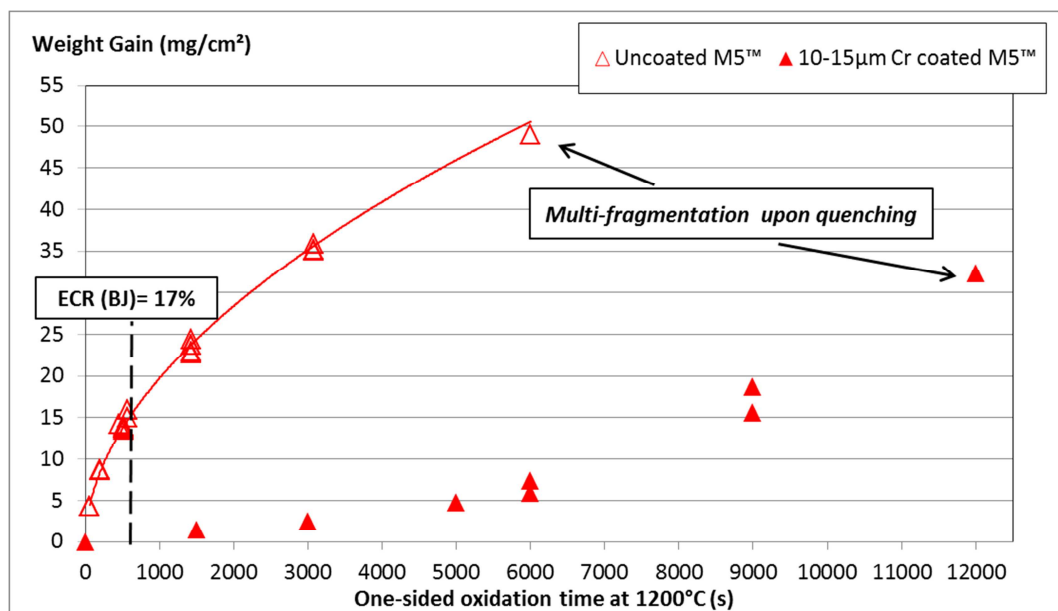


Fig. 6 Weight gain measured after one-sided steam oxidation at 1200°C and direct water quenching down to RT

It is obvious from figure 6 that the Cr coating induces a significant reduction of the overall HT oxidation kinetics of the M5™ cladding, thus offering a significant additional “coping time” before achieving full embrittlement of the cladding leading to fragmentation upon final (direct) water quenching from 1200°C.

Complementary PQ mechanical tests are on-going, including impact tests at RT and ring Compression tests at 20 and 135°C. However, some preliminary impact tests at RT have been done and are compared in Figure 7 to the results obtained for the uncoated reference material already presented and discussed in Refs. 8-10. The evolution of the PQ impact energy as a function of the oxidation time at 1200°C confirms the beneficial effect of the chromium coating on the residual ductility/toughness of HT oxidized claddings, as already observed in the case of a Zircaloy-4 substrate after one-sided steam oxidation at 1000-1200°C (Refs. 1-3).

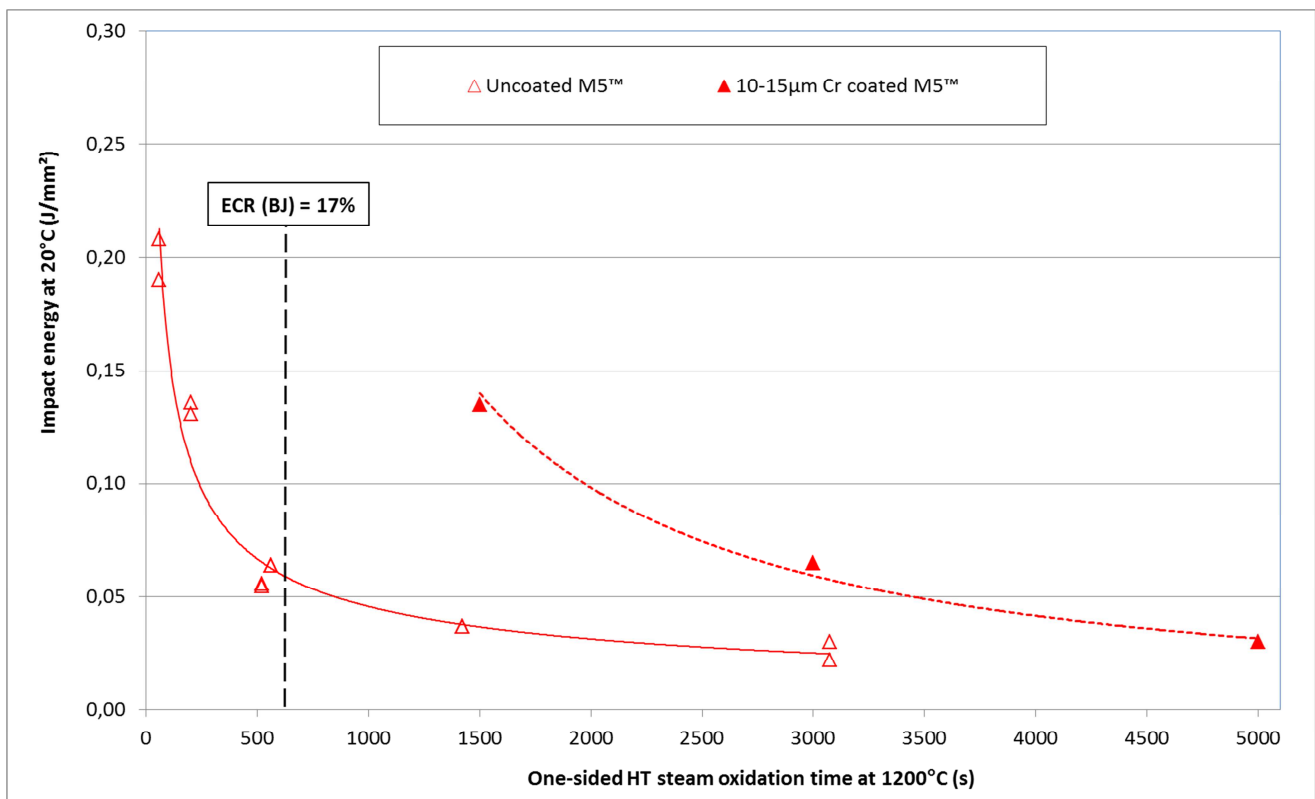


Fig. 7 Post-Quenching impact energy measured at RT as a function of (one-sided) steam oxidation time at 1200°C

Finally, some PQ metallurgical examinations, including EPMA (Electron Probe Micro Analysis) measurements of the oxygen diffusion profiles are on-going. Figure 8 shows oxygen diffusion profiles measured by EPMA within the substrate after one-sided steam oxidation for ~25 min (i.e., for ~1500s) at 1200°C on both uncoated and Cr coated M5™ clad segments (with welded end plugs). The oxidation time here is two times higher than the one corresponding to ECR BJ value of 17% for the uncoated materials.

For the uncoated reference material on the one hand, it can be observed the formation of thick outer brittle oxide (ZrO_2) and $\alpha_{Zr}(O)$ layers corresponding to more than half of the wall clad thickness, and significant oxygen diffusion within the thin residual prior- β_{Zr} inner layer achieving ~0,5 wt.%. From previous studies (Refs. 9-11), this last value appeared to be close to the oxygen solubility limit in the β_{Zr} phase at 1200°C and is slightly higher than the “critical” value (i.e., ~0,4 wt.%) inducing a ductile-to-brittle transition at RT of the quenched prior- β_{Zr} structure, which is consistent with the negligible PQ clad toughness measured (~0,03 J/mm²). For the Cr-coated M5 sample on the other hand, there is no formation of outer brittle ZrO_2 and $\alpha_{Zr}(O)$ layers and negligible oxygen diffusion within the Zr substrate from the outer clad surface; for this particular sample one can only observe some slight oxygen diffusion from the inner (uncoated) clad surface, likely due to some residual gaseous oxygen initially trapped inside the closed clad segment (with welded plugs). The Cr-coated M5™ cladding thus preserves its RT residual ductility/toughness as illustrated by its quite high PQ Charpy Impact energy value (~0,15J/mm², see Fig. 7).

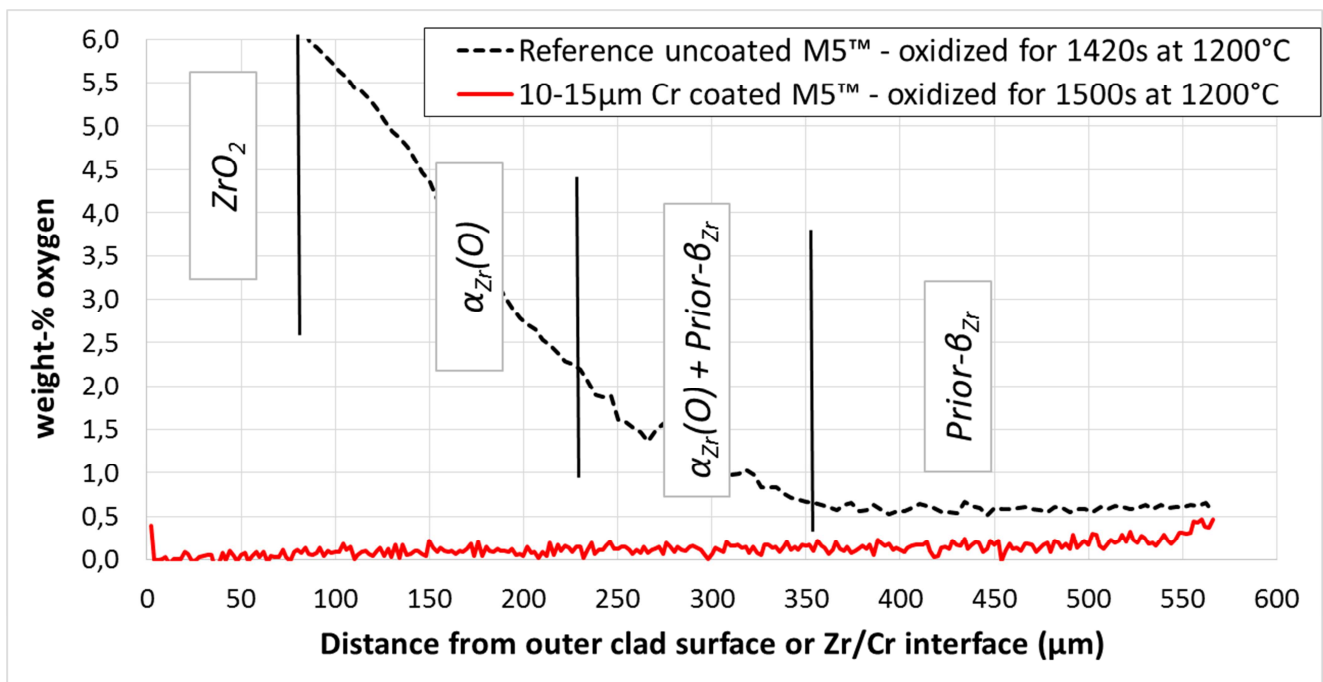


Fig. 8 Oxygen diffusion profiles measured by EPMA within the substrate after one-sided steam oxidation for ~25 min at 1200°C on both uncoated and 10-15µm Cr coated M5™ clad segments

IV. CONCLUSIONS

Internal pressure creep and temperature ramp tests were performed in steam environment on 50 cm long 10-15µm Cr coated M5™ claddings for burst temperatures and internal pressures typical of LOCA transients. As already observed after preliminary tests on Cr-coated cladding samples with a Zircaloy-4 substrate, the results showed a HT strengthening effect of the Cr coating, associated with smaller clad ballooning. Excellent Cr-coating adhesion was also confirmed, even at the balloon location where high cladding deformation is achieved. Additionally, one-sided steam oxidation tests have been performed on Cr-coated M5™ in steam at 1200°C. They have confirmed that, for design based accident and for extended design conditions, the HT oxidation resistance of the material was enhanced by the presence of a 10-15µm Cr coating, which prevented oxygen diffusion into the metallic zirconium-based substrate thus inducing better residual impact properties. PQ ring compression tests are on-going to confirm the enhanced PQ behavior of Cr-coated M5™ compared to the uncoated cladding materials.

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