BEHAVIOR OF Cr-COATED M5 CLADDINGS DURING AND AFTER HIGH TEMPERATURE STEAM OXIDATION FROM 800°C UP TO 1500°C (LOSS-OF-COOLANT ACCIDENT & DESIGN EXTENSION CONDITIONS)

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ABSTRACT

One-sided steam oxidation tests have been conducted at various temperatures between 1000 and 1500°C on several facilities on 12-15µm thick Cr-coated M5 claddings. Microstructural observations and micro-chemical analysis have been performed after oxidation and quenching. Some post-quenching ring compression tests have been also carried out to assess the residual strength/ductility of the Cr-coated materials oxidized at High Temperature (HT). It was confirmed that in the 1000-1300°C oxidation temperature range, the oxidation resistance of the coated materials was enhanced, with a significant additional "coping period" at HT before the material became macroscopically brittle during and/or after quenching. The study was then extended to steam oxidation temperatures higher than 1300°C (Design Extension Conditions). Those tests have confirmed that a eutectic reaction occurred between the zirconium-based substrate and the residual metallic Cr coating above 1300°C. For the DEC-type conditions applied, the tested Cr-coated clad segments did not fail upon the final water quenching while some uncoated reference segments did.

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1. INTRODUCTION, MATERIALS AND EXPERIMENTAL PROCEDURES

Within the CEA-Framatome-EDF nuclear fuel joint program, chromium coated zirconium based fuel claddings are developed and studied as an "Enhanced Accident Tolerant Fuel" (EATF) cladding short-term concept for nuclear Light Water Reactors (LWR). Previous studies [1]-[4] performed on both Cr-coated Zircaloy-4 and M5 based claddings have shown that the oxidation resistance of the material in steam at High Temperature (HT) was significantly enhanced by the presence of a 10-15µm Cr coating, which substantially delayed oxygen diffusion into the metallic zirconium-based substrate and thus the embrittlement of the material. But, until now, those studies

mainly focused on HT steam oxidation performed at 1200°C which corresponds to the maximum "Peak Cladding Temperature" (PCT) considered in safety LOCA criteria. In view of increasing the database to have better insights into the coping time and temperature of this EATF concept, the study has been extended to lower and higher oxidation temperatures, including "Design Extension Conditions" (DEC), up to 1500°C. For these last conditions, one important issue is the occurrence of a eutectic reaction between the Cr coating and the zirconium based substrate, which may occur at temperatures above 1300°C, and its potential (unknown) consequences on the HT oxidation and associated embrittlement/failure behaviors.
The studies presented here were carried out on M5 cladding tube samples with a 12-15µm-thick Cr coating on their outer surface. The typical microstructure of as-received Cr-coated M5 has been already presented in [4]. We just recall here that for the chromium deposition, a specific PVD (Physical Vapor Deposition) type process has been developed and applied. The Cr coatings obtained are fully dense and homogenous in thickness, with a very good bonding to the M5 substrate. Moreover, it has to be recalled that the as-received M5 microstructure is not affected by the coating process so that its already assessed properties are preserved.
To insure a good robustness of the results and to extend the data at oxidation temperatures higher than those already tested, three different HT steam oxidation and quenching facilities have been used, that is:

- the reference CEA "DEZIROX 1" facility on which more than two thousands HT steam oxidation tests have been conducted so far, mostly on uncoated nuclear fuel claddings, including low-tin Zircaloy-4, M5, pre-hydrided and/or pre-corroded or not… [5]-[8];
- the HT oxidation test facility recently developed and used at Framatome-Paimboeuf with some results shown in another article [13];
- a new CEA HT steam oxidation facility called "I2TOx", able to perform HT tests under inert or controlled steam environment up to 1600°C. In this new experimental device, complex thermal cycling can be applied with continuous control of the sample temperature, gas flow and humidity, heating rate up to at least 1°C/s and fully automatized final water quenching.

2. OXIDATION UP TO 1200°C (LOCA CONDITIONS AND SLIGHTLY BEYOND)

For this set of experiments, one-sided steam oxidation tests (end caps welded under secondary vacuum at both extremities of the tube samples) have been performed at 1000, 1100 and 1200°C for oxidation times ranging from a few minutes up to a few hours. Measured weight gains and overall thicknesses of ZrO_2 and/or Cr_2O_3 oxide layers are plotted as a function of the square root of time in Figure 1, for uncoated reference M5 and 12-15 µm Cr coated M5 clad segments. Additionally, the "Cathcart-Pawell" (CP) [9] oxidation rate relationship developed for (uncoated) Zr based alloy materials is plotted for comparison. For the figure corresponding to steam oxidation at 1200°C, the typical oxidation time (~600s) corresponding to the historical LOCA regulatory limit based on an Equivalent Cladding Reacted (ECR) of 17% calculated using the "Baker-Just" (BJ) correlation [10] has been also indicated. It can be observed that:

- the results obtained both at CEA and at Framatome –Paimboeuf on two different HT steam oxidation facilities are consistent.;
- whichever the oxidation temperature, the 12-15µm thick Cr coating induces a significant reduction of the overall HT oxidation of the M5 cladding. This is especially highlighted at 1000 and 1100°C, for oxidation times up to 5 hours: the oxidation level of coated M5 is very limited, with outer oxide layers thinner than 10 µm, while for these conditions, the uncoated reference material displays heavy oxidation with outer zirconia and oxygen stabilized α_{Zr}(O) layers of several tens up to hundreds of micrometers, leading to significant embrittlement of the (uncoated) claddings.

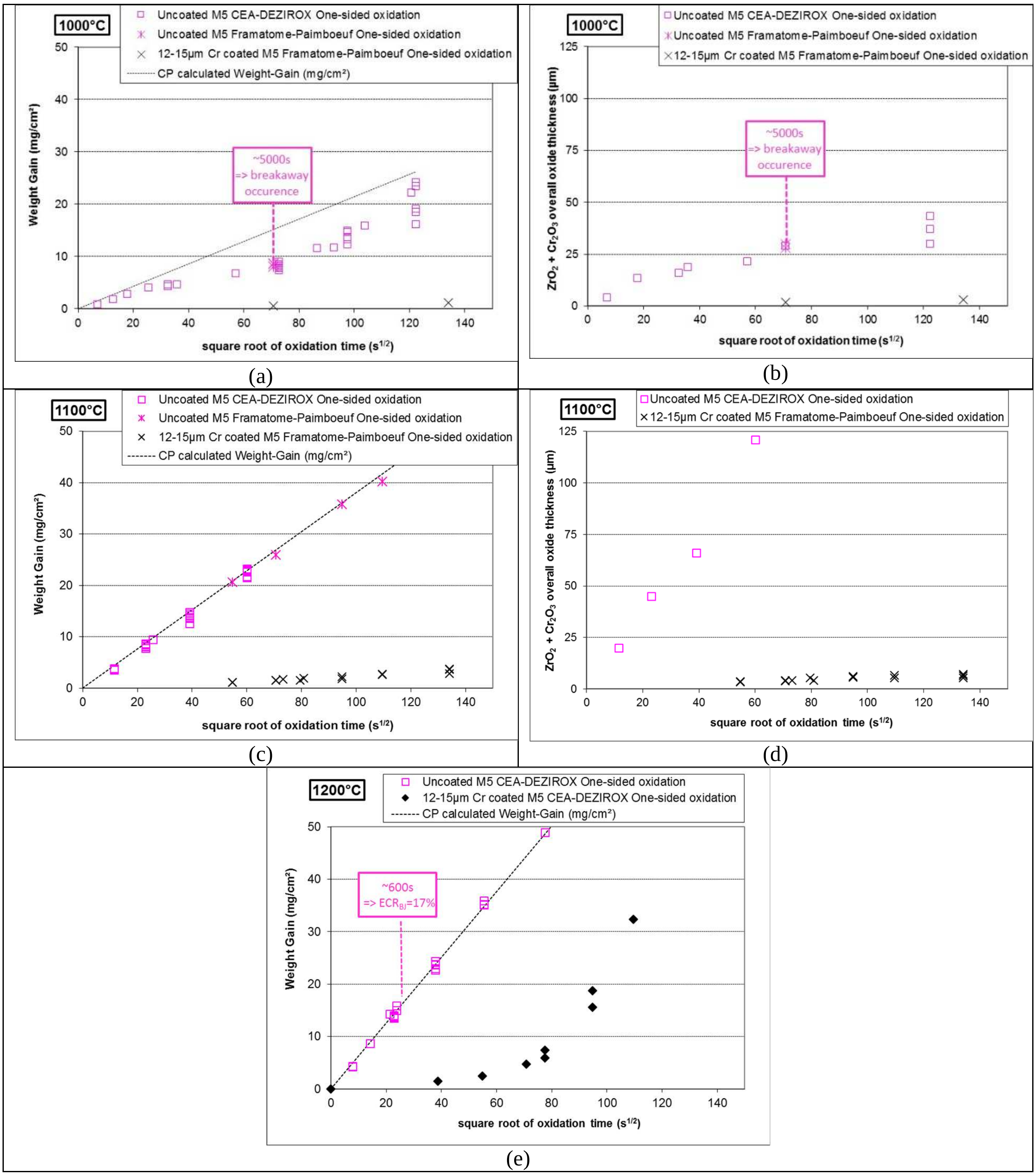


Fig 1. Evolution of weight gain and of overall oxide thickness of uncoated and 12-15µm Cr coated M5 cladding segments as a function of the square root of the steam oxidation time

Post-Quenching (PQ) mechanical tests were carried out on both uncoated and 12-15µm Cr coated M5 clad segments after one-sided steam oxidation at 1200°C. The PQ impact properties have already been presented and discussed in the last WRFPM/Topfuel meeting [4]. Since then, some complementary PQ Ring Compression Tests (RCT) have been performed at both Room Temperature (RT) and 135°C. Evolutions of the measured maximum applied load and plastic displacement (normalized to the initial clad diameter)[1] up to rupture, as a function of the oxidation time at 1200°C, are plotted in Figure 2. When compared to the results obtained for reference uncoated M5 [6], RCT results confirm the beneficial influence of the 12-15µm Cr coating on the coping time before achieving macroscopic PQ embrittlement. As already discussed for the PQ impact properties of Cr-coated M5 [4], this improvement of PQ mechanical properties can be related to the additional delay before significant oxygen diffusion into the underlying prior-β_{Zr} layer, which is known to be one of the main parameter responsible for the decrease of the cladding strength upon quenching and of the PQ residual ductility after HT steam oxidation [7].

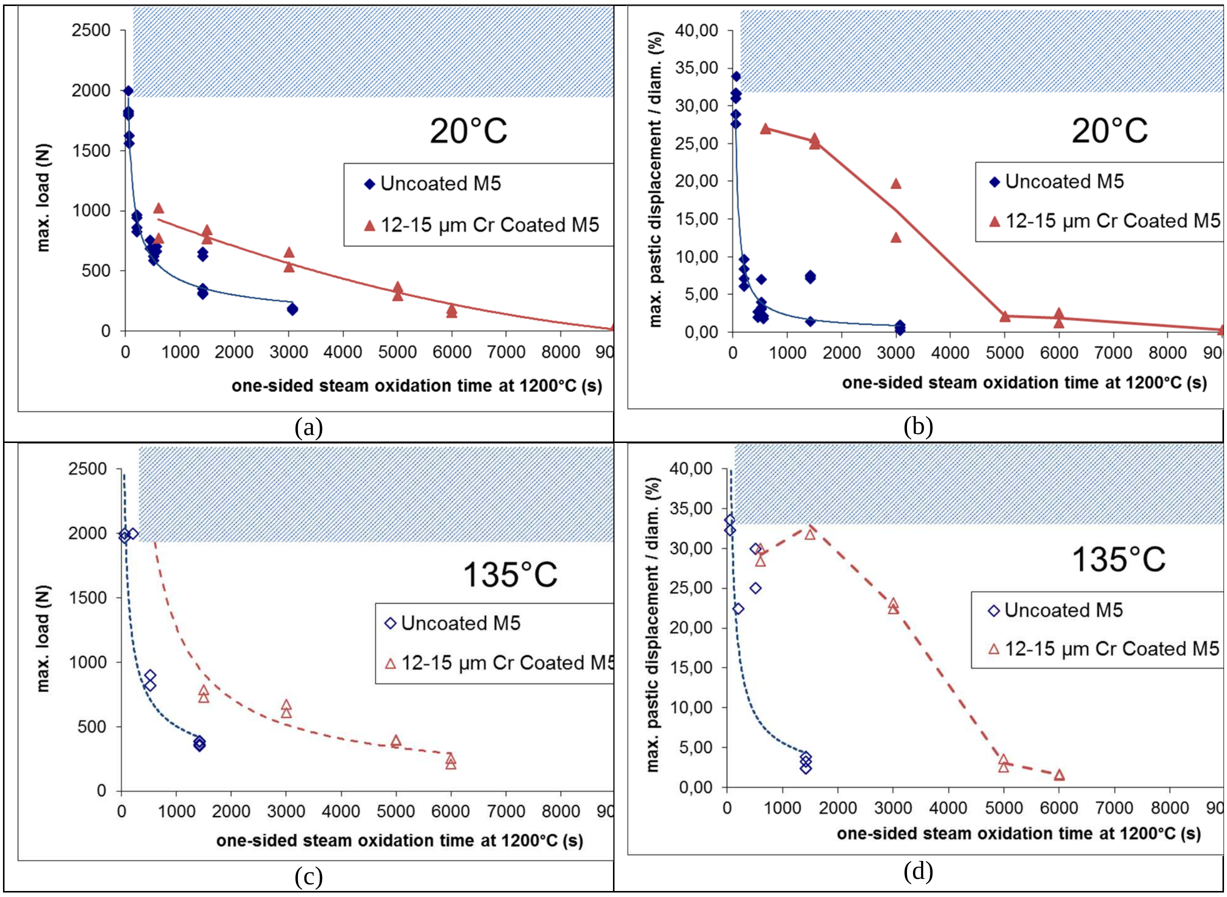
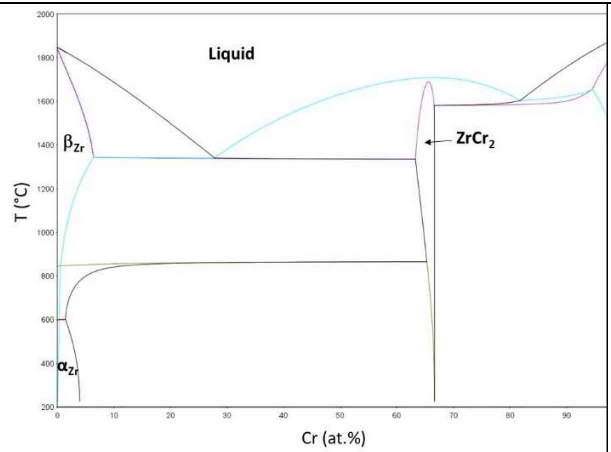


Fig 2: Post-Quenching Ring Compression Test properties evolution
as a function of steam oxidation time at 1200°C [6]

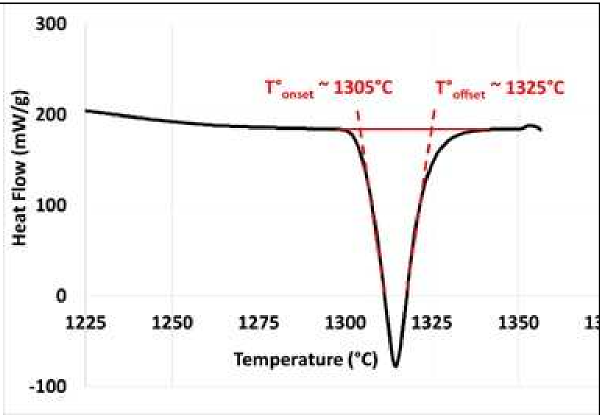
[1] When the test is stopped before sample failure (due to displacement and load limits), the reported mechanical properties are lower than the actual material properties at failure (the displacement/load limit is represented by the hatched area in Fig. 2)

3. HT STEAM OXIDATION BETWEEN 1300°C AND 1500°C AND Zr-Cr EUTECTIC REACTION (DESIGN EXTENSION CONDITIONS)

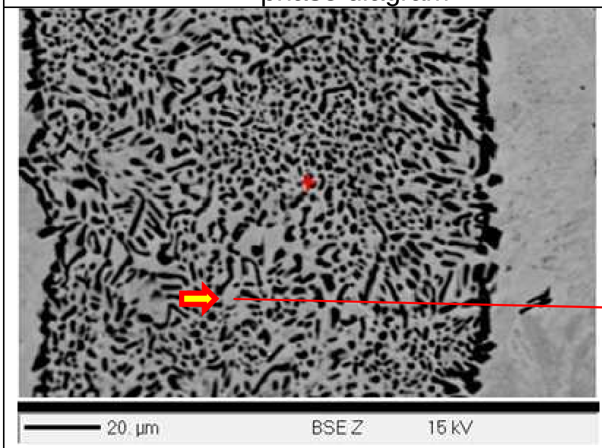
The potential detrimental consequences of the Zr-Cr eutectic reaction which may occur at very high temperatures is one important issue of the Cr-coated Zr based cladding EATF concept for DEC. Indeed, the pseudo-binary M5-Cr phase diagram calculated using the Thermo-Calc® software with the updated CEA "Zircobase" thermodynamic database [12] predicts that this reaction should occur at 1340°C (Fig. 3 (a)). Before doing very HT steam oxidation tests (T≥1300°C), calorimetric measurements have been performed under (inert) helium environment on Cr-coated M5 substrates to get some insights into the temperatures at which the eutectic Zr-Cr reaction occurs. Heating and cooling rates of 10°C/min have been applied, corresponding to near equilibrium conditions. A part of the thermogram obtained on Cr-coated M5 is shown in Fig. 3 (b). The Zr-Cr eutectic reaction is clearly highlighted by an endothermic peak between ~1305°C and ~1325°C. Additionally, Figures 3 (c) and 3 (d) illustrate the typical post-test eutectic microstructure and micro-chemical profiles obtained by Electron Probe Micro Analysis (EPMA). As anticipated from the equilibrium phase diagram, the eutectic liquid phase has decomposed during the slow cooling into prior-β_{Zr} (enriched in oxygen) and $ZrCr_2$ intermetallic phases.



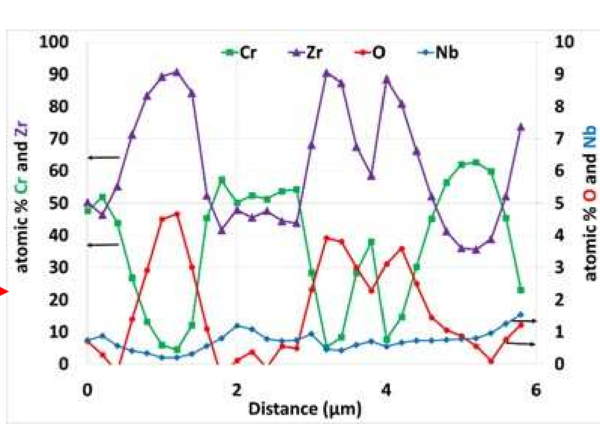
(a) Calculated pseudo-binary M5-Cr phase diagram



(b) Partial view at HT of the experimental thermogram obtained by calorimetric measurements on Cr-coated M5



(c) Back-Scattered Electron micrograph of the solidified eutectic area of Cr-coated M5 after HT calorimetric test



(d) EPMA chemical profiles measured inside the solidified eutectic zone

Fig 3. Calculated pseudo-binary M5-Cr phase diagram, partial thermogram from calorimetric measurements, associated microstructures and chemical profiles underlying the M5-Cr eutectic reaction occurrence at temperature above 1300°C

In a second step, steam oxidation tests have been performed at 1300°C, 1400°C and 1500°C for 600s, 100s and 50s respectively, followed by direct water quenching. For all the tests, heating rate of 1°C/s has been applied. Heating began under flowing helium (neutral environment) and steam flow was introduced at 600°C or at 1300°C, until the final water quenching. Table 1 summarizes the different testing conditions applied and the main results. It can be observed that for uncoated M5, calculations of ECR using an oxidation kinetics correlation derived from results obtained previously on M5 at CEA give values close to the experimental ones. It must be mentioned that all these calculations have been performed taking into account the temperature overshoot measured *in-situ*, sometimes observed when reaching 1300°C and above, induced by the fast and exothermic oxidation reaction that takes place in these very high oxidation temperatures. This means that the oxidation kinetics correlation used is still valid for the actual dynamic anisothermal HT oxidation conditions experienced here, up to at least 1500°C. Additionally, it shows that the new HT oxidation facility used here gives results consistent with the HT oxidation database previously obtained at CEA on M5 using other HT oxidation facilities (and mainly under isothermal oxidation conditions).

However, and as indicated in the last column of Table 1, for the different HT conditions tested here, Cr-coated clad segments did not fail upon the final water quenching while some uncoated reference segments did. Then, to get more insights into the microstructural and micro-chemical evolution of the tested Cr-coated M5 clad segments, some detailed PQ metallurgical examinations were conducted and are presented here after.

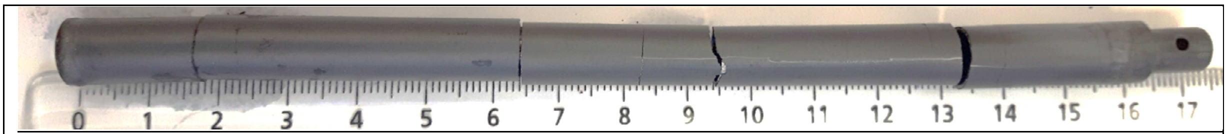
Cr-coated or not?	T(°C) of steam introduction upon heating at 1°C/s	Temperature range achieved (*) (°C)	Oxidation time (s)	Measured Weight Gain (mg/cm²)	ECR calculated from weight gain (%)	Calculated ECR for M5 (***) (%)	Calculated Baker-Just-ECR (%)	Failed or not upon quenching?
No	600°C	1300-1320	600	24.8	19.1	20.3	29.0	No
Yes		1300-1320	600	2.8-2.9 (**)	2.2	-	-	No
No		1400-1420	100	20	15.4	16.9	23.4	No
Yes		1400-1450	100	19.0	14.6	-	-	No
No		1500-1530	50	28.7	22.1	23.7	31.7	Yes or No (****)
Yes		1500-1550	50	Not measured		-	-	No
No	1300°C	1300-1350	600	31.1	23.9	20.6	29.0	Yes
Yes		1300-1310	600	2.4	1.8	-	-	No
No		1400-1450	100	25.8	19.8	18.4	24.8	Yes
Yes		1400-1450	100	19.6	15.1	-	-	No

(*) taking into account the measured temperature overshoot, due to contribution of the HT exothermic oxidation reaction
(**) two different tests performed, thus showing good reproducibility
(***) calculation derived from CEA/Framatome/EDF M5 database (proprietary)
(****) small crack at the end caps weld location, likely to be not representative of the sample gauge length behavior

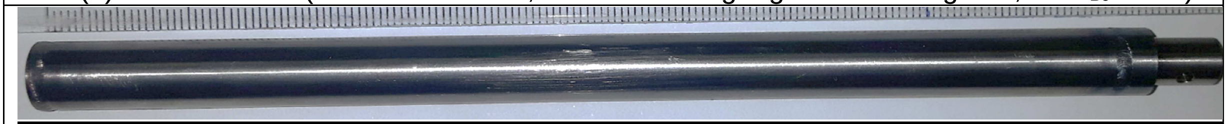
Tab 1: Steam oxidation testing conditions at very HT and main results obtained (heating at 1°C/s in all cases)

HT oxidation at 1300°C just below the Zr-Cr eutectic temperature (with steam introduction at 1300°C) – The PQ aspect of the uncoated and Cr-coated M5 tested clad segments is illustrated in Figure 4. It has to be mentioned that for these particular oxidation conditions, uncoated M5 experienced some temperature overshoot (~ + 50°C) when the steam was introduced at 1300°C, while the Cr-coated M5 did not. This indicates that the Cr-coating may

have a positive influence by decreasing the PCT in these extreme HT oxidation conditions, then mitigating the risk of catastrophic (self-driven) clad oxidation escalation.
Additionally, it can be observed that multi-failures of the uncoated materials occurred upon the final water quenching due to the high ECR achieved, while for the Cr-coated M5, the measured weight gain was very low (2.4 mg/cm² which corresponds to a measured ECR lower than 2%). Consistently, the Cr-coated clad segment integrity was fully preserved. These results confirm the capacity of the Cr coating to prevent the Zr based substrate from early oxidation and oxygen ingress which are known to induce quenching and PQ clad embrittlement.



(a) Uncoated M5 (overshoot ~50°C, measured weight gain = 31.1 mg/cm², ECR_{BJ}=29%)



(b) 12-15µm Cr coated M5 (no temperature overshoot, weight gain = 2.4 mg/cm²)

Fig 4. PQ aspects of two uncoated/coated M5 segments
after one-sided HT steam oxidation for 600s at ~1300°C

HT oxidation above the Zr-Cr eutectic temperature – Figure 5 shows the typical PQ aspect of coated M5 segments after one-sided HT steam oxidation at temperatures above the temperatures at which the Zr-Cr eutectic reaction occurs. For such very HT oxidation conditions, the PQ Cr-coated clad surface is characterized by a "crocodile skin" morphology with some continuous blisters forming an external protruding pattern. This "crocodile skin" aspect is due to small displacement of the liquid at the surface (shell); this phenomenon should be due to potential liquid "capillary" effects and local swelling associated with the solid-to-liquid volume change.

Fig 5. Typical PQ aspect of a Cr-coated M5 after HT oxidation at 1400°C

Figure 6 shows an illustration of EPMA examinations through the PQ clad wall thickness, at the location of one protruding blister. From the mapping of oxygen and chromium, one may observe that the protruding blister corresponds to the formation at HT of a (prior-)liquid "pocket" with a typical dendritic substructure induced upon the final solidification/quenching. This zone consists of both chromium-depleted prior-β_{Zr} dendrites and chromium-enriched inter-dendritic zones, containing around 30at.% of chromium. Such microstructure can be understood by considering again the pseudo-binary M5-Cr phase diagram (Figure 7). Thus, the different metallurgical evolutions upon heating beyond 1300°C, annealing for 100s at ~1400-1450°C[2] and then water quenching down to room temperature, can be summarized as follows:

(a) ***upon heating beyond 1300°C***, fast inter-diffusion between Zr and Cr occurs, then the intermediate metallic $ZrCr_2$ layer reacts with the β_{Zr} substrate to form the eutectic liquid phase;

(b) ***upon annealing for 100s at 1400-1450°C***, the liquid (eutectic) phase is progressively enriched in zirconium coming from the Zr-substrate (considering that no more Cr is available due to its early consumption to form eutectic liquid phase upon heating in the 1305-1325°C temperature range);

[2] The same metallurgical evolutions were observed for temperature incursion/oxidation up to 1500-1550°C

(c) ***upon quenching from 1400-1450°C***, β_{Zr} dendrites precipitate in association with enrichment in Cr of the inter-dendritic residual Zr-Cr liquid phase as the temperature decreases; then, the residual Zr-Cr liquid phase solidifies when the temperature decreases below the "eutectic point" of the phase diagram[3], which corresponds to ~30%at. of chromium, consistently with the EPMA measurements. Additionally, EPMA oxygen mapping shows that continuous outer scales of ZrO_2 and α_{Zr}(O) have grown during the HT oxidation process. The homogeneity and uniformity of these outer scales over the whole clad outer surface are remarkable. It can be thus observed that the local oxidation kinetics were outstandingly the same at the liquid eutectic and the Cr-depleted locations. It indicates that the formation of a liquid Zr-Cr phase at the outer surface of the Cr-coated clad at very HT (>1300°C) may not drastically modify the zirconium based cladding HT oxidation mechanisms and kinetics.

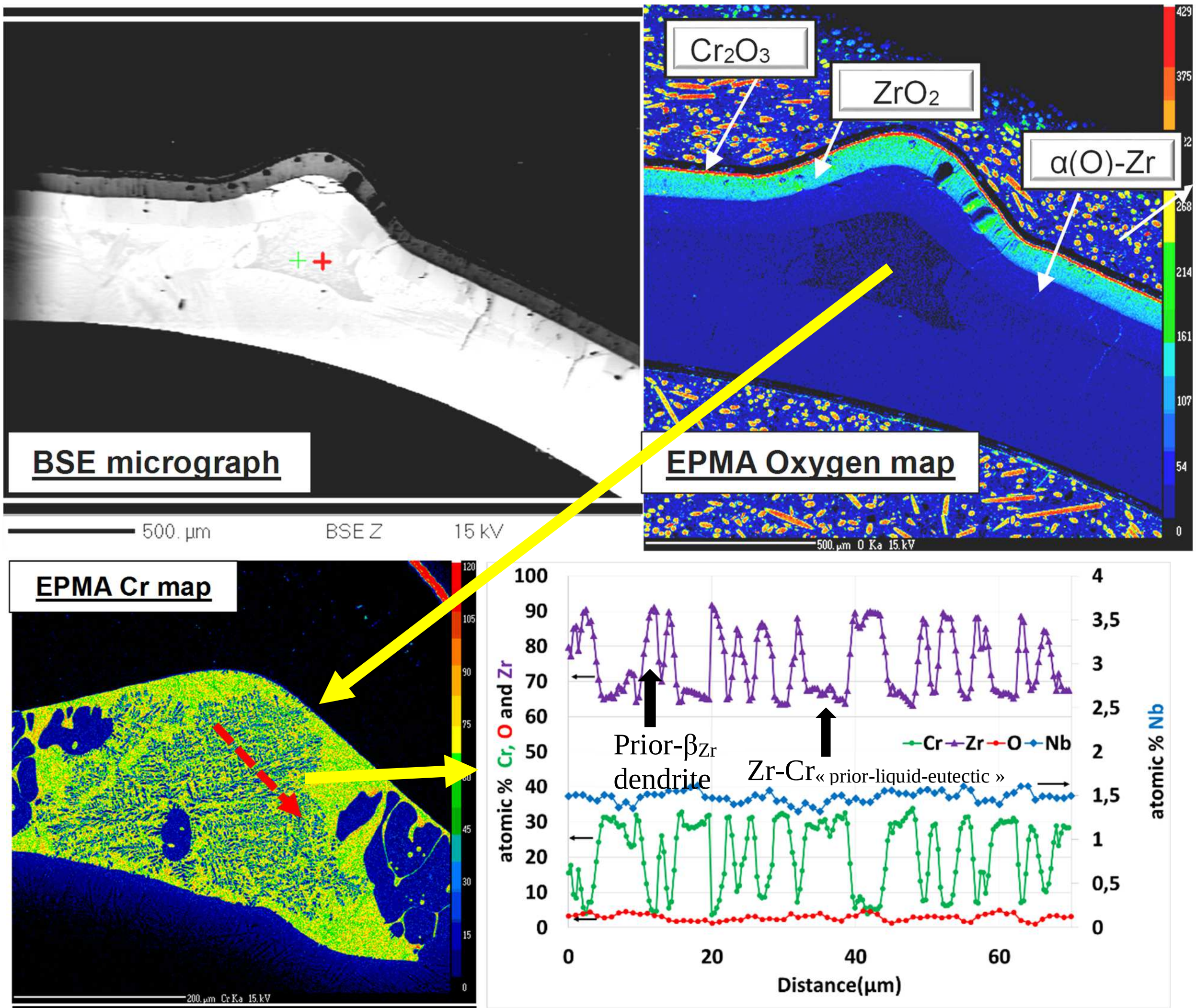


Fig 6. EPMA chemical element mapping and quantitative profiles obtained at the vicinity of a protruding blister of Cr-coated M5 cladding segment that has been one-sided steam oxidized for 100s at ~1400-1450°C and water quenched down to RT

[3] In fact, when compared to the equilibrium phase diagram and due to the high cooling rate, some over-cooling may occur before solidification of the inter-dendritic Zr-Cr liquid phase

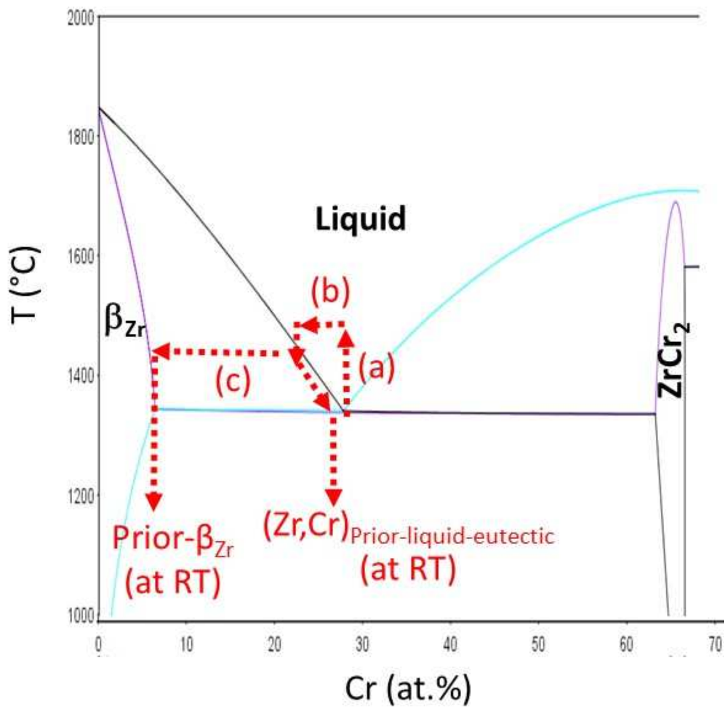


Fig 7. Partial portion of the calculated binary M5-Cr phase diagram and schematic metallurgical evolutions upon heating beyond 1300°C, annealing for 100s at 1400-1450°C, and then quenching from 1400-1450°C

4. CONCLUSIONS

Various one-sided HT steam oxidation tests have been performed between 1000 and 1500°C on M5 cladding segments with a 12-15µm thick outer Cr-coating. Some additional PQ mechanical testing and metallurgical examinations were carried out to get better insights into the PQ behavior and microstructures of the tested Cr-coated cladding segments. A special attention has been paid to the eutectic reaction that occurs between Zr and Cr for HT oxidation temperatures above 1300°C (DEC).

- In the 1000-1300°C oxidation temperature range, it was confirmed that the 12-15µm thick Cr-coating increased significantly the oxidation resistance of the cladding and, when compared to reference uncoated claddings, increased the "coping time" at HT significantly, before the material became macroscopically brittle during and/or after quenching.
- Complementary calorimetric measurements in near-thermodynamic equilibrium conditions have highlighted the eutectic reaction that occurs between the residual metallic Cr coating and the Zr based substrate above 1300°C, consistently with thermodynamic calculations.
- For the different DEC-type conditions applied, the tested Cr-coated clad segments did not fail upon the final water quenching while some uncoated reference segments did, even when samples reach temperatures beyond the eutectic temperature.
- One important observation was that the local oxidation kinetics was outstandingly the same at the liquid eutectic protruding blisters and at the neighboring Cr-depleted clad surface zones, and does not induce additional temperature escalation when compared to the reference uncoated materials. It is thus believed that the formation of a liquid Zr-Cr phase at the outer surface of the Cr-coated clad at very HT (>1300°C) under steam environment may not drastically modify the HT oxidation mechanisms and kinetics of the zirconium based cladding. Then, the oxidation kinetics correlations already established for uncoated reference cladding materials could be used as a

conservative approach to anticipate the behavior of Cr-coated claddings at temperatures above 1300°C, i.e., for DEC.

- Finally, it is believed that the outer ZrO_2 and α_{Zr}(O) scales that rapidly grow due to the steam oxidation process at very HT may have some beneficial effects, by acting as an efficient confinement barrier. Thus, for DEC, this would prevent from further (underlying) liquid Zr-Cr eutectic phase spatial relocation and/or potential reaction/bonding with adjacent rods (or with other components such as grids, guide tubes…) of the nuclear fuel sub-assembly.

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