Qualitative approach to understand the behaviors of oxidation, hydriding, and the buildup of corrosion products (CRUD) for CrAl-ODS-Zr alloy ATF cladding

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1. Introduction

The oxidation, hydriding, and the buildup of corrosion products (CRUD, Chalk River Unknown Deposit) are directly correlated with the fuel performance during normal operation, anticipated operational occurrences (AOOs), and accident conditions. The oxidation and hydriding degrade cladding ductility particularly in accident situations. The oxidation also decreases in thermal conductivity and load-bearing thickness. In addition, excessive oxidation is continued oxide spallation which can lead to a local cold spot which acts as a sink for hydrides, creating a local, extremely brittle hydride lens. CRUD act as a heat transfer barrier and induces an increase in cladding temperature. They lead to CRUD induced localized corrosion (CILC) or axial offset anomaly (AOA). To avoid these risks, the acceptance criteria in regulatory standard review plan (SRP) 4.2 described that oxidation, hydriding, and the buildup of corrosion products (CRUD) should be limited based on mechanical testing to demonstrate that each component maintains acceptable strength and ductility [1,2]. Also, these allowable levels and demonstration of acceptability should be discussed on the safety analysis report and their effects be accounted for in the thermal and mechanical fuel analyses. The effect of CRUD on thermal-hydraulic considerations and neutronic (AOA) considerations should be reviewed. In this regard, specific design limits for oxidation and hydriding (excepting CRUD) have established for Zr-based cladding.

But these limits are relevant to Zr/ZrO_2, but the outer oxide for coated accident tolerant fuel (ATF) cladding will be Cr_2O_3. Accordingly, they couldn't be simply applied to analysis for coated cladding because the relevant knowledge is lack due to limited data. In this paper, the oxidation, hydriding, and the buildup of corrosion products (CRUD) behaviors of ATF cladding is qualitatively studied and its effect on fuel in-reactor behavior is discussed for the phenomenon identification and ranking table (PIRT) development study. They are performed for the development of the ATF nuclear fuel performance model and code. The type of the ATF cladding to be covered in this study is Zr-alloy cladding with the partially oxide dispersion strengthened (ODS) and CrAl alloy coated layer, as shown in **Fig. 1**.

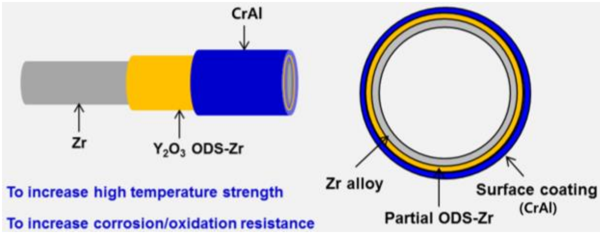


Fig. 1 Structure of CrAl-ODS-Zr alloy cladding [3,4]

2. Oxidation, hydriding, and the buildup of corrosion products (crud) for Zr-based cladding

The oxidation of Zr-based cladding in PWR environment during normal operation is dependent on the various parameters (e.g. temperature, $Zr(Fe,Cr)_2$, hydrogen segregation at oxide/matrix interface, dissolved oxygen, irradiation, Li concentration). Based on the operation experiences, the design limits of oxide thickness and hydrogen concentrations at end-of-life use 100 μm and 500-600 ppm, respectively [5]. The excessive oxidation can cause oxide spallation and the locally massive hydride formation, but their effects does not reflect on the current limits. And oxidation is most important parameter limiting the length of time that fuel rod can safely be left in reactors.

Based on extensive test results, oxidation rates of Zr could be approximated pre-transition region and post-transition region following cubic rate law and linear rate law, respectively, even if cyclic transitory region exists (**Fig. 2**). Most models on the fuel performance codes evaluating oxidation under normal operation (e.g. FRAPCON, EPRI/KWU/CE, ESCORE, EPRI SLI, NE PLC, COCHISE etc) are based on Garzarolli model [6] (dot line in **Fig. 2**) which used approximate integral method.

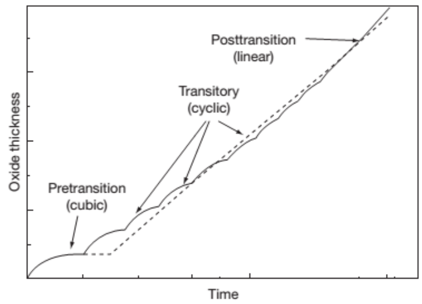


Fig. 2 Schematic diagram of the oxidation rate of Zr-alloy during normal operation [7]

The fraction of the hydrogen liberated by the oxidation (metal-water corrosion reaction that is absorbed locally by the cladding could be approximated to constant values for PWR conditions. On FRAPCON, they depend on the material type (e.g. 0.15 for Zry-4, 0.1 for M5, 0.175 for ZIRLO/Opt. ZIRLO) [8].

CRUD deposition is caused by van der Waals force between cladding and corrosion products. There is no relevant design limit. On FRAPCON, the initial thickness and deposition rates provided by user input are applied to temperature analysis, because there is no deposition model.

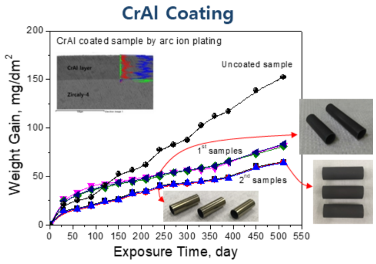
3. Oxidation, hydriding, and the buildup of corrosion products (CRUD) for CrAl-ODS-Zr alloy ATF cladding

3.1. CrAl-ODS-Zr alloy ATF cladding [3,4]

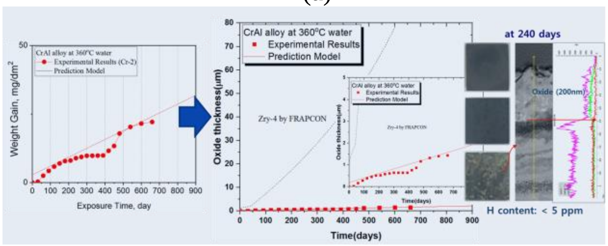
The surface modified Zr cladding concept in KAERI has been developing as a one of the candidates for ATF cladding because the corrosion/oxidation resistance and the high-temperature strength of Zr alloy can be improved by applying a surface modified technology, as shown in **Fig. 1**. Two technologies of outer surface coating and a partial ODS structure at the intermediated region between the outer CrAl coated layer and Zr alloy tubes are applied in this concept. In detail, the corrosion/oxidation resistance during normal operation and under accident conditions can be increased by the surface coating method (arc ion plating, AIP), and the high-temperature strength of the cladding can be increased by the partial ODS method with Y_2O_3 particles.

3.2. Oxidation, hydriding, and the buildup of corrosion products (CRUD)

On the evaluation of the oxidation, hydriding, and the CRUD buildup, only outermost layer (CrAl) exposed to primary water need to be considered as long as coating layer maintains intact without cracking and delamination. Throughout 360-520 ℃ water/steam autoclave test results, many organizations reported that the coated ATF cladding using Cr, CrN, CrAl has 2~100 times improved oxidation resistance than existing Zr-alloy cladding and good hydriding resistance due to protective Cr_2O_3 layer [9]. Also for CrAl coated cladding, a highly improved oxidation resistance without local flaking and galvanic corrosion observed on the 360 ℃ simulated PWR water loop tests (**Fig. 3**). Based on this results, an oxidation prediction model was developed considering only uniform corrosion as shown in **Fig. 3 (b)**.



(a)



(b)

Fig. 3 Oxidation properties of CrAl coated cladding (a) Autoclave test under 360℃ simulated PWR environment, (b) Prediction model [10,11]

But most of these data are based on ex-reactor test data, they should be confirmed by post-irradiation examination of lead-test rods and evaluated based on this in-reactor data. In addition, coating cracking and defects induces locally high oxidation, hydriding and the formation of brittle hydride lens. These concerns can be solved by the optimization of cladding fabrication process and setting of appropriate limits.

In terms of hydriding, protective Cr_2O_3 prevent to diffuse hydrogen into Zr matrix and very low hydrogen pickup is anticipated, as mentioned before. But M. Ševeček et al reported that Cr-coated cladding has similar hydrogen concentration in spite of low oxidation rate (**Fig. 4**) [12]. They imply that Cr-coated cladding can have high hydrogen pickup fraction, and the relevant mechanism was not confirmed yet. Another possible explanation is just scatter in the range of low hydrogen concentration. Further examinations and in-reactor tests are necessary to confirm.

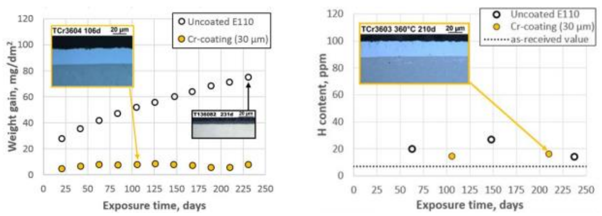


Fig. 4 Ex-reactor oxidation and hydriding properties of Cr-coated E110 cladding (360℃, 197 bar, simulated WWER environment) [12]

On CRUD buildup test of CrAl coated Zry-4 cladding using static autoclave at 360℃ for 200 days, CrAl coating significantly decreases the deposition rate than

Zry-4. The CRUD buildup test for CrAl coated cladding using simulated PWR water loop is on-going. They result in beneficial effects on the thermal conductivity. Meanwhile, Westinghouse reported that Cr-coated cladding has roughly same propensity to collect CRUD as standard ZIRLO [13]. Additional ex-reactor and in-reactor tests should be performed, because there are only results in limited conditions.

In comparison with Zr-alloy cladding, the thickness of Zr-alloy in CrAl-ODS-Zr alloy cladding is almost maintained. Therefore, it is considered that the existing design limits (e.g. 100 μm oxide thickness, 600 ppm hydrogen) could be similarly applicable to Zr matrix. Lower limits conservatively considering additional margin is preferable due to uncertainties in hydrogen pickup fraction. Additional limits need to prevent the cracking and delamination of coatings. Otherwise, separate limits could be proposed based on the oxidation/mechanical tests for coated cladding. Meanwhile, there is no design limit on CRUD deposition for Zr-alloy cladding and lower CRUD deposition rates for CrAl-ODS-Zr alloy cladding are expected. But CRUD deposition should be evaluated by post-irradiation examination of lead test rods and monitored in plants.

4. Summary

The oxidation, hydriding, and the buildup of corrosion products (CRUD) behaviors of CrAl-ODS-Zr alloy ATF cladding has been studied by qualitative approach. CrAl-ODS-Zr alloy ATF cladding would have superior resistance for oxidation and hydriding, although they should be confirmed by post-irradiation examination of lead-test rods and evaluated based on this in-reactor data. The existing design limits could be similarly applicable to Zr matrix, and lower limits conservatively considering additional margin is preferable. In addition, cracking and delamination which are inherent concerns for coating should be evaluated. Meanwhile, there is no necessity for specific limit of CRUD buildup, and CRUD deposition rates should be evaluated and monitored in plants.

Acknowledgement

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