Experimental report

01/04/2024

Proposal:	**1-04-245**
Council:	10/2022
Title:	Phase transformations in Cr-coatedzirconium nuclear fuel cladding studied by in-situ neutron diffraction
Research area:	Materials

This proposal is a new proposal

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Samples: Zr-Nb-Cr-O

Instrument	Requested days	Allocated days	From	To
D1B	3	2	04/04/2023	06/04/2023

Abstract:

Cr-coating of the classical Zr-based claddings is a new concept supposed to bring more safety in case of an accident in a nuclear power plant. It is important to study the phase transformations occurring in such alloys during the temperature transients encountered in accidental conditions.
Model alloys have been synthesized aiming to reproduce the different levels of chromium reached in the cladding after an accidental excursion at high temperature. Studying these model alloys allow to reproduce the phase transformations occurring in the complete cladding.
In-situ neutron diffraction allows to study not only the phase transformation occurring as a function of temperature but also the partitioning of the different elements via the measurement of lattice parameters.
We will study two model samples plus the complete cladding in-situ. In addition, ex situ measurements will be performed on samples previously quenched with a quenching rate not obtainable in in-situ conditions.

Context

Nuclear energy is expected to play a key role in the future to accompany the energy transition. Many efforts are devoted to the improvement of safety in general and to the development of accident tolerant fuels, in particular. Coating classical zirconium based fuel claddings with chromium significantly improves the safety of nuclear power plants in accidental conditions.

Such Enhanced Accident Tolerant Fuel (E-ATF) concept consists in a 15µm thick PVDcoating of chromium at the surface of the conventional zirconium-niobium claddings. The aim of this coating is to protect the fuel assembly from oxygen and hydrogen ingress during accidental high temperature transient that can cause serious embrittlement and failures.

However, in typical accidental conditions such as Loss Of Coolant Accident (LOCA), the maximum temperature can reach 1200°C (HT) involving α-Zr (hcp) transformation into β-Zr (bcc) and chromium diffusion into the cladding inducing a substantial diffusion profile throughout the whole cladding thickness and major evolutions of metallurgical and mechanical properties (Fig. 1).

Then, different cooling scenarii are considered when the Emergency Cooling Systems operate:

(1) A direct water quenching from HT,

(2) A two-steps cooling from HT to intermediate temperature (~900°C-600°C) at relatively slow cooling rates (1°C/s-10°C/s) followed by water quenching.

With multi-scale examination, it has been shown [1] that the mechanical properties of the Cr - coated claddings after LOCA are extremely sensitive to the applied cooling scenario.

The aim of this work is to understand the metallurgical and phase transformations aspects of Cr-coated E-ATF during LOCA. In order to reproduce the typical concentrations observed in the chromium diffusion profile in the cladding, industrial alloys Zr1wt%Nb-1500wppmO (M5Framatome) were melted with different chromium concentrations (Fig. 1). Each model alloy representing a layer of the actual cladding is studied independently in order to obtain, by reconstruction and after modeling, an overall understanding of the cladding behavior during cooling. Phase transformations and intermetallic (ZrCr2) precipitation during cooling are still a matter of great uncertainties, especially in the case of the LOCA's two-steps cooling (2) and have a consequence on the final results.

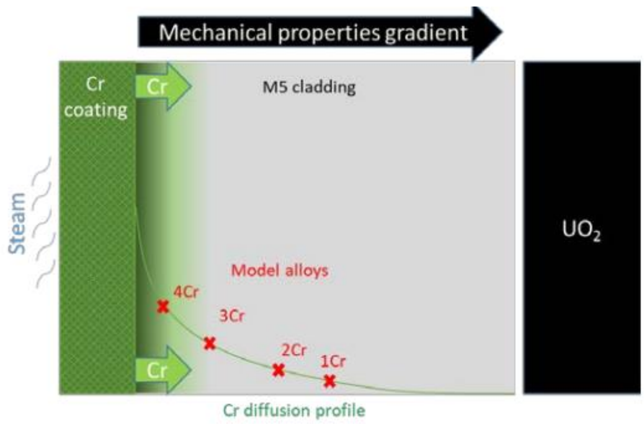

Figure 1. Schematic representation of Cr-coated M5 with Cr diffusion profile and model alloys positions

Aim of the experiment

The aim of this experiment was to fully characterize the phase transformations, intermetallic precipitation and compositional evolutions during a LOCA two-steps cooling scenarii for different Cr concentrations in order to get a deep understanding of the phenomena happening on a real coated cladding. In this purpose, homogeneous model alloys was compared to a reference Cr-coated M5 under the same conditions. To reproduce the cooling scenarii, this experiment consisted in both in-situ and ex-situ measurements. First, the in-situ experiment reproduced the slow cooling from 1200°C to 600°C allowing the observation of the β phase at high temperature that cannot be retained after quenching. Second, the ex-situ experiment was performed on previously water quenched (from different temperatures between 1200°C and 600°C) samples since the furnace cooling kinetics cannot reproduce a water quench.

Results and discussion

We were able to make significant progress in our understanding of phase equilibria during cooling from HT thanks to the two beam days provided by ILL. We conducted three in situ experiments while cooling down from HT to room temperature. By refining the HT β_{Zr} phase lattice parameter (Figure 1) in comparison with the Calphad formalism, we were able to gain a thorough understanding of the phase transformation sequence and the related chemical partitioning. Furthermore, the ILL facility constant cooling demonstrates that this β_{Zr} phase persists at lower temperatures. It was not anticipated by Calphad calculation and appears to be the result of substantial Nb and Cr partitioning that takes place during the $\beta_{Zr} \rightarrow \alpha_{Zr}$ phase transformation.

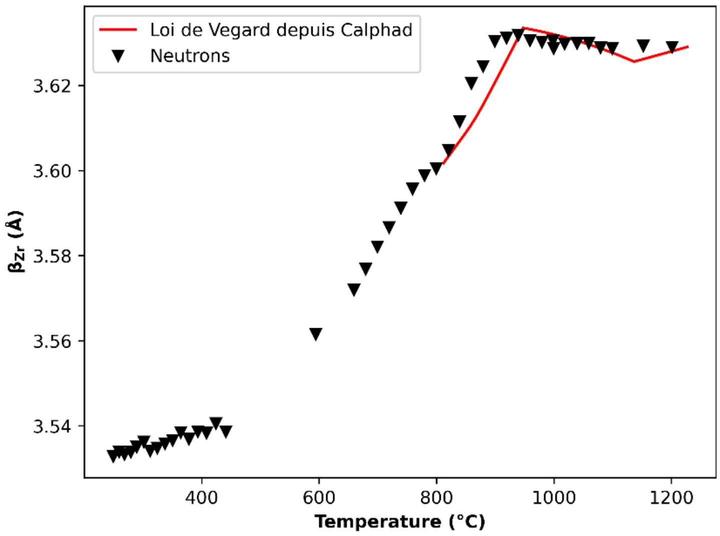

Figure 2. Refinement of βZr lattice parameter (black dots) evolution during cooling and display a good agreement to Caphad (red curve)

Several metastable phases that were unclear with conventional XRD may now be readily identified thanks to the ex-situ experiment on quenched samples. These phases were successfully refined on the neutron diffraction pattern, and we were able to determine a complex metastable phase transition sequence from ordering the HT βZr phase to α_{Zr} displacive martensite transformation by coupling neutron diffraction and high resolution TEM (Figure 3). These stages appear to be crucial for the ultimate mechanical characteristics of the cladding behavior following a LOCA transient, and those observations are the first step toward comprehending the cladding material ultimate features.

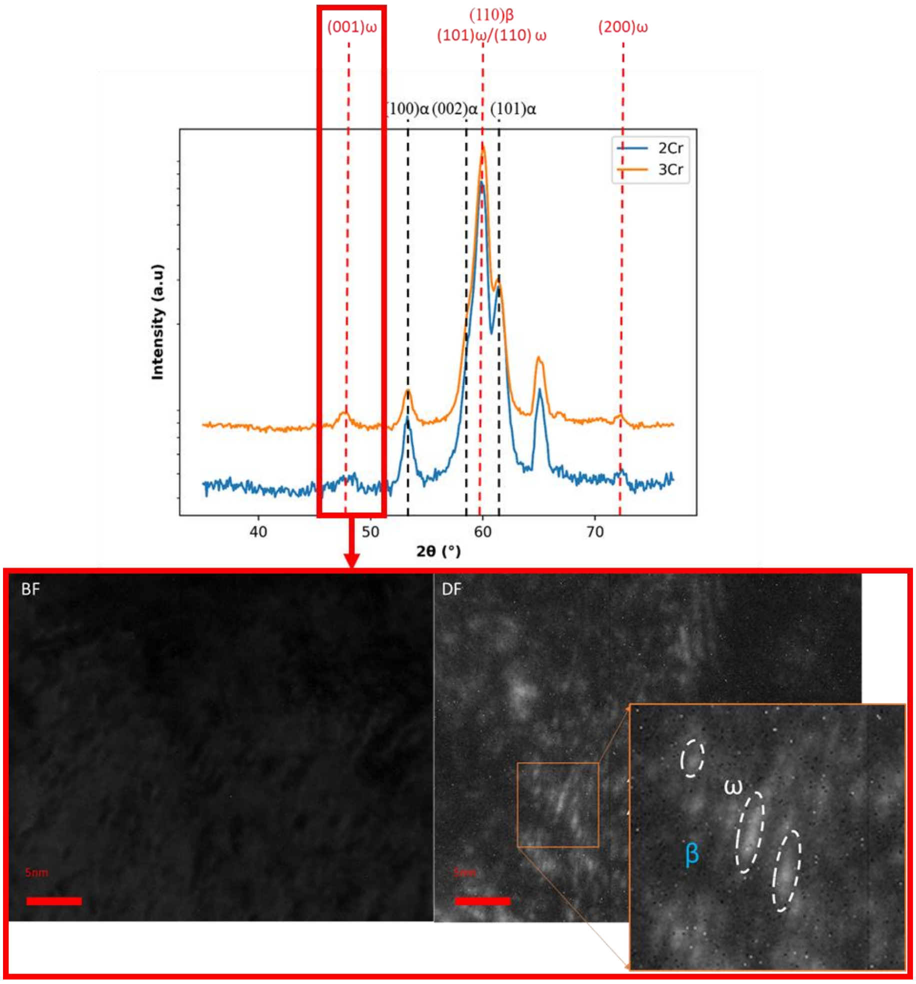

Figure 3. Neutron diffraction pattern and TEM (Bright and Dark field) study of the (001)ω and demonstrating the existence of the ω phase

An article about the experiments will be redacted in the coming months.

Acknowledgments

We would like to thank Laetitia Laversenne local contact on D1B as well as the technical staff and the staff other member for their help during the experiment.

References

[1] J.-C. Brachet *et al.*, « Effect of Chromium Content on the On-Cooling Phase Transformations and Induced Prior-bZr Mechanical Hardening and Failure Mode (in Relation to Enhanced Accident-Tolerant Fuel Chromium-Coated Zirconium-Based Cladding Behavior upon and after High-Temperature Transients) », *Zirconium in the Nuclear Industry: 20th International Symposium*, p. 433-459, 2022.