Metallurgical evolutions of zirconium alloys containing high hydrogen contents during cooling from high temperature

T. Le Hong, M. Le Saux, Jc. Brachet, J. Crepin, Q. Barres, T. Guilbert, R. Guillou, J.-M. Joubert, C. Toffolon-Masclet, I. Turque

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Thai LE HONG [1,2*], Matthieu LE SAUX [1], Jean-Christophe BRACHET [1], Jérôme CREPIN [2], Quentin BARRES [1], Thomas GUILBERT [1], Raphaëlle GUILLOU [1], Jean-Marc JOUBERT [3], Caroline TOFFOLON-MASCLET [1], Isabelle TURQUE [1]

[1] DEN-Service de Recherches Métallurgiques Appliquées (SRMA), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France
[2] MINES ParisTech, PSL Research University, Centre des Matériaux, CNRS UMR 7633, BP 87, 91003 Evry, France
[3] Institut de Chimie et des Matériaux Paris-Est, UMR 7182 CNRS-Université Paris-Est Créteil, 2-8 rue Henri Dunant, 94320 Thiais, France
[*] Main Author, E-mail: hong-thai.le@cea.fr, hong-thai.le@mines-paristech.fr

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Introduction

In pressurized water nuclear reactors, under hypothetical Loss-Of-Coolant Accident (LOCA) conditions, zirconium alloy fuel cladding tubes could be exposed to steam at high temperature (up to 1200°C). In some conditions (*e.g.* after burst occurrence), the material could absorb an important amount of hydrogen, up to thousands of wt.ppm locally, before being cooled and water quenched [1]. Structural and metallurgical evolutions undergone by the material during cooling have an effect on its mechanical properties, which have to remain sufficient for safety reasons. Data about these metallurgical evolutions during cooling from high temperature are scarce for high hydrogen contents [2, 3].

The purpose of this study is to improve both experimental database and understanding of the effects of high hydrogen contents, up to 3000 wt.ppm, on the metallurgical transformations of zirconium based alloys, during cooling/quenching from high temperature (β_{Zr} domain).

Materials and experimental procedure

The specimens were mostly prepared from low tin Zircaloy-4 and M5™[1] fuel cladding tubes. "Van Arkel" Zirconium sheet samples containing a very low amount of oxygen (~100 wt.ppm) was also used for a selected number of characterizations in order to separate the effects of hydrogen and oxygen (Zircaloy-4 and M5™ contain 0.13-0.14 wt.% of oxygen).The materials were charged in hydrogen at 800°C to various contents between 1000 and 3000 wt.ppm. The hydrogen-charged samples were heat-treated at about 1000°C in order to characterize the properties of the (prior-) β_{Zr} phase, and then were subjected to various cooling rates to study the potential effect of the cooling scenario on zirconium phase transformation and hydrogen precipitation.

Neutron and X-ray diffraction (XRD) analyses were performed at room temperature after cooling, or *in situ* upon step-cooling from the β_{Zr} domain. These investigations provided information on the material structure (phases, lattice parameters) and its evolution with temperature as a function of the alloy, the hydrogen content and the cooling scenario. In order to understand the effects of hydrogen on the evolution of lattice parameters and to decorrelate from the oxygen effects, XRD was performed at room temperature on as-received and hydrogen-charged "Van Arkel" Zirconium after heat-treatement in the β_{Zr} domain followed by various cooling scenarios. The diffraction data were analyzed by the Rietveld refinement method.

Calorimetry and dilatometry measurements were also carried out to investigate metallurgical changes of the model hydrogen-charged materials in near-equilibrium and dynamic conditions.

The experimental results were compared to thermodynamic predictions obtained in equilibrium conditions by the Thermo-Calc software associated with the Zircobase thermodynamic database [4].

[1] M5 is a registered trademark of AREVA NP in the USA or others countries

Conclusion

The following conclusions were obtained, amongst others:

- Phases transformations of zirconium and hydrides precipitation during cooling were quantified. According to neutron diffraction results (Figure 1), in the materials containing about 3300 wt.ppm of hydrogen, the body-centered-cubic β_{Zr} phase transforms into the hexagonal α_{Zr} phase during cooling, progressively at the beginning of cooling then rapidly around 500°C due to an eutectoid transformation in Zircaloy-4 and a monotectoid reaction in M5.
- δ-ZrH_{2-x} hydrides start to precipitate at about 540°C for Zircaloy-4 and 520°C for M5. The α_{Zr}, β_{Zr} and δ-ZrH_{2-x} phases co-exist between about 500 and 540°C and between about 480 and 520°C in the case of Zircaloy-4 and M5, respectively.
- Thermodynamic predictions are in good agreement with these results.
- The precipitation of γ-ZrH hydrides, potentially metastable, was observed at low temperatures (≤ 350°C) in materials with high (1000 and 3000 wt.ppm) and lower (300 wt.ppm) hydrogen contents, for both slow and fast cooling.
- According to results of both X-ray and neutron diffraction, the a and c parameters of the α_{Zr} hexagonal lattice increase with increasing the mean hydrogen content at room temperature.

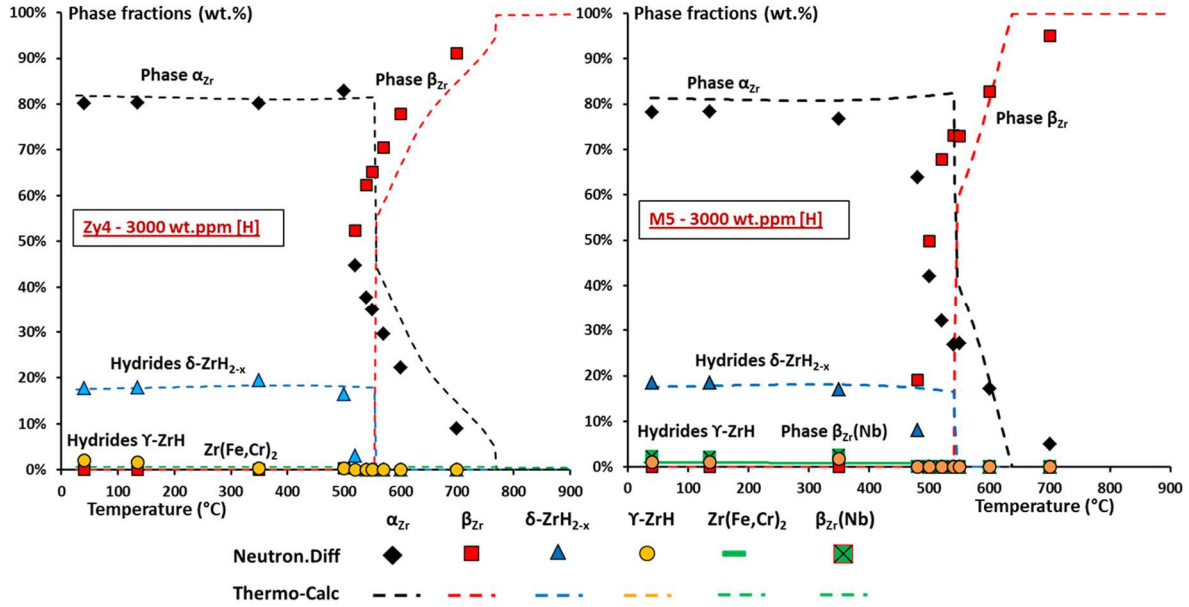

Figure 1: **Evolution of phase weight fractions as a function of temperature obtained by neutron diffraction (symbol) *in situ* during step-cooling from 700°C and thermodynamic calculations (dotted curves) for Zircaloy-4 (left) and M5 (right) containing about 3000 wt.ppm of hydrogen**

Acknowledgment

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