"IN SITU" NEUTRON SCATTERING STUDY OF HYDROGEN-CONTAINING ZIRCALOY-4 ALLOYS

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Aims of the study

The fuel cladding of Pressurized Water Nuclear Reactors (PWR), made in Zircaloy-4 (zirconium-based alloy, containing in weight typically 1.4% Sn, 0.2% Fe and 0.1% Cr), is sensitive to hydrogen absorption in the usual working conditions (i.e. under H_2O at 300°C). Hydride platelets may form, which are an important embrittlement factor of the cladding, and also which induce a swelling when they dissolve in the α-h.c.p. Zircaloy matrix. Moreover, recent studies suggest that these hydrides may be an accelerating factor of corrosion. This aspect will be all the more important as the new working PWR conditions will be more demanding.
It is therefore essential to characterize and understand the mechanisms of hydride formation and dissolution, in particular under neutron irradiation : this is the object of a research programme undertaken by the "Direction of Nuclear Reactors" of CEA, which includes a neutron scattering study at LLB.
The large coherent and incoherent cross-sections of hydrogen make this tool very powerful to determine the hydrogen content and characterize the hydrides ; indeed, the incoherent cross-section gives rise to a continuous background in diffraction spectra, which is **proportional** to the hydrogen content, and is (nearly) independent of scattering angle ; the coherent cross-section contributes significantly to the structure factor of the hydride phase, i.e. to the intensity of its diffraction peaks. Zirconium is a specially favorable element for this study, because its neutron absorption coefficient and incoherent scattering cross-sections are very weak : the diffraction spectra of H-free samples show very low background.

Results

In a first stage, we have shown, on the powder diffractometer G4.1 (equipped with a 800 cell linear multidetector), that the incoherent scattering contribution, obtained from the measurement of the background on samples originating from cladding tubes, allows to determine **non destructively** the total amount of incorporated hydrogen (Fig. 1), with very good sensitivity and precision (< 20 ppm weight). The principle of measurement consists to calibrate in absolute value the incoherent signal measured on a reference vanadium sample of cylindrical shape, after subtraction of the instrumental background ; this allows to calibrate the signal difference between the hydrogenated sample and an hydrogen free sample.
On the other hand, the diffraction peaks of the hydride (f.c.c. δ-ZrH_2) and Laves phase precipitates ($Zr(Fe,Cr)_2$) can be easily detected and analysed, for very weak (< 1% atomic) H, Fe and Cr contents, which is not possible in conventional X-ray diffraction.
In a second stage, we have performed "in situ" measurements at various temperatures (between 20 and 500 °C) under secondary vacuum, on a section of Zircaloy-4 cladding tube containing 642 ppm weight hydrogen (length of the sample : 50 mm, diameter : 9.5 mm). The typical measuring time for a single spectrum was 2 hours. In a single experiment (total duration : 5 days), we have been able to obtain simultaneously from the analysis of diffraction spectra the following informations :
- total hydrogen content,
- hydrogen content in hydride form,
- crystallographic characterization of the $Zr(Fe,Cr)_2$ and ZrH_2 precipitates,
- solubility of H, dissolution of hydrides (Fig. 2),
- influence of H on the thermal expansion of Zircaloy-4 (Fig. 3).

Desorption of hydrogen out of the sample under secondary vacuum was observed above 450 °C, by a decrease of the incoherent background signal.

Conclusions and future prospects

Neutron scattering is the only experimental technique which allows to measure non-destructively the total hydrogen content in Zircaloy tubes. But, more than a simple hydrogen content determination at room temperature, the neutron scattering technique, when combined use is made of the incoherent background and of the diffraction peaks, is also a very rich technique, sensitive and reliable, and quite appropriate to follow "in situ" at high temperature the precipitation/dissolution phenomena of zirconium hydrides, even for very weak contents of precipitates.
Future work will be the examination of neutron irradiated samples in PWR conditions (influence of irradiation on hydrogen solubility and on the structure of precipitates) and the study of the behaviour of the cladding in accidental situation (loss of primary cooling), which will require measurements at higher temperature (≈1000 °C).

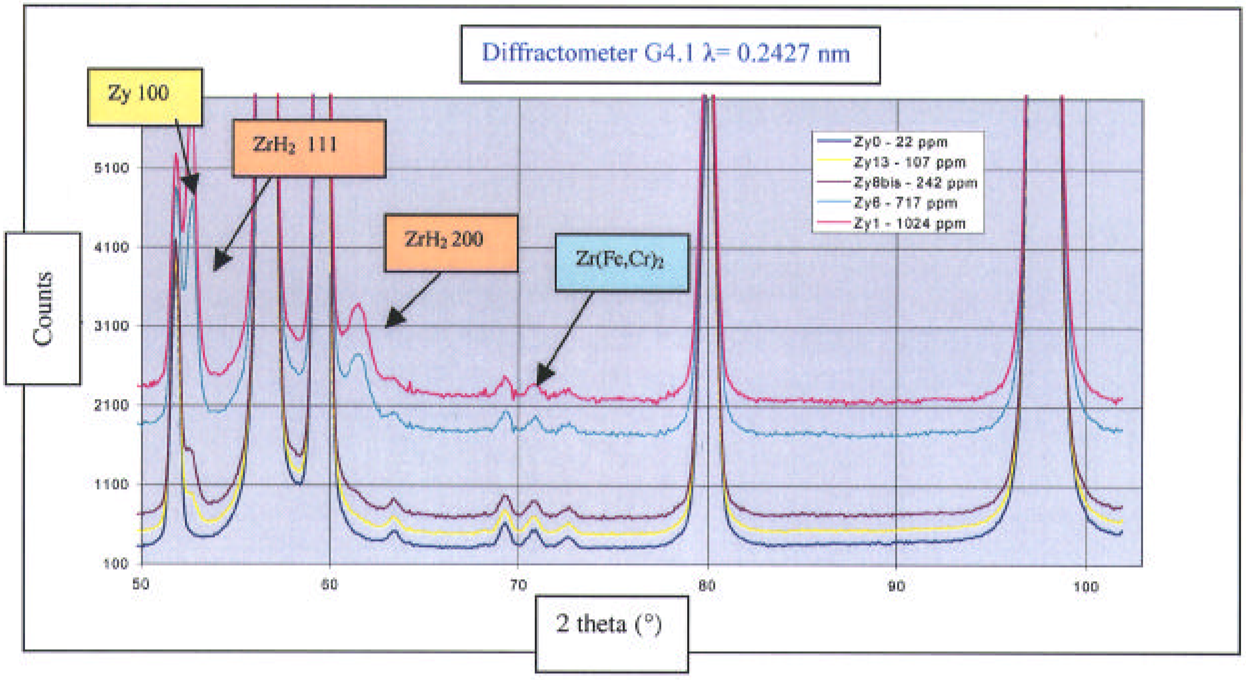

Figure 1 : Powder diffraction diagrams measured for several Zircaloy samples. One observes the increase of background with the hydrogen content, and the weak diffraction lines of δ-ZrH_2 hydride and Laves phase.

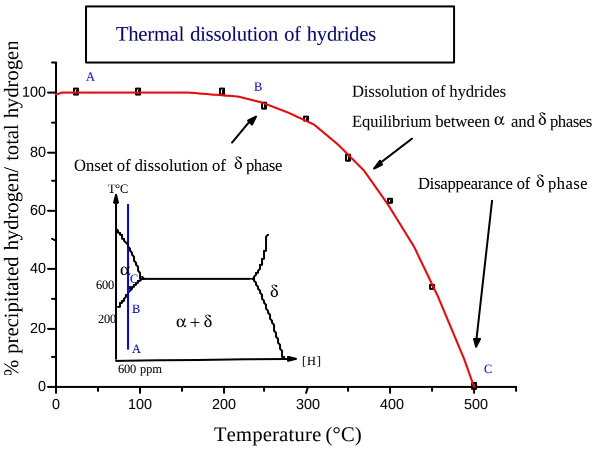

Figure 2 : Proportion of hydrogen content in hydride form (d-phase) versus temperature, for a sample containing 642 ppm weight hydrogen. This quantity decreases with increasing temperature, according to the phase diagram shown in inset : above 500°C, dissolution of the hydrides is complete and the sample is a single-phase Zr-based (a) hexagonal solid solution. It allows to determine the hydrogen solubility curve in the studied material, between room temperature and 500°C, and to deduce a value for the enthalpy of dissolution of the d-hydrides in Zircaloy-4 : DH = 41.5 kJ / mol.

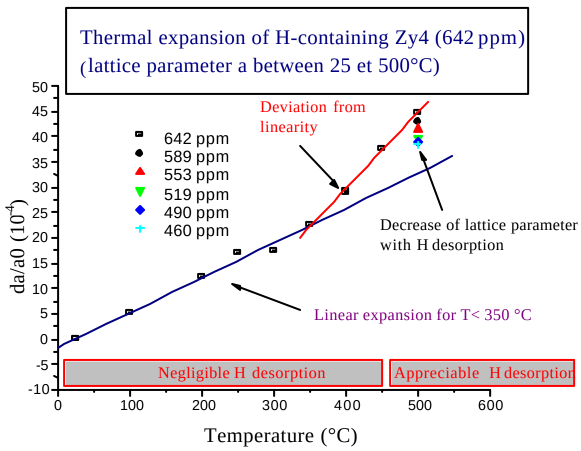

*Figure 3 : Temperature dependence of the lattice parameter **a** of Zircaloy-4 (sample containing 642 ppm weight hydrogen). A similar curve is found for the lattice parameter **c**. We attribute the increase of slope above 350°C to the dissolution of hydrides, which introduces interstitial hydrogen atoms in the a-Zircaloy matrix and a supplementary swelling. This explanation is confirmed by the observed decrease of lattice parameter during an isothermal stay at 500°C, due to hydrogen desorption out of the sample.*

References

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[2] J.H. Root, R.W.L. Fong « Neutron diffraction study of the precipitation and dissolution of hydrides in Zr-2.5Nb pressure tube material » Journal of Nuclear Materials 232 (1996) 75-85.