



**The Abdus Salam
International Centre for Theoretical Physics**



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**Joint ICTP-IAEA Advanced School on the Role of Nuclear Technology
in Hydrogen-Based Energy Systems**

13 - 18 June 2011

**Typical alloys for Nuclear Plant Technology studied for Corrosion by Nuclear Neutron
Diffraction**

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Grenoble
France*

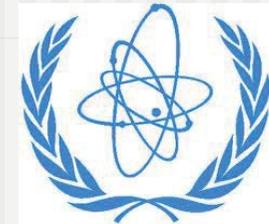
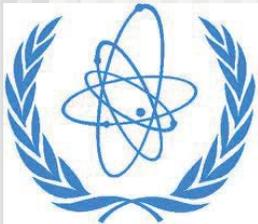
ZIRCALOY'S

**Typical alloys for Nuclear Plant Technology
studied for Corrosion by Nuclear Neutron Diffraction**

Daniel Fruchart

**Institut Néel, MCMF, IICE
Grenoble – France**

Collaboration with Cezus Co, China and Brazil



ZIRCALOY'S

Zircaloy's > 98 % zirconium

High mechanical resistance

High strength at high temperature (1850°C)

Mechanically usable

Rather corrosion resistant

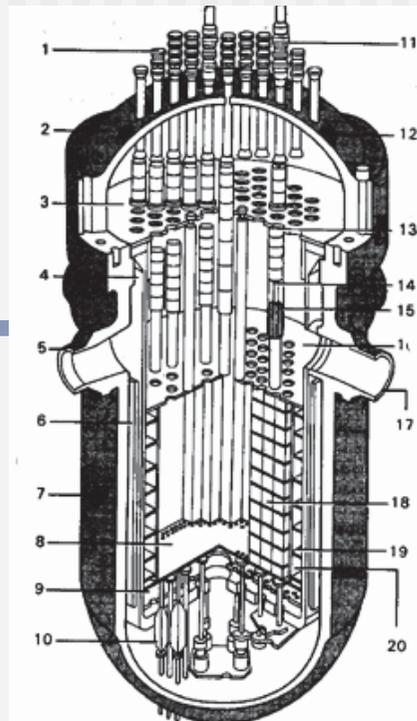
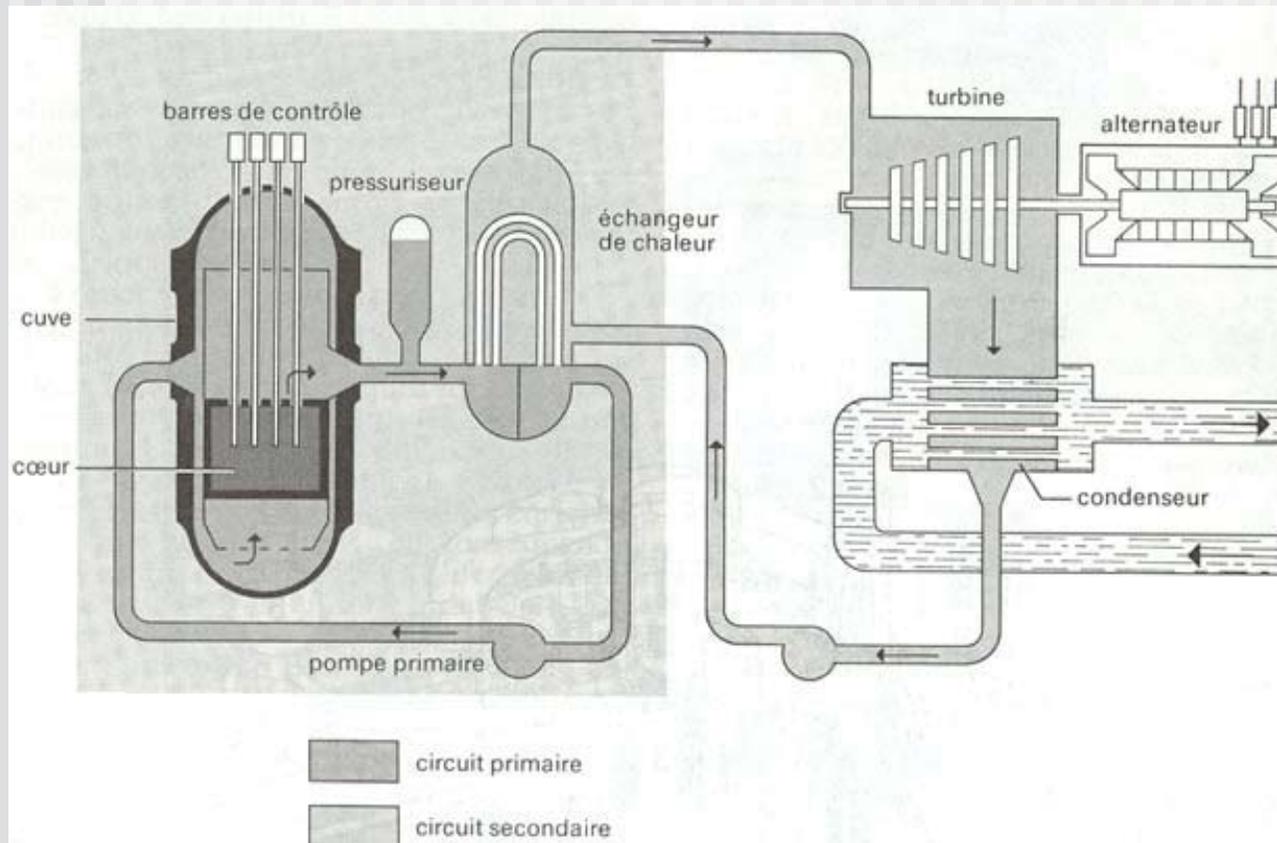
Relative abundance

Transparency for neutron (0.004 cm⁻¹)

iron (0.12 cm⁻¹)

ZIRCALOY'S

PWR : 155b - 345 °C



- 1 puits d'instrumentation
- 2 couvercle de la cuvette du réacteur
- 3 plaque de maintien supérieure
- 4 enveloppe du cœur
- 5 ajutage d'entrée
- 6 écran thermique
- 7 cuvette
- 8 plaque inférieure de supportage du cœur
- 9 plaque de répartition de débit
- 10 tube guide d'instrumentation
- 11 mécanisme de grappe de contrôle
- 12 anneau de levage
- 13 tube guide de grappe de contrôle
- 14 tige de commande des grappes
- 15 grappes de contrôle
- 16 plaque supérieure du cœur
- 17 ajutage de sortie
- 18 assemblages de combustibles
- 19 maintien radial du déflecteur
- 20 déflecteur

puissance thermique 2775 MW
 puissance électrique 925 MW
 rendement 33,2 %
 combustible 157 assemblages
 masse d'oxyde d'uranium 82,2 t
 enrichissement initial
 moyen de l'uranium 2,43 %
 enrichissement des recharges 3,25 %
 température de l'eau :
 - entrée 286 °C
 - sortie 323 °C
 pression dans la cuvette 155 bar

1300 MW: ~ 50 T UO₂ (3%) in Zyr tubes, φ 9.5 mm, wall 0.8 mm

ZIRCALOY'S

(at. %)	Sn	Ni	Fe	Cr	Nb	Cu-Mo-O
Zyr 2	1.3	0.05	0.13	0.10		
Zyr 4	1.3	-	0.14	0.11		
Zyr 2.5Nb(1)	1.3				2.5(1)	
Zyr M*	1.3	-	Yes	Yes	Yes	
other Zyr						1.8...
Zyr NZ2	1.0	-	0.30	0.10	0.3	0.08
Zyr NZ8	1.0	-	0.30	-	1.0	0.08

* Brazil, Canada, **China**, **France**, Germany, Japan, Russia, USA...

ZIRCALOY'S

* **Highly textured material** (rolled, extruded....)

α -Zr - hexagonal phase : hard mechanical phase

β -Zr - bcc phase for $T > 800$ °C

β -Zr - bcc phase when alloyed with Nb

* **Alloying elements** : solid solution at high temperature but precipitate to a fine microstructure for nice mechanical strength at RT

ZIRCALOY'S

* **Needs of better Zyr** : to use in higher temperature reactor for better thermodynamic efficiency (> 35 %) and for longer life-time (> 30 y.)

* **Corrosion** : near to super critical water regime, dry steam in PWR

* **Reaction** : $\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2$ (or **4 H??**)

at least 2 types of **zircona** can be formed
tetragonal dense ZrO_2
monoclinic expanded ZrO_2



ZIRCALOY'S

* Role of precipitates on the corrosion process?

Zyr 2 : Ni eases the H diffusion in bulk via Zr-Ni precipitates

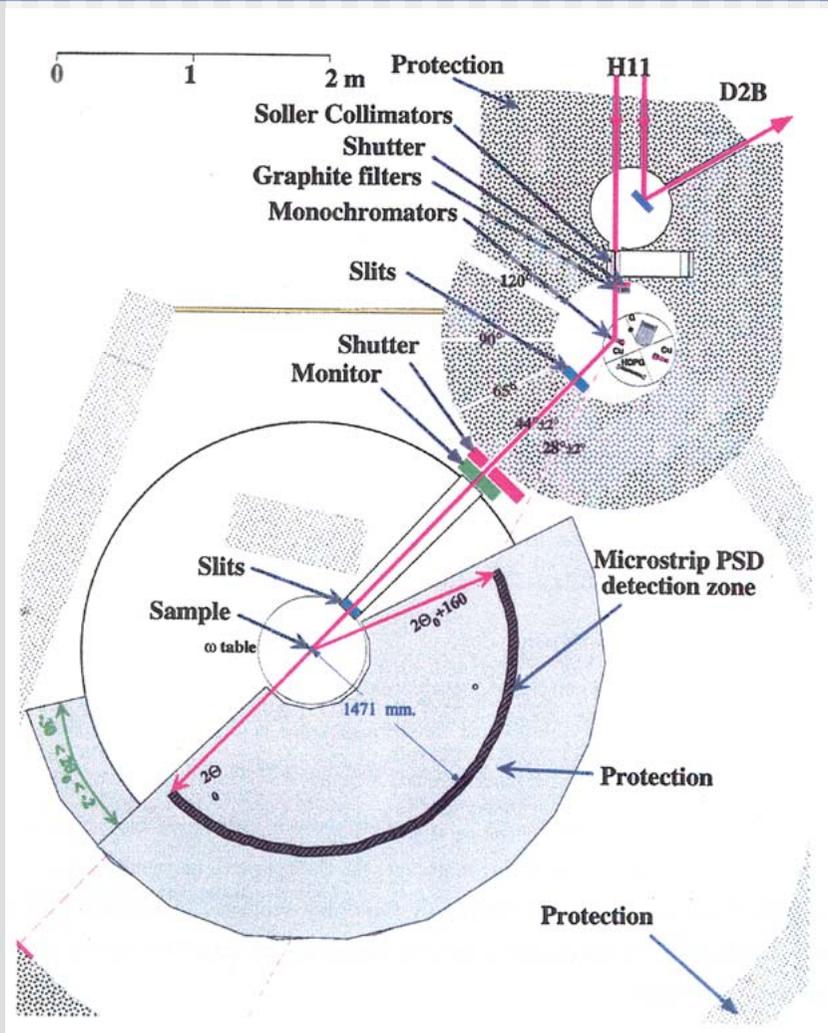
Zyr 4 : $\text{Zr}(\text{Fe,Cr})_2$ precipitates trap H at working temperature, they release H to form brittle ZrH_2 hydrides when cooling down

Zyr 2.5Nb : the β -Zr better diffuse hydrogen than the α -Zr

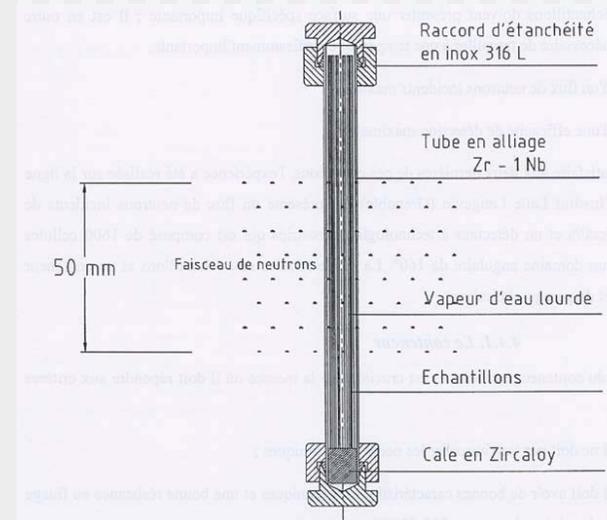
Ex-situ and **in situ neutron diffraction experiments**

ZIRCALOY'S

Fundamental Experiments



50 strips Zyr-4
 2 mm wide, 0.12 mm thick,
 D_2O for 48 h., $T = 420^\circ C$, 155 b
 1 record every 3 min.



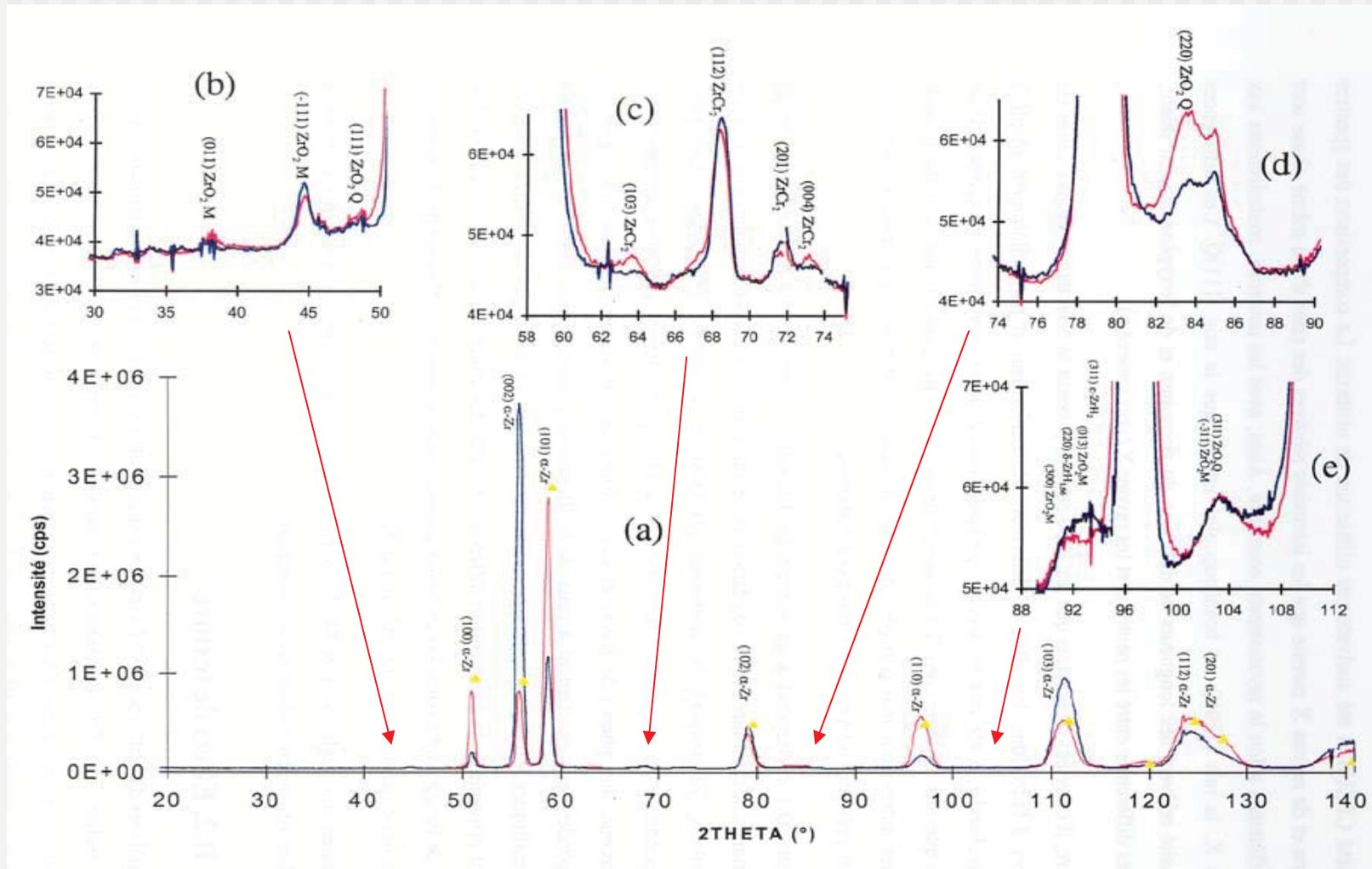
échantillons :
 longueur : 85 mm
 largeur : 1 - 2 mm
 épaisseur : 0,12 - 0,14 mm
 masse totale : 10,00 g
 surface totale : 2,3 - 2,8 dm²

conteneur :
 longueur : 120 mm
 diamètre interne : 8,36 mm
 diamètre externe : 9,52 mm
 volume intérieur : 6,3 ml
 surface totale : 0,28 dm²

quantité d'eau lourde introduite : 0,2746 g

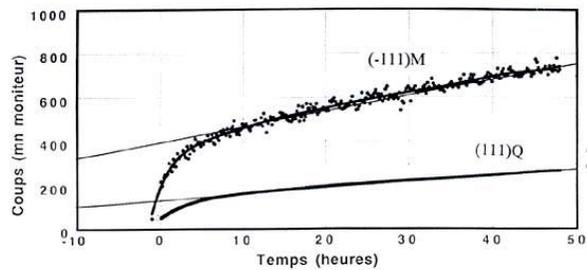
ZIRCALOY'S

Neutron Diffraction Patterns

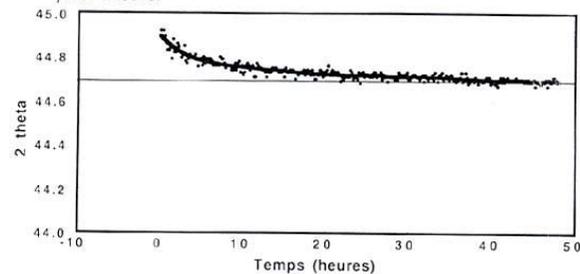


ZIRCALOY'S

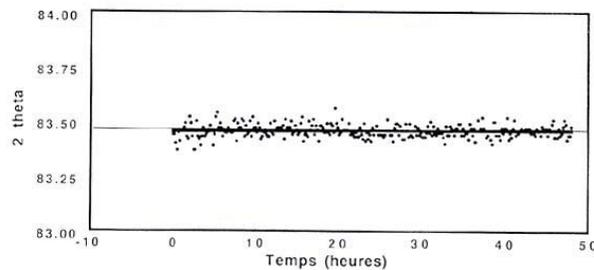
Results : T = 432°C, 150 b stream pressure, for 48h.



évolution en fonction du temps de l'intensité des raies (-111)M et (111)Q pendant le palier à 432°C.

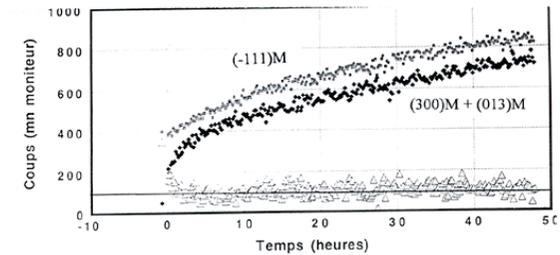


évolution en fonction du temps de l'angle de Bragg de la raie (-111)M pendant le palier à 432°C.

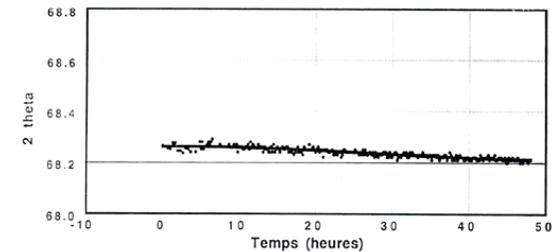


évolution en fonction du temps de l'angle de Bragg de la raie (220)Q pendant le palier à 432°C.

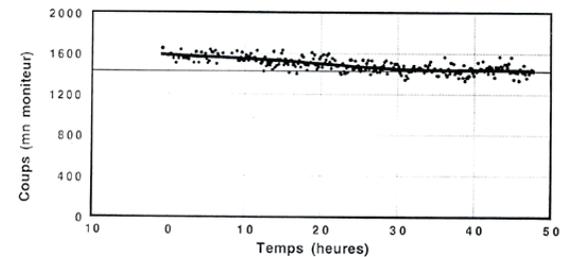
Kinetic of formation of zirconia and AB₂ hydride



évolution en fonction du temps de l'intensité de la raie (-111)M et de l'ensemble des raies (300)M et (013)M (non déconvoluées) durant le palier à 432°C. Les triangles correspondent à la différence entre les deux.



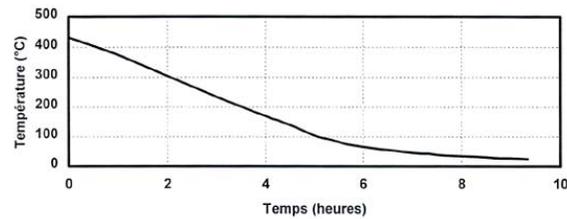
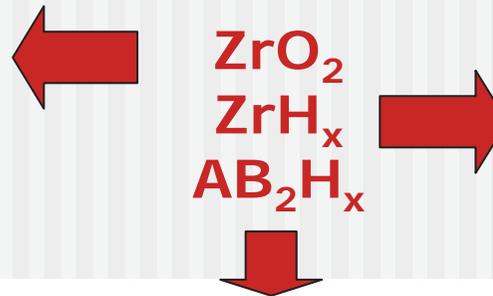
évolution en fonction du temps de l'angle de Bragg de la raie (112) de la phase Zr(Fe,Cr)₂ durant le palier à 432°C.



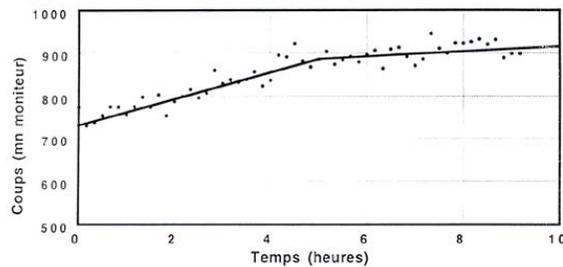
évolution en fonction du temps de l'intensité de la raie (112) de la phase Zr(Fe,Cr)₂ durant le palier à 432°C.

ZIRCALLOY'S

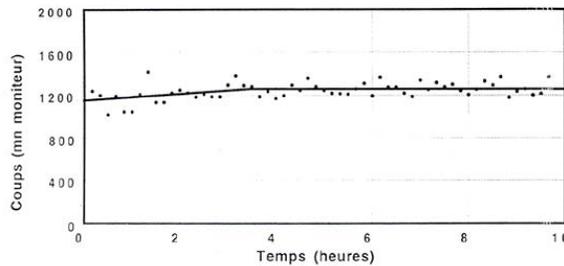
Results : cooling down from 432°C to 20°C in 9 h.



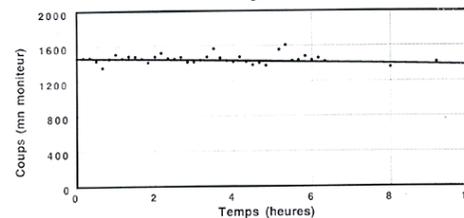
évolution de la température pendant le refroidissement entre 432°C et l'ambiante.



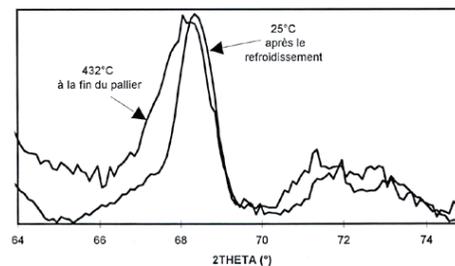
évolution en fonction du temps de l'intensité de la raie (-111)M pendant le refroidissement.



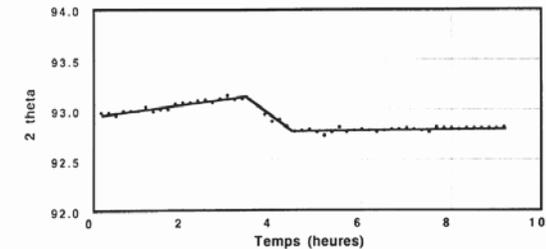
évolution en fonction du temps de l'intensité de la raie (220)Q pendant le refroidissement.



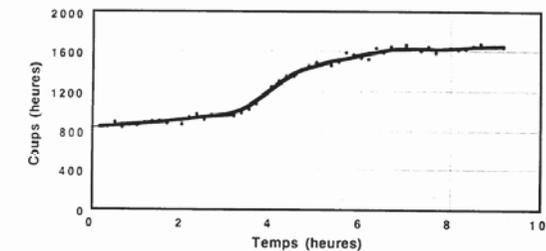
évolution en fonction du temps de l'intensité de la raie (112) de la phase Zr(Fe,Cr)₂ pendant le refroidissement.



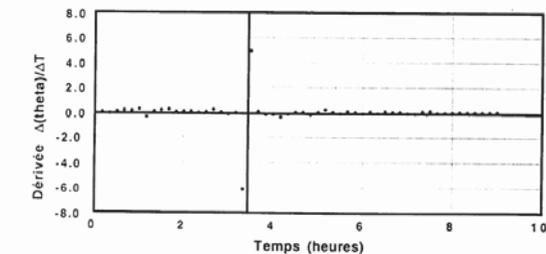
spectre de diffraction de la zone de la phase de Laves avant et après le refroidissement montrant l'asymétrie de la raie (112) à chaud.



évolution en fonction du temps de "l'angle du maximum d'intensité" de l'ensemble des raies (300)M et (013)M et de la raie (311) de l'hydruze ε-ZrH₂ pendant le refroidissement.



évolution en fonction du temps de l'intensité de l'ensemble des raies (300)M et (013)M et de la raie (311) de l'hydruze ε-ZrH₂ pendant le refroidissement.



évolution en fonction du temps de la dérivée de l'angle de Bragg de la figure D.15, durant la descente en température.

NZ2 and NZ8

(In-situ) Neutron Diffraction Experiments

X-Ray diffraction

Grazing incidence

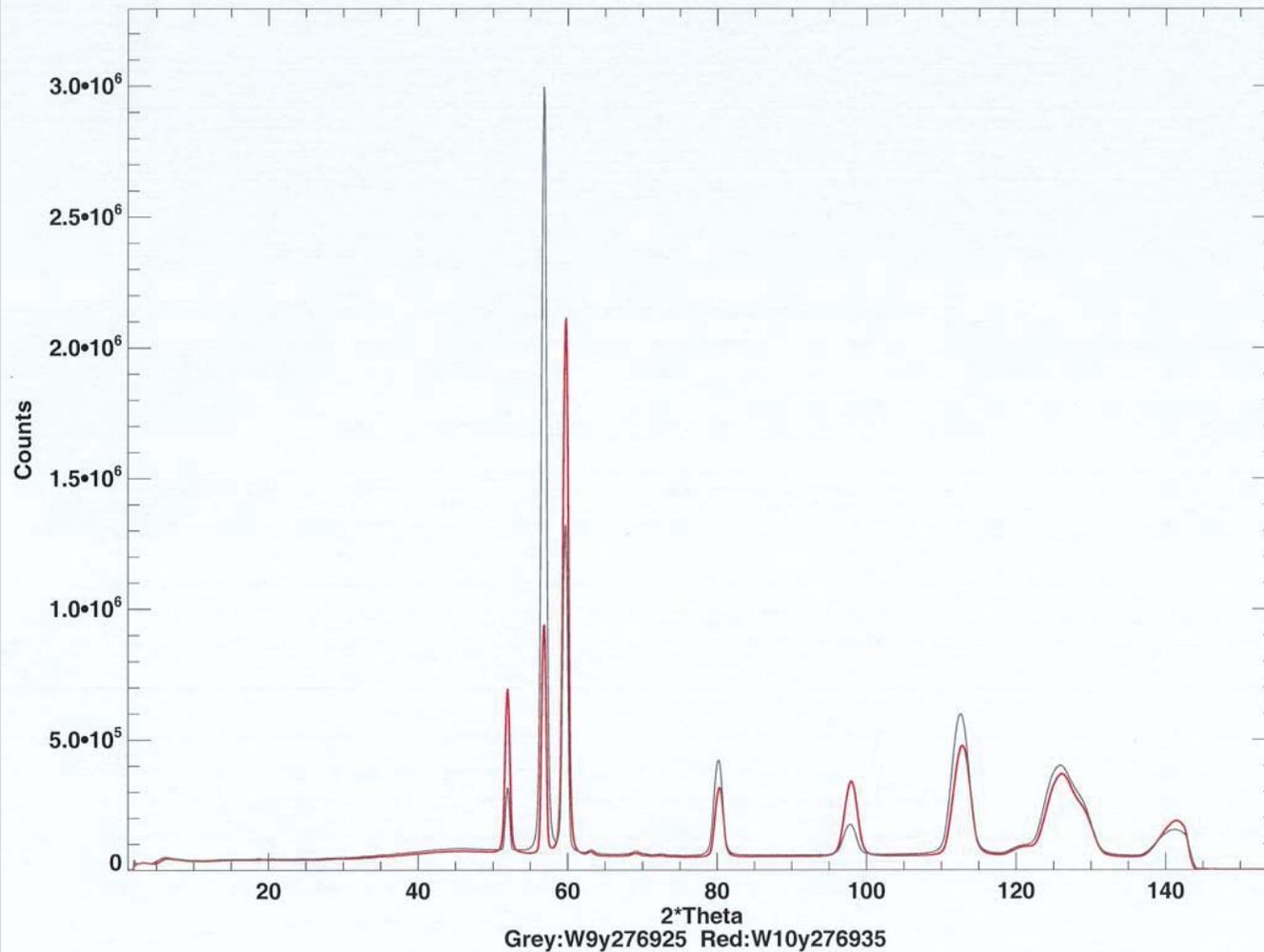
Large Angle Diffraction

Texture analysis

NPA – TEM – SEM - μ -Analyses

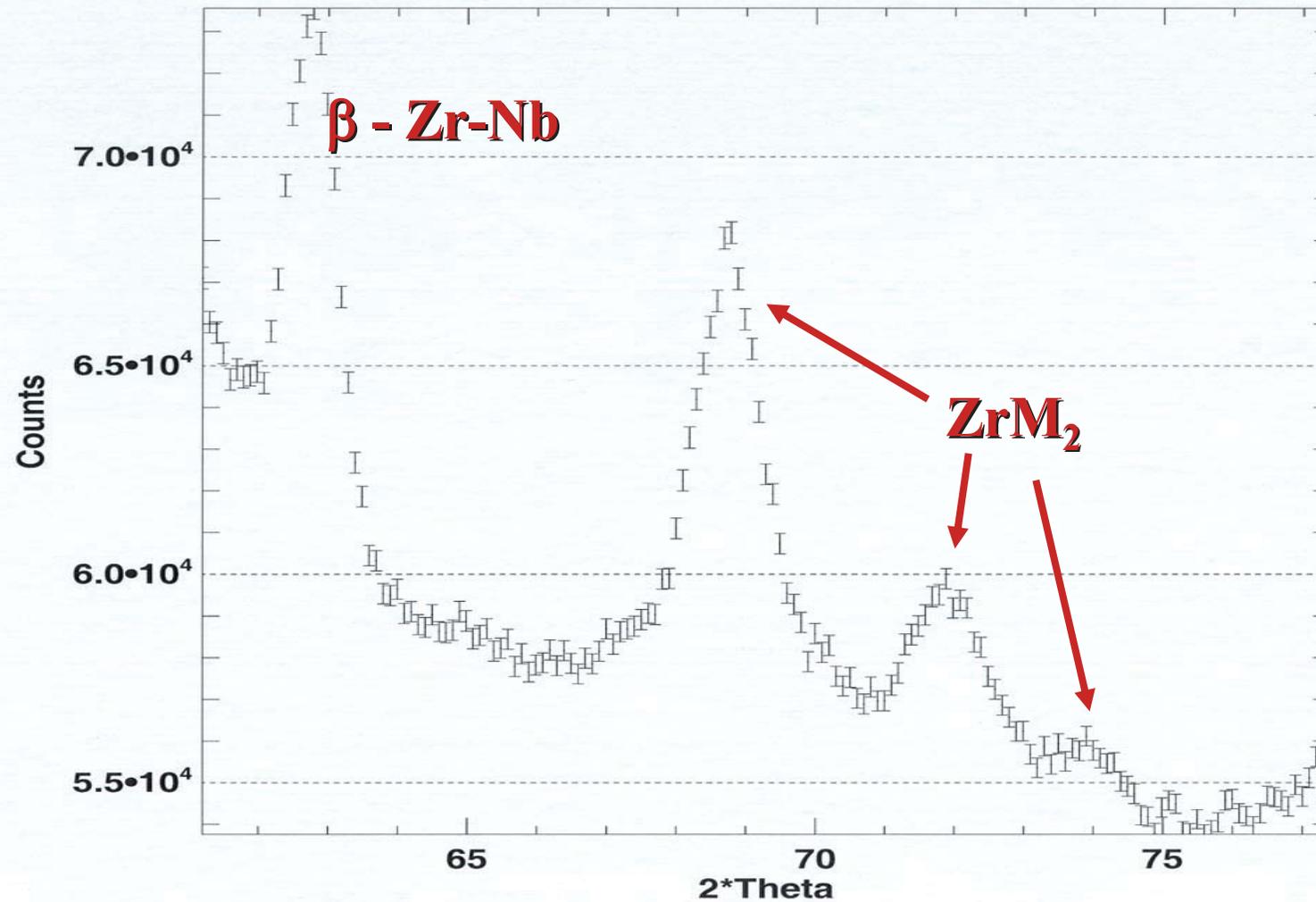
Raman spectroscopy

Neutron Diffraction Analysis NZ2

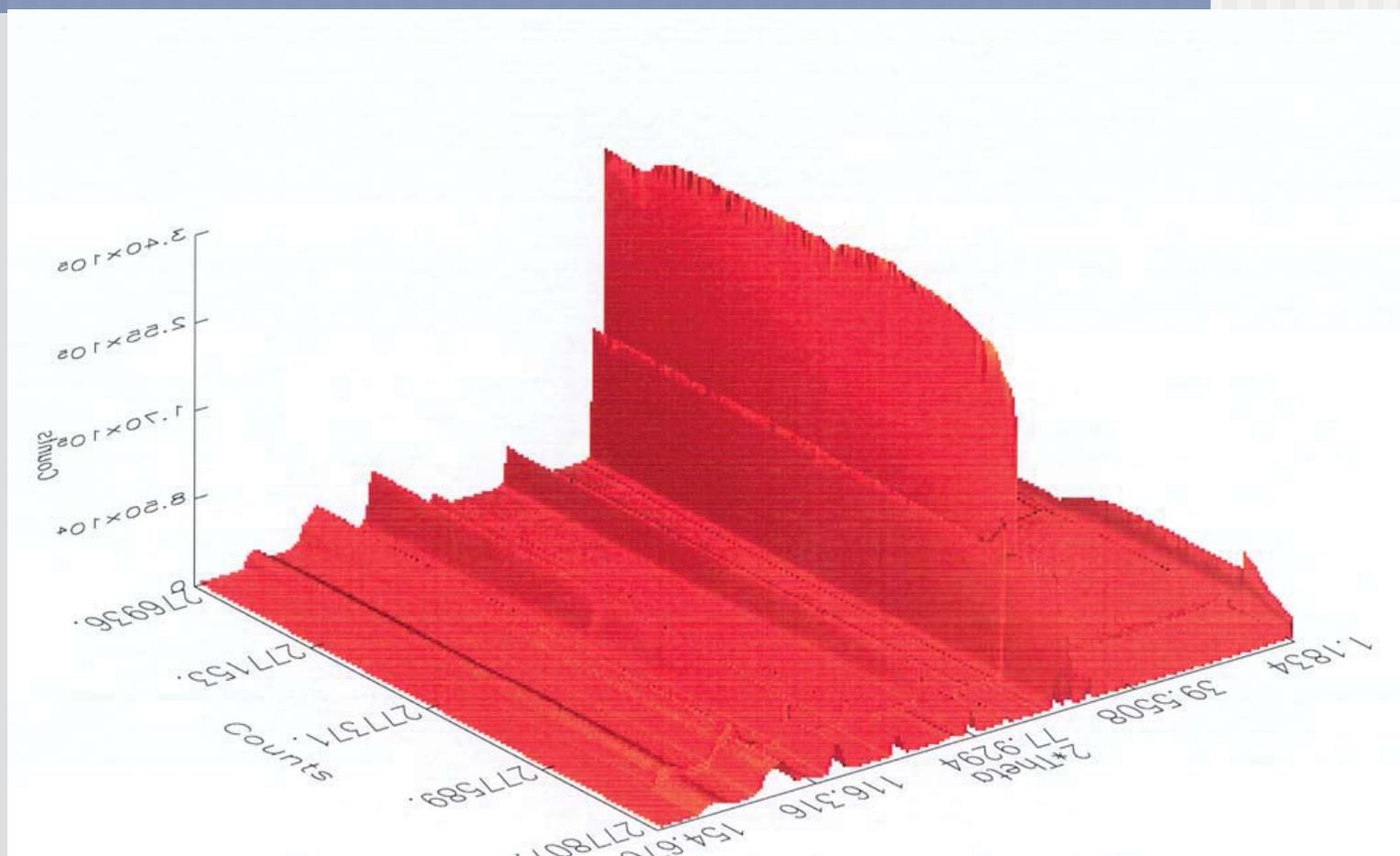


Texture

In-situ Neutron Diffraction – 420°C

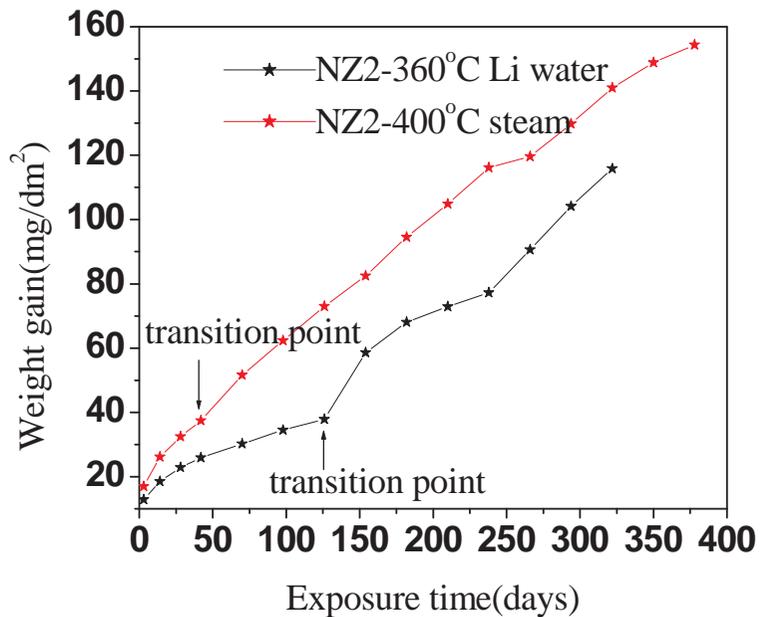


In-situ Neutron Diffraction – 420°C

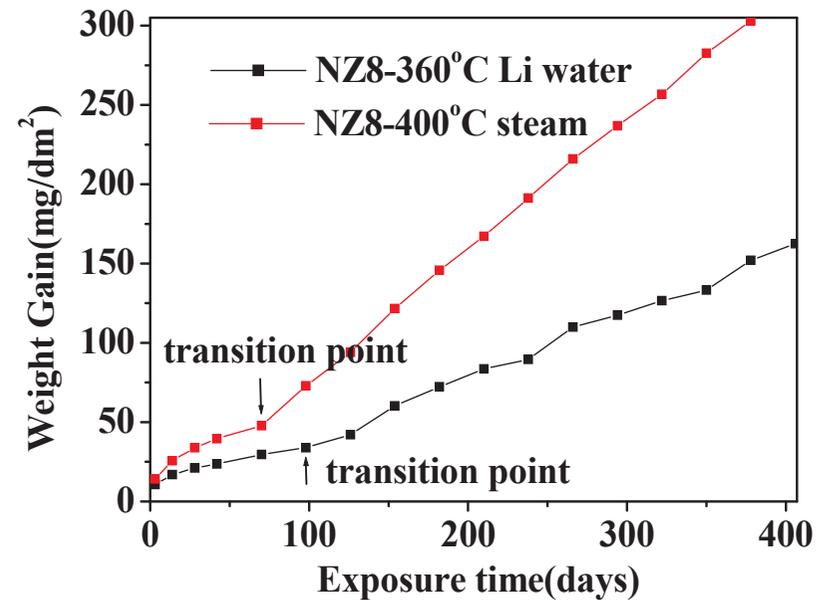


27 h

Corrosion kinetics



Corrosion kinetics of NZ2 and NZ8 alloys
in 360°C Li water

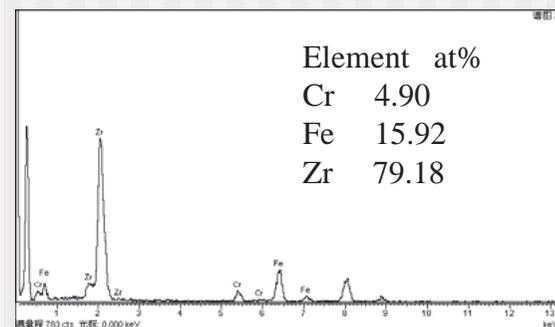
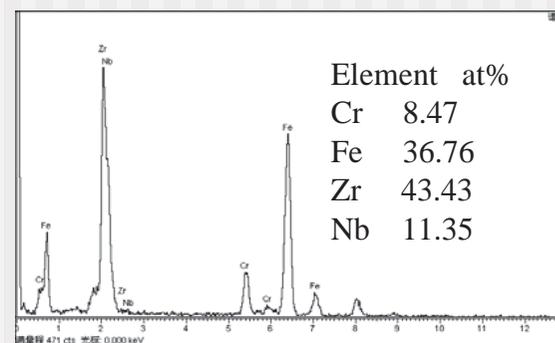
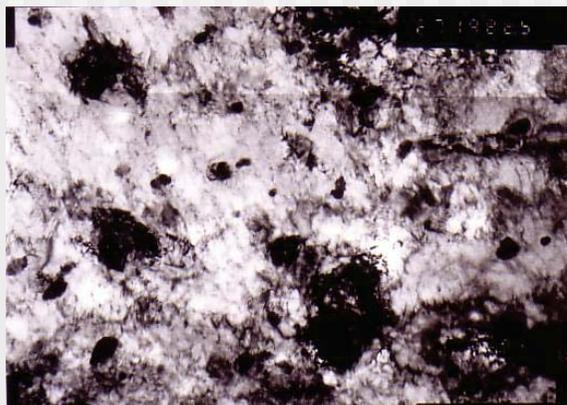
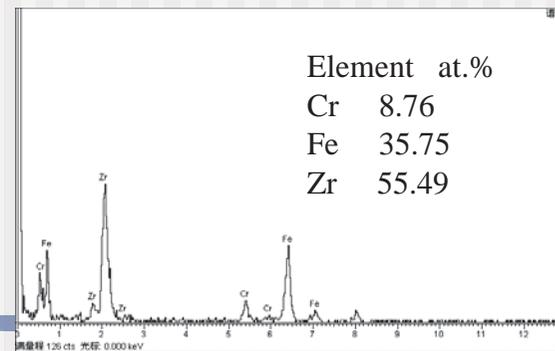


Corrosion kinetics of NZ8 alloy in 360°C Li
water and in 400°C steam

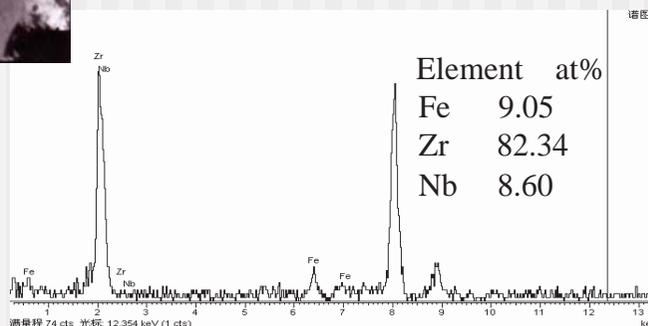
NZ2 better resistant to steam

Precipitates analysis

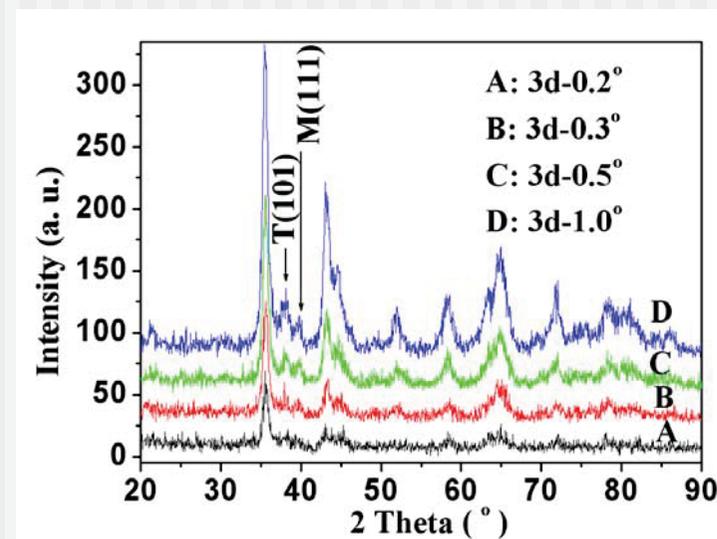
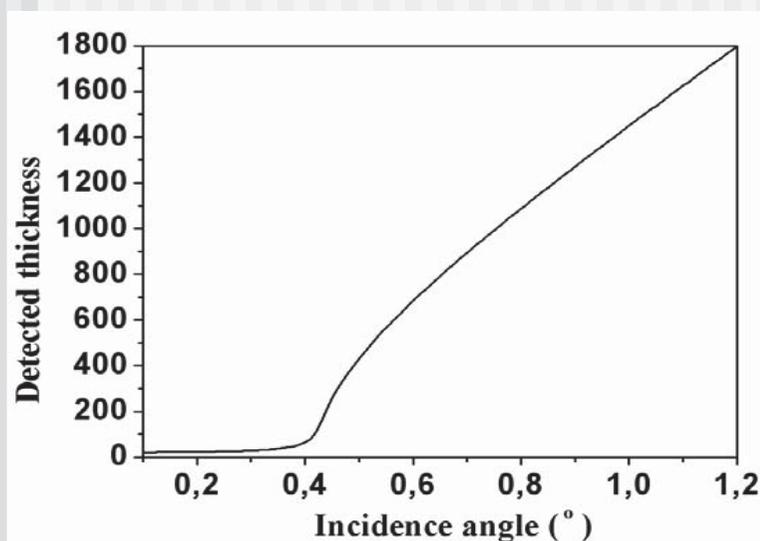
NZ2



NZ8



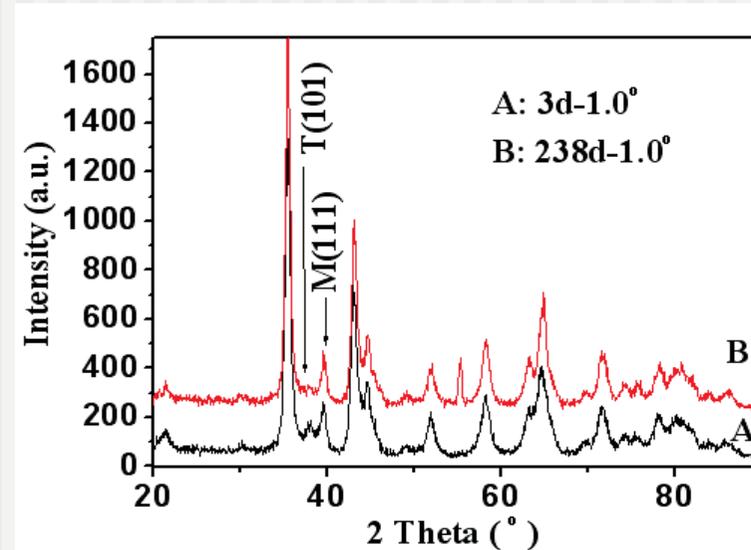
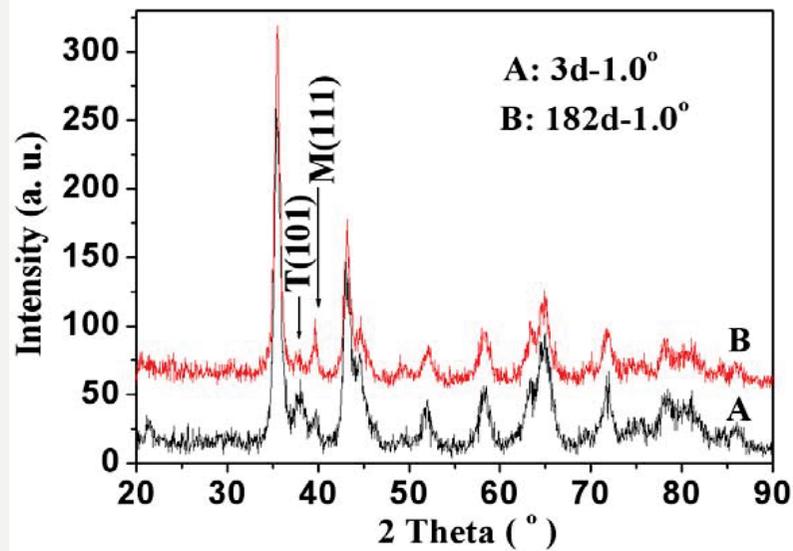
Grazing incidence XRD analysis NZ2



Grazing incidence XRD patterns of the oxide film surface of NZ2 alloy exposed to 360°C Li water for 3d

Grazing incidence XRD analysis NZ2

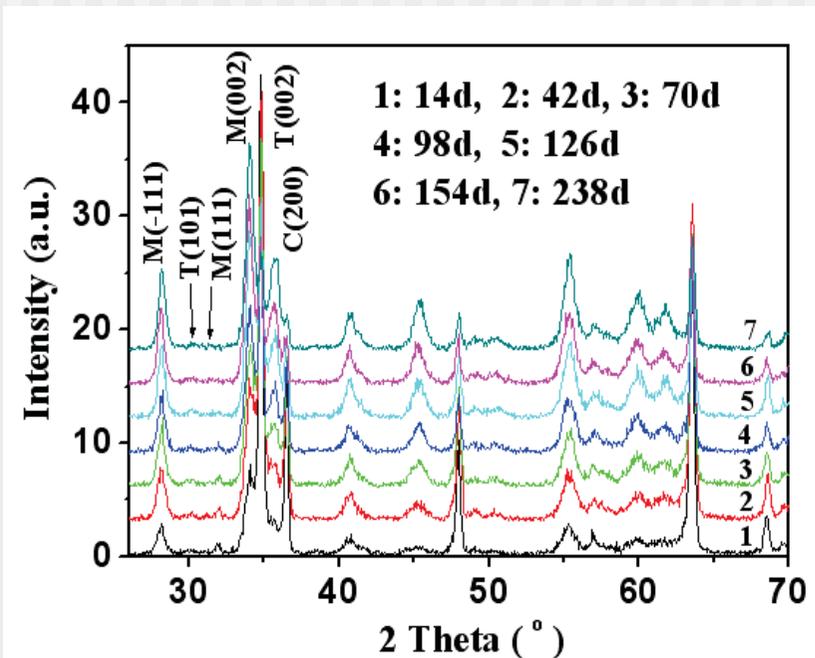
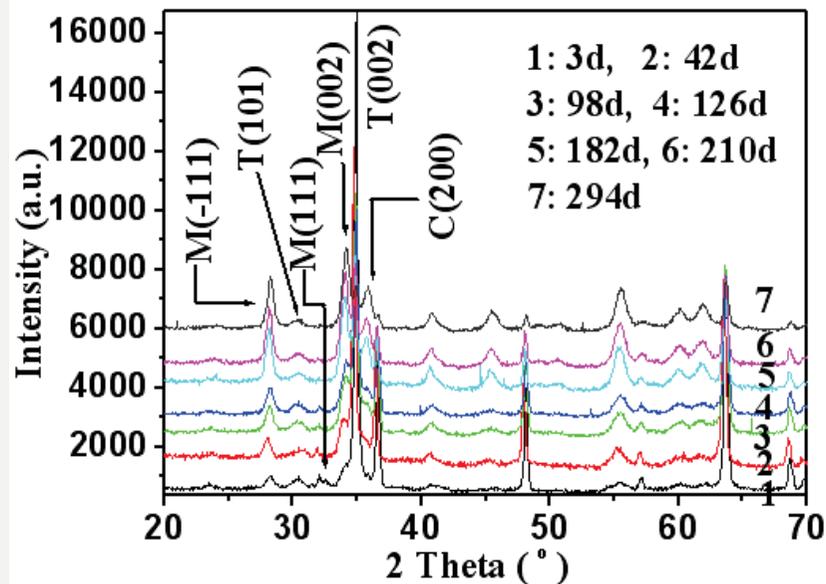
Grazing angle XRD patterns of the oxide film surface of NZ2 alloy exposed to 360°C Li water for different time



Grazing angle XRD patterns of the oxide film surface of NZ2 alloy exposed to 400°C steam for different time

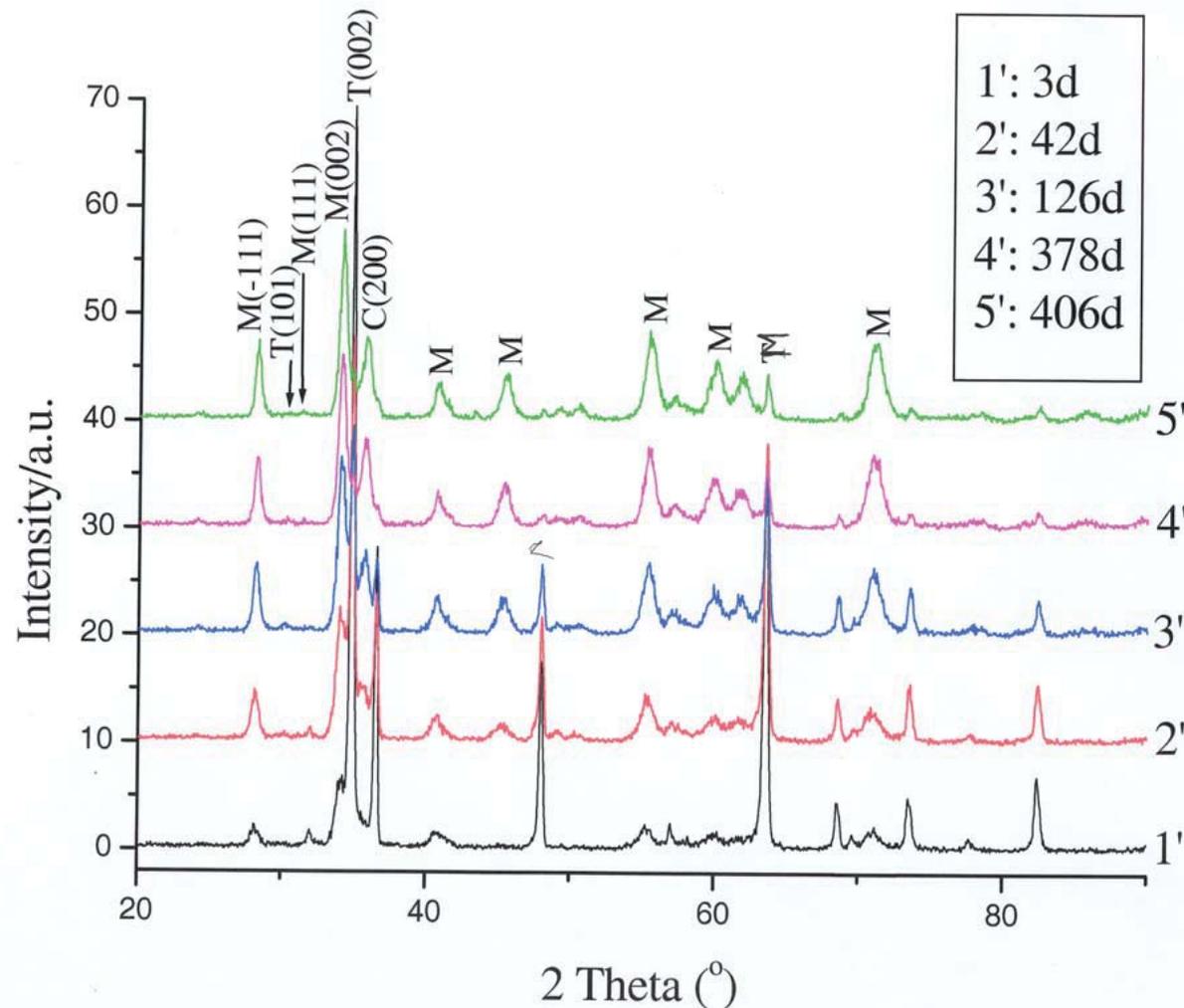
Grazing incidence XRD analysis NZ2

Normal XRD patterns of the oxide film of NZ2 alloy exposed to 360°C Li water for different time



Normal XRD patterns of the oxide film of NZ2 alloy exposed to 400°C steam for different time

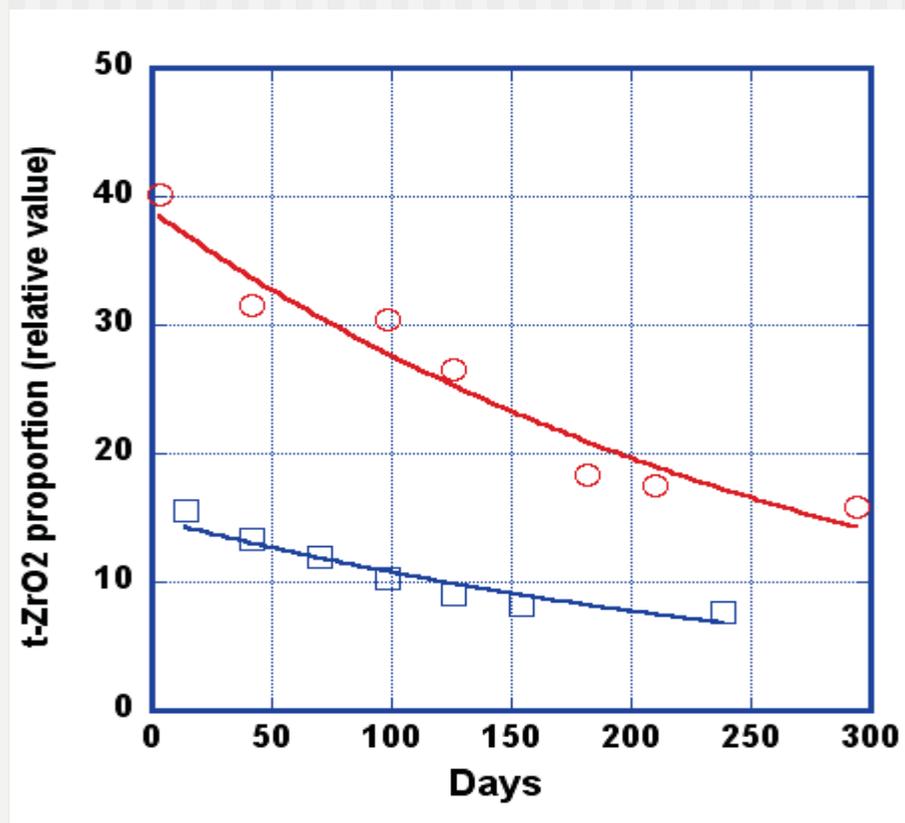
X-Ray Diffraction Grazing Incidence NZ2



NZ2
different
Duration

Development
of
3 types
Zirconia
T - C - M

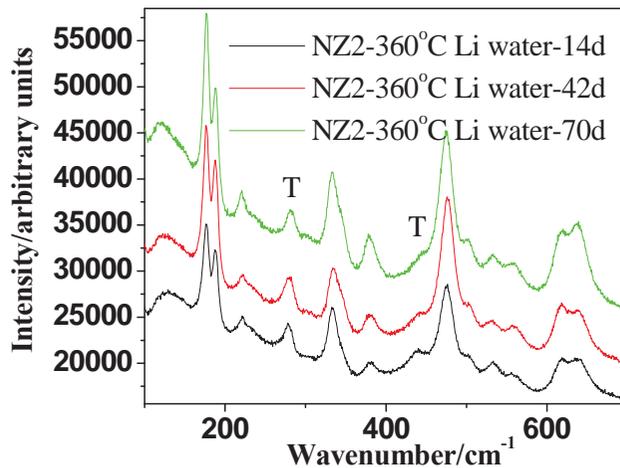
Corrosion rate analysis NZ2



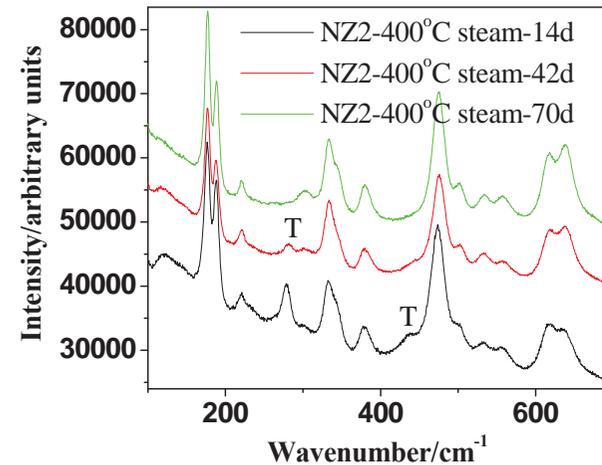
Relationship of corrosion time and the t-ZrO₂ content in oxide film of NZ2 alloy: (circle) corroded at 360°C Li water and (square) corroded at 400°C in steam

Raman analysis

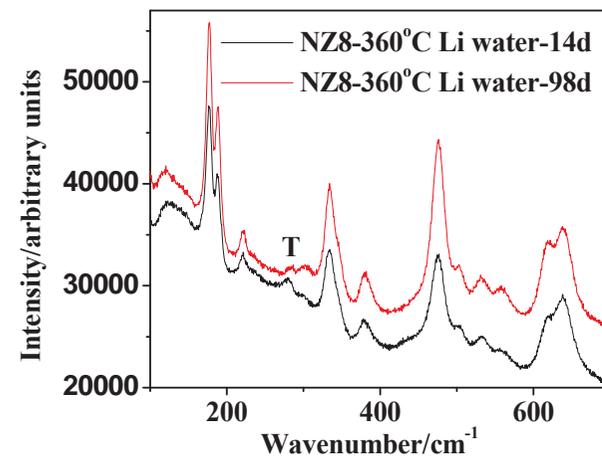
Raman spectra of oxide film at the difference distances from surface, which was gained by exposing NZ2 alloy to 360°C Li water for 70d



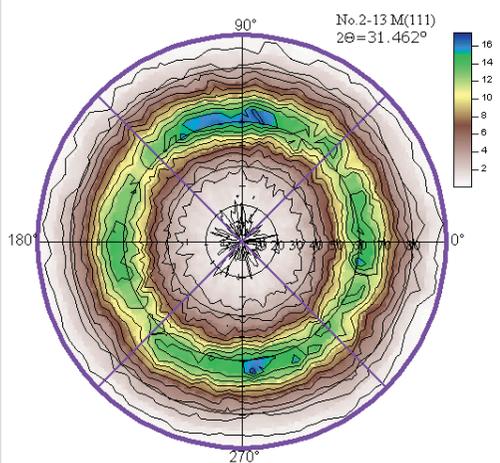
Raman spectra of oxide film of NZ2 alloy exposed to 360°C Li water for 14d, 42d and 70d



Raman spectra of oxide film for NZ8 alloy exposed to 360°C Li water for 14d and 98d

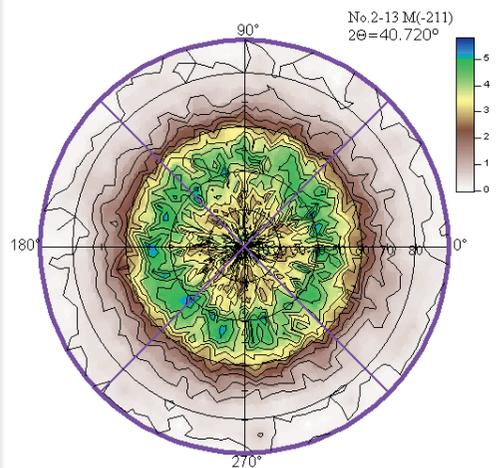


Texture XRD analysis NZ2



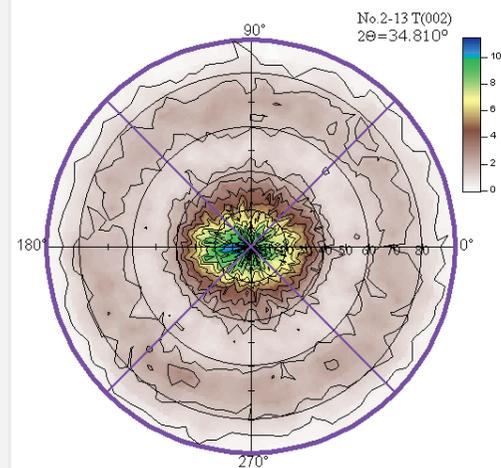
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dimanche 9 déc. 2007



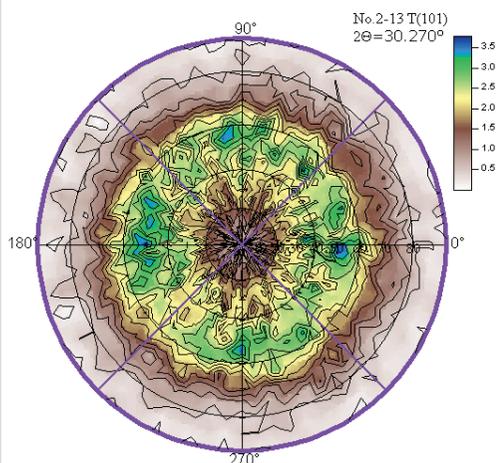
Institut Neel - CNRS - Grenoble

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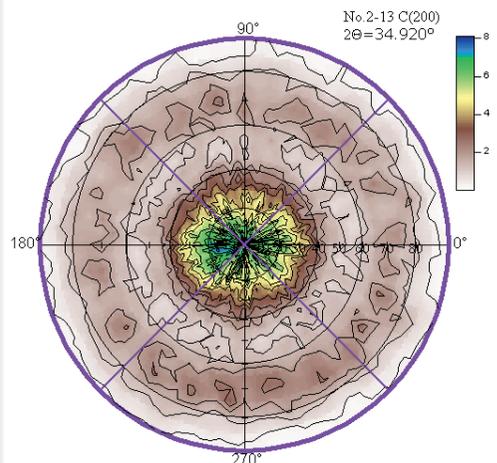
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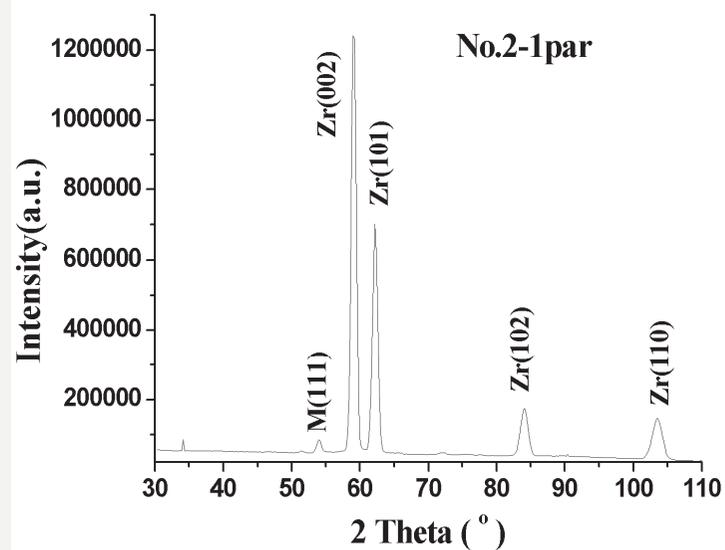


Institut Neel - CNRS - Grenoble

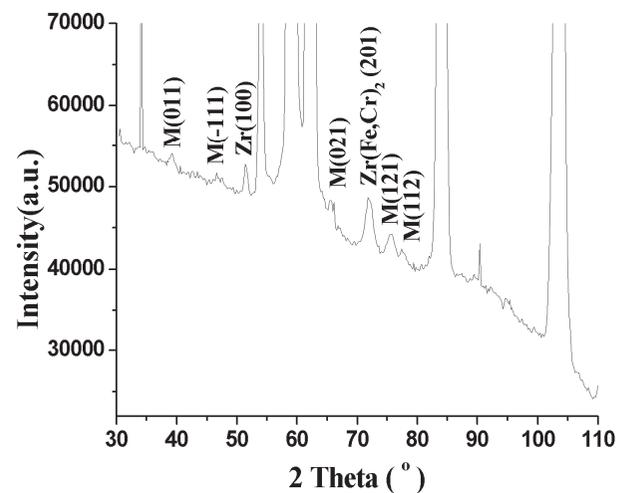
dimanche 9 déc. 2007

Some of the 27 pole figures recorded of the oxide film of NZ2 alloy corroded in 360°C Li water for 294d

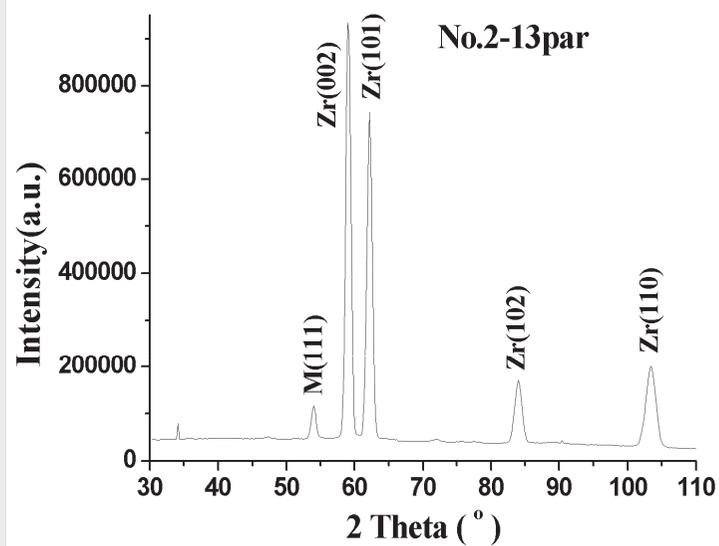
Neutron diffraction analysis



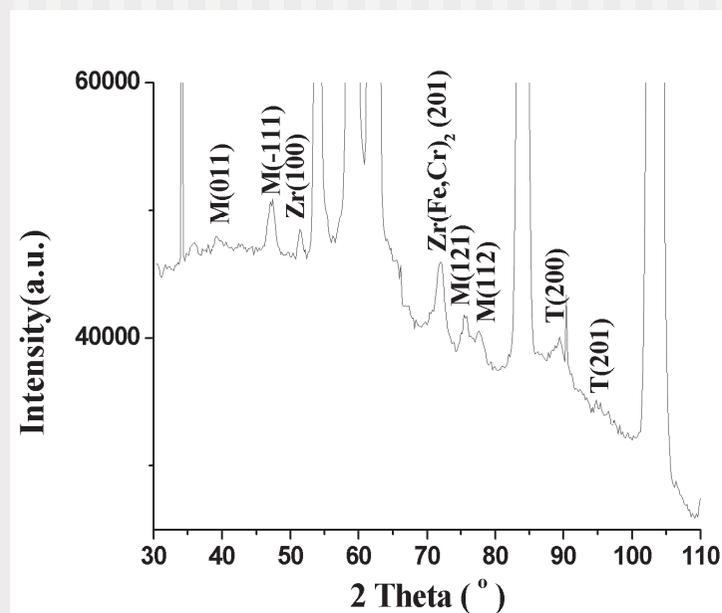
Neutron diffraction patterns recorded for 3d in 360°C Li water



Neutron diffraction analysis



Neutron diffraction patterns recorded for 294d in 360°C Li water



Conclusion

In-situ neutron diffraction analysis

XRD low + high angles

Analysis of the texture

SEM + microanalysis

TEM

Raman

**To determine the best corrosion resistant Zircaloy
that a hydrogen-assisted phenomena via precipitates**

