MH 2004

Directional Metal-Hydrogen Bonding in Interstitial Hydrides, I - $ErNi_3H_x$ ($0<x<3.7$)

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with a use of facilities

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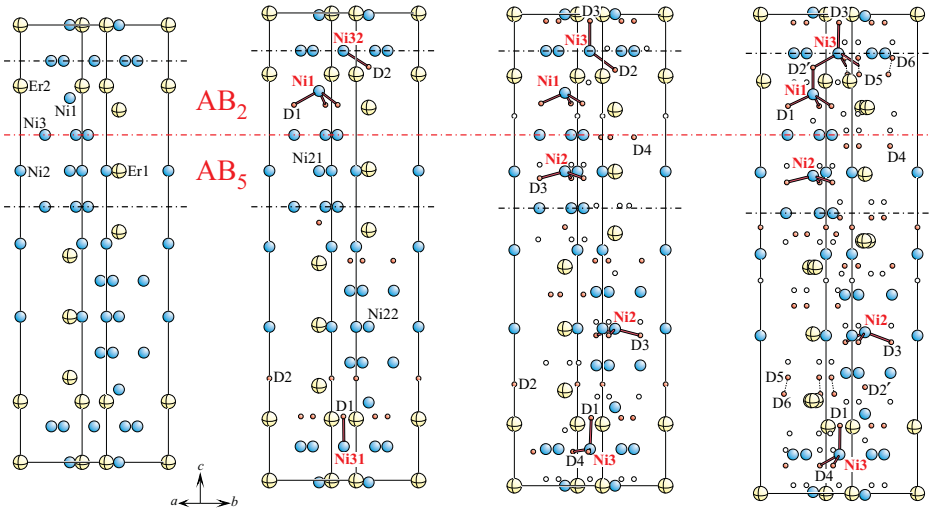


alloy $ErNi_3$ | β1-deuteride $ErNi_3D_{1.23}$ | β2-deuteride $ErNi_3D_{1.97}$ | γ-deuteride $ErNi_3D_{3.75}$

Known before

1. Pressure-composition diagrams
2. Cell parameters for at least two phases
3. Structural study was not done earlier due to high equillibrium hydrogen pressure for $ErNi_3H_x$ phases

Synthesis

Alloy:
$ErNi_3$ - arc-melting, annealing at 800C

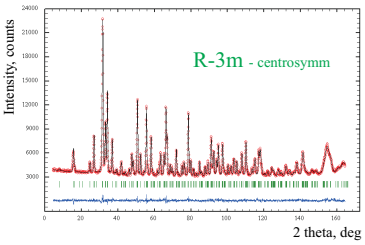
Deuterides: autoclave hydrogenation
$β1\text{-}ErNi_3D_{1.23-1.33}$ - up to 150C, up to 20 bar D2
$β2\text{-}ErNi_3D_{\sim1.97}$ - up to 150C, up to 80 bar D2
$γ\text{-}ErNi_3D_{\sim3.75}$ - 80C->20C, long exposure to 100 bar D2

Cell expansion:
alloy-β1 transition – the unit cell expands along *c*;
β1-β2 transition – expansion is almost isotropic;
β2–γ transition – expansion along *a*.

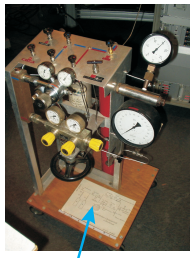
D atom sites:
alloy-β1 transition – hydrogen fills AB_2 unit;
β1-β2 transition – hydrogen fills AB_5 unit;
β2–γ transition – hydrogen fills AB_5 unit, rearrangement of D-positions.

The symmetry of the structure lowers from R-3m to R3m upon hydrogenation!!!

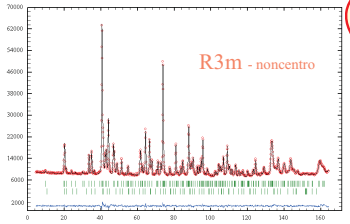
alloy $ErNi_3$ – annealed 800C – NPD 1.15 Å



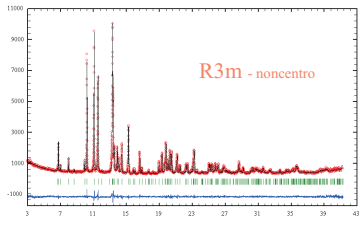
On-site deuteration

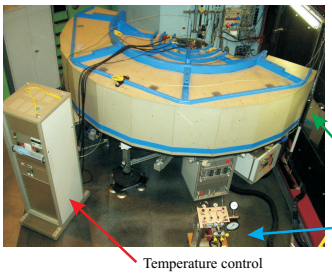


β1-$ErNi_3D_{1.23}$ – 10 bar, 150C->20C – NPD 1.49 Å



β1-$ErNi_3D_{1.23}$ – 20 bar, 80C->20C – synchr 0.50 Å

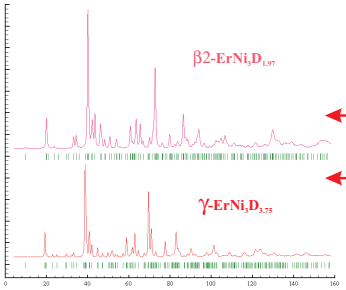




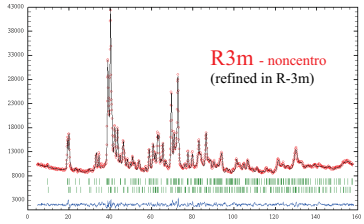
Ni atoms environment:
tends to be tetrahedral NiD_4
or pyramidal NiD_3 – incomplete tetrahedron;
similar to NiD_4 in $LaMg_2NiD_7$ and Mg_2NiD_4;
different from those in cobalt analogues YCo_3D_x and $ErCo_3D_x$

Neutron and synchrotron powder diffraction on samples just taken out from deuterium atmosphere (10-20 bar)
HRPT instrument at PSI, 1.494 Å
SNBL beamline at ESRF, 0.5001 Å
high angular and structural resolution

Composition:
1. Three deuteride phases $ErNi_3D_x$ (β1, β2, γ) occur in the $ErNi_3$-D system.
2. Their ranges of existence are x=1.23-1.33 (β1), x~2 (β2) and x>3.44 (γ). No α-solid solution.



β2-$ErNi_3D_{1.97}$ + γ-$ErNi_3D_{3.75}$ – 100 bar, 80C->20C – NPD 1.49 Å



Structure refinements in non-centrosymmetric *R3m* such as with the β1-phase were not feasible because of the small reflections/parameters ratio.

Neutron powder diffraction on a sample just taken out from 100 bar of deuterium gas
HRPT instrument at PSI, 1.494 Å

Symmetry:
Deuteration of $ErNi_3$ leads to a loss of inversion symmetry - the first time reported for a rhombohedral AB_3-H system.

It has been experimentally ascertained for the β1-phase.