

CRISTALLOGRAPHIC STRUCTURES OF AUSTENITIC AND MARTENSITIC HYDRIDES OF $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{Ni}$ INTERMETALLIC COMPOUND

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TiNi alloy is polymorphic. It exhibits a martensitic transition near room temperature between a cubic CsCl-type (austenite) and a monoclinic TiNi-type (martensite) structure. This transformation is at the origin of its shape memory effect. In addition, TiNi has good hydrogen storage properties under normal conditions of pressure and temperature. In austenitic form, TiNi absorbs 1.4 H/f.u. under atmospheric pressure. No plateau is observed in the pressure composition isotherm curve (PCI) showing that hydrogen is absorbed in solid solution [1]. Hydrogenation properties of the martensite form are unknown. By adjusting a partial substitution of Ti by Zr and by using different elaboration techniques (melt spinning and induction melting), we were able to stabilize the two different crystallographic forms at room temperature for the same composition: $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{Ni}$. The austenitic phase exhibits hydrogenation properties close to those of cubic TiNi. The martensitic phase absorbs up to 2.8 H/f.u. and shows a pressure plateau ranging between 1 and 2.5 H/u.f. This plateau indicates the presence of two hydride phases in equilibrium. These results lead to the conclusion that hydrogenation properties of TiNi-type alloy are strongly influenced by the structural polymorphism [2] of the parent alloy.

Crystallographic structures of $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{NiD}_{1.6}$, obtained from austenite and of $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{NiD}_{1.3}$, $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{NiD}_{1.8}$ and $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{NiD}_{2.8}$, prepared from martensitic alloy have been studied by X-ray and neutron diffraction. Hydrogenation of the austenitic alloy $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{Ni}$ does not change the CsCl-type structure of the metallic sublattice. The deuteride $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{NiD}_{1.6}$ can be indexed with the space group $Pm\bar{3}m$ and deuterium atoms occupy 50% of the octahedral sites $3d$. Partial occupation of sites $3d$ seems related to a short distance (2.25 Å) between two neighboring sites $3d$. The cell volume increases of 10 % during hydride formation. In contrary to the binary compound TiNi that undergoes a tetragonal distortion after

absorption, Ti substitution by Zr seems to limit the appearance of such distortion.

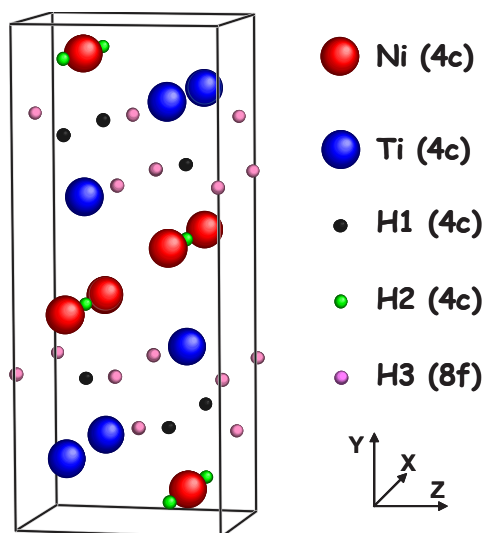


Figure 1. Structure of the martensitic-type hydrides $\beta\text{-Ti}_{0.64}\text{Zr}_{0.36}\text{NiD}$ and $\gamma\text{-Ti}_{0.64}\text{Zr}_{0.36}\text{NiD}_{2.5}$ (S.G. $Cmcm$). For the β phase, site H1 is fully occupied. In the γ phase, site H3 is fully occupied and site H2 is half filled (50%).

Hydrogenation of martensitic $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{Ni}$ induces a symmetry change from a monoclinic TiNi-type to an orthorhombic CrB-type structure. Two hydride phases are clearly observed (S.G. $Cmcm$) with two different compositions $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{NiD}$ and $\text{Ti}_{0.64}\text{Zr}_{0.36}\text{NiD}_{2.5}$. The first hydride (phase β) shows a cell volume increase of 5.4% and the second (phase γ) of 12.2%. For the β phase, hydrogen occupies all the tetrahedral sites $4c$ (H1 in Figure 1) whereas in the γ phase, hydrogen totally fills tetrahedral sites $8f$ (H3) and half fills pyramidal sites $4c$ (H2). This configuration is very similar to that observed for the compound ZrNi, that forms a stoichiometric γ hydride (ZrNiH_3) obtained by a complete filling of sites H2 and H3.

References

- [1] R. Burch, N. B. Mason, *J. Chem. Soc. Faraday Trans. I*, **75** (1979) 561.
 [2] F. Cuevas, M. Latroche et al., *J. Alloys Comp.*, **330-332** (2002) 250.