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Crystal structural properties of Ti_3SnD

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Abstract

Ti_3Sn crystallises in hexagonal Ni_3Sn type structures. Upon deuteration a primary interstitial solid solution of deuterium in Ti_3Sn has been identified. At higher deuterium concentrations a cubic hydride phase is formed with the limiting composition Ti_3SnD. The structural properties of these phases have been refined from neutron powder diffraction intensities using the Rietveld method. The crystal structure of Ti_3SnD has been confirmed to crystallize in the $CaTiO_3$ type structure, space group $Pm3m$, with the unit cell parameter $a = 4.1769(4)$ Å. The deuterium atoms occupy Ti_6 octahedral voids in the cubic structure to 95.7(6)% and 72(6)% in the hexagonal.

Keywords: Metal hydride; Ti_3Sn; Crystal structure; Hydrogen; Neutron diffraction

1. Introduction

Ti_3Sn crystallises in the hexagonal Ni_3Sn type structure with a narrow homogeneity range [1]. Rudman et al. [2] has studied the hydrogen absorption and reported, based on X-ray data, a cubic hydride phase of the filled Cu_3Au type structure, $CaTiO_3$, with the unit cell parameter $a = 4.17$ Å. The phase transition, Ni_3Sn type to $CaTiO_3$ type, has also been reported for the hydride formation of Ti_3Al [3].

In the present investigation the phase transition from hexagonal Ni_3Sn type to cubic filled Cu_3Au type in the Ti_3Sn–D system has been studied.

2. Experimental

2.1. Sample preparation

Ti_3Sn was synthesised by arc-melting appropriate amounts of titanium rod (99.99%) and tin ingot (99.995%) in an argon atmosphere. The sample was powdered by heat-treatment in a deuterium atmosphere. The deuterium were then removed from the powder by heating in vacuum and then the sample was heat-treated for 7 days at 1173 K in an evacuated quarts ampoule. The metal hydride phase was obtained by heating the sample to 923 K for 12 h in 70 kPa deuterium pressure followed by slow cooling to room temperature.

2.2. X-ray diffraction

Phase analysis and unit cell dimensions were determined by using X-ray powder diffraction techniques. Powder patterns were recorded in a Guinier–Hägg type focusing camera with $CuK\alpha_1$-radiation and with silicon as internal standard ($a = 5.43088$ Å).

2.3. Neutron powder diffraction

Neutron powder diffraction intensities were recorded at 10 K for the deuterated sample and 295 K for the pure sample at the R2 reactor (Studsvik, Sweden). The samples were contained in a vanadium cylinder and the measurements were performed using a multi-detector system with 35 independent detectors mounted 4° apart measuring intensities in 2Θ steps of 0.08°. The neutron flux at the sample was approximately 10^6 cm^{-2} s^{-1} from a parallel double Cu (220) monochromator system, with a wavelength of 1.472 Å. The 2Θ ranges covered were 8.00–139.39° for both measurements.

2.4. Crystal structure analysis and refinements

Structure refinements of the X-ray and neutron powder diffraction profiles were performed according to the Rietveld method [4] using the program FULLPROF [5]. The

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2Θ ranges for the refinements were 12.00–139.39°. The pseudo-Voigt function was used to describe the peak shape. The background of the neutron diffractogram was described by a polynomial expression.

2.5. Ti_3Sn

2.5.1. Neutrons

Fourteen parameters were refined in the final refinement cycles: scale factor (1), 2Θ zero-point (1), atomic coordinate (1), temperature factors (2), unit cell parameters (2), background parameters (4), profile shape parameter (1), asymmetry parameter (1) and half-width parameters (3). The neutron wavelength was refined to 1.472 Å using unit cell parameters determined from X-ray powder diffraction and with Si as an internal standard.

2.6. Ti_3SnD

2.6.1. Neutrons

The following parameters were refined in the final refinement cycles: scale factor (2), 2Θ zero-point (1), atomic coordinate (1), unit cell parameters (3), profile shape parameter (1), half-width parameters (6), background parameters (4) and occupancy (1). The occupancy of the metal positions was refined but did not significantly differ from ideal values. The isotropic temperature factor of the deuterium atoms was varied and found most stable for 0.5 $Å^2$. For the titanium and tin atoms the isotropic temperature factor were refined to small negative values and these were therefore fixed to $B = 0$ $Å^2$.

3. Results and discussion

The unit cell dimensions for pure Ti_3Sn were determined to $a = 5.9178(6)$ Å and $c = 4.7650(7)$ Å which is in good agreement with previous structure determinations [1]. The composition was $Ti_{3.0}Sn$.

All deuterated samples contained two phases, an interstitial solid solution and a hydride phase. The final structure parameters from neutron data of the pure and deuterated samples are listed in Table 1. The observed and calculated neutron powder diffraction profiles of Ti_3Sn–Ti_3SnD_x are shown in Fig. 1. The cubic phase crystallises in the perovskite structure, $CaTiO_3$, space group *Pm*3*m*, with the unit cell parameter $a = 4.1769(4)$ Å which is in accordance with results by Rudman et al. [2]. The cubic structure of Ti_3Sn has a total of four octahedral holes per unit cell where one is surrounded by six titanium atoms and the other three have four titanium and two tin atoms at the vertices. The deuterium atoms occupy the Ti_6 octahedra and the deuterium content was determined to approximately, Ti_3SnD. The occupancy of the voids was found from refinements to be 95.7(6)%. The crystal structure of the cubic hydride phase is shown in Fig. 2.

In the hexagonal unit cell of Ti_3Sn there are eight octahedra of which six are surrounded by four titanium and two tin atoms and the other two have titanium atoms at all vertices. The tetrahedral holes in the structure are all surrounded by one tin and three titanium atoms. Full occupancy of the Ti_6 octahedral position results in a deuterium content of Ti_3SnD. From refinements it was found that deuterium occupy the Ti_6 octahedron not only

Table 1
Final structure parameters for Ti_3Sn and Ti_3SnD from neutron powder diffraction intensities

Atom	Position	*x*	*y*	*z*	B_{iso}
Ti_3Sn 295 K					
$R_p = 0.059$	$R_{wp} = 0.083$	$R_{exp} = 0.030$			
$R_{Bragg} = 0.071$					
$P6_3/mmc$ (no. 194)					
Ti	6*h*	0.8353(6)	0.6707(6)	1/4	0.3(1)
Sn	2*c*	1/3	2/3	1/4	0.35(8)
Ti_3Sn–D 10 K					
$R_p = 0.044$	$R_{wp} = 0.057$	$R_{exp} = 0.029$			
Ti_3SnD_x					
$R_{Bragg} = 0.33$					
$P6_3/mmc$ (no. 194)					
Ti	6*h*	0.841(5)	0.683(5)	1/4	0
Sn	2*c*	1/3	2/3	1/4	0
D[a]	2*a*	0	0	0	0.5
Ti_3SnD					
$R_{Bragg} = 0.047$					
*Pm*3*m* (no. 221)					
Ti	3*c*	1/2	1/2	0	0
Sn	1*b*	0	0	0	0
D[b]	1*a*	1/2	1/2	1/2	0.5

[a] 72(6)% occupancy on the position.

[b] 95.7(6)% occupancy on the position.

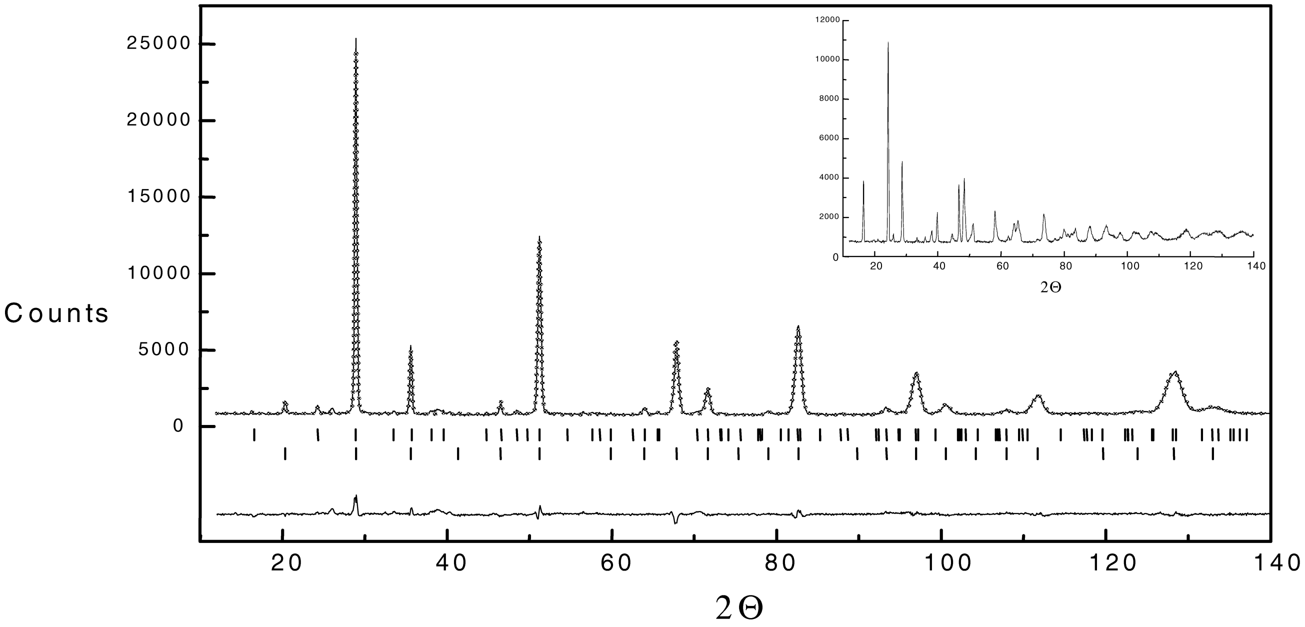

Fig. 1. Final observed (full line), calculated (points) and difference (full line) neutron diffraction profile for Ti_3SnD and in the right corner Ti_3Sn.

in the hydride phase but also in the solid solution structure. The voids are occupied in the latter to 72(6)%. The hexagonal unit cell parameters were determined to $a = 5.9160(8)$ Å and $c = 4.8219(6)$ Å using X-ray data at room temperature. On deuteration of the hexagonal phase the unit cell volume expands 1.64(8) $Å^3$ which is caused only by an increase of the *c*-axis. The Ti_6 octahedra share faces and are all located along the *c*-axis, which explains the elongation of this axis in the solid solution. The shortest D–D distances when deuterium atoms fill all Ti_6 octahedra are 2.4 Å in the hexagonal structure and 4.17 Å in the cubic. The distances between titanium and deuterium atoms in the Ti_6 octahedra are 2.09 Å for both the cubic and the hexagonal structures.

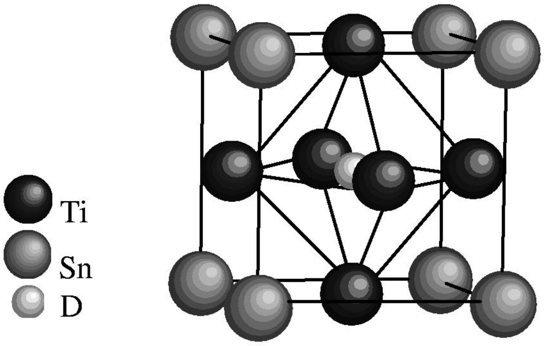

Fig. 2. Crystal structure of cubic Ti_3SnD, *Pm*3*m* (no. 221), $a = 4.1769(4)$ Å.

The phase transition, Ni_3Sn to filled Cu_3Au-type, has been reported in the Ti_3Al systems not only for the hydride but also for the carbide Ti_3AlC [6] and the nitride Ti_3AlN_x [7], but to our knowledge no cubic carbide or nitride have been reported for Ti_3Sn.

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