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# Structural properties of the nanoscopic $Al_{85}Ti_{15}$ solid solution observed in the hydrogen-cycled $NaAlH_4 + 0.1TiCl_3$ system

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## Abstract

The twice-hydrogen-cycled $NaAlH_4 + xTiCl_3$ ($x < 0.15$) system has been studied by high-resolution X-ray synchrotron diffraction and transmission electron microscopy. Intense low $d$-spacing shoulders are formed on Al reflections, indicating the formation of a face-centred cubic $Al_{85}Ti_{15}$ solid solution of unit cell dimension 4.0356 Å. The $Al_{85}Ti_{15}$ solid solution is found as isolated 4–25 nm nanocrystallites on the $NaAlH_4$ surface. The $Al_{85}Ti_{15}$ phase is highly $\langle 110 \rangle \{111\}$ edge dislocated to $\sim 6 \times 10^{16}$ m$^{-2}$. Local energy-dispersive spectroscopy shows an Al:Ti ratio consistent with an $Al_{85}Ti_{15}$ composition, confirming an extended solubility of Ti in Al. Structural analysis indicates a quenched $L1_2$ superlattice obtained by Al and Ti sublattice swapping, yielding an equivalent A1 $Fm\overline{3}m$ model to describe the $Al_{85}Ti_{15}$ crystal structure.
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## 1. Introduction

The binary Al–Ti system has been of great interest to the metallurgical community as the source of potential light-weight materials for aerospace applications [1]. Much work has focused on the $Al_3Ti$ phase, which possesses attractive properties such as a low, $\sim 3.3$ g cm$^{-3}$ density, a high hardness with a yield stress of 980 MPa [2], and a high melting temperature, $\sim 1400$ °C. It has also proved an interesting system in which to study the temperature-dependent super-structure symmetry interconversion of the $D0_{22}$, $D0_{23}$ and $L1_2$ structure types [3]. Due to a lack of ductility below 620 °C [4], studies have focused on converting the tetragonal $D0_{22}$ phase to the cubic $L1_2$ phase by partial substitution with transition metals [2,5,6], giving a ternary cubic $L1_2$ phase with a high number of accessible slip systems.

Early models of B substitution in $Ni_3Al$ [7,8] indicated enhanced ductility was due to B substituting on the unoccupied body centre of the unit cell and subsequently reducing the covalent directionality of the face centred Al atoms. However, channelling-enhanced microanalysis [9,10] of 0.5 at.% (Zr, Hf, W) $L1_2$ Cr-stabilized $Al_3Ti$ indicated clearly that the body centre remains unoccupied. Other studies [11] have focused on developing duplex-type microstructures, where dislocation sources are activated at the interface between precipitates in the $L1_2$ $Al_3Ti$ matrix, such as $Al_2Ti$ or AlTi precipitates, or by dispersing $Al_3Ti$ precipitates within a more ductile Al matrix [12,13].

For $Al_{(1-x)}Ti_x$ with $x < 0.25$, there exists no known stable phase in the binary phase diagram [14]. Early work on quenched melt spins stated the solubility limit for Ti in Al as 2 at.% [15]. In later studies, this solubility limit has been quoted as 4 at.% [16], 10 at.% [17], and even up to 27 at.% [18] in sputter-deposited films. By comparison, other Al based $Al_{(1-x)}M_x$ (M = metal) solid solutions have clear sol-

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ubility limits [19]. Some solubility limits for Ti in Al are based on the observation of apparently single-phase laboratory source X-ray diffraction patterns [16,17]. However, such typically medium-resolution data can disguise the presence of multiple phases, and Rietveld modelling of the Al:Ti ratio is inherently correlated with the scale factor. Although a partially ordered $L1_2$ structure is suggested for $x < 0.25$ by several authors [13,16], clear quantitative information on the local Al:Ti ratio obtained by a supporting spectroscopic technique such as electron-dispersive spectroscopy (EDS) is typically not provided. Further, there exist no diffraction patterns in the literature showing clear $L1_2$ superlattice reflections, and all presented diffraction patterns appear with $Fm\bar{3}m$ type symmetry. The correct structure and maximum solubility of Ti for $Al_{(1-x)}Ti_x$ with $x < 0.25$ remains an open question.

Two different diffraction studies provide key pieces of information about the likely $Al_{(1-x)}Ti_x$ crystal structure. The first study [13] shows clear $L1_2$ superstructure reflections for a single-phase $Al_{90}Zr_{10}$ sample. This study also states that $Al_{90}Ti_{10}$ and $Al_{90}Hf_{10}$ possess similar $L1_2$ structure, although no diffraction patterns are shown. The second study [3] provides the variation of unit cell dimension of $Al_{(1-x)}Ti_x$ as a function of Ti content for an assumed cubic unit cell. The strong variation of unit cell dimension with Ti in [3] indicates that Ti continues to be solved into Al up to 25 at.%. Based on Zr and Ti residing in the same group of the periodic table, we then expect similar bonding behaviour and a similar structure for Ti; however, the absence of superlattice reflections requires an explanation.

The $NaAlH_4$ system is primarily of interest as a hydrogen storage material [20]; however, the formation of isolated nanoscopic crystalline $Al_{(1-x)}Ti_x$ ($x < 0.25$) phases on the $NaAlH_4$ surface provides an interesting new test bed for the Al–Ti system at the 4–25 nm scale. In this work we combine high-resolution X-ray synchrotron diffraction and transmission electron microscopy (TEM) to show that the $Al_{85}Ti_{15}$ phase displays a lattice parameter and Al:Ti ratio in excellent agreement with the predicted 85:15 phase in Ref. [3]. The absence of $L1_2$ superlattice reflections for $Al_{85}Ti_{15}$ is explained with structure factor calculations for $L1_2$ sublattice exchange of Ti and Al which quench the superlattice reflections completely. Similar sublattice exchange in the $Al_{(1-x)}Zr_x$ system reproduces the observed diffraction data in Ref. [13] which shows the Zr system retaining the $L1_2$ superlattice reflections, as expected due to Zr possessing a larger X-ray scattering factor than Ti, and with much less Zr solved into the Al sublattice.

This paper is organized as follows. Section 3.1 describes the methods used to produce isolated nanocrystals of $Al_{(1-x)}Ti_x$ ($x < 0.25$) phases, and presents high-resolution images of their dislocation structure and local EDS analysis of elemental Al:Ti ratios. Section 3.2 discusses the potential crystallographic symmetry of such phases, based on model structure factor calculations of sublattice exchange in the $Al_{(1-x)}Ti_x$ ($x < 0.25$) and $Al_{(1-x)}Zr_x$ ($x < 0.25$) structures.

## 2. Materials and methods

$NaAlH_4$ was purchased from Albermarle Corporation (Lot No. 22470404-01). $TiCl_3$ was purchased from Sigma–Aldrich Chemicals Inc. (>99.99% purity). At all times, all powders have been handled under inert Ar atmosphere in a dry glovebox, with <1 ppm $O_2$ and $H_2O$. Milled $NaAlH_4$ powders with $TiCl_3$ additive were prepared in 1 g quantities in a Fritsch P7 planetary mill (PM), with a ball to powder ratio (bpr) of 20:1, at 750 rpm for a period of 1 h, and in 2 g quantities in a Spex 6750 Freezer mill, milled at intensity 15 for a period of 2 h, in a standard SPEX cryo vial, with a 32 g SS440c impactor. Hydrogen (H) cycling was performed in a Sieverts apparatus, rated to 200 bar and 600 °C. Samples for diffraction measurements were removed directly after milling, and after 2 and 5 H cycles (typically H cycled at 140 °C with 150 bar aliquot). Synchrotron radiation powder X-ray diffraction data were recorded at the Swiss–Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Samples were contained in rotating 0.8 mm boron–silica glass capillaries. High resolution data ($\Delta d/d \sim 4 \times 10^{-4}$) was typically collected at 295 K between 5 and 35° $2\theta$, in steps of 0.0025°. A wavelength of 0.4998 Å was obtained from a channel-cut Si (1 1 1) monochromator. Medium resolution ($\Delta d/d \sim 3 \times 10^{-3}$) in situ annealing data were collected on a two-dimensional image plate (MAR345) over the $2\theta$ range 3–34° with step size 0.015° and exposure time of 30 s. A wavelength of 0.7111 Å was used. TEM was performed with a JEOL 2010F field emission gun operating at 200 kV, or with a Philips CM30 operating at 100–300 kV. TEM samples were loaded inside the glovebox and transferred into the column of the microscope by two different methods. (i) An oxygen-tight transfer cap was used, with the cap being removed inside a glovebag attached to the holder entrance of the microscope. The glovebag was pumped and flushed with pure $N_2$ to prevent sample oxidation. (ii) A Gatan environmental cell TEM holder was used. A vacuum gate valve on the environmental chamber allowed the sample to be withdrawn and isolated in the chamber during transfer, which prevented contamination or contact with air. Method (i) was most frequently used. X-ray synchrotron diffraction patterns were analyzed by the Rietveld method, using the software RIETICA [21]. Diffraction line profiles were fitted with a full Voigt function, with the instrumental shape determined by a NIST $LaB_6$ 660a lineshape standard, further annealed to 1800 °C. Backgrounds were modelled with type I Chebyshev polynomials.

## 3. Results

### 3.1. Methods to produce nanoscopic $Al_{(1-x)}Ti_x$ ($x<0.25$) phases from $NaAlH_4 + xTiCl_3$

Crystalline $Al_{(1-x)}Ti_x$ $x < 0.25$ solid solutions can be crystallized from the $NaAlH_4 + xTiCl_3$ system by three