Short Communication

Preparation and Structure of Al_3Ti

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The phase diagram of the binary system Al-Ti shows three intermetallic compounds, Al_3Ti, $Al_{11}Ti_5$ and AlTi, which are all formed peritectically. The system has no congruently melting compounds.[1] This situation makes the crystal growth from the melt of the intermetallic compounds difficult. Al_3Ti has a narrow composition range and a peritectic transition temperature at 1340 °C, where Al_3Ti is in equilibrium with $Al_{11}Ti_5$ and a melt containing approximately 25 atomic % Ti. It is possible to grow a single crystal from a solution by a modified Czochralski growth method, when the composition of the solution is only a few atomic % different from that of the crystal in equilibrium with the solution. This was demonstrated by the crystal growth of Mo_3Si.[2] At the peritectic temperature the vapor pressure of Al is approximately 9 Pa,[3] and a loss of aluminium from the melt should not be a problem in the crystal growth experiment.

The crystal structure of Al_3Ti belongs to the tetragonal DO_{22}-type and is a superstructure derived from the cubic close packed structure of aluminium.[4] As the DO_{22}-type structure may be of interest in connection with superconductivity of binary and ternary phases,[5] it was decided to grow and characterize a single crystal of Al_3Ti.

A binary alloy with the nominal composition 25 atomic % Ti, 75 atomic % Al was made in a cold crucible from 99.7 % Ti (Pierce Inorganics, S.V., Holland) and 99.999 % Al (Schweizerische Aluminium AG, Neuhausen a Rhf.). A cold crucible where the volumen of the melt can be kept constant during the modified Czochralski growth experiment[2] was applied in an ADL-MP crystal growth unit.[6] An ambient He-pressure of 0.7 MPa was used to reduce any evaporation of Al from the melt. A single crystal of Al_3Ti was grown from the melt of the binary alloy mentioned above with a growth rate of 3 mm h^{-1}. An attempt to grow from a melt with a nominal composition smaller than 25 atomic % Ti at a temperature of 1100 °C was not succesful, yielding platelike dendrites of Al_3Ti.

An X-ray Guinier photograph was taken of a sample of the Al_3Ti crystal with a Guinier camera using $CuK\alpha_1$ (λ = 1.5405981 Å) radiation and Ge (a = 5.6576 Å) as an internal standard. From the

Table 1. Temperature factor parameters. Standard deviations in parentheses.

$h^2+k^2+l^2 >$	No. of reflections	Ti-atom $U_{11}(=U_{22})$ ×10⁴	U_{33}	Al1-atom $U_{11}(=U_{22})$ ×10⁴	U_{33}	Al2-atom $U_{11}(=U_{22})$ ×10⁴	U_{33}	R %
0	127	51(2)	48(3)	77(2)	122(3)	61(1)	72(2)	1.6
20	103	54(2)	51(2)	79(2)	126(3)	69(2)	76(2)	1.4
40	71	58(2)	55(3)	80(2)	130(3)	73(2)	80(2)	1.2
60	50	56(2)	58(2)	80(3)	132(3)	74(2)	82(2)	1.0
80	34	54(4)	60(3)	83(5)	131(4)	75(3)	83(3)	0.9
100	25	58(6)	63(4)	87(7)	133(5)	76(5)	87(4)	1.0

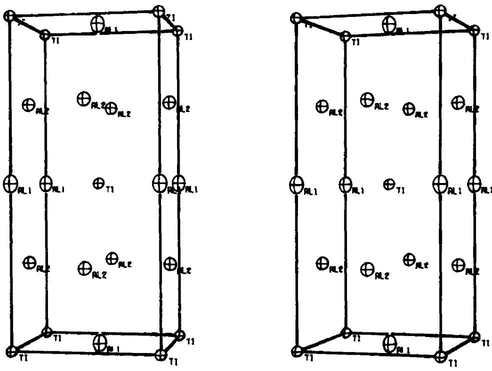

Fig. 1. Stereoplot of Al_3Ti. Ellipsoids at 75 % propability level.

powder pattern the tetragonal unit cell was found: $a = 3.8537(3)$, $c = 8.5839(13)$ Å. The unit cell reported previously[4] was twice that cell, with $a = 5.425$ and $c = 8.579$ Å. Laue photographs taken with ratiation from a tungsten X-ray tube showed the crystal to be of good quality.

A single crystal with dimensions 2×2×1.5 mm^3 was spark-eroded from the large crystal of Al_3Ti and used in a neutron diffraction single crystal investigation. The four-circle diffractometer at Risø was used to measure a total of 774 reflections, using $\lambda = 1.018$ Å neutrons and the ω-2θ scan technique. A single crystal neutron diffraction instead of an X-ray diffraction investigation was made because more precise temperature factor parameters are obtained in neutron diffraction than in X-ray diffraction.

Two standard reflections were measured for each 50 reflections in a half sphere out to $\sin\theta/\lambda = 0.85$. After correction for absorption ($\mu = 0.14$ cm^{-1}) and data reduction, the number of independent reflections with $I > 3\sigma(I)$ was 127. The least squares program *LINUS*[7] was used in the structure factor calculations with the scattering lengths 0.345 and −0.330 (in units of 10^{-12} cm) respectively[8] for Al and Ti.

The spacegroup is *I4/mmm* (no. 139), containing 2 formula units/cell. The atoms in the structure are in special positions with no positional parameters (Al1 in *2b*, Al2 in *4d* and Ti in *2a*). Refinement of the occupancies of the atoms showed that the crystal was stoichiometric within experimental errors.

The diffraction data may yield detailed information concerning the temperature factor parameters of the atoms. A series of calculations of these parameters were made including all reflections and only high angle reflections (Table 1). Characteristic for the results obtained is that the U_{33} temperature factor parameter for Al1 is significantly larger than U_{33} for Al2. This is also observed in Fig. 1, which shows the thermal ellipsoids in the [001] direction.

The intertatomic distances in the structure are: (standard deviation less than 0.001 Å)

Al1-Al1	3.854 Å,	Al2-Al2	2.725 Å,
Ti-Ti	3.854 Å,	Al1-Al2	2.884 Å,
Al1-Ti	2.725 Å,	Al2-Ti	2.884 Å.

In Al-metal the Al-Al distances are 2.86 Å; the shortest Al-Al distance in Al_3Ti is thus significantly shorter than in pure aluminium. The Al1 atom has its thermal ellipsoid elongated after its longest interatomic distance.

A specimen of a single crystal of Al_3Ti was used to investigate a possible transition to superconductivity at low temperatures using an induction method.[9] The sample showed no transition to superconductivity down to 4.5 K. Al-metal shows transition to superconductivity at 1.175 K and Ti-metal at 0.39 K.[10]

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