Crystallography

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Abstract

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X-RAY STUDY OF THE CRYSTAL STRUCTURE OF THE COMPOUNDS TiSi AND TiGe

At the present time a large number of structures of titanium compounds have been studied. The absence of data on the structure of the compounds TiSi and TiGe is a substantial gap in the crystal chemistry of binary titanium compounds with elements of subgroup IVB. The aim of the present investigation is to determine the crystal structure of the compounds TiSi and TiGe.

For the preparation of the chemical compounds, the following starting materials were used: iodide titanium (99.7%), silicon (99.7%), and germanium (99.9%). The synthesis of the compounds was carried out both by powder sintering and by melting in an arc electric furnace with a copper hearth and a tungsten electrode.

Preliminary X-ray studies showed that the compounds TiSi and TiGe are isostructural, like the previously studied compounds of these systems $TiSi_2$ ([1]) and $TiGe_2$, as well as Ti_5Si_3 and Ti_5Ge_3 ([2]). By means of X-ray phase analysis, chemical analyses, and determination of the lattice constants, the exact correspondence of the TiSi compound to the stoichiometric composition (36.95 wt.% Si = 50.00 at.%) was confirmed, and the absence of solubility of titanium and silicon in it was established.

The study of the structure of the TiSi compound was carried out on single crystals that were extracted from shrinkage cavities of an ingot containing about 44 wt.% Si. Melting was performed in a quartz tube evacuated to 10^{-4} mm Hg and placed in the inductor of a high-frequency generator. Inside the tube, on crushed quartz, there was placed a graphite heater in the form of a cylinder ending below in a truncated cone, calcined at 1100° for 4 hours in a vacuum of 10^{-3} mm Hg. The shape and dimensions of the graphite heater were found experimentally; the aim was to create gradual directed cooling of the melt from top to bottom. A thoria crucible was placed inside the graphite heater, in which the alloy was melted, and outside the heater there was a quartz cylindrical screen to prevent the wall of the quartz tube from coming into contact with the heater.

The TiSi compound forms by a peritectic reaction, and for the formation of its primary crystals the composition of the alloy was taken as 44 wt.% Si ([3]). In an alloy of this composition, primary crystals of the TiSi compound separate from the liquid; around them an eutectic subsequently crystallizes, consisting of a mixture of TiSi + $TiSi_2$ crystals. The TiSi crystals are located in shrinkage

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Fig. 2. Unit cell of the compound. Large circles are titanium atoms, small ones are silicon atoms.

Figure 2: Fig. 2. Unit cell of the compound. Large circles are titanium atoms, small ones are silicon atoms.

cavities inside the ingot and have the form of plates, to which in some cases a small number of $TiSi_2$ crystallites, separated during eutectic crystallization, are attached. Selection of a TiSi single crystal suitable for investigation and containing no eutectic constituent was carried out visually and, more reliably, by Laue photographs.

Analysis of Laue patterns and rotation X-ray photographs showed that the TiSi compound has rhombic symmetry. The unit-cell constants were obtained from calculation of the rotation X-ray photographs and refined with the aid of

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Debyegrams. The following values of the constants were obtained for the TiSi and TiGe compounds (in kX):

Compound	a	b	c
TiSi	$3,61_1$	$4,96_0$	$6,47_9$
TiGe	$3,80_1$	$5,22_4$	$6,82_0$

The density of the compounds was determined by the pycnometric method and was found to be, for TiSi, $\rho_{\text{exp}} = 4.21 \pm 0.05$ g/cm^3; $\rho_{\text{X-ray}} = 4.34$ g/cm^3. The number of atoms in the unit cell is therefore 8.

Fig. 2. Unit cell of the compound. Large circles are titanium atoms, small ones are silicon atoms.

By indexing the rotation X-ray photographs and fiber diagrams, it was established that the structures of the TiSi and TiGe compounds belong to the space groups C_{2v}^1 or D_{2h}^1. The agreement of the observed and calculated $\sin^2\theta$ values is good.

Analysis of the interference intensities showed that the most probable arrangement of the atoms is in planes with the parameter $x = 0$, $1/2$, and 1, and especially at the vertices of the unit cell. Verification of the preliminary model of the atomic arrangement was carried out by an approximate calculation of the intensities for a statistical arrangement of atoms in the cell, since the scattering power of titanium and silicon atoms differs only slightly. This kind of preliminary consideration considerably facilitated the choice of a model for the arrangement of atoms in the unit cell. In Fig. 1 the graph of calculated intensities is shown by the dashed line.

intensities for a statistical arrangement of the atoms in the cell. Knowledge of the atomic coordinates made it possible to establish that the structure of the TiSi compound belongs to the space group C_{2v}^1. Refinement of the atomic coordinates was carried out with the aid of Patterson–Harker series (projection on the z axis) and Patterson series (projection on the xy plane). The coordinates of the atoms in the unit cell of the TiSi compound have the following values:

Atom												
Ti	0	0	0	0.5	0.5	0.5	0	0	0.5	0.5	0.5	0
Si	0.5	0	0.412	0.5	0	0.588	0	0.350	0.250	0	0.350	0.750

The unit cell with the titanium and silicon atoms placed in it is shown in Fig. 2.

The calculated intensities of the Debye pattern, obtained with allowance for the Thomson, Lorentz, multiplicity, absorption, and temperature-correction factors, agree well with those measured experimentally, as is evident from Fig. 1.

Lauegrams were taken with molybdenum radiation, kforograms with Mo–K_α radiation, and rotation X-ray patterns and Debye patterns with Cu–K_α radiation.

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Note: Figure translations are in progress. See original paper for figures.