must be considered in computing the bond length standard deviation. The description of the disposition of these distances with respect to interatomic angles follows.

The $M(f)$ atoms are located at the vertices of hexagons whose plane is parallel to (100) (Fig. 1(a)). The longer 2·460 Å bonds are directed parallel to $y$ and the 2·427 Å bonds are perpendicular to (011) and (01$\bar{1}$). Angles in the hexagon deviate slightly from 120° so that the four angles formed by the intersection of a long and a short $M(f)$–$M(f)$ bond are equal to 119° 37′ and the two angles formed by the intersection of two shorter $M(f)$–$M(f)$ bonds are equal to 120° 46′.

The $M(e)$ atoms are located on hexagons parallel to (011) and (01$\bar{1}$) which include one boron atom (Fig. 1(b)). Of the six sides of the hexagon two are the shorter $M(e)$–$M(e)$ 2·389 Å bonds parallel to $x$, two are the longer $M(e)$–$M(e)$ 2·456 Å bonds, perpendicular to (131) and ($\bar{1}$31) or (13$\bar{1}$) and ($\bar{1}$3$\bar{1}$) and two are the 2·2 Å $M(e)$–B bonds. Of the six angles two are formed by intersection of a long and a short $M(e)$–$M(e)$ and equal 120° 40′, two are formed by intersection of a short $M(e)$ bond and an $M(e)$–B bond and equal 107° 15′, one is formed by intersection of two longer $M(e)$–$M(e)$ bonds and equals 118° 40′, and one is formed by intersection of two $M(e)$–B bonds and equals 145° 30′.

All $M(e)$ to $M(f)$ distances can be depicted as sides of a distorted tetrahedron as originally described by Kiessling (1950). All of these distances are long (greater than 2·7 Å), relative to the $M(e)$–$M(e)$ and $M(f)$–$M(f)$ distances. The articulation of the longer $M(f)$–$M(e)$ distances with the shorter $M(e)$–$M(e)$ and $M(f)$–$M(f)$ distances results in distorted tetrahedra so that the triangular faces of these tetrahedra are isosceles rather than equilateral, with two larger angles of about 64° and one smaller one of about 52°.

The boron atoms, as also noted by Kiessling (1950), lie in strings perpendicular to (031) or (03$\bar{1}$) alternating at intervals of $\frac{1}{4}a$ with a boron–boron distance of 2·1 Å.

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# The structure of (Ti, Re) Si₂.

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Nearly all transition metals form disilicides. Of special interest are the disilicides with metals of the fourth to sixth group of the periodic system. They crystallize with three different crystal structure types which are geometrically related. They can be described as different stacking variations of graphite-like, metal-centered Si nets. The three types are:

$C54$ or TiSi₂ type: A 4-layer stacking type, which occurs with TiSi₂.

$C40$ or CrSi₂ type: A 3-layer stacking type, which has been reported for VSi₂, NbSi₂, TaSi₂, CrSi₂.

$C11$ or MoSi₂ type: A 2-layer stacking type, which has been found with MoSi₂, WSi₂ and ReSi₂.

These disilicide types and their mutual solubility have been studied extensively over the last ten years by Nowotny and his co-workers (Nowotny, 1963). It was found that the occurrence of these structure types is influenced by a valence electron factor and it is possible to change the structure type by replacing part of the metal and non-metal component with other elements having more or fewer valence electrons.

No investigations have been made before with ReSi₂. It was of interest to investigate how the rules developed for the 4th, 5th and 6th group disilicides would apply to ReSi₂. Therefore, a study of the phases and their
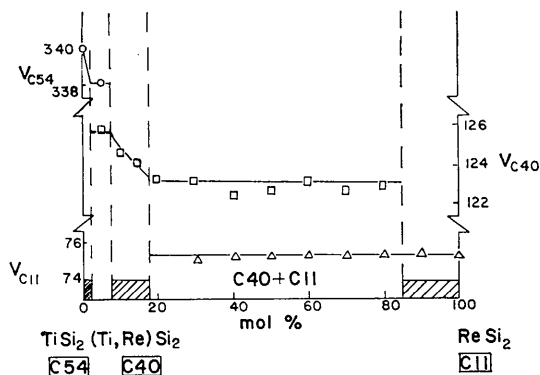


Fig. 1. Unit-cell volume (Å³) of the phases in the pseudobinary system TiSi₂–ReSi₂ at 1300 °C.

homogeneity ranges in the pseudo-binary system $ReSi_2$–$TiSi_2$ was undertaken.

The thirteen specimens were prepared by ball milling stoichiometric mixtures of the powdered elements and hot pressing them at 1300 °C. After that the alloys were annealed under hydrogen at 1300 °C for 72 hours.

As shown in Fig. 1, in the pseudo-binary system $TiSi_2$–$ReSi_2$, a ternary phase occurs with approximate composition $Ti_{0.9}Re_{0.1}Si_2$. The powder pattern can be indexed with a hexagonal unit cell with

$$a = 4.70_5, \quad c = 6.50_5 \quad \text{and} \quad c/a = 1.38 .$$

With the reflections $00l$: $l = 3n$ only, five enantiomorphous space group pairs are possible. From these the space group $P6_422$ ($D_6^5$) was selected with six silicon atoms in equipoint $6(i)$ with $x = 1/6$, and titanium and rhenium atoms randomly distributed over equipoint $3(c)$. Table 1

Table 1. *Intensity calculation for* $(Ti_{0.9}Re_{0.1})Si_2$ *with* $CrSi_2$ *structure*

Cr $K\alpha$ radiation

| $hki l$ | $d$ (Å) | $1000 \sin^2 \theta_c$ | $1000 \sin^2 \theta_o$ | $I_c$ | $I_o$ |
|---|---|---|---|---|---|
| $10\bar{1}0$ | 4.076 | 79.0 | 81.4 | 5 | $vvw$ |
| $10\bar{1}1$ | 3.454 | 110.0 | 111.1 | 30 | $m$ |
| $10\bar{1}2$ | 2.543 | 202.9 | 204.2 | 12 | $w$ |
| $11\bar{2}0$ | 2.353 | 237.1 | 238.9 | 15 | $w$ |
| $11\bar{2}1$ | 2.213 | 268.0 | 269.3 | 100 | $vs$ |
| $0003$ | 2.170 | 278.7 | 277.8 | 35 | $m$ |
| $20\bar{2}0$ | 2.038 | 316.1 | 320.1 | 6 | $vw$ |
| $10\bar{1}3$ | 1.915 | 357.8 ⎫ | 361.4 | 1 ⎫ | $s$ |
| $11\bar{2}2$ | 1.907 | 360.9 ⎭ | | 62 ⎭ | |
| $11\bar{2}3$ | 1.595 | 515.8 | 514.6 | 10 | $w$ |
| $21\bar{3}0$ | 1.540 | 553.2 | — | <1 | — |
| $10\bar{1}4$ | 1.511 | 574.5 | 571.9 | 2 | $vvw$ |
| $21\bar{3}1$ | 1.499 | 584.2 | 586.5 | 5 | $vvw$ |
| $20\bar{2}3$ | 1.485 | 594.9 | 594.3 | 6 | $vvw$ |
| $21\bar{3}2$ | 1.392 | 677.1 | 678.0 | 5 | $vvw$ |
| $30\bar{3}0$ | 1.359 | 711.3 | 714.0 | 5 | $vvw$ |
| $11\bar{2}4$ | 1.338 | 732.6 | 728.9 | 38 | $m$ |
| $30\bar{3}1$ | 1.330 | 742.3 | 743.5 | 39 | $m$ |
| $21\bar{3}3$ | 1.256 | 832.0 | — | 2 | — |
| $30\bar{3}2$ | 1.254 | 835.2 | 835.4 | 47 | $m$ |
| $10\bar{1}5$ | 1.240 | 853.2 | — | 3 | — |
| $22\bar{4}0$ | 1.177 | $\alpha_1$ ⎰ 946.8 | 947.1 ⎱ | 96 | $s$ |
| | | $\alpha_2$ ⎱ 949.9 | 950.9 ⎰ | | $m$ |

shows the agreement between calculated and observed intensities. The structure of $Ti_{0.9}Re_{0.1}Si_2$ is of the $C40$–$CrSi_2$ type.

The lattice parameters of all phases found are given in Table 2. $ReSi_2$ dissolves about 15 mol.% $TiSi_2$ without much change in the lattice parameters of the $C11$ structure. The ternary phase exists from about $Ti_{0.93}Re_{0.07}Si_2$ to approximately $Ti_{0.82}Re_{0.18}Si_2$, while the $TiSi_2$ phase has a homogeneity limit below 5 mol.% $ReSi_2$.

The obtained results can be interpreted by a valence electron factor. $TiSi_2$ crystallizes with the 4-layer stacking type. By replacing some of the Ti atoms with the electron-richer Re atoms the intermediate 3-layer stacking type is obtained, while pure $ReSi_2$ chooses the 2-layer stacking type. The sequence of the occurring phases in the pseudo-binary system $TiSi_2$–$ReSi_2$ agrees well with the similar results obtained for the pseudo-binary sections $TiSi_2$–$MoSi_2$ and $TiSi_2$–$WSi_2$ (Nowotny, Kudielka & Parthé, 1956). In both cases a ternary phase exists — (Ti,Mo)$Si_2$ and (Ti,W)$Si_2$ — crystallizing with the 3-layer stacking type.

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Table 2. *Lattice parameters of* (Ti,Re)$Si_2$ *alloys*

| Composition of alloy | $C54$ type Orthorhombic | | | $C40$ type Hexagonal | | $C11$ type Tetragonal | |
|---|---|---|---|---|---|---|---|
| | $a$ | $b$ | $c$ | $a$ | $c$ | $a$ | $c$ |
| $TiSi_2$ | $8.27_9$ Å | $4.81_9$ Å | $8.56_8$ Å | — | — | — | — |
| $(Ti_{0.95}Re_{0.05})Si_2$ | $8.26_5$ | $4.79_1$ | $8.54_3$ | $4.71_2$ Å | $6.53_5$ Å | — | — |
| $(Ti_{0.9}Re_{0.1})Si_2$ | — | — | — | $4.70_5$ | $6.50_5$ | — | — |
| $(Ti_{0.85}Re_{0.15})Si_2$ | — | — | — | $4.69_3$ | $6.51_3$ | — | — |
| $(Ti_{0.8}Re_{0.2})Si_2$ | — | — | — | $4.68_7$ | $6.48_3$ | + | + |
| $(Ti_{0.7}Re_{0.3})Si_2$ | — | — | — | $4.68_0$ | 6.49 | $3.12_7$ Å | $7.68_3$ Å |
| $(Ti_{0.6}Re_{0.4})Si_2$ | — | — | — | $4.67_9$ | 6.46 | $3.12_7$ | $7.69_8$ |
| $(Ti_{0.5}Re_{0.5})Si_2$ | — | — | — | $4.68_1$ | 6.47 | $3.12_8$ | $7.69_5$ |
| $(Ti_{0.4}Re_{0.6})Si_2$ | — | — | — | $4.68_2$ | 6.49 | $3.13_4$ | $7.68_0$ |
| $(Ti_{0.3}Re_{0.7})Si_2$ | — | — | — | $4.68_1$ | 6.46 | $3.13_2$ | $7.68_9$ |
| $(Ti_{0.2}Re_{0.8})Si_2$ | — | — | — | $4.67_7$ | 6.49 | $3.13_8$ | $7.66_2$ |
| $(Ti_{0.1}Re_{0.9})Si_2$ | — | — | — | — | — | $3.13_7$ | $7.67_0$ |
| $ReSi_2$ | — | — | — | — | — | $3.13_8$ | $7.66_6$ |