The Crystal Structure of Ni_3Si_2 with some Notes on Ni_5Si_2

GUNVOR PILSTRÖM

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of Ni_3Si_2 has been determined from single crystal data. The unit cell is orthorhombic and contains 16 formula units. The space-group is $Cmc\ 2_1$. The unit cell dimensions determined by powder diffraction techniques are: $a = 12.229\text{ Å}$, $b = 10.805\text{ Å}$ and $c = 6.924\text{ Å}$. The nickel atoms are situated in four eight-fold and four four-fold positions and the silicon atoms are situated in three eight-fold and two four-fold positions.

The single crystal data have also been used to determine the symmetry and unit cell dimensions of Ni_5Si_2 for which a trigonal unit cell has been found. This phase has a small homogeneity range. Thus Ni_5Si_2 in equilibrium with $\delta\text{-Ni}_3\text{Si}$ has the cell dimensions, $a = 6.670\text{ Å}$ and $c = 12.267\text{ Å}$ whereas in equilibrium with Ni_3Si the dimensions are $a = 6.670\text{ Å}$ and $c = 12.332\text{ Å}$.

The existence of Ni_3Si_2 was first established in 1906 by Guertler and Tammann¹ who made a thermal and microscopic investigation of the Ni-Si system. They found that Ni_3Si_2 is formed by a peritectoid reaction at 830°C . Iwasé and Okamoto², who revised the Ni-Si diagram in 1936, found that the peritectoid reaction takes place at 845°C . In 1939 Ôsawa and Okamoto³ published an X-ray analysis of the Ni-Si system. The unit cell of Ni_3Si_2 was stated to be orthohexagonal with the unit cell dimensions $a = 6.605\text{ kX}$, $b = 7.627\text{ kX}$ and $c = 9.574\text{ kX}$, and a cell content of 45 atoms.

Ni_5Si_2 was also stated to be orthohexagonal with the unit cell dimensions $a = 13.29\text{ kX}$, $b = 7.672\text{ kX}$ and $c = 9.752\text{ kX}$, and a cell content of 90 atoms. In the present investigation single crystal examinations show that the unit cell of Ni_5Si_2 is in fact trigonal. The cell dimensions, determined by the powder method, vary slightly with composition. Ni_5Si_2 in equilibrium with $\delta\text{-Ni}_3\text{Si}$ gives values for a and c of 6.670 and 12.267 Å , respectively, compared with values of 6.670 and 12.332 Å obtained for the phase in equilibrium with Ni_3Si .

EXPERIMENTAL

The materials used for alloy preparations were: Nickel sponge (98.2%) obtained from Johnson Matthey Co., Ltd, London and silicon (99.9%) obtained from Pechiney & Cie Paris.

Table 1. Powder data for Ni_3Si_2 . ($\text{CrK}\alpha_1$ radiation).

hkl	$\sin^2\Theta_{\text{obs}} \times 10^4$	$\sin^2\Theta_{\text{calc}} \times 10^2$	I_{obs}	I_{calc}	hkl	$\sin^2\Theta_{\text{obs}} \times 10^4$	$\sin^2\Theta_{\text{calc}} \times 10^2$	I_{obs}	I_{calc}
110	200	200	m	138	023	2 912	2 909	w	65
200	350	351	w	32	422	a)	2 945	w—	27
020	449	449	w—	13	600	3 156	3 155	st +	625
111	—	473		4	151	—	3 167	b)	22
021	—	722		0.1	440	—	3 198	b)	122
220	—	800		10	530	—	3 201	b)	73
310	—	901		3	242	3 241	3 241	st +	1170
221	1 073	1 073	w +	52	223	—	3 260	b)	51
002	—	1 094		0.3	313	3 361	3 362	st +	989
130	—	1 098		0.1	512	3 396	3 397	st	493
311	1 174	1 174	w—	18	441	—	3 472		8
112	1 294	1 294	m +	294	531	3 476	3 475	m +	312
131	1 372	1 372	m	120	133	3 555	3 558	c)	120
400	1 403	1 402	w—	18	350	3 593	3 596	st	613
202	1 442	1 444	w—	32	602	—	3 604	b)	44
022	1 544	1 543	w	42	351	3 873	3 869	w +	54
040	—	1 796		0.1	621	—	3 877		12
330	1 798	1 799	w +	138	152	—	3 988		6
420	1 848	1 851	w	45	060	—	4 041		2
222	1 889	1 893	w—	27	620	—	4 165		1
312	a)	1 995	w—	17	043	4 257	4 256	w +	79
041	—	2 069		0.2	333	—	4 259		9
331	a)	2 072	w—	29	442	} 4 294	4 292		542
421	—	2 125		0.1	532		4 295	st	38
240	—	2 147		11	423	—	4 312	b)	22
132	a)	2 191	w—	23	061	—	4 314	b)	27
510	—	2 303		0.1	004	4 378	4 374	m +	331
241	—	2 420		3	260	—	4 392		4
402	—	2 496		17	710	—	4 407		7
511	a)	2 577	w—	21	114	—	4 574		10
113	—	2 660		0	243	—	4 607		4
042	} 2 897	2 890		151	261	—	4 665		18
332		2 893	m	23	352	a)	4 689	w—	23
150	—	2 894		3	204	—	4 725		6
					024	—	4 823		25

a The line is too diffuse to be measured accurately.

b The line is too near a strong line to be discernible.

c This line is overlapped by a line of the calibration standard.

An arc melted alloy with the nominal composition Ni_3Si_2 was annealed at 830°C for 30 days. X-Ray powder photographs were taken in a Guinier-type focusing camera with $\text{CrK}\alpha_1$ radiation. Si was used as an internal standard ($\lambda_{\text{CrK}\alpha_1} = 2.2896 \text{ \AA}$, $\text{Si}: a = 5.4306 \text{ \AA}$). The accuracy of the lattice parameter values is estimated to be 0.03 %. For the structure determination a small fragment was selected from the annealed alloy. Photographs were taken in a Weissenberg camera with $\text{MoK}\alpha$ radiation. Intensity data were obtained using a multiple film technique with iron foil interleaved between the films. The c -axis was used as the rotation-axis and the layer-lines 0–6 were recorded. The intensities of 367 non-equivalent reflexions were estimated visually. The calculations of Fourier series and structure factors were made with the aid of the electronic digital computer BESK using programmes devised by Westman *et al.*⁴ and by Åsbrink *et al.*⁵. The constants $A_i, B_i, C_i, a_i, b_i, c_i$ in the expression for the atomic scattering factors f_i (given by Åsbrink *et al.*⁵) have been determined by Appel⁶ as follows:

	A_i	B_i	C_i	a_i	b_i	c_i
Ni	9.664	10.559	7.537	0.321	3.479	25.262
Si	2.8315	6.8065	4.5870	0.3235	2.2965	51.770

THE DETERMINATION OF THE STRUCTURE OF Ni_3Si_2

From single crystal and powder photographs the unit cell of Ni_3Si_2 was found to be orthorhombic with the dimensions: $a = 12.229$ Å, $b = 10.805$ Å, $c = 6.924$ Å. Powder data are given in Table 1. Ôsawa and Okamoto³ found the density (D_m) to be 6.32 g cm^{-3} and from this the unit cell was assumed to contain 16 formula units, giving the calculated X-ray density 6.74 g cm^{-3} . (Densities given by these authors for other compounds show that they have usually obtained values that are in fact too low.)

The Weissenberg films showed the systematic extinctions: $F(hkl)$ for $h + k = 2n + 1$ and $F(h0l)$ for $l = 2n + 1$. The possible space-groups were $Cmcm$, $Ama2$ and $Cmc2_1$. The Patterson section $P(X0Z)$ showed that $Cmc2_1$ was the most probable space-groups. During the refinement of the structure there was nothing which indicated that another space-group should be chosen.

The Patterson sections $P(X0Z)$ and $P(XY\frac{1}{2})$ gave rough x and y parameters. As the electron density projection $\rho(xy)$ was the only centrosymmetric one this projection was first refined. There were no Harker peaks to give the z -coordinates. As the x and y -coordinates obtained from $\rho(xy)$ were good apart from some overlapping and the measured density shows that the structure must be fairly densely packed it was possible to get rough z -parameters from spatial considerations. The z -coordinate of Ni_5 was arbitrarily put at 0. The whole of the three-dimensional intensity data was finally used for refining all the parameters. The refinement was made by calculating $\rho(F_{\text{obs}})$ and $\rho(F_{\text{calc}})$ and was taken to a point at which all shifts were smaller than the standard deviations. The standard deviations were calculated using the formula given by Cruickshank⁷. As only one electron density projection is centrosymmetric the values of standard deviations given are twice those calculated for a centrosymmetric space-group. For final parameters and standard deviations see

Table 2. Atomic parameters for Ni_3Si_2 .

	x	y	z
8 Ni_1 in 8(b)	0.1732	0.1177	0.518
8 Ni_2 in 8(b)	0.1723	0.1189	0.900
8 Ni_3 in 8(b)	0.1972	0.2467	0.217
8 Ni_4 in 8(b)	0.1824	0.4975	0.225
4 Ni_5 in 4(a)		0	0
4 Ni_6 in 4(a)		0.2345	0.024
4 Ni_7 in 4(a)		0.2330	0.400
4 Ni_8 in 4(a)		0.3814	0.714
8 Si_I in 8(b)	0.120	0.059	0.214
8 Si_{II} in 8(b)	0.152	0.344	0.506
8 Si_{III} in 8(b)	0.151	0.343	0.920
4 Si_{IV} in 4(a)		0.157	0.712
4 Si_V in 4(a)		0.409	0.218

Table 2a. Standard deviations of the atomic parameters ^a of Ni₃Si₂.
$$\begin{aligned}
 \sigma_x(\text{Ni}) &= 0.0003 \\
 \sigma_y(\text{Ni}) &= 0.0005 \\
 \sigma_z(\text{Ni}) &= 0.002 \\
 \sigma_x(\text{Si}) &= 0.001 \\
 \sigma_y(\text{Si}) &= 0.001 \\
 \sigma_z(\text{Si}) &= 0.006
 \end{aligned}$$

^a The standard deviation for Ni₁ is 0 as this atom defines the origin.

Tables 2 and 2a. An isotropic temperature factor with $B = 0.22 \text{ \AA}^2$ was applied. The reliability index $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ was 0.118 after the last refinement.

DESCRIPTION OF THE STRUCTURE OF Ni₃Si₂

The structure of Ni₃Si₂ is very complicated and thus difficult to describe. It may be visualized, however, as consisting of flat and puckered layers perpendicular to the a -axis. The flat layers lie in the mirror planes $x = 0$ and $x = \frac{1}{2}$. The puckered layers, which are at $x \simeq \pm 1/6$ and $x \simeq \pm 1/3$ are symmetrically equivalent. Fig. 1 shows the nickel atoms in these layers projected on the bc -plane. Fig. 2 shows a flat layer and Fig. 3 a puckered layer in which both nickel and silicon atoms are present.

Fig. 1. The nickel atoms projected on the bc plane. Four unit cells are shown.

Fig. 2. The pattern of atoms in the mirror plane $x = 0$ (or $x = \frac{1}{2}$). The circles are nickel atoms, the dots are silicon atoms. The Arabic figures are the indices of the nickel atoms and the Roman figures those of the silicon atoms. Four unit cells are shown.

Table 3 gives interatomic distances and Table 4 and Figs. 4 (a) — (m) show the environments of each atom. Most of the Ni-Ni distances lie in the range 2.47—2.76 Å and in particular, there are a number with values of about

Fig. 3. The figure corresponds to Fig. 2 for the puckered layer. Unit cell is outlined with respect to x near $1/6$.

Table 3. Interatomic distances in Ni_3Si_2 (Å) <3.3.

	—Ni ₁	—Ni ₂	—Ni ₃	—Ni ₄	—Ni ₅	—Ni ₆	—Ni ₇	—Ni ₈	—Si _I	—Si _{II}	—Si _{III}	—Si _{IV}	—Si _V
Ni ₁ —		2.65 2.68	2.53 2.56	2.59 2.99	2.47		2.59		2.29 2.43	2.46	2.30	2.54	
Ni ₂ —	2.65 2.68		2.50 2.61	2.49 3.15	2.56	2.60			2.35 2.40	2.31	2.44	2.51	
Ni ₃ —	2.53 2.56	2.50 2.61		2.72		2.76	2.73		2.24	2.33 2.55	2.37 2.53		2.98
Ni ₄ —	2.59 2.99	2.49 3.15	2.72 3.07					2.59	2.50	2.32 2.58	2.22 2.72		2.43
Ni ₅ —	2.47(2)	2.56(2)				2.54	2.61		2.18(2) 2.55(2)			2.24 2.61	
Ni ₆ —		2.60(2)	2.76(2)		2.54		2.60	2.67	2.74(2)		2.30(2)	2.32	2.32
Ni ₇ —	2.59(2)		2.73(2)		2.61	2.60		2.70	2.72(2)	2.33(2)		2.31	2.29
Ni ₈ —				2.59(2)		2.67	2.70			2.38(2)	2.37(2)	2.43	2.26
Si _I —	2.29 2.43	2.35 2.40	2.24	2.50	2.18 2.55	2.74	2.72		2.94			2.75	
Si _{II} —	2.46	2.31	2.33 2.55	2.32 2.58			2.33	2.38			2.87 3.20	3.10	2.81
Si _{III} —	2.30	2.44	2.37 2.53	2.22 2.72		2.30		2.37		2.87 3.20		3.09	2.86
Si _{IV} —	2.54(2)	2.51(2)			2.24 2.61	2.32	2.31	2.43	2.75(2)	3.10(2)	3.09(2)		
Si _V —			2.98(2)	2.43(2)		2.32	2.29	2.26		2.81(2)	2.86(2)		

Table 4. Coordinations of the atoms of Ni_3Si_2 .

Atom	Ni neighbours		Si neighbours	
	No.	mean distance (Å)	No.	mean distance (Å)
Ni ₁	8	2.63	5	2.41
Ni ₂	8	2.65	5	2.40
Ni ₃	7	2.63	6	2.50
Ni ₄	7	2.80	6	2.46
Ni ₅	6	2.54	6	2.39
Ni ₆	7	2.65	6	2.45
Ni ₇	7	2.65	6	2.45
Ni ₈	4	2.64	6	2.37
Si _I	10	2.44	2	2.85
Si _{II}	8	2.41	4	3.00
Si _{III}	8	2.41	4	3.01
Si _{IV}	9	2.45	6	2.98
Si _V	7	2.53	4	2.84

2.60 Å. This value corresponds to $2r_{\text{Ni}} + 0.1$ Å. A similar investigation of the Ni-Si distances shows that most of them lie between 2.20 and 2.55 Å and in particular, there are a number with values in the range 2.30–2.33 Å. This corresponds to $r_{\text{Ni}} + r_{\text{Si}} - 0.10 = 2.32$ Å.

The environments of the individual atoms are very irregular and dissimilar. It may be observed that the coordination of Ni_1 is practically identical with

that of Ni_2 . The same is true for Ni_6 and Ni_7 and for Si_{II} and Si_{III} . Ni_5 and Ni_8 have the most regular coordinations of all atoms. Ni_5 is surrounded by a fairly regular icosahedron of six nickel and six silicon atoms and Ni_8 coordinates a tetrahedron of nickel atoms and an octahedron of silicon atoms. The six silicon neighbours of Ni_4 , Ni_6 and Ni_7 may also be described as forming a distorted octahedron.

It is of interest to compare this structure with those of NiSi and δ -Ni₂Si. The nickel atoms in NiSi coordinate a nickel tetrahedron and a silicon octahedron (Toman)⁸ analogously to the environment of Ni₈ in Ni₃Si₂. The mean distance between each nickel atom and its four nickel neighbours is 2.67 Å in NiSi and 2.64 Å in Ni₃Si₂. The corresponding mean distance to the six silicon atoms is 2.37 Å in both structures. In δ -Ni₂Si the nickel atoms are surrounded

Fig. 4. (a)–(h) show the surroundings of the nickel atoms and (i)–(m) the surroundings of the silicon atoms. A large circle is a nickel atom, a small circle a silicon atom. Double circles refer to superimposed atoms. Atoms connected to the central atom by lines of uniform thickness are coplanar (within ± 0.1 Å). Arabic figures denote the indices of the nickel atoms and Roman figures those of silicon atoms. The minus signs refer to atoms below the median plane and plus signs to atoms above this plane. Distances from the central atom to the neighbours are given (in Å).

by eight nickel and five silicon atoms (Toman)⁹ like Ni_1 and Ni_2 in Ni_3Si_2 but the environments are dissimilar.

Acknowledgements. This work has been financially supported by the *Swedish State Council of Technical Research* and by the *Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force*, through its European Office under Contract No. AF 61(052)-40. Facilities for the use of the electronic digital computer BESK were granted by the *Swedish Board for Computing Machinery*.

The author wishes to thank professor G. Hägg for his kind interest. Thanks are also due to Dr. B. Aronsson and Dr. S. Rundqvist for valuable advice and stimulating discussions.

REFERENCES

1. Guertler, W. and Tammann, G. *Z. anorg. Chem.* **49** (1906) 93.
2. Iwasé, K. and Okamoto, M. *Sci. Repts Tōhoku Imp. Univ., K. Honda Anniv. Vol.* (1936) 777.
3. Ōsawa, A. and Okamoto, M. *Sci. Repts Tōhoku Imp. Univ.* **27** (1939) 326.
4. Westman, S., Blomqvist, G. and Åsbrink, S. *Arkiv Kemi* **14** (1959) 535.
5. Åsbrink, S., Blomqvist, G. and Westman, S. *Ibid* **14** (1959) 545.
6. Appel, K. Technical Note from the *Quantum Chemistry Group, University of Uppsala*.
7. Cruickshank, D. W. J. *Acta Cryst.* **2** (1946) 65.
8. Toman, K. *Ibid* **4** (1951) 462.
9. Toman, K. *Ibid* **5** (1952) 329.

Received December 7, 1960.