The Nb-Si (Niobium-Silicon) System

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Equilibrium Diagram

The most thorough investigation of the Nb-Si system is the DTA study of [80Koc], and the assessed Nb-Si diagram (Fig. 1) in general follows these results. The system contains seven stable phases: (1) the liquid (L); (2) the bcc W-type terminal solid solution, (Nb); (3) tetragonal Ti_3P-type Nb_3Si; (4) tetragonal W_5Si_3-type βNb_5Si_3; (5) tetragonal Cr_5Si_3-type αNb_5Si_3; (6) hexagonal $CrSi_2$-type $NbSi_2$; and (7) the diamond cubic terminal solid solution, (Si). Special points of Fig. 1 are listed in Table 1.

(Nb) Terminal Solid Solution

The melting point of pure Nb is 2469 °C [Melt], 3 °C lower than that reported by [80Koc]. It is generally agreed that a small amount of Si is soluble in (Nb), although the exact level is less certain. Figure 2 shows the solubility limits of Si in (Nb) determined by various investigators; as can be seen, a wide variety of choices are available for the solvus line. Measured solubilities tend to be lower in the more recent investigations of [80Koc] and [91Men], but [91Coc1] claims a maximum solid solubility of 4.36 at.% Si. The assessed solvus line drawn in Fig. 1 and 2 adheres most closely to the results of [65Gol] and [91Men], the most thorough investigations of this equilibrium. The single data point reported by [65Gol] is the only existing measurement for (Nb) solidus compositions, and thus a tentative straight line has been drawn to represent this boundary.

Nb_3Si

Initially, the composition and stoichiometry range of this compound was a matter of some doubt. As Table 2 points out, several investigators in this system reported the existence of a lower silicide with an "Nb_4Si" stoichiometry, and a variety of formation and decomposition temperatures; this composition was used in the Nb-Si diagram in [Moffatt]. However, [65Ros] and [67Pan] both reported the existence of a tersilicide rather than Nb_4Si, and [69Dea] demonstrated that Nb_4Si was stable only in carbon-contaminated alloys. The impact of slight impurity levels on phase stabilities in silicide systems is well-known; [84Pan] has shown that other impurities (Al, Cu, Ge) tend to suppress Nb_3Si formation in Nb-Si alloys. Results obtained with purer samples [80Koc, 89Lip, 91Coc1, 91Coc2, 91Men] found only Nb_3Si in the system, and the consistent confirmation of its Ti_3P-type structure and negligible solubility range recommend its choice as the lowest stable silicide in this system.

Nb_3Si is formed by a peritectic reaction; the formation temperature of 1975 °C is 5 °C lower than that reported by [80Koc], a correction reflecting the overestimation in that work of the melting points of pure Nb and Si. The temperature at which the eutectoid decomposition of Nb_3Si occurs is less certain, as the kinetics of this reaction are extremely slow. Because of this, the isothermal results of [91Men] are preferred to the DTA-obtained eutectoid temperature of [80Koc] and [75Flu].

Table 1 Special Points of the Assessed Nb-Si Phase Diagram

Reaction	Compositions of the respective phases, at.% Si			Temperature, °C	Reaction type
$L \leftrightarrow (Nb)$		0		2467	Melting
$L \leftrightarrow (Nb) + Nb_3Si$	17.5	3.5	25	1915	Eutectic
$L + \beta Nb_5Si_3 \leftrightarrow Nb_3Si$	19.5	37.5	25	1975	Peritectic
$Nb_3Si \leftrightarrow (Nb) + \alpha Nb_5Si_3$	25	1.6	35.5	1765	Eutectoid
$L \leftrightarrow \beta Nb_5Si_3$		37.5		2515	Melting
$Nb_3Si + \beta Nb_5Si_3 \leftrightarrow \alpha Nb_5Si_3$	25	37.5	37.5	1935	Peritectoid
$\beta Nb_5Si_3 \leftrightarrow \alpha Nb_5Si_3 + NbSi_2$	39.5	38.5	66.7	1645	Eutectoid
$L \leftrightarrow \beta Nb_5Si_3 + NbSi_2$	57	40.5	66.7	1895	Eutectic
$L \leftrightarrow NbSi_2$		66.7		1935	Melting
$L \leftrightarrow NbSi_2 + (Si)$	98	68.8	100	1395	Eutectic
$L \leftrightarrow (Si)$		100		1414	Melting

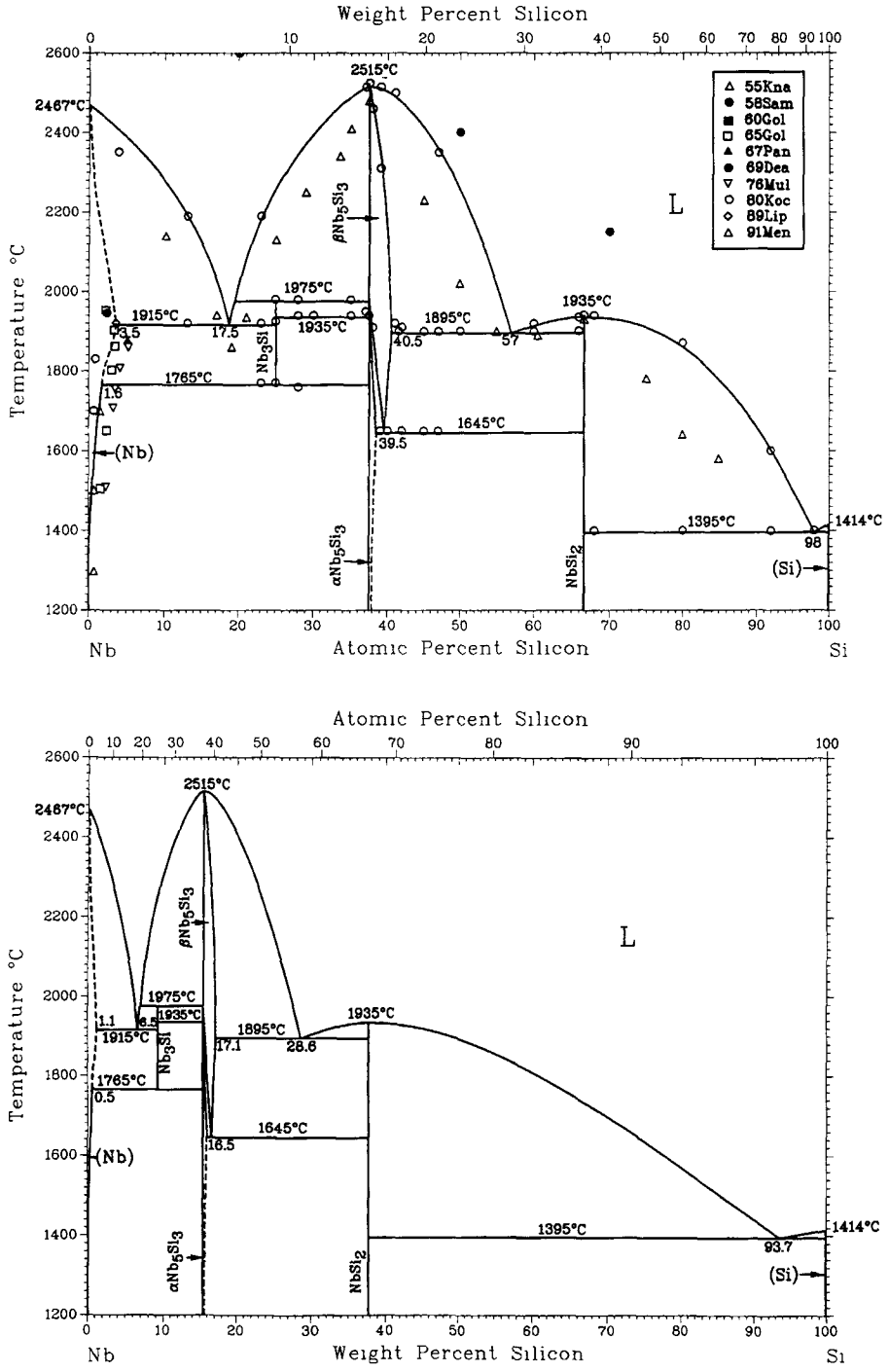

Fig. 1 Assessed Nb-Si phase diagram.

Nb_5Si_3

The "Nb_2Si" reported by [48Bra] and [54Har], and the "Nb_3Si_2" described by [55Par2] and [55Par3], are apparently this phase in actuality. The correct stoichiometry was first identified by [55Kna] and [55Gea], and repeatedly confirmed by others; [56Kie] and [60Gol] showed the presence of polymorphism in this phase. The stoichiometry ranges and invariant temperatures for both the α and β forms of Nb_5Si_3 are less certain. [61Aly] and [79Pan] report wider solid solubility ranges for these phases than [80Koc]. However, [61Aly] and [79Pan] also reported the existence of stable Nb_4Si, leading to the presumption that the samples used by [80Koc] were purer, leading to more credible results. [80Koc] is also the only in-

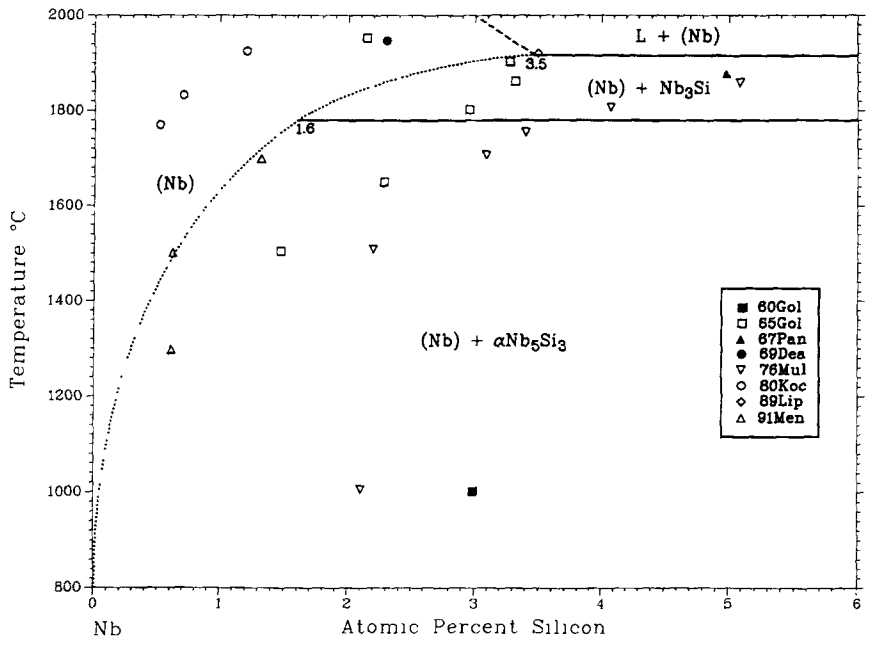

Fig. 2 Measured solubilities of Si in (Nb). Dotted line represents assessed solvus.

Table 2 Experimental Results for the Lowest Niobium Silicide

Investigation	Reported lowest silicide	Upper stability limit and type of equilibrium	Lower stability limit
[55Kna]	Nb_4Si	1950 °C (peritectic)	None
[56Bre]	$NbSi_{0.55}$ (at 1727 °C)	NA	NA
[58Sam]	Nb_4Si	2600 °C (congruent)	None
[60Gol]	Nb_4Si	1930 °C (peritectic)	>1100 °C
[61Aly,62Aly,67Aly]	Nb_4Si	NA	>1250 °C
[67Pan]	Nb_3Si	1880 °C (peritectic)	1800 °C
[69Dea]	Nb_3Si	1945 °C (peritectic)	1800 °C
[79Pan]	Nb_4Si (X_{Si} = 0.18 to 0.225)	1960 °C (peritectic)	1720 °C
[80Koc]	Nb_3Si	1980 °C (peritectic)	1770 °C
[91Coc1,91Coc2]	Nb_3Si	NA	NA

vestigation to have uncovered a transformation temperature range for Nb_5Si_3, which would be expected given the solid solubility range. As a result, the latter results are recommended in Table 1, again after lowering the transformation and melting points by 5 °C. The congruent melting point of βNb_5Si_3 is also in reasonable agreement with that reported by [79Pan].

$NbSi_2$

The negligible solid solubility range for this compound shown in Fig. 1 reflects higher levels of confidence in the experimental results of [80Koc] over those of [61Aly], who reported a solubility range of 64.9 to 68.8 at.% Si, and [79Pan], who reported a range of 65.0 to 68.8 at.% Si. Congruent melting points ranging between 1930 and 1950 °C have been reported by [55Kna], [56Kie], [79Pan], and [80Koc]; the recommended melting point of 1935 °C is 5 °C lower than that of [80Koc], and 5 °C higher than that reported by [55Kna] and [79Pan].

(Si)

The melting point of pure Si reported by [80Koc] is 6 °C higher than the adopted value of 1414 °C [Melt]. The solubility of niobium in solid Si is negligible [60Gol].

Liquidus

Figure 1 includes the liquidus data reported by [55Kna], [56Kie], and [80Koc]; the recommended liquidus line follows the results of the latter, again adjusted by 5 °C. The (Nb)-Nb_3Si eutectic composition of 17.5 at.% Si given by [80Koc] (Fig. 1) is less than that estimated by [89Lip] (18.7 at.% Si) based on X-ray and metallographic data.

Metastable Phases

The difficulties in transition-metal—silicon system research caused by impurity contamination are well-known, and the effect of impurities on reported Nb-Si equilibria are apparent in the generation of several phases in the system that have proven to be metastable in purer samples. These include:

- Nb_4Si, which is stabilized by interstitial impurities [69Dea], and suppressed by some substitutional impurities [65Sav]. [58Sam] describes it as an isomorph of ε-Fe_3N.
- γNb_5Si_3, a hexagonal (Mn_5Si_3) structure first reported by [54Sch], and later by [58Sam] and [59Arz]. Like Nb_4Si, it is apparently stabilized by interstitials [62Aly].
- Nb_3Si-m″, an fcc form isomorphous to $AuCu_3$ reported by [63Gal]. [81Wan] used shock compression to create a similar structure in purer samples.
- Nb_3Si_2, produced by the reaction of Nb with Cu-Si-Sn alloys by [78Dew]. This phase was demonstrated to be distinct from Nb_5Si_3, although no crystal structure was identified. It should not be confused with the "Nb_3Si_2" reported by [55Par2] and [55Par3], which was in fact the same as the 5:3 compound.

Table 3 Nb-Si Crystal Structure Data

Phase	Composition, at.% Si	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(Nb)	0 to 3.5	*cI*2	$Im\bar{3}m$	*A*2	W	[King1]
Nb_3Si	25	*tP*32	$P4_2/n$	...	Ti_3P	[64Sch]
αNb_5Si_3	36.7 to 39.8	*tI*32	*I*4/*mcm*	$D8_1$	Cr_5Si_3	[55Par1]
βNb_5Si_3	37.5 to 40.5	*tI*32	*I*4/*mcm*	$D8_m$	W_5Si_3	[61Now]
$NbSi_2$	64.9 to 68.8	*hP*9	$P6_422$	*C*40	$CrSi_2$	[41Wal]
(Si)	100	*cF*8	$Fd\bar{3}m$	*A*4	C(diamond)	[King1]
Metastable phases						
Nb_7Si	8 to 13	*c***	...	...	...	[81Haa]
Nb_4Si	20	*hP**	...	*C*6?	ε-Fe_3N	[58Sam]
Nb_3Si-m	10 to 22	*cP*8	$Pm\bar{3}n$	*A*15	Cr_3Si	[72Ham]
Nb_3Si-m′	10 to 27	*cF*4	$Fm\bar{3}m$	*A*1	Cu	[81Wan]
Nb_3Si-m″	25	*cP*4	$Pm\bar{3}m$	$L1_2$	$AuCu_3$	[63Gal]
Nb_3Si I	25	*t***	...	...	...	[73Leg]
γNb_5Si_3	37.5	*hP*16	$P6_3/mcm$	$D8_8$	Mn_5Si_3	[54Sch]

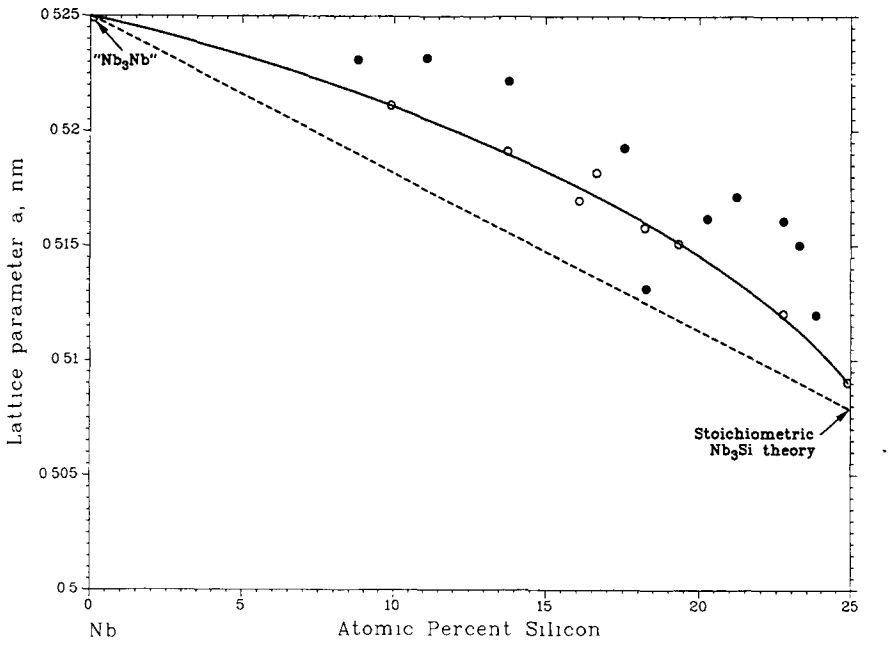

Fig. 3 Experimentally measured lattice parameter values for *A*15 Nb_3Si as a function of Si content. Open-circle values are in reasonable agreement with best-fit line; closed-circle values are in greater disagreement. Reprinted by permission from *Cryogenics*, December 1986, Butterworth Scientific Limited.

Table 4 Nb-Si Lattice Parameter Data at Room and Elevated Temperature

Phase	Composition, at.% Si	Lattice parameters, nm *a*	*c*	Comment	Reference
(Nb)	0	0.33002	. .		[Pearson3]
	0	0.3299	...	At 1300 °C	[55Kna]
	~2	0.3308	...	Si-saturated	[55Kna]
	0	0.32995	...	At 1000 °C	[60Gol]
	~3	0.3304	...	Si-saturated	[60Gol]
Nb_3Si	25	1.023	0.519		[64Sch, 65Ros]
		1.023	0.5189		[67Pan]
		1.021	0.519		[69Dea]
		1.0224	0.5189	$R = 0.032$	[75Wat2]
		1.0230	0.5180		[80Koc]
αNb_5Si_3	36.7 to 39.8	0.655	1.186		[55Par2]
		0.656	1.186		[58Sam]
		0.659	1.189		[59Arz]
		0.654	1.184		[62Aly]
		0.6571	1.1889		[80Koc]
βNb_5Si_3	37.5 to 40.5	0.999	0.506		[55Par1]
		0.997	0.508	$NbSi_2$-saturated	[55Par3]
		1.000	0.507		[58Sam]
		1.003	0.511		[59Arz]
		1.0006	0.50615		[61Now]
		1.006	0.5082	At 380 °C	[61Now]
		1.0052	0.5076	At 650 °C	[61Now]
		1.0040	0.5081		[80Koc]
$NbSi_2$	66.7	0.4785	0.6576		[41Wal]
		0.478	0.656		[58Sam]
		0.47971	0.6592		[59Swa]
		0.4785	0.658		[62Aly]
		0.4803	0.6604		[63Bri]
		0.4796	0.6584		[63Ver]
		0.4819	0.6592	$R = 0.077$	[72Kub]
		0.4791	0.6588		[80Koc]
		0.47834	0.65673		[88Eng]
		0.4804	0.6601	At 200 °C	[88Eng]
		0.4813	0.6613	At 400 °C	[88Eng]
		0.4822	0.6627	At 600 °C	[88Eng]
		0.4831	0.6641	At 800 °C	[88Eng]
		0.4841	0.6658	At 1000 °C	[88Eng]
(Si)	100	0.54306	...		[King1]
Metastable phases					
Nb_7Si	8	0.5195	...		[81Haa]
	13	0.5186	...		[81Haa]
Nb_4Si	18 to 22.5	0.359	0.446		[58Sam]
Nb_3Si·m	10.5	0.5196	...		[81Haa]
	17.8	0.5135	...		[82Fel]
	18.8	0.515	...		[79Wat]
	19	0.515	...		[80Sur]
	19	0.5155	...		[82Wan]
	19.3	0.5123	...		[81Haa]
	22	0.5155	...		[80Tog]
	25	0.5091	...		[82Oli]
	~25	0.503-0.517	...		[83Iwa, 86Dew]
Nb_3Si·m′	10	0.388	...		[85Wan]
	17	0.417	...		[85Wan]
	22	0.422	...		[85Wan]
	27	0.426	...		[85Wan]
Nb_3Si m″	25	0.4211	...		[63Gal]
γNb_5Si_3	37.5	0.752	0.523		[54Sch]
		0.752	0.524		[58Sam]
		0.752	0.530		[59Arz]
High-pressure phase					
Nb_3Si I	25	0.6593	1.2652		[73Leg]

A second driving force behind the generation of metastable phases in the Nb-Si system has been the effort to produce Cr_3Si-type Nb_3Si (here designated Nb_3Si·m), which it was thought would exhibit superconductivity at relatively high temperatures. This has in fact been accomplished by a variety of methods; the reader is referred to the reviews of [83Iwa] and [86Dew] for a complete listing. Nb_3Si·m produced by these efforts is Nb-rich, with silicon percentages ranging from 8.6 [75Kaw] to 25 [82Oli]; it can be stabilized by interstitial impurities [80Tog]. An Nb-rich hexagonal form (Cu-type) of Nb_3Si (Nb_3Si·m′) also has been produced by [88Wan]. [81Haa] and [82Haa] have reported a distinct cubic Nb_7Si phase, with lattice parameters similar to Cr_3Si-type Nb_3Si and a composition range of 8 to 13 at.% Si. One popular method of producing new

forms of Nb_3Si has been the crystallization of amorphous films, which tend to be more easily formed in alloys of this composition range [89Lip]; at cooling rates of 10^{12} K/s, the glass formation range extends from 8 to 27 at.% Si [88Wan]. Other examples of amorphous alloy formation in the Nb-Si system include the work of [77Tsu], [79Wat], [80Mas], [80Sur], and [89Mil].

Pressure

The reaction of elemental Nb and Si at higher temperatures and pressures examined by [73Leg] produced several new crystalline forms of Nb_3Si. These include a bcc W-type phase similar to (Nb), and tetragonal Nb_3Si I. The crystallization of amorphous alloys by [81Wan] generated metastable fcc $Nb_{78}Si_{22}$, which may be related to the $AuCu_3$ structure produced by [63Gal].

Crystal Structures and Lattice Parameters

Tables 3 and 4 list the available data for the stable and metastable phases of the Nb-Si system. As previously discussed, Nb_4Si is listed here as a metastable phase. The effect of silicon content on the lattice parameter of solid-solution (Nb) has been measured by [55Kna], [60Gol], and [89Lip]; no such measurements have yet been made for either phase of Nb_5Si_3. [61Now] has measured the thermal expansion coefficients of βNb_5Si_3, and [63Nes], [63Ver], and [88Eng] have done the same for $NbSi_2$. Figure 3, reproduced from the review of [86Dew], shows that the measured lattice parameter of Cr_3Si-type Nb_3Si varies with the composition of the amorphous alloy from which it is produced, although it is not certain that the composition of the crystallized phase necessarily matched that of the amorphous material.

Table 5 Measured Heats of Formation in Nb-Si Liquid Solutions

[85Sud], 1910 K		[81Bet], 3000 K	
X_{Nb}	$\Delta_f H$, kJ/mol	X_{Si}	$\Delta_f H$, kJ/mol
0.02	-3.7	0.05	-7.81
0.04	-5.3	0.10	-15.51
0.06	-6.1	0.15	-22.89
0.08	-6.6	0.20	-29.92
0.10	-6.8	0.25	-36.55
0.12	-5.9	0.30	-42.74

Table 6 Experimental and Estimated Heats of Formation of Niobium Silicides

	$\Delta_f H$, kJ/mol	
Source	αNb_5Si_3	$NbSi_2$
[56Bre]	(-13 to -98)	(-24 to -78)
[72Gor]	-63.8	
[73Cha]	-60.7	-46.0
[79Kau]	-65.3	-90.7
[81Nie]	-56	-46

Thermodynamics

Although large gaps remain in the database for this system, the amount of experimental thermodynamic data is more extensive for Nb-Si solid and liquid alloys than for several other transition metal-silicon systems. Four investigations on the enthalpies of mixing in Nb-Si melts have been reported [71Dub, 77Koz, 81Bet, 85Sud]; however, results from only the latter two are readily available. Table 5 lists the enthalpies of mixing in Si-base liquids at 1910 K reported by [85Sud], and in Nb-base melts at 3000 K measured by [81Bet] (also see [80Fro] and [83Fro]). The wide difference in experimental temperatures and compositions makes the comparison of results infeasible.

Experimental information on the thermodynamics of Nb-Si compounds also has been occasionally reported. The standard enthalpy of formation of Nb_5Si_3 has been determined by [72Gor]; these results are compared in Table 6 with the estimates of [56Bre], [73Cha], [79Kau], and [81Nie]. Heat capacities have been measured for $NbSi_2$, αNb_5Si_3, and Nb_4Si by [70Bon] and [71Bon], using a drop calorimetry technique over the temperature range 1200 to 2200 K; confirmation of these results at lower temperatures would be of value.

Magnetism

Superconductivity is exhibited by four phases in the Nb-Si system: (Nb), Nb_3Si, Nb_3Si·m, and Nb_3Si·m″. Of these, Nb_3Si·m″ has the lowest superconducting transition temperature, 1.5 K [63Gal]. Values for Nb_3Si range from 5.3 to 8.0 K [69Dea, 76Mul], whereas that of (Nb) decreases from 9.2 K to the level of Nb_3Si as the dissolved Si content increases. A wide range of superconducting transition temperatures (3.4 to 18 K) have been reported for Nb_3Si·m, approaching the theoretical level of 25 K only for those samples crystallized from alloys containing the stoichiometric fraction of Si [86Dew]. Both [83Iwa] and [86Dew] point out that the superconducting transition temperature for Nb_3Si·m depends on sample preparation method as well as stoichiometry; however, developments in superconductivity research suggest that this question will not likely be pursued as vigorously in the future.

Cited References

41Wal: H.J. Wallbaum, "Disilicides of Niobium, Tantalum, Vanadium, and Rhenium," *Z. Metallkd., 33*, 378-381 (1941) in German. (Crys Structure; Experimental)

48Bra: G. Brauer, "Metal-Borides, -Silicides, -Germanides and -Stannides," *FIAT Rev. Ger. Sci., 1939-1946: Inorganic Chem., 2*, 100-108 (1948) in German. (Equi Diagram; Review)

54Har: G.F. Hardy and J.K. Hulm, "The Superconductivity of Some Transition Metal Compounds," *Phys. Rev., 93*, 1004-1016 (1954). (Equi Diagram; Experimental)

54Sch: H. Schachner, E. Cerwenka, and H. Nowotny, "New Silicides of M_5Si_3-Type with $D8_8$-Structure," *Monatsh. Chem., 85*, 245-254 (1954) in German. (Equi Diagram, Meta Phases, Crys Structure; Experimental)

55Gea: G.A. Geach and F.O. Jones, "Interactions in Mixtures of Hard Metals at Very High Temperatures," *Plansee Proc., 1955*, 80-91 (1955). (Equi Diagram; Experimental)

55Kna: A.G. Knapton, "The System Niobium-Silicon and the Effect of Carbon on the Structures of Certain Silicides," *Nature, 175*, 730 (1955). (Equi Diagram; Experimental; #)

55Par1: E. Parthé, B. Lux, and H. Nowotny, "Structure of the Silicides M_5Si_3," *Monatsh. Chem., 86*, 859-867 (1955) in German. (Crys Structure; Experimental)

55Par2: E. Parthé, H. Nowotny, and H. Schmid, "Structure Investigation on Silicides," *Monatsh. Chem., 86*, 385-396 (1955) in German. (Equi Diagram, Crys Structure; Experimental)

55Par3: E. Parthé, H. Schachner, and H. Nowotny, "Contribution to the Structure of Transition Metal Silicides," *Monatsh. Chem., 86*, 182-185 (1955) in German. (Equi Diagram, Crys Structure; Experimental)

56Bre: L. Brewer and O. Krikorian, "Reactions of Refractory Silicides with Carbon and Nitrogen," *J. Electrochem. Soc., 103*, 38-50 (1956). (Equi Diagram, Thermo; Experimental)

***56Kie:** R. Kieffer, F. Benesovsky, and H. Schmid, "Contribution to the Synthesis of the Systems Vanadium-Silicon and Niobium-Silicon," *Z. Metallkd., 47*, 247-253 (1956) in German. (Equi Diagram, Crys Structure; Experimental; #)

58Sam: G.V. Samsonov, V.S. Neshpor, and V.A. Ermakova, "Properties of the Niobium-Silicon System," *Zh. Neorg. Khim., 3*, 868-878 (1958) in Russian. (Equi Diagram, Crys Structure; Experimental; #)

59Arz: P.M. Arzhany, R.M. Volkova, and D.A. Prokoshkin, "On the Structure and Phase Composition of the Diffusion Coating of Silicon on Niobium," *Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk. Met. Toplivo*, No. 6, 127-129 (1959) in Russian. (Meta Phases, Crys Structure; Experimental)

59Swa: H.E. Swanson, N.T. Gilfrich, M.I. Cook, R. Stinchfield, and P.C. Parks, "Standard X-Ray Diffraction Powder Patterns," *NBS Circ., 539*, 1-70 (1959). (Crys Structure; Experimental)

60Gol: H.J. Goldschmidt, "The Constitution of the Iron-Niobium-Silicon System," *J. Iron Steel Inst. (London), 194*, 169-180 (1960). (Equi Diagram; Experimental; #)

61Now: H. Nowotny and E. Laube, "Thermal Expansion of High-Melting Phases," *Planseeber. Pulvermetall., 9*, 54-59 (1961) in German. (Crys Structure; Experimental)

61Aly: S.I. Alyamovskii, P.V. Gel'd, and I.I. Matveenko, "Phase Components of the System Nb-Si," *Tr. Ural'sk. Politekhn. Inst. Sb.*, No. 114, 149-151 (1961) in Russian. (Equi Diagram; Experimental)

62Aly: S.I. Alyamovskii, P.V. Gel'd, and I.I. Matveenko, "Concentration Regions of Stability of Silicides of Niobium at 1250 °C," *Zh. Neorg. Khim., 7*, 836-843 (1962) in Russian. TR: *Russ. J. Inorg. Chem., 7*, 432-435 (1962). (Equi Diagram, Crys Structure, Meta Phases; Experimental)

63Bri: L.H. Brixner, "X-Ray Study and Thermoelectric Properties of the $NbSi_xGe_{2-x}$ and the $TaSi_xGe_{2-x}$ Systems," *J. Inorg. Nucl. Chem., 25*, 257-260 (1963). (Crys Structure, Magnetic; Experimental)

63Gal: F. Galasso and J. Pyle, "Nb_3Si, a Superconductor with the Ordered Cu_3Au Structure," *Acta Crystallogr., 16*, 228-229 (1963). (Meta Phases, Crys Structure, Magnetism; Experimental)

63Nes: V.S. Neshpor and M.I. Reznichenko, "The Thermal Expansion of Some Silicides," *Ogneupory, 28*, 134-137 (1963) in Russian. (Crys Structure; Experimental)

63Ver: L.F. Verkhorobin and N.N. Matyuskenko, "The Thermal Expansion of Disilicides of Some Transition Metals," *Poroshk. Metall.*, No. 6, 51-53 (1963) in Russian. TR: *Sov. Powder Metall. Met. Ceram.*, No. 6, 468-469 (1963). (Crys Structure; Experimental)

64Sch: K. Schubert, A. Ramam, and W. Rossteutscher, "Some Structure Data of Metallic Phases (11)," *Naturwissenschaften, 51*, 506-507 (1964) in German. (Crys Structure; Experimental)

65Gol: H.J. Goldschmidt, E.A. Catherall, and R.A. Taylor, "Investigation into the Tungsten-Rich Region of the Tungsten-Silicon System and into Related Metal-Silicon Systems," *Technical Report AFML-TR-65-270* (1965). (Equi Diagram, Crys Structure; Experimental)

65Ros: W. Rossteutscher and K. Schubert, "Structural Investigations in Some $T^{4...5}$-$B^{4..5}$ Systems," *Z. Metallkd., 56*, 813-822 (1965) in German. (Crys Structure; Experimental)

65Sav: E.M. Savitskii, V.V. Baron, M.I. Bychkova, S.A. Bakuta, and E.I. Gladyshevskii, "Phase Diagram and Properties of Nb-Mo-Si Alloys," *Izv. Akad. Nauk SSSR, Met.*, No. 2, 159-166 (1965) in Russian. TR: *Russ. Metall.*, No. 2, 91-96 (1965). (Equi Diagram; Experimental)

67Aly: S.I. Alyamovskii, P.V. Gel'd, F.P. Shveikin, and I.I. Matveenko, "Lower Silicide of Niobium, Nb_3Si," *Izv. Akad. Nauk SSSR, Neorg. Mater., 3*, 729-732 (1967) in Russian. TR: *Inorganic Mater. (USSR), 3*, 649-652 (1967). (Equi Diagram, Crys Structure; Experimental)

67Pan: V.M. Pan, V.V. Pet'kov, and O.G. Kulik, "Phase Diagram of the Nb-Nb_5Si_3 System and the Crystalline Structure of the Compound Nb_3Si," *Metalloved., Fiz.-Khim. Metallofiz. Sverkhprovodnikov 1967*, 161-165 (1967) in Russian. TR: *Physics and Metallurgy of Superconductors*, E.M. Savitskii and V.V. Baron, Ed., Nauka, Moscow (1967). (Equi Diagram, Crys Structure; Experimental; #)

***69Dea:** D.K. Deardorff, R.E. Siemens, P.A. Romans, and R.A. McCune, "New Tetragonal Compounds Nb_3Si and Ta_3Si," *J. Less-Common Met., 18*, 11-26 (1969). (Equi Diagram, Crys Structure, Magnetism; Experimental)

70Bon: V.P. Bondarenko, V.I. Zmii, E.N. Fomichev, A.A. Kalashnik, and R.P. Slyusar', "Determination of the Enthalpy and Specific Heat of Tantalum and Niobium Disilicides in the 1200-2100 °K Temperature Range," *Teplofiz. Vys. Temp., 8*, 910-912 (1970) in Russian. TR: *High Temp. (USSR), 8*, 856-857 (1970). (Thermo; Experimental)

71Bon: V.P. Bondarenko, L.A. Dvorina, N.P. Slyusar', and E.N. Fomichev, "Enthalpy of Niobium Silicides Nb_4Si and Nb_5Si_3 at 1200-2200 °K," *Poroshk. Metall., 11*, No. 11, 48-51 (1971) in Russian. (Thermo; Experimental)

71Dub: A.S. Dubrovin, O.S. Gorelkin, Yu.Ya. Demidov, N.A. Chirkov, L.S. Kostylev, and O.D. Kolesnikova, "Calorimetric Study of the Heats of Solution of Silicon and Aluminum in Aluminothermal Alloys," *Metalloterm. Protsessy Khim. Met., Mater. Konf. 1971*, A.T. Dogvinenko, Ed., 121-130 (1971) in Russian. (Thermo; Experimental)

72Gor: C.S. Gorelkin, A.S. Dubrovin, O.D. Kolesnikova, and N.A. Chirkov, "Measurement of the Heat of Formation of Intermetallic Compounds by the Sintering Method in an Isothermal Calorimeter," *Zh. Fiz. Khim., 46*, 754-757 (1972) in Russian. TR: *Russ. J. Phys. Chem., 46*, 431-432 (1972). (Thermo; Experimental)

72Ham: R.H. Hammond and Z. Hazra, *Proc. Low Temperature Conf. 13*, (1972), K.D. Timmerhaus, W.J. O'Sullivan, and E.F. Hammelm, Ed., Plenum Press, New York, 465 (1974). (Meta Phases, Crys Structure; Experimental)

72Kub: R. Kubiak, R. Horyn, H. Broda, and K. Lukaszewicz, "Refinement of the Crystal Structure of $NbSi_2$, $NbGe_2$, and $TaGe_2$," *Bull. Acad. Pol. Sci., 20*, 429-436 (1972). (Crys Structure; Experimental)

73Cha: T.G. Chart, "Thermochemical Data for Transition Metal-Silicon Systems," *High Temp.—High Press., 5*, 241-252 (1973). (Thermo; Review)

73Leg: J.-M. Leger and H.T. Hall, "Pressure and Temperature Formation of A_3B Compounds, I. Nb_3Si and V_3Al," *J. Less-Common Met., 32*, 181-187 (1973). (Meta Phases, Pressure, Crys Structure; Experimental)

75Flu: F. Flükiger, private conversation reported by [75Wat1].

75Kaw: H. Kawamura and K. Tachikawa, "Synthesis of the A15 Nb_3Si Film by the Chemical Vapor Deposition," *Phys. Lett. A, 55*, 65-66 (1975). (Meta Phases, Crys Structure; Experimental)

75Wat1: R.M. Waterstrat, "Observations on Nb_3Si and the Relative Stability of *A*15 Versus Ti_3P-Type Structures, *J. Less-Common Met., 43*, 105-115 (1975). (Equi Diagram; Experimental)

75Wat2: R.M. Waterstrat, K. Yvon, H.D. Flack, and E. Parthé, "Refinement of Nb_3Si and Nb_3As," *Acta Crystallogr. B, 31*, 2765-2769 (1975). (Crys Structure; Experimental)

76Mul: P. Müller, "Structure and Superconductivity of Niobium-Rich Niobium-Silicon Alloys," *Kristall. Tech., 11*, K3-K6 (1976) in German. (Equi Diagram, Magnetism; Review; #)

77Koz: Yu.S. Kozlov, N.A. Vatolin, V.I. Zhuchkov, O.V. Demidovich, and Yu.B. Malt'sev, "Calorimetric Study at High Temperatures of Niobium-Base Liquid Alloys," *Vses. Konf. Kalorim., [Rasshir. Tezisy Dokl.], 7th, 1*, 55-56 (1977) in Russian. (Thermo; Experimental)

77Tsu: C.C. Tsuei, W.L. Johnson, R.B. Laibowitz, and J.M. Viggiano, "The Ratio of Energy Gap to Transition Temperature in Amorphous Superconductors," *Solid State Commun., 24*, 615-618 (1977). (Meta Phases; Experimental)

78Dew: D. Dew-Hughes and T.S. Luhman, "The Thermodynamics of *A*15 Compound Formation by Diffusion from Ternary Bronzes," *J. Mater. Sci., 13*, 1868-1876 (1978). (Meta Phases; Experimental)

79Kau: L. Kaufman, "Coupled Phase Diagrams and Thermochemical Data for Transition Metal Binary Systems - VI," *CALPHAD, 3*, 45-76 (1979). (Thermo; Theory; #)

79Pan: L.A. Panteleimonov, Yu.D. Seropegin, I.A. Guseva, and I.V. Osipova, "Physicochemical Study of the Reaction of Niobium with Silicon," *Vestn. Mosk. Univ., Khim., 20*, 271-275 (1979) in Russian. (Equi Diagram; Experimental; #)

79Wat: R.M. Waterstrat, F. Haenssler, and J. Müller, "Nb-Si *A*15 Compounds Produced by Liquid Quenching," *J. Appl. Phys., 50*, 4763-4766 (1979). (Meta Phases, Crys Structure; Experimental)

80Fro: M.G. Frohberg and G. Betz, "The Measurement of Heats of Solution of High Melting Metallic Systems in an Electromagnetic Levitation Field," *Arch. Eisenhuttenwes., 51*, 235-240 (1980) in German. (Thermo; Experimental; #)

***80Koc:** Yu.A. Kocherzhinskiy, L.M. Yupko, and E.A. Shishkin, "The Nb-Si Diagram," *Izv. Akad. Nauk SSSR, Met.*, No. 1, 206-209 (1980) in Russian. TR: *Russ. Metall.*, No. 1, 184-188 (1980). (Equi Diagram, Crys Structure; Experimental; #)

80Mas: T. Masumoto, A. Inoue, S. Sakai, H. Kimura, and A. Hoshi, "Superconductivity of Ductile Nb-Based Amorphous Alloys," *Trans. Jpn. Inst. Met., 21*, 115-122 (1980). (Meta Phases; Experimental)

80Sur: C. Suryanarayana, W.K. Wang, H. Iwasaki, and T. Masumoto, "High-Pressure Synthesis of A15 Nb_3Si Phase from Amorphous Nb-Si Alloys," *Solid State Commun., 34*, 861-863 (1980). (Meta Phases, Crys Structure; Experimental)

80Tog: K. Togano, H. Kumakura, and K. Tachikawa, "Metastable *A*-15 Phase in Liquid-Quenched Nb-Si Binary Alloys, *Phys. Lett. A, 76*, 83-85 (1980). (Meta Phases, Crys Structure; Experimental)

81Bet: G. Betz and M.G. Frohberg, "Calorimetric Measurements of Refractory Metals and Alloys by Using Levitation Melting," *Metall, 35*, 299-303 (1981) in German. (Thermo; Experimental; #)

81Haa: E.L. Haase and O. Meyer, "High T_c Phases in the Nb-Si, Nb-Ge, and the Nb-Ge-Si Systems," *IEEE Trans. Mag., 17*, 541-544 (1981). (Meta Phases, Crys Structure; Experimental)

81Nie: A.K. Niessen and F.R. de Boer, "The Enthalpy of Formation of Solid Borides, Carbides, Nitrides, Silicides and Phosphides of Transition and Noble Metals," *J. Less-Common Met., 82*, 75-80 (1981). (Thermo; Theory)

81Wan: W.K. Wang, Y. Syono, T. Goto, H. Iwasaki, A. Inoue, and T. Masumoto, "Formation of FCC Solid Solution in Nb-Si System under Shock Compression," *Scr. Metall., 15*, 1313-1316 (1981). (Meta Phases, Crys Structure; Experimental)

82Fel: R.D. Feldman, "Growth of *A*15 Nb-Si by Epitaxy and Composition Grading," *Thin Solid Films, 87*, 243-258 (1982). (Meta Phases, Crys Structure; Experimental)

82Haa: E.L. Haase and J. Ruzicka, "Irradiation Damage of *A*15-Nb_3Si and Nb_7Si," *J. Low Temp. Phys., 47*, 461-466 (1982). (Meta Phases; Experimental)

82Oli: B.W. Olinger, L.R. Newkirk, and J.C. King, "Mechanisms for a Rapid Phase Transformation of Nb_3Si from the Ti_3P Structure to the Cr_3Si (*A*15) Structure," *Acta Crystallogr. A, 38*, 151-154 (1982). (Meta Phases, Crys Structure; Experimental)

82Wan: W.K. Wang, H. Iwasaki, C. Suryanarayana, T. Masumoto, N. Toyota, T. Fukase, and F. Kogiku, "Crystallization Characteristics of an Amorphous $Nb_{81}Si_{19}$ Alloy under High Pressure and Formation of the *A*15 Phase," *J. Mater. Sci., 17*, 1523 (1982). (Meta Phases, Crys Structure; Experimental)

83Fro: M.G. Frohberg and G. Betz, "Enthalpy Measurements on Refractory Metals and Alloys by Levitation Calorimetry," *Ber. Bunsenges. Phys. Chem., 87*, 782-785 (1983). (Thermo; Experimental)

83Iwa: H. Iwasaki, "*A*15-Nb_3Si Produced by Transformation from Amorphous State at High Pressures and Temperatures," *Sci. Rep. Res. Inst., Tōhoku Univ. A, 31*, 1-15 (1983). (Meta Phases, Crys Structure, Magnetism; Review)

84Pan: V.M. Pan, V.I. Latysheva, O.G. Kulik, A.G. Popov, and E.N. Litvinenko, "Nb-$NbAl_3$-Nb_5Si_3 Phase Diagram," *Izv. Akad. Nauk SSSR, Met.*, No. 4, 225-226 (1984) in Russian. TR: *Russ Metall.*, No. 4, 233-235 (1984). (Equi Diagram; Experimental)

85Sud: V.S. Sudavtsova, G.I. Batalin, and V.S. Tutevich, "Thermodynamic Properties of Binary Si-(V, Nb, Mo) Melts," *Zh. Fiz. Khim., 59*, 2156-2158 (1985) in Russian. TR: *Russ. J. Phys. Chem., 59*, 1282-1283 (1985). (Thermo; Experimental)

85Wan: W.K. Wang and F. Spaepen, "Face-Centered-Cubic Nb-Si Solid Solutions Produced by Picosecond Pulsed Laser Quenching," *J. Appl. Phys., 58*, 4477-4479 (1985). (Meta Phases, Crys Structure; Experimental)

86Dew: D. Dew-Hughes, "Is Nb_3Si a 25 K Superconductor?" *Cryogenics, 26*, 660-664 (1986). (Meta Phases, Magnetism; Review)

88Eng: I. Engström and B. Lönnberg, "Thermal Expansion Studies of the Group IV-VII Transition-Metal Disilicides," *J. Appl. Phys., 63*, 4476-4484 (1988). (Crys Structure; Experimental)

88Wan: W.K. Wang, C.J. Lobb, and F. Spaepen, "Formation of Metastable Nb-Si Phases by Picosecond and Nanosecond Pulsed Laser Quenching," *Mater. Sci. Eng., 98*, 325-328 (1988). (Meta Phases; Experimental)

89Lip: M.D. Lipschutz, A.B. Gokhale, and G.J. Abbaschian, "Supercooling Effects in Nb-Rich Nb-Si Alloys," *Refractory Metals: State-of-the-Art 1988*, P. Kumar and R.L. Ammon, Ed., Minerals, Metals and Materials Society/AIME, Warrendale, PA, 167-182 (1989). (Equi Diagram; Experimental; #)

89Mil: D.J. Miller, J.W. Sears, and H.L. Fraser, "Characterization of Metastable Phases in a Rapidly Solidified Nb-22Si Alloy," *Acta Metall., 37*, 999-1007 (1989). (Meta Phases; Experimental)

91Coc1: B. Cockeram, M. Saqib, R. Omlor, R. Srinivasan, L.E. Watson, and I. Weiss, "Characterization of Silicide Precipitates in Primary Nb Phase in Nb - 10% Si In-situ Composites," *Scr. Metall. Mater., 25*, 393-398 (1991). (Equi Diagram; Experimental; #)

91Coc2: B. Cockeram, H.A. Lipsitt, R. Srinivasan, and I. Weiss, "Phase Relationships in Nb-18.7 a/o Si In-Situ Composite," *Scr. Metall. Mater., 25*, 2109-2114 (1991). (Equi Diagram; Experimental)

***91Men:** M.G. Mendiratta and D.M. Dimiduk, "Phase Relations and Transformation Kinetics in the High Nb Region of the Nb-Si System," *Scr. Metall. Mater., 25*, 237-242 (1991). (Equi Diagram; Experimental; #)

*Indicates key paper.

#Indicates presence of a phase diagram.

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