Copper – Niobium – Silicon

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Introduction

Copper is a component of many composites, which contain superconductive A15 phases. This induced significant interest in ternary systems of the NbSi-M type, including Cu-Nb-Si. Unfortunately, the existence of the ternary $Nb_5Cu_4Si_4$ phase, the crystal structure of which was determined by [1968Gan], makes this system useless for "bronze" technology. Nevertheless, the solubility of $NbSi_2$ in liquid copper was studied by [1972Jan]. Some controversy exists on the existence of the $Nb_5Cu_4Si_4$ phase. Although the existence of $Nb_5Cu_4Si_4$ was confirmed by [1979Sav1, 1979Cha], the authors of [1981Zan] reported that no ternary phases could be observed in their phase equilibria studies. [1981Zan] explained the appearance of $Nb_5Cu_4Si_4$ by non-equilibrium crystallization conditions. Such an explanation, however, is in contradiction with the findings of [1979Sav1] on annealed alloys. [1982Pan] studied the influence of alloying with copper on the phase formation in the Nb-Si system and reported on the existence of a further ternary phase: Nb_4CuSi. At 1500°C this phase was said to be in equilibrium with Nb based solid solution and Nb_5Si_3. The ternary compound $Nb_5Cu_4Si_4$ was also detected in several as-cast specimens with the crystal structure and lattice parameters virtually the same as presented by [1968Gan] and [1979Sav1]. [1982Pan] reported that $Nb_5Cu_4Si_4$ melts at 1170 ± 10°C. [1992Mat] studied the silicide formation and phase separation from Cu/Nb and Nb/Cu bilayers on silicon. The formation of the ternary phase $Nb_5Cu_4Si_4$ was observed after annealing Cu/Nb at 700°C and Nb/Cu at 800°C.
Phase equilibria and physical property investigations of Cu-Nb-Si alloys were further stimulated by theoretical predictions of [1974Pal] that a hypothetical, stoichiometric Nb_3Si with A15 structure may reach a superconducting transition temperature T_C of about 25 to 29 K. This prediction was confirmed by [1975Pan], who obtained a metastable compound Nb_3Si with A15 structure under a high-pressure shock wave: the onset temperature of the transition in the superconducting state was measured at 18.5 K.
There were two suggestions about how to form Nb_3Si with A15 structure: (i) using the possibility to stabilize the Nb_3Si compound with A15 structure by alloying Nb-Si with Cu (but [1978Sav] and [1982Pan] have shown that in equilibrium alloys copper does not stabilize the A15 type structure); (ii) formation of a metastable phase due to strong non-equilibrium crystallization during rapid cooling from the liquid state. The latter idea was confirmed by [1978Sav, 1979Sav1, 1979Sav2, 1980Sav]: indeed high cooling rates from the melt in the presence of Cu lead to the appearance of some quantity of superconductive phase. The superconducting properties of various intermetallic phases in equilibrium and metastable states were shortly reviewed by [1983Sav].
The methods and experimental techniques used in experimental studies of Cu-Nb-Si alloys are summarized in Table 1.
There was only one attempt to calculate phase equilibria in the Cu-Nb-Si system. However, these calculations by [1992Rei] for 25 and 700°C did not take into account the presence of the ternary phases and therefore are considered inaccurate.

Binary Systems

The Cu-Si phase diagram is taken from [2002Leb]. The Cu-Nb phase diagram is accepted from [2002Rom]. The Nb-Si phase diagram is from [Mas2], who excluded γNb_5Si_3 with Mn_5Si_3 type as a metastable phase from the binary system. For a complete listing of metastable binary Nb-Si phases see [Mas2]. A critical assessment and thermodynamic calculation of the Nb-Si system is due to [2002Fer].

Solid Phases

Solid phases observed in this system are given in Table 2. Existence of two ternary phases is accepted: τ_1, $Nb_5Cu_4Si_4$ and τ_2, Nb_4CuSi.

Liquidus Surface

The liquidus surface was presented by [1981Zan]. It is not accepted here because ternary phases were not observed in this investigation and were not shown in the liquidus surface.

Isothermal Sections

The partial 800°C isothermal section has been constructed by [1979Sav2]. It is presented in Fig. 1 after minor modifications described below. The isothermal section at 1500°C for the entire composition range is presented in Fig. 2 basically from [1982Pan]. In both isothermal sections some modifications of the original diagrams have been made to ensure agreement with the lower solubility of Cu in (Nb) and narrower regions of αNb_5Si_3 and liquid in the accepted binary systems.

Notes on Materials Properties and Applications

In cast and annealed Cu-Nb-Si alloys supeconductivity above 4.2 K is exhibited only by the Nb base solid solution. Simultaneous alloying of Nb with Si and Cu, decreases the T_C of Nb to 7.9 K at the total content of alloying elements of 2-3 at.% and to 7.3 K at 40%. This is somewhat below the T_C of the saturated Nb base solid solution in the binary Nb-Si system (8.5 K) [1976Mue]. After rapid quenching and tempering ternary Cu-Nb-Si alloys, the T_C of the Nb based supersaturated solid solutions decreases to less then 4.2 K. This is due to enhanced solubility of Cu and Si in Nb during quenching from liquid state, and due to the appearance of thermal stresses. Rapidly quenched alloys of Nb with 20-27 at.% Si and 20-30 at.% Cu had two transitions in the superconducting state: one at 7.7 K, corresponding to transition of Nb base solid solution, the other at 13.85-14.1 K for a small amount (10-20 vol%) of metastable Nb_3Si with A15 structure. This superconductive phase was not observed in binary Nb-Si alloys quenched with the same rate. Whereas rapid quenching of alloys of the Nb-Si system is insufficient to stabilize the superconducting metastable phase, the effect of the high cooling rate in the presence of copper promotes the appearance of the superconductive metastable phase with T_C = 14.1 K. However, this value is less than the one for the metastable Nb_3Si produced under an extremely high pressure shock wave [1975Pan], for which the onset of the superconducting state was measured at 18.5 K.

Miscellaneous

One way to produce superconductors with high T_C was proposed by [1983Sav]. It consists in producing superconducting alloys in amorphous state with further crystallization by heat treatment.

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Table 1: Investigations of the Cu-Nb-Si Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1968Gan]	Single crystal X-ray determination of crystal structure of $Nb_5Cu_4Si_4$	Annealing at 1100°C, 36Nb-32Cu-32Si (at.%)
[1972Jan]	Dissolving of $NbSi_2$ in liquid Cu	1200°C, Cu-$NbSi_2$, (Cu)
[1978Sav, 1979Sav2, 1980Sav]	Optical microscopy, SEM, EMPA, magnetic susceptibility	As-cast, annealed at 800°C, and rapidly quenched from liquid state alloys (10^6-10^7 K·s^{-1}), < 40 at.% Si and < 80 at.% Cu

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[1981Zan]	Optical microscopy, X-ray analysis, EMPA	800, 875°C, entire ternary system
[1982Pan]	Optical microscopy, X-ray analysis	1500°C, < 80 at.% Si and < 40 at.% Cu
[1992Mat]	Auger electron spectroscopy, Rutherford backscattering spectrometry, X-ray diffraction, TEM	200 - 800°C, Nb/Cu and Cu/Nb bilayers electron-beam evaporated on silicon

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cu) < 1084.62	*cF*4 *Fm*$\bar{3}$*m* Cu	*a* = 361.46	0 to 11.1 at.% Si [2002Leb]
(Si) < 1414	*cF*8 *Fd*$\bar{3}$*m* C-diamond	*a* = 543.06	0 to 0.003 at.% Cu [2002Leb]
(Nb) < 2469	*cI*2 *Im*$\bar{3}$*m* W	*a* = 330.04	dissolves up to 1.2 at.% Cu at 1080°C [2002Rom]
Cu_7Si 842 - 552	*hP*2 $P6_3/mmc$ Mg	*a* = 256.05 *c* = 418.46	11.05 to 14. 5 at.% Si; at 12.75 at.% Si [2002Leb]
Cu_6Si 853 - 787	*cI*2 *Im*$\bar{3}$*m* W	*a* = 285.4	14.2 to 16.2 at.% Si at 14.9 at.% Si [2002Leb]
Cu_5Si(h) 824 - 711	*t***	*a* = 881.5 *c* = 790.3	17.6 to 19.6 at.% Si [2002Leb] sample was annealed at 700°C [V-C2]
Cu_5Si(r) < 729	*cP*20 $P4_132$ βMn	*a* = 619.8	17.15 to 17.6 at.% Si [2002Leb]
$Cu_{15}Si_4$ < 800	*cI*76 *I*$\bar{4}$3*d* $Cu_{15}Si_4$	*a* = 961.5	21.2 at.% Si [2002Leb, V-C2]
$Cu_3Si(h_2)$ 859 - 558	*hR** *R*$\bar{3}$*m* or *t***	*a* = 247 α = 109.74° *a* = 726.7 *c* = 789.2	23.4 to 24.9 at.% Si [2002Leb] [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$Cu_3Si(h_1)$ 620 - 467	*hR** $R\bar{3}m$	*a* = 472 α = 95.72°	23.2 to 25.2 at.% Si [2002Leb]
$Cu_3Si(r)$ < 570	*o***	*a* = 7676 *b* = 700 *c* = 2194	23.3 to 24.9 at.% Si [2002Leb]
Cu_5Si	*t***	*a* = 647 *c* = 873	at 17 at.% Si metastable [2002Leb]
Nb_3Si 1980 - 1770	*tP*32 $P4_2/n$ Ti_3P	 *a* = 1023.0 *c* = 518.0	25 at.% Si [Mas2] R.T. [V-C2]
βNb_5Si_3 2520 - 1650	*tI*32 *I*4/*mcm* W_5Si_3	 *a* = 1002.6 *c* = 507.17	37.5 to 40.5 at.% Si [Mas2] R.T. [V-C2]
αNb_5Si_3 < 1940	*tI*32 *I*4/*mcm* Cr_5B_3	*a* = 657.1 *c* = 1188.9	37.5 to38.5 at.% Si [Mas2] R.T. [V-C2]
$NbSi_2$ < 1940	*hP*9 $P6_222$ $CrSi_2$	*a* = 481.9 *c* = 659.2	66.7 at.% Si [Mas2] R.T. [V-C2]
Nb_3Si	*cP*8 $Pm\bar{3}n$ Cr_3Si	*a* = 515.5	$Nb_{3.24}Si_{0.76}$, high pressure [V-C2]
Nb_3Si	*cP*4 $Pm\bar{3}m$ $AuCu_3$	*a* = 422.0	[V-C2], metastable ?
Nb_5Si_3	*hP*16 $P6_3/mcm$ Mn_5Si_3	*a* = 753.6 *c* = 524.9	Carbon stabilized phase [V-C2]
* τ_1, $Nb_5Cu_4Si_4$ < 1170	*tI*26 *I*4/*m* $Nb_5Cu_4Si_4$	*a* = 1019.08 *c* = 360.04	36Nb-32Cu-32Si (at.%), [1968Gan, V-C2] melting point [1982Pan]
* τ_2, Nb_4CuSi < at least 1500	*tP*12 *P*4/*mmc* Nb_4CoSi	*a* = 620.5 *c* = 506.8	formed above 1500°C [1982Pan, V-C2]

Fig. 1: Cu-Nb-Si.
Partial isothermal section at 800°C

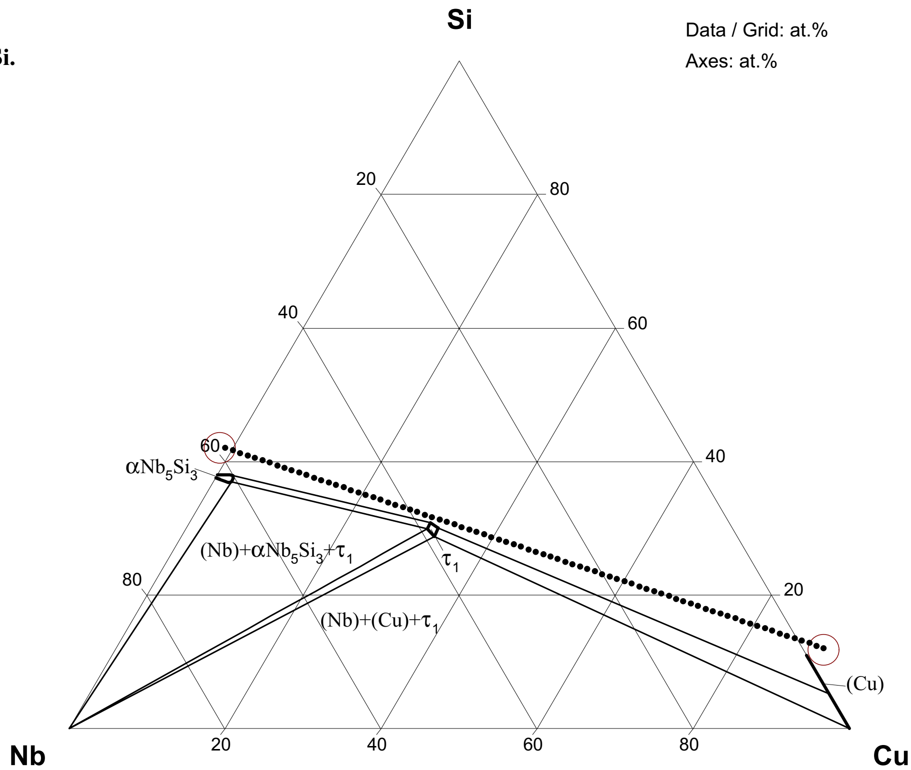

Fig. 2: Cu-Nb-Si.
Isothermal section at 1500°C