Copper – Nickel – Silicon

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Introduction

The phase diagram Cu-Ni-Si is of considerable industrial significance, it contains the Corson alloy, an alloy of Cu with about 1 mass% Si and 3 mass% Ni, which age-hardens by precipitation of Ni_2Si or Ni_3Si during annealing between 450 and 550°C. This alloy is produced in large scale for electric switches and plugs. The Cu-Ni-Si system is relatively complex. Corson [1927Cor1, 1927Cor2, 1930Cor1, 1930Cor2] was first exploring the system experimentally. Okamoto [1938Oka, 1939Oka1, 1939Oka2, 1939Oka3] investigated the system by thermal, metallographic, X-ray, dilatometric, and hardness measurements. Several isothermal and vertical sections were presented. The liquidus projection and coordinates of the corresponding four-phase equilibria were also reported [1939Oka2]. In the area between 10 and 20 mass% Ni and 12 to 15 mass% Si a ternary phase was reported by [1939Oka2]. For the γ phase of the Cu-Si system he reported Ni solubility up to 25 mass%. The γ,Cu_5Si(r) phase which in the binary Cu-Si system is formed on cooling by a peritectic reaction $\kappa + \delta \rightleftharpoons \gamma$ at 730°C with more than 10 mass% Ni crystallizes primarily from liquid containing more than 2 mass% Ni. For the $Ni_{31}Si_{12}$ and θ,Ni_2Si phases Okamoto [1939Oka2] reported large Cu solubilities of 35 and 20 mass%, respectively. [1959Las], however, concluded from X-ray investigations of the Ni Silicides that Ni_2Si, $Ni_{31}Si_{12}$, and Ni_3Si do not dissolve significant amounts of copper. [1973Sok] report appreciable Cu solubility only for θ,Ni_2Si, but much less than [1939Oka2]. Other experimental investigations are restricted to some details. [1957Nov, 1958Nov] gave isotherms of the liquidus and (Ni,Cu) solvus in the Cu corner. These isotherms, however, show a severe inflection incompatible with the findings of Corson, Okamoto and Sokolovskaya et al. [1971Sok, 1973Sok], who measured the solubility of Si in the whole range of the α,(Ni,Cu) solid solution and gave a complete isothermal section at 500°C. In this isothermal section ternary solubilities are shown for the βMn type γ,Cu_5Si(r) phase (~15 at.% Ni), the η,$Cu_3Si(h_2)$ phase (~10 at.% Ni) and the θ,Ni_2Si(h) phase (~10 at.% Cu). [1977Lug] investigated the vertical section at 10 at.% Si by thermal analysis. [1975Tep] identified the particles precipitating during age hardening of the Corson alloy to be the orthorhombic Ni_2Si (δ_1) phase. [2000Wit] measured the partial enthalpies of liquid by high temperature solution calorimetry at 1627°C.
Reviews of the experimental determination of the ternary phase diagram were given by [1949Jae], [1979Cha], [1979Dri]. The age hardening abilities of Cu-Ni-Si alloys containing 3 and 5% Ni+Si in the atomic ratio Ni:Si=2:1 were studied by [1935Jen]. Based on microscopic investigations, the authors proposed a ternary phase on the Cu rich side of the system with a widely variable composition.

Binary Systems

The Cu-Ni and Cu-Si binary systems are accepted from [2002Leb1] and [2002Leb2], respectively. The transformations between η, η´ and η´´ were not investigated in the ternary system, therefore these three phases are not distinguished in this assessment and treated as a single phase called η. The Ni-Si system is accepted from [Mas2].

Solid Phases

The system is dominated by a fcc α,(Ni_xCu_{1-x}) solution which dissolves up to 15 mass% Si on the Ni rich side and 10 mass% Si on the Cu rich side. Corson [1930Cor2] presented solubility limits of Si in (Ni,Cu) of the whole Cu-Ni range for 975, 825 and below 500°C. At a Cu:Ni ratio of 6:1 a solubility minimum of 0.9 mass% Si was reported for 975°C. Solubility limits of α,(Ni_xCu_{1-x}) were shown in graphs by [1931Jon] for 500 and 900°C, by [1939Oka3] for 900 and 450°C, [1957Nov, 1958Nov] for 700, 800, 900 and 1000°C, by [1971Sok, 1973Sok] for 500°C. Although these solubilities are given in small graphs only, some disagreement is detectable. On the ternary solubilities of the binary intermediate phases is even more discrepancy in literature. Okamoto [1939Oka2] reported large solubilities in the binary γ phase

(25 mass% Ni), in the ξ,$Ni_{31}Si_{12}$ phase (34 mass% Cu) and in the θ,Ni_2Si(h) phase (30 mass% Cu). [1959Las], however, at least for ξ,$Ni_{31}Si_{12}$ stated the Cu solubility to be small.
A ternary phase with appreciable range of homogeneity around a composition of about Cu_3NiSi was postulated by Okamoto [1939Oka2] without determining structural details. There is no other experimental verification of this phase. [1949Jae] in his compilation interpreted also the Ni rich part of the γ,Cu_5Si(r) phase given by [1939Oka2] as a ternary phase. Also [1957Nov] mentioned it as a ternary phase. Crystallographic data for all solid phases are given in Table 1.

Quasibinary Systems

Corson [1927Cor1, 1927Cor2] reported the section Cu-Ni_2Si to be quasibinary with a eutectic at about 1030°C, 9 mass% Ni_2Si in the α(Cu) solid solution and 12 mass% Ni_2Si in the liquid phase (values taken from graph). In all later publications dealing with this part of the system [1935Jen, 1938Oka, 1939Oka2, 1957Nov, 1959Las] all sections between α(Cu) and any of the Ni-silicides were assumed to be not quasibinary.

Invariant Equilibria

[1939Oka2] reported temperatures and liquid compositions of the invariant equilibria containing liquid. However, these data have to be taken with care, as the homogeneity ranges of some phases of [1939Oka2] are not commonly accepted. As no better data for coordinates and types of invariant reactions are available Okamoto's table is reproduced here as Table 2.

Liquidus Surface

A liquidus projection of the whole system was reported by [1939Oka2] (reproduced in Fig. 1). The same problems exist as with the invariant equilibria. The review articles [1949Jae, 1979Cha, 1979Dri] accepted this liquidus surface.

Isothermal Sections

Isothermal section of the Cu rich corner were given by [1939Oka1] at 450°C up to 25 mass% Ni and 20 mass% Si and at 1010, 950 and 800°C up to 10 mass% Ni and 7 mass% Si [1939Oka3]. [1957Nov] gave isothermal sections of the Cu corner up to 8 mass% Ni+Si for 1000, 900, 800 and 700°C. [1973Sok] gave a 500°C isothermal section of the whole system. The shapes of the α(Cu) solid solution boundary differs between the three investigators. All three agree on equilibria α(Cu)+Ni_3Si, α(Cu)+$Ni_{31}Si_{12}$ and α(Cu) + γ,Cu_5Si(r), the latter assumed to be a ternary phase by [1957Nov]. [1973Sok], however, reports an equilibrium α(Cu)+Ni_2Si at 500°C between the 2nd and 3rd equilibrium, which was not found by the other two groups, by [1939Oka3] even not at 450°C. [1975Tep] found Ni_2Si(r) to be the phase precipitating during age hardening and that is an argument for Sokolovskaya version [1973Sok]. As there are not sufficient arguments to solve the disagreements, no "critically assessed" isothermal section can be given. In Fig. 2 the 500°C section of [1973Sok] is reproduced.

Temperature – Composition Sections

Vertical sections were presented by [1927Cor1, 1927Cor2] (Cu side of Cu-Ni_2Si), [1938Oka] (4 complete and 4 qualitative ones without scaling the composition axis), [1939Oka2] (16 complete and 12 partial ones), [1957Nov] (six ones restricted to the Cu corner), [1972Che] (30 mass% Cu, 40 mass% Si and 1 mass% Si), [1973Sok] (one, between Ni_2Si and Cu) and [1977Lug] (one, at 10 at.% Si). None of the sections of different authors is for the same composition line. Comparison of neighboring sections, however, reveals some disagreement. The Cu side of the section from Cu to Ni_2Si from [1927Cor1, 1927Cor2] is reproduced in Fig. 3. The "invariant line", however, has to be interpreted as a narrow normal three-phase field L+(Cu)+Ni_2Si.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α, (Ni_xCu_{1-x})	*cF*4 $Fm\bar{3}m$		$0 \le x \le 1$
(Ni) < 1455	Cu	a = 352.40	pure Ni at 25°C [Mas2]
(Cu) < 1084.62		a = 361.46	pure Cu at 25°C [Mas2]
(Si) < 1414	*cF*8 $Fd\bar{3}m$ C (diamond)	a = 543.06	at 25°C [Mas2]
κ, ~Cu_7Si 842 - 552	*hP*2 $P6_3/mmc$ Mg	a = 256.05 c = 418.46	[V-C2]
β, ~Cu_6Si 853 - 787	*cI*2 $Im\bar{3}m$ W	a = 285.4	14.6 to 16.7 at.% Si [Mas2]
γ, ~Cu_5Si(r) < 729	*cI*20 $P4_132$ βMn	a = 619.8	17.1 to 17.6 at.% Si [Mas2]
δ, ~Cu_5Si(h) 824 - 711	*t***	a = 881.5 c = 790.3	17.6 to 19.6 at.% Si [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ε, $Cu_{15}Si_4$ < 800	*cI*76 $I\bar{4}3d$ $Cu_{15}Si_4$	*a* = 961.5	21.2 at.% Si [2002Leb2]
η, ~$Cu_3Si(h_2)$ 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 [2002Leb2] [V-C2]
η´, ~$Cu_5Si(h_1)$ 620 - 467	*hR** $R\bar{3}$	*a* = 472 α = 95.72°	23.2 to 25.2 at.% Si [Mas2]
η´´, ~Cu_5Si(r) < 570	*o***	*a* = 7676 *b* = 700 *c* = 2194	23.3 to 24.9 at.% Si [Mas2]
β_3, $Ni_3Si(h_2)$ 1170 - 1115	*oP*16 *Pnma* Fe_3C	*a* = 550 *b* = 650 *c* = 435	[Mas2, V-C2]
β_2, $Ni_3Si(h_1)$ 1115 - 990	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 280.8	[Mas2, V-C2]
β_1, Ni_3Si(r) < 1035	*cP*4 $Pm\bar{3}m$ $AuCu_3$	*a* = 350.5	[Mas2, V-C2]
γ_1, Ni_5Si_2 < 1242	*hP*43 *P*321 $Ni_{31}Si_{12}$	*a* = 666.7 *c* = 1227.7 *a* = 667.1 *c* = 1228	[V-C2] [V-C2]
θ, Ni_2Si(h) 1306 - 825	*hP*6 $P6_3/mmc$ Ni_2In	*a* = 383.6 *c* = 494.8 *a* = 380.5 *c* = 489.0	[V-C2] [V-C2]
δ_1, Ni_2Si(r) < 1255	*oP*12 *Pnma* Co_2Si	*a* = 499 *b* = 372 *c* = 706 *a* = 497.9 *b* = 375.4 *c* = 706.5	[V-C2] [V-C2]
ζ, Ni_3Si_2 < 830	*oC*80 $Cmc2_1$ Ni_3Si_2	*a* = 1222.9 *b* = 1080.5 *c* = 692.4	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ρ, NiSi < 992	*oP*8 *Pnma* MnP	*a* = 518 *b* = 334 *c* = 559 *a* = 519 *b* = 333 *c* = 562.8	[V-C2] [V-C2]
β$NiSi_2$ 993 - 981	-	-	-
α$NiSi_2$ < 981	*cF*12 $Fm\bar{3}m$ CaF_2	*a* = 538 *a* = 538.3 *a* = 540.6	[V-C2]
* τ, ~Cu_3NiSi	-	-	[1939Oka2]

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Cu	Ni	Si
L + β_3 ⇌ α + γ_1	1071	U_1	L	47.8	36.6	15.6
β$NiSi_2$ ⇌ α$NiSi_2$, L, (Si)	980	D_1	L	3	38	59
L + γ_1 ⇌ α + γ	940	U_2	L	70.1	13.63	16.27
L + γ_1 ⇌ θ + γ	880	U_3	L	47.9	24.1	28.0
L + θ + γ ⇌ τ	859	P_1	L	53.9	18	28.1
L + γ ⇌ α + β	858	U_4	L	81.14	2.45	16.41
L + γ + β ⇌ δ	835	P_2	L	79.8	1.94	18.26
L + γ ⇌ ε + τ	832	U_5	L	68.5	6.7	24.8
L ⇌ δ + γ + ε	820	E_1	L	77.3	2.5	20.2
L + θ ⇌ ρ + τ	790	U_6	L	42.8	23.16	34.04
L + ε ⇌ τ + (Si)	774	U_7	L	58.3	8.8	32.9
L ⇌ ρ + β$NiSi_2$ + τ	770	E_2	L	45.56	18.83	35.61
L ⇌ (Si) + β$NiSi_2$ + τ	769	E_3	L	55.74	11.37	32.89

Fig. 1: Cu-Ni-Si.
Liquidus surface projection

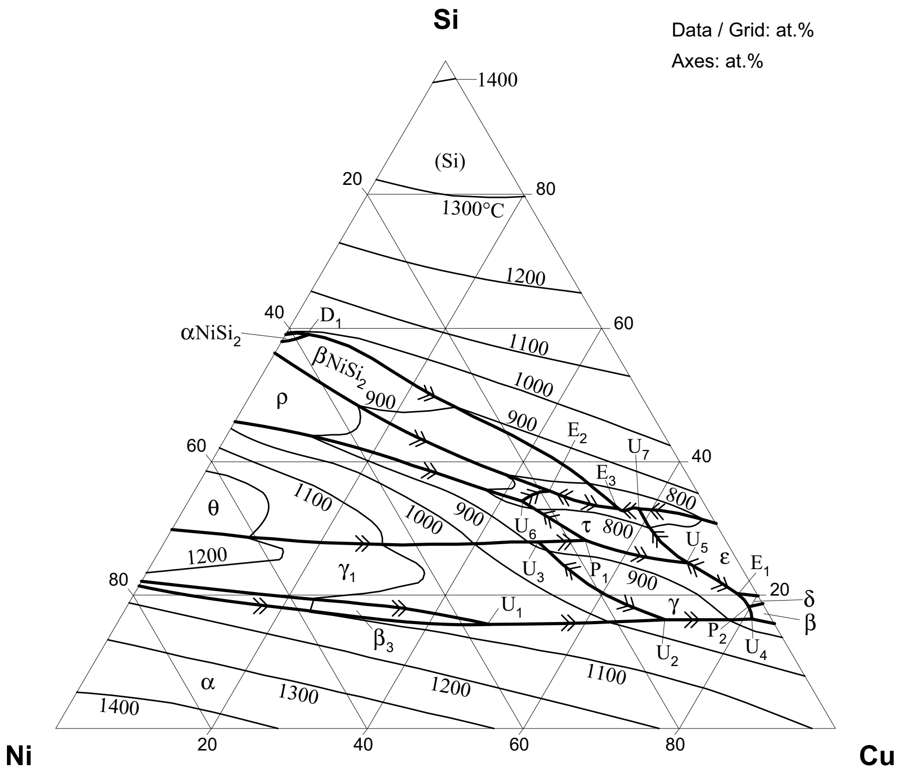

Fig. 2: Cu-Ni-Si.
Isothermal section at 500°C

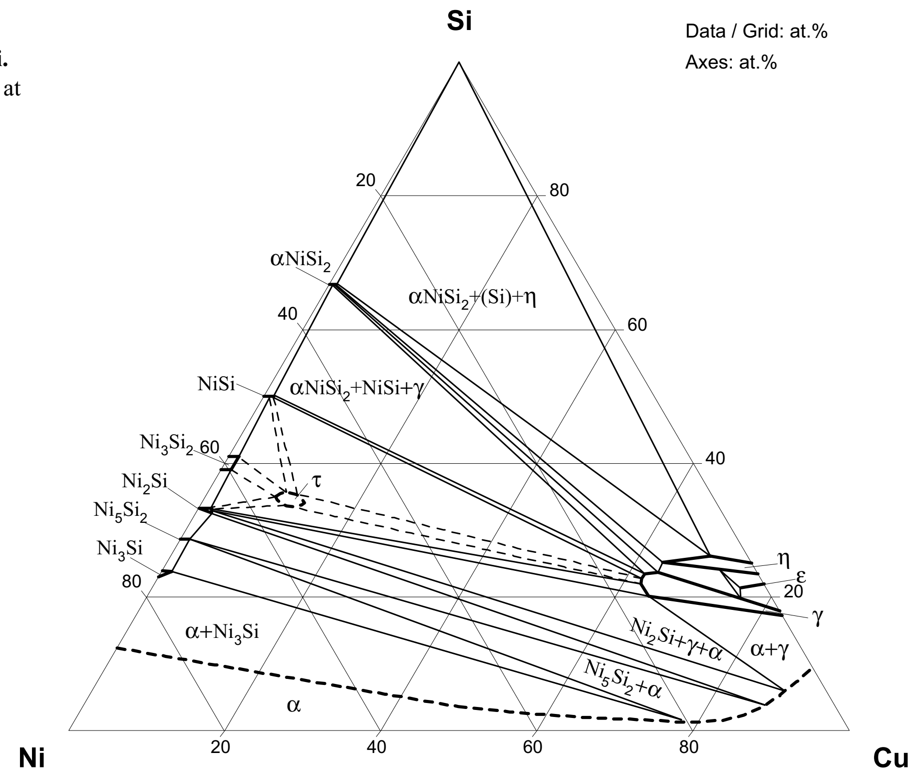

Fig. 3: Cu-Ni-Si.
Cu - Ni_2Si vertical section