Cobalt – Copper – Silicon

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Introduction

Copper alloys are of general interest to the electrical industry because of copper's very high electrical and thermal conductivity. The Co-Cu-Si system has been under study since the late 1920s through the so called 'Corson Alloys'. Cu rich compositions can be strengthened considerably through the precipitation of Co_2Si within the Cu rich matrix following a suitable aging treatment [1927Cor1, 1927Cor2, 1930Cor1, 1930Cor2]. This feature of Cu rich alloys of this system raised the prospect of the fabrication of stronger cabling wire. However, there has been surprisingly little study of the phase diagram. Initial studies were carried out by [1927Cor1, 1927Cor2, 1930Cor1, 1930Cor2] which were confined to the Cu rich part of the diagram, although the presence of a Cu-Co_2Si quasibinary section was speculated. Later, [1968Gro] presented two isopleths for 1 and 2.5 mass% Co, respectively, but again, only for Cu rich alloys. [1975Rev1] presented Cu rich isothermal sections for 700, 900 and 1000°C. They used 67 different alloys which had been prepared by vacuum induction melting followed by hot working and cold drawing into wires. The wires were sealed in evacuated silica ampoules before annealing and subsequent examination by optical microscopy, X-ray analysis and mechanical and electrical property measurement. This work was also reported by [1979Dri, 1979Cha, 1988Las]. More recently, [1985Alb1] used in situ resistivity measurements to determine the solubility of Co_2Si in the Cu-Co_2Si quasibinary system; the results being in good agreement with [1975Rev1]. The majority of investigations of this system however, relate to the precipitation of the Co_2Si phase and its strengthening properties [1927Cor1, 1927Cor2, 1930Cor1, 1930Cor2, 1933Wil, 1975Tep, 1985Alb2, 1988Len, 2001Don, 2002Var, 2003Var1, 2003Var2]. Mechanical property measurement [1933Wil], TEM [1975Tep, 1988Len] and DSC measurements were used to study the precipitation kinetics.
Overview of the works related to phase realtions and crystal structure is given in Table 1.

Binary Systems

The binary systems are taken from [2006Ans] (Co-Cu), [2002Leb] (Cu-Si), and [Mas2] (Co-Si).

Solid Phases

The solid phases of the system are listed in Table 2. No ternary phases were reported by [1979Cha] in their review of the system. [1988Las] reported that Co_2Si precipitated after aging selected alloys at 400-500°C, in agreement with much earlier work [1927Cor2, 1930Cor2].
[1985Alb2] studied precipitation in high Cu content alloys, and found it to begin between 400°C and 600°C, with Co being formed first, clustering and acting as a nucleation site for Si, followed by formation of Co_2Si. The reaction rates were found to be faster with increasing Si content of the alloy, with excess Si remaining in the (Cu) solid solution.

Quasibinary Systems

There is a quasibinary section between Cu and Co_2Si [1930Cor3,1975Rev1]. The solubility of Co_2Si in (Cu) in this section was given as 2.35 mass% at 1050°C, 1.9 mass% at 1000°C, 1.1 mass% at 900°C, 0.55 mass% at 800°C and 0.3 mass% at 700°C. The work of [1985Alb1] is in good agreement.

Liquidus, Solidus and Solvus Surfaces

[2002Zab] calculated the liquidus surface using thermodynamic parameters for the accepted constituent binary phase diagrams. As this was prepared by extrapolation from the binary systems using no ternary equilibrium data, the surface is not reproduced here.

Isothermal Sections

[1975Rev1] prepared isothermal sections for Cu contents greater than 95 mass% for 700°C (Fig. 1), 900°C (Fig. 2) and 1000°C (Fig. 3), observing three-phase fields between: (Cu) + Co_2Si + CoSi and (Cu) + (Co) + Co_2Si at 700°C; L + (Cu) + CoSi; (Cu) + Co_2Si + CoSi and (Cu) + (Co) + Co_2Si at 900°C; L + (Cu) + Co_2Si and (Cu) + (Co) + Co_2Si at 1000°C. These results at 700°C were in agreement with [1988Las], and at 900°C in agreement with [1979Dri]. The sections at 900 and 1000°C (Figs. 2 and 3) have been modified slightly to maintain consistency with the accepted binary phase diagrams.

Temperature – Composition Sections

[1968Gro] produced temperature-composition sections at 1 and 2.5 mass% Co. However, as there are contraventions with the phase rule (as pointed out by [1979Cha]) they are not reproduced here.

Thermodynamics

In order to try and understand the hardening mechanism, the kinetics of the precipitation of Co_2Si were calculated in the quasibinary section: Cu - 0.65 at.% Co - 0.33 at.% Si (Cu - 1 at.% Co_2Si) [2002Var]. The results from enthalpimetric calculations agreed with the DSC experiments: Co atoms cluster, followed by Si preciptation, to finally form Co_2Si. This agreed with the results of [1975Rev2, 1985Alb2, 1988Len]. The effective activation energy of both Co and Si precipitation was found as ~1.5eV. [2001Don] subsequently showed the Co and Co_2Si precipitations to be two overlapping exothermic reactions. The enthalpies of the reactions were proportional to the precipitate volume fractions.

Notes on Materials Properties and Applications

Copper alloys are of interest for the effect of various alloying additions on their electrical properties. This system, amongst others, is beneficial because there is a strengtheing mechanism (precipitation of Co_2Si) which allowed for stronger electrical alloys. The Corson process was a heat treatment and quenching schedule which optimised the precipitation for specific alloys [1927Cor2], as well as retaining reasonable electrical properties [1927Cor1]. This was achieved by using the Cu-Co_2Si quasibinary section [1930Cor2], and undertaking various heat treatments and quenching, *e.g.* from 400-600°C. More age hardening studies were carried out by [1933Wil]. Using TEM, [1975Tep] showed that at maximum strength, the Co_2Si particles have an orthorhombic lattice.

[1998Shi] observed in-plane four-fold symmetry in the magnetisation and magnetoresistance in Co/Cu multilayers electrodeposited on Si(001) substrates covered in a thin evaporated Cu seed layer. This could be of relevance for electronic devices.

[1992Var] measured fatigue crack propagation rates in Cu - 0.67 at.% Co - 1.1 at.% Si and Cu - 0.34 at.% Co - 0.95 at.% Si alloys, to investigate the influence of precipitation processes and the mechanisms of crack propagation.

Details of materials properties studies in Co-Cu-Si alloys are given in Table 3.

Miscellaneous

[1992Dau] observed a decagonal phase in $(Al,Si)_{65}Co_{20}Cu_{15}$ alloys.

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

Reference	Method Experimental Technique	Temperature/Composition/Phase Range Studied
[1927Cor1, 1927Cor2, 1930Cor1, 1930Cor2]	Metallography	Various
[1968Gro]	Metallography, chemical analysis, X-ray diffraction, dilatometry.	Various; > 90 mass% Cu
[1975Rev1]	Metallography, kinetics	400-1000°C; Cu-1.62 % Co- 0.38 % Si
[1975Rev2]	Metallography, X-ray diffraction, mechanical properties and electrical resistance.	700°C, 900°C and 1000°C; > 95 mass% Cu
[1975Tep]	TEM, X-ray diffraction	Cu-1.73 Co - 0.85% Si (at.%)
[1979Dri]	Metallography, X-ray analysis.	900°C; > 95 mass% Cu
[1985Alb1, 1985Alb2]	Electrical resistance and thermoelectric force measurements.	< 1000°C; Cu - 0.3 - 1.75 at.% Co - 0.05 - 1.9 at.% Si
[1988Las]	Metallography, X-ray analysis, X-ray diffraction.	700°C; > 95 mass% Cu; Ageing at 400°C, 450°C and 500°C.
[1988Len]	Electrical resistivity, thermoelectric power, mechanical testing, TEM, DSC.	400-600°C; Cu - 0.63 - 0.56 at.% Co - 0.27 - 1.91 at.% Si
[2001Don]	DSC, Kissinger calculations	Cu - 0.5 - 1.0 at.% Co_2Si

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αCo)	*cF*4 $Fm\bar{3}m$ Cu	*a* = 356.88 *a* = 354.47	at 520°C [V-C2] Dissolves ~17 at.% Cu at ~1360°C [2006Ans], 16.5 at.% Si at 1250°C [Mas2]
(εCo) < 422	*hP*2 $P6_3/mmc$ Mg	*a* = 250.71 *c* = 406.86	at 25°C [Mas2]
(Cu) < 1084.62	*cF*4 $Fm\bar{3}m$ Cu	*a* = 361.46	at 25°C [Mas2] Melting point [1994Sub]. Dissolves 11.1 at.% Si at 853°C [2002Leb], 9.1 at.% Co at 1113.3 [2006Ans].
(Si) < 1414	*cF*8 $Fd\bar{3}m$ Diamond	*a* = 543.06	[Mas2]. Dissolves 0.003 at.% Cu [2002Leb], negligible Co [Mas2]
Co_3Si 1214 - 1193	*hP*8 $P6_3/mmc$ Mg_3Cd	*a* = 497.6 ± 0.2 *b* = 406.9 ± 0.6	[Mas2, V-C2]
αCo_2Si ≲ 1320	*oP*12 *Pnma* Co_2Si	*a* = 491.9 *b* = 372.5	[Mas2, V-C2]
βCo_2Si 1334 - 1238	-	-	[Mas2]
CoSi < 1460	*cP*8 $P2_13$ FeSi	*a* = 445.0	[V-C2]
$CoSi_2$ < 1326	*cF*12 $Fm\bar{3}m$ CaF_2	*a* = 535.3	[V-C2]
κ, 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]
β, ~Cu_6Si 853 - 787	*cI*12 $Im\bar{3}m$ W	 *a* = 285.4	14.2 to 16.2 at.% Si at 14.9 at.% Si. [2002Leb]
δ, 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 [2002Leb]
γ, Cu_5Si(r) < 729	*cP*20 $P4_132$ βMn	*a* = 619.8	17.15 to 17.6 at.% Si [2002Leb]

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 [2002Leb]
η, $Cu_3Si(h_2)$ 859 - 558	*hR** $R\bar{3}m$ or	*a* = 247 α = 109.74° *a* = 726.7 *c* = 789.2	23.4 to 24.9 at.% Si [2002Leb] [V-C2]
η', $Cu_3Si(h_1)$ 620 - 467	*hR** $R\bar{3}$	*a* = 472 α = 95.72°	23.2 to 25.2 at.% Si [2002Leb]
η'', $Cu_3Si(r)$ < 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]

Table 3: Investigations of the Co-Cu-Si Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1927Cor1]	Resistivity measurements	Electrical resistivity
[1930Cor1]	Hardness and tensile tests	Hardness and tensile test data
[1930Cor2]	Corrosion tests, resistivity measurements, hardness tests	Corrosion rates, electrical resistivity from 400°C, 500°C and 600°C, hardesses
[1975Rev1]	Resistivity measurements and tensile tests	Electrical resistance and tensile yield stress
[1975Tep]	Tensile tests	UTS and proof stress
[1988Len]	Electrical resistivity, thermoelectric power, simultaneous tortion and extension	Electrical resistivity, thermoelectric power, tortional yeild stress
[1992Var]	Fatigue	Fatigue crack propagation rates
[1998Shi]	XRD, TEM	Magnetoresistance
[2003Var1, 2003Var2, 2002Var]	DSC	Thermodynamics (heat contents), kinetics, order of preciptation events

Fig. 1: Co-Cu-Si.
Partial isothermal
section at 700°C

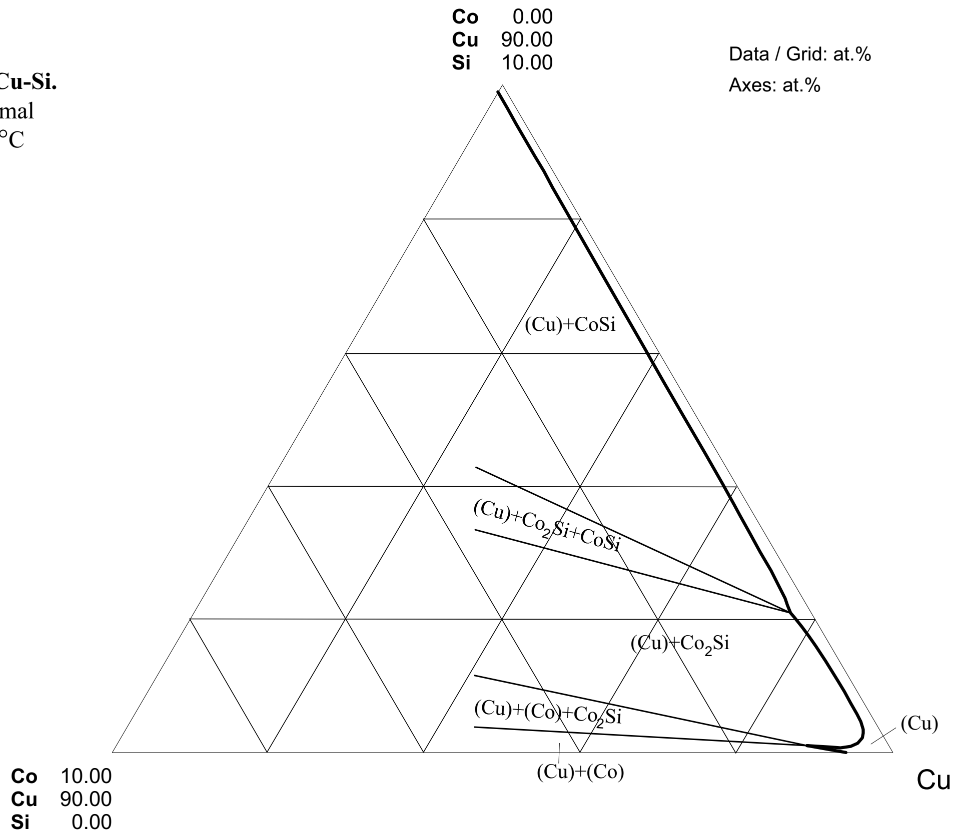

Fig. 2: Co-Cu-Si.
Partial isothermal
section at 900°C

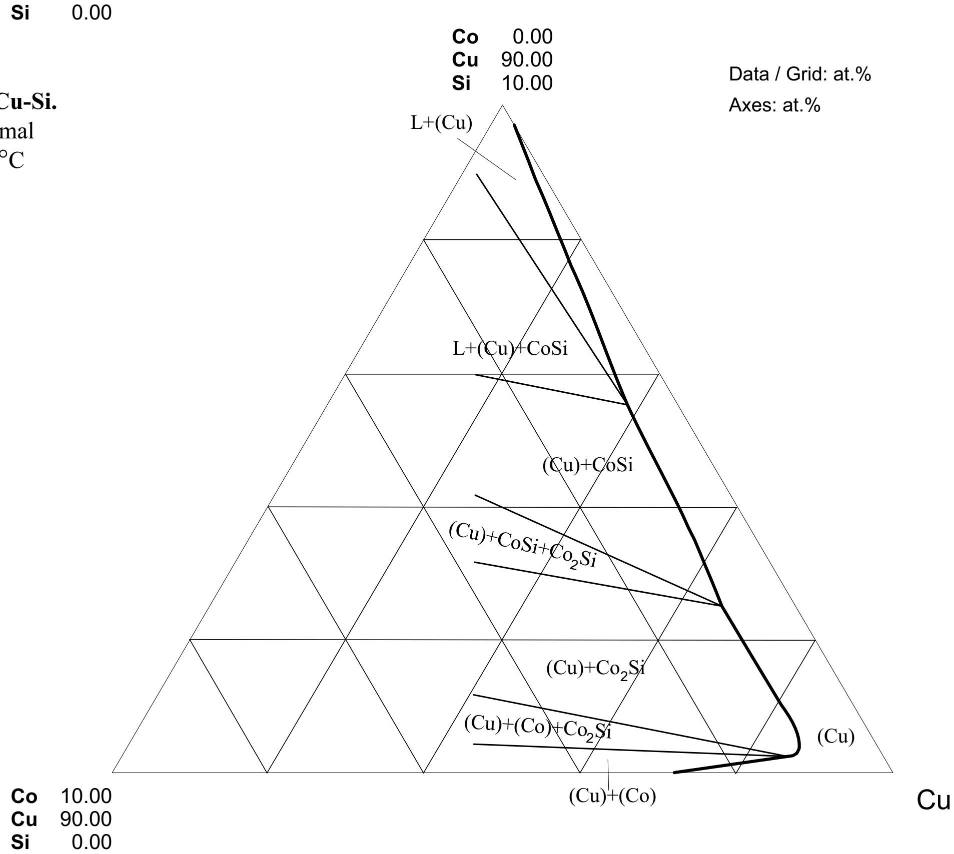

Fig. 3: Co-Cu-Si. Partial isothermal section at 1000°C