Chromium – Copper – Silicon

Riccardo Ferro, Svitlana Ilyenko

Introduction

A partial, tentative isothermal section at 800°C (in the concentration range Cr-Cr_5Si_3-Cu) has been constructed in the experimental investigation by [1979Sav]. A few more papers, however concerning the Cr-Cu-Si system have been published: mainly experimental as [1972Jan, 1987Roi] or giving computed data as [1992Rei, 1995Xia].
In the experimental investigations the alloys were generally prepared in vacuum melting furnaces from pure metal mixtures [1995Xia] or by arc melting in purified He on water-cooled copper hearth [1979Sav] and subjecting the alloys to several remelting. According to [1979Sav] the compositions of the resulting alloys were established by chemical analysis. After melting the alloys were heat treated at 800°C for 200 h in evacuated quartz capsules. Rapid quenching experiments were also carried out.
A special technique was used by [1972Jan] in a study of the solubility of several disilicides (of Cr but also of Ti, V, Nb, Ta, Mo, W) in metal melts (Cu or Ag or Au). Special crucibles were prepared by pressing (and then sintering) the disilicide powder in an appropriate finger die. The disilicide crucibles were then used for melting the other metals, which were subsequently analyzed for the Si content.

Binary Systems

Phase diagrams of the binary boundary systems are accepted as evaluated in the MSIT Binary Evaluation Program: Cr-Cu from [2002Ans], Cu-Si from [2002Leb] and Cr-Si from [2006Leb].

Solid Phases

Data concerning the crystal structures of the solid phases are listed in Table 1. Notice that these are unary or binary phases. No ternary phases have been found [1979Sav]. According to [1972Jan] Cr (as the other metals of Group VI) forms no ternary silicide with Cu.

Isothermal Sections

A partial schematic isothermal section at 800°C in the composition range Cu-Cr-Cr_5Si_3 was presented by [1979Sav]. It is shown in Fig. 1 after correcting the homogeneity ranges of all phases at the binary boundary sides according to the accepted binary systems. Isothermal section at 800°C was also reported by [1995Vil] referencing the same work of [1979Sav], however in fact the diagram in [1995Vil] differs from that in [1979Sav]. Obviously it was modified by [1995Vil] without mentioning this or it was taken from another unknown source. This diagram is not considered in the present evaluation.
Isothermal sections in the Cu rich corner at 700 and 1000°C have been reported by [1987Roi]. However, an agreement with the accepted binary systems is poor regarding the solubility data for the (Cu) solid solution. These sections are not accepted in the present evaluaion.
Complete isothermal sections of the system have been computed. Tie lines have been calculated by [1992Rei] at 700°C, see Fig. 2. Stable tie lines were mapped on the premise of comparing the net Gibbs free energies of a competing pair of tie lines at their respective point of intersection. The data of the Gibbs energies relevant to the elements and binary compounds and used in the computation were taken from different compilations. In an investigation [1995Xia] on wetting of Si_3N_4 by liquid Cr alloys, properties of Cr-Cu-Si alloys were considered and an isothermal section at 1160°C of the ternary phase diagram was calculated using MTDATA. It is presented in Fig. 3. It should be noted that we introduced in Fig. 3 a three-phase filed (Cr)+L+Cr_3Si which was missed in the calculation by [1995Xia]. Both calculated sections, at 700°C (Fig. 2) and at 1160°C (Fig. 3) can be considered as tentative as they do not consider solubility ranges of binary phases and their extensions into the ternary.

Notes on Materials Properties and Applications

Because of the limited solubility in Cu, relatively economical cost and microstructure stability at high temperature, Cr is a promising reinforcing metal for Cu based in situ composites [2001Sun]. Cu-15Cr (mass%) in situ composite is superior to any monolithic Cu and conventional Cu alloys in terms of the combination of tensile strength and electrical conductivity. For the further performance improvement, Si has been selected by [2001Sun] as an alloying element for Cu-15Cr (mass%) in situ composites because the addition of Si increases the softening temperature and high temperature strength of Cu-dilute Cr alloy. [2001Sun] showed that the addition of 0.5 mass% Si produces solution hardening of Cr phase (solubility of Si in Cr is about 1.8 mass% after solution treatment at 1000°C) and formation of 4 vol% Cr_3Si, it has been found that both Cr_3Si and Si rich layer attach to (Cr) phase. The higher hardness of Cr phase in Cu-15Cr-0.5Si alloy makes the Cr phase more difficult to deform, i.e. the drawn structure of Cu-15Cr-0.5Si in situ composite is coarser [2001Sun]. The tensile strength of as drawn Cu-15Cr-0.5Si in situ composites is lower than that of Cu-15Cr in situ composites at higher drawing strain. However the strength of Cu-15Cr-0.5Si in situ composites is higher than that of Cu-15Cr in situ composites at the same interphase spacing due to the higher hardness of Cr phase [2001Sun].
Adhesive characteristics (wettability and formation of a transitional zone at the phase boundary) of the Cr-Cu alloys with addition of 7mass% Si in the temperature range 1100 to 1300°C have been studied in [2001Les].
[1995Xia] outlined that Cr-Cu-Si alloys did not have very good wetting on Si_3N_4, however, additions of Ni improve this property.
Superconducting properties of Cr-Cu-Si alloys have been studied by [1979Sav]. Mechanical properties have been studied in [1930Cor].

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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
(Cu) < 1084.62	*cF*4 $Fm\bar{3}m$ Cu	*a* = 361.46	at 25°C [Mas2] melting point [1994Sub]
(α'Cr)	*tI*2 *I*4/*mmm* α'Cr	*a* = 288.2 *c* = 288.7	at 25°C, HP [Mas2]
(αCr) < 1863	*cI*2 $Im\bar{3}m$ W	*a* = 288.48	at 25°C [Mas2]
(δSi)	*hP*4 $P6_3/mmc$ αLa	*a* = 380 *c* = 628	at 25°C, 16 GPa -> 1 atm [Mas2]
(γSi)	*cI*16 $Im\bar{3}m$ γSi	*a* = 663.6	at 25°C, 16 GPa [Mas2]
(βSi)	*tI*4 $I4_1/amd$ βSn	*a* = 468.6 *c* = 258.5	at 25°C, 9.5 GPa [Mas2]
(αSi) < 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	at 12.75 at.% Si [2002Leb] 11.05 to 14.5 at.% Si
β, ~ Cu_6Si 853 - 787	*cI*2 $Im\bar{3}m$ W	*a* = 285.4	at 14.9 at.% Si [2002Leb] 14.2 to 16.2 at.% Si
δ, Cu_5Si(h) 824 - 711	*t***	*a* = 881.5 *c* = 790.3	sample annealed at 700°C 17.6 to 19.6 at.% Si [2002Leb]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ, Cu_5Si(r) < 729	*cP*20 $P4_132$ βMn	*a* = 619.8	17.15 to 17.6 at.% Si [2002Leb]
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 *t***	 *a* = 726.7 *c* = 789.2	23.4 to 24.9 at.% Si [2002Leb] [2002Leb]
η', $Cu_3Si(h_1)$ 620 - 467	*hR** $R\bar{3}$		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]
Cr_3Si < 1780	*cP*8 $Pm\bar{3}n$ Cr_3Si	*a* = 455.6	[V-C2] 20.8 to 25.3 at.% Si [2006Leb]
βCr_5Si_3 1666 - 1488	?	?	37.5 - 37.7 at.% Si [2006Leb]
αCr_5Si_3 < 1488	*tI*32 *I*4/*mcm* W_5Si_3	*a* = 917.0 *c* = 463.6	[V-C2] 37.5 at.% Si [2006Leb]
CrSi < 1424	*cP*8 $P2_13$ FeSi	*a* = 462.2	[V-C2] 50 at.% Si [2006Leb]
$CrSi_2$ < 1438	*hP*9 $P6_222$ $CrSi_2$	*a* = 442.83 *c* = 636.80	[V-C2] 66.3 - 68 at.% Si [2006Leb]

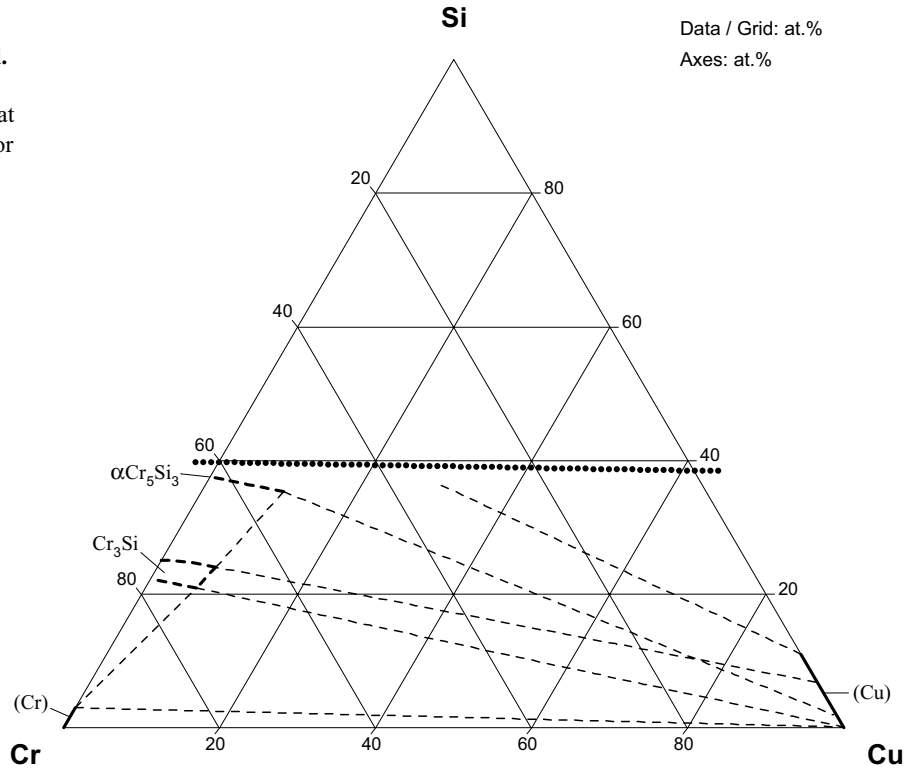

Fig. 1: Cr-Cu-Si. Tentative partial isothermal section at 800°C in the Si poor region

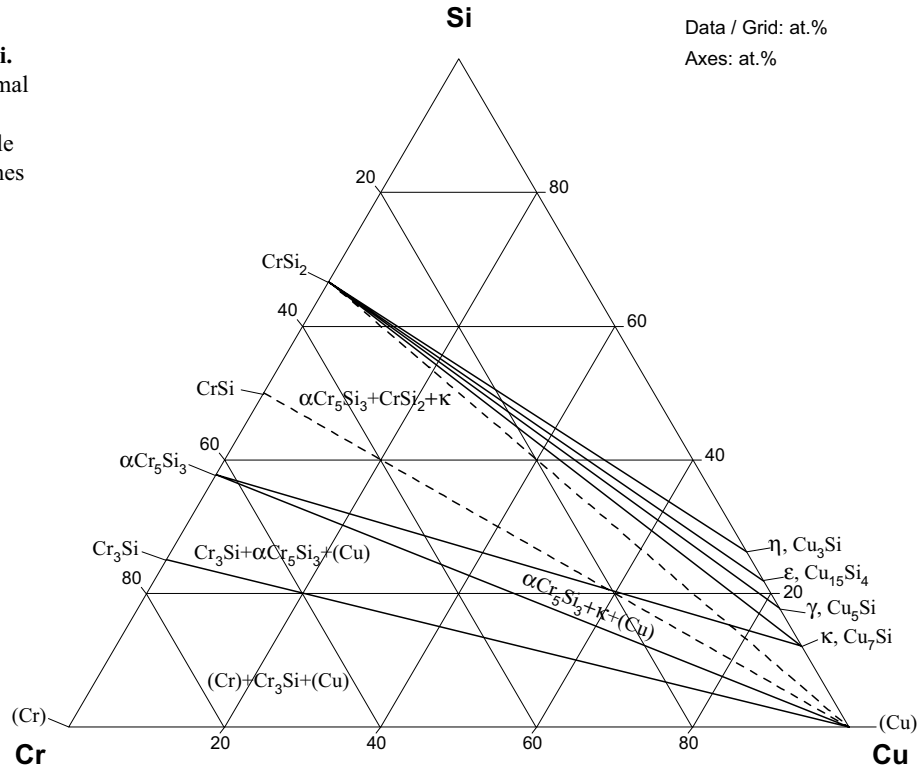

Fig. 2: Cr-Cu-Si. Calculated isothermal section at 700°C. Alternative possible trends of the tie-lines are shown (dotted lines)

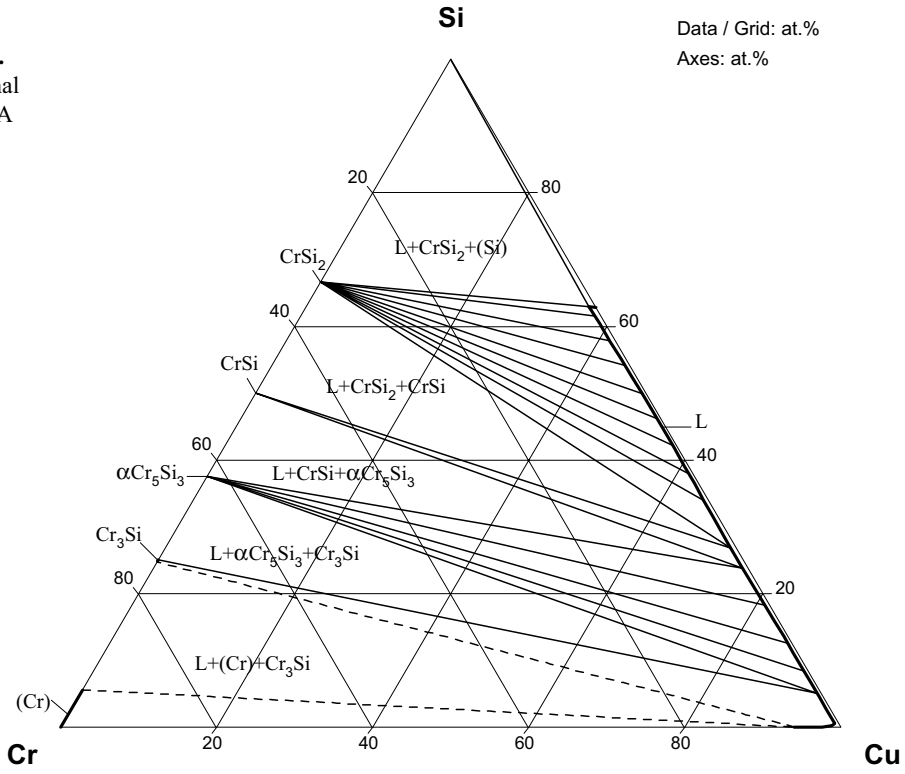

Fig. 3: Cr-Cu-Si. Computed isothermal section at 1160°C. A few tie-lines are shown in the two-phase fields