



Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: www.elsevier.com/locate/calphad

Calorimetric measurements and assessment of the binary Cu–Si and ternary Al–Cu–Si phase diagrams

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ARTICLE INFO

Article history:

Received 18 January 2016

Received in revised form

1 March 2016

Accepted 2 March 2016

Keywords:

Cu–Si

Al–Cu–Si

Dynamic scanning calorimetry

Thermodynamic modelling

CALPHAD

ABSTRACT

Using dynamic scanning calorimetry the temperature, composition and reaction enthalpy of a number of invariant reactions in the Cu–Si and Al–Cu–Si systems were determined. The temperatures and compositions are in good agreement with previous experimental data. Reaction enthalpies have not been previously measured. The Cu–Si system was thermodynamically modelled in detail using all available data. Experimental data are well reproduced, including the presently measured reaction enthalpies. Compared to the best previous thermodynamic description some improvements could be achieved. The Al–Cu–Si system was tentatively modelled using a new model for the γ -Al₄Cu₉ phases and without using large ternary interactions with large temperature dependencies. The Cu-rich part is very complex and the complete system could be reasonably described. Though it was not possible to present a detailed assessment in this work there are important improvements compared to previous thermodynamic descriptions.

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1. Introduction

The Cu–Si and Al–Cu–Si systems are sub-systems of the Al–Cu–Mg–Si system, which is a central system for aluminium alloys. The phase diagrams of these systems have been investigated already in the early 1900s and there is currently renewed interest and both diagrams have recently been investigated experimentally [1–4]. The Cu–Si system contains a number of intermetallic phases in the Cu-rich part and the phase diagram is by now for most parts fairly precisely known, although some question marks do remain (see Section 2.1). The thermodynamic properties of the liquid have been extensively measured, whereas the thermodynamic properties of the solid phases are not well known. In order to gain more information we measure the enthalpies of the melting reactions involving the intermetallic phases using dynamic scanning calorimetry (DSC). The Cu–Si system has been modelled thermodynamically several times [5–8], most recently by Gierlotka and Azizul Haque [8]. All descriptions reproduce the phase diagram well and most precisely so the description by Gierlotka and Azizul Haque [8]. However, with the exception of the description by Shin et al. [7], the thermodynamic properties of the solid phases differ considerably from the available experimental and theoretical information. Here we model the Cu–Si system taking into account recent experimental data [1], our own calorimetric measurements

and all previous data. The Al–Cu phase diagram is very complex and was recently experimentally investigated by Ponweiser et al. [9]. The system was very recently thermodynamically modelled by Liang and Schmid-Fetzer [10]. This description is a substantial improvement compared to the previous description [11,12], in particular concerning the modelling of the γ -Al₄Cu₉ phases.

The Cu-rich part of the Al–Cu–Si system is very complex and, in spite of recent detailed investigations [2–4], not completely known. The hcp (κ -CuSi) and the γ -Al₄Cu₉ phases extend far into the ternary and the bcc phase extends across the system from Al–Cu to Cu–Si as a high-temperature phase. Ponweiser and Richter [2] identified a ternary phase at 700 °C, but its temperature range of stability could not be determined. For some reason they did not identify the bcc phase, which clearly must be a stable phase at 700 °C. At 500 °C they are in agreement with the very detailed work by Riani et al. [4] and with the work of He et al. [3]. In this work we re-determine the temperature and composition of a number of invariant reactions and measure the reaction enthalpies by DSC. The ternary system was modelled recently by He et al. [3]. In addition to large ternary interactions with large temperature dependencies the extension of the γ -Al₄Cu₉ phases could not be reproduced with the model used. Here we provide a preliminary model of the Al–Cu–Si system based on a very recent description of the Al–Cu system from Liang and Schmid-Fetzer and on our new description of the Cu–Si system. Although we are not able to provide a finished description of the Al–Cu–Si system at this point we think that the insights into the modelling are important and should be shared.

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2. Review of literature data

2.1. Cu–Si

The Cu–Si system was reviewed by Olesinski and Abbaschian [13] in 1986 in some detail and we will only repeat the main points here. The phase diagram is shown in Fig. 1 and the phases are listed in Table 1. The phase diagram was investigated already in 1907 [17] and again in 1919 [18]. Although these early phase diagrams have a number of strange features the liquidus temperatures are surprisingly accurate in spite of the very impure Si available at that time. High purity Si only became available much later. A very detailed and accurate investigation of the phase diagram was made by Smith [19,20] in 1928 and 1929. He developed a thermal analysis method which resulted in very clear and sharp peaks. At that time the hcp phase was thought to be part of the fcc-(Cu) solid solution, resulting in a rather strange shape of that phase field. Otherwise, the phase

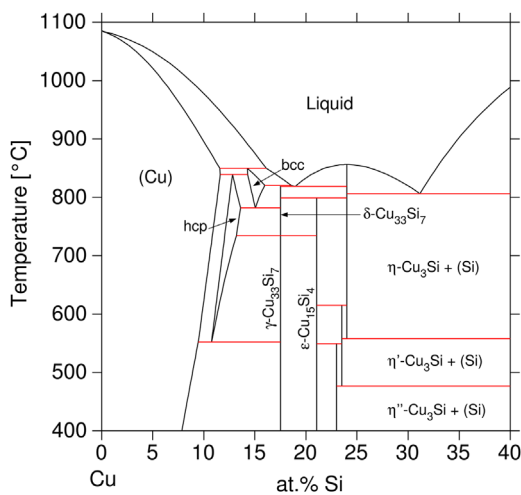


Fig. 1. Cu-rich part of the Cu–Si phase diagram calculated with the present thermodynamic description.

diagram is close to the currently accepted phase diagram. The ϵ -Cu₁₅Si₄ phase was found somewhat later by Iokibe [21], who also found a second transition of the η -Cu₃Si phase, and by Arrhenius [22]. The existence of two transitions of the η -Cu₃Si phase was confirmed by Mima and Hasegawa [23], who investigated the phase field of the η -Cu₃Si phases (η , η' and η'') and their transitions in some detail. The hcp phase was first identified by Sautner [24] and the phase field was investigated in detail by Smith [25] and by Andersen [26]. The most accurate data for the (Cu) solvus are provided by Andersen [26] using X-ray diffraction (XRD). The phase diagram was recently investigated again by Sufryd et al. [1], confirming previous results with some smaller modifications. It has been questioned if the ϵ -Cu₁₅Si₄ phase is a stable phase in the Cu–Si system [4] and this is discussed in detail by Sufryd et al. [1] concluding that it is stable. It is often not found in as solidified samples since it forms slowly and does not form directly from the liquid phase. In diffusion couples ϵ -Cu₁₅Si₄ and γ -Cu₃₃Si₇ are only found after extended annealing and detailed microscopic investigation [27] since they grow orders of magnitude slower than Cu₃Si. Sufryd et al. [1] also found δ -Cu₃₃Si₇ and γ -Cu₃₃Si₇ to both have narrow solid solution ranges centred around 17.5 at% Si. This means that the composition of γ -Cu₃₃Si₇ is shifted to slightly higher Si content than previously accepted [13,20]. The (Si) liquidus for compositions above 40 at% Si has only been measured by Rudolfi [17] and by Matsuyama [28] in good mutual agreement. Considering that the melting temperature of pure Si from [28] only differs by 6 K from the currently accepted value the data can be considered sufficiently accurate in spite of their age. With the exception of the lower transitions of the Cu₃Si phase (η' -Cu₃Si/ η'' -Cu₃Si) all invariant equilibria are known to within about ± 2 K.

The solubility of Cu in (Si) is very small, even at high temperature, but since it is of interest for semiconductor applications it has been measured a number of times [29–33]. All measurements are in good agreement except the measurement by [32], which is somewhat too low, and the lowest temperature point by [29], which is too high. Cu shows a high rate of diffusion in (Si) and is found to dissolve interstitially [30], but no crystallographic details are given.

Table 1

Phases in the Cu–Si and Al–Cu–Si systems. The reference refers to the crystal structure of the phase.

Phase	Prototype	Pearson symbol	Space group	Model	Database name	Ref.
(Cu), fcc, α	Cu	<i>cF4</i>	<i>Fm-3m</i>	(Al,Cu,Si)	FCC_A1	[13]
hcp, κ	Mg	<i>hP2</i>	<i>P6₃/mmc</i>	(Al,Cu,Si)	HCP_A3	[13]
bcc, β	W	<i>cI2</i>	<i>Im-3m</i>	(Al,Cu,Si)	BCC_A2	[13]
γ -Cu ₃₃ Si ₇ , Cu ₅₆ Si ₁₁	β -Mn	<i>cP20</i>	<i>P4₁32</i>	Cu ₃₃ Si ₇	CU33SI7_A13	[13]
δ -Cu ₃₃ Si ₇	–	<i>tP*</i>	?	Cu ₃₃ Si ₇	CU33SI7_HT	[14]
ϵ -Cu ₁₅ Si ₄	Cu ₁₅ Si ₄	<i>cI76</i>	<i>I-43d</i>	Cu ₁₅ Si ₄	CU15SI4_D86	[16]
η -Cu ₃ Si (ht), Cu ₁₉ Si ₆	–	<i>hR*</i>	<i>R-3m</i>	Cu _{0.76} Si _{0.24}	CU3SI_HT	[66]
η' -Cu ₃ Si (it)	η' -Cu ₃ Si	<i>hR9</i>	<i>R-3</i>	Cu _{0.765} Si _{0.235}	CU3SI_MT	[66]
η'' -Cu ₃ Si (lt)	–	<i>oC*</i>	?	Cu _{0.77} Si _{0.23}	CU3SI_LT	[66]
(Si)	C	<i>cF8</i>	<i>Fd-3m</i>	(Al,Si)(Cu,Va)	DIAMOND_A4	[13]
α_2 -AlCu ₃	long-period superstructure based on Al ₃ Ti and Au ₃ Cu	–	–	Al _{0.23} Cu _{0.77}	ALCU3_D022	[9]
γ_2 -Al ₄ Cu ₉ , γ_0	Cu ₅ Zn ₈	<i>cI52</i>	<i>I-43m</i>	Cu ₄ Cu ₆ (Al,Cu,Si) ₁₆	AL4CU9_D82	[9]
γ_1 -Al ₄ Cu ₉	Al ₄ Cu ₉	<i>cP52</i>	<i>P-43m</i>	Cu ₄ Cu ₆ (Al,Cu,Si) ₁₆	AL4CU9_D83	[9]
δ -Al ₅ Cu ₈ , Al ₂ Cu ₃ , Al ₁₇ Cu ₃₃	Al ₅ Cu ₈	<i>hR52</i>	<i>R3m</i>	Al ₅ Cu ₈	AL5CU8	[9]
ϵ_1 -(Al,Cu) (ht)	?	?	?	(Al,Cu,Si)	BCC_A2	[9]
ϵ_2 -AlCu _{2-x} (lt)	InNi ₂	<i>hP6</i>	<i>P6₃/mmc</i>	(Al,Cu)Cu	ALCU_B82	[9]
ζ_1 -Al ₉ Cu ₁₁ (ht), Al ₃ Cu ₄	–	<i>hP42</i> or <i>oF88</i>	<i>P6₃/mmm</i> or <i>Fmm2</i>	(Al,Cu) ₉ Cu ₁₁	AL9CU11	[9]
ζ_2 -Al ₉ Cu ₁₁ (lt), Al ₃ Cu ₄	Al ₉ Cu ₁₁	<i>oI24</i>	<i>Imm2</i>	(Al,Cu) ₉ Cu ₁₁	AL9CU11	[9]
η_1 -AlCu (ht)	–	<i>oP16</i> or <i>oC16</i>	<i>Pban</i> or <i>Cmmm</i>	(Al,Cu)Cu	ALCU_ETA_1	[9]
η_2 -AlCu (lt)	AlCu	<i>mC20</i>	<i>C2/m</i>	Al _{0.48} Cu _{0.52}	ALCU_ETA_2	[9]
θ -Al ₂ Cu	Al ₂ Cu	<i>tI12</i>	<i>I4/mcm</i>	Al ₂ (Al,Cu)	AL2CU_C16	[9]
(Al), fcc	Cu	<i>cF4</i>	<i>Fm-3m</i>	(Al,Cu,Si)	FCC_A1	[9]

Note: As short-hand notation the greek letters as given above are used for the phases in the Al–Cu system. This is consistent with the notation in [10]. For the phases in the Cu–Si system greek letters with a subscript “S” are used.

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