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Phase equilibria in the system Au–Cu–Si and structural characterization of the new compound $Au_{5\pm x}Cu_{2\pm x}Si$

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ABSTRACT

The ternary Au–Cu–Si system was investigated by means of powder X-ray diffraction (XRD) for phase identification, scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) for microstructures and chemical compositions, light optical microscopy (LOM), and differential thermal analysis (DTA) for the determination of thermal effects. Three isothermal sections were constructed at 250 °C, 400 °C and 650 °C. A new ternary compound τ, $Au_{5\pm x}Cu_{2\pm x}Si$, was identified and its crystal structure was determined by means of single crystal X-ray diffraction. It adopts a new crystal structure type in space group *Pnma*, Pearson symbol *oP*32 and shows a composition range between $Au_{5.6}Cu_{1.4}Si$ and $Au_{4.4}Cu_{2.6}Si$ at 250 °C. Lattice parameters were found to vary between $a = 9.64–9.50$ Å, $b = 7.61–7.64$ Å and $c = 6.90–6.89$ Å from the Au-rich to the Au-poor composition limit. Three vertical sections, at 10 and 30 at.% Si and at 10 at.% Cu, were constructed based on DTA data and four invariant ternary phase reactions were identified. A partial ternary reaction scheme (Scheil diagram) and a partial liquidus projection are given.

1. Introduction and literature review

The binary system Au–Si shows a very deep eutectic point (363 °C at 18.6 at.% Si), many hundred degrees below the melting points of Au (1064 °C) and Si (1414 °C) [1]. Such extreme stabilization of the liquid phase towards low temperatures is very rare and it has attracted considerable attention from the fundamental point of view as well as for a number of technical applications. Several metallic glasses have, for instance, been reported based on Au–Cu–Si alloys; among them Au–Cu–Si–Ag–Pd alloys have showed good processability, high corrosion resistance, good mechanical properties and an excellent wear and scratch resistance, making them a highly suitable candidate for jewelry applications [2–4]. Au–Si based alloys have also been of interest in the field of nanotechnology, being subject for extensive research in catalyzed growth of Si nanowires or nanotubes from gold nanoparticles *via* the so-called vapor–liquid–solid (VLS) mechanism [5–10]. The reason for this interest is because of their potential compatibility in silicon-based integrated circuit technology. A third field of interest concerns soldering processes for joining applications, *e.g.* in highly loaded microelectromechanical systems or optoelectronic devices, which have not been investigated extensively up to now. Studies for the related Au–Ge alloys, however, show that such applications may be quite promising [11]. For Au–Si alloys, Tiensuu et al. reported on the application of eutectic Au–Si for assembling three-dimensional Si based microelectromechanical devices with average fracture stresses of up to 65 MPa [12].

The above mentioned applications and the development of new technologies involving Au–Si alloys require a deep knowledge of the underlying phase diagrams of Au–Si–X ternary or even higher order systems. For joining applications, Cu is an alloying element of particular interest, as this metal is among the most commonly used metallization layers in electronics. The current work is therefore devoted to an experimental investigation of phase equilibria in the ternary Au–Cu–Si system. A brief literature review of the current knowledge on ternary Au–Cu–Si and the limiting binary systems is given below.

All three binary subsystems (Au–Cu, Cu–Si and Au–Si) are generally well known have been assessed by Okamoto and Massalski [1]. The Au–Cu phase diagram show a continuous fcc (Cu-type) solid solution with a melting point minimum at 44 at.% Cu and 910 °C. The formation of several low temperature phases at Au_3Cu, AuCu and $AuCu_3$ stoichiometry has been reported at temperatures between 410 and 240 °C [1]. The Cu–Si phase diagram is more complex, exhibiting numerous phases in the Cu-rich part of the system which was re-investigated recently [13]. Cu shows a large solubility for Si

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Table 1
Experimental phase compositions and cell parameters of selected samples for the isothermal sections at 250 °C, 400 °C and 700 °C determined in the present study.

Sample comp./at.%	Annealing/°C	XRD		EDX/at.%		
		Phase	Lattice parameter/Å	Si	Cu	Au
$Au_{45}Cu_{10}Si_{45}$	250	Si	$a = 5.4292$	99.9	0	0.1
		τ	$a = 9.6451$, $b = 7.6133$, $c = 6.8957$	10.6	18.0	71.4
		(Au,Cu)	$a = 4.0256$	0	6.9	93.1
$Au_{40}Cu_{30}Si_{30}$	250	Si	$a = 5.4281$	99.9	0.1	0
		τ	$a = 9.4714$, $b = 7.5893$, $c = 6.7546$	11.0	28.7	60.3
		γ	$a = 6.5627$	14.4	44.8	40.8
$Au_6Cu_{64}Si_{30}$	250	η	$a = 4.0781$, $c = 7.3655$	23.6	72.0	4.2
		γ	$a = 6.3455$	18.6	65.5	16.0
		Si	$a = 5.4272$	–[a]	–[a]	–[a]
$Au_{48}Cu_{44}Si_8$	250	(Au,Cu)	$a = 3.9108$	0.9	48.6	50.5
		γ	$a = 6.5613$	14.3	45.8	39.9
		τ	$a = 9.5038$, $b = 7.6394$, $c = 6.8897$	9.7	34.1	56.2
$Au_{20}Cu_{10}Si_{70}$	250	τ	$a = 9.4855$, $b = 7.5918$, $c = 6.7629$	11.8	29.7	58.5
		Si	$a = 5.4295$	100	0	0
$Au_7Cu_9Si_{83}$	250	Si	$a = 5.4316$	100	0	0
		γ	$a = 6.5420$	17.1	47.8	35.1
$Au_7Cu_9Si_{83}$	250	Si	$a = 5.4286$	99.4	0.6	0
		η	$a = 4.0658$, $c = 7.3439$	24.3	72.9	2.8
$Au_{66}Cu_{26}Si_8$	250	τ	$a = 9.5665$, $b = 7.5749$, $c = 6.7904$	10.7	25.9	63.4
		(Au,Cu)	$a = 3.9731$	0	28.3	71.7
$Au_{40}Cu_{40}Si_{20}$	400	Si	$a = 5.4282$	100	0	0
		γ	$a = 6.5790$	14.7	45.6	39.7
		L		16.7	29.1	54.2
$Au_5Cu_{33}Si_{62}$	400	Si	$a = 5.4284$	99.7	0.3	0
		γ	$a = 6.3829$	19.3	64.5	16.1
		η	$a = 4.0890$, $c = 7.3747$	23.8	70.3	5.9
$Au_{20}Cu_{40}Si_{40}$	400	Si	$a = 5.4283$	99.8	0.2	0
		γ	$a = 6.4649$	15.6	56.4	28.0
$Au_{37}Cu_{55}Si_8$	400	(Au,Cu)	$a = 3.8457$	3.9	54.2	41.9
		γ	$a = 6.4420$	14.9	59.0	26.1
$Au_8Cu_{71}Si_{21}$	400	γ	$a = 6.3429$	18.9	68.3	12.8
		η	$a = 4.0726$, $c = 7.3459$	23.5	73.7	2.8
$Au_1Cu_{77}Si_{22}$	400	ε	$a = 9.7225$	21.6	77.5	0.9
		η	$a = 4.0162$, $c = 7.3409$	24.0	74.8	1.2
$Au_{14}Cu_{56}Si_{30}$	650	γ	$a = 6.3922$	22.8	65.7	11.5
		L		18.2	54.6	27.2
		Si	$a = 5.4289$	99.7	0.3	0
$Au_6Cu_{74}Si_{20}$	650	γ	$a = 6.3020$	17.0	73.7	9.3
		η	$a = 4.0683$, $c = 7.3522$	23.1	74.0	2.9
$Au_8Cu_{79}Si_{13}$	650	γ	$a = 6.2792$	16.0	78.1	5.9
		(Au,Cu)	$a = 3.6858$	9.3	79.8	10.9

[a] Not determined due to fine microstructure.

up to 11 at.%, while the solubility of Si in Cu is negligible. The congruently melting η-phase (Cu_3Si) occurs in 3 different modifications. The cubic ε-phase, appears at approximately 78.5 at.% Cu and is formed in a peritectoidic reaction. Between 83 and 84 at.% Cu the two phases γ (stable below 740 °C) and δ (above 740 °C) are present. Two additional high temperature phases, β (bcc) and κ (hcp) are found around 85 and 87 at.% Cu, respectively. The Au–Si system is a simple eutectic system with its deep eutectic found at 18.6 at.% Si and 363 °C. The solubility of Si in Au has been determined metallographically to be less than 2 at.% Si. Amorphous phases have been reported in a wide composition range and the eutectic Au–Si alloy was the first ever discovered metallic glass [14], which can be formed even by simple water quenching.

Compared to the binaries, data on the ternary Au–Cu–Si system are insufficient and only a handful of minor studies have been published. Among them, a projection of the liquidus surface can be found based on some 20 samples measured by DTA in an atmosphere of dry nitrogen. Three fields of primary crystallization were reported; a solid solution of (Au,Cu) (fcc), Si and the intermediate phase η-Cu_3Si with a eutectic at $Au_{74.7}Cu_{6.1}Si_{19.2}$ at.% and 337 °C [15]. A later review article also added hypothetical ternary transition reactions to add up with data on the Cu–Si binary [16]. Another study used X-ray powder diffraction and metallography to determine the solubility limit of Si in the (Au,Cu) solid solution. A solubility of 1–4 at.% Si was suggested depending on the Au/Cu ratio [17]. Unknown diffraction lines were also found from the compound $Au_{37.5}Cu_{37.5}Si_{25}$ when investigating its glass forming abilities [18]. A more recent study focused on the phase formation during annealing of Au/Cu bilayers on Si substrates where the presence of Cu_3Si (η) and "Cu_4Si" (ε) at 200 °C and 400 °C was confirmed [19].

2. Experimental

A total number of 90 samples were prepared from copper wire (99.999%, Alfa Aesar), silicon lump (99.9999%, Alfa Aesar) and gold (Granulates Ögussa 99.99%, rod Alfa Aesar 99.99% and film Ögussa 99.9%). The copper was reduced with H_2 at 300 °C for approximately 3 h before use, in order to clean the surface from Cu_2O. The calculated amounts of the elements (total weight 500 mg) were weighed with a semi-micro balance with an accuracy of at least 0.5 mg. The occurring mass loss during the whole sample preparation procedure was usually below 1% and therefore not considered to affect the sample composition significantly.

Arc-melting was applied to melt the elements into a sample pill in an argon atmosphere using a water-cooled copper plate and zirconium as getter material. Sample pills were turned over and remelted two times for proper homogenization. The samples were