Short Communication

Ternary Phases in the System Au–Cu–Sn

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This short communication gives a brief account of three, hitherto unknown, genuine ternary phases in the Au–Cu–Sn system. A comprehensive report on the Au–Cu–Sn phase diagram (including aspects such as temperature and composition dependences of intermediate phases, tie-lines etc.) as well as reaction kinetic features for some of the phases concerned will be published in due course. The study of the Au–Cu–Sn system is part of a program on ternary tin systems aimed at various goals; these include the fundamental nature of crystal growth in tin flux melts, and more applied aspects such as the reaction between soft solder and metals. In addition, tin phases often provide challenging characterization problems for metallography, X-ray diffraction etc.

When the present program was planned and started, only two rather peripheral studies[1,2] on the Au–Cu–Sn system were available. Shortly before the present report was concluded a third paper[3] came to hand which deals with low-temperature diffusion of Sn into Au–Cu alloys. The composition of two new ternary phases was reported: $Au_{25}Cu_{55}Sn_{20}$ and $Au_{33.3}Cu_{33.3}Sn_{33.3}$. These compositions belong to the phase regions B and C, respectively, in the present paper.

Samples were made by melting (heated at 1100–1200 °C for ca. 1 min under vigorous shaking) appropriate amounts of 99.95 % Au (K. A. Rasmussen), 99.9 % Cu (J. T. Baker) and 99.98 % Sn (E. Merck) in sealed, evacuated silica-glass tubes. This initial heat treatment was concluded by quenching the samples from the molten state into ice water. Most of the samples were afterwards annealed at 360 °C and in some cases also at various other temperatures. The homogeneity, composition and structural state of the samples at room temperature were examined by powder X-ray (Guinier) diffraction, metallography, scanning electron microscopy (SEM), density measurements and differential thermal analysis (DTA). For details of the experiments and documentation of results reference is made to the forthcoming comprehensive report[4] on our findings.

The isothermal section of the Au–Cu–Sn phase diagram at 360 °C shown in Fig. 1 includes the three genuine ternary phases of the system. For want of a suitable rational notation we have adopted the notation A, B and C. As also seen from the illustration most of the binary phases of the Au–Sn and Cu–Sn systems extend into the ternary region.

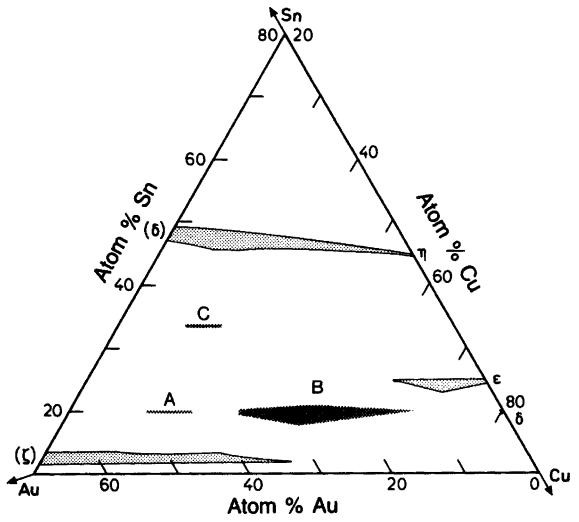

Fig. 1. Isothermal portion of the Au–Cu–Sn phase diagram at 360 °C. A, B and C refer to genuine ternary phases. Notations for binary phases (of which most extend into the ternary region) correspond to those for the binary systems.

Phase A comprises 20 atom % Sn, but has an appreciable range of homogeneity with respect to Au and Cu. At 360 °C this phase is stable between the $Au_{43}Cu_{37}Sn_{20}$ and $Au_{49}Cu_{31}Sn_{20}$ (viz. 43–49 atom % Au). However, phase limits are very susceptible to temperature, the homogeneity range extending to $Au_{15}Cu_{65}Sn_{20}$ at 550 °C. Phase A is quenchable, and powder X-ray diffraction diagrams obtained from quenched samples at room temperature are indexed (cf. the data for $Au_{200}Cu_{600}Sn_{200}$ in Table 1) on a b.c.c. unit cell. The unit cell dimension varies linearly with the atom % Au from a = 912.1(5) pm for $Au_{15}Cu_{65}Sn_{20}$ to a = 948.4(6) pm for $Au_{48}Cu_{32}Sn_{20}$. The pycnometric density of 11.20 g cm^{-3} for $Au_{200}Cu_{600}Sn_{200}$ (quenched from 550 °C) shows that the unit cell comprises 52 (51.6 according to the density) atoms. It will later be documented that the crystal

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Table 1. Powder data for ternary Au–Cu–Sn phases.

Phase A[a]			Phase B[b]			Phase C[c]				
I/I_0	d/pm	$h^2+k^2+l^2$	I/I_0	d/pm	$h^2+k^2+l^2$	I/I_0	d/pm	h	k	l
3	291	10	6	471	2	15	389	1	0	1
6	265	12	6	384	3	20	323	0	0	4
7	245.3	14	29	298	5	3	296	1	0	3
100	216.4	18	17	271.9	6	55	288	1	1	0
5	187.4	24	100	221.9	9	30	263	1	1	2
5	180.2	26	71	210.5	10	22	218.3	1	0	5
8	153.1	36	25	200.7	11	100	215.1	0	0	6
2	148.9	38	6	177.9	14			1	1	4
4	135.4	46	6	156.9	18	45	203.7	2	0	0
4	132.6	48	9	148.8	20	8	180.3	2	1	1
5	129.9	50	5	141.9	22	35	172.3	2	0	4
6	125.0	54	6	133.1	25			1	1	6
16	113.1	66	14	130.5	26	6	168.2	1	0	7
			5	128.1	27	8	161.5	0	0	8
			13	123.6	29	16	149.0	2	1	5
						20	147.9	2	0	6
						25	144.1	2	2	0
						3	140.9	1	1	8

[a] $Au_{200}Cu_{600}Sn_{200}$; quenched from 550 °C; b.c.c.; a = 918.4(3) pm. [b] $Au_{200}Cu_{600}Sn_{200}$; quenched from 360 °C; primitive cubic; a = 665.6(2) pm. [c] $Au_{330}Cu_{337}Sn_{333}$; body-centred tetragonal, a = 407.3(2), c = 1292.1(6) pm.

structure of phase A is of the γ-brass type (space group $I\bar{4}3m$).

Phase B also has a tin content of ca. 20 atom %, but for this phase there is observed a slight variation between 18 and 20.5 atom % Sn. For a fixed Sn content of 20 atom % the homogeneity range varies from $Au_{12}Cu_{68}Sn_{20}$ to $Au_{36}Sn_{44}Sn_{20}$ at 360 °C. The Au content can be increased further on turning to lower annealing temperatures ($Au_{45}Cu_{35}Cu_{20}$ at 300 °C). Phase B has the distinct character of a low-temperature phase relative to phase A.

Powder X-ray diffraction diagrams of samples of phase B are indexed on a primitive cubic unit cell. (The data for $Au_{200}Cu_{600}Sn_{200}$ presented in Table 1 may serve as an example.) For phase B the unit cell dimension also varies linearly with the atom % Au [from a = 661.3(5) pm for $Au_{15}Cu_{65}Sn_{20}$ to a = 682.3(5) pm for $Au_{45}Cu_{35}Sn_{20}$] for samples quenched from 300 °C. The pycnometric density of 11.39 g cm^{-3} for $Au_{20}Cu_{60}Sn_{20}$ corresponds to 20 (20.0 according to the density) atoms per unit cell. It will be shown later that the crystal structure of phase B is of the β-manganese type (space group $P2_13$).

Phase C contains basically equal atomic amounts of Au, Cu and Sn, but a certain variation of the Au/Cu ratio was observed. C is really a low-temperature phase which is stable below ca. 370 °C. X-Ray diffraction diagrams of phase C are indexed (cf. the data for $Au_{330}Cu_{337}Sn_{333}$ in Table 1) on a tetragonal body-centred unit cell. It will be shown later that the structure of phase C is of the La_2Sb type (space group $I4/mmm$). The unit cell dimensions of samples close to the phase limits at 360 °C are a = 407.3(2) and c = 1292.1(6) pm for $Au_{330}Cu_{337}Sn_{333}$ and a = 408.8(3) and c = 1300.7(6) pm for $Au_{370}Cu_{297}Sn_{333}$. [The pycnometric density of 11.68 g cm^{-3} for the former sample shows that the unit cell contains 12 (11.96 according to the density) atoms.]

Both γ-brass and β-manganese type structures belong to the class of so-called electron compounds. For the γ-brass structure the ideal electron-to-atom ratio e/a is 21/13 = 1.62, but a variation between 1.54 and 1.70 has been observed.[5] For the β-manganese type the ideal value is e/a = 3/2, but values of up to 1.75 have been found.[6] For valences of 1 for Au and Cu and 4 for Sn the phase region A, containing 20 atom % Sn, attains e/a = 1.60. The e/a ratio for phase region B varies from 1.54 (18 atom % Sn) to 1.62 (20.5 atom % Sn). Hence it seems safe to conclude that the ternary phases A and B are representative members of the class of electron compounds. For phase C e/a = 2.0, and there are indeed a number of electron compounds known[7] with e/a around this value. Possibly, this phase may also belong to the electron compounds.

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