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Determination of the thermodynamic properties of (gold+copper+silicon) melts by Knudsen-cell mass spectrometry

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Abstract

The excess Gibbs free energies in ternary alloys Au–Cu–Si have been determined by means of the high-temperature Knudsen-cell mass spectrometry, with the use of the 'ion-current ratio method' at constant molar fraction of silicon X_{Si}=0.1, 0.25, 0.50 and 0.75 at the mean temperature 1750 K. The minimum of the excess Gibbs free energy of formation of liquid ternary alloys is located at X_{Si}=0.25, X_{Cu}=X_{Au}=0.375 and amounts the value of -14.5 kJ mol^{-1}. This indicates a stabilisation of the ternary liquid phase which could be correlated with a better glass forming tendency. © 1998 Elsevier Science B.V.

Keywords: Gibbs energy; Metallic glasses; Silicon alloys; Knudsen-cell mass spectrometry

1. Introduction

The fact that the ability of the metal–nonmetal binary alloys to form metallic glasses by quenching the melt is correlated to the chemical order in the liquid has often been evoked in the literature [1]. It is known that the compositions of the melt quenched glasses are generally those at or near the low lying eutectic points [2]. The Au–Si binary system in which the existence of the chemical short-range order in the liquid state agrees with the presence in the phase diagram of a deep eutectic can be given as an example [3]. Then it is interesting to know how the addition in a liquid binary system A–B of a third element C modifies the equilibrium between the different interactions A–A, B–B and A–B and consequently the stability of the three-component system. The object of this investigation is to determine the Gibbs free energies of the formation in the ternary liquid alloys Au–Cu–Si by the Knudsen effusion method associated with a mass spectrometer. In previous studies performed by the same method [3,4], a coherent set of thermodynamic properties of the binaries Au–Si and Cu–Si has been published.

2. Experimental

Ternary alloys were prepared by mixing together weighed quantities of the pure metals (Koch-Light, mole fraction of metallic impurities $<10^{-3}$). The alloys were vaporized from an electron-bombardment-heated Knudsen cell with 1 mm diameter orifices and orifice-to-sample ratio of about 1/100. Experiments were made using a graphite outer crucible and a vitreous carbon (Carbone-Lorraine CV2500) inner crucible. The apparatus used for the measure-

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ments is a single-focusing mass spectrometer (Varian-Mat, type CH5, Bremen). The basic equations connecting the measured ionic intensity to the vapor pressure of each species inside the Knudsen cell are given in detail elsewhere [5]. An automatic optical pyrometer (Pyrophot II, The Pyrometer Instrument) was used to measure the brightness temperature of a hole drilled on the side of the graphite cell. Calibrations were performed in situ by observing the melting temperatures of Ag, Au, Pt and Pd.

In order to check that the vaporization process does not modify the initial mole fraction of the sample (especially for copper-rich alloys), the crucibles were systematically weighted before and after the experiment.

Numerous methods have been proposed in the literature to determine the activities by the Knudsen-cell mass spectrometry [6]. The method employed here, described for the first time in the case of Fe–Ni–Cr ternary system [7], consists of measuring only the ratio of the two ionic intensities at a given temperature and at constant value of the third constituent. In this case, no calibration of the apparatus versus the vapor pressure is needed.

For binary systems, the method presented in the following requires the measurement of the ionic intensity ratio $I_\mathrm{i}^+/I_\mathrm{j}^+$ of the components of the alloy ij for a molar fraction x_i and this in the whole concentration range. The activity coefficient γ_i is obtained from the following relationship:

$$\ln \gamma_{\mathrm{i},x_\mathrm{i}} = -\int_{x_\mathrm{i}=1}^{x_\mathrm{i}} x_\mathrm{j} d \ln \frac{I_\mathrm{j}^+ x_\mathrm{i}}{I_\mathrm{i}^+ x_\mathrm{j}} \tag{1}$$

This method avoids the determination of the sensitivity of the apparatus. The study of the variation of this ratio with the temperature leads to the molar enthalpy of formation following:

$$\Delta \bar{H}_\mathrm{i} = -R \int_{x_\mathrm{i}=1}^{x_\mathrm{i}} x_\mathrm{j} d \left[\frac{d \ln \frac{I_\mathrm{j}^+}{I_\mathrm{i}^+}}{d\left(\frac{1}{T}\right)} \right] \tag{2}$$

In a ternary system A–B–C, the exact differential of excess molar Gibbs free energy at constant P and T is given by:

$$dG^E = G_A^E dX_A + G_B^E dX_B + G_C^E dX_C \tag{3}$$

Since $\sum dX_\mathrm{i}=0$, it follows that at constant mole fraction of the component A:

$$(\partial G^E / \partial X_\mathrm{B})_{X_\mathrm{A}} = G_\mathrm{B}^E - G_\mathrm{C}^E \tag{4}$$

Substituting the activity coefficients and integrating from the A–C binary section to a ternary composition X_B lead to:

$$G_{X_B}^E = RT \int_{X_B=0}^{X_B} \ln \frac{\gamma_\mathrm{B}}{\gamma_\mathrm{C}} dX_\mathrm{B} + G^E_{\mathrm{A-C},\mathrm{X_A}} \tag{5}$$

In terms of the ion current ratio, it becomes:

$$G_{X_\mathrm{B}}^E = RT \int_{X_\mathrm{B}=0}^{X_\mathrm{B}} \ln \frac{I_\mathrm{B}^+ X_\mathrm{C}}{I_\mathrm{C}^+ X_\mathrm{B}} dX_\mathrm{B} + KX_\mathrm{B} + G^E_{\mathrm{A-C,X_A}} \tag{6}$$

The constant K, which includes calibration factors, is evaluated by carrying out the integration across to the A–B binary, thus:

$$K = \frac{1}{1 - X_\mathrm{A}} \left[(G^E)_{A-B,X_\mathrm{A}} - (G^\mathrm{E})_{\mathrm{A}-C,X_\mathrm{A}} - RT \int_0^{1-X_\mathrm{A}} \ln \frac{I_\mathrm{B}^+ X_\mathrm{C}}{I_\mathrm{C}^+ X_\mathrm{B}} dX_\mathrm{B} \right] \tag{7}$$

where I_B^+ and I_C^+ are the ionic intensities of the B and C species at constant X_A, respectively. Finally, the results can be obtained versus two reference systems: either in the binary section at constant X_C with reference to both limiting binaries or in the ternary alloy if the values of the limiting binary alloys are known.

3. Results

To our knowledge, the only thermodynamic data on the ternary liquid Au–Cu–Si system published up to now concern the enthalpies of formation measured by calorimetry [8] and data on the liquidus [9].

From Table 1, it can be readily seen from the comparison of the relative values of the ionic intensities of the three constituents, that the two ionic intensity method described above is well adapted to this ternary system. The tabulated measurements are carried out on the heating and cooling mode. In this study, the intensities of the following ions, $I_{63\mathrm{Cu}}$ and

Table 1
Values of the ionic intensities $I_{28\mathrm{Si}}$, $I_{63\mathrm{Cu}}$ and $I_{197\mathrm{Au}}$ versus temperature (heating and cooling) at $X_{\mathrm{Si}}=0.25$, $X_{\mathrm{Au}}=0.202$ and $X_{\mathrm{Cu}}=0.548$

T/K	$I_{28\mathrm{Si}}$	$I_{63\mathrm{Cu}}$	$I_{197\mathrm{Au}}$
1340	–	0.002	–
1415	–	0.009	–
1464	–	0.022	0.0003
1517	0.00015	0.054	0.0006
1578	0.00030	0.135	0.00145
1630	0.00065	0.280	0.0031
1677	0.0013	0.515	0.0055
1724	0.0025	0.915	0.0123
1696	0.0021	0.675	0.00855
1669	0.00125	0.44	0.006
1637	0.0008	0.275	0.0036
1584	0.00045	0.183	0.00235
1568	0.00025	0.111	0.00135

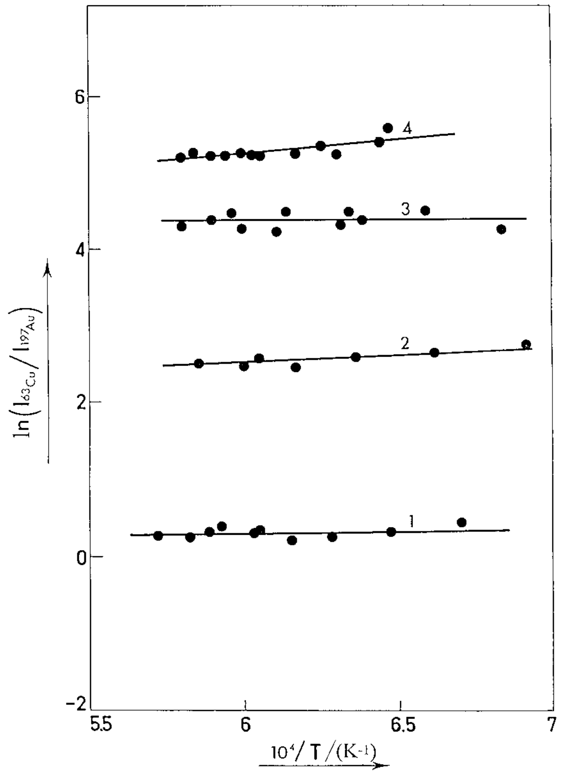

Fig. 1. Logarithm of the ratio of the ionic intensities of $I_{63\mathrm{Cu}}$ and $I_{197\mathrm{Au}}$ plotted against the reciprocal temperature, $1/T$, in 0.25 $X_{\mathrm{Si}}+0.75[(1-x)_{\mathrm{Au}}+x_{\mathrm{Cu}})]$ for the different mole fractions x_{Cu}.(1) 0.132; (2) 0.448; (3) 0.730; (4) 0.838.

$I_{197\mathrm{Au}}$ ionised with an energy of 12 eV, are recorded in the temperature range 1300 to 1800 K. Fig. 1 presents the logarithm of the ratio of the ionic intensities of $I_{63\mathrm{Cu}}$ and $I_{197\mathrm{Au}}$ plotted against the reciprocal temperature, $1/T$, in the case of 0.25 $X_{\mathrm{Si}}+0.75[(1-x)_{\mathrm{Au}}+x_{\mathrm{Cu}})]$ for the following mole fractions $x_{\mathrm{Cu}}=0.132$, 0.448, 0.730 and 0.838. The same sets of measurements are carried out on three additional binary sections defined by the constant value of $X_{\mathrm{Si}}=0.1$, 0.5 and 0.75. Results for the logarithm of the ratio, ln $[I_{63\mathrm{Cu}}x_{\mathrm{Au}}/I_{197\mathrm{Au}}x_{\mathrm{Cu}}]$, versus the molar fraction x_{Cu} in the binary sections defined by $X_{\mathrm{Si}}=0.1$, 0.25, 0.5 and 0.75 at $T=1750$ K, taken as a mean temperature, are displayed in Fig. 2. The coefficients A and B of the straight lines for four different binary sections at constant X_{Si}, ln $[I_{63\mathrm{Cu}}x_{\mathrm{Au}}/I_{197\mathrm{Au}}x_{\mathrm{Cu}}]=\mathrm{A}+\mathrm{B}x_{\mathrm{Cu}}$ at 1750 K are presented in Table 2. According to Eq. (6), the knowledge of the excess Gibbs free energies of the limiting binaries (in this case, Au–Si [3] and Cu–Si [4]) and the integration of this function

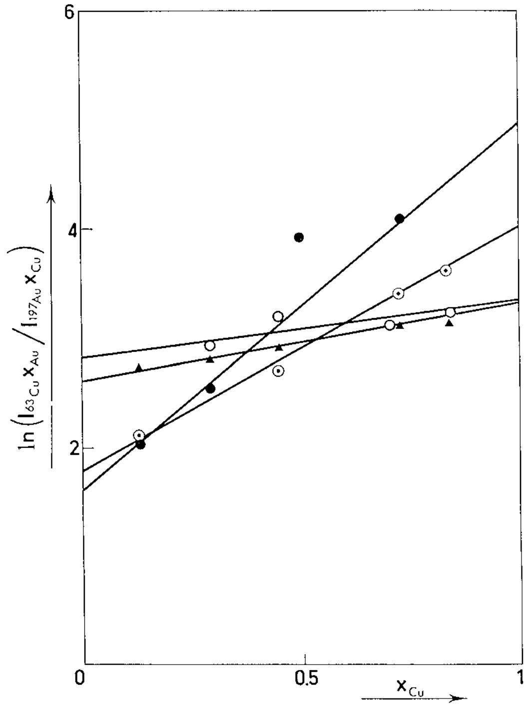

Fig. 2. Variation of the logarithm of the ratio ln $[I_{63\mathrm{Cu}}\,x_{\mathrm{Au}}/I_{197\mathrm{Au}}\,x_{\mathrm{Cu}}]$ versus the molar fraction x_{Cu} in the binary section at $T=1750$ K for different values of X_{Si}. (●): $X_{\mathrm{Si}}=0.1$; (⊙): $X_{\mathrm{Si}}=0.25$; (▲): $X_{\mathrm{Si}}=0.50$; (○): $X_{\mathrm{Si}}=0.75$.

Table 2
Coefficients A and B of the straight lines ln $[I_{63\mathrm{Cu}}x_{\mathrm{Au}}/I_{197\mathrm{Au}}x_{\mathrm{Cu}}] = \mathrm{A}+\mathrm{B}x_{\mathrm{Cu}}$ at 1750 K for four different mole fractions X_{Si}.

X_{Si}	A	B
0.1	1.6	3.67
0.25	1.8	2.93
0.5	2.6	1.4
0.75	2.76	2.24

across the corresponding binary section lead to the determination of the excess Gibbs free energies of formation of the ternary alloys. The variations of the integral excess Gibbs free energy, ΔG^E at 1750 K, at constant binary section for X_{Si}=0.1, 0.25, 0.50, 0.75 are plotted on the Fig. 3 versus the mole fraction. The corresponding numerical values are listed in Table 3. Lastly, the excess Gibbs free energies with reference to pure metals are plotted according to an iso-enthalpic representation in Fig. 4.

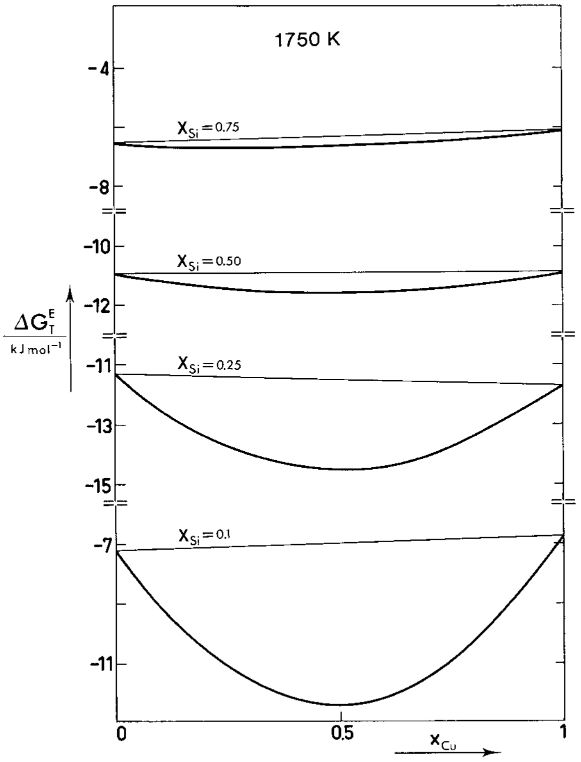

Fig. 3. Variation of the integral excess Gibbs free energy, ΔG^E, at T=1750 K, at constant binary section for X_{Si}=0.1, 0.25, 0.50, 0.75.

Table 3
Excess Gibbs molar free energies on the four binary sections at constant X_{Si} in the ternary alloys at 1750 K

x_{Cu}	X_{Cu}	X_{Au}	ΔG^E/J mol^{-1}
X_{Si}=0.1			
0	0	0.9	−7190
0.1	0.09	0.81	−9095
0.2	0.18	0.72	−10 570
0.3	0.27	0.63	−11 610
0.4	0.36	0.54	−12 220
0.5	0.45	0.45	−12 390
0.6	0.54	0.36	−12 130
0.7	0.63	0.27	−11 445
0.8	0.72	0.18	−10 320
0.9	0.81	0.09	−8770
1	0.9	0	−6780
X_{Si}=0.25			
0	0	0.750	−11 360
0.1	0.075	0.675	−12 475
0.2	0.150	0.600	−13 350
0.3	0.225	0.525	−13 990
0.4	0.300	0.450	−14 385
0.5	0.375	0.375	−14 540
0.6	0.450	0.300	−14 460
0.7	0.525	0.225	−14 135
0.8	0.600	0.150	−13 575
0.9	0.675	0.075	−12 770
1	0.750	0	−11 730
X_{Si}=0.5			
0	0	0.50	−10 920
0.1	0.05	0.45	−11 150
0.2	0.10	0.40	−11 325
0.3	0.15	0.35	−11 450
0.4	0.20	0.30	−11 525
0.5	0.25	0.25	−11 550
0.6	0.30	0.20	−11 520
0.7	0.35	0.15	−11 445
0.8	0.40	0.10	−11 315
0.9	0.45	0.05	−11 135
1	0.50	0	−10 905
X_{Si}=0.75			
0	0	0.250	−6580
0.1	0.025	0.225	−6630
0.2	0.050	0.200	−6600
0.3	0.075	0.175	−6675
0.4	0.100	0.150	−6665
0.5	0.125	0.125	−6635
0.6	0.150	0.100	−6585
0.7	0.175	0.075	−6515
0.8	0.200	0.050	−6420
0.9	0.225	0.025	−6310
1	0.250	0	−6180

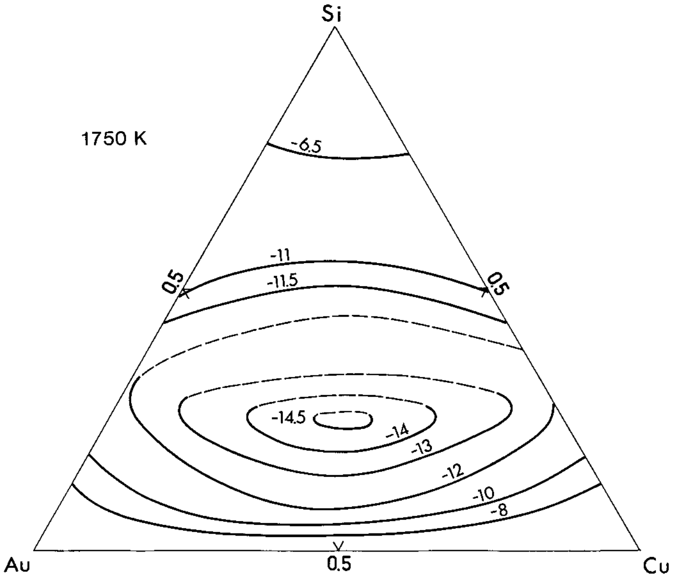

Fig. 4. Iso-excess Gibbs free energies of formation at T=1750 K with reference to pure gold, copper and silicon liquid metals in kJ mol^{-1}.

The following remarks can be noted:

–the excess Gibbs free energies of formation of the ternary alloys are negative in the whole experimental composition range at 1750 K,

–the curves are symmetrical versus the equimolar fraction of the binary alloys Au–Si and Cu–Si,

–the minimum is shifted towards metal-rich (Au or Cu) range and is located at X_{Si}=0.25, X_{Cu}=X_{Au}=0.375 and the value of ΔG^E amounts -14.5 kJ mol^{-1}.

The corresponding excess Gibbs free energies of the minima are -11.76 kJ mol^{-1} at x_{Si}=0.35 for Au–Si alloys and -12.2 kJ mol^{-1} at x_{Si}=0.33 for Cu–Si alloys at the same temperature indicating a negative ternary effect. From these results, a stabilisation of the ternary liquid phase is pointed out; in terms of the integral Gibbs free energy values, this effect is enhanced due to the negative contribution of the ideal term. It suggests a lowering of the range of thermal stability of the ternary liquid which could be correlated with a better glass forming tendency.

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