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THERMODYNAMIC BEHAVIOUR OF A COPPER-GERMANIUM-SILICON SOLDER ALLOY

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The thermodynamic behaviour of a Cu-80 at.%, Ge-17 at.%, Si-3 at.% solder alloy was investigated at 1200 K. Germanium activity, determined experimentally via the electromotive force (EMF) method, showed pronounced negative deviations from Raoult's law, indicating strong attractive liquid-phase interactions. Silicon activity, evaluated using CALPHAD modelling, revealed significant stabilisation. Consequently, copper activity, derived through Gibbs-Duhem integration, exhibited positive deviations from ideality. The experimental results show excellent agreement with theoretical estimates, providing new thermodynamic data that highlight the potential of Cu-Ge-Si alloys for high-temperature soldering in microelectronics.

Keywords: solder alloy, copper-germanium-silicon, thermodynamics, electromotive force method, CALPHAD modelling

1. Introduction

The development of lead-free soldering materials for high-temperature applications represents a major direction in microelectronics and power electronics, where thermal stability and interfacial compatibility are essential for the reliability of the joints. Classic tin-based alloys present significant limitations under these conditions, especially due to microstructural instability and the formation of brittle intermetallic compounds. Copper-rich alloys, alloyed with elements such as germanium and silicon, are considered promising alternatives. Germanium contributes to improving wettability and modifying phase equilibria, whilst silicon

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plays an important role in stabilising metal-semiconductor interfaces and limiting unwanted reactions.

Although the thermodynamic properties of the Cu-Ge and Cu-Ge-Si systems have been extensively investigated at very high temperatures, the experimental data available in the intermediate temperature range are limited. In particular, information regarding the activities of the components in the liquid phase at approximately 1200 K is insufficient [1,2]. In this context, the present paper aims to determine the thermodynamic activities in the Cu80 at.% Ge17 at.% Si3 at.% alloy at 1200 K by the electromotive force method, verify the consistency of the data through the Crohen criterion, and correlate the results with the predictions of the CALPHAD modelling. The obtained results provide new relevant information for the design of soldering materials intended for high-temperature applications [3].

2. Methodology

The determination of the thermodynamic activities of germanium in the Cu80 at.% Ge17 at.% Si3 at.% alloy was carried out by the electromotive force (EMF) method, using an electrochemical cell with a reference electrode made of pure germanium and a working electrode represented by the investigated alloy. The solid electrolyte was ZrO_2 stabilised with Y_2O_3, chosen due to its high ionic conductivity and chemical stability at high temperatures. The electrical contact with the external circuit was made through platinum conductors. The cell was placed in a tubular electric furnace, capable of ensuring a stable thermal regime in the investigated temperature range. The working temperature, 1200 K, was kept constant during the measurements, and the electromotive force values were recorded after reaching thermodynamic equilibrium.

For the study of the composition's influence, the EMF determinations were performed for a series of alloys corresponding to germanium atomic fractions between 0.1 and 1.0, the latter representing the reference state. The thermodynamic activities were calculated based on Nernst's equation, using pure germanium as a reference at the same temperature. The internal consistency of the experimental data was verified by applying the Crohen criterion. The obtained values confirmed the reversibility of the electrode reaction and demonstrated the reliability of the EMF measurements [4].

The direct determination of silicon activity was not experimentally possible; this was evaluated indirectly by CALPHAD-type thermodynamic modelling, using Redlich-Kister parameters available in the literature. The copper activity was subsequently obtained by numerical integration of the Gibbs-Duhem relation, using the activities of germanium and silicon and imposing the reference condition for pure copper [4]. For this purpose, an electrochemical cell of the type: Ge (pure) | solid electrolyte | Cu-Ge-Si, represented in Figure 1.1, was constructed.

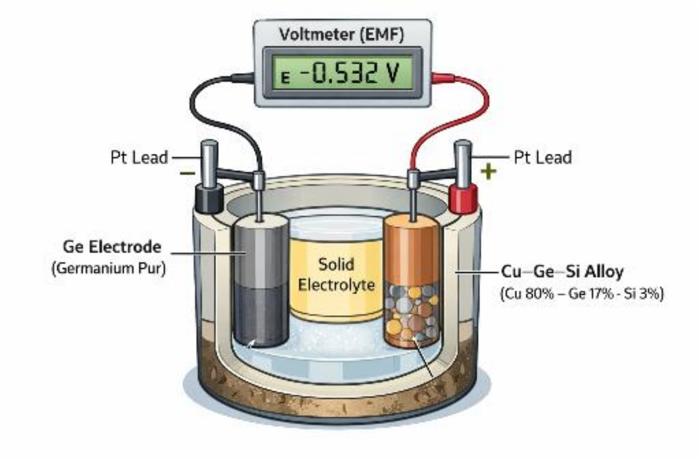

Fig. 1.1. Diagram of the electromotive cell used to determine the germanium activity in the Cu-Ge-Si alloy by the EMF method

3. Experimental Results and Discussion

The experimentally measured electromotive force values, the calculated thermodynamic activities, the logarithm of the germanium thermodynamic activity, as well as the calculated values of the Crohen criterion at the temperature of 1200 K are presented in Table 1.1.

Table 1.1

Experimentally measured electromotive force, thermodynamic activity of germanium, logarithm of activity, and Crohen criterion values at 1200 K

xGe	E(V)	E(mV)	aGe	lnaGe	CCrohen
0.0	0.000	0	0.000	-	-
0.1	0.0796	80	0.046	−3.079	38.7
0.2	0.0524	52	0.132	−2.028	38.7
0.3	0.0383	38	0.227	−1.482	38.7
0.4	0.0292	30	0.323	−1.130	38.7
0.5	0.0233	24	0.406	−0.901	38.7
0.6	0.0170	17	0.518	−0.658	38.7
0.7	0.0126	13	0.613	−0.489	38.8
0.8	0.0090	9	0.707	−0.347	38.6
0.9	0.0057	6	0.802	−0.221	38.8

The Crohen criterion is satisfied, as the ratio aGe −lnaGe remains practically constant and equal to the theoretical value nF/RT over the entire analysed range. Figure 1.2 shows the thermodynamic activity of germanium as a function of the molar fraction.

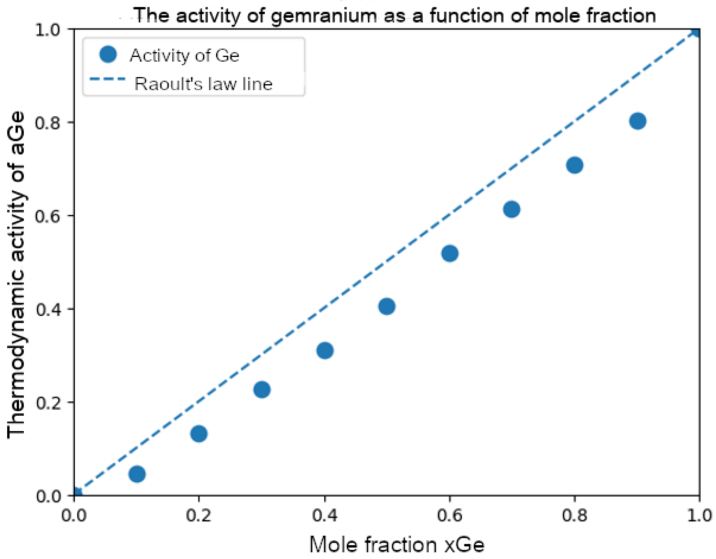

Fig. 1.2. Thermodynamic activity of germanium as a function of atomic fraction at 1200 K

Figure 1.2 shows the thermodynamic activity of germanium as a function of the molar fraction. The graph of the thermodynamic activity of germanium as a function of the molar fraction highlights its monotonic increase with composition, from values close to zero in the dilute range up to unity for pure germanium, according to the adopted reference state. The experimental points are systematically situated below the straight line corresponding to Raoult's law over the entire intermediate composition range, indicating negative deviations from the ideal behaviour. This evolution reflects the existence of attractive interactions between germanium and the metallic matrix, which determine the thermodynamic stabilisation of the solution and lead to activity values lower than the molar fraction. The continuity of the curve and the low dispersion of the points confirm the internal consistency of the data obtained by the EMF method. The observed trend is in agreement with the results reported in the literature and with the predictions provided by the CALPHAD modelling for copper-rich systems, supporting the validity of the experimentally determined values and their suitability for further uses in thermodynamic descriptions of the Cu-Ge-Si system.

To perform the comparison under the same temperature conditions, the experimentally determined germanium activity values at 1200 K were compared with a CALPHAD curve calculated at the same temperature, 1200 K, based on the published thermodynamic parameters for the Cu-Ge binary system. The Cu-Ge liquid phase is described in the literature by a substitutional solution model, and the excess Gibbs energy is expressed using a Redlich-Kister polynomial. Since direct experimental data for liquid-phase germanium activities at 1200 K are limited, the

CALPHAD curve at 1200 K was utilised as a thermodynamic reference for comparison.

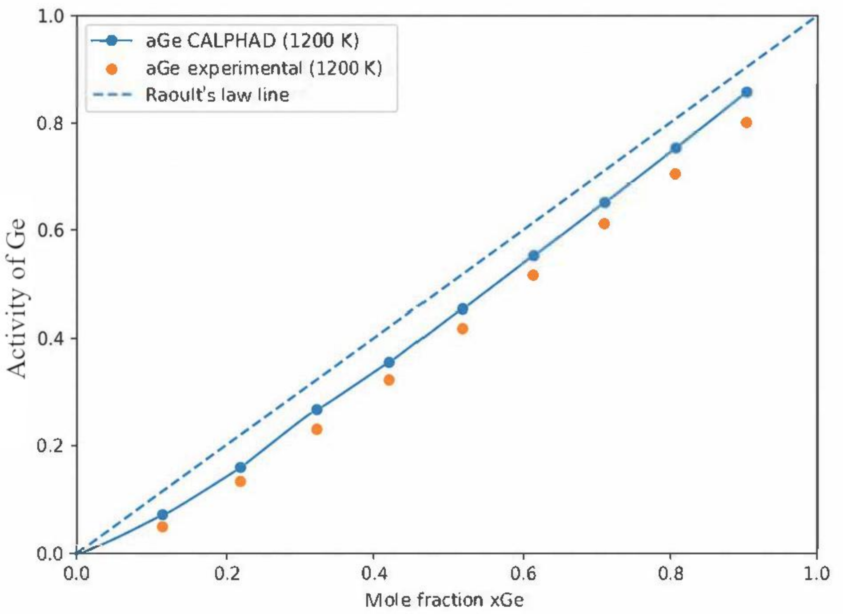

Fig. 1.3. Germanium activity: experimental data at 1200 K vs. CALPHAD values recalculated at 1200 K

The figure highlights a good agreement between the thermodynamic activity values of germanium determined at 1200 K and the values obtained through CALPHAD modelling recalculated at the same temperature, based on the thermodynamic parameters available in the literature for the Cu-Ge system. Both datasets exhibit a monotonically increasing variation with the germanium mole fraction and fall below the line corresponding to Raoult's law, indicating negative deviations from ideal behaviour.

The experimental values obtained at 1200 K are slightly lower than those estimated by CALPHAD at the same temperature. This difference can be attributed both to the effect of the ternary Cu-Ge-Si composition, through the presence of silicon in the investigated alloy, and to the limitations associated with modelling based on the binary Cu-Ge system. The numerical proximity of the points and the maintenance of the same variation trend confirm the thermodynamic consistency of the experimental results and support the validity of the adopted methodology.

Overall, the comparison shows that the data obtained in the present work are compatible with the thermodynamic description reported in the literature and can be utilised for subsequent thermodynamic modelling of the Cu-Ge-Si system. The activity coefficients of germanium, γ_{Ge}, were determined based on the fundamental relationship between activity and mole fraction:

$$aGe = \gamma Ge \cdot xGe.$$

The variation of the activity coefficient as a function of composition at 1200 K is illustrated in Fig. 1.4.

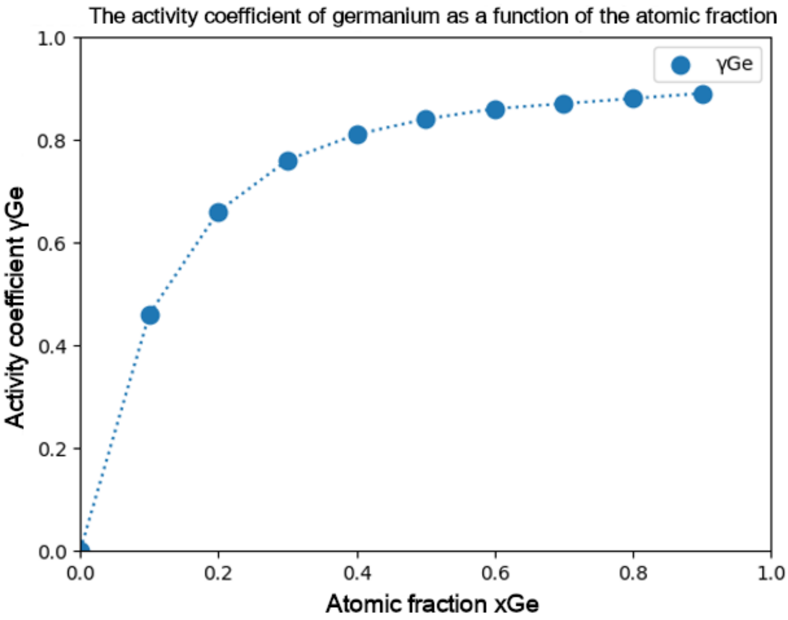

Fig. 1.4. Variation of the activity coefficient of germanium as a function of atomic fraction at 1200 K

The activity coefficient of germanium is sub-unitary over the entire investigated composition range, confirming the non-ideal character of the solution and the negative deviations from the ideal behaviour. The direct determination of the silicon activity by the EMF method is difficult experimentally, due to its tendency to form passive films and the low stability of ionic species in available electrolytes. Consequently, the silicon activity was evaluated indirectly by CALPHAD-type thermodynamic modelling, using Redlich-Kister parameters reported in the literature [6]. Based on the chemical potential thus obtained, the activity was calculated using the relationship:

$$\mu Si = \mu°Si + RT \ln(aSi) \tag{1.1}$$

where:

μSi is the chemical potential of silicon in the alloy, $\mu°Si$ is the chemical potential of silicon in the reference state, R is the gas constant, T is the absolute temperature.

For the analysed composition, the estimated values of silicon activity at 1200 K are of the order of 10^{-3}, respectively $aSi \approx 0.0025$, which indicates a pronounced stabilisation of silicon in the copper-rich matrix [11]. Given the low atomic fraction, the variation of silicon activity in the investigated composition range exerts a limited influence on the overall balance of chemical potentials.

The copper activity cannot be determined directly by the electromotive force (EMF) method, because it does not constitute the electrochemically active species in the cell used. Consequently, the values were obtained indirectly, by integrating the Gibbs-Duhem relation for the ternary Cu-Ge-Si system, using the experimentally determined germanium activities and the silicon activities estimated by the CALPHAD method [7]. The numerical integration was performed imposing the reference condition aCu=1 for pure copper.

$$xCu\ d(\ln aCu) + xGe\ d(\ln aGe) + xSi\ d(\ln aSi) = 0 \qquad (1.2)$$

The germanium activity is known from the electromotive determinations presented in the table, whilst for silicon, direct experimental data are not available [8]. However, the silicon content is low (xSi = 0.03), and at such dilute concentrations, the contribution of the term containing silicon is significantly smaller than that associated with the Cu-Ge pair [10]. Therefore, the usual approximation for dilute solutions is adopted:

$$d(\ln aSi) \approx 0 \qquad (3)$$

The activity values obtained by this method are represented graphically in Figure 1.5.

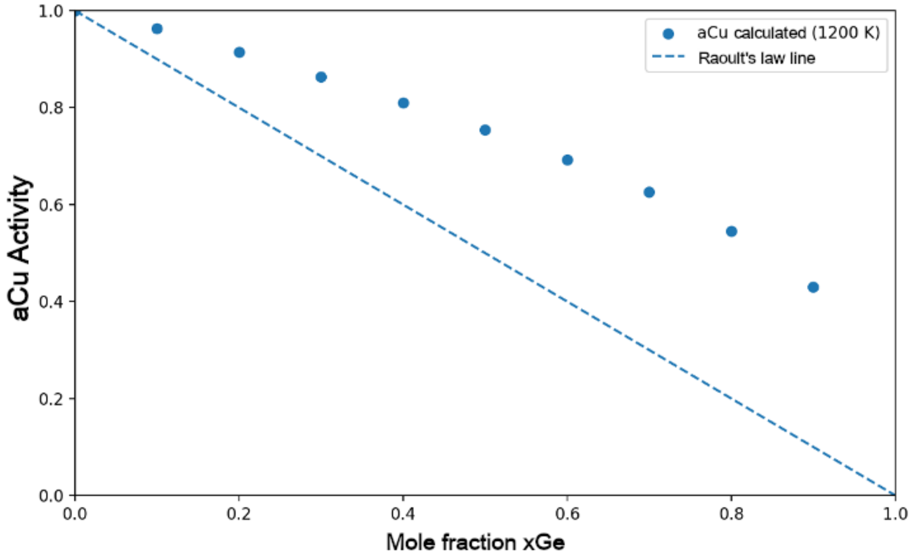

Fig. 1.5. Variation of copper activity as a function of atomic fraction at 1200 K

The copper activity values determined by integrating the Gibbs-Duhem relation must be analysed taking into account the method's sensitivity to uncertainties associated with the input data, especially in the range where one of the components is present in low concentrations. The integration procedure can lead to the propagation and amplification of numerical errors, but the overall trends remain physically relevant. Over the entire investigated composition range, the copper activity is situated below the values corresponding to the ideal behaviour described by Raoult's law. The progressive decrease of aCu with the increase in the germanium atomic fraction highlights a non-ideal behaviour with a negative deviation, specific to favourable chemical interactions between copper and the alloying elements.

This evolution is consistent with the pronounced thermodynamic stabilisation of germanium and silicon, reflected by their low activities. As a result of the constraint imposed by the Gibbs-Duhem relation, the decrease in the chemical potentials of the minority components determines the decrease in the activity of copper in the solution [13].

The obtained trend is compatible with the data reported in the literature and with the predictions provided by CALPHAD-type modelling for liquid copper-rich alloys at high temperatures. The activity coefficients of copper were calculated using relationship (1.2); their obtained value variation as a function of composition at 1200 K is illustrated in Fig. 1.6.

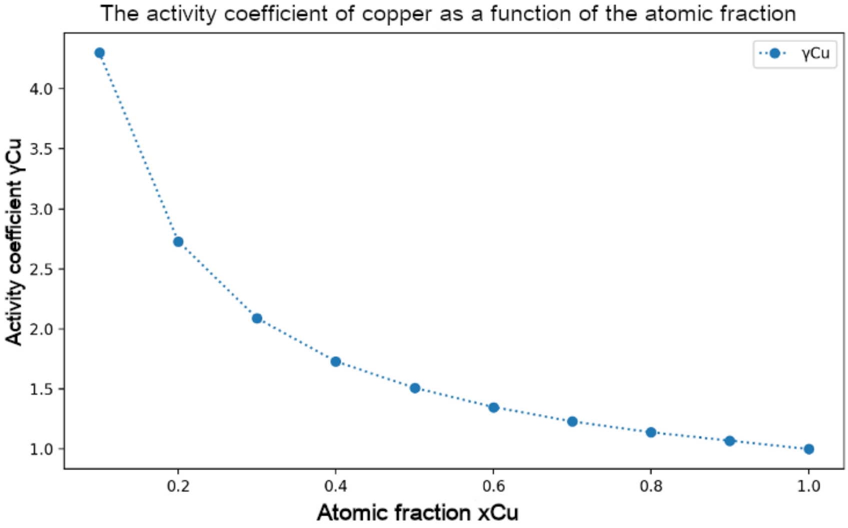

Fig. 1.6. Variation of the activity coefficient of copper as a function of atomic fraction at 1200 K

The graph of the variation of the copper activity coefficient as a function of the atomic fraction highlights clear deviations from the ideal behaviour, especially in the range of low copper concentrations. For high values of xCu, the activity coefficient remains close to unity, which indicates the predominance of Cu-Cu type interactions and a high thermodynamic stability of copper in the liquid solution.

As the atomic fraction of copper decreases, γCu increases progressively, reaching values of over 4 in the most dilute range investigated. This evolution reflects the accentuation of the non-ideal character of the liquid phase and highlights the fact that the environment rich in germanium and silicon becomes increasingly less favourable for the copper atoms. Consequently, the chemical potential of copper increases compared to the situation corresponding to an ideal solution.

The observed behaviour is consistent with the preferential stabilisation of germanium and silicon in the alloy. The decrease in the activities of these components determines, through the constraint imposed by the Gibbs-Duhem relation, the relative increase in the activity coefficient of copper.

These thermodynamic characteristics have direct practical implications for real soldering processes. The pronounced thermodynamic stabilisation of germanium and silicon, correlated with the increase in the chemical potential of copper, actively enhances the wetting behaviour of the solder on metallic substrates. Furthermore, this stabilisation limits excessive interfacial diffusion, effectively restricting the uncontrolled growth of brittle intermetallic compound (IMC) layers at the joint interface. By controlling these interfacial reactions, the thermodynamic stability directly correlates with improved mechanical properties and reliability of the resulting solder joints, ensuring their structural integrity and shear strength under thermal cycling in demanding microelectronic applications.

4. Conclusions

The experimental measurements carried out at 1200 K by the electromotive force method have highlighted the strongly non-ideal character of the liquid phase in the Cu-Ge-Si alloy. The germanium activity is systematically situated below the values predicted by Raoult's law, which indicates intense attractive interactions between germanium and the copper-rich matrix.

The validity of the experimental data is supported by the satisfaction of the Crohen criterion, which confirms the reversibility of the electrode reaction and the internal consistency of the EMF measurements.

The comparison with the predictions obtained by the CALPHAD modelling shows a very good agreement regarding the trend of activity variation with composition. The observed numerical differences are compatible with the influence of temperature, and the parallelism of the curves confirms the robustness of the methodology used.

Silicon exhibits extremely low activities ($\approx 10^{-3}$), which demonstrates a pronounced thermodynamic stabilisation in the alloy. As a result of the Gibbs-Duhem relation, this stabilisation leads to the relative increase of the activity and especially of the activity coefficient of copper, which becomes strongly greater than unity in the dilution range.

Although the Gibbs-Duhem integration can amplify numerical errors at low copper concentrations, the overall evolutions remain physically coherent and compatible with the literature.

From an application point of view, the pronounced stabilisation of germanium and silicon, correlated with the increase in the chemical potential of copper, favours the control of interfacial processes [11,12]. Under these conditions, the Cu-Ge-Si system emerges as a viable option for the development of soldering materials used at high temperatures in microelectronics and power electronics.

While the current investigation establishes a robust thermodynamic profile at 1200 K, extending this analysis to a broader temperature range (e.g., 1000 K to 1300 K) represents an important direction for future research. Evaluating the system across multiple isotherms will allow for the calculation of partial molar enthalpies and entropies of mixing, providing a more comprehensive understanding of the temperature dependence of the liquid-phase interactions and aiding in the optimisation of the alloy for specific industrial processing windows.

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