PHYSICAL REVIEW B **77**, 125426 (2008)

Characteristics of liquid-liquid immiscibility in Al-Bi-Cu, Al-Bi-Si, and Al-Bi-Sn monotectic alloys: Differential scanning calorimetry, interfacial tension, and density difference measurements

Ivan G. Kaban* and Walter Hoyer
Institute of Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany

(Received 22 October 2007; published 26 March 2008)

Phase separation in ternary monotectic alloys $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{90}X_{10}$ (X=Cu, Si, Sn; wt %) has been investigated. Experimental work included differential scanning calorimetry and measurements of the liquid-liquid (l-l) interfacial tension and difference in densities of coexisting phases. It is established that the interfacial tension between Al-rich and Bi-rich liquid phases increases when either Cu or Si is added and it decreases when Sn is added to the $\mathrm{Al}_{34.5}\mathrm{Bi}_{65.5}$ binary. This is related to the size of miscibility gap and is explained by increasing composition gradient across the (l-l) interface upon addition of either Cu or Si and its decreasing upon addition of Sn to the Al-Bi binary. The drop of interfacial tension in liquid $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{90}\mathrm{Sn}_{10}$ against $\mathrm{Al}_{34.5}\mathrm{Bi}_{65.5}$ is also caused by adsorption of Sn at the interface. Temperature dependences of the interfacial tension and density difference in the alloys studied follow a power law in reduced temperature (T_C-T) at approach of the critical point with exponents close to the values predicted by the renormalization group theory of critical behavior.

DOI: 10.1103/PhysRevB.77.125426 PACS number(s): 68.05.−n, 68.35.Rh, 64.60.F−

I. INTRODUCTION

Aluminum and its alloys with Cu, Mg, Si, or other elements have found wide application in building, automotive, and aerospace industry, especially due to their low specific weight, high corrosion resistance, and mechanical properties. At present, aluminum is the second most widely used metal after steel.[1] However, there are aluminum alloys, so-called monotectic alloys, which have been extensively studied during the last several decades but still are not utilized despite very promising properties and characteristics.[2,3] Perhaps, one of the most technically important applications of Al-based demixing alloys would be self-lubricating sliding bearings for automotive applications being capable to substitute for conventional bearing material Cu-Sn-Pb if a hard Al or Al-Cu/Si matrix with finely dispersed particles of a soft metal like Bi could be produced. However, by passing through the miscibility gap, monotectic alloys decompose into two liquid phases and consist of two layers after solidification on Earth. This makes them useless for the technical applications, where a homogeneous structure is required.

It has been supposed for a long time that demixing and layering during cooling of monotectic alloys are conditioned by a difference in densities of constituents and the gravity force. However, the first investigations under reduced gravity conditions revealed that gravity is not the only reason for the phase separation in monotectic alloys. A crucial role in the structure development here is played also by a droplet migration, called Marangoni motion, which is driven by the interfacial tension (IFT) gradients along the surfaces of droplets. Thus, the microstructure observed in cast monotectic alloys is a result of a complex interplay of nucleation, growth, Stokes and Marangoni motion, the interaction of the individual flow fields around the moving droplets, and their interaction with the solidification front and its morphology.[3] The gradients of interfacial tension are related to the temperature gradients in alloy during cooling and are thus unavoidable in the casting process. Therefore, an idea to compensate the Marangoni effect (at least in part) by gravity induced sedimentation in continuous casting process on Earth has appeared.[4] To define the required process parameters in terms of quantities, a knowledge of various physical properties such as the diffusion coefficient, viscosity, density and density difference of the coexisting phases, and the interfacial tension is required. These physical properties are also indispensable for the theoretical description and modeling of the structure development in monotectic alloys.[3,5]

Liquid-liquid (l-l) interfacial tension in binary Al-Bi monotectic system has been studied recently.[6] Investigation of the ternary Al-Bi-Cu, Al-Bi-Si, and Al-Bi-Sn alloys is important in a view of possible technical applications as bearings. Al-Cu, Al-Si, or Al-Sn is more interesting than pure Al for the matrix because of mechanical properties. Besides, ternary monotectic alloys may consist of more equilibrium phases than binaries, and this opens a window for generating entirely new monotectic microstructures.[7] Naturally, there is also a pure scientific interest to the impact of Cu, Si, or Sn on interfacial properties between Al-rich and Bi-rich liquid phases. Recently, we have investigated the composition dependences of IFT in ternary alloys $\mathrm{Al}_{34.5-x}\mathrm{Bi}_{65.5}\mathrm{Cu}_x$ and $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{100-x}\mathrm{Si}_x$ (wt %) near the monotectic temperature and temperature dependences of IFT in the alloys containing 11.25% Cu and 5% Si.[8,9] In the present work, we study three ternary alloys based on $\mathrm{Al}_{34.5}\mathrm{Bi}_{65.5}$ and containing 10 wt % of Cu, Si or Sn, respectively. Phase transitions are investigated by differential scanning calorimetry. Liquid-liquid interfacial tension and difference in densities of coexisting phases are measured by a tensiometric technique.

II. EXPERIMENTAL DETAILS

Al-Bi-Cu, Al-Bi-Si, and Al-Bi-Sn monotectic alloys studied in this work were prepared from high-pure Al, Bi, Cu, Si, and Sn (99.999%). Liquid-liquid interfacial tension $\sigma_{\alpha\beta}$ and difference in macroscopic densities of two coexisting liquid phases $\Delta\rho_{\alpha\beta}$ have been measured by a tensiometric method.

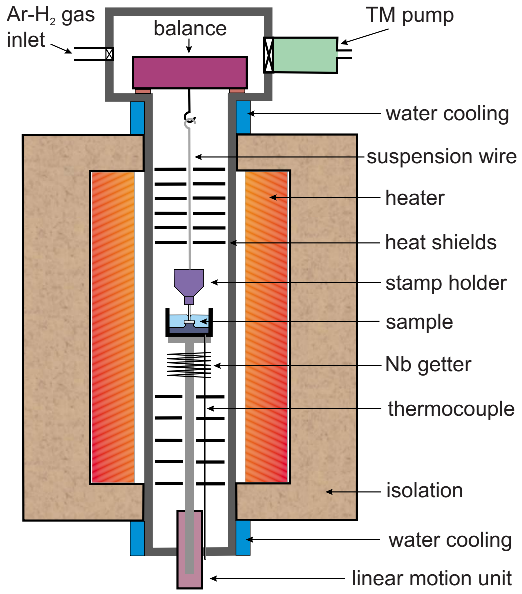

FIG. 1. (Color online) Scheme of the tensiometer.

Determination of the interfacial tension is based on a relation between the force exerted on the cylindrical alumina stamp detached to the liquid-liquid interface and the shape of the meniscus formed. The force caused by the meniscus in the vertical direction (which equals to the weight of liquid displaced by the meniscus) is measured experimentally, and the meniscus is modeled by numerical solution of the Young–Laplace equation of capillarity. The density difference $\Delta\rho_{\alpha\beta}$ is calculated from the buoyancy force exerted by the liquid phases on the stamp immersed. A detailed description of the measuring technique can be found in Refs. 6 and 8–12.

The measurements were performed in the tensiometer schematically shown in Fig. 1. Before heating, the chamber was evacuated better than 1×10^{-5} mbar and filled with a gas mixture of Ar-10H$_2$ (vol. %) with a total pressure of ~1 bar. A niobium getter was used to reduce the amount of oxygen that gets into the chamber through leaks during measurements. The heating system consisted of a concentric heater outside the chamber, power supply, and electronic temperature control device. The graphite crucible (5 cm inner diameter, 4 cm height) was moved by an ultrahigh vacuum manipulating system. The force exerted on the stamp was measured by a balance with an accuracy of ±1 mg. Relative error of the density difference is estimated to be 3%. The error of interfacial tension is 5%–8% near the monotectic temperature.

Phase transitions in the monotectic alloys were studied with the differential scanning calorimeter NETZSCH DSC 404 C. Temperature calibration of the calorimeter was performed using Ag, Al, Bi, Cu, Ge, In, Si, and Sn of high purity. Samples for calorimetric measurements (~170 mg of mass) were prepared by arc melting under argon atmosphere after initial vacuuming of the furnace up to about 10^{-3} mbar. Samples with total weight loss in preparation below 2 mg were chosen for the measurements. differential scanning-colorimetry (DSC) scans were obtained during nonisothermal heating and cooling with a rate of 20 K/min under an Ar flow. The heating-cooling cycles were carried out several times and with several different samples, and a good reproducibility of the peak positions (within ±5 K) has been observed.

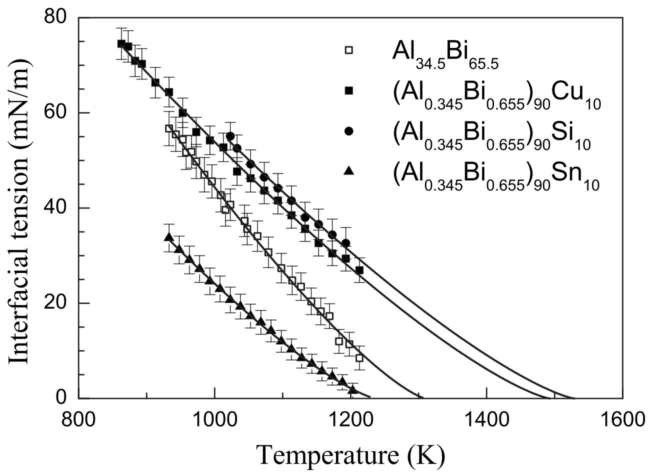

FIG. 2. Temperature dependences of the liquid-liquid interfacial tension in the alloys studied. (The data for $Al_{34.5}Bi_{65.5}$ binary are taken from Ref. 6.) The *lines* are fits to the experimental data: $\sigma_{\alpha\beta}=\sigma_0(1-T/T_C)^{1.3}$ mN/m (see text and Table I for details).

III. RESULTS

Figure 2 shows the experimental values of the (l-l) interfacial tension $\sigma_{\alpha\beta}$ in the ternary monotectic alloys $(Al_{0.345}Bi_{0.655})_{90}Cu_{10}$, $(Al_{0.345}Bi_{0.655})_{90}Si_{10}$, and $(Al_{0.345}Bi_{0.655})_{90}Sn_{10}$ (wt %) together with the respective data for liquid $Al_{34.5}Bi_{65.5}$ (wt %) taken from Ref. 6. The interfacial tension between Al-rich and Bi-rich liquid phases strongly depends on the kind of element added to the $Al_{34.5}Bi_{65.5}$ binary: $\sigma_{\alpha\beta}$ is remarkably increased over the whole temperature interval when either Cu or Si is added, and it is decreased when Sn is added.

Experimental temperature dependences of the density difference of coexisting liquid phases $\Delta\rho_{\alpha\beta}$ in $Al_{34.5}Bi_{65.5}$ binary[6] and $(Al_{0.345}Bi_{0.655})_{90}X_{10}$ ternary alloys are plotted in Fig. 3. It is seen from $\sigma_{\alpha\beta}(T)$ and $\Delta\rho_{\alpha\beta}(T)$ that the critical temperature T_C is also increased with addition of either Cu or Si, and it is decreased with Sn addition.

DSC cooling scans for $Al_{34.5}Bi_{65.5}$, $(Al_{0.345}Bi_{0.655})_{90}Cu_{10}$, $(Al_{0.345}Bi_{0.655})_{90}Si_{10}$, and $(Al_{0.345}Bi_{0.655})_{90}Sn_{10}$ are plotted in Fig. 4. The phase separation is manifested as a small step in exothermic direction in the DSC curves for all alloys studied except the alloy containing Si. The onset temperatures of phase separation T_{sep} and monotectic reaction T_M extracted from DSC curves are given in Table I. T_{sep} for $Al_{34.5}Bi_{65.5}$ alloy (critical composition as it follows from the phase diagram)[13] is just 2 K above the literature value of critical temperature, which indicates a very good agreement and, consequently, a reliability of the present DSC measurements.

IV. DISCUSSION

A. Immiscibility and interfacial tension

Interfacial tension, also called as the specific interfacial free energy, is a unique physical property that characterises

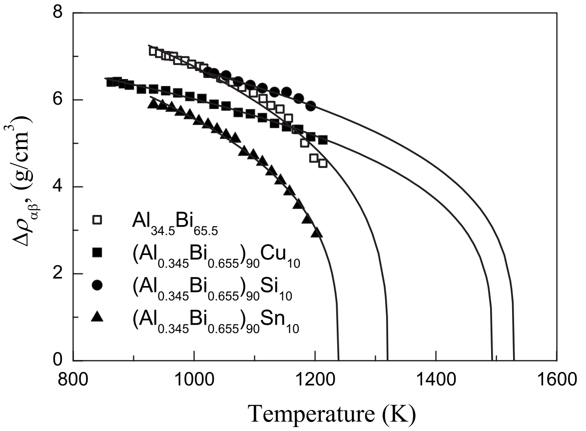

FIG. 3. Temperature dependences of the density difference $\Delta\rho_{\alpha\beta}$ in the alloys studied. (The data for $Al_{34.5}Bi_{65.5}$ binary are taken from Ref. 6.) The lines are fits to the experimental data: $\Delta\rho_{\alpha\beta}=\rho_0(1-T/T_C)^{\beta}$ g/cm^3 (see text and Table II for details).

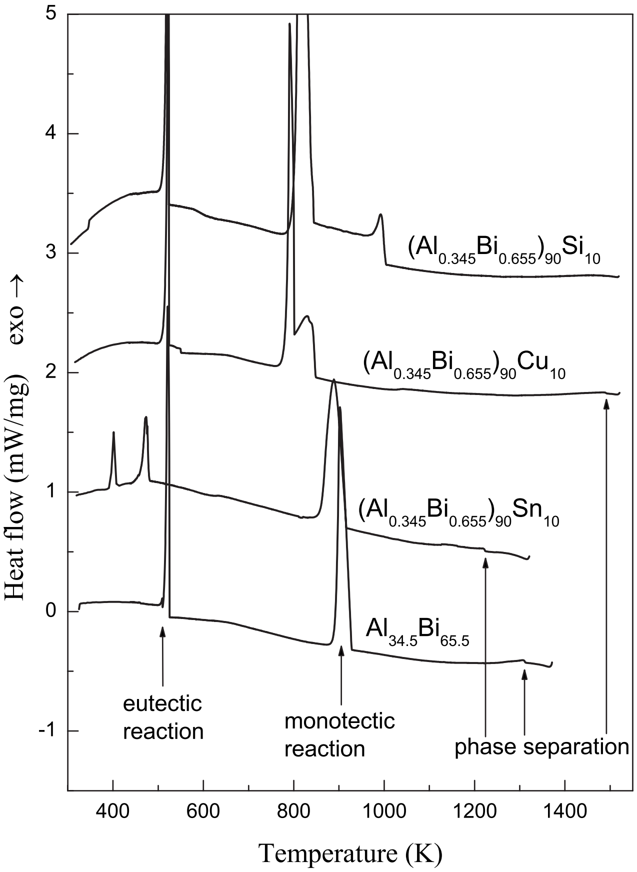

FIG. 4. DSC curves obtained at 20 K/min cooling rate.

an interface between two coexisting phases.[14–16] It is thermodynamically defined as the difference, per unit area of interface, between the free energy of the whole system with the interface and the free energy of a homogeneous system, which could be formed by the same atoms with the same chemical potentials. Hence, IFT can be calculated by the methods of statistical theromodynamics if an appropriate model is chosen. Cahn and Hilliard[15] applied the van der Waals model of diffusive interfaces[14] and obtained the following expression for IFT at a flat interface between phases α and β:

$$\sigma_{\alpha\beta}=N_V\int_{-\infty}^{+\infty}[\Delta f(c_i)+\kappa(dc_i/dx)^2]dx. \tag{1}$$

Here, N_V is the number of molecules per unit volume, c_i is the mole fraction of one of the two components, and κ is a gradient energy coefficient associated with the gradient of composition dc_i/dx. $\Delta f(c_i)$ is regarded as a free energy referred to a standard state of an equilibrium mixture of α and β. For the calculations of (l-l) interfacial tension in the $Al_{34.5}Bi_{65.5}$ binary, we refer to our recent paper.[8]

Hoyt[17] extended the Cahn–Hilliard theory[15] to multicomponent systems and derived the expression [Eq. (2)] for interfacial tension similar to Eq. (1),

$$\sigma_{\alpha\beta}=N_V\int_{-\infty}^{+\infty}\left[\Delta f(c_1,c_2,\ldots,c_{n-1})+\sum_{i}^{n-1}\sum_{j}^{n-1}\kappa_{ij}\nabla c_i\nabla c_j\right]dx, \tag{2}$$

where n stays for the number of components, $\nabla=\partial/\partial x$.

Following the theory, interfacial tension is a functional of the concentration profile(s) at the interface. According to Eqs. (1) and (2), the more smaller the composition variation across the interface is, the smaller will be the contribution of the gradient energy term to the IFT and vice versa. Obviously, the concentration profile across (l-l) interface depends (among other factors) on the composition of bulk phases and size of the miscibility gap. It is reasonable to expect a decrease of the concentration gradient with narrowing miscibility gap and its increase with widening miscibility gap. This suggests the change of (l-l) interfacial tension in the same direction.

Bi-Cu binary system has a metastable miscibility gap below liquidus, and Bi-Si binary is characterized by a very large miscibility gap.[13] Addition of either Cu or Si to the Al-Bi binary significantly enhances the liquid-liquid separation so that the miscibility region covers almost the entire concentration triangle in both Al-Bi-Cu (Refs. 18 and 19) and Al-Bi-Si (Refs. 20 and 21) ternary systems, and the critical temperature remarkably increases. Practically, all Cu (respectively Si) stays in the Al-rich phase, and the solubility of Al in Bi decreases rapidly with increasing Cu (Si) concentration. Thus, the increase of interfacial energy between Al-rich and Bi-rich liquid phases with addition either Cu or Si to the $Al_{34.5}Bi_{65.5}$ (Fig. 2) is explained by the reasons discussed above. The same arguments account for the smaller IFT between coexisting liquids in the ternary Al-Bi-Sn alloy against Al-Bi binary. Indeed, unlike Bi-Cu and Bi-Si, Bi and Sn form a simple eutectic system with unlimited solubility in the liquid state.[13] The sizes of the miscibility gap (both width and height) decrease remarkably when Sn is added to the Al-Bi binary.[7,19,22]

B. Adsorption at the interface

The above analysis shows the dependence of interfacial tension on bulk composition of coexisting liquids. It is also

TABLE I. (A) Phase separation temperature T_{sep} and monotectic temperature T_M extracted from the DSC cooling scans. Experimental uncertainty is ±5 K. (B) Temperature dependences of the liquid-liquid interfacial tension $\sigma_{\alpha\beta}$: the fits to the experimental data. T is the absolute temperature, T_C is the critical temperature, μ is the critical-point exponent, and σ_0 is a constant. Uncertainties are determined by the fitting.

	DSC experiment, cooling, 20 K/min		Fit $\sigma_{\alpha\beta}=\sigma_0(1-T/T_C)^{\mu}$ (mN/m)			
Alloy	T_M (K)	T_{sep} (K)	Fitting range (K)	T_C (K)	σ_0 (mN/m)	μ
$Al_{34.5}Bi_{65.5}$[a]	928	1312	933–1213	1310±4	290.6±3.9	1.30[b]
				1310[c]	288.1±8.9	1.29±0.02
$(Al_{0.345}Bi_{0.655})_{90}Cu_{10}$	849	1491	863–1213	1493±7	227.6±2.6	1.30[b]
$(Al_{0.345}Bi_{0.655})_{90}Si_{10}$	1004		1023–1193	1529±14	226.8±6.9	1.3[b]
$(Al_{0.345}Bi_{0.655})_{90}Sn_{10}$	902	1216	933–1203	1237±2	206.8±1.6	1.30[b]
				1238±5	208.7±9.4	1.31±0.04[d]

[a] Reference 6.

[b] $\mu=1.30$ is fixed by the fitting.

[c] $T_C=1310$ K is fixed.

[d] All parameters (σ_0, T_C, and μ) are free.

known that concentration of constituents at the interface differs from that in bulk phases due to a preferential accumulation of one species over the others. This phenomenon, denoted as interfacial adsorption or segregation, was firstly described by Gibbs.[23] He derived the adsorption equation which relates changes in interfacial energy $\sigma_{\alpha\beta}$ to corresponding changes in thermodynamic variables, such as temperature and chemical potential, and involves the excess quantities associated with the interface. The isothermal Gibbs adsorption equation as applied to the interface in a multicomponent system is[16,23,24]

$$d\sigma_{\alpha\beta}=-\sum_i \Gamma_i d\mu_i, \tag{3}$$

where μ_i is the chemical potential of the ith specie and Γ_i is the surface excess of component i per unit area. Thus, variation of the interfacial tension due to adsorption at the interface can be estimated if the concentration of components in the bulk and at the interface is known. Unfortunately, it is very difficult to determine the amount of adsorbed material at an interface directly. There exist a limited number of such experiments performed at solid-solid interfaces (e.g., segregation of gold at copper-silver interphase boundaries studied by the scanning Auger electron spectroscopy)[25] and at liquid-vapor interfaces (e.g., x-ray reflectivity investigations of the surface segregation in liquid metallic alloys by the Harvard X-Ray Group).[26] Grimm *et al.*[27] determined concentration profiles in the immiscible system water/acetic acid/toluene by means of a charge coupled device-camera, which captured the laser induced fluorescence from the components marked with a fluorophore. Investigations of the liquid-liquid interfaces in metallic mixtures are extremely difficult because of high temperatures and opacity. Huber *et al.*[28] managed to determine the structure of the liquid-liquid interface between Ga-rich bulk phase and Bi-rich wetting film in the monotectic Bi-Ga alloy by x rays and calculate the (l-l) interfacial tension.

Deficiency of the experimental data, on the one side, and technological importance and theoretical interest, on the other side, have advanced the theoretical modeling and computer simulation of the interfacial structure and segregation. In the literature, various thermodynamic, semiempirical, and empirical models of surfaces and interfaces can be found.[14–17,29–33]

Chatain and co-workers[34,35] suggested a simple criterion to estimate tensioactivity of a component C at the interface in a three-component system A-B-C by calculating the adsorption separately from A-rich (α) and B-rich (β) liquids. Only composition of bulk phases and partial excess free energies at infinite dilution are to be known in their approach. Tensioactivity of component C can be expressed by the parameter

$$\tau_{\alpha\beta}=\frac{K_{\alpha\beta}\tau_\alpha+\tau_\beta}{1+K_{\alpha\beta}}, \tag{4}$$

where τ_α and τ_β represent the changes of energy during adsorption of element C, respectively, from the volume of liquid α and liquid β to the interface. $K_{\alpha\beta}$ is a partitioning coefficient, which describes the distribution of component C (with concentration X_C) between liquid α and liquid β by infinite solution,

$$K_{\alpha\beta}=\left(\frac{X_C^\alpha}{X_C^\beta}\right)_{X_C\to 0}. \tag{5}$$

A negative value of $\tau_{\alpha\beta}$ corresponds to the segregation of component C at the interface between α and β liquid phases. The more negative is $\tau_{\alpha\beta}$, the more significant is the adsorption and the more distinctive is the drop of the interfacial tension $\sigma_{\alpha\beta}$. For positive values of $\tau_{\alpha\beta}$, the solute C will desorb from the interface.

We have determined with Eq. (4) the tensioactivity parameter $\tau_{\alpha\beta}$ for Al-Bi-Cu, Al-Bi-Si, and Al-Bi-Sn ternary systems. Partial excess free energies at infinite dilution were calculated from the excess Gibbs free energies for binary systems[36–40] forming a respective ternary system. It is found that $\tau_{\alpha\beta}/\mathrm{RT} \approx -2$ for Sn in the Al-Bi-Sn system at 933 K. Thus, the drop of interfacial tension observed in ternary $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{90}\mathrm{Sn}_{10}$ alloy as compared to the $\mathrm{Al}_{34.5}\mathrm{Bi}_{65.5}$ binary is caused not only by the decrease of miscibility gap width but also by adsorption of Sn at the (*l*-*l*) interface. The same has been concluded by Chatain *et al.*[34] for activity of Sn in ternary Zn-Pb-Sn monotectic system. Tensioactivity parameters for other ternary systems at 933 K are $\tau_{\alpha\beta}/\mathrm{RT} \approx 2$ for Cu in Al-Bi-Cu and $\tau_{\alpha\beta}/\mathrm{RT} \approx 4$ for Si in Al-Bi-Si. Positive values of $\tau_{\alpha\beta}$ are indicatives of increasing interfacial tension upon addition of either Cu or Si to the Al-Bi binary. These findings are consistent with the experimental observations (Fig. 2).

C. Temperature dependence of the interfacial tension

As the temperature in a two-phase liquid system increases, the interface between the coexistent phases thickens and becomes diffuse until, at the critical point, it disappears and two liquids merge into one homogeneous fluid. The liquid-liquid interfacial tension also decreases with increasing temperature and it vanishes at the critical point. The temperature dependence of interfacial tension can be described by the power law,

$$\sigma_{\alpha\beta} = \sigma_0 (1 - T/T_C)^{\mu}, \tag{6}$$

where σ_0 is a constant, T is the absolute temperature, T_C is the critical temperature, and μ is the so-called critical-point exponent. According to the classical theory of van der Waals[14] or the later work of Cahn and Hilliard[15] $\mu = 3/2$, while the renormalization group theory of critical behavior[16,41] gives $\mu = 1.26$. A review of critical-point phenomena can also be found in Refs. 42 and 43.

Critical-point exponent for (*l*-*l*) interfacial tension has been estimated on the base of experimental data rather extensively for nonmetallic mixtures. This is explained by the fact that IFT can be determined there practically until the critical point, as this was done by Guha *et al.*[44] for the system cyclohexane-acetonitrile by the capillary rise method, for example. The value of μ found in the majority of works on nonmetallic mixtures equals 1.26 within the experimental uncertainty.

To our knowledge, interfacial tension in liquid metallic systems with a miscibility gap has been measured in a wide temperature interval just in a few studies.[6,8–12,45] The values of critical-point exponent established are rather scattered. For example, Chatain *et al.*[45] found $\mu = 1.36$ for Ga-Pb monotectic system. Merkwitz and co-workers obtained $\mu = 1.19$ for Ga-Pb system[10,11] and $\mu = 1.45$ for Al-In system.[10,12]

We have shown earlier[6] that the experimental temperature dependence of the (*l*-*l*) interfacial tension for liquid $\mathrm{Al}_{34.5}\mathrm{Bi}_{65.5}$ is well described by Eq. (6) with $\sigma_0 = 289$ mN/m and $\mu \approx 1.3$. The critical temperature $T_C = 1310$ K from the Al-Bi phase diagram[13] was taken for the fit in Ref. 6. Also, $\sigma_{\alpha\beta}(T)$ for ternary alloys $\mathrm{Al}_{23.25}\mathrm{Bi}_{65.5}\mathrm{Cu}_{11.25}$, $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{95}\mathrm{Si}_5$, and $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{95}\mathrm{Sn}_5$ was established in recent studies[8,9] to follow the power law [Eq. (6)] with $\mu = 1.3$. Therefore, the same value of critical point exponent ($\mu = 1.3$) was applied by fitting the experimental values of IFT in the present work. Critical temperature T_C was a fitting parameter along with constant σ_0. Besides, in the case of $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{90}\mathrm{Sn}_{10}$, where the experimental data were obtained practically over the whole miscibility gap, all three parameters in Eq. (6)—σ_0, T_C, and μ—have been fitted simultaneously. The fitting curves are shown in Fig. 2 and the parameters are listed in Table I.

It is important to note that fitting the experimental data for ternary $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{90}\mathrm{Sn}_{10}$ alloy yields $\mu = 1.31 \pm 0.04$, which is close to the renormalization theory value ($\mu = 1.26$). Temperature interval studied experimentally was about half of the miscibility gap height for the alloys with Cu and Si. Thus, it was not possible to fit $\sigma_{\alpha\beta}(T)$ for this alloys with all free parameters in Eq. (6) with an acceptable accuracy. However, the experimental temperature dependences are very well described by function (6) if μ is set to be equal to 1.3.

Another interesting and important finding is that fitting both parameters (σ_0 and T_C) in Eq. (6) for the $\mathrm{Al}_{34.5}\mathrm{Bi}_{65.5}$ binary gives a critical temperature $T_C = 1310 \pm 4$ K which agrees with the phase diagram[13] as well as with our DSC measurement. A good agreement between T_{sep} (DSC) and T_C (IFT fit) is also observed for the $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{90}\mathrm{Sn}_{10}$ alloy. The difference of 22 K can be partly explained by experimental inaccuracy. It can also be a result of undercooling of the sample during DSC measurement. The coincidence of T_{sep} (1241 K) and T_C (1243 K) values for $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{90}\mathrm{Cu}_{10}$ alloy is obviously a casual result mainly related to a short temperature range of the measured IFT as compared to the height of miscibility gap. Unfortunately, we were not able to establish the phase separation temperature for $(\mathrm{Al}_{0.345}\mathrm{Bi}_{0.655})_{90}\mathrm{Si}_{10}$ alloy by DSC. We assume that also for this alloy, T_C determined by $\sigma_{\alpha\beta}(T)$ fit can be somewhat different from a real value.

D. Temperature dependence of the density difference

Similar to the (*l*-*l*) interfacial tension, difference in densities of coexisting phases $\Delta\rho_{\alpha\beta}$ in an immiscible system vanishes on approach to the critical point. If distance to the critical point is measured as the difference $T_C - T$, then

$$\Delta\rho_{\alpha\beta} = \rho_0 (1 - T/T_C)^{\beta}, \tag{7}$$

where ρ_0 is a constant and β is the critical-point exponent which equals $\frac{1}{2}$ in the classical (mean-field) approximation, and it is $\sim\frac{1}{3}$ in the renormalization theory.[16,42,43]

It has been shown in a number of experimental works that β equals $\frac{1}{3}$ within experimental error in nonmetallic immiscible systems. One of the best examples often cited is the experimental work of Thompson and Rice.[46] Density measurements in CCl_4-$\mathrm{C}_7\mathrm{F}_{16}$ system were performed to within $10^{-6} T_C$ there, and β was found to be 0.33 ± 0.02. Temperature dependences of the density difference in metallic monotectic systems have not been studied so extensively yet. The

TABLE II. Temperature dependences of the experimental density difference $\Delta\rho_{\alpha\beta}$ in the alloys studied: the fits to the experimental data. T is the absolute temperature, T_C is the critical temperature, β is the critical-point exponent, and ρ_0 is a constant (T_C was fixed during fitting). Uncertainties are determined by the fitting.

	Fit $\Delta\rho_{\alpha\beta}=\rho_0(1-T/T_C)^\beta$ (g/cm^3)			
Alloy	Fitting range (K)	T_C (K)	ρ_0 (g/cm^3)	μ
$Al_{34.5}Bi_{65.5}$[a]	923–1213	1310	10.68 ± 0.19	0.31 ± 0.01
$(Al_{0.345}Bi_{0.655})_{90}Cu_{10}$	863–1213	1493	8.30 ± 0.06	0.29 ± 0.01
$(Al_{0.345}Bi_{0.655})_{90}Si_{10}$	1023–1193	1529	9.12 ± 0.17	0.29 ± 0.02
$(Al_{0.345}Bi_{0.655})_{90}Sn_{10}$	933–1203	1237	9.51 ± 0.12	0.32 ± 0.01

[a] Reference 6.

data reported are very limited and scattered. Egelstaff and Ring[47] estimated the critical exponent for some metallic binaries from the coexistence curves and found a whole range of values for β: 0.3 for Ga-Pb, 0.35 for Ga-Tl, and 0.5 for Al-In and Ga-Hg. Later, Schürmann and Parks[48] determined the critical exponent β for Ga-Hg alloy of critical composition by resistivity measurements and found that it is 0.335 ± 0.005. Jost *et al.*[49] measured the density in liquid Li-Na mixture of critical composition and established that $\beta = 0.50 \pm 0.015$ as the temperature approaches T_C. We have found that the density differences in Ga-Pb and Al-In monotectic systems reported by Merkwitz and co-workers[10–12] are well described by Eq. (7) with critical exponent $\beta = 0.26 \pm 0.01$ and $\beta = 0.29 \pm 0.02$, respectively.

It order to prove which value of critical-point exponent is valid for metallic immiscible alloys studied in the present work, the experimental density differences were fitted with Eq. (7). The critical temperatures T_C extracted from the temperature dependences of interfacial tension (Table I) were taken for the fitting. The fits are shown in Fig. 3, while the values of critical-point exponent β and pre-exponential factor ρ_0 obtained are listed in Table II. The critical-point exponent β for binary $Al_{34.5}Bi_{65.5}$ and ternary $(Al_{0.345}Bi_{0.655})_{90}Sn_{10}$ alloys is found to be 0.31 ± 0.01 and 0.32 ± 0.01, respectively. For the other ternary alloys β is slightly lower: 0.29 ± 0.02. It should be mentioned again that the error of critical temperature obtained by fitting of $\sigma_{\alpha\beta}(T)$ for alloys containing Cu and Si is rather high because of a short temperature range where the experimental data are measured. Naturally, if the values of T_C for $(Al_{0.345}Bi_{0.655})_{90}Cu_{10}$ and $(Al_{0.345}Bi_{0.655})_{90}Si_{10}$ alloys would be higher than those taken for $\Delta\rho_{\alpha\beta}(T)$ fits plotted in Fig. 3 then the critical exponent β would also be larger. In general, we may say that the critical-point exponent β for all monotectic alloys studied in this work is very close to $\frac{1}{3}$—the value that follows from the renormalization theory.

V. SUMMARY

It is established experimentally that the liquid-liquid interfacial tension increases when either Cu or Si is added to the $Al_{34.5}Bi_{65.5}$ alloy and it is decreased when Sn is added. Also the critical temperature is increased with either Cu or Si additions and it is reduced with addition of Sn to the Al-Bi. Changes of the (l-l) interfacial tension in the systems studied can be related to the size of miscibility gap. If molecular miscibility decreases, the interfacial tension is increased and vice versa. This is explained by increasing (decreasing) composition gradient across the (l-l) interface when a third element is added to the Al-Bi binary.

The drop of interfacial tension observed in ternary $(Al_{0.345}Bi_{0.655})_{90}Sn_{10}$ alloy as compared to the $Al_{34.5}Bi_{65.5}$ binary is caused not only by the narrowing of miscibility gap but also by the adsorption of Sn at the (l-l) interface. It is shown that the tensioactivity of elements at the liquid-liquid interface in monotectic alloys can be predicted on the base of excess Gibbs free energies for binary systems forming a respective ternary system.

The temperature dependences of (l-l) interfacial tension in binary $Al_{34.5}Bi_{65.5}$ and ternary $(Al_{0.345}Bi_{0.655})_{90}Cu_{10}$, $(Al_{0.345}Bi_{0.655})_{90}Si_{10}$, and $(Al_{0.345}Bi_{0.655})_{90}Sn_{10}$ monotectic alloys are well described by the power function $\sigma_{\alpha\beta}=\sigma_0(1-T/T_C)^\mu$ with the critical-point exponent $\mu = 1.3$, which is close to the value ($\mu = 1.26$) predicted by renormalization theory. The difference in densities of coexisting phases $\Delta\rho_{\alpha\beta}$ in all alloys studied also follows the power law in reduced temperature at approach of the critical point with an exponent close to the value ($\frac{1}{3}$) of renormalization theory. The results of present study confirm that the values of critical-point exponents for metallic monotectic alloys do not depend on the chemical interactions.

ACKNOWLEDGMENTS

This study was supported by the German Research Foundation (DFG) in the Priority Programme "DFG-SPP 1120: Phase transformations in multi-component melts" under Grant No. HO 1688/8-2. We are indebted to Rainer Schmid-Fetzer, Joachim Gröbner, and Djordje Mirkovic for valuable information and discussions of phase equilibria in the monotectic systems.

---

*Author to whom correspondence should be addressed. ivan.kaban@physik.tu-chemnitz.de

[1] *Aluminium Handbook*, Fundamentals and Materials Vol. 1, 1st ed., edited by C. Kammer (Aluminium, Düsseldorf, 1999).

[2] B. Predel, J. Phase Equilib. **18**, 327 (1997).

[3] L. Ratke and S. Diefenbach, Mater. Sci. Eng., R. **15**, 263 (1995).

[4] B. Prinz and A. Romero, in *Immiscible Liquid Metals and Organics*, edited by L. Ratke (DGM-Informationsgesellschaft, Oberursel, 1993), p. 281.

[5] L. Ratke, S. Drees, S. Diefenbach, B. Prinz, and H. Ahllborn, in

Materials and Fluids Under Low Gravity, edited by L. Ratke, H. Walter, and B. Feuerbacher (Springer, Berlin, 1996), p. 115.

[6] I. Kaban, W. Hoyer, and M. Merkwitz, Z. Metallkd. **94**, 831 (2003).

[7] J. Gröbner and R. Schmid-Fetzer, JOM **57**, 19 (2005).

[8] W. Hoyer and I. Kaban, Rare Met. **25**, 452 (2006).

[9] I. Kaban, W. Hoyer, and M. Kehr, Int. J. Thermophys. **28**, 723 (2007).

[10] M. Merkwitz, Ph.D. thesis, TU Chemnitz, 1997.

[11] M. Merkwitz, J. Weise, K. Thriemer, and W. Hoyer, Z. Metallkd. **89**, 247 (1998).

[12] M. Merkwitz and W. Hoyer, Z. Metallkd. **90**, 363 (1999).

[13] T. B. Massalski, J. L. Murray, K. H. Bennet, and H. Baker, *Binary Alloy Phase Diagrams* (American Society for Metals, Metals Park, OH, 1986), Vol. 1.

[14] J. D. Van der Waals, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **13**, 657 (1894).

[15] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).

[16] S. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).

[17] J. J. Hoyt, Acta Metall. Mater. **38**, 1405 (1990).

[18] U. R. Kattner and B. P. Barton, J. Phase Equilib. **13**, 629 (1992).

[19] D. Mirkovic, J. Gröbner, and R. Schmid-Fetzer, Spring Meeting of the German Physical Society Condensed Matter Division, Berlin, 2008, presentation MM 2.1 (unpublished).

[20] Yu. Sun-Keun, Ph.D. thesis, Universität Stuttgart, 1994.

[21] J. Gröbner (private communication).

[22] R. Schmid-Fetzer, in *Ternary Alloys*, edited by G. Petzow and G. Effenberg (VCH, Weinheim, 1990), Vol. 3, p. 438.

[23] J. W. Gibbs, *The Scientific Papers of J. Willard Gibbs*, Thermodynamics Vol. 1 (Dover, New York, 1961), p. 219.

[24] B. Widom, Physica A **95**, 1 (1979).

[25] S. A. Dregia, P. Wynblatt, and L. Bauer, J. Vac. Sci. Technol. A **5**, 1746 (1987).

[26] V. S. K. Balagurusamy, R. Streitel, O. G. Shpyrko, P. S. Pershan, M. Meron, and B. Lin, Phys. Rev. B **75**, 104209 (2007).

[27] A. Grimm, K. Mühlfriedel, and K.-H. Baumann, Chem. Eng. Technol. **74**, 1582 (2002).

[28] P. Huber, O. Shpyrko, P. S. Pershan, B. Ocko, E. DiMasi, and M. Deutsch, Phys. Rev. B **68**, 085409 (2003).

[29] M. Hillert, Acta Metall. **9**, 525 (1961).

[30] E. Defay and I. Prigogine, *Surface Tension and Adsorption* (Longmans, London, 1966).

[31] P. Wynblatt, A. Saul, and D. Chatain, Acta Mater. **46**, 2337 (1998).

[32] C. Serre, D. Chatain, P. Wynblatt, M. Muris, and M. Bienfait, Metall. Mater. Trans. A **32**, 2851 (2001).

[33] G. B. McFadden and A. A. Wheeler, Proc. R. Soc. London, Ser. A **458**, 1129 (2002).

[34] D. Chatain, C. Vahlas, and N. Eustathopoulos, Acta Metall. **32**, 227 (1984).

[35] D. Chatain and N. Eustathopoulos, J. Chim. Phys. Phys.-Chim. Biol. **81**, 587 (1984).

[36] A. J. McAlister, Bull. Alloy Phase Diagrams **5**, 247 (1984).

[37] R. W. Olesinski and G. J. Abbaschian, Bull. Alloy Phase Diagrams **6**, 359 (1985).

[38] J. Niemelä, G. Effenberg, K. Jack, and P. J. Spencer, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **10**, 77 (1986).

[39] B.-J. Lee, C.-S. Oh, and J.-H. Shim, J. Electron. Mater. **25**, 983 (1996).

[40] N. Saunders, in *COST-507: Thermochemical Database for Light Metal Alloys*, edited by I. Ansara, A. T. Dinsdale, and M. H. Rand (European Communities, Luxemburg, 1998), p. 28; J. Gröbner, H. L. Lukas, and F. Aldinger, *ibid*, p. 79; S. G. Fries and H. L. Lukas, *ibid*, p. 81.

[41] S. Fisk and B. Widom, J. Chem. Phys. **50**, 3219 (1969).

[42] H. E. Stanley, *Introduction to Phase Transitions and Critical Point Phenomena* (Oxford University Press, Oxford, 1987).

[43] C. Domb, *Critical Point: A Historical Introduction to the Modern Theory of Critical Phenomena* (Taylor & Francis, London, 1996).

[44] S. Guha, V. C. Vani, Y. Jayalaxmi, A. Kumar, B. R. Gopal, and E. S. R. Gopal, J. Solution Chem. **16**, 691 (1987).

[45] D. Chatain, L. Martin-Garin, and N. Eustathopoulos, J. Chim. Phys. Phys.-Chim. Biol. **79**, 569 (1982).

[46] D. R. Thompson and O. K. Rice, J. Am. Chem. Soc. **86**, 3547 (1964).

[47] P. A. Egelstaff and J. W. Ring, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, I. S. Rowlinson, and C. S. Rushbrooke (North-Holland, Amsterdam, 1968), p. 253.

[48] H. K. Schürmann and R. D. Parks, Phys. Rev. Lett. **26**, 367 (1971).

[49] J. Jost, D. Heydt, J. Spehr, and H. Ruppersberg, J. Phys.: Condens. Matter **6**, 321 (1994).