

LIQUID-LIQUID INTERFACIAL TENSION IN IMMISCIBLE BINARY Al-BASED ALLOYS

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The liquid-liquid interfacial tension in the demixing Al-Bi, Al-In and Al-Pb systems has been measured in a wide temperature interval. The absolute values of the interfacial tension have also been calculated with the help of different models. A systematic difference between the experimental and calculated values at the monotectic temperature by a factor of ~1.5 is observed. The temperature dependencies of the interfacial tension in the investigated systems are shown to be well described by the models of Cahn-Hilliard and Chatain-Eustathopoulos.

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1. Introduction

Aluminium-based monotectic alloys are intensively investigated during last decades as possible new bearing materials. The idea is to obtain aluminium matrix with finely distributed particles of *e.g.* indium, bismuth or lead as a soft phase with lubricating function. However this is still far from the practical application because the miscibility phenomenon poses problems during solidification [1,2].

The liquid-liquid interfacial energy effects play a crucial role in solidification processes of the monotectic alloys. Therefore, for understanding, description, and mathematical modelling as well as for prediction of the structure development during solidification in immiscible systems the liquid-liquid interfacial tension and its temperature dependence are to be known.

In this work we present the experimental results of the liquid-liquid interfacial tension in the Al-Bi, Al-In, Al-Pb monotectic systems determined with a sophisticated force method. Besides, the interfacial tension in these systems is calculated with the help of different models. The correlation between the theoretical and experimental values is studied. This can help to estimate the absolute values of the interfacial tension and its temperature dependence in the systems where the experimental measurements are very difficult or even impossible.

2. Experimental

The interfacial tension in the Al-Bi, Al-In and Al-Pb monotectic systems was studied by the force method described in [3, 4]. Due to a special construction of the alumina stamp submerging into the melts the influence of the free surface of the Al-rich liquids on the experimental data was significantly reduced. The weight of the meniscus formed by the stamp at the interface was measured as a function of the stamp's height. After subtraction of the buoyancy force and geometrical corrections for limited sample volume and shape of the stamp, the volume of the meniscus in dependence on the height of the contact line was determined. On the other hand, the meniscus was modelled for different values of the capillary constant $a = \sigma_{\alpha\beta}/\Delta\rho_{\alpha\beta}g$ ($\sigma_{\alpha\beta}$ is the interfacial tension

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between phases α and β , $\Delta\rho_{\alpha\beta}$ is the difference of the densities of the two liquids, and g is the gravitational acceleration). From comparison of the experimental and theoretical volume curves the capillary constant was determined, and then the interfacial tension was calculated.

The measurements have been performed in a vertical high temperature chamber (1 m of length and 0.1 m of inner diameter) made from a special alloy. The crucible was moved by an ultrahigh vacuum manipulating system. The weight of the stamp was measured by a balance with an accuracy of ± 1 mg.

The samples were prepared from an Al rod and granules of Bi, In and Pb of very high purity (99.999 %). Before heating the chamber was evacuated to better than 1×10^{-5} mbar and then filled with a gas mixture of Ar-10 % H_2 with a total pressure of 1 bar. Nb getter was used additionally for reducing the oxygen that may get into the chamber through leakage during measurements.

3. Results and discussion

The liquid-liquid interfacial tensions for the Al-Bi, Al-In and Al-Pb systems in dependence on the temperature are shown in Fig. 1. The experimental values are fitted with the power function

$$\sigma_{\alpha\beta} = a \cdot (1 - T/T_c)^\delta \quad (1)$$

where a is a constant and δ is the so-called critical exponent. For a practical use such analytical expression is very convenient. However the problem consists in determination of the values a and δ . The classical theory of critical phenomena [5,6] gives $\delta = 1.5$ and the renormalisation theory [7] suggests $\delta = 1.26$. Which value of δ satisfies a given system could be decided only by comparison with experiment. This is well seen from Fig. 1. Besides, the experimental data are required for estimation of the constant a . Since measurements of the interfacial tension are not always possible, a theoretical method, which yields correct values of the interfacial tension (at least at the monotectic temperature), is needed.

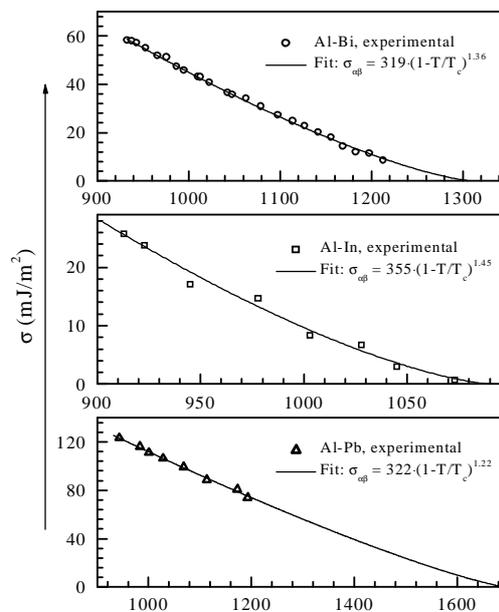


Fig. 1. Liquid-liquid interfacial tension in the Al-Bi, Al-In and Al-Pb systems.

Antonow suggested [8] that liquid-liquid interfacial tension $\sigma_{\alpha\beta}$ between two liquids α and β can be calculated as the difference between their surface tensions σ_β and σ_α . At first sight this seems

to be the easiest way. However, experimental data on the surface tension of individual phases constituting different immiscible systems do not exist and it is also not simple to measure them.

Among the pure theoretical models the simplest is that of Becker [8] where a demixing system is considered as a regular solution with sharp interface between two phases, and interactions between the atoms are restricted to nearest neighbours. Following this idea the interfacial tension is equal to an additional energy resulting from the asymmetry of the bonds across the interface.

Chatain and Eustathopoulos (Chatain-Eustathopoulos) have described an immiscible system as two liquids separated by a coherent interface [10-12]. The interfacial area is modelled by a definite number of monatomic layers. The interfacial tension is determined as the difference of the free energy of the whole immiscible system and the free energy of a homogeneous system, which could be formed by the same atoms with the same chemical potentials.

Cahn and Hillard (Cahn-Hillard) supposed that there is no sharp interface between two liquids in an immiscible system and that the concentration profile normal to the interface changes continuously [6]. The Gibbs free energy is assumed to depend not only on the temperature, pressure and local composition but also on the composition gradient, which must be small as compare to the reciprocal of the interatomic distance. After application of the van der Waals model of diffusive interfaces to binary mixtures they have obtained an expression for the interfacial tension in approximation of the regular solution.

In order to calculate the interfacial tension in the frame of the models described above one must presume the structure of the interface. It was proposed in [10] to identify the liquid-liquid interface with the (111)-plane of the face-centered cubic lattice. For comparing, the dimensionless expression $(\sigma_{\alpha\beta} \cdot \Omega_m / W)$ within the three models with such interfacial layer structure was determined [3,13]. Fig. 2 shows this expression as a function of the reduced temperature T/T_c . It is seen that the model of Becker is restricted to temperatures where the composition at the interface can be assumed to change at a jump, and the model of Cahn-Hillard is restricted to temperatures where continuous (smooth) transition from one to other phase is observed. The model of Chatain-Eustathopoulos as if unifying the models of Becker and Cahn-Hillard gives values $(\sigma_{\alpha\beta} \cdot \Omega_m / W)$, which tend to those of Becker's model at low temperatures and practically coincide with the values of Cahn-Hillard's model at high temperatures.

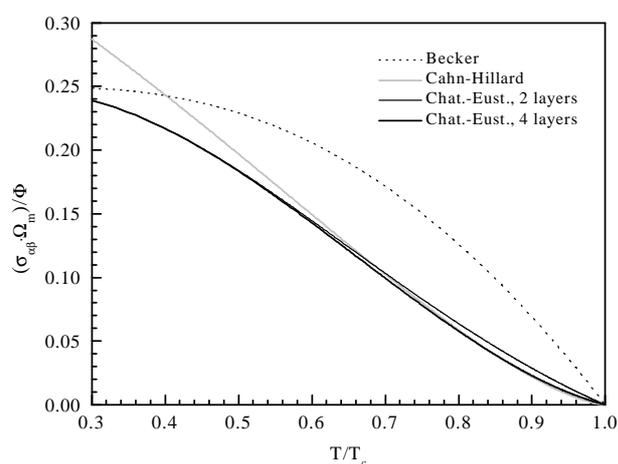


Fig. 2. $(\sigma_{\alpha\beta} \cdot \Omega_m / W)$ as a function of the reduced temperature.

The absolute values of the interfacial tension in the Al-Bi, Al-In and Al-Pb systems at the monotectic temperatures calculated with the help of the multilayer model of Chatain and Eustathopoulos in the regular solution approximation are given in Table 1. It is seen that the calculated values are approximately 1.5 times less than those measured experimentally. It is noteworthy that this difference between the experimental values of the interfacial tension and those calculated with the continuous models (Cahn-Hillard, Chatain-Eustathopoulos) was observed for the binary monotectic systems investigated so far in [3,13].

Table 1. The experimental and theoretical values of the liquid-liquid interfacial tension at the monotectic temperature: T_m – the monotectic temperature, T_c – the critical temperature, $W = 2 \cdot R \cdot T_c$, Ω_m – the molar interface, $\sigma_{\alpha\beta}^{th}$ – the theoretical and $\sigma_{\alpha\beta}^{ex}$ – the calculated values of interfacial tension near the monotectic temperature.

System	T_m (K)	T_c (K)	W (kJ/mol)	Ω_m (m ² /mol)	$\sigma_{\alpha\beta}^{th}$ (mJ/m ²)	$\sigma_{\alpha\beta}^{ex}$ (mJ/m ²)	$\sigma_{\alpha\beta}^{ex} / \sigma_{\alpha\beta}^{th1}$
Al-Bi	930	1310	21.8	$58 \cdot 10^3$	36	56.7	1.57
Al-In	912	1110	18.4	$53 \cdot 10^3$	17	25.5	1.50
Al-Pb	932	1695	28.1	$57 \cdot 10^3$	81	125.5	1.55

To compare the temperature dependencies of the interfacial tension in the Al-Bi, Al-In and Al-Pb systems determined experimentally with the theoretical predictions, the measured data were fitted to the values $(\sigma_{\alpha\beta} \cdot \Omega_m / W)$ calculated with the models of Cahn-Hillard and Chatain-Eustathopoulos with simple division by the constant values of 1.57, 1.50 and 1.55, respectively. It is seen that both models describe the temperature dependence of the interfacial tension very well.

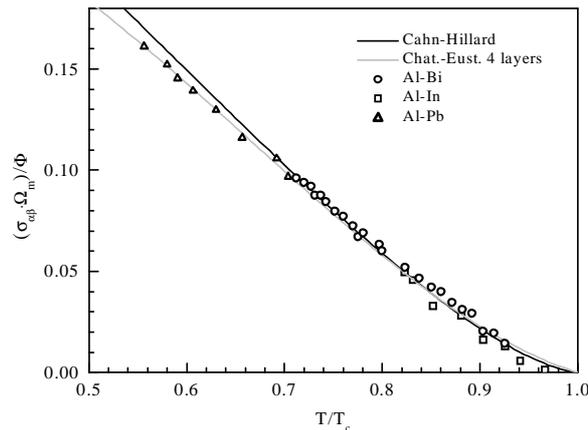


Fig. 3. Temperature dependence of the experimental values of the interfacial tension for Al-Bi, Al-In and Al-Pb immiscible systems fitted to the expression $(\sigma_{\alpha\beta} \cdot \Omega_m / W)$.

4. Conclusions

Analysis of the liquid-liquid interfacial tension in the demixing Al-Bi, Al-In and Al-Pb systems determined experimentally and comparison with the values calculated with the help of models of Becker, Cahn and Hillard, and Chatain and Eustathopoulos resulted in the following:

The temperature dependencies of the liquid-liquid interfacial tension in the Al-Bi, Al-In and Al-Pb binary systems are well described by the continuous model of Cahn-Hillard or multilayer model of Chatain-Eustathopoulos. The temperature dependence of the interfacial tension within the model of Becker is not realistic.

The absolute values of the interfacial tension calculated within the models of Cahn-Hillard and Chatain-Eustathopoulos in the approximation of a regular solution with liquid-liquid interface as (111)-plane of the face-centered cubic lattice for the Al-Bi, Al-In, Al-Pb systems is ~1.5 times less than the respective experimental data. Obviously this parameter might be applied to the theoretical calculations to determine a value of the interfacial tension in the systems where experimental measurements are not possible.

Acknowledgements

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