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Surface tension of binary and ternary aluminium alloys of the systems Al–Si–Mg and Al–Zn–Mg

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The surface tension and density of liquid binary and ternary aluminium alloys of the systems Al–Si–Mg and Al–Zn–Mg (Si, Mg and Zn contents less than 19, 8 and 20 wt %, respectively) have been measured by means of the maximum bubble pressure method. A semi-empirical theory, which relates the surface tension to bulk thermodynamic properties, is used to calculate the surface tension of the binary alloys and discuss the experimental data. For the ternary alloys, the present results indicate that in the range of compositions explored here, the properties of the ternaries can be obtained from those of the binaries. Comparison with results previously reported by other authors is made.

1. Introduction

The surface tension of liquid metals [1, 2] is both a fundamental property and a parameter of great technological importance. In particular, the surface tension of liquid aluminium and its alloys is an essential input in developing any casting model [3, 4] and in understanding the wettability at the aluminium/ceramic system, a property of crucial relevance in the fabrication of metal matrix composites [5]. Despite its importance, the amount of work addressed to measure the surface tension of commercial and ternary alloys [4], is much less than that dedicated to the binary systems [6–15].

In this work we present results for the surface tension, σ, and density, ρ, of aluminium alloys of the ternary systems Al–Si–Mg and Al–Zn–Mg obtained by means of the maximum bubble pressure (MBP) method. Partial accounts of the results discussed here were reported previously [14, 15]. The experimental data will be used to elucidate whether σ and ρ of the ternary alloys can be obtained from data for the binary systems [15]; this question is of both practical and fundamental interest. A semi-empirical theory, which relates the surface tension to bulk thermodynamic properties [16–18], will be used to calculate the surface tension of the binary alloys and discuss the experimental data.

As a final remark, we should point out that all data presented here for the surface tension of the liquid alloys should be associated with the oxidized surface, in the sense of [19]. This assessment is supported by recent findings [20] which indicate that the changes in the maximum pressure observed previously [14, 15] that were related to changes in surface tension, do in fact correspond to modifications in the wetting conditions at the metal–capillary tip interface. The conclusion drawn previously [20] is that the MBP method does not allow us to establish a clear relation between surface tension and the degree of oxidation, and that the only reliable values are those for the oxidized surface.

2. Experimental procedure

As a detailed description of the MBP experimental apparatus utilized in this work can be found elsewhere [14], here we shall only mention some of the main features of the present experiments. Alumina Degussit A123 capillaries with external diameter around 2 mm and wall thickness ~ 0.25 mm were used; actual diameters were measured with an accuracy of ± 0.001 mm by means of high-precision gauge techniques. The inmersion depth was varied in the range 15–30 mm, whereas the bubbling rate was fixed at around 10–20 bubbles/min. To speed up the stabilization of the maximum pressure, argon N55 plus 100 p.p.m. oxygen was used as bubbling gas (see [21]). The immersion depth was measured by means of a high-precision micrometre to within ± 0.005 mm; a sudden pressure rise allowed determination of the zero point with an error of ± 0.01 mm.

The alloys investigated in this work were prepared in alumina crucibles of inner diameter around 50 mm,

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TABLE I Density, ρ, and surface tension, σ as measured in this work ($T = 973$ K), for Al–Si, Al–Zn and Al–Mg alloys.

Si (wt %)	ρ (g cm^{-3})	σ (mJ m^{-2})	Zn (wt %)	ρ (g cm^{-3})	σ (mJ m^{-2})	Mg (wt %)	ρ (g cm^{-3})	σ (mJ m^{-2})
1	2.38	866	2.5	2.42	865	0.8	2.37	856
3	2.39	865	5.8	2.46	862	3	2.34	822
5	2.40	858	9.8	2.52	857	5	2.33	798
8	2.41	855	19.5	2.71	846	8	2.31	781
12	2.43	847	–	–	–	–	–	–
19	2.46	838						

TABLE II Slopes of the straight lines, or at the origin of the curves (*), fitted to the experimental and theoretical results for the surface tension of the aluminium binary alloys considered in this work, as a function of the element content. The data corresponding to [6, 7] were derived from the figures reported therein

	Experimental values (mJ m^{-2})				Theory (mJ m^{-2})
	This work	[9, 10]	[13]	[6, 7]	This work
Si	− 1.6	− 2.17	− 2.5	–	–
Zn	− 1.2	− 1.44	–	− 3.3*	− 1.1*
Mg	− 22.0*	− 41.9	–	− 13.0*	− 21.0*

the same as that subsequently used to carry out the MBP measurements. Aluminium of commercial purity (~ 99.98%) was used all throughout; typical amounts of impurities (wt %) were 0.015 Si and 0.005 Fe. The maximum contents in the binary alloys were: Mg 8 wt %, Si 19 wt %, and Zn 20 wt %. For the ternary alloys, the following compositions were considered. Al–Mg–Si: Mg 0.5, 1, 1.5, 2 and 3 wt % and Si 5 and 8 wt %. Al–Zn–Mg: Mg ~ 3 wt % and Zn 5, 12 and 20 wt %. To reduce the magnesium losses, the experiments on Al–Mg alloys were carried out in the shortest period possible; the magnesium content was also determined after a set of measurements; losses were always less than 5% of the initial magnesium content. No salt fluxes were used; instead the oxide layers were removed, before introducing the capillary into the liquid metal, by means of ceramic rods. The liquid metal temperature was varied in the range 973–1173 K and controlled within ± 2 K.

The surface tension was calculated from a relation derived by Cantor [21] and modified by Schrödinger [22], assuming that the bubbles had spherical shape, slightly deformed due to the metallostatic pressure, and detached with a diameter that coincided with the outer diameter of the capillary ($2r$). Only the first correction term [21, 22] was found to be important in the present measurements; in such a case the surface tension is given by

$$\sigma = \frac{rP}{2}\left(1 - \frac{2}{3}\frac{r\rho g}{P}\right) \qquad (1)$$

where ρ is the density of the liquid alloy, g the acceleration of gravity and P is given by,

$$P = P_{\mathrm{m}} - \rho g h \qquad (2)$$

where P_{m} is the maximum (measured) pressure and h the immersion depth.

The method also allows the measurement of the density, ρ, of the liquid metal by varying the immersion depth

$$\rho = \frac{\Delta P}{g \Delta h} \qquad (3)$$

where ΔP is the pressure change due to an increment Δh in the immersion depth.

The errors for the surface tension and density were estimated to be ± 6 mJ m^{-2} and ± 0.04 g cm^{-3}, respectively. We finally note that, although the error in determining the density by means of the MBP is relatively high, essentially due to the high σ/ρ ratio of aluminium, the results (see below and [14, 15]) are in good agreement with those obtained by other authors.

3. Binary alloys

3.1. Experimental results

The results for the binary alloys investigated in this work are summarized in Tables I and II and Figs 1–3.

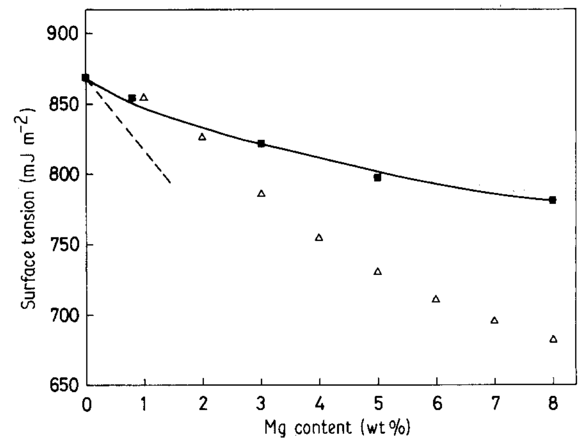

Figure 1 (■) Experimental data for the surface tension of Al–Mg alloys as a function of the magnesium content at 973 K. The results reported by Lang [9, 10 (– – –)] and those obtained by means of the semi-empirical theory (△) described in the text are also shown. The analytic expression of the fitted curve (—) is $\sigma = \sigma(\mathrm{Al}) - 72 \ln (1 + 0.3x)$ mJ m^{-2}, where x is the magnesium content (wt %)

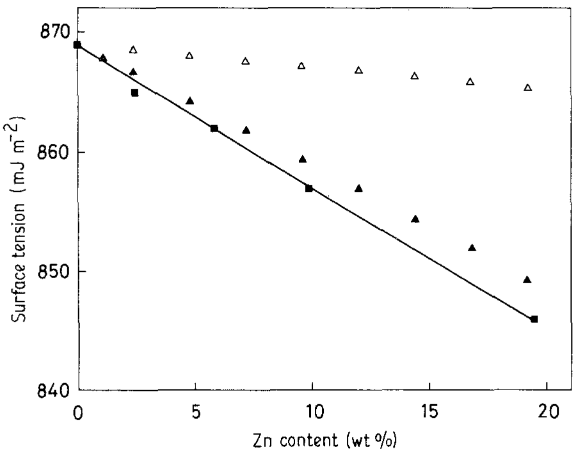

Figure 2 (■) Experimental data for the surface tension of Al–Zn alloys as a function of the zinc content at 973 K. The results obtained by means of the semi-empirical theory (△, ▲) described in the text are also shown (the results corresponding to two different values of the surface tension of pure zinc are reported, see text). The analytical expression of the fitted curve (——) is $\sigma = \sigma(\mathrm{Al}) - 1.2x\ \mathrm{mJ\,m^{-2}}$, where x is the zinc content (wt %).

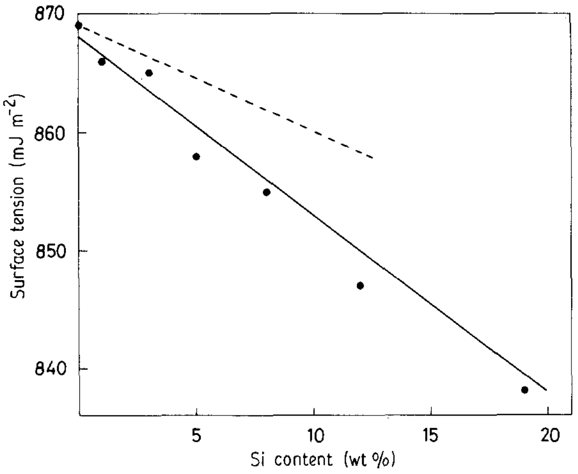

Figure 3 (●) Experimental data for the surface tension of Al–Si alloys as a function of the silicon content at 973 K. The fitted curve (——) is $\sigma = \sigma(\mathrm{Al}) - 1.6x\ \mathrm{mJ\,m^{-2}}$, where x is the silicon content (wt %). The result given by Equation 11 (– – –) is also shown.

Some of the data already reported [14, 15] have been checked and found to be within experimental error.

In the three alloys, the density varies linearly with the content of the alloying element. The results at $T = 973$ K (Table I) can be fitted by

$$\rho_{\text{Al-A}} = (2.376 + \alpha_A x_A)\,\mathrm{g\,cm^{-3}} \qquad (4)$$

where $\rho_{\text{Al-A}}$ stands for the density of the alloy Al-A, x_A is the content of element A (wt %) and $\alpha_A = -0.009$, 0.014 and $-0.0044\ \mathrm{g\,cm^{-3}}$ for A = Mg, Zn and Si, respectively. In the case of zinc, the fitting is only valid for contents lower than ~ 10 wt %; beyond this concentration the density of the alloys increases much more steeply. We also note that only the results for Al–Mg are in good agreement with the linear mixture rule [2]; for silicon, Equation 1 should be valid at most up to the concentration at which the alloy becomes solid (~ 21.5 wt % at $T = 973$ K).

The surface tension in two of the alloys (silicon and zinc) varies linearly with the concentration. At $T = 973$ K the data are satisfactorily fitted by

$$\sigma_{\text{Al-A}} = (869 + \beta_A x_A)\,\mathrm{mJ\,m^{-2}} \qquad (5)$$

where $\beta_A = -1.6$ and $-1.2\ \mathrm{mJ\,m^{-2}}$ for A = Si and Zn (Fig. 1) respectively. In the case of magnesium the surface tension shows a logarithmic dependence with the concentration, x (Fig. 2); at $T = 973$ K the fitted function is

$$\sigma_{\text{Al-Mg}} = [869 - 72\ln(1 + 0.3x)]\,\mathrm{mJ\,m^{-2}} \qquad (6)$$

As regards the validity of the linear mixture rule for the Al–Zn system we note that Equation 5 gives a surface tension for pure zinc of $749\ \mathrm{mJ\,m^{-2}}$. This value is rather close to that reported earlier [2], i.e. $734\ \mathrm{mJ\,m^{-2}}$, but far below that given by Falke *et al.* [23] (~ $839\ \mathrm{mJ\,m^{-2}}$). The question resides upon whether the temperature coefficient of pure zinc is negative, as reported in [2], or positive [23]. Although the present results (see also next subsection) favour a negative temperature coefficient, we cannot discard a change in the sign of this coefficient at high zinc contents (below 10 wt % it is negative and very similar to that of pure aluminium, see [15]). In comparing these data with previous results we first note a remarkable agreement for silicon and zinc (Table II).

The surface tension of pure aluminium is much more strongly modified by magnesium additions. At low magnesium contents, σ varies more steeply than predicted by the linear mixture rule; however, if Equation 6 is extrapolated to high concentrations, we note that the rate of change decreases with x, giving a value for the surface tension of pure magnesium of $620\ \mathrm{mJ\,m^{-2}}$, considerably higher than the data reported in the literature [2], around $542\ \mathrm{mJ\,m^{-2}}$. The steep change of σ at low concentrations indicates that segregation of magnesium to the surface should be very important, as expected from elementary thermodynamic considerations [2]. This trend has also been observed by Lang [9, 10] and Korol'Kov [8], although both authors found that σ varied much more rapidly with x than reported in this work (see also Table II). Our results are in better agreement with those of Pelzel, [6, 7] and Smenchenko [24]; the value reported by the latter for an alloy with a magnesium content of 10 wt %, $775\ \mathrm{mJ\,m^{-2}}$, is very close to the result given by Equation 6, ~ $768\ \mathrm{mJ\,m^{-2}}$.

3.2. Semi-empirical theories

We first discuss the results obtained by means of a semi-empirical theory that gives the surface tension of the binary alloy in terms of the surface tensions of the pure elements and bulk thermodynamic data for the binary system [1, 16, 17]. As a consequence, this approach can only be used to discuss the results for Al–Mg and Al–Zn alloys. In this theory the surface tension of the alloy A_xB_{1-x} is written as

$$\sigma = \sigma_A + \frac{RT}{S}\ln\frac{\gamma_A^s x^s}{\gamma_A^b x^b} \qquad (7a)$$

$$\sigma = \sigma_B + \frac{RT}{S}\ln\frac{\gamma_B^s(1 - x^s)}{\gamma_B^b(1 - x^b)} \qquad (7b)$$

where the $\gamma^{s,b}_{A,B}$ are the surface (s) and bulk (b) activities of elements A and B, $x^{s,b}$ the surface and bulk contents of element A, and σ_A and σ_B the surface tensions of the pure elements. S is the average atomic area which has been assumed to be equal for the two elements [1], R the gas constant and T the absolute temperature.

To apply Equation 7a and b we first need to determine the surface magnitudes. To this end we follow the method of Fowler and Guggenheim [16]; these authors wrote the following expressions for the surface activities

$$\ln \gamma^{i}_{A} = \frac{z^{i}}{2} \ln \frac{\beta^{i} - 1 + 2x^{i}}{x^{i}(1 + \beta^{i})} \qquad i = b, s \quad (8a)$$

$$\ln \gamma^{i}_{B} = \frac{z^{i}}{2} \ln \frac{1 + \beta^{i} - 2x^{i}}{(1 - x^{i})(1 + \beta^{i})} \qquad (8b)$$

where z^{i} is the coordination number at the bulk or surface (for the coordination numbers of the alloys, an average of those corresponding to the two elements was taken in the calculations) and β^{i} is given by

$$\beta^{i} = [4x^{i}(1 - x^{i})\exp(2W^{i}/z^{i}RT) + (1 - 2x^{i})^{2}]^{1/2} \qquad (9)$$

where W^{i} is the pair interaction energy $W^{i} = E^{i}_{AB} - (E^{i}_{AA} + E^{i}_{BB})/2$, where $E^{b,s}$ are the bond energies (bonds AA, AB or BB) at the bulk and the surface, respectively. The bulk pair interaction energy can be directly fitted to the experimental data for the bulk magnitudes [25]. For the surface quantities, it is assumed that a local approximation works, namely, $W^{s} = W^{b}$ [18]. This allows us to write the surface activities in terms of known bulk quantities and the surface composition, x^{s}. To determine the latter it is required that the two expressions for the surface tension of the alloy, Equation 7a and b, give the same results. The resulting equation can be solved numerically for x^{s}. Once determined the function that relates x^{s} and x^{b}, the surface activities can be calculated by means of Equations 8a and b, and, finally, the surface tension by means of Equation 7.

The results for Al–Zn and Al–Mg alloys are summarized in Figs 1 and 2 and in Table II. In the case of zinc the results obtained by using two different values [2, 23] for the surface tension of pure zinc at $T = 973$ K are shown (Fig. 2). Comments similar to those made in the previous subsection are pertinent here; again our results favour a negative temperature coefficient for σ of pure zinc [2] (see also above). In the case of magnesium (Fig. 1) we note that whereas at contents below 2 wt % the theoretical results are very close to the experimental data, beyond that point theory gives a much faster variation of σ. We speculate with the possibility that the surface tension of pure magnesium is known with insufficient accuracy [2]. We base our conclusion upon the fact that other calculations that do not use the surface tension of magnesium as an input, give much smaller changes of σ with the magnesium content [26, 27]; for instance, in [27] the value reported for a 10 wt % Mg is 735 mJ m^{-2}, rather close to that given by equation 6, around 768 mJ m^{-2}.

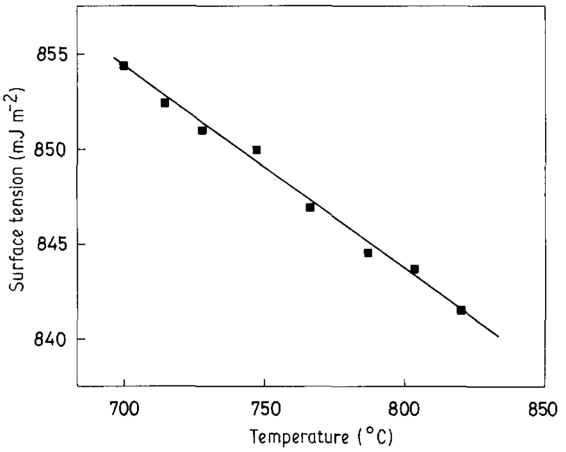

Figure 4 Temperature dependence of the surface tension of Al–8 wt % Si alloys as measured in this work

As a final point we discuss a simple estimation of the surface tension of Al–Si alloys. The idea is to correlate the changes induced in the surface tension of pure aluminium by silicon additions with those of the liquidus temperature, and relies upon the very small dependence of the temperature coefficient of σ ($d\sigma/dT$) on silicon content reported in the literature [21]. To check the latter result we have measured the temperature coefficient of σ for two alloys with silicon contents of 5 and 8 wt % (the results for the latter are illustrated in Fig. 4); in both cases the coefficient is around -0.11 mJ m^{-2} K^{-1}, close to the value for pure aluminium obtained by us [28] and other authors [29], namely, ~ 0.12 mJ m^{-2} K^{-1}. Then we fit the function that relates the difference between the liquidus temperature, T_l, and the actual temperature, T, (see Fig. 5) to the Si content of the alloy, x_{Si}, by

$$\Delta T = T - T_l \simeq 8x_{Si}, \quad x_{Si} < 12.5 \text{ wt \%} \qquad (10)$$

The surface tension of the alloy is then written as

$$\sigma_{Al-Si} = \sigma_{Al} + \left(\frac{d\sigma}{dT}\right)_{Al} \Delta T \simeq \sigma_{Al} - 0.9x_{Si} \text{ mJ m}^{-2} \qquad (11)$$

a result which is in remarkable agreement with the experimental data (see Table II). We note, however, that the same argument applied to the magnesium and zinc alloys fails. It gives linear coefficients of -0.14 and -0.6 mJ m^{-2} for zinc and magnesium contents in the ranges 0–30 and 0–10 wt %, respectively, in sharp disagreement with the experimental data (see Table II). We should finally remark on a serious drawback of this argument. As T_l increases beyond the eutectic point, Equation 11 would also predict an increase in σ. We have found no experimental indication of this prediction (Fig. 3). Thus, we conclude that this reasoning only works at low concentrations of silicon (below the eutectic point).

4. Ternary alloys

The results for the two ternary systems investigated in this work are reported in Table III and Figs 6 and 7.

TABLE III Density, ρ, and surface tension, σ, as measured in this work for the ternary alloys Al–Mg–Zn and Al–Mg–Si ($T = 973$ K)

x	x (wt %)	Mg (wt %)	ρ (g cm^{-3})	σ (mJ m^{-2})
Zn	5.2	2.7	2.44	815
	11.7	3.1	2.52	808
	2.0	3.2	2.69	793
Si	5	0.5	2.39	848
	5	1	2.38	840
	5	1.5	2.37	830
	5	2	2.37	822
	5	3	2.36	812
	8	1	2.40	831
	8	2	2.39	815
	8	3	2.37	800

In both figures the curves obtained by using the results for the binary alloys (Equations 5 and 6) are also plotted; at a constant temperature (973 K in this case) we write for a given magnitude $X (X = \rho, \sigma)$

$$X_{\mathrm{Al-A-B}} = X_{\mathrm{Al}} + \Delta X_{\mathrm{Al-A}} + \Delta X_{\mathrm{Al-B}} \quad (13)$$

where $\Delta X_{\mathrm{Al-A,B}}$ are the increments in the magnitude, X_{Al}, induced by A or B additions, respectively. The agreement between the experimental data and the results given by Equation 13 is very remarkable. Small discrepancies are well within the experimental error and might be related to errors in the determination of the magnesium content (as mentioned above, magnesium losses can be around 5%). The main conclusion is that the density and the surface tension of the ternary alloys investigated here can be obtained from data for the binaries; effects derived from the interaction between the elements are very weak, if any, and undetectable within the present experimental accuracy.

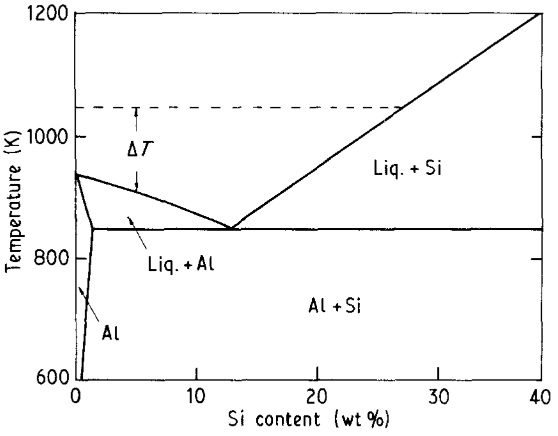

Figure 5 Phase diagram of the Al–Si system. The function ΔT (actual temperature minus liquidus temperature at a given concentration) in terms of which the surface tension of the alloys can be written (see text) is also shown.

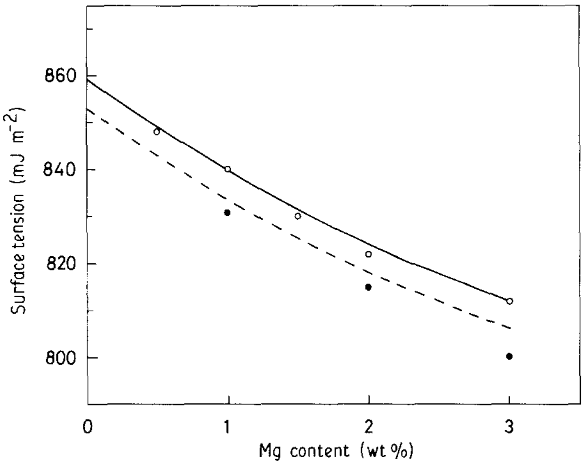

Figure 6 (○, ●) Experimental data for the surface tension of Al–Si–Mg alloys as a function of the magnesium at 973 K. The curves correspond to the results obtained from the data for the two binary alloys (see text). (○, ——) 5 wt % Si, (●, - - -) 8 wt % Si.

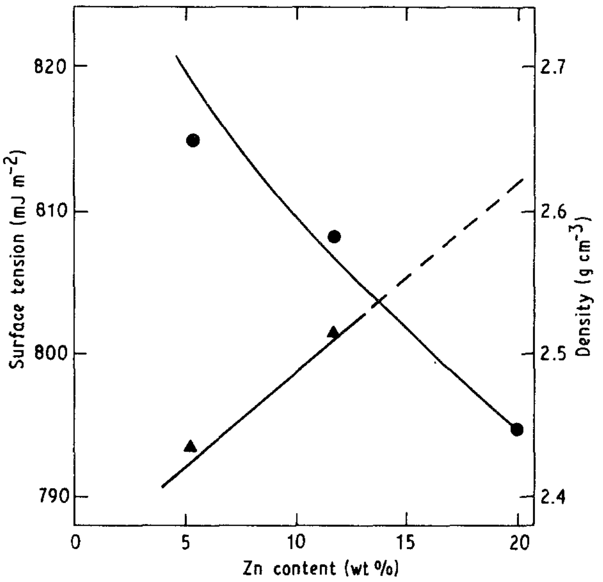

Figure 7 Experimental data for ▲ the density and ● surface tension of Al–Zn–Mg alloys as a function of the zinc content at 973 K. The curves correspond to the results obtained from the data for the two binary alloys; the curve for the density is displayed as broken beyond ~ 13 wt %, to indicate that the fitting for Al–Zn alloys is only valid below that content (see text). The magnesium content is kept fixed ~ 3 wt% (see Table III).

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References

1. M. SHIMOJI, "Liquid Metals" (Academic Press, London, New York, 1977) pp. 351–4.
2. B. C. ALLEN, in "Liquid Metals", edited by S. Z. Beer (Marcel Dekker, New York, 1972) p. 161.
3. The Metals Society (eds) "Solidification and Casting of Metals" (J. W. Arrowsmith Ltd., London, 1979).
4. A. M. KOROL'KOV, "Casting Properties of Metals and Alloys" Translated from Russian (Consultants Bureau, New York, 1963).
5. F. DELANNAY, L. FROYEN and A. DERUYTTERE, *J. Mater. Sci.* **22** (1987) 1.
6. E. PELZEL, *Berg-Und Hüttenmän. Monats.* **93** (1948) 247.

7. *Idem, ibid*, **94** (1949) 10.
8. A. M. KOROL'KOV, *Otdelenie, Teknicheskik Nauk* **2** (1965) 35.
9. G. LANG, *Aluminium* **49** (1973) 231.
10. *Idem, ibid.* **50** (1974) 731, and references therein.
11. L. GOUMIRI, J. C. JOUD, P. DESRÉ and J. M. HICTER, *Surf. Sci.* **83** (1979) 471.
12. P. LATY, J. C. JOUD and P. DESRÉ, *ibid.* **69** (1977) 508.
13. V. SOMOL, F. FRANZ and L. KUBICEK, *Kovove Materialy* **23** (1985) 223.
14. C. GARCIA-CORDOVILLA, E. LOUIS and A. PAMIES, *J. Mater. Sci.* **21** (1986) 2787.
15. A. PAMIES, E. LOUIS and C. GARCIA-CORDOVILLA, in "8th Internationale Leichtmetalltagung", edited by Austria Metall., AG, A-5282, Ranshofen, Austria (Leoben-Wien, 1987) pp. 493–5.
16. R. H. FOWLER and E. A. GUGGENHEIM, "Statistical Thermodynamics" Cambridge University Press, Cambridge, 1932).
17. T. P. HOAR and D. A. MELFORD, *Trans. Faraday Soc.* **53** (1957) 315.
18. R. SPEISER, D. R. POIRIER and K. YEUM, *Scripta Metall.* **21** (1987) 687.
19. L. GOUMIRI and J. C. JOUD, *Acta Metall.* **30** (1982) 1397.
20. J. GOICOECHEA, C. GARCIA-CORDOVILLA, E. LOUIS and A. PAMIES, *Scripta Metall.* **25** (1991) 479.
21. M. CANTOR, *Ann. Physik* **283** (1892) 399.
22. E. SCHRÖDINGER, *ibid.* **46** (1915).
23. W. L. FALKE, A. E. SCHWANEKE and R. W. NASH, *Metall. Trans.* **8B** (1977) 301.
24. V. K. SMENCHENKO, "Surface Phenomena in Metals and Alloys" (Pergamon Press, New York, 1961).
25. R. HULTGREN, P. D. DESAI, D. T. HAWKINS, M. GLEISER and K. K. KELLEY, "Selected values of the thermodynamics properties of binary alloys" (American Society for Metals, Metals Park, OH, 1973).
26. J. E. SCHOUTENS, *J. Mater. Sci.* **24** (1989) 2681.
27. H. A. PAPAZIAN, *High Temp. Sci.* **18** (1984) 119.
28. A. PAMIES, C. GARCIA-CORDOVILLA and E. LOUIS, *Scripta Metall.* **18** (1984) 869.
29. L. GOUMIRI, J. C. JOUD and P. DESRÉ, *Surf. Sci* **83** (1979) 471.

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