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The surface tension of liquid pure aluminium and aluminium–magnesium alloy

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This paper discusses the results of several experiments designed to further illustrate the recent findings of the present authors according to which, if a virtually leak-fee maximum bubble pressure system is used to measure the surface tension of liquid aluminium, a surface tension around 1100 mJ m^{-2} is first obtained, decreasing to the oxidized value (around 865 mJ m^{-2}) as the experiment proceeds and oxygen enters the system mainly through the capillary walls. The peculiarities and difficulties inherent to the maximum bubble pressure method are illustrated. For instance, a study of the time needed for the surface tension to decrease to the oxidized value as a function of temperature reveals the important role played by the vapour pressure in the process. This is further illustrated by considering Al–Mg alloys, as magnesium has a different heat of vaporization and a much larger vapour pressure than aluminium at the measuring temperatures. Results for the changes in density and surface tension for the oxidized and unoxidized cases induced by magnesium (up to 8 wt %) are also presented and compared to previous data.

1. Introduction

The recent results concerning the surface tension (σ) of liquid aluminium reported by Goumiri and Joud [1] and the present authors [2] have opened new and interesting possibilities in the field. In the last decade it was thought that a highly reliable value for σ of pure liquid aluminium has been achieved, it was around 865 mJ m^{-2} at the melting point [1, 3]. Instead, the above mentioned authors [1, 2] have demonstrated that the latter value corresponds to oxidized aluminium (above a monolayer of oxide, see [1]) whereas for unoxidized aluminium a value higher than 1050 mJ m^{-2} should be expected. These remarkable results indicate that many data concerning the surface tension of liquid metals and alloys should be revised. On the other hand the experimental equipment used to measure surface tension [4–7] have to be improved in order to fit the strict conditions required for the study of unoxidized liquid metals [1, 2]. In these studies many new peculiarities and difficulties should arise and those have to be identified and overcome.

The purpose of this paper is two-fold. First the results of several experiments devised to improve our understanding of the problems arising in the measurement of surface tension of unoxidized and oxidized aluminium by means of the maximum bubble pressure (MBP) method will be presented and discussed. Second, results for the surface tension and density of binary Al–Mg alloys with magnesium contents up to 8 wt %, will be reported. Magnesium is an interesting alloying element as it noticeably modifies the surface tension of liquid aluminium [8], and, on the other hand, it is used in many commerical alloys. In addition the results for Al–Mg alloys will also contribute to the first aim of the present report.

2. Experimental procedures and materials

In [2] it was found that if the whole MBP system was purged just before the capillary was introduced into the molten metal a high surface tension value around 1091 mJ m^{-2} at $T = 873$ K was obtained; then, as the experiment proceeded, σ decreased saturating around 869 mJ m^{-2}. These results were interpreted in terms of surface oxidation of liquid aluminium, namely, the high σ value corresponds to nearly unoxidized aluminium, whereas as the experiment proceeds oxygen enters the system, mainly through non-metallic parts of the system (capillaries), reacting with liquid aluminium. Oxygen diffusion might be favoured by the very low gas flows used in the measurements and the sudden pressure drops associated with bubble detachment. Before proceeding, it is worth to remark that those results cannot be understood in terms of wetting. In fact wetting would increase with time, not decrease, leading to an increase in pressure and therefore in the apparent values of σ. On the other hand, when the metal wets the capillary, an irregular signal (fluctuations in pressure) is usually observed [4]; in the present experiments a highly regular signal was always detected.

As the above mentioned behaviour had not been observed previously, it is worthwhile to comment on the outstanding characteristics of the present system which might likely be the cause of those new results. The experimental set-up used in this work was designed

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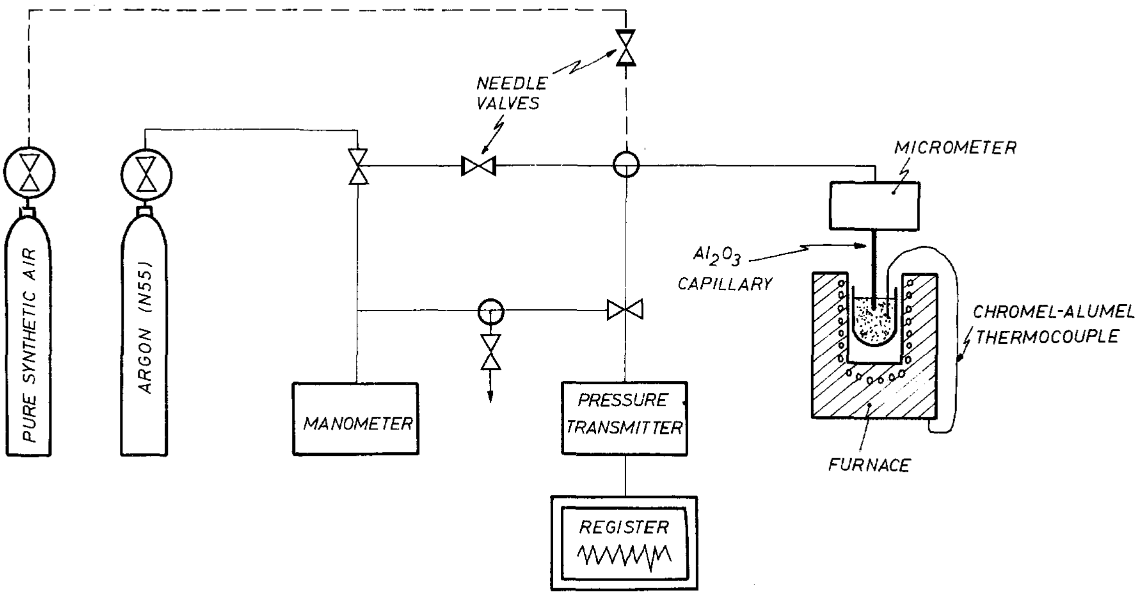

Figure 1 Sketch of the experimental set up used in this work.

and assembled in our laboratory and was similar to others described by previous authors [6, 7]. A sketch of the system is shown in Fig. 1. For connections and tubing, top quality steel parts were used. Gas flows were controlled by means of double pattern fine metering valves. Differential pressure (referred to atmospheric pressure) was measured by means of a Phillips PCS-Transmitter P. Alumina Degussit A123 capillaries with external diameters around 2.0 mm and walls of 0.25 mm were used. Actual diameters were measured at several points around the capillary tips with an accuracy of ± 0.001 mm; only capillaries with diameters defined within ± 0.005 mm were used. The capillaries were joined to the stainless steel tubing by means of flexible graphite ferrules. The immersion depth was measured by means of a high precision micrometer within ± 0.005 mm, and varied in the range 15 to 30 mm; when introducing the capillary, a sudden pressure rise allowed to determine the zero point within ± 0.01 mm.

N55 argon (99.9995%) was used as bubbling gas. As it contains less than 1 p.p.m. of oxygen, it should in principle be pure enough to measure σ for nearly unoxidized aluminium. In fact, it can be estimated that at least 500 p.p.m. of oxygen are required to build up a monolayer of oxide on the bubble surface. Therefore there is no need for further purification of N55 argon. What should be instead done is to reduce leaks to a minimum. As mentioned above, this was accomplished in the present experimental set up by using stainless steel parts, and by joining the capillaries to the tubes by means of graphite ferrules. The latter point is of crucial relevance, as joining ceramic capillaries to steel parts is a major problem; those ferrules provide a very easy, reliable, way to avoid leaks at that joint. The authors think that the use of graphite ferrules is the most important innovation introduced in the present system, in comparison with previous ones.

If the graphite ferrules are in good condition, the easiest way for oxygen to enter the system is through the capillary walls. Alumina is a highly porous material and therefore oxygen can easily diffuse through it. As mentioned above, the diffusion process might be favoured by the low gas flows used in the measurements and the sudden pressure drops occurring when bubbles detach. The role played by the latter can be checked by noticing that, as the bubbling rate is increased, the surface tension decreases faster from the value corresponding to the unoxidized surface, indicating that bubble detachment favours oxygen diffusion. To avoid or reduce oxygen contamination, very severe modifications of the present experimental set-up are likely required. Working under high vacuum conditions may be a way, although any method suitable for decreasing the surface porosity of the alumina capillaries, such as metallization, may also help. In this paper, no attempts were made to avoid oxygen contamination, instead the way in which that occurred, among other characteristics of the results obtained with the previous experimental set up [2], were utilized to improve our understanding of some peculiarities and difficulties inherent to the measurement of σ by means of the MBP method.

High purity aluminium 99.999% supplied by Goodfellow Metals was used. Aluminium–magnesium alloys with magnesium contents of 0.8, 3, 5 and 8 wt % were prepared in our laboratory. Typical amounts of impurities in weight per cent were the following: 0.02 Si and 0.005 Fe. Experiments on Al–Mg alloys were carried out in the shortest period in order to reduce magnesium losses to a minimim. No salt fluxes were used instead the oxide layers were removed, before introducing the capillary, by means of ceramic rods. The magnesium content was also determined after a set of measurements; losses were always lower than 5% of the initial magnesium content. Alumina capillaries proved to work properly also for Al–Mg alloys; no signs of wetting were detected (see next section). Argon with oxygen amounts in the range 10 to 200 p.p.m. was also used. The liquid metal temperature was varied in the range 973 to 1176 K and controlled within ± 2 K. The time needed for σ to decrease from the value corresponding to unoxidized aluminium, down to that for the oxidized surface (Δt) was also measured and the kinetics of the process studied. As the bubbling rate affects Δt, it was fixed (after having measured the density, see below) at 30 bubbles $\min^{-1}$. The bubbling rate can be easily fixed by keeping the gas flow and immersion depth constant.

The surface tension σ was calculated from the Cantor relation [9] as modified by Schrödinger [10]. These authors, assuming that bubbles had spherical shape (of diameter coinciding with the external diameter of the capillary, $2r$) slightly deformed due to the metallostatic pressure, derived the following expression for σ

$$\sigma = \frac{rP_0}{2}\left\{1 - \left(\frac{2}{3}\right)\left(\frac{r\varrho g}{P_0}\right) - \left(\frac{1}{6}\right)\left(\frac{r\varrho g}{P_0}\right)^2\right\} \quad (1)$$

where ϱ is the liquid metal density, g the acceleration of gravity, and P_0 is given by

$$P_0 = P - \varrho gh \quad (2)$$

h being the immersion depth and P the maximum (measured) pressure. Only the first correction term in Equation 1 was found to be important.

The method allows also to measure the density of the liquid metal by varying the immersion depth. The density will then be calculated from

$$\varrho = \frac{\Delta P}{g\Delta h} \quad (3)$$

where ΔP is the pressure change due to an increment Δh in the immersion depth. The density of both pure aluminium and Al–Mg alloys were determined in this way. The results for ϱ of pure aluminium are very satisfactory, as remarked in [2]. Finally it should be mentioned that the estimated errors for the surface tension and density are $\pm 6\,\mathrm{mJ\,m^{-2}}$ and $\pm 0.04\,\mathrm{g\,m^{-3}}$ respectively.

3. Results and discussion

3.1. Pure aluminium

In order to obtain further support for the interpretation of the results reported in [2] in terms of surface oxidation, a very small amount of pure air was allowed to enter the system. The results are very revealing: surface tension abruptly drops to the value corresponding to oxidized aluminium and then it raises up again to the value it should have had, had not air been allowed to enter the system (Fig. 2). This experiment is rather difficult, as to avoid a full contamination of the system allowing σ to recover the high value (Fig. 2), only a very small amount of air has to be injected into the system.

An aspect of the problem which might be in principle studied by means of the MBP method is the change in σ as a function of the fraction of a monolayer of oxide, by varying the O_2 content of the bubbling gas. The basis for this study is that it seems at first reasonable to assume that all O_2 molecules contained in a bubble should be deposited on the metal surface (notice the high surface reactivity of aluminium and the high average kinetic energy of gas molecules at 1000 K). Therefore σ was measured at $T = 975\,\mathrm{K}$ by using argon with different amounts of O_2 up to 200 p.p.m. The results are shown in Fig. 3. It is noticed that, (a) the initial value of σ does not change with the O_2 content within experimental error, which is rather high for unoxidized aluminium, and (b) increasing amounts of O_2 decrease the time Δt needed for σ to drop to the value corresponding to oxidized aluminium. None of these points can be easily understood; the results discussed in the next paragraph may throw light on the first of them and it will be considered later on in this paper.

To clarify the way in which aluminium oxidizes during the MBP experiment, the effect of temperature (T) on Δt was studied. Δt was defined as the time

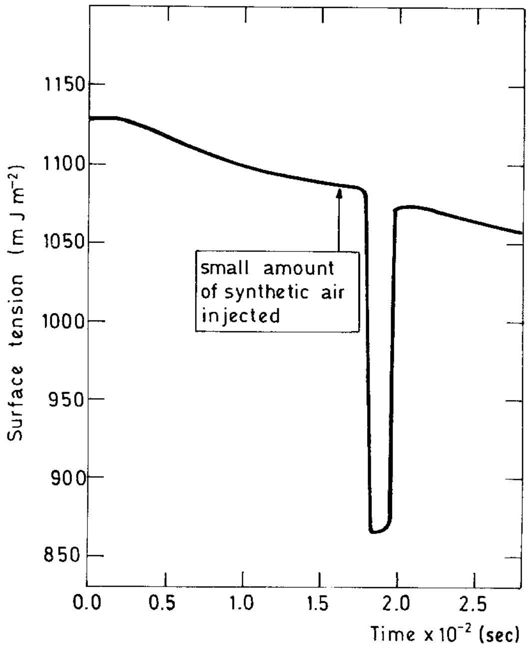

Figure 2 Surface tension of high purity aluminium (99.999%) as a function of bubbling time. The arrow shows the time at which a very small amount of air was allowed to enter the system. Bubbling gas: N55 argon, $T = 1073\,\mathrm{K}$.

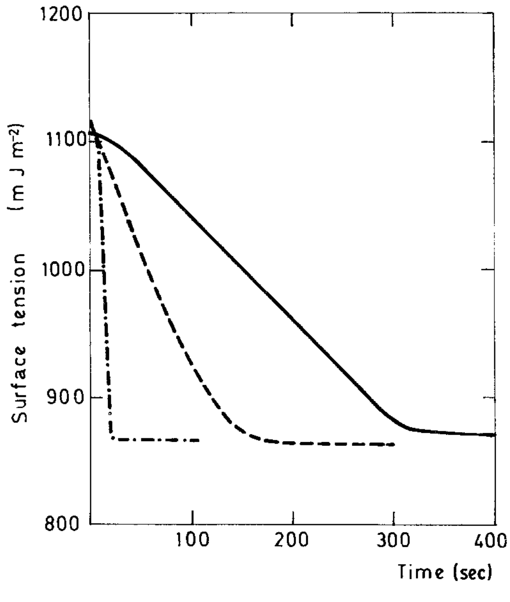

Figure 3 Surface tension of high purity aluminium (99.999%) as a function of bubbling time. Bubbling gas: N55 argon with several contents of oxygen. (———) Ar + 62 p.p.m. O_2, (– – –) Ar + 100 p.p.m. O_2, (–·–·–) Ar + 220 p.p.m. O_2.

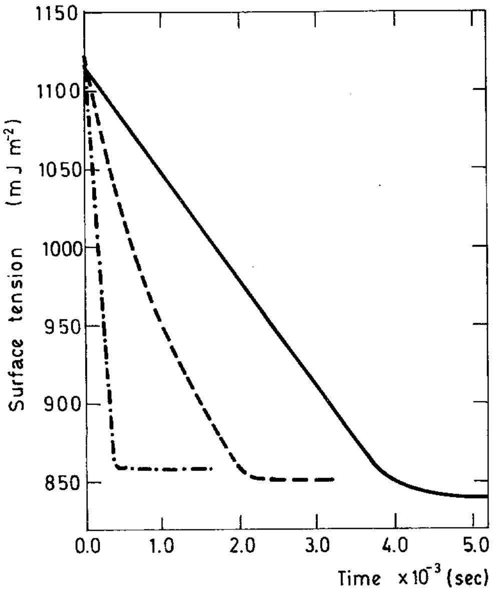

Figure 4 Surface tension of high purity aluminium (99.999%) as a function of bubbling time and temperature. Bubbling gas: N55 argon + 100 p.p.m. O_2. (———) 1173 K, (– – –) 1123 K, (–·–·–) 1073 K.

TABLE I Time needed (Δt) for surface tension to decrease from the value corresponding to the unoxidized surface to that for the oxidized surface at different temperatures, for pure aluminium and an Al–0.8 wt % Mg alloy (see Figs 4 and 5). Bubbling gas Ar + 100 p.p.m. O_2. Bubbling rate 30 bubbles min^{-1}. The activation energy ΔE (kJ mol^{-1}) of the process is also given (see text)

Pure aluminium		ΔE	Al–0.8 wt % Mg		ΔE
T (K)	Δt (sec)		T (K)	Δt (sec)	
973	74	205	942	186	149
1023	141		973	758	
1073	468		1023	1057	
1123	2145		1073	2450	
1176	4260		–	–	

needed for a 98% decrease in surface tension from the higher value (unoxidized) to the lower (oxidized). It was observed that Δt increased exponentially with T. Fig. 4 shows the results for a bubbling gas containing Ar + 100 p.p.m. O_2 (lower contents of O_2 lead to very high values of Δt at high temperatures and therefore need very long experiments). These experimental data can be adjusted by

$$\Delta t \;=\; \nu \exp\left(-\Delta E/RT\right) \qquad (4)$$

where R is the gas constant, T the absolute temperature and ν and ΔE are adjusted to the experimental data (see Table I and Fig. 5). The result for ΔE is 205 kJ mol^{-1}. The explanation for this peculiar behaviour can be found by recalling that vapour pressure also varies exponentially with temperature in a narrow range of T [11]. The activation energy of the process is known as the heat of vaporization for that range of T and it can be calculated to be 124 kJ mol^{-1} for the vapour pressure data of [12] and 333 kJ mol^{-1} extrapolating those of [11]. It is remarkable that the activation energy of the process shown in Fig. 4 is in between the experimental values for the heat of vaporization. The explanation of Fig. 4 may then be the following. Aluminium in the gas phase reacts with O_2 decreasing the amount of oxide formed on the aluminum surface. As T increases the amount of Al–gas increases and therefore Δt increases. The weakness of the argument is that the experimental vapour pressure values are too low for aluminium to saturate 200 p.p.m. of O_2, as the results of Fig. 3 indicate to happen. In this context it should be pointed out that experimental values for the vapour pressure show a large spread and that kinetics of vaporization could also play a role.

A final point concerns the reasons for the decrease in Δt as the O_2 content is increased (Fig. 3). This is the most obscure point of the results reported here. Although a fully satisfactory explanation for this behaviour has not been found, it is likely that the amount of O_2 trapped in the porous alumina capillaries [13] increases with the O_2 content of the bubbling gas. This is only a possibility which has not been investigated any further. Before proceeding to discuss the results for Al–Mg alloys, it is worth to comment on the value of σ for unoxidized aluminium. The results of Goumiri and Joud [1] indicate that σ varies very rapidly during the first stages of oxidation. Then as the imperviousness of the system critically depends on how the capillary is fitted (condition of the graphite ferrules, among other factors), the error in σ for unoxidized aluminium is higher than the experimental error given above. These comments indicate that σ values for unoxidized aluminium should be critically considered. The average of more than 20 measurements is given in Table II. It is interesting to note that this value is even closer to the theoretical value of Chacón *et al.* [14] than that reported in [2].

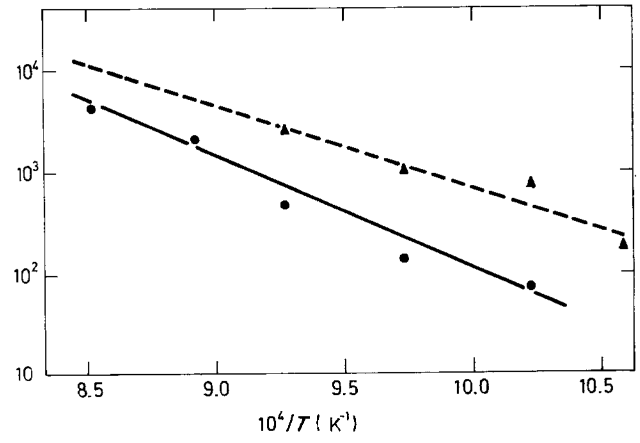

Figure 5 Time needed for the surface tension to decrease from the value corresponding to the unoxidized surface down to that for the oxidized surface (Δt) for pure aluminium and Al–Mg alloy. Bubbling gas: N55 Ar + 100 p.p.m. O_2. (●) Al 99.999%, (▲) Al–0.8 wt % Mg.

TABLE II Density (ϱ) and surface tension (δ) measured at 973° C by means of the maximum bubble pressure method, for several Al–Mg binary alloys

Magnesium content (wt %)	ϱ (g cm^{-3})	σ (mJ m^{-2})	
		unoxidized	oxidized
0.0	2.382	1122	869
0.8	2.37	1100	856
3	2.34	1070	822
5	2.33	1042	798
8	2.31	1014	781

3.2. Aluminium–magnesium alloys

The first point to be considered is the possible wetting of alumina capillaries by Al–Mg alloys. Although a result similar to that reported in Fig. 1 for pure aluminium, has been obtained for Al–Mg alloys, it has been possible to check that the condition of the capillary tip is more critical for these alloys than for pure aluminium. In fact defects on the tip, roughness and lack of dryness, among other factors, may promote wetting of the capillary by Al–Mg alloys. Nonetheless, if the capillary tip was carefully prepared, no signs of wetting were detected. These signs could be irregular results [4], sticking of metal on the capillary tip, (etc.).

Results for the density and the surface tension are reported in Table I. The density of the alloys vary linearly with the magnesium content; the adjusted function is

$$\varrho = (2.376 - 0.009x)\ \mathrm{g\,cm^{-3}} \qquad (5)$$

where x is the wt % Mg. It can be easily checked that, as expected, this result is in good agreement with the linear mixture rule [5].

On the other hand the results for the surface tension follow a logarithmic law, instead of the linear relation found by Lang [8]. Fig. 6 shows the experimental points, and the adjusted functions. The functions adjusted for oxidized and unoxidized surfaces, are rather similar, notwithstanding the large errors inherent to the measurements for unoxidized surfaces. On the other hand, our results show that the surface tension of binary Al–Mg alloys varies with the magnesium content much more steeply than predicted by the linear mixture rule [5]. This indicates that segregation of magnesium to the surface should be very important, as expected from elemental thermodynamic considerations [5]. This tendency has been also observed by Lang [8] and Korol'Kov [15], although both authors found that σ varied much more rapidly with x than reported in Fig. 6. The present results are in better agreement with those reported by Pelzel [16, 17].

The final question concerns the change in surface tension upon oxidation. Fig. 7 shows data for alloys with different magnesium contents. The most remarkable result is that as the magnesium content increases, the time Δt needed for the surface tension to decrease from the value corresponding to the unoxidized surface, down to that for the oxidized surface, increases. This result is a further support for the role of vapour pressure in this process. In fact, the vapour pressure of magnesium at around 1000 K is nine orders of magnitude higher than that for alumiunium [11], explaining the increase in Δt as the magnesium content increases. Further evidence can be obtained by studying the kinetics of the process. Results for Δt as a function of temperature for the most dilute alloy (0.8 wt %) are given in Table I and Fig. 5. The activation energy is much lower than in the case of aluminium, in agreement with the lower heat of vaporization that magnesium has: 50.6 and 123 kJ mol^{-1} for the vapour pressure data of [12] and [11], respectively. All these results support the assumption made in this work, which remarks on the essential role of vapour pressure in determining the way in which σ decreases down to the value corresponding to the oxidized surface.

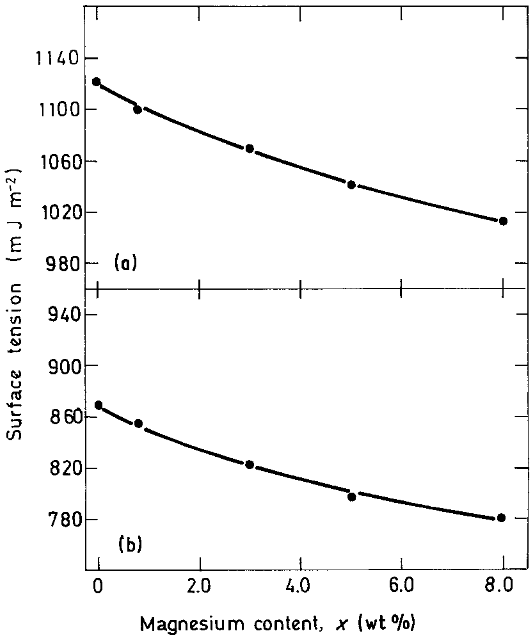

Figure 6 Surface tension (σ) of Al–Mg alloys as a function of the magnesium content. Data for (a) unoxidized $\sigma = \sigma\,(\mathrm{Al}) - 96.7 \ln (1 + 0.26x)$ and (b) oxidized $\sigma = \sigma\,(\mathrm{Al}) - 71.8 \ln (1 + 0.31x)$; the adjusted functions are shown. T = 973 K.

4. Concluding remarks

The following conclusions emerge from the results presented in this paper:

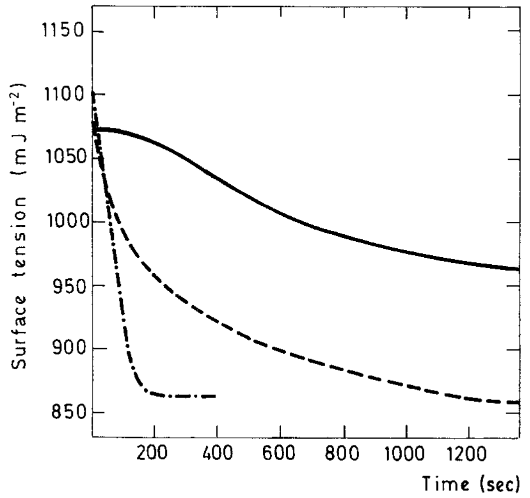

Figure 7 Surface tension of Al–Mg alloys as a function of bubbling time. T = 1023 K, bubbling gas Ar + 100 p.p.m. O_2. (—) Al–3 wt % Mg, (– – –) Al–0.8 wt % Mg, (–·–) Al 99.999%.

(a) The injection of a small amount of air in the MBP system leads to an abrupt drop in σ (down to the value corresponding to oxidized aluminium), followed by a sudden increase to the value it should have had, had no air been injected into the system. These results give further support to the interpretation of the data of [2] in terms of oxidation of the aluminium surface (see Fig. 1 of [2]).

(b) There are two effects of increasing amounts of oxygen in the bubbling gas (up to 200 p.p.m.), (i) the value of surface tension corresponding to unoxidized aluminium does not decrease, (ii) Δt decreases as the oxygen content is increased. While point (i) can be understood in terms of the aluminium vapour pressure (see next point), a fully satisfactory explanation for (ii) has not been found.

(c) As the temperature is increased, Δt increases. This can be interpreted recalling that the vapour pressure increases exponentially, and that the oxidation reaction in the gas phase slows down the formation of oxides on the liquid surface and therefore the drop in surface tension. In fact by plotting Δt against temperature, an exponential relation is found with activation energy similar to the heat of vaporization of aluminium. Further support for this interpretation is provided by the results for Al–Mg alloys, for which Δt increases with the magnesium content. In fact, this result can be explained by considering that the vapour pressure of magnesium at around 1000 K is nine orders of magnitude higher than that of aluminium.

(d) As regards the results for binary Al–Mg alloys, several comments are in order. The density of aluminium is only slightly changed by magnesium. Instead, the surface tension for both the unoxidized and the oxidized surfaces, substantially decreases as the magnesium content is increased. The present results indicate that there is no linear relationship between surface tension and magnesium content as previously reported by Lang [8], but it is rather a logarithmic function (for magnesium contents up to 8 wt %).

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