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Liquid–liquid interfacial tension measurements applied to molten Al-halide systems

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After a brief review of the theory concerning the formation of a meniscus by a flat, vertical blade, the equipment and testing procedure used are described. The value of the interfacial tension between molten aluminium and flux (made of the equimolar mixture, NaCl–KCl) at 740° C is $\gamma = 792$ dyn cm^{-1}. The influence of the addition of various fluorides (NaF, KF, LiF, Na_3AlF_6) to the NaCl–KCl flux on the interfacial tension value between aluminium and flux was then studied. For a given molar fraction of salt addition, the interfacial tension decreases when the resulting effect increases in the following order: $Na_3AlF_6 < LiF < NaF < KF$. The results obtained with the addition of Na_3AlF_6 and NaF match those obtained previously by Kurdyumov *et al.*

1. Introduction

In the melting cycle of aluminium alloys, it is often necessary to eliminate solid inclusions present inside the molten metal. One of the classical methods used is the treatment of the molten metal with a liquid flux. The term flux covers a whole range of alkaline and alkaline earth–halide mixtures. During the fluxing operation, the solid inclusions are absorbed at the metal–flux interface, then trapped in the liquid flux phase. The thermodynamic conditions of this process have been studied by several authors, e.g. Kozakewitch and co-workers [1, 2], and Kurdyumov *et al.* [3]. They take into account the solid inclusion preferential angle of wetting by the liquid flux as well as the liquid–solid interfacial tension and the liquid–liquid interfacial tension.

High temperature liquid–liquid interfacial tension measurements are not easy. Several methods have already been used:

(1) drop shape method [1, 2]: X-rays are used to reveal the shape of a drop of metal melted under slag and placed on a flat support;

(2) capillary depression method [4, 5]: examination of the liquid–liquid interface in a capillary tube is also carried out by X-ray radiography;

(3) meniscus elongation method [3]: we used this method to measure the interfacial tensions between molten aluminium and the alkaline halide mixtures which are commonly used under the name of flux in industrial practice for the treatment of aluminium alloys.

2. Measurement principle

Let there be two liquids, L_1 and L_2, separated by an interface (S), as shown in Fig. 1. Laplace's Law, which symbolizes the equilibrium between the pressure forces and the surface tension, can be written at any point P of the interface.

$$\gamma_{LL}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) - \Delta\rho g y = \text{constant} \quad (1)$$

where $\Delta\rho$ is the difference between the densities of the liquids L_1 and L_2, γ_{LL} the interfacial tension between the liquids L_1 and L_2, R_1 and R_2 the principal radii of curvature at the point P, and y the distance from P to a horizontal plane (H)

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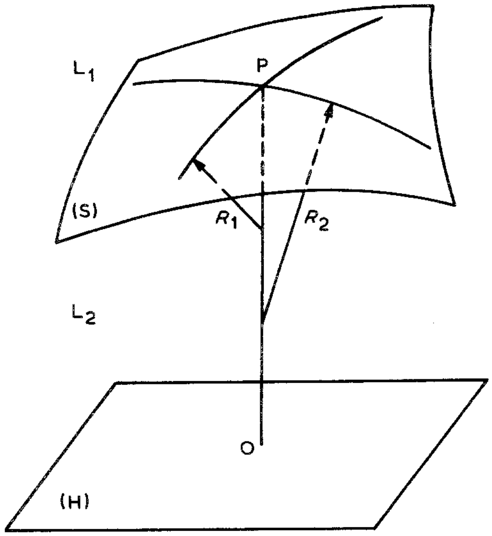

Figure 1 Interface (S) between two liquids L_1 and L_2.

taken as a reference. g is the acceleration due to gravity.

The differential Equation 1 can be solved when the interface has a simple geometry. This is the case when a plane interface is deformed by a thin, plane and infinitely long blade, while assuming in addition that the blade is held vertically. Fig. 2 shows a section of the interface by a plane perpendicular to the blade. $0y$ is the trace of the blade. At any point P of the interface, the surface (S) radius of curvature in any horizontal direction parallel to the plane of the blade is infinite. The other principal radius of curvature can be written $R_1 = \mathrm{d}s/\mathrm{d}\phi$.

If the undeformed planar interface at which the meniscus levels off, at an infinite distance from the blade, is taken as the reference plane, Equation 1 becomes:

$$y = \frac{\gamma_{\mathrm{LL}}}{\Delta\rho g}\frac{d\phi}{ds}.$$

The solution of this equation leads to a mathematical relation, in a parametric form, of the meniscus section shown in Fig. 2 (cf. Bouasse [6]):

$$y = 2\left(\frac{\gamma_{\mathrm{LL}}}{\Delta\rho g}\right)^{1/2} \sin\frac{\phi}{2} \tag{2}$$

$$x = 2\left(\frac{\gamma_{\mathrm{LL}}}{\Delta\rho g}\right)^{1/2}\left(\cos\frac{\phi}{2} - \cos\frac{\phi_0}{2} + \frac{1}{2}\ln\frac{\tan(\phi/4)}{\tan(\phi_0/4)}\right) \tag{3}$$

$$\phi_0 = \frac{\pi}{2} - \theta_0,$$

θ_0 being the junction angle of the interface and the blade. The force applied to the blade is equal to the difference between the weights of the

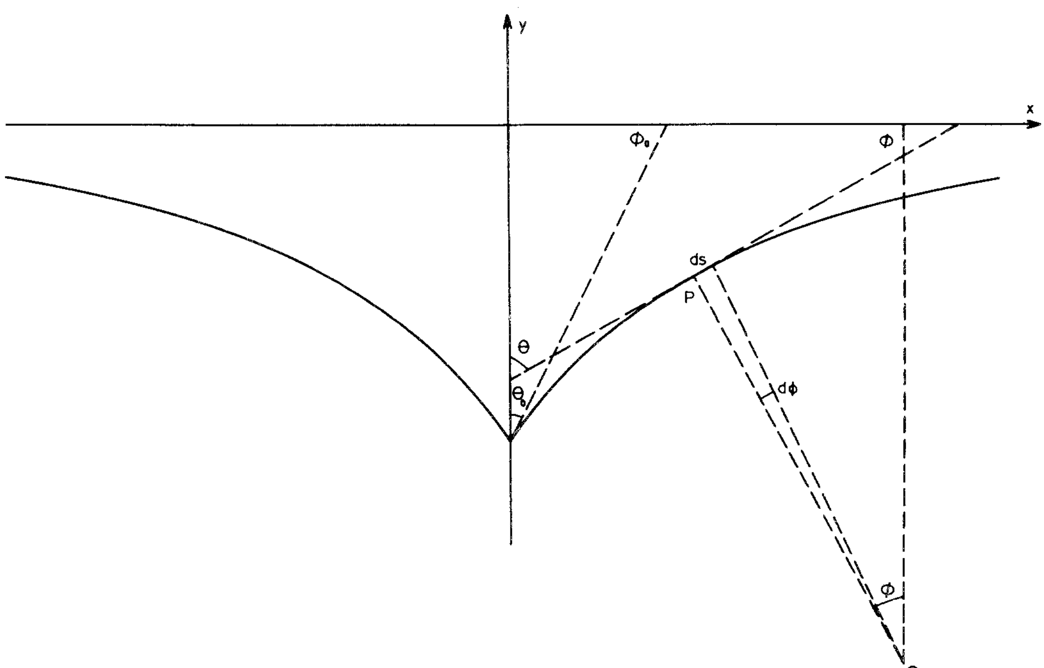

Figure 2 Cross-section of the interface.

volume of the liquids displaced during the formation of the meniscus. Per unit of length of wet perimeter, this force is equal to:

$$f = \Delta\rho g \int_{-\infty}^{0} y \mathrm{d}x \tag{4}$$

with

$$y = \frac{\gamma_{\mathrm{LL}}}{\Delta\rho g} \frac{\mathrm{d}\phi}{\mathrm{d}s} \qquad \mathrm{d}x = \mathrm{d}s \cos\phi$$

$$f = \Delta\rho g \int_0^{\pi/2 - \theta_0} \frac{\gamma_{\mathrm{LL}}}{\Delta\rho g} \cos\phi \, \mathrm{d}\phi$$

$$f = \gamma_{\mathrm{LL}} \cos\theta_0 \tag{5}$$

At the contact point with the blade ($x = 0$, $\phi = \phi_0, \theta = \theta_0$), Equation 2 can be written:

$$y = 2\left(\frac{\gamma_{\mathrm{LL}}}{\Delta\rho g}\right)^{1/2} \sin\frac{\phi_0}{2}$$

$$= \sqrt{\left[(1-\sin\phi_0)\frac{2\gamma_{\mathrm{LL}}}{\Delta\rho g}\right]} \tag{6}$$

and by eliminating ϕ_0 between Equations 5 and 6, the following relation for γ_{LL} is obtained:

$$\gamma_{\mathrm{LL}} = \frac{f^2}{\Delta\rho g y^2} + \frac{\Delta\rho g y^2}{4}. \tag{7}$$

The capillary force applied to the blade, the meniscus height y, as well as the difference in the densities, $\Delta\rho$, of the two liquids can be determined experimentally, and their measurements permit the determination of γ_{LL}. The curve $f = f(y)$ representing the force applied to the blade as a function of the penetration depth is determined point by point.

Fig. 3 is an example of the experimentally derived curves. These curves can be broken down into three sections denoted OA, AB, BC.

2.1. Section OA

The blade, when totally immersed into liquid L_1, is not in contact with liquid L_2. The slope is characteristic of the variation of Archimedes' buoyancy force resulting from the penetration in L_1 of the rod connecting the blade to the balance (positions 1 to 3).

2.2. Section AB

This section involves several physical effects caused by the displacement of the blade below the level of the initial interface (positions 4, 5, 6):

(a) the variation of the buoyancy force on the rod identical to that observed in section OA;

(b) the variation of the buoyancy force on the blade caused by the difference of the density of liquids L_1 and L_2;

(c) the force due to the interfacial tension during the formation of the meniscus, the formula of which is derived from Equation 7

$$f = y\sqrt{\left(\Delta\rho g \gamma_{\mathrm{LL}} - \frac{\Delta\rho^2 g^2 y^2}{4}\right)}$$

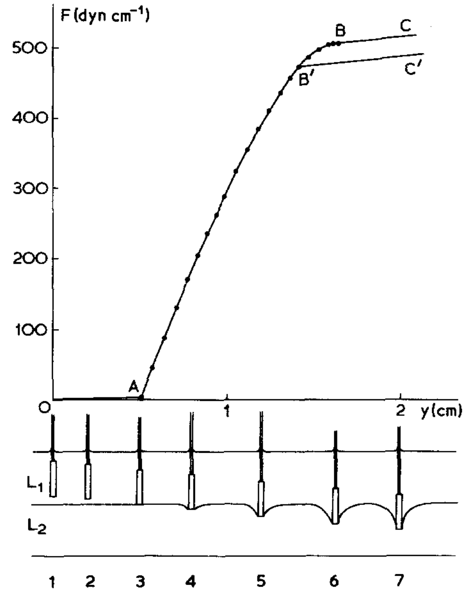

Figure 3 Buoyancy force supported by the blade as a function of the penetration depth.

2.3. Section BC

Starting from position 6, the blade penetrates the meniscus without deforming it. The capillary force is constant and the linear variation of the recorded force is due only to the variations of the buoyant force (effects previously noted a and b).

The capillary force and the meniscus height vary only in Section AB of the experimental curve; it is this part of the curve which is used in order to determine the interfacial tension γ_{LL}. The mathematical function representing section AB can be written:

$$f = y\sqrt{\left(\Delta\rho g \gamma_{\mathrm{LL}} - \frac{\Delta\rho^2 g^2 y^2}{4} + ay\right)} \tag{8}$$

where a is the buoyancy force coefficient, per unit of depth of penetration and per unit of wet perimeter of the blade.

Starting from the experimental points, the value $[(f - ay)/y]^2$ is plotted as a function of y^2.* The resulting curve is a straight line, the equation of which is derived from Equation 8:

$$\left(\frac{f-y}{y}\right)^2 = \Delta\rho g \gamma_{LL} - \frac{\Delta\rho^2 g^2 y^2}{4}.$$

The slope and the intercept on the ordinate axis led to the value of γ_{LL}.

The method described consists in treating the experimental values by theoretical equations, under the assumption that the following conditions are fulfilled: (1) infinite and isothermal medium, (2) infinitely long and infinitesimally thin blade. These conditions are not experimentally attainable; this leads to systematic errors in the determination of γ_{LL}. However, some of these errors are very small, like the error due to the size of the crucible.

2.3.1. Error due to the crucible

The two liquids are contained in a crucible of radius R. According to Equations 2 and 3, the meniscus formed by the blade levels off to the plane level of the liquid–liquid interface at an infinite distance from the blade. Thus $y = 0$, $\phi = 0$ and $x = \infty$.

Experimentally, the values of x are finite and limited to the radius of the crucible R. The crucible that we use is such that when $x = R$, $y = 1/100y$ (max) for $\gamma_{LL} = 800\,\text{dyn cm}^{-1}$, Thus, with a very good accuracy, Equation 7 remains valid for obtaining the value of γ_{LL}.

The formation of the meniscus displaces a volume of liquid which brings about a variation of the level of the liquid–liquid interface used as a reference for the measurement of the meniscus height. The maximum error made on the measurement of the height is around 2.5×10^{-2} cm, but the resulting error on the value of the interfacial tension is always lower than 0.1%.

2.3.2. Error due to the blade

The previous calculations suppose that the blade has an infinite length; actually the blade has finite dimensions, which leads to edge effects. However, for two blades with the same thickness but different lengths, the edge effects are the same. Thus, the difference of the buoyancy forces must be taken into consideration in order to derive the magnitude of the effect supported by a blade, the length of which is equal to the difference between the lengths of the two previous blades and this time without any edge effect.

2.3.3. Error due to the temperature

The working temperature must be measured with accuracy, as the magnitude of γ is very sensitive to this parameter; thus, Kurdyumov *et al.* [3] have observed that, within the 740 to 800° C temperature range, the variations of the interfacial tension Al-flux (50% NaCl–50% KCl by weight) is around $2\,\text{dyn cm}^{-1}\,{}^\circ\text{C}^{-1}$ (768 to $645\,\text{dyn cm}^{-1}$). Furthermore, this temperature must be homogeneous and constant during the test. In our set-up, we have thermal gradients; the temperature variation is 2° C between the centre and the edge of the crucible and 4° C between the bottom and the top.

In addition, during the experiment the displacement of the crucible in the heating zone creates a temperature variation of 5° C between the top and the bottom positions of the crucible. This temperature variation can be suppressed by controlling the electrical power supplied as a function of the crucible position. The error produced by these temperature uncertainties on the value of γ_{LL} is thus around $10\,\text{dyn cm}^{-1}$.

3. Equipment and testing procedure

Fig. 4 shows the equipment used. The furnace (1) heats up the charge with six ring-positioned resistors (2) supplied with three-phase alternating 220 V. The control is of the "on and off" type. The crucible (3) containing the charge has the following dimensions: diameter, 22.5 cm; height, 13.5 cm; thickness, 1.5 cm. This crucible must be chosen so as to be non-reactive with respect to the liquids to be studied. The blades (4) which are used to form the meniscus are cemented to the end of alumina rods of 0.2 cm diameter. In order to ensure a good rigidity to the rod–blade assembly, an additional weight of about 200 g (5) is fixed to the rod. The rod–blade–weight set-up is suspended from the tray of an electromagnetic balance (6) by a metallic wire. The balance is placed on a support located at the top of a bracket

*Fig. 3 was obtained for $\gamma_{LL} = 480\,\text{dyn cm}^{-1}$, $a = 22\,\text{dyn cm}^{-2}$ and $\Delta\rho = 0.76\,\text{g cm}^{-3}$; junction angle θ being zero, the curve OABC is observed; if $\theta = 20°$ the curve OAB′C′ is observed, with B′C′ parallel to BC.

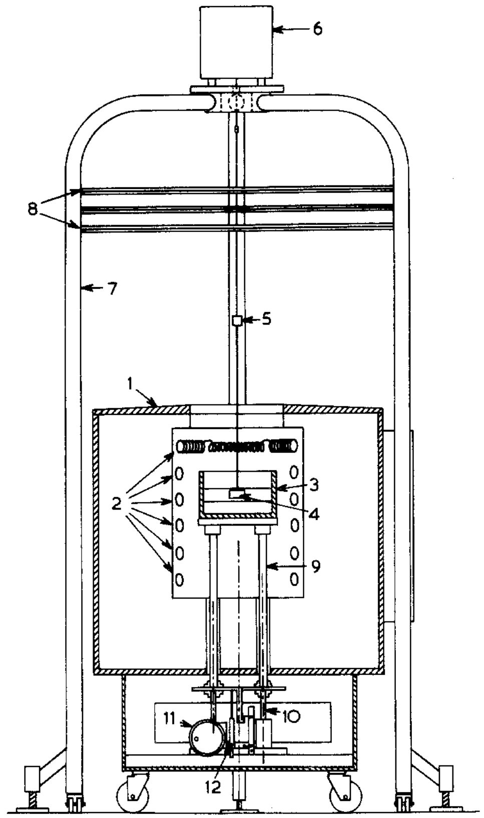

Figure 4 Furnace.

(7) 1 m above the top opening of the furnace. A series of three screens (8) allows the balance to be used at temperatures below 35° C.

The position of the blades being stationary, the crucible has to be mobile in order to vary the penetration depth. Therefore, the crucible support (9) is affixed to a jack (10), the vertical displacement of which is driven either electrically, by means of a motor, or manually through a crankshaft (11), when the motor is not in gear. The displacement measurement is made with a differential transformer transducer (12).

We determined experimentally the interfacial tensions between liquid aluminium and fluxes containing basically sodium and potassium chlorides. The charges are calculated so as to obtain two liquid layers each about 4 cm thick. The aluminium, which requires skimming, is melted first. After skimming, the flux is added, then melted. When the flux has reached a very good homogeneity and when the chosen operating temperature is stabilized, the blade is completely immersed in the flux without, however, being put in contact with the liquid aluminium. The balance which measures the apparent weight of the blade and its accessories is then brought to zero in order to show only the apparent weight variation when the blade is immersed. The crucible is then moved until the blade comes into contact with the liquid aluminium. This contact point must be determined accurately.

Buoyancy force measurements are then carried out for immersion depths increasing by 1 mm steps until the blade crosses the interface. The same operation is then repeated for the second blade which has a different length, but the same thickness.

4. Experimental results

The fluxes which were studied are made of equimolar mixtures of NaCl–KCl to which amounts of addition elements such as NaF, KF, LiF, Na_3AlF_6 are added. Knowledge of the densities of the various fluxes is indispensable in order to make use of the buoyancy force measurements. For this reason, we used the direct Archimedes method to measure the densities.

The plunger of sintered alumina which was used, was calibrated at 23° C in toluene.

The dilatation coefficient of alumina, according to Bockris *et al.* [7] is:

$$a = 10^{-6}(5.7 + 4.25 \times 10^{-3}\,\Delta t - 1.25 \times 10^{-6}\,\Delta t^2).$$

The results obtained, shown in Fig. 5, take into account both capillary thrust arising from the crossing of the flux–air interface by the rod connecting the plunger to the balance and the variation of the liquid level height resulting from the immersion of the plunger.

The working temperature is 740° C. It can be observed that at 740° C the density of the flux made of an equimolecular mixture NaCl–KCl, increases when additional elements such as NaF, LiF, KF, Na_3AlF_6 are added.

The density of aluminium has been the subject of many studies and we will take the following variation law:

$$\rho(\mathrm{Al}) = 2.369 - 3.11 \times 10^{-4}(T - T_\mathrm{m})$$

as quoted by Lucas [8]. The densities being known, the use of the curves representing the buoyancy thrust supported by the blade as a function of the penetration depth leads to the results shown in Fig. 6.

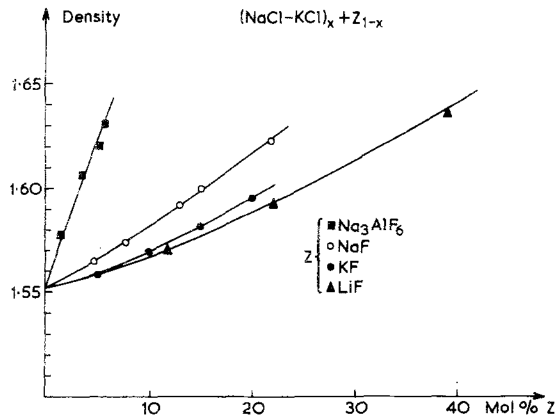

Figure 5 Densities of the salts used at 740° C.

The value of the interfacial tension, derived from our measurements, existing between liquid aluminium and the flux, made of the simple equimolecular mixture NaCl–KCl is 792 dyn cm^{-1} at 740° C. It can be seen that the addition of fluorides (NaF, KF, LiF, Na_3AlF_6) to the equimolecular NaCl–KCl mixture decreases the value of the interfacial Al-flux tension and that $d\gamma/dx$ (x being the molar fraction of the addition element) is larger for small percentages than for larger ones.

If our results are compared to those of Kurdyumov *et al.* [3] (Fig. 6), relative to interfacial tensions between equal mixtures of aluminium and NaCl–KCl (weight for weight) with Na_3AlF_6 and with NaF added, a very good agreement can be observed.

4. Conclusions

The meniscus elongation method at the liquid–liquid interface can be used to determine the interfacial tension. Applied to the liquid salts systems, this method has enabled us to measure the interfacial tension between aluminium and the equimolecular NaCl–KCl mixture which constitues the base of industrial fluxes and to determine the influence of salt additions on this interfacial tension.

With the addition of a given molar fraction of alkaline fluorides, the interfacial tension is markedly decreased, the resulting effect increasing in the following order:

$$Na_3AlF_6 < LiF < NaF < KF.$$

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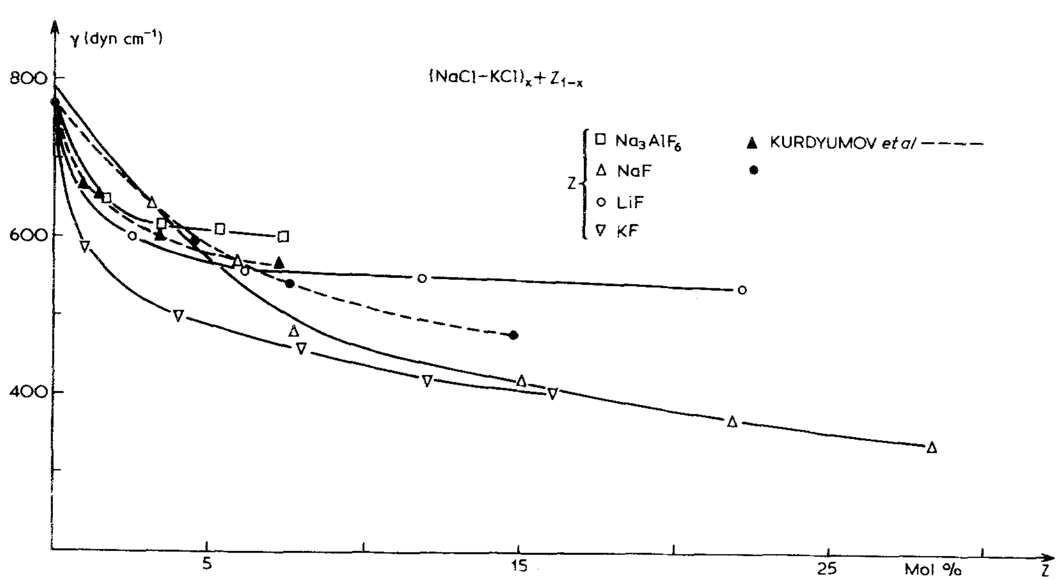

Figure 6 Variation of the interfacial tension as a function of the flux composition; comparison with Kurdyumov *et al.*'s results [3].

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