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Interfacial Tension between Aluminum and Chloride−Fluoride Melts

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A technique was developed for the measurement of the interfacial tension between liquid metals and molten salts at elevated temperatures. The technique is based on the measurement of the capillary depression occurring when a capillary, which is moved vertically down through the molten salt layer, passes through the salt/metal interface. The depression is measured by simultaneous video recording of the immersion height of the alumina capillary and the position of a liquid meniscus in a horizontal tube connected to the alumina capillary. The interfacial tension was measured for (a) aluminum and an equimolar melt of NaCl + KCl with several salt additions at 1000 K, (b) aluminum and NaCl + NaF at 1123 K, and (c) aluminum and NaCl + KF at 1123 K. It was found that the interfacial tension decreases with increasing amount of NaF, increases with the increasing amount of $MgCl_2$ additions, remains unchanged with AlF_3 additions, and slightly decreases with the addition of MgF_2 and Na_3AlF_6.

Introduction

Scrap and recycled aluminum have to be remelted and refined before being made into useful new products. This often involves melting the aluminum under a molten salt cover in order to prevent oxidation and to enhance the coalescence and recovery of the molten metal. In this process the interfacial tension between the aluminum and the salt is of significant importance in terms of both metal recovery and dross dewetting. Since scrap metal always has an oxide layer, it is required, by either mechanical or chemical means, to break this layer to allow the metallic droplets to coalesce.

Interfacial Tension Techniques

For the measurement of interfacial tensions, several techniques exist. However, at high-temperatures the choice of measurement technique is limited. Since most high temperature fluids are corrosive and often nontransparent to visual light, the sessile drop technique can rarely be used. However, by the use of X-rays, the shape of sessile drops immersed in another liquid may be determined (Utigard and Toguri, 1985). On the basis of the curvature of the drop and the density difference between the two fluids, the interfacial tension can be calculated. However, depending on the density difference between the metal and the salt, X-rays leads to a fuzzy outline of the drop shape and together with the sensitivity of the drop outline on the interfacial tension, this technique is limited to an accuracy of about 5 to 10%.

The pin detachment method, which is based on the measurement of the force needed to detach a pin from the interface between the salt and the metal, has also been used to measure the interfacial tension of high-temperature fluids. The pin itself must be very well wetted by the liquid metal in order to justify the assumption of a contact angle of 0° between the pin and the metal. Recently, the interfacial tension between aluminum and cryolite melts was measured by this technique using a titanium diboride pin (Fan and Østvold, 1991). A serious problem is that TiB_2 tends to react with aluminum and start to dissolve, thereby changing the properties of the metal. Another problem is that impurities in the TiB_2 may change the wetting properties and therefore the calculated interfacial tension.

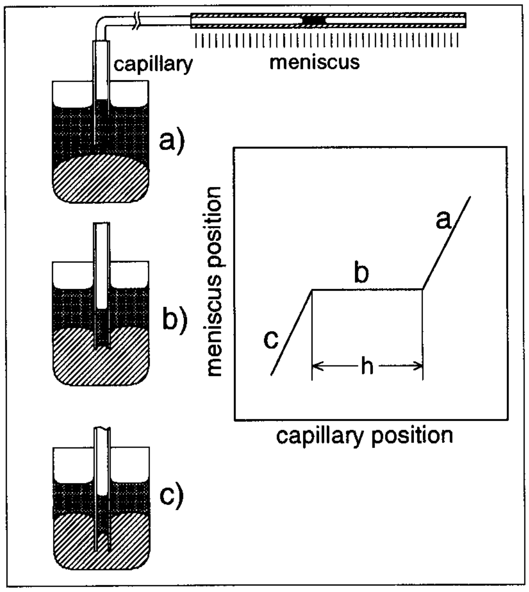

Figure 1. Principle of the interfacial tension measurements based on the capillary depression method.

The drop weight method has been used to determine interfacial tensions in molten slag/metal systems (Gammal and Mullenberg, 1980) and for aluminum + salt systems (Ho and Sahai, 1990). This method is based on measuring the size of individual metallic drops which are forced through a small orifice into the molten salt. The drop size is usually determined by recording the mass increase of the crucible holding the salt as individual drops are forced through the orifice and into the melt. One problem with this technique is that the metal and the molten salt are not necessarily in thermodynamic equilibrium before the metal is forced into the salt. This may lead to rapid exchange reactions as the metal enters the salt, possibly leading to interfacial tension changes (Richardson, 1982;

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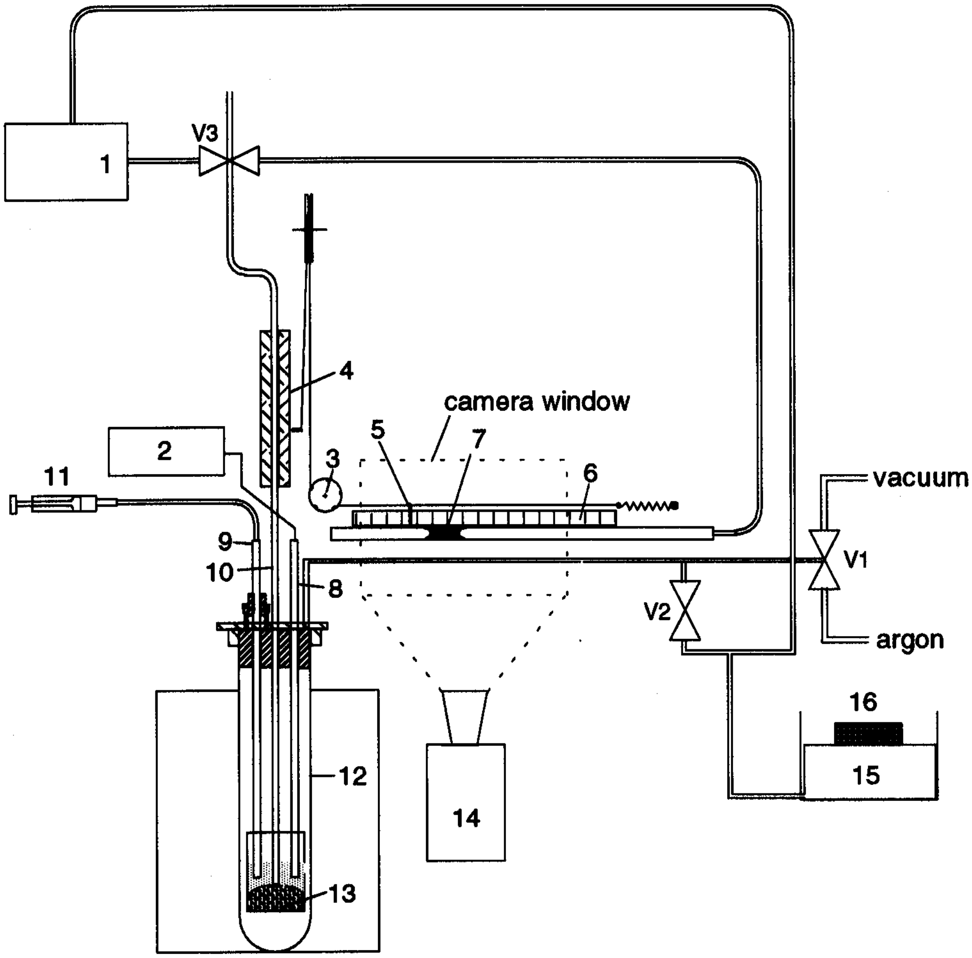

Figure 2. Schematic representation of the experimental technique: (1) small gas pump, (2) temperature display, (3) pulleys, (4) immersion mechanism, (5) capillary position pointer, (6) scale, (7) liquid meniscus, (8) thermocouple, (9) metal sampling tube, (10) immersion capillary alumina tube, (11) metal sampling syringe, (12) mullite reaction tube, (13) MgO crucible, (14) high-resolution video camera with S-VHS VCR and video monitor, (15) gas buffer, (16) gas buffer load.

Utigard, 1987). It is known that while reactions take place, the interfacial tension may significantly decrease.

The maximum bubble pressure method, which is a technique somewhat similar to the drop weight method, has also been used at high temperatures. With this technique, it is required to measure the pressure necessary to force small drops of a molten metal through an orifice into the molten salt (Reding, 1971). On the basis of the density difference and the maximum "drop" pressure, the interfacial tension can be calculated using the Schroedinger equation (Schroedinger, 1914). This technique is very demanding and therefore rarely used. In addition, it has the problem of exchange reactions taking place as the two liquids come into contact, leading to interfacial tension gradients and possible wetting changes.

Another method used for interfacial tension measurements is based on the capillary depression phenomenon which takes place when a nonwetted tube is moved through an interface. This method, which has been used to measure the aluminum + cryolite interfacial tension (Dewing and Desclaux, 1977), is based on measuring the position of the metal/salt interface in the tube. As the tube is moved down through the salt layer before reaching the metal interface, the molten salt entering the tube displaces a certain volume of gas (Figure 1, region a). Since the tube is nonwetted by the metal, no metal will enter the tube as it reaches and passes through the salt/metal interface and as long as the tube immersion is less than the capillary depression. Therefore, during this period there is no further displacement of the gas within the tube (region b). However, as the tube is pushed further down, metal suddenly starts to enter the tube, and again gas is displaced from the tube (region c). By connecting the capillary tube to a horizontal glass tube in which there is a liquid meniscus, the position of the salt/metal interface can be determined on the basis of the movement of this meniscus.

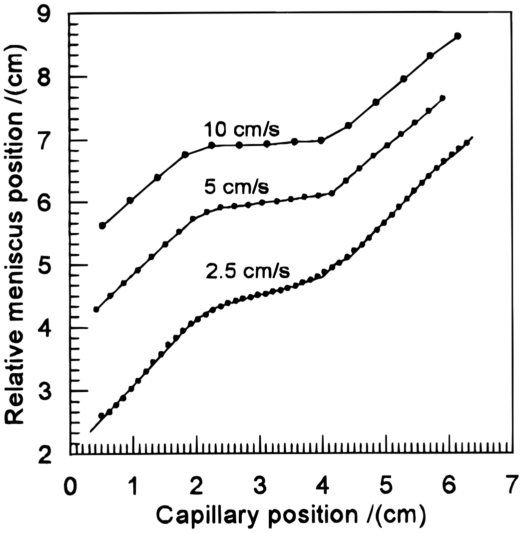

Figure 3. Meniscus position versus the capillary immersion depth at different immersion speeds.

Table 1. Interfacial Tension σ between Aluminum and Chloride−Fluoride Metals at Various Mole Fractions of the Components

100x						100x					
NaCl	KCl	NaF	T/K	σ/(mN/m)	S_d/(mN/m)	NaCl	KCl	NaF	T/K	σ/(mN/m)	S_d/(mN/m)
50.0	50.0	0.00	1000	738.3	10.4	48.2	48.2	3.52	1000	577.8	7.7
50.0	50.0	0.08	1000	719.0	3.1	47.4	47.4	5.28	1000	550.3	10.4
49.9	49.9	0.16	1000	709.4	2.7	46.4	46.4	7.17	1000	529.2	7.9
49.6	49.6	0.79	1000	688.1	8.1	45.4	45.4	9.18	1000	508.4	13.8
49.2	49.2	1.57	1000	666.6	12.3	42.5	42.5	14.96	1000	494.8	20.8

100x					100x				
NaCl	NaF	T/K	σ/(mN/m)	S_d/(mN/m)	NaCl	NaF	T/K	σ/(mN/m)	S_d/(mN/m)
100.0	0.00	1123	742.8	18.1	99.3	0.69	1123	654.5	13.3
99.9	0.07	1123	720.3	10.2	98.6	1.39	1123	604.1	28.8
99.9	0.14	1123	699.6	5.7	97.2	2.76	1123	577.9	18.6

100x					100x				
NaCl	KF	T/K	σ/(mN/m)	S_d/(mN/m)	NaCl	KF	T/K	σ/(mN/m)	S_d/(mN/m)
100.0	0.00	1123	755.1	28.0	99.5	0.50	1123	684.6	18.6
99.9	0.05	1123	748.6	32.3	99.0	1.01	1123	648.4	17.7
99.9	0.10	1123	726.3	28.9	98.0	2.01	1123	623.3	12.3

100x							100x						
NaCl	KCl	NaF	$MgCl_2$	T/K	σ/(mN/m)	S_d/(mN/m)	NaCl	KCl	NaF	$MgCl_2$	T/K	σ/(mN/m)	S_d/(mN/m)
50.0	50.0	0.00	0.00	1000	726.3	25.5	47.3	47.3	3.92	1.38	1000	720.2	11.7
49.6	49.6	0.00	0.70	1000	738.6	8.4	46.3	46.3	3.96	3.49	1000	755.0	19.1
49.3	49.3	0.00	1.41	1000	746.8	15.6	44.5	44.5	4.01	7.08	1000	774.4	15.2
48.2	48.2	0.00	3.55	1000	758.3	11.2	40.7	40.7	4.13	14.56	1000	780.5	9.4
46.4	46.4	0.00	7.20	1000	753.9	23.7	27.8	27.8	4.52	39.85	1000	793.1	23.3
42.6	42.6	0.00	14.87	1000	794.0	23.5	46.2	46.2	7.69	0.00	1000	528.0	16.1
29.4	29.4	0.00	41.12	1000	818.8	23.9	45.8	45.8	7.71	0.68	1000	555.9	9.1
48.0	48.0	3.90	0.00	1000	615.8	22.1	45.5	45.5	7.73	1.36	1000	608.7	18.6
47.7	47.7	3.91	0.69	1000	660.1	18.4	44.4	44.4	7.79	3.44	1000	690.0	13.9

100x							100x						
NaCl	KCl	NaF	$MgCl_2$	T/K	σ/(mN/m)	S_d/(mN/m)	NaCl	KCl	NaF	$MgCl_2$	T/K	σ/(mN/m)	S_d/(mN/m)
42.6	42.6	7.89	6.96	1000	745.3	10.4	26.3	26.3	8.76	38.66	1000	760.0	10.7
38.8	38.8	8.09	14.27	1000	744.9	14.3							

100x						100x					
NaCl	KCl	MgF_2	T/K	σ/(mN/m)	S_d/(mN/m)	NaCl	KCl	MgF_2	T/K	σ/(mN/m)	S_d/(mN/m)
50.0	50.0	0.00	1000	763.4	16.5	47.3	47.3	5.32	1000	712.9	24.0
49.5	49.5	1.07	1000	742.7	18.4						

100x						100x					
NaCl	KCl	Na_3AlF_6	T/K	σ/(mN/m)	S_d/(mN/m)	NaCl	KCl	Na_3AlF_6	T/K	σ/(mN/m)	S_d/(mN/m)
50.0	50.0	0.00	1000	766.0	12.9	49.7	49.7	0.64	1000	688.8	13.4
49.8	49.8	0.32	1000	732.1	15.4	49.2	49.2	1.64	1000	684.1	17.4

100x						100x					
NaCl	KCl	AlF_3	T/K	σ/(mN/m)	S_d/(mN/m)	NaCl	KCl	AlF_3	T/K	σ/(mN/m)	S_d/(mN/m)
50.0	50.0	0.00	1000	775.9	10.8	49.2	49.2	1.59	1000	779.6	10.2
49.6	49.6	0.79	1000	776.2	6.5	48.0	48.0	4.00	1000	785.8	6.9

This technique has the disadvantage that, as the capillary tube moves down into the crucible, the average temperature inside the tube increases, leading to gas expansion and movement of the measuring meniscus. Dewing and Desclaux tried to avoid this problem by moving the capillary rapidly to a certain immersion and then measuring the distance traveled by the meniscus during its initial rapid movement, assuming that the gas expansion will reflect itself by a subsequent slower movement of the meniscus. By immersing the capillary tube to various depths, they were able to obtain a curve of the meniscus movement versus the depth of capillary immersion, which allowed them to determine the capillary depression. Since the movement of the meniscus was measured visually, personal judgment had to be made as to when the rapid movement of the meniscus had stopped. One advantage of this method is that ceramic tubes such as alumina are nonwetted by most metals and are nearly inert in most low-temperature molten salts. Another advantage is that the metal and the salt can be kept in contact with each other long enough before the start of the interfacial tension measurement, allowing for chemical equilibrium to be reached. Because of these advantages, it was decided to develop a revised and improved version of this technique for the measurement of the interfacial tension between aluminum- and chloride-based molten salts.

Experimental Section

To eliminate the manual reading of the meniscus, a system was developed so that the position of the capillary immersion tube as well as that of the measuring meniscus

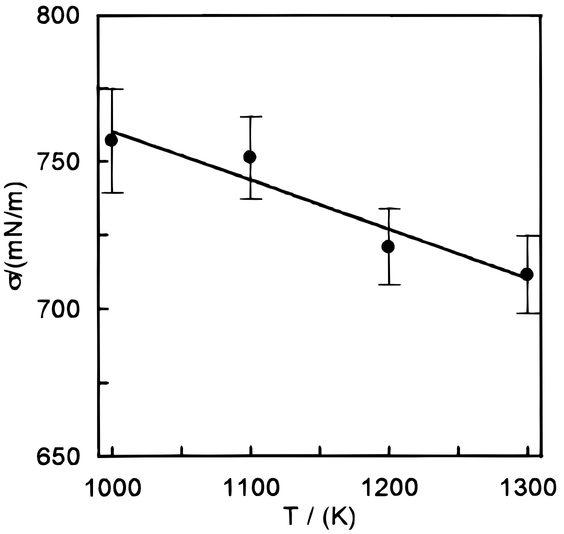

Figure 4. Interfacial tension between Al and an equimolar melt of NaCl and KCl as a function of temperature.

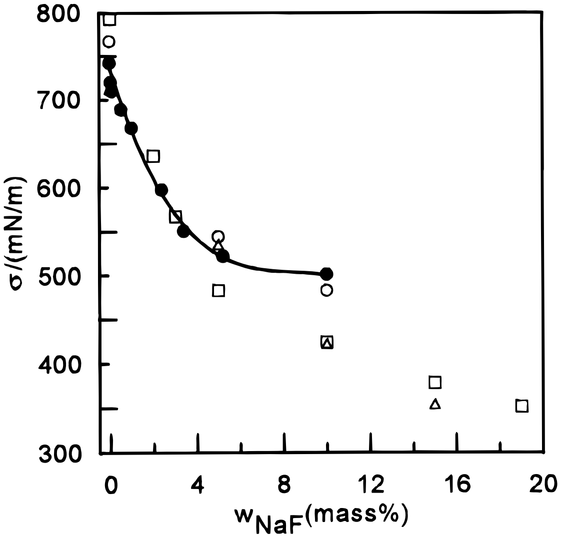

Figure 5. Interfacial tension at 1000 K as a function of the NaF content: (□) Martin-Garin et al., 1979; (△) Kurdyumov et al., 1973; (○) Ho and Sahai, 1990; (●) this work.

could be continuously recorded by a video camera. A schematic diagram of the experimental setup is given in Figure 2. The measuring capillary alumina tube has an i.d. of 4.3 mm and an o.d. of 6.35 mm, and is connected to the 2.5 mm i.d. horizontal glass tube containing the meniscus liquid through a plastic tube. The capillary positioning device was designed to exhibit sufficient force to move the capillary smoothly through the gastight gasket which is required in order to prevent air leakage into the reaction tube. The vertical movement of the alumina capillary was displayed by a pointer along the same scale as the meniscus position. By zooming in on this scale with a video camera set with a shutter speed of 1/1000 s, sharp images with a high resolution were obtained. These images were recorded on a super VHS VCR.

To work with an inert atmosphere, the furnace compartment was sealed, allowing for evacuation followed by refilling with high-purity argon. A gas buffer made from polyethylene provided pressure equalization between the reaction tube and the surroundings, allowing us to operate with a slight inside overpressure during periods when no measurements were taken.

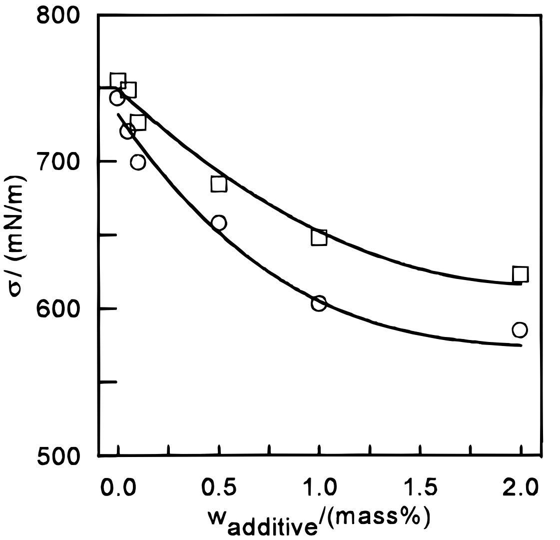

Figure 6. Interfacial tension between aluminum and NaCl-NaF and NaCl-KF melts at 1100 K as a function of NaF and KF contents: (○) NaF; (□) KF.

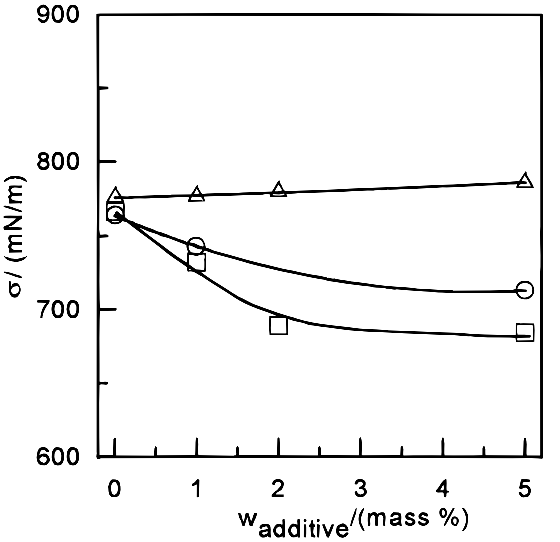

Figure 7. Interfacial tension between aluminum and NaCl−KCl melts at 1000 K as a function of MgF_2, AlF_3, and Na_3AlF_6 contents: (○) MgF_2; (□) Na_3AlF_6; (△) AlF_3.

Experimental Procedure

Preparation of the samples was carried out in a drybox filled with high-purity nitrogen. While in the drybox, the metal and the salt flux were added to a magnesium crucible (i.d. = 69 mm, h = 120 mm), which was then placed into a one-end closed mullite tube (i.d. = 4 in.). This reaction tube was sealed by a water-cooled brass head, through which the measuring capillary, thermocouple, and sampling tube could be immersed. Before heating, the reaction tube was repeatedly evacuated and then filled with high-purity argon. After stabilization at the required temperature, the gas buffer load was removed, all valves were set to the desired direction, the VCR was started for recording and the capillary positioning device was actuated.

The relay unit performed one sweep which consisted of lowering the capillary tube at a rate of 5 cm/s to the bottom position, followed by lifting to the upper resting position. The whole sweep lasted approximately 2 s. Immersion rates above 10 cm/s caused increasing scatter in the measurement. This may be due to disturbances at the salt/metal interface or to the fact that the camera scanning

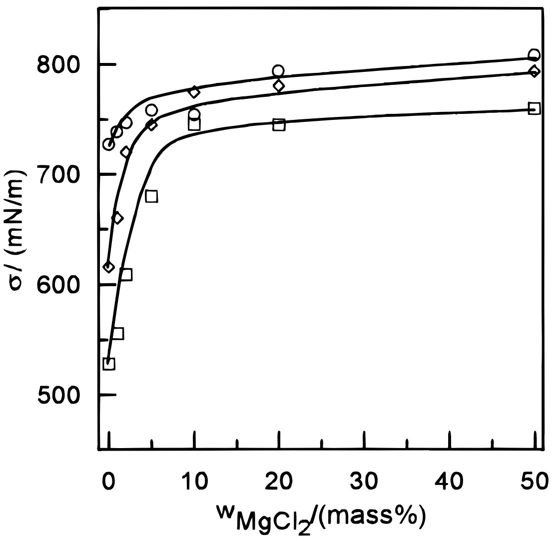

Figure 8. Interfacial tension between aluminum and NaCl−KCl melts at 1000 K with additions of NaF as a function of $MgCl_2$ content: (○) no NaF added; (◇) 2.5 wt % NaF; (□) 5 wt % NaF.

speed was limited to only 30 frames/s, giving a poor resolution of the meniscus position. On the other hand, immersion speeds below 1 cm/s caused noticeable thermal expansion of the gas within the capillary tube, affecting the position of the recording meniscus. Figure 3 shows the obtained results for sweeps using 1, 5, and 10 cm/s immersion speeds. On the basis of this figure as well as other tests, it was decided to carry out the tests with an immersion speed of 5 cm/s. At this speed, the immersion takes about 1 s and approximately 25 measurement points are recorded during the course of each measurement. Since some melt was left in the capillary tube after being pulled out of the melt, a small gas pump was used to expel this remaining melt. For each melt composition, 10 sweeps were recorded and subsequently transcripted manually frame by frame to a spreadsheet for subsequent evaluation.

Calculation Procedure

During the computational procedure, several corrections have to be made as outlined by Dewing and Desclaux. To decrease the magnitude of these corrections, it is preferable to use as large a diameter crucible as possible. In our experiments the crucible i.d. was 70 mm, height 100 mm. The amount of aluminum and salt was chosen so that, after its melting, there was 40 mm of layer aluminum and 30 mm layer of molten salt in the crucible.

The first correction results from when the tube is immersed into the metal: it displaces some of the metal, and the metal level in the crucible rises. To compensate for this, the depth of immersion measured from the point where the tube first touched the metal must be divided by $[1 - (r'/r_c)^2]$, where r' is the external radius of the capillary and r_c is the crucible radius. Before proceeding with the other corrections, the uncorrected capillary depression should be divided by this factor.

A second correction is due to the curvature of the interface before the tube touches it. The capillary depression has to be calculated on the basis of a hypothetical flat, undistorted surface. The real interface lies below this hypothetical interface and the excess pressure that exists immediately below the interface is $2\sigma/r_1$, where r_1 is the radius of curvature of the surface at that point before the tube is immersed, and σ is the interfacial tension.

The third correction is due to changes in the shape of the interface caused by the capillary. As the tube enters the aluminum, an interfacial tension force is formed along the outer edge of the tube. The resulting interfacial tension force is spread evenly over the cross section of the crucible, leading to a pressure change of $2\sigma r'/r_c^2$.

Since the alumina immersion capillary is completely nonwetted by aluminum, it was assumed that it forms a contact angle of 180° with the aluminum. The interfacial tension can then be calculated from the following equation:

$$\sigma = \frac{g\rho h}{2\left(\frac{1}{r} - \frac{1}{r_1} - \frac{r'}{r_c^{\,2}}\right)} \qquad (1)$$

where σ is the interfacial tension, r is the internal radius of the measuring capillary, r_1 is the radius of the aluminum surface curvature at the center of the crucible, r' is the external radius of the capillary, r_c is the internal radius of the crucible, g is the acceleration of gravity, ρ is the density of aluminum, and h is the capillary depression. To estimate r_1 for our 70 mm diameter crucible, the following relation was used.

$$r_1/\text{mm} = 53 + 75\left[\frac{\Delta\rho/(\text{kg/m}^3)}{\sigma/(\text{mN/m})}\right]^2 \qquad (2)$$

$\Delta\rho$ is the density difference between the melt and aluminum. r_1 varied between 100 and 180 mm.

This relation was developed by superimposing sessile drops of various shapes with an equatorial diameter of 70 mm (equal to crucible i.d.) and with a contact angle of 90°. The sessile drop shapes were then digitized and the apex diameter was calculated using the program developed by Rotenberg et al. (1983). On the basis of the results for the various drop shapes, a regression analysis was used to obtain the above equation. The interfacial tension (σ) was found by iterative calculations. These calculations were insensitive to the initial guess, and they converged very quickly. If these corrections had not been made, the maximum error in the calculated interfacial tension would have been 4%.

To determine the effect of uncertainties of the various parameters on the calculated interfacial tension, a set of sensitivity calculations were carried out. It was found that a 1% uncertainty in either the capillary diameter, the capillary depression, or the density of the aluminum causes a 1.0 to 1.1% uncertainty in the calculated interfacial tension. A 1% uncertainty in the density of the melt or in the temperature leads to an uncertainty in the interfacial tension of less than 0.1%.

Results and Discussion

The interfacial tension data obtained in this investigation are summarized in Table 1. Figure 4 shows that the interfacial tension between aluminum and an equimolar melt of NaCl + KCl decreases linearly from about 760 mN/m at 1000 K to about 712 mN/m at 1300 K. The error bars represent the standard deviation (~2.0%) based on 10 separate immersions for each melt temperature. As seen in Figure 5, the interfacial tension decreases significantly with increasing NaF content. This effect, which is explained by sodium enrichment of the salt/aluminum interface, has previously also been found by other investigators (Ho and Sahai, 1990; Kurdyumov et al., 1973) and also in the aluminum−cryolite system (Dewing and Desclaux, 1977; Utigard and Toguri, 1985). When NaF is present, the following exchange reaction with aluminum takes place

$$\frac{1}{3}\mathrm{Al} + \mathrm{NaF} = \frac{1}{3}\mathrm{AlF_3} + \mathrm{Na} \qquad K_{\mathrm{eq}} = 1.9 \times 10^3 \quad (3)$$

Since sodium has a very low surface tension, it tends to concentrate at the interface, causing a drop in the interfacial tension. Figure 6 shows that KF also sharply decreases the interfacial tension. This can be explained by potassium enrichment at the salt/metal interface, in a fashion similar to that of NaF.

Figure 7 shows that additions of MgF_2 and Na_3AlF_6 decrease slightly the interfacial tension, while AlF_3 has no effect on it. The only additive which increases the interfacial tension was $MgCl_2$. As seen in Figure 8, $MgCl_2$ additions to a melt with no NaF caused the interfacial tension to increase from about 730 to 805 mN/m. This increase may be explained by the following reaction:

$$\mathrm{MgCl_2} + 2\mathrm{Cl^-} = \mathrm{MgCl_4}^{2-} \quad (4)$$

By the formation of this complex, it appears that the interaction between the salt and the aluminum decreases, leading to an increasing interfacial tension. Figure 8 shows that $MgCl_2$ additions lead to an increase in the interfacial tension also when NaF was present. This can be explained by the exchange reaction

$$\mathrm{MgCl_2} + 2\mathrm{NaF} = \mathrm{MgF_2} + 2\mathrm{NaCl} \qquad K_{\mathrm{eq}} = 3.6 \times 10^8 \quad (5)$$

In this way, the activity of NaF decreases and thereby also the sodium activity in the metal.

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