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# Interfacial Tension between Aluminum and Cryolite Alumina Melts

**Michal Korenko***

Department of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska cesta 9, SK-845 36 Bratislava, Slovakia

The interfacial tension (IFT) between aluminum and cryolite melts containing different salt additions ($AlF_3$, NaF, $Na_2SO_4$, $NaVO_3$) has been measured by the capillary depression method under the condition of electrolysis. The interfacial tension was found to be strongly dependent on the $n(NaF)/n(AlF_3)$ ratio (cryolite ratio, CR). The addition of $Na_2SO_4$ decreases the IFT of the alumina/electrolyte interface. We also found a different influence of conditions of electrolysis on IFT in the systems with and without $Na_2SO_4$. In the systems without $Na_2SO_4$, the IFT decreases with increasing current density, and vice versa in the systems with $Na_2SO_4$. Addition of $NaVO_3$ has no effect on the IFT between aluminum and the cryolite−alumina electrolytes.

## Introduction

Surface phenomena play a crucial role in metallurgical processes. In the Hall−Héroult process (industrial aluminum electrolysis), the interfacial tension (IFT) between aluminum and the electrolyte influences the stability and shape of the interface which, in turn, may control the rate of back dissolution of aluminum into the electrolyte. It is now generally accepted that the loss in the current efficiency is mainly controlled by the rate of dissolution of aluminum into the bath phase.[1,2] Thus all factors which affect the bath/metal boundary will influence the current efficiency. The IFT also determines the ability of the interface to support undissolved alumina particles which prevents or decreases the formation of alumina sludge between the carbon lining and the liquid aluminum cathode. The IFT also plays a significant role in the refining and the recycling of aluminum. 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.

As indicated by Grjotheim et al.[1] and Thonstad et al.,[2] information concerning the effect of electrolysis on IFT is limited. The interfacial tension between aluminum and cryolite melts has previously been investigated mostly by Russian authors Zhemchuzhina and Belyaev, Gerasimov and Belyaev, Portevin and Bastien, and Belyaev[3−6] (Figure 1). However, the results have been found to be sufficiently discrepant that more work was desirable. Later investigations were carried out by Dewing and Desclaux,[7] Utigard and Toguri,[8,9] Grjotheim et al.,[10] Fan and Østvold,[11] Korenko and Ondercin,[12] and Korenko.[13] Despite all of these studies, the influence of different impurities on the IFT between aluminum and electrolytes is rarely known. The same can be said about the influence of the passing current on the interfacial tension in aluminum electrolysis.

## Experimental Section

There are several methods for IFT measurement. However, at high temperature, the choice of the measurement techniques is limited. Good reviews of the possible methods for determination of IFT in high temperature molten systems can by found in the work by Silný and Utigard[14] and Danek.[15] In the following paragraphs, we will present a short compilation from these works to offer a survey of possible techniques.

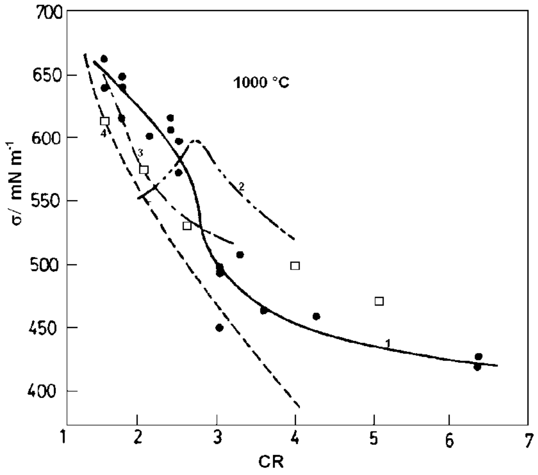

**Figure 1.** Interfacial tension of aluminum in cryolite melts as a function of cryolite ratio (CR) at 1000 °C. 1, Utigard and Toguri;[9] 2, Zhemchuzhina and Belyaev;[3] 3, Gerasimov and Belyaev;[4] 4, Dewing and Desclaux;[7] □, Zhanguo Fan and Østvold.[11]

Since most high temperature liquids are corrosive and often nontransparent to visible light, the sessile drop method can seldom be used. However, by the usage of an X-ray beam, the shape of sessile drops immersed in another liquid may be determined.[8,9] Another method for IFT measurements is the pin detachment method. A serious problem is the material compatibility and the corrosion issues between the pin and the investigated systems which may tend to change the wetting properties and therefore the IFT.[15]

Also, the drop weight method can be generally used for the determination of IFT between aluminum and the molten electrolyte. This method is based on measuring the size of individual metallic drops which are forced through a small orifice into the molten salts. However, the main problem with this technique is that the metal and the molten salts are not necessarily in thermodynamic equilibrium before the metal is forced into the salts.

The maximum bubble pressure method, which is a technique somewhat similar to the drop weight method, has also been used

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* Corresponding author. E-mail: uachmiko@savba.sk.

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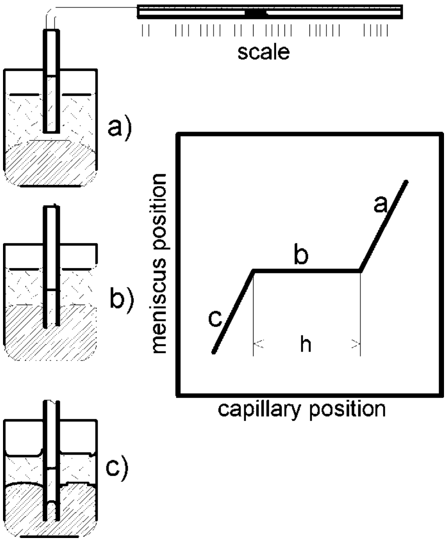

**Figure 2.** Principle of the method (according to work by Silný and Utigard[14]).

at high temperatures. The principle of the technique is based on the measurement of pressure necessary to force small drops of a molten metal through an orifice into the molten salts. Like in the former case, this technique is very demanding and therefore rarely used.

Among the simple, classical methods of determining the surface or interface tension is capillary rise or depression. This method was used in this work.

***Technique.*** The method used in this work is based on the capillary depression phenomenon, which takes place when a tube that is not wetted by a metallic phase is moved through the aluminum/melt interface. This method was used to measure the aluminum/cryolite interfacial tension by Dewing and Desclaux,[7] and it is based on measuring the position of the metal/salt interface in the tube. 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, based on the movement of this meniscus. The situation and the principle of the method are well described in Figure 2 (borrowed from the work by Silný and Utigard[14]). As the sinter-corundum 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 2, region a). Since the tube is not wetted by the metal, no metal will enter the tube as it reaches and passes through the salt/metal interface and is pushed further down until the maximal capillary depression is reached, the metal starts to enter the tube, and again gas is displaced from the tube (Figure 2, region c).

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[7] 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 would be reflected by a subsequent slower movement of the meniscus. By immersing the capillary tube to various depths, they were able to obtain a rough 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 applied as to when the rapid movement of the meniscus had ceased. One advantage of this method is that ceramic tubes such as alumina are not wetted 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 long enough before the start of the interfacial tension measurement, allowing chemical equilibrium to be reached. The next significant advantage of the capillary technique is the possibility of usage of the technique under the conditions of electrolysis. Because of these advantages, we developed a revised and improved version of this technique, which was first presented by Silný and Utigard.[14] We are using video recording equipment and a PC for the exact measurement of the interfacial tension between aluminum and molten salts.

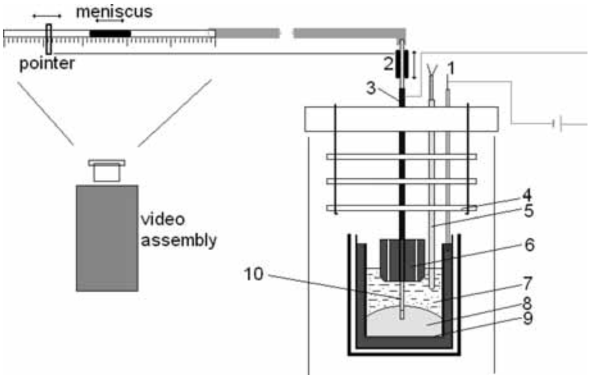

**Figure 3.** Schematic representation of the experimental setup. 1, cathode connection; 2, positioning device; 3, anode connection; 4, radiation sheets; 5, thermocouple; 6, graphite anode; 7, electrolyte; 8, aluminum; 9, Mo plate; 10, alumina tube for depression measuring.

***Experimental Details.*** 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 indicator meniscus were continuously recorded by a digital video camera. A schematic diagram of the experimental setup is given in Figure 3. The measuring alumina capillary tube has an ID of 4.9 mm, an OD of 7.2 mm, and is connected via a plastic tube to the 2.5 mm ID horizontal glass tube containing the meniscus liquid. Graphite crucibles with a (59 to 60) mm ID and height of 110 mm were used. The amounts of aluminum and salt were chosen so that after melting there was a 40 mm layer of aluminum and a 30 mm layer of molten salt in the crucible.

The measuring alumina tube was placed inside the anode connection tube (Figure 3). This connection tube was made of stainless steel, and at the end of the tube, the graphite anode was placed. The anode was made from very pure graphite. The measuring alumina tube thus moves through the connection tube and anode. Such an assembly enables measuring of the capillary depression in situ during the electrolysis. Each measurement under the condition of electrolysis was done after 15 min current exposition. Because an inert atmosphere of nitrogen was used, the furnace compartment was hermetically closed.

The automatic capillary positioning device was designed to exhibit sufficient force to move the capillary smoothly through the gastight gasket, which is required to prevent air leakage into the reaction tube. A pointer along the same scale as the meniscus position displayed the vertical movement of the alumina capillary. By zooming in on this scale with a video camera equipped with a fast shutter, sharp, high-resolution images were obtained. These images were digitized frame by frame and read into the computer. Typicallly, 10 sweeps were recorded for each melt composition, when no current was applied, and 5 sweeps under the conditions of electrolysis. Further details of the technique and calculation procedure may be found elsewhere.[14]

**Table 1. Interfacial Tension between Aluminum and Cryolite−Alumina Electrolytes at 1000 °C**[a]

| $x(Na_3AlF_6)$ | $x(NaF)$ | $x(AlF_3)$ | $x(Al_2O_3)$ | $x(Na_2SO_4)$ | $x(NaVO_3)$ | CR | $j$ / $A \cdot cm^{-2}$ | IFT / $mN \cdot m^{-1}$ | $S_d$ / $mN \cdot m^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.4340 | 0 | 0.5160 | 0.0500 | 0 | 0 | 1.37 | 0 | 647 | 12 |
| 0.6950 | 0 | 0.2150 | 0.0900 | 0 | 0 | 2.29 | 0 | 551 | 13 |
| 0.6950 | 0 | 0.2150 | 0.0900 | 0 | 0 | 2.29 | 0.018 | 530 | 14 |
| 0.6950 | 0 | 0.2150 | 0.0900 | 0 | 0 | 2.29 | 0.037 | 545 | 12 |
| 0.6950 | 0 | 0.2150 | 0.0900 | 0 | 0 | 2.29 | 0.056 | 516 | 11 |
| 0.6950 | 0 | 0.2150 | 0.0900 | 0 | 0 | 2.29 | 0.074 | 532 | 14 |
| 0.6950 | 0 | 0.2150 | 0.0900 | 0 | 0 | 2.29 | 0.092 | 519 | 12 |
| 0.6950 | 0 | 0.2150 | 0.0900 | 0 | 0 | 2.29 | 0.112 | 516 | 16 |
| 0.5820 | 0.3680 | 0 | 0.0500 | 0 | 0 | 3.63 | 0 | 465 | 15 |
| 0.5820 | 0.3680 | 0 | 0.0500 | 0 | 0 | 3.63 | 0.060 | 445 | 18 |
| 0.5820 | 0.3680 | 0 | 0.0500 | 0 | 0 | 3.63 | 0.112 | 427 | 19 |
| 0.3909 | 0.5591 | 0 | 0.0500 | 0 | 0 | 4.43 | 0 | 450 | 5 |
| 0.3909 | 0.5591 | 0 | 0.0500 | 0 | 0 | 4.43 | 0.074 | 416 | 16 |
| 0.3909 | 0.5591 | 0 | 0.0500 | 0 | 0 | 4.43 | 0.112 | 405 | 15 |
| 0.3368 | 0.6132 | 0 | 0.0500 | 0 | 0 | 4.82 | 0 | 426 | 11 |
| 0.4154 | 0 | 0.4940 | 0.0505 | 0.0401 | 0 | 1.37 | 0 | 547 | 15 |
| 0.6641 | 0 | 0.2058 | 0.0900 | 0.0401 | 0 | 2.29 | 0 | 451 | 12 |
| 0.6641 | 0 | 0.2058 | 0.0900 | 0.0401 | 0 | 2.29 | 0.040 | 485 | 13 |
| 0.6641 | 0 | 0.2058 | 0.0900 | 0.0401 | 0 | 2.29 | 0.060 | 510 | 14 |
| 0.5579 | 0.3520 | 0 | 0.0500 | 0.0401 | 0 | 3.63 | 0 | 375 | 15 |
| 0.5579 | 0.3520 | 0 | 0.0500 | 0.0401 | 0 | 3.63 | 0.030 | 385 | 12 |
| 0.5579 | 0.3520 | 0 | 0.0500 | 0.0401 | 0 | 3.63 | 0.060 | 410 | 16 |
| 0.3224 | 0.5875 | 0 | 0.0500 | 0.0401 | 0 | 4.82 | 0 | 371 | 17 |
| 0.4972 | 0 | 0.4528 | 0.0500 | 0 | 0.0400 | 1.57 | 0 | 633 | 12 |
| 0.7857 | 0 | 0.1243 | 0.0900 | 0 | 0.0400 | 2.59 | 0 | 526 | 13 |
| 0.655 | 0.2950 | 0 | 0.0500 | 0 | 0.0400 | 3.45 | 0 | 458 | 15 |
| 0.4336 | 0.5164 | 0 | 0.0500 | 0 | 0.0400 | 4.19 | 0 | 436 | 10 |
| 0.3253 | 0.6247 | 0 | 0.0500 | 0 | 0.0400 | 4.92 | 0 | 444 | 11 |

[a] $x(a)$, molar ratio of the component $a$; CR, cryolite ratio, molar ratio $n(NaF)/n(AlF_3)$; $j$, current density; IFT, interfacial tension; $S_d$, standard deviation.

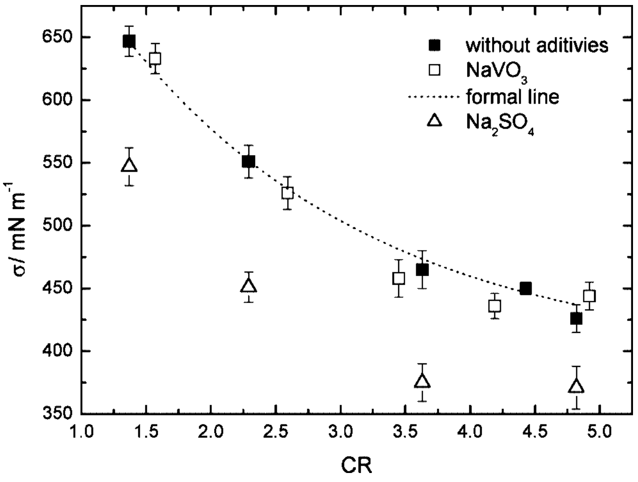

**Figure 4.** Interfacial tension between aluminum and cryolite melts at 1000 °C (zero current). ■, $Na_3AlF_6$ + $AlF_3$ (NaF) + 9.00 (5.00) mass % $Al_2O_3$; □, $Na_3AlF_6$ + $AlF_3$ (NaF) + 9.00 (5.00) mass % $Al_2O_3$ + 4.00 mass % $NaVO_3$; Δ, $Na_3AlF_6$ + $AlF_3$ (NaF) + 9.00 (5.00) mass % $Al_2O_3$ + 4.01 mass % $Na_2SO_4$.

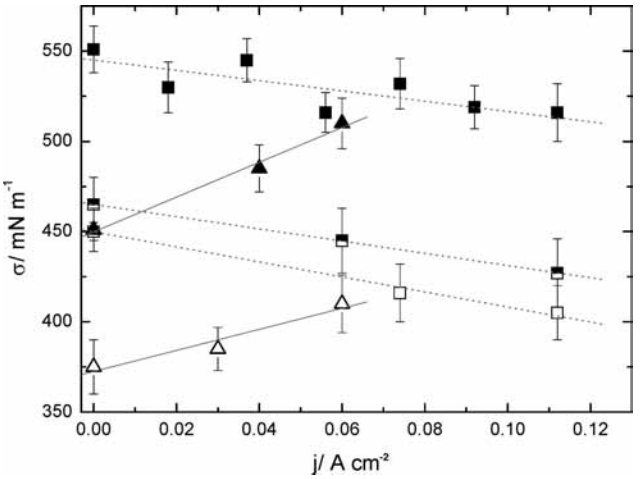

**Figure 5.** Interfacial tension between aluminum and cryolite electrolytes under condition of electrolysis, i.e., interfacial tension as a function of current density at 1000 °C. Δ, $Na_3AlF_6$ + NaF + 5.00 mass % $Al_2O_3$ + 4.01 mass % $Na_2SO_4$, CR = 3.63; ▲, $Na_3AlF_6$ + $AlF_3$ + 9.00 mass % $Al_2O_3$ + 4.01 mass % $Na_2SO_4$, CR = 2.29; □, $Na_3AlF_6$ + NaF + 5.00 mass % $Al_2O_3$, CR = 4.43; ⬒, $Na_3AlF_6$ + NaF + 5.00 mass % $Al_2O_3$, CR = 3.63; ■, $Na_3AlF_6$ + $AlF_3$ + 9.00 mass % $Al_2O_3$, CR = 2.29. All curves are linear formal lines.

## Materials

Aluminum: HiChem s.r.o., Czech Republic, shots, min. 99.99 % purity, max. content of Mg of 40 ppm, Si of 15 ppm, Cu of 20 ppm, and Fe, Mn, Cr, Ti, and Zn of 5 ppm.

$Na_3AlF_6$: Greenland, handpicked, dried at 300 °C.

$AlF_3$: resublimated, min. 99.5 % purity.

NaF: Merck p. a., dried at 250 °C.

$Al_2O_3$: Merck p. a., dried at 300 °C.

$Na_2SO_4$: Merck p. a., dried at 300 °C.

$NaVO_3$: Merck p. a., dried at 300 °C.

The preparation of the samples was carried out in a drybox filled with high purity nitrogen.

## Results and Discussion

The IFT data obtained in this investigation are summarized in Table 1. The error bars represent the standard deviation based on 10 separate immersions. Figure 4 shows the collection of results obtained at zero current. As seen from Figure 4, the IFT decreases significantly with increasing CR (cryolite ratio $n(NaF)/n(AlF_3)$). This effect, which is explained by sodium enrichment of the metal/melts interface, has also been found by all previous investigators.[3–13] Since sodium has a very low surface tension, it tends to concentrate at the interface, causing a drop in the

IFT. The data obtained in this work agree at high CR mostly with Utigard and Toguri[9] and at lower CR with Fan and Østvold[11] (Figure 1).

In Figure 4, the strong negative influence of addition of $Na_2SO_4$ on the IFT of the aluminum/electrolyte interface can also be seen. The quantification of this influence is a decrease of IFT by 100 $mN \cdot m^{-1}$ (ca. 15 %) upon addition of ca. 4 mass % of $Na_2SO_4$. Addition of $NaVO_3$ has no effect on the IFT between aluminum and the cryolite−alumina electrolytes.

In Figure 5, the influence of polarization on the IFT can be seen in the aluminum/cryolite−alumina melts, with and without $Na_2SO_4$. The systems were investigated in the conditions of electrolysis of 15 min duration at each current density. The applied current has different influences on the investigated systems. In the systems without $Na_2SO_4$, the IFT decreases with an increase of current density and vice versa in the systems with $Na_2SO_4$. These results are very interesting. The draft explanation of such a behavior (which is, more or less speculative) can be found in the work by Korenko.[13]

## Literature Cited

(1) Grjotheim, K.; Krohn, C.; Malinovský, M.; Matiašovský, K.; Thonstad, J. *Aluminium Electrolysis. Fundamentals of the Hall−Héroult Process*; Aluminium - Verlag: Düsseldorf, 1982.

(2) Thonstad, J.; Fellner, P.; Haarberg, G. M.; Híveš, J.; Kvande, H.; Sterten, Å. *Aluminium Electrolysis*, 3rd ed.; Aluminium - Verlag: Düsseldorf, 2001.

(3) Zhemchuzhina, E. A.; Belyaev, A. I. *Fiz. Khim. Rasplav. Solei I Shlakov*, Akad. Nauk SSSR, Uralsk., zpub Filial, Inst. Elektrokhim., Tv. Vses. Saveshch.: Sverdlovsk,1960 (Russ.), cited according to Grjotheim et al.[1]

(4) Gerasimov, A. D.; Belyaev, A. I. Interfacial tension at the contact of metal and electrolyte in the electrolytic production and refining of aluminum. *Izv. Vyssh. Ucheb. Zaved., Tsvet. Met.* **1958**, *1*, 50 (Russ.), according to *Chem. Abstr.* **1959**, *53*, 19630c.

(5) Portevin, A.; Bastien, P. Unknown title. *Met. Ind.* **1955**, *48*, 716 (Russ.), cited according to Grjotheim et al.[1]

(6) Belyaev, A. I. *Elektrolit alyuminievykh vann*; Metalurgizdat: Moscow,1961 (Russ.), cited according to Grjotheim et al.[1]

(7) Dewing, E. W.; Desclaux, P. The Interfacial Tension Between Aluminum and Cryolite Melts Saturated with Alumina. *Metall. Trans. B* **1977**, *8B*, 555–561.

(8) Utigard, T.; Toguri, J. M. Interfacial Tension of Aluminum in Cryolite Melts. *Metall. Trans. B* **1985**, *16B*, 333–338.

(9) Utigard, T.; Toguri, J. M. Electrocapilarity in the Aluminum Reduction Cell. *Metall. Trans. B* **1986**, *17B*, 547–552.

(10) Grjotheim, K.; Kvande, H.; Qiu, Z.-X.; Fan, L. Interfacial Phenomena in Molten Salt Electrolysis. *Aluminium* **1989**, *65*, 157–162.

(11) Fan, Z.; Østvold, T. Interfacial Tension Measurements between Liquid Aluminum and Cryolite Melts. *Aluminium* **1991**, *67*, 287–291.

(12) Korenko, M.; Ondercin, M. Interfacial tension between aluminum and cryolite melts during electrolysis of the systems $Na_3AlF_6$–$AlF_3$(NaF)–$Al_2O_3$. *J. Appl. Electrochem.* **2006**, *36*, 1347–1352.

(13) Korenko, M. Influence of Sulphur Impurities on the Interfacial Tension between Aluminum and Cryolite Alumina Melts. *Z. Naturforsch.* **2007**, *62a*, 309–314.

(14) Silný, A.; Utigard, T. A. Interfacial Tension between Aluminum and Chloride−Fluoride Melts. *J. Chem. Eng. Data* **1996**, *41*, 1340–1345.

(15) Danek, V. *Physicochemical analysis of molten electrolytes*; Elsevier: Amsterdam, 2006; Chapter 6.

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