

Interfacial tension between aluminum and cryolite melts during electrolysis of the systems $\text{Na}_3\text{AlF}_6\text{--AlF}_3$ (NaF)– Al_2O_3

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Received 4 March 2005; accepted in revised form 3 April 2006

Key words: aluminum electrolysis, cryolite, interfacial tension

Abstract

The interfacial tension between aluminum and cryolite melts containing different salt additions has been measured by the capillary depression method. The technique is based on the measurement of the capillary depression occurring when the 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. The interfacial tension was found to be strongly dependent on the $n(\text{NaF})/n(\text{AlF}_3)$ ratio (cryolite ratio, CR). At the cryolite ratio 2.28 (80 wt.% Na_3AlF_6 + 10 wt.% AlF_3 + 10 wt.% Al_2O_3 // Al, $t = 1000$ °C) the interfacial tension was 546 mN m^{-1} , while it was 450 mN m^{-1} at the cryolite ratio 4.43 (80 wt.% Na_3AlF_6 + 10 wt.% NaF + 10 wt.% Al_2O_3 // Al, $t = 1000$ °C). Experiments under current flow conditions were also performed. During the electrolysis the interfacial tension at $n(\text{NaF})/n(\text{AlF}_3)$ ratio 2.28 decreased from 546 mN m^{-1} at zero current to 518 mN m^{-1} at 0.112 A cm^{-2} . The same trend was observed in the system with a cryolite ratio 4.43. The interfacial tension decreased from 450 mN m^{-1} at zero current to 400 mN m^{-1} at 0.112 A cm^{-2} . The consequent increase in interfacial tension of these systems caused by interruption of electrolysis was observed. Electrolysis of the system 25 wt.% NaF + 75 wt.% NaCl (eutectic mixture)/Al indicated no influence of applied current on the interfacial tension at 850 °C.

1. Introduction

In the Hall–Heroult cell for electrolysis of alumina, the interfacial tension between aluminum and the electrolyte influences 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 current efficiency is mainly controlled by the rate of dissolution of aluminum into bath phase [1]. Thus all factors which affect the bath/metal boundary will have an influence on the current efficiency.

As indicated by Grjotheim et al. [2] and Thonstad et al. [1], information concerning the effect of electrolysis on interfacial tension is limited. Thus the present investigation was undertaken mostly to study the effect of current flow on the interfacial tension.

The interfacial tension between aluminum and cryolite melts has previously been investigated mostly by Russian authors Zhemchuzhina, Gerasimov, Portevin and Belyaev [3–6]. Later, investigations were carried out by Dewing and Desclaux [7], Utigard and Toguri [8, 9], Grjotheim et al. [10] and Zhanguo and Østvold [11].

2. Experimental

2.1. Methods and experimental apparatus

The method used for interfacial tension measurements 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 of 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. 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 1, 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 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

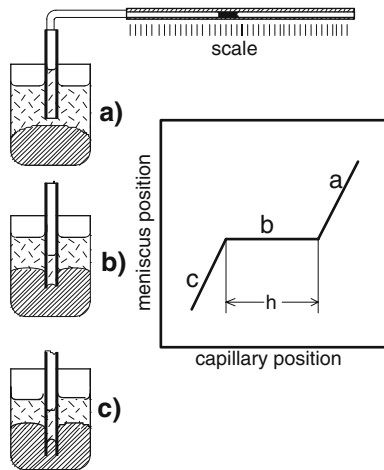


Fig. 1. Principle of the method (according to [12]).

the tube (Figure 1, Region b). However, as the tube is pushed further down until the maximal capillary depression is reached, metal starts to enter the tube, and again gas is displaced from the tube (Figure 1, 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 will 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 vs 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 the 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. Because of these advantages, we developed a revised and improved version of this technique, which was first presented by Silný and Utigard [12]. Video recording equipment and a PC are used for the exact measurement of the interfacial tension between aluminum and molten salts.

A schematic diagram of the experimental setup is given in Figure 2. The measuring alumina capillary tube has an ID of 4.9 mm, the OD is 7.2 mm, and is connected via a plastic tube to the 2.5 mm ID horizontal glass tube containing the meniscus liquid. The measuring alumina tube was placed inside the anode connection

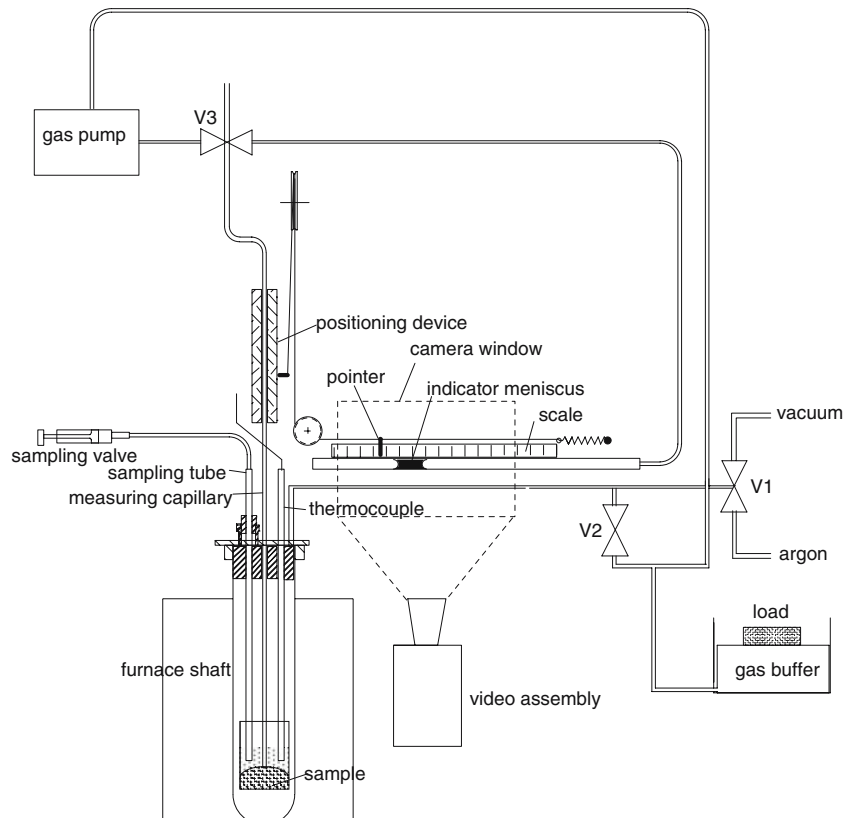


Fig. 2. Schematic representation of the experimental setup.

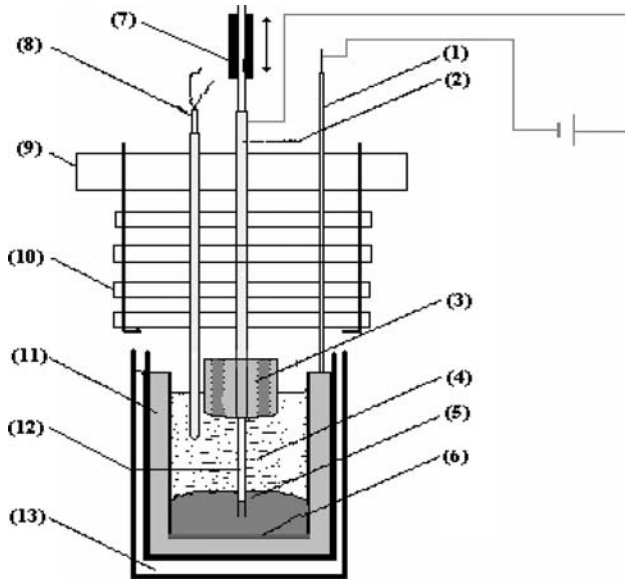


Fig. 3. Detail of the electrolysis cell. 1 – cathode connection, 2 – anode connection, 3 – graphite anode, 4 – electrolyte, 5 – aluminum, 6 – Mo plate, 7 – part of the positioning device, 8 – TC, 9 – furnace flange, 10 – radiation sheets, 11 – graphite crucible, 12 – alumina tube for depression measuring.

tube (Figure 3). This connection tube was made of stainless steel and at the end of this tube, the graphite anode was placed (Figure 3). The measuring alumina tube thus moves through the connection tube and anode. Such assembly enables measuring of the capillary depression during the electrolysis.

Because an inert atmosphere was used, the furnace compartment was hermetically closed, allowing evacuation followed by re-filling with argon. A gas buffer made from a flexible polyethylene bag, provided pressure equalization between the reaction tube and the surroundings, allowing operation with slight over-pressure inside during periods when no measurements were taken.

Further details of the technique and calculation procedure may be found elsewhere [12].

2.2. Materials

Aluminum – HiChem s.r.o., Czech Republic, shots, min. 99.99% purity, max. content of Mg: 40 ppm, Si: 15 ppm, Cu: 20 ppm, Fe, Mn, Cr, Ti, Zn: 5 ppm
 Na_3AlF_6 – Greenland, handpicked, dried at 300 °C
 AlF_3 – resublimated, purity min. 99.5%
 NaF – Merck p.a., dried at 250 °C
 Al_2O_3 – Merck p.a., dried at 300 °C
 NaCl – Merck p.a., dried at 300 °C

The preparation of the samples was carried out in a dry-box filled with high purity nitrogen. Graphite crucibles with 59–60 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 reaction tube was closed by a water-cooled

brass head, through which the measuring capillary, thermocouple and sampling tube could be immersed.

3. Result and discussion

3.1. $\text{Na}_3\text{AlF}_6 + \text{AlF}_3 + \text{Al}_2\text{O}_3/\text{Al}$

Figure 4 shows the dependence between the interfacial tension of the system 80 wt.% $\text{Na}_3\text{AlF}_6 + 10$ wt.% $\text{AlF}_3 + 10$ wt.% $\text{Al}_2\text{O}_3/\text{Al}$ and current density. It follows that interfacial tension decrease with increasing current density. During the electrolysis the interfacial tension at $n(\text{NaF})/n(\text{AlF}_3)$ ratio (CR) 2.28 decreases from 546 mN m^{-1} at zero current to 518 mN m^{-1} at 0.112 A cm^{-2} . It is generally accepted [1, 4, 6–8, 11] that the interfacial tension in these systems is strongly dependent on the $n(\text{NaF})/n(\text{AlF}_3)$ ratio (CR). It is also accepted that current is transported to the interface mainly by Na^+ ions. As a result of the ionic migration of sodium cations and the cathode reaction, concentration gradient of hypothetical NaF species arises at the metal/electrolyte interface. This concentration gradient decreases the interfacial tension. Thonstad and Rolseth [13] produced the diagram given in Figure 5 to illustrate the mass transfer in the boundary layer. For simplicity, oxide-containing species are neglected.

Figure 6 shows the influence of current interruption on the interfacial tension in this system. The interfacial tension increases after current interruption asymptotically.

Also the equilibrium content of sodium in molten aluminum is dependent on CR [1]. Felner and Danielik [14] and Danielik [15] showed that the sodium content in the aluminum increases during electrolysis. Comparison of the shift of CR near the aluminum cathode caused by electrolysis in Danielik's work [15] (calculated according to the concentration of sodium in the molten aluminum cathode during the electrolysis) and in this work

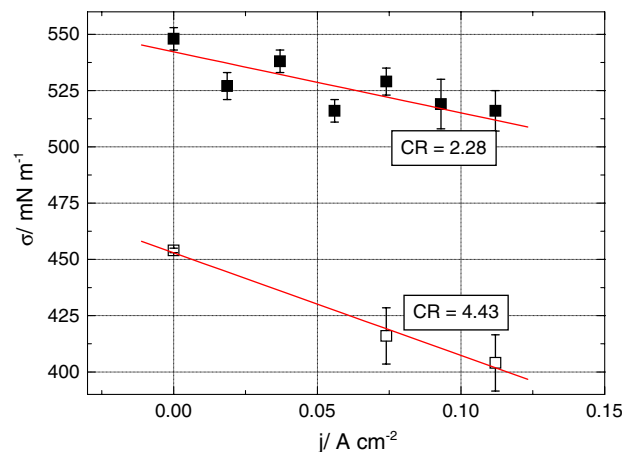


Fig. 4. Interfacial tension as a function of current density and CR. 80 wt.% $\text{Na}_3\text{AlF}_6 + 10$ wt.% NaF (AlF_3) + 10 wt.% $\text{Al}_2\text{O}_3/\text{Al}$, $t = 1000$ °C.

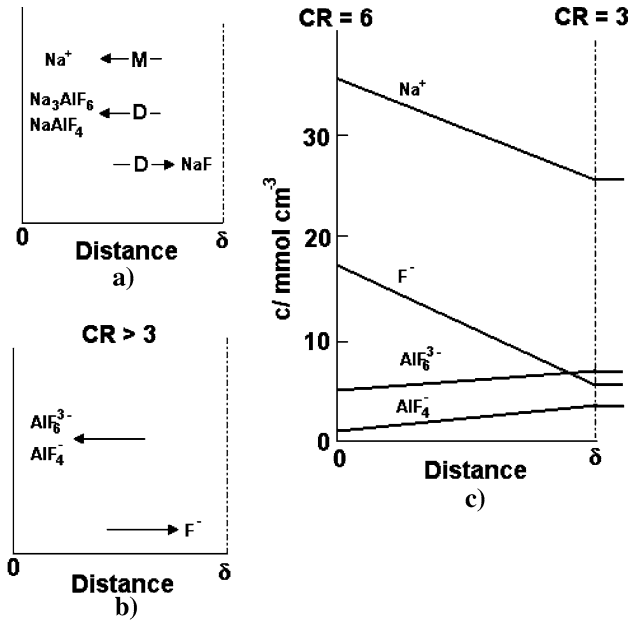


Fig. 5. Schematic illustration of mass transfer taking place in the stagnant cathode diffusion layer by diffusion (D) and migration (M): (a) formal treatment; (b) net ionic transport; (c) calculated concentration gradients in cryolite [13].

(calculated according to the interfacial tension data) is shown in Figure 7. The results agree well.

3.2. $Na_3AlF_6 + NaF + Al_2O_3/Al$

Figure 4 shows the dependence between the interfacial tension and applied current for the systems 80 wt.% $Na_3AlF_6 + 10$ wt.% $NaF + 10$ wt.% Al_2O_3/Al (CR = 4.43). As in the above case, the interfacial tension decreases with increasing current density from

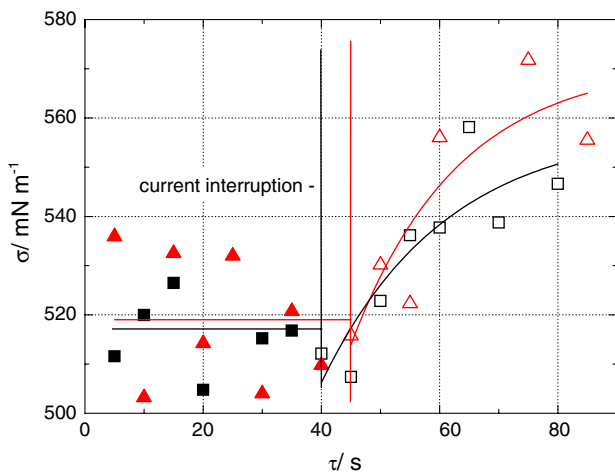


Fig. 6. Interfacial tension before and after current interruption. 80 wt.% $Na_3AlF_6 + 10$ wt.% $AlF_3 + 10$ wt.% Al_2O_3/Al , $t = 1000$ °C, CR = 2.28. Squares - $j = 0.056$ A cm^{-2} , triangles - $j = 0.093$ A cm^{-2} , full symbols - interfacial tension before current interruption, open symbols - interfacial tension after current interruption.

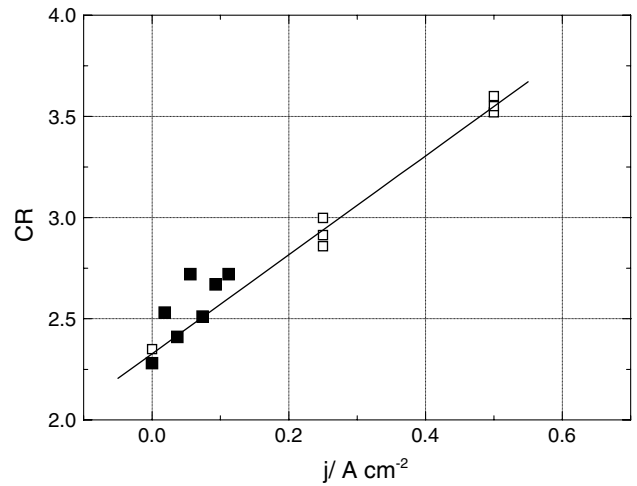


Fig. 7. Shift of CR near Al-cathode vs current density. $Na_3AlF_6 + AlF_3 + Al_2O_3/Al$, $t = 1000$ °C. Open symbols - Danielik [15], full symbols - this work.

450 $mN m^{-1}$ at zero current to 400 $mN m^{-1}$ at 0.112 A cm^{-2} .

Figure 8 summarizes the date of the interfacial tension in cryolyte systems as a function of CR (no applied current). The data from this work are in good agreement mostly with Utigard and Toguri [8] and Zhanguo Fan and Østvold [11].

Figure 9 shows the influence of the current interruption on the interfacial tension after electrolysis at 0.074 A cm^{-2} . The interfacial tension increases asymptotically as in above case.

All investigations suggest the prime role of the activity of sodium for processes taking place at the metal/electrolyte interface. The sodium activity influences the

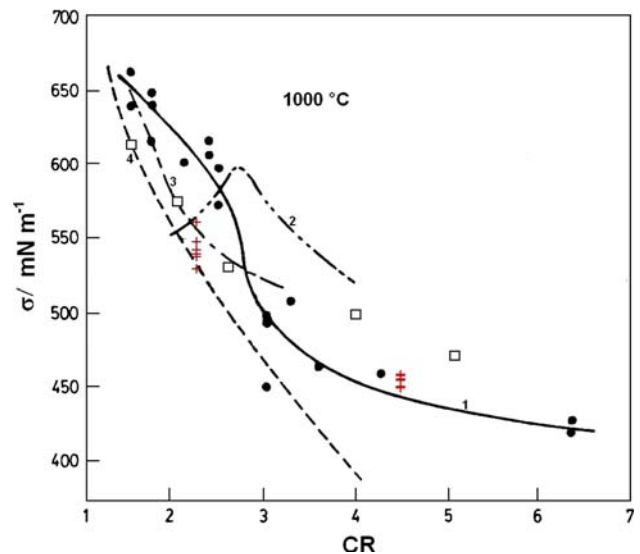


Fig. 8. Interfacial tension of aluminum in cryolite melts as a function of CR. 1 - Utigard Toguri [8], 2 - Zhemchuzhina and Belyaev [3], 3 - Gerasimov and Belyaev [4], Dewing and Desclaux [7], □ - Zhanguo Fan and Østvold [11], + - present study.

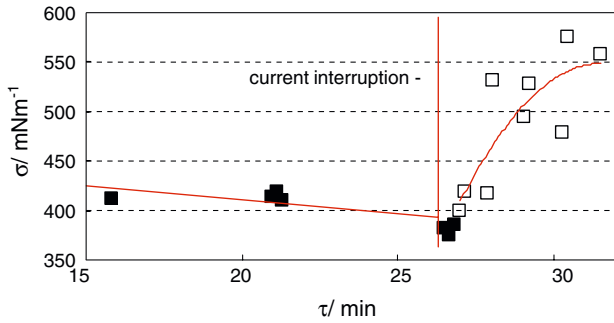


Fig. 9. Interfacial tension before and after current interruption. 80 wt.% Na_3AlF_6 + 10 wt.% NaF + 10 wt.% $\text{Al}_2\text{O}_3/\text{Al}$, $t = 1000^\circ\text{C}$, $\text{CR} = 4.43$ ■ – interfacial tension before current interruption, □ – interfacial tension after current interruption.

contamination of primary aluminum by sodium, cathodic overvoltage and interfacial tension [1], as well.

3.3. $\text{NaCl} + \text{NaF}/\text{Al}$

Experiments were also carried out on a eutectic mixture of NaF and NaCl (25 wt.% NaF + 75 wt.% NaCl/Al) at 850°C . The dependence between duration of electrolysis (50 min at 0.037 A cm^{-2}) and change in interfacial tension of the system was recorded. During electrolysis in this system sodium was produced at the molten aluminum cathode by electrodeposition. In this case, no influence of current and current interruption on the interfacial tension was observed (Figure 10). This fact may be due to a too high concentration of sodium ions in the electrolyte. In such a system the further electrodeposition of sodium has no effect on the interfacial tension. Figure 11 summarizes the interfacial tension data (at zero current) from literature [16] and this work.

4. Conclusions

The apparatus for the interfacial tension measurement in molten aluminum and salt systems based on the capillary depression method has been described. This method is suitable for measurements in the electrolysis conditions. The following conclusions can be made: The

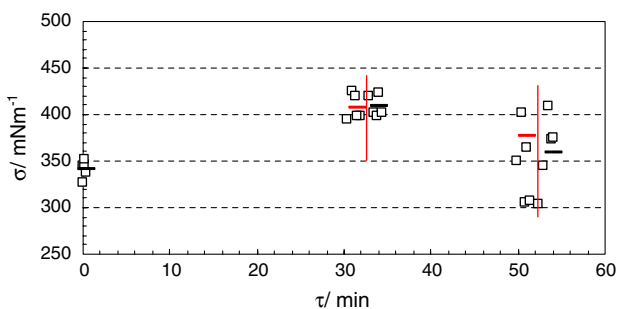


Fig. 10. Interfacial tension in the systems 25 wt.% NaF + 75 wt.% NaCl/Al as a function of duration of electrolysis. $j = 0.037\text{ A cm}^{-2}$, $t = 850^\circ\text{C}$. Vertical lines – interruption of current.

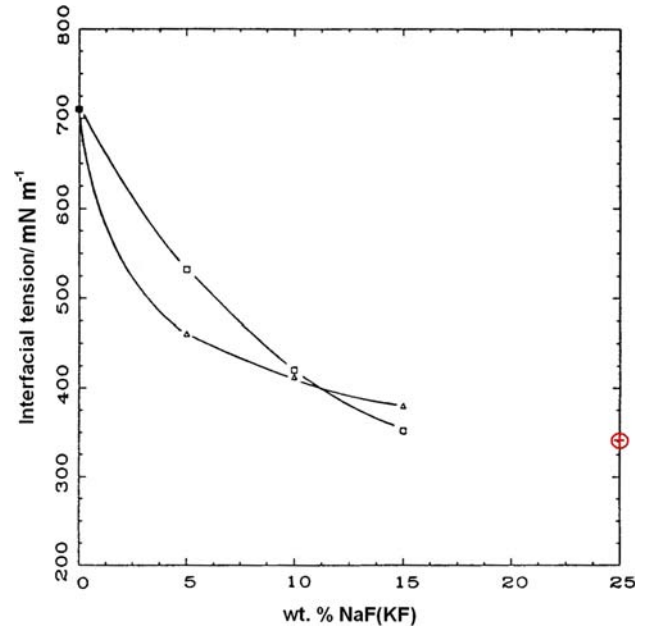


Fig. 11. Interfacial tension in the systems $\text{NaCl}-\text{NaF}$ (KF) as a function of salt composition [16], $t = 850^\circ\text{C}$, □ – NaF , Δ – KF , \oplus – this work.

interfacial tension was found to be strongly dependent on the CR. At the CR 2.28 (80 wt.% Na_3AlF_6 + 10 wt.% AlF_3 + 10 wt.% $\text{Al}_2\text{O}_3/\text{Al}$, $t = 1000^\circ\text{C}$) the interfacial tension was 546 mN m^{-1} , in contrast to 450 mN m^{-1} at the CR 4.43 (80 wt.% Na_3AlF_6 + 10 wt.% NaF + 10 wt.% $\text{Al}_2\text{O}_3/\text{Al}$, $t = 1000^\circ\text{C}$). During electrolysis the interfacial tension at CR ratio 2.28 decreases from 546 mN m^{-1} at zero current to 518 mN m^{-1} at 0.112 A cm^{-2} . The same trend was observed in the system with CR 4.43 (80 wt.% Na_3AlF_6 + 10 wt.% NaF + 10 wt.% $\text{Al}_2\text{O}_3/\text{Al}$, $t = 1000^\circ\text{C}$). The interfacial tension decreases from 450 mN m^{-1} at zero current to 400 mN m^{-1} at 0.112 A cm^{-2} . The decrease in the interfacial tension during electrolysis is due to increase in sodium concentration near the molten aluminum cathode caused by the applied current. No influence of current on the interfacial tension in the system 25 wt.% NaF + 75 wt.% NaCl (eutectic mixture)/ Al was observed.

Acknowledgements

This work was supported by the Science and Technology Assistance Agency under contract No. APVV –51-008104 and by Slovak Grant Agency VEGA 2/4071/04.

References

1. J. Thonstad, P. Fellner, G.M. Haarberg, J. Híveš, H. Kvande and Å Sterten, *Aluminium Electrolysis*, 3rd edn., (Aluminium-Verlag, Dueseldorf, 2000).

2. K. Grjotheim, C. Krohn, M. Malinovský, K. Matiašovský and J. Thonstad, *Aluminium Electrolysis. Fundamentals of the Hall-Héroult Process* (Aluminium-Verlag, Düsseldorf, Germany, 1982).
3. E.A. Zhemchuzhina and A.I. Belyaev, *Fiz. Khim. Rasplav. Solei i Shlakov*, Akad. Nauk SSSR, Uralsk. Filial, Inst. Elektrokhim., Tv. Vses. Saveshch., Sverdlovsk, 1960 (1962) p. 207.
4. A.D. Gerasimov and A.I. Belyaev, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Met.* **1** (1958) 50.
5. A. Portevin and P. Bastien, *Met. Ind.* **48** (1955) 683, 716.
6. A.I. Belyaev, *Elektrolit alyuminievykh vann* (Metalurgizdat, Moscow, 1961).
7. E.W. Dewing and P. Desclaux, *Metall. Trans.* **8B** (1977) 555.
8. T. Utigard and J.M. Toguri, *Metall. Trans. B* **16B** (1985) 333.
9. T. Utigard and J.M. Toguri, *Metall. Trans. B* **17B** (1986) 547.
10. K. Grjotheim, H. Kvande, Qiu Zhu-Xian and Fan Liman, *Aluminium* **65** (1989) 157.
11. Zhanguo Fan and T. Østvold, *Aluminium* **67** (1991) 287.
12. A. Silný and T.A. Utigard, *J. Chem. Eng. Data* **41** (1996) 1061.
13. J. Thonstad and S. Rolseth, *Electrochim. Acta* **23** (1978) 223.
14. P. Fellner and V. Danielik, *Proc. Int. Harald Øye Symp.*, Trondheim, Norway (1995) p. 389.
15. V. Danielik, PhD Thesis, SUT Bratislava (1997).
16. H.K. Francis and S. Yogesh, 'Light metals' (1990), p. 717.