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Electrolyte superheat during electrolytic production of Al

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Abstract

Different variations of electrolysis control schemes, that take into consideration the degree of electrolyte superheat of each individual electrolytic cell, have found a wide application in primary aluminium production. The objective of this work is to ascertain the correctness of the current superheat determination with the use the industrial mobile sensors for simultaneous measurement of electrolyte temperature and its melting/fusion temperature and to evaluate theoretically the necessary value of the superheat. The results correspond with published data, showing that in order to provide necessary heat for melting and dissolution of 1% of alumina in the electrolyte a electrolyte superheat of 13,9ºC is needed. On the other side as a result of the dissolution of 1% of alumina the melting/fusion temperature of electrolyte is decreased by 5,4ºC. This means that during dissolution of alumina the superheat (SH) is reduced by almost 9ºC. At a given superheat value of electrolyte of about 10ºC, which is recommended by many scientists and production engineers, and also taking into consideration the imperfection of sampling and the presence of unaccounted solid particles in the electrolyte during analysis, the possibility to establish negative values of electrolyte superheat is extremely increased.

1. Motivation and Project Target

High energy expenditure during Al production by electrolysis of cryolite aluminous melts stimulates researches in field of electrolysis improvement. Among the results of these numerous researches are the improvements in electrolytic cell design, different feeding systems of electrolytic cell with alumina and means to control electrolysis. The generally recognized method of feeding of electrolytic cell with alumina is the method based on dependence of electrolytic cell voltage on concentration of alumina in electrolyte (Figure 1). But various effects call the present determination method for melting/fusion temperature of electrolytes during a cooling into question.

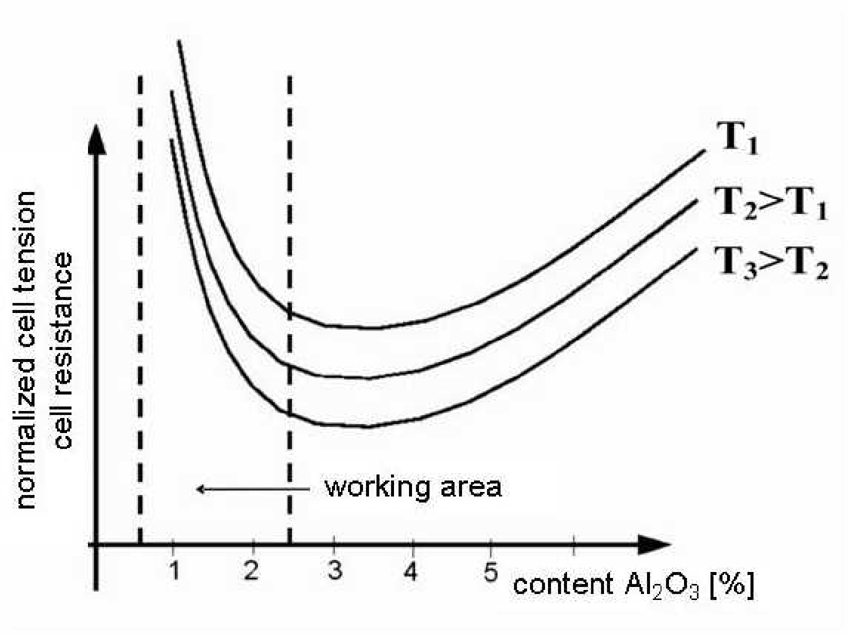

Figure 1: Dependence of electrolytic cell voltage on alumina concentration in electrolyte

From the dependence of cell voltage on alumina concentration in electrolyte it follows that the introduction of up to 3% of alumina into electrolyte leads to increase of electrolyte's electro conductivity (electrolytic cell voltage decreases). Further addition of alumina to electrolyte decreases its electro conductivity (electrolytic cell voltage increases). To support/provide clear correlation between electrolytic ell voltage and alumina concentration on electrolyte it is recommended to preserve alumina concentration in electrolyte at values not higher then the values corresponding to min electrolytic cell voltage. Low concentrations of alumina in electrolyte (less then 1%) may lead to anode effect. High concentrations of alumina in electrolyte (more then 3%) may lead to sludge formation in electrolyte. That's why alumina concentration in electrolyte is kept in the range 1-3%.

Different variations of electrolysis control schemes, that take into consideration the degree of electrolyte superheat of each individual electrolytic cell depending on electrolyte composition, the amount of cathode metal as well as the actual technological conditions, have found a wide application lately [1]. Electrolyte superheat degree (SH) means the difference between the temperature of the bath/electrolyte (T_B) and its melting/fusion temperature (T_{liq})

$$SH = T_B - T_{liq} \tag{1}$$

Many researches show that every 10 ºC of superheat the current efficiency decreases by 1%. In some cases even a value of 2% is reported [2,3,4]. Because of this fact different scientists propose smaller and smaller electrolyte superheat degrees in practice:

1977:	15 ºC	by Trotzkyi and Zheliaznov give the superheat value [5]
1994:	10-15 ºC	by Richards [6]
1995:	5-15 ºC	by Solheim [7]
1999:	5-10 ºC	by Utigrd [8]

In 2005 on the basis of simulation/modeling for future electrolytic cells the following SH values are forecasted depending a cell power [9]:

Electrolytic cell power	**265 kA**	**300 kA**	**350 kA**	**400 kA**	**500 kA**	**740 kA**
SH /ºC/	2,4 – 3,6	6,7 – 6,8	6,7 – 7,8	8,0 – 9,0	9,4 – 9,7	9,8 – 10,0

Along with the straight and easily observable dependence between current efficiency and SH there are as well other dependencies which are more difficult to evaluate. So the largest heat losses from electrolytic cell happen through side walls. The value of these losses also depends on SH [10];

$$W = \frac{T_0 - T_{liq}}{k * \sum R} \qquad (2)$$

where T_0 – temperature of the electrolytic cell surface, T_{liq} – melting/fusion temperature of the electrolyte, k – heat transfer coefficient from the surface into air; ΣR – sum of thermal resistances.

It follows that crust formation on the inner walls also depends on SH because such accretions act as a heat insulator [10]. If SH increases, accretion melts partly or completely and the heat-insulating refractory begins to erode. This may cause the necessity to switch off the electrolytic cell for a moment. It means that along with the decrease of the current efficiency SH also influences on the life time of each electrolytic cell. SH gives more information than electrolyte temperature and cryolite ratio (CR) can serve. SH is the integrated indicator of energetic and material balance of the bath. Heat-input and -losses affect the electrolyte temperature strongly. And the material balance of the electrolyte of a given composition is reflected in its melting/fusion temperature [11].

The reason why SH until now has not found a wide application in the control of electrolysis lies in the complexity of its determination. Traditionally SH in industrial baths is determined as the difference between the measured electrolyte temperature and the calculated (on the basis of chemical composition) fusion/melting temperature. This led to considerable errors. Since SH was determined not very precise, it could not be used for precise control of electrolysis. With technological development it has become now possible to determine SH with an acceptable precision in industrial baths. Therefore SH begins to be widely used for control of Al electrolysis [12]. The use of SH for control of electrolysis has allowed to create a multifunctional control system, that makes it possible to determine and prevent technological disarrangements of bath at the early stage of their appearance. Moreover this control system has allowed to exclude deviations in temperature regime of the bath and to stabilize electrolyte composition. This made possible to lower the electrolysis temperature and to work with electrolytes having low cryolite ratios. And this correspondingly helps to decrease energy consumption and to increase current efficiency [13].

For SH determination special sensors were elaborated. These sensors allow to determine the temperature of the electrolyte in the electrolytic cell and its melting/fusion temperature at the same time by taking of one single sample. Classical thermo analysis is used when temperature is registered continuously with time. While melting/fusion (crystallization) of a melt generally heat is absorbed (released) and this decreases the heating (cooling) rate. In order to simplify and unify the process and to decrease the time for measurement of both the electrolyte temperature and its melting/fusion temperature "Heraeus" installed crucible and thermo element together in their devices (Cry-O-Therm Sensor, thermo element Pt10Rh/Pt) and "Intalcom" (thermo element NiCr/NiAl). Thus crucible is at the same time sampling device. For the measurement a hole is made in the electrolyte crust. The sensor is carefully immersed into the electrolyte and is heated up for a certain time. Then the sensor with the electrolyte sample is taken out of the electrolyte. During cooling of the sample the temperature change with time is fixed (Fig. 2). At the first inflection point on the cooling curve the temperature of electrolyte in electrolytic cell, at the second inflection point the electrolyte melting/fusion temperature is determined.

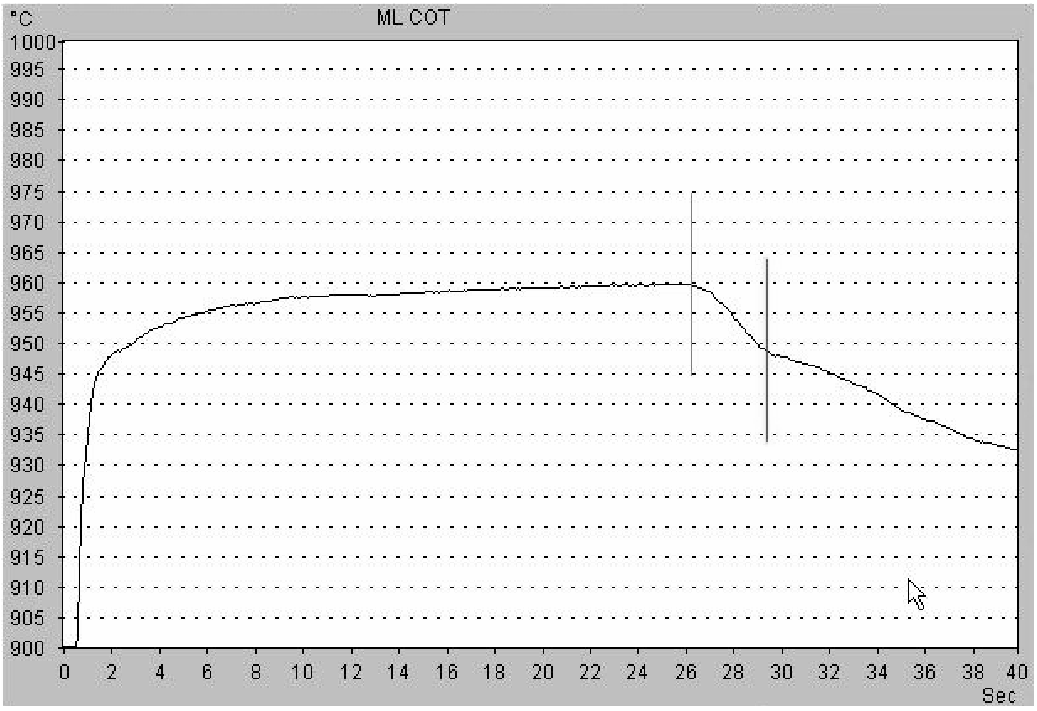

Figure 2: An example of poly thermal curve obtained using the sensor by company Heraeus

The sample cooling rate makes up more then 150°C per minute. However an unusual/abnormal tendency of cryolite aluminous melts for supercooling is well-known [14]. The value of supercooling is directly proportional to the cooling rate. So the increase of the cooling rate from 3-8°C to 25-35°C per minute lead to a divergence in melting/fusion temperature determination of about 30°C [15]. These effect calls the present determination method for melting/fusion temperature of electrolytes during a cooling with a rate of >150°C into question.

The objective of this work/research is to find out and ascertain the correctness of the current SH determination with the use the above mentioned mobile sensors for simultaneous measurement of electrolyte temperature and its melting/fusion temperature, i.e. SH, and to evaluate theoretically the necessary value of SH.

2. Investigations

2.1 Thermochemical Modelling

In order to ascertain the correctness of the current SH determination method thermodynamic calculations (FactSage^{TM} – TEACH Version I.0, Juli 2005 [17]) were conducted for evaluation of the influence of alumina addition to cryolite on the change of its phase composition at 960ºC. Thereby the cryolite ratio was varied from 2,3 to 2,7. The received data (Fig. 3) show that an introduction of alumina with the temperature 250°C into a cryolite melt at 960°C separates the solid phase-cryolite out of the melt. This effect is of cause depending on the cryolite ratio and the amount of introduced alumina.

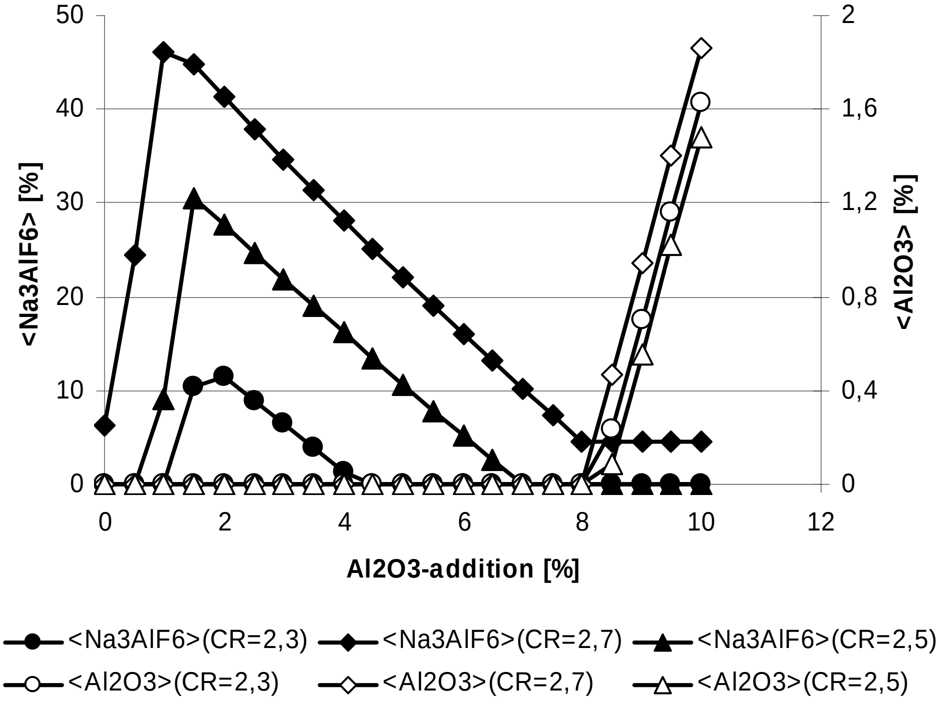

Figure 3: The influence of addition of alumina with temperature 250°C to cryolite melt with temperature 960°C and cryolite ratios (CR) from 2,3-2,7 on the amount and composition of the formed precipitated phases

The maximum amount of solid phase is formed when 2% of alumina is added to cryolite independently from the cryolite ratio. The higher the cryolite ratio, the larger the amount of formed solid phase is (when CR = 2,7 more then 45% of the system´s cryolite, when CR = 2,3 more then 10% of the system´s cryolite is precipitated after an addition of 2% of alumina). If the alumina concentration exceeds 2%, the amount of solid phase-cryolite decreases until the alumina concentration reaches 8%. At that point the minimal amount of solid phase is separated out. A further increase of the alumina concentration causes again the formation of a solid phase, but this time it´s alumina.

From Fig. 1 and Fig. 3 it follows that at alumina concentration of 2% in electrolyte the largest amount of solid phase is observed and electrolyte has the max electro conductivity.

Each introduction of alumina into a cryolite melt changes additionally the liquid phase composition (Fig. 4 and 5). While introducing 2% of alumina into the melt cryolite (Na^+, AlF_6^{3-}) gradually disappears and becomes replaced by NaF and AlF_3.

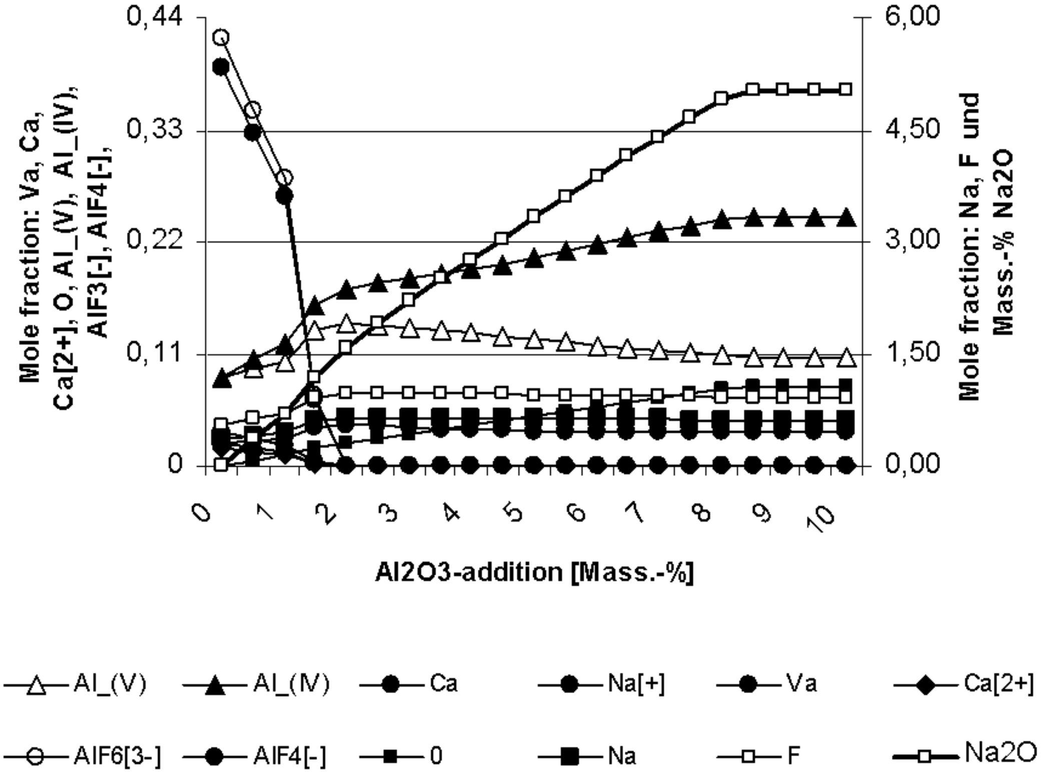

Figure 4: Liquid phase composition of cryolite aluminous melt (CR = 2,3) at 960°C with the amount of introduced alumina

Along with it the number of vacancies (Va) and concentration of Ca[2+], AlF_6[3-], AlF_4[-] and Na[+] ions decrease greatly in the melt. Their concentration fall almost to zero at 1,5-2% of alumina.* The further increase of alumina amount in the melt leads to increase of Na_2O, O, Na, F, Ca, Al_(IV) and Al_(V) concentrations.

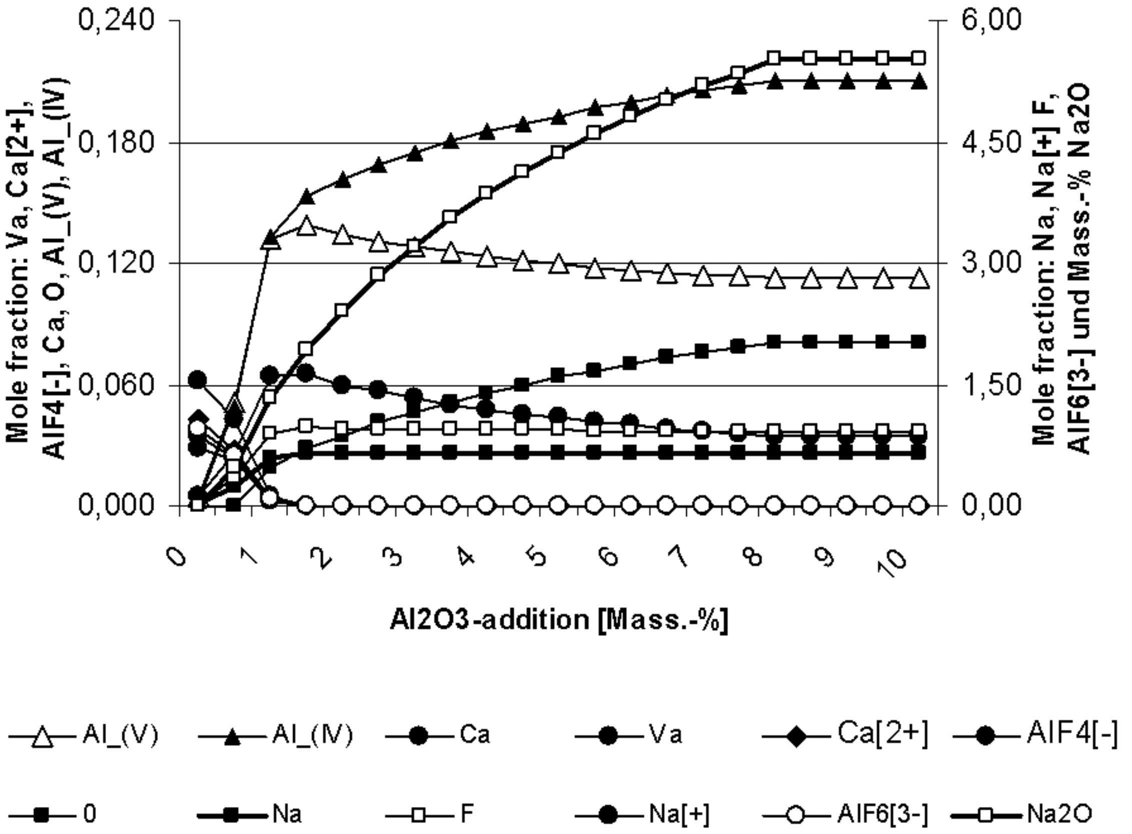

Figure 5: The change of liquid phase composition of cryolite aluminous melt (CR = 2,7) at 960°C with the amount of introduced alumina

Concentrations of Na, F and Ca reach their maximum value at 2% of alumina and later do not change. Concentration of Al_(IV) and Al_(V) continue to rise until 8% of alumina is added and then remain constant. The increase of cryolite ratio from 2,3 to 2,7 does not influence on the shape of curves.

Comparison of Fig. 1 and Fig. 3-5 shows that the possible increase of electrolyte electro conductivity with introduction into it of up to 2% of alumina may be caused by decrease concentration of ions AlF_4[-], AlF_6[3-], Na[+]and vacancies Va in liquid phase. The decrease of electrolyte electro conductivity with introduction of more then 2% of alumina may be caused by concentration growth of large oxygen containing ions Al_[V] и Al_[IV] in the melt.

2.2 Experimental Validation

These thermochemical basic data are the starting point for examination of industrial melting/fusion temperatures taken from production electrolytes. This investigation also includes the determination and presence of solid phase at electrolysis temperature. For this purpose one Al factory in Germany (plant A) was selected, where SH measurements are made with the “Heraeus” sensor (Cry-O-Therm Sensor, thermo element Pt10Rh/Pt), and one Al factory in Russia (plant B), where SH measurements are made with the “Intalcom” sensor (thermo element NiCr/NiAl). In both plants samples of electrolyte were taken directly from the pot lines to determine SH. These samples were subsequently reduced to fine particles and homogenized under Ar atmosphere. 20-100g of these averaged analytical samples was subjected to a large scale DTA analysis.

Simultaneously to these measurements DTA analysis of 200mg sister samples were made on the derivatograph NETZSCH STA 409C/CD. In both cases measurements were made in Ar atmosphere. The thermo-couples were preliminary calibrated through melting/fusion temperatures of zone molten Al, pure sodium chloride and anoxic Cu. The cooling rate amounted to 3-5 degree Celsius per minute. On fig. 6 a typical cooling curve of the large scale DTA analysis with a 30 g sample is given. As it can be seen the melting/fusion temperature of the electrolyte is about 992,6ºC. A second strong effect, which corresponds to beginning of crystallization of the double eutectic, is observable at 960,7ºC. The latter value is taken in industrial sensor measurements for the alloy melting/fusion point.

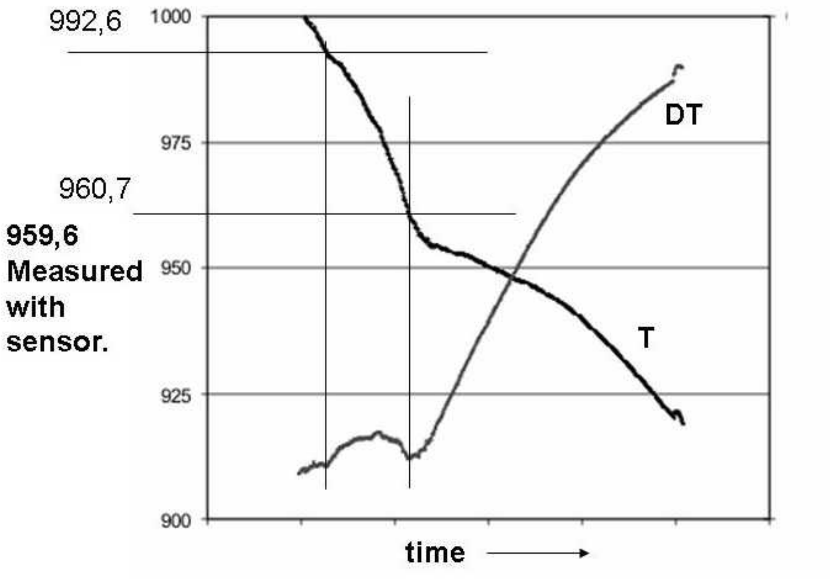

Figure 6: Typical cooling curves of a DTA analysis of 30g samples

The measured temperatures of electrolytes T_0 and their melting/fusion temperatures T_{liq} measured locally in industrial cells (plant A and B) using the above types of sensors are presented in Table 1. ΔT (varying from 5 to 15°C) represents the super heat value entering the control software**.** In the same table the true melting/fusion temperatures T_1 and the temperatures of the second thermal effects T_2 (most probably the crystallization of a two phase eutectic transformation) are given. These measurements were conducted with probes of the same electrolytes and data was obtained from DTA analysis on 2 different devices. Convergence of the thermal effects detected by cooling curves on the 30g DTA analysis device and on the analytical 200mg device (derivatograph NETZSCH STA 409C/CD) coincide with an accuracy in the range of 1ºC.

As it can be seen from table 1, the industrial detected fusion temperature is not the right value, it is equal to the two phase eutectic transformation! It follows from this data that the melting/fusion temperatures of the electrolyte, measured in industrial conditions by sensors are significantly underestimated. Our DTA analysis support the suggestion that the cooling rates of melt in industrial sensors cannot be used for precise determination of melting/fusion temperatures of cryolite aluminous melts. This is due to the unusual/abnormal tendency of cryolite aluminous melts for supercooling. A second reason may be that the electrolyte operates already in the two phase area below melting/fusion temperature because only thermal effect during crystallization is detected by the measurements.

Table 1: Comparison of electrolyte melting/fusion temperatures measured in industrial cells (plant A - “Heraeus” sensor Cry-O-Therm Sensor, thermo couple Pt10Rh/Pt), plant B - “Intalcom” sensor, thermo couple NiCr/NiAl) with own DTA-analysis results (thermo couple Pt10Rh/Pt, platinum crucible)

Plant and cell number		**Industrial measurements with the help of sensors**			**30 g DTA-analysis at Aachen**		
		T_0	**T_{liq}**	**ΔT**	**T_1**	**T_2**	**ΔT**
A	2095	950,4	943,4	+7	949,2 949,7[1]	941,2 941,9[1]	+1,2
	2091	968,3	959,6	+8,7	992,6	960,7	-24,3
B	267	948	933	+15	943,8	933,6	+4,2
	224	950	937	+13	972,7 973,1[1]	949,3 950[1]	-22,7
	259	947	942	+5	969,1	938,6	-22,1

[1] – measurement on 200 mg analytic equipment derivatograph NETZCSH STA 409C/CD

Our calculations correspond with the data of work [15], showing that in order to provide necessary heat for melting and dissolution of 1% of alumina in the electrolyte a electrolyte superheat of 13,9ºC is needed. On the other side as a result of the dissolution of 1% of alumina the melting/fusion temperature of electrolyte is decreased by 5,4ºC. This means that during dissolution of alumina the superheat (SH) is reduced by almost 9ºC. At a given superheat value of electrolyte of about 10ºC, which is recommended by many scientists and production engineers, and also taking into consideration the imperfection of sampling and the presence of unaccounted solid particles in the electrolyte during analysis, the possibility to establish negative values of electrolyte superheat is extremely increased, as shown in Table 1 in the last column.

3. Conclusions

Thermodynamic analysis of the cryolite-alumina system at 960°C and measurements of melting/fusion temperatures of industrial electrolytes by DTA show solid phase-cryolite will be present in cryolite aluminous melt at typical working temperatures of 960°C.

The importance of consideration of electrolyte superheat during Al electrolysis is beyond doubt.

A very contradictory correlation between electrolyte electro conductivity, amount of solid phase and ion composition of electrolyte was established.

Control of electrolysis with consideration of electrolyte superheat, measured even with the help of the existing mobile sensors, contributes to stabilization of heat and mass balances in electrolytic cell. But it is necessary to improve the design of the mobile sensors for SH measurement in order to increase measurement precision.

Further investigations to determine optimal SH-values depending on electrolyte composition, way of alumina feeding into it, electrolytic cell design are necessary.

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