

## THE EFFECT OF CRYOLITE ON THE FORMATION OF ALUMINUM CARBIDE AT THE CARBON ALUMINUM INTERFACE

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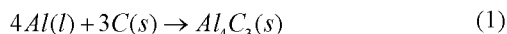
### Abstract

The effect of cryolite on the formation of aluminum carbide was studied by an aluminum-carbon diffusion couple experiment. The interface between the aluminum and carbon was coated by a thin layer of cryolite, and the diffusion couple experiments were performed at 1030 °C in stagnant argon atmosphere. The microstructure of the relatively thick and porous aluminum carbide formed at the solid-liquid interface was investigated by optical and scanning electron microscopy. It was shown that the presence of cryolite has a pronounced effect on the formation of carbide, although fluorides could not be found at the interface after the experiment. The porous and needle like morphology of the carbide layer suggests the mass transport during growth is through the gas or liquid phase. The stability of cryolite and possible gas species involved in the growth process have been analyzed thermodynamically to identify possible gaseous species present at both global equilibrium and metastable conditions.

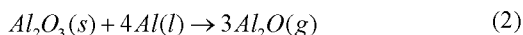
### Introduction

One of the most common reasons for the shut down of aluminum electrochemical cells is the degradation of the cathode lining [1]. In modern aluminum electrolysis technology the lifetime of the pot is mainly determined by cathode wear, which has become more significant with the use of graphitized cathode blocks [2]. The cathode wear mechanism has received increasing attention because aluminum producers are increasing the amperage of the cells and the tendency to shift to graphitized cathodes with higher electrical conductivity. The wear has been related to pure mechanical wear or to the formation of aluminum carbide ( $Al_4C_3$ ), which might be formed chemically or electrochemically. Aluminum carbide may dissolve into the bath. [3]. Despite the importance of cathode wear, the wear mechanism(s) is still not fully understood [1].

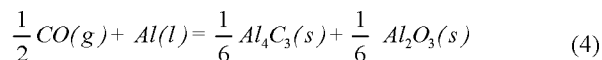
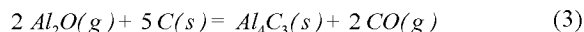
Aluminum may react directly with carbon to form aluminum carbide according to reaction (1),



The reaction is thermodynamically favored at the temperature corresponding to the operation of the cell ( $\Delta G^\circ = -147$  kJ (970 °C)) [4], but poor wetting between liquid aluminum and carbon materials hinders the reaction to proceed [5]. In diffusion couple, the surface of aluminum is covered by a thin protective layer of aluminum oxide. This layer can be removed and aluminum carbide can be formed at temperatures higher than 1100 °C [6]. The protective oxide is removed thermally by the following reaction (2),



but the reaction (2) is known not to occur at temperatures relevant for the electrolysis [7]. The removal of the oxide layer and the initial stage of aluminum carbide formation were studied in recent work by the authors [6]. The vapor pressure of aluminum suboxide in reaction (2) reaches the value  $\sim 10^{-6}$  bar at temperature 1100 °C, which allows the evaporation of the thin oxide layer at atmospheric conditions. Then  $Al_4C_3$  may form by the reactions between aluminum suboxide and carbon (3), and CO and Al (4).



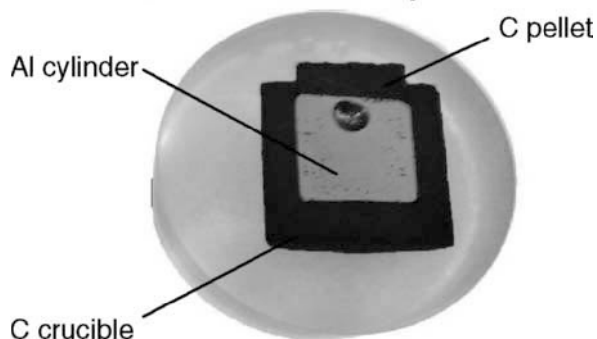
Here, the formation of aluminum oxycarbide is neglected for simplicity. In the previous study two layers of aluminum carbide were observed at temperatures higher than 1100 °C [6]. The first layer towards aluminum was shown to contain more oxygen, possibly due to formation of oxycarbides (Figure 2). The second layer growing towards carbon had lower oxygen content and was regarded as almost pure aluminum carbide.

In aluminum electrolysis cell the cryolite bath dissolves the oxide layer and improves the wetting of liquid Al on carbon materials [8]. Molten cryolite is also a solvent of  $Al_4C_3$  and can thereby reduce the diffusion barrier between Al and C induced by a layer of  $Al_4C_3(s)$  [9]. The influence of cryolite on the interfacial reaction between molten aluminum and carbon is investigated in the temperature range 1030-1100 °C in this paper. The experimental findings are analyzed with support from a thermodynamic analysis of possible reactions and vapor pressures at global equilibrium and metastable conditions.

### Experimental

The influence of cryolite on the interaction of molten aluminum and carbon was studied by performing diffusion couple experiments. Cryolite was introduced by submerging of an Al cylinder into the suspension of fine cryolite powder and 100% ethanol. A small amount of cryolite (10-20 mg) was introduced in order to serve only as a wetting agent, not as a solvent of aluminum carbide. The coated Al cylinder was cast into the carbon crucible and dried. The aluminum cylinder was made of aluminum with high purity (99.99 %). Fully graphitized carbon IG-15 (Toyo Tanso, graphitization temperature of 3000 °C with a bulk density of 1.9 g/cm<sup>3</sup>) was chosen because of its high degree of graphitization. Natural cryolite was used for the initial experiments, but was later replaced with synthetic cryolite (Sigma-Aldrich) in order to reduce the agglomeration of fine fluoride particles. A carbon pellet was placed on the top to improve the contact between the reactants (Figure 1). The crucible was placed into a fused silica-liner [6] and experiments were

performed in a stagnant argon atmosphere. The liner was evacuated down to 2 mbar and re-filled with Ar gas (-5.0 Yara Praxair, 2 ppm O<sub>2</sub> and 3 ppm H<sub>2</sub>O) to 0.8 bar to reach less than 1 bar total pressure. The diffusion couples were heat treated at 1030 °C (the melting point of cryolite is 1012 °C), and the duration of the experiments was from 3 hours to 3 days. The heating rate was 300 °C per hour and the glass-liner with the sample was quenched in water at the end of the experiments.



**Figure 1:** Cross section of the aluminum carbon diffusion couple embedded in epoxy.

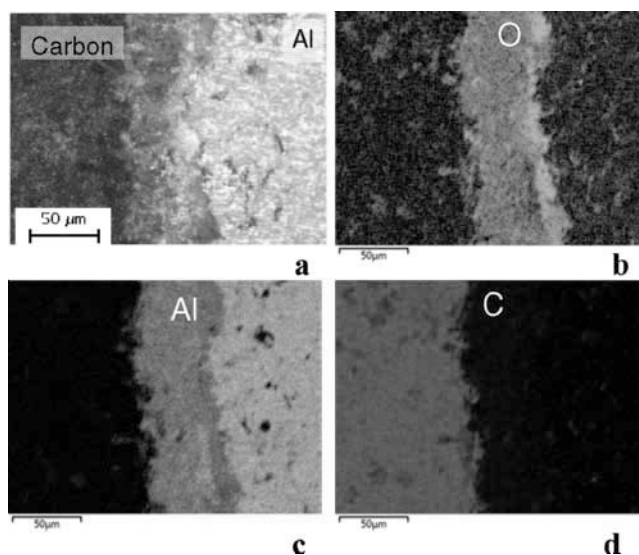
#### Characterization of the diffusion couples

After the experiment the diffusion couple was embedded in epoxy resin and cut into two to get a cross section (Figure 1). The cross section was then ground using silicon carbide abrasive paper and polished using diamond sprays down to ¼ μm on polishing cloth (Struers). 100 % ethanol was used as a lubricant for grinding and polishing, to reduce reaction of the reaction layer with humidity. The Al-C interface was analyzed both by optical microscope using a polarizing filter (polmet) and electron microscopy (LV-SEM HITACHI S-3500N). Scanning electron microscopy (SEM) and element mapping was done by energy dispersive spectroscopy (EDS) using a HITACHI-S 3400 SEM. The interface of the diffusion couples after the reaction was analyzed by X-ray diffraction (Bruker D8 Focus).

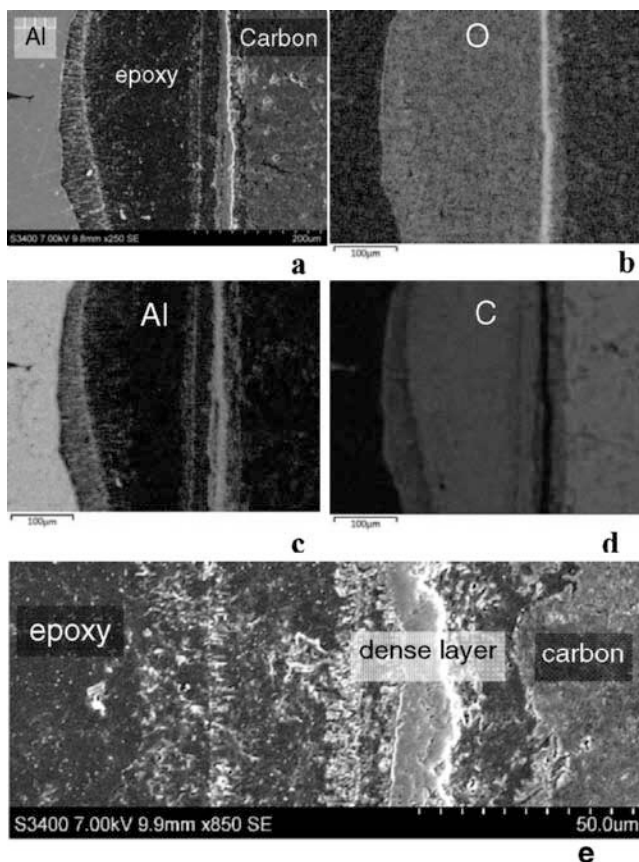
#### Results

In the previous work two layers of aluminum carbide were observed at temperatures higher than 1100 °C [6]. An example of the two layers formed at the Al-C interface is shown in Figure 2.

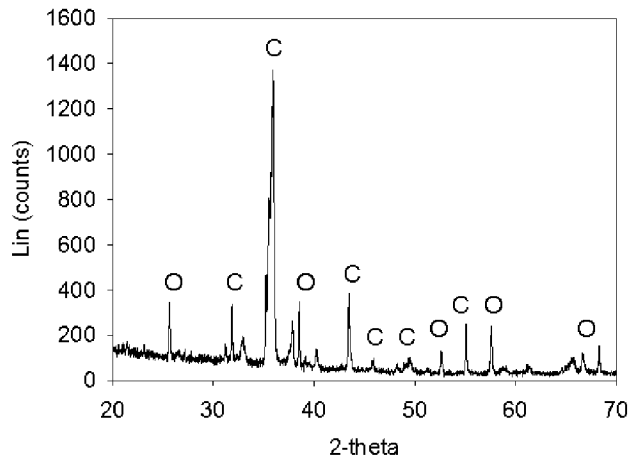
A typical Al/C interface with small amount of cryolite at the interface is shown in Figure 3. Aluminum carbide was found on the interface already after 3 hours. The thickness of the aluminum carbide layers was uneven along the interface reflecting the variation in the local amount of cryolite. A gap between Al and C due to the solidification of Al<sub>11</sub> during cooling became infiltrated with epoxy during sample preparation. EDS analysis of the layers showed the formation of aluminum carbide, with considerable amount of oxygen present (Figures 3 and 8). XRD of the aluminum and carbon surfaces confirmed the presence of aluminum carbide. Aluminum oxide was also present according to XRD, but no oxycarbides could be found (Figure 4). Cryolite or fluorides could not be detected by EDS or XRD at any of the interfaces.



**Figure 2:** a) Optical image of two layers of aluminum carbide at the liquid aluminum solid carbon interface without cryolite, 1200 °C, 10 days. The first layer with higher oxygen content towards Al and the second layer with lower oxygen content towards C. Element mapping of b) oxygen, c) aluminum and d) carbon.



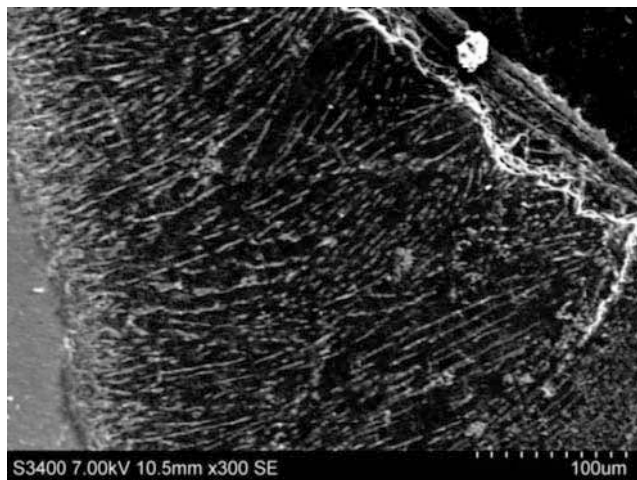
**Figure 3:** a) SEM image and element maps of b) oxygen, c) aluminum and d) carbon of a typical Al/C interface after 3 days at 1030 °C with cryolite. e) SEM image; the detail of more compact denser layer towards the carbon material.



**Figure 4:** XRD spectrum of Al surface (the contact surface with C). The peaks belong to aluminum carbide (C) and aluminum oxide (O).

The aluminum oxide found at the interface originates either due to oxidation of the carbide after exposure to air, from oxygen impurities in the Ar gas or the initial oxide layer on Al. No significant difference between the experiments performed for 3 hours and 3 days experiments were observed, which suggests that the reaction is fast and the layers are formed during first hours.

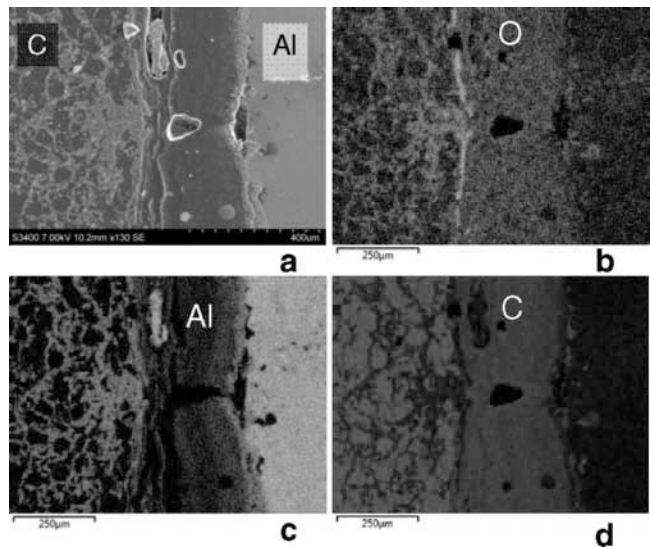
$Al_4C_3$  grains with needle-like morphology could always be observed towards aluminum (Figures 3- 8). The layer of  $Al_4C_3$  needles was observed at all the interfaces, but the thickness varied, from 10 to 300  $\mu m$ . The occurrence and length of the aluminum carbide needles depended on the local amount of cryolite. In some experiments, an excessive amount of cryolite was introduced onto the top of aluminum cylinder, which resulted in thicker layer with long carbide needles (Figure 5).



**Figure 5:** Optical image of the thick needle-like  $Al_4C_3$  layer (compared to Figures 3, 7 and 8) found on the place with high amount of introduced cryolite after 3 hours.

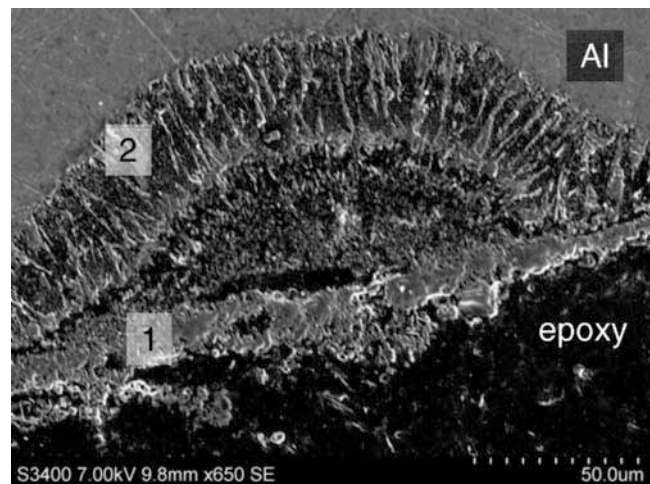
Towards the carbon materials a relatively denser layer was observed (Figures 3, 7 and 8). The thickness is varying from 10 to 20  $\mu m$ . The oxygen content in this denser layer was always higher than in the layer with needles (Figure 3).

Aluminum or aluminum carbide were usually not observed in the pores of the carbon material, because of its low porosity and the dense layer, which acts as a diffusion barrier. In some special cases however, when the layer was found not in contact, aluminum carbide was found in the pores of carbon (Figure 6).

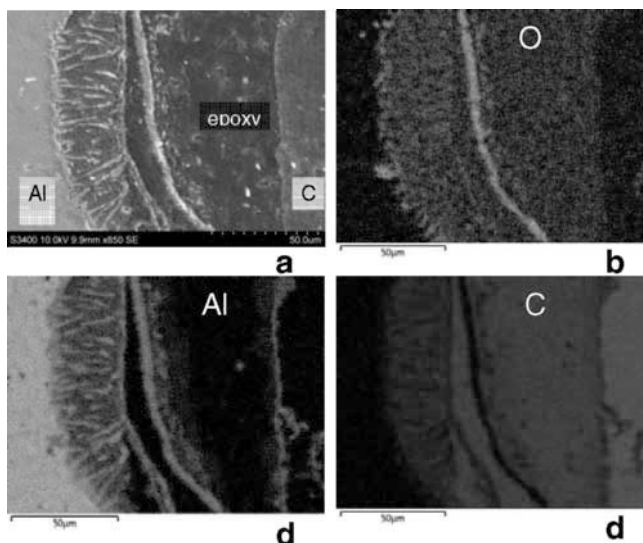


**Figure 6:** a) SEM image of aluminum carbide penetration into the pores of carbon. Element mapping of b) oxygen, c) aluminum and d) carbon.

There were also regions which displayed a somewhat different microstructure than these two characteristic layers. EDS analysis of the reaction product in these cases showed aluminum carbide with very high carbon content, which reflects the mixture of epoxy with carbide. The molten aluminum shrunk during cooling, and the significant volume reduction caused usually fracture of the layers with the carbide needles. Some carbide particles that had detached from both layers were found in the resulting gap in the diffusion couple, which became surrounded by epoxy and appear like an extra layer (Figure 3).



**Figure 7:** Two layers at the liquid aluminum solid carbon interface; dense layer (1) and needle-like layer (2).



**Figure 8:** a) SEM image and element maps of b) oxygen, c) aluminum and d) carbon of a typical Al/C interface after 3 hours at 1030 °C with cryolite.

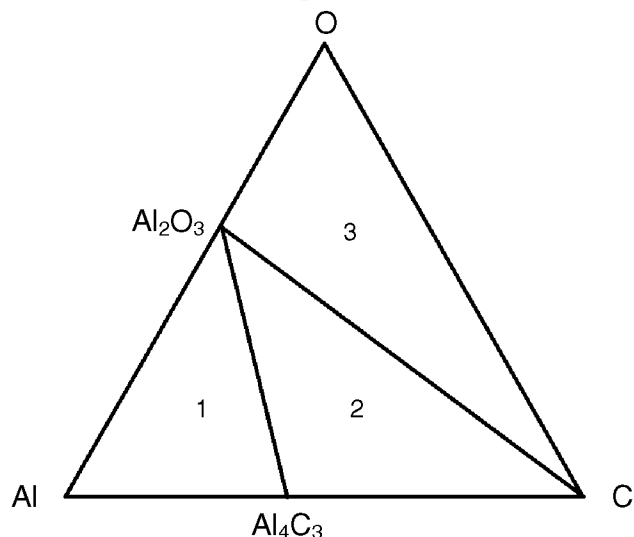
### Discussion

Thermodynamic calculations (FactSage 6.2) were performed to determine the vapor composition in Al-C-O system with cryolite at various conditions. Aluminum oxycarbide phases were not included in the calculations due to lack of thermodynamic data. The partial pressures of the gaseous species are helpful for understanding the mechanism of aluminum carbide formation and the influence of cryolite. The ternary phase diagram of Al-C-O system can be divided into 3 subsystems (Figure 9). In triangle 1, aluminum carbide is in equilibrium with excessive, unreacted aluminum and aluminum oxide. The vapor composition is fixed according to Gibbs phase rule in the entire region, independent of oxygen content in the system. Triangle 2 represents excess of carbon, and the vapor composition is again fixed according to the Gibbs phase rule. In triangle 3 excess amount of oxygen is present and the only gaseous species is CO and CO<sub>2</sub> in equilibrium with Al<sub>2</sub>O<sub>3</sub>. In the diffusion couple experiments, carbon and aluminum are not consumed and global equilibrium is not reached. Locally the vapor pressure can deviate substantially from the global equilibrium values. The three subsystems represent the metastable conditions in the vicinity of excess carbon, aluminum and oxygen.

The partial pressures in two subsystems with excess aluminum and carbon are rising with the temperature (Figure 10). They are fixed within the region and oxygen content does not influence the vapor composition according to the Gibbs phase rule. The vapor pressures increase with nearly two orders of magnitude by increasing the temperature to 1200 °C.

The calculated vapor pressures of volatile species when cryolite is in contact with Al and C and traces of Al<sub>2</sub>O<sub>3</sub> are given in Table 1. These calculations demonstrate the volatility of sodium and fluorine, in line with the experimental findings, where any of cryolite species were not found at the interfaces after the termination of the experiments. Cryolite will be therefore relatively quickly being transported away from the C-Al interface during the experiment. The main effect of cryolite is therefore to dissolve the oxide scale on the Al surface and to facilitate

reactions between Al and C, either through the gas phase or by the direct contact between the two phases as discussed further below.



**Figure 9:** Phase diagram of Al-C-O ternary system with 3 subsystems.

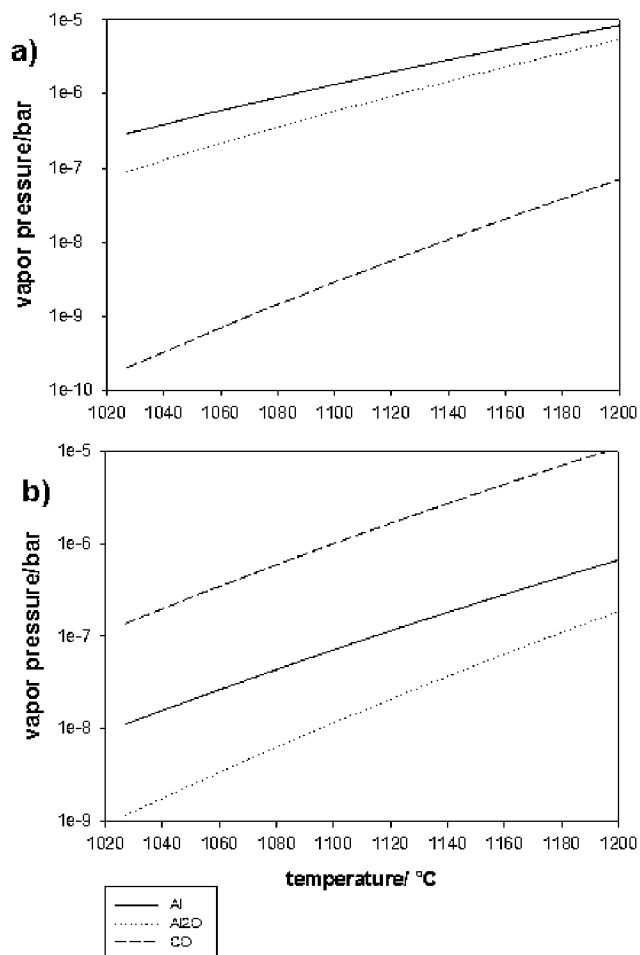
**Table 1:** Partial pressures of species above cryolite in Al-C-O system at a temperature of 1030 °C.

System	Excess Al	Excess C
	Partial pressure / bar	
Na	$4.2 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$
AlF	$1.05 \cdot 10^{-2}$	$1.2 \cdot 10^{-3}$
NaAlF <sub>4</sub>	$6.2 \cdot 10^{-3}$	$6.2 \cdot 10^{-3}$

The gas transport mechanism was proposed in previous work [6]. The protective oxide layer can be evaporated at temperatures higher than 1100 °C and can initiate aluminum carbide formation (Reactions 3-4). Vapor pressures of aluminum and aluminum suboxide reach the value  $10^{-6}$  at 1100 °C in the vicinity of aluminum and CO pressure reaches this value at 1100 °C in the vicinity of carbon (Figure 10). Al vapor and Al<sub>2</sub>O can transport aluminum to carbon and CO can transport carbon to aluminum. The presence of cryolite has no influence on the vapor pressures of Al, Al<sub>2</sub>O and CO. The partial pressures are low ( $\sim 10^{-7}$ ) at experimental temperature 1030 °C and their involvement in aluminum carbide formation is less likely than in the previous study at 1200 °C [6].

Aluminum carbide was formed already at 1030 °C and has different morphology than the carbide observed after the experiment without cryolite at higher temperatures. Cryolite is generally considered as a wetting agent and solvent of the aluminum oxide protective layer and aluminum carbide [8]. Experimentally cryolite was shown to disappear, explained by the estimated high vapor pressures when cryolite is in equilibrium with Al<sub>0</sub>. The dissolution of Al and Al<sub>2</sub>O<sub>3</sub> in molten cryolite will reduce the vapor pressures but not sufficiently to hinder the evaporation. The dissolution was not included in the calculations, but cryolite is known as a good solvent of aluminum oxide [10]. Thus in the initial stage of the reaction the aluminum oxide layer can dissolve in cryolite and dissolution re-precipitation of the oxide may occur before the cryolite is evaporated. Then the transport of aluminum to the carbon can be fast through the liquid layer of cryolite. However, formation of a dense aluminum

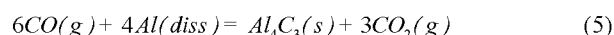
carbide layer can slow down the reaction, which can be then diffusion controlled. Grjotheim et al. studied  $Al_4C_3$  formation with a large amount of cryolite [11]. The reaction and dissolution proceeded until saturation, which was reached after a couple of hours. The solubility of aluminum carbide in cryolite is around 1 wt. % [9]. Then the diffusion controlled growth of a carbide layer was suggested on the carbon surface.



**Figure 10:** Vapor pressures of selected species in two subsystems: a) excess Al (triangle 1) and b) excess C (triangle 2).

Needle-like aluminum carbide, which was found towards the aluminum, suggests precipitation and growth from a liquid or gas phase. Precipitation from liquid aluminum at cooling was observed in experiments without cryolite, large aluminum carbide grains with regular shape were formed [6]. At 1030 °C the solubility of carbon in aluminum is low and the precipitation is not likely [12]. Discussed gas transport mechanisms from the previous work are less likely at lower temperatures. They are also independent of the presence of cryolite, but the differences between aluminum carbides observed with and without cryolite are evident. Occurrence and length of the needles have been shown to be dependent on the local amount of cryolite (Figure 5). Thus the effect of cryolite and its involvement in the reaction is believed to be very important. Aluminum carbide needles might have precipitated from cryolite. The needles were always oriented perpendicular to Al/C interface, regardless of the position in the crucible (bottom, top, and sidewall). The deposition could proceed by vapor-solid-liquid growth mechanism [13]. The direction of

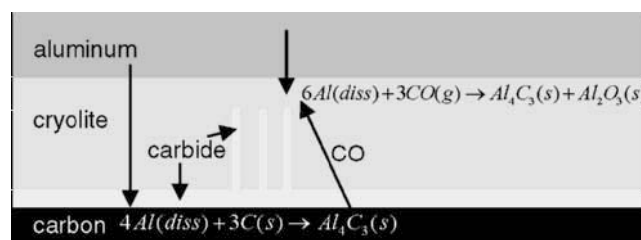
the growth is suggested to be towards aluminum. The dense carbide layer might act as a good substrate for the growth of the needles. Cryolite as a liquid phase is saturated with aluminum carbide ( $\approx 1$  wt. %) [9] and aluminum ( $\approx 0,1$  wt. %) [14]. The only carbon containing gas, which can be involved in the reaction with dissolved Al, is CO. The partial pressure of CO in the system is low, but on the outside of the crucible (local equilibrium) the pressure is higher ( $10^{-5}$  bar) and depends on oxygen concentration in the system. When CO is introduced to the cryolite, it reacts with dissolved aluminum (Reaction 4). Formation of aluminum carbide in saturated cryolite leads to precipitation of  $Al_4C_3(s)$ . The precipitation can take place by further growth of the needles. This is determined by the anisotropy of the crystal, the growth is preferred to proceed in one direction. Solubility of  $Al_2O_3$ , the by product of the reaction, is 10-20 times higher, therefore precipitation should not occur in the initial stage. Alumina content reduces aluminum carbide solubility in cryolite [9]. Evaporation of cryolite also leads into  $Al_4C_3$  precipitation, which might contribute to the growth of the needles. When cryolite is evaporated, the formation of the needles stops. Oxygen content in the system is limited and will in the end cause formation of  $Al_2O_3$ . If  $Al_4C_3$  is formed by reaction (5), the by product  $CO_2$  can be transported back to carbon, react to CO and bring the carbon back.



This reaction is however not thermodynamically favored according to the calculations ( $\Delta G^\circ = 28,6$  kJ (1030 °C)).

The dense layer towards carbon has relatively high oxygen content and it is not clear to identify from EDS mapping whether it is highly oxidized aluminum carbide or aluminum oxide. The small amount of carbon in this layer might have come from the carbon coating of the sample. On the Figure 8 the dense, relatively thick and oxygen rich layer is detached from the carbon surface and thinner, aluminum carbide layer is towards carbon. This suggest the dense, oxygen rich layer to be aluminum oxide, which might be formed by precipitation from cryolite either by evaporation or from the reaction (4) as a by product of the formation of carbide needles. The thin aluminum carbide layer is probably formed by direct contact of aluminum and carbon on the carbon surface. In the initial stage, before cryolite was evaporated completely, aluminum could be transported relatively fast through the layer of liquid cryolite. Formed aluminum carbide can be dissolved into the bath. The experiment with duration of 3 hours showed, that saturation of cryolite with carbide and the formation of the carbide layer towards carbon are very fast processes.

The proposed mechanisms for formation of aluminum carbide at the carbon aluminum interface is illustrated Figure 11.



**Figure 11:** Proposed mechanism of aluminum carbide formation.

## Conclusion

Al/C diffusion couple experiments with cryolite have shown that aluminum carbide is formed on the interface already at 1030 °C. Without presence of cryolite, at least 1100 °C is needed to form aluminum carbide. Compact aluminum carbide layer was observed towards carbon. Needles of aluminum carbide were found towards aluminum, the length depends on the local amount of cryolite. Small amount of cryolite has evaporated and was not found on Al/C interface after the experiment. Cryolite has probably dissolved the protective aluminum oxide layer and the wetting of aluminum on carbon was improved. The layer towards carbon is suggested to form by aluminum transported to the carbon surface by the diffusion through the cryolite layer. The needles are probably precipitated from the cryolite. Vapor-liquid-solid growth mechanism is suggested. Cryolite saturated with aluminum is fed with CO and aluminum carbide can be deposited on the top of the needles. Evaporation of saturated cryolite might also lead to aluminum carbide precipitation and the growth of the needles.

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