

## FUNDAMENTALS OF ALUMINIUM CARBIDE FORMATION

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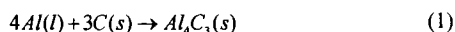
### Abstract

The fundamentals of formation of aluminum carbide were studied by aluminum-carbon diffusion couple experiment. The diffusion couples consisted of liquid aluminum and graphitized carbon, and the diffusion couple experiments were performed at temperatures 1000-1200°C in stagnant argon atmosphere. The formation of aluminum carbide layer at the solid-liquid interface was confirmed by X-ray diffraction and electron and optical microscopy. The kinetics of the formation of the carbide layer was investigated in detail and formation of carbide by solid-gas reactions is discussed.

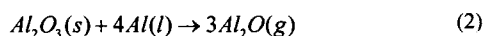
### Introduction

One of the most common reasons for the shut down of aluminum cells is the wear of the cathode lining. In modern electrolysis technology the lifetime of the pot is mainly determined by cathode wear, which has been shown to depend on the carbon material and is now known to be faster for graphitized carbon materials compared to anthracitic carbon materials [1]. The cathode wear mechanism has recently received considerable attention, but there are no consensus regarding the mechanism [2]. The wear has been related to pure mechanical wear, to the formation of aluminum carbide ( $Al_4C_3$ ), which may dissolve in the aluminum pad, and finally electrochemical wear, which can be related to the current density [3]. The wear in industrial cell is uneven, it varies from place to place. Typical is double-w wear profile [4]. Despite the importance of aluminum carbide formation in the cathode lining, the mechanism is not known in detail.

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



The reaction is thermodynamically favored at the temperature corresponding to the operation of the cell ( $\Delta G^\circ = -147$  kJ (970°C)) [5], but the lack of direct contact between liquid aluminum and the carbon cathode hinders the reaction to proceed. It is not possible to form detectable amounts of the carbide below 1000°C without the presence of the bath [6]. It is also well known that liquid aluminum does not wet carbon. The surface of aluminum is covered by a thin protective layer of aluminum oxide [7], which can be removed by the following reaction,



The wetting of aluminum and carbon has been studied by Landry et al. [7]. At an early stage, the interaction is characterized by high wetting angle ( $\theta_0$ ) between  $Al/Al_2O_3$  [7]. During the evaporation, reaction (2), the wetting angle is decreasing and when the oxide layer is removed, the contact between aluminum and carbon is

enabled. The interaction is then characterized by the wetting angle between  $Al/C$ . At elevated temperatures it has been shown that the reaction between  $Al$  and  $C$  takes place on the interface, where aluminum carbide is directly formed. The wetting angle decreases during the reaction and the final wetting angle between  $Al/Al_4C_3$  is reached. The  $Al-C$  wetting properties depend also on the type of carbon material. The higher the atomic density of carbon substrate in contact with aluminum, the higher the adhesion energy and the lower the contact angle. Roughness is also important, and a polished surface is better wetted than a rough surface [7]. In an aluminum electrolysis cell the cryolite bath serves as a wetting agent, it dissolves the oxide layer and changes the surface properties of carbon [2]. However, the bath wets  $Al$  better than the carbon material and hinders direct contact between molten aluminum and the cathode. In addition, intercalation of  $Na$  in carbon changes the wetting angle between the bath and carbon cathode [1]. In this paper initial results on the fundamentals of aluminum carbide formation are reported. The direct reaction between molten aluminum and carbon is studied in the temperature range 1000-1200°C, significantly higher than the operation temperature of aluminum cells, but these temperatures are necessary in order to study the kinetics of the reaction.

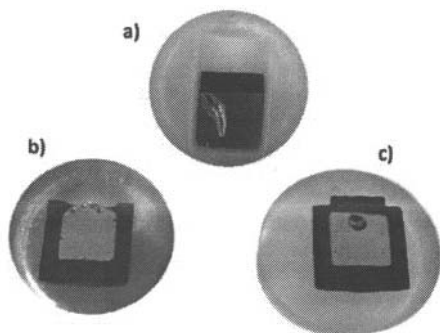
### Experimental

The interaction of molten aluminium and carbon was studied by using diffusion couple experiments. Initial experiments were performed by pressing pellets of  $Al$  and  $C$  together in an alumina crucible (Haldenwanger), see Fig. 1c. The crucible was placed into a fused silica-liner, which was flushed with  $Ar$  gas as shown in Fig. 2.  $Ar$  5.0 (Yara Praxair) contains 2 ppm of oxygen and 3 ppm of water. In order to reduce the possible effect of the oxygen impurities, similar experiments were also performed, in stagnant argon atmosphere. In this case the silica-liner was evacuated down to 2 mbar and kept at 2 mbar or re-filled with  $Ar$  to 0,8 bar total pressure. A modification of the set-up was conducted by removal of the alumina crucible, which might influence the reaction and made polishing of the diffusion couple more difficult. In this case a carbon crucible from the tested material was prepared, see Fig. 1b. The aluminum cylinder (super purity of 99.99 %) was forced into the crucible and covered with a carbon pellet, as illustrated in Fig. 1c. Extra load (alumina cylinder) on the top was applied to improve the contact at elevated temperatures.

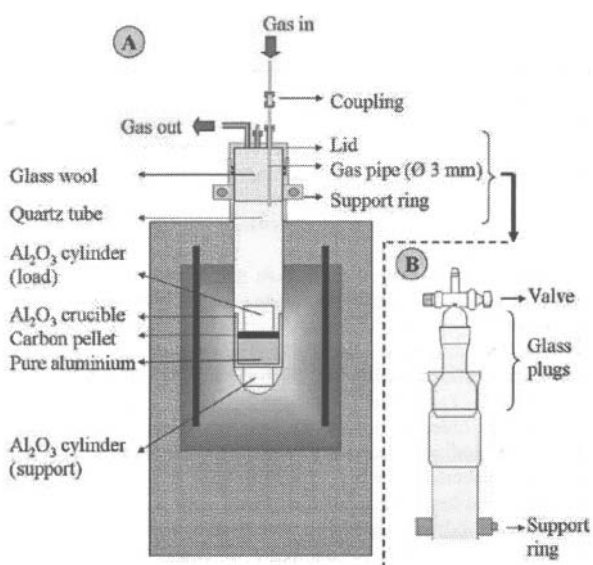
Two different carbon materials were used in the study. The first experiments were conducted using electrode graphite (Svensk specialgratit AB) with a density of  $1.54$  g/cm<sup>3</sup>. Later, fully graphitized carbon IG-15 (Toyo Tanso, graphitization temperature of 3000°C with a bulk density of  $1.9$  g/cm<sup>3</sup>) was chosen because of its high degree of graphitization.

Experiments were performed in a temperature range of 1000-1200°C, and the duration of the experiments was varying from 1 to 10 days. For some tests the temperature was kept at 1200°C for

one hour and afterwards lowered to 1000°C for the rest of the experiment. The initial first hour was introduced in an attempt to remove the protective oxide layer at the Al(l) surface. The heating rate was 300°C per hour and the glass-liner with the sample was quenched in water or gaseous nitrogen at the end of the experiments.



**Fig. 1:** Diffusion couples embedded in epoxy; a) diffusion couple in alumina crucible b) diffusion couple in graphite crucible c) diffusion couple in a graphite crucible and carbon lid.



**Fig. 2:** Experimental set-up with alumina crucible and flux of Ar (A) and top of the glass tube for experiments with stagnant Ar (B).

#### Characterization of the diffusion couples

After the experiment the diffusion couple was embedded in epoxy resin and cut in two to get a cross section. The cross section was then grinded by a silicon carbide abrasive paper and polished using diamond sprays down to  $\frac{1}{4} \mu\text{m}$  on polishing cloth (Struers). 100 % ethanol was used as a lubricant for grinding and polishing, because aluminium carbide reacts with water. The Al-C interface was analyzed by optical microscope using a polarizing filter (polmet), electron microscopy (LV-SEM HITACHI S-3500N), energy dispersive spectroscopy (EDS) (HITACHI-S 3400) and X-

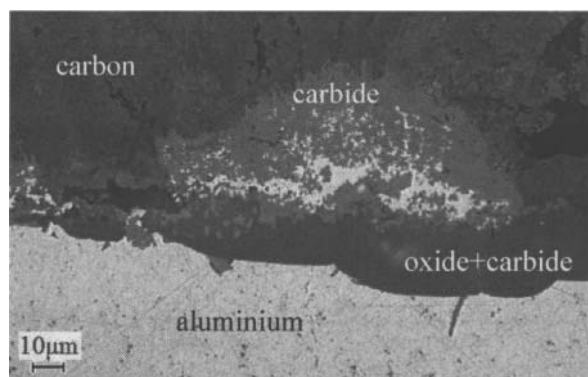
ray diffraction (Bruker D8 Focus). Thermodynamic calculations have been performed using FactSage 5.0.

#### Results

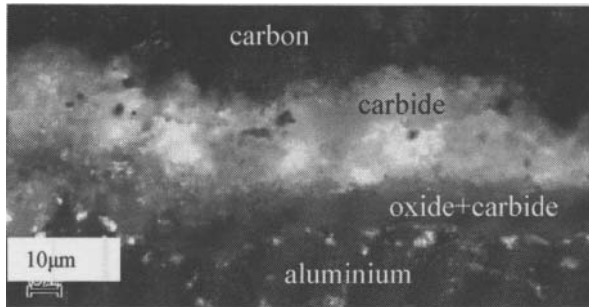
Typical cross sections of the aluminum/carbon interface at various conditions are shown in Figs. 3-9. Formation of aluminum carbide took place at the Al/C interface at temperatures between 1100 and 1200°C. The thickness and microstructure of the layer was observed to be dependent on the reaction conditions (time, temperature, stagnant or flowing Ar and total pressure). The  $\text{Al}_4\text{C}_3$  layer appeared inhomogeneous along the C-Al interface, but in most of the diffusion couples it was possible to measure an average thickness. Large single crystals of aluminum carbide could also be observed in the Al layer.

In the experiments, where the diffusion couple was mounted in an alumina crucible and with argon flux through the liner, a thin, uneven layer, with accumulation of carbide shown as large crystals/polycrystalline areas, was already observed after 1 day at 1200°C as shown in Figs. 3 and 5. Beside a thin initial layer, voids or pores in the inhomogeneous carbon material seams to be filled with the reaction product during the initial reaction. With increasing time the reaction product continue to grow and become more even in thickness over time, see Fig 5b and c. The thickness was 40-50 and 80-100  $\mu\text{m}$  after 4 and 16 days, respectively. The micrographs provide evidence that the layer is not homogeneous and consist of two layers, the first containing both O and C, indicating formation of an oxycarbide and a second layer towards the carbon materials with a low O-content. The two layers are shown in Fig. 4. The carbide layer in the vicinity of the carbon surface is more yellowish as compared to the transparent layer towards the aluminum surface. The presence of O and C was confirmed by EDS, but a quantitative determination of the O and C content is difficult due to the porous nature of the layer and possible influence of hydration/oxidation of  $\text{Al}_4\text{C}_3$  during sample preparation. The origin of the oxygen in one of the layers cannot be ruled out, it might be impurity in Ar or from the alumina crucible.

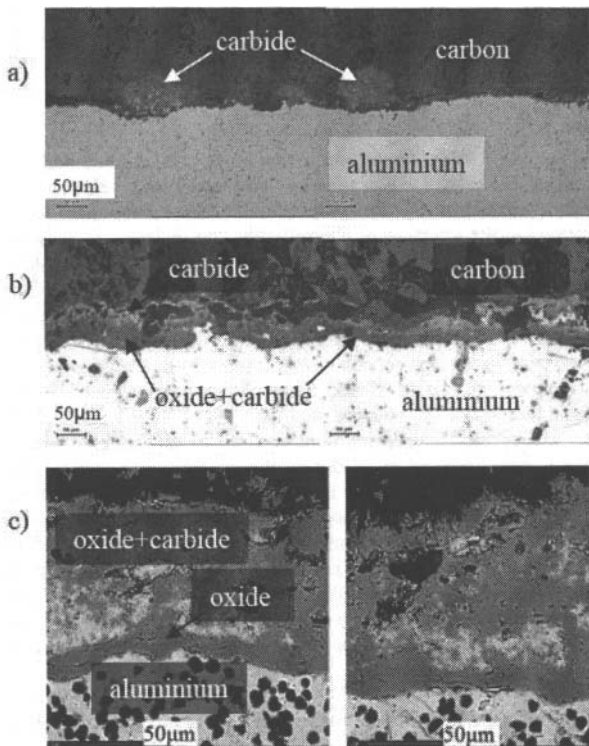
The thickness of the carbide layer formed after 4 days at 1000°C were difficult to determine. In this experiment the diffusion couple was initially heated for 1 h at 1200°C in order to possibly remove the oxide scale at the Al surface. A thin polycrystalline layer of carbide could be observed, see Fig. 6



**Fig. 3:** Optical macrograph of the Al/C interface after 24 h at 1200°C. The diffusion couple was mounted in a alumina crucible and Ar was flushed during the experiment.



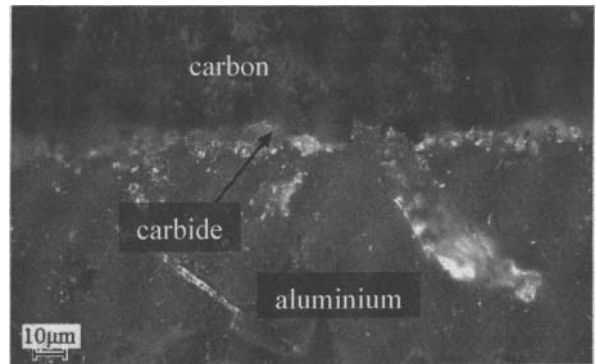
**Fig. 4:** Optical micrograph of the Al/C interface after 96 h at 1200°C. The diffusion couple was mounted in a alumina crucible and Ar was flushed during the experiment.



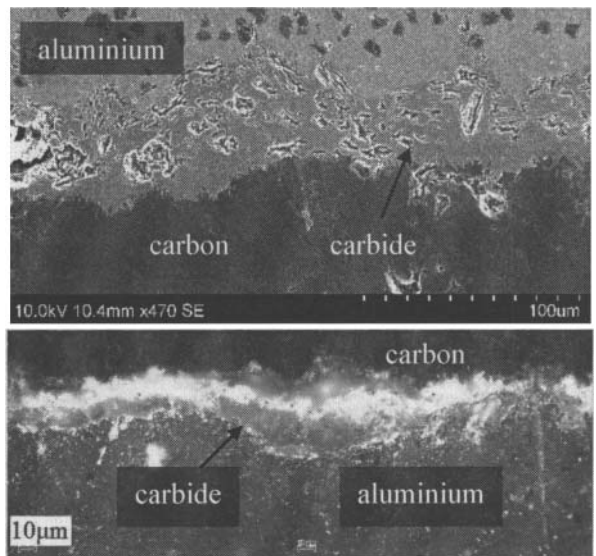
**Fig. 5:** Optical and SEM macrographs of the Al/C interfaces at 1200°C. (a) 1 day, (b) 4 days, (c) 16 days. Experiments were performed in an alumina crucible and flushing Ar. All phases are labeled, the black spots in the aluminium layer are diamonds from polishing.

The experiments in stagnant Ar atmosphere showed lower oxygen content in the first layer near the aluminum surface in comparison with experiments performed in flux of Ar. An example is shown in Fig. 7. A higher content of oxygen was confirmed by EDS in the more transparent grains.

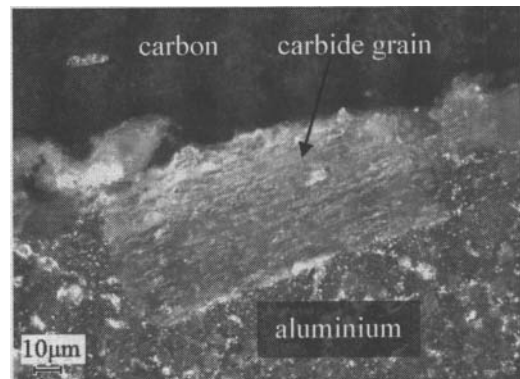
Large apparently single crystals of  $Al_4C_3$  were observed inside the Al layer in most of the diffusion couples. A typical example is shown in Fig. 8, where a  $\sim 60 \times 120 \mu m$  large  $Al_4C_3$  crystal can be recognized. This crystal has most likely been formed during cooling and has precipitated from C dissolved in Al(l). C has clearly been dissolved into Al(l) during the experiments.



**Fig. 6:** Optical micrograph of the Al/C interface after 4 days at 1000°C and initially heat treated for 1 h at 1200°C. Experiment in alumina crucible and flushing Ar.



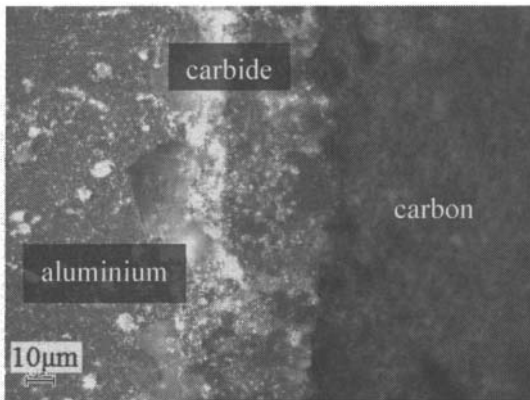
**Fig. 7:** SEM a) and optical micrograph b) of the Al/C interface after 5 days at 1200°C. Experiments were performed in alumina crucible and stagnant Ar atmosphere.



**Fig. 8:** Optical microscope image of Al/C interface, large  $Al_4C_3$  grain after slow cooling to room temperature.

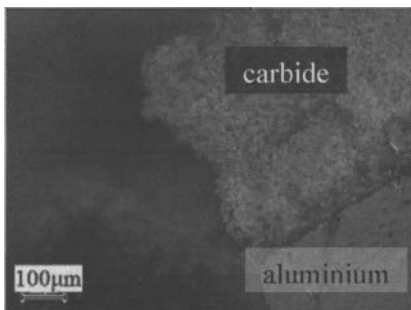
A diffusion couple using carbon crucible and stagnant Ar atmosphere is shown in Fig. 9. Qualitatively the results are comparable to the ones with the alumina crucible in terms of general carbide formation, but more experiments are needed to get a quantitative comparison.

The experiments using the graphite crucible were performed in stagnant Ar, while most of the experiments using the alumina crucible was performed using Ar flux. In these experiments the type of carbon materials has also not been varied in a systematic way, hence, it is yet not possible to compare the carbide growth rate using two analyzed carbon materials. The carbide thickness in Ar flux was typically 50-80  $\mu\text{m}$  after 8 days and in stagnant argon 80-100  $\mu\text{m}$  after 16 days.

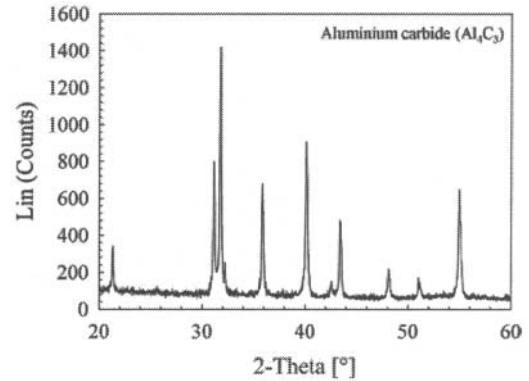


**Fig. 9:** Optical micrograph of the Al/C interface after 10 days at 1150°C. Graphite crucible (IG-15) and stagnant Ar atmosphere.

In some experiments using the same set-up poor reproducibility of the thickness of the  $\text{Al}_4\text{C}_3$  layer was observed. An example is shown in Fig. 10 where a porous 500  $\mu\text{m}$  thick layer of  $\text{Al}_4\text{C}_3$  could be observed. It was also possible in this case to confirm that the layer was  $\text{Al}_4\text{C}_3$  by X-ray diffraction, see Fig. 11. The explanation for the poor reproducibility is not clear at the present stage, and will be followed up in future work. The porous nature of the layer is, however, strongly suggesting that the majority of the  $\text{Al}_4\text{C}_3$  is formed from the gas phase and not due to a direct reaction between Al and C.



**Fig. 10:** Optical micrograph of a thick porous layer of  $\text{Al}_4\text{C}_3$ , formed after 3 days at 1200°C and total pressure of 0.002 bar Ar.



**Fig. 11:** XRD profile for sample from the 0.002 bar test. All reflections belong to  $\text{Al}_4\text{C}_3$ . No reflections for oxide phases like  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_4\text{O}_4\text{C}$  or  $\text{Al}_2\text{OC}$  are present.

### Discussion

In an ideal diffusion couple experiment with a good and flat contact between the two reactants, the solid state reactions are either controlled by diffusion through the intermediate layer formed at the interface or controlled by the reactions if transport through the layer is not controlling the kinetics. In the Al-C diffusion couple there is several factors which challenge the interpretation of the data. First, one of the reactants is a liquid, and transport of the product through the liquid cannot be ruled out. However, in the last version of the set-up, liquid Al is completely surrounded by liquid C and transport of C through Al is not important when Al become saturated by C. The large carbide crystals precipitated during cooling (Fig. 8) give clear evidence that C has dissolved in Al during the experiment. Secondly, the carbon material is relatively inhomogeneous with large variations in the grain size and with pores of different size. Due to this the first reaction layer appears inhomogeneous during the first 3 days as shown in Fig. 5. It was not straight forward to determine an average thickness, because the layer is only some  $\mu\text{m}$  thick and the second layer is not developed. However, after 4 days the second layer starts to appear and an average thickness is measurable.

The first experiments were performed with argon flux containing 2 ppm  $\text{O}_2$  and 3 ppm  $\text{H}_2\text{O}$ . If one assume that these traces of oxygen will be involved in the reaction between Al and O one must take into consideration the possibility to form Al oxycarbides in addition to pure carbide. The presence of oxygen in the initial (first) layer was confirmed by EDS, and this layer was also recognizable with the optical microscope (Figs. 3 and 4). According to calculations, oxygen and water present in argon can oxidize 1 micron layer of aluminium carbide per day in an argon flux of 1.6 l/h (carbon pellet diameter = 15 mm), which corresponds to the experimental observations. The calculation has been done for the case of total oxidation. To avoid oxygen, the experimental setup with no flux was introduced (closed system) as shown in Fig. 1b, where it was possible to run experiments in vacuum or stagnant atmosphere. EDS analysis of the carbide layer formed in stagnant argon at 0.8 bar showed specific oxidized areas (corresponding with transparent grains), but the content of oxygen was lower compared to flux of argon. Since the aluminium is initially covered with an oxide layer, complete elimination of the influence of oxygen is impossible in these experiments.

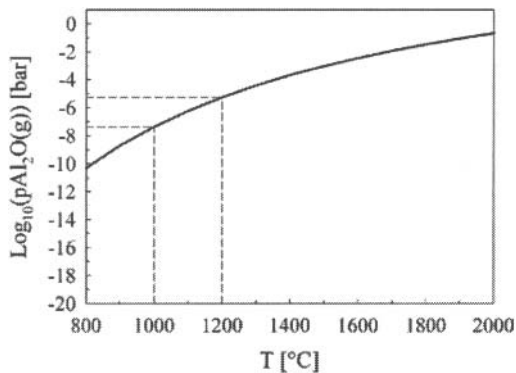
In order to understand the influence of oxygen, several thermodynamic calculations have been performed using the software package FactSage 5.0. In these calculations, formation of oxycarbide was not possible due to lack of thermodynamic data.

In general, the number of degrees of freedom of the system can be found by the Gibbs phase rule,

$$Ph + F = C + 2 \quad (3)$$

where Ph is the number of phases in thermodynamic equilibrium, F is the degree of freedom, C is the number of involved components and 2 corresponds to pressure and temperature. Let us first consider the binary Al-O system with Ar as an inert gas (C=3) at a constant temperature. The total pressure of the system is fixed (F=0) when the gas is in equilibrium with  $Al_2O_3(s)$  and Al(l) since  $Ph+F=3$  and  $Ph=3$ . The equilibrium composition of the gas is then fixed with  $Al_2O(g)$  as the dominating gas species, as predicted in equation (2). It is suggested that the protective  $Al_2O_3$  layer at the aluminium surface is removed or cracked either mechanically, due to the expansion of aluminium at elevated temperatures, or chemically through the evaporation of  $Al_2O(g)$ . The latter will be discussed further below.

Fig.12 shows that the vapor pressure of the sub-oxide  $Al_2O(g)$  increases with increasing temperatures, and reaches  $10^{-5}$  bar at temperatures above 1100°C, where the oxide layer evaporates thermally away from the Al(l) surface. This explains observations made by Landry et al. [7] and explain why it is so difficult to get direct contact between Al and C and formation of carbide. Carbide was only found at temperatures above 1100°C. The partial pressure of  $O_2(g)$  in the Al-O system at 1100-1200°C is  $10^{-34}$  and  $10^{-31}$ , respectively, demonstrating the reducing conditions due to the presence of Al(l).



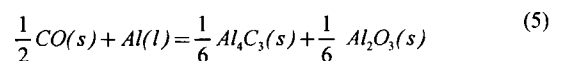
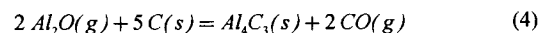
**Fig. 12:** The calculated equilibrium vapor pressure of  $Al_2O$  sub-oxide as function of temperature in the system Al-O, corresponding to reaction (2). The temperature range for experiments performed here is marked with dashed lines.

The next step was to investigate what may contribute to a change in volatility of the oxide scale. Here, an air leakage or oxygen impurities in stagnant argon, as mentioned above, were considered. If the oxygen in the system reacts with carbon to form  $CO(g)$ , one may expect that the volatility of aluminium increases, which changes the vapor pressure of  $Al_2O(g)$ . This is however not the case. The partial pressure of  $Al_2O(g)$  remains constant according to reaction (2) as long as  $Al_2O_3(s)$  is present. Equilibrium calculations have shown that additions of small

amounts of C to the Al-O system increases the  $CO(g)$  pressure until  $Al_4C_3(s)$  starts to form. In this case the gas composition is fixed again (constant pressure of  $Al_2O(g)$ ) according to Gibbs phase rule. This scenario does not change until one of the condensed phases is consumed or disappears. Any excess of carbon (after the formation of  $CO(g)$ ) will react with Al(l) to form  $Al_4C_3(s)$ . This proceeds until Al(l) is consumed and an equilibrium between  $Al_2O_3(s)$ ,  $Al_4C_3(s)$  and C(s) is established. Here the formation of oxycarbides is neglected, but the main conclusion that the volatility of  $Al_2O(g)$  would not be greatly influenced by the presence of C is valid. The removal of the alumina scale from Al(l) is therefore most likely controlled by temperature and the diffusion of  $Al_2O(g)$  away from the Al surface.

In Fig. 13, possible mechanism is proposed, how the protective  $Al_2O_3$  layer is removed from the Al(l) surface and how the carbide formation may take place. The gaseous sub-oxide  $Al_2O(g)$  can diffuse towards the carbon surface, enabling transport of Al through the gas phase. At the carbon surface  $Al_2O(g)$  reacts to form carbide (or oxycarbide) and  $CO(g)$ . Contrary, the released  $CO(g)$  transports C to the aluminium surface, where  $CO(g)$  can react to form  $Al_4C_3(s)$  and generate  $Al_2O(g)$ . Oxygen can then circulate between both interfaces, and one may imagine that the two reactions at the two different surfaces generate two different  $Al_4C_3(s)$  microstructures.

From this scenario, a possible explanation for the formation of two different layers, as shown in Fig. 4, is proposed. It is assumed that aluminium carbide grows at both interfaces according to the sub-reactions (4) and (5). Reaction (5) leads to an oxide rich carbide layer in the vicinity of the aluminium surface. At the present stage the possibility of formation of oxycarbides ( $Al_2OC$  and/or  $Al_4O_4C$ ) cannot be ruled out. This will be followed up in future work, including these species in the thermodynamic analysis. From literature it is known that aluminium oxycarbides appear transparent [8, 9]. In Figs. 4, 8 and 9 it is evident that the first layer consists of transparent grains and EDS measurements have shown the presence of oxygen in this layer. However, reaction (4) may explain the oxide free carbide layer at the carbon surface.



In initial experiments it was not possible to identify the original position of the C/Al interface in order to elucidate the growth rate by these two proposed reaction mechanisms. Both reactions are heterogeneous, involving both a gas and condensed phases. The presence of liquid Al is expected to have a strong detrimental effect on the microstructure of the layer formed at the Al interface. Dissolution - precipitation due to the solubility of  $Al_4C_3(s)$  in Al(l) may also influence the microstructure and destabilization of the oxycarbide due to the low O solubility in Al(l). On the other surface the microstructure of carbon material is expected to influence the microstructure of the carbide form. Here both grain orientation (graphite like grains), grain and pore size are expected to be important. These effects will be followed up in future studies.

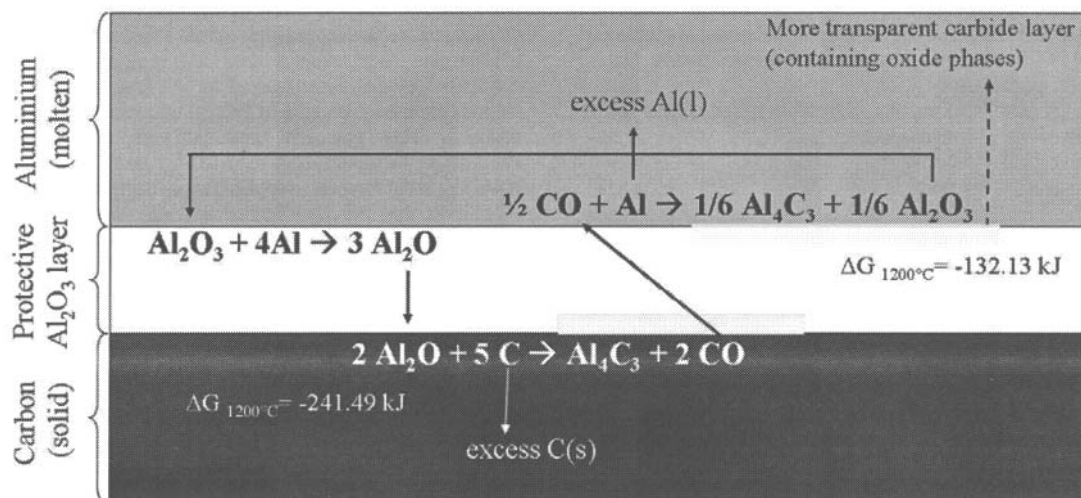


Fig. 13: Proposed gas transport mechanism of aluminium carbide formation.

The initial expectation was that the diffusion couples would provide evidence for the solid state diffusion through a carbide layer at the interface. Estimation of the diffusion coefficient by  $D=4L^2/t$ , where  $L$  is the thickness and  $t$  is the time, give diffusion coefficient of the order of  $10^{-10} \text{ m}^2/\text{s}$ . Such high diffusion coefficients are highly unlikely in the carbide with strong covalent bonds, which strongly supports the preliminary conclusion that gas diffusion is involved in the growth. For gas assisted diffusion, higher temperatures are necessary throughout the experiment to produce Al<sub>2</sub>O sub-oxide (see Fig. 12), and finally aluminium carbide. The attempt to remove the oxide layer at 1200°C for 1 hour and lowering the temperature to 1000°C in the course of the experiment in argon flux was show the presence of a carbide layer, but quantitative determination of the thickness was challenging after only 4 days of reaction.

The large single crystal like grains, with regular shape (Fig. 7) were observed on the interface only after slow cooling (4h), not after quenching in water or gaseous nitrogen flow. It is proposed that their formation is due to nucleation and growth from the molten aluminium during cooling. The solubility of carbon (as aluminum carbide) in liquid aluminium is approximately 200-250 ppm at 1200°C, 40 ppm at 1000°C and less than 10 ppm at 800°C [10]. The carbide deposition from dissolved carbon in aluminium proceeds continuously during cooling, where the cooling rate influences the microstructure of the precipitate.

### Conclusion

Initial experiments using Al/C diffusion couples have shown that aluminium carbide is formed at the interface. The reaction was influenced by several factors such as the atmosphere and the presence of solid alumina. The reaction rate has been shown to be retarded initially due to the oxide scale on molten aluminium, and thick layers of carbide were only observed at 1200°C. The microstructure of the layer formed at the interface showed evidence of two different layers between Al and C, and in one of the layers the presence of oxygen was confirmed by EDS, suggesting that this layer contained oxycarbide. A possible

reaction mechanism was suggested involving mass transport between the Al and C surface by Al<sub>2</sub>O(g) and CO(g). The two different heterogeneous reactions at the two surfaces could possibly explain the two layers formed in the diffusion couples.

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