

# Behaviour of Aluminium Carbide in Al-Melts During Re-melting

Mertol Göknelma, Trygve Storm Aarnæs, Jürgen Maier, Bernd Friedrich, and Gabriella Tranell

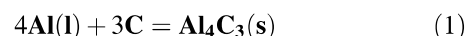
## Abstract

The presence of non-metallic inclusions in aluminium has become a more critical issue with increasing demands on surface quality and low final wall thicknesses of products. Aluminium carbide particles form during the primary aluminium production due to the contact between aluminium and carbon/carbonaceous species in the electrolysis cell. These particles are typically very small ( $<3 \mu\text{m}$ ), however, they may have crucial impacts on the mechanical and optical properties of products when they agglomerate due to poor wetting/high surface tension with/in aluminium melts. The carbide concentration is typically reduced after metal re-melting. The current paper experimentally examines this concentration change and the measured effect of re-melting temperature, atmosphere and rate of carbide reduction during holding of the liquid metal. The study showed that electrolysis metal, initially containing approximately 35 ppm  $\text{Al}_4\text{C}_3$ , retained carbide contents after re-melting in alumina crucibles at 700, 750 or 800 °C at similar levels (2–12 ppm) as previously reported as corresponding to carbon saturation in the melt. The study also illustrated that the carbide level is rapidly decreased during re-melting, and that the reduction is faster in air than in argon, suggesting that the removal takes place via direct oxidation of carbide particles close to—or at the melt surface.

## Introduction

During the production of aluminium, various impurities enter the melt and lead to a degradation of the metal product. Impurities may originate from the raw materials, but they can also be introduced through the atmosphere, refractories, or other materials in contact with the melt [1]. In aluminium production, carbon is introduced to the metal mainly through direct and indirect contact with anode and cathode materials in the electrolysis cell [2].

During cooling towards solidification of the metal in the casthouse, the solubility of carbon decreases with subsequent formation of aluminium carbide ( $\text{Al}_4\text{C}_3$ ) inclusions precipitating as a second phase present in the metal [3], according to the reaction:



The inclusions formed through this reaction may be harmful to the properties of the final product as carbide inclusions are hard and brittle, which can lead to mechanical failure of thin products. They are also highly reactive and will react with moisture in the air, forming  $\text{Al}(\text{OH})_3$ , which leads to product surface imperfections [4].

The carbon solubility in molten aluminium plays an important role in the formation of aluminium carbide. While there has been some disagreement among researchers on the level of solubility [4–6], data from the studies of Rødseth et al. [6] and Dorward [4] are in reasonable agreement on the relation between the measured *carbide* content of metal equilibrated with solid carbon at temperatures in the range 685–1100 °C and solidified. Dorward's solubility data may be represented by the Eq. (2):

$$C_{\text{Al}_4\text{C}_3}[\text{ppm}] = 3.18 \times 10^7 \exp(-15800/T[\text{K}]) \quad (2)$$

while the data of Rødseth is represented by the Eq. (3):

$$C_{\text{Al}_4\text{C}_3}[\text{ppm}] = 8.33 \times 10^7 \exp(-16742/T[\text{K}]) \quad (3)$$

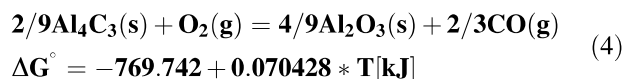
M. Göknelma (✉) · T. Storm Aarnæs · G. Tranell  
Department of Materials Science and Engineering, Norwegian  
University of Science and Technology, 7491 Trondheim, Norway  
e-mail: mertol.gokelma@ntnu.no

J. Maier · B. Friedrich  
IME Process Metallurgy and Metal Recycling, RWTH Aachen  
University, Intzestraße 3, 52056 Aachen, Germany

In these and other studies, it has generally been assumed that there is negligible solid solubility of carbon in aluminium, which would imply that all carbon dissolved at high temperature will precipitate as carbides during solidification.

In general, there are multiple ways of removing inclusions in aluminium, neither of which have been successfully applied to carbides; Filtration aims to remove inclusions by trapping them on top of, or within, the filter while the liquid may pass unhindered. Aluminium carbide particles have a size from 0.5 to 5  $\mu\text{m}$  [7], which makes them difficult to capture through filtration. Sedimentation is a different removal strategy, where the melt is held for some time, allowing inclusions to settle to the bottom of the melt-carrying vessel. However, it is unsuited in this case since the density difference between aluminium carbide and liquid aluminium is too small (2.375  $\text{g}/\text{cm}^3$  vs. 2.360  $\text{g}/\text{cm}^3$  [8]) to allow for effective settling. It has been suggested that inclusion flotation, aided by a purge gas could be a viable option for carbide removal [4]. It has also been reported that re-melting aluminium leads to a decrease in the carbide content [4]. While this phenomenon has been observed industrially, little research into the mechanisms behind—and kinetics of this decrease has been reported in the open literature. The three theoretically possible paths that can decrease the carbide content of a melt, in systems absent of moisture, may be listed as:

1. Particle flotation or attachment to crucible walls
2. Direct carbide oxidation with subsequent emission of CO through reaction (4):



3. Reaction between dissolved carbon in the melt and oxygen in the atmosphere with associated emission of CO:



and subsequent dissolution of carbide into the melt (reverse reaction of (1)), maintaining a carbon equilibrium content with atmosphere and reactor.

The goal for this work was to examine and explain in more detail the change in carbide content of aluminium after re-melting at different temperatures, gas atmospheres, pressure conditions and holding times.

## Experimental

### Materials

The starting point for all the experimental investigation was a cast bar of metal extracted directly from primary aluminium tapped from an electrolysis cell, containing approximately 35 ppm carbide, as determined by the gas chromatography method. The bar was sectioned into pieces for the experiments described below, taking care so that all samples had approximately the same amount of bar surface area and weight.

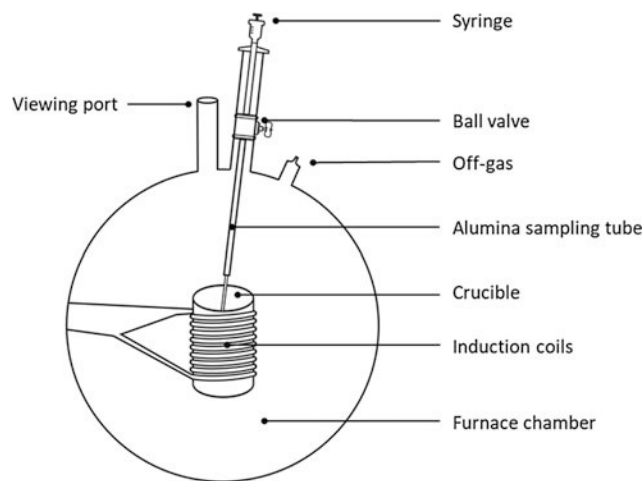
### Experimental Equipment and Procedures

In order to investigate the effect of re-melting temperature, furnace atmosphere and holding time on the carbide content, two furnace set-ups were used in the experiments. A small vacuum induction furnace with controllable atmosphere was used to study the effect of temperature and pressure conditions. A larger induction furnace with a removable hood was used to evaluate the rate of carbide content reduction during re-melting and holding.

#### Vacuum Induction Furnace Re-melting

In each experiment, a sintered alumina crucible (diameter 57 mm, height 100 mm) with 150 g of aluminium was placed inside a graphite crucible. The temperature of the melt was monitored by an alumina-clad thermocouple. The setup is schematically shown in Fig. 1.

The furnace was evacuated and flushed with Ar (6N purity), and subsequently refilled with argon to the



**Fig. 1** Schematic drawing of the re-melting setup in an induction furnace with a vacuum chamber

appropriate pressure (trials 1–2 under partial vacuum and trials 3–12 with slight over pressure). The metal was heated to a temperature of 700, 750 or 800 °C and held for 30 min respectively. Temperature was monitored online with a thermocouple immersed in the melt. Samples in trials 1–4 were taken in situ with an alumina tube, fitted with a syringe in the beginning and the end of the holding time. The remaining samples were taken after solidification (Table 1).

### Large Induction Furnace Re-melting

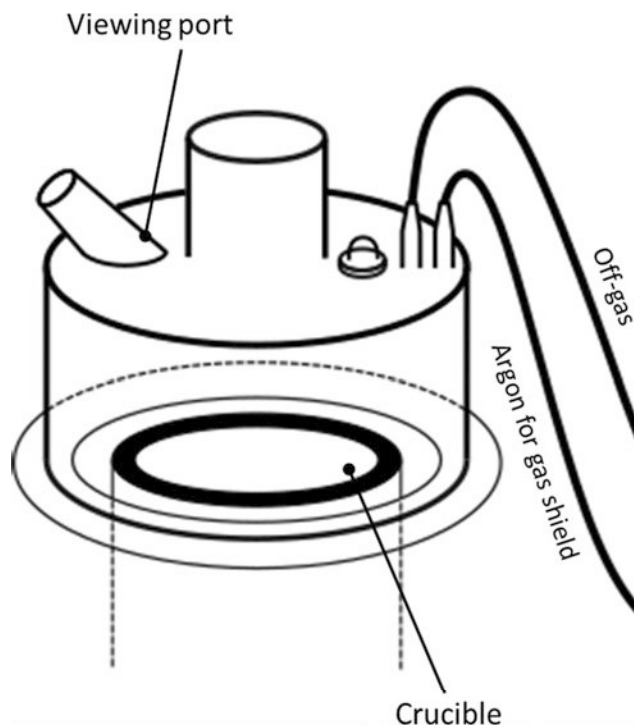
The second setup used for the re-melting experiments was in a larger induction furnace. In this set-up, an alumina crucible (diameter 98 mm, height 139 mm) was also placed inside a graphite crucible. A hood with sampling ports was fitted to the alumina crucible rim. A schematic drawing of the setup is displayed in Fig. 2.

Before each experiment, the crucible and thermocouple tubes were coated with boron nitride, so the molten aluminium would not stick. Approximately 1 kg of aluminium was used for each experiment, inserted into the crucible followed by the crucible being placed inside the furnace. After the metal melted and reached the target temperature, the melt was held for 30 min. The experiments were performed at two different oxygen contents (open air or argon with air) in the atmosphere above the melt. The main parameters are shown in Table 2. After trial 15 and 16, the metal was sampled after solidification. The rest of the samples were taken with a syringe from the liquid aluminium.

One additional experiment ( $\approx 2$  kg melt) was performed without the hood, in air atmosphere, with frequent melt sampling, from the liquid aluminium with a syringe, to observe the change in carbide concentration as a function of time. Nine samples were taken in 34 min of holding (30 min after reaching 700 °C) as shown in Table 3.

### Carbide Analysis of Starting Material and Re-melted Samples

The carbide content of both the starting material and samples of re-melted material at different temperatures were determined by the Hydro Aluminium laboratories at Sunndalsøra, Norway. Each sample was cleaned and placed in a reaction



**Fig. 2** Schematic drawing of the re-melting setup in an induction furnace with continuous gas flush

bulb which was evacuated to a pressure of  $10^{-5}$  torr. Hot sodium hydroxide solution was added to dissolve the sample. Aluminium carbide will decompose in contact with the water in the solution and form methane according to:



After the reaction finished, 5 ml of the gas was removed through the septum with a syringe and injected into the gas-chromatograph. By utilising the ideal gas law, the amount of carbide was calculated by comparing the methane peak with the peak of a reference gas with a known methane content [5].

## Results and Discussion

Carbide concentration contents of all analysed samples are shown in Table 4.

**Table 1** Experimental parameters for re-melting in the small vacuum induction furnace

Trial	Temperature (°C)	Furnace atmosphere	Holding time (min)	Pressure
1–2	700	Argon with <100 ppm O <sub>2</sub>	30	490–500 mbar
3–7	700			Normal
8–9	750			
10–12	800			

**Table 2** Experimental parameters for re-melting in large induction furnace

Trial	Temperature (°C)	Furnace atmosphere	Holding time (min)
13–15	700	Argon with 700 ppm O <sub>2</sub>	30
16	800		
17–21	700	Argon with 4% O <sub>2</sub>	

**Table 3** Sampling time and temperature data for trial 22 during holding the melt at approximately 700 °C

Temperature (°C)	680	700	720	715	702	700	700	700	700
Time (min)	1	3	6.5	10.5	13	18	23	28	33

**Table 4** Aluminium carbide concentrations measured in metal from re-melting tests

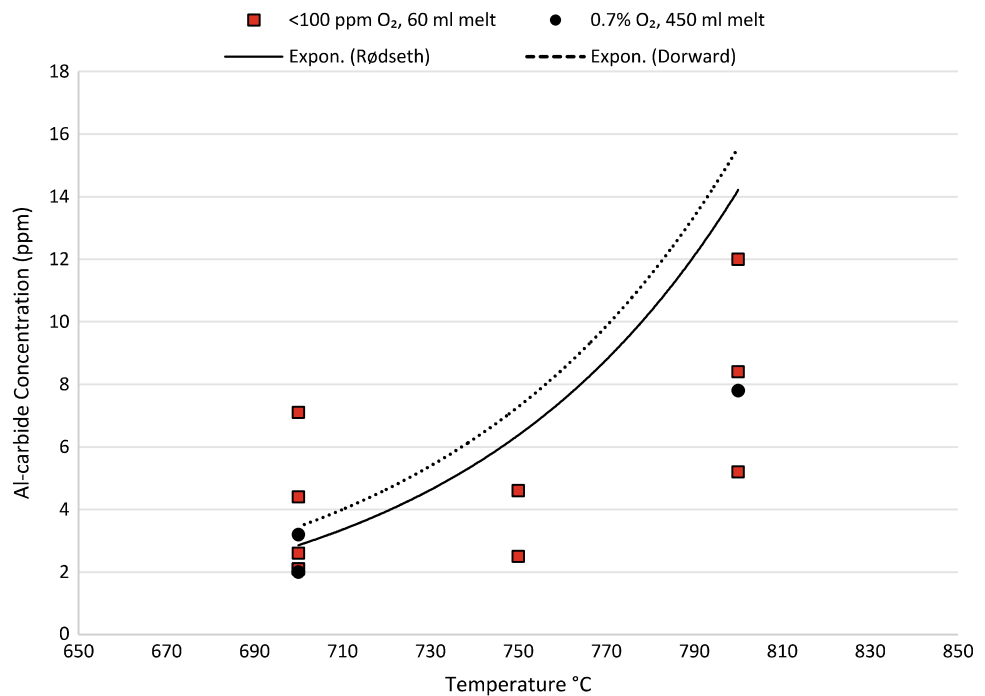
#	O <sub>2</sub> conc. in the furnace	T (°C)	Al-carbide concentration in ppm										Melt quantity (g)	Press.
			Time (min) after melting											
1	<100 ppm	700	Sample too small for analysis					2.9					150	490–500 mbar
2			17.8					5.4						
3			15.8					4.4						
4			11.5					2.1						
5			–					7.1						
6			–					2.6						
7			–					2.1						
8		750	–					4.6						
9			–					2.5						
10		800	–					5.2						
11			–					8.4						
12			–					12						
13	700		–					2					1000	
14			–					2						
15		–					3.2							
16		800	–					7.8						
17	700		5.6					–						
18		7.9					–							
19		8.6					–							
20		4.7					–							
21		9.0					–							
22	Open air	700	1	3	6.5	10	13	18	23	28	33	2000		
			4.5	2.3	2.7	2.4	3.4	2.0	2.1	2.2	2.1			

The resulting melt carbide contents will be discussed in terms of melt temperature, oxygen content in the atmosphere, pressure and holding time.

### Effect of Melt Temperature

Figure 3 shows the aluminium carbide concentration after re-melting at 700, 750 and 800 °C respectively. The average

**Fig. 3** Remaining  $\text{Al}_4\text{C}_3$  in ppm 33 min after re-melting at various temperatures and in different experimental set-ups (trials 3–16)



of the final concentrations were 3.8 (st.dev: 1.9), 3.6 (st.dev: 1.5) and 8.5 (st.dev: 3.4) ppm respectively. Although a considerable deviation is seen between parallels, all samples show significantly lower carbide content than the starting material. A higher carbide content—i.e. less carbide reduction—can be seen for re-melting/holding at 800 °C, as compared with 700 and 750 °C. While a purely physical removal effect (flotation and sticking of particles, route 1) would not explain the temperature dependence, both routes 2 and 3 are temperature dependent as they are governed by the (equilibrium) carbon content in the metal under given conditions. The measured carbide contents lie at, or below the reported carbide contents by both the Rødseth et al. [6] and Dorward [9] studies. It should, however, be noted that these were carbon saturated systems. In our study, the melt is in contact with an alumina crucible and an oxygen-containing atmosphere. As such, it is likely that the metal after re-melting is not carbon saturated and hence, will naturally yield a lower measured carbide content. While the solid solubility of carbon in aluminium has not been widely discussed, a Japanese group [10] in the 1960's reported some degree of solid solubility of carbon in aluminium, approximately an order of magnitude lower than the carbide content of melts equilibrated at 1000 °C.

### Effect of Melt Holding Time

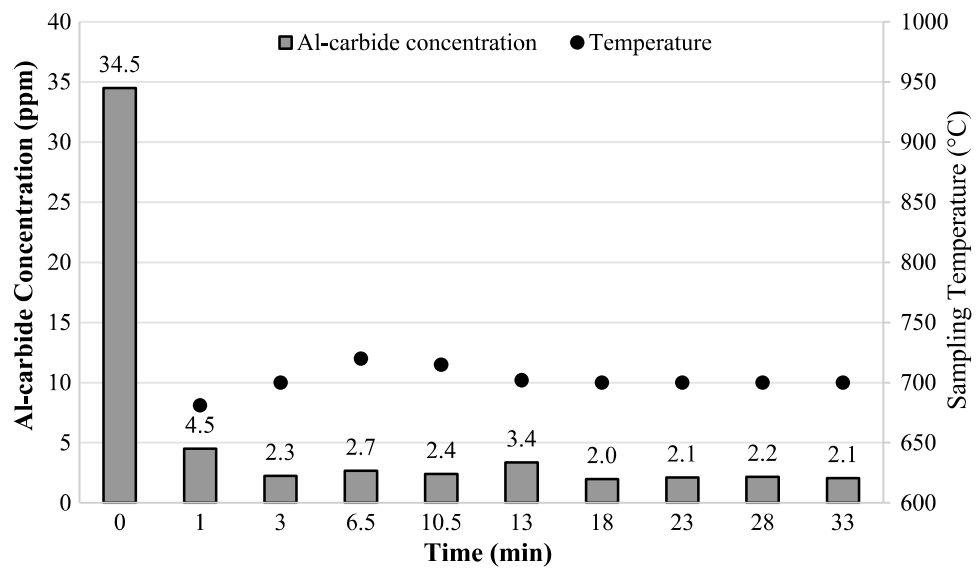
Figure 4 gives us a closer look at the kinetics of the carbide concentration change during re-melting and holding in open

air atmosphere at 700 °C. A very rapid reduction was observed in the first minute after the aluminium was molten, with further reduction in the following couple of minutes. After stabilisation of the temperature at 700 °C, the aluminium carbide concentration reached a representative level of just above 2 ppm throughout the following 30 min. The rapid carbide concentration change indicates fast reaction, suggesting route 2 as the most likely reaction mechanism. Since wetting between carbides and metal is poor, the carbides might be pushed to the surface during melting where they react quickly with atmospheric oxygen or attach to the crucible wall. Dissolution of solid carbide particles into the melt is considered a slower process, making route 3 less likely. Initial experiments where the off-gas composition over the melt was measured by FTIR, yielded a CO peak immediately after melting, indicating fast oxidation of carbides present at—or in vicinity of the metal surface.

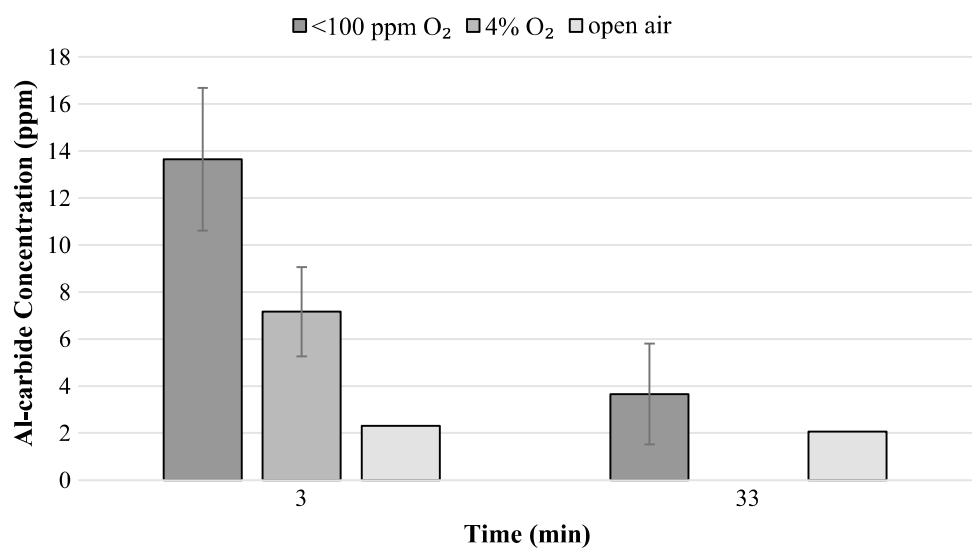
### Effect of Oxygen Content Above the Melt

Figure 5 shows the aluminium carbide concentration change during re-melting under argon atmosphere (with <100 ppm  $\text{O}_2$ ), in Ar with 4%  $\text{O}_2$  and in open air at 700 °C. The final carbide concentrations (after 30 min holding time) in these experiments are comparable (at around 2 ppm) however, samples taken when the melt reached 700 °C (3 min.) showed higher carbide concentrations in Ar atmosphere and in the Ar with 4%  $\text{O}_2$  atmosphere than obtained under open air. While the carbide concentration was measured at 15 ppm in average (st. dev = 3.2)

**Fig. 4** Kinetic change in  $\text{Al}_4\text{C}_3$  concentration during re-melting and holding at  $\approx 700^\circ\text{C}$



**Fig. 5** Change in Al-carbide concentration 3 and 33 min after melting in trial 1–7 (average values) and 17–22



in three parallels in the setup with low oxygen concentration, the trial re-melted in open air showed values very close to final concentration in the first minutes after re-melting. The faster removal rate in the presence of air also suggests route 2 through reaction (3) where non-wetted carbide particles close to the melt surface oxidize rapidly after re-melting.

### Effect of Vacuum

Operating under partial vacuum was tested whether it is beneficial for melt decarburization. However, as illustrated by Figs. 4 and 5, the removal mechanism is already fast during re-melting. Hence, although the number of experiments is not enough to draw firm conclusions, no observable

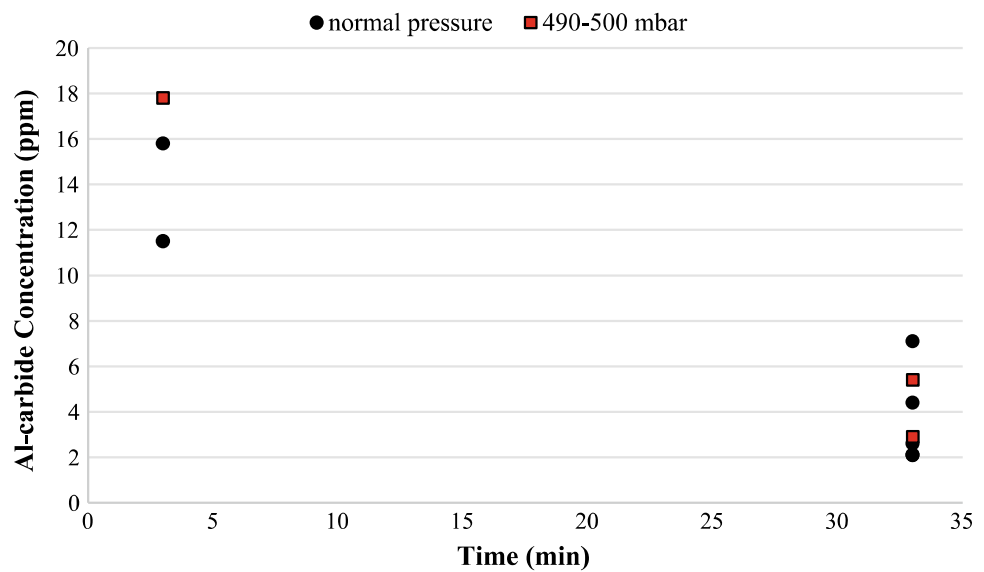
effect on rate or extend of decarburization was found in the current small furnace set-up, as illustrated by Fig. 6.

### Conclusions

The effects of temperature, atmosphere, pressure and holding time on the aluminium carbide ( $\text{Al}_4\text{C}_3$ ) content of re-melted aluminium with an initial carbide content of approximately 35 ppm, was investigated experimentally. The results of the study showed that:

- The carbide content in re-melted aluminium is dependent on re-melting temperature and the lowest carbide contents found were 2.1 ppm at  $700^\circ\text{C}$ , 2.5 ppm at  $750^\circ\text{C}$

**Fig. 6** Change in Al-carbide concentration during re-melting under normal pressure and reduced pressure at 700 °C (experiments 1–7)



and 5.2 ppm at 800 °C in a vacuum induction furnace set-up with a furnace atmosphere of Ar containing <100 ppm O<sub>2</sub>. These values correspond broadly to—or slightly below reported literature data on carbide contents in C-saturated Al melts.

- The reduction in melt carbide concentration is rapid in an open atmosphere furnace. Already 3 min after melting, the carbide was close to the final content of around 2 ppm at 700 °C. The fast reaction indicates direct oxidation of carbide particles which may have been pushed to the melt surface due to poor wetting between carbide and melt.
- Reduction in carbide content is slower in Ar (<100 ppm oxygen content) and Ar containing 4% O<sub>2</sub> than in open air, supporting a removal mechanism of carbide oxidation to Al<sub>2</sub>O<sub>3</sub> and CO at the melt surface.
- While only a few experiments were carried out, no observable effect of furnace pressure was found, with similar resulting carbide concentrations in samples re-melted under argon at atmospheric pressure and reduced pressure after 30 min holding time.

**Acknowledgements** The authors wish to thank staff at Hydro Aluminium Sunndalsøra for supplying electrolysis metal and for carrying out all carbide analyses. The assistance of Henning Dahl, carrying out a part of the experiments, is gratefully acknowledged. Fruitful

discussions with Snorre Kjørstad Fjeldbo around carbides in aluminium, is also much appreciated. The work was funded through the “BEST” project, jointly financed by the Research Council of Norway, Hydro Aluminium, Alcoa Norway, Gränges Aluminium and Hycast.

## References

1. Engh, T (1992) Principles of Metal Refining. Oxford Science Publications
2. R.C. Dorward. Aluminium carbide contamination of molten aluminium. *Aluminium*, 49(10):686{689, October 1973.
3. Novak B, Tschöpe K, Ratvik AP, Grande T (2012) Fundamentals of Aluminum Carbide Formation. *Light Metals*:1343–1348
4. Dorward R (1973) Aluminium carbide contamination of molten aluminium. *Aluminium*, 49(10):686–689
5. Simensen C (1989) Comments on the solubility of carbon in molten aluminum. *Metallurgical Transactions A*, 20(1):191
6. Rødseth J, Rasch B, Lund O, Thonstad J (2002) Solubility of carbon in aluminium and its effect upon the casting process. *Light Metals*:883–888
7. Simensen C (1978) Gas-chromatographic analysis of carbides in aluminium and magnesium. *Fresenius' Zeitschrift Für Analytische Chemie* 292(3):207–212
8. Outotec (2017) HSC 9 (software)
9. Dorward R (1990) Discussion of “comments on the solubility of carbon in molten aluminum”. *Metallurgical Transactions A*, 21 (1):255–257
10. Obinata I and Komatsu N (1964), Solubility of carbon in liquid aluminium, *Journal of Japan Institute of Light Metals*, 14(4), pp. 226–230