Carbothermic Reduction of Alumina: A Review of Developed Processes and Novel Concepts

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Abstract

The Hall-Héroult process for the electrolytic reduction of alumina was developed at the end of the 19th century and is still currently the only industrial process for the production of aluminium. Today this process is ranked among the most energy and CO_2 intensive industrial processes, consuming about 1 % of the globally produced electric energy and producing 2.5 % of the world's anthropogenetic GHG emissions. The direct carbothermic reduction of alumina has been proposed as an alternative process which can substantially improve the sustainability of primary aluminium production. Processes developed so far suffered from critical design issues, which resulted in low aluminium yields, primarily due to aluminium carbide and -oxycarbide formation and aluminium vaporization. Novel concepts currently being developed under the ENEXAL collaborative research project have the potential to overcome such problems by applying fundamental thermodynamic principles and innovative reactor designs. Thermochemical calculations predict that by carrying out the carbothermic reduction under vacuum, not only will the required reaction temperature be considerably lowered, but also the formation of gaseous Al should occur without the accompanying formation of Al_2O, Al_4C_3, and of Al-oxycarbides. Alternatively, liquid Al can be produced by a combination of high temperatures and high excess of carbon thereby again avoiding carbide and sub-oxide formation. The implementation of such carbothermic reduction processes in aluminium production could lead to energy savings of up to 21 %, GHG emissions reductions of up to 52 % and exergy efficiency increase of up to 10 percentile points. Additionally, the prospect of utilizing concentrated

solar energy to provide process heat can render the primary aluminium production truly sustainable. This paper presents a thermodynamic study of the Al-C-O system, a short review on the alumina carbothermic processes developed so far and two novel carbothermic reductions concepts along with preliminary experimental results.

1 Introduction

Aluminium is a light-weight, durable, flexible, corrosion-resistant metal with high electrical and thermal conductivity, which is used in a vast array of products in all areas of modern life. As a result, aluminium is the world's second most-used metal after steel and the aluminium production industry is the largest, in volume of metal produced, in non-ferrous metal industry [1]. In 2006, the world's aluminium production was approximately 50 million tonnes, greatly exceeding the 17 million tonnes of copper, 8 million tonnes of lead and 0.4 million tonnes of tin produced worldwide [2]. From this 50 million tonnes the ratio of secondary (recycled) to primary (produced from bauxite ore) aluminium was 44 % and this ratio has been constantly increasing over the last 4 decades. But since the total aluminium demand has also increased and is estimated that it will keep on increasing [3], the complete abandonment of primary aluminium production is still far away.

The primary aluminium industry is the world's largest industrial consumer of energy. A 'cradle-to-gate' life cycle assessment suggests that the gross energy requirement of current primary aluminium production, including mining, crushing and transportation, is 211 MJ/kg Al, and the global warming potential is 22.4 kg CO_{2equiv}/kg Al [4]. Primary aluminium industry consumes about 1 % of the globally produced electric energy and about 7 % of the total energy consumed by industry worldwide [5].

The main electricity consumption in the primary aluminium production (approximately 56 MJ/kg of Al [5-6]) happens in the Hall-Héroult process (Table 1), where aluminium is produced by the electrolytic reduction of high grade alumina (Al_2O_3) in a molten salt (cryolite) bath at 960 °C. Assuming coal-based electricity generation which is the case used in many primary aluminium plants worldwide, approximately 170 MJ [7] of energy are consumed for the electrolytic reduction and an additional 14.84 kg of CO_2 are indirectly released through coal burning for each kg of aluminium produced in this way (Table 1). Thus the Hall-Héroult process is – by design – the most energy intensive stage in the primary production of aluminium, consuming up to 188 MJ/kg Al, while its total (direct and indirect) CO_2 and CO_2 equivalent emissions (PFCs) are up to 18.66 kg/kg of Al produced or 2.5 % of the world's anthropogenetic CO_2-equivalent emissions [7]. The exergy efficiency of the Hall-Héroult process is also very low (n_{ex} = 15.86 %) [7], given that large sums of exergy from carbon are used to produce high-exergy content electricity, part of which is then lost in cells' overpotentials as non-recoverable waste heat. Finally, the electrolytic cells used in the process need to be periodically replaced, producing a carbon based solid waste (0.02 kg/kg Al) known as Spent Pot Lining (SPLs), which is classified as a hazardous waste, due to its chemical content in fluorides and cyanides.

Table 1: The Hall-Héroult Process (all species are considered to enter and exit the system boundaries at 25 °C)

ELECTRICITY PRODUCED IN:		HYDROELECTRIC PLANTS		COAL BURNING PLANTS	
		Mass	Exergy*	Mass	Exergy
INPUT	Alumina	1.93 kg	0.80 MJ	1.93 kg	0.80 MJ
	Carbon Anodes	0.45 kg	15.37 MJ	0.45 kg	15.37 MJ
	Na_3AlF_6	0.03 kg	0.01 MJ	0.03 kg	0.01 MJ
	AlF_3	0.04 kg	0.05 MJ	0.04 kg	0.05 MJ
	TOTAL INPUT (IN1)	**2.45 kg**	**16.23 MJ**	**2.45 kg**	**16.23 MJ**
UTILITIES	Electricity		56.24 MJ		56.24 MJ
	Coal for producing electricity			5.11 kg	170.27 MJ
	Fuel for Anode baking	0.06 kg	2.66 MJ	0.06 kg	2.66 MJ
	TOTAL UTILITIES (IN2)		**58.90 MJ**	**5.17 kg**	**172.94 MJ**
PRODUCT	Aluminium	1.00 kg	30.00 MJ	1.00 kg	30.00 MJ
	TOTAL PRODUCT (OUT1)	**1.00 kg**	**30.00 MJ**	**1.00 kg**	**30.00 MJ**
WASTE	CO_2 from Electrolysis	1.53 kg	0.69 MJ	1.53 kg	0.69 MJ
	CO_2 from anode baking	0.12 kg	0.05 MJ	0.12 kg	0.05 MJ
	CF_4 (g)	2.99E-04 kg	1.62E-03 MJ	2.99E-04 kg	1.62E-03 MJ
	C_2F_6(g)	2.45E-05 kg	1.77E-04 MJ	2.45E-05 kg	1.77E-04 MJ
	Spent Pot Lines (SPL)	0.02 kg	0.35 MJ	0.02 kg	0.35 MJ
	CO_2 from Electricity	0.00 kg	0.00 MJ	14.84 kg	6.68 MJ
	TOTAL WASTE (OUT2)	**1.67 kg**	**1.10 MJ**	**16.51 kg**	**7.78 MJ**
WASTE HEAT (IN1+IN2-OUT1-OUT2)			**44.04 MJ**		**151.39 MJ**
Total Energy consumption (Utilities + Carbon Anodes)		**74.27 MJ**		**188.30 MJ**	
Total CO_2-eq emissions		**3.82 kg**		**18.66 kg**	
Exergy Efficiency of process		**39.93 %**		**15.86 %**	

Economically, the Hall-Héroult process is a highly expensive process, viable only in very large plants, as its' electrical energy cost accounts for approximately 30 % of the total primary aluminium production cost [8], while due to its basic volumetric inefficiency [5] (since the reduction process takes places practically in a two dimensional plane between the electrodes) its implementation requires large reactor surfaces, which translates into high capital and operational costs.

1.1 The carbothermic reduction of alumina

A basic non-electrochemical alternative to the Hall-Héroult process is the carbothermic reduction of alumina, which has been proposed by various researchers in the last 50 years [5].This process is theoretically described by the following chemical reaction occurring at temperatures higher than 2100 °C:

$$Al_2O_3 + 3C = 2Al + 3CO_{(g)} \quad (1)$$

Assuming such a process happening in an Electric Arc Furnace with at least 90 % Aluminium yield then, as shown in Table 2, compared to the Hall-Héroult process described above, the carbothermic reduction of alumina could achieve 21 % energy savings (including the energy of the coal used in the reductive process) and 52 % direct GHG emissions reductions (including the elimination of PFC emissions). Assuming utilization of coal based electricity generation the total energy savings would increase to 32 % and the overall exergy efficiency of the process would be 23 %, as more carbon would be utilized directly in the chemical reduction process rather than being burned to produce electricity to power the electrochemical reduction process. Additionally the hot CO gas produced from the process would be a potential heat and energy source, while the process would be free of solid wastes.

Table 2: Hypothetical carbothermic reduction of Alumina assuming 90 % reaction efficiency in an EAF at 2200 °C (all species are considered to enter and exit the system boundaries at 25 °C)

ELECTRICITY PRODUCED IN:		POWERED FROM HYDROELECTRIC PLANTS		POWERED FROM COAL BURNING PLANTS	
		Mass	Exergy*	Mass	Exergy
INPUT	Alumina	2.10 kg	0.87 MJ	2.10 kg	0.87 MJ
	Carbon	0.74 kg	25.23 MJ	0.74 kg	25.23 MJ
	TOTAL INPUT (IN1)	**2.84 kg**	**26.11 MJ**	**2.84 kg**	**26.11 MJ**
UTILITIES	Electricity		33.69 MJ		33.69 MJ
	Coal for producing electricity			3.06 kg	102.01 MJ
	TOTAL UTILITIES (IN2)		**33.69 MJ**	**3.06 kg**	**102.01 MJ**
PRODUCT	Aluminium	1.00 kg	30.00 MJ	1.00 kg	30.00 MJ
	TOTAL PRODUCT (OUT1)	**1.00 kg**	**30.00 MJ**	**1.00 kg**	**30.00 MJ**
WASTE	CO from process	1.56kg	15.29 MJ	1.56 kg	15.29 MJ
	CO_2 from Electricity Production	0.00 kg	0.00 MJ	8.89 kg	4.00 MJ
	TOTAL WASTE (OUT2)	**1.56 kg**	**15.29 MJ**	**10.45 kg**	**19.29 MJ**
WASTE HEAT (IN1+IN2-OUT1-OUT2)			**14.51 MJ**		**78.83 MJ**
Total Energy consumption (Utilities + Carbon)		**58.92 MJ**		**127.24 MJ**	
Total CO_2 emissions (including oxidation of CO to CO_2)		**2.44 kg**		**11.33 kg**	
Exergy Efficiency of process		**50.17 %**		**23.42 %**	

Economically such a process could reduce the capital cost of the primary aluminium industry up to 50 % [5, 9], due to an increase of volumetric processing (as the reaction would take place in a bulk reactor, utilizing all three dimensions) thus making primary aluminium mini-mills viable.

However till this day no industrial application of a carbothermic reduction process has been successfully applied, as the occurrence of side-reactions in the Al-C-O system, reduce substantially the final aluminium production yield. At temperatures lower than 2100 °C reaction (1) is hindered by the formation of the aluminium carbides (Al_4C_3) and aluminium oxy-carbides (Al_2OC and Al_4O_4C)

which eventually form an alumina-carbide melt phase. At higher temperatures aluminium carbides are unstable, but aluminium content is lost in the gaseous phase as aluminium vapours and aluminium sub-oxide Al_2O vapours. It should also be noted that in the end, the liquid aluminium phase produced is in reality an Al-C alloy with approximately 20 % mole in carbon [10], which when cooled will re-form carbides, which have to be separated from the aluminium and recycled in the process.

2 Developed carbothermic reduction processes

Theoretical concepts for the carbothermic reduction of alumina date back more than a century, while attempts to establish a viable process have been made in the past by major aluminium industries like PECHINEY, ALCAN and ALCOA [11].

In the 1960's, PECHINEY created an electric arc furnace plant, where alumina reacted with carbon at 2400 to 2500 °C, producing a gaseous mixture of aluminium suboxide, aluminium and carbon monoxide. This gas phase was further reduced with excess carbon forming aluminium carbides, which were decomposed at high temperature in a vacuum to produce aluminium [11]. This process was eventually abandoned due to its very high energy cost (67.5 MJ/kg Al) [12].

Since then, the major research focus of ALCAN in the 1980's and more recently of ALCOA have revolved around Cochran's idea of a process in two stage reactor [13] where at first at temperatures lower than 2000 °C an aluminium carbide – alumina slag is formed and then at temperatures higher than 2000 °C this slag is further reduced producing an aluminium carbon alloy. These two steps can be described as:

Slag formation: $3Al_2O_3 + 9C = (Al_4C_3{\cdot}Al_2O_3)_{slag} + 6CO_{(g)}$ $\quad 1900\ °C < T < 2000\ °C \quad (2)$

Alloy formation: $(Al_4C_3{\cdot}Al_2O_3)_{slag} = 6(Al)_{alloy} + 3CO_{(g)}$ $\quad T > 2000\ °C \quad (3)$

The idea behind the separation of the reduction in two steps stems from the need to limit aluminium volatizing and dusting problems, by limiting the volume of CO gas that goes through the liquid Al-C alloy [13]. Cochran's process involved in the first stage the creation of a liquid phase (alumina-carbide slag rich in alumina) in contact with solid carbon and alumina. Gradually all the available carbon is oxidized, producing 2/3 of the total CO gas and theoretically avoiding aluminium vaporization. By the end of the first stage a second liquid phase has formed (alumina-carbide slag rich in carbides), which is treated in higher temperatures in order to gradually produce a lighter liquid Al-C alloy phase and the remaining quantity of CO gas [13]. To achieve good phase separation and avoid large aluminium losses in the gaseous phase, precise control of reactor temperature or precisely tuned multiple reactors are needed, leading to significant reactor design and operational problems.

The latest development in this process was made by a collaborative ALCOA-ELKEM project, where a novel complex reactor (Advanced Reactor Process-ARP) [12, 14-15] was developed. The ARP resolved some of the technological problems of previous groups (like heat supply and slag transfer) and introduced an additional Vapour Recovery Reactor (VRR) [15-16] to recycle the aluminium and aluminium sub-oxide vapours evolved in both steps. This VRR is essentially a carbon stack, which cools the off-gases passing through it and therefore allows the capturing of all aluminium content as aluminium carbides and oxy-carbides, which are then recycled in the alloy production reactor (step 2). In this way not only are aluminium losses reduced but steps 1 and 2 can run simultaneously as the VRR acts as a "self-stabilization" unit effectively regulating fluctuations in carbon and aluminium content between steps 1 and 2.

ALCOA-ELKEM calculate the electrical energy requirements for the operation of their ARP to 34.2 MJ/kg of Al (a value very close to the theoretical estimation given in Table 2) and estimate that the overall capital cost of such a plant would be 30 % less than a convention Hall-Héroult plant with equal production capacity [12]. However, the ARP still suffers from the major drawback of producing and circulating large quantities of aluminium carbides between different reactors thereby reducing the process efficiency and potentially creating significant technological problems associated with mass transfer.

3 Thermodynamic analysis

To improve or redesign the process for the carbothermic reduction of alumina, it is necessary first to identify the mechanisms that limit the reductive process. The key obstacle is the formation of aluminium carbides and of the alumina-carbide slag, both of which can be avoided if the process takes place at temperatures higher than 2200 °C and atmospheric pressure, where such phases are thermodynamically unstable. Utilizing the FactSage^{TM} 6.1 software, a thermodynamic analysis conducted in NTU-Athens shows that in the Al_2O_3+3C system above 2200 °C at thermodynamic equilibrium only 40 % of aluminium is retrievable as liquid (Al-C) alloy, while the remaining 60 % is found in the gaseous phase as aluminium vapour ($Al_{(g)}$) and aluminium sub-oxide ($Al_2O_{(g)}$) (Figure 1). In total, only 66 % of the alumina is reduced to metallic aluminium, as 33 % of the aluminium content is found as aluminium sub-oxide, a metastable chemical specie with aluminium in the +1 oxidation state.

It is also worth noticing, that in the calculated speciation of the system (Figure 2), there exists unreacted solid carbon which is not dissolved in the Al-C liquid phase. Taking into account that the software's predictions for the Al-C phase diagram are in complete agreement with published results [10], it is clear that thermodynamically the reduction of Al_2O from carbon

$$Al_2O_{(g)} + C = 2Al_{(l)} + CO_{(g)}, \qquad \Delta G_{(2200\,^{\circ}C)} = -32.23\ kJ \tag{4}$$

cannot take place in full, despite its highly negative Gibbs free energy potential. It is therefore obvious that other reactions hinder the completion of reaction (4) thus forming an equilibrium mixture.

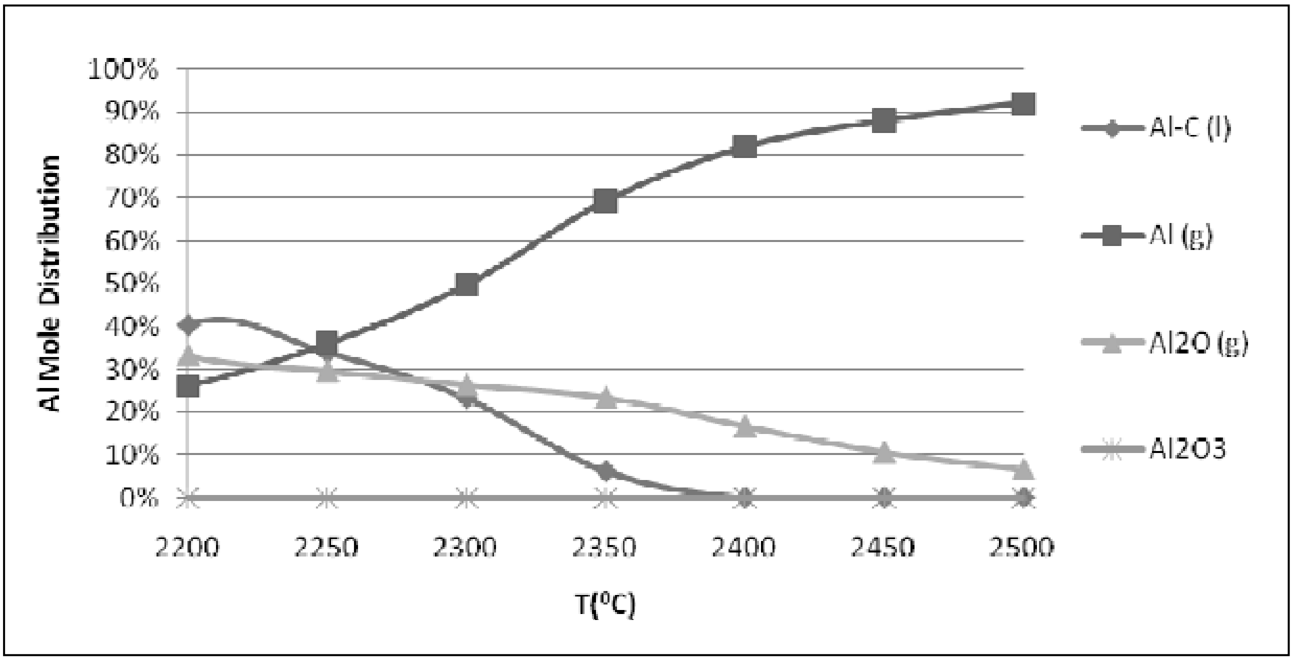

Figure 1: Calculated distribution of aluminium content at thermodynamic equilibrium for various temperatures in a system with initial molar composition of $1Al_2O_3 + 3C$

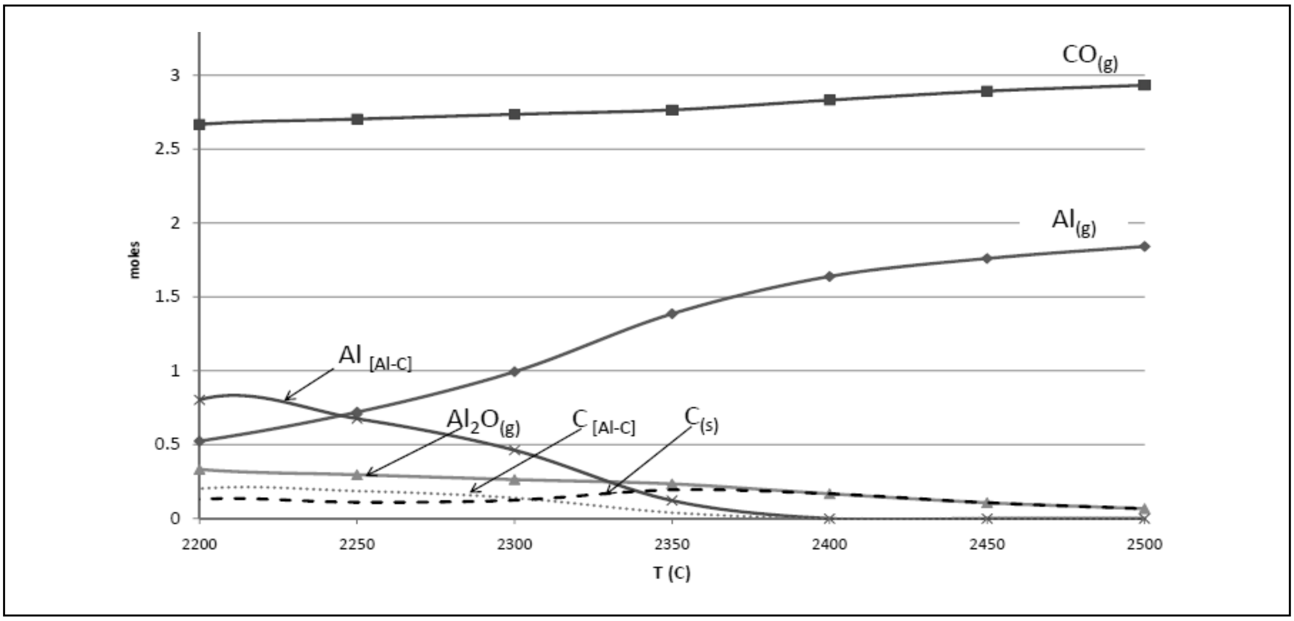

Figure 2: Calculated molar speciation at thermodynamic equilibrium for various temperatures in a system with initial molar composition of $1Al_2O_3$+3C. Species with the [Al-C] subscript are dissolved in the liquid Al-C alloy phase

In Figure 3 the alumina reduction yields for different initial carbon amounts shows that the presence of excess carbon does not change this equilibrium mixture, which as seen, is almost constant throughout the temperature region from 2200 °C to 2400 °C. Above the later temperature, where the Al-C liquid phase completely evaporates, Al_2O and C begin to be consumed again increasing the total aluminium reduction yield, which approaches 100 % at 2500 °C.

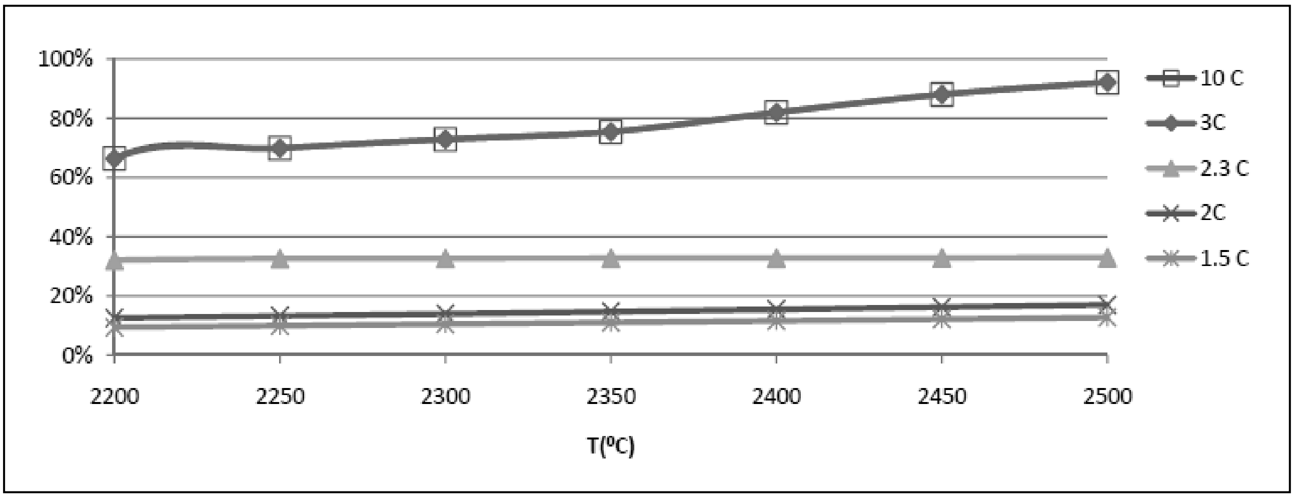

Figure 3: Calculated reduction yield of alumina to metallic aluminium species (Al-C alloy and $Al_{(g)}$) at thermodynamic equilibrium for various temperatures in system with initial molar composition of $1Al_2O_3$+xC

To comprehend further this mechanism, which prohibits the full reduction of alumina and favours $Al_2O_{(g)}$ production, the effect of oxygen in the system is examined.

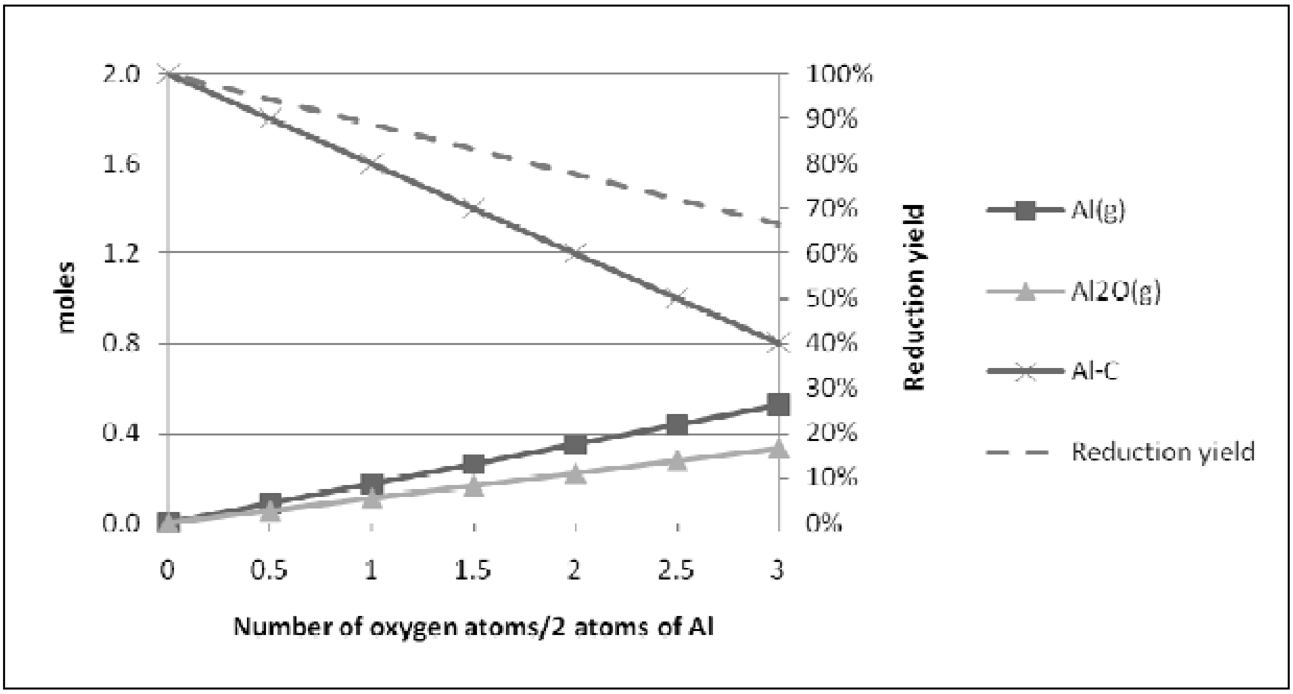

Figure 4: Calculated aluminium molar speciation and alumina to metallic aluminium reduction yield at 2200 °C in system with varying initial aluminium to oxygen atomic ratio and excess carbon. For ratio 3 oxygen atoms / 2 Al atoms the initial system is equivalent to the composition of Al_2O_3+10C, for 2 oxygen atoms / 2 Al atoms to ½·(Al_4O_4C+19C), for 1 oxygen atoms / 2 Al atoms to Al_2OC+9C, and for 0 oxygen atoms / 2 Al atoms to ½·(Al_4C_3+17C)

As seen in Figure 4, as more oxygen atoms are removed from the system the moles of liquid Al-C and the total alumina reduction yield are both increased, reaching their maximum possible values when all oxygen atoms are removed from the system, e.g. when one starts from a 100 % aluminium carbide system. Figure 4, therefore presents a thermodynamic justification for staging the carborthermic reduction in two steps, as by removing 2/3 of the oxygen content from the Al_2O_3+10C system at lower temperatures one can retrieve the double amount of liquid Al-C at 2200 °C. At the same time however, due to the formation of the alumina-carbide slag phase, it is impossible to completely convert all of the alumina to aluminium carbides [17] and therefore the two stage carbothermic reduction cannot achieve (under thermodynamic equilibrium) a 100 % aluminium reduction.

Figure 4 also shows a correlation between oxygen atoms presence and aluminium sub-oxide formation. This correlation is defined by the following reaction

$$4Al_{(l)}+Al_2O_{3(l)} = 3Al_2O_{(g)}, \qquad \Delta G_{(2230\ °C)} = -178.8\ J \qquad (5)$$

the occurrence of which is documented in [18] and is essentially the comproportionation reaction of aluminium species: $2Al^{[0]} + Al^{[+3]} = 3Al^{[+1]}$. Metallic aluminium is present in the system either as liquid Al-C alloy or as aluminium vapours, aluminium in the +3 oxidation state is present in the system as alumina (Al_2O_3) or as aluminium carbide (Al_4C_3) and oxy-carbides, while aluminium in the +1 oxidation state can only exist as aluminium sub-oxide (Al_2O). Returning to Figure 4, in systems with no oxygen atoms present there are obviously no $Al^{[+1]}$ species and therefore the comproportionation reaction cannot take place. As the ratio of oxygen atoms in the system increases, reaction (5) takes place oxidizing part of the metallic aluminium that had been previously reduced carbothermically and thus an equilibrium mixture between metallic aluminium, aluminium sub-oxide vapours and carbon is formed (reactions (1),(4) and (5)).

As seen in Figure 5, reaction (5) is favoured entropically when metallic aluminium is in the liquid phase (at temperatures between 2200 and 2400 °C) as from 4 liquid molecules 3 gaseous are evolved in an endothermic reaction. At higher temperatures, where metallic aluminium is in the gaseous phases the reaction becomes exothermic and reduces 4 gaseous molecules into 3. Therefore the reaction is no longer favoured both entropically and energetically and is practically reversed. This explains why, as seen in Figures 1 to 3, the reduction yield of alumina is increased in the absence of the Al-C liquid phase.

Finally, while reaction (5) seems to explain the presence of aluminium sub-oxide vapours in thermodynamic equilibrium with solid carbon and its dependence on the oxygen ratio of the system, there still remains a question on the presence of the aluminium vapours in the system. Thermodynamically aluminium evaporates above 2500 °C (boiling point 2518 °C) and therefore one would expect much smaller amounts of vapours at 2200 °C. Additionally, in Figure 4 it is evident that the oxygen ratio of the system also affects the amounts of aluminium vapours in the system, proving that their presence is not the result of high aluminium vapour pressure. Instead, taking into account the similar trend of $Al_{(g)}$ and $Al_2O_{(g)}$ presented in Figure 4, the presence of aluminium vapours in the system can be attributed to the coupling of reaction (5) with aluminium vaporization as can be seen in the overall reaction

$$4.1Al_{(l)} + Al_2O_{3(l)} = 3Al_2O_{(g)} + 0.1Al_{(g)}, \qquad \Delta G_{(2238\,°C)} = -155.4\ J \qquad (6)$$

which is again favoured entropically, and when compared to reaction (5), occurs under similar temperatures and Gibbs free energy potentials.

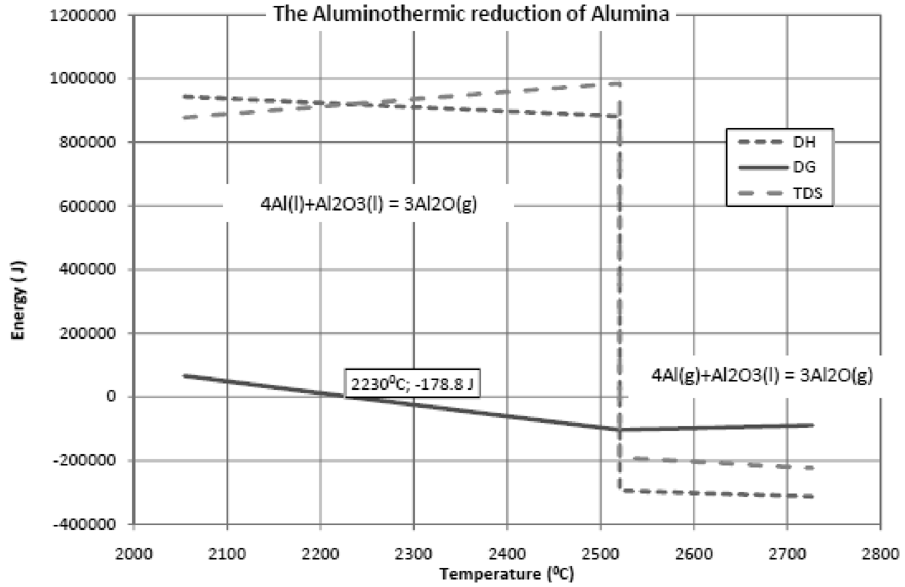

Figure 5: Calculations of the changes in Gibbs free energy potential, enthalpy and dissipative heat for reaction (5) under different temperatures and atmospheric pressure

In conclusion, the present thermodynamic study indicates that at temperatures higher than 2200 °C:

- The reduction yield of alumina does not depend on carbon excess and is controlled by the formation of aluminium sub-oxide vapours.
- The presence of sub-oxide vapours in the system is justified thermodynamically and not kinetically (e.g. through phase separation in the reactor).
- The production of aluminium sub-oxide vapours is favoured in the presence of liquid aluminium in contact with alumina, while this is reversed in the presence of gaseous aluminium.
- The amounts of aluminium vapours in the system depend on the amount of aluminium sub-oxide vapours and are not the result of high aluminium vapour pressure.

Based on these conclusions, thermodynamically it seems that to achieve high aluminium reduction yields one must avoid the formation of aluminium sub-oxide either by moving into conditions that favour gaseous rather than liquid aluminium production or by removing the liquid aluminium phase from the system before it can back react with alumina bearing phases.

4 New proposed processes under the ENEXAL project

Under the EC-funded "Novel technologies for enhanced energy and exergy efficiencies in primary aluminium production industry (ENEXAL)" collaborative research project novel concepts for the carbothermic reduction of alumina are being researched, aiming at overcoming the complexity and difficulties of the previously developed processes [19]. In accordance with the thermodynamic conclusions presented above two different paths will be explored. The first path relies on staging the carbothermic reduction of alumina under vacuum, where the production of aluminium vapours will be favoured and liquid aluminium formation will be avoided. The second path relies on improving the existing EAF technology in such a way that liquid aluminium is removed from the reaction zone and fumed Al_2O and Al is condensed in an integrated shaft type attachment, both continuously. The vacuum carbothermic reduction process in the ENEXAL project is being studied and optimized by ETH-Zurich and the Weizmann Institute, while the shaft-EAF process will be studied and optimized by RWTH-Aachen and NTU-Athens.

4.1 "Vacuum carbothermic reduction"

In experiments carried out at the Paul Scherrer Institute using mixtures of Al_2O_3 and charcoal (molar ratio 1:3) under Ar at atmospheric pressure in a quartz-tube reactor, heating by 30 sec pulses from an 18 kW induction furnace resulted in the production of elementary Al, as well as Al_2O_3, Al_4C_3, and the oxy-carbides Al_2OC and Al_4O_4C. The formation of these species was proven by gas chromatography for the released CO, and by XRD analysis for the solid products on the cold reactor wall [20]. By induction furnace heating of a mixture with initial molar ratio $Al_2O_3/C = 1$, the XRD spectrum of the material obtained from the cold reactor wall showed only peaks due to Al and Al_4C_3 but the overall yield of the reaction was significantly suppressed [21].

Thermochemical calculations predict that by carrying out the carbothermic reduction under vacuum, not only will the required reaction temperature be considerably lowered, but in addition the formation of gaseous Al should occur without the accompanying formation of $Al_2O_{(g)}$, Al_4C_3, and of Al-oxycarbides. This can be illustrated in the equilibrium diagram for the reaction at 0.1 mbar presented in Figure 6, where at around 1500 °C one gets almost full conversion of Al_2O_3 to $Al_{(g)}$ and $CO_{(g)}$.

In an effort to achieve both energy savings and CO_2 emission avoidance, the carbothermic reduction of Al_2O_3, was performed under vacuum using concentrated solar energy as the source of high-temperature process heat [22]. Exploratory experimental runs using a solar reactor were carried out at temperatures in the range 1027 to 1727 °C and total pressures in the range 3.5 to12 mbar, with reactants Al_2O_3 and bio-charcoal directly exposed to simulated high-flux solar irradiation, yielding up to 19 % Al by condensation of product gases, accompanied by the formation of Al_4C_3 and Al_4O_4C within the crucible [23]. Based on the measured CO generation, integrated over the duration of the experimental run, the reaction extent reached 55 % at 1727 °C. When the reducing agent is derived from a biomass source, the solar-driven carbothermal reduction is CO_2 neutral.

The purpose of the ENEXAL project is to execute the reduction of alumina under vacuum with the aid of concentrated solar radiation which will directly illuminate powder mixture of alumina and bio-charcoal.

The products of the reaction between the alumina and the charcoal at these conditions are Al vapours which can partially condense on the walls of the reactor which are cooled to around 700 °C and liquid aluminium is collected at the bottom of the reactor. The CO and the balance of the Al vapours are pumped out through additional condenser and filtration. The pure CO exhausted from the system can be converted to hydrogen in the water-gas shift reaction ($CO+H_2O \rightarrow H_2+CO_2$).

In a further potential application of vacuum carbothermic reduction to aluminium, the direct reduction of iron-free bauxite minerals was predicted by thermochemical calculations to be feasible, and would occur without significant interference by the accompanying Si or Ti minerals. With iron-rich bauxites, a preliminary step of iron removal would be necessary. This circumstance still needs to be tested experimentally [24].

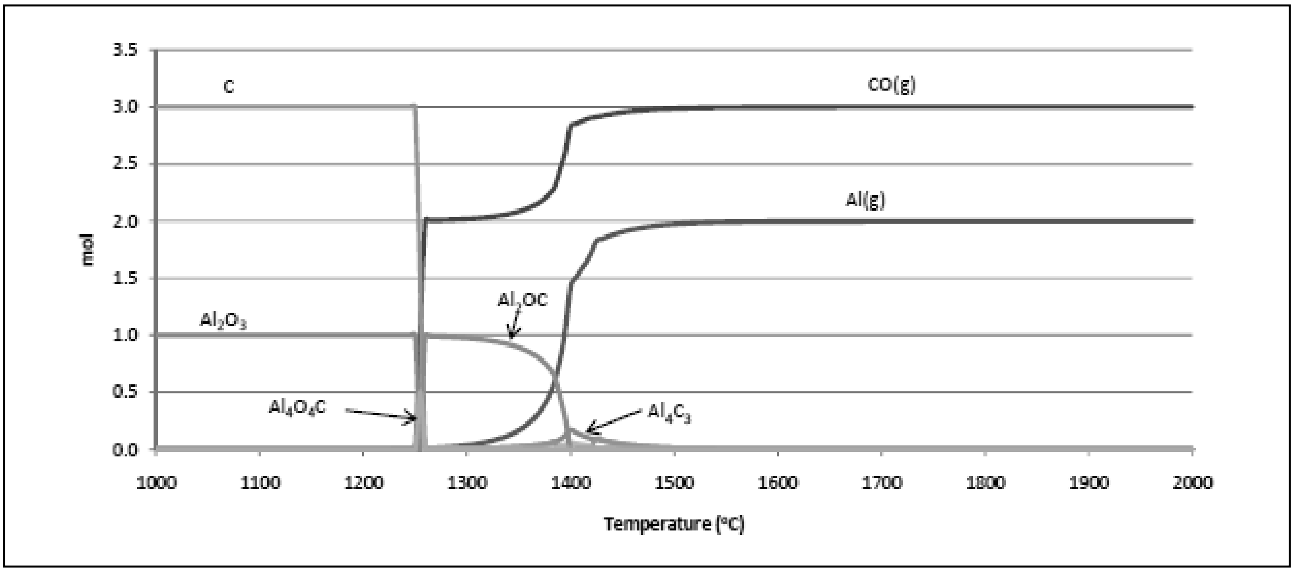

Figure 6: The equilibrium diagram for the reaction of alumina with carbon at 0.1 mbar as calculated in FactSage™ 6.1 software

4.2 "The Shaft-EAF" concept

The concept of using electric arc furnaces (EAF) for carbothermic reduction of aluminium is not new. In the last decades several scientific projects have dealt with the idea of producing aluminium in electric arc furnaces, but only the production of AlSi alloys has reached industrial scale for some years in Germany during the Second World War and Russia [25-26].

The main challenges of a Si-free aluminium EAF process are the high evaporation of aluminium and aluminium sub-oxide as well as the generation of aluminium carbides. Most process ideas using EAF are focussed on a fast continues tapping of the produced aluminium out of the hot zone to prevent the aluminium for evaporation and to minimize carbide formation. A packed bed formed by Al_2O_3/C-pellets is used for condensation of evaporated products to minimize the losses and the extent of which depends on the size and the height of the packed pellet bed. The main problem with such designs is that due to the high carbon concentration in the pellet bed the aluminium and aluminium suboxide condensed vapours react with carbon forming aluminium carbides and oxycarbides. In fact the rate of aluminium carbides formation in the upper condensation zone can be higher than the amount of aluminium carbide consumption in the main reaction zone.

The current project aims on a modification of the electric arc shaft furnace. The condensation zone will be divided in two zones in order to create a better temperature profile allowing for minimisation of the reaction between aluminium and carbon, while the reaction between condensed aluminium and carbon will be prevented through an innovative pellet bed design. The main idea is to condensate most of the aluminium in zones without carbon, but one of the problems of the investigated process concept remains the re-evaporation of aluminium during the process, as aluminium which is condensed in the upper pellet bed will return to the hot zone together with the unreacted charge. With changes and optimizations in the furnace construction and operation, this re-evaporation cycle will be controlled and minimized so that produced aluminium is protected against overheating.

The current trials in the frame of ENEXAL are conducted in one of the IME-laboratory electric arc furnaces. The needed modifications were kept as simple as possible to design the anticipated temperature profile inside the shaft. The maximum power of the furnace is 100 kW and the total volume of the graphite crucible is 10 l. The bottom electrode is a water cooled copper electrode and the top electrode consists of graphite. The position of the top electrode can be infinitely hydraulically adjusted. The diameter of both electrodes is 50 mm. The furnace can be tapped or tilted. The crucible is mounted into the furnace on a coke bed in order to assure a sufficient electrical conductivity between crucible and bottom electrode. The advantage of the graphite crucible is a higher thermal stability as conventional linings as well as reduced contamination by impurities from the lining material. Furthermore the graphite crucible can be changed easier than a ceramic lining and due to the low cross section a higher energy density can be maintained.

5 Conclusions

The carbothermic reduction of alumina is potentially a process which could reduce substantially the heavy environmental footprint of the primary aluminium industry by reducing energy consumption by 21 %, GHG emissions by 52 % and increasing the overall exergy efficiency by 10 percentile points. However its implementation is hindered substantially by side and back reactions limiting the efficiency of aluminium production. The present study shows that even if the formation of aluminium carbides is avoided or controlled, there exists a mechanism that prevents the full reduction of alumina to aluminium, through the formation of aluminium sub-oxide vapours. As shown through thermodynamic calculations this mechanism is not the result of reactions kinetics, but exists even under thermodynamic equilibrium, due to the comproportionation reaction of aluminium species.

Under the ENEXAL project two novel concepts for the carbothermic reduction of alumina will be examined, which aim to achieve high aluminium yields by operating under conditions that hinder the abovementioned mechanism. The "Vacuum carborthermic reduction" aims at retrieving all aluminium content in the gaseous phases while the "Shaft-EAF" concept aims at optimizing an Electric Arc Furnace in such a way that any aluminium sub-oxide and aluminium vapours formed are treated within the furnace.

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