

Vacuum Carbothermic Reduction of Alumina

*Martin Halmann^a, Aldo Steinfeld^b, Michael Epstein^c, Enrico Guglielmini^d,
Irina Vishnevetsky^e*

a Weizmann Institute of Science, Rehovot, Israel, m.halmann@weizmann.ac.il. Corresponding author.

b ETH Zurich, Zurich, Switzerland, aldo.steinfeld@ethz.ch.

c Weizmann Institute of Science, Rehovot, Israel, michael.epstein@weizmann.ac.il.

d ETH Zurich, Zurich, Switzerland, genrico@ethz.ch.

e Weizmann Institute of Science, Rehovot, Israel, irina.vishnevetsky@weizmann.ac.il.

Abstract:

The current industrial production of aluminum from alumina is based on the electrochemical Hall-Héroult process, which has the drawbacks of high greenhouse gas emissions, reaching up to 0.70 kg CO₂-equiv/kg Al, and large energy consumption, about 0.055 GJ/kg Al. Considerable efforts have been applied to produce aluminum by the alternative process of the carbothermic reduction of alumina. Thermodynamic equilibrium calculations and experiments by induction furnace heating indicated that this reaction can be achieved under atmospheric pressure only above 2200°C. Thermodynamics predict the advantage of much lower required reaction temperatures by alumina reduction under vacuum. This was experimentally demonstrated under simulated concentrated solar illumination, and by induction furnace heating. At a temperature of about 1550°C and a CO partial pressure less than 0.1 mbar, the reactants were almost completely consumed, with only minor remaining solids in the reactor crucible. Deposits condensed on the cold reactor walls contained up to 59-71 wt % of Al, in addition to Al₄C₃, Al-oxycarbides and Al₂O₃.

Keywords:

Alumina, Aluminum, Carbon, Carbon Monoxide, Carbothermic Reduction, Vacuum

1. Introduction

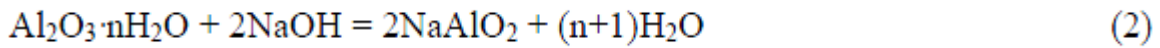
Aluminum is the most abundant metallic element in the Earth's crust, amounting to 8.3% by weight of the crust. Aluminum metal has been first isolated in 1825 by the Danish chemist Hans Christian Ørsted. This metal, and particularly its alloys, has become of considerable importance due to its unique properties of light weight, high thermal and electric conductivity, and corrosion resistance [1]. Because of the high calorific value of aluminum, 31 MJ/kg Al, a future important role could be that of an energy carrier and energy storage material. Thus, the well-known alkaline decomposition of aluminum or aluminum alloys such as Al-Si to release hydrogen:



could be applied for hydrogen fuel cells in the transportation sector [2, 3].

The production of primary (new) aluminum is the largest in volume in the non-ferrous metal industry. In 2010 the world primary aluminum production reached 24 million metric tons, accounting for 1% of the world anthropogenic greenhouse gas emissions, while the production of iron and steel contributed 5.4%. Current aluminum production is based on two main stages, developed in the late 19th century:

a) The Bayer process for producing Al₂O₃ from a mixture of minerals composing the deposits of bauxite. A simplified overall equation describing this process is:



in which in the above forward reaction, carried out in digesters, the alumina is solubilized to sodium aluminate at temperatures of 140-240°C, while most of the oxides of iron, silicon and titanium remain insoluble, and are separated as “red mud”. The solution of sodium aluminate is then cooled to 45-70°C, resulting in the reverse reaction of Eq.1, with precipitation of hydrated alumina, which then is calcined at 1150-1300°C to Al₂O₃ [3] The Bayer process often requires a stage of mineral beneficiation, which involves the removal of fines and the separation of iron oxides by hydrochloric acid leaching, and also co-produces a strongly alkaline waste (red mud) which is a serious environmental hazard (major accident in Hungary, 4 October 2010), and also requires large areas. The Bayer process uses about 25% of the total energy consumption of aluminum production.

b) The Hall-Héroult electrolytic smelting process for converting Al₂O₃ to Al. The high-temperature electrochemical Hall-Héroult process in molten cryolite using sacrificial carbon anodes (releasing CO₂, prepared from calcined coke with pitch as binder) has the drawbacks of considerable environmental pollution due to perfluorocarbon (PFC) release, high greenhouse gas emissions, reaching 0.70 kg CO₂-equiv/kg Al even in modern smelters, and large electrical energy consumption, about 15.4 MWh (or 55.4 GJ) per metric ton Al. If the CO₂ emission from coal-fired electric power generation is included, the Hall-Héroult process may cause the emission of up to 8 kg CO₂-equiv/kg Al, while the Bayer process uses up to 0.035 GJ/ton Al [1, 4]. In the present study, thermochemical equilibrium calculations were made using the FACTSAGE and HSC computer codes [5, 6]. Reaction enthalpies were derived using the data of NIST [7].

2. Reactions at atmospheric pressure

Considerable efforts had been applied to produce aluminum from alumina by the alternative process of the carbothermic reduction of alumina, according to the overall reactions [8-14],



Thermodynamic equilibrium calculations and experiments by induction furnace heating indicated that these reactions can be achieved under atmospheric pressure only above 2200°C [14]. The reduction of alumina to Al under Ar and CH₄ at atmospheric pressure had been studied by radio-frequency generated induction-coupled plasma, at above 10,000°C. The reduction products collected on a water-cooled surface contained Al and Al₄C₃ [15]. The drawback of the very high reaction temperature is partly compensated by producing syngas as a valuable by-product, and by not requiring vacuum pumping [16]. Experiments using mixtures of Al₂O₃ and charcoal under Ar at atmospheric pressure in a quartz-tube reactor heated by 30 sec pulses from an 18 kW induction furnace resulted in the condensation on the cold region of the reactor tube of elementary Al, as well as variable amounts of Al₂O₃, Al₄C₃, and the oxy-carbides Al₂OC and Al₄O₄C. In the best result in one of the experiments the Al content in the deposit was 29% [14, 17].

3. Reactions under vacuum

According to the Le Chatelier principle, the extent of a chemical reaction should be favored by a decrease in the total gas pressure. Thus, under vacuum conditions, the equilibrium of Eq. (3) should be shifted to the right and the onset temperature for the metal production should be significantly lowered. Thermodynamic equilibrium calculations indeed predict the advantage of much lower required reaction temperatures by alumina reduction under vacuum, as shown in Fig. 1 [17, 18].

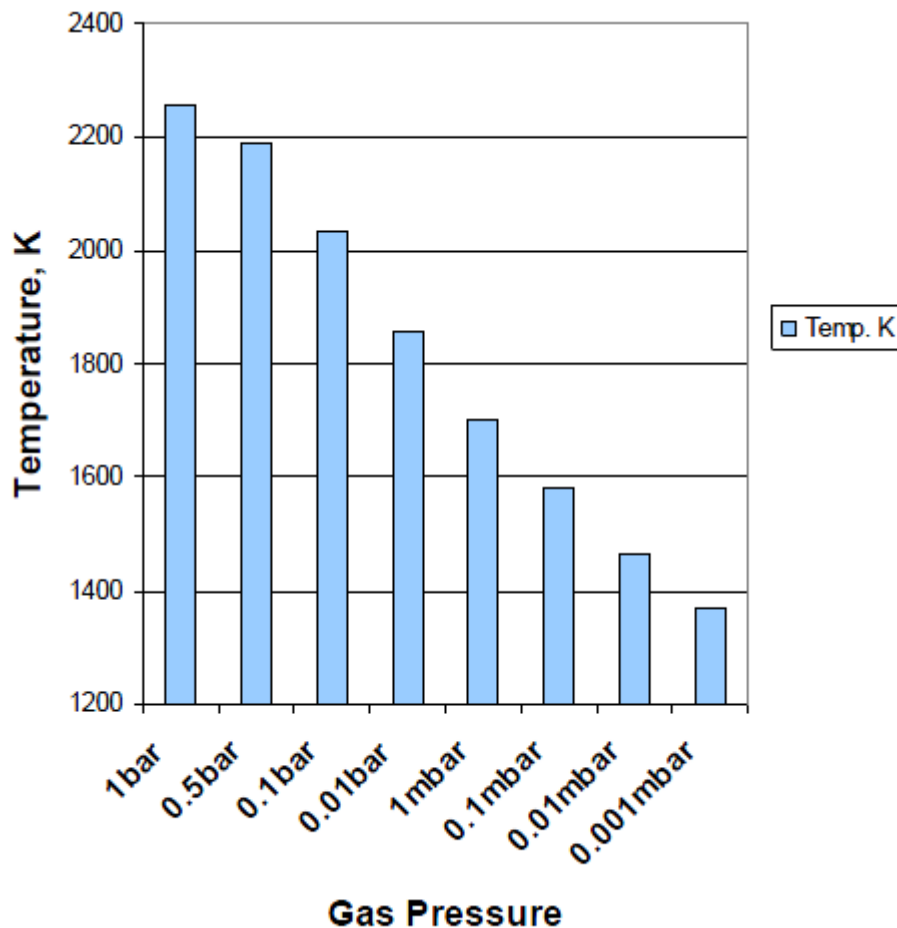


Fig.1. Calculated onset temperature for Al(g) production as function of pressure in the system $Al_2O_3 + 3C$.

This had been experimentally demonstrated under simulated concentrated solar illumination [18] and by induction furnace heating [19, 20]. The direct vacuum carbothermic reduction has also been applied to the alumina contained in bauxite [21-23]. In a study of the vacuum carbothermal processing of low-iron bauxite, a mixture of calcined bauxite and charcoal heated up to 1600°C at an initial pressure of 0.01 mbar in a corundum reactor tube resulted in the condensation of β -SiC, Al_4O_4C , Al, Al_4C_3 , and α -alumina on the cold wall of the reactor, and in a residue of α -alumina, TiC, and FeO in the hot zone of the reactor [21]. In a related study, the production of Al-Si alloys had been studied by the vacuum carbothermal reduction of bauxite tailings containing mainly Al_2O_3 , SiO_2 , and Fe_2O_3 in a graphite furnace at pressures down to 10^{-9} bar and temperatures up to 2000°C, resulting in the formation of an Al-Si-Fe alloy, as well as carbides and elementary Al and Si. The proposed mechanism involves the intermediate formation and decomposition of carbides, in which the presence of Fe seemed to have a catalytic effect [22].

4. Induction furnace experiments

In experiments with induction furnace heating, using a 25 kW desktop Induction Heater, at a temperature of about 1550°C, an argon carrier gas flow rate of 100 ml/min, a pumping speed of 250 m^3/h , and a CO partial pressure less than 0.1 mbar, the reactants were almost completely consumed, with only minor amounts of solids remaining in the reactor crucibles. Details of the experimental setup and of the reaction procedure have been reported [19]. Aluminum vapors left the crucible and condensed on colder places of the reactor. The content of elementary aluminum at the deposition site depends on the rate of the reverse reaction. The reverse reaction is promoted by the temperature and its rate is higher in hotter places. A number of test results are detailed in Table 1. It can be seen that at temperatures of 1520°C and 1720°C and maximal CO partial pressures of about 0.1 mbar

and 1 mbar respectively the forward reactions are almost fully completed with negligible residual amount (about 1% of the initial mass of the reactant mixture) left in the crucible, which consists of crystalline or amorphous carbon and a few percent of aluminum carbide. At lower temperature the residue in the crucible is larger and amounts about 12% of the original loaded material (see Test No 1, Table1).

The best results were observed at deposit places with a temperature of about 1000-1150°C, starting with pellets made of a stoichiometric mixture of reactants, made of nano-particles of alumina and beech charcoal. The content of elementary Al in the deposit (59wt%) was measured by XRD quantitative analysis. When the alumina nano-powder in the pellets was replaced by 10µm alumina powder with 10 wt % addition of sugar as a binder, 71 wt % of elementary Al was obtained, together with aluminum carbide, oxy-carbide and oxide (see Fig.2).

Table 1. Amounts and composition of crucible residues after induction furnace heating.

Test No	Reaction temperature [°C]	Maximal CO partial pressure [mbar]	Initial Mass of reactant mixture [g]	Residue in crucible [g]	Content of residue
1	1380	0.05	2.76	0.33	33% Al ₂ O ₃ 41% Al ₄ C ₃ 19% Al ₄ O ₄ C 24% Graphite
2	1520	0.09	2.15	0.02	1% Al ₄ C ₃ 50% Graphite 49% amorphous carbon
3	1720	1.2	3.62	0.04	7.6% Al ₄ C ₃ 92.4% Graphite

5. Discussion

A major issue involved in aluminum carboreduction in vacuum is the actual electrical energy consumed by the vacuum pumps which is substantially higher than the theoretical work of isothermal compression. The minimum theoretical work in isothermal expansion of the product gases, assumed to be brought from atmospheric pressure P_0 to vacuum pressure P is

$$W = nRT_{\text{reaction}} \ln P_0/P [\text{kJ/mol Al}_2\text{O}_3] \quad (5)$$

where n is the increase in the number of gas moles formed per mole of aluminum oxide including the amount of argon carrier gas moles, if any, $R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$ is the gas constant, and T_{reaction} is the absolute temperature of the reaction. The total net enthalpy input can be estimated from

$$\Delta H = H_{2\text{Al}}(T_{\text{reaction}}) + H_{3\text{CO}}(T_{\text{reaction}}) + H_{\text{kAr}}(T_{\text{reaction}}) - H_{\text{Al}_2\text{O}_3}(20^\circ\text{C}) - H_{3\text{C}}(20^\circ\text{C}) - H_{\text{kAr}}(20^\circ\text{C}) \quad (6)$$

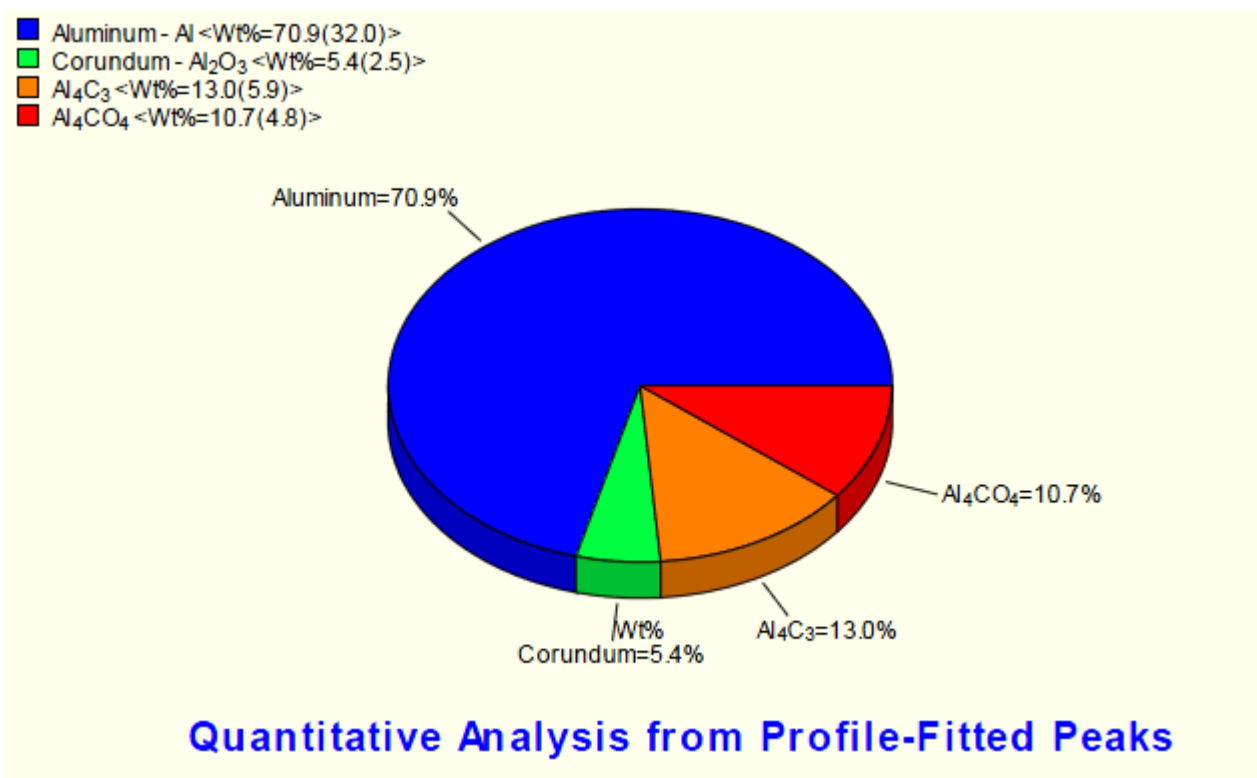


Fig.2 Results of quantitative analysis of a sample from a deposit site at a temperature of about 1000°C.

The hypothetical heat input for the reaction of Eq. (1) to $2\text{Al}(\text{g}) + 3\text{CO}(\text{g})$ at $T = 1800 \text{ K}$ without carrier gas was calculated to be $2,242 \text{ kJ/mol Al}_2\text{O}_3$. The minimum work of expansion from normal pressure to $P = 10^{-4} \text{ bar}$ is $689 \text{ kJ/mol Al}_2\text{O}_3$. The total theoretical energy input would be 0.054 GJ/kg Al , comparable to that in modern smelters by the Hall-Héroult process of about 0.052 GJ/kg Al [1]. At higher reaction temperature 2000K and 1mbar pressure the total theoretical energy is 0.0522 GJ/kg Al which is similar to the energy consumption in the industrial process. However, the real pumping energy consumption can significantly exceed the theoretical work of exothermal expansion and at a CO partial pressure of less than $0.2\text{-}0.3 \text{ mbar}$ (depending on amount of carrier gas used) the actual pumping energy would exceed the energy consumed in the industrial Hall-Héroult process which in itself is at least in two times higher than the theoretical figure which is 0.023 GJ/kg Al [24]. The pumping energy was estimated according to [25] for a dry vacuum system based on a Roots blower and a multi-stage Roots backing pump. As can be seen in Fig. 3, in order for the pumping energy to be lower than the energy consumption in the current industrial process, the operating pressure must be higher than about 0.2 mbar of the CO partial pressure. In order that the total energy input into the process (pumping plus the process heat and the sensible heat to bring the reactants to the reaction temperature) to be similar to the industrial process, the CO partial pressure should be about 1 mbar . This entails an increase of about 200°C in the reaction temperature. That was proved experimentally when the forward reaction was successfully completed during 20 min as the CO partial pressure was increased from $0,08 \text{ mbar}$ up to 1.4 mbar and the reaction temperature was increased from 1550°C to about 1750°C respectively.

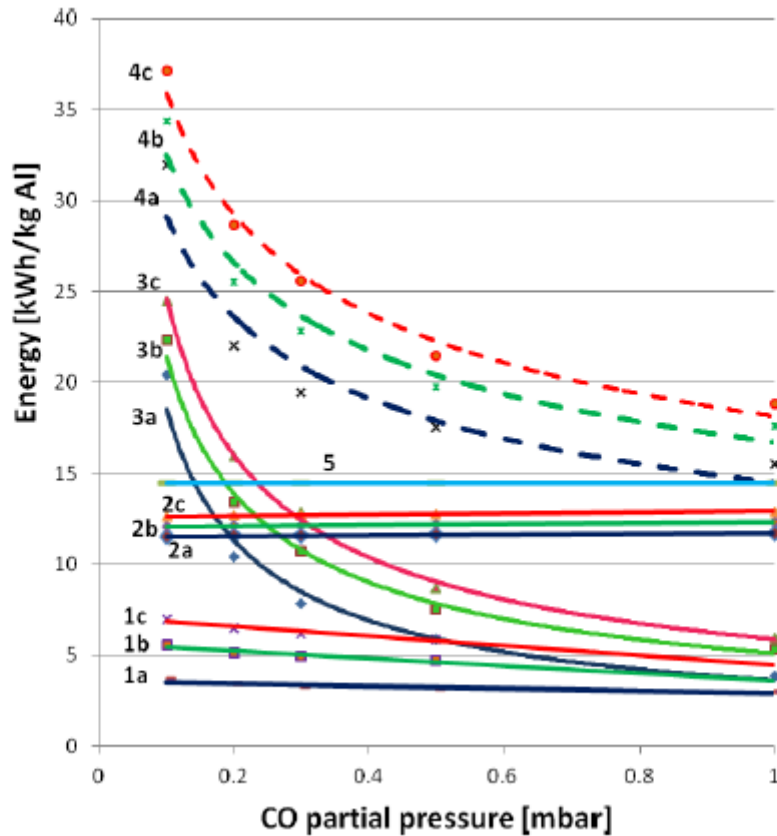


Fig.3 Real energy consumption for production of 1 kg Al per hour as function of the CO partial pressure. 1-theoretical work for exothermal expansion; 2-net total process energy (chemistry plus sensible heat), 3– pumping energy; 4 –total energy; 5 – energy consumption in Hall-Héroult industrial electrolytic process (a- 55.5 mol CO +0mol Ar per hour, b-55.5 mol CO +55.5mol Ar, c– 55.5 mol CO +100mol Ar).

The main difficulty in the carbothermic reduction of alumina is of preventing the re-oxidation or carbonization of the gaseous aluminum that condenses on the walls of the reactor where the temperature is still sufficiently high to promote the reverse reaction. XRD analyses of samples taken from different sites in the reactor confirm that the amount of elementary aluminum in the deposit strongly depends on the temperature at the specific site. The problem could be that at continuous irradiation of the reaction crucible to a high temperature (1800°C), the forward reaction (3) is too fast relative to the rate of pumping out of the CO and of the Ar carrier gas. As a result aluminum vapor condenses on hotter areas and the residence time of the CO molecules is sufficient to allow them to react back. It is therefore important to design the pumping speed appropriately and in addition to the speed at the inlet of the pump, the resistance to flow in the connecting pipes, traps, etc, should be considered in order to obtain fast removal of the gases from the reactor. One possible approach would be to slow down the *average* forward reaction rate, while irradiating to a high reaction temperature. This could be achieved by pulsing the irradiation. With a smaller rate of Al(g) and CO production, the yield of Al(s) collection and CO removal could be improved. Also, the average electrical energy consumption would be decreased. This technique of pulse irradiation had been successfully applied in previous studies of alumina reduction at atmospheric pressure in pulsed-arc reactors or induction furnaces [12, 14, and 16]. A moving-bed electric arc furnace for carbothermic reduction of Al₂O₃ with petroleum coke was patented, producing Al containing only 9-12% Al₄C₃ [26, 27]. Concentrated solar energy could be used to provide the energy required to preheat the reactor and the reactants to the operating temperature and to supply the endothermic energy required for the chemical reaction [12, 18].

Acknowledgement

The research leading to these results has received partial funding from the European Union Seventh Framework Programme ([FP7/2007-2013]) under grant agreement ENER/FP7EN/249710/ENEXAL.

References

- [1] Balomenos, E., Panias, D., Paspaliaris, J., Energy and exergy analysis of the primary aluminium production processes – A review on current and future sustainability. *Mineral Processing and Extractive Metallurgy Review*, 2011; 32 (2): 69-89.
- [2] Soler, I., Candela, A.M., Macanas, J., Munoz, M., Casado, J., In situ generation of hydrogen from water by aluminium corrosion in solutions of sodium aluminate. *J. Power Sources*, 2009; 192: 21-26.
- [3] Shkolnikov, E.I., Zhuk, A. Z., Vlaskin, M. S., Aluminum as energy carrier: Feasibility analysis and current technologies overview. *Renewable and Sustainable Energy Reviews*, 2011; 15: 4611-4623.
- [4] International Aluminum Institute, Aluminum for Future Generations/2009 Update. Available at: <http://www.world-aluminium.org>.
- [5] FactSage Thermochemical Software & Database Package, Centre for Research in Computational Thermochemistry, Ecole Polytechnique de Montreal, Canada, <http://www.crct.polymtl.ca>.
- [6] HSC Chemistry Computer Code V.6.0, Roine, A., Outokumpu Technology, Pori, Finland.
- [7] NIST National Institute of Standards and Technology, Standard Reference Data Program, Chemistry Webbook, available at <http://webbook.nist.gov/chemistry>.
- [8] Choate W., Green J., Technoeconomic assessment of the carbothermic reduction process for aluminum production, *Light Metals*, 2006; 445-450. See also: Choate, W.T. and Green, J.A.S., 2003. U.S. Energy Requirements for Aluminum Production, Historical Perspective, Theoretical Limits and New Opportunities, available at http://www1.eere.energy.gov/industry/aluminum/pdfs/al_theoretical.pdf.
- [9] Steinfeld, A., High-temperature solar thermochemistry for CO₂ mitigation in the extractive metallurgical industry. *Energy*, 1997; 22: 311-316.
- [10] Cox, J.H., L.M., The aluminum-oxygen-carbon system. *Can. J. Chem.*, 1963; 41: 671-683.
- [11] Murray J.P., Steinfeld, A., Fletcher, E.A., Metals, nitrides, and carbides via solar carbothermal reduction of metal oxides. *Energy*, 1995; 20: 695-704.
- [12] Murray J.P., Aluminum production using high-temperature solar process heat. *Solar Energy*, 1999; 66: 133-142.
- [13] Fruehan T. J., Li Y., Cargin G., Mechanism and rate of reaction of Al₂O, Al, and CO vapors with carbon, *Metallurgical and Materials Transactions B*, 2004; 35B (4): 617-623.
- [14] Halmann M., Frei A., Steinfeld A., Carbothermal reduction of alumina: Thermochemical equilibrium calculations and experimental investigation. *Energy*, 2007; 32: 2420-2427.
- [15] Rains R. K., Kadlec R. H., The reduction of Al₂O₃ to aluminum in a plasma, *Metall. Transact.*, 1970; 1: 1501-1506.
- [16] Halmann M., Epstein M., Steinfeld A., Carbothermic reduction of alumina by natural gas to aluminum and syngas: A thermodynamic study. *Minerals Processing & Extractive Metallurgy Review*. Available online: 12 Jul 2011.
- [17] Halmann M., Frei A., Steinfeld A., Vacuum carbothermic reduction of Al₂O₃, BeO, MgO-CaO, TiO₂, ZrO₂, HfO₂+ZrO₂, SiO₂, SiO₂+Fe₂O₃, and GeO₂ to the metals. A thermodynamic study, *Mineral Processing and Extractive Metallurgy Review*, 2011; 32: 247 – 266.

- [18] Kruesi M., Galvez M.E., Halmann M., Steinfeld A., Solar aluminum production by vacuum carbothermal reduction of alumina – Thermodynamic and experimental analyses, *Metallurgical and Materials Transactions B, Process Metallurgy and Materials Processing Science*, 2011; 42(1): 254-260.
- [19] Vishnevetsky I., Epstein M., Metal oxides reduction in vacuum: Setup development and first experimental results, *Proc. SolarPaces, Granada, Spain, Sept. 20-23, 2011*.
- [20] Feng Yue-bin, Yang Bin; Dai Yong-nian. Carbothermal reduction of alumina in a vacuum, *Advanced Materials Res.*, 2011; 156-157: 1688-1691 *Trans. Tech. Publications, Switzerland*.
- [21] Goldin, B.A.; Grass, V. E., Ryabkov, Yu.I., Vacuum carbo-processing of low-iron bauxites, *Glass and Ceramics*, 1998; 55 (9-10): 323-325. Translation of *Steklo I Keramika*, 1998; No. 10: 25-27.
- [22] Yang, Dong; Feng, N-X; Wang, Y-W; Wu, X-I. Preparation of primary Al-Si alloy from bauxite tailings by carbothermal reduction process, *Trans. Nonferrous Metals Soc. China*, 2010; 20: 147-152 (in English).
- [23] Halmann, M., Epstein, M., Steinfeld, A. Bauxite components vacuum carbothermic reduction: A thermodynamic study. *Minerals Processing & Extractive Metallurgy Review*. Available online 29 June 2011.
- [24] Beck, T. R., Electrolytic production of aluminum. *Electrochemistry Encyclopedia*, 2008; <http://electrochem.cwru.edu/encycl/art-a01-al-prod.htm>.
- [25] *The Vacuum Technology Book*, 2011. Pfeiffer Vacuum (a catalogue), Volume 1, www.pfeiffer-vacuum.net
- [26] Kirby, R. M., Carbothermic reduction furnace, 1982. US Patent 4,334,917.
- [27] Kirby, R. M., Saavedra, A. F., Viability of carbothermic alumina reduction. *J. Metals*, 1988; 40 (11): 32-36.