

Experimental Verification of the Thermodynamics of Critical Aspects of the Carbothermic Reduction of Alumina. Part II: Thermogravimetric Study of the Reaction of Al₂O₃-C Mixtures and the Al₂O₃-Al₄C₃ Phase Diagram

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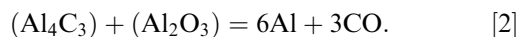
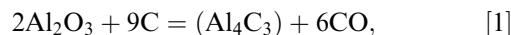
The thermodynamics of several aspects of the carbothermic reduction of alumina have been examined. In Part I, the results of measuring the evolved CO from the reaction between Al₂O₃ and C mixtures were used to determine the temperature and carbon contents for carbide formation at alumina saturation and at carbide saturation in the Al₂O₃-Al₄C₃ system. In this part of the paper, results are presented for a thermogravimetric study of the reactions of Al₂O₃ with carbon, as well as those for the determination of the Al₂O₃ liquidus line and the Al₂O₃-Al₄O₄C eutectic in the Al₂O₃-Al₄C₃ phase diagram. The critical temperature for Al₂O₃ and C to react, producing gas at 1 atm., was in agreement with that predicted from thermodynamics and measured in Part I of this paper. However, the Al₂O₃ liquidus appeared to be steeper and the eutectic temperature lower than the predicted phase diagram.

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I. INTRODUCTION

IN Part I of this paper, certain aspects of the thermodynamics of the carbothermic reduction of alumina were discussed and investigated experimentally. In brief, the two main reactions in the process are carbide or slag-making (1) and metal-making (2).



The Al₂O₃ and Al₄C₃ may be in solution or as pure components and the Al is a solution containing carbon. In addition, reactions producing Al and Al₂O vapors are critical. In order to verify our current knowledge, the conditions for Reaction [1] to occur were measured. Reaction [1] occurs when the total pressure of CO, Al₂O, and Al exceeds 1 atm. If the thermodynamics of Reaction [1] are verified, it is not unreasonable to assume the conditions for Reaction [2] to occur, can also be reasonably well calculated. This is because the thermodynamic quantities required are similar, except that for Reaction [2] the activities in the Al-C system must be known. Reasonably good models exist for the Al-C system.

The experimental results presented in Part I were in generally good agreement with the predicted results using our current knowledge of the thermodynamics. It should be noted that our current knowledge is based on solution models for the Al₂O₃-Al₄C₃ system and the free energies of several reactions. Previously, there were no experimentally determined conditions for Reaction [1] to occur.

The experimental results agreed with the temperature for Reaction [1], as well as for the temperatures and compositions in the liquid region and at carbide saturation. However, the carbon content for initial carbide formation at Al₂O₃ saturation did not agree with the accepted phase diagram. In this part of the paper, results are presented for the reaction of Al₂O₃ and carbon in a high-temperature resistance-heated vacuum furnace, as well as those for certain aspects of the phase diagram which were examined in the induction furnace described in Part I.

II. LITERATURE REVIEW

As mentioned previously,^[1] the conditions for Reaction [1] to occur were based on solution models and calculated values for the thermodynamics of some reactions. For the Al₂O₃-Al₄C₃ phase diagram, there has been extensive discussion and analysis, but there are limited experimentally determined temperatures, phases, and compositions. A detailed discussion of the phase diagram is given elsewhere,^[2] and only the aspects relevant to the present work are discussed in detail here.

Foster *et al.*^[3] proposed an early version of the phase diagram. They used thermal analysis and past experimental examinations. They identified two oxycarbide

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phases: $\text{Al}_4\text{O}_4\text{C}$ and Al_2OC . There have been differing opinions regarding the stability of Al_2OC . Motzfeld *et al.*^[4] believe it is not stable in the simple system and that nitrogen as an impurity stabilizes the phase. In any case, this phase is not critical in the carbothermic process.

The other main controversy involves the location of the eutectic and peritectics. For example, Foster *et al.*^[3] estimated the Al_2O_3 – $\text{Al}_4\text{O}_4\text{C}$ eutectic to be at 2113 K (1840 °C). Qui and Metselaar^[5] estimated it to be 2123 K (1850 °C) based on their solution model and the measurements by Lihmann.^[6] Other researchers^[7–10] estimated the eutectic to be about 2173 K to 2178 K (1900 °C to 1905 °C). Pelton and coworkers^[11–13] did an extensive analysis of the system and computed the phase diagram including the eutectic and peritectics. A summary of the measured and/or calculated eutectics and peritectics is presented in Table I. Two versions of the phase diagram are shown in Figures 1 and 2. In the calculated portion of the phase diagrams, several thermodynamic data are necessary. These are listed in the original publications and by Walker.^[2] There have been limited experimental results on the critical points other than the eutectic and peritectics. Ginsberg and Sparwald^[7] made Al_2O_3 and Al_4C_3 liquidus line measurements, while Lihmann^[6] made a single measurement for the Al_4C_3 liquidus line. The calculated phase diagrams by Pelton and coworkers^[11,12] are similar to that given in Figure 2 by Motzfeld and coworkers. The diagram calculated by Qui and Metselaar is similar to that proposed by Foster. The main difference is that both Qui and Metselaar and Foster have a lower eutectic temperature.

The objective of the phase diagram investigation in this work was limited to the location of the Al_2O_3 – $\text{Al}_4\text{O}_4\text{C}$ eutectic, the Al_2O_3 liquidus, and the intersection of the slag-making operating line with the Al_2O_3 liquidus. The second aspect of the study examined the temperature at which Reaction [1] occurs spontaneously when the total pressure of CO, Al_2O , and Al gases equals 1 atm. In Part I, this same reaction was studied by measuring the amount of CO evolved. In this part of the paper, the reaction was studied using a vacuum thermobalance (TGA), which measured the weight change when reacting Al_2O_3 and carbon mixtures. The current understanding of the thermodynamics of Reaction [1] was discussed in Part I of this paper.

III. EXPERIMENTAL

A. Experimental System and Procedure for the TGA

The apparatus used for these experiments was located at the Elkm Research Center, Kristiansand, Norway. Ketil Motzfeldt, at the Norwegian University of Science and Technology in Trondheim, Norway, specifically designed this for these types of experiments. It essentially consists of a graphite-tube furnace and, above it, an electronic balance, enclosed in separate but connected water-cooled compartments. The enclosure is vacuum tight and permits operation in neutral or reducing atmospheres at pressures from about 10^{-8} to slightly above 1 atm., and temperatures to about 2473 K (2200 °C). A detailed schematic is shown in Figure 3.

Inside of the water-cooled furnace was a graphite tube between the graphite heating elements. Furnace heating was controlled by regulating the voltage output to these graphite resistance-heating elements. A small graphite crucible, containing the sample, was suspended from the balance. Temperature measurement was conducted using a pyrometer which was situated off to the side of the furnace and sighted off of a mirror, down through a quartz window, down through the holes in the heat shield, and finally through a hole in the crucible lid and directly onto the sample material surface. The instrument used for this was a multi-wavelength pyrometer (SpectroPyrometer) from FAR Associates. The instrument is believed to be more accurate than those used in previous studies of these systems. Some of the Al_2O and Al vapors evolved from the sample during heating would condense on the quartz window, resulting in a dropping of the observed temperature reading with time. To overcome this problem and accurately measure temperature during the entire test, the furnace was configured with multiple quartz windows. When one became dirty, the top of the furnace was rotated to a clean window. Once the furnace was evacuated (bringing the pressure down to 10^{-4} atm), several options were available for the tests. The chamber could be filled to atmospheric pressure, or to some pressure less than this, with an inert gas, such as argon, or CO.

The experiments were performed using high-purity materials in order to remove any affect that impurities may have on the thermodynamics of the Al_2O_3 – Al_4C_3 system. The alumina powder used for these tests was

Table I. Calculated and Estimated Temperature and Composition of the Eutectic and Peritectics in the Al_2O_3 – Al_4C_3 System

	Eutectic Al_2O_3 – $\text{Al}_4\text{O}_4\text{C}$		Peritectic $\text{Al}_4\text{O}_4\text{C}$ – Al_2OC T [K (°C)]	Peritectic Al_2OC – Al_4C_3 T [K (°C)]
	T [K (°C)]	$X_{\text{Al}_4\text{C}_3}$		
Foster <i>et al.</i> ^[3]	2113 (1840)	0.118	2163 (1890)	2273 (2000)
Qui and Metselaar ^[5]	2123 (1850)	0.122	2143 (1870)	2263 (1990)
Ginsberg <i>et al.</i> ^[7]	2173 (1900)	0.11	2223 (1950)	2273 (2000)
Motzfeldt and coworkers ^[8–10]	2178 (1905)	0.12	not included	not included
Chartrand <i>et al.</i> ^[11]	2181 (1908)	0.101	2206 (1933)	2272 (1999)
Degterov and Pelton ^[12]	2181 (1908)	0.108	2212 (1939)	2253 (1980)

Motzfeld *et al.* consider $\text{Al}_4\text{O}_4\text{C}$ – Al_4C_3 peritectic at 2218 K (1945 °C) and $X_{\text{Al}_4\text{C}_3} = 0.165$.

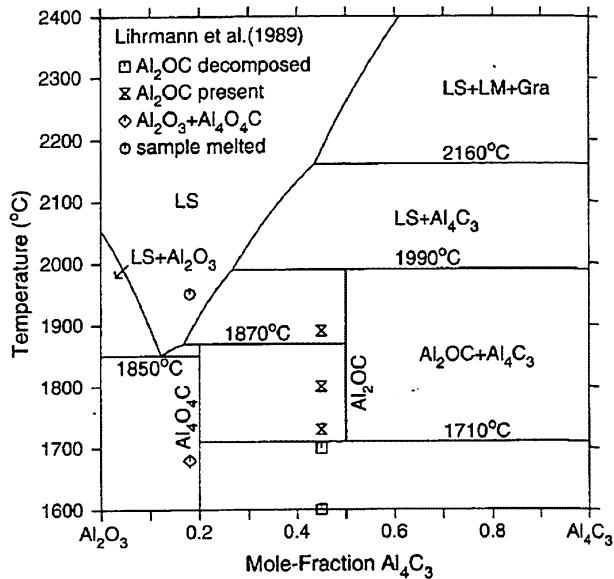


Fig. 1—Calculated phase diagram of Qui and Metselaar^[5] including experimental data of Lihrmann.^[6]

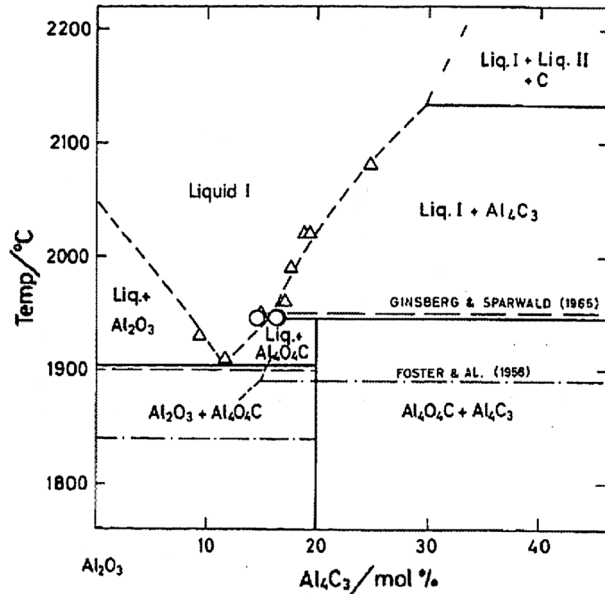


Fig. 2—Calculated phase diagram of Motzfeldt and Sandberg^[10] including experimental data of Ginsberg *et al.*^[7] (triangles) and Gjerstad^[8] (circles).

purchased from Alpha Aesar, with a mean particle size of 51 μm and a purity of 99.99 pct. The source of carbon for these experiments was graphite powder purchased from Goodfellow, with mean particle size of 60 μm and a purity of 99.997 pct. In addition, an experiment was performed using pet-coke as the carbon source in place of the high-purity graphite. This was done in order to investigate the effect that the carbon source has on the reactions.

The original experimental approach, referred to as “Slow-Heating,” utilized a starting sample of 2.5 g of Al_2O_3 and 1.5 g of Graphite. For the modified

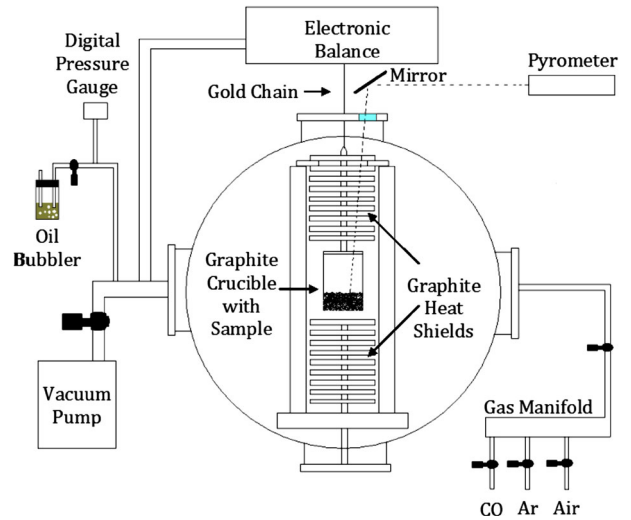


Fig. 3—Detailed schematic of the TGA apparatus used to measure the weight loss from Al_2O_3 -C reactions.

approach, referred to as “Fast-Heating,” the total sample mass was increased to 8 g, utilizing a starting sample of 5 g Al_2O_3 and 3 g graphite. After weighing the essential components, the crucible assembly was inserted into the furnace chamber and suspended from the balance using a gold chain. Then, the pyrometer was sighted onto the reactants surface using a laser-sighting device. The furnace and balance were assembled and sealed, the electronic balance was zeroed, and the cooling water flow to the furnace was turned on. The furnace was evacuated using the rotary vacuum pump.

After checking for leaks, argon was used to purge the furnace and the furnace was re-evacuated using the vacuum pump. Finally argon or CO gas was slowly flowed into the chamber until the pressure gauge gave a reading of slightly above 1 atm. At this point, the furnace exhaust to the oil bubbler was closed as well as the rotary pump valve and gas inlet valve. Some experiments were performed at reduced total pressure of CO. For these experiments, the CO gas was slowly flowed into the chamber until the pressure reading was around 0.5 atm. Next, the furnace power was turned on and furnace heating began. The furnace was heated fairly rapidly to 2073 K (1800 °C) with little or no weight loss. Heating beyond this temperature either remained rapid (fast-heating) or was slowed down (slow-heating) while continuously measuring the temperature. If the pressure significantly exceeded 1.0 atm., *e.g.*, 1.05 atm., due to the CO evolved, the pump was used to remove some of the CO bringing the pressure back to 1 atm.

B. Experimental Procedures and Equipment for the Phase Diagram Measurements

The overall objective here was to measure additional phase diagram data for the Al_2O_3 - Al_4C_3 system. This included evaluating the location for the Al_2O_3 - $\text{Al}_4\text{O}_4\text{C}$ eutectic, the Al_2O_3 liquidus line, as well as the intersection of the slag-making operating line with this liquidus

line. The methodology used is illustrated schematically in Figure 4. It involved heating a high-purity Al_2O_3 – Al_4C_3 powder mixture, having an initial composition to the left of the Al_2O_3 – $\text{Al}_4\text{O}_4\text{C}$ eutectic, and collecting liquid samples at increasing temperatures above the eutectic temperature. Theoretically, liquid slag should begin to form once the eutectic temperature is reached (shown as point “A”), the amount of liquid which forms being dependent on both the starting composition and the application of the lever rule in this two phase (Al_2O_3 –liquid slag) region. Upon reaching the eutectic temperature, all the Al_4C_3 in the starting charge should form a liquid slag along with a portion of the Al_2O_3 . As temperature is increased above the eutectic, increasing amounts of liquid slag will form, resulting from additional Al_2O_3 dissolving into the slag. The expectation was that with increasing temperature above the eutectic, the concentration of Al_4C_3 within the slag would decrease while the total quantity of slag in the crucible increases. If samples of this slag are taken at known temperatures, then the position of the liquidus line can be determined from the compositions of these slag samples (shown as “B” and “C”). Eventually, with continued temperature rise, a temperature will be reached corresponding to the slag-making operating line. Here, the Al_2O_3 in the reactor can begin to react with the graphite walls of the crucible to form additional Al_4C_3 , as well as evolving CO, Al, and Al_2O gases. This operating line represents the temperature where the total pressure of the product gases (CO, Al, Al_2O) is equivalent to 1 atm. pressure and so the driving force for the slag-making reaction taking place is large enough that this reaction proceeds to a significant extent. So, a secondary aim of this work was to identify the position of this operating line (shown as point “D”) by measuring the CO evolved from the reactants.

The experimental setups for these experiments were the same as those described in detail in Part I,^[1] where gas evolution experiments were conducted to investigate the Al_2O_3 –C reactions. Experiments were performed using Reactor B (minimized N_2).

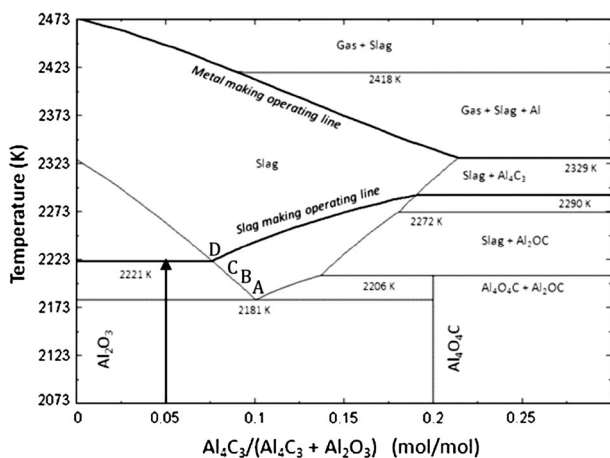


Fig. 4—Schematic illustrating the methodology used for making Al_2O_3 – Al_4C_3 phase diagram measurements.

Two different approaches were used for the reactants in these experiments. One, involved using Almatix T-162 alumina balls (1/4”) and Al_4C_3 powder (325 mesh or less than $44\ \mu\text{m}$) purchased from Sigma Aldrich as the starting charge. The purity of the Al_4C_3 powder was 99.99 pct. The experiments were performed using 360 g of the 1/4” alumina balls along with 40 g of the Al_4C_3 powder, giving a mixture with a starting Al_4C_3 mol fraction of 0.072. The use of alumina balls with the Al_4C_3 powder did not lead to contamination of the slag samples since the alumina balls were too large to be drawn up with the samples. The second approach involved using around 305 g of crushed solidified Al_2O_3 – Al_4C_3 slag from a prior experiment as the starting charge. The slag used for this had a final measured aluminum carbide mole fraction of 0.0908 (3.09 wt pct C) prior to cool-down.

The procedures for performing the experiments were similar as for the gas evolution experiments described in Part I. The reactants were rapidly heated to 2073 K (1800 °C) in an argon–krypton gas mixture (1 SLPM Ar + 8.5×10^{-3} SLPM Kr), while a sample of the off-gas was continually analyzed by a mass spectrometer. The krypton acted as a tracer gas, from which the amount of evolved CO was computed from the mass spectrometer data and the precise measurement of the krypton flow rate. Some experiments were performed by maintaining the argon flow beyond 2073 K (1800 °C), while others were performed by replacing the argon flow with CO (1 SLPM) at this temperature.

Upon reaching 2073 K (1800 °C), the furnace power was adjusted so as to achieve a very slow rate of temperature increase for the remainder of the experiment. Starting around 2123 K (1850 °C), the reactant mixture was probed with the tungsten rod to check for liquid slag formation. After probing the reactants, the furnace power was adjusted to maintain constant temperature for around 15 to 20 minutes, at which point the reactants were probed for a second time. This was done in this way in 283 K (10 °C) temperature increments, throughout the experiment.

When liquid slag was observed to form in the reactor, two samples of this liquid were taken. One sample was analyzed for its carbon concentration using a Leco Carbon Analyzer. The second sample was used to determine the nitrogen contents. Additional samples were taken in this way as temperature gradually increased. When the mass spectrometer indicated that significant CO evolution had started, indicating that the slag-making operating line had been reached, a final pair of slag samples was taken. At this point, the experiment was determined to be complete, and the furnace was shut-off. Argon gas was used in the reactor during cooldown, and the pyrometer was left on.

IV. EXPERIMENTAL RESULTS

A. Weight Loss Experiments

The “slow-heating” experiments involved very gradual heating of a starting sample with 2.5 g Al_2O_3 and

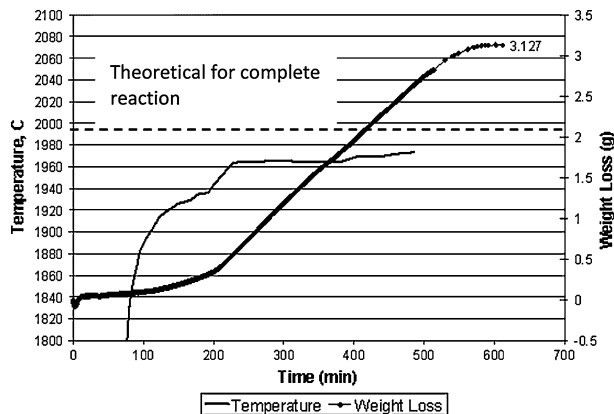
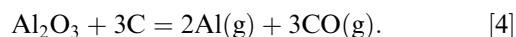
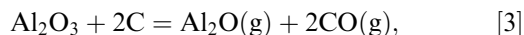


Fig. 5—Measured weight loss and temperature for the “slow-heating” experiment using high-purity Al_2O_3 and graphite in 1 atm. CO.

1.5 g graphite at 1 atm. CO pressure. Several of these experiments were performed, and all exhibited the same basic trends.

An example of the result is shown in Figure 5 as temperature and weight loss vs time. Here, the temperature is represented by the thin line and the measured sample weight loss by the thicker line. A significant increase in weight loss was observed to occur at 2187 K (1914 °C). The temperature gradually increased during the test, until the weight loss had stopped at a temperature of around 2245 K (1972 °C). The total measured weight loss for this experiment was 3.127 g. The dashed line represents the theoretical weight loss for complete reaction of the alumina in the reactants without taking the weight loss from the aluminum vapor species into account.

The measured weight loss was far more than expected based on theoretical calculations using the slag-making Reaction [1], which indicates that 2.059 g of weight loss is expected for complete Al_2O_3 consumption. This calculation did not consider the weight losses associated with Al_2O and Al vaporization. The reactions forming these vapors also consume alumina, and can be written as



Of these two reactions, Reaction [3] forming Al_2O is expected to be dominant. So this reaction alone can be considered for this discussion, but those for Al vapor formation apply as well.

After this experiment, there was a significant quantity of condensate on the inner walls of the chamber. These areas are much cooler than the reactant containing crucible. Also, this condensate has been observed to form in the past and was found to form from Al_2O and Al condensation or back reactions with CO.^[14] It was hypothesized that these Reactions [3] and [4] are controlled by the transfer of Al_2O and Al to cooler portions of the furnace. As the Al_2O and Al back-react,

their vapor pressures decrease causing Reactions [3] and [4] to proceed. Al_2O and Al are being removed from the system allowing more to form. On the other hand, the reaction to form carbide[1] is expected to be heat transfer controlled at temperatures greater than 2223 K (1950 °C).

The sample that remained after the test was analyzed by X-ray diffraction (XRD), and was found to be pure graphite. Unexpectedly, both the Al_2O_3 and any Al_4C_3 , which had formed, were both absent from the final sample. An additional reaction can be written which might explain this



This seems to indicate that during heating, eventually the temperature for slagmaking is reached, producing Al_2O_3 - Al_4C_3 slag according to Reaction [1]. Reactions [3–4], forming Al_2O , Al, and CO vapors also take place at this point. The slag that forms reacts according to Reaction [5], forming additional Al_2O vapor along with solid carbon. The rate at which slag is formed, being dependent on heat transfer, is slow due to the slow-heating rate. So, the Al_4C_3 which is formed by the slag-making Reaction [1] is consumed in Reaction [5] to produce additional Al_2O . The condensation of Al_2O and Al lowers their pressures pushing Reactions [3–5] to the right until all the Al_2O_3 has reacted. In essence, the overall reaction for the process becomes the combination of Reactions [1] and [5], which is equivalent to Reaction [3].

If the overall reaction for the process under these “slow-heating” conditions is assumed to be Reaction [3], then for a starting sample of 2.5 g Al_2O_3 and 1.5 g carbon, the expected total weight loss would be approximately 3.09 g. This is reasonably close to the experimentally measured weight loss of 3.127 g. This indicates that for “slow-heating” conditions, the overall reaction for the process will indeed be Reaction [3].

In order to overcome the problems associated with the “slow-heating” experiments (*i.e.*, the formation of excessive Al and Al_2O vapors), the procedure was modified. The change was to increase both the sample size and the heating rate. For these tests, the sample size was doubled, and the heating time to reach 2245 K (1972 °C) was reduced from 10 hours down to 1 hour. By increasing the heating rate, the slag-making reaction will occur at a relatively fast rate, and so the slag will form before Al_2O vaporization becomes significant. By doubling the starting reactant quantities, this insured that there would be a considerable quantity of slag, which forms during the experiment. So, while Reactions [3–5] may take place for these experiments, there is sufficient slag formed so that it will not be completely consumed in forming Al_2O and Al vapors.

This “fast-heating” approach involved identifying the slag-making temperature, as the temperature where the weight loss increases dramatically. The temperature for carbide saturation is much more difficult to identify. The only way available to find this is by an inflection in the heating rate. When carbide saturation is reached, the

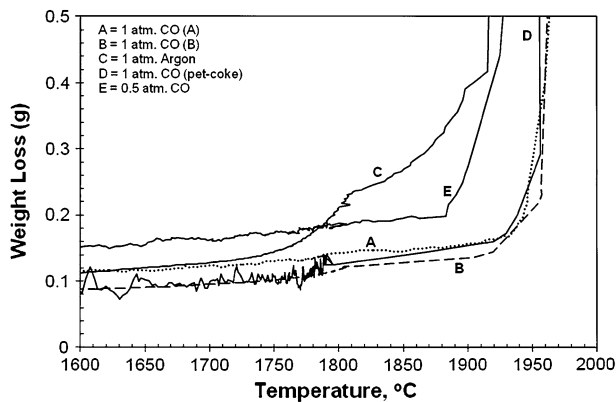


Fig. 6—Measured weight loss as a function of temperature for the “fast-heating” experiments.

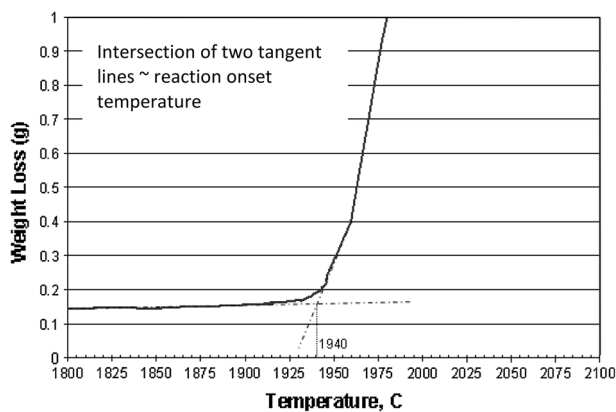


Fig. 7—Illustration showing the method used for estimating the temperature where the slag/carbide-making reaction starts. Data shown here are for high-purity reactants at 1 atm. CO.

Table II. Experimental and Calculated Temperatures for Carbide Formation from Al_2O_3 and C

Test Details	Experimental Onset Temperature [K (°C)]	FactSage Predicted Temperature [K (°C)]
1 atm. CO (A)	2213 (1940)	2221 (1948)
1 atm. CO (B)	2229 (1956)	2221 (1948)
1 atm. CO (Pet-coke)	2206 (1933)	n/a
1 atm. argon	2189 (1916)	n/a
0.5 atm. CO	2187 (1914)	2176 (1903)

Table III. Experimental and Calculated Weight Loss Values for Complete Reaction of Al_2O_3 and C

Experiment	Measured Weight Loss (g)	Calculated Weight Loss (excluding $\text{Al}_2\text{O} + \text{Al}$) (g)	FactSage Predicted Weight Loss (including $\text{Al}_2\text{O} + \text{Al}$) (g)
1 atm. CO	4.414	4.118	4.821

temperature of the sample should remain constant until all the Al_2O_3 is consumed in making pure solid Al_4C_3 .

The measured weight loss as a function of temperature for five experiments is shown in Figure 6. This plot is just a section of the total weight loss data, and so these samples all lost more weight than is shown. This is shown as a magnified view in order to better identify those temperatures where the slag-making reaction starts. The main variables for these tests were the gas pressure, gas composition, and carbon source. Two experiments (A and B) were performed with the high-purity Al_2O_3 and graphite at 1 atm. pressure of CO. The difference between these two tests is the furnace power setting that was used. A lower power setting was used for sample (A) than for sample (B). Other experiments include using the same high-purity materials at 1 atm. pressure in argon (C) and at 0.5 atm. pressure of CO (E). A final test was performed using high-purity alumina along with pet-coke as the carbon source at 1 atm. pressure of CO (D).

The method used to estimate the temperature where slag formation starts for each of the five experiments was to identify the intersection of two tangent lines from the weight loss vs temperature data. An example of this is illustrated in Figure 7 for Experiment (A) using the high-purity reactants at 1 atm. CO. The estimated temperatures for the start of this reaction are shown in Table II.

These experimental data indicate that the slag-making reaction starts within the temperature range of 2213 K to 2229 K (1940 °C to 1956 °C) when high-purity graphite is reacted with high-purity alumina at 1.0 atm. total pressure of CO. Under the same gas conditions when pet-coke is used instead of graphite, the slag-making reaction starts at a lower temperature 2206 K (1933 °C). A possible explanation for this difference is that the activity of the carbon in pet-coke may be different than that for graphite. Another possibility is that this resulted from the higher ash content in pet-coke than for graphite. When high-purity reactants are used with a total reduced pressure of 0.5 atm. CO, the reaction starts at an even lower temperature 2187 K (1914 °C) since CO can be produced at the lower pressure now. This is also true for the sample run at 1 atm. of argon, but here argon is an ill-defined CO pressure.

One of these “fast-heating” experiments was run until the sample weight loss had stopped. This was done for sample (A) at 1 atm. CO. A total weight loss of 4.414 g was measured for this sample. The calculated theoretical weight loss for the reaction, excluding the weight loss

from Al_2O and Al vapor reactions, is 4.118 g. The FactSage thermodynamic software package can be used to predict the overall weight loss, including Al_2O and Al vaporization. These calculations were made for the final temperature where weight loss was observed to stop, which for this experiment was 2290 K (2017 °C). This is useful to examine the comparison between the predicted values and the experimentally observed, thus providing insight into the reasonableness of the thermodynamic data from which the predictions are made. These calculations are summarized in Table III.

From these calculations, it was found that the measured weight loss from the experiment was less than that predicted by FactSage when Al_2O and Al weight losses are included, but more than the calculated theoretical weight loss when excluding the contribution from Al_2O and Al vaporization. It is difficult to make conclusions about whether this indicates that less ($\text{Al}_2\text{O} + \text{Al}$) or CO evolve during the slag-making reaction than FactSage predicts, since it is unclear what amount of the experimentally measured weight loss came from CO or the $\text{Al}_2\text{O} + \text{Al}$ vapors.

B. Phase Diagram Determination Experiments

Several different experimental approaches were used. The two main differences were the reactants used (Al_2O_3 - Al_4C_3 mixture or crushed solidified Al_2O_3 - Al_4C_3 slag) and the gas used for experiments once the temperature surpassed 2073 K (1800 °C) (argon or CO). Experiment (A) involved heating a mixture of Al_2O_3 and Al_4C_3 ($X_{\text{Al}_4\text{C}_3} = 0.072$) in 1 atm. CO. During heat-up, most of the carbide was oxidized producing Al_2O_3 and carbon. This, in retrospect, is predicted by thermodynamics since the temperature is below the slag or carbide-making operating line during heat-up. Essentially Reaction [1] was going from right to left. Later, when the resulting Al_2O_3 -C was reacted in 1 atm. argon, it produced carbide (with no evidence of metallic aluminum present) at a temperature below the carbide-making operating line due to the argon lowering the resulting CO pressure. The CO was being produced at a lower pressure than 1 atm., however, the CO pressure is ill defined.

Two additional experiments were conducted in argon rather than CO. Experiment (B) involved using the very same starting reactants that were used in (A), while Experiment (C) utilized crushed solidified slag as the starting charge. For Experiment (B), a completely molten slag was formed by heating Al_2O_3 and Al_4C_3 reactants to 2232 K (1959 °C). The slag was then cooled very slowly and liquid samples taken until the slag was completely solidified at 2158 K (1885 °C) and 3.62 wt pct C ($X_{\text{Al}_4\text{C}_3} = 0.107$). This is below the expected eutectic temperature of 2181 K (1908 °C) and in reasonable agreement with the expected carbon content of 3.425 wt pct C ($X_{\text{Al}_4\text{C}_3} = 0.101$). There was no evidence of metallic aluminum being present in any of the samples from this experiment.

For Experiment (C), crushed solidified slag was heated very slowly. The first liquid was found at 2159 K (1886 °C) and contained 3.17 wt pct C

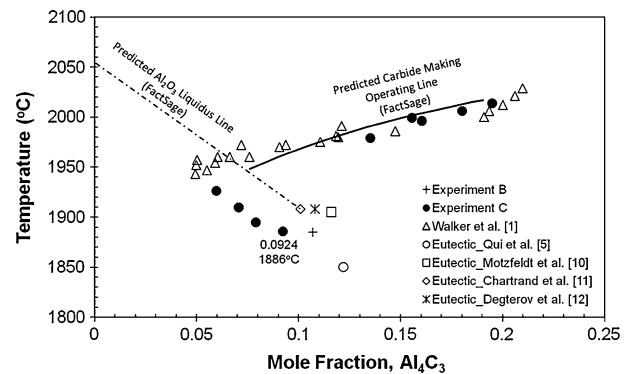


Fig. 8—Measured phase diagram data, including the slag/carbide-operating line measurements from Part I^[1] as well the eutectic measurements from prior researchers.

($X_{\text{Al}_4\text{C}_3} = 0.0924$). This should be the eutectic point. The temperature of the sample was gradually increased beyond this point, and samples of the liquid slag were obtained along the way. These samples should represent the Al_2O_3 saturated liquidus line. Heating continued and additional liquid slag samples were obtained which are believed to represent a portion of the slag/carbide-making operating line. Again, there was no evidence of metallic aluminum being present in of the samples from this experiment. The data from Experiment (B) and Experiment (C) are shown in Figure 8, together with the slag/carbide-making operating line measurements from Part I, selected phase diagram data (eutectic) from prior investigators, and the predictions from FactSage.

The measured data from Experiment (C) appear to be in agreement with the measurements from Part I, both in terms of the slag (carbide) making operating line as well as for the Al_2O_3 liquidus line. Both indicate that the predicted operating line is reasonable, but that the Al_2O_3 liquidus line is steeper than predicted.

With regards to Experiment (C), one item requires mention. Theoretically, the slag composition for this experiment could only move along the alumina liquidus line up to the point where the slag carbide concentration matched that for the starting slag. The slag which was used as the starting charge had a measured carbon content of 3.09 wt pct C ($X_{\text{Al}_4\text{C}_3} = 0.091$) when it was formed, prior to cooling it down, solidifying, and crushing it. The carbon content of this slag was not re-measured prior to its use in Experiment (C). The results from this experiment extend up along the alumina liquidus line beyond this point. A possible explanation for this could be that the carbon content of starting charge was different (lower) at the start of this experiment vs its measured value from the liquid slag prior to cooling it down and solidifying it. This slag would have solidified as solid $\text{Al}_4\text{O}_4\text{C}$ plus Al_2O_3 , rather than as Al_2O_3 - Al_4C_3 slag. It is possible that some of this solid $\text{Al}_4\text{O}_4\text{C}$ had reacted with moisture during the approximate 1-week time before its use in Experiment (C). This reaction can be written as



While a reaction such as this may be unlikely to occur for solidified $\text{Al}_2\text{O}_3\text{-Al}_4\text{C}_3$ slag, it has been observed to readily occur for solid Al_4C_3 , and $\text{Al}_4\text{O}_4\text{C}$ is expected to behave similarly.

V. GENERAL DISCUSSION

The eutectic composition was measured ($X_{\text{Al}_4\text{C}_3} = 0.092$ to 0.107) near to the FactSage-predicted composition ($X_{\text{Al}_4\text{C}_3} = 0.101$), while the eutectic temperature may be lower than predicted from the models [2158 K to 2159 K (1885 °C to 1886 °C) rather than 2181 K (1908 °C)], except that of Qui and Metselaar, which predicts an even lower eutectic temperature 2123 K (1850 °C) than found in this study. This indicates that the alumina liquidus line may be steeper than computed by FactSage using the most relevant thermodynamic models and databases. This is supported by both the alumina liquidus line measurements reported here as well as the measurements in Part 1 where the slag compositions at alumina saturation were found to have significantly lower carbon (Al_4C_3) than FactSage predicts.

Whereas the difference appears small, it significantly changes the activity composition relationship for Al_4C_3 and Al_2O_3 . The present work could be interpreted to indicate the activities of C^{4-} and O^{2-} in the sub-lattice model, which show large negative deviations from ideal behavior. The interaction terms could be adjusted within the slag solution model to make the interactions between species stronger. This would enable the alumina liquidus line to be steeper, as the experimental data suggest. This presents two problems. One, this would change the predicted operating line significantly, while recent experimental data (Part 1) support the path of the predicted operating line. Second, is that this would widen the gap between the equilibrium P_{CO} vs temperature curves for liquid slag, carbon, and Al_2O_3 or Al_4C_3 . Currently, the experimental P_{CO} measurements of Motzfeldt and Sandberg^[10] are used for this, and these are a key component of the calculated phase diagram. These would have to be modified without supporting experimental data in doing so. Besides stronger interactions between species, other possible explanations for the steeper liquidus line are errors in the free energy of melting of Al_2O_3 and Al_4C_3 , and the free energy of formation for Al_4C_3 .

There are at least two possible experimental reasons that may explain the results in the present study. One is an error in analysis for carbon. However, multiple samples were analyzed and two different Leco machines were used. Specific standards were used and this technique has been used extensively in the past. Another is that the multi-wavelength pyrometer may read temperatures 283 K to 293 K (10 °C to 20 °C) lower than actual. However, the experiments predicted the temperature for the initial slag or carbide-making reaction as well as the carbide saturation temperature. Furthermore, the pyrometer agreed within 278 K (5 °C) with the W-Re thermocouple (C type). Obviously, additional work is required to resolve this discrepancy and to fully

understand how it affects the thermodynamics, especially since the model parameters are obtained from the phase diagram.

VI. CONCLUSIONS

The reaction between Al_2O_3 and carbon in the temperature range of about 2123 K to 2293 K (1850 °C to 2020 °C) was investigated using a high-temperature vacuum furnace TGA. The temperature at which the carbide-forming reaction starts was found to be 2213 K to 2229 K (1940 °C to 1956 °C) at very low nitrogen levels. This is in agreement with the FactSage prediction of 2221 K (1948 °C). The required temperature decreased with CO pressure in the furnace as predicted.

Experiments were performed to determine the liquidus at Al_2O_3 saturation as well as the location of the $\text{Al}_2\text{O}_3\text{-Al}_4\text{O}_4\text{C}$ eutectic. The results indicated a somewhat steeper liquidus and a lower eutectic temperature than predicted based on the current understanding of the thermodynamics.

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