UCRL-11699

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

CARBOTHERMIC REDUCTION OF ALUMINA:
A THERMODYNAMIC ANALYSIS

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

To be published in Canadian Metallurgical Quarterly

UCRL-11699

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

Carbothermic Reduction of Alumina: A Thermodynamic Analysis

Wayne L. Worrell

October 7, 1964

Carbothermic Reduction of Alumina: A Thermodynamic Analysis*

Wayne L. Worrell**

Abstract

Using new thermodynamic data for Al_4C_3, stability relationships in the Al-C-O system have been determined. A Pourbaix-Ellingham diagram has been constructed and is used to evaluate the equilibrium carbothermic-reduction process. The analysis indicates that liquid aluminum can never be obtained and that appreciable amounts of $Al_2O(g)$ are present in the vapor. An analysis is also made of an alternate reduction path in which aluminum vapor is produced by the decomposition of aluminum carbide. The Al_4O_4C and Al_2OC oxycarbide phases are considered to be metastable, but their possible influence on the equilibrium reduction process is briefly discussed.

* This work was performed under the auspices of the United States Atomic Energy Commission.

** Wayne L. Worrell is Lecturer and Research Metallurgist, Department of Mineral Technology, College of Engineering, and Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California.

Introduction

Many of the proposed substitutes for the electrolytic reduction of alumina include a carbothermic reduction step. In the 1964 AIME Extractive Metallurgy Division's lecture, Stroup[1] discussed the past history and anticipated developments of carbothermic reduction in the production of aluminum.

A thermodynamic analysis of the Al-C-O system is very useful in evaluating the potential feasibility of such a process. Such an analysis was published recently by Morfopoulos[2] who erroneously concluded that the concentration of $Al_2O(g)$ was negligible at practical reduction temperatures. It is the purpose of this paper to re-evaluate the equilibrium relationships in the Al-C-O system, using new stability data for Al_4C_3.

A very concise method of picturing stability regions in a metal-carbon-oxygen system is to construct a Pourbaix-Ellingham diagram. Such diagrams have been used previously in a thermodynamic analysis of the metal-carbon-oxygen systems of vanadium, columbium, and tantalum[3] and of chromium, molybdenum, and tungsten.[4] In this paper a similar diagram is constructed for the Al-C-O system and is used to evaluate the practicality of carbothermic reduction.

Thermodynamic Data

Thermodynamic Data for the binary compounds and gases occurring in the Al-C-O system are presented in Table I in the form of linear Gibbs-energy-of-formation* equations. These equations are

---

* In accord with the decision of the Commission on Physical-Chemical Symbols and Terminology of the IUPAC, the term Gibbs energy of formation is adopted to represent the free energy of formation at constant temperature and pressure.

---

applicable in the specified temperature ranges and are used in the subsequent calculations.

The Gibbs-energy-of-formation equations for $Al_2O_3(s)$, $Al_2O(g)$, $AlO(g)$, $CO(g)$, and $CO_2(g)$ were calculated from the data given in Elliott and Gleiser[5]. The data for Al(g) is taken from the critical evaluation of Hultgren, Orr, Anderson and Kelley[6].

The thermodynamic data for Al_4C_3 were calculated using a newly determined heat-of-formation, which is 15.6 kcal more negative than that tabulated in Elliott and Gleiser[5]. Mah[7] has obtained -53.4 ± 2.0 kcal/mole, and King and Armstrong[8] report -43.0 ± 0.7 kcal/mole for the heat of formation of Al_4C_3. However, a large percentage of King and Armstrong's combustion product was the δ - Al_2O_3 phase. Using Kleppa's[9] recently measured enthalpy change for the δ - Al_2O_3 to α - Al_2O_3 transformation, they have recalculated their data and have obtained a revised value of -49.7 ± 1.2 kcal/mole.[10]

Furukawa, et al,[11] have measured the heat capacity and enthalpy of Al_4C_3 from 15° to 1173°K and have tabulated values for the entropy and enthalpy from 0 to 2000°K. Using this new thermal data, a value of -51.2 kcal/mole for the heat of formation at 298°K of Al_4C_3 is obtained from the high-temperature equilibrium study of Campbell[12]. The averaging of the three values yields -51.5 ± 1.0 kcal/mole for the heat of formation at 298°K of Al_4C_3. The Gibbs-energy-of-formation equations for Al_4C_3 were obtained by combining this average value with the newly tabulated thermal data of Furukawa, et al.[11]

Phase Relationships

In 1956 Foster, Long and Hunter[13] reported the existence of two oxycarbides, Al_4O_4C and Al_2OC, in the Al-C-O system. Cox and Pidgeon[14] attempted to measure the thermodynamic properties of these two ternary compounds, but the validity of their results is very questionable. In two of their investigated reactions, the attainment of equilibrium is impossible, while in the third, the influence of $Al_2O(g)$ and $Al(g)$ in the vapor phase complicates the interpretation of their results. In a previous thermodynamic analysis of the Al-C-O system, Morfopoulos[2] concludes that there are serious inconsistencies in Cox and Pidgeon's results.[14]

This author feels that the work of Foster, Long and Hunter[13] amply demonstrates the existence of the Al_4O_4C and Al_2OC phases but that it does not prove conclusively that these are stable phases. Indeed it appears that they may be metastable phases through which Al_2O_3 passes on being reduced to Al_4C_3. The transformation of Al_2O_3 to Al_4C_3 can be pictured as:

$$Al_4O_6 \rightarrow Al_4O_4C \rightarrow Al_4O_2C_2 \rightarrow Al_4C_3$$

where each carbon replaces two oxygens. It is perhaps significant that none of the "equilibrium" photomicrographs of Foster, Long and Hunter[13] showed only two phases; an additional non-equilibrium phase was always present in varied amounts. Thus, the Al_4O_4C and Al_2OC phases are considered to be metastable and will not be considered in the subsequent thermodynamic analysis.

Pourbaix-Ellingham Diagram

To provide a complete picture of the thermodynamically stable regions in metal-carbon-oxygen systems, Worrell and Chipman[3, 4] have described and constructed Pourbaix-Ellingham diagrams in which the two co-ordinates are oxygen potential ($-RT \ln P_{O_2}$) and temperature. In a Pourbaix-Ellingham diagram for a three-component system, the phase rule requires that at equilibrium two condensed phases define an area, three condensed phases determine a line, and four condensed phases specify a point.

To obtain a well-defined area at the end of the reduction process, the initial carbon to oxygen mole ratio is specified to be more than sufficient to reduce the oxide but not enough to convert all the metal to carbide. Thus, the lowest region in the subsequent Pourbaix-Ellingham diagram represents an area in which aluminum and aluminum carbide are the stable condensed phases.

In the Al-C-O system, alumina and carbon are the stable condensed phases at low temperatures and oxygen potentials (a low value of $-RT \ln P_{O_2}$ corresponds to a high oxygen pressure at a constant temperature). As the temperature or oxygen potential increases, a phase region appears in which alumina and aluminum carbide are the stable condensed phases.

The three-condensed-phase (Al_2O_3 - Al_4C_3 - C) equilibrium line is defined by the reaction:

$$2Al_2O_3 + 3C \rightleftharpoons Al_4C_3 + 3O_2(g) \qquad (1)$$

$$-RT \ln P_{O_2} = 249,600 - 46.7T \quad \text{(below 932°K)} \qquad (1a)$$

$$-RT \ln P_{O_2} = 247,100 - 44.1T \quad \text{(above 932°K)} \qquad (1b)$$

Equations (1a) and (1b) were calculated using the data tabulated in Table I and represent the top line shown in Figure 1, which is the Pourbaix-Ellingham diagram for the Al-C-O system.

The Al_2O_3 - Al_4C_3 - Al equilibrium line is defined by the following reaction:

$$Al_2O_3 \rightleftharpoons 2Al + \frac{3}{2}O_2(g) \qquad (2)$$

$$-RT \ln P_{O_2} = 266,800 - 49.7T \quad \text{(below 932°K)} \qquad (2a)$$

$$-RT \ln P_{O_2} = 268,400 - 51.7T \quad \text{(above 932°K)} \qquad (2b)$$

Equations (2a) and (2b) represent the line which separates the Al_2O_3 - Al_4C_3 and the Al_4C_3 - Al phase areas in Figure 1.

The vertical line at 932°K represents the equilibrium between solid and liquid aluminum.

Vapor equilibrium lines for 1, 10^{-2}, 10^{-4}, 10^{-6}, and 10^{-8} atm are shown as dashed lines in Figure 1. The one atm line would intersect the Al_2O_3 - Al_4C_3 - C equilibrium line at a temperature above the observed eutectic melting of Al_2O_3 and Al_4C_3[13].

Along each of the reduced vapor pressure lines two points, A and B, are indicated. Above the A points, 99.9% (or greater) of the vapor is carbon monoxide, while aluminum gas accounts for 99.9% (or greater) of the vapor below the B points. In the region between the A and B points, the vapor is a mixture of CO(g), Al(g) and Al_2O(g).

The vapor equilibrium lines indicate that a liquid aluminum phase can never be obtained in an equilibrium reduction process. At any specified reduction pressure, the temperature at which carbon can reduce Al_2O_3 to Al_4C_3 is higher than that necessary for Al_4C_3 and Al_2O_3 to form Al(ℓ). Because the vapor pressure of aluminum in equilibrium with Al_2O_3, Al_4C_3 and Al(ℓ) at the temperature necessary for carbide formation is greater than the reduction pressure, the equilibrium pressure of aluminum never reaches the value necessary to maintain a liquid aluminum phase. For example, if the reduction pressure is 10^{-4} atm, Figure 1 indicates that the minimum temperature for carbide formation is 1565°K, but the 10^{-4} atm line crosses the Al_2O_3 - Al_4C_3 - Al(ℓ) line at 1515°C.

Carbothermic Reduction of Alumina

In the previous section it was shown that one would never obtain the liquid aluminum phase in an equilibrium reduction process. However, the equilibrium vapor above Al_4C_3 and Al_2O_3 could contain a significant amount of Al(g), which could then be subjected to a distillation process. The two pertinent reactions are:

$$Al_2O_3 + Al_4C_3 \rightleftharpoons 6Al(g) + 3CO(g) \qquad (3)$$

$$\log(P_{CO})(P_{Al})^2 = -59,700/T + 23.65$$

$$5Al_2O_3 + 2Al_4C_3 \rightleftharpoons 9Al_2O(g) + 6CO(g) \qquad (4)$$

$$\log(P_{CO})(P_{Al_2O})^{\frac{3}{2}} = -57,500/T + 25.15$$

The equilibrium vapor composition can be determined by combining equations (3) and (4) with the restriction that the total reduction pressure must equal $P_{CO} + P_{Al_2O} + P_{Al}$. Calculated equilibrium vapor compositions are tabulated in Table II for the minimum temperature necessary to form Al_4C_3 at a specified reduction pressure. It would be a very difficult if not impossible task to distill pure aluminum from vapor having these tabulated compositions.

An alternate reduction path to that indicated above could be enacted by initially charging a carbon to oxygen mole ratio more than enough to convert all the metal to carbide. The alumina would be completely reduced to Al_4C_3 before the carbon phase disappeared, and the phase area below the Al_2O_3 - Al_4C_3 - C equilibrium line would

be Al_4C_3 and C instead of Al_4C_3 and Al_2O_3 as shown in Figure 1. On further heating, the aluminum vapor arising from the decomposition of Al_4C_3 might be easily condensed because CO(g) and Al_2O(g) would not be present in the vapor. The vapor pressure of aluminum in equilibrium with Al_4C_3 and C can be calculated from the following decomposition reaction:

$$Al_4C_3 \rightleftharpoons 4Al(g) + 3C \qquad (5)$$

$$\log P_{Al} = -19,350/T + 7.16$$

The temperature at which the aluminum pressure is equal to a specified reduction pressure is tabulated in Table III. Using both the Knudsen and torsion effusion methods, Meschi and Searcy[15] have studied reaction (5) between 1500 and 1800°K. The aluminum pressure calculated from their measurements is also shown in Table III for each tabulated temperature.

Meschi and Searcy's pressures are lower than the calculated equilibrium ones by a factor of three. This discrepancy is most likely related to an outer carbon layer forming as Al_4C_3 decomposes. The formation of this layer could lower the observed pressures since aluminum would have to diffuse through this carbon layer to reach the vapor phase. Meschi and Searcy observed such a carbon layer of several millimeters in thickness at the top of every sample. This carbon layer would most likely cause difficulty in reaching a particular reduction pressure at the equilibrium temperature. However, one may be able to attain a given reduction pressure by increasing the temperature of the system above that tabulated in Table III.

It should be emphasized that the previous thermodynamic analysis of the carbothermic reduction of aluminum is valid only when equilibrium conditions are maintained. Although this may not occur in the Al-C-O system, this analysis at least indicates the general direction of the reduction reactions and some possible difficulties in their applications. Indeed the observations of the Al_4O_4C and Al_2OC phases[13] indicate that the reduction of alumina to Al_4C_3 may be extremely sluggish. These phases probably cause the actual reduction process to deviate considerably from the calculated equilibrium one. For example, the presence of either or both of the oxycarbides could reduce the amount of $Al_2O(g)$ in the vapor from that tabulated in Table II.

References

1. Stroup, P. T., Met. Soc. AIME, 230, 1963, 356.

2. Morfopoulos, V. C. P., Cand. Met. Quart., 3, 1964, 95.

3. Worrell, W. L. and Chipman, J., Trans. Met. Soc. AIME, 230, 1964.

4. Worrell, W. L., submitted for publication in Trans. Met. Soc. AIME, 1964.

5. Elliott, J. F., and Gleiser, M., Thermochemistry for Steelmaking, Vol. I, Addison-Wesley Pub. Co., Reading, Massachusetts, 1960.

6. Hultgren, R., Orr, R. L., Anderson, P. P., and Kelley, K. K., Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley and Sons Inc., New York, New York, 1963.

7. Mah, A. D., U. S. Bur. of Mines, R. I. 6415, 1964.

8. King, R. C., and Armstrong, G. T., N.B.S. Report No. 8186, Jan., 1964, Chapter I.

9. Kleppa, O. J. and Yokokawa, T., J. Am. Chem. Soc., 86, 1964, 2749.

10. Private Communication to K. K. Kelley from G. T. Armstrong, 1964.

11. Furukawa, G. T., Douglas, T. B., Saba, W. G., and Victor, A. C., N.B.S. Report No. 8186, Jan., 1964, Chapter II.

12. Campbell, C. S., Met. Soc. Cont., 7, 1961, 412.

13. Foster, L. M., Long, G., and Hunter, M. S., J. Am. Cer. Soc., 39, 1956, 1.

14. Cox, J. H., and Pidgeon, L. M., Can. J. Chem., 41, 1963, 671.

15. Meschi, D. J., and Searcy, A. W., J. Phys. Chem. 63, 1959, 1175.

Table I

Thermodynamic Data for the Condensed Binary Phases and Gases Occurring in the Al-C-O System

Reaction	Gibbs Energy of Formation (cal.)	Temperature Range °K
$2Al(s) + \frac{3}{2} O_2(g) \rightleftharpoons Al_2O_3(s)$	-400,200 + 75.0T	298-932
$2Al(\ell) + \frac{3}{2} O_2(g) \rightleftharpoons Al_2O_3(s)$	-402,600 + 77.6T	932-2000
$2Al(\ell) + \frac{1}{2} O_2(g) \rightleftharpoons Al_2O(g)$	- 44,500 - 14.5T	1000-2000
$Al(\ell) + \frac{1}{2} O_2(g) \rightleftharpoons AlO(g)$	+ 4,500 - 14.0T	1000-2000
$Al(\ell) \rightleftharpoons Al(g)$	+ 72,500 - 27.0T	1000-2000
$4Al(s) + 3C(s) \rightleftharpoons Al_4C_3(s)$	- 51,500 + 10.0T	298-932
$4Al(\ell) + 3C(s) \rightleftharpoons Al_4C_3(s)$	- 63,800 + 23.0T	932-2000
$C(s) + \frac{1}{2}O_2(g) \rightleftharpoons CO(g)$	- 26,760 - 21.0T	298-2000
$C(s) + O_2(g) \rightleftharpoons CO_2(g)$	- 94,260 - 0.3T	298-2000

Table II

Composition of the Equilibrium Vapor Above Al_2O_3 and Al_4C_3 at the Indicated Pressure and Temperature

Reduction Pressure (atm)	Temperature (°K)	%CO	%Al_2O	%Al
10^{-2}	1840	72	23	5
10^{-4}	1565	84	10	6
10^{-6}	1365	85	5	10
10^{-8}	1205	86	2	12

Table III

Calculated and Observed Aluminum Pressures in Equilibrium with Aluminum Carbide and Carbon

Reduction Pressure (atm)	Calculated Temperature (°K) (Equation 5)	Observed Pressures (atm) (Reference 15)
10^{-2}	2110	3×10^{-3}
10^{-4}	1735	3×10^{-5}
10^{-6}	1470	3×10^{-7}
10^{-8}	1275	3×10^{-9}

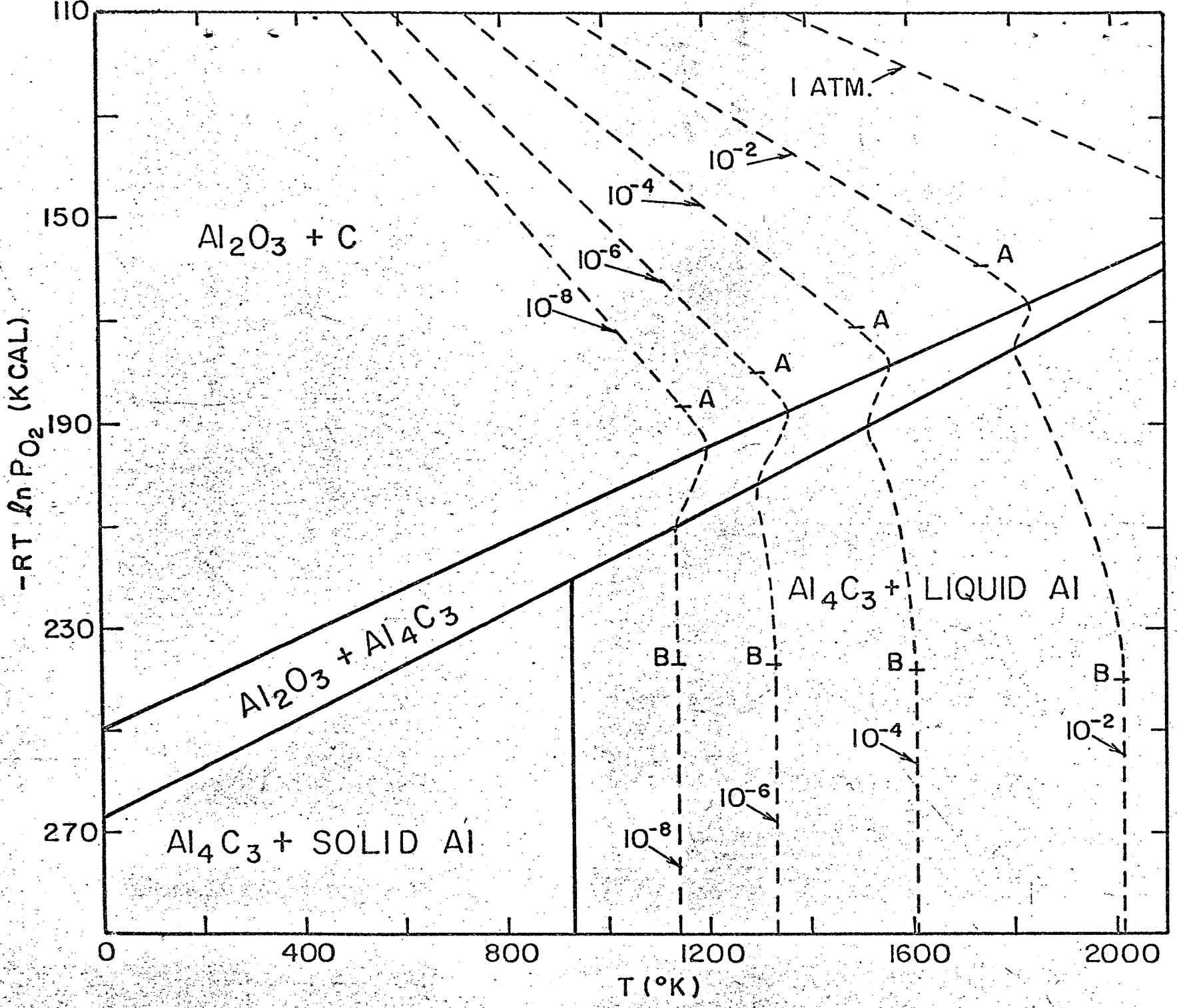

Figure 1. Pourbaix-Ellingham Diagram for the Al-C-O System.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.