



## Comment on “Thermodynamics of the Al-C-O Ternary System” [*J. Electrochem. Soc.*, 153, E119 (2006)]

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In the recent paper by Heyrman and Chatillon, *J. Electrochem. Soc.*, 153, E119 (2006), the authors have done a remarkable job in reviewing almost everything written on the Al-C-O system during the last 50 years. No objection is raised to the final conclusion of their work. It appears, however, that in their discussion the authors have included a number of investigations where the results are notoriously wrong or misleading. Thus the present communication aims at, in part to point out some of the fallacies, in part also to contribute with information that appears unknown to the authors. To retain brevity, only the most salient features will be considered.

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### The Stable Compounds

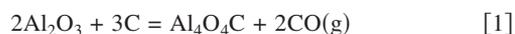
In addition to the well-known compounds  $\text{Al}_2\text{O}_3$  and  $\text{Al}_4\text{C}_3$ , the authors state in the first part of their paper that “Two oxycarbides,  $\text{Al}_4\text{CO}_4$  and  $\text{Al}_2\text{OC}$ , exist - -.” As regards the second, this is not quite correct. It has been demonstrated beyond doubt that in the pure Al-C-O system, the compound  $\text{Al}_2\text{OC}$  does not appear as a thermodynamically stable phase. For instance, as shown by Herstad<sup>2</sup> some 40 years ago, reaction between Al(l) and CO(g) gives  $\text{Al}_4\text{O}_4\text{C}$  and  $\text{Al}_4\text{C}_3$ , but no  $\text{Al}_2\text{OC}$ . However, admixture of only a few percent of  $\text{N}_2$ (g) results in the formation of the said compound. It appears that the solid “ $\text{Al}_2\text{OC}$ ” is stabilized by the presence of a small amount of N atoms in the structure. It is recalled that the compound as written is isoelectronic with  $\text{Al}_2\text{N}_2$ , and the various “ $\text{Al}_2\text{OC}$ ” phases identified show X-ray patterns very similar to that of AlN.

A further evidence of the nonexistence of  $\text{Al}_2\text{OC}$  as a stable phase in the Al-O-C system is given by the equilibrium investigations of Herstad<sup>2,3</sup> and Sandberg<sup>4,5</sup> (also reviewed by Motzfeldt et al.<sup>6</sup>). Measurements throughout the range from 1500 to 2100°C showed no trace of any compound except  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_4\text{O}_4\text{C}$ , and  $\text{Al}_4\text{C}_3$ . Thus, out of the four phase diagrams in Fig. 1 from Heyrman et al.,<sup>1</sup> only alternative (b) is reasonably correct.

### Previous Work, and the Rôle of Nitrogen

Scientific investigation of the system Al-O-C began with the work of Foster et al.<sup>7</sup> 50 years ago, disclosing the existence of the oxycarbides  $\text{Al}_4\text{O}_4\text{C}$  and  $\text{Al}_4\text{O}_2\text{C}_2$  (or  $\text{Al}_2\text{OC}$ ). It was a pioneering investigation, done in a graphite tube furnace, but with a furnace enclosure that almost certainly was not gas tight. The same was true with a number of other investigations in the following years. Thus it is reasonable, as evidenced from their results, that they all had some nitrogen entering into their inert atmosphere, with the consequent formation of “ $\text{Al}_2\text{OC}$ ” as explained above.

Cox and Pidgeon<sup>8</sup> were among the first to use some sort of vacuum system, but there is evidence to show that it was badly leaking. It is of interest to compare the two reactions



and



Because of the marked stability of the nitride, the equilibrium pressure of CO(g) from Reaction 2 is higher than that from Reaction 1 already at an  $\text{N}_2$  pressure of 0.001 bar (at temperatures to about 1800°C), according to calculations by Herstad.<sup>2</sup> He also found that the pressure measurements of Cox,<sup>9</sup> when plotted as  $\log P_{\text{CO}}$  against inverse temperature, scatter around a straight line corresponding to Reaction 2 for  $P_{\text{N}_2} = 0.01$  bar. (This does not mean that the partial pressures of  $\text{N}_2$  really were that high.)

In contrast, the investigations of Herstad, Sandberg and associates<sup>2-5</sup> were done with furnaces in vacuum-tight, water-cooled

enclosures, properly degassed to  $10^{-8}$  bar before admitting the desired gas. In fact, the long story of the alleged existence of “ $\text{Al}_2\text{OC}$ ” is a prime example to show that it is worth the effort aiming at clean work, which includes high-vacuum technique.

The work of Lihmann et al.<sup>10</sup> deserves special mention. Their experimental approach was that of a ceramist: cold-pressing of samples of aluminum oxide, carbide, and nitride of known compositions, firing in inert atmosphere to the desired temperature (eventually extended annealing) and subsequent examination by X-ray diffraction. In particular they investigated a series of samples along the join from  $\text{Al}_2\text{OC}$  to AlN. Their investigations confirmed that small amounts of the nitride stabilized the formation of the “ $\text{Al}_2\text{OC}$ ” phase. Pure  $\text{Al}_2\text{OC}$  (no AlN added) was found to be thermodynamically stable only in a limited temperature region between 1715 and 2000°C. Considering this strange behavior, and the possibility that some nitrogen has crept into their seemingly pure oxide-carbide mixtures, it appears more probable that  $\text{Al}_2\text{OC}$  is thermodynamically unstable at all temperatures, in line with the previous conclusion.

### A Method for Equilibrium Measurements

From the assessment of Heyrman and Chatillon<sup>1</sup> it appears that they consider the measurements of Motzfeldt and Sandberg<sup>4,5</sup> to be the most dependable. On the other hand, Heyrman et al. are rather vague with respect to the method used. Hence some words on this point.

It is true that Herstad<sup>2</sup> started out by observing static pressures of CO, in a furnace enclosure that had a total volume of  $\sim 80$  L. This means that a gas evolution of, say, 100 mL<sup>3</sup> (STP) will give a pressure difference of roughly 0.1 percent, i.e., hardly noticeable on a mercury manometer. Furthermore, a temperature change in the furnace enclosure of only a fraction of a degree will obscure the effect. On the other hand, the same 100 mL<sup>3</sup> of gas evolved from a sample will reduce the sample mass by roughly 100 mg, while an analytical balance easily detects a change of 1 mg. Thus a thermogravimetric method is at least two orders of magnitude more sensitive than direct pressure measurements. With this in mind, the equipment was modified to accommodate a balance on top of the graphite-tube furnace; at first one with an optical readout (Herstad<sup>2</sup>), later on an electronic balance (Sandberg<sup>5</sup>).

Increasing weight means that Reaction 1 proceeds to the left with absorption of gas, decreasing means reaction to the right. Measurements were made by altering the applied CO pressure in steps at constant furnace temperature. Each value of constant CO pressure was kept for some minutes, until a constant rate of weight change was observed. As the run went on, rates of weight change were plotted against the corresponding gas pressures. The equilibrium pressure is located where the curve for mass loss rate crosses the zero line.

The method is simple and very accurate, and a number of equi-

librium points may be determined in a single day. And yet, to my knowledge it has not been employed by anybody else for this or similar systems.

The accuracy of the pressure determinations is difficult to match by a corresponding accuracy in temperature. For example, Reaction 1 changes its equilibrium pressure by 1 to 2 millibar for each degree change in temperature.

With this in mind, utmost care was taken in temperature determinations. A “disappearing-filament” optical pyrometer<sup>a</sup> was used, rather old but reliable when properly handled. It was checked against the melting points of platinum (1772°C) and alumina (2054°C), with the proper corrections for absorption in the sighting window and mirror. Deviations from true temperature are estimated to be well within  $\pm 10^\circ$ .

### Thermodynamic Modeling

Heyrman and Chatillon<sup>1</sup> repeatedly refer to the thermodynamic evaluation by Qui and Metselaar<sup>11</sup> without any reservation. This is vexing.

The thermodynamic model of Qui and Metselaar is presented with reference to the two-sublattice model of Hiller et al.,<sup>12</sup> which again is based on Temkin’s concept of ionic mixtures.<sup>13</sup> Hillert et al. extended Temkin’s concept to include also nonstoichiometry and neutral species, but this extension is superfluous in the present case where all compounds are strictly stoichiometric.

Temkin<sup>13</sup> assumed that a molten mixture of ionic compounds may be regarded as one lattice of cations and one of anions. In the molten state, cations exchange with other cations, and the same for anions, but a cation and an anion cannot exchange positions. An implication not specifically mentioned by Temkin is that the ions are of moderate charge,  $\pm 1$  or  $\pm 2$ .

An example may illustrate this. The melting point of MgO is very high, 2850°C, apparently because of the strong attraction between the small, divalent ions Mg<sup>2+</sup> and O<sup>2-</sup>. Alumina, with the trivalent ion Al<sup>3+</sup>, might be expected to melt even higher, but this is not so (it melts at 2054°C). This may be explained by assuming that the melting of alumina takes place to monovalent ions



From this point of view, small divalent ions are doubtful, and tri- and tetravalent ions hardly exist as freely interchangeable species in a melt. Thus a compound like Al<sub>4</sub>C<sub>3</sub> has no congruent melting point at all.

Qui and Metselaar<sup>11</sup> on the other hand, ignorant of Temkin’s original idea, construct a model where the melt consists of the ions Al<sup>3+</sup>, O<sup>2-</sup>, and C<sup>4-</sup>. It is almost like suggesting that sodium carbonate on melting dissociates to 2 Na<sup>+</sup>, C<sup>4+</sup>, and 3 O<sup>2-</sup>.

One of the results of this model building is shown in their Fig. 4, where their calculated equilibrium gas pressures of CO are shown as functions of inverse temperature. In particular, in the region where molten oxycarbide is one of the phases, the curves calculated by Qui and Metselaar deviate markedly from the experimental (and rather accurate) points of Sandberg.<sup>5</sup> Unfortunately, the same diagram is also reproduced by Heyrman and Chatillon, their Fig. 4.<sup>1</sup> Both parties apparently have more faith in theory than in facts.

Dismissing the work of Qui and Metselaar, it may still be of interest to devise a model for the molten phase in the Al-O-C system, based on Temkin’s idea of ionic mixtures. Two of the ions are already given by Eq. 3. The third ion appears from the dissociation of the oxycarbide



<sup>a</sup> Type 8622-C from Leeds & Northrup, Inc., Philadelphia, USA, purchased to the lab. in Trondheim in 1950 and still (2006) in good shape. A modern version based on the same principle, DFP 2000, is marketed by Spectrodyne, Inc., Philadelphia, USA.

The dissolution of aluminum carbide in the melt is thought to take place by the reaction



Thus, the molten phase of this system may be described as a mixture of the three simple, monovalent ions AlO<sup>+</sup>, AlO<sub>2</sub><sup>-</sup>, and AlC<sup>-</sup>.

To perform a calculation, the ionic fraction  $N_x$  of each species is calculated from the given overall composition. Next, the activity of any one of the neutral species shown in Eq. 3-5 is calculated from the product of the ionic fractions, analogous to other reaction equilibria. The principle is simple, while the expressions for the activities in this case turn out to be somewhat complex and thus are not reproduced here; the reader is referred to the original paper.<sup>14</sup>

From this model in combination with a few known data, the phase diagram for the system Al<sub>2</sub>O<sub>3</sub>-Al<sub>4</sub>C<sub>3</sub> was constructed. The liquidus line on the Al<sub>4</sub>C<sub>3</sub> side is of particular interest, as this is the region where liquid aluminum may be obtained by carbothermal methods. The calculated liquidus turned out to be somewhat steeper than in the previously suggested phase diagram, which was reproduced as Fig. 1b of Heyrman et al.<sup>1</sup>

An independent check on the results from the model calculations may be obtained by calculation of the liquidus lines by means of the experimental CO pressures of Sandberg.

Once again the details of the calculation may be left for the original paper.<sup>14</sup> The result, however, is interesting; the liquidus line derived from Sandberg’s measurements show a close similarity to that derived from the model. An adjustment of 2% in Sandberg’s measured pressures, and the two would be identical. This agreement does not prove anything, but it is a strong indication that the liquid phase in this system really behaves like an ideal Temkin mixture.

### Thermodynamic Data

The title of the paper by Heyrman and Chatillon<sup>1</sup> indicates that their aim was to derive thermodynamic data for the oxycarbides.

For Al<sub>4</sub>O<sub>4</sub>C at the standard temperature of 298 K they find

$$\Delta H_f^\circ = -2313.5 \pm 15.4 \text{ kJ mol}^{-1}$$

$$S^\circ = 97.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

Sandberg, from his data, also derived tables of thermodynamic values, although they were never published except in his thesis.<sup>4</sup> For Al<sub>4</sub>O<sub>4</sub>C at 298 K, based on the “third-law method”

$$\Delta H_f^\circ = -2316.3 \text{ kJ mol}^{-1}; \quad S^\circ = 97.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

It is seen that the two sets of data are close to identical, as they ought to be as they are derived from essentially the same data.

For Al<sub>2</sub>OC, Heyrman and Chatillon<sup>1</sup> did not succeed in deriving any data. This must be regarded as comforting, since the compound does not exist

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