Molten Aluminium Oxycarbide, Considered as an Ionic Mixture

Ketil Motzfeldt *, Bjørn Sandberg ** and Stein Julsrud ***

** NTNU, Trondheim, Norway*
*** Elkem International, Tokyo, Japan*
**** Norsk Hydro, Research Centre, Porsgrunn, Norway*

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ABSTRACT

A critical review is given of the system Al_2O_3-Al_4C_3, including a discussion of solid compounds in the system. The liquid phase is considered as a mixture of the three ions AlO^+, AlO_2^- and AlC^-. A revised phase diagram is delineated, based also on experimental gas pressures at equilibrium in the presence of solid carbon.

COMPOUNDS

The investigation of Foster, Long and Hunter about 50 years ago /1/ represented a major improvement in the knowledge of the system Al_2O_3-Al_4C_3 by calling attention to the oxycarbides Al_4O_4C and Al_2OC. The stable existence of the former has since been confirmed by a number of workers, while the stability of the latter has been in doubt. In the experimental investigations of Cox and Pidgeon /2/ and Ginsberg and Sparwald /3/ Al_2OC was identified in the products. On the other hand, Herstad /4,5/ did not find it in the products of reaction between alumina and carbon. Further to demonstrate the stability relationship, Herstad studied the reaction of molten aluminium with controlled amounts of carbon monoxide. The expected reaction would be

$$2\,Al(l) + CO(g) = Al_2OC\,(s)$$

With pure CO gas, however, the products were always mixtures of Al_4O_4C and Al_4C_3 with no trace of Al_2OC. But when about 6 percent (or more) of nitrogen was added to the gas, a solid solution of Al_2OC and AlN was formed, as evidenced by X-ray powder patterns and chemical analysis. It was concluded that the nitride stabilizes the oxycarbide phase Al_2OC, the two compounds being isomorphous. The reason why previous workers identified Al_2OC in their products might be that they had leaks in their vacuum system (or no vacuum system at all), so that contamination of nitrogen could occur.

More recently, Lihrmann *et al.* /6/ in a thorough study of the Al_2OC phase concluded that it is stabilized in the presence of 5 mol% (or more) of AlN, while pure Al_2OC is stable only at temperatures above 1715°C (up to the peritectic decomposition around 2000°C). This range of stability, however limited, is in doubt since Sandberg /7,8/ in his careful equilibrium measurements in the range 1650 to 2100°C found no evidence of the oxycarbide Al_2OC. Hence we choose to ignore it altogether. We are thus left with the three solid compounds Al_2O_3, Al_4O_4C and Al_4C_3 in our system, and at higher temperature a liquid phase.

Experimental investigations in this system have usually been done with carbon (graphite) as a container material. It is then tacitly assumed that the solubility of carbon in the other solids as well as in the melt is negligible. The presence of carbon, however, gives rise to various reactions and partial pressures of the gases CO, Al_2O and Al which should not be neglected.

PHASE TRANSITIONS

Foster *et al.* /1/ placed the eutectic at about 1840°C and the peritectic decomposition of Al_4O_4C at 1890°C. Their work, however, was of an exploratory nature, with equipment not well suited for accurate temperature determinations. Ginsberg *et al.* /3/ determined the two temperatures as 1900°C and 1950°C, respectively. This is in good accord with the more accurate determinations of Gjerstad /9/ who fixed the eutectic Al_2O_3-Al_4O_4C at 1905°C and the peritectic decomposition of Al_4O_4C at 1945°C.

THE LIQUID PHASE

It is generally recognized that a carbothermal process for the production of aluminium will involve reactions in the molten mixture /10/. This gives some special importance to the liquid phase of this system. It is generally agreed that it is best considered as an ionic mixture.

Temkin's Model

M.Temkin /11/ introduced the concept of perfect ionic solutions, for which the heat of mixing is zero and the change in entropy is determined solely by the number of possible permutations among different cations, and correspondingly among different anions. This concept has formed the basis for all later work on molten salt mixtures.

The Two-Sublattice-Model.

Based on Temkin's approach, Hillert *et al.* /12/ developed the "two-sublattice-model" with the intent of bridging the gap between ionic and non-ionic systems. Qiu and Metselaar /13/ unfortunately adopted the idea of the two sublattices without regard for the underlying assumption of random permutation. Thus they assume that the molten phase in the system Al_2O_3-Al_4C_3 may be considered as a mixture of the ions Al^{3+}, O^{2-} and C^{4-}. But it is very unlikely that a highly charged ion like C^{4-} may exist as a separate and permutable species in the melt; most likely it would unite with a neighbour of the opposite sign and form AlC^-. Likewise the triply charged Al^{3+} is unlikely as a "free" ion in the melt (cf. below). Altogether the ionic model of Qiu and Metselaar must be discarded. In addition their proposed phase diagram is in error with respect to temperatures of transition as well as other details. Their various diagrams, a total of 14, are on the verge of fiction.

The Melting of Oxides.

Two divalent ions of opposite sign, like Mg^{2+} and O^{2-}, exert strong mutual attractive forces. Hence solid MgO, with the sodium chloride lattice, has a very high melting point, 2800°C. The triply charged Al^{3+} ion will have an even stronger attraction for oxygen ions and thus alumina should have a still higher melting point. But it does not; Al_2O_3 melts at 2054°C. The reason must be that it has a simpler way of melting:

$$Al_2O_3(s) = AlO^+ + AlO^{2-} \qquad (1)$$

This mechanism of melting of alumina was first proposed by Elyutin *et al.* /14/ on the basis of observations of electrical conductivity and viscosity.

A MODEL FOR THE MELT

The equation for the melting of alumina is given above, Eqn. (1). The dissociation of the oxycarbide may take place by the reaction

$$Al_4O_4C\ (s) = 2\ AlO^+ + AlO_2^- + AlC^- \qquad (2)$$

Aluminium carbide does not melt as such, but it does dissolve to some extent in molten alumina. This may be assumed to take place by the reaction

$$Al_4C_3\ (s) + AlO_2^- = 2\ AlO^+ + 3\ AlC^- \qquad (3)$$

Thus we have an ionic mixture consisting of the three monovalent ions AlO^+, AlO_2^- and AlC^-. Considering an initial mixture consisting of $(1 - x)$

moles of Al_2O_3 and x moles of Al_4C_3, the ion fractions in the molten mixtures will be:

$$N_{AlO^+} = 1 \text{ (always)}; \; N_{AlO_2^-} = \frac{1-2x}{1+x}; \; N_{AlC^-} = \frac{3x}{1+x} \qquad (4)$$

According to the Temkin model of an ideal ionic solution, the activity of a component in the solution is given by the product of its ion fractions. In the present case it is merely the product of anion fractions:

$$a_{Al_2O_3} = N_{AlO_2^-} = \frac{1-2x}{1+x} \qquad (5)$$

$$a_{Al_4O_4C} = N_{AlO_2^-} N_{AlC^-} = \frac{3x(1-2x)}{1+x)^2} \qquad (6)$$

$$a_{Al_4C_3} = N^3_{AlC^-} / N_{AlO_2^-} = \frac{27x^3}{(1-2x)(1+x)^2} \qquad (7)$$

THE PHASE DIAGRAM

The liquidus line in a phase diagram represents the equilibrium between a given component in the liquid and the same component in the solid phase. In the present case the solid phases are pure compounds with unit activity, and thus the general equilibrium condition is very simple:

$$\Delta G^o = \Delta H^o - T\Delta S^o = - RT \ln a_{comp} \qquad (8)$$

where a_{comp} stands for the activity of either alumina, oxycarbide or carbide as given by Eqns. (5) to (7).

In the case of alumina we may use directly the data given by the JANAF Tables /15/ for solid and liquid alumina. This gives the activity at various temperatures, and hence the composition $x = (1 - a)/(2 + a)$. The result is a nearly straight line from the melting point down to the eutectic at 1905°C (2178 K) with a calculated composition $x = 0.116$.

The liquidus on the oxycarbide side is fixed by noting that we know two points: The eutectic as given above, and the peritectic point which we set at 1945°C (2218 K) and composition $x = 0.165$. From Eqn. (8) this gives two equations with two unknowns, and we find

$$\Delta S_2^o = 47.1 \text{ J/K mol:} \; \Delta H_2^o = 130{,}500 \text{ J/mol}$$

These values are used with Eqn. (8) in the form

$$T = \frac{\Delta H^c}{\Delta S^o - R \ln a} \qquad (8A)$$

where the activity is calculated from Eqn. (6) for various values of x. The result is a nicely rounded curve with a hypothetical maximum at 1952°C as shown in Fig. 1.

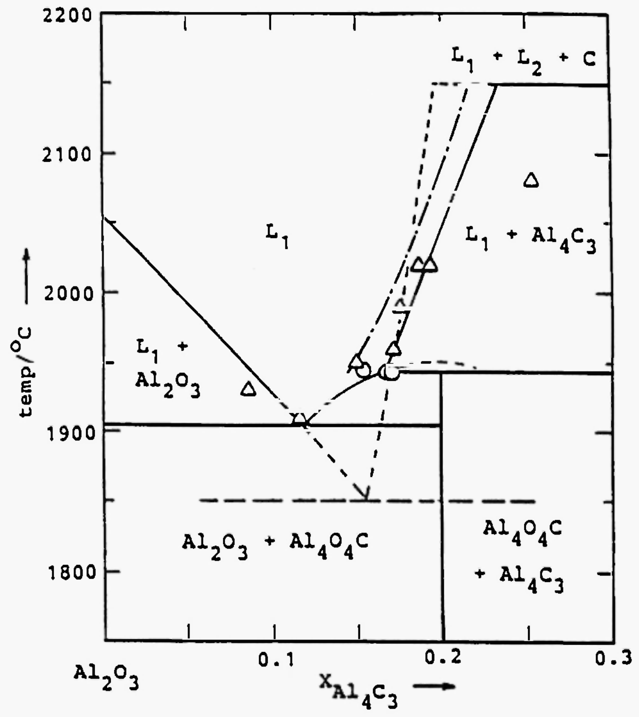

Fig. 1: The phase diagram Al_2O_3-Al_4C_3 (left third only shown, accepting that Al_2OC does not exist as a stable phase). *Triangles*: Ginsberg and Sparwald /3/. *Circles*: Gjerstad /9/. Dashed, dotted and full lines: See text.

Regarding the liquidus on the carbide side, it was noted in a previous communication /16/ that Sandberg, when cooling samples within the region of primary crystallization of the carbide, observed no halt at 1905°C, but instead a metastable eutectic between carbide and oxide at 1840°C /7,8/. Allowing for some undercooling, the eutectic was set at 1850°C (2123 K) with the composition of the alumina liquidus calculated for that temperature. The resulting liquidus is shown as a dashed line in the phase diagram, Fig. 1. It is seen, however, that this carbide liquidus appears exceptionally steep, and the two points employed to fix it are rather uncertain. Thus another method is called for.

Sandberg /7, 8/ determined the equilibrium pressures of carbon monoxide for a total of five different reactions in this system. Here we are particularly interested in the reaction above the peritectic temperature:

$$2\ Al_2O_3\ (\text{in liquid}) + 9\ C = Al_4C_3 + 6\ CO\ (g) \qquad (9)$$

$$K = P^6_{CO} / a^2_{Al_2O_3} \quad \text{or} \quad a_{Al_2O_3} = P^3_{CO} / \sqrt{K} \qquad (10)$$

With K calculated from JANAF data and P_{CO} at various temperatures taken from Sandberg /7/, $a_{Al_2O_3}$ and hence $x = (1 - a)/(2 + a)$ is determined. The result, indicated with a dash-dot line in Fig. 1, shows remarkable agreement when considering that it is obtained by an entirely different type of observations.

A still better fit to the experimental points may be obtained by a slight lowering of the CO pressures from Sandberg. It is not unreasonable to assume that his measured pressures may be slightly high because of the partial pressures of Al_2O and Al produced concurrent with CO in the reaction, Eqn. (9). But a mere 2 percent reduction of his measured pressures suffice to bring the liquidus to go through the chosen peritectic point. With this point in combination with a notion of the proper slope from Sandberg's measurements we may also calculate a set of thermodyamic data for the dissolution of the carbide, reaction (3):

$$\Delta S^0_3 = 96\ \text{J/K mol}; \ \Delta H^0_3 = 250\,000\ \text{J/mol}$$

The full line in Fig. 1 is calculated with these data, using Eqn. (7) and (8A). The calculated liquidus appears as an essentially straight line although there is no obvious reason why it should be straight. The liquidus line ends at the temperature of peritectic decomposition of the carbide, 2150°C. Above this temperature the system consists of two liquid phases plus solid carbon, and it cannot be represented as pseudo-binary. At this temperature the total equilibrium gas pressure will be about 3.0 bar.

DISCUSSION

The ionic model of the melt, as presented in Eqns. (1) to (3), appears reasonable, as do the results obtained for the phase diagram. On the other hand, the thermodynamic data presented here for reactions (2) and (3) should be regarded as rather uncertain. In particular it is noted that the two dissociation reactions (2) and (3) produce the same number of "free" ions per formula unit (i.e., four) and hence one would expect their entropy changes to be of similar magnitude. This is in contrast to the values given above where both entropy and enthalpy changes of reaction (2) are about one-half of those for reaction (3).

A note should be added regarding our model for the melting of alumina, Eqn. (1). In a recent X-ray study of molten alumina, Ansell *et al.* /17/ found that the melting is accompanied by a drastic change in structure, from octahedral coordination in α-alumina to tetrahedral in the melt. This structural change may be one reason for the relatively low melting point of alumina. It does not, however, have any direct bearing on our simple model for ionization during melting.

The present liquidus line on the carbide side and the corresponding line on the alumina side do not agree with the metastable eutectic, which is nevertheless believed to be real. We do not know the reason for this discrepancy nor do we know whether the carbide liquidus has been correctly placed in Fig. 1. The only way to find out is by experiment. Experimental investigations of this phase diagram could preferably be done under an overpressure, e.g., some 10 bars of argon, to impede the gas-producing reactions that take place in this system at elevated temperatures.

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