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Formation of Aluminium Carbide by Carbothermal Reduction of Alumina: Role of the Gaseous Aluminium Phase

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Abstract

Formation of aluminium carbide by carbothermal reduction of alumina under an atmospheric pressure of argon involves the following reactions occurring from 1400°C:

(i) *The decomposition of alumina:*

$$2Al_2O_3 \rightleftharpoons 4Al + 3O_2$$

and the correlative formation of carbon monoxide:

$$3O_2 + 6C \rightleftharpoons 6CO$$

(ii) *The intermediate formation of the oxycarbide Al_2OC for partial pressures of carbon monoxide of about 5×10^{-3} Pa:*

$$4Al + 2CO \rightleftharpoons 2Al_2OC$$

(iii) *The final production of Al_4C_3, when the partial pressure of carbon monoxide becomes lower, accompanying the decomposition of the oxycarbide, may be by:*

$$4Al + 3C \rightleftharpoons Al_4C_3$$

Gaseous aluminium can be detected experimentally by an emission spectrometer from the lowest temperatures (1400°C) and all along the different steps.

Die Bildung von Aluminiumkarbid durch die karbothermische Reduktion von Aluminiumoxid unter Argon-Atmosphärendruck beinhaltet die folgenden, bei 1400°C ablaufenden Reaktionen:

(i) *Den Zerfall des Aluminiumoxids:*

$$2Al_2O_3 \rightleftharpoons 4Al + 3O_2$$

und die damit verbundene Bildung von Kohlenmonoxid:

$$3O_2 + 6C \rightleftharpoons 6CO$$

(ii) *Die zwischenzeitliche Bildung des Oxykarbids Al_2OC bei einem CO-Partialdruck von ungefähr 5×10^3 Pa:*

$$4Al + 2CO \rightleftharpoons 2Al_2OC$$

(iii)

Schließlich die Bildung von Al_4C_3, wenn der CO-Partialdruck abnimmt, begleitet von der Zersetzung des Oxykarbids:

$$4Al + 3C \rightleftharpoons Al_4C_3$$

Gasförmiges Aluminium kann experimentell mit Hilfe eines Emissionsspektrometers von Beginn an (1400°C) während des gesamten Prozesses nachgewiesen werden.

La synthèse du carbure d'aluminium par réduction carbothermique de l'alumine sous pression atmosphérique d'argon met en évidence différentes réactions apparaissant dès 1400°C:

(i) *La décomposition de l'alumine:*

$$2Al_2O_3 \rightleftharpoons 4Al + 3O_2$$

et la formation parallèle de monoxyde de carbone:

$$3O_2 + 6C \rightleftharpoons 6CO$$

(ii) *La formation intermédiaire de l'oxycarbure Al_2OC pour des pressions partielles de monoxyde de carbone de l'ordre de 5×10^3 Pa:*

$$4Al + 2CO \rightleftharpoons 2Al_2OC$$

(iii) *En dernier lieu, la production du carbure Al_4C_3, liée à la décomposition de l'oxycarbure lorsque la pression partielle de monoxyde de carbone diminue, possiblement selon:*

$$4Al + 3C \rightleftharpoons Al_4C_3$$

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L'aluminium vapeur peut être détecté expérimentalement par un spectromètre d'émission à des températures aussi peu élevées que 1400°C et tout au long de ces différentes étapes.

1 Introduction

The carbothermic reduction of alumina is one of the oldest ways of obtaining aluminium carbide. Nevertheless the mechanism of the reaction remains unknown. As far as it has been established[1-3] that this reaction produces important amounts of gaseous phases, the authors have tried to approach the reaction mechanism by the analysis of these phases with an emission spectrometer. For the reaction occurring at temperatures as low as 1400°C[4-5] it can be seen that this method is somewhat original.

2 Thermodynamics

On the basis of the thermodynamical data of the JANAF tables[6] the authors have drawn the stability diagram of the alumineous phases liable to exist during the reaction:

$$2Al_2O_3 + 9C \rightarrow Al_4C_3 + 6CO \qquad (1)$$

according to the partial pressure of carbon monoxide at 2100 K (Fig. 1).

Considering a closed system at a chosen temperature of 2100 K and under a total pressure (P_t) of 10^5 Pa, the equilibrium pressures of each species were calculated as a function of the partial pressure of carbon monoxide (P_{CO}). Hence, the boundaries between the predominance ranges of the different species were determined. For instance, the stability range of Al_4C_3 is determined by the following equations whose equilibrium constants K are given by JANAF tables:

$$2Al_2O_3 + 9C \rightleftharpoons Al_4C_3 + 6CO \qquad K_1 = 10^{-4\cdot268}$$

$$Al_4C_3 \rightleftharpoons 4Al_{(g)} + 3C \qquad K_2 = 10^{-8\cdot706}$$

$$Al_4C_3 + 2CO \rightleftharpoons 2Al_2O_{(g)} + 5C \qquad K_3 = 10^{-2\cdot638}$$

From these the equilibrium conditions were deduced:

$$K_1 = \frac{P_{CO}^6}{P_t^6}$$

i.e.

$$\log P_{CO} = \tfrac{1}{6}\log K_1 + \log P_t = 4\cdot289$$

If $P_{CO} < 10^{4\cdot384}$ Pa the formation of carbide is favoured.

$$K_2 = \frac{P_{Al}^4}{P_t^4}$$

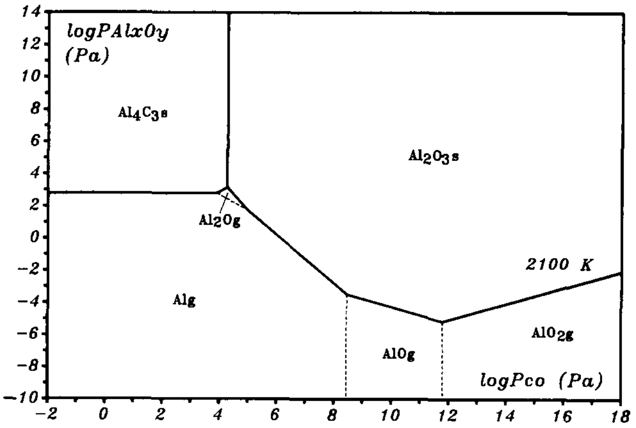

Fig. 1. Stability diagram of the alumineous phases according to the partial pressure of carbon monoxide at 2100 K.

i.e.

$$\log P_{Al} = \tfrac{1}{4}\log K_2 + \log P_t = 2\cdot824$$

whatever P_{CO} is. If $P_{Al} > 10^{2\cdot824}$ Pa the carbide is the most stable species, but if P_{Al} is inferior to this value, carbon is mixed with some carbide, in equilibrium with gaseous aluminium.

$$K_3 = \frac{P_{Al_2O}^2}{P_{CO}^2}$$

i.e.

$$\log P_{Al_2O} = \log P_{CO} + \tfrac{1}{2}\log K_3 = \log P_{CO} - 1\cdot319$$

The boundary is an oblique line with the stability range of Al_4C_3 in the upper part. The area determined by the section bounded by the three so-drawn straight lines (upper left part of Fig. 1) is that of the predominance of the carbide Al_4C_3. These lines are not to be considered out of this part, because other equilibria, not presented here, are determinant.

Concerning the dotted lines (Fig. 1) between the gaseous species, these are established by assuming that their partial pressures are identical.

So, for the highest pressures of carbon monoxide, alumina is in equilibrium with gaseous AlO_2, then, lowering the carbon monoxide pressure, with AlO, and, subsequently, with gaseous aluminium. For the lowest partial pressures of carbon monoxide the carbide Al_4C_3 appears in equilibrium with gaseous aluminium. In a very narrow range of carbon monoxide pressures (near 10^4 Pa) alumina is in equilibrium with Al_2O. This gaseous phase only appears above 1800 K.

3 Experimental

The apparatus consisted of an electric furnace with a graphite resistor in which mixtures of alumina and lamp black, according to eqn (1), were put into a vitreous carbon crucible. The temperature was controlled by an optical pyrometer and the furnace was heated under an atmospheric pressure of flowing argon. The outflowing gases phases went through an infrared analyser to detect their carbon monoxide or dioxide content.

In the side of the furnace, a window of quartz allowed sighting of the top of the powder bed, through a small hole made in the side of the crucible. In front of this window was disposed a spectrometer (JOBIN-YVON THR 1000) with a photomultiplier and an informatic treatment of the signal. The range of detection was from 190 to 870 nm.

The powders used were alumina provided by Fluka (Ø 0·3 μm, specific area = 5·7 m^2/g) containing less than 0·01% of total impurities, and lamp black from Prolabo S.A. with residual ashes <0·75% (Ø = 0·2–0·3 μm, specific area = 30 m^2/g). The powders were mixed in an agate mortar and small amounts (200 mg) were put into the crucible for heating according to the following conditions: heating rate of 20 K/min and argon flowing at 110 liters/h.

4 Results

Without powder in the crucible, the furnace heated under flowing argon at 1800°C gave a continuous spectrum with an important intensity between 400 and 850 nm (Fig. 2). So, it would have been very difficult to detect any weak signal in this range, and the analysis was limited to the UV range from 200 to 400 nm.

When heating the mixture in the furnace, several discrete peaks were obtained appearing from 1400°C (Fig. 3). Table 1 provides their wavelengths and their relative intensities at 1500°C. These peaks correspond to those of the emission spectrum of aluminium,[7–10] also given in Table 1.

When increasing the temperature, a correlative increase of the intensity of the emission lines was observed (Fig. 4), and, from 1600°C, a reversion of the ultimate lines was noticed, characteristic of an important self-absorption.

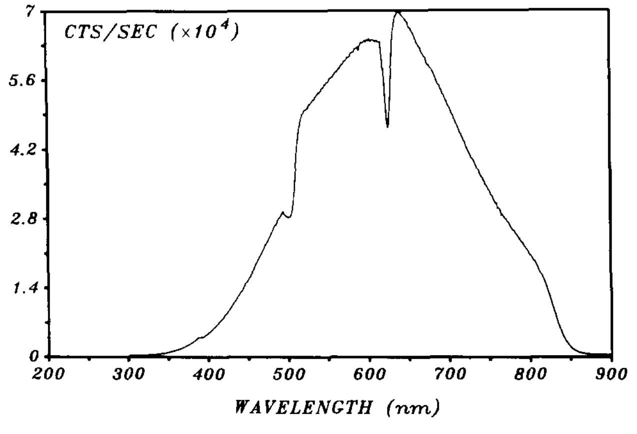

Fig. 2. Continuous spectrum of the furnace heated at 1800°C.

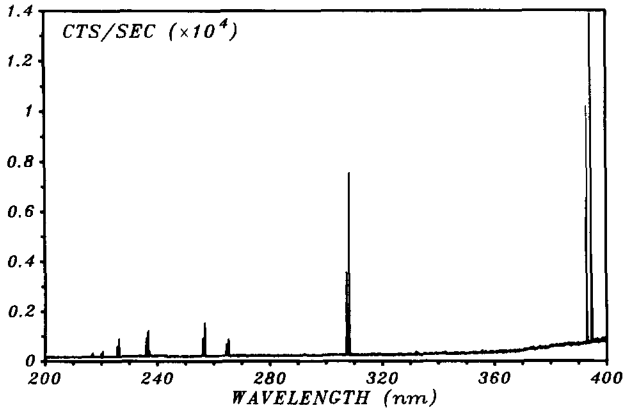

Fig. 3. Emission spectrum appearing when heating a mixture C/Al_2O_3 at 1500°C.

Then the isothermal development of the reaction was followed at 1800°C by observing the changes of the intensities of the two ultimate emission lines (394·40 and 396·15 nm). Figure 5 shows that the intensities of the peaks were maximal after 20 min at this stage, then decreased rapidly for 1 h and more slowly subsequently.

When the temperature was increased between 1450°C and 1750°C, the quantity of carbon mon-

Table 1. Comparison between the emission lines observed at 1500°C and those of aluminium vapour

Emission lines observed (nm)	*Intensities observed*[a]	*Emission lines of aluminium (nm) from Refs 7–10*
216·88	M	216·88
217·40	M	217·40
220·46	M	220·46
221·00	M	221·00
225·99	W	225·99
226·35	M	226·35
226·92	M	226·91
		226·92
236·71	S	236·71
237·21	M	237·21
237·32	S	237·31
		237·34
237·84	M	237·84
256·80	S	256·80
257·51	S	257·51
		257·54
265·25	S	265·25
266·04	S	266·04
305·01	VW	305·01
		305·47
305·71	VW	305·72
		306·43
		306·62
308·22	VS	308·22
309·28	VS	309·27
		309·28
394·40	VS	394·40
396·15	VS	396·15

[a] vw = very weak; w = weak; m = medium; s = strong; vs = very strong.

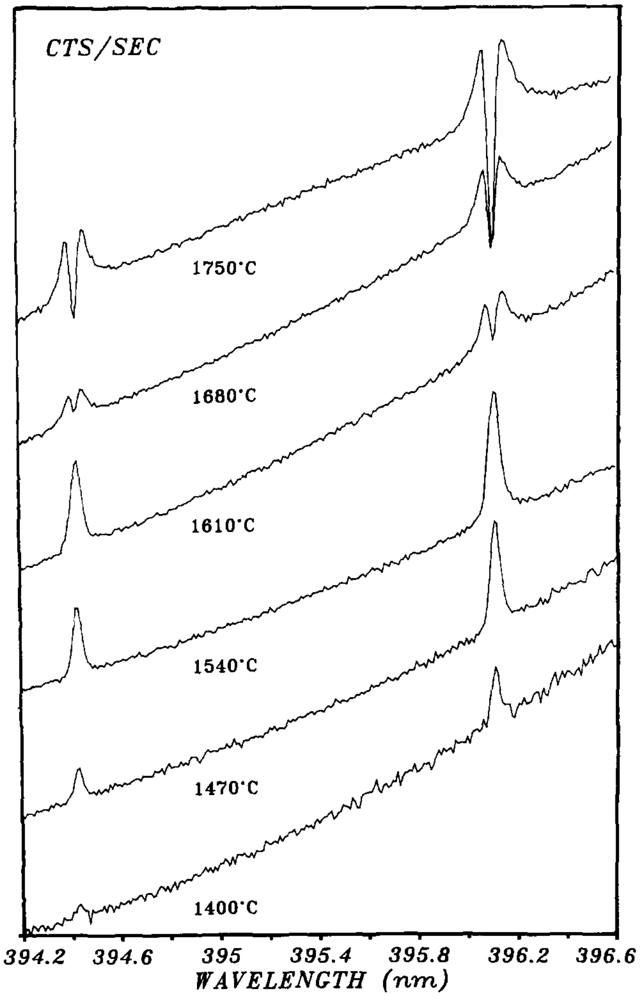

Fig. 4. Modifications of the two ultimate emission lines when heating a mixture alumina–carbon between 1400°C and 1800°C in argon.

oxide first formed rapidly grew to reach a maximum content in the furnace atmosphere of 0·32 vol.% (Fig. 6). Then its formation became slower and its content lowered (0·18 vol.% at 1800°C).

When the reaction was stopped after short times (5 min), two products were identified: the oxycarbide Al_2OC and traces of carbide Al_4C_3, but no alumina was found as it had totally reacted. For longer times, the quantity of carbide formed increased as long as it remained Al_2OC, i.e. for durations of about 1 h at 1800°C. Above those times (Table 2), only the carbide was obtained and losses of weight due to the progressive decomposition of carbide continued to be observed. For instance, after 5 h, the total weight loss was 70·5% at 1800°C, while the theoretical weight loss due to the outflow of carbon monoxide is only 53·86% according to eqn (1), and a mixture of carbon and aluminium carbide remained in the crucible.

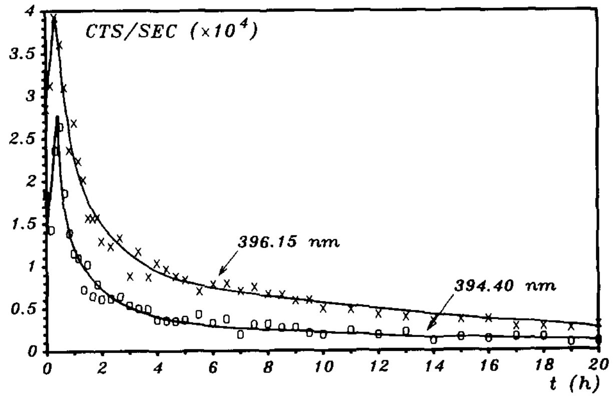

Fig. 5. Changes of the intensities of the two ultimate emission lines during the isothermal reaction at 1800°C in argon.

As a complement, and for testing the influence of the partial pressure of carbon monoxide and of the carbon on the formation of aluminium emission

Table 2. Total weight loss and X-ray analysis for different times at 1800°C

t (h)	$\Delta m/m_0$ *(%)*	*Identified phases*
0·08	27·2	Al_2OC–Al_4C_3–C
1	53·0	Al_4C_3–Al_2OC–C
2	66·5	Al_4C_3–C
5	70·5	Al_4C_3–C
10	72·5	Al_4C_3–C

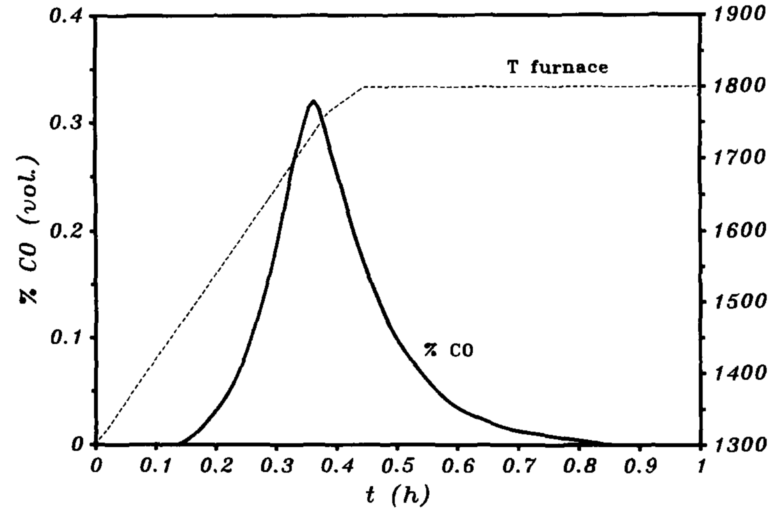

Fig. 6. Carbon monoxide content during the reaction.

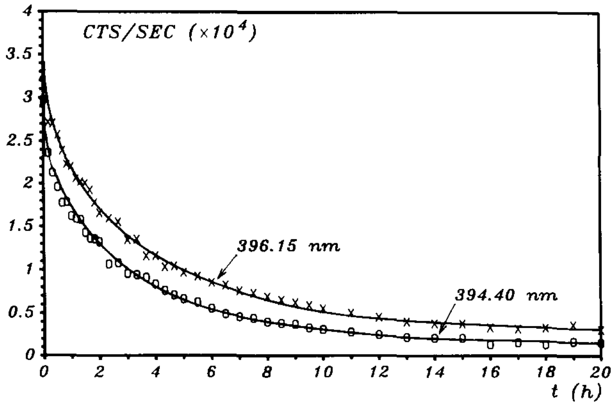

Fig. 7. Intensities of the two ultimate emission lines during the isothermal reaction at 1800°C, under a mix of argon/carbon monoxide (5%) gas flowing.

lines, first the pure argon gas flowing was substituted by a mix of argon with 5 vol.% carbon monoxide. Then, keeping the pure argon atmosphere, alumina was heated alone in the crucible.

The addition of carbon monoxide in flowing argon delayed the beginning of the aluminium emission lines until 1600°C was reached (instead of at 1400°C without CO). During the first hour of heating at 1800°C (Fig. 7), the increase of aluminium emission lines was not observed but rather they continuously decreased in intensity over 20 h. The weight loss was lower (60% instead of 70·5% after 5 h) and the X-ray diffraction analysis showed that a final mixture of Al_2OC (major constituent) and Al_4C_3 was obtained instead of Al_4C_3 alone.

When heating pure alumina in argon up to 1800°C in the same quantity (130·7 mg) that was introduced when using 200 mg of the C/Al_2O_3 mixture the aluminium emission lines were again observed (Fig. 8). At the beginning, they were a little less intense than when alumina was mixed with carbon, but their intensities decreased more slowly with time, so that they were more intense after short times (1 h). No initial increase was observed. Although no carbon was introduced, carbon monoxide formation was observed, but more slowly than when using oxide/carbon mixtures. The maximum content (0·30 vol.%) appeared close to 1800°C before decreasing continuously, and more slowly (Fig. 9). When opening the furnace after cooling, it was noticed that the alumina had quite completely disappeared.

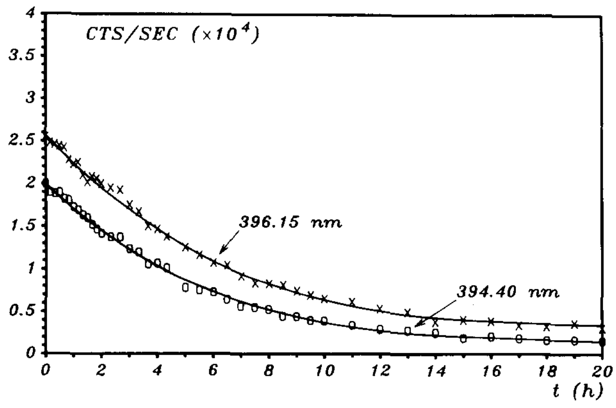

Fig. 8. Intensities of the two ultimate emission lines when heating pure alumina at 1800°C in argon.

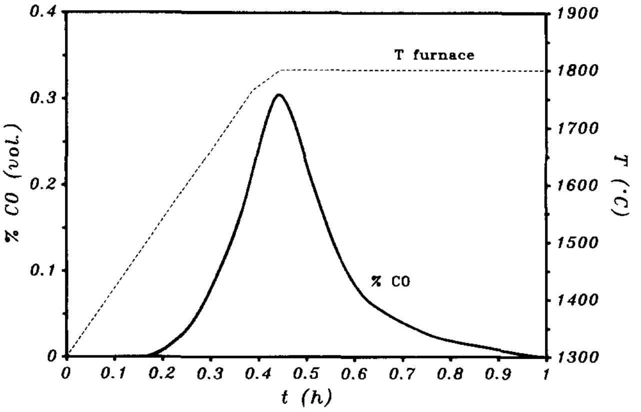

Fig. 9. Carbon monoxide content when heating alumina.

5 Discussion

The overall results clearly show that, by the spectrometric analysis method, gaseous aluminium can be identified above the alumina, according to the equation:

$$2Al_2O_3 \rightleftharpoons 4Al + 3O_2 \tag{2}$$

whether alumina is alone or mixed with carbon. Even when alumina is alone, the partial pressure of oxygen in the furnace is fixed by the following equilibrium:

$$2C + O_2 \rightleftharpoons 2CO \tag{3}$$

because of the great excess of carbon due to the conception of the furnace (with a graphite resistor and graphite thermal insulations). It explains why quite the same emission of carbon monoxide was observed with or without added carbon. Nevertheless it is possible that the transport of oxygen from the crucible to the resistor (for instance) explains the shift towards high temperatures of the outflow of carbon monoxide (compare Figs 6 and 9). The carbon monoxide content measurements lead to the evaluation of its partial pressure in the furnace at low values, below $P_{CO} = 3 \times 10^2$ Pa under the experimental conditions. So the calculated equilibrium partial pressure of gaseous aluminium P_{Al} reaches $2{\cdot}9 \times 10^5$ Pa by using the constants of equilibria (2) and (3).[6] The so-formed aluminium is, for instance, likely to condense on the cold surfaces of the furnace, explaining the progressive disappearance of alumina. During this reaction, the alumina grains become smaller and smaller, lowering their external surface: the dilution by argon becomes more important, and the aluminium emission lines logically become weaker and weaker as observed.

For the alumina and carbon mixtures, the reaction begins at 1400°C and, on reaching 1800°C, alumina is quite completely transformed into Al_2OC (it was observed that there is no more alumina after 5 min of isothermal treatment). It is clear that an intermediate reaction according to the overall equation:

$$2Al_2O_3 + 6C \rightarrow 2Al_2OC + 4CO \qquad (4)$$

first occurs, mainly during the nonisothermal treatment. Comparing eqn (4) to eqn (1) it appears that the major part of the carbon monoxide emission accompanies this first reaction, explaining why this emission is already decreasing before the maximum temperature is reached. During that time, the constant presence of aluminium vapour (Fig. 4) shows that the formation of Al_2OC necessarily results from the reaction of aluminium (vapour) with carbon monoxide:

$$2Al + CO \rightarrow Al_2OC \qquad (5)$$

This equilibrium is shifted in the direction of the decomposition of the oxycarbide when the partial pressure of monoxide is lowered. This happens after a short time at 1800°C, since P_{CO} falls (Fig. 6). Then reaction (2) providing oxygen is over, and consequently carbon monoxide formation occurs through reaction (3). So, following eqn (5), important amounts of aluminium vapour are released after short times of being maintained at 1800°C, explaining the initial increase of the aluminium emission lines shown in Fig. 5. Then the oxycarbide Al_2OC goes on decomposing by this route until gaseous aluminium is present (about 1 h at 1800°C). This mechanism explains the continuation of the aluminium emission lines observed while Al_2O_3 has completely disappeared.

It can be observed that a threshold exists for the carbon monoxide content in order to obtain Al_2OC: even when alumina is alone, a carbon monoxide emission takes place, but its partial pressure is not sufficient to allow formation of aluminium oxycarbide.

Gaseous aluminium released at 1800°C by eqn (5) is then likely to react with residual carbon to form the carbide according to eqn (6):

$$4Al + 3C \rightleftharpoons Al_4C_3 \qquad (6)$$

So, both equilibria (5) and (6) would coexist while Al_2OC is not completely converted into Al_4C_3, gaseous aluminium being provided by eqn (5) and consumed through eqn (6). During the progressive disappearance of aluminium oxycarbide, the aluminium emission lines logically decrease.

This explanation agrees with the experimental results but only a fine study of the conversion of Al_2OC into Al_4C_3 would confirm this hypothesis. Nevertheless, when the carbide is formed at these temperatures, the equilibrium pressure of aluminium above the carbide is not negligible, reaching $6{\cdot}2 \times 10^2$ Pa at 1800°C.[6] So, it is not surprising that aluminium emission lines continue to be observed for a long time. Aluminium vapour probably also condenses on the cold parts of the furnace, slowly shifting, after a long time, equilibrium (6) in the direction of the decomposition of the carbide and explaining why losses of weight greater than the theoretical value and increasing with time are observed.

When using an atmosphere of argon with 5% carbon monoxide, the partial pressure of oxygen is fixed (eqn (3)) at a higher value than previously ($5{\cdot}7 \times 10^{-13}$ Pa), so lowering through equilibrium (2) the partial pressure of aluminium (4.3×10^3 Pa). The consequence is a slowing of the conversion of alumina into oxycarbide and, subsequently, a relative stabilization of the oxycarbide, according to eqn (5). Logically, the initial intense evolution of aluminium is no longer observed, but the slower decomposition of the oxycarbide is seen. Indeed, the oxycarbide is not completely stabilized, because the partial pressure of equilibrium of aluminium vapour above Al_2OC is probably close to 10^3 Pa (Fig. 1), and the argon flowing naturally induces a non-negligible decomposition. This explains why the weight loss, after 5 h, although smaller than without additional carbon monoxide (60% instead of 70·5%), is higher than the theoretical (35·9%).

6 Conclusion

This study brings the first direct experimental proof for the existence of gaseous aluminium above alumina at temperatures as low as 1400°C. When heating mixtures of alumina and carbon higher than 1400°C the reaction begins quickly and important amounts of carbon monoxide evolve. For carbon monoxide pressures of about 5×10^3 Pa, the gaseous aluminium formed reacts with CO, giving Al_2OC. Then when P_{CO} becomes lower the aluminium carbide is the most stable phase, and it was obtained in the present study.

Since no thermodynamic data were available for the oxycarbide Al_2OC, it could not be placed with precision in the diagram of Fig. 1. It would probably appear in a narrow range of carbon monoxide pressure close to 10^3–10^4 Pa, in the darkened area of Fig. 10.

The authors have a good confirmation of the existence of this stability range of Al_2OC at about that pressure of carbon monoxide, since the

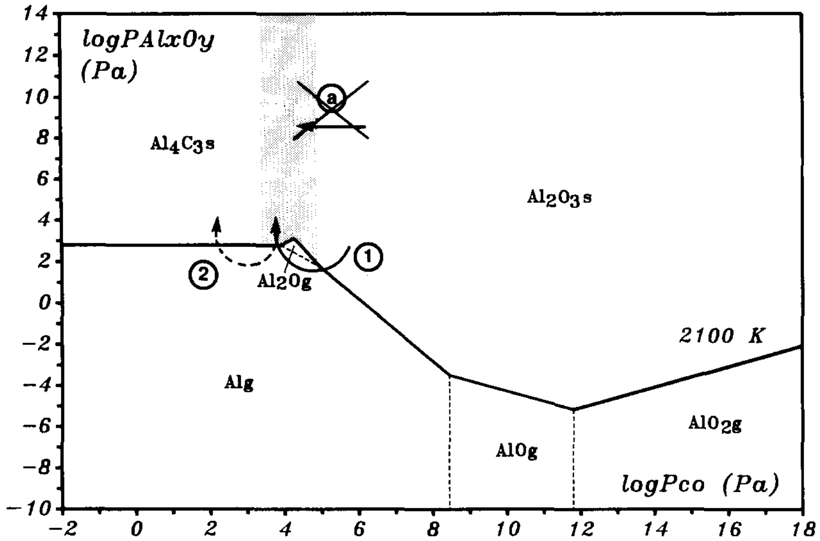

Fig. 10. Schematic possible route for the synthesis of aluminium carbide (with estimated stability range of Al_2OC, from the present work).

oxycarbide was obtained quite alone when the alumina and carbon mixtures were heated under an imposed partial pressure of carbon monoxide of 5×10^3 Pa.

Another difference is that the Al_2O gaseous phase was not observed. It is obvious that the present apparatus was not fit to detect such molecules, but, firstly, its presence would be exclusive of that of gaseous aluminium and, secondly, the global succession of reactions occurs at temperatures lower than 1500°C, where Al_2O is not thermodynamically stable. So, it is very unlikely that Al_2O quantitatively exists under the present experimental conditions.

Now, if the authors wanted to put the experimental results for the synthesis mechanism of Al_4C_3 on the stability diagram of Fig. 10, taking into account the added area of Al_2OC, the solid–solid route (arrow **a** in Fig. 10) can be eliminated and the route shown by arrow **1**, for the first step of the reaction, retained, providing the oxycarbide as an intermediate phase. The second step (dotted arrow **2**) corresponds to the authors' hypothesis of another gas–gas reaction favoured by a lowering of the partial pressure of carbon monoxide.

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