Formation of Aluminum Nitride by the Reaction Between Aluminum Oxide and Nitrogen Plasma Jet*

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Aluminum nitride was formed by the reaction between the aluminum oxide and the nitrogen plasma jet from a transferred plasma torch. The plasma jet was produced by passing rapidly nitrogen gas of ordinary pressure through an electric arc standing between a graphite crucible anode and a cooled tungsten cathode. Nitrogen plasma jet reacted rapidly with the pellet, made of aluminum oxide and graphite powder, placed on the crucible. The nitrogen flow rate was 1.5~4 l/min at power input of 4~7 kW. Greyish powder was deposited on the crucible, on the copper coil over the crucible and on the wall of the reaction chamber. It was confirmed that the powder was AlN including unreacted aluminum oxide and graphite. Influences on the nitriding reaction were studied for the mixing mole ratio of graphite to aluminum oxide, the current intensity, the nitrogen flow rate and the reaction time.

1. Introduction

Marynowski¹⁾ predicted the possibility of forming AlN through the chemical reaction between aluminum oxide and nitrogen plasma jet. De Vynck²⁾ prepared Al(CN)₃ by the reaction between aluminum oxide and nitrogen plasma jet containing propane.

The authors have also studied on TaN³⁾, Mo₂N⁴⁾, W₂N⁴⁾, TiN⁵⁾, AlN⁶⁾, and ZrN⁷⁾, which are formed by the reaction between corresponding metal rods and the nitrogen plasma jet using a transferred plasma torch. This paper deals with the result on the formation of aluminum nitride by the reaction between aluminum oxide and the nitrogen plasma jet conducted in this way.

2. Experimental

Materials : The pellets of 15 mm in diameter and 3 mm in thickness were made by the following way. Al₂O₃ and graphite were mixed

in estimated ratio. 1 g of the mixed powder was pressed using pitch as binder and was baked at about as 1100°C for 4 hours. Argon and nitrogen of high purity were used.

Apparatus : The apparatus for the reaction was described previously.³⁾ The pellets were set on the graphite crucible placed on the copper

1. Plasma torch 2. Graphite crucible
3. Pellet 4. Cooling coil

Fig. 1 Reaction apparatus

*Studies of Chemical Reactions at High Temperatures (Part 6).
The original written in Japanese in *Denki-kagaku* 36, 41 (1968).

block as shown in Fig.1. The arc was radiated between the tungsten cathode in the torch and the graphite crucible. The nozzle diameter of the plasma torch was 7 mm.

Methods : The reaction of nitride formation was carried out in the same way as described previously.³⁾ The products were confirmed by X-ray diffraction and chemical analysis.

Fig. 2 Potential - current curves
current intensity (A)

Fig. 3 Relation between power input and nitrogen flow rate

3. Results and Discussions

3.1 Energy for Nitride Formation

a) Characteristics of the plasma torch. The characteristics of the plasma torch were examined for graphite crucible as anode. Potential - current curves are shown in Fig.2. The power input increased with increasing nitrogen flow rate as shown in Fig.3.

b) Energy for the nitrogen plasma jet. From Fig.3, the relation between the nitrogen flow rate and the energy of the nitrogen plasma jet ($\text{kW}\cdot\text{min}/\text{l}$) was calculated, the results being shown in Fig.4. The energy per unit volume of the gas decrease with increasing nitrogen flow rate. From Fig.4, one can easily suppose that the sufficient energy is supplied to nitrogen gas to form atomic nitrogen or nitrogen cation. Therefore, the nitrogen plasma jet would consist in N , N^+ electron and small amount of N_2 .

Fig. 4 Relation between energy and nitrogen flow rate

3.2 Confirmation of the Products

When the nitrogen plasma jet reacted with the pellet, greyish powder was deposited on the crucible, on the coil and on the walls of the chamber. The cake formed on the crucible by the reaction was also grey.

Each product was weighed and the composition was determined by X-ray diffraction and

Fig. 5 X-ray diffraction patterns of products on the various parts of the furnace

chemical analysis.

Typical X-ray diffraction patterns are shown in Fig.5. The product deposited on the crucible was confirmed to be AlN, while the cake formed on the crucible was AlN containing unreacted Al_2O_3 and graphite. The product deposited on the coil and on the wall of the chamber were amorphous.

3.3 Temperature Measurement

The surface temperature of the pellet and

Fig. 6 Relation between surface temperature and current intensity

the graphite crucible under the nitrogen plasma jet were measured with a micropyrometer. The relation between the surface temperature and the current intensity is shown in Fig.6. The measured values were corrected on the basis of Wien's equation.

The surface temperature of the pellet rose with increasing current intensity. The surface temperature of the graphite crucible also rose with the increase of current intensity up to 80A. When the current intensity exceeded 80A, the surface temperature of the crucible became nearly constant.

Table 1 Influence of C/ Al_2O_3 on AlN Formation

C/ Al_2O_3	Coil and wall		Crucible		Residue of pellet	
	Yield (g)	AlN content (%)	Yield (g)	AlN content (%)	Yield (g)	AlN content (%)
0	0.678	1.91	0.179	1.82	—	—
0.5	0.420	4.79	0.233	3.58	—	—
1.0	0.279	6.87	0.213	9.32	—	—
2.0	0.306	4.51	0.202	16.7	—	—
3.0	0.268	8.23	0.113	69.1	0.007	58.3
4.0	0.250	7.70	0.102	62.4	0.015	51.8
6.0	0.286	12.0	0.073	67.3	0.141	21.2

Reaction condition: 80sA, 3 l/min, 2 min.

3.4 Influences of Various Conditions on the Reaction of AlN Formation

As a degree of the reaction amount, aluminum conversion rate (Al C.R.) is defined as follows:

Al C.R. (%) = (Al as AlN in total product (g)/Al as Al₂O₃ in original pellet (g)) x 100

a) Influences of the mixing ratio of carbon to Al₂O₃ (C/Al₂O₃). The influence of C/Al₂O₃ on the yield and the content of AlN in the product are listed in Table 1. The relation between Al C.R. and C/Al₂O₃ is shown in Fig. 7. The Al C.R. of the product on the coil and of the cake formed on the crucible increased gradually with increasing C/Al₂O₃. Al C.R. of the product deposited on the crucible increased with

increasing C/Al₂O₃ up to C/Al₂O₃ = 3. When C/Al₂O₃ exceeded 3, Al C.R. of the product deposited on the crucible became almost constant. Al C.R. of total products increased with increasing C/Al₂O₃.

X-ray diffraction patterns of products deposited on the crucible at few various ratio (C/Al₂O₃) are shown in Fig.8. When C/Al₂O₃ exceeded 3, main product was AlN. From these results obtained by chemical analysis and X-ray diffraction method, the reaction seems to proceed rapidly for C/Al₂O₃ larger than 3.

b) Influence of the current intensity The

Fig. 7 Relation between Al C.R. and C/Al₂O₃

C : Graphite, α-A : α-Al₂O₃, β-A : β-Al₂O₃, N : AlN
Al₂O₃ : I 0, II 0.5, III 1, IV 2, V 3, VI 4, VII 6.

Fig. 8 X-ray diffraction diagrams obtained for various C/Al₂O₃

Table 2. Influence of the Current Intensity on AlN Formation

Current Intensity (A)	Coil and wall		Crucible		Residue of pellet	
	Yield (g)	AlN content (%)	Yield (g)	AlN content (%)	Yield (g)	AlN content (%)
60	0.192	12.4	0.098	48.6	0.316	16.5
70	0.230	13.6	0.075	45.4	0.080	34.6
80	0.286	12.0	0.073	67.3	0.141	21.2
90	0.247	15.6	0.080	51.5	0.128	22.3
100	0.339	17.1	0.091	65.4	0.006	52.6

Reaction conditions: C/Al₂O₃ = 6, 3 l/min, 2 min.

Fig. 9 Relation between Al C.R. and current intensity

influence of the current intensity on the yield and content of AlN in the product are listed in Table 2. The relation between Al C.R. and the current intensity is shown in Fig.9. Al C.R. of products deposited on the coil and on the crucible gradually increased with the increasing current intensity. Al C.R. of the cake formed on the crucible decreased with increasing current intensity. However, Al C.R. of the total products are kept nearly constant in spite of the variation of the current intensity, if the nitrogen flow rate had been held at an appropriate value.

c) Influence of the nitrogen flow rate The

Fig. 10 Relation between Al C.R. and nitrogen flow rate

influence of the nitrogen flow rate on the yield and the content of AlN of the product is listed in Table 3. The relation between Al C.R. and the nitrogen flow rate is shown in Fig.10. Al C.R. of the product deposite on the coil and on the crucible gradually increased with increasing nitrogen flow rate. Al C.R. of the cake formed on the crucible linearly decreased with increasing nitrogen flow rate. Al C.R. of the total products became maximum at about 2 l/min of the nitrogen flow rate.

d) Influence of the reaction time The influence of the reaction time on the yield and the content of AlN of the product is listed in Table 4. The relation between Al C.R. and the reaction

Table 3. Influence of the Nitrogen Flow Rate on AlN Formation

N ₂ Flow Rate (l/min)	Coil and wall		Crucible		Residue of pellet	
	Yield (g)	AlN content (%)	Yield (g)	AlN content (%)	Yield (g)	AlN content (%)
1.5	0.153	11.9	0.042	65.2	0.494	10.9
2.0	0.171	18.9	0.063	52.0	0.351	13.2
3.0	0.286	12.0	0.073	67.3	0.141	21.2
4.0	0.287	13.2	0.124	35.8	0.025	62.3

Reaction conditions: C/Al₂O₃ = 6, 80A, 2 min.

Fig. 11 Relation between Al C.R. and Reaction time

time is shown in Fig.11. Al C.R. with respect to the product deposited on the coil increased linearly with increasing reaction time. Al C.R. of the product deposited on the coil increased with increasing reaction time up to 60 sec. At this point it became nearly constant in spite of the elongation of the reaction time. Al C.R. of the cake formed on the crucible was kept nearly constant in spite of the variation of the time. Al C.R. of the total product increased with increasing reaction time.

Substances on the surface of the cake which was formed on the crucible were offered to X-ray diffraction and chemical analysis. Results obtained are given in Fig.12 and Table 5, which

Reaction time : I. 15sec, II. 30sec, III. 60sec, IV. 120sec.
Reaction conditions : C/Al₂O₃ = 6, 80A, 3l/min

Fig. 12 X-ray diffraction patterns of products sampled from the surface of the cake at various reaction time

Table 5 Relation Between the Reaction Time and AlN Formation on the Pellet Surface

Reaction time (sec)	Sample weight (g)	AlN content (%)
15	0.110	19.0
30	0.125	25.3
60	0.134	24.3
120	0.141	21.2

Reaction condition: C/Al₂O₃ = 6, 80A, 3 l/min.

indicate that the crystallization of AlN proceeds with the lapse of the reaction time.

Table 4 Influence of the Reaction Time on AlN Formation

Reaction Time (sec)	Coil and wall		Crucible		Residue of pellet	
	Yield (g)	AlN content (%)	Yield (g)	AlN content (%)	Yield (g)	AlN content (%)
30	0.070	9.82	0.020	61.3	0.683	4.72
60	0.117	12.5	0.080	60.2	0.366	8.58
90	0.233	12.0	0.079	56.3	0.182	15.9
120	0.286	12.0	0.073	67.3	0.141	21.2

Reaction conditions: C/Al₂O₃ = 6, 80A, 3 l/min.

3.5 Discussion on AlN Formation

As mentioned above, the nitrogen plasma jet is supposed to consist in N , N_2^+ electron and a small amount of N_2 . Heavy heating by plasma jet will cause the melting of Al_2O_3 . AlN formation will proceed through the reaction between N (or N^+) and the molten Al_2O_3 . The mixing ratio of carbon to Al_2O_3 (C/Al_2O_3) is also very effective to the reaction of AlN formation. The reaction of AlN formation was found to proceed faster when C/Al_2O_3 becomes to 3. When $C/Al_2O_3 = 3$, the content of AlN in the product deposited on the crucible was highest and X-ray diffraction pattern shows that the product is almost AlN.

- 1 : $Al_2O_3 + 3/2C + N_2 \rightleftharpoons 2AlN + 3/2CO_2$
 2 : $Al_2O_3 + 3/2C + 2N \rightleftharpoons 2AlN + 3/2CO_2$
 3 : $Al_2O_3 + 3C + N_2 \rightleftharpoons 2AlN + 3CO$
 4 : $Al_2O_3 + 3C + 2N \rightleftharpoons 2AlN + 3CO$

Fig. 13 Relation between ΔF of the reaction of AlN formation and temperature

When C/Al_2O_3 exceeded 3 the diffraction lines of graphite appeared. Therefore we concluded that suitable C/Al_2O_3 for the reaction of AlN formation is 3.

The temperature dependencies of the free energy change were calculated for probable reactions of AlN formation and are shown in Fig.13⁸⁾. Inspection of Fig.13 suggest the formation of AlN at 3000°K to proceed through the reaction,

Since AlN begin to sublime over 2000°C, AlN formed on the surface of the pellet would be sublimated and deposited on the coil, on the wall of the chamber and on the crucible. The products on the coil and on the wall of the chamber may be cooled suddenly and thus deposited as amorphous. On the other hand, the product on the crucible suffers gradual cooling to be able to crystallize.

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