

Effects of Magnesium Catalyst on the Nitridation of Aluminum Melt in the Synthesis of Aluminum Nitride Powder

Hyo-Jin Kim[†], Sung-Hun Kim[†], Sung-Min Lim, Jong-Hyun Seo, Kon-Bae Lee^{1,*},
Jae-Chul Lee², Jae-Pyoung Ahn^{*}

Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 130-650, Korea

¹*School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Korea*

²*Department of Materials Science and Engineering, Korea University, Seoul 136-701, Korea*

[†]Equally contributed first authors.

*Correspondence to:

Ahn JP,
Tel: +82-2-958-5536
Fax: +82-2-958-9674
E-mail: jpahn@kist.re.kr

Lee KB,
Tel: +82-2-910-4230
Fax: +82-2-910-4320
Email: kblee@kookmin.ac.kr

Received June 11, 2014

Revised June 27, 2014

Accepted June 27, 2014

Aluminum nitride (AlN) powder was easily synthesized by the direct nitridation of Al melt containing ~20 wt.% Mg catalyst and the nitriding behavior was investigated by thermodynamic calculation and through observations of electron microscopy and X-ray diffraction. The addition of Mg catalyst decreased the nitriding temperature below 1,000°C, which is comparable to the high nitriding temperature of 1,400°C required in carbothermal method. It was caused by a significant increase of the solubility of nitrogen gas due to the increase of Mg catalyst in Al melt. The dissolved nitrogen gas met Mg catalyst and was transformed into metastable Mg₃N₂. Finally the metastable phase reacted with Al to AlN.

Key Words: AlN powder, Mg catalyst, Nitridation

INTRODUCTION

Aluminum nitride (AlN) powder is a high value-added basic material with excellent characteristics. AlN has numerous attractive properties including high thermal conductivity (220 W/m·K), good electrical resistance ($14 \times 10^{13} \Omega \cdot \text{cm}$), low dielectric loss, ideal thermal expansion ($4 \times 10^{-6}/\text{K}$) match with silicon, and good mechanical strength (430 MPa). Therefore, AlN is the ideal material for high density, high-power, and high-speed integrated circuit applications (Selvaduray & Sheet, 1993; Okada et al., 2000; Zhang et al., 2001; Haibo et al., 2005). Carbothermal reduction of alumina powder is a representative method already applied industrially, and it has the advantage of

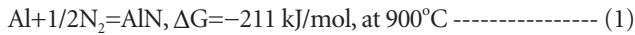
synthesis of uniform particles. However, this method requires a reaction temperature as high as 1,700°C~1,800°C and also high purity alumina powder as a reactant is necessary for synthesis of high purity AlN powder making it an expensive material (Okada et al., 2000). In recent, it is required to develop more economical processes that can produce AlN powders of high thermal conductivity for heat-sink applications in high temperature and high power microelectronic devices. For example, AlN powder is used as filler for high-heat-conductive thick-film. Because the purity of AlN is not so important in this application, low-cost AlN may be also a very good candidate for AlN substrates boned metallic thin film, heat sink substrates for the light emitting diodes (LEDs) and power

This work was supported by a grant from the Fundamental R&D Program for Core Technology of Materials (10037309, Metal matrix composites by gas reaction control) funded by the Ministry of Knowledge Economy, Republic of Korea and the Priority Research Centers Program through the National Research Foundation of Korea funded by the Ministry of Education, Science, and Technology (2012-0006680) and the Leading Foreign Research Institute Recruitment Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (MSIP) (2013K1A4A3055679).

© This is an open-access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted noncommercial use, distribution, and reproduction in any medium, provided the original work is properly cited.
Copyrights © 2014 by Korean Society of Microscopy

transistors, for power control parts of hybrid car, etc (Pi et al., 2009).

In this study, we report a large-scale production method capable of synthesizing relatively low cost AlN powder in a very short time using Al melt. Generally, it is well-known that nitridation in a gas bubbling method with nitrogen gas through Al melt is possible to occur according to following reaction.



However, because this process is very slow, it cannot use to produce AlN in commercial-scale. Therefore, it is necessary to develop a new process for production of the low cost AlN. We developed a new method for large-scale producing the AlN powder of low cost. In this method, Mg is added into Al melt as a catalyst for acceleration of the nitridation. This result is different from previous reports used Al melt added the Mg, which were showed a relatively low nitridation below 5% (Kumari et al., 2011). However, we can obtain nearly complete nitridation with Mg contents. Therefore, the effect of Mg on the mechanism of accelerated formation of AlN in the Al-Mg system was analyzed from scanning electron microscope (SEM) and transmission electron microscope (TEM) observation and thermodynamic interpretation.

MATERIALS AND METHODS

Nitriding was carried out in an induction furnace, as schematically shown in Fig. 1. The ingots of 1,050 Al and ~20 wt.% Mg were loaded in the crucible (alumina or graphite) and the furnace was heated to $700^\circ\text{C} \sim 1,000^\circ\text{C}$ and held for 1~10 hours under a flowing nitrogen atmosphere in the retort

furnace to maintain 1 bar of furnace pressure. The melts were occasionally stirred with carbon rod if needed. After completion of nitriding, reaction products were cooled and then pulverized by the crushing process.

The microstructure and phase analysis of the products were characterized using X-ray diffraction (XRD), SEM, and TEM. In addition, thermodynamic behavior with temperature, pressure, and Mg addition were interpreted by Thermodynamical program (Thermo-Calc Software Inc., Sweden).

RESULTS AND DISCUSSION

In order to identify nitrogen state in Al-N binary system, i.e.,

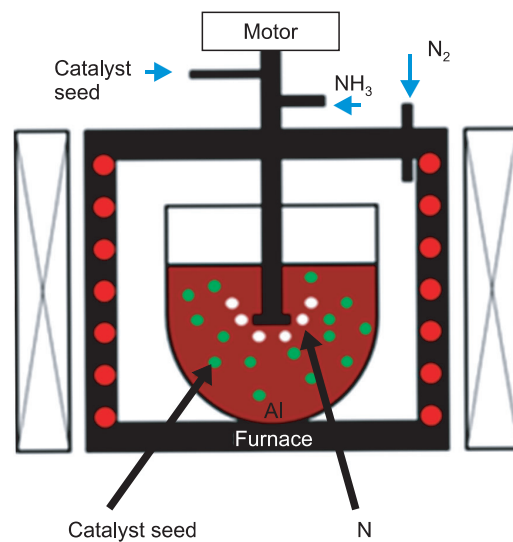


Fig. 1. Schematic diagram of electrical furnace used in the direct nitridation of Al melt.

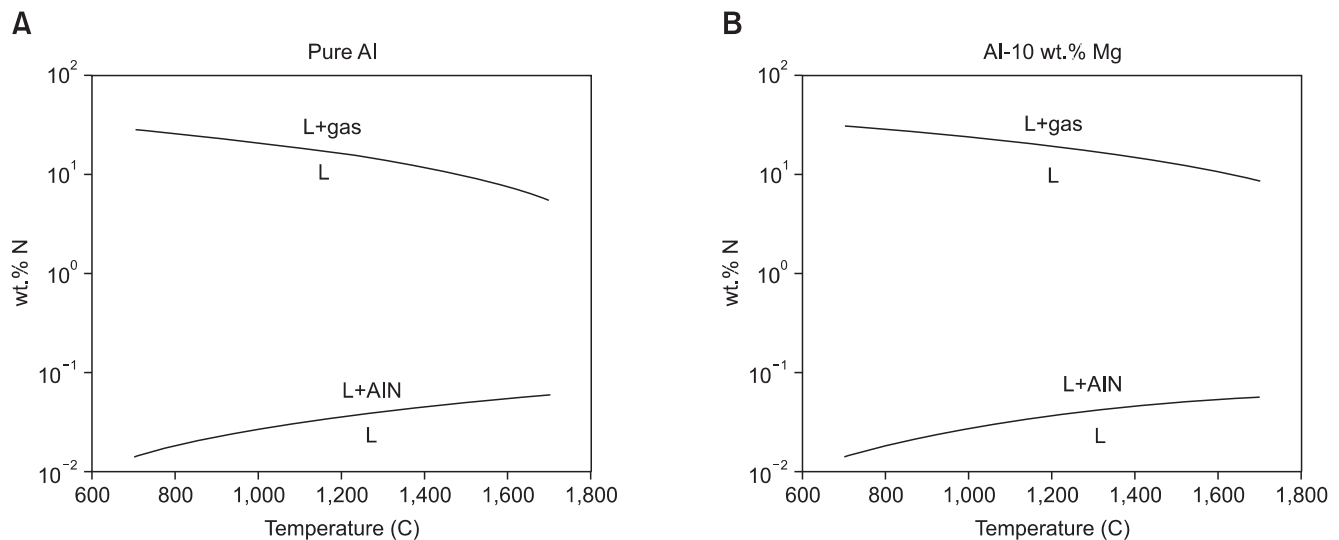


Fig. 2. Solubility of nitrogen gas in Al-N binary system under the gas pressure of (A) $P_{\text{N}_2} = 1$ bar and (B) $P_{\text{N}_2} = 10$ bar.

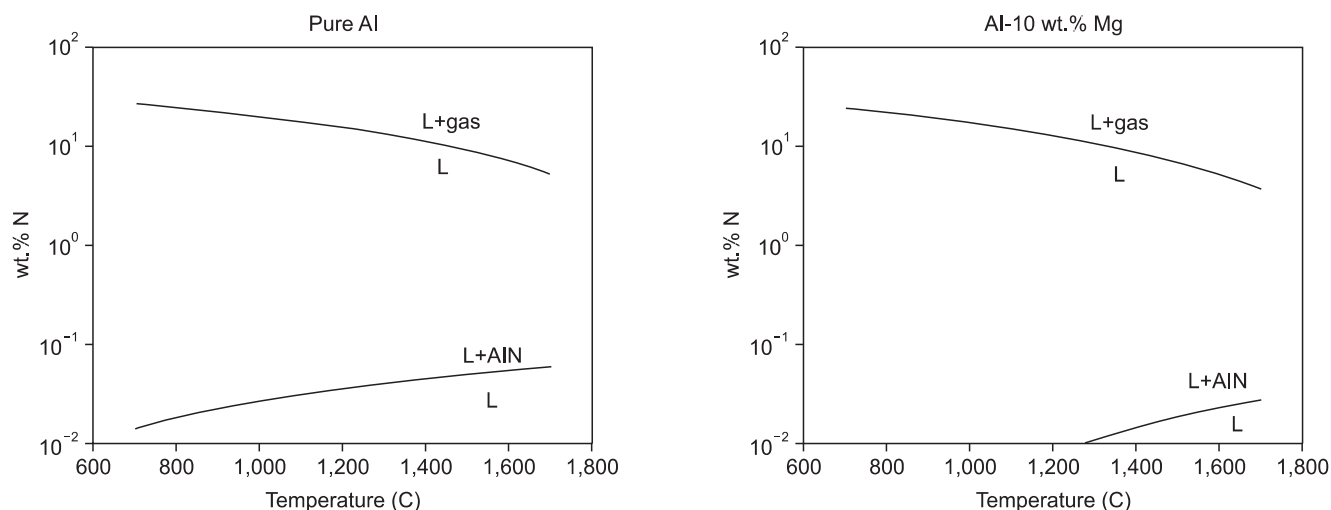


Fig. 3. Solubility of nitrogen gas to AlN as a function of nitriding temperature under $P_{N_2}=1$ bar and Al-10 wt.% X-N (X=catalyst).



Fig. 4. Optical image of AlN powder synthesized under the condition of Al-10 wt.% Mg-N.

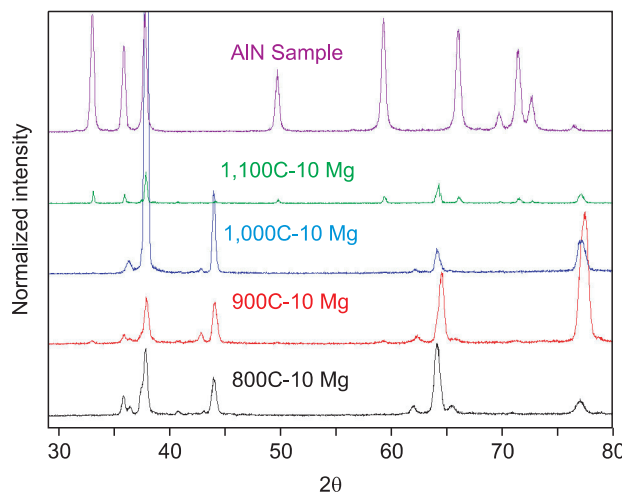


Fig. 5. X-ray diffraction pattern of AlN powder synthesized for 1 hour at various temperature under the condition of Al-10 wt.% Mg-N.

whether it is gas or AlN state, the effect of partial pressure of nitrogen on solubility of nitrogen in both nitrogen gas and AlN was analyzed as shown in Fig. 2. There is no significant difference in solubility of nitrogen with partial pressure of nitrogen gas in both case. When the partial pressure of nitrogen gas was 1 and 10 bar, solubility of nitrogen in the AlN was increased with temperature. However, because it was decreased in the nitrogen gas, one may expect that formation of the AlN can be enhanced with temperature increase. In addition, because dissolution of the nitrogen gas around AlN formed may be increased with temperature, it can promote the growth of AlN.

From the thermodynamic interpretation, it can be seen that there is no large difference in phase equilibrium and nitrogen solubility due to pressure change in Al-N binary system. However, because dissolution of the nitrogen gas increase

and decrease in both the AlN and the nitrogen gas with temperature increase, respectively, it is believed that it may affect the growth of AlN already formed.

Fig. 3 shows the variation of nitrogen solubility for both gas and AlN in the case of the 10 wt.% Mg addition, as well as in pure Al. Contrary to the pure Al, when Mg is added into Al, while nitrogen solubility for gas is not changed, that for AlN decreased. This means indirectly that nitrogen is more stable being dissolved within the Al melt rather than the AlN. It also shows that nitrogen for AlN cannot dissolve in AlN below 1,200°C~1,300°C. Because nitrogen solubility for gas is not changed, however, most of the nitrogen is dissolved into the Al melt and thus driving force for nitriding increases. When Mg is added into the Al melt, variation of the nitrogen solubility with both temperature and pressure may cause

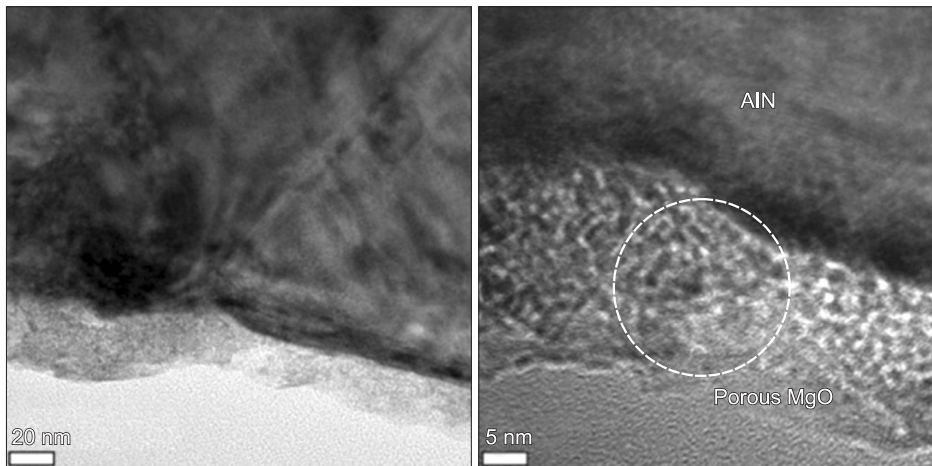
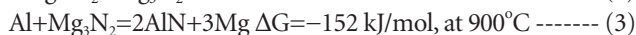


Fig. 6. Transmission electron microscope image of AlN powder synthesized for 1 hour at 700°C under the condition of Al-10 wt.% Mg-N. AlN particles have a well-developed wurtzite phase and the surface consists of amorphous MgO layer.

another reactions such as (2) and (3) reaction. Mg in the melt react with nitrogen to form intermediate phase (Mg_3N_2), followed by a substitution or replacement reaction to produce AlN.



AlN synthesized in this study is easily pulverized by ball milling, as shown in Fig. 4. This means that unreacted liquid Al does not exist between AlN particles.

Fig. 5 shows XRD patterns of the AlN powder formed, when 10 wt.% Mg is added to Al melt, revealing the formation of small amount of MgO as well as AlN. It is believed that MgO is formed by the oxidation of Mg_3N_2 exposed to air after the cooling to room temperature. This can be clearly confirmed by TEM observation, as shown in Fig. 6, indicating the existence of amorphous MgO layer (about 20 nm) on the surface of AlN particle. The thickness of MgO layer decreases with increase temperature and it is only several nm at 1,000°C, meaning the occurrence of more vaporization of the Mg at higher temperature.

The extent of conversion AlN of Al increases with synthesizing temperature, as shown in Fig. 5. Full conversion occurred at

temperature over 900°C and residual content of the Mg is less than 1% at 1,000°C. Formation of the AlN also depends on the fabrication time and perfect nitridation occurred at the time longer than 5 hours at 900°C. In addition, it can be seen that a ratio of the Al to N in the AlN formed increases to 1:1 with temperature.

CONCLUSIONS

We developed a new method for large-scale producing the AlN powder by an addition of Mg as a catalyst for nitridation of Al melt. As expected, while nitriding below 10% occurred at low Mg content, nearly perfect nitridation can obtain even at 700°C as Mg content increase to 10 wt.%. This is caused by an increase of the solubility of nitrogen gas due to the increase of Mg content in the Al melt. The nitrogen gas dissolved in Al melt is transformed into Mg_3N_2 and then it react with Al to AlN.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

REFERENCES

- Haibo J, Chen K, Heping Z, Agathopoulos S, Fabrichnaya O, and Ferreira J M F (2005) Direct nitridation of molten Al(Mg, Si) alloy to AlN. *J. Cryst. Growth* **281**, 639-645.
- Kumari S S, Pillai U T S, and Pai B C (2011) Synthesis and characterization of in situ Al-AlN composite by nitrogen gas bubbling method. *J. All. Comp.* **509**, 2503-2509.
- Okada T, Toriyama M, and Kanzaki S (2000) Direct nitridation of aluminum compacts at low temperature. *J. Mater. Sci.* **35**, 3105-3111.
- Pi J W, Lee J K, and Kim S R (2009) Technology and products of AlN. *Ceramists* **12**, 38-45.
- Selvaduray G and Sheet L (1993) Aluminium nitride: review of synthesis methods. *Mater. Sci. Technol.* **9**, 463-473.
- Zhang Y, Liu J, He R, Zhang Q, Zhang X, and Zhu J (2001) Synthesis of aluminum nitride nanowires from carbon nanotubes. *Chem. Mater.* **13**, 3899-3905.