# Synthesis of Aluminium Nitride Nano-powder using Induction Plasma Technology: Effect of Feedstock Molar Ratio and Reactor Pressure

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Abstract: The context of this research is to replace ammonia plasma nitridation by urea plasma nitridation as ammonia is a dangerous precursor and urea is very safe. The effect of feedstock molar ratio (Al:Urea) and the reactor pressure on the formation of aluminium nitride (AlN) nano-powder were investigated using radio frequency (RF) induction plasma technology. The Al: Urea molar ratio has a significant effect in supplying the nitrogen for the nitriding reaction for the AlN synthesis. In addition, pressure affects the residence time of the precursors in the plasma. Therefore, the focus of this project is to optimize these parameters. In the experimental planning setup, the following reaction conditions were used: Al:Urea molar ratio of 1:2, 1:4 and 1:6, while the reactor pressure was 67, 30, 15, or 9 kPa. Factsage thermodynamic software was used to simulate the formation of AlN in plasma. The synthesised AlN powders were evaluated by X-ray diffraction (XRD) for various phases present and Scanning electron microscopy (SEM) for morphological analysis. The XRD patterns show formation of AlN with hexagonal structure and SEM images indicate the formation of nanometric powders in the size range of 40 - 100 nm with spherical and semispherical shapes. The experimental results show that increasing the Al:Urea molar ratio and plasma pressure decreases the formation of AlN. The molar ratio of 1:4 and pressure of 9 kPa resulted in the maximum production of AlN using RF plasma method.

Keywords: Aluminum nitride (AlN), RF plasma spray, aluminium, Urea, molar ratio, nano materials, pressure

#### 1. Introduction

AlN has become the key component of semiconductor equipment, crucibles for handling corrosive chemicals and reaction vessels [1]. This is due to its high thermal conductivity [2], low thermal expansion coefficient [3], chemical/physical stability at fairly high temperature regions, high hardness [4] and high resistance of molten metals, wear and corrosion [1, 5, 6].

The conventional synthesis methods of AlN powder are carbothermal reduction-nitridation of alumina [7], direct nitridation of Al powder [8, 9], non-transferred arc plasma method [10], chemical routes [11] and Microwave-assisted Urea Route [12], Pulsed Laser Ablation [13] and transferred type arc plasma [14].

Recently, synthesis using thermal plasma technology has become popular because of the fast reaction rate due to the high plasma temperature [3], its flexibility in the choice of various feedstock materials [15], its high conversion rate and energy efficiency [3, 10], its rapid quenching [16, 17] which facilitates the synthesis of a homogeneous size distribution of ultra-fine AlN particles.

Considering urea as a source of nitrogen, it is critical to optimize the molar ratio of Al:Urea and the plasma reactor pressure for maximising the production of AlN. In this project, aluminium and urea were injected as precursors in the surrounding active nitrogen plasma. Phase and microstructure characterization were investigated by X-ray diffraction (XRD) and Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX).

# 2. Experimental procedures

2.1. Feedstock powder preparation

Aluminium metal powder (99.9%, Atlantic equipment engineers) with average grain size of  $1 - 5 \mu m$  and urea grains (Sigma-V1428) were used as the raw materials. The molar ratio (MR) of Al:Urea precursor used were 1:2, 1:4, and 1:6. These were mixed and stirred in the oven at 130°C for 30 minutes, and were constantly stirred during both the melting and cooling periods in order to avoid segregation into two phases, as aluminium is heavier than urea, and urea melts at 133 °C. After cooling, the mixture was ground and classified through a No. 200 (75  $\mu$ m) sieve. The backscattered SEM image indicating the distribution of the Al and Urea is shown in Figure 1.

In another experiment, the aluminium powder and urea in molar ratio of 1:4 were ground while being mixed in hexane medium and left in an ultrasonic bath for 5 minutes. Afterward, it was stirred for 2 hours and kept at ambient temperature to dry overnight. Similarly, the dried mixture was ground and classified through a No. 200 (75  $\mu$ m) sieve. Finally, the mixture was dried in oven at 60 °C for 24 hours to evaporate the excess hexane. The backscattered SEM image indicating the distribution of the Al and Urea is shown in Figure 2.

2.2. Materials synthesis procedure

The radio frequency (RF) plasma system was used for synthesizing AlN using a feedstock in powder form. The plasma system consists of a purpose-made plasma reactor and atomisation probe (both of which were fabricated inhouse), a PL-50 torch (supplied by TEKNA System Co., Sherbrooke, Canada), and power supply (from Lepel Co., USA) was used in this project.



Figure 1: Backscattered SEM image of the Al and urea precursors prepared by melting urea



Figure 2: SEM imaging of Al and urea precursor prepared in a hexane medium

In this study, the effect of plasma pressures of 67, 30, 15, 9 kPa as well as Al: urea molar ratio of 1:2, 1:4 and 1:6 on the synthesized powder are investigated. The plasma spray conditions are summarized in Table 1, where the plasma power was maintained at 45 kW, and the total sample feed rate into the plasma was 0.5 g.min<sup>-1</sup>. The gas flow rates were set as follows: Ar carrier gas at 1.0 l.min<sup>-1</sup> and the central gas (Ar) at 21.0 l.min<sup>-1</sup>, while the sheath gas

consisting of a mixture of Ar = 40.0,  $H_2 = 2.0$  and  $N_2 = 22.0$  l.min<sup>-1</sup>.

## 2.3. Materials characterisation

Evaluation of the crystal structure of the synthesised AlN powder was performed on an X-ray diffractometer "Philips PAN analytical X'pert PRO MRD", using Cu K $\alpha$ 1 radiation with a wavelength,  $\lambda = 1.54$  Å. The chemical composition of the samples were obtained using Rietveld method.

Morphology and particle size of the synthesised powder were investigated using the Scanning Electron Microscope (SEM, Hitachi S-4700). Particle size measurements were carried out using the ImageJ Analyzer software.

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Run #	Al:Urea molar ratio	Preparation condition	Pressure (kPa)
1	6	Melting	30
2	4	Hexane medium	30
3	4	Melting	30
4	2	Melting	30
5	4	Melting	67
6	4	Melting	30
7	4	Melting	15
8	4	Melting	9

Carrier gas (Ar) = 1 l.min<sup>-1</sup>; Central gas (Ar) = 21 l.min<sup>-1</sup>; Sheath gas (Ar/H<sub>2</sub>/N<sub>2</sub>) = 40/2/22 l.min<sup>-1</sup>; Feed rate = 0.5 g.min<sup>-1</sup>; Power = 45 kW.

# 3. Results and discussion

Prior to the experiments, production of AlN through the plasma process was simulated by Factsage thermodynamic computation software to examine the possibility of its formation under plasma chemistry and condition, as shown in Figure 3. Two coupled databases selected for this simulation were FactPS and FTlite. The interaction between plasma gas composition and solid precursors (Al and Urea) were calculated as a function of temperature where the thermodynamic equilibrium is achieved. However, the plasma is not in equilibrium condition since the high gradient temperature is existing in the plasma experiment.

Figure 3 shows that the formation of AlN begins at about 2400°C and reaches to its maximum at 2200 °C. In addition, the formation of CO, NH<sub>3</sub>, CO<sub>2</sub> gases are considered as the plasma gas species belong to the both precursors and plasma gases including carrier gas, sheath gas.



Figure 3: Thermodynamic plots showing predicted compositions during AlN production through plasma.

Figure 4 shows the X-ray diffraction patterns of the plasma-synthesised AlN powders using different molar ratios, while Figure 5 displays typical results obtained by SEM imaging.



Figure 4: XRD pattern of synthesise powder with different molar ratio (MR)

The XRD results indicated that no trace of AlN formation was observed with Al:Urea MR of 6, but by decreasing the molar ratio the peaks gradually appeared. When using a molar ratio of 4, the intensity of AlN peaks were at their highest, but by decreasing the MR to 2, the peaks were less intense. According to Rietveld semiquantitative method 15 % AlN is produced in Run# 3 with MR of 4. Thus, the Al:Urea MR of 4 was considered to be the optimum composition of the reactants. This was therefore selected as the MR for the raw materials precursors for the rest of the experiments.

Furthermore, the chosen method for preparing the precursors was by melting the urea in the oven since it yielded results that were more coherent. Indeed, melting produced a more homogenous mixture of the Al-urea when compared to the experiment prepared using hexane-based media. The SEM results demonstrate that the morphology of the synthesised powders is either spherical or semi spherical in nature. By measuring the particle size of the AlN powder by ImageJ software, the size is between 40 - 100 nm.



Figure 5: SEM image of the plasma-synthesised powder with Al:Urea molar ratio of 1:4.

XRD diffraction patterns of the plasma-synthesised sample using different pressures are shown in Figure 6. The XRD patterns reveal that by decreasing the pressure from 67 to 30 kPa, the peaks related to the by-product components including  $Al_2O_3$  were eliminated. The peaks related to Al and AlN in the synthesised sample at pressure 15 kPa appeared due to decreasing the residence time of the sample in the plasma.



Figure 6: XRD pattern of plasma synthesised powder at various pressures.

Since plasma is more confined at the pressure of 67 kPa than at lower pressure values, the density of reactant particles is higher in the torch. Therefore, the oxygen of urea has more opportunity to react with the aluminium and

to produce alumina. Confining the plasma increases the probability of contact between the particles, which facilitates the reactivity of nitrogen at high pressure. However, nitrogen is not a suitable candidate for the nitriding reaction because of re-bonding of nitrogen atoms once the decomposition of nitrogen gas occurs. Whereas the presence of  $H_2$  can hamper the rebonding process, its effect was found to be minor.

By decreasing the pressure from 67 to 9 kPa, the nitrogen derived from the decomposition of Urea reacted more easily with aluminium. Since AlN decomposes between 2200 - 2300 °C and it forms between 2500 - 2600 °C, by reducing the pressure, the residence time becomes shorter, consequently, the particles leave the high temperature zone more quickly. As a result, the reduced pressure lowers the decomposition rate of the AlN. According to Rietveld semi- quantitative method 20 % AlN is produced in Run# 8 with pressure of 9kPa.

Formation of amorphous AlN and cubic AlN could be explained by fast quenching of powders when they pass through the hot plasma region. On the hand, presence of aluminium peak in the XRD pattern does not necessarily means that the material is 100% Al it could be related to aluminium nitride in amorphous phase. Furthermore, it is most likely that by applying a post treatment method, amorphous and cubic meta stable phases of AlN transform to the most stable phase (hexagonal).

Similarly, Figure 7 depicts a typical SEM image of the plasma-synthesised samples at different pressures, with the spherical morphology of the powder being conspicuous. The mean particle diameter of the collected powder was about 10 - 40 nm.



Figure 7: Representative SEM image of the plasmasynthesised powder at 9 kPa pressure.

#### 4. Conclusion

This work involves the synthesis of aluminium nitride nano-powder by RF plasma spray technology. Preliminary experimental results have shown that the ideal molar ratio of the Al:Urea reactants is 1:4 and the plasma chamber pressure of 9 kPa is the optimum experimental set up for the synthesis of AlN. Rietveld XRD method predicts a 20% AlN composition for this optimised run (#8), however some non-crystalline AlN is present and post treatments are needed to recrystallize the AlN. In future, apart from post heat treatments, other plasma parameters including the injection process will be investigated in order to achieve a higher plasma synthesized product purity.

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### 6. References

[1] M. Yamada, H. Nakamura, T. Yasui, M. Fukumoto, and K. Takahashi, Journal of Materials Transansaction **47**, 7 (2006).

[2] S. M. Oh and D. W. Park, Journal of Thin Solid Films **316**, 1–2 (1998).

[3] M.-C. Sung, Y.-M. Kuo, L.-T. Hsieh, and C.-H. Tsai, Journal of Material Research.**32**, 7 (2017).

[4] K. Kim, Jornal of Crystal Growth, **283**, 3–4 (2005).

[5] K. Baba, N. Shohata, and M. Yonezawa, Appl. Phys. Lett., **54**, 23, (1989).

[6] D. Smolen and P. Dominik, Mater. Ceram. (2013).

[7] K. Komeya, E. Mitsuhashi, T. Meguro Journal of the Ceramic Society of Japan **101**, 4 (1993)

[8] A. C. Da Cruz and R. J. Munz, KONA Powder Part. J., **17** (1999).

X.-X. Mao, J. Li, H.-L. Zhang, Y.-G. Xu, and S.-W. Wang, Wuji Cailiao Xuebao/Journal Inorg. Mater., 32,10, (2017).

[10] T.-H. Kim, S. Choi, and D.-W. Park, J. Korean Phys. Soc., **63**,10 (2013).

[11] R. Baxter, N. Hastings, a. Law, and E. J. Glass," Anim. Genet., **39**, 5, (2008).

[12] J. Bin Ahn, D. S. Kim, Y. K. Kim, and J. G. Lee, Appl. Mech. Mater., **851** (2016).

[13] C. Grigoriu, M. Hirai, K. Nishiura, W. Jiang, and K. Yatsui, J. Am. Ceram. Soc. **83**, 10 (2000).

[14] M. Iwata, K. Adachi, S. Furukawa, and T. Amakawa, J. Phys. D. Appl. Phys., **37**, 7 (2004).

[15] K. I. Kim, S. C. Choi, J. H. Kim, W. S. Cho, K. T. Hwang, and K. S. Han, Ceram. Int., **40**, 6 (2014).

[16] H. Ageorges, S. Megy, K. Chang, J. M. Baronnet, J. K. Williams, and C. Chapman, Plasma Chem. Plasma Process., 13, 4 (1993).

[17] N. Venkatramani, Curr. Sci., 83, 3 (2002).