

# Aluminium Nitride Synthesis in Air from Aluminium and Graphite Mixtures Mechanically Activated

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## Abstract

*From the powder mixtures of aluminium metal and natural graphite ground in a planetary ball mill, aluminium nitride was formed in air as the consequence of self-ignition and following self-propagation reactions. The mechanism for AlN formation in air is discussed by taking into consideration the possible reactions. © 1997 Elsevier Science Limited.*

## 1 Introduction

Aluminium nitride (AlN) and AlN-based materials have attracted attention in advanced ceramics.<sup>1</sup> In our previous papers,<sup>2,3</sup> the formation of aluminium nitride was reported by exposing the powder mixtures of aluminium metal and natural graphite after mechanical activation by grinding in air. The ground powders were found to self-ignite and the reactions to propagate in the powders. The main reaction product was aluminium nitride, probably containing a small amount of oxygen (aluminium oxynitride). The main question was why nitride can be formed in air, instead of aluminium oxide.

In the present paper the experimental results with various powder mixtures of aluminium metal and carbon were summarized in order to understand the formation process of aluminium nitride in air and the formation mechanism was discussed.

## 2 Experimental

The aluminium metal powder with a purity of 99.9% and a particle size of 61–104  $\mu\text{m}$  was selected. Natural graphite with a flake size of 5  $\mu\text{m}$  was used. The mixtures of aluminium and carbon in various ratios were ground in a P-7 planetary ball mill, using a 25 ml jar and four balls of tungsten

carbide. The powder mixtures after grinding were transferred into either a porcelain saucer or graphite crucible and exposed to air. The products, after self-ignition and self-propagated reactions, were examined by X-ray powder diffraction, optical microscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. The experimental details were reported in our previous papers.<sup>2,3</sup>

## 3 Results and Discussion

### 3.1 Formation process

The scheme of reaction process was summarized as follows; most of the ground powders spontaneously ignited at several spots on the surface of the powder after exposure to air, evolving red heat, and propagated toward neighbouring regions, then reacted violently, evolving white heat. The reactions started by self-ignition through self-propagation ending in the formation of porous lumps.

In order to understand the propagating reactions, the ground sample was transferred in a graphite crucible with a diameter of 30 mm and a depth of 40 mm. Ignition was observed to occur at the limited surface and the exothermic reactions to propagate into the crucible, but the supply of air was reasonably supposed to occur through the surface. The lump obtained after the reaction was sliced along the depth and examined by XRD. The results are summarized in Fig. 1. At the top of the lump, only oxygen containing compounds, alumina and aluminium oxycarbide, are observed. However, it has to be mentioned that from just below the surface to the bottom of the crucible aluminium nitride is always formed. With the depth increase, aluminium oxynitride and aluminium carbide, compounds containing less oxygen, are formed, but no oxide is detected. Near the bottom of the crucible, un-reacted aluminium metal remains.

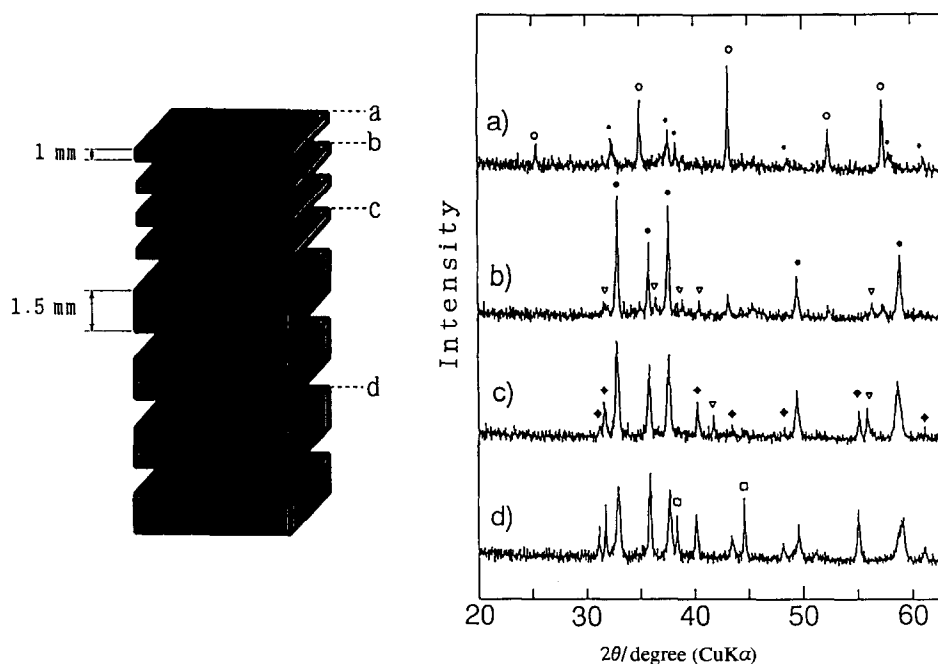


Fig. 1. X-ray powder patterns of the products formed by self-ignition and self-propagation reactions as the function of the depth in the graphite crucible. The ratio of Al:C was 3:1. ●:AlN, ○:α-Al<sub>2</sub>O<sub>3</sub>, \*:Al<sub>2</sub>OC, ▽:AlONs, ◆:Al<sub>4</sub>C<sub>3</sub>, □:Al.

The lattice constants  $a_0$  and  $c_0$  of aluminium nitrides obtained changed from 0.3115 and 0.4983 to 0.3142 and 0.5003 nm, respectively, and tended to decrease with the change in the sampling position from the surface to the bottom. The lattice constants were explained by assuming the formation of the solid solutions between AlN and Al<sub>2</sub>OC with wurtzite structure, and their change with depth suggested that more pure AlN was formed at the deeper position, which is in agreement with the experimental fact that the less oxygen containing compounds were formed at the deeper position.

From the experimental results summarized above, it is concluded that self-ignition and successive self-propagation of the reactions are essential for the formation of aluminium nitride in the reaction products. By the self-ignited reactions which occur near the surface of the sample, oxygen gas in the air is consumed to form oxygen-containing aluminium compounds, oxide, oxycarbide and oxynitride, but nitrogen can penetrate into the sample and react with mechanically activated aluminium powders to form aluminium nitride, which is reasonably supposed to be initiated by the heat due to self-ignited reactions and then to self-propagate into the sample because of its exothermic nature.

### 3.2 Formation conditions

For the formation of aluminium nitride in the final products, the mixing ratio of aluminium metal to natural graphite was important. The appropriate range of Al/C was determined to be from 5.75:1.25 to 4:3. No reaction occurred and only

aluminium balls of a few mm in size, of which the surfaces were covered by carbon, were obtained when the Al/C ratio was more than 6:1. When the ratio was less than 4:3, self-ignition was observed but the reactions did not propagate into the powders, and the main product was aluminium carbide.

For the self-ignition of the powders, natural graphite was found to be important. After grinding, no crystalline diffraction peaks in XRD pattern were detected, as shown in Fig. 1, which suggested the change of natural graphite to the amorphous state. It is known that the finely ground natural graphite is easily oxidized and evolves red heat by exposing it to air. When the ground powder was exposed to either nitrogen or argon, no ignition occurred, but it was self-ignited by the introduction of oxygen gas in the atmosphere. Therefore, the oxidation of mechanically activated natural graphite is an essential condition to start the self-ignition.

For the self-propagation of the reactions, the degree of mechanical activation, in other words the particle sizes of graphite and aluminium, was important. When the mixtures of aluminium with the size of 61–104 μm and natural graphite with the flake size of 5 μm were used in appropriate ratio, a grinding period of more than 75 min was necessary in order to have successive self-ignition and self-propagation of the reactions, and consequently to have aluminium nitride. If natural graphite with a larger size, such as 400 μm was used, a longer grinding time was needed to reach aluminium nitride.

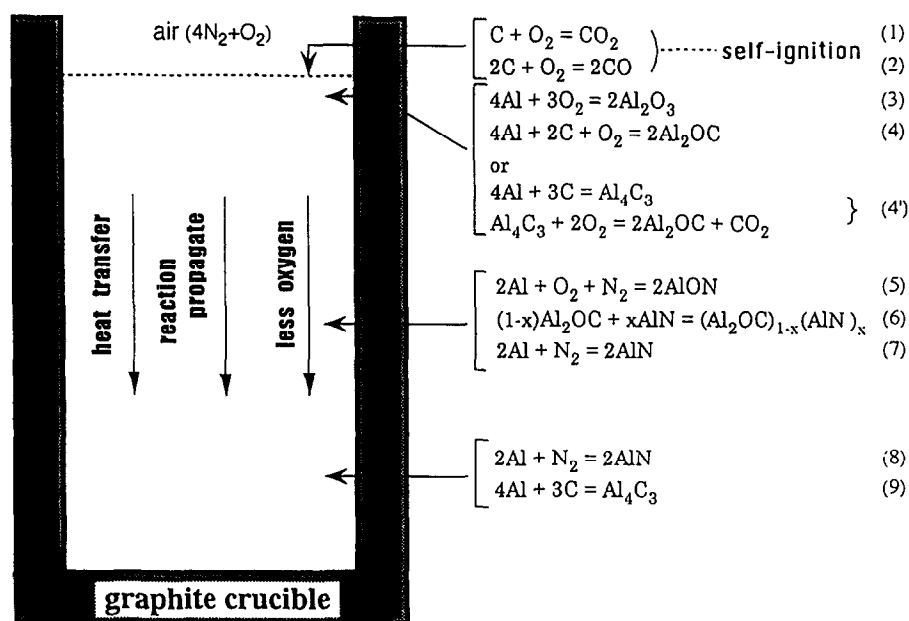


Fig. 2. Reactions during self-ignition and self propagation in the graphite crucible as the function of depth.

All of the particles of aluminium metal were coated with carbon in an amorphous state derived from natural graphite. This seems to be efficient enough to transfer the heat evolved by the oxidation of carbon and also to protect the aluminium particles from the oxidation.

### 3.3 Formation mechanism

The possible reactions for the reaction products are mentioned in Fig. 2 as the function of the depth in the graphite crucible and the formation mechanism of aluminium nitride in air is discussed.

On the surface of the powder lump, the amorphous carbon on aluminium particles reacts exothermically with oxygen in the air (eqns (1) and (2)), this being the initiation of the following reactions. In order to cause the oxidation, carbon has to be not only in an amorphous state but also mechanically activated. The heat evolved by the oxidation of carbon is efficiently transferred to aluminium particles because of intimate contact between carbon and aluminium, and causes the reactions of aluminium. Near the surface, there is still a large amount of oxygen, and so aluminium changes to either its oxide ( $\alpha$ -alumina, eqn (3)) or oxycarbide ( $Al_2OC$ , eqns (4) or (4')). Because all of these reactions at the surface are exothermic, the evolved heat was transferred to the inside of the crucible and therefore the reaction propagates into the powder lump.

A large amount of oxygen seems to be consumed very near the surface, because no alumina was detected below 1 mm depth from the surface. At mid-depth, a trace of oxygen seems to be kept as aluminium oxynitride (eqn (5)) and in a solid solution between aluminium oxycarbide and nitride (eqn (6)). Also the formation of aluminium nitride

occurs (eqn (7)), but it is supposed from its lattice parameters to contain certain amounts of oxygen and carbon in its structure.

Aluminium nitride (eqn (8)) formed near the bottom of the crucible, well-insulated from oxygen, contains much less oxygen in the lattice. Because of the presence of amorphous carbon without oxygen and also of heat transferred from the upper part, aluminium carbide is also formed (eqn (9)).

### 4 Conclusion

From the powder mixtures of aluminium metal and natural graphite ground in a ball mill, the formation of aluminium nitride was found. Starting from aluminium with the size of 61–104  $\mu m$  and natural graphite with the flake size of 5  $\mu m$ , and selecting the mixing ratio of Al/C in a range of 5.75:1.25 to 4:3, the self-ignition and self-propagation reactions occurred in air after grinding for more than 75 min. The possible reactions and mechanism for the preferential formation of aluminium nitride in air were discussed.

### References

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