

Nitridation reaction of aluminum powder in flowing ammonia

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Abstract

AlN powder was prepared by the nitridation of metal Al in flowing NH₃. The effects of reaction temperature and the temperature gradient of the reaction zone on the nitridation of Al were investigated. Comparative analysis of products formed in different reaction zones and reaction temperatures suggested that the nitridation reaction of liquid Al particles in flowing NH₃ was through the following mechanisms: NH₃ dissociated into reactive nitrogen (N) and hydrogen (H) radicals at the surface of Al particles. N reacted with Al to form AlN, while H promoted the decomposition of NH₃, which provided enough energy for the dissociation of NH₃. All of the experimental results had been discussed on the basis of this model, which indicated high reaction temperature or positive temperature gradient was favorable for the nitridation of Al.

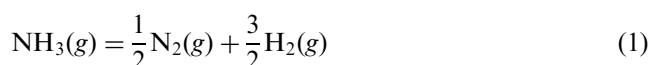
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1. Introduction

Aluminum nitride (AlN) has been acknowledged as a very important ceramic material in industrial applications due to its high thermal conductivity, high electrical resistivity, low thermal expansion coefficient than alumina ceramics, good thermal shock resistance and good corrosion resistance.^{1–6} There are two primary processes commercially used for the manufacture of AlN powder: (i) the direct nitridation of metallic aluminum in nitrogen (N₂), and (ii) the carbothermal reduction and nitridation of alumina. Comparatively the former method is known to have the advantages of simplicity and cost-effectiveness, but metallic Al tends to aggregate due to its lower melting point (660 °C) than the nitridation temperature. Another major obstacle is that a coherent nitride skin forms on the surface of metal Al in the absence of an additive and does not allow a complete nitridation. Extensive efforts have been taken to overcome these obstacles. Additive such as Mg² has been reported to be able to avoid a dense nitride layer, however residual impurities are difficult to

avoid. In the development of direct nitridation, processes such as floating nitridation¹ and nitridation of Al vapor³ have been developed to resolve such problems. A mixture of N₂ and ammonia (NH₃) instead of pure N₂ is sometime used to decrease the reaction temperature and to achieve a higher conversion of Al,^{4,5} which is attributed to the lower N–H bond energies in NH₃ compared with the N–N bond energies in N₂; therefore, less energy is required to break bonds.⁶ NH₃, however, is not stable at the temperatures where AlN is the only condensed phase. It decomposes according to



at temperatures above 200–300 °C at atmospheric pressure. Once NH₃ decomposes into molecular N₂ and H₂, the reactivity with Al decreases. Chang et al.⁶ have proved theoretically that the direct reaction of NH₃ with liquid Al was thermodynamically favored. Hoch et al.⁷ has suggested that NH₃ gas should reach the oxide and react as NH₃ before it has a chance to decompose because of the fine particle size of the solid reactants. But he has also noted that this sequence of events should have to be tested in the reaction vessel. However, other researchers have pointed out that the dissociation of NH₃ occurring in parallel with nitridation should be

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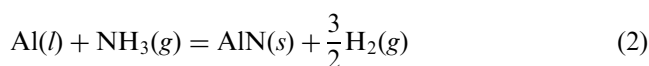
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carefully taken into account in studying the nitridation reaction. Huseby⁸ has claimed that, with an NH₃ atmosphere heated to 727 °C, at equilibrium more than 99.9% of the NH₃ would dissociate and the dissociation occurred at surfaces. It has been found that at the contact of metallic iron with NH₃, not only direct nitridation with NH₃ but also dissociation of NH₃ into nitrogen and hydrogen gas molecules should occur on the surface, and larger specific surface of nanoparticles enhanced NH₃ dissociation.⁹ Thus far, understanding of the nitridation reaction of Al in NH₃ has still been limited and no experiment is reported to investigate the reaction mechanisms, although it is important to understand the reaction mechanisms in order to improve the process for commercial application.

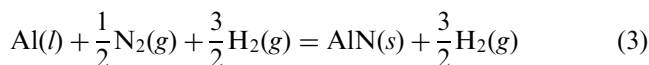
In the present study, the nitridation reaction of liquid Al particles in flowing NH₃ is investigated. NH₄Cl and KCl are used as the additives to ensure the complete nitridation of Al powder, which is discussed in detail in another paper.¹⁰ In brief, NH₄Cl and KCl do not participate in the nitriding reaction as additives. NH₄Cl prevents the agglomeration of liquid Al particles and KCl avoids the formation of a dense nitride layer on the Al surface, so the large reaction area between Al and ammonia is ensured. Thus the nitridation fully proceeds as it can, without being interrupted by foreign factors (e.g. formation of passivate layer). Based on this, the main purpose of this paper is to determine the reaction mechanism between NH₃ and liquid Al particles. For this purpose, a special reactor with two reaction zones, whose temperature gradients are opposite, is used. The effect of the temperature gradient and the reaction temperature is also investigated to elucidate the reaction mechanism.

2. Thermodynamic considerations

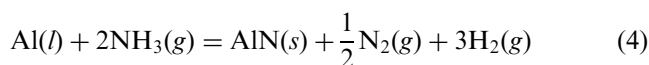
The nitridation reaction of Al in flowing NH₃ can be written as



If the ammonia decomposes previous to the nitridation reaction, the reaction can be written as



If the dissociation of NH₃ occurs at the surface of liquid Al particles in parallel with nitridation, it may be suggested as



The Gibbs free-energy changes for reactions (2)–(4) between 727 and 1727 °C are plotted in Fig. 1. The data

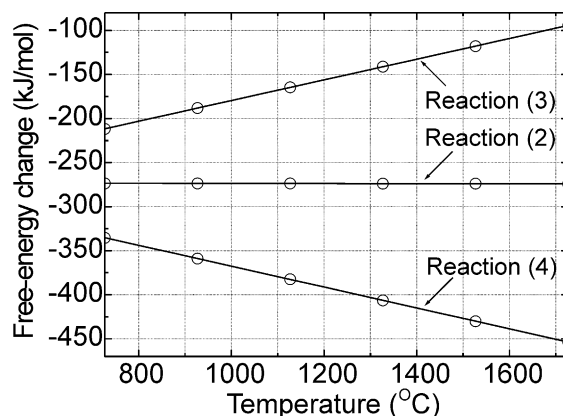


Fig. 1. Gibbs free-energy change for reactions (2)–(4) under isothermal conditions at 1 atm.

on free energy of formation are obtained from the JANAF tables.¹¹ It can be seen from Fig. 1 that the free-energy change associated with reactions (4) is significantly more negative than reaction (2) and (3), and can provide a driving force for dissociation of NH₃ when in contact with Al, thus enhance its thermal dissociation into reactive nitrogen radicals (NH₂, NH, and N). The dissociation energies E_D of the N–H bonds in NH₃ molecule are 427, 375 and 356 kJ/mol, respectively (see Table 1). The free-energy changes associating with the dissociation reactions are somewhat lower than E_D according to Eq. (5), for $\Delta S^\circ > 0$.

$$\Delta G^\circ = E_D - T\Delta S^\circ \quad (5)$$

It is obvious that only reaction (4) can provide enough energy for the dissociation of NH₃. According to thermodynamic calculations using ΔG° data of reaction (4) in Fig. 1, the necessary dissociation temperatures in equilibrium ($\Delta G = 0$) at atmosphere pressure are also listed in Table 1. It can be supposed that Al hardly be nitrided under atmosphere pressure if the reaction temperature is lower than 900 °C. Because $\Delta G^\circ < E_D$, the necessary nitridation temperature may be somewhat lower than the calculated in Table 1.

The free-energy change of reaction (4) is more negative at higher temperature, so it is expected that the conversion of Al increase with reaction temperature. Furthermore, since the dissociation of NH₃ is an endothermic and stepwise reaction, the temperature distribution in the reactor should be of important impact

Table 1

The dissociation energy (E_D) of N–H bonds in NH₃ molecule and the necessary dissociation temperatures according to reaction (4)

Reaction	E_D (kJ/mol)	Dissociation temperature (°C)
NH ₃ (g) = NH ₂ (g) + H(g)	427	1502
NH ₂ (g) = NH(g) + H(g)	375	1063
NH(g) = N(g) + H(g)	356	902

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