University of Wollongong

Research Online

Faculty of Engineering and Information
Sciences - Papers: Part A

Faculty of Engineering and Information
Sciences

1994

Low temperature synthesis of Al-AlN composites from a nanostructure made by controlled magneto-ball milling of Al in ammonia

Andrzej Calka

University of Wollongong, acalka@uow.edu.au

J I. Nikolov

Australian National University

G H. J Wantenaar

Australian Defence Force Academy

Follow this and additional works at: <https://ro.uow.edu.au/eispapers>

Part of the [Engineering Commons](#), and the [Science and Technology Studies Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Low temperature synthesis of Al-AlN composites from a nanostructure made by controlled magneto-ball milling of Al in ammonia

Abstract

The formation of an AlN compound in ball milled Al powder in ammonia was studied. In this work a magneto-ball milling device with controlled ball movement was used. The end milling product was an Al based nanostructure. This product can be transformed into an AlN-Al nanocomposite upon heating below the melting point of Al. It was found that the level of unreacted Al is dependent on milling time. The maximum amount of AlN was 88.28 wt %. The structure of as-milled and annealed samples was investigated using x-ray diffractometry and transmission electron microscopy. Differential thermal analysis was performed on as-milled samples.

Keywords

made, low, nanostructure, aln, al, synthesis, milling, ball, controlled, temperature, composites, ammonia, magneto

Disciplines

Engineering | Science and Technology Studies

Publication Details

Calka, A., Nikolov, J. I. & Wantenaar, G. H. J. (1994). Low temperature synthesis of Al-AlN composites from a nanostructure made by controlled magneto-ball milling of Al in ammonia. *Journal of Applied Physics*, 75 (10), 4953-4955.

Low temperature synthesis of AlAIN composites from a nanostructure made by controlled magnetoball milling of Al in ammonia

A. Calka, J. I. Nikolov, and G. H. J. Wentenaar

Citation: *Journal of Applied Physics* **75**, 4953 (1994); doi: 10.1063/1.355785

View online: <http://dx.doi.org/10.1063/1.355785>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/75/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Phase evolution in carbide dispersion strengthened nanostructured copper composite by high energy ball milling](#)

AIP Conf. Proc. **1476**, 378 (2012); 10.1063/1.4751632

[Ammonia synthesis at low temperatures](#)

J. Chem. Phys. **112**, 5343 (2000); 10.1063/1.481103

[Hightemperature phase transformations of iron anhydrous ammonia system realized by ball milling at room temperature](#)

J. Appl. Phys. **79**, 3956 (1996); 10.1063/1.361822

[Low temperature synthesis of boron nitride from condensed diborane and ammonia using synchrotron radiation](#)

Appl. Phys. Lett. **60**, 2561 (1992); 10.1063/1.106913

[Production of compositionally gradient AlAIN films by reactive sputtering and their mechanical and electrical properties](#)

J. Appl. Phys. **71**, 3278 (1992); 10.1063/1.350975

AIP | Journal of
Applied Physics

Journal of Applied Physics is pleased to
announce **André Anders** as its new Editor-in-Chief

Low temperature synthesis of Al-AlN composites from a nanostructure made by controlled magneto-ball milling of Al in ammonia

A. Galka and J. I. Nikolov

Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 2600, Australia

G. H. J. Wantenaar

Physics Department, Australian Defense Force Academy, Campbell, ACT 2600, Australia

(Received 31 August 1993; accepted for publication 17 January 1994)

The formation of an AlN compound in ball milled Al powder in ammonia was studied. In this work a magneto-ball milling device with controlled ball movement was used. The end milling product was an Al based nanostructure. This product can be transformed into an AlN-Al nanocomposite upon heating below the melting point of Al. It was found that the level of unreacted Al is dependent on milling time. The maximum amount of AlN was 88.28 wt %. The structure of as-milled and annealed samples was investigated using x-ray diffractometry and transmission electron microscopy. Differential thermal analysis was performed on as-milled samples.

I. INTRODUCTION

Aluminum nitride is a wide-band semiconductor that shows a high thermal conductivity, low dielectric constant, high mechanical strength, and an expansion coefficient similar to silicon.¹ Therefore, aluminum nitride is considered a useful substrate material for electronic devices.

Conventional synthesis routes for aluminum nitride are direct nitridation of metallic aluminum² and carbothermic reaction of alumina, carbon, and nitrogen.³ Direct nitridation involves heating aluminum powder in the presence of N₂ or NH₃ at temperatures above 1200 °C. Alternatively, carbothermic reduction involves reacting finely mixed Al₂O₃ and carbon powder in N₂-containing gas at temperatures between 1100 and 1800 °C. Aluminum nitride may also be synthesized by plasma nitridation of aluminum,⁴ a reaction of aluminum chloride with ammonia,⁵ and by pyrolytic routes.⁶ In all of those processes, the quality of product powder is limited by the impurity level. This strongly affects the thermal conductivity which is always well below the theoretically predicted value. The reason for this behavior is the existence of point defects in the aluminum nitride lattice, mainly due to oxygen impurities. Therefore, an important requirement for AlN to be considered as a substrate material is that it be free from metallic and nonmetallic impurities.

This article describes a novel magneto-ball milling method of low temperature synthesis of AlN. This method is based on the formation of an Al based nanostructure which transforms into an AlN-Al composite upon low temperature annealing.

II. EXPERIMENTAL METHOD

It has been known that nanostructured materials can be formed by ball milling.⁷ They are comprised of very small crystals with a nearly perfect order and a second component comprising all the atoms in the interfacial regions combined in strongly distorted structures.⁷ Such a structure can be produced by ball milling Al in ammonia. However, it has been well known that room temperature ball milling of soft metals such as Al using commercial high energetic ball mills (espe-

cially designed for pulverization of metals, alloys, and ceramics) without the aid of lubricants is almost impossible. In such devices the local temperature rises cause predominantly cold welding and suppress the fracturing process. Therefore, in this work we used a ball milling device (Uni-Ball-Mill) that provides better control of milling parameters such as milling energy, ball movement pattern, and shearing to impact ratio.^{8,9} Schematic representation of this type of milling device is seen in Fig. 1. This is a planetary ball mill that consists of a few hardened steel balls confined in a stainless-steel cell. The ball movement during the milling process is confined to the vertical plane by cell walls and is controlled by an external magnetic field generated by FeNdB magnets. The intensity and direction of the field can be externally adjusted to allow the ball trajectories, impact energy, and the shearing energy to be varied in a controlled manner. By selecting appropriate milling conditions we were able to reduce the cold welding of Al powder particles and enhance the fracturing, thereby producing a large volume of the interfacial component of the nanostructure with an Al crystal size reduced to 25 nm.

In this work elemental powder of aluminum (99%, -150 mesh) was milled in a dry ammonia atmosphere under a pressure of 3 MPa. The ball-to-powder ratio was 10/1. The samples were analyzed after 150, 300, and 600 h of milling. The structural development was examined by means of x-ray diffractometry (XRD) using Co K α radiation and transmission electron microscopy (TEM). Thermal properties were studied using a Shimadzu DTA-50 thermal analyzer working in a differential scanning calorimetry (DSC), continuous heating mode. All samples were annealed in argon atmosphere with a heating rate of 20°/min. The temperature range used was from 30 up to 1000 °C. After 600 h of milling the iron contamination has been found to be 0.5 at. %, as determined by Rutherford backscattering spectroscopy (RBS) using 2 MeV He⁺ ions. The oxygen content in ball milled samples is limited by the extent of oxygen in the starting material.

FIG. 1. Schematic representation of milling device used in this work.

III. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of as-milled Al powders (left side in Fig. 2) ball milled for (a) 150, (b) 300, and (c) 600 h. After milling for 150 h only the expected Bragg peaks of elemental Al powder are observed [Fig. 2(a)]. Prolonged milling up to 300 or 600 h causes formation of interfacial components of the nanostructure that are seen in Figs. 2(b) and 2(c) (left side) as broad diffraction features (above the dash line) overlapping with the Al peaks. It should be noted that the interfacial component of the nanostructure causes an incoherent x-ray scattering that is relatively weak in comparison to the diffracted signal. Therefore, the weak x-ray feature seen in Figs. 2(b) and 2(c) (left side) may correspond to the major sample volume (as it can be seen in Fig. 3). The ball milling causes increases in the width of the Al peaks but the peak position remains unchanged. Using the Scherrer formula, the calculated grain size is 25 nm. It has been known that the XRD peak broadening can be affected by grain size and strain. However, in the case of ductile materials such as Al and Cu the mean strain induced by ball milling is relatively small ($<0.2\%$), thus the errors in the present study are believed to be on the order of 10%–25%

FIG. 2. XRD patterns of Al milled in an ammonia atmosphere for (a) 150, (b) 300, and (c) 600 h (left column) and annealed in DSC (right column).

FIG. 3. The dark-field image and corresponding selected area diffraction pattern of the sample milled for 600 h.

for grain sizes of about 25 nm.¹⁰ These results indicate a nanostructural character of as-milled materials.

Figure 3 shows the dark-field image (DFI) and the selected area diffraction pattern (SADP) of a sample milled for 600 h. The DFI shows small crystals in a large volume of featureless material. The SADP shows the broad halo characteristic of the amorphous phase and white spots that can be indexed to the fcc aluminum structure.

Figure 4 shows DSC traces of samples ball milled for (a) 150, (b) 300, and (c) 600 h. For the sample milled for 150 hours [Fig. 4(a)] two thermal effects are seen, an endothermic effect due to the melting of Al (peak temperature at 664 °C) and an exothermic effect above the melting temperature of Al (peak temperature at 700 °C) corresponding to the formation of AlN. The sample milled for 300 h shows a complicated DSC trace. The endothermic effect corresponding to melting Al overlaps with the exothermic effect due to the formation of AlN which, in this sample, is shifted to lower temperature (onset at 559 °C, peak temperature at 636 °C). Moreover, an additional broad endothermic feature is seen within the temperature range 200–560 °C. This effect is frequently seen in samples heated or milled in a hydrogen or ammonia atmosphere and can be attributed to the decomposition of ammonia molecules¹¹ or the desorption of hydrogen.¹² A prolonged milling time of up to 600 h causes additional changes in the thermal properties [Fig. 4(c)]. Further shifting (towards lower temperature) of the exothermic effect associated with formation of AlN is observed. In this sample the transformation of the nanophase into AlN starts at 503 °C and shows the maximum reaction rate at 580 °C (peak temperature). Most of this reaction is completed below the melting point of Al. A very weak endothermic peak associated with melting Al (peak temperature at 653 °C) indicates the presence of small amounts of unreacted aluminum. The extended endothermic effect at lower temperatures looks more pronounced than that of the sample milled for 300 h.

All the samples described were heated to 1000 °C. The reason for this was twofold: (i) to ensure no further phase transformations induced by heating take place, and (ii) to develop larger grain size for more pronounced XRD patterns.

FIG. 4. DSC curves of Al milled in ammonia for (a) 150, (b) 300, and (c) 600 h.

In Fig. 2(b) the corresponding XRD patterns obtained from heated in DSC samples (Fig. 4) are presented. The sample milled for 150 h and heated in DSC up to 1000 °C [Fig. 4(a)] shows set of diffraction peaks indexed to Al and AlN phases [Fig. 2(a), right side]. The broadening of the Bragg peaks is due to the fine grain size. Using the Scherrer formula, the calculated grain size is 15 nm for the AlN phase and 25 nm for the Al. These results indicate a nanocomposite Al-AlN type structure. A similar XRD pattern was obtained for a sample milled for 300 h [Fig. 2(b), right side]. However, the lower intensity of Al peaks indicates less of the aluminum matrix and more of the AlN phase. The XRD pattern of the sample milled for 600 h and annealed in DSC [Fig. 2(c), right side] shows only peaks attributed to the AlN phase. Although the Al peaks are not visible on the XRD pattern, the DSC trace shows the presence of a small endothermic

FIG. 5. The bright-field image and corresponding selected area diffraction pattern of the sample milled for 600 h and annealed in DSC up to 600 °C.

peak due to the melting of Al, confirming the presence of unreacted Al in this sample. Indeed, the TEM micrograph (bright-field image) of the sample milled for 600 h and annealed in DSC up to 600 °C (below the melting point of Al) shows dark crystals of AlN (10–25 nm in size) and bright areas of unreacted Al (Fig. 5). In this study we determined the amount of unreacted Al by measuring the melting heat of Al in the annealed samples. The results are as follows: in annealed samples milled for 150 h: 45.3 wt %, 300 h: 22.23 wt %, and 600 h: 11.72 wt % of unreacted Al.

IV. CONCLUSIONS

On the basis of these results one can conclude that controlled ball milling of Al in ammonia leads to the formation of an Al based nanostructure. This material transforms into an Al-AlN nanocomposite type of structure upon heating below the melting point of Al. By using different atmosphere and/or milling times, a range of nanocomposites with different ratios of AlN to the Al matrix can be synthesized. The maximum amount of the AlN phase obtained in this study was 88.28 wt %. As far as the authors know this is the first time that AlN was synthesized from nanostructured aluminum by room temperature ball milling and a subsequent annealing at a temperature below the melting point of Al. We believe that the amount of the AlN phase can be increased by selecting the appropriate milling condition. Using this method, we believe that nitrides of other soft metals such as Ga, Cu, and Sn can be synthesized.

- ¹W. Werdecker and F. Aldinger, IEEE Trans. Components Hybrids, Manuf. Technol. **7**, 399 (1984).
- ²D. Fister, Ceram. Eng. Sci. Proc. **6**, 1305 (1985).
- ³M. Billy and J. Mexmain, Sprehsaal **118**, 245 (1985).
- ⁴G. Long and L. M. Foster, J. Am. Ceram. Soc. **42**, 53 (1959).
- ⁵I. Kimura, N. Hotta, N. Nukui, N. Saito, and S. Yasukawa, J. Mater. Sci. Lett. **7**, 66 (1988).
- ⁶G. Pouskopuleli, Ceram. Inst. **15**, 213 (1989).
- ⁷H. Gleiter, Prog. Mater. Sci. **33**, 223 (1989).
- ⁸A. Calka and A. P. Radlinski, Mater. Sci. Eng. A **134**, 1350 (1991).
- ⁹Manufacturer: ANUTECH, The Australian National University.
- ¹⁰G. W. Nieman and J. R. Weertman, J. Mater. Res. **6**, 1012 (1991).
- ¹¹Unpublished results.
- ¹²K. Aoki and X.-G. Li, Appl. Phys. Lett. **61**, 2422 (1992).