NASA/TM—2017-219472

Synthesis and Thermal Conductivity of Exfoliated Hexagonal Boron Nitride/Alumina Ceramic Composite

Ching-cheh Hung, Janet Hurst, Diana Santiago, Maricela Lizcano, and Marisabel Kelly
Glenn Research Center, Cleveland, Ohio

April 2017

NASA STI Program . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program plays a key part in helping NASA maintain this important role.

The NASA STI Program operates under the auspices of the Agency Chief Information Officer. It collects, organizes, provides for archiving, and disseminates NASA's STI. The NASA STI Program provides access to the NASA Technical Report Server—Registered (NTRS Reg) and NASA Technical Report Server—Public (NTRS) thus providing one of the largest collections of aeronautical and space science STI in the world. Results are published in both non-NASA channels and by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counter-part of peer-reviewed formal professional papers, but has less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., "quick-release" reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or co-sponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

For more information about the NASA STI program, see the following:

- Access the NASA STI program home page at http://www.sti.nasa.gov

- E-mail your question to help@sti.nasa.gov

- Fax your question to the NASA STI Information Desk at 757-864-6500

- Telephone the NASA STI Information Desk at 757-864-9658

- Write to:
  NASA STI Program
  Mail Stop 148
  NASA Langley Research Center
  Hampton, VA 23681-2199

NASA/TM—2017-219472

Synthesis and Thermal Conductivity of Exfoliated Hexagonal Boron Nitride/Alumina Ceramic Composite

Ching-cheh Hung, Janet Hurst, Diana Santiago, Maricela Lizcano, and Marisabel Kelly
Glenn Research Center, Cleveland, Ohio

National Aeronautics and
Space Administration

Glenn Research Center
Cleveland, Ohio 44135

April 2017

Acknowledgments

The authors thank the NASA Advanced Air Transportation Technology Project (AATT) for supporting this research and NETZSCH Instruments North America, LLC, for thermal conductivity measurement.

This report contains preliminary findings, subject to revision as analysis proceeds.

This work was sponsored by the Advanced Air Vehicle Program at the NASA Glenn Research Center

Level of Review: This material has been technically reviewed by technical management.

Available from

NASA STI Program
Mail Stop 148
NASA Langley Research Center
Hampton, VA 23681-2199

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
703-605-6000

This report is available in electronic form at http://www.sti.nasa.gov/ and http://ntrs.nasa.gov/

Synthesis and Thermal Conductivity of Exfoliated Hexagonal Boron Nitride/Alumina Ceramic Composite

Ching-cheh Hung, Janet Hurst, Diana Santiago, Maricela Lizcano, and Marisabel Kelly
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Summary

Exfoliated hexagonal boron nitride (hBN)/alumina composite can be fabricated by following the process of (1) heating a mixture of hBN, $AlCl_3$, and NaF in nitrogen for intercalation; (2) heating the intercalated product in air for exfoliation and at the same time converting the intercalate ($AlCl_3$) into Al_2O_3, (3) rinsing the oxidized product, (4) coating individual exfoliated hBN platelets that contain Al_2O_3 with new layers of aluminum oxide, and finally, (5) hot pressing the product into the composite. The composite thus obtained has a composition of approximately 60 wt% hBN and 40 wt% alumina. Its in-plane and through-plane thermal conductivity were measured to be 86 and 18 w/mK, respectively, at room temperature.

Introduction

A method of intercalating hexagonal boron nitride (hBN) with ferric chloride ($FeCl_3$) was developed recently (Ref. 1). Sodium fluoride (NaF) was used as an activation agent to activate this reaction. The intercalated product can be further treated by heating in 750 °C air to produce an hBN-Fe_2O_3 mixture where nanosized Fe_2O_3 particles in this mixture were observed to be between the layers of the hBN platelets.

The above phenomenon for $FeCl_3$ led to the idea that perhaps aluminum chloride ($AlCl_3$) could also react with hBN similarly in the presence of NaF, producing an hBN-Al_2O_3 mixture where nanosized Al_2O_3 particles are inside the hBN platelets. This hypothesis came from the observation that $FeCl_3$ is very similar to $AlCl_3$ in terms of intercalation: Graphite can be intercalated by both of them by the same mechanism at a temperature below their melting points (or sublimation point) (Ref. 2), and unless an activating agent is present, both of them are inert to hBN (Ref. 3).

If the above hBN-Al_2O_3 mixture could indeed be made, it may be further processed to fabricate exfoliated boron nitride/alumina ceramic composites, potentially a high thermal conductivity electrical insulator. Specifically, it could be coated with an additional layer of Al_2O_3 using a recently developed method and then hot pressed into an hBN/alumina composite (Ref. 4). The hBN phase in this composite can be very thin because Al_2O_3 particles are between the hBN layers, and the chemical composition of the composite can be changed by adjusting the hBN-to-$AlCl_3$ ratio of the original reactants for this process. Since hBN platelets with varying sizes, shapes, and composition lead to composites with different mechanical, thermal, and electrical properties, use of exfoliated hBN with varying degrees of exfoliation could lead to composites with tailored mechanical, thermal, and electrical properties for different applications.

This report describes in detail the process to synthesize exfoliated boron nitride/alumina composite described above. The intermediate and final products of this synthesis process were characterized using x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). Thermal conductivity of the final exfoliated hBN/alumina composite was also measured.

Methods

A typical run to fabricate an exfoliated hBN/alumina composite involves the sequence of (1) heating a mixture of hBN, $AlCl_3$, and NaF in nitrogen for intercalation, (2) heating the intercalated product in air for exfoliation and at the same time converting the intercalate ($AlCl_3$) into Al_2O_3, (3) rinsing the oxidized product, (4) coating individual platelets with aluminum oxide (Ref. 4), and finally, (5) hot pressing the product into the composite (Ref. 4).

For the particular run to fabricate the composite described in this report, a mixture of hBN, hydrated $AlCl_3$ (1 wt% water), and NaF (mass ratio 1:1.25:0.18) was heated in nitrogen at a pressure of 1 atm. $AlCl_3$ was hydrated to enhance adhesion of the aluminum compound on the hBN surface during intercalation (Ref. 4). The sample was first held at room temperature for 14 h, then held between 50 and 80 °C for 8 h, then held between 110 and 170 °C for 24 h, and finally held between 190 and 230 °C for 16 h. Note that $AlCl_3$ has a sublimation point of 180 °C and a melting point of 192 °C. The above temperature ranges for reactions were designed so that sufficient time was allowed for the reaction to reach completion before excess $AlCl_3$ was evaporated at a temperature above its sublimation point.

The product was then removed from the nitrogen environment and slowly heated in air from room temperature to 750 °C in 16 h and then held at 750 °C for 1 h. The slow heating was for the purpose of minimizing change of the intercalated structure during oxidation. After such heating in air, the product was rinsed with demineralized water and examined using XRD and FESEM. Incomplete oxidation was observed. The product was therefore further heated (5 °C/min), first at 1050 °C for 1 h in a quartz flask, with its opening sealed by quartz wool, cooled, and then set in open air at 850 °C for 1 h. After that, the product was examined again using XRD and FESEM, and was confirmed to be an hBN-alumina mixture. It was then treated with the steps of mixing with hydrated $AlCl_3$ (1 wt% water) followed by heating in air to form an aluminum oxide coating, and finally hot pressing at 1950 °C and 69 MPa for 1 h in nitrogen, producing an hBN/alumina ceramic composite (Ref. 4).

The hBN used in this research is the highly crystalline PT110 powder from Momentive Performance Materials, Inc. The platelets were 20 to 80 μm wide and 5 to 10 μm thick. NaF were used as purchased. The hydrated $AlCl_3$ was obtained by exposing the hygroscopic $AlCl_3$ to ambient air to pick up moisture until its mass increased to a predetermined value.

A Bruker D8 Advance X-Ray Diffractometer was used for XRD data. A Hitachi S-4700II FESEM was used for SEM images and energy dispersive spectrum (EDS) data.

Through-plane thermal conductivity of a sample disk was measured using a NETZSCH LFA 447 instrument. Another such sample was sent to the instrument manufacturer for an independent thermal conductivity measurement. The method of in-plane thermal conductivity measurement can be found elsewhere (Ref. 4).

Results and Discussion

Table I lists the steps of the process to fabricate exfoliated boron nitride/alumina composites, the purpose of these steps, and the chemical composition of the intermediate product obtained at the end of each step. This is further described in details as follows:

(1) Product after heating the original reactant in nitrogen (Fig. 1). FESEM and XRD of the product thus obtained are shown in Figure 1. XRD indicates the presence of NaF. The hBN platelets appear to be completely coated by material containing Al, Na, Cl, F, and O (Table I). Some degree of insertion of this material into the spaces between the layers can also be observed in the FESEM image.

If $AlCl_3$ in the original reactant mixture was anhydrous (without prehydration), heating the reactant yielded different products. In that case XRD indicated the presence of hBN and $NaAlCl_4$, and EDS indicated the absence of F. Further study will be needed to explore the potential of this product.

(2) Product after 750 °C heating in air and then rinsing (Fig. 2). EDS shows all chlorine was removed, but some fluorine and sodium remained in the hBN. XRD data indicated that it was Na_3AlF_6 and a small amount of $Al_4B_2O_9$. FESEM found hBN layers about 20 nm thick, but no separation spaces between them can be found. Additionally, XRD shows small alumina peaks. All of these observations indicate incomplete oxidation and incomplete exfoliation. The large number of nanosized particles on the sides and faces of the hBN platelets, as shown in FESEM images, are believed to be a mixture of alumina, Na_3AlF_6, and $Al_4B_2O_9$.

(3) Product after 1050 °C heating in low-oxygen air (Fig. 3). The low-oxygen environment was created by placing the samples in a quartz flask and sealing the opening of the flask with quartz wool. It was for the purpose of further oxidation of the intercalate while avoiding oxygen attack on partially exfoliated hBN at 1050 °C. After such heating, XRD shows only hBN and alumina peaks, with alumina peaks having become much larger, indicating oxidation indeed occurred at this environment. However, a small amount of fluorine still remained in the sample.

Another effect of this 1050 °C heating was additional exfoliation. Separated hBN layers 20 nm or thinner was a common feature and were shown in the FESEM image in Figure 3.

Also, the FESEM image in Figure 3 shows that the large number of nanoparticles before this 1050 °C heating, as shown in Figure 2, disappeared. This is believed to be the result of the combined effects of nanoparticle melting and exfoliated hBN wetting as well as evaporation and oxidation at this temperature. Note that Na_3AlF_6, one of the chemicals in the form of nanoparticles on the sides and faces of the hBN platelets, has a melting point of 950 °C. The other such chemical, $Al_4B_2O_9$, decomposes at 1035 °C (Ref. 5).

An unexpected effect of this reaction is that the sample was contaminated by quartz (from the flask). The EDS spectrum shows a small Si peak. However, XRD did not detect any silicon-containing compound. Silicon contamination may lower the melting point of Na_3AlF_6 described in the previous paragraph. For the purpose of understanding the effects of this contamination, the reaction described here was repeated using an alumina container instead of a quartz flask. In terms of XRD, the product thus obtained showed no difference from the one that was contaminated by Si. It is concluded that the presence of silicon in the sample does not affect the process described in this report and does not affect the conclusions presented here.

(4) Product after 850 °C heating in air (Fig. 4). Both XRD and FESEM show that this heating did not cause much change. EDS, however, shows that the heating removed residual fluorine from the sample.

(5) Products after Al_2O_3 coating on hBN (Fig. 5). This step does not cause detectable changes in terms of XRD, indicating the structure of the hBN remains the same. FESEM, though, shows the exfoliated hBN was completely coated by a new layer of amorphous material. All small features, including the thin separated hBN layers, are no longer visible.

(6) Product after hot press at 1950 °C and 69 MPa (Fig. 6). The composite thus formed is hBN (60 wt%) and alumina (40 wt%) according to mass data. In addition, XRD indicates the presence of trace amounts of B_2O_3 and its hydrated form HBO_2. Note that the interface chemical $9Al_2O_3 \cdot 2B_2O_3$, observed by Zhang et al. (Ref. 6) and Wang et al. (Ref. 7) in their hBN-Al_2O_3 studies, was not detected in the samples obtained in this research. This is expected as $9Al_2O_3 \cdot 2B_2O_3$ would decompose into alumina and B_2O_3 at this hot press temperature (Ref. 5). Also note that a composite of 90 wt% hBN and 10 wt% alumina were obtained previously when the same process was applied to an as-received commercial hBN instead of the exfoliated ones (Ref. 4). The XRD (002) to (100) peak ratio, an indicator of preferred orientation, was calculated to be 0.0042. This is much lower than the 0.14 value for the randomly oriented hBN (I/I_0 value, Powder Diffraction File Reference code: 04-004-1056) and indicates a preferred orientation of the hBN in the composite. This is consistent with thermal conductivity data obtained by the instrument manufacturer (Disk A) and in-house at NASA Glenn (Disk B), which indicate an in-plane thermal conductivity value much higher than the through-plane value (Table II).

Conclusion

The method of using NaF as an activating agent to intercalate hexagonal boron nitride (hBN) with $FeCl_3$ was successfully modified to intercalate hBN with $AlCl_3$. This new intercalated product was further exfoliated by heating in air, rinsing, coating with new layers of Al_2O_3, and hot pressing into an hBN-alumina composite with room-temperature in-plane and through-plane thermal conductivity values of 86 and 18 w/mK, respectively.

References

1. Hung, Ching-cheh, et al.: Exfoliation of Hexagonal Boron Nitride via Ferric Chloride Intercalation. NASA/TM—2014-218125, 2014. http://ntrs.nasa.gov
2. Forsman, W.C., et al.: Graphite Intercalation Chemistry: An Interpretive Review. Synth. Met., vol. 5, no. 2, 1983, pp. 77–100.
3. Rudorff, W.: Graphite Intercalation Compounds. Advances in Inorganic Chemistry and Radiochemistry, H.J. Emeleus and A.G. Sharpe, eds., Vol. 1, Academic Press Inc., New York, NY, 1959, pp. 223–266.
4. Hung, Ching-cheh, et al.: Highly Thermally Conductive Hexagonal Boron Nitride/Alumina Composite Made From Commercial Hexagonal Boron Nitride. J. Am. Ceram. Soc., vol. 100, no. 2, 2016, pp. 515–519.
5. Siba, Ray P.: Preparation and Characterization of Aluminum Borate. J. Am. Ceram. Soc., vol. 75, no. 9, 1992, pp. 2605–2609.
6. Zhang G.J., et al.: Reactive Synthesis of Alumina-Boron Nitride Composites. Acta Mater., vol. 52, no. 7, 2004, pp. 1823–1835.
7. Wang, Wei-Li, et al.: Microstructure and Mechanical Properties of Alumina Ceramics Reinforced by Boron Nitride Nanotubes. J. Eur. Ceram. Soc., vol. 31, 2011, pp. 2277–2284.

TABLE I.—COMPOSITION OF INTERMEDIATE AND FINAL PRODUCTS OF FABRICATING BORON NITRIDE/ALUMINA COMPOSITES DETECTED BY ELECTRON DISPERSION SPECTROSCOPY
[From field emission scanning electron microscope operated at 15 kV.]

Fabrication step	Purpose	Element peaks[a]							
		B	N	O	F	Na	Al	Cl	Si
Reactants hBN, $AlCl_3$, and NaF		–	–	–	–	–	–	–	–
(1) Room temperature to 230 °C heating in nitrogen	Intercalation	S	S	L	VS	VS	L	L	0
(2) 750 °C heating in air and rinse	Exfoliation	S	L	L	S	S	L	0	0
(3) 1050 °C heating in low-oxygen air		L	L	S	VS	S	L	0	S
(4) 850 °C heating in air		S	L	L	0	S	L	0	S
(5) Al_2O_3 coating on hBN (Ref. 4)	Coating	S	L	L	0	S	L	VS	0
(6) Hot pressing at 1950 °C and 69 MPa in nitrogen	Hot pressing	L	L	S	0	VS	L	VS	VS

[a]L: largest three peaks.
VS: very small, peaks are barely visible.
S: all other peaks.
0: no peak.
–: not measured.

TABLE II.—THERMAL-CONDUCTIVITY-RELATED PROPERTIES OF FABRICATED EXFOLIATED hBN/ALUMINA COMPOSITES

Sample	Density at 25 °C, g/cm^3	Direction	Temperature, °C	Specific heat, (J/g-°C)	Diffusivity, mm^2/s	Conductivity, W/mK
Disk A	2.45	Through-plane	25	0.880	8.43	18.2
			100	1.01	6.01	14.9
			500	1.45	2.58	9.2
			1000	1.73	1.56	6.6
		In-plane	25	0.880	39.9	86.0
			100	1.01	28.3	70.0
			500	1.45	10.7	38.0
			1000	1.73	3.28	13.9
Disk B	2.190	Through-plane	35	0.971	10.82	23.0

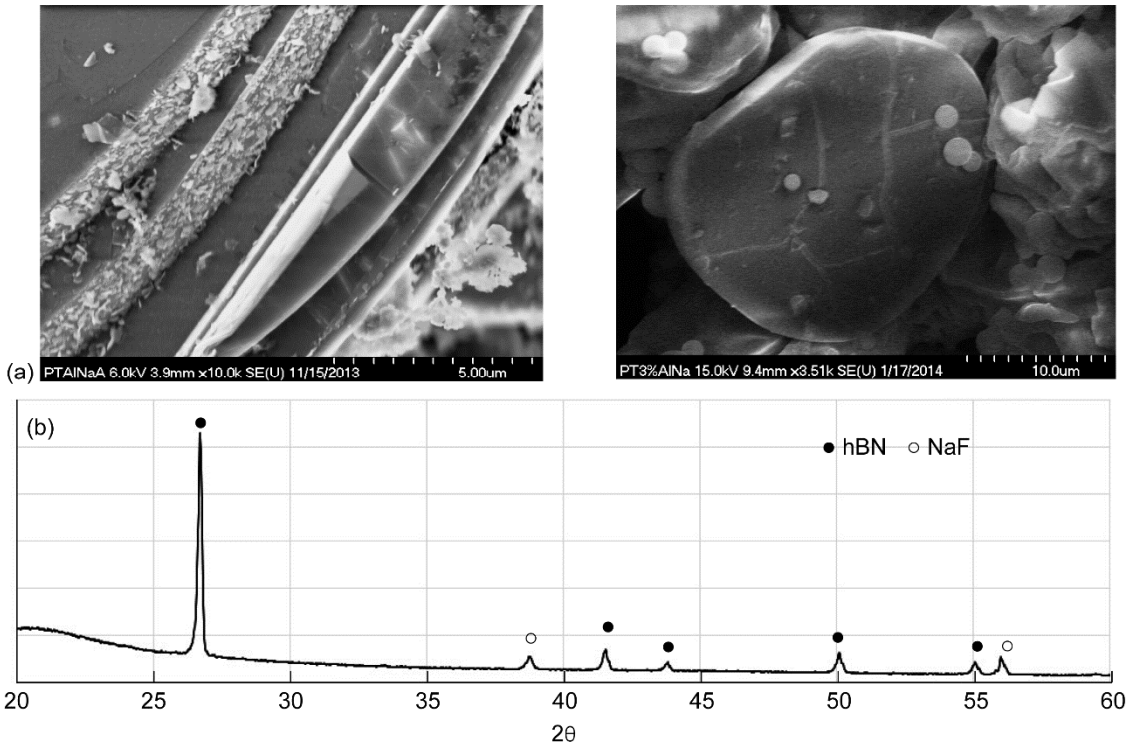

Figure 1.—Intermediate product after 110 to 230 °C heating of hexagonal BN (hBN), $AlCl_3$, and NaF reactants in nitrogen to fabricate hBN/alumina composite. See Step (1), Table I. (a) Field emission scanning electron microscopy (FESEM) images. (b) X-ray diffraction (XRD) spectrum.

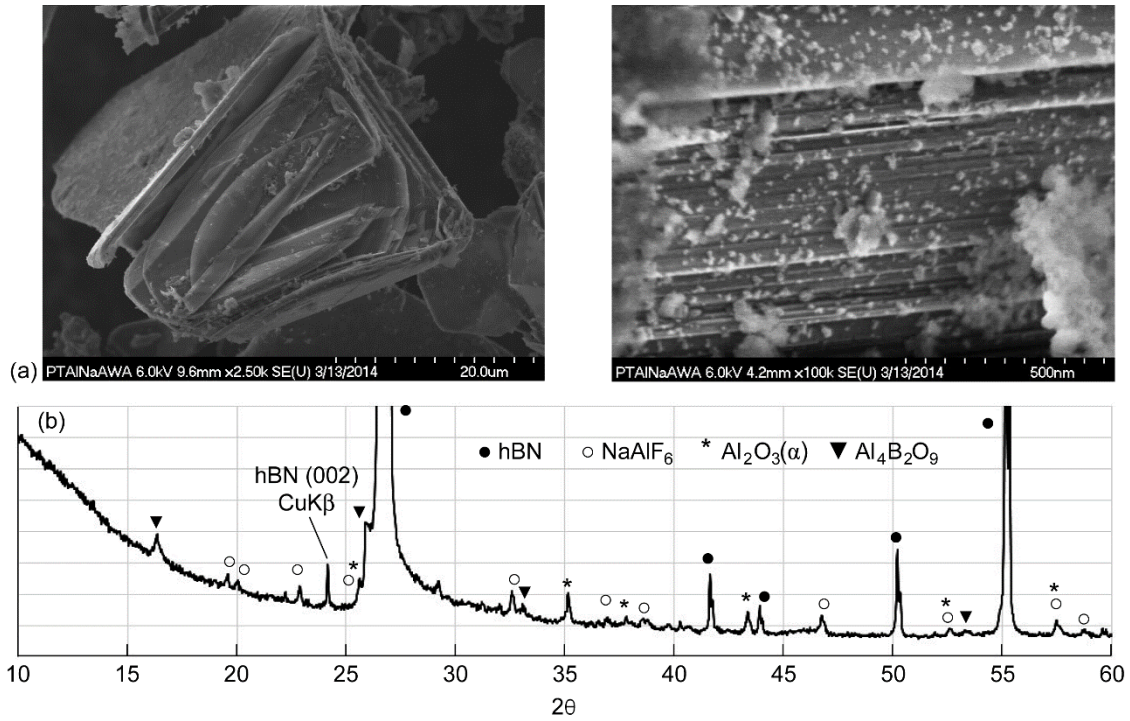

Figure 2.—Intermediate product after 750 °C heating in air and rinsing to fabricate hBN/alumina composite. See Step (2), Table I. (a) Field emission scanning electron microscopy (FESEM) images. (b) X-ray diffraction (XRD) spectrum.

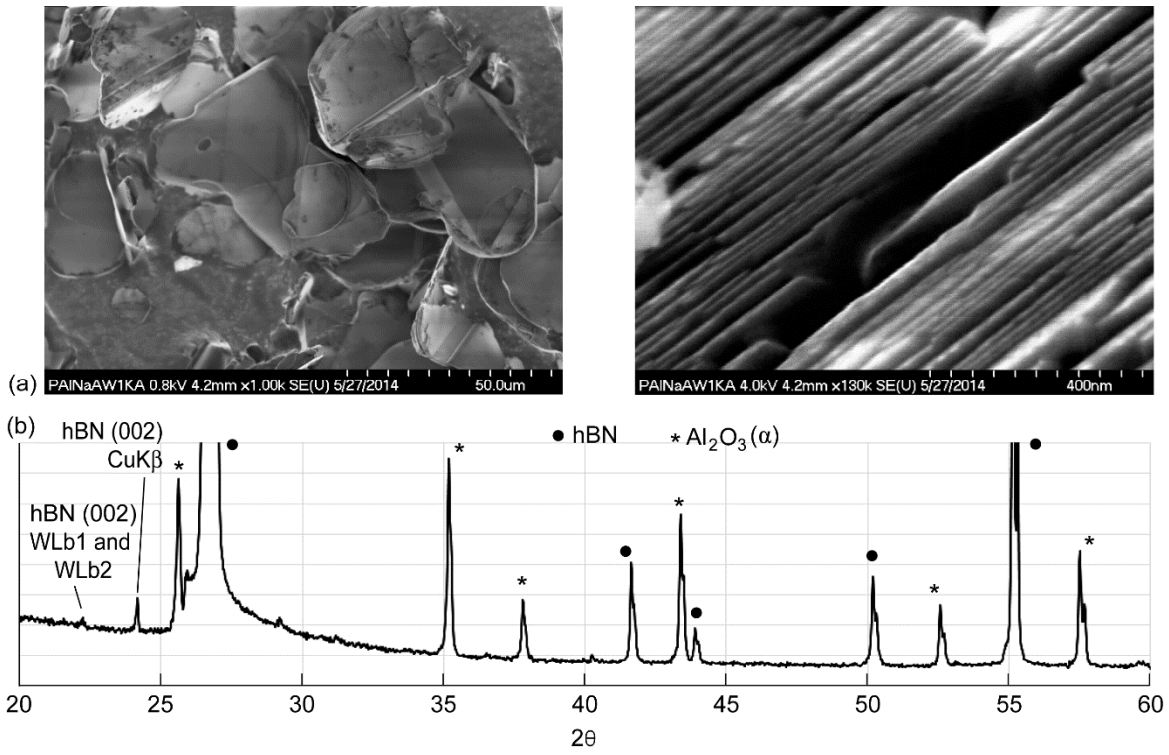

Figure 3.—Intermediate product after 1050 °C heating in low-oxygen air to fabricate hBN/alumina composite. See Step (3), Table I. (a) Field emission scanning electron microscopy (FESEM) images. (b) X-ray diffraction (XRD) spectrum.

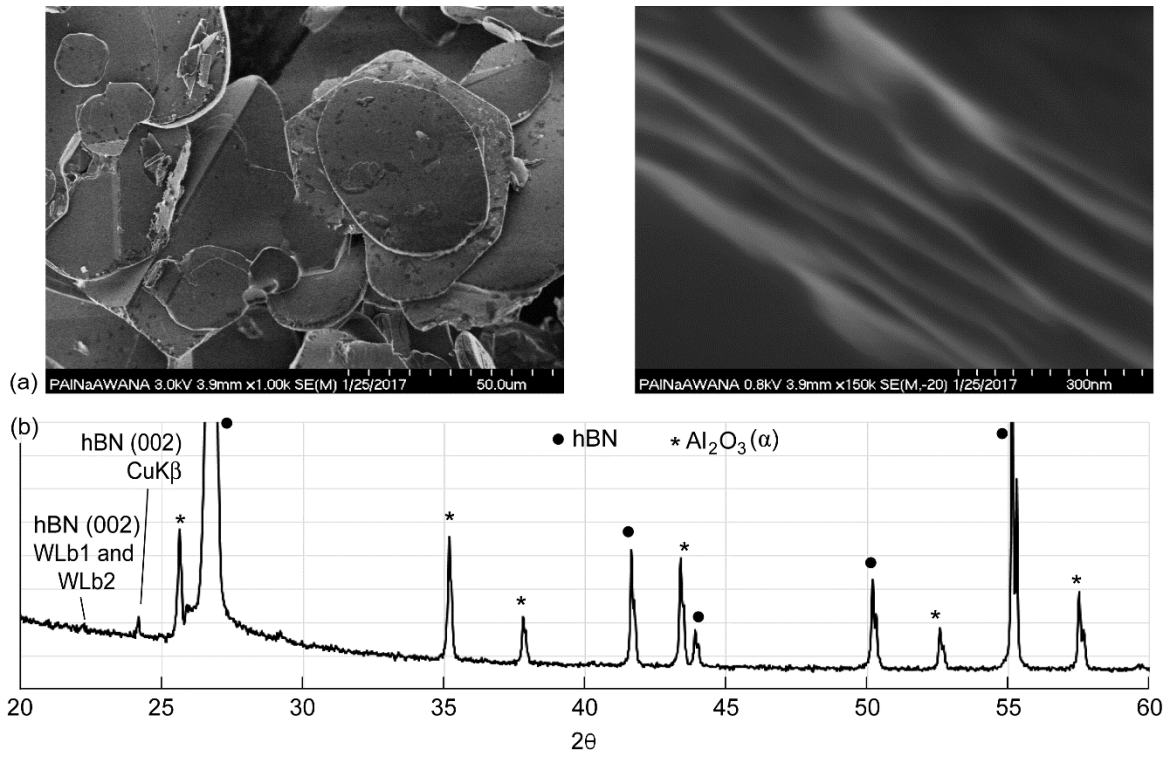

Figure 4.—Intermediate product after 850 °C heating in air and rinsing to fabricate hBN/alumina composite. See Step (4), Table 1. (a) Field emission scanning electron microscopy (FESEM) images. (b) X-ray diffraction (XRD) spectrum.

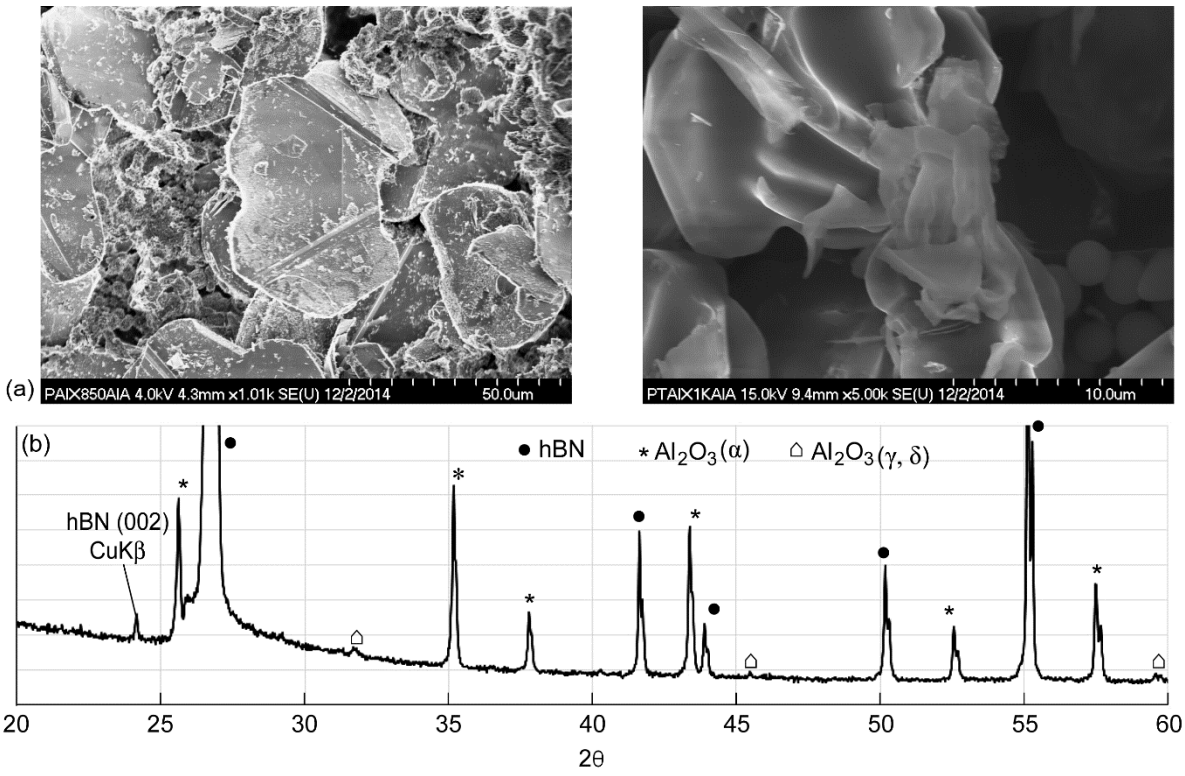

Figure 5.—Intermediate product after coating hBN with Al_2O_3 rinsing to fabricate hBN/alumina composite. See Step (5), Table I. (a) Field emission scanning electron microscopy (FESEM) images. (b) X-ray diffraction (XRD) spectrum.

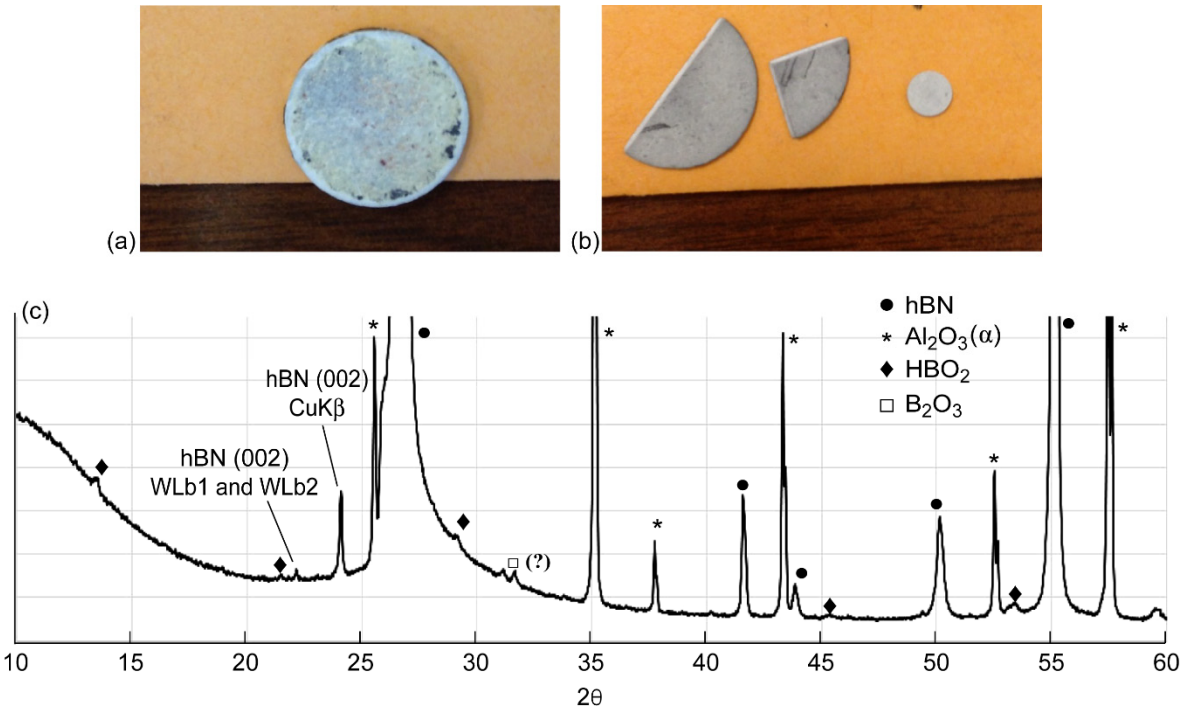

Figure 6.—Final hBN/ceramic composite after final step of hot pressing at 1950 °C and 69 MPa in nitrogen to fabricate hBN/alumina composite. See Step (6), Table I. (a) Hot-pressed composite disk 19 mm in diameter. (b) Machined and polished samples, 0.7 mm thick. Largest sample is 19 mm in diameter. (c) X-ray diffraction (XRD) spectrum.