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Title: Fabrication of Al/AlN in-situ nanocomposite through planetary ball milling and hot extrusion of Al/BN: microstructural evaluation and mechanical behavior

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Keywords: Al/AlN nanocomposite; planetary ball milling; hot extrusion; mechanical properties; microstructure; In-situ phase

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Abstract: In this study, Al/AlN in-situ nanocomposites were fabricated using Al/BN as the starting composite powders. The impact of adding hexagonal boron nitride (BN) to the Al matrix of commercial purity on the microstructure and mechanical behavior of the fabricated in-situ nanocomposites was investigated. Samples including 1, 2, and 4 wt.% boron nitride nanoparticles were produced by planetary ball milling of the composite powders and a post-process of hot extrusion. Scanning transmission electron microscopy revealed that boron nitride nanoparticles dissolved as a solid solution of B and N in the Al matrix at the as-milled state. Through the process of hot extrusion, AlN as the in-situ phase was formed by a reaction between Al and N. These led to improve the mechanical properties as well as grain refinement of Al/AlN nanocomposite. The average grain size of the fabricated composites with the use of 1, 2 and 4 wt.% BN was measured about 910, 823, and 760 nm respectively. It was found that combined strengthening mechanisms of grain refinement, a solid solution of mostly B and AlN in-situ phase formation improved the mechanical properties of Al/AlN nanocomposite. With the use of 1, 2, and 4 wt.% BN, the tensile strength of nanocomposite samples increased approximately 40, 56, and 57% in comparison with pure Al, respectively. The remarkable change in microstructure and mechanical properties of the nanocomposite was obtained when the content of BN is up to 2 wt.%.

Cover letter

Journal of Alloys and Compounds

Dear Editor

Prof. Cook

I wish to submit an original research article entitled "*Fabrication of Al/AlN in-situ nanocomposite through planetary ball milling and hot extrusion of Al/BN: microstructural evaluation and mechanical behavior*" for consideration by " *Journal of Alloys and Compounds* ". This work has not been published before; it is not under consideration for publication anywhere else; and publication has been approved by all co-authors and the responsible authorities at the institute(s) where the work has been carried out.

We believe that this manuscript is appropriate for publication by "*Journal of Alloys and Compounds* " since this research article contains an efficient fabrication method for Al/AlN in-situ nanocomposite following deep microstructural investigations and phase evaluations. Furthermore, as a novelty, we try to correlate the microstructure features to the mechanical. Some of the key factors in the proposed fabrication method are its low cost of production, its easy manufacturing, and no size limitation. Also, the optimum parameters for the fabrication of the nano-composite with the best mechanical properties are defined.

Thank you very much for your consideration of this manuscript,

Sincerely,

R. Ebrahimi

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Prime Novelty Statement

The current manuscript provides a detailed phase evaluation and microstructure investigation of Al/AlN in-situ nanocomposite fabricated through planetary ball milling and hot extrusion as a cheap and applicable fabrication route. The microstructure changes correlate to the mechanical behavior in order to determine the impact of various strengthening mechanisms.

Response to Reviewers

Shiraz University

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Title:

Fabrication of Al/AlN in-situ nanocomposite through planetary ball milling and hot extrusion of Al/BN: microstructural evaluation and mechanical behavior

Dear editor

Professor *Livio Battezzati*

The authors thank the reviewers for the time and effort which they invested in reading, in detail, our work. This document summarizes changes made in response to the reviewer comments. Each reviewer comment is addressed separately. Changes made in the manuscript are highlighted in blue. We believe that the changes made, in light of the reviewers' comments, have significantly enhanced the quality of the submitted manuscript.

Reviewer #1:

But there are several minor typos and some information are lacking. Please consider the following suggestions.

[Text overall]

several typos, missing spaces and discontinuously unit use and form

Answer: The manuscript is modified to overcome typos, missing spaces and discontinuously unit and form.

0 Abstract:

Study used hexagonal BN, so Authors should clarify it in abstract too. What Al is used? Purity

Answer: The authors thank the reviewer for the comment. The bellow sentence is added to the abstract:

" The impact of adding hexagonal boron nitride (BN) to the Al matrix of commercial purity on the microstructure and mechanical behavior of the fabricated in-situ nanocomposites was investigated."

2 Experimental Procedure:

[1st paragraph] Add purity of used Al-powder. Small variances and impurities at this state have big impact at overall properties.

Answer: The purity al-powder was 99.75 % . Therefore, it is added to the first line of the experimental procedure.

[1st p.] h-BN composition percentage of B 54.5% and N 45.5% does not add up by 99% purity.

Answer: The authors acknowledge the reviewers' comment. The composition of h-BN powders was determined qualitatively by EDS analysis. Therefore, the measurement is not accurately and the composition percentage was deleted from manuscript in the experimental section, First paragraph, lines 3.

[2nd p.] Study highlights the importance of the ball milling process. But the information given are not sufficient to recall the production step properly. Please add mill type; container material, its diameter and height; mill ball density, material and diameter; extent of container filling; milling temperature.

Answer: the supplementary information of the ball milling process was added in the experimental section, second paragraph, lines 2-7:

"Mixtures of composite powders contain the Al powders with different content of boron nitride (1, 2 and 4 wt.%), and 1 wt.% stearic acid as process control agent (PCA) were prepared using a Fritsch P5 planetary ball mill. The composite powders were loaded with balls (10 mm diameter made of 100Cr6 with density of 7.81 g/cm^3) in a hardened chromium steel round-ended cup. The full volume, diameter, and deepest height of cup are 130 ml., 70 mm, and 45 mm respectively. Also, 50 % of the cup is left empty during milling process. The milling process was carried out at room temperature in pure argon atmosphere for 300 min milling time with rotational speed of 430 RPM and powder to ball weight ratio of 1:20."

[3rd p.] Used hot extrusion process speed would be interesting information.

Answer: The samples were extruded with process speed of 0.2 mm/sec. This data was added to manuscript in the experimental procedure section, Third paragraph, lines 6-7.

[4,5th p.] Polishing time for TEM samples not given. Stats indicate the same parameter as the following EBSD samples were used? Continuous use of SI Units: TEM polishing temperature are written in °C, EBSD in K.

Answer: The bellow sentence is added to the experimental procedure:

"The specimens were finally polished by ion beam using Gatan 691 precision ion polishing system (PIPS) for ~1 min."

[6th p.] Vickers 10kg load? Correct units are kgf or N

Answer: The correction has been made in experimental procedure section, last paragraph, line 4 as the following phrase.

3. Results:

3.1.

[2nd p.] What are grains A, B, C? It is not clear to understand. Are they the three grains shown in Fig.3? But there is no description either. Authors should precise it further. Either at Fig. 3 or in the text.

Answer: The authors thank the reviewer for this comment. The corresponding grains was shown in Fig. 3. Therefore, grains A, B, and C are recognizable in the Fig. 3 of the revised manuscript.

4. Discussion:

4.2.

[1st p.] true value strain. Should add units into the clips

Answer: The correction has been made in discussion section as of bellow:

"The true strain value in the hot extrusion process (~2.3 mm/mm) is higher than the required critical strain for happening dynamic recrystallization in Al matrix (~ 0.5 mm/mm)"

[2nd p.] Adding the time of the 580°C heat treatment would improve quality of reading

Answer: The heat treatment process was explained in experimental procedure section, third paragraph, lines 4-5 through the following sentence:

"The pressed samples were sintered at 580 °C for 45 min to fabricate the final dense samples with 10 mm diameter"

Figures

Fig. 3 Please highlight/marker the grains A, B, C

Answer: It is corrected.

Fig. 7(b) Are the mentioned rods of Al4C3 different sizes or just different orientated rods regarding the researched plain?

Answer: As can be seen in Figs. 6 and 8, Al4C3 phase has different size (in length and inter planar spacing) and orientation.

Yours sincerely,

Ramin Ebrahimi

*Manuscript
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Fabrication of Al/AlN in-situ nanocomposite through planetary ball milling and hot extrusion of Al/BN: microstructural evaluation and mechanical behavior

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Abstract

In this study, Al/AlN in-situ nanocomposites were fabricated using Al/BN as the starting composite powders. The impact of adding hexagonal boron nitride (BN) to the Al matrix of commercial purity on the microstructure and mechanical behavior of the fabricated in-situ nanocomposites was investigated. Samples including 1, 2, and 4 wt.% boron nitride nanoparticles were produced by planetary ball milling of the composite powders and a post-process of hot extrusion. Scanning transmission electron microscopy revealed that boron nitride nanoparticles dissolved as a solid solution of B and N in the Al matrix at the as-milled state.

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Through the process of hot extrusion, AlN as the in-situ phase was formed by a reaction between Al and N. These led to improve the mechanical properties as well as grain refinement of Al/AlN nanocomposite. The average grain size of the fabricated composites with the use of 1, 2 and 4 wt.% BN was measured about 910, 823, and 760 nm respectively. It was found that combined strengthening mechanisms of grain refinement, a solid solution of mostly B and AlN in-situ phase formation improved the mechanical properties of Al/AlN nanocomposite. With the use of 1, 2, and 4 wt.% BN, the tensile strength of nanocomposite samples increased approximately 40, 56, and 57% in comparison with pure Al, respectively. The remarkable change in microstructure and mechanical properties of the nanocomposite was obtained when the content of BN is up to 2 wt.%.

Keywords: *Al/AlN nanocomposite; planetary ball milling; hot extrusion; mechanical properties; microstructure; In-situ phase*;

1. Introduction

Recently, the fabrication of bulk Al-matrix composites with use of BN particles have strongly been considered due to their light weight (lower than pure Al), superior strength at room temperature even at low contents of BN as a reinforcement, and good thermal stability at elevated temperatures [1-3]. Consequently, these composites are good candidates for automotive and aerospace applications in comparison to the other Al matrix composite materials.

Hexagonal boron nitride (h-BN) has exceptional features in comparison to other ceramic particles. These exceptional features are its low density (2.3 g/cm^3 and lower than pure Al), its ability to dissolve in the Al matrix during high energy milling and its ability to be formed in-situ

phases during the annealing state of fabrication (sintering, spark plasma sintering and hot extrusion) [4, 5].

The structure of Al/BN composite powders and their solid solution formation during planetary ball milling were studied by a number of researchers [5-7]. It is well documented that high energy planetary ball milling can lead to the dissolution of BN in the Al matrix as a solid solution. On the other hand, it has been suggested that the possible AlN and AlB_2 as the in-situ phases are created during a heating state in the Al matrix as the following [4, 5].

$$3Al + 2BN \rightarrow 2AlN + AlB_2 \quad (1)$$

Hot extrusion and spark plasma sintering have been used successfully to fabricate Al/BN bulk samples from composite powders [1-3, 8]. For instance, Firestein *et al*. [1] synthesized Al/BN nanocomposite by the homogeneous mixing of composite powders and spark plasma sintering. In this study, the nanocomposite samples with 4.5 wt.% of BN nanoparticles showed 50% increase in the tensile strength compared with the pure Al as a reference sample. In the other study, Firestein *et al*. [2] have fabricated in-situ nanocomposite by planetary ball milling to prepare Al/BN powder and then spark plasma sintering. They found that AlN and AlB_2 as the hard inclusions and the grain refinements due to ball milling process enhanced the tensile strength by about 130 % compared with the pure Al.

An alternative for the process of spark plasma sintering is the process of hot extrusion that has several potential advantages including: the low cost of production, the easy manufacturing, no size limitation [9, 10], the high shearing stresses during the process which is enough to break the nanometric oxide layer covering powder particles, and the occurrence of the dynamic recrystallization during the process [11]. Gostariani *et al*. [3], fabricated nanocomposite by

planetary ball milling of Al/BN composite powders following a conventional hot extrusion. The tensile strength of the nanocomposite containing minimum content of BN (1 wt.% BN) improved by 40% in comparison with the pure Al. In another research, Gostariani *et al* [12], investigated the hot deformation behavior of mechanically milled and hot extruded Al-1 wt.% BN using hot compression tests at different temperatures and strain rates. It is found that the dynamic recrystallization is responsible for the fine-grained microstructure of the hot deformed samples. The nanocomposite resisted against abnormal grain growth and led to the stability of ultrafine structure after hot deformation.

Most of the researches on the Al-matrix composite with use of BN particle have focused on the improvement of mechanical properties wherein the microstructure evolution and strengthening mechanisms are rarely evaluated. Therefore, the present study aims to correlate the microstructure evolution to the mechanical behavior of Al/AlN in-situ nanocomposites contain different amount of BN and fabricated by planetary ball milling and hot extrusion.

2. Experimental Procedure

Commercial pure Al powders with the purity of 99.75 % having irregular morphology with an average particle size of 45 µm were employed as the matrix material (Fig.1 (a)). Hexagonal boron nitride (h-BN) nanoparticles (Lower Friction Co., 99 % purity, the average size of 70 nm) were added as the ceramic particle to fabricate Al/AlN in-situ nanocomposite (Fig. 1(b)).

Mixtures of composite powders contain the Al powders with different content of boron nitride (1, 2 and 4 wt.%), and 1 wt.% stearic acid as process control agent (PCA) were prepared using a Fritsch P5 planetary ball mill. The composite powders were loaded with balls (10 mm diameter made of 100Cr6 with density of 7.81 g/cm^3) in a hardened chromium steel round-ended cup. The

full volume, diameter, and deepest height of cup are 130 ml, 70 mm, and 45 mm respectively. Also, 50 % of the cup is left empty during milling process. The milling process was carried out at room temperature in pure argon atmosphere for 300 min milling time with rotational speed of 430 RPM and powder to ball weight ratio of 1:20. In order to increase compressibility, the milled powder was annealed at 200 $^{\circ}$C for 60 min. Then, the composite powders were pressed by a compressive pressure of 190 MPa in a cylindrical die with 35 mm diameter. The pressed samples were sintered at 580 $^{\circ}$C for 45 min to fabricate the final dense samples with 10 mm diameter. Finally, these dense samples were extruded with the speed of 0.2 mm/sec and extrusion ratio of 12:1. According to the 1, 2, and 4 wt.% of BN in the initial composite powders, the extruded nanocomposites named Al-1 wt.% BN, Al-2 wt.% BN, and Al-4 wt.% BN respectively. A pure Al specimen was prepared with the similar fabrication method (ball milling and hot extrusion processes) to use as a reference sample for comparison of mechanical properties.

A scanning electron microscope (SEM) of type Philips XL 30 and a transmission electron microscope (TEM) of type Philips 100 kV were used to the investigation of the particle size and morphology of pure Al powders and boron nitride particles, respectively. The microstructures of the extruded samples were studied by a TEM/STEM (STEM, JEOL JEM-2100F) equipped with an energy-dispersive X-ray spectrometry (EDS) and the operating voltage of 200 kV. Thin foils for TEM observations were prepared with mechanical polishing to the thickness of 100μm. Then the thin foils were twin-jet polished using the TenuPol-5 facility (Struers Co., Ltd.) in an electrolyte solution of 20 vol. % $HClO_4$ acid and 80 vol. % of ethanol with the voltage of 35 V at -20 $^{\circ}$C. The specimens were finally polished by ion beam using Gatan 691 precision ion polishing system (PIPS) for ~1 min.

Electron back-scattering diffraction (EBSD) was used for the quantitative analysis of the microstructure. The EBSD observations were performed by a JEOL 7001 F scanning electron microscope (FE-SEM) equipped with a field emission gun operating at 20 kV. For the EBSD measurements, the INCA suite 4.09 software package was used. EBSD analysis was carried out on an area of $45 \times 60\ \mu m^2$at pixel $0.052\ \mu m^2$. Misorientations below 2° were not measured in the post-processing data analysis. Before the observations, the samples were sectioned through the extrusion direction and then ground using different SiC abrasive papers followed by final polishing with diamond compounds and the polishing cloths. Electro-polishing of all EBSD samples were performed in a solution of 20 vol. % of $HClO_4$ and 80 vol. % of ethanol with a DC voltage of 35 V for 20 sec at -20 $^{\circ}$C.

Mechanical properties of the extruded samples were measured by the tensile and the hardness tests. The tensile test specimens with 6 mm diameter and 30 mm gauge length were prepared according to ASTM E8. The tensile tests were performed at room temperature and constant cross-head speed of 0.5 mm/min. To investigate hardness, Vickers method under 10 kgf applied load was used.

3. Results

3.1. Microstructure Observations Using TEM

Figure 2 (a, b, and c) shows the TEM micrographs with the corresponding selected area diffraction (SAD) patterns of the extruded nanocomposites contains 1, 2, and 4 wt.% BN respectively. Although some elongated cells are observed along the extrusion direction, the high fraction of microstructures consists of equiaxed cells in the range of nano to ultrafine size. The average cell size of the nanocomposite decreases with the increasing of boron nitride particles.

The average cell size of nanocomposites containing 1, 2 and 4 wt.% BN is determined as ~750, ~550and ~300 nm respectively. As can be seen, the continuous ring shape of the Al phase in SAD pattern confirms the good refinement in the microstructure of the Al matrix.

Various types of cell boundaries can be detected in the fabricated nanocomposites. For instance, different cell boundaries in the nanocomposite containing 4 wt.% BN is shown in Fig. 3. Three high angle boundaries, as well as a triple junction, are observed in Fig. 3(a). The cell wall thickness of the aforementioned boundaries is low. Interestingly, these three adjunct grains have different morphologies. While piled-up dislocation in grain A shows the high stored strains in it, only, some single dislocations are detectable in grains B and C which attributes to the relaxation happens in these grains. A low angle grain boundary with a thick cell wall is shown in Fig. 3(b). This cell wall has the average thickness of ~20 nm with high mobility.

3.2. Microstructure Observations Using EBSD

Since TEM observations mainly represent a smaller area of a specific region and also it is less quantitative, the EBSD observations were carried out to have a generalized quantitative investigation of the microstructural features. Fig. 4 shows the inverse pole figure as a scale of EBSD orientation color maps and the corresponding boundary maps of different composite taken from a plane perpendicular to the extrusion direction. As observed for all the samples the microstructure consists of the grains with a random orientation distribution and almost equiaxed shapes. Furthermore, most of the boundaries are high angle grain boundaries (HAGBs).

The microstructural parameters, from the EBSD (Figs. 4), such as grain size (equivalent circle diameter), mean misorientation angle (θ_m) and the fraction of high-angle grain boundaries (f_{HAGBs}) were measured and presented in Fig. 5. With increasing the content of BN nanoparticles,

the grain size decreases and the mean misorientation angle of the boundaries and the fraction of HAGBs increase. The average grain size of the nanocomposites containing 1, 2 and 4 wt.% BN measured about 910, 823 and 760 nm respectively. However, the change of the aforesaid parameters is so slight by increasing the BN more than 2 wt.%. In other words, the maximum change in the grain size, f_{HAGBs}, and θ_m are detected in the composites containing 2 wt.% of BN.

3.3. Phase Evaluation

It is not possible to characterize the newly created phases in the nanocomposite by X-ray diffraction due to the limitation of the phase analysis (higher than 5 vol. %). Therefore, the phase evaluation of the extruded nanocomposite has been investigated using TEM/STEM observations with an energy-dispersive X-ray spectrometry corresponding to selected area diffraction patterns (SADP). Fig. 6 shows the TEM micrograph of the Al-1 wt.% BN nanocomposite. The spherical initial BN nanoparticles were not observed in the microstructure. Instead, a rod-shape phase with nanometric diameter and length is dispersed uniformly in the matrix (Fig. 6(a)). This rod-shape phase was detected in various sizes, from $15 \times 150\ nm$ to $20 \times 70\ nm$ (see Fig. 6(b)).

Figure 7 displays a SAD pattern of Al-4 wt.% BN nanocomposite with two different magnifications. The different diffraction reflections of Al phase are determined in Fig. 7(a). By discarding the Al phase, the other rings relate to the newly created phases in the Al matrix as determined in Fig. 7(b). It demonstrates the complete elimination of the initial BN reinforcement in the extruded Al matrix. In addition, the diffraction reflections of AlN (100) and Al_4C_3 phases indicate the in-situ creation of them through the extrusion process. On the other hand, AlB_2 which is expected to be formed in-situ was not detected in TEM and SAD observations.

To recognize the nature of the rod-shape phase of Fig. 6, high-resolution STEM micrographs of two of them are shown in Fig.8. The inter-planar spacing of the rod-shape phases is found to be about 0.55 nm and 0.83 nm, which is corresponding to the (006) and (003) planes of Al_4C_3 respectively.

Fig. 9 shows the bright field TEM images and the corresponding results of EDS analysis results of the matrix and in-situ phases in the Al-4 wt.% BN nanocomposite. As can be seen in Fig.8 (a), in spite of the limitations of EDS to characterize the light elements; the nitrogen content of in-situ phases obviously increases compared with the matrix. Therefore, the microstructure observation corresponding to EDS result confirms the formation of AlN which was previously confirmed by the analysis of SAD patterns (see Fig. 7(b)). On the other hand, Fig. 9(b) confirms the high amount of the carbon in the rod-shape phase which was expected to be Al_4C_3. Furthermore, the results of the EDS line scanning confirm the formation of both, the AlN and Al_4C_3 as the in-situ phases. The green line in Fig. 10(a) confirms the high nitrogen content of the spherical shape phase. Also, the gray line in Fig. 10(b) shows the high carbon content of the rod-shape phase.

3.4. Mechanical Properties

The variation of ultimate tensile strength (UTS) and elongation of the composites by increasing the BN content is plotted in Fig. 11. The UTS of the samples contains zero amount of BN gradually increases from 212 MPa to 297 MPa by adding 1 wt.% of BN to the composite. By adding this amount of BN the elongation of the pure Al sample decreases from ~15% to ~7.7%. This means an improvement in the UTS by the amount of 40% and a decrease in the elongation by ~50% by addition of only 1 wt.% of BN. By adding another 1 wt.% of BN nanoparticles the

UTS increases to 330 MPa wherein the elongation decreases to 5.8%. In other words, an addition of 2 wt.% of BN nanoparticles to the pure Al improved its UTS by ~56% with the cost of ~62% decrease in the elongation. Further addition of BN content does not affect the UTS strongly but cause a significant decrease in the elongation. As seen, in the Al-4 wt.% BN nanocomposite the UTS and elongation are 333 MPa and 1.7% respectively

The average values of Vickers hardness of the extruded specimens are presented in Fig. 12. For the composites contains 0, 1, 2 and 4 wt.% of BN the hardness was calculated as 65, 102, 112 and 124 HV respectively. Therefore by adding 1, 2 and 4 wt.% of BN to the Al matrix, its hardness increases by 55%, 70%, and 90% respectively.

4. Discussion

4.1. Phase Evaluation

Phase transformations such as the dissolution of BN during milling in the Al matrix and the in-situ phase formation in subsequent annealing has been investigated as the challenging topic in the fabrication of Al/BN composite, particularly at elevated temperatures [5-7, 13]. Dissolution of BN in Al matrix in the milling process and the formation of AlN and AlB_2 in-situ phases during the annealing process of Al-15 wt.% BN were reported previously in several studies [6, 7]. In lower contents of BN, the elimination of BN during the milling process is facilitated but the probability of the formation of in-situ phases in the hot extrusion post-processing becomes lower. However, the current study confirms the formation of the spherical in-situ AlN, even at the low BN amount of 4% (refer to Figs. 7-10). Nevertheless, the other in-situ phase of AlB_2 was not detected in the observations. Therefore, due to the dissolution of BN in the milling, it seems that the reaction of Eq. (1) between Al and BN did not happen at the extrusion process. In the

other words, the BN decomposed to B and N elements and then dissolved as a solid solution in the Al matrix [5]. Then, AlN as the in-situ was formed at the extrusion temperature by the following equation:

$$Al + N = AlN \quad (2)$$

Figure 9(a) and Fig. 10(a) show the creation of AlN phase as the spherical shape and nanometric size which is also reported by Firestein *et al*. [2]. However, the high fraction of N and all the B content remained as a solid solution in the Al matrix. The possibility of reaction between Al and B through Eq. (3) is lower than the reaction of Eq. (2) due to its lower Gibbs free energy [14].

$$Al + 2B \rightarrow AlB_2 \quad (3)$$

As can be obviously observed in Figs. 6 and 8, an unwanted in-situ phase of Al_4C_3 which was formed in a rod shape, is created by the reaction between C (is obtained from dissolution of stearic acid in the matrix during milling process [15, 16]) and Al through the following equation:

$$4Al + 3C \rightarrow Al_4C_3 \quad (4)$$

4.2. Microstructure Observation

According to the TEM micrographs of the extruded samples (Fig. 2), the matrix of nanocomposite samples consists of recrystallized nano/ultrafine grains. The true strain value in the hot extrusion process (~2.3 mm/mm) is higher than the required critical strain for happening dynamic recrystallization in Al matrix (~0.5 mm/mm) [17] and cause to occur the dynamic recrystallization during the hot extrusion process. In addition, the refined microstructure of the nanocomposites remained in the form of ultrafine / nano grains after hot extrusion at 580 ˚C.

This means that the Al/AlN in-situ nanocomposite has thermal stability against the abnormal grain growth.

As can be seen in Fig. 3, the grain boundaries in the Al matrix act as main obstacles to decrease the dislocation motion and accumulate of dislocation and pile up. After hot deformation of high SFE materials, the tendency to dislocation substructure formation increases. The three-dimensional dislocation tangles turn into two-dimensional dislocations with the more than 10° crystallographic misorientation [18]. The dislocation substructures are obtained from cell structure and convert to high angle sub boundaries which are surrounded by high angle boundaries (see Fig. 3(b)).

According to Fig. 3, the density of dislocation of Al-4 wt.% BN was calculated by following equation [19]:

$$\bar{l} = {}^{1}/_{\rho^{0.5}} \tag{5}$$

where $\bar{l}$ and ρ are average separation between dislocation and density of dislocation, respectively [19]. Based on this equation, the density of dislocation in the different region of matrix such as: in the cell walls, accumulated behind the grain boundaries and in the grain interior are measured as $\sim 1.8\times10^{16}$ m^{-2}, $\sim 7\times10^{14}$ m^{-2}, and $\sim 1.5\times10^{14}$ m^{-2} respectively.

The EBSD observations in Fig. 4 revealed that recrystallization is the dominant mechanism to develop the ultrafine microstructure with high angle boundary. Although the grains of the matrix in nanocomposite samples were refined about 30% by increasing the BN content from 1 to 4 wt.%, the occurrence of grain refinement in the extrusion process were not significant. In the other words, the main grain refinement happens in the milling process and the addition of BN

has less effect on the grain refinement. Through the high energy ball milling of Al-BN composite powders, the boron nitride with weak Van der Waals bonding between its layers is easily affected by ball milling and decomposes to boron and nitrogen elements [5, 20]. These elements are placed at the defects in the Al matrix which are, in turn, increased by ball milling and resulting in occurrence of the mechanical alloying. This phenomenon led to refine the composite powder microstructure with the dislocation network and subgrain formation. On the other hand, the solid solution and the in-situ phases decreased the movement of grain boundary and also prevented abnormal grain growth in the bulk microstructure and resulted in the stability of ultrafine microstructure in the elevated temperature of the extrusion process. In addition, due to the absence of initial reinforcement and also high temperature of extrusion, the grain refinement with the particle stimulated nucleation (PSN) mechanism is not possible.

4.3. Mechanical Properties

Based on the microstructure observations, the mechanical properties of the extruded samples increased by the combined strengthening mechanisms of; grain boundary strengthening, solid solution formation, and presence of AlN and Al_4C_3 as the in-situ phases. Furthermore, the dispersion of Al_2O_3 phase in the matrix was unavoidable and enhanced the mechanical properties of the extruded samples. This phase is obtained from the Al_2O_3 layer which is covering the Al powders and fragments during ball milling of Al powders and disperses in Al matrix [21].

According to Hall-Petch equation [22], due to the ultrafine grain microstructure of the extruded samples, the increase in the mechanical properties of the nanocomposites is expected. The grain refinement, dispersion of Al_2O_3 and Al_4C_3 in-situ phase formation promote the mechanical

properties of all extruded samples such as pure Al (reference sample) and nanocomposite samples.

According to Orowan- Ashby model, the increasing in the UTS of all extruded samples such as Al-4 wt.% BN results from the presence of Al_4C_3 can be estimated by [23]:

$$\Delta\sigma = \frac{MGb}{2.36\,\pi}.\ln\left(\frac{\phi}{2b}\right).\frac{1}{\lambda-\phi} \quad (6)$$

where M is the Taylor factor which can be considered as 3.06 for the current case of randomly oriented FCC structure, G=26 GPa is shear modulus, b=0.286 nm is the Burgers vector, and ϕ is the equivalent diameter ($\phi = \sqrt{\frac{3D^2L}{2}}$). According to Fig. 8, the parameters of D and L for rod shape of Al_4C_3 have measured about 15.5 and 90 nm, respectively and the equivalent diameter is estimated as 180 nm. λ is the inter particle spacing ($\lambda = \phi\sqrt{\frac{\pi}{6\,V_{Al4C3}}}$). In this parameter, V_{Al4C3} is the volume fraction of Al_4C_3 phase which is calculated as following Eq.(7) [23]:

$$V_{Al4C3} = \frac{2.25.\alpha.m}{2.25.\alpha.m + \frac{\rho_{Al4C3}}{\rho_{Al}}.(100-2.25.\alpha.m)} \quad (7)$$

where m is weight percentage of total stearic acid (m=1 for 1 wt.% stearic acid). ρ_{Al4C3} is 2.36 g/cm^3. When the reaction between Al and stearic acid occurred completely, the parameter of α equals to the unit (α=1). With the use of Eq. (6) to (7), the contribution of Al_4C_3 phase to the strengthening of the extruded matrix is estimated as 28 MPa.

As can be seen in Figs. 3 and 5, the increasing in the grain boundaries cause to bound the dislocation movement and increasing the dislocation density behind the boundaries and consequently the enhancement in the strength.

By using Eq.(5) and estimate the dislocation density within the grains, the improvement in the strength due to dislocation strengthening mechanism in Al-4 wt.% BN is calculated about 55 MPa by using the following relationship[24]:

$$\Delta\sigma = M\alpha Gb\sqrt{\rho} \quad (8)$$

where α is a constant which is 0.2 for FCC metals, and $\rho=1.5\times10^{13}m^{-2}$ is the calculated density of the dislocations in the grain.

Another parameter which is involved in the strengthening of the composite is the grain boundary strengthening (Hall-Petch mechanism) which is expressed [24]:

$$\Delta\sigma = {}^{k}/_{\sqrt{D}} \quad (9)$$

where K is the locking parameter (Hall- Petch constant) and it was deemed 0.04 MPa/$\sqrt{m}$ for pure Al. Therefore, the contribution of the grain boundary into the increase of the strength of Al-4 wt.% BN is calculated about 46 MPa.

Based on the Eq.(10), improvement of the yield strength of nanocomposite samples contains 1 and 4 wt.% BN with the grain size of 910 nm and 760 nm estimated about 4 MPa[23].

$$\Delta\sigma = k({D_C}^{-0.5} - {D_m}^{-0.5}) \quad (10)$$

In the Eq. (10), D_c and D_m are the average grain size of the extruded nanocomposite samples with the use of 4 and 1 wt.% BN, respectively.

Therefore, the effect of grain refinement on the increasing of the mechanical properties of the nanocomposite in comparison with the reference sample (pure Al) is minor and can be ignored. In fact, the improvement of hardness and tensile strength of the Al/AlN in-situ nanocomposites

attribute to the solid solution and the formation of AlN in-situ phase. In the solid solution of B and N elements in the Al matrix, the difference of atomic size of solute (B and N) and solvent (Al) is considerable. Therefore, the strain field on the lattice of the surrounding matrix impedes the dislocation motion in the matrix and an additional stress needs to overcome the solute stress field which is collectively known as solid solution strengthening [19]. The comparison of Al-4 wt.% BN with pure Al (reference sample) showed that the contribution of solid solution mechanism to strengthen the Al-4 wt.% BN nanocomposite was estimated about 130 MPa. Therefore, the solid solutioning and occurrence of the AlN in-situ phase had the most positive effect on the improvement of the mechanical properties of extruded nanocomposite samples.

Interestingly, the trends in the variation of the mechanical properties (Figs. 11 and 12) are consistent with the trend of change in the microstructural features (Fig. 5). In the other words, although the grain refinement and improvement in the mechanical properties continues by increasing the content of BN, maximum changes in the microstructure and strength occurs after addition of 2 wt.% of BN. Considering the significant decrease in the elongation of the samples contains 4 wt.% of BN, it can be said that the best combination of strength and ductility attributes to the composites contains 2 wt.% of BN.

Conclusion

In this research, the microstructure evaluation and the mechanical behavior of the Al/AlN in-situ nanocomposites fabricated by Al/BN composite powders using planetary ball milling and hot extrusion were investigated. TEM/STEM observations indicated that the boron nitride dissolved as a solid solution in the Al matrix. Through the process of solid solution, the BN decomposed to B and N and mechanical alloying happened. Although the AlN as in-situ phase was created by the reaction of Al and N at hot extrusion process, the element of B remained as a solid solution in

the matrix. These phenomena led to refine microstructure and increase the dislocation density in the matrix. The EBSD results confirmed the development of the recrystallized ultrafine microstructure of nanocomposite with the thermal stability against grain growth during the high-temperature extrusion process. The average grain size of bulk extruded nanocomposite samples including 1, 2, and 4 wt.% BN was obtained as 910, 823, and 760 nm, respectively. By increasing the amount of BN nanoparticles from 1 to 2 and then 4 wt.%, the tensile strength enhanced about 40%, 56%, and 57% respectively, in comparison to that of the pristine pure Al sample. In addition, the hardness values of nanocomposite reached to 102, 112 and 124 HV which are about 55%, 70%, and 90% respectively greater than the milled pure Al (65 HV).The improvement of mechanical properties in extruded nanocomposite attribute to the combined effects of grain refinement, formation of the in-situ phase and solid solutioning.

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Figure Captions

Fig.1. (a) SEM image of pure Al (b) TEM image of boron nitride (BN) nanoparticles.

Fig.2. TEM micrographs with the corresponding SAD patterns of the extruded nanocomposite samples with various compositions of Al/BN (a) Al-1 wt.% BN (b) Al-2 wt.% BN (c) Al-4 wt.% BN.

Fig.3. TEM observation on grain boundary microstructure of the extruded Al-4 wt.% BN showing (a) a triple junction with accumulated dislocation near a grain boundary (b) high magnification views on low angle boundary surrounded by high angle boundaries.

Fig.4. Inverse pole figure EBSD orientation color maps and the corresponding boundary maps in the extrusion direction of (a) Al-1 wt.% BN, (b) Al-2 wt.% BN and (c) Al-4 wt.% BN.

Fig.5. Variation of (a) grain size, (b) fraction of HAGBs and mean misorientation angle in Al-BN nanocomposites by increasing BN content.

Fig.6. a) TEM micrograph of Al-1 wt.% BN representing (a) the uniform distribution and (b) different size of a rod-shape in-situ phase.

Fig.7. A SAD pattern of Al-4 wt.% BN nanocomposite; (a) different diffraction reflections of Al phase and (b) the in-situ created phases.

Fig.8. High resolution STEM images of the in-situ Al_4C_3 with orientation of (a) (006) and (b) (003).

Fig.9. Bright field TEM images and the corresponding results of EDS analysis of the matrix and in-situ phases in Al-4 wt.% BN nanocomposite; (a) AlN phase and (b) Al_4C_3 phase.

Fig.10. Bright field TEM images with the corresponding result of the EDS line scanning confirms the formation of (a) AlN and (b) Al_4C_3 in-situ phases. The blue, green and gray colors represent Al, N and C elements respectively. Arrows show a decrease in Al content and increase in (a) N and (b) C content at the area occupied by the in-situ phase.

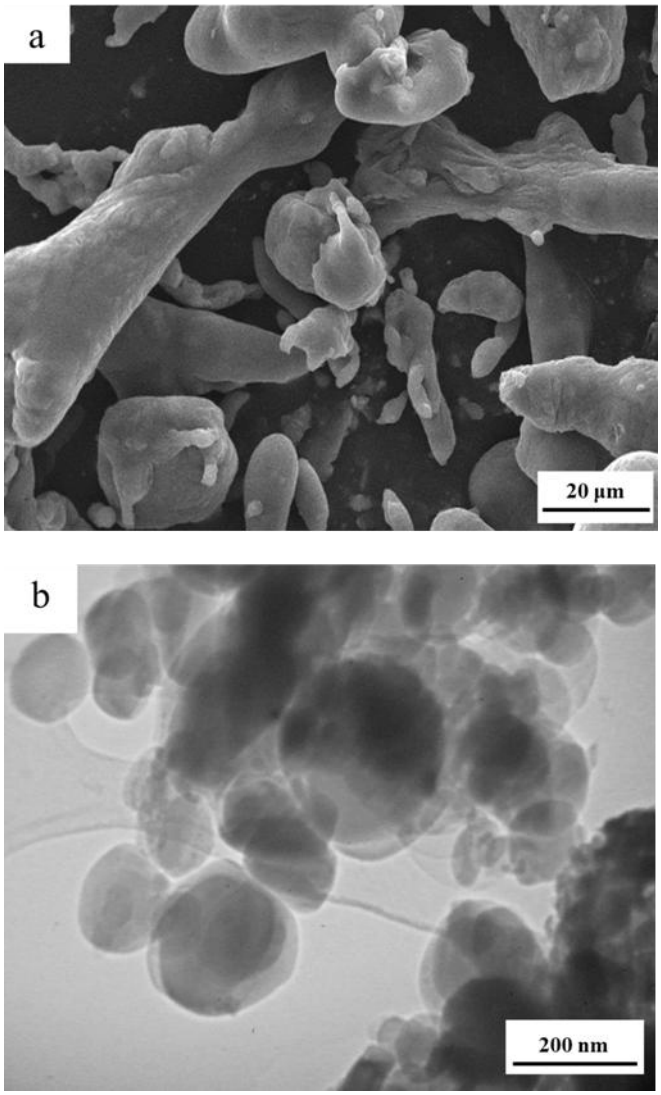
Fig.11. Variation of ultimate tensile strength (UTS) and elongation of the extruded samples by increasing the BN content

Fig.12. Variation of Vickers hardness of the extruded samples by increasing the BN content

Highlights

- Al/AlN nanocomposites were fabricated by planetary ball milling and hot extrusion.
- BN particles were dissolved as solid solution in matrix at the as-milled state.
- The in-situ AlN phase was created during hot extrusion process.
- The high fraction of N and all the B were remained as solid solution in matrix.
- The solid solution and AlN phase improve the mechanical property of nanocomposite.

Figure



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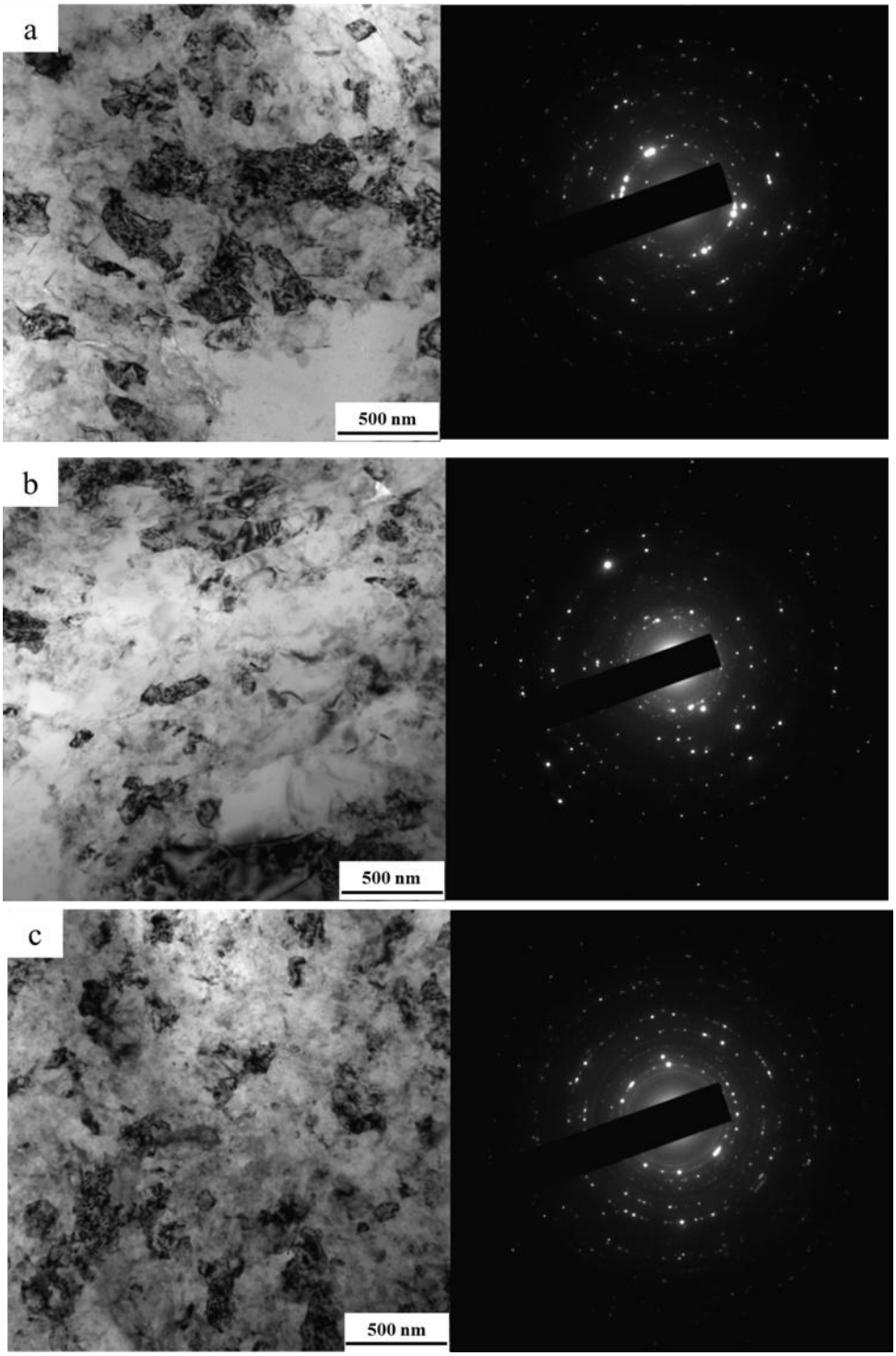


Fig.2. TEM micrographs with the corresponding SAD patterns of the extruded nanocomposite samples with various compositions of Al/BN (a) Al- 1 wt. % BN (b) Al-2 wt. % BN (c) Al-4 wt. % BN

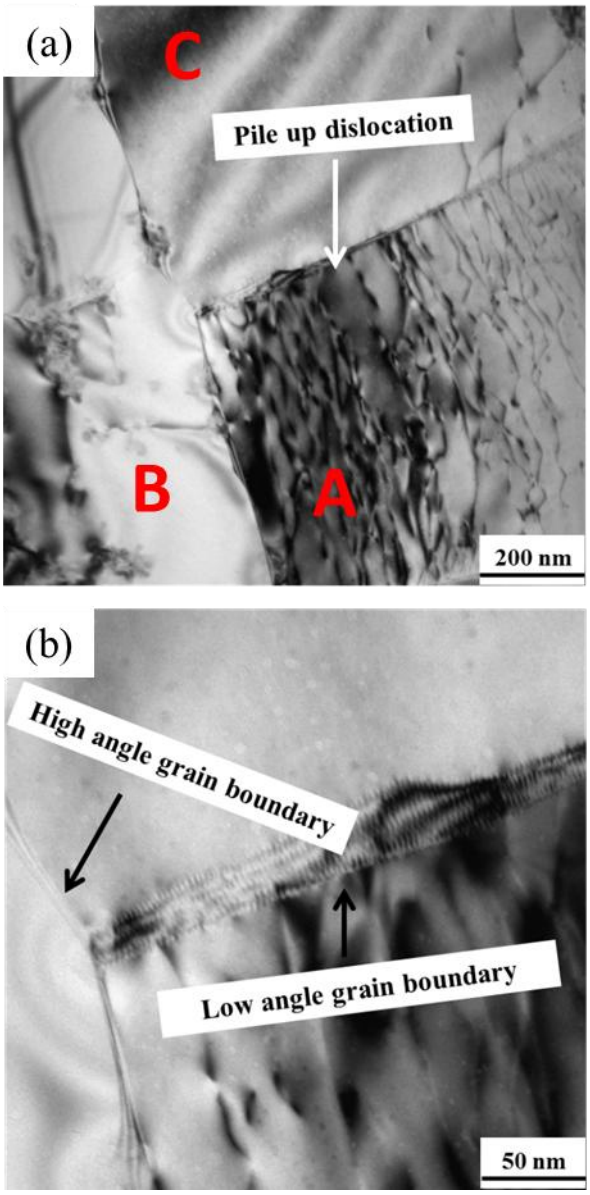
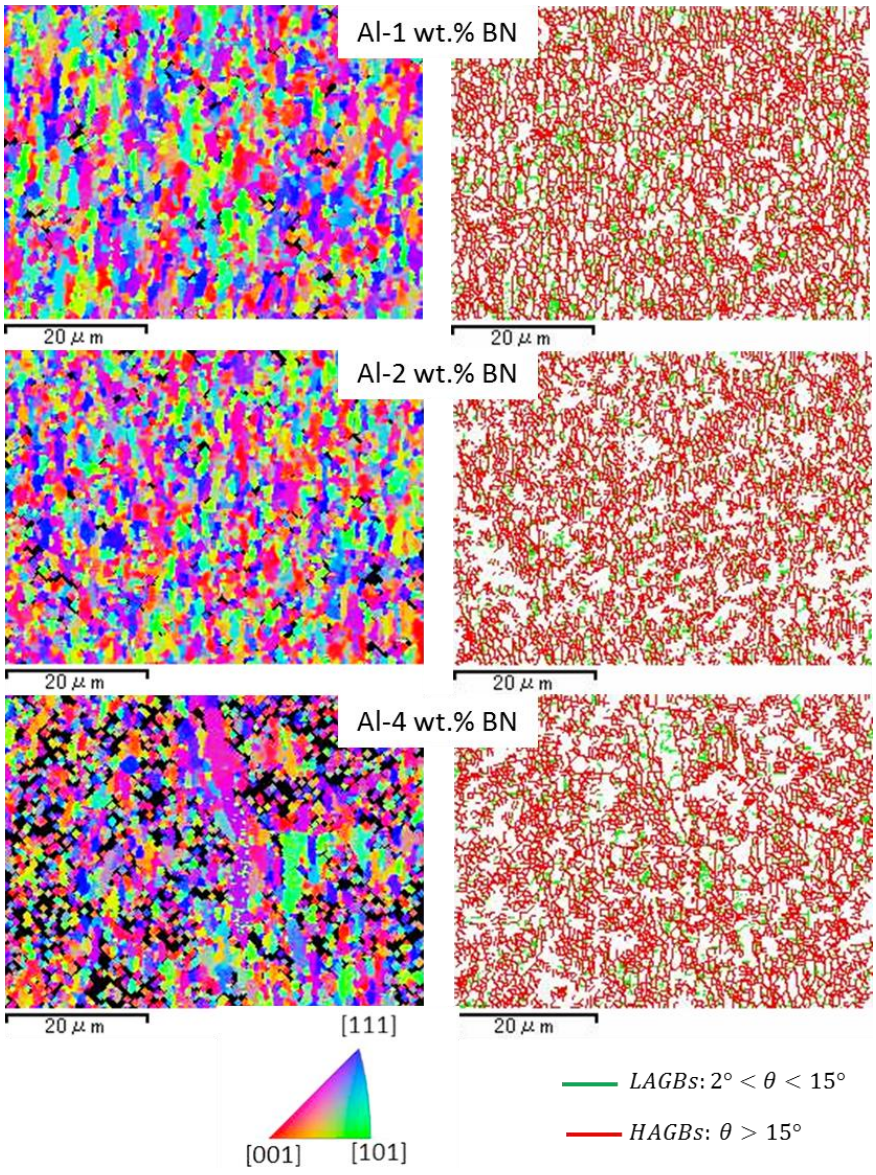


Fig.3. TEM observation of the grain boundaries of the extruded Al-4 wt. % BN; (a) a triple junction with accumulated dislocation near a grain boundary;(b) high magnification views on low angle boundary surrounded by high angle boundaries



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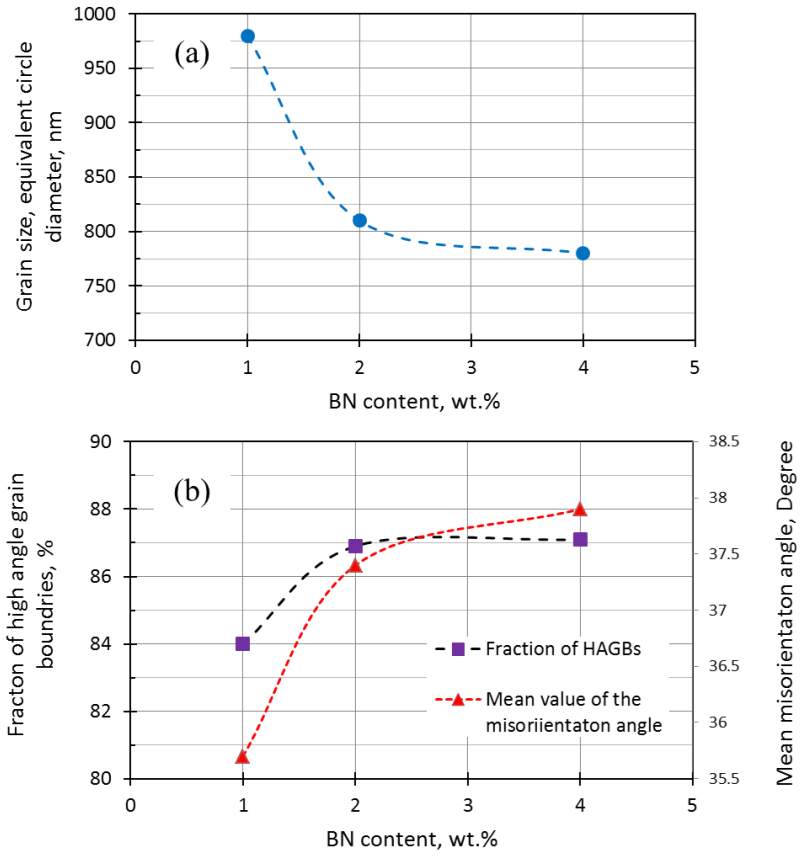

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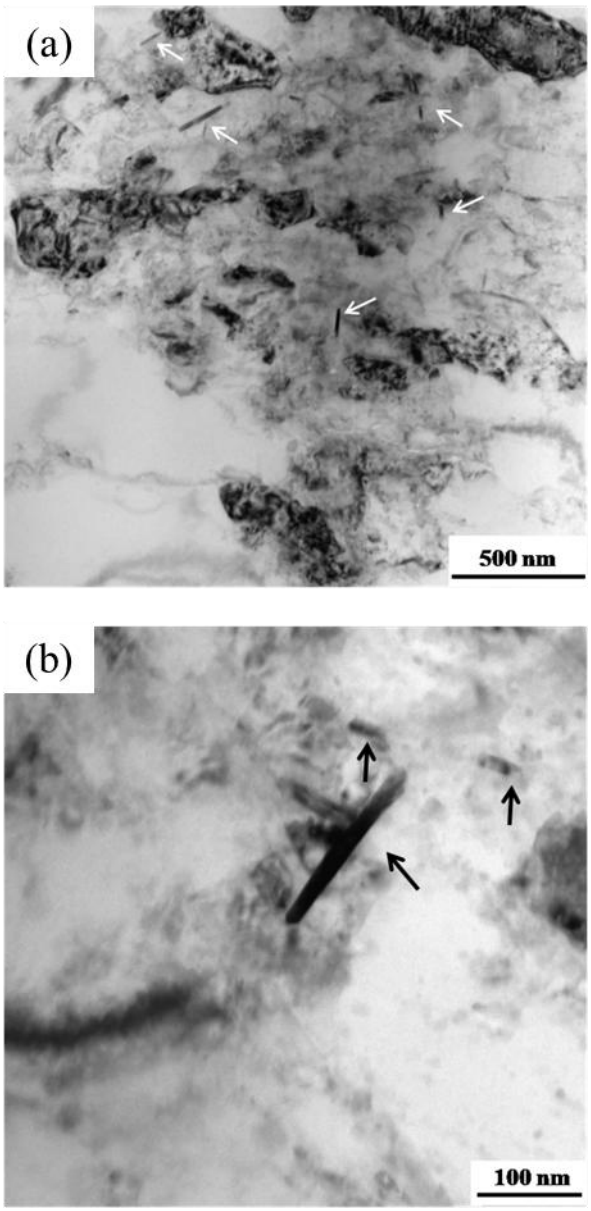

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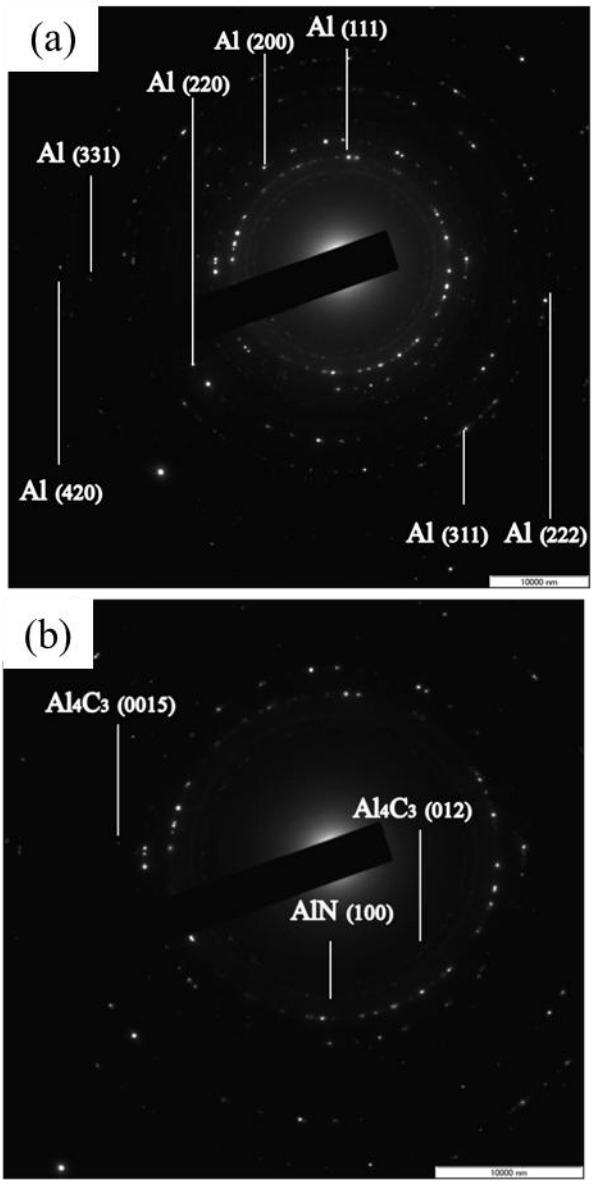
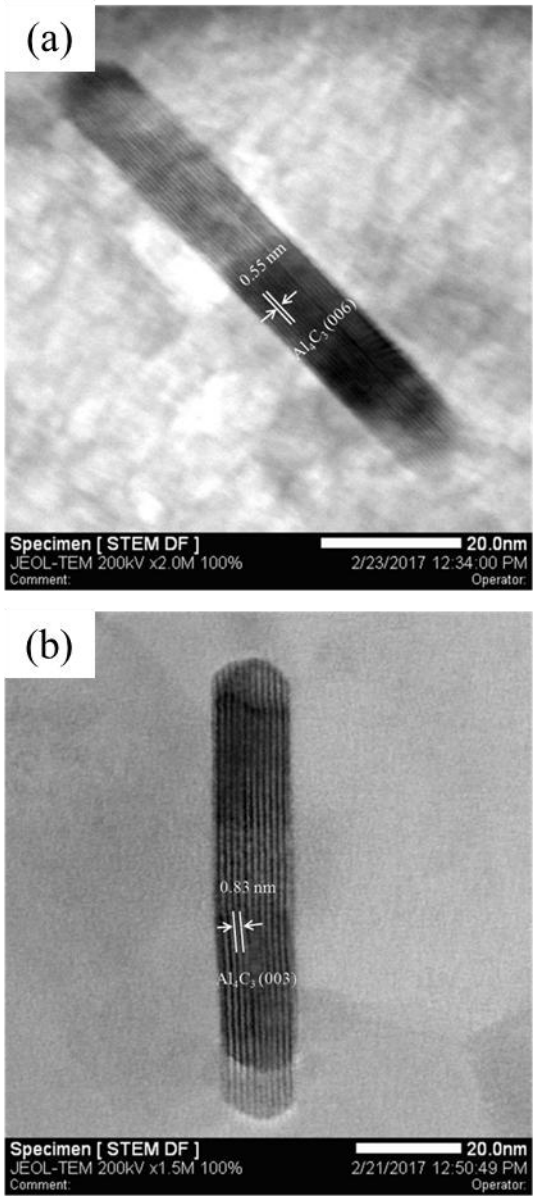


Fig.7. ASAD pattern of Al-4 wt. % BN nanocomposite; (a)different diffraction reflections of Al phase and (b) the in-situ created phases



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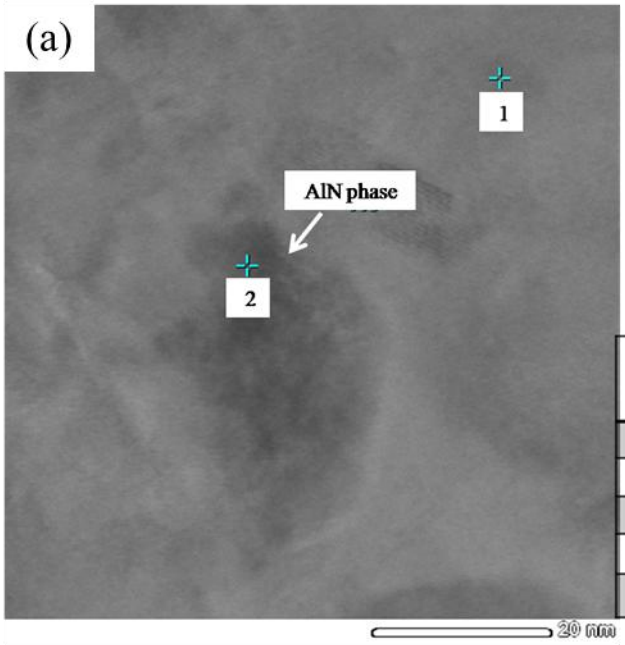
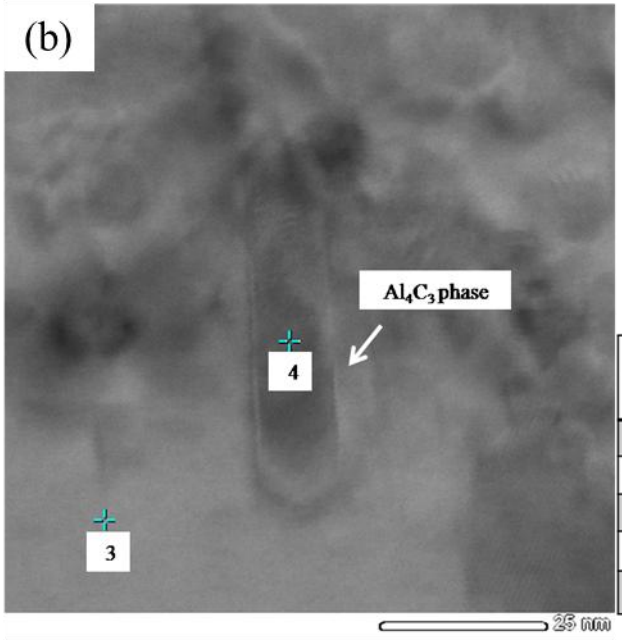
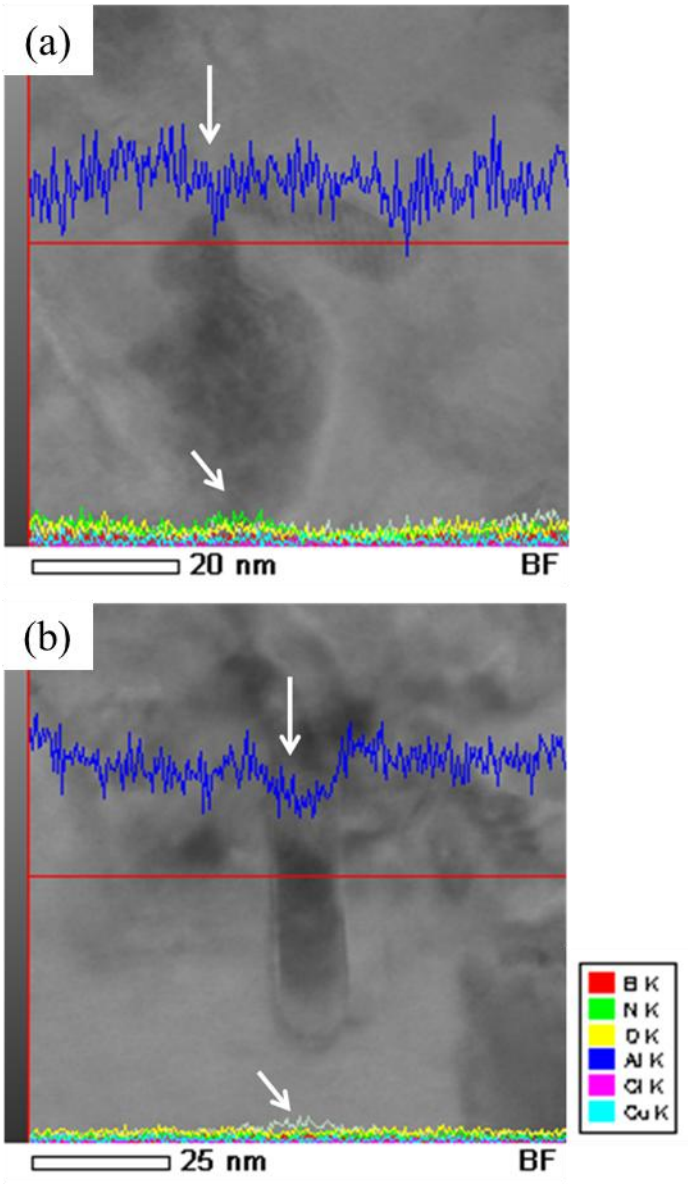


Elements	Atomic Percent (point 1)	Atomic Percent (point 2)
B	1.52	-
N	8.23	11
O	3.36	2.76
Al	83.72	83.19
Cu	3.17	3.05



Elements	Atomic Percent (point 3)	Atomic Percent (point 4)
C	14.24	24.81
N	1.21	2.55
O	1.58	2.32
Al	81.24	68.71
Cu	1.73	1.61

Fig. 9.Bright field TEM images and the corresponding results of EDS analysisof the matrix and in-situ phases in Al- 4 wt. % BN nanocomposite; (a) AlN phase and(b) Al_4C_3 phase



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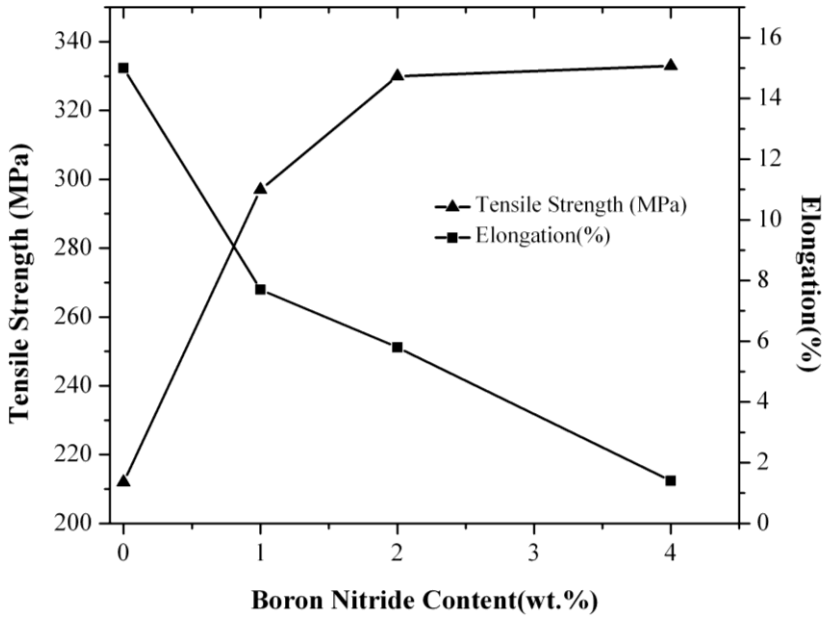

Fig.11. Variation of ultimate tensile strength (UTS) and elongation of the extruded samples by increasing the BN content

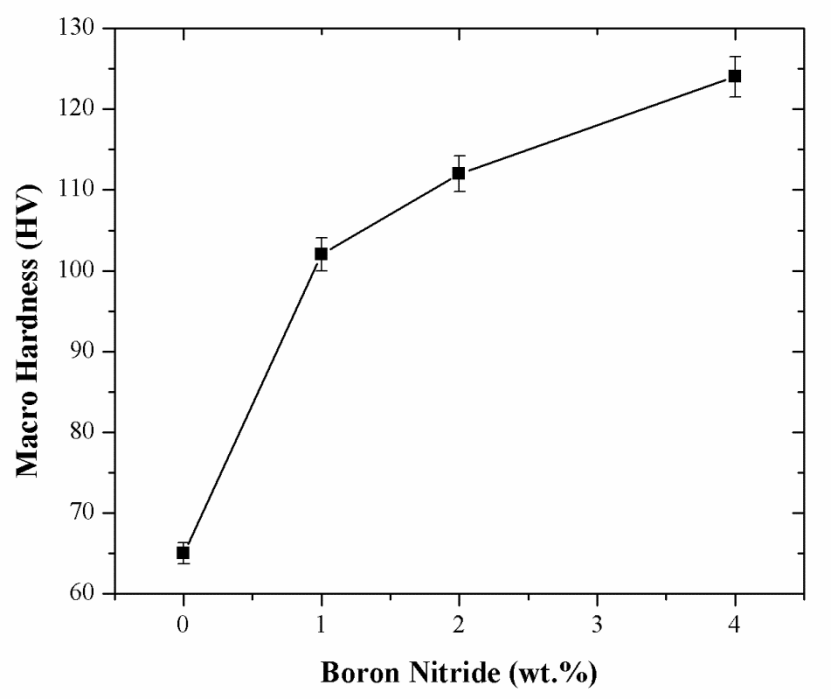

Fig. 12.Variation of Vickers hardness of the extruded samples by increasing the BN content