

Al-AIN TRI-MODAL COMPOSITES PREPARED BY MECHANICAL ALLOYING

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Abstract. Al/AIN particulate composites were prepared by mechanical alloying (MA) of Al powder in NH₃ or N₂ atmosphere. The AIN phase formed only by a combination of MA in NH₃ and subsequent sintering. To improve the mechanical properties of the resulting Al/AIN bimodal composites, the mechanically alloyed Al powder was mixed with pristine Al powder and sintered. This resulted in (Al/AIN)/Al trimodal particulate composites with interesting properties. The outer part of the composites was hardened during sintering, showing the possibility of surface hardening by simple sintering in Al alloys.

1. INTRODUCTION

Aluminum nitride (AIN) is an interesting ceramic material for many structural and electronic applications. AIN is a wide-band semiconductor with high mechanical strength, high hardness, high thermal conductivity, low density, low dielectric constant and low thermal expansion coefficient similar to silicon. Several methods have been proposed to synthesize AIN, such as direct nitridation in flowing ammonia at high temperature [1], pressureless liquid metal infiltration [2], plasma spray deposition [3], squeeze casting [4], gas-reduction [5], *etc.* However, these methods need high temperature and they are quite complicated, limiting the mass production and wide application of this material. Mechanical alloying (MA), a high-energy milling, has also been employed to synthesize AIN or AIN/Al composites [6,7]. This method is relatively easy to produce composite powders with fine microstructure. However, the powders synthesized by this method are very hard to compact due to work-hard-

ening, grain refinement and dispersion-strengthening effects induced during MA. Furthermore, the hot-consolidated materials are in general very brittle and have low toughness.

In the present work, we have synthesized Al/AIN particulate composites by MA and simple press-sinter PM processing. To improve the toughness and ductility of bimodal composites, we have prepared tri-modal composites from a powder mixture of pristine Al powder and Al/AIN bi-modal composite powder prepared by prior MA.

2. EXPERIMENTAL PROCEDURE

The starting material is commercial-grade Al powder (99.9%, 29 μm). The MA process was carried out in a Szegvari Attritor equipped with a water cooling system. The ball to powder ratio is 50:1. The diameter of the stainless steel balls is 6.4 mm. The speed of the rotator is 300 r.p.m. N,N'-ethylenebisstearamide (C₃₈H₇₆N₂O₂, 3 wt.%) was used both as a process control agent (PCA) to avoid

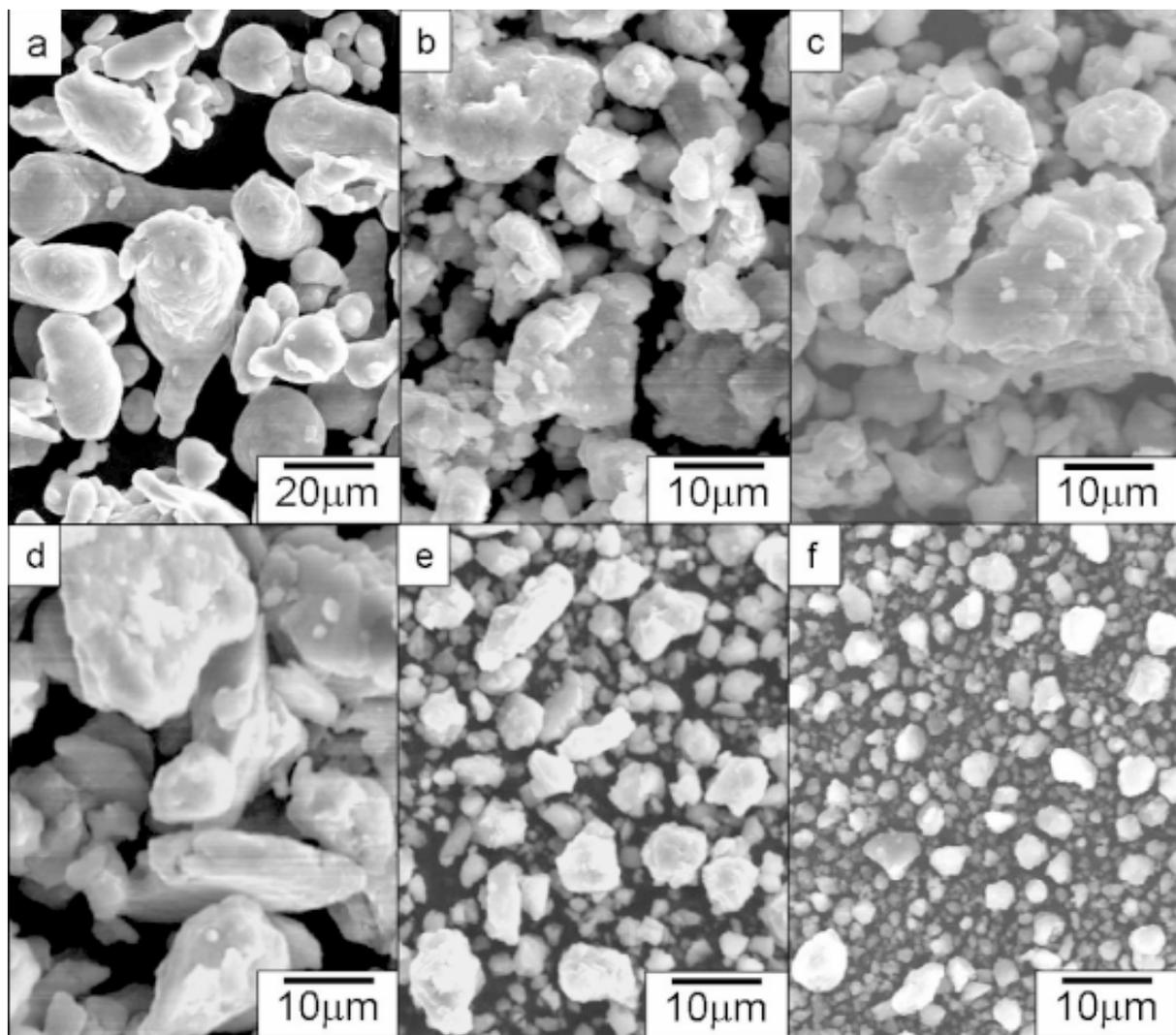
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Table 1. Milling condition of different specimens.

Sample name	A	B	C	D
PCA	$C_2H_7NO_2$	$C_6H_4N_2O_7$	$C_{38}H_{76}N_2O_2$	
Amount of PCA (wt.%)	3.0	4.4	3.0	
Milling atmosphere	Ar	Ar	N_2	NH_3

Table 2. Mean particle size of different specimens.

Sample name	A	B	C	D
Milling time (h)	12	12	12	6
Gas pressure (atm)	1.2	1.2	1.2	1.2
Particle size (μm)	20.5	21.8	27.0	8.0

**Fig. 1.** The morphology of as-received pure Al (a) and the specimen A, B, C, and D milled for 12 h (b, c, d and f). (e): The specimen D milled for 6 h.

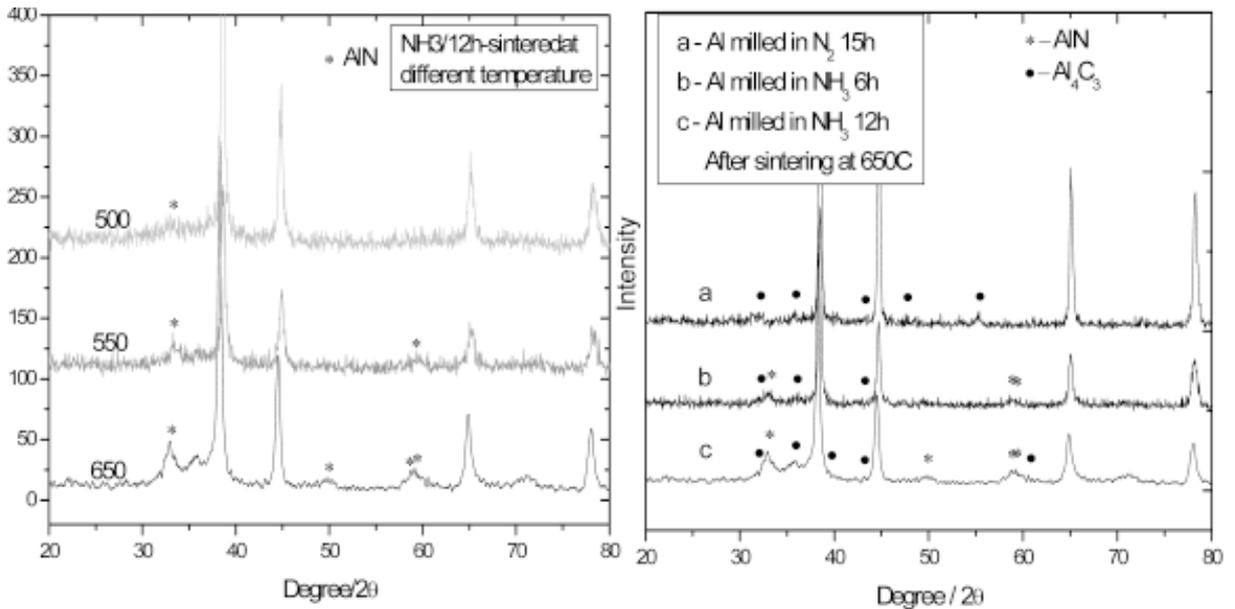


Fig. 2. XRD patterns of typical MA powders (left: specimen D).

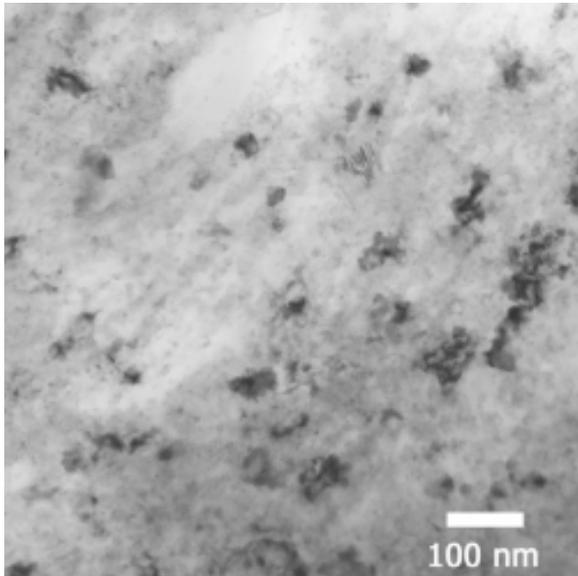


Fig. 3. TEM image of the specimen D, sintered at 650 °C for 1 h.

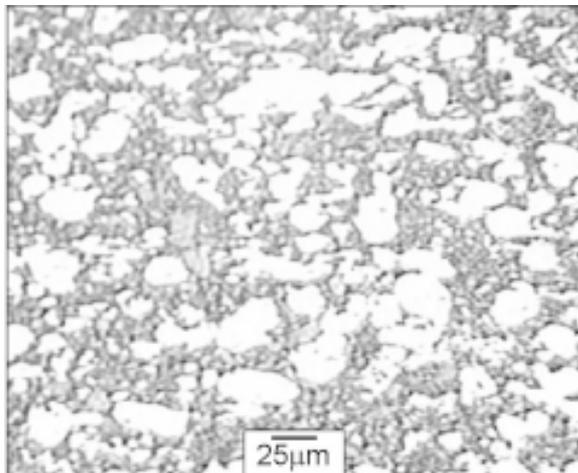


Fig. 4. Optical image of (Al/AlN)/Al tri-modal composite, prepared from the mixture of MA Al powder (specimen D) + 50% Al, sintered at 650 °C for 1 h.

excess cold welding of Al powder during the milling process and nitrogen source. For comparison, $C_2H_7NO_2$ and $C_6H_4N_2O_7$ were also used as PCA. MA was carried out in Ar, N_2 , or NH_3 . The milling conditions of different specimens are summarized in Table 1. The MA powders were subsequently die-compacted at a pressure of 750 MPa. The compacts were then sintered at 650 °C for 1 hour in N_2 or Ar. The sintered specimens were characterized by a variety of techniques, such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission-scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM).

3. RESULTS AND DISCUSSION

Fig.1 shows the SEM morphology of the ball-milled powders. The mean particle size after ball-milling is summarized in Table 2. The results show that milling atmosphere played an important role in particle refinement during milling. The particle size is markedly reduced when milling in NH_3 (Figs.1e and 1f), while almost no refinement took place in the case of milling in Ar or N_2 (Figs.1b~1d) regardless of PCA composition. Another important observation made during ball-milling is that increasing the gas pressure of NH_3 (from 1.1 to 1.3 atm.) promoted particle refinement. It seems that the de-

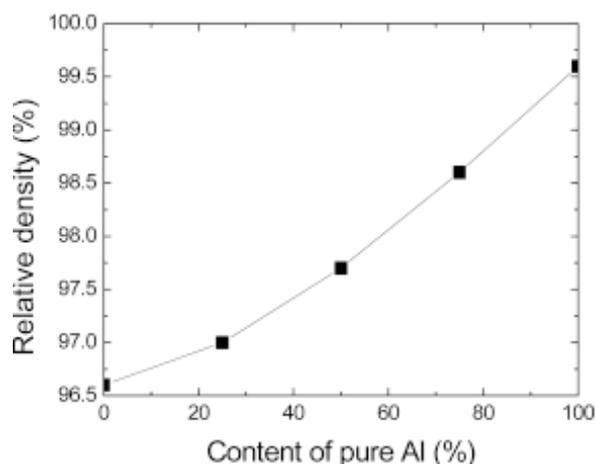


Fig. 5. Relative density of (Al/AlN)/Al tri-modal composites as a function of pristine Al content.

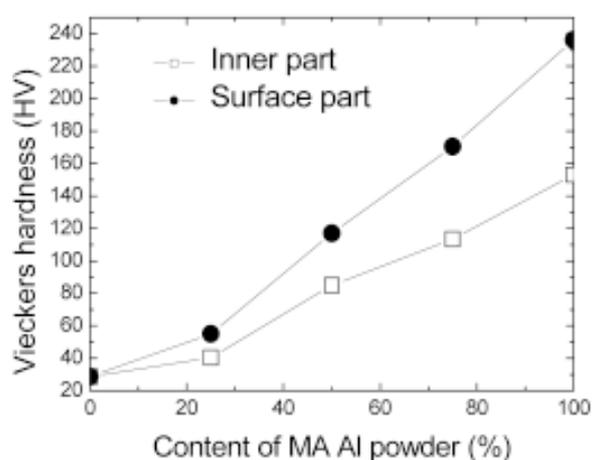


Fig. 6. Difference in hardness between the surface and inner part of the sintered (Al/AlN)/Al tri-modal composites as a function of MA Al powder content.

composition of NH_3 into reactive nitrogen (N) and hydrogen (H) radicals at the surface of Al particles alters the ductility of Al.

The formation of AlN was examined by XRD. The diffraction peak of AlN was not observed in any as-ball-milled powder regardless of milling conditions. The powders milled in Ar or N_2 (specimens A–C) showed no AlN peaks, but weak peaks of Al_4C_3 which stem from the PCA. Other dispersoid phases such as Al_2O_3 may be too weak to be detected by XRD. The results of TEM and XPS spectra examination showed the existence of various kinds of amorphous or crystalline Al-C-N-O compounds on the surface of the MA powders after sintering at 650°C . These include Al oxy-carbonitride ($\text{Al}_{2-x}\text{C}_{1-x}\text{N}_x\text{O}_{1-x}$), Al oxy-carbide ($\text{Al}_4\text{O}_4\text{C}$), Al oxy-nitride ($\text{Al}_{27}\text{O}_{39}\text{N}$ or $\text{Al}_{10}\text{N}_8\text{O}_3$), Al carbide (Al_4C_3) and Al oxide (Al_2O_3). The AlN peaks appeared only for the powders ball-milled in NH_3 (specimen D) after sintering at temperature above 500°C (Fig. 2). They did not appear until the sintering temperature reached 500°C . As the sintering temperature increased above 500°C , the peaks of Al_2O_3 appeared first, followed by AlN, Al_4C_3 , Al oxy-nitride, and Al oxy-carbide, consecutively. The relative intensity of AlN peaks also increased with increasing sintering temperature. For specimen D which was milled in NH_3 , AlN was a major dispersoid phase after sintering at 650°C for one hour (TEM image in Fig. 3). It is presumed that NH_3 adsorbed on the surfaces of Al powder dissociated to atomic nitrogen (N) which then reacted with Al. Oxygen

and carbon from the PCA also reacted with Al, forming amorphous or crystalline Al-O-C-N compounds. These compounds undergo a transformation during sintering, forming crystalline Al_4C_3 , Al_2O_3 and AlN. The volume fraction of major dispersoid AlN which was estimated from the XRD intensity ratio $I_{\text{Al}(200)}/I_{\text{AlN}(100)}$ increased with increasing milling time: e.g. ~12 and 40% after milling for 12 and 50 hours, respectively.

For Al/AlN particulate composite, we have used the powder milled for 12 hours in NH_3 (specimen D) which has about 10 vol.% of AlN dispersoid. The powder was die-compacted and sintered at 650°C in Ar or N_2 atmosphere. The sintered product, namely bi-modal particulate composite of Al/AlN, consists of nano-sized AlN dispersoids as well as various minor Al-O, Al-C-O-N, and Al-N-O (10–50 nm) particles embedded in the fine grained Al matrix (grain size $0.3\text{--}1\ \mu\text{m}$). The microhardness of the sintered composite was 232.6H_v which is about 7 times higher than that of sintered pure Al (26.8H_v) prepared under the same processing condition. The observed high hardness is mainly due to the combined effect of grain refinement of Al and dispersion-strengthening by dispersoids.

Although this Al/AlN bimodal composite was very strong, it was very brittle and had low in toughness. Furthermore, the compressibility of the powder which is practically important in industrial PM processing is poor. To overcome these disadvan-

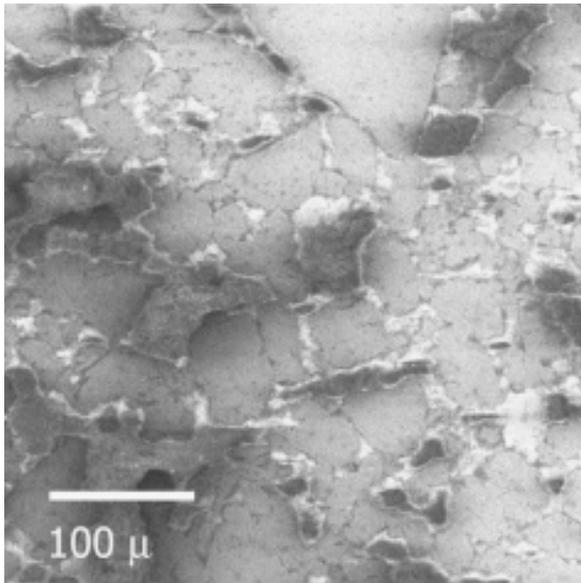


Fig. 7. SEM microstructure of the sintered (Al/AlN)/50%Al tri-modal composites at the surface region.

tages, tri-modal (Al/AlN)/Al composite was prepared by mixing the MA powder (specimen D) with pure pristine Al powder. A typical microstructure is shown in Fig. 4. The optical micrograph of the sintered material consists of pure Al grains (bright phase) and Al/AlN bimodal composite grains (dark phase). A higher magnification by TEM revealed that the dark grains consist of Al and dispersoids. Although the hardness and strength of the composites decreased by adding pristine Al to once ball-milled MA powder, the compressibility of powder as well as ductility and toughness markedly increased. This resulted in a better green and sintered density (Fig. 5) compared with the bimodal composites.

An interesting feature observed during hardness test of the composites was the surface hardening of the Al/AlN composites. After sintering either in N_2 or Ar for an hour, we observed that the surface of the sample was much harder than the inner part. This phenomenon was observed both in bi-modal and tri-modal composites. The thickness of the hardened layer depends on the sintering temperature and duration, but typically 1–3 mm. The hardness difference between two regions became pronounced when increasing the amount of MA Al powder which was previously ball-milled in NH_3 for 12 hours (Fig. 6). In the case of pure Al powder

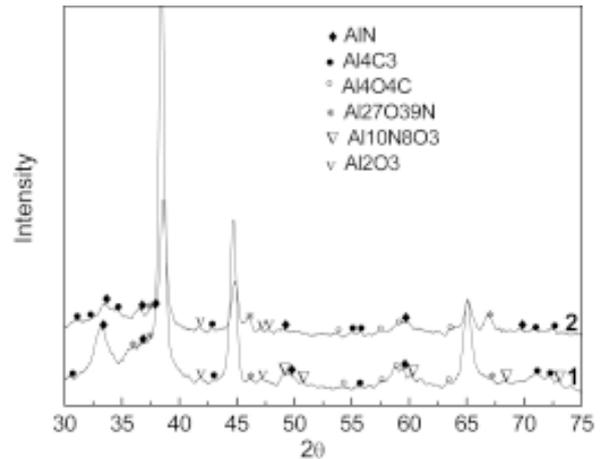


Fig. 8. XRD pattern of the inner (1) and the surface region (2) of the (Al/AlN)/50%Al tri-modal composites after sintering.

sintered under the same condition, no such effect was observed.

To clarify the cause of the observed surface hardening, the surface and the inner region of the composite were examined. By optical micrography, the hardened surface region was darker than the inner part, indicating a higher volume fraction of dispersoid phases at the surface. The surface region examined by FE-SEM showed that this region contains a variety of dispersing phases not only along the grain boundaries but also ultra-tiny particles within the Al grains (Fig. 7). The detailed identification of each particle was difficult due to their fine size. However, XRD result (Fig. 8) showed a difference in phases between the outer and inner regions. The main difference was that $Al_{10}N_8O_3$ is present in the inner part, with their absence in the surface region. $Al_{27}O_{39}N$ phase was detected in both regions, but the outer region showed more intense $Al_{27}O_{39}N$ peaks than the inner part. The fine particles of the oxygen-rich $Al_{27}O_{39}N$ phase in the surface region should be formed in the presence of residual oxygen in commercial N_2 or Ar gas which were used as milling atmosphere or dissociated oxygen in the ball-milled powder. The oxygen might react with the nitrogen-rich compound $Al_{10}N_8O_3$ to form the oxygen-rich $Al_{27}O_{39}N$. The $Al_{27}O_{39}N$ phase was darker in the micrograph and has a higher hardness than $Al_{10}N_8O_3$.

The observed surface hardening by simple sintering seems to be very important practically be-

cause, unlike steels, no heat treatment has been so far known to surface-harden Al alloys. Using this effect, one can obtain a variety of Al alloys with different hardness across the part. For instance, a sintering gas with different O₂ content could be used to adjust the thickness of the hardening layer.

In summary, Al/AlN composites were synthesized by mechanical alloying. Among various mechanical alloying parameters, AlN phase formed only when Al is ball milled in NH₃ and subsequently sintered at a temperature above 500 °C. The bimodal composite was seven times harder than pure Al because of the presence of various dispersoids such as Al oxide, Al oxy-carbide, Al oxy-nitride and, in particular, AlN. Compared to the bimodal composites, trimodal composites exhibited improved ductility, hardness and compressibility. Surface hardening was observed during the sintering of the Al/AlN composites. This showed a potential application to surface hardening treatment in Al alloys.

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