Journal of Alloys and Compounds 629 (2015) 184–187

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Letter

Nano-scale AlN powders and AlN/Al composites by full and partial direct nitridation of aluminum in solid-state

Lei Jia [a,*], Katsuyoshi Kondoh [b], Hisashi Imai [b], Motohiro Onishi [b], Biao Chen [b], Shu-feng Li [a]

[a] *School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, China*
[b] *Joining and Welding Research Institute, Osaka University, Osaka 567-0047, Japan*

ARTICLE INFO

Article history:
Received 1 December 2014
Received in revised form 25 December 2014
Accepted 27 December 2014
Available online 9 January 2015

Keywords:
Nitride materials
Metal matrix composites
Gas–solid reaction
Mechanical properties

ABSTRACT

Full and partial nitridation of Al powders were obtained by heating commercial pure Al powders at different temperatures for different time under pressure-less H_2 and N_2 atmosphere. Then the fully nitrided powders were wet ball milled to prepare AlN powders while the partially nitrided powders were consolidated, and then extruded into AlN/Al composites. In-situ formation of AlN on the surface of Al powders was successfully controlled in the nitridation process. AlN dispersoids transformed from particle-like to needle-like, and finally to fully reacted AlN clusters consisted of their nano-scale fine particles. As a result, AlN powders with a mean particle size of about 200 nm and a purity of 98.63 wt% could be prepared, and AlN/Al composites with adjustable combinations of strength and elongation can be fabricated as well.

1. Introduction

Aluminum nitride (AlN) has been considered as an attractive ceramic material due to its excellent mechanical and functional properties, such as high strength and modulus, high thermal and low electrical conductivities, and good wear resistance [1,2]. AlN are mainly used as substrate for multichip modules and packaging materials for integrated circuits and etc. [3–5], and as reinforcement for metal matrix similar as SiC, Al_2O_3 [6]. These would in turn require high pure, ultra-fine AlN powders and good dispersion of them in Al matrix, respectively [6–9]. So far, a number of methods have been reported to prepare AlN powders, including direct nitridation of Al and carbon thermal reduction of Al_2O_3 with carbon mixture powders, but high energy such as plasma, microwaves, spray pyrolysis and organic additives such as chlorides and fluorides were always required, giving rise to the formation of impurities and the increase of cost [1,10–13]. Additionally, it is also difficult for traditional powder metallurgy method to obtain the well-dispersed AlN particles on the surface of Al powders, liking Al–SiC and Al–Al_2O_3 systems [14].

In our previous investigation, in-situ direct nitridation was used to prepare AlN/Al composites, where AlN was in-situ formed and dispersed uniformly on the surface of Al alloy powder [15,16]. Similar methods were also reported in the literatures [17,18]. However, the complete nitridation was not realized by in these works, resulting in a mixture of AlN and Al powder. Therefore, an idea can be drawn, if the nitridation degree could be regulated during in-situ direct nitridation process, high purity AlN powders and AlN/Al mixture powders with a uniform dispersion of AlN can be prepared, which should be better suitable for the preparation of AlN/Al composites.

Based on the above propose, pure Al powders were directly nitrided at low temperatures and different nitridation degrees were realized by controlling the nitridation temperature and time in the present work. Nano-scale AlN powders with high purity and AlN/Al composites were finally prepared, and the morphological evolution of AlN during the nitridation process was characterized.

2. Experimental details

Pure Al powders (99.9 wt%, 20 μm) were nitrided in a horizontal electrical-resistance furnace (AMF-2-500) under an atmospheric pressure. Firstly, Al powders placed in an alumina tube were heated to the designed temperatures (580 or 600 °C) at a heating rate of 20 °C/min, and held for 20 min under the protection of high-purity H_2 with a flowing rate of 2 L/min to remove the naturally formed oxide films and avoid oxidation behavior during the above heating process. Then, the flowing H_2 gas was shut off and Al powders were nitrided for different time under a normal pressured high-purity N_2 gas with a flowing rate of 4 L/min. Finally, the fully nitrided powder were dispersed by wet-ball milling for 120 min with ethanol, in which ZrO_2 milling balls were used at a ball to powders ratio of 10:1 and a rotation speed was 200 rpm. The partially nitrided powders were consolidated by sparking plasma sintering (SPS) at 600 °C for 30 min, and then extruded at a ratio of 37:1 to prepare AlN/Al composites.

Tensile samples with a diameter of 3.0 mm and gauge length of 15 mm were machined from the as-extruded rods, and then tested on a universal testing machine (AG-150) at the ambient temperature, where the strain rate was

---

* Corresponding author. Tel.: +86 29 82312505.
E-mail address: xautjialei@hotmail.com (L. Jia).

http://dx.doi.org/10.1016/j.jallcom.2014.12.220
0925-8388/

5×10^{-4} s^{-1}. The crystal structure of the nitrided powders was determined by an X-ray diffraction spectrometer (XRD-6100) with Cu Kα target. The morphologies were characterized by a field-emission scanning electron microscope (FESEM-6500F) and a transmission electron microscope (TEM-2010). The nitrogen contents were analyzed by an inserted gas fusion nitrogen–oxygen determination instrument (EMGA-830).

3. Results and discussion

Fig. 1 shows SEM morphologies of pure Al powders before and after nitridation at different temperatures and time. Obvious grooves present on the surface of as-received raw pure Al powders before nitridation (Fig. 1a), suggesting the raw Al powders have no oxide film. After nitridation at 580 °C for 60 min, Fig. 1b indicates some sub-micron particles with the cactus-shape and nano-scale fine particles with the spot-shape are formed on the powder surface. At 600 °C for 30 min shown in Fig. 1c, the needle-like products uniformly cover the surface of Al powders. With increase in the nitridation time, the number of nitridation products increases continuously, and the powder surface becomes increasingly loose, suggesting that serious nitridation phenomena occurred (Fig. 1d and e). After heating at 600 °C for 120 min, the powders are fully nitrided, and agglomerated into clusters consisting of nano-scale particles (Fig. 1f).

Fig. 2 shows the corresponding XRD patterns (a) and N contents of raw Al powders and each nitrided powder (b). It is evident that no nitridation occurs at 580 °C, however, the obvious AlN peaks are detected at 600 °C. Their intensity increases with the prolongation of nitridation time. Additionally, the N content of the nitrided powders also increases continuously, indicating a continuous nitridation reaction occurred on the surface of Al powders. This can be also confirmed by the above SEM images shown in Fig. 1. After nitridation at 600 °C for 120 min, all of the diffraction peaks agree well with a standard value of AlN phase except a weak peak at about 45° when the N content of the nitrided Al powders is approximately 33.68 wt%. It indicates that the AlN powders with purity up to 98.63 wt% can be prepared by full nitridation of pure Al powders at a solid-state and press-less H_2 and N_2 atmosphere.

As mentioned in Figs. 1f and 2, high purity AlN powders can be prepared by full nitridation of pure Al powders at 600 °C for 120 min, but the AlN powers are easily agglomerated as clusters consisting of large numbers of nano-scale particles. Subsequently, AlN powders were further wet ball milled, resulting in nano-sized particles as shown in Fig. 3a. From the bright-field image, it is further determined that in-situ AlN powders synthesized have a mean diameter of about 200 nm. Meanwhile, the SAED pattern presents a series of poly-crystal rings, corresponding to h-AlN (Fig. 3b). From these results, it is believed that nano-scale AlN powders can be successfully synthesized by direct nitridation along with the subsequent wet ball milling from pure Al powders.

The AlN/Al composite were prepared by powder metallurgy utilizing the partially nitrided powders, in which AlN disperse uniformly on the surface of Al powders. Fig. 4a shows the statistical result of ultimate tensile strength (UTS) and elongation (δ) as well as the typical nominal S–S curves of AlN/Al composites prepared

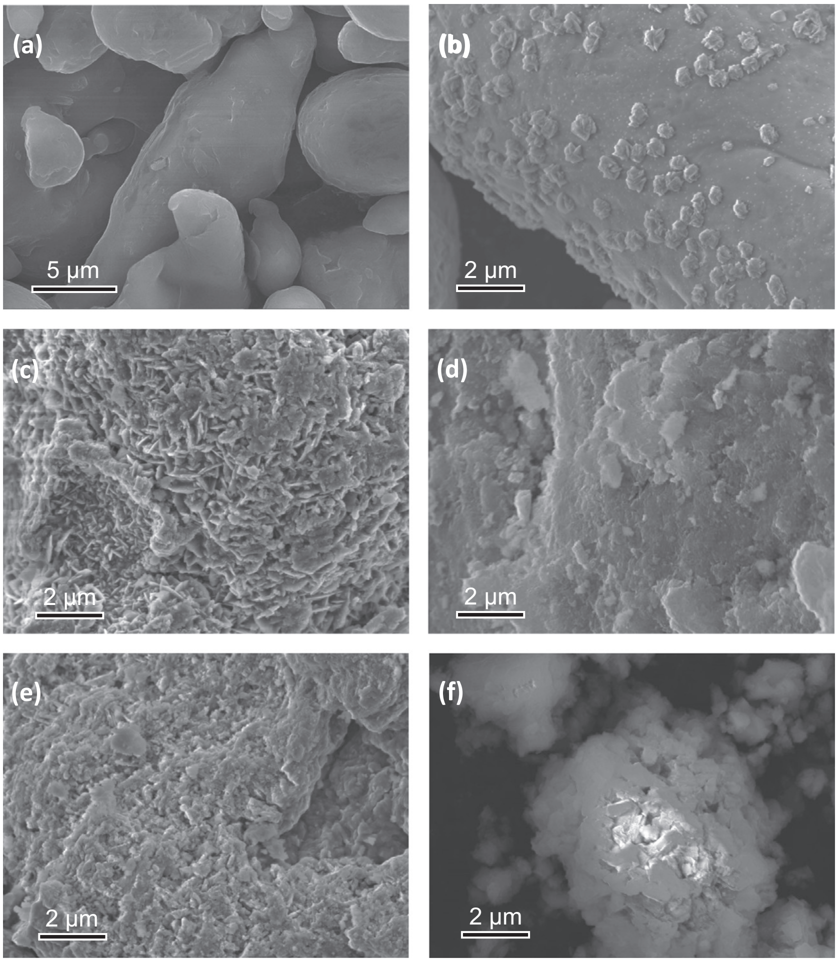

Fig. 1. SEM morphologies of Al powder (a) before and (b–f) after nitridation by different crafts, where (b) nitridation at 580°Cfor 60 min, (c–f) nitridation at 600 °C for 30, 40, 60 and 120 min, respectively.