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In-situ synthesis of co-continuous aluminum-aluminum nitride composites by arc plasma induced accelerated displacement reaction

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ABSTRACT

We investigate in-situ formation of co-continuous aluminum (Al)-aluminum nitride (AlN) composites with attractive mechanical and thermal properties by newly developed arc plasma-induced accelerated displacement reaction (APADR). The core innovation of the process is that it combines a simple pressureless infiltration with a thermodynamically favorable displacement reaction of silicon nitride (Si_3N_4) and molten Al under arc-plasma induced ultra-high temperature. The fast volume displacement nitridation via APADR resulted from improved wettability and enhanced diffusion of dissolved nitrogen. Thus, within a minute of APADR, Al matrix composites (AMCs) containing AlN over 50 vol% were successfully fabricated by the infiltration of Al melt into Si_3N_4 particulate preforms with different particle size distributions. The microstructures of the composites exhibited co-continuous three-dimensional network structures with strong interfacial bonding and high interfacial thermal conductance, which resulted in a unique combination of relatively high flexural strength and high thermal conductivity. In particular, the AMCs containing nitrides of 73 vol% exhibited a low coefficient of thermal expansion, close to that of GaAs or GaN used for high-power semiconductor devices, which is the lowest value ever reported among the nitride reinforced AMCs. These results would give us a promising strategy for in-situ processing routes to fabricate continuous nitride reinforced AMCs with high dimensional and mechanical stability for heat spreader applications.

1. Introduction

Al matrix composites (AMCs) have been widely used in the fields such as ground transportation, electronic packaging, aerospace and infrastructure industries [1–5]. Among them, the base materials for electronic packaging, i.e., heat spreaders, require conflicting thermal properties such as high thermal conductivity (TC) and low coefficient of thermal expansion (CTE) at the same time. To solve this problem, various AMCs with high volume fraction of ceramic reinforcements (≥50 vol%) have been developed by several processing techniques such as powder metallurgy [6], centrifugal casting [7] or pressure infiltration [8]. However, it is very difficult to form those AMCs by a simple and economical way while preventing interfacial reactions [3–5].

Aluminum nitride (AlN) has received significant attention as a second phase for the AMCs due to its thermodynamic compatibility with Al, high modulus, high TC and low CTE [9–18]. Although AMCs containing 60–85 vol% AlN could be fabricated by spark plasma sintering [9,10] or infiltration process [11], the processes require a significant external pressure up to 300 MPa due to the poor wettability between molten Al and AlN [19]. Thus, extensive studies have been focused on the fabrication of AlN reinforced AMCs with high volume fraction of AlN by in-situ processing routes that are advantageous for strong interfacial bonding between the constituents [3,4]. For example, directed melt nitridation process offers co-continuous AMCs with varying metal/ceramic ratios by treating a molten alloy in a static/flowing nitrogen gas atmosphere [16], and gas bubbling method yields particulate AMCs containing relatively large amount of AlN when ammonia gas is injected into Al melt [17,18]. However, both processes require several hours for the nitridation of Al melt at elevated temperatures higher than 1273 K, which is time-consuming and economically unfavorable. Another example is a displacement reaction that is carried out by immersing a ceramic precursor in a molten alloy where the precursor is

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transformed into a thermodynamically more stable phase [20–23]. According to the standard Gibb's free energies of formation for nitrides [Fig. 1(a)], the formation of AlN is favorable by the displacement reaction between molten Al and technical ceramics like silicon nitride (Si_3N_4) as follows [24]:

$$2Al_{(l)} + 1/2Si_3N_{4(s)} \rightarrow 2AlN_{(s)} + 3/2[Si]_{Al},\ \Delta H_f^{\circ} = -293\ \text{kJ/mol at } T = 1500\ K \quad (1)$$

where Si diffuses out of Si_3N_4 during the reaction and dissolves in the Al melt. While the AlN formation in Equation (1) has been reported by several works [25–28], there has been little attention paid to fabricate AlN reinforced AMCs with the displacement reaction of molten Al and Si_3N_4. The reason is that a Si_3N_4 substrate exhibits non-wetting contact angles, $\theta > 90^{\circ}$ with a drop of molten Al below 1273 K [Fig. 1(b)] [28,29]. The poor wettability of Si_3N_4 and molten Al is responsible for weak adhesion, which confines the displacement reaction between them. The contact angles decrease with the addition of alloying elements like Mg in Al [29], but Mg addition results in deleterious effects on the TC of AMCs [30]. Thus, it is essential to increase the processing temperature higher than 1273 K where molten Al wets Si_3N_4 and the displacement reaction given by Equation (1) favorably takes place.

In this study, we investigate in-situ synthesis of continuous AlN reinforced AMCs through newly developed arc plasma-induced accelerated displacement reaction (APADR). Within a minute by APADR process, the AMCs with 55 and 73 vol% nitrides were fabricated by the fast volume displacement nitridation through pressureless infiltration of Al melt into Si_3N_4 particulate preforms with different particle size distributions. The distinctive co-continuous microstructure and resultant properties such as flexural strength, CTE, and TC were systematically characterized. In particular, the AlN formation mechanism and microstructure change depending on Si_3N_4 particulate preforms in newly developed APADR process were carefully discussed.

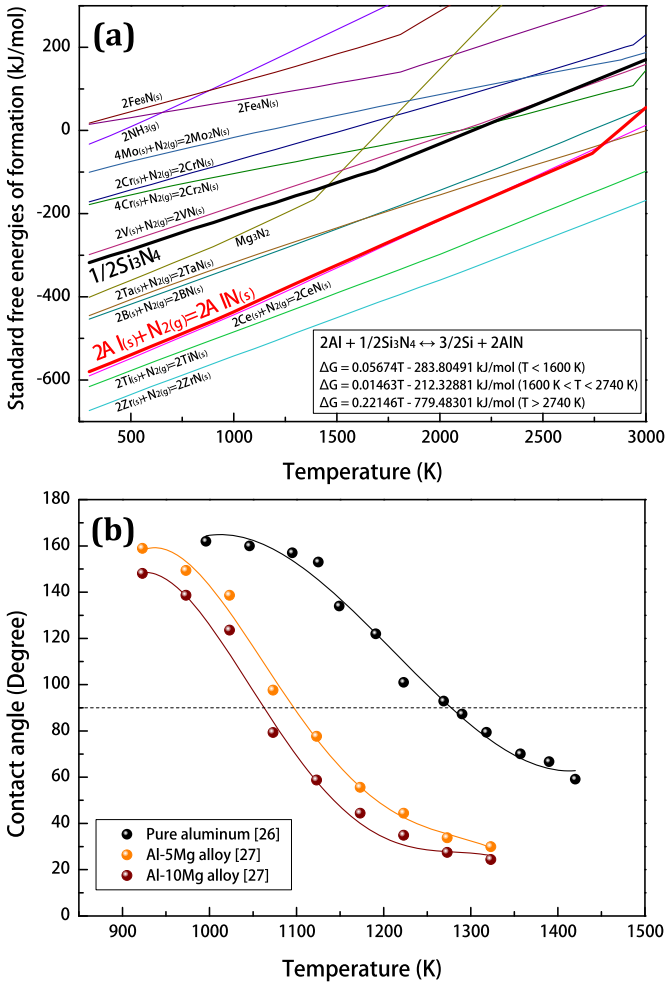

Fig. 1. (a) Standard Gibb's free energies of formation for nitrides [24] and (b) variation of contact angles between molten alloys and Si_3N_4 substrate as a function of temperature [28,29].

2. Experimental

Si_3N_4 particulate preforms were prepared by cold pressing Si_3N_4 powder with median diameter (D_{50}, the diameter of particle at 50% in the cumulative particle size distribution) of 0.7 μm (UBE industries, Tokyo, Japan) and 14.8 μm (LTS research laboratories, Orangeburg, NY, USA, −325 mesh). The size distribution of the powder was measured by a particle size analyzer (Microtrac MT3000, Nikkiso, Tokyo, Japan). Disk-shaped preforms with diameter of 13 mm and height of 2 mm were prepared by compacting the powder in a steel die and cold isostatic pressing at a global pressure of 200 MPa. The preforms were then dried in an oven at 423 K for 12 h to remove moisture. Preforms with two different particle size distributions were prepared; (a) unimodal particle size distribution (UPSD) consisting of relatively fine particles (D_{50} = 0.7 μm), and (b) bimodal particle size distribution (BPSD) consisting of coarse (D_{50} = 14.8 μm) and fine (D_{50} = 0.7 μm) particles with 7: 3 vol ratio [31]. Green density of these preforms was calculated from the sample weight and geometric dimensions, which were 45 vol% and 65 vol%, respectively.

The APADR process was carried out by arc melting with a constant arc voltage of 20 V and arc current of 150 A. First, a button-shaped Al ingot was prepared by arc melting pure Al pieces (99.999% purity) under a Ti-gettered Ar atmosphere (99.999% purity, total pressure of 40 kPa), and then the ingot, placed on a Si_3N_4 preform, was arc melted [Fig. 2(a)]. The preform was covered and reacted with molten Al, leaving a reaction layer at the rim of the preform [Fig. 2(b)]. After the as-melted Al–Si_3N_4 ingot was turned over, the ingot was arc-melted again for a minute [Fig. 2(c)]. It should be noted that the distance between tungsten electrode and the ingot was kept larger than 2 mm and arc plasma was generated on the periphery of the ingot to avoid the collapse of the preform. Within a minute of the arc melting, the preform was immersed and completely infiltrated with the Al melt, leaving disk-shaped AMCs embedded in the Al ingot [Fig. 2(d)]. During the infiltration, a small amount of Al was evaporated due to the arc plasma-induced ultra-high temperature over 2000 K (measured by pyrometer [32] and inferred from the evaporation of Al (boiling point: 2743 K)) and the exothermic heat of reaction in Equation (1). It should be noted that the displacement reaction of the dissociated N from Si_3N_4 to AlN is instantaneous due to the absence of activation energy for chemisorption. Furthermore, solubility of N in Al at 2000 K was estimated to be about 0.3 at.% [13], indicating that dissolution of the dissociated N is thermodynamically favorable. Thus, the arc melting method can be an effective route to dissolve significant amount of N into Al melt and improve wettability, and AlN can be explosively in situ formed by displacement reaction, which leads to fast volume nitridation of Al. The resultant composites fabricated by reaction of the UPSD and BPSD preforms will be denoted as UPSD and BPSD composite, respectively.

Phase constitution of the resulting composites was characterized by X-ray diffraction (XRD; New D8 Advance, Bruker, Karlsruhe, Germany) using monochromatic Cu Kα radiation for a 2θ range of