Materials Science & Engineering A 557 (2012) 59–68

Contents lists available at SciVerse ScienceDirect

Materials Science & Engineering A

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

In situ synthesis of alumina-matrix oxide/oxide composites by reactive sintering

Zhong-Chun Chen [a],*, Sri Nugroho [b], Makoto Ezumi [a], Takahiro Akao [a], Tetsuhiko Onda [a]

[a] *Department of Mechanical and Aerospace Engineering, Graduate School of Engineering, Tottori University, Koyama-minami 4-101, Tottori 680-8552, Japan*
[b] *Department of Mechanical Engineering, Diponegoro University, Semarang, Indonesia*

ARTICLE INFO

Available online 29 June 2012

Keywords:
In situ synthesis
Oxide/oxide composites
Al_2O_3
Ba-β-Al_2O_3
Reactive sintering

ABSTRACT

In situ processing is an attractive and cost-effective approach to fabricate ceramic matrix composites with high performances. In this paper, the in situ synthesis of alumina-matrix oxide/oxide composites reinforced with Ba-β-Al_2O_3 or Ba-β-Al_2O_3/ZrO_2 phases through reactive sintering of Al_2O_3/$BaCO_3$ or Al_2O_3/$BaZrO_3$ powder mixtures is briefly reviewed. The in situ synthesized composites exhibited a microstructural feature of elongated Ba-β-Al_2O_3 and equiaxed ZrO_2 particles, which were distributed in Al_2O_3 matrix homogeneously. The TEM observations suggest that the longitudinal interface between Ba-β-Al_2O_3 phase and Al_2O_3 matrix is parallel to the basal planes of the Ba-β-Al_2O_3 phase. The formation of the elongated Ba-β-Al_2O_3 particles is likely to be due to the preferred diffusion of Ba cations along (0001) basal planes. Furthermore, the diffusion of Ba cations dominates the in situ reaction processes. The presence of Ba-β-Al_2O_3 and ZrO_2 phases resulted in crack deflection and crack bridging, thus improving the fracture toughness of the Al_2O_3 matrix composites.

1. Introduction

Ceramic matrix composites (CMCs) have attracted much attention for high-temperature structural applications. Many of these applications, such as gas turbine and aerospace engines, require long-term exposure to oxidizing environments. Accordingly, oxidation resistance of the CMCs becomes one of the important issues. The CMCs in these applications need to have a good combination of mechanical (*e.g.*, strength, fracture toughness, and creep resistance), chemical (*e.g.*, oxidation and corrosion resistance), thermo-physical (*e.g.*, thermal shock resistance) properties, and also long-term stability during service at elevated temperatures [1]. An oxide/oxide composite consisting of oxide matrix and oxide reinforcement is a potential candidate due to its damage tolerance and inherent resistance to degradation in the oxidizing atmospheres at high temperatures.

In the past 20 years, considerable efforts have been made to highlight oxide fiber-reinforced oxide matrix composites [2–8]. In these oxide/oxide composites, a tailored interphase, or interface between fibers and surrounding matrix, plays a crucial role in determining the mechanical properties such as strength and fracture toughness of the composites. The interphase must be weak enough to allow fiber/matrix interfacial debonding and subsequent fiber pullout during fracture [9]. A fiber/matrix interfacial layer in CMCs is generally obtained through incorporation of a coating layer on fibers. In oxide/oxide systems, various oxide compounds have been proposed as candidates for coating materials, which include (1) simple oxides, such as SnO_2 [10–12], ZrO_2 [13,14], TiO_2 [15], and CeO_2 [16]; (2) complex oxides which have a high probability of low cohesion with matrix or fiber due to the polarization of oxygen bonds by high valence cations [8], for example, vanadates, phosphates or niobates, having a general formula MXO_4 ($M=La$, Y or Nd; $X=P$, Nb or V) [17–19]; and (3) hexaaluminates with a layered crystal structure, such as $CaAl_{12}O_{19}$ and $LaAl_{11}O_{18}$ [2,3,20]. These oxide coatings are chemically inert at elevated temperatures with respect to both Al_2O_3 fiber and Al_2O_3 matrix.

However, the incorporation of reinforcements with high aspect ratios (such as fibers and whiskers) may cause some difficulties in achieving full density, due to the constraint of network formed by the reinforcements. Consequently, pressure-assisted sintering, typically hot-pressing technique, is often used to obtain fully dense composites. Applications of these reinforcements and complicated fabrication processes including fiber coating lead to high costs. Moreover, there are some difficulties in handling and in distributing fibers or whiskers into a matrix homogeneously. Therefore, it is desired to generate elongated reinforcements with high aspect ratios through an in situ process during materials processing.

Conventional fibers or whiskers reinforced composites are so-called “ex situ” composites, that is, the reinforcements are

---

* Corresponding author. Tel./fax: +81 857 31 5707.
E-mail address: chen@mech.tottori-u.ac.jp (Z.-C. Chen).

0921-5093/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msea.2012.05.106

synthesized externally and then introduced into a matrix. In the case of "in situ" composites, the reinforcements are synthesized internally within a matrix during materials processing. In the last decades, much attention has been paid for using an in situ toughened approach to enhance the mechanical properties of ceramic materials. Second phases or grains with an elongated morphology (platelet, plate-like or needle-like) are formed in situ during materials processing, thus resulting in microstructural toughening. For example, the in situ formation of elongated β-Si_3N_4 grains with high aspect ratios in silicon nitride materials gave rise to self-reinforcement with toughness values >10 MPa $m^{1/2}$ [21,22]. Obviously, in situ processing is an attractive and cost-effective approach to obtain CMCs with high performances.

Concerning the in situ processing of CMCs, a lot of fabrication methods have been proposed. The main techniques include (i) eutectic reactions [23–26], (ii) solid-state precipitation [27,28], (iii) phase transformation [21], and (iv) chemical reactions [29–32]. This paper is limited to the in situ processing of alumina-matrix oxide/oxide composites fabricated by chemical reactions.

In alumina-matrix composites, many elongated second phases used as reinforcements are aluminate compounds with a layered β-alumina structure (such as $LaAl_{11}O_{18}$ [30,33] and $SrAl_{12}O_{19}$ [34]) or a magnetoplumbite (MP) structure ($LaMgAl_{11}O_{19}$ [29] and $CaAl_{12}O_{19}$ [31]). These aluminates, which have a β-alumina, MP or related layered structure, are commonly referred to as hexaaluminates [35]. These hexaaluminates having an elongated morphology may lead to improvement in fracture toughness. Many alkali, alkaline-earth, and rare-earth cations can stabilize the hexaaluminate structure in either β-alumina or MP form [35,36]. β-alumina and the MP structure are very similar, and both crystal structures consist of layered spinel blocks ($Al_{11}O_{16}^{+}$) with stabilizing cations and oxygen anions in mirror planes between the spinel layers [35]. Hexaaluminates have a unique plate-like morphology due to a specific anisotropy in their growth kinetics. Tsukuma and Takahata [33] incorporated $LaAl_{11}O_{18}$ platelets in TZP/Al_2O_3 by adding small amounts of La_2O_3, and the resultant composite exhibited higher strength and fracture toughness at elevated temperatures. By using different hexaaluminates as second phases, Chen and Chen [29] obtained alumina-based composites with toughness values 50% higher than monolithic alumina. In addition, An and Chan [31] investigated in situ toughening in the alumina-calcium hexaaluminate (CA_6) system. They found an increase in the aspect ratio of the CA_6 second phase resulted in more pronounced *R*-curve behavior, and enhanced toughening was the result of crack bridging by the elongated CA_6 grains.

In the present paper, the in situ processing of alumina-matrix composites containing barium hexaaluminate or barium hexaaluminate/zirconia reinforcing phases is reviewed. These composites were synthesized through reactive sintering of $Al_2O_3/BaCO_3$ or $Al_2O_3/BaZrO_3$ powder mixtures at high temperatures. The emphasis was focused on densification behavior, microstructure, and mechanical properties of in situ synthesized alumina-matrix composites.

2. Chemical reactions between alumina and barium zirconate

Alumina is one of the important and cost-effective oxide ceramics. It is widely used in mechanical, electronic, electrical, metallurgical, chemical, and medical industries because of its superior characteristics such as high strength and hardness, excellent wear resistance and heat resistance. Meanwhile, $BaZrO_3$ has a cubic perovskite structure and a high melting point (~2600 °C). It is an important technological material and has found widespread applications in dielectrics, piezoelectrics, electrooptic materials, catalysts, proton conductors, and crucible material for crystal growth of high-T_c superconducting compound $YBa_2Cu_3O_{7-\delta}$ [37–39].

In 1998, Gladysz et al. [40] first reported the preparation of alumina/barium zirconate ($BaZrO_3$) laminated composites and their microstructural development around the interface between Al_2O_3 and $BaZrO_3$. During hot pressing, $BaZrO_3$ reacts with Al_2O_3 to form a series of in situ reaction products: ZrO_2, $BaO \cdot Al_2O_3$, and $BaO \cdot 6Al_2O_3$. Such reactions resulted in the formation of mutiple, weak, and stable interfaces in the $Al_2O_3/BaZrO_3$ laminated composites. The resulting interfaces between various reaction zones were sharp and weak enough to allow for crack deflection and delamination during three-point bend tests. Microstructural observations showed that $BaZrO_3/ZrO_2$ interface was most likely to deflect cracks.

According to the above results, $BaZrO_3$ may be used as a candidate coating material for Al_2O_3 fiber/Al_2O_3 matrix composites. Generally, the absence of chemical reactions at the interfaces between fiber and coating layer or between matrix and coating layer is thought to be one of the important criterions in fabricating tough CMCs. In other words, a coating material depends on an inert phase with respect to Al_2O_3 to produce a mechanically weak interface. However, $BaZrO_3$ reacts with Al_2O_3 and produces a series of weak interfaces with the potential improvements in fracture toughness.

Koopman et al. [41] examined the feasibility of $BaZrO_3$ as a candidate material for interfacial coating in Al_2O_3 fiber/Al_2O_3 matrix composites. They used a sol–gel technique to coat $BaZrO_3$ onto Al_2O_3 fibers (Saphikon^{TM} and Nextel^{TM} 610). The coated fibers were embedded into Al_2O_3 powder and consolidated by hot pressing to obtain Al_2O_3 fiber/Al_2O_3 matrix composites. The results showed that the reactions between $BaZrO_3$ coating and Al_2O_3 occurred and indentation-induced cracks propagated along the reaction zone interfaces. Unlike common interphase materials, $BaZrO_3$ coating resulted in multiple interfaces through reactions with Al_2O_3 fiber and Al_2O_3 matrix during hot pressing [41].

Barium aluminates have several types of stoichiometric compositions, such as barium monoaluminate ($BaO \cdot Al_2O_3$), tri-barium monoaluminate ($3BaO \cdot Al_2O_3$), barium tetraaluminate ($BaO \cdot 4Al_2O_3$), and barium hexaaluminate ($BaO \cdot 6Al_2O_3$) [42]. Of which barium hexaaluminate has attracted much attention in some potential applications including catalytic combustion [43] and gas sensor [44] because of its high chemical, physical, and thermal stability as well as high ionic conductivity and high resistance to sintering and thermal shocks.

In addition to stoichiometric aluminates, barium can form a large number of complex nonstoichiometric Ba–O–Al aluminates. Groppi et al. [43] pointed out that materials with the β-Al_2O_3 structure could be obtained in the range of 9.1–14.6 of the Al/Ba ratio. In fact, it has been well established that barium hexaaluminate is actually constituted by two distinct phases with defective β-Al_2O_3 structure, *i.e.* Ba-β_I-Al_2O_3 and Ba-β_{II}-Al_2O_3 · β_I with a composition of $Ba_{0.75}Al_{11}O_{17.25}$ (Al/Ba = 14.67) is poorer in barium, while β_{II} with a composition of $Ba_{2.33}Al_{21.33}O_{34.33}$ (Al/Ba = 9.15) is richer in barium [35,43,45–48]. Furthermore, according to the phase diagram of Al_2O_3-$BaAl_2O_4$ proposed by Kimura et al. [45], only β_I phase exists together with Al_2O_3, provided the molar fraction of BaO is less than 10%. The present work is focused on the Ba-β_I-Al_2O_3 phase and it is expressed as Ba-β-Al_2O_3 hereinafter.

In order to further understand the chemical reactions between $BaZrO_3$ and Al_2O_3, Chen et al. [49] introduced $BaZrO_3$ coating on Nextel^{TM} 610 fibers by sol–gel method. The coated fibers were heat-treated at different temperatures ranging from 1100 °C to