

Processing and Characterization of Barium Hexaaluminate Reinforced Alumina Matrix Composites (バリウムヘキサアルミネート分散強化型アルミナセラミックス複合材料の作製と評価)

著者	Sri Nugroho
号	53
学位授与番号	4144
URL	http://hdl.handle.net/10097/42558

氏名	すり ぬぐろほ
授与学位	Sri Nugroho 博士(工学)
学位授与年月日	平成21年3月25日
学位授与の根拠法規	学位規則第4条第1項
研究科, 専攻の名称	東北大学大学院工学研究科(博士課程) 金属フロンティア工学専攻
学位論文題目	Processing and Characterization of Barium Hexaaluminate Reinforced Alumina Matrix Composites (バリウムヘキサアルミネート分散強化型アルミナセラミックス複合材料の作製と評価)
指導教員	東北大学教授 川崎 亮
論文審査委員	主査 東北大学教授 川崎 亮 東北大学教授 粉川 博之 東北大学教授 藤田 文夫 東北大学准教授 陳 中春

論文内容要旨

Component for high temperature structural applications, such as in gas turbine and aerospace engines, heat exchangers, and hot gas fillers are conventionally made from Fe-, Ni-, Co-based superalloys with operating temperatures around 1100°C that is near their upper use temperature. Accordingly, the use of cooling air is necessary, thus resulting in reduced efficiency and performance of the system. Since these applications require long-term exposure to oxidizing environments, the materials have to be featured by a combination of mechanical (e.g., strength, fracture toughness, and creep resistance), chemical (e.g., oxidation and corrosion resistance), thermo-physically properties (e.g., thermal shock resistance), and also long-term stability during service at elevated temperatures. An all-oxide ceramic composite consisting of oxide fibers, oxide matrix, and an oxide interphase(s), is a potential candidate due to its damage tolerance and inherent resistance to degradation in oxidizing atmospheres at high temperatures. Because of a reduced need or no need for cooling air, the applications of all-oxide CMCs lead to an increase in thermal efficiency and a reduction in pollutant emissions (NO_x, CO, and unburned hydrocarbons). One of the most popular all-oxide composites is alumina fiber reinforced alumina matrix composites. However, processing of this material faces some drawbacks, such as difficulty in dispersing fiber homogeneously, need for surface treatment of the fiber, hard to consolidate due to networking structure and high cost. In order to overcome this problem, in-situ synthesis is applied to obtaining composites that have similar structure and properties as fiber-like reinforced matrix composites.

In this work, barium hexaaluminate (Ba-β-Al₂O₃ or BaO·7.3Al₂O₃) was studied further for potential application as reinforcement for alumina-matrix composites through in situ synthesis of alumina-barium carbonate and alumina-barium zirconate powders. Due to limited information on densification behavior and mechanical properties data on bulk single phase of Ba-β-Al₂O₃.

synthesis and formation mechanism of Ba- β -Al₂O₃ powder followed by densification of synthesized powders by spark plasma sintering (SPS) and pressureless sintering (PLS) were first conducted. Then, using the same starting powders and processing, 30%vol Ba- β -Al₂O₃/Al₂O₃ and 30%vol [Ba- β -Al₂O₃-ZrO₂]/Al₂O₃ composites were produced from in situ reaction of (Al₂O₃-BaCO₃) and (Al₂O₃-BaZrO₃), respectively.

So far, some research works have concerned with the solid-state synthesis [1] and formation mechanisms [2,3] of Ba- β -Al₂O₃ phase. However, to the best knowledge of the present authors, different from conventional solid-state reaction technique, in this research, a high-energy planetary ball milling method was applied to reduce the particle sizes and enhance the reactivity of constituent powders. Besides, the formation mechanism of Ba- β -Al₂O₃ phase has never been reported before from the viewpoint of morphological evolution with temperature changes. Thus the first goals of this research are to synthesize monophasic Ba- β -Al₂O₃ powder through mechanically-activated milling and solid-state reaction of alumina and barium carbonate powder mixtures and to get further understanding of its formation mechanism. Ba- β -Al₂O₃ was synthesized through this following equation:



Based on TG, DSC and XRD results, mechanically activated milling results in decrease in decomposition temperature of BaCO₃ and promotes further reaction between Al₂O₃ and BaCO₃ powders [4]. Almost single phase Ba- β -Al₂O₃ can be synthesized through high energy ball milling for 9 ~ 12 hours, followed by heat treatment at 1500°C for 2 hours. The formation of Ba- β -Al₂O₃ phase includes three stages: (i) decomposition of BaCO₃, (ii) formation and growth of spherical BaO·Al₂O₃ particles, and (iii) reaction between Al₂O₃ and BaO·Al₂O₃ to form Ba- β -Al₂O₃ with an elongated morphology. Figure 1 shows a schematic illustration of the reaction sequence and formation mechanism of the Ba- β -Al₂O₃ phase during heat treatment.

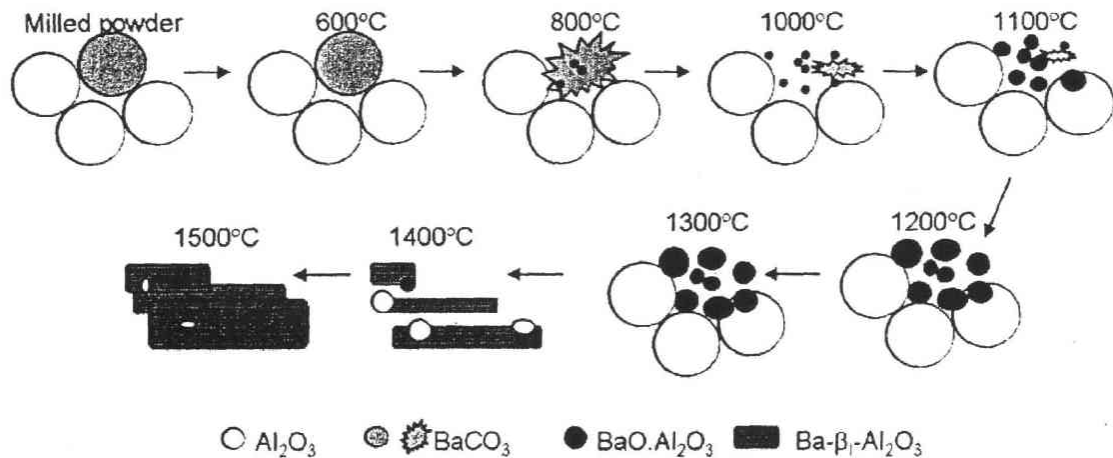


Fig. 1. Schematic illustration showing the formation of elongated Ba- β -Al₂O₃

Ba- β -Al₂O₃ is very difficult to be densified due to its peculiar layered structure and its elongated morphology. Many attempts have been made to obtain dense sample of Ba- β -Al₂O₃ but the results were unsatisfactory. Debsikdar [5] stated that the pressureless-sintered density of this material up to 1550°C for 24 h was, less than 60%. Work by He et.al. [6] and Dunn et.al. [7] in the

same year, almost dense barium hexaaluminate could be consolidated by PLS but it needs very high temperature of sintering and long sintering time. Due to this difficulty, to the best of our knowledge, therefore, it is still little research discussing the mechanical properties of this material. Besides, densification by using SPS methods is not yet done. Based on the formation mechanism of Ba- β -Al₂O₃ discussed above, dense Ba- β -Al₂O₃ samples were consolidated from two different powders compounds, i.e., [BaO·Al₂O₃ + Al₂O₃] (route 1) and Ba- β -Al₂O₃ (route 2) powders by SPS and PLS. A single phase of bulk Ba- β -Al₂O₃ with full density can be produced from SPS-ed route-1 powders at 1500°C-30min. SPSed route-2 powder at 1500°C-60min only produced 91% of theoretical density. Route-1 powder was easier to be densified than route 2, because it has spherical and very fine powders. The phases for route 1 and route 2 are [Ba- β -Al₂O₃ + trace of Al₂O₃] and Ba- β -Al₂O₃, respectively. The hardness and fracture toughness of this material were 14.6 GPa and 1.6 MPa.m^{1/2}, respectively. PLS at 1500°C for 2 h was not able to produce dense bulk Ba- β -Al₂O₃ derived neither from route-1 nor route-2 (with relative density less than 80%TD). The fracture images showed that it has transgranular mode of fracture.

In alumina based composites, the elongated second phases used as reinforcements are, generally, aluminate compounds with a layered β -alumina structure (such as LaAl₁₁O₁₈ [8], BaO·6.9Al₂O₃ [9], SrAl₁₂O₁₉ [10]) or a magnetoplumbite (MP) structure (LaMgAl₁₁O₁₉ [11] and CaAl₁₂O₁₉ [12]). Tagaoka [9] has synthesized 22vol% BaO·6.9 Al₂O₃/ Al₂O₃ composites by PLS however there is no further study on its mechanical properties. The main goals of this chapter are to in-situ synthesize and characterize 30vol% Ba- β -Al₂O₃/Al₂O₃ composite by SPS and to examine its mechanical properties.

The same Al₂O₃ and BaCO₃ powders were used as starting material, with the nominal composition of composites after sintering is 30vol%Ba- β -Al₂O₃/Al₂O₃ (see eq. 2).



Based on the result of densification of bulk Ba- β -Al₂O₃, powder of [BaO·Al₂O₃+Al₂O₃] (resulted from heat treatment of Al₂O₃ + BaCO₃ powder following eq. 2) was used for SPS. The Ba- β -Al₂O₃ reinforced Al₂O₃ matrix composite with 100%TD can be fabricated by SPS above 1400°C for 30min from [BaO·Al₂O₃+Al₂O₃] as starting powders. Figure 2 shows clearly dense composite and platelike morphology of Ba- β -Al₂O₃ in the composite. It is seen that alumina has smooth surface and on the other hand Ba- β -Al₂O₃ phase has rough surface and layered structure. Ba- β -Al₂O₃ phase attached perfectly in the surrounding alumina matrix.

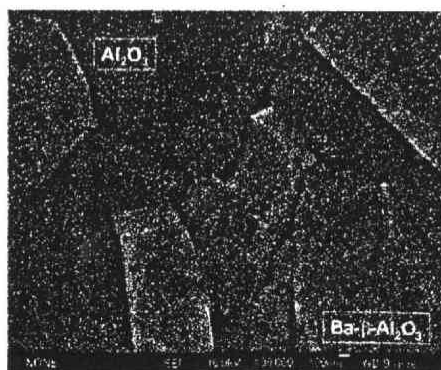


Fig. 2 Morphology of Ba- β -Al₂O₃ in the composite showing platelike and layered structure

The hardness and fracture toughness of Ba- β -Al₂O₃/Al₂O₃ composite were 18.03 GPa and 3.45 MPa.m^{1/2}, respectively. The incorporation of Ba- β -Al₂O₃ phase results in a slight improvement in fracture toughness of the composite due to crack deflection and crack bridging.

Recently, Chen et.al. [13,14] have also worked on in situ synthesis of alumina matrix composites by reactive sintering of Al₂O₃ and BaZrO₃ powder mixtures through this following equation:



The composite containing 30vol% [Ba- β -Al₂O₃ + ZrO₂] showed an optimum combination of mechanical properties. In this chapter, further research on synthesis of 30vol% [Ba- β -Al₂O₃-ZrO₂]/Al₂O₃ composites by two different densification procedures, i.e. (process-1) planetary ball milling + SPS and (process-2) rotary ball milling + PLS, will be thoroughly studied. The objective of this work is to examine the effect of processing parameter (ball milling and sintering methods) on densification behavior, formation of reinforcements, microstructural development and mechanical properties during consolidation. Ba- β -Al₂O₃/ZrO₂ reinforced Al₂O₃ matrix composite with almost 100% TD could be in situ synthesized by using PLS at 1500°C – 2h (process-1) or SPS at minimum 1400°C–30 min (process-2). Process-2 could produce Ba- β -Al₂O₃/ ZrO₂/ Al₂O₃ composite with higher toughness (5 MPa.m^{1/2}) than one by process-2 (4.1 MPa.m^{1/2}). This might be due to the higher aspect ratio of reinforcement formed and crack propagation mainly in interface of matrix/reinforcement. Compare with Ba- β -Al₂O₃/Al₂O₃ composite (3.4 MPa.m^{1/2}), Ba- β -Al₂O₃/ZrO₂/Al₂O₃ composite produced by process-1 or process-2, has higher fracture toughness. Besides due to difference in aspect ratio and crack propagation sites, it also was due to the existence of ZrO₂ particule embedded in Ba- β -Al₂O₃ phase. The crack propagation behavior of three different Ba- β -Al₂O₃ reinforced alumina matrix composites could be seen in the figure 3 below.

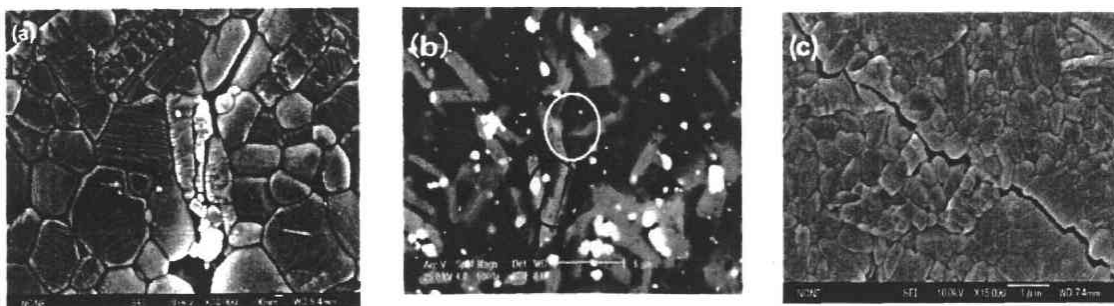


Fig. 3. (a) Ba- β -Al₂O₃/Al₂O₃ composite (b) Ba- β -Al₂O₃/ZrO₂/Al₂O₃ composite by process-1 (c) Ba- β -Al₂O₃/ZrO₂/Al₂O₃ composite by process-2

The formation of Ba- β -Al₂O₃ and ZrO₂ phases as reinforcement of the composite could improve fracture toughness of composite through crack bridging and crack deflection mechanism. The microstructure of in situ synthesized Ba- β -Al₂O₃/ZrO₂/Al₂O₃ composite is stable until 1400°C.

References:

1. Masato Machida, Koichi Eguchi, and Hiromichi Arai, *Journals of American Ceramics Society* 71[12] 1142-47 (1988).
2. G. Groppi, C. Cristiani, P. Forzatti and M. Belloto, *J. Mater. Sci.* **29** (1994), p. 3441
3. N. Iyi, S. Takekawa and S. Kimura, *Journal of Solid State Chemistry, Volume 83, Issue 1, November 1989, Pages 8-19*
4. Sri Nugroho, Zhongchun Chen, Akira Kawasaki, MOD. Jarfigo, submitted in the *Journal of Alloys and Compounds*, under review.
5. J.C. Debsikdar, O.S. Sowemimo, *journal of material science letters* 11 (1992) 637-638.
6. G. He, T. Goto, T. Narushima and Y. Iguchi, *Solid State Ionics*, Volume 121, Issues 1-4, June 1999, Pages 313-319
7. S. Dunn, R.V. Kumar and D.J. Fray *Solid State Ionics* 124 (1999), p. 133.
8. C.B. Solano, L. Esquivias, *J. Am. Ceram. Soc.*, 82 [5] 1318-24 (1999)
9. T. Nagaoka, Y. Iwamoto, *J. Am. Ceram. Soc.*, 83 [7] 1613-16 (2000)
10. M. Yasuoka, K. Hirao, M.E. Brito, S. Kanzaki, *J. Am. Ceram. Soc.* 78 (1995) 1853.
11. P.E.D. Morgan, J.A. Miles, *J. Am. Ceram. Soc.* 69 (1986) C157
12. L. An, H.C. Ha, H.M. Chan, *J. Am. Ceram. Soc.* **81** [12] 3321-24 (1998)
13. Z. Chen, K.K. Chawla, M. Koopman, *Mater. Sci. Eng. A.* 367 (2004) 24-32.
14. Z. Chen, T. Okazawa, K. Ikeda, *Ceram. Trans.* 192 (2006) 11-21.

論文審査結果の要旨

地球温暖化防止は急務の課題であり CO₂ ガスの排出量を低減するためエネルギー機器の作動温度の高温化が急ピッチで進められている。そのための鍵は高温構造用セラミックスであり、耐熱温度の限界に近づいた超耐熱合金の代替材料として不可欠となっている。しかし、大きな問題点は破壊靱性値が低いことであり、機器の信頼性を確保するためにはその改善が必要となる。バリウムヘキサアルミネートは層状構造をもつ酸化物セラミックスであり層間剥離が容易なことから、強度や破壊靱性は低いものの選択的に亀裂を伝播させることが期待できる。したがって、高温構造用セラミックスに分散することができれば、急峻に立ち上がる R-曲線挙動を実現できる可能性があり破壊靱性の向上に有効と考えられる。一方、バリウムヘキサアルミネートは難焼結性であり、その単相焼結体の作製例は少なく、破壊靱性などの基本的性質のデータが乏しい。また、それらの均一分散混合も困難なことから新しい創製プロセスの研究開発も必要とされている。以上の観点から、本研究では、大気中の高温構造用セラミックスを想定して Al₂O₃ セラミックスをマトリックスに選択し、バリウムヘキサアルミネート単相焼結体の合成と評価を行った上で、in-situ 反応焼結プロセスによってバリウムヘキサアルミネート分散強化型 Al₂O₃ 複合セラミックスの作製を試みたものである。破壊靱性値および機械的性質の評価とともに高靱性化メカニズムについても言及している。

第1章は序論であり、研究の背景および目的を述べている。

第2章では、メカノケミカル反応を利用した高エネルギーボールミル法と熱処理を組み合わせ、バリウムヘキサアルミネート単相粉末の合成を試みた。詳細に合成過程を調べ、形成メカニズムを明らかにするとともに単相粉末の合成に成功したことを述べている。

第3章では、パルス通電焼結法によりバリウムヘキサアルミネート単相粉末の焼結固化を試み、焼結体の機械的性質の評価を行った。バリウムヘキサアルミネート単相粉末の焼結緻密化は非常に困難であったが、中間生成物としての BaO- Al₂O₃ に Al₂O₃ を混合することにより、若干 Al₂O₃ が残るがほぼ理論密度の単相焼結体を得られることを明らかにした。加えて、機械的性質として硬さおよび破壊靱性値を求めている。

第4章では、上記結果を基にバリウムヘキサアルミネート分散強化型 Al₂O₃ 複合セラミックスを in-situ 反応焼結により合成した。期待した破壊靱性の向上は少なかったが、アスペクト比が低いことが一因であると考察している。

第5章では、Al₂O₃ と BaZrO₃ 混合粉末の in-situ 反応焼結によりバリウムヘキサアルミネートと ZrO₂ 分散強化型 Al₂O₃ 複合セラミックスを合成し、その評価を行った。常圧焼結法によっても緻密化できることを示し、異方性粒成長によって高いアスペクト比が得られることを明らかにした。これにより亀裂架橋、デフレクションなどの靱化メカニズムが有効に働き十分な破壊靱性値の改善ができることを明らかにした。

第6章は、本研究をまとめた総括である。

以上要するに本論文は、in-situ 反応焼結プロセスによるバリウムヘキサアルミネート分散強化型 Al₂O₃ 複合セラミックス作製の基礎研究を実施し、合成機構の詳細な考察とともに高靱性化メカニズムを示したもので、基礎的研究ばかりでなく工学的応用についても言及しており、材料システム、工学の発展に寄与することが少なくない。

よって、本論文は（工学）の学位として合格と認める。