Available online at www.sciencedirect.com

Journal of the European Ceramic Society 25 (2005) 1251–1257

www.elsevier.com/locate/jeurceramsoc

High temperature strength and thermal stability for melt growth composite

Narihito Nakagawa*, Hideki Ohtsubo, Atsuyuki Mitani,
Kazutoshi Shimizu, Yoshiharu Waku

Ube Research Laboratory, Ube Industries Ltd., 1978-5 Kogushi, Ube City, 755-8633 Yamaguchi, Japan

Abstract

Melt growth composites (MGCs) have a microstructure, in which continuous networks of single-crystal Al_2O_3 phases and single-crystal oxide compounds (YAG ($Y_3Al_5O_{12}$), GAP ($GdAlO_3$)) interpenetrate without grain boundaries. Therefore, the MGCs have excellent high-temperature strength characteristics, creep resistance, superior oxidation resistance and thermal stability in the air atmosphere at very high temperature. To achieve ultra-high thermal efficiency and low NO_x emission for gas turbine systems, we produced turbine nozzle vanes that does not require cooling and heat shield panels for combustor liners. The thermal stability and mechanical properties of these parts have been studied. The high-temperature strength characteristics and the thermal stability of components were also no changes after heat treatment for 500 h at 1700 °C in an air atmosphere. The favorable properties of melt growth composite have been discussed for possible application in gas turbine system.

Keywords: Al_2O_3; $GdAlO_3$; Mechanical properties; Thermal properties

1. Introduction

Directionally solidified eutectic ceramics has been extensively investigated to improve the microstructure and the mechanical properties for application at high temperatures.[1–4] It has been reported that a unidirectionally solidified Al_2O_3/YAG eutectic ceramics has superior flexural strength, creep resistance at high temperatures,[5–7] and is a candidate for high-temperature structural materials. However, this material contains many grain boundaries or colonies between Al_2O_3 and YAG, which are expected to impair the mechanical property.[8]

On the other hand, authors have already reported a eutectic composite such as $Al_2O_3/Y_3Al_5O_{12}$ (YAG) or $Al_2O_3/GdAlO_3$ (GAP) or $Al_2O_3/Er_3Al_5O_{12}$ (EAG) with neither colonies nor grain boundaries, using a unidirectional solidification. The eutectic composite has a new microstructure, in which continuous networks of single-crystal Al_2O_3 phases and single-crystal oxide compounds (YAG, GAP, EAG) interpenetrate without grain boundaries. Therefore, the eutectic composite has excellent high-temperature strength characteristics, creep resistance, superior oxidation resistance and thermal stability at 1700 °C in an air atmosphere.[9–15] These materials were called melt growth composite (MGC).

Several useful applications of the MGCs can be recently considered, for example, gas turbines and power generation systems at very high temperatures. Feasibility study on the MGCs to the high temperature section of the gas turbine has been examined at a national project during 2001–2005 in Japan. In this paper, we investigate the high-temperature strength characteristics and the thermal stability of gas turbine MGC parts such as hollow-type turbine nozzle vanes and heat shield panels for combustor liners and discuss for possible application in gas turbine system.

2. Experimental

2.1. Manufacturing of raw powder

Using commercially available Al_2O_3 powder (AKP-30, produced by Sumitomo Chemical Co. Ltd.), Y_2O_3 powder and Gd_2O_3 powder (Y_2O_3-RU, Gd_2O_3-RU, sub-micron type, produced by Shin-Etsu Chemical Co. Ltd.), wet ball milling

---

* Corresponding author. Tel.: +81 836 31 6139; fax: +81 836 31 6153.
E-mail address: 26359u@ube-ind.co.jp (N. Nakagawa).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.01.030

of $Al_2O_3/Y_2O_3 = 82/18$ or $Al_2O_3/Gd_2O_3 = 78/22$ mole ratio was undertaken to obtain a uniform composite powder slurry. The slurry obtained was dried in a rotary evaporator to remove the ethanol.

2.2. Unidirectional solidification of Al_2O_3/YAG MGC

Fig. 1 shows schematic drawing of the Bridgman-type apparatus for unidirectional solidification. All the unidirectional solidification experiments were carried out by using the advanced alloy crystalline structure controlling equipment at the Japan Ultra-high Temperature Materials Research Center (573-3 Okiube, Ube City, Yamaguchi Prefecture 755-0001, Japan). Preliminary melting to obtain a board-shape ingot was performed in a molybdenum (Mo) mold. The Mo mold was heated by high-frequency induction coils. A board-shaped ingots obtained were inserted into a Mo mold which is divided into two parts. One split mold is the same configuration as the another one with a cavity of dimensions of about 44 mm × 120 mm × 3 mm. The external appearance of the Mo split mold is a semi-column with 26 mm in radii and 150 mm in length. Two Mo split molds were installed in a cylinder of Mo (57 mm in outside diameter by 210 mm in length by 2 mm thickness) in a vacuum chamber. The Mo cylinder was heated by heating a graphite susceptor heated by high-frequency induction coils. After sustaining at 1930 °C (about 100 °C above melting point) for 30 min, the cylinder of Mo was lowered at the speed of 5 mm/h to complete the unidirectional solidification. The size of Al_2O_3/YAG MGC plates is 45 mm in width by 90 mm in length by 6 mm in thickness as shown in Fig. 2.

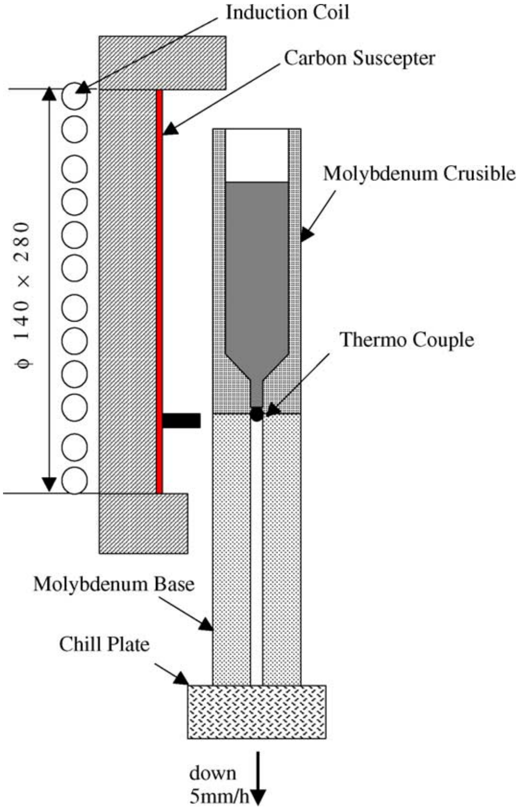

Fig. 1. Schematic drawing of the Bridgman-type unidirectional solidification apparatus.

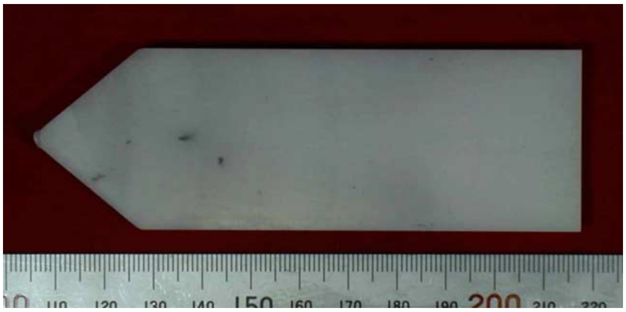

Fig. 2. A boarded-type ingot of Al_2O_3/YAG MGC.

2.3. Unidirectional solidification of $Al_2O_3/GdAlO_3$ MGC

Preliminary melting to obtain an ingot was applied in a molybdenum crucible (52 mm in inside diameter by 210 mm in length by 2 mm thickness) heated by high-frequency induction coils. Ingots obtained were inserted into the molybdenum molds (53 mm in inside diameter by 210 mm in length by 2 mm thickness). And the mold was inserted into a vacuum chamber, where a graphite susceptor was heated by high-frequency induction coils. After sustaining the melt temperature at 1870 °C (about 100 °C above melting point) for 30 min, the molybdenum crucible was lowered at 5 mm/h to induce the unidirectional solidification. The size of Al_2O_3/GAP eutectic composite rods of 53 mm in diameter by 70 mm in length was obtained as shown in Fig. 3.

Fig. 3. A column ingot of Al_2O_3/GAP MGC.

2.4. Fabrication of MGC components for gas turbine system

The heat shield panels for the combustor liner were finished by machining using diamond wheel from the Al_2O_3/YAG MGC plate. On the other hand, an external appearance of hollow-type turbine nozzle vanes were finished by machining using diamond wheel and then a hollow part was finished by ultra sonic machining from the Al_2O_3/GAP MGC column. Finally, the surfaces of these parts were polished.

2.5. Mechanical test method

The specimens used for four-point flexural tests were selected so that their axial direction was parallel to the direction of the unidirectional solidification. The dimensions of the flexural test specimen were 3 mm × 4 mm × 36 mm with a 30 mm span. The tests were carried out using the high-temperature uniaxial tension-compression and flexural test system (modified creep and fatigue machine, type 8562 produced by Instron) at the Japan Ultra-high Temperature Materials Research Center. The testing jigs were made of graphite. The four-point flexural strength was measured from room temperature to high temperature for the $Al_2O_3/Y_3Al_5O_{12}$ eutectic composite and the $Al_2O_3/GdAlO_3$ composite in an argon atmosphere at a crosshead speed of 0.5 mm/min.

The thermal stability of the microstructure of the MGCs was evaluated from microstructural changes after heat treatments in an air atmosphere at 1700 °C for up to 500 h in furnace using scanning electron microscope (SEM). Microstructure of MGCs was observed by using scanning electron microscope (SEM). Change in the representative size, surface roughness and weight of MGCs components was also evaluated after heat treatment in an air atmosphere at 1700 °C. High-resolution transmission microscopic (HRTEM) observation of the MGCs was carried out using a JEM-2010 microscope, while the electron probe microanalysis (EPMA) was conducted with a JMX-8621MX.

3. Results and discussion

3.1. Microstructure of $Al_2O_3/Y_3Al_5O_{12}$ and $Al_2O_3/GdAlO_3$ eutectic composites

Fig. 4 shows SEM images of the microstructure of cross-section perpendicular to the solidification direction of Al_2O_3/YAG and Al_2O_3/GAP MGCs. The Al_2O_3/YAG and Al_2O_3/GAP MGCs consist of Al_2O_3 phases and YAG phases, and Al_2O_3 phases and GAP phases, respectively; these were determined from X-ray diffraction patterns. The white areas in the SEM images are the YAG phases for the Al_2O_3/YAG MGC and GAP phases for the Al_2O_3/GAP MGC, and the black areas is the Al_2O_3 phase for both MGCs from EPMA analysis. The dimensions of phases of the Al_2O_3/YAG MGC are 20–30 μm, which is defined as the typical length to the short axis of each domain seen in the cross-section perpendicular to the solidification direction. On the other hand, that of the Al_2O_3/GAP MGC was around 5 μm smaller than that of the Al_2O_3/YAG MGC. Homogeneous microstructures with no pores or colonies are observed in both MGCs.

Fig. 5 shows SEM photographs which illustrates the three-dimensional configuration of the YAG phases (Fig. 5(a)) and the GAP phase (Fig. 5(b)) in Al_2O_3/YAG and Al_2O_3/GAP MGCs, respectively, from which Al_2O_3 phases had been removed by heat treating in graphite powders at 1600 °C for 2 h. The configuration of the GAP phase and the YAG phase is a three-dimensionally connected porous structure of irregular shape. We, therefore, conclude that the present MGCs have a microstructure consisting of three-dimensionally continuous and complexly entangled single-crystal Al_2O_3 and single crystal YAG for the Al_2O_3/YAG MGC, and single-crystal Al_2O_3 and single crystal GAP for the Al_2O_3/GAP MGC.[15]

3.2. Temperature dependence of flexural strength of MGCs

Fig. 6 shows the temperature dependence of the flexural strength of Al_2O_3/YAG and Al_2O_3/GAP MGCs from

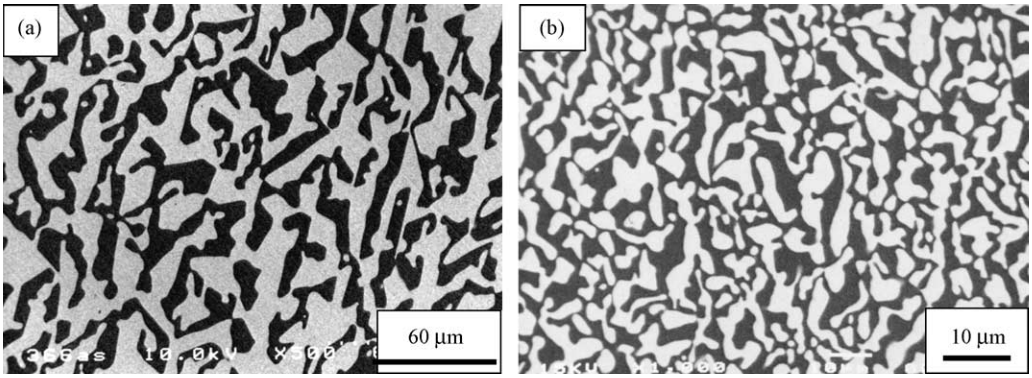

Fig. 4. SEM images of microstructure of cross-section perpendicular to the solidification direction of the Al_2O_3/YAG and Al_2O_3/GAP MGCs: (a) Al_2O_3/YAG MGC and (b)Al_2O_3/GAPMGC.

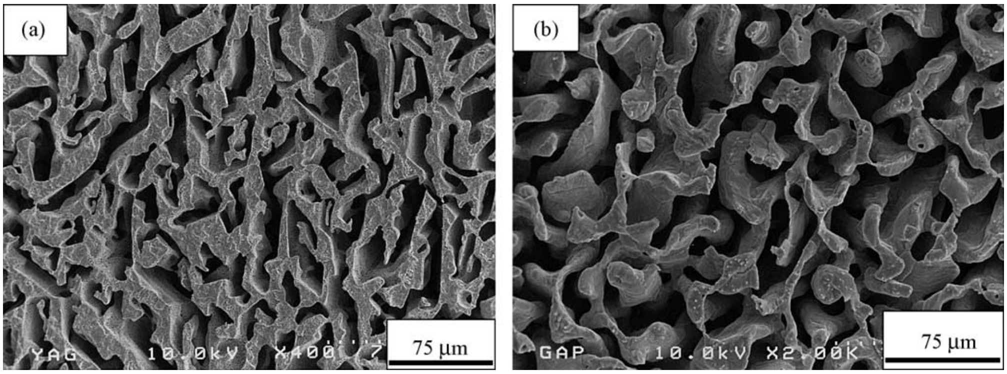

Fig. 5. SEM photographs of the three-dimensional configuration of the YAG phases (a) in the Al_2O_3/YAG MGC and the GAP phases (b) in the Al_2O_3/GAP MGC.

room temperature to very high temperatures in comparison with that of a sintered Si_3N_4 ceramics (SN282)[16] and superalloy (CMSX®-10).[17] The strength of Si_3N_4 is four-point flexural strength. And the strength of a superalloy is tensile strength. The Al_2O_3/YAG MGC maintains its room temperature strength up to 1800 °C (just below its melting point of about 1830 °C), with a flexural strength in the range of 300–350 MPa. On the other hand, the flexural strength of the Al_2O_3/GAP MGC shows approximately 600 MPa from 1400 to 1600 °C, twice 300–350 MPa of the Al_2O_3/YAG binary MGC. In comparison, Ni-based single-crystal superalloys (CMSX®-10) currently being used as turbine blades at the present time show a large drop in strength with an increase of temperature above around 800 °C. The Si_3N_4 ceramics has the higher flexural strength than that of the MGCs at room temperature, but its strength decreases gradually with an increase of temperatures above around 800 °C. In addition, the Si_3N_3 ceramic shows the poor oxidation resistance at high temperatures, hence it is a major impediment to use for oxidative environment at high temperatures. In contrast to this, MGCs are particularly desirable for oxidative environment at high temperatures.

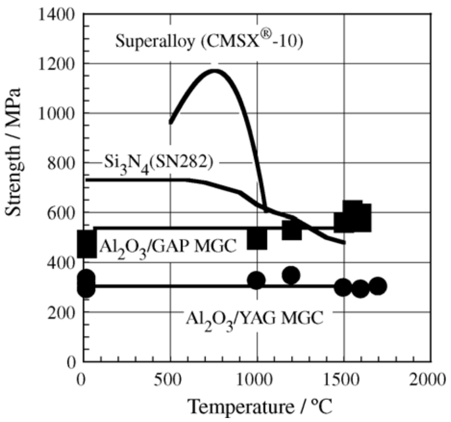

Fig. 6. Temperature dependence of the flexural strength of the MGCs compared with a superalloy (CMSX®-10) and a Si_3N_4 ceramic. Strength shows four-point flexural strength for MGCs and a Si_3N_4 ceramic, and tensile strength for a superalloy.

It has been reported that a unidirectionally solidified eutectic ceramics has superior flexural strength, creep resistance at high temperatures.[6,18–20] We also have been reported that the Al_2O_3/GAP eutectic composite shows yielding behavior under high stress at 1600 °C.[15] Fig. 7 shows a typical stress-displacement curve of a four-point flexural test obtained at 1600 °C from a specimen parallel to the solidification direction of the Al_2O_3/GAP MGC large ingot with 53 mm in diameter and 70 mm in length. The Al_2O_3/GAP MGC shows similar yielding behavior to that of the reported composite[15] and its strength at 1600 °C is about 600 MPa somewhat smaller than about 700 MPa.[15]

3.3. Thermal stability of MGCs

Fig. 8 shows the SEM images of microstructure of cross-section perpendicular to the solidification direction of the Al_2O_3/YAG and Al_2O_3/GAP MGCs after 0–500 h of heat treatment at 1700 °C in an air atmosphere. In case of Al_2O_3/YAG MGC (Fig. 9(a)–(c)), even after 500 h of heat treatment no grain growth of microstructure was observed. While in case of Al_2O_3/GAP MGC (Fig. 9(d)–(f)), a slight grain growth was observed. However, both MGCs were shown to be comparatively stable without void formation

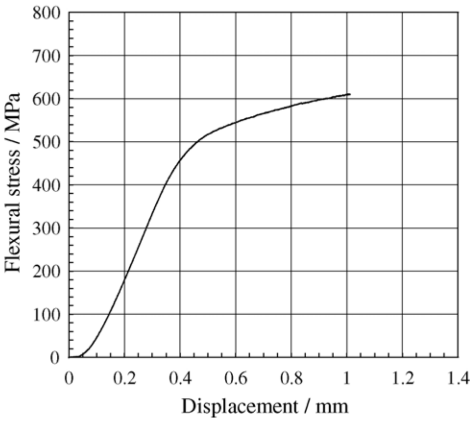

Fig. 7. Typical stress-displacement of the Al_2O_3/GAP MGC obtained from four-point flexural tests at 1600 °C.

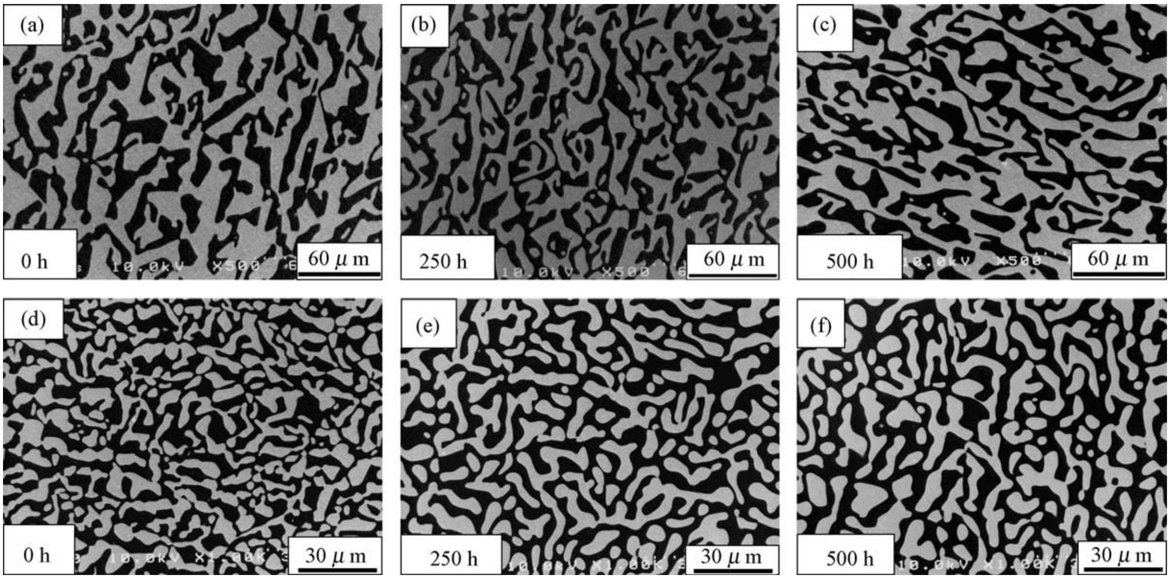

Fig. 8. SEM images showing microstructural change of cross-section perpendicular to the solidification of MGCs before and after heat treatment until 500 h at 1700 °C in an air atmosphere: (a–c) the Al_2O_3/YAG MGC and (d–f) the Al_2O_3/GAP MGC.

during lengthy exposure at high temperature of 1700 °C in an air atmosphere. This stability resulted from the thermodynamic stability at that temperature of the constituent phases of the single-crystal Al_2O_3, the single-crystal YAG and the single-crystal GAP, and the thermodynamic stability of the interface.

Fig. 9 shows a relationship between flexural strength at room temperature and the time of heat treatment at 1700 °C in an air atmosphere. The Al_2O_3/YAG MGC has about 300–370 MPa of the flexural strengths after the heat treatment for 500 h at 1700 °C in an air atmosphere. This strength is the same value as the as received. While, the Al_2O_3/GAP MGC has about 500–600 MPa of the flexural strengths after the heat treatment for 500 h at 1700 °C in an air atmosphere. Both MGCs exhibited good thermal stability at very high temperature of 1700 °C in an air atmosphere.

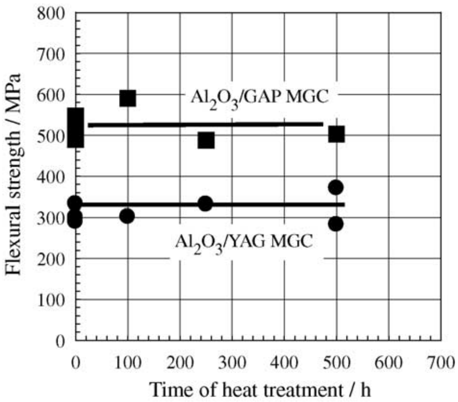

Fig. 9. Relationship between flexural strength at room temperature and time of heat treatment at 1700 °C in an air atmosphere.

3.4. Applications of the MGC's for gas turbine engines

To improve energy efficiency and curb the emission of pollutants such as CO_2 and NO_x, we examined an application of MGC to gas turbine high temperature components. Fig. 10 shows locations of turbine nozzle vanes and combustor liners supposed to be MGC application and a general view of the gas turbine system. The size of the gas turbine system was chosen as relatively small as a 5000 kW-class. The MGC application to these parts can be expected to improve simultaneously thermal efficiency and low NO_x lean burn combustion. The estimated thermal efficiency will become around 38% at 1700 °C of turbine inlet temperature (TIT) and 30 of engine compression ratio with non-cooled turbine nozzle vane.[21] On the other hand, the ordinary gas turbine system with a 5 MW class has thermal efficiency of 29% at 1100 °C of TIT and 15 of engine compression ratio with cooled turbine nozzle vanes. Consequently, we can expect to improve approximately 9% of thermal efficiency by applying MGC to gas turbine nozzle vanes.

External appearance of a hollow-type turbine nozzle vane and a heat shield panel of MGC components are shown in Fig. 11. The hollow-type turbine nozzle vane was made of the Al_2O_3/GAP MGC and the heat shield panel was made of the Al_2O_3/YAG MGC. Table 1 shows changes in representative dimensions, surface roughness and weight of both parts before and after heat treatment for 500 h at 1700 °C in an air atmosphere. These MGC parts have outstanding oxidation resistance with no change in dimensions, surface roughness and weight after heat treatment for 500 h at 1700 °C in an air atmosphere.

These excellent high-temperature characteristics of the MGCs are closely linked to such factors as: (1) the MGCs has unique microstructures consisting of three-dimensionally

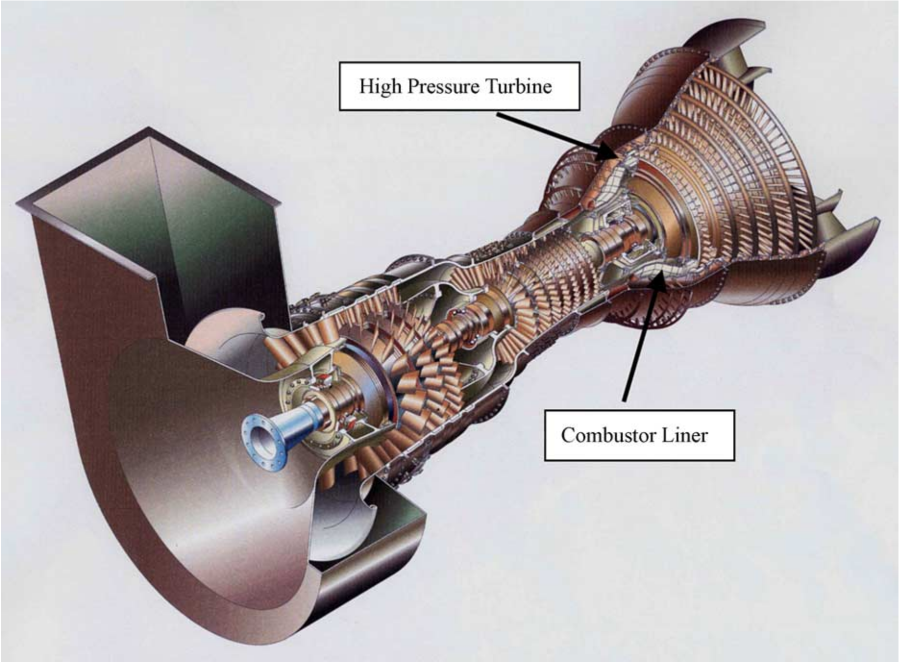

Fig. 10. Schematic of locations of MGC parts and a general view of gas turbine system.

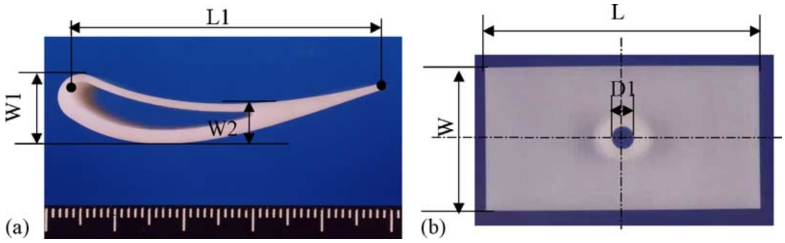

Fig. 11. Samples of the MGC gas turbine components: (a) hollow-type turbine nozzle vane and (b) heat shield panel for a combustor liner.

continuous and complexly entangled single-crystal Al_2O_3 and single-crystal YAG for the Al_2O_3/YAG MGC or single-crystal Al_2O_3 and single-crystal GAP for the Al_2O_3/GAP MGC. (2) No amorphous phase were formed at the interface between constituent phases as seen in Fig. 12 showing a high-resolution TEM image of interfaces observed in the Al_2O_3/GAP MGC, and interfaces formed

Table 1
Changes in representative dimensions, surface roughness and weight of MGC components after heat treatment until 500 h at 1700 °C in an air atmosphere

Length	0 h	250 h	500 h	Dimensional change
L1 (mm)	43.971	43.975	43.977	0.006
W1 (mm)	10.614	10.620	10.614	0.000
W2 (mm)	5.389	5.390	5.385	−0.004
Weight (g)	26.783	26.782	26.770	−0.012
Ra (μm)	0.46	0.56	0.77	0.31
L (mm)	74.539	74.528	74.534	0.005
W (mm)	38.060	38.064	38.066	−0.006
D1 (mm)	5.553	5.558	5.557	−0.003
Weight (g)	18.561	18.562	18.564	0.003
Ra (μm)	0.61	0.63	0.64	0.03

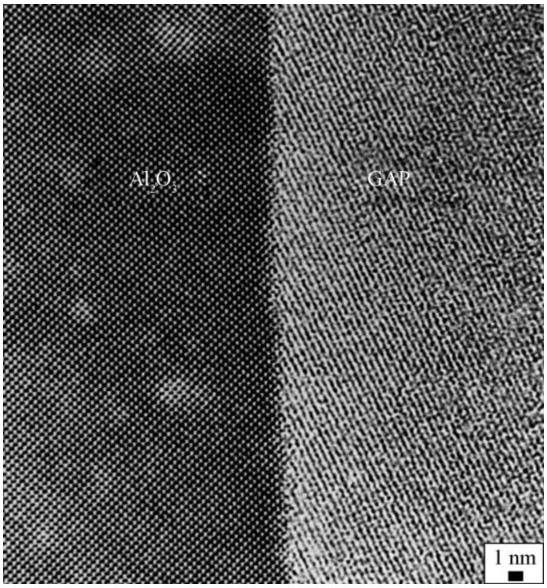

Fig. 12. A high-resolution TEM image of interfaces between the Al_2O_3 phases and GAP phases in Al_2O_3/GAP MGC.

are thermodynamically stable and comparatively good coherency.

4. Conclusions

The gas turbine components of Al_2O_3/YAG and Al_2O_3/GAP MGCs can be successfully fabricated by using Bridgman-type furnace and evaluated those high-temperature characteristics. The present MGCs have a unique microstructure consisting of three-dimensionally continuous and complexly entangled single-crystal Al_2O_3 and single-crystal oxide compounds (YAG or GAP) without grain boundaries. The dimensions of microstructure are 20–30 μm for Al_2O_3/YAG MGC and around 5 μm for Al_2O_3/GAP MGC.

The Al_2O_3/YAG MGC maintains its room temperature strength up to 1800 °C (just below its melting point of about 1830 °C), while the Al_2O_3/GAP MGC shows excellent strength characteristics at very high temperatures, showing substantially yielding behavior under high stress.

A hollow-type turbine nozzle made of the Al_2O_3/YAG MGC and heat shield panel of combustor liner made of the Al_2O_3/GAP MGC show superior oxidation resistance with no changes in representative dimensions, surface roughness and weight after heat treatment for 500 h at 1700 °C in an air atmosphere. This is attributed to the MGC's unique microstructure without grain boundaries and its interfacial effect. Therefore, these MGC is expected to be widely used in mechanical engineering at very high temperatures in the future.

Acknowledgments

The authors would like to express their thanks to the New Energy and Industrial Technology Development Organization (NEDO) and the Ministry of Economy, Trade and Industry (METI), who gave them the opportunity to conduct "Research on Technology for MGC Ultra-High-Efficiency Gas-Turbine."

References

1. Schmid, F. and Viechnicki, D., Oriented eutectic microstructures in the system Al_2O_3/ZrO_2. *J. Mater. Sci.*, 1970, **5**, 470–473.
2. Ashbrook, R. L., Directionally solidified ceramics eutectics. *J. Am. Ceram. Soc.*, 1977, **60**(9–10), 428–435.
3. Pastor, J. Y., Paza, P., Llorca, J., Pena, J. I., Merino, R. I. and Orera, V. M., Mechanical properties of directionaly solidified Al_2O_3–ZrO_2 (Y_2O_3) eutectics. *Mater. Sci. Eng.*, 2001, **A308**, 241–249.
4. Martinez Fernandez, J., Sayir, A. and Farmer, S. C., High temperature creep deformation of directionally solidified $Al_2O_3/Er_3Al_5O_{12}$. *Acta Mater.*, 2003, **51**, 1705–1720.
5. Viechnicki, D. and Schmid, F., Eutectic solidification in the system $Al_2O_3/Y_3Al_5O_{12}$. *J. Mater. Sci.*, 1969, **4**, 84–88.
6. Mah, T. and Parthasarathy, T. A., Processing and mechanical properties of $Al_2O_3/Y_3Al_5O_{12}$ (YAG) eutectic composite. *Ceram. Eng. Sci. Proc.*, 1990, **11**, 1617–1627.
7. Parthasarathy, T. A., Mah, T. and Matson, L. E., Creep behavior of an $Al_2O_3/Y_3Al_5O_{12}$ eutectic composite. *Ceram. Eng. Soc. Proc.*, 1990, **11**, 1628–1638.
8. Parthasarathy, T. A., Tai II, M. and Matson, L. E., Deformation behavior of an $Al_2O_3/Y_3Al_5O_{12}$ eutectic composite in comparison with sapphire and YAG. *J. Am. Ceram. Sci.*, 1993, **76**, 29–32.
9. Waku, Y., Nakagawa, N., Ohtsubo, H., Ohsora, Y. and Kohtoku, Y., High temperature properties of unidirectionally solidified Al_2O_3/YAG composites. *J. Jpn. Inst. Met.*, 1995, **59**, 71–78.
10. Waku, Y., Otsubo, H., Nakagawa, N. and Kohtoku, Y. Y., Sapphire matrix composites reinforced with single crystal YAG phases. *J. Mater. Sci.*, 1996, **31**, 4663–4670.
11. Waku, Y., Nakagawa, N., Wakamoto, T., Ohtsubo, H., Shimizu, K. and Kohtoku, Y., High-temperature strength and thermal stability of a unidirectionally solidified Al_2O_3/YAG eutectic composite. *J. Mater. Sci.*, 1998, **33**, 1217–1225.
12. Waku, Y., Nakagawa, N., Wakamoto, T., Ohtsubo, H., Shimizu, K. and Kohtoku, Y., The creep and thermal stability characteristics of a unidirectionally solidified Al_2O_3/YAG eutectic composite. *J. Mater. Sci.*, 1998, **33**, 4943–4951.
13. Nakagawa, N., Waku, Y., Wakamoto, T., Ohtsubo, H., Shimizu, K. and Kohtoku, Y., The creep, oxidation resistance characteristics of a unidirectionally solidified $Al_2O_3/Er_3Al_5O_{12}$ eutectic composites. In *Proceedings of the 6th International Symposium on Ceramic Materials and Components for Engines*, 1997, pp. 701–708.
14. Nakagawa, N., Waku, Y., Wakamoto, T., Ohtsubo, H., Shimizu, K. and Kohtoku, Y., High temperature properties and thermal stability of a unidirectionally solidified $Al_2O_3/Er_3Al_5O_{12}$ eutectic composites. *J. Jpn. Inst. Met.*, 2000, **64**, 101–107.
15. Waku, Y., Nakagawa, N., Wakamoto, T., Ohtsubo, H., Shimizu, K. and Kohtoku, Y., A ductile ceramic eutectic composite with high strength at 1873 K. *Nature*, 1997, **389**, 49–52.
16. Yoshida, M., Tanaka, K., Kubo, T., Terazone, H. and Tsuruzone, S., Development of ceramic components for ceramic gas turbine engine (CGT302). In *Proceedings of the International Gas Turbine and Aeroengine Congress and Exhibition*. The American Society of Mechanical Engineers, 1998, pp. 1–8.
17. Erickson, G. L., *The development and application of CMSX-10*. The Minerals, Metals & Materials Society, 1996, pp. 35–44.
18. Stubican, V. S. and Bradt, R. C., Eutectic solidification in ceramic systems. *Ann. Rev. Mater. Sci.*, 1981, **11**, 267–297.
19. Sayir, A. and Farmer, S. C., Fracture characteristics of single crystal and eutectic fibers. In *Fiber Fracture*, ed. M. Elices and J. Llorca. Elsevier Science, 2002. pp. 109–122.
20. Sayir, A., Farmer, S. C., Dicksons, P. O. and Yum, H. M., High temperature mechanical properties of Al_2O_3/ZrO_2 (Y_2O_3) fibers. *Mat. Res. Soc. Symp. Proc.*, 1995, **365**, 21–27.
21. Fujiwara, K., Nakagawa, N., Kobayashi, K., Yokoi, S., Kihara, T. and Takamatsu, H., Research on application of melt growth composite ceramics to gas turbines, In: *Proceedings of ASME TURBO EXPO 2003*. GT2003-38029.