JOURNAL OF MATERIALS SCIENCE 31 (1996) 4663–4670

Sapphire matrix composites reinforced with single crystal YAG phases

Y. WAKU, H. OHTSUBO, N. NAKAGAWA, Y. KOHTOKU
Ube Research Laboratory, Corporate Research & Development, UBE Industries, Ltd., 1978-5, Kogushi, Ube City, Yamaguchi, 755, Japan

An investigation of fabrication technology on eutectic composites consisting of Al_2O_3 phases and YAG ($Y_3Al_5O_{12}$) phases was carried out by applying the unidirectional solidification process. Unidirectionally solidified eutectic composites consisting of $\langle 1\,1\,0 \rangle$ sapphire phases and $\langle 4\,2\,0 \rangle$ single crystal YAG phases could be fabricated successfully by lowering a Mo crucible at a speed of 5 mm h^{-1} under a pressure of 10^{-5} mmHg of argon. These eutectic composites have excellent high-temperature properties up to 1973 K. For example, the flexural strength is 360–500 MPa independent of testing temperature from room temperature to 1973 K. Oxidation resistance at 1973 K in an air atmosphere is superior to SiC and Si_3N_4 and the microstructure of these eutectic composites is stable even after heat treatment at 1773 K for 50 h in an air atmosphere.

1. Introduction

There are severe demands on high-performance materials, such as high-temperature strength, oxidation resistance up to 1800 K and toughness. These requirements must be satisfied to allow these materials to be used in advanced aerospace structures, automobiles and high efficiency gas generators [1]. Future aerospace propulsion systems will require materials that are lighter, stiffer, and stronger at high temperature than currently available materials. The benefits of lighter engine materials and reduced cooling requirements include higher thrust-to-weight ratios and increased thermodynamic efficiency due to higher operating temperatures [2].

Even though advanced monolithic ceramic materials like Si_3N_4 and SiC have been regarded as strong candidate materials for high-temperature gas turbine applications, it becomes obvious that these materials not only show low toughness, reliability, oxidation resistance and relatively low high-temperature strength, but also give rise to enormous manufacturing costs [3].

In contrast, a SiC/SiC composite produced by a chemical vapour infiltration process (CVI process) developed by Societé Européenne de Propulsion (SEP) in France has been investigated in this application at high temperatures up to 1673 K [4, 5] and is generally considered as a unique material for possible use at high temperatures up to 1673 K. But this composite not only has relatively low oxidation resistance above 1673 K, but also gives rise to enormous manufacturing costs.

To date, it has been considered that oxide ceramics are unsatisfactory materials for applications at temperature above 1300 K because of easy plastic deformation at high temperature ranges [6]. But since these oxide ceramics have more superior oxidation resistance properties than ordinary ceramics, such as SiC and Si_3N_4, if improvements giving high-temperature strength above 1300 K became possible, then oxide ceramics could be used more widely in aerospace, automobile and high efficiency gas generator applications.

The unidirectional solidification of metal alloys has been extensively investigated over the past century. The impetus has been chiefly to control and improve the microstructure for application at elevated temperatures. This has led to the unidirectional solidification of metals of eutectic composition. These have been proven to yield oriented lamellar or fibrous composite microstructures, possessing excellent thermal stability and a coherent interphase bonding which is impossible to achieve in composites formed by conventional methods [7].

The same improved microstructural properties, such as thermal stability of microstructures, fine control of crystal grain size, segregation and structure of grain boundary, may be expected in oxide ceramics if unidirectional solidification technology can be applied. The first objective of this study is to develop a new unidirectional solidification processing technology for high performance advanced ceramic composites instead of the powder sintering method generally used in the production of engineering ceramics. The second objective is to develop high performance Al_2O_3/YAG oxide ceramic composites which will be stable at high temperatures above 1773 K in an air atmosphere. In the present study, to attain the above two objectives, unidirectional solidification experiments of Al_2O_3/Y_2O_3 system are investigated, including an optimum composition study and evaluation of high temperature properties, such as high temperature strength, oxidation resistance and thermal stability of the microstructure, for unidirectional solidified eutectic composites.

2. Experimental details

2.1. Procedure of mixed powder

Using commercially available α-Al_2O_3 powder (Sumitomo Chemical Co., Ltd., AKP-30) and Y_2O_3 powder (Shin-etsu Chemical Co., Ltd., Y203-SU, submicron type), wet ball milling using ethanol was carried out to obtain a homogeneous mixed powder. The slurry obtained was dried in a rotary evaporator to remove the ethanol. After pre-forming the mixed powder into a shape $10\,\phi \times 10$ mm, arc pre-melting is carried out.

2.2. Composition study

To reveal the feasibility of manufacturing oxide ceramics composites *in situ* by means of the unidirectional solidification process, a study to determine the optimum composition for Al_2O_3 and Y_2O_3 oxide ceramic binary system was carried out taking account of the formation of macro- and micro-cracks initiated during the solidification and cooling process. Melting was performed by using a Mo crucible heated by a carbon heater in an argon gas atmosphere with hot-pressing equipment (FUJIDENPA CE 50 by Fuji Denpa Industries). Melting temperatures 50–100 K higher than the melting point in the equilibrium phase diagram were adopted [8]. Cooling rates for the solidification process were controlled at approximately $100\ \mathrm{K\,min^{-1}}$.

2.3. Unidirectional solidification

All experiments were carried out by using the advanced alloy crystalline structure controlling equipment (FEZ) at the Japan Ultra-High Temperature Materials Research Center. A schematic of the unidirectional solidification apparatus is shown in Fig. 1.

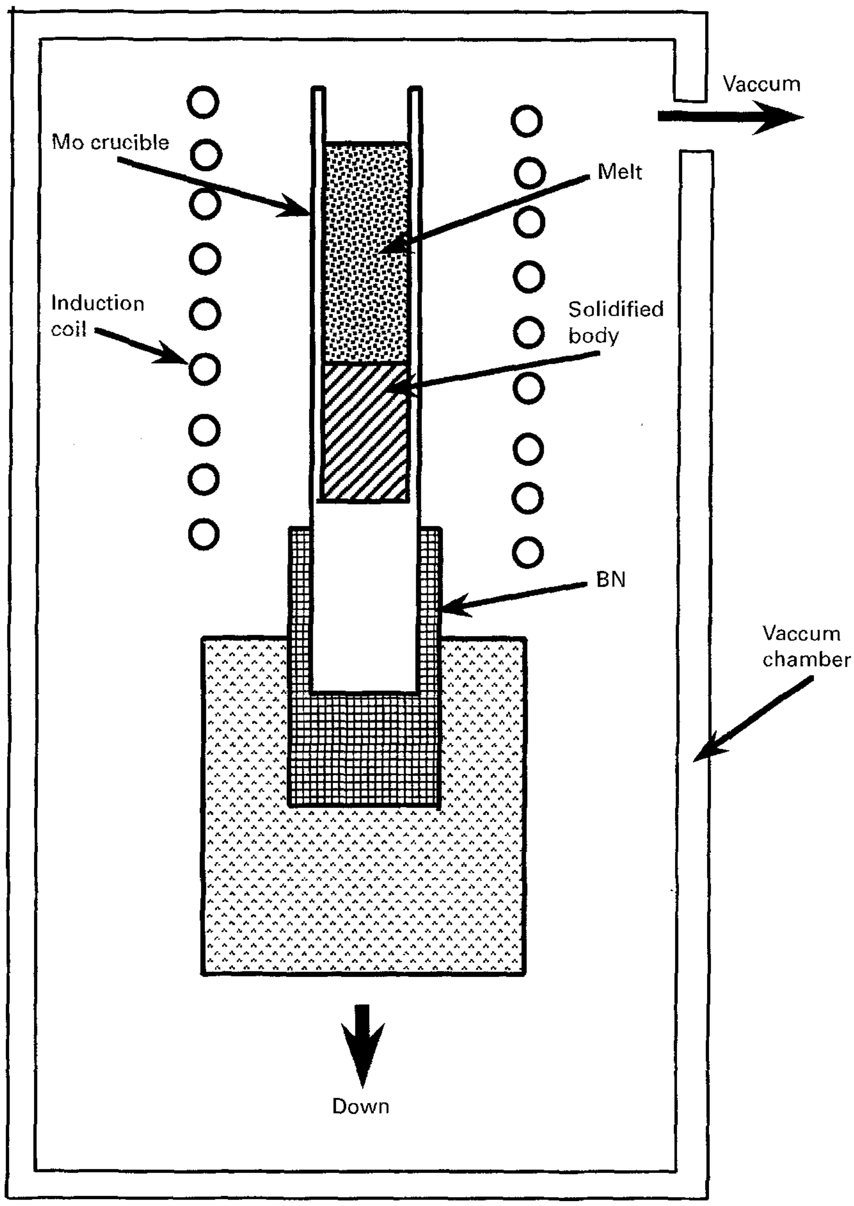

Figure 1 Schematic of the unidirectional solidification apparatus.

The powders obtained by crushing the arc-melted ingots were put in the Mo crucible and placed in a chamber. The melting experiment was performed in the Mo crucible heated by high-frequency induction heating under a pressure of 10^{-5} mmHg of argon, and then, after holding for 30 min at 2123 K, unidirectional solidification was carried out by lowering the Mo crucible at a speed of 5 mm h^{-1} in the same argon gas atmosphere.

2.4. Evaluation method
Three-point flexural tests were carried out by using specimens (3 mm × 4 mm × 36 mm) having the long axis parallel to solidification direction. The equipment used in this study is the high temperature uniaxial tension compression and bending test system (modified creep and fatigue machine, Instron type 8562) at the Japan Ultra-High Temperature Materials Research Center. Tests of flexural strength were conducted in an argon gas atmosphere at room temperature to 1973 K. The crosshead speed was 0.5 mm min^{-1}.

Structural analyses were undertaken using a Rigaku-Denki RAD-RB type X-ray diffraction apparatus. The high resolution transmission microscopic observations of the interface structures between the Al_2O_3 and YAG phases was undertaken using a Japan Electron JEM-2010. EPMA analyses were undertaken using a Japan Electron JMX-8621MX. Oxidation resistance of the resultant unidirectional solidified eutectic composites was evaluated from weight change before and after a given constant holding time at 1973 K in an air atmosphere. To compare with commercially available SiC and Si_3N_4 ceramics, the same heat-treatment conditions as for the unidirectional solidified eutectic composite were applied. The thermal stability of the unidirectional solidified eutectic composites was investigated by observing the change in the microstructures before and after heat treatment at 1973 K for 50 h in air atmosphere.

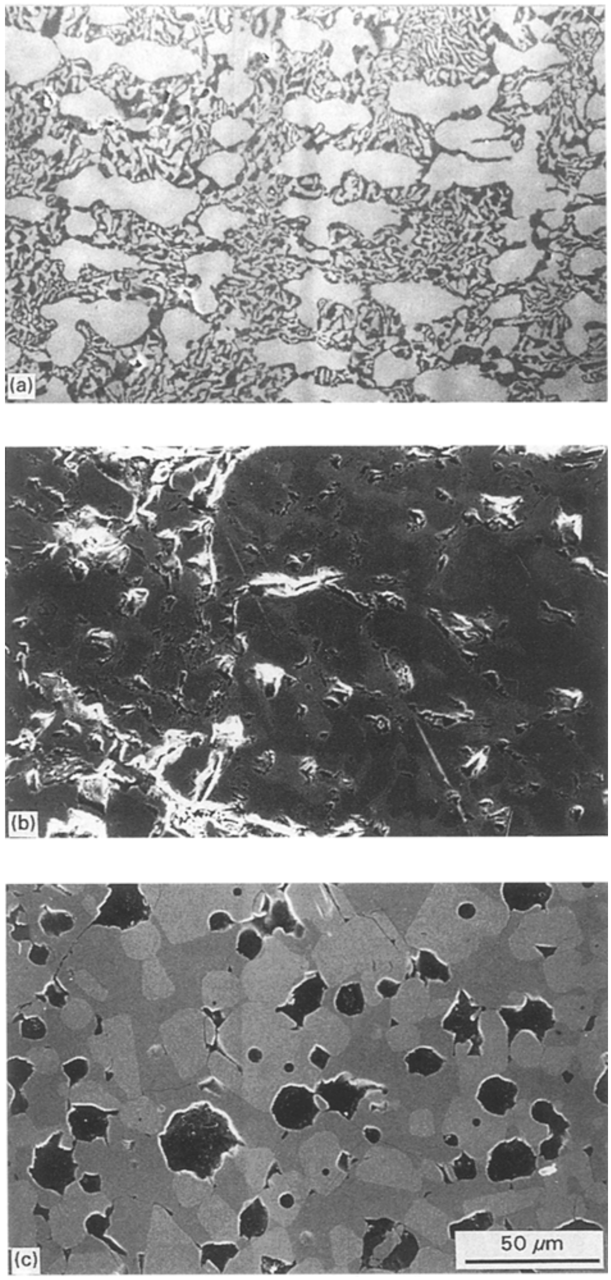

Figure 2 Photomicrographs of cast composites. (a) 78.6/21 mol %, (b) 40/60 mol % and (c) 19/81 mol % of α-Al_2O_3/Y_2O_3.

3. Results and discussion
3.1. Composition study
Fig. 2 shows optical photomicrographs of solidified composites with α-Al_2O_3/Y_2O_3 = 78.6/21.4, 40/60 and 19/81 mol ratio, respectively, and the results of X-ray diffraction are presented in Table I. Table I indicates that the compound phases observed in this study almost coincide with those of the Al_2O_3–Y_2O_3 binary equilibrium phase diagram [8]. Composites made of $2Y_2O_3 \cdot Al_2O_3$ and $3Y_2O_3 \cdot 5Al_2O_3$ (YAG) compounds can be observed with Al_2O_3/Y_2O_3 = 40/60 mol ratio. For Al_2O_3/Y_2O_3 = 78.6/21.4 mol ratio, it can be observed that not only α-Al_2O_3 phases and YAG ($Al_5Y_3O_{12}$) compound are formed by the eutectic reaction, but also a few vol % primary YAG compound. From this fact, it can be considered that the eutectic composition investigated experimentally in this study shifted toward the hyper-eutectic composition side from that in the binary equilibrium phase diagram [8]. On the other hand, it may be that we observe not eutectic phases but dual phase of Y_2O_3 and $2Y_2O_3 \cdot Al_2O_3$ which together give Al_2O_3/Y_2O_3 = 19/81 mol ratio.

TABLE I Compositions of α-Al_2O_3/Y_2O_3 investigated in this study and the present compound phases indicated from the X-ray diffraction patterns

Composition	Phases
78.6 mol % Al_2O_3/21.4 mol % Y_2O_3	α-Al_2O_3 + $5Al_2O_3 \cdot 3Y_2O_3$
40 mol % Al_2O_3/60 mol % Y_2O_3	$5Al_2O_3 \cdot 3Y_2O_3$ + $Al_2O_3 \cdot 2Y_2O_3$
19 mol % Al_2O_3/81 mol % Y_2O_3	Y_2O_3 + $Al_2O_3 \cdot 2Y_2O_3$

There are a lot of macro-cracks and micro-cracks in the solidified composites with Al_2O_3/Y_2O_3 = 40/60 and 19/81 mol ratio due to thermal coefficient mismatch between constituent phases and thermal stress induced during the cooling process after solidification as shown in Fig. 2. But in the case of $Al_2O_3/Y_2O_3 = 78.6/21.4$ mol ratio, no cracks can be observed in the solidified composites due to the small difference in thermal coefficient mismatch between the Al_2O_3 phases and the YAG phases. Therefore, this composition system may be expected to be produced *in situ* by the unidirectional solidification process, with the composite consisting of α-Al_2O_3 phases and YAG phases and to have superior high temperature mechanical properties. From several compositional experients, it is also clear that the binary composition for the perfect eutectic reaction is $Al_2O_3/Y_2O_3 = 82/18$ mol ratio which is slightly different from the binary equilibrium phase diagram [8].

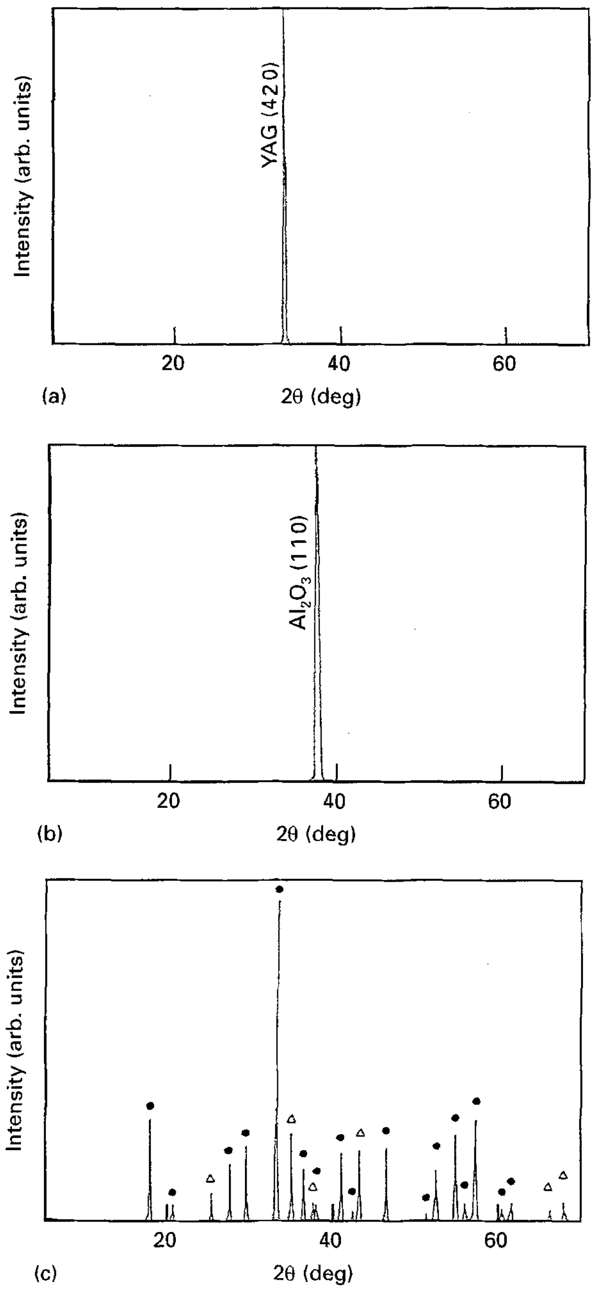

Figure 3 X-ray diffraction patterns of unidirectionally solidified eutectic composites at (a) plane perpendicular to the solidification direction, (b) at a plane 76° inclined to the solidification direction, and (c) powder fragmented from unidirectionally solidified composites (● YAG; △ Al_2O_3).

3.2. Unidirectional solidification

Fig. 3a and b show X-ray diffraction patterns of the eutectic composite obtained from a cross-section perpendicular to and a cross-section declined by about 76 degrees from the solidification direction of the composite, respectively. Fig. 3c also shows an X-ray diffraction pattern from crushed powder of the unidirectional solidified composite, which is the same sample as used for the X-ray diffraction of Fig. 3a and b. It can be easily deduced from comparison between Fig. 3a, b and c that the unidirectional solidified eutectic composites consisted of $\langle 110 \rangle$ single crystal Al_2O_3 (sapphire) and $\langle 420 \rangle$ single crystal YAG. In other words, this eutectic composite fabricated by the *in situ* process of unidirectional solidification is a $\langle 110 \rangle$ sapphire matrix composite reinforced with $\langle 420 \rangle$ single crystal YAG. This material is expected to have superior high temperature properties, such as creep strength and high temperature strength, because both $\langle 110 \rangle$ sapphire and $\langle 420 \rangle$ single crystal YAG have excellent high temperature strength.

Optical photomicrographs of the cross-section parallel to and perpendicular to the solidification direction of the eutectic composite are shown in Fig. 4. For the cross-section parallel to the solidification direction, the microstructure consisting of single crystal Al_2O_3 and single crystal YAG is elongated toward the solidification direction. In contrast, the mirostructure of the cross-section perpendicular to the solidification

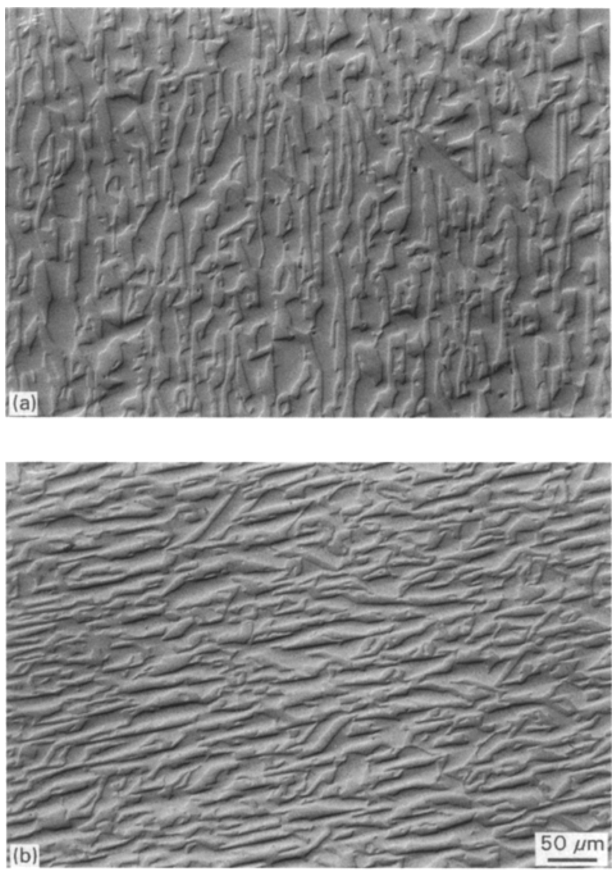

Figure 4 Photomicrographs of the cross-section (a) parallel to and (b) perpendicular to the solidification direction for the unidirectionally solidified eutectic composites.

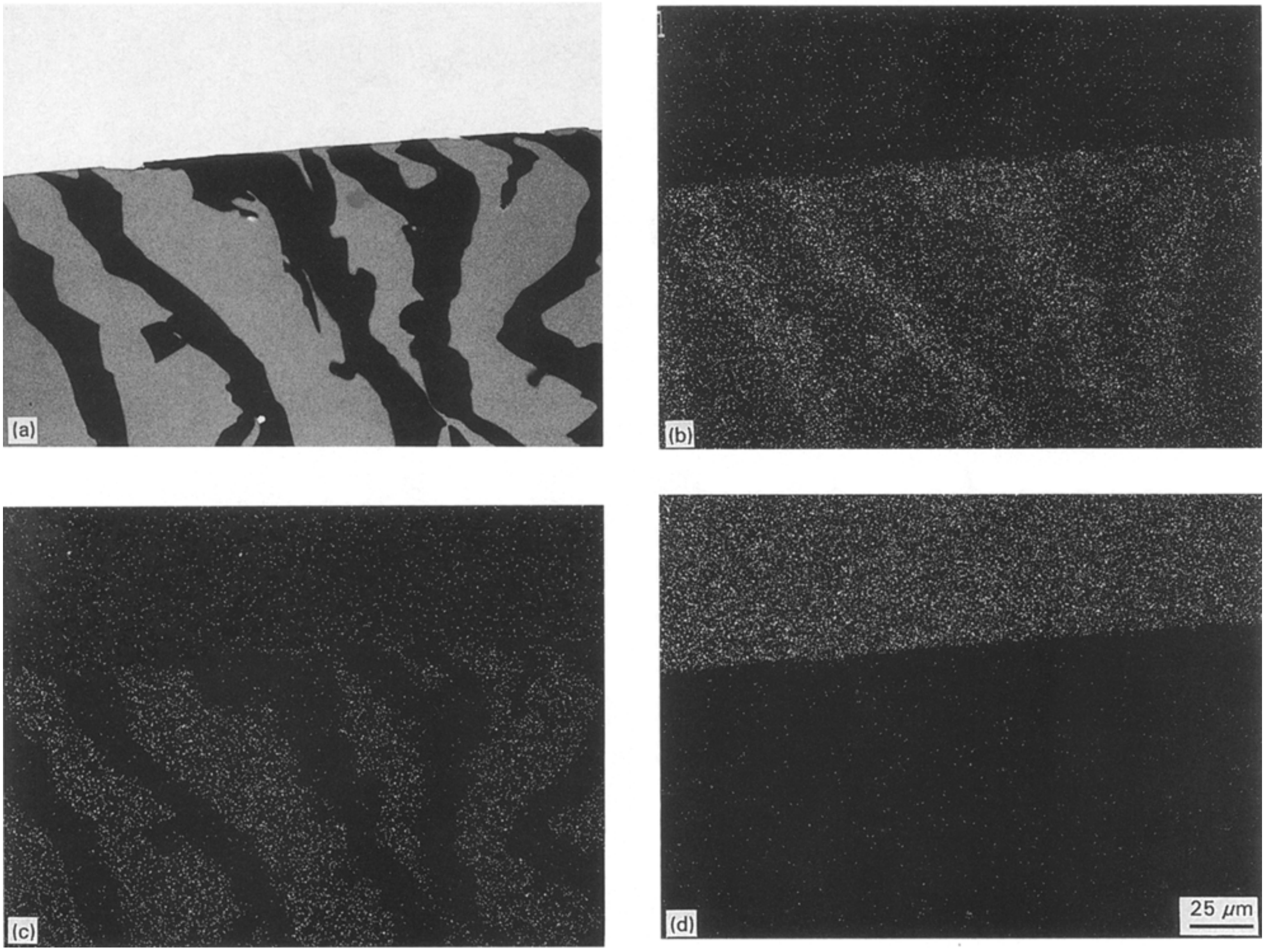

Figure 5 SEM image and EPMA analysis of the microstructure of the unidirectionally solidified eutectic composites. (a) SEM image, (b) EPMA analysis of Y element, (c) EPMA analysis of Al element and (d) EPMA analysis of Mo element.

direction consisted of the same constituent phases as the cross-section parallel to the solidification but is elongated toward the Mo crucible regardless of the solidification direction. Fig. 5 shows a SEM image and EPMA analysis for the microstructure of an unidirectionally solidified eutectic composite including the Mo crucible. The white areas in the SEM image is the YAG phase, and the dark area is the Al_2O_3 phase from the EPMA analysis. No reaction products at the interface between the Mo crucible and the solidified composite are observed and there is a distinct interface between the Mo crucible and the solidified body. These results show that the Mo material may be used as a casting die, and also that this unidirectional solidified eutectic composite may possibly be used for net-shape fabrication of complex products.

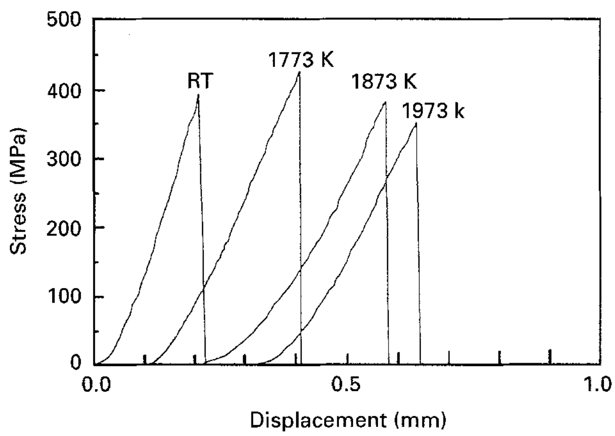

Figure 6 Typical stress–displacement curves of the unidirectionally solidified eutectic composites.

3.3. High temperature properties

Dependence of three-point flexural strength on testing temperature from room temperature to 1973 K is investigated in an argon atmosphere. Typical stress–strain curves measured are shown in Fig. 6. The unidirectional solidified eutectic composite indicates an elastic fracture behaviour not showing obvious plastic deformation even at 1973 K. Fig. 7 shows SEM photographs of the fracture surface of a flexural specimen conducted at room temperature, 1673, 1773 and 1873 K, respectively. The eutectic composite tends to indicate transgranular fracture, not the intergranular fracture generally observed in sintered ceramics. In the case of room temperature, the fracture surface is relatively smooth, independent of the Al_2O_3 phases and YAG phases, and is characterized by its featureless appearance, but the crystallographic nature of the fracture surface becomes apparent with increasing testing temperature.

Temperature dependence of the flexural strength from room temperature to 1973 K is shown in Fig. 8

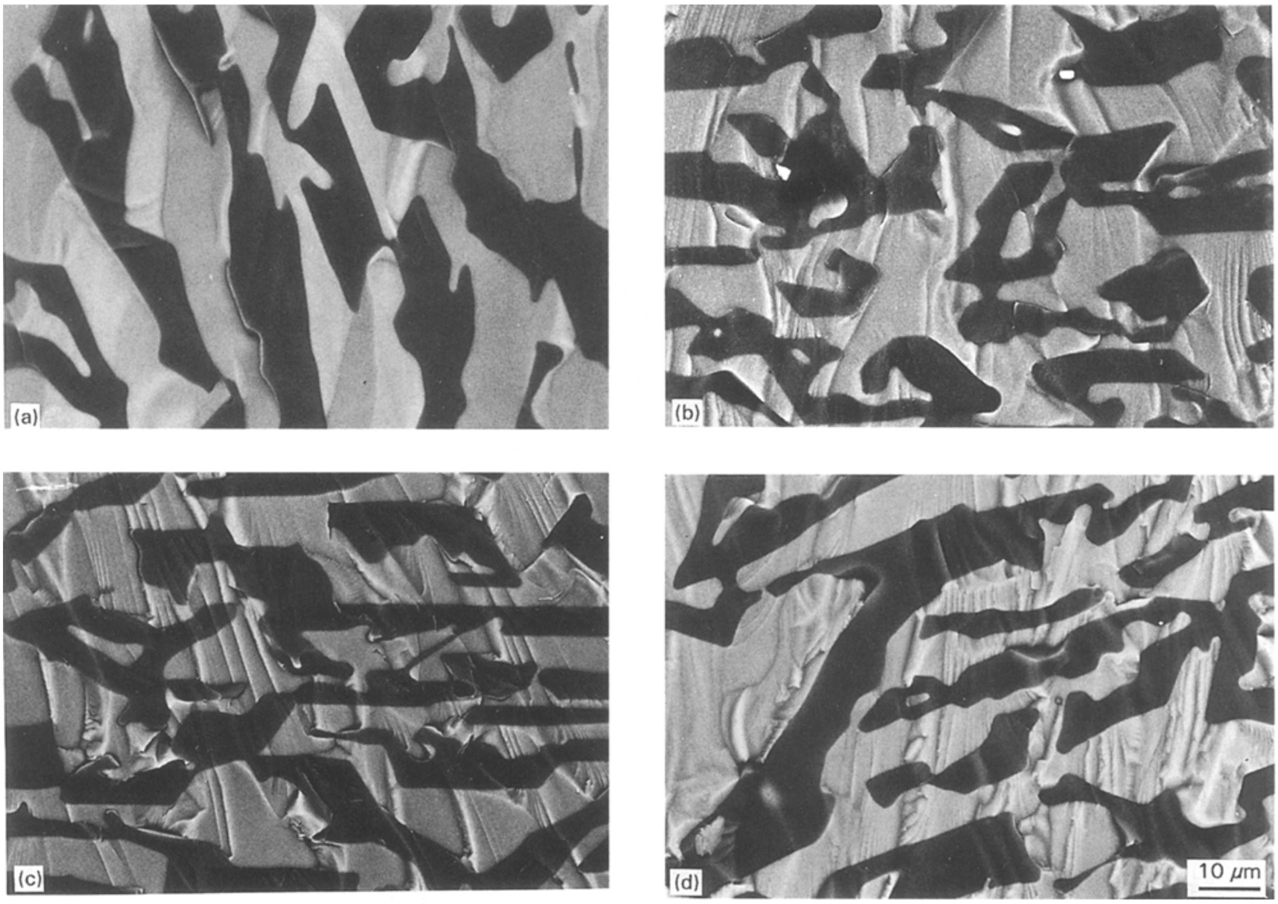

Figure 7 SEM photographs showing the fracture surface of flexural test specimens conducted at (a) room temperature, (b) 1673 K, (c) 1773 K and (d) 1873 K.

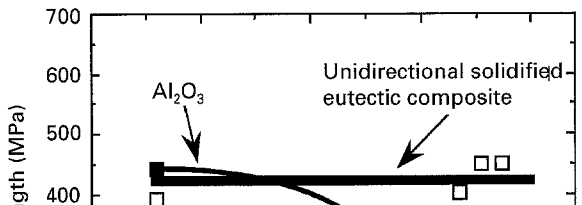

Figure 8 Temperature dependence of flexural strength of the unidirectionally solidified eutectic composites compared with Al_2O_3, mullite ceramics and SiC/SiC2D composite from room temperature to 1973 K.

in comparison with ordinary oxide ceramics and (mullite [9] and Al_2O_3 [10]) and advanced ceramic composites such as the well known SiC/SiC composites [11]. The flexural strength of the unidirectional solidified eutectic composite is about $360 \sim 500$ MPa and independent of testing temperature from room temperature to 1973 K. In comparison, mullite ceramics, an oxide considered to be satisfactory for relatively high temperature applications, show a large drop on increasing the testing temperature to 1573 K [9]. Al_2O_3 ceramics show degradation in high temperature strength above 1273 K [10]. Meanwhile, the high temperature strength of the unidirectionally solidified eutectic composite at 1673 K is almost equal to or above that for SiC/SiC2D [11] fabricated by the chemical vapour infiltration method of the Societé Européenne de Propulsion (SEP) in France, which is thought to have the maximum high temperature strength at the present time. However, it is difficult to use SiC/SiC composites above 1673 K in an air atmosphere because their oxidation resistance and high temperature strength start to decrease with increasing temperature. However, the high temperature flexural strength up to 1973 K of the unidirectional solidified eutectic composite is almost the same as that at 1673 K.

According to Kotchick and Tressler [12], plastic deformation behaviour of sapphire shows that basal slip $\{001\}$ $\langle 110 \rangle$ is active under 1173 K, prismatic slip $\{110\}$ $\langle 110 \rangle$ is active under 1323 K and pyramidal slip $\{101\}$ $\langle 011 \rangle$ is active above 1873 K. Above 1873 K, macro-plastic deformation can be observed because the von Mises criterion is satisfied, i.e. five independent slip systems become active as the temperature increases.

It is generally considered that the existence of amorphous phases at the interface and grain boundary may decrease high temperature strength [13, 14].

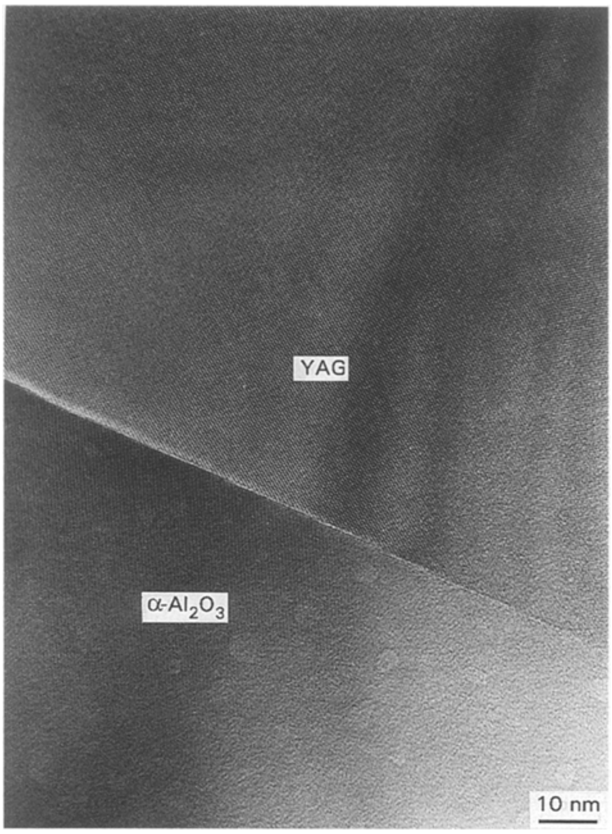

Figure 9 HRTEM image of the interface between Al_2O_3 phase and YAG phase of the unidirectionally solidified eutectic composites.

Fig. 9 shows a HRTEM image of the interface between Al_2O_3 phases and YAG phases. The existence of amorphous phases was not observed and relatively compatible interfaces are formed. From the above, it may be concluded that the superior high temperature strength was obtained by the following means: good crystal orientation of the matrix, consisting of $\langle 1\,1\,0\rangle$ single crystal Al_2O_3 and $\langle 4\,2\,0\rangle$ YAG, which can hardly be deformed plastically even at the high temperature of 1873 K; no amorphous phases formed at the interface between Al_2O_3 phases and YAG phases, which can easily cause plastic deformation; and the effect of the eutectic composite consisting of single crystal Al_2O_3 and YAG, which are stable at high temperature.

3.4. Oxidation resistance

Fig. 10 shows changes in the weight gain of the unidirectional solidified eutectic composite after heat treatment for 50 h at 1973 K in an air atmosphere in comparison with ordinary SiC and Si_3N_4 ceramics. Si_3N_4 and SiC ceramics show collapses of shapes after 10 h and after 50 h, respectively, and both ceramics show unstable oxidation resistance properties due to the chemical reaction of $Si_3N_4 + 3O_2 \rightarrow 3SiO_2 + 2N_2$ and $2SiC + 3O_2 \rightarrow 2SiO_2 + 2CO$ [15].

Meanwhile, it is found that the unidirectionally solidified eutectic composite has excellent oxidation resistance properties up to 1973 K in an air atmosphere as indicated by the absence of weight gain, shown in Fig. 10.

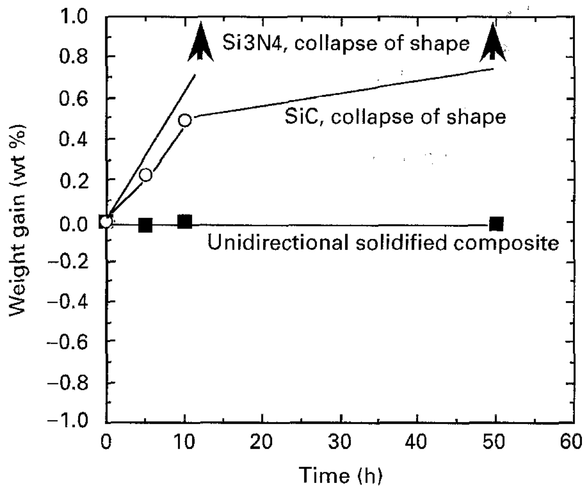

Figure 10 Changes in weight gain of the unidirectionally solidified composites after heat treatment at 1973 K for 50 h in an air atmosphere compared with ordinary SiC and Si_3N_4 ceramics.

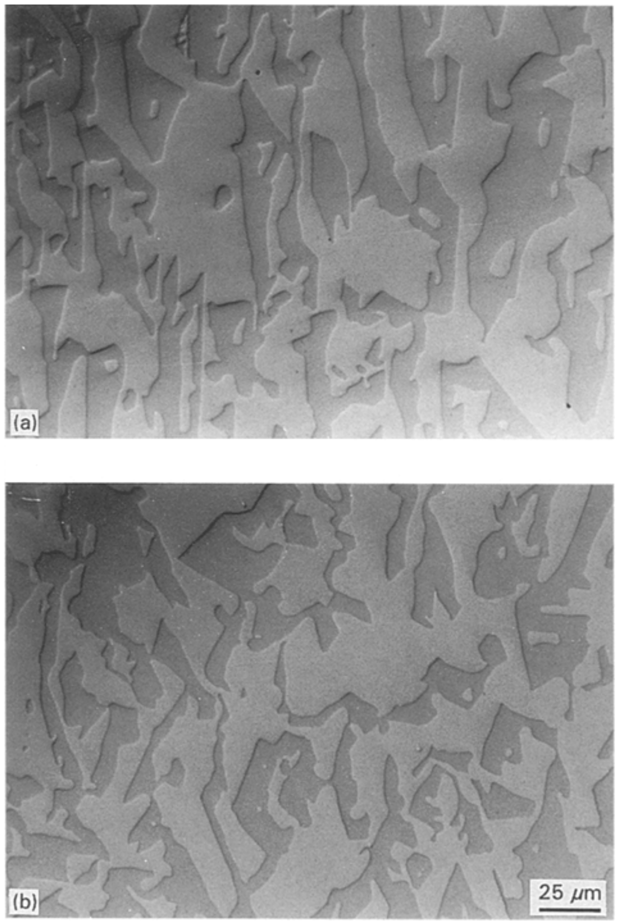

Figure 11 Photomicrographs before and after heat treatment for 50 h at 1973 K in an air atmosphere.

3.5. Thermal stability of microstructure

Fig. 11 shows optical photomicrographs before and after 50 h in air atmosphere at 1973 K. No change in microstructure can be observed. This is probably due to the single crystal nature of both the Al_2O_3 phases and the YAG compound, which are stable materials at high temperature because of their relatively small diffusion rate. It can be concluded that the unidirectionally solidified eutectic composite might be stable even in applications at 1973 K in an air atmosphere.

4. Conclusion

By using commercially available Al_2O_3 and Y_2O_3 powders, unidirectional solidification was carried out, and the main results obtained are:

1. An eutectic composite consisting of Al_2O_3 phases and YAG phases can be fabricated by the *in situ* process of unidirectional solidification with 82 mol % Al_2O_3 and 18 mol % Y_2O_3.
2. The microstructure of this unidirectionally solidified eutectic composite consisted of $\langle 1\,1\,0 \rangle$ single crystal Al_2O_3 (sapphire) and $\langle 4\,2\,0 \rangle$ single crystal YAG.
3. No temperature dependence of the flexural strength of this composite was observed from room temperature to 1973 K and its flexural strength is 360–500 MPa. This value of flexural strength at 1873–1973 K in an air atmosphere can be regarded as the maximum currently in the world.
4. From oxidation resistance tests, it is found that the unidirectionally solidified eutectic composite has an excellent oxidation resistance with almost no change in weight after 50 h at 1973 K in an air atmosphere, which differs from current Si_3N_4 and SiC ceramics which are unstable under these conditions. The thermal stability of the microstructure of the unidirectional solidified eutectic composite is superior to comparable current ceramics. No grain growth was observed after 50 h in an air atmosphere at 1973 K.
5. As described above, the unidirectionally solidified single crystal Al_2O_3 single crystal YAG eutectic composite can be regarded as an ultra-high temperature composite having high temperature strength, oxidation resistance and stability of microstructure. It is concluded that this composite can be applied stably between 1773 and 1973 K in an air atmosphere.

References

1. Y. WAKU and T. NAGASAWA, in Proceedings of Symposium on Processing Fabrication of Advanced Materials III sponsored by the Structural Materials Division (SMD) of The Minerals, Metals & Materials Society (TMS) Materials Week '93, Pittsburgh, Pennsylvania, 17–21 October, 1993, edited by V. A. Ravi, T. S. Srivatsan and J. J. Moore, p. 271.
2. R. BOWMAN and R. NOEBE, *Adv. Mater. Process.* **8** (1989) 35.
3. Y. WAKU and T. NAGASAWA, in Proceedings of Symposium on Processing Fabrication of Advanced Materials III sponsored by the Structural Materials Division (SMD) of The Minerals, Metals & Materials Society (TMS) Materials Week '93, Pittsburgh, Pennsylvania, 17–21 October, 1993, edited by V. A. Ravi, T. S. Srivatsan and J. J. Moore, p. 271.
4. J. W. WARREN, *Ceram. Eng. Sci. Proc.* **6** (1985) 64.
5. P. J. LAMICQ, G. B. BERNHART, M. M. DAUCHIER and J. G. MACE, *Amer. Ceram. Soc. Bull.*, **65** (1986) 336.
6. A. N. STROH, *Adv. Phys.* **6** (1957) 418.
7. V. S. STUBICAN, R. C. BRADT, F. L. KENNARD, W. J. MINFORD and C. C. STORREL, "Tailoring Multiphase and Composite Ceramics" (Plenum Press, New York and London, 1986).
8. E. M. LEVIN, C. R. ROBBINS and H. F. McMURDIE "Phase Diagrams for Ceramists 1969 Supplement" (The American Ceramics Society, USA, 1969).
9. M. MIZUNO, *J. Amer. Ceram. Soc.* **74** (1991) 3017.
10. R. W. DAVIDGE and A. G. EVANS, *Mater. Sci. Eng.* **6** (1970) 281.
11. P. LAMICQ, in Proceedings of Japan–Europe Symposium on Composite Materials, Nagoya, June 1993, edited by R & D Institute of Metals and Composites for Future Industries in Japan (Japan Industrial Technology Association, Tokyo, 1993) p. 4.
12. D. W. KOTCHICK and R. E. TRESSLER, *J. Amer. Ceram. Soc.* **63** (1980) 429.
13. D. R. CLARKE, *ibid.* **62** (1979) 236.
14. J. ECHIGOYA, S. HAYASHI, K. SASAKI and H. SUTO, *J. Jpn. Inst. Metals* **48** (1984) 430.
15. T. SATO, S. OHTAKI, T. ENDO and M. SHIMADA, *J. Soc. Mater. Sci. Jpn.* **37** (1988) 77.

Received 20 October 1994
and accepted 13 February 1996