Solidification Microstructure of Y_2O_3 -Added Al_2O_3 - ZrO_2 Eutectic*

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The microstructure of the Al_2O_3 - ZrO_2 eutectic with addition of a small amount of Y_2O_3 has been studied. The eutectic composition was determined as 59 mol% Al_2O_3 -36.8 mol% ZrO_2 -4.2 mol% Y_2O_3 . The added Y_2O_3 (2.1-5.3 mol%) dissolved only in the ZrO_2 phase and the crystal structure of this phase changed from monoclinic to tetragonal+cubic depending on the amount of Y_2O_3 . Several orientation relationships were found between the ZrO_2 and Al_2O_3 phases. The Al_2O_3 - ZrO_2 eutectic contained twins in the ZrO_2 phase. Cracks were observed in the Al_2O_3 matrix and at the Al_2O_3 / ZrO_2 interface. The orientation relationship between monoclinic ZrO_2 and Al_2O_3 can be interpreted to be affected by the difference in the thermal expansion coefficient between ZrO_2 and Al_2O_3 .

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I. Introduction

The Al_2O_3 - ZrO_2 composite has been paid a considerable attention as a high strength ceramics with high toughness⁽¹⁾⁽²⁾. The Al_2O_3 - ZrO_2 system has an eutectic at about 39 mol% ZrO_2 . The directional solidification has been carried out to obtain the anisotropic microstructure of aligned fibers along the growth direction⁽³⁾⁽⁴⁾. It is reported that a fine oriented structure, so called a directionally solidified structure, is obtained when the thermal gradient at the solid-liquid interface is about 10^6 K/m (1000 C/cm)⁽⁵⁾. The directionally solidified eutectic consists of ZrO_2 fibers which are of the monoclinic crystal structure in an Al_2O_3 matrix. Pure monoclinic ZrO_2 is brittle, so that it is necessary to stabilize by MgO, CaO and Y_2O_3 to improve its mechanical

strength for commercial use. The aim of the present paper is to investigate the microstructure of the Al_2O_3 - ZrO_2 eutectic with a small amount of Y_2O_3 melted by the Bridgman method and the orientation relationship between Al_2O_3 and ZrO_2 phases using a transmission electron microscope.

II. Experimental Procedure

Materials used in this investigation were 99.9% Al_2O_3 , 99.9% ZrO_2 and 99.9% Y_2O_3 powders (Rare metallic Co LTD). The starting materials were prepared for solidification by blending weighed powders of compositions shown in Table 1 and Table 2, pressing into rods 6 mm in diameter and 80 mm in length and sintering at 1620 K for 3.6 ks (1 h) in air. Four kinds of specimens as listed in Table 1 were melted, in order to determine the eutectic

Table 1 Compositions used for the determination of eutectic composition.

specimen code	Al_2O_3 (mol%)	ZrO_2 (mol%)	Y_2O_3 (mol%)
a	67	28.8	4.2
b	64	31.8	4.2
c	59	36.5	4.2
d	56	39.8	4.2

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Table 2 Compositions of Al_2O_3 - ZrO_2 - Y_2O_3 eutectics used in this experiment.

specimen code	Al_2O_3 (mol%)	ZrO_2 (mol%)	Y_2O_3 (mol%)
0Y	59	41	0
5Y	59	38.9	2.1
13Y	59	35.7	5.3

composition of the Al_2O_3 - ZrO_2 system with addition of a small amount of Y_2O_3 . The compositions used for the eutectic determination were selected in consideration of the phase diagrams of Schmid and Viechnicki⁽³⁾ and Alper *et al.*⁽⁶⁾. The melting was accomplished by a modified Bridgman method⁽⁷⁾ in a commercial crystal growing furnace, in which a Mo crucible was heated by an induction coil. The temperature at the melt zone was measured by an optical pyrometer to be about 2173 K. Solidified ingots were cut perpendicular to the growth direction, polished and then observed by an optical microscope. Thin foils were prepared by sectioning the solidified ingot and grinding the section down to 0.1 mm using a diamond polisher. The sections were then ion-beam-thinned in argon at the acceleration voltage of 5 kV and the beam current of 1 mA. Electron microscopy was conducted with a JEM200B and a JEOL 2000EX.

III. Experimental Results and Discussion

Figure 1 shows optical photographs of transverse sections of samples listed in Table 1, which were solidified at the rate of 2.8×10^{-6} m/s (10 mm/h). (a) to (d) of Fig. 1 correspond to specimen codes a to d listed in Table 1, respectively. In this figure the Al_2O_3 phase appears black and the ZrO_2 phase white. The primary phase of Al_2O_3 or ZrO_2 is observed in Fig. 1(a), (b) and (d). There is no primary phase in the structure of Fig. 1(c), which composition should be close to the eutectic one. The 59 mol% Al_2O_3 -36.8 mol% ZrO_2 -4.2 mol% Y_2O_3 was determined as the eutectic composition of Al_2O_3 - ZrO_2 - Y_2O_3 system with addition of 4.2 mol% Y_2O_3 .

The distribution of Y_2O_3 in the eutectic sample of (c) listed in Table 1 was analyzed by a

Fig. 1 Optical micrographs of Al_2O_3 - ZrO_2 - Y_2O_3 . (a) to (d) correspond to a to d in Table 1, respectively.

Table 3 Compositions of Al_2O_3 and ZrO_2 phases in Al_2O_3 - ZrO_2 - Y_2O_3 eutectics.

Specimen code		Al_2O_3 (mol%)	ZrO_2 (mol%)	Y_2O_3 (mol%)
0Y	A	94.3	5.7	0
	Z	8.2	91.8	0
C1	A	98.9	1.0	0.1
	Z	8.5	82.2	9.3
C2	Z	8.8	77.9	13.3

A: Al_2O_3 phase Z: ZrO_2 phase C1: ZrO_2 phase in a cell C2: ZrO_2 phase near cell boundary

transmission electron microscope equipped with an energy dispersive X-ray spectroscope (EDS). Table 3 gives the compositions of Al_2O_3 and ZrO_2 phases of the eutectic estimated from the EDS analysis. The solubilities of ZrO_2 and Y_2O_3 in the Al_2O_3 phase are 1 mol% and 0.1 mol%, respectively. Those of Al_2O_3 and Y_2O_3 in the ZrO_2 phase are 8.5 mol% and 9.3 mol%, respectively. This indicates that Y_2O_3 dissolves only in the ZrO_2 phase but not in the Al_2O_3 phase. The solubility value of 9.3 mol% Y_2O_3 in the ZrO_2 phase (C1 in Table 3) was obtained from the ZrO_2 phase in the center of cell, but the ZrO_2 phase in the cell boundary gives a higher Y_2O_3 content than that in the cell as shown in Table 3 (C2), which indicates the occurrence of segregation during solidification. The composition of Al_2O_3 - ZrO_2 eutectic was also shown as 0Y in Table 3. The solubility of Al_2O_3 in the ZrO_2 phase was 8.2 mol%, which was almost the same as that with addition of 4.2 mol% Y_2O_3 . The concentration of ZrO_2 in the Al_2O_3 phase was 5.7 mol%.

The compositions used in this experiment were determined by the experiment mentioned above and are listed in Table 2. The specimen codes of 0Y, 5Y and 13Y correspond to the concentrations of Y_2O_3 which should be dissolved in the ZrO_2 phase. X-ray diffraction (XRD) patterns were taken from crashed powders of the solidified samples. All the diffraction peaks were given the indices of α - Al_2O_3 , cubic ZrO_2 or monoclinic ZrO_2 . No other crystal structures were found. The crystal structure of ZrO_2 phase was changed from monoclinic to cubic with increasing Y_2O_3 content. The volume ratio of cubic phase to monoclinic phase was estimated from the integrated intensities of

Fig. 2 Dependence of volume fraction of cubic structure in ZrO_2 phase on the Y_2O_3 content and X-ray diffraction profiles of 5Y.

(111)cubic and (111)monoclinic peaks⁽⁸⁾. An example is shown for 5Y in Fig. 2, in which XRD profiles of (111)cubic and (111)monoclinic peaks are shown. Figure 2 shows the dependence of the volume fraction of cubic structure in the ZrO_2 phase on the Y_2O_3 content. It is increased with the increase of the Y_2O_3 content and is about 80% for 5Y. This dependence of volume fraction of the cubic phase corresponds to the added Y_2O_3 dissolved only in the ZrO_2 phase⁽⁹⁾. Figure 3 shows electron micrographs and electron diffraction patterns of samples of 0Y, 5Y and 13Y. The ZrO_2 phase in the solidified Al_2O_3 - ZrO_2 eutectic is monoclinic and consists of many twins. Cracks are observed at the Al_2O_3 /m ZrO_2 interfaces and within the Al_2O_3 matrix. These cracks may be introduced by the volume expansion of the ZrO_2 phase due to the martensitic transformation of cubic or tetragonal phase to monoclinic phase during the cooling. The ZrO_2 phase in 5Y takes the structure of tetragonal precipitates in the cubic matrix as seen in Fig.

Fig. 3 Electron micrographs and electron diffraction patterns for 0Y(a)(d), 5Y(b)(e) and 13Y(c)(f).

3(b) and (e), which is detected by transmission electron microscopy not by XRD technique. The structure of 13Y consists of a single phase of cubic ZrO_2 . Both eutectics of 5Y and 13Y do not contain any cracks in them, as observed in 0Y.

The orientation relationship between Al_2O_3 and ZrO_2 phases was investigated by electron diffraction for the sample of 13Y, in which the crystal structure of ZrO_2 phase is cubic. Figure 4 shows an electron diffraction pattern taken from the eutectic. This figure indicates that the direction of incident beam is $[0001]Al_2O_3$, which is parallel to $[001]ZrO_2$, and the $(1120)Al_2O_3$ plane is parallel to $(100)ZrO_2$ plane. This orientation relationship does not always hold. Figure 5 shows the distribution of $\langle 001 \rangle ZrO_2$ direction of ZrO_2 phase, in which the direction of $\langle 001 \rangle ZrO_2$ declines toward the $\langle 1\bar{1}00 \rangle Al_2O_3$ direction from $\langle 0001 \rangle$ direction within 45° . The orientation relationships of $[0001]Al_2O_3 // [001]ZrO_2$ and $(11\bar{2}0)Al_2O_3 // (110)ZrO_2$

Fig. 6 Electron micrographs of twins in ZrO_2 phase of Al_2O_3 - ZrO_2 eutectic. (a) Bright field image, (b) dark field image using spot 1 in (d), (c) dark field image using spot 2 in (d), (d) electron diffraction pattern taken from both ZrO_2 and Al_2O_3 phases and (e) key diagram for (d).

addition of Y_2O_3 (1–5.3 mol%) from monoclinic to tetragonal+cubic and cubic depending on the amount of Y_2O_3 addition.

(3) Several orientation relationships were found between Al_2O_3 and ZrO_2 phases.

(4) The Al_2O_3 - ZrO_2 binary eutectic contained twins in the ZrO_2 phase, and cracks were observed at Al_2O_3 / ZrO_2 interfaces and within the Al_2O_3 matrix.

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REFERENCES

- (1) N. Claussen: J. Am. Ceram. Soc., **59** (1976), 49.
- (2) F. F. Lange: J. Mater. Sci., **17** (1982), 247.
- (3) F. Schmid and D. Viechnicki: J. Mater. Sci., **5** (1970) 470.
- (4) R. L. Ashbrook: J. Am. Ceram. Soc., **60** (1977), 428.
- (5) V. S. Stubican and R. C. Bradt: Ann. Rev. Mater. Sci., **11** (1981), 267.
- (6) Phase Diagrams for Ceramists 1975 Supplement, The American Ceramic Soc. INC. p. 136.
- (7) J. Echigoya, H. Suto and S. Hayashi: Trans. JIM **26** (1985), 895.
- (8) D. L. Porter and A. H. Heuer: J. Am. Ceram. Soc., **62** (1979) 298.
- (9) H. G. Scott: J. Mater. Sci., **10** (1975), 1527.
- (10) G. K. Bansal and A. H. Heuer: Acta Met., **20** (1972), 1281.
- (11) Thermophysical Properties of Matter Vol. 13, Plenum, New York (1977).
- (12) E. Bischoff and M. Ruhle: J. Am. Ceram. Soc., **66** (1983), 123.
- (13) R. N. Patil and E. C. Subbarao: J. Appl. Crystallogr., **2** (1969), 281.