Microstructural Change of 11 mol% MgO–ZrO₂ by Aging

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The structural change of 11 mol% MgO–ZrO₂ by aging has been investigated using the dilatometric, X-ray diffraction and transmission electron microscopic techniques. Above 1413 K, the cubic ZrO₂ decomposed to MgO+tetragonal ZrO₂ eutectoidically. Below 1413 K, two kinds of decomposition have taken place. One is the precipitation of tetragonal phase in the cubic matrix. The other is the eutectoidic decomposition to MgO+monoclinic ZrO₂. The eutectoidic temperature was estimated at 1503 K. The equilibrium and metastable phase diagrams have been discussed in the ZrO₂ rich part of the MgO–ZrO₂ system.

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I. Introduction

The partially stabilized zirconia (PSZ) is known as the ceramic material having high strength as well as high toughness(1). The toughness in magnesia stabilized zirconia is accompanied by the transformation of tetragonal precipitates to the monoclinic one under applied stress in the cubic matrix. Since the mechanical properties are closely related to its microstructure, many workers have studied the structure change including precipitation and decomposition in the ZrO₂ rich portion of the ZrO₂–MgO system by aging(2)-(6). They have shown that the metastable phases appear at the hypoeutectoid composition of 8–11 mol% MgO–ZrO₂ by aging at 1073–1673 K, which do not exist in the equilibrium phase diagram proposed by Grain(2). (See Fig. 1). For example, the precipitation of the tetragonal phase and Mg₂Zr₅O₁₂ have been seen in the sample of 8–11 mol% MgO–ZrO₂ by aging at temperatures under 1373 K, at which the monoclinic phase should appear(5). The authors have reported that the eutectoidic reaction of MgO + monoclinic ZrO₂ directly from the cubic ZrO₂ in a hypereutectoid sample of 18 mol% MgO–ZrO₂(8). In spite of various studies on the precipitation and decomposition of the ZrO₂–MgO system, it seems that systematic investigations on the phase diagram including the metastable one are lacking.

The aim of present work is to observe the structure of MgO–stabilized zirconia of 11 mol% MgO aged in the temperature range of 1273 to 1573 K and to propose the equilibrium and metastable phase diagrams of the ZrO₂–MgO system.

II. Experimental

The material used for this study was an 11 mol% MgO–ZrO₂ commercial powder (Daiichi Kigenso LTD), which was sintered at 1973 K in air for 86.4 ks to form a single phase cubic ZrO₂ solid solution and then air-quenched at the rate of about 300 degree/s. The phase diagram for the MgO–ZrO₂ system (Fig. 1) shows that this temperature is in the single phase range at the composition of 11 mol% MgO. To prevent the vaporization of MgO from the surface of samples, it was annealed in an Al₂O₃ crucible with MgO powder. The sintered samples were cut into discs. The disc was aged isothermally at the temperatures between 1173 and 1623 K for 1.2 to 2592 ks and quenched in air. They were polished mechanically and thinned by
argon ion bombardment for transmission electron microscopic observations. The specimens were aged in a dilatometer at the temperature range of 1373 to 1473K for 86.4 to 612 ks, and then differential dilatation between the specimens and a reference specimen of cubic ZrO₂ was recorded as a function of temperature during cooling from the aging temperature to determine the transition temperature from the tetragonal to monoclinic phases. The cooling rate was 0.08 degree/s.

### III. Results and Discussion

1. Microstructures

   (1) Solution treated alloy

   The X-ray diffraction profile of the as-sintered 11 mol% MgO-ZrO₂ sample is shown in Fig. 2. All peaks are given by indexes of cubic ZrO₂ and there is no separation of 400, the peak of which should be splitted into two peaks with the presence of a tetragonal phase. Each peaks is sharp and diverges into two, K₁ and K₂. This means that the as-sintered alloy has low defects and a low concentration fluctuation. Figure 3 shows an electron diffraction pattern taken from the [121] beam direction of as sintered alloy. Since the \{213\} type tetragonal reflection is not seen, there is no tetragonal phase. The grain size after sintering was about 100 μm. The magnesia was distributed uniformly from edge to edge and there was no evidence of the vaporization of magnesia from the surface.

   (2) Aged alloy above tetragonal-monoclinic transition temperature

   Figure 1 shows the phase diagram of the MgO-ZrO₂ system proposed by Grain(2). The aging temperatures used in the present experiment are also shown in this figure. The microstructure of 11 mol% MgO aged at the temperature of 1573K for 432 ks is shown in Fig. 4, at which the phase diagram suggests that cubic ZrO₂ decomposes to MgO + tetragonal ZrO₂. It consists of MgO rods elongated along the same direction and ZrO₂ phase with twins. This is a quite similar feature obtained by the eutectoidic decomposition except that the matrix is heavily twinned(6)(8). Since an electron diffraction pattern indicates that the ZrO₂ matrix is a monoclinic phase, the twinned structure in the matrix may be due to the tetragonal to monoclinic transformation during cooling. So, the microstructure obtained by the aging at the temperature of 1573K

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† Because the 11 mol% MgO-ZrO₂ shows the complicate decomposition behavior by aging, it is not appropriate to use it for the determination of the transition temperature. The transition temperature was determined using eutectic samples, which consist of 18 mol% MgO-ZrO₂, from the thermal expansion curves during cooling after aging at 1393, 1413 and 1473 K for 86 ks in dilatometer. It was 1413 K.
K was the result of the MgO+tetragonal ZrO$_2$ eutectoidic reaction and the 11 mol\% MgO-ZrO$_2$ is close to the composition of the tetragonal ZrO$_2$+MgO eutectoid. It is interesting to point out that the twins are perpendicular to the MgO rods and consist of (100) twins known from a diffraction pattern of the matrix. This fact suggests that the tetragonal ZrO$_2$ decomposed from cubic ZrO$_2$ was a single crystal before its transformation to monoclinic ZrO$_2$. The transformation of tetragonal ZrO$_2$ in eutectoid may be affected by the difference in the thermal expansion coefficient between MgO and tetragonal ZrO$_2$\(^8\)(9). The surface relief accompanied by the transformation was seen at the ZrO$_2$/MgO interface. Cracks were also observed at the interface indicated by arrows in Fig. 4. The direction of the long axis of MgO rods is on the (111)MgO plane and parallel to the \langle100\rangle direction of monoclinic ZrO$_2$. It should be noted that the image of Fig. 4 is the end-on condition. Since the habit plane of the tetragonal monoclinic phase transformation is \{100\}mono/\{100\}teta\(^{10(11)}\), the monoclinic ZrO$_2$ in Fig. 4 was parallel to the (001) tetragonal and perpendicular to the (100) tetragonal plane before the transformation. Such being the case, the interface between MgO and tetragonal ZrO$_2$ has the relation of (111)MgO//(001)teta ZrO$_2$ by the eutectoidic decomposition of cubic ZrO$_2$. This is the same relationship given in the lamellar interface of directionally solidified MgO–ZrO$_2$ eutectic\(^{9(12)(13)}\).
Aged alloy below the transition temperature

Figure 5 shows the optical micrograph taken from the alloy aged at 1373 K for 18 ks. It is seen that the decomposition takes place from the grain boundaries. This decomposition started at the grain boundary shows the eutectoidic feature by the aging of this temperature as shown in Fig. 6. This eutectoidic decomposition is the reaction of monoclinic ZrO$_2$ + MgO from cubic ZrO$_2$ as will be shown later and has already been observed in the 18 mol% MgO hypereutectoidic alloy$^{(9)}$. Careful observation reveals a fine precipitation in grains. An electron diffraction pattern, which is taken from the [110] beam direction, shows the extra reflections of {112} tetragonal as seen in Fig. 7(b). The dark field image taken from the 112 tetragonal reflection shows the tetragonal precipitates of about 20 nm size in the cubic matrix (Fig. 7(a)). The precipitation of the tetragonal phase is considerably faster than the eutectoidic reaction nucleated from the grain boundary. This result is supported from the previous work$^{(4)}$. Since the hypereutectoidic alloy of 18 mol% MgO-ZrO$_2$ did not show any tetragonal precipitation by aging in this temperature range, this metastable tetragonal precipitation has occurred at the composition near 11 mol% MgO-ZrO$_2$.

Figure 8 shows bright field images of precipitates showing the aging time dependence of precipitate size at the temperature of 1373 K. The beam direction is [001] cubic for all images of Fig. 8. As the aging time increases, the tetragonal precipitates increase in size. Within the aging time of 86.4 ks, the tetragonal precipitate kept its crystal structure and did not transform to the monoclinic phase as shown in Fig. 8. On the other hand, the precipitates aged longer than 253 ks were about 130 nm in size and transformed already to the monoclinic phase (Fig. 9). The electron diffraction pattern taken from area (a). Beam direction is [110].
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The diffraction pattern from both the precipitates and the matrix shows the monoclinic reflections in it. A dark field image taken by the monoclinic reflection reveals the transformed monoclinic precipitates. Figure 10 shows the aging time dependence of precipitate size measured from Figs. 8 and 9. The precipitate gives the lenticular shape, so that the precipitate size should be defined by both the long axis and the short axis. The size of both axes increases linearly with the increase of the aging time. The aspect ratio does not change and is 3.6-3.9, which is close to the value of 4 giving the minimum strain energy. The critical size of transformation from the tetragonal to monoclinic phase obtained from the present experiment is 150 nm in the long axis.

Fig. 8  Bright field images of 11 M aged at temperatures of 1373 K for (a) 1.44 ks, (b) 18 ks and (c) 86.4 ks. All images are taken by the beam direction [001]. (d) Electron diffraction pattern taken from 11 M aged at 1373 K for 86.4 ks.

Fig. 9  Electron micrographs of 11 M aged at the temperature of 1373 K for 252.9 ks. (a) Bright field image, (b) dark field image taken by monoclinic reflections circled in diffraction pattern (c).
axis and 35 nm in the short axis of a lenticular shape. Heuer and Rühle reported the critical size in 8 mass% MgO PSZ to be 250 nm and 50–100 nm in the long and short axes, respectively. This critical value is a little larger than that of the present work. One reason for this is the difference in MgO concentration of the precipitates due to the difference in aging temperature. The other is the difference in density and distribution of the tetragonal precipitates due to the difference in MgO concentration of the matrix. Figure 11 shows the thermal expansion curves of samples after aging in dilatometer. In the case of the aging time less than 259 ks, the dilatation changes monotonically with temperature and the precipitates retain their crystal structure up to room temperature. The starting temperature of the transformation with which to observe the dilatation are 973 and 1003 K for the aging times of 259 and 612 ks, respectively. This shows that the starting temperature increases with the aging time. Care must be taken to determine the transformation temperature of the tetragonal precipitates, because it gives a quite different temperature by the aging temperature and time.

The longer aging time changes the structure of the matrix to the eutectoidic one of MgO+monoclinic ZrO2, which is observed near grain boundaries as shown in Fig. 6. This is already observed in the sample of 18 mol% MgO–ZrO2. It is interesting to note that the cubic ZrO2 with tetragonal precipitates also decompose to MgO+ monoclinic ZrO2 eutectoidically.

The lower aging temperature such as 1273 K leads to the precipitation of the δ phase as observed by several workers. This phase has the composition of Mg2Zr5O12 and the typical electron diffraction pattern is shown in Fig. 12. The temperature nucleating the δ phase is only below 1273 K, though Hannink has reported that the sample aged at 1373 K reveals the δ phase.

After Zener, it is possible to estimate the eutectoidic temperature from the spacing of the MgO rod of the eutectoidic structure. The relation between the rod spacing, s, and the eutectoidic temperature, Te, is given by

$$ s = \frac{2 Te y}{\rho Q \Delta T} $$

where $\Delta T$, $y$, $\rho$ and $Q$ indicate the supercooling, the interfacial energy, the density and the heat of transformation, respectively. Therefore a plot on log paper of the rod spacing vs the amount of undercooling should give a straight line with a slope of $-1$. Figure 13 shows the rod spacing vs the amount of supercooling relation in the case of $Te = 1493$, 1503 and 1513 K, respectively. The eutectoidic temperature of 1503 K gives the slope of $-1$, so that the eutectoidic temperature of 11 mol% MgO–ZrO2 was estimated at 1503 K. This is a value very close to the eutectoidic temperature.
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2. Phase diagram in the ZrO₂-MgO system

The present experimental results of structural observations can be compared with the equilibrium phase diagram proposed by Grain, Fig. 1. The differences between the present work and Grain's are as follows.

1. The transition temperature of the tetragonal to monoclinic phases is 1458±45 K, which is a little lower than 1513 K proposed by Grain.

2. The sample of 11 mol% MgO-ZrO₂ seems to be of eutectoid composition. This is evidenced by the aging of 11 mol% MgO-ZrO₂ at the temperature of 1573 K, by which the tetragonal ZrO₂+MgO eutectoidic decomposition can be seen as shown in Fig. 4. The composition proposed by Grain is 13 mol% MgO-ZrO₂, which is a little higher in concentration of MgO than the present result.

3. The solubility of MgO in tetragonal ZrO₂ at the temperature of 1473 K is determined as being less than 1% by EDS analysis (Fig. 14). There are no traces of MgO peaks in monoclinic ZrO₂ aged at 1373 K, which shows no solubility of MgO in monoclinic ZrO₂. The equilibrium phase diagram obtained from the present work is shown in Fig. 15.

When the aging time is less than 86.4 ks, the precipitation of the tetragonal phase from the cubic matrix can be seen even if the aging temperature is within the region of monoclinic ZrO₂+MgO. The tetragonal phase observed here may be caused by the precipitation from the metastable tetragonal+cubic area which is formed by the extrapolation of cubic+tetragonal and monoclinic+tetragonal lines below the temperature of 1673 K. The phase was observed below the temperature of 1273 K and both of the δ phase and the tetragonal phase exists at the same time at this aging temperature. Since the δ phase is identified as Mg₂Zr₁₀O₁₂, the composition of the δ phase is ZrO₂–28 mol% MgO. These results give the metastable phase diagram for the tetragonal and δ phases as shown in Fig. 16.

As reported previously(8), the cubic phase of 18 mol% MgO–ZrO₂ was decomposed to monoclinic ZrO₂+MgO directly. The eutectoidic temperature was estimated at about
This type of decomposition of monoclinic ZrO$_2$+MgO from the cubic matrix was also observed in the sample of 11 mol% MgO-ZrO$_2$ and the eutectoidic temperature was estimated from the Zener equation to be 1503 K. The eutectoidic temperature, $T_e$, is estimated from the supercooling, $\Delta T$, at the eutectoidic composition, care must be taken to determine whether $T_e$ obtained by the present work is the eutectoidic temperature or not. The eutectoidic temperature of the cubic phase to monoclinic ZrO$_2$+MgO should be on the extrapolated line of the cubic+MgO/cubic boundary in the temperature region of tetragonal ZrO$_2$+MgO. Thus the composition of 11 mol% MgO-ZrO$_2$ is just or very close to the eutectoidic composition. Since the direct transformation of cubic to monoclinic ZrO$_2$ exists only metastably, the transformation temperature of cubic ZrO$_2$ without MgO to monoclinic phase is not clear. But the structure of tetragonal ZrO$_2$ is very similar to that of cubic ZrO$_2$, so that the free energy of both phases may be very close to each other$^{(1)3}$. This
suggests that the transformation temperature of cubic to monoclinic is very close to that of tetragonal to monoclinic phases. The metastable phase diagram is shown in Fig. 17 for the eutectoidic decomposition of monoclinic ZrO$_2$+MgO from the cubic ZrO$_2$ matrix.

IV. Conclusion

The structural change of 11 mol% MgO-ZrO$_2$ by aging has been investigated using the dilatometric, X-ray diffractions and transmission electron microscopic techniques. The results obtained are summarized as follows.

(1) Above 1413 K, the cubic ZrO$_2$ decomposed to MgO+tetragonal ZrO$_2$ eutectoidically, the latter of which was transformed to the monoclinic ZrO$_2$. This temperature of 1413 K was a little lower than that proposed by Grain.

(2) Below 1413 K, two different kinds of decomposition have taken place. One is the precipitation of tetragonal phase in the cubic matrix. The other is the eutectoidic decomposition of the cubic or cubic+tetragonal phase to MgO+monoclinic ZrO$_2$. The former which is the metastable reaction was much faster than the later.

(3) The tetragonal precipitates grew with the aging time and transformed to the monoclinic phase at the size of 150 nm in the long axis at the aging temperature of 1373 K during cooling. The transformation starting temperature moved to a higher temperature with the increase of aging time.

(4) The eutectoidic temperature of MgO+monoclinic ZrO$_2$ was estimated at 1503 K from the Zener’s method.

(5) The concentration of MgO in tetragonal and monoclinic ZrO$_2$ at 1473 and 1373 K was determined to be less than 1 mol% by EDX analysis.

(6) Below 1273 K, the precipitation of the $\delta$ phase as well as tetragonal precipitates in the cubic matrix can be seen at the early stage of aging. Both precipitates are metastable at this temperature, finally the MgO+monoclinic ZrO$_2$ eutectoidic reaction has covered the sample after long aging.

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