Tetragonal phase formed in liquid quenched ZrO₂-9 mol% MgO and its thermal stability

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Ceramics were formed by the addition of magnesia to zirconia in the composition range of 0 to 50 mol%, and these ceramic materials were liquid quenched using an infrared image furnace and a twin roll process. The composition and structure of the liquid-quenched film samples were examined using X-ray diffraction and transmission electron microscopy. The results confirmed the formation of a high-temperature metastable phase (t'-phase) in ZrO₂-9 mol% MgO partially stabilized zirconia (PSZ). The t'-phase that formed underwent a transition to the stable tetragonal phase (t-phase) during a suitable annealing treatment, but it was found not to undergo a phase transformation to the monoclinic phase (m-phase) in the presence of external stress. The t'-phase was confirmed to have three variants.

Key-words : Mg-PSZ, Liquid-quench, TEM, XRD, EDS, t'-phase, Thermal stability

1. Introduction

Since zirconia ceramics have crystallographically unique properties, a great deal of research has already been carried out into areas such as their application to high-strength, toughened ceramics that require such properties, or what is called partially stabilized zirconia. However, most of the studies have concerned the t→m martensite transformation that occurs at low temperature, and various associated phenomena, although zirconia actually exhibits three different crystal phases (m-phase, t-phase and c-phase) at temperatures up to its melting point. We believe that it is also important to clarify the mechanism involved in the high-temperature t→c phase transformation, in order to form a deeper understanding of the characteristics of zirconia. However, since this transformation occurs at a high temperature of 2620 K, this type of research has a short history, and many problems remain to be solved.

This research began in 1975, with a report by Scott1) that this phase transition occurred in a non-diffusive manner. Since then, Ruhle et al.2) have described this phase transition as being non-martensitic, and having the character of a massive transformation. In addition, Miller et al.3) reported on the characteristics of powder samples produced by plasma spraying, such as the fact that a t-phase that includes a great deal of Y₂O₃ is formed in a non-equilibrium state, and that this does not easily undergo a transition to the m-phase. This phase is named the t'-phase, and it is distinguished from the normal t-phase that undergoes a martensite transformation to a conventional m-phase. On the other hand, Sakuma et al.4),5) added 0 to 8.7 mol% Y₂O₃ to ZrO₂, fabricated button samples by arc melting and investigated the relationship between the mechanical properties and the microstructure. ZrO₂ that contains 4 mol% or more Y₂O₃ has a reduced fracture toughness, and this is thought to be because it is difficult for a t-phase with a high Y₂O₃ content in solid solution to undergo an external-stress-induced transition to the m-phase, implying the formation of the t'-phase. In addition, Noma et al.6) have fabricated film samples by liquid quenching of melts using an arc image furnace and hammer and anvil apparatus with ZrO₂-3 mol% Y₂O₃ and confirmed the presence of the t'-phase. The cooling rate for the samples exceeded 10⁴ K/sec. The phases formed were identified by powder X-ray diffraction (XRD). The results showed that only the t-phase was present, indicating that it does not transform to the m-phase under the influence of external stress. In these studies on the high-temperature phases of PSZ, samples that have been fabricated by temporary melting are typically used, but even though the composition of these samples is uniform, the crystal grains can sometimes develop to a macroscopic size. For example, Sakuma et al.7),8) reported that when samples of ZrO₂-4.0 mol% Y₂O₃ that had been arc melted and then annealed for 10 min at 1773 K were observed by electron microscopy with an electron beam incidence of (011), an equally spaced dark and light striped pattern frequently appeared in the sample in two directions. They called this a modulated structure and posited that the formation mechanism is related to spinodal decomposition. The above research on the high-temperature phase of ZrO₂ was mainly carried out on liquid-quenched PSZ with Y₂O₃ in solid solution, sometime subjected to subsequent annealing, and the results obtained can be summarized as follows. (1) When PSZ samples of ZrO₂ containing 3 to 7 mol% Y₂O₃ in solid solution are quenched from a temperature equal to or greater than that of the c-phase, which is the stable high-temperature phase, a t'-phase appears in the quenched sample, which is thought to be a due to a non-diffusive transformation from the c-phase. (2) This t'-phase has a crystal structure that differs slightly from that of the t-phase that is typically observed in samples obtained by conventional powder sintering. While the t-phase undergoes a t→m transformation under the influence of external stress, for the t'-phase a stress-induced t→m transformation does not easily occur. In addition, the t'-phase exhibits a microstructure with a peculiar morphology that differs from that of the t-phase. (3) Thermodynamically, the t'-phase is thought of as a metastable phase, which undergoes a transition to the t-phase when a suitable annealing treatment is carried out. (4) Although the formation mechanism formation of the t'-phase.

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for the t'-phase is basically thought to be a non-diffusional transformation from the c-phase, there are some reports suggesting that it is a martensitic transformation and others that it is a massive transformation, and no conclusion has so far been reached. The above is an overview of the experimental results on the high-temperature phase of Y2O3-PSZ that have been made reported so far. In addition, the t'-phase has also been reported to be formed in PSZ with Er2O3 added, suggesting the possibility of its formation in other materials. However, morphology of t'-ZrO2 precipitates in Mg-PSZ has been mainly studied. Since such a study has not yet carried out for Mg-PSZ, it is of considerable interest to compare the results with those for Y2O3-PSZ.

Therefore, in this study, we used samples of ZrO2-9 mol % MgO (Mg-PSZ), which has also been the subject of a large amount of research and development as a high-strength, high-toughness ceramic. Referring to the many reports for Y2O3-PSZ, a large amount of research and development as a high-strength, high-toughness ceramic. Referring to the many reports for Y2O3-PSZ.

3. Experimental results

3.1 Changes in microstructure due to differences in solute (Mg) concentration in the liquid-quenched material

To determine the composition range and conditions for formation of high-temperature crystal phases (t, c or a phase related to these) that are stable at room temperature following rapid quenching, we prepared six types of samples with 0, 0.5, 2, 9, 13, and 50 mol % MgO added to the ZrO2. Figure 2 shows the typical microstructure of each of the liquid-quenched samples. Twin crystals having a pure ZrO2 m-phase can be seen at various locations in Fig. 2(a), and, from their diffraction patterns, it was found that these correspond to the m-phase. Figures 2(b) and 2(c) are for samples with 0.5 and 2 mol % MgO, respectively, but there is no great difference from the pure ZrO2 structure shown in Fig. 2(a). In Fig. 2(e), the twin crystal structure has become somewhat finer than in the previous two samples, and the diffraction pattern clearly shows only the m-phase in both cases. However, in the quenched sample with 9 mol % MgO shown in Fig. 2(d), long, narrow sheet-like crystal structures with widths of 50 to 200 nm and lengths of several microns or less are observed in the parent phase. Furthermore, the diffraction pattern indicates that the m-phase has completely disappeared, leaving a tetragonal,

Fig. 1. Equilibrium state diagram for ZrO2-MgO.
cubic crystal structure. When the amount of MgO added was further increased to 13 mol % [Fig. 2(e)], the cubic crystal became stable based on the equilibrium state diagram shown in Fig. 1.

The microstructure was characterized by coarse crystal grains with some defects. In addition, diffuse scattering unique to the c-phase of PSZ began to appear in the diffraction pattern.

Figure 2(f) shows the microstructure of a quenched sample with equal molar concentrations of ZrO$_2$ and MgO, and even though no equilibrium state diagram has been produced at present for this, Fig. 1 predicts that it can be quenched from a c-phase ZrO$_2$ solid solution near the eutectic composition of MgO. It also exhibits a lamellar microstructure reflecting the eutectic state. The above are the characteristics of the microstructures appearing in the six types of quenched Mg-PSZ material used in the present study, and the sheet-like crystal phase thought to be the high-temperature crystal phase for this system only appeared in the quenched 9 mol % MgO sample [Fig. 2(d)]. For the other samples, only the stable phase predicted from the state diagram appeared, and no amorphous or other phases were present. In addition, the thickness of the samples obtained by liquid quenching was reduced from 50 to 20 μm as the MgO content increased, and the white samples gradually increased in transparency. This is thought to be because the melting point of the samples increased with decreasing MgO content, making quenching more difficult.

3.2 X-ray diffraction in liquid-quenched ZrO$_2$-9 mol % MgO

The long, narrow sheet-like crystals in the liquid quenched PSZ material with 9 mol % MgO were observed by TEM, and XRD was used to identify the crystal phase and changes in the crystal structure after annealing. Figure 3 shows the results of measurements on these samples. Figures 3(a) and 3(b) were obtained from the liquid-quenched parent material and (c) through (e) from samples that had been annealed at 1673 K. Diffraction peaks appeared in an angular range of $2\theta = 27$ to 29°, near the m-phase $\{111\}$ peak and $2\theta = 70$ to 80°, near the t-phase $\{400\}$ and $\{004\}$ peaks. Table 1 summarizes the diffraction peak positions. In Fig. 3(a), for the as-quenched thin-film sample, in addition to the peak for the $\{400\}$ planes of the stable c-phase, a diffuse peak corresponding to the t'-phase ($c/a = 1.007$ to 1.009) that is thought to be the high-temperature crystal phase is clearly present. Figure 3(b) shows results for samples that were peeled by mechanical pulverization of the thin-film samples. No particular changes are found in the m-phase peaks themselves, which are the same as in Fig. 3(a). Therefore, the liquid-quenched parent material does not undergo a phase transformation in the presence of mechanical stress at room temperature. Comparing the lattice constants to those for the c- and t-phases (c-phase: $a = 0.5080$ nm, t-phase: $a = 0.5077$ nm, $c = 0.5183$ nm) that are widely reported for the stable, high-temperature phases, we can conclude that the phases appearing in the quenched parent material do not correspond to the stable t-phase. Figure 3(c) is for a quenched parent sample annealed in air for 0.6 ksec at 1673 K, and Fig. 3(d) is for a similar sample pulverized using a mortar in the same manner as (b). In the annealing treatment, the sample was rapidly inserted into a furnace where the temperature had already been set at 1673 K, and after the treatment time was complete, it was rapidly removed into air at room temperature, to keep changes in the crystal phase due to cold removal to a minimum. It can be seen that the [004] t'-peak found in Fig. 3(a) and though to correspond to the t'-phase disappears in Fig. 3(c), and a [004] t'-peak for a new stable t-phase can be found. Furthermore, in Fig. 3(d), the intensity of the [004] t'-peak is reduced, and an m-phase [111] m-peak appears instead. This provides further evidence that the t-phase that was produced by annealing is the conventional stable phase that transforms into the m-phase under external stress. It also suggests that the thermodynamically metastable t'-phase was present in the quenched parent material corresponding to Fig. 3(a). In other words, as can be seen from the state diagram (Fig. 1), annealing for 0.6 ksec at 1673 K causes the t-foot in the

![Fig. 3](image-url). XRD spectra of liquid-quenched ZrO$_2$-9 mol % MgO. (a) Liquid-quenched parent material: shows formation of c- and t-phases; (b) sample of powdered quenched parent material: no differences from (a) seen; (c) quenched parent material annealed at 1673 K for 0.6 ksec: t'→t phase decomposition has occurred; (d) pulverized sample (c): stress-induced transition from t'→m phase occurs; (e) sample (c) annealed at 1673 K for 1.8 ksec: t'→t→m phase decomposition occurs due to heat treatment.
quenched parent material to be broken down to the c + t-phases. Figure 3(e) shows the XRD spectrum following a long annealing time of 1.8 ksec at 1673 K. As with Fig. 3(c), a small (004) t-peak is clearly visible and no t′-phase peak is found. An m-phase peak can also be clearly seen. This may be due to t→t′ phase growth during the longer annealing period, after which the t-phase undergoes a phase transition to the m-phase during cooling.

These XRD results indicate the formation of a t′-phase distinguishable from the normal t-phase, which is the conventional stable phase for liquid-quenched Mg-PSZ with 9 mol % MgO. Furthermore, this t′-phase is thought to be a thermodynamically metastable phase, and undergoes a transition to the stable t-phase under suitable annealing conditions. It is also confirmed that no easy transformation of the t′-phase occurs due to stress, unlike the stress-induced t→m martensite transformation at room temperature.

3.3 TEM and EDX analysis of metastable t′-phase formed in liquid-quenched ZrO2-9 mol % MgO

The XRD results confirmed the formation of a previously unreported t′-phase in liquid-quenched samples with 9 mol % MgO. We therefore carried out detailed TEM observations of the samples to examine the microstructure of this phase and structural changes due to annealing. Figure 4 shows an optical micrograph of the sample surface. It can be seen that the structure of this sample is broadly divided into two parts, a banded structure formed by lines running diagonally from the upper left to the lower right in the micrograph and a massive structure without any bands. TEM images from these two regions are shown in Fig. 5. Image A is a bright-field image of the t′-phase observed with the electron beam incident along the (111) direction, and B is the corresponding diffraction pattern. Figures 5(a) through 5(c) and 5(d) through 5(f) are dark-field images obtained from three different (112) and (220) reflections shown in B. The reason for choosing a (111) electron beam incident direction is described below. From the results of high-temperature X-ray22) and neutron diffraction23) studies, the structure of the t-phase was determined to be that shown in Fig. 6. The eight oxygen atoms of the unit cell (white circles) are pulled by the Zr atoms (solid black circles), which are displaced along the Z-axial direction, and just as if shuffling had occurred, the oxygens are displaced (along the Z-axial direction). As a result, a (112) reflection that should be forbidden for the fluorite structure is excited during electron diffraction. Therefore, if we assume that the t′-phase is formed

Table 1. Relationship between XRD peak position and interplanar spacing d for c-, t- and m-phases of ZrO2

|  | d (nm)  | 2θ (degree) |
|---|---------|-------------|
| Cubic (c) (400) | 0.1271 | 74.6 |
| Stable tetragonal (t) (400) | 0.1268 | 74.81 |
| (004) | 0.1293 | 73.12 |
| Metastable tetragonal (t′) (400) | 0.1268-0.1271 | 74.6-74.8 |
| (004) | 0.128 | 74 |
| Monoclinic (m) (111) | 0.3151 | 28.3 |

Fig. 4. Optical micrograph of liquid-quenched ZrO2-9 mol % MgO. A banded structure is seen running from the upper left to the bottom right and a massive structure also appears.

Fig. 5. TEM images of banded structure formed in liquid-quenched ZrO2-9 mol % MgO. Image A is a bright-field image of an area having the banded structure seen in Fig. 4. A sheet-shaped t′-phase having three variants is observed. Image B is a diffraction pattern with an incident electron beam orientation of (111). Images (a) through (c) are dark-field images using the [112] forbidden reflection, and the three orientation variants of the t′-phase are easily seen. Images (d) through (f) are dark-field images using (220) reflections.
via the c-phase, we can consider the presence of three different t'-phase variants each with a c-axis corresponding to the directions of the three main axes of the c-phase (X, Y and Z in the figure). In addition, we can consider only the (111) orientation to be the one where the (112) type reflections from each of the three variants simultaneously satisfy the diffraction conditions, and we can confirm the presence of each of the variants by obtaining dark-field images for the (112) reflections. From the above, we find that the sheet-like t'-phase seen in bright-field image A clearly has variants in three directions if we examine the dark-field images shown in Figs. 5(a) through 5(c). It is also noteworthy that bright-field image A can be formed by combining these three dark-field images. It can also be seen from the images that the habit plane for the sheet-like structure of the t'-phase is \{110\}. Figures 5(d) through 5(f) are dark-field images from the \{220\} reflections. Since these reflections arise from both the c- and t-phases, they produce bright contrast over the entire region of the dark field images. Figure 7 shows TEM images of a region of the massive structure seen in Fig. 4. The arrangement of images in this figure is identical to that in Fig. 5. In contrast to Fig. 5 where the sheet-like t'-phase was observed, no such structure was found in the images; instead, a fine tweed-like structure appears over the entire sample.

In both the \{112\} dark-field images in Figs. 7(a) through 7(c) and the \{220\} dark-field images in (d) through (f), the structures are dispersed and have a bright contrast, by which alone the crystallographic correlations between the structures cannot be found. The presence of both the banded and massive structures in liquid-quenched PSZ with 9 mol% MgO may be due to non-uniformity in the cooling rate of the samples and stress induced during the twin rolling. Figure 8 shows the results of TEM observations (using the same method as described previously) of the quenched side of samples produced as follows. Rather than using twin rolling as the cooling method, hemispherical samples are dropped naturally onto a copper plate cooled with liquid nitro-

Fig. 6. Schematic diagram of t-ZrO$_2$ crystal structure. The eight oxygen atoms of the unit cell are displaced along the Z-axial direction.

Fig. 7. TEM images of massive structure formed in liquid-quenched ZrO$_2$-9 mol% MgO. Image A is a bright-field image of the area seen as a massive structure in Fig. 4, and a fine tweed-like structure is observed. Image B is a (111) diffraction pattern. Images (a) through (c) are dark-field images using the \{112\} forbidden reflections, and (d) through (f) are dark-field images using \{220\} reflections.

Fig. 8. Microstructural observations of ZrO$_2$-9 mol% MgO liquid-quenched on a copper plate. Image A shows the microstructure formed in the sample when the material is fabricated using a quenching method where the sample is dropped onto a copper plate. As in Fig. 7, a tweed-like structure is observed. B is a (111) diffraction pattern.
3.4 Changes in microstructure of the t'-phase formed in liquid-quenched ZrO$_2$-9 mol % MgO due to annealing

From the XRD results described earlier, we can assume that the t'-phase formed by liquid quenching is thermally unstable. Therefore, we carried out detailed TEM observations of the changes in the microstructure of the t'-phase due to annealing. Figure 10 shows the microstructure of the t'-phase for different annealing times at a temperature of 1673 K. Figures 10(a) through 10(e) correspond to annealing times in air of 0.3, 0.6, 1.8, 3.6 and 10.8 ksec, respectively. Moreover, the annealing temperature of 1673 K is in the neighborhood of the boundary between the two phase regions for the t + c-phases and t + MgO in the equilibrium phase diagram (Fig. 1). This is a suitable temperature for observing the process of changes in the t'-phase due to heating. The annealing method used was rapid heating and cooling whereby the quenched sample was placed into a furnace for a precise period, where the furnace temperature had been set to 1673 K in advance as in section 3–2 above. Following 0.3 ksec annealing [Fig. 10(a)], the growth of a fine lens-shaped t-phase from the t'-phase was clearly seen. The length of the long axis of the lens-shaped t-phase was 30 to 60 nm at this time. The uniformity in the t-phase growth direction can also be seen in the figure, with the long axes in each of the variants aligned with each other. Following annealing for 0.6 ksec [Fig. 10(b)], the length of the t-phase was 50 to 80 nm, growing to 100 to 150 nm and 150 to 300 nm with further increases in annealing time [Figs. 10(c) and 10(d)]. Following 10.8 ksec [Fig. 10(e)] the lens-shaped t-phases that had grown in the direction of the long axis began to collide with each other, and further growth in that direction become impossible. A process making the thickness in the direction of the short axis increase can also be observed. In this process from the t'- to t-phase, the boundaries of each t'-phase variant can still be clearly identified up to a time of 1.8 ksec in Fig. 10(c), but thereafter in (d) and (e) they become obscure. In terms of the crystal structure, the formation of the m-phase within the t-phase can be seen in the diffraction pattern in Fig. 10(e). Figure 11 shows TEM data for this t'→t growth process with the electron beam incident along the (111) direction to the sample as in Figs. 5 and 9. The same heating time of 0.6 ksec as in Fig. 10(b) was selected. As can be seen from the dark-field images obtained from the [112] forbidden reflection in Figs. 11(a) through 11(c), the total area of the sheet-shaped variants appears as bright contrast. Both the stable t-phase and the parent t'-phase maintain this reflection. This shows that oxygen ion displacement for the t'- and t-phases occurs in the same manner. On the other hand, these variants are not present in the massive structures, so the microstructural changes due to annealing are different from those in the banded structures. Figures 12(a) and 12(b) show the changes in microstructure during annealing (0.6 ksec at 1673 K) in the banded structures and massive structures, respectively. The kind of structure that correlates to the space between the longitudinal direction of the t-phase and the variant crystal wall seen in Fig. 12(a) is not observed in the area of the massive structure in Fig. 12(b). The long axis of the lens-shaped t-phase precipitates corresponds to the a-axis of the parent phase (c-phase). This can be understood by the fact that, when the c-axis (long axis) of the t-phase aligns with the a-axis (short axis) of the parent phase, the misfit strain of the precipitated phase is lowest. This is a phenomenon that has typically been observed with other metal alloys and ceramics. Figure 13 shows the microstructure when the sample with the banded structure where the t'-phase was observed is annealed even longer for 1.8 ksec at 1673 K.

![Fig. 9. EDX analysis of t'-phase formed in liquid-quenched ZrO$_2$-9 mol % MgO. Images (a) and (b) show the t'-phase before and after spot analysis. In (b), contamination of the sample due to the analysis can be seen. A through P on the right side are the analytical values for each of the points shown in Photo (b).](image-url)
Figure 13(a) and 13(b) are a bright-field image (©111ª electron beam incidence) and a dark-field image from the {112} forbidden reflection, and (a) is the corresponding diffraction pattern. As can be seen in the dark-field image, areas with no contribution from the {112} reflection are observed at the locations indicated by arrows in the bright-field image and between the lens-shaped t-phases. This is presumably due to the fact that the t→t phase process due to the heat treatment is observed.

4. Discussion

From the XRD and TEM results, we conclude that a thermodynamically metastable t'-phase with three variants is formed when ZrO$_2$-9 mol % MgO is rapidly quenched from a molten liquid. The characteristics of the t'-phase include (1) not being transformed to the m-phase by external stress; (2) having variants that are roughly uniform in MgO concentration and can be thought of as a non-diffusive transformation from the c-phase; (3) having the three variants formed by displacement of oxygen
atoms; and (4) breaking down to the stable t-phase and c-phase during prolonged annealing at 1673 K. As was noted in the introduction, this can be thought of as roughly similar to the t'-phase in the ZrO$_2$-Y$_2$O$_3$ system, whose crystal structure has already been reported, even though in terms of microstructure, Mg-PSZ has its own peculiar characteristics. The tetragonalities (c/a) of the t- and t'-phases in the ZrO$_2$-Y$_2$O$_3$ system have been reported to be 1.006 and 1.016, respectively, and are somewhat smaller than the values obtained in the present study, but are within the range that can be interpreted as differences in the solute atoms. These types of studies on Mg-PSZ have already been attempted by Bender et al.,24) (cooling rate of approximately 5000 to 35,000 K/sec), but there has been no report of the existence of a t'-phase. Therefore, if we consider that the t'-phase found in the present study is crystallographically the same as that in the ZrO$_2$-Y$_2$O$_3$ system, we can take a similar approach to discussing problems such as its formation mechanism, crystallography, and structure. Even if the t'-phase is formed from the c-phase by a non-diffusive transformation due to quenching, a clear conclusion cannot necessarily be drawn as to its parent phase, nor whether it is formed by a massive transformation as suggested by Heuer et al., or a martensite transformation. For example, if the parent phase of the structure seen in Fig. 5 is the c-phase as described by Gupta25) and Sakuma,26,27) the t'-phase is formed by partial transformation of the c-phase, and it can be thought of as arising from a typical martensite transformation mechanism. From the results of the present study, the boundaries with the parent phase at the ends of the sheet-like t'-phase have a very pronounced contrast; therefore, even though we can structurally consider formation by a martensite transformation, the [112] forbidden reflection also arises from the parent phase, and it is difficult to consider it a stable c-phase.

Lanteri et al.,28) have reported that a contrast similar to an anti-phase domain boundary (APB) seen in ordered alloys appears in dark-field images obtained from {112} reflections for the parent phase. These structures are all t'-phase structures, and the variants discussed in this paper are taken as being parent phase - t'-phase internal twins (90° twins, with these twins being accommodation twins rather than transformation twins). Furthermore, we can observe a tiny split in the diffraction spots by analyzing high index reflections. However, it is certain that the {112} forbidden reflections also arise from areas thought to be the parent phase, but no structure similar to an APB or splits in the diffraction spots were observed. In addition, if we suppose that the displacement (shuffling) of oxygen atoms in the Z-axial direction occurs (c'-phase) while the cubic symmetry of the parent phase is maintained, as has been recently suggested by Sugiyama et al., it is possible to explain the appearance of the forbidden reflection. Although this does not conflict with the results of the present study, no final or conclusive evidence has been obtained.

The above discussion has been based on results already obtained for ZrO$_2$-Y$_2$O$_3$ systems, but various problems still remain. (1) Conditions for formation of the t'-phase: Since a twin roll was used as the liquid quenching method in the present study, considerable compression stress was applied to the samples by the roll during quenching. We cannot determine whether the main factor in t'-phase formation was the effect of quenching alone, or whether it was caused also by the effects of stress. (2) Effects of solute concentration on formation of the t'-phase: The t'-phase was only observed in samples with a 9 mol% MgO concentration, and the EDX results also indicated a concentration of 8 to 9 mol%. It was confirmed that the t'-phase was not formed in the samples with 2 and 13 mol% MgO, but we need to confirm whether or not it is possible for it to form in samples in the neighborhood of 9 mol% MgO such as the 5 and 11 mol% MgO samples. (3) Effects of the t'-phase on mechanical properties: Since the t'-phase is not easily transformed into the m-phase by external stress, the stress relaxation mechanism caused by the stress-induced t→m martensite transformation that has typically been used effectively in toughening PSZ does not apply here. Therefore, it can be assumed that some sort of heat treatment is necessary, but whether this can be tied to increasing strength and toughness of the materials is a question for the future. However, even though these unsolved problems remain, this study is the first to make it clear that the t'-phase can be obtained by carrying out liquid quenching with a system other than PSZ with Y$_2$O$_3$. The possibility is extremely high that a similar t'-phase can be obtained in systems other than MgO (e.g., PSZ with CaO added), and moving forward, it can be said that the path has been widened for new developments and a variety of solutions for these problems.

5. Conclusion

We carried out liquid quenching of a sintered product in which 0, 0.5, 2, 9, 13 and 50 mol% MgO were added to ZrO$_2$ using twin rolling, and we evaluated the microstructure and crystal structure of the film samples obtained in this manner. As a result, we confirmed that a t'-phase with characteristics roughly similar to the t'-phase observed in ZrO$_2$-Y$_2$O$_3$ systems was formed in liquid-quenched ZrO$_2$-9 mol% MgO. From this we can assume that the formation of this t'-phase is not peculiar to the ZrO$_2$-Y$_2$O$_3$ system, and that it will occur in various ZrO$_2$ materials (for example, ZrO$_2$-CaO, ZrO$_2$-CeO$_2$, etc. where there is a solid solution of a stabilizer in the ZrO$_2$). Based on these results, we can draw the following conclusions about the characteristics of the t'-phase formed in the quenched ZrO$_2$-9 mol% MgO material.

(1) The formation of the t'-phase requires a large cooling rate, but besides that, it can be assumed that three-dimensional compression stress during cooling contributes to its formation.

(2) The t'-phase is thought to be a thermodynamically metastable phase, but transformation to the m-phase does not
occur easily in the presence of external stress.

(3) The t’-phase is made up of three variants, and the MgO concentration is uniform among them. In addition, the MgO concentration is higher than that in the stable lens-shaped t-phase.

(4) The t’-phase is a thermally unstable phase, and it breaks down easily during annealing. For example, for annealing at 1673 K, a t’→c + t-phase breakdown occurs, and the orientation of the t-phase obtained at that time reflects its previous history.

(5) It is clear that there are three variants present in the t’-phase, but there is still some uncertainty as to the nature of the parent phase, and c, t’ and c’ phases have been proposed. Further investigation is necessary to resolve these issues.

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