PII: S0272-8842(97)00016-3

Ceramics International 24 (1998) 307–312
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0272-8842/98 $19.00+.00

In-situ TEM Observations of Tetragonal to Monoclinic Phase Transformation in ZrO_2–2 mol% Y_2O_3 Ceramics

G. Y. Lin
Institute of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China

T. C. Lei & Y. Zhou
School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China

(Received 16 September 1996; accepted 3 December 1996)

Abstract: In-situ TEM observations of tetragonal to monoclinic phase transformation in ZrO_2–2 mol%Y_2O_3 ceramics were performed under the action of electron beam heating. The results show that the nucleation and growth of m-ZrO_2 martensite and its final morphology are dependent upon the microscopic content and distribution of Y_2O_3. In microareas with lower Y_2O_3 content and homogeneous distribution, the m-ZrO_2 martensite nucleates and grows by twins, finally forming parallel laths. But in microareas with higher Y_2O_3 content and heterogeneous distribution, single plate of m-ZrO_2 martensite is first formed, and simulates the appearance of other martensite plates, finally forming N or Z shaped skeleton. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Phase transformation toughening via the martensitic tetragonal(t) to monoclinic(m) phase transformation in ZrO_2 is one of the most effective ways of improving the fracture toughness of ceramics[1,2] and results in the development of the most hopeful zirconia-toughened ceramics used in engineering.[3] The effects and mechanisms of phase transformation toughening are directly dependent on the nature of t–m ZrO_2 transformation and the related microstructure. However, careful studies on the process and mechanisms of t–m phase transformation have been very scarcely reported because the martensitic transformation is usually too rapid to observe clearly. For this reason, the t-ZrO_2 particles are partially stabilized by adding proper stabilizer and by selecting suitable t-ZrO_2 grain and adjusting the operating voltage and current of TEM so that the t–m transformation speed can be controlled and in-situ TEM observations of the whole process of this transformation become possible.[4,5] The nucleation and growth of m-ZrO_2 martensite in hot-pressed ZrO_2–2 mol%Y_2O_3 ceramics are carefully examined and the effecting factors of transformation method and final product morphology are discussed in this paper.

2 EXPERIMENTAL

The ZrO_2–2 mol%Y_2O_3 ceramics was prepared by hot-pressing ZrO_2–2 mol%Y_2O_3 powders fabricated by coprecipitation–filtration with an average particle size of about 0.65 µm (having 34% t-ZrO_2 and 66% m-ZrO_2) at 1600°C under 25 MPa for 1 h. The selected temperature for hot-pressing lies in the single tetragonal phase region of ZrO_2–Y_2O_3 diagram.[6] The TEM foils were prepared as following: sheets with a thickness of about 0.5 mm were cut from the hot-pressed specimen and then ground to a thickness of about 50 µm and divided into discs of 3 mm diameter. The ground discs were gripped between two pieces of copper nets and glued together with resign. The well-glued specimens were thinned by an ion-thinner of Gatan model-600 at a small angle of 10°. The centre of the copper net was denuded and a copper ring was remained. This copper ring then becomes a supporting skeleton which protects the foil from breakage during operation. The t–m ZrO_2 transformation in ZrO_2–2 mol% Y_2O_3 ceramics was induced and observed by using a Philips CM-12 transmission electron microscopy operated at 120 KV.

3 RESULTS AND DISCUSSION

The XRD examinations[7] show that there is 27% m-ZrO_2 in the ZrO_2–2 mol% Y_2O_3 ceramics after hot pressing although hot pressing was performed at 1600°C, which lies in the single t-phase region according to the ZrO_2–Y_2O_3 phase diagram.[6] This indicates that part of the t-phase may transform into m-phase after cooling to room temperature (but to an amount much less than 66%). The intercept method reveals that the average particle size of ZrO_2 in the ZrO_2–2 mol% Y_2O_3 ceramics is 2.35 μm after hot-pressing.

A series of TEM photographs of the whole process of nucleation and growth of a typical plate-type martensite were shown in Fig. 1. It can be found that a plate of m-ZrO_2 martensite nucleated at grain boundaries by means of heterogeneous nucleation under electron beam bombardment. When the martensite plate grew completely across a grain, it was stopped at a grain boundary and the resulting stress concentration caused by volume expansion and shear, induced a differently oriented plate to nucleate and begin to grow. Sometimes the length of a plate stopped growing before it grew completely across a grain and a new oriented plate was induced to nucleate and grow (Fig. 1(b) and (e)), which meant that some location in the grain hinders the martensite transformation. However, the plate could grow across the subgrain boundary (Fig. 1(c)). The old plates also grew in width by means of shear at the same moment of forming a new one, but the speed was very low. Every plate almost stopped growing in width after 7 min and the t–m ZrO_2 phase transformation in this grain wasn't complete under electron beam bombardment even after removal of the condenser aperture and a further condensation of the electron beam onto the grain for 20 min. The reversal transformation didn't happen, either, which was observed in ZrO_2–2.5 mol% Y_2O_3 ceramics by Mecartney and Rühle.[4] and Heuer *et al.*[8] Finally, the grain was composed of t + m dual phases, the plates of m-ZrO_2 martensite formed N or Z shaped skeleton.

Figure 1 also shows the dynamic process of the nucleation and growth of microcracks in ZrO_2–2 mol% Y_2O_3 ceramics. There was already a long microcrack in the triangular grain boundary before the dynamic phase transformation in Fig. 1(a). It was probably caused by the t–m phase transformation of near other grains. Figure 1(d)–(f) show the dynamic process of the nucleation and growth of microcracks. The microcracks were formed in the grain boundary induced by the stress concentration caused by the volume expansion and shear as the martensite plate nucleates and grows. The microcracks always nucleated at the cross top of two plates, which indicated that there was higher stress intensity at the cross top. The microcracks could further grow in length and width as the martensite phase transformation went on. The sizes of this kind of microcracks are small compared with the sizes of ZrO_2 particles so that they may play a role in toughening ceramics.[9]

Figure 2 shows another pattern of the nucleation and growth of m-ZrO_2 martensite in ZrO_2–2 mol% Y_2O_3 ceramics. The martensite laths formed first also at grain boundaries, but it was different from Fig. 1 that two martensite laths (Fig. 2(a)), not only one, nucleated simultaneously and the two martensite laths continually grew in both length and width by means of shear along a certain plane (Fig. 2(b)). At the same time, new martensite laths continually nucleated and grew, and always two and two nucleated simultaneously, grew together (Fig. 2(c) and (d)). Another difference from Fig. 1 is that the new martensite laths nucleated independently by means of twins (Fig. 2(a) and (c)), but didn't form at the top of old laths by self-triggering. Of course stress concentration caused by the volume expansion and shear could enhance the nucleation and growth. The two laths nucleated simultaneously should grow to constitute twins on their common plane as twin plane. The two neighbouring laths, but not nucleated simultaneously, would also grow to constitute twins along a certain habit plane by means of shear (as shown in Fig. 2). Therefore, the final morphology of m-ZrO_2 was parallel lath-shaped martensite with twin relationship in this grain (Fig. 2(f)). This kind of transformation nucleating and growing by means of twins could decrease the total change of shape and release elastic strain because of the self-co-ordination effect so that its transformation speed was faster under the action of electron beam heating and didn't easily cause microcracks to be nucleated at the grain boundary. The microcrack in Fig. 3(b) may be due to the larger volume expansion caused by t–m phase transformation of some neighbouring particles and the end product of some particles also forming N or Z shaped skeleton.

It is found that there are two kinds of typical types of m-ZrO_2 martensite from t–m phase

Fig. 1. A series of TEM photographs showing the dynamic process of nucleation and growth of m-ZrO_2 martensite in ZrO_2–2 mol%Y_2O_3 ceramics: (a) 20 s; (b) 60 s; (c) 90 s; (d) 150 s; (e) 5 min; (f) 10 min.

transformation not only under electron beam bombardment (Figs 1 and 2) but also during cooling after sintering (Fig. 3), one is plate type of martensite forming N or Z shaped skeleton, another is parallel lath type of martensite. The EDAX analysis results indicate that it is dependent upon the microscopic distribution of Y_2O_3 content (as shown in Fig. 3). The Y_2O_3 content is always higher and its distribution is heterogeneous (the Y_2O_3 content may be up to 3.81 mol% in some

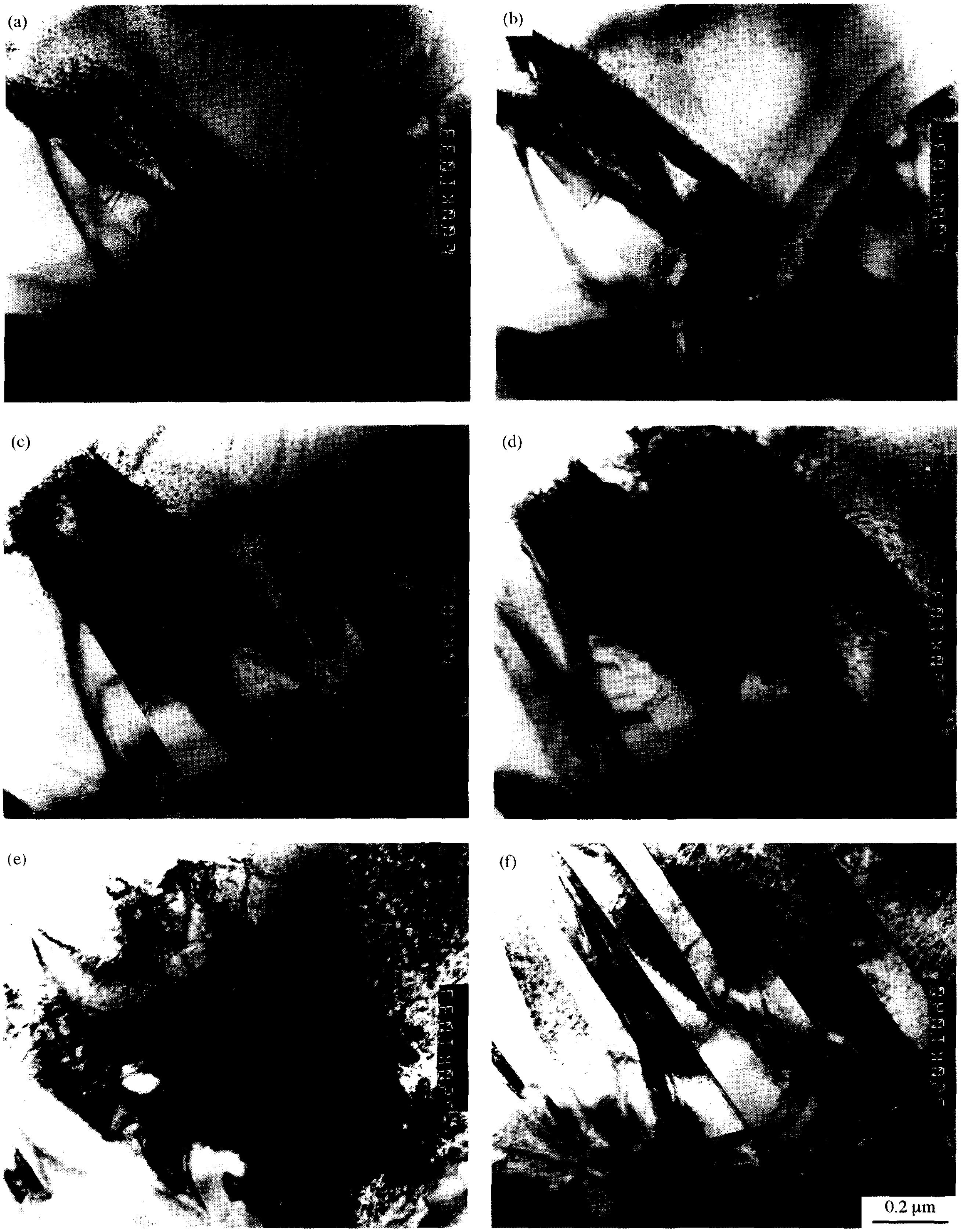

Fig. 2. A series of TEM photographs showing the dynamic process of nucleation and growth of m-ZrO_2 martensite in ZrO_2–2 mol%Y_2O_3 ceramics: (a) 15 s; (b)30 s; (c) 60 s; (d) 120 s; (e) 200 s; (f) 300 s.

microareas, but is only 1.34 mol% in some other microareas) in the grain with N or Z shaped skeleton of m-ZrO_2 [Fig. 3(a)]. However, the Y_2O_3 content is always lower and its distribution is homogeneous, which is between 1.39 mol% and 1.93 mol% in the grain with parallel lath type of m-ZrO_2 [Fig. 3(b)]. It is close to the average value (2 mol%) of the composition. Therefore, it can be seen that m-ZrO_2 might first nucleate and grow at the grain boundary or the microareas with lower Y_2O_3 content in

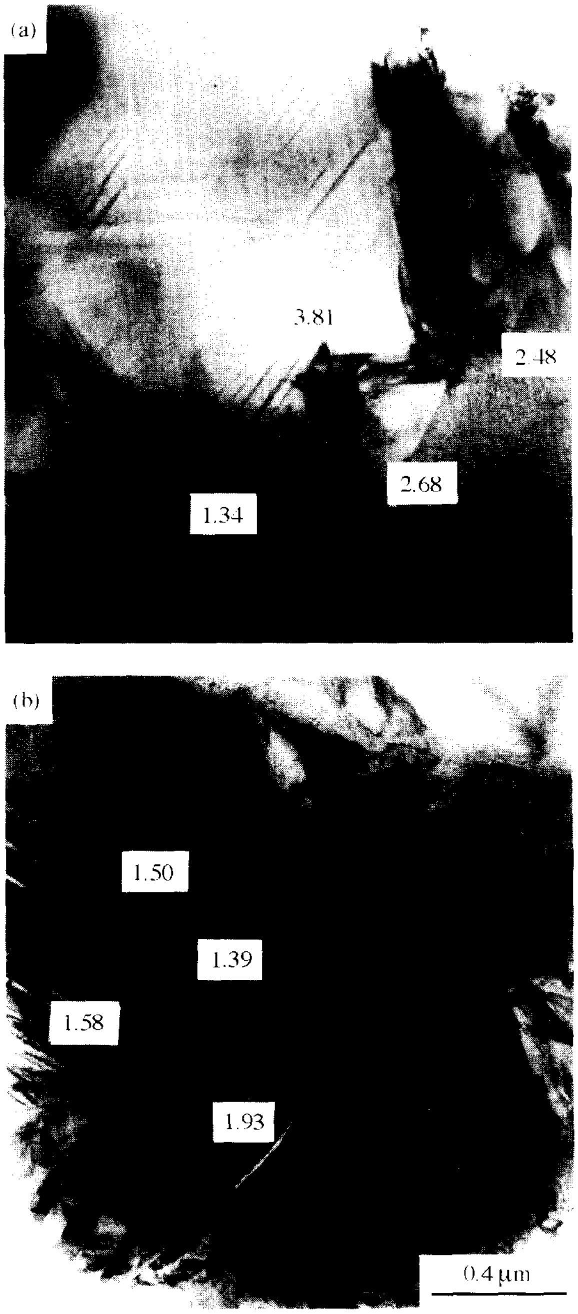

Fig. 3. TEM photographs showing the morphology of m-ZrO_2 martensite in ZrO_2–2mol%Y_2O_3 ceramics and Y_2O_3 contents (in mol%) in the microareas: (a) N or Z shaped skeleton plate type of m-ZrO_2 martensite; (b) parallel lath type of m-ZrO_2 martensite.

the t-ZrO_2 grains with higher Y_2O_3 content and heterogeneous distribution then the nucleation and growth of m-ZrO_2 were stopped at the microareas with higher Y_2O_3 content and some martensite plates couldn't grow across the whole grain (Fig. 1(b) and (c)) or grow in width by shear to transform the whole grain into m-ZrO_2, so that the grain is composed of t + m dual phases and m-ZrO_2 finally forms N or Z shaped skeleton. This is because the higher the Y_2O_3 stabilizer in ZrO_2, the larger the difference between tetragonal phase structure and monoclinic phase structure and more difficulty in inducing t–m phase transformation. However, m-ZrO_2 can nucleate and grow by means of twins with lower energy rampart in every microarea of the t-ZrO_2 grains with lower Y_2O_3 content and homogeneous distribution and finally forms parallel lath type of martensite. Yoshizawa and Sakuma have also discovered that the Y_2O_3 contents in microareas are very heterogeneous in ZrO_2–4mol%Y_2O_3 ceramics, they may be from 1.9mol% to 5.6mol%.[10] Finally, it should be pointed out that the effect of Y_2O_3 content on the m-ZrO_2 morphology in ZrO_2–Y_2O_3 ceramics is very similar to that of carbon content on the martensite morphology in steels. The martensite in low carbon steels always forms parallel lath type of martensite structure and the martensite in middle and high carbon steels always forms N or Z shaped skeleton plate type of martensite structure after quenching.[11]

4 CONCLUSIONS

1. The t–m ZrO_2 phase transformation in ZrO_2–2mol%Y_2O_3 ceramics can be induced by the electron beam bombardment of TEM. The m-ZrO_2 always nucleates at the t-ZrO_2 grain boundaries.
2. The patterns of nucleation and growth of m-ZrO_2 martensite and its final morphology in ZrO_2–2mol%Y_2O_3 ceramics are dependent upon the microscopic Y_2O_3 content and its distribution. In the t-ZrO_2 grains with lower Y_2O_3 content and homogeneous distribution, the m-ZrO_2 martensite nucleates and grows by twins in a higher speed and finally forms parallel lath type of martensite. But in the t-ZrO_2 grains with higher Y_2O_3 content and heterogeneous distribution, single plate of m-ZrO_2 is first formed at the beneficial microareas and stimulates the appearance of other martensite plates, the plates grow in width by shear at a very low speed, and finally form N or Z shaped skeleton throughout the grains.
3. The effect of Y_2O_3 content on the m-ZrO_2 morphology in ZrO_2–Y_2O_3 ceramics is very similar to that of carbon content on the martensite morphology in steels.
4. The microcracks are formed in the grain boundary induced by the t–m phase transformation, which may play a role in toughening ceramics.

REFERENCES

1. EVANS, A. G. & CANNON, R. M., Toughening of brittle solids by martensite transformation. *Acta Metall.*, **34**(5) (1986) 761–800.

2. RÜHLE, M., CLUSSEN, N. & HEUER, A. H., Transformation and microcracking toughening as complement process in ZrO_2-toughened Al_2O_3. *J. Am. Ceram. Soc.*, **69**(2) (1986) 195–197.
3. CLUSSEN, N., Microstructure design of zirconia-toughened ceramics (ZTC). In *Advances in Ceramics, Vol. 12, Science and Technology II*, ed. N. Clussen, M. Rühle & A. H. Heuer. The American Ceramics Society, Columbus, OH, 1984, pp. 325–352.
4. MECARTNEY, M. L. & RÜHLE, M., In-situ TEM observations of the monoclinic to tetragonal phase transformation in tetragonal ZrO_2. *Acta Metall.*, **37**(7) (1989) 1859–1863.
5. LEE, R. R. & HEUER, A. H., In-situ martensitic transformation in a ternary MgO–Y_2O_3 ZrO_2 alloy: I. Transformation in tetragonal ZrO_2 precipitates. *J. Am. Ceram. Soc.*, **71**(8) (1988) 701–706.
6. GREEN, D. J., HANNINK, R. H. J. & SWAIN, M. V., *Transformation Toughening of Ceramics*. CRC Press, Boca Raton, FL, 1989, pp. 97–101.
7. LIN, G. Y., LEI, T. C., WANG, S. X. & ZHOU, Y., Microstructure and mechanical properties of SiC whiskers reinforced $ZrO_2(2\,mol\%\,Y_2O_3)$ based composites. *Ceram. Int.*, **22**(3) (1996) 199–205.
8. HEUER, A. H., RÜHLE, M. & MARSHALL, D. B., On the thermoelastic transformation in tetragonal zirconia. *J. Am. Ceram. Soc.*, **73**(4) (1990) 1084–1093.
9. GREEN, D. J., Critical microstructure for microcracking in Al_2O_3–ZrO_2 composites. *J. Am. Ceram. Soc.*, **65**(5) (1982) 610–614.
10. YOSHIZAWA, Y. & SAKUMA, T., Evolution of microstructure and grain growth in ZrO_2–Y_2O_3 alloys. *ISIJ Int.*, **29** (1989) 746–752.
11. ZHAO, L. C., *Principles of Metallography*. Harbin Institute of Technology Press, 1987, pp. 81–98 (in Chinese).