SYNTHESES OF MONOCLINIC AND TETRAGONAL ZrO_2 AT HIGH TEMPERATURES

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ABSTRACT

Single crystals of ZrO_2 in tetragonal crystal forms were synthesized by flux methods. The tetragonal crystal was transformed into a single or twinned monoclinic phase during cooling. The observed orientational relations between the two phases is c_t/c_m and $\{100\}_m//\{100\}_t$. Three kinds of orientational relations were observed on heating transformation; c_t is parallel to c_m , b_m and a_m^* . The equilibrium temperature of the monoclinic and the tetragonal phases is $1,145 \pm 10^\circ\text{C}$.

Introduction

The monoclinic-tetragonal phase transformation of ZrO_2 displays many of the characteristics associated with the martensitic phase transformation of such a type as observed in the Fe-Ni alloys, namely, diffusionless-shear mechanism, broad hysteresis, athermal characteristics, surface deformation, and deformation twinning.

The surface deformation associated with the thermal transformation was observed by Fehrenbacher & Jacobson (1965). They examined sintered ZrO_2 grains under the vacuum hot-stage microscope. The writer also observed the surface deformations on $\{100\}_m$ and $\{110\}_m$ of the single crystals when they were heated above $1,160^\circ\text{C}$. A shape change, deformation twinning and the orientation relation between monoclinic and tetragonal phases were determined by Bailly (1964) by electron microscopy. It was revealed that c_t is parallel to c_m , and $\{100\}_m$ is parallel to $\{100\}_t$.

Table 1. Summary of the reported data on the transformation of ZrO_2 .

	monoclinic $\rightarrow$ tetragonal	tetragonal $\rightarrow$ monoclinic
temperature (measured with powder)	1,150°C—1,250°C (on heating)	1,070°C—700°C (on cooling)
twin	not observed * {not observed $\begin{cases} \{101\}_t \\ \{100\}_m \\ \{110\}_m \end{cases}$	{not observed $\begin{cases} \{100\}_m \\ \{110\}_m \end{cases}$
crack	not observed	observed
surface deformation	observed (lenticular) * (lectangular)	not observed
**orientation relation	$c_m // c_t$ $\{100\}_m // \{100\}_t$	$c_m // c_t$ $\{100\}_m // \{100\}_t$
dislocation movement	observed	observed
habit plane	absent	absent

* Results of the writer's investigation.

** Monoclinic and tetragonal structures are based on face-centered fluorite-like cells.

Main results of the previous workers are listed in Table 1. The present investigation is concerned primarily with the synthetic study of the monoclinic and the tetragonal single crystals at high temperatures, and the orientation relations between the two phases.

Crystal syntheses

Synthesis A:

A mixture of PbF_2 (99.99% pure, 3 g) and ZrO_2 (99.9% pure, 0.3 g) was sealed in a platinum tube of 8 mm in diameter. The sealed tube was heated at 1,255°C in an electric resistance furnace, and then cooled to 1,180°C. The cooling rate was 15°C/hour. The specimen was then quenched to room temperature.

Synthesis B:

The starting material composed of PbF_2 (3 g) and ZrO_2 (0.2 g) was melted at $1,255^\circ\text{C}$ in a platinum tube, and then quenched to room temperature. The quenched specimen was heated at $1,130^\circ\text{C}$ for 20 hours.

Synthesis C:

Anhydrous borax (2 g) and ZrO_2 (0.2 g) was mixed in a platinum crucible and heated at $1,250^\circ\text{C}$ for 5 hours, and then cooled rapidly to $1,140^\circ\text{C}$. Crystals were synthesized at $1,140^\circ\text{C}$ by the evaporation of the flux.

Synthesis D:

The synthetic method is the same as synthesis C except for the temperature of evaporation of the flux. Crystals were synthesized at $1,165^\circ\text{C}$.

Characteristics of the obtained crystals

Synthetic crystals were examined at room temperature by the two-circle Goldschmidt goniometer, under the polarizing microscope and in X-ray oscillation method.

The tetragonal ZrO_2 is unquenchable. Therefore, the synthetic crystals have the structure of monoclinic symmetry. The morphological symmetry of some crystals was observed as tetragonal.

Crystals obtained by synthesis A:

Many fine crystals, $0.1\text{ mm} \times 0.1\text{ mm} \times 0.5\text{ mm}$ in dimensions, were obtained by this method. These crystals exhibit well-developed faces. Some crystals are bladed, but many are columnar. The surface deformation was not observed. The morphological symmetry of the columnar crystals was determined as tetragonal. The observed crystal faces were $\{100\}_t$, $\{110\}_t$, and $\{111\}_t$, the axial ratio being 1:1.02. The typical crystal form is shown in Fig. 1A. The morphological symmetry of some bladed crystals were also determined as tetragonal.

The crystals with tetragonal outerforms have the structure of monoclinic symmetry which was confirmed by optical and X-ray studies. Many crystals exhibit polysynthetic twinning on $\{100\}_m$, and single crystals are rare. The morphological, optical and X-ray studies demonstrated the following crystallographic orientational relations: c_t/c_m and $\{100\}_m//\{100\}_t$.

Crystals obtained by synthesis B:

Many platy crystals were obtained by this method. The outerform of the crystals is monoclinic. The typical crystal form is shown in Fig. 1B.

Crystals obtained by synthesis C:

Crystals with monoclinic forms were obtained by this method. The crystals are tabular with well-developed $\{110\}_m$ and $\{100\}_m$. $\{010\}_m$ is absent or only poorly developed. $\{011\}_m$ is observed with all the examined crystals. Outerforms of the crystals are simply twinned on $\{100\}_m$. The angle β is about 99° .

Crystals obtained by synthesis D:

Columnar crystals were obtained by this method. The morphological and optical characters of them are similar to those of the crystals obtained by synthesis A.

Many experiments not described above were carried out by the flux methods. Crystals with tetragonal symmetry were obtained when experiments were carried out above $1,160^\circ\text{C}$.

Fig. 1. Morphology of ZrO_2 crystals.
A, Tetragonal form (synthesis A);
B, Monoclinic form (synthesis B).

Equilibrium temperature of the two phases

Thermal transformation of ZrO_2 was examined by the high-temperature X-ray diffractometer. Examined powders were made from the synthetic crystals. A small amount of the tetragonal phase was detected when the monoclinic ZrO_2 was heated at $1,150^\circ\text{C}$.

The synthetic study of the monoclinic single crystals described above revealed that crystals with monoclinic outcrops were synthesized at $1,140 \pm 10^\circ\text{C}$.

These experimental results suggest that the equilibrium temperature of the two phases is $1,145 \pm 10^\circ\text{C}$.

Heating experiments of monoclinic ZrO_2

Monoclinic single crystals were heated slowly to $1,180^\circ\text{C}$ and quenched to room temperature. A single crystal was then changed into polycrystalline monoclinic ZrO_2 . Observation of the heated crystals under the polarizing microscope demonstrated that c_m -axis of the original single crystal is parallel to c_m , b_m and a_m^* -axes of finely twinned new crystals. Surface deformations with rectangle forms were observed on the crystal faces.

This result confirms that there are three kinds of orientational relations between the monoclinic and the tetragonal phases.

Conclusions

Single monoclinic crystals with tetragonal crystallographic symmetry were obtained above $1,160^\circ\text{C}$. The orientational relations between the two modifications are as follows: $c_m//c_t$ and $\{100\}_m//\{100\}_t$.

When monoclinic crystals were heated and transformed into the tetragonal phase, other orientational relations were observed.

Equilibrium temperature of the monoclinic and the tetragonal phases is $1,145 \pm 10^\circ\text{C}$.

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