

A New Face-Centered Cubic Phase in the ZrO₂-ZrN System

SOTOMITSU IKEDA, TAKESHI YAGI, NOBUO ISHIZAWA,
NOBUYASU MIZUTANI,* AND MASANORI KATO

*Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute
of Technology, Oh-Okayama, Meguro-Ku, Tokyo 152, Japan*

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A face-centered cubic (fcc) phase with quadrupled cell dimension of the rock salt-type ZrN has been found in the ZrO₂-ZrN system by the powder X-ray diffraction method and electron microscopy. The fcc phase coexists with Zr₇O₁₁N₂, ZrN, and ZrO₂ in the ZrO₂-ZrN system with ZrN fraction ranging from 30 to 90 mole%. The cell dimension of the fcc phase has been refined to $a = 18.334(2)$ Å in the 70 mole% ZrO₂-30 mole% ZrN compound and $a = 18.329(3)$ Å in the 30 mole% ZrO₂-70 mole% ZrN compound. The fcc phase is supposed to be chemically denoted as ZrN(O), substituting a small amount of nitrogen atoms with oxygen atoms in the ZrN host lattice in an ordered form. © 1988 Academic Press, Inc.

1. Introduction

Three phases are reported for the ZrO₂-ZrN system, γ (Zr₂ON₂, cubic, $a = 10.135$ Å), β (Zr₇O₈N₄, rhombohedral, $a = 9.540$ Å, $c = 8.834$ Å), and β' (Zr₇O₁₁N₂, rhombohedral, $a = 9.560$ Å, $c = 17.60$ Å) (1, 2). All of these structures are derived from the fluorite-type ZrO₂ structure, while ZrN has the rock salt-type structure with $a = 4.574$ Å (3). Compounds in this oxynitride system near the end member of ZrO₂ have a microstructure in which the tetragonal and monoclinic ZrO₂ particles are dispersed in a matrix having a modulated β' structure (4, 5). Since such a microstructure has an analogy to that of the cation-substituted partially stabilized ZrO₂ as found in ZrO₂-Y₂O₃, -CaO or -MgO systems, the present oxynitride compound is also expected to have several properties required for the new ce-

ramic materials with high strength and high toughness. This paper describes an unknown phase (temporarily called an X phase) which has been found during a course of the survey of synthesis and characterization of the zirconium oxynitride system (6).

2. Experimental

Compounds of the ZrO₂-ZrN system were synthesized by the reaction sintering method in the range of ZrN fraction from 0 to 100 mole% at 10-mole% intervals. A mixture of ZrO₂ (Toyosoda, purity 99.9%, specific area 15 m²/g) and ZrN (Soekawa; purity 99%) powders at an appropriate composition was ground in an alumina ball mill with methanol for 20 hr, dried at 60°C, passed through a 60-mesh sieve, and pressed isostatically at 1000 kg/cm². The mixture was heated at 1600°C for 20 hr in a reducing atmosphere with a flow of dehy-

*To whom all correspondence should be addressed.

drated and oxygen-desorbed gas mixture of N₂ (150 cm³/min) and H₂ (50 cm³/min).

Powder X-ray diffraction data were obtained by a diffractometer (Philips PW1700) using graphite-monochromated CuK α radiation. The step scanning technique was employed with step size 0.20° and counting

time 5 sec. The K α ₂ component was stripped by the Rachinger method (7). Peak positions were calibrated by using Si powder (NBS 640) as an external standard. After eliminating ambiguous peaks which can be identified as the other coexisting phases, the remaining 20 peaks (4° < 2 θ < 60°) of

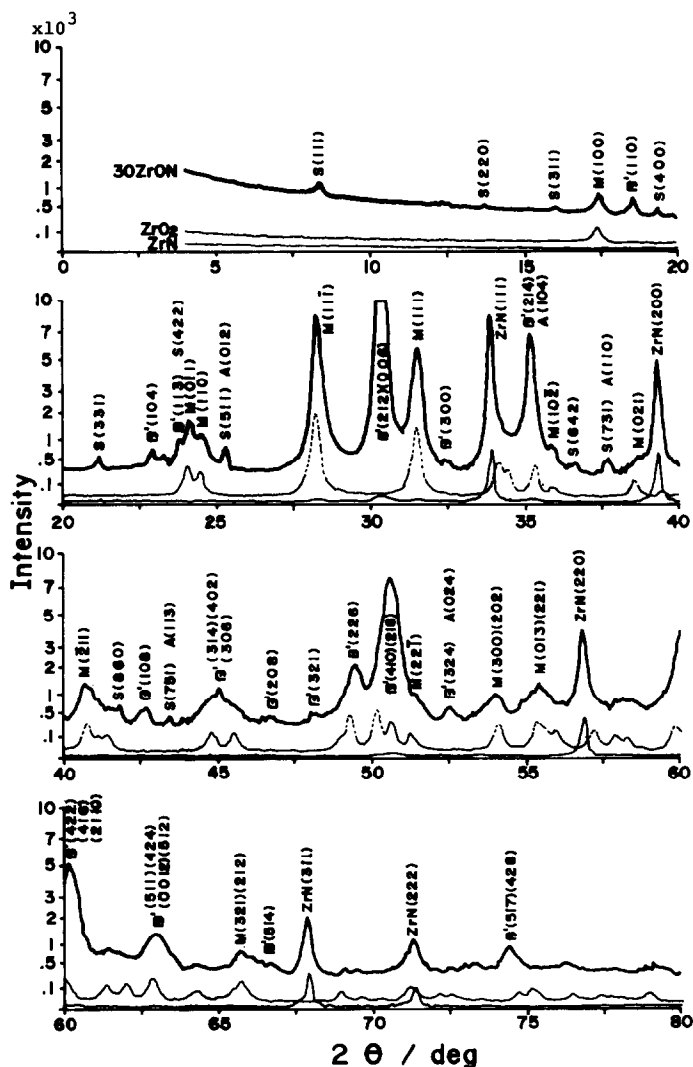


FIG. 1. X-Ray powder diffractogram (CuK α) of the 70 mole% ZrO₂-30 mole% ZrN compound (30ZrON). Peaks are labeled with the abbreviation of S for the X phase, M for the monoclinic zirconia, and A for α -Al₂O₃. Diffractograms of the pure M and ZrN phases are also superimposed in a reduced scale for comparison. The highest peak reaches approximately 3×10^4 counts/step (212 and 006 of β').

the compound containing 70 mole% ZrN were used as the input data for the program ITO to find the unit cell. This program was originally written by Visser (8) on the basis of the Ito method (9). A face-centred cubic (fcc) unit cell of $a = 18.329(3)$ Å was solved with the figure of merit (8) of 8.2. All other dubious unit cells were discarded or reduced to the same fcc cell in the course of the iteration procedure between the indexing and the cell parameter refinement (10).

A microscopic analysis was then carried out using a transmission electron microscope (JEOL 200CX) to examine the presence of the *X* phase in the zirconium oxynitride. Samples were sliced from the sintered rod by a diamond cutter, thinned first by hand to 15–50 μm, and finally by an ion beam thinning machine (Edward IBT200).

3. Results and Discussion

The X-ray powder diffraction pattern of the oxynitride with 30 mole% ZrN is shown in Fig. 1. The powder data are summarized in Table I. The compound consists of rhombohedral β' phase ($Zr_7O_{11}N_2$) and monoclinic and tetragonal ZrO_2 as major components, ZrN and *X* phase as minor components, and $\alpha-Al_2O_3$ as a trace component. The last one is a contamination due to the milling process. The *X* phase was found in the compositional range between 30 and 90 mole% ZrN. No other phases such as $\beta(Zr_7O_8N_4)$ or $\gamma(Zr_2ON_2)$ were found. The cell dimension of the *X* phase is refined to 18.334(2) Å for the compound with 30 mole% ZrN and 18.329(3) Å for 70 mole% ZrN.

Presence of the *X* phase was ascertained by electron microscopy as shown in Figs. 2–4. A large and smooth domain indicated by an arrow in Fig. 2 has a diffraction pattern shown in Fig. 3 which is indexed by the

TABLE I
OBSERVED AND CALCULATED POWDER X-RAY
DIFFRACTION DATA FOR THE *X* PHASE IN THE 70
mole% ZrO_2 –30 MOLE% ZrN COMPOUND

<i>h</i>	<i>k</i>	<i>l</i>	I_{obs}	d_{obs}	d_{calc}
1	1	1	13	10.536	10.584
2	2	0	1	6.478	6.481
3	1	1	4	5.515	5.527
4	0	0	4	4.578	4.583
3	3	1	10	4.201	4.206
4	2	2	17	3.738	3.742
5	1	1	17	3.525	3.528
3	3	3			
4	4	0	6	3.238	3.241
6	2	2	<1	2.761	2.764
4	4	4	100	2.645	2.646
6	4	2	<1	2.450	2.450
7	3	1	9	2.384	2.387
5	5	3			
8	0	0	10	2.291	2.292
6	6	0	10	2.161	2.160
8	2	2			
7	5	1	4	2.117	2.117
5	5	5			
8	8	0	23	1.621	1.620

same fcc lattice with quadrupled cell dimension of ZrN as found in the X-ray study. The β' phase and the ZrO_2 polymorphs were found in the grains having complicated microstructures as shown in the lower part of Fig. 2. A high-resolution image of Fig. 4 indicates that the *X* phase forms homogeneous and well-crystallized domains in the compound. The *X* phase was generally found in a region surrounding the ZrN particles. Thus, the *X* phase is supposed to have a structure containing a small amount of oxygen atoms in the ZrN host lattice, and its chemical composition will be written as $ZrN(O)$.

Computations were carried out using a HITAC M280 computer at the Computer Center of Tokyo Institute of Technology.



FIG. 2. Micrograph of 30 mole% ZrO_2 -70 mole% ZrN compound, with the X phase indicated by an arrow.

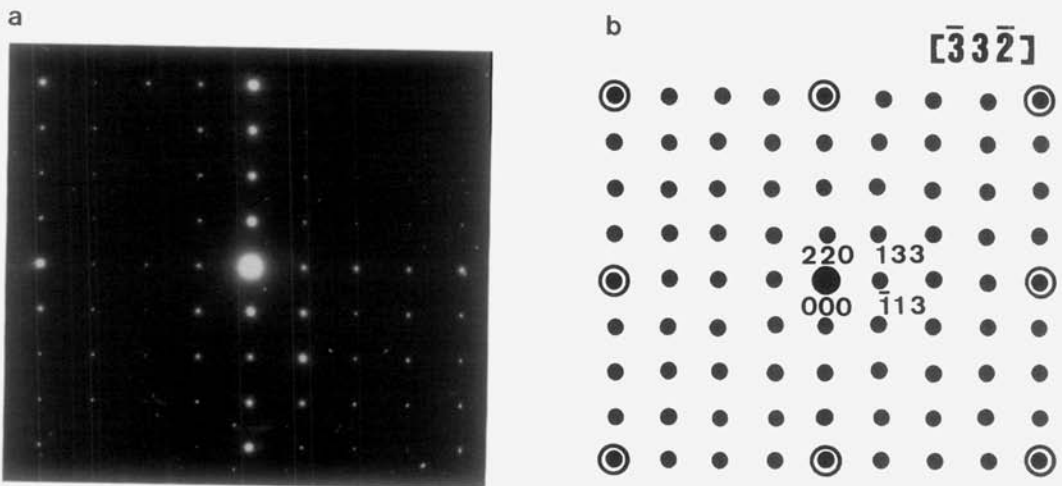


FIG. 3. Selected area diffraction pattern (a) of the X phase indicated by an arrow in Fig. 2 and its schematic representation (b). Doubled circles in (b) coincide with the reciprocal points of ZrN .

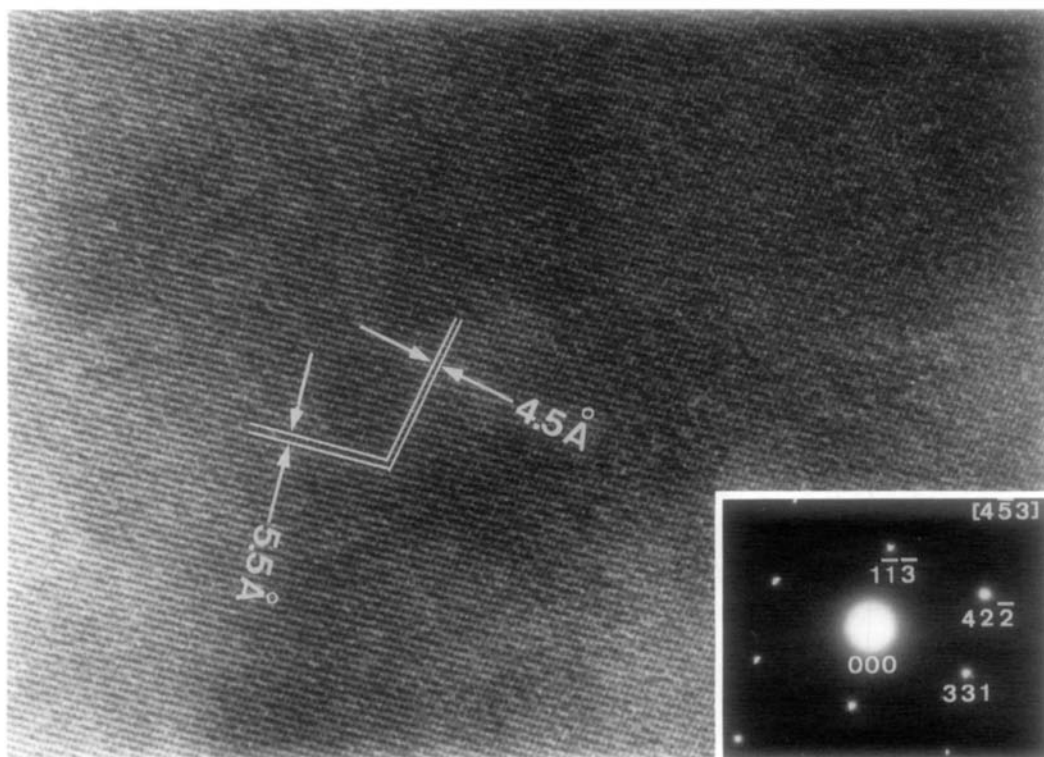


FIG. 4. High-resolution image of the X phase in the 30 mole% ZrO_2 -70 mole% ZrN compound indicated 4.5 and 5.5 Å periodicities which correspond to (331) and $(1\bar{1}\bar{3})$ interplanar spacings, respectively.

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