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NOTES

EXAFS Study on Binary Oxide-Powder Composed of TiO_2 and ZrO_2

Binary oxide composed of TiO_2 and ZrO_2 was prepared by two different methods. In one method, the binary oxide (A) was prepared by a simultaneous hydrolytic decomposition of titanium tetra-isopropoxide (Kishida Chemical Co.) and zirconium tetra-*n*-propoxide (Alpha Products) dissolved in benzene. The hydrolysis was carried out at room temperature using an excess amount of distilled water in dry nitrogen stream. The precipitate thus obtained was dried at 110°C in an oven, followed by calcination at 500–800°C in air for 2 h. The weight ratio of TiO_2/ZrO_2 in the binary oxide powder was varied from 10/90 to 90/10 by changing the amounts of respective alkoxides in a proper ratio. In the second method, which will be designated as P, pure TiO_2 and ZrO_2 were physically mixed and ground, and subsequently calcined in a similar manner as A. Pure oxide of each kind was prepared by the hydrolysis of respective alkoxide.

For the binary oxide P the X-ray diffraction peaks due to TiO_2 (anatase) and ZrO_2 (monoclinic) were always observed with the rational intensity ratio according to the concentration. While for the binary oxide A no diffraction peaks were observed when the weight ratio of TiO_2/ZrO_2 was in the range between 25/75 and 75/25 and the calcination temperature was lower than 650°C. The X-ray diffraction peaks due to $ZrTiO_4$ began to be observed when the oxide A was calcined at the temperatures higher than 650°C. The results mentioned above were very similar to those obtained by Wang *et al.* (*1*) for TiO_2–ZrO_2 binary oxide prepared by coprecipitation of a mixed solution of titanium tetrachloride and zirconium tetrachloride in anhydrous alcohol with aqueous ammonia.

The local structure around Zr ions in the binary oxide A calcined at 500°C was studied by means of EXAFS. The EXAFS spectrometer employed in this work has been previously reported (*2*). Briefly, it consists of a rotating anode X-ray generator (Rigaku Denki Co., RU-200), a spectrometer with a Johansson cut bent Ge(311) crystal, a pure Ge solid state detector and counting electronics. The X-ray source with an Ag target was operated at 30 kV and 50 mA in order to minimize the effect of the higher order reflections. In the analysis of the EXAFS spectra, the oscillatory part was subtracted, then converted to *k* space and Fourier transformed by the standard method, as described earlier (*3*). A typical spectrum and associated Fourier transform of the powder A calcined at 500°C, TiO_2/ZrO_2 ratio being 50/50, are shown in Fig. 1, as well as those for reference compounds ZrO_2 and $ZrTiO_4$. In the Fourier transforms of binary oxides A, a peak near 1.6 Å (phase shift uncorrected), which represents Zr—O distance, is always dominant. The peak was back-transformed using the formula derived from single scattering theories (*4*), and the Zr—O distance *R* and the oxygen coordination number *N* were obtained by the least-squares calculation. The dependence of *R* and *N* on the composition and the calcination temperature are shown in Table 1. The interatomic distance of Zr—O and the coordination number of oxygen around Zr ions in the binary oxide A calcined at 500°C are in very good accordance with those in pure ZrO_2, as shown in Table 1. This led us to the conclusion that local structure around Zr ions is very similar to that of ZrO_2 crystal. However, there must be no long range order, because the second peak in the Fourier transform is

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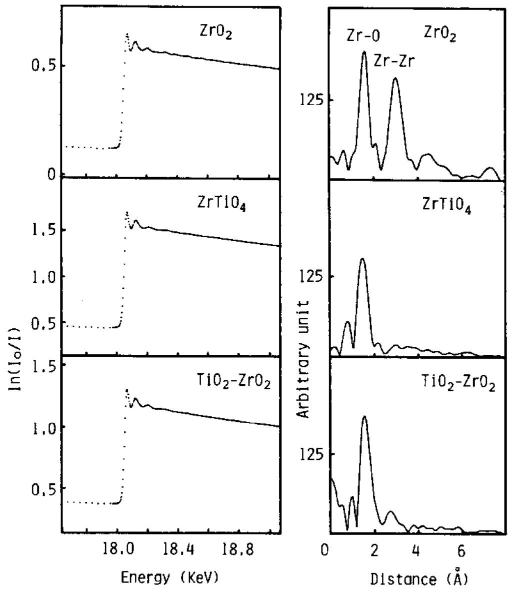

FIG. 1. EXAFS spectra and associated Fourier transforms of ZrO_2, $ZrTiO_4$ and coprecipitated TiO_2–ZrO_2 binary oxide A (50/50).

very much weaker than that of pure ZrO_2. The size of ZrO_2 structure in the binary oxide A calcined at 500°C was estimated about 20 Å according to the formula proposed by Greegor and Litle (5). With the elevation of the calcination temperature, the Zr—O distance decreased to ca. 2.03 Å and at the same time the coordination number of oxygen around Zr ions gradually decreased (see Table 1). The interatomic distance between Zr and O and the coordination number around Zr ions in ZrO_2 are 2.11 Å in average and 7, respectively, and those in $ZrTiO_4$ are 2.03 and 6. Therefore, the reductions of the Zr—O distance and the coordination number with elevating the calcination temperature indicate that the local structure around Zr ions approaches that of $ZrTiO_4$. When the calcination temperature exceeds 650°C, X-ray diffraction pattern due to $ZrTiO_4$ appears, indicating the growth of the crystal. On the other hand, X-ray diffraction patterns due to both ZrO_2 and TiO_2 crystal were always observed in the physically mixed and ground sample (binary oxide P). This clearly proves that Ti and Zr ions in the binary oxide A prepared from metal alkoxides are homogeneously dispersed.

The change in the distribution of Ti and Zr ions in the surface vicinity of the binary oxide A was examined by AES (JEOL, Jump-10) using sputtering technique with Ar^+. Electrons generated at an accelerating voltage of 3 kV with a current of 25 mA were used to ionize argon. Although the sputtered depth was not measured, the sputtering time was varied up to 7 min. In the AES spectrum of the binary oxide A, the signals assigned to Zr(*MNN*), Ti(*LMM*), and O(*KLL*) were observed at 148, 388, and 512 eV, respectively. The composition ratio of Zr/Ti can be estimated from the ratio of the peak intensities, I_{148}/I_{388}. The change in the ratio with the prolonged sputtering for the binary oxide A calcined at 500°C, the TiO_2/ZrO_2 being 50/50, is given in Fig. 2. Although a little condensation of Ti ions in the vicinity of the surface was observed, both Ti and Zr ions were proved to be homogeneously distributed in the bulk of the oxide A. In a binary oxide system, the oxide whose heat of for-

TABLE 1

Structural Parameters of Coprecipitated TiO_2–ZrO_2 Binary Oxide A at Various Temperatures

Ti : Zr	Temp. (°C)	N	*R* (Å)	λ	σ (Å)
25 : 75	500	7.0	2.07	2.30	0.06
	550	7.1	2.04	2.30	0.06
	600	4.8	2.06	2.30	0.02
	650	4.9	2.03	2.30	0.02
50 : 50	500	7.5	2.10	2.30	0.05
	550	6.7	2.05	2.30	0.02
	600	6.6	2.11	2.30	0.03
	650	5.8	2.03	2.30	0.04
	750	4.6	2.00	2.30	0.03
75 : 25	500	7.3	2.11	2.30	0.04
	600	5.7	2.01	2.30	0.03
	650	5.2	2.01	2.30	0.05
Reference materials					
ZrO_2		7	2.11	2.41	0.03
$ZrTiO_4$		6	2.03	2.28	0.03

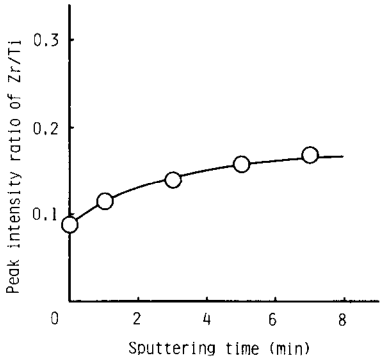

FIG. 2. Change in the AES peak intensity ratio of Zr/Ti with the sputtering time; the sample is a coprecipitated TiO_2–ZrO_2 binary oxide A (50/50).

mation is larger than the other oxide might be condensed in the surface vicinity (6). The heat of formation of TiO_2 is 436.0 kcal/mol (7) and is larger than that of ZrO_2, 258.2 kcal/mol (8), indicating the surface condensation of Ti ions in the binary oxide A.

Thus, the relatively homogeneous dispersions of Ti and Zr ions in TiO_2–ZrO_2 binary oxide were achieved by the simultaneous hydrolysis of the mixed solution of titanium tetra-iso-propoxide and zirconium tetra-*n*-propoxide dissolved in benzene.

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