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EFFECT OF WATER VAPOUR ON THE THERMAL EVOLUTION OF THE METASTABLE PHASES OF ZIRCONIUM DIOXIDE

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ABSTRACT

The role of water vapour on sintering and the tetragonal-to-monoclinic phase transformation of ZrO_2 was studied using different polycrystalline zirconia samples obtained from either thermal decomposition of zirconium nitrate or thermal dehydration of zirconia gels. The samples were heat-treated up to temperatures ranging from 873 to 1173 K in a dynamic vacuum, atmospheric air and a flow of water vapour saturated oxygen. It was found that water vapour accelerates sintering and facilitates conversion of the metastable tetragonal phase into the monoclinic (thermodynamically stable) modification. A metastable cubic phase ($a_0 = 510$ pm) was also found in some low-temperature ZrO_2 samples.

INTRODUCTION

Three stable polymorphs of zirconium dioxide are known, with monoclinic, tetragonal and cubic structures. The monoclinic phase, space group $P2_1/c$ [1], is stable up to 1373 K, when it transforms enantiotropically into the tetragonal phase, space group $P4_2/nmc$ [2]. Above 2600 K, ZrO_2 adopts the cubic, fluorite-type, structure.

The high-temperature modifications of pure ZrO_2 cannot be retained on quenching. However, several authors have reported on metastable tetragonal [3–11] and cubic [8–13] phases of this compound which can exist indefinitely at room temperature. These phases have, apparently, the same lattice parameters as the corresponding high-temperature analogues.

The low-temperature metastable modifications of zirconium dioxide, which on heating transform monotropically into the thermodynamically stable monoclinic phase, appear when zirconia is prepared by calcining a salt [3,11] an alkoxide [8], or a hydrous zirconia gel [4–10] under mild conditions. Formation of these phases has been variously explained in terms of non-stoichiometry [7,14], the retention of tenaciously held water or a foreign anion [10], the effect of pH during precipitation of the parent zirconia gel [15], or as a crystallite size effect [3,16]. Although these factors can possibly account for some particular situations, the fact remains that thermal decom-

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position of various zirconium compounds under slightly different conditions leads to ZrO_2 powders with different crystallographic characteristics [10,17,18]. Murase and Kato [19] have recently drawn attention to the role of water vapour on the tetragonal-to-monoclinic phase transformation. They found that water vapour greatly accelerates conversion into the monoclinic phase. The experimental results described in the present paper lend support to this theory, which can explain why calcination of precursors under different conditions leads to zirconia powders of variable crystalline phase. Water vapour retained from the calcination atmosphere appears to be a determining factor.

EXPERIMENTAL

Sample preparation and thermal treatment

Five series of samples were prepared as follows. Zirconium nitrate (supplied by Carlo Erba) with a nominal purity of 99.9% was subjected to thermolysis, either in air or under a dynamic vacuum, for 48 h at 573 K. The resulting materials were subsequently subjected to cumulative thermal treatments for 12 h at increasing temperature, as shown in Table 1. These thermal treatments were carried out, as for the starting material, either in static air or in a dynamic vacuum (ca. 10^{-2} Pa). Samples thus prepared will be hereafter designated by the letters NA (air-calcined series) or NV (vacuum-calcined series) followed by a number which indicates the temperature of the last heat treatment in degrees Kelvin (see Table 1). Thus, NA773 and NV773 are zirconium nitrate samples calcined (in air or vacuum, respectively) for 48 h at 573 K, followed by 12 h at 648 K and finally 12 h at 773 K.

In another series of experiments, hydrous zirconia gel was prepared by precipitation, at room temperature, of an aqueous solution (about 0.1 M) of zirconium nitrate (Carlo Erba, 99.9%) with 12 M aqueous ammonia (Merck pro analysi) to a final pH of 10.5. The gel thus obtained was filtered off and washed free from nitrates (brucine test) with double-distilled water. This was followed by removal of water by sublimation at 260 K in a dynamic vacuum. The resulting xerogel was heated for 48 h at 573 K, followed by cumulative periods of 12 h at increasing temperature, as shown in Table 1. Calcinations were performed either in static air or under a dynamic vacuum, as before. Samples will be termed HAx (air-calcined series) or HVx (vacuum-calcined series), where x denotes the temperature of the last heat treatment.

Samples NW648, NW773 and NW873 were obtained from zirconium nitrate fired at 573 K for 48 h (sample NA573) and subsequently subjected to cumulative periods of 12 h at 648, 773 and 873 K. These calcinations were

TABLE 1

Surface area and crystalline phases of different zirconia samples

Sample	Calcination temperature (K)	Surface area (m^2 g^{-1})	Crystalline phases
HA648	648	79	T, (M)
HA773	773	51	T, (M)
HA873	873	44	T, (M)
HA973	973	29	(T), M
HA1073	1073	26	(T), M
HV648	648	167	C
HV773	773	106	C
HV873	873	–	C
HV973	973	47	T+C, (M)
HV1173	1173	17	(T), M
NA648	648	68	(T+C), M
NA773	773	28	T, M
NA873	873	20	T, M
NA1023	1023	–	T, M
NV648	648	108	C
NV773	773	67	C
NV873	873	43	T+C, (M)
NV1023	1023	5	T, M
NW648	648	–	T, (M)
NW773	773	25	T, M
NW873	873	15	T, M

C, cubic; M, monoclinic; T, tetragonal; parentheses denote phases in minor proportion.

carried out under a flow of oxygen saturated with water vapour at room temperature.

Characterization

To determine the crystalline phases present, all samples were analysed by X-ray diffraction using a powder diffractometer equipped with a graphite crystal monochromator and Cu K_α radiation. BET surface areas were determined by nitrogen adsorption at 77 K, using a volumetric apparatus of conventional design.

RESULTS AND DISCUSSION

The X-ray diffractograms of samples NA573, NV573, HA573 and HV573 showed only a very broad diffraction band covering from 22 to 38° (2θ), which indicates a very low degree of crystallinity. However, for NA573 and NV573 total disappearance of the lines corresponding to the parent zirconium nitrate suggested that thermolysis was complete.

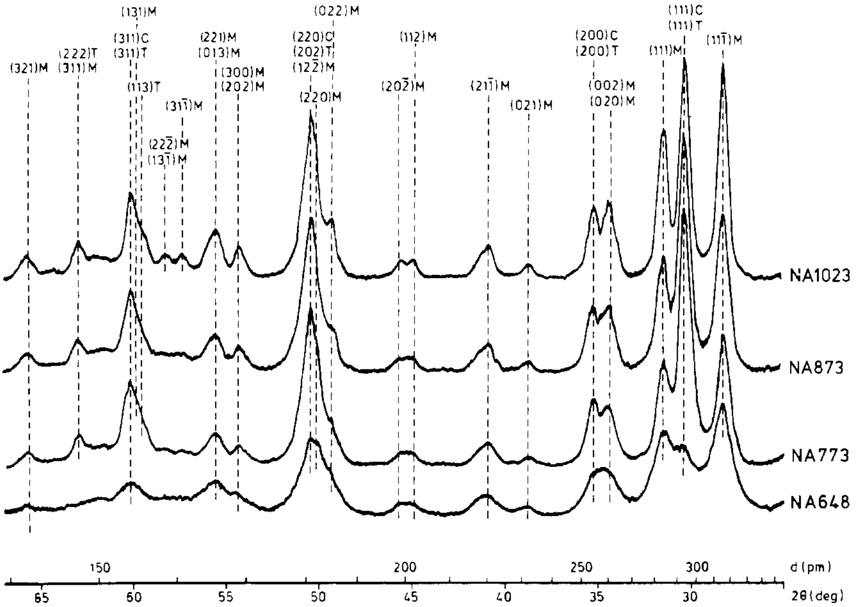

Fig. 1. X-ray diffraction patterns of samples of the NA-series.

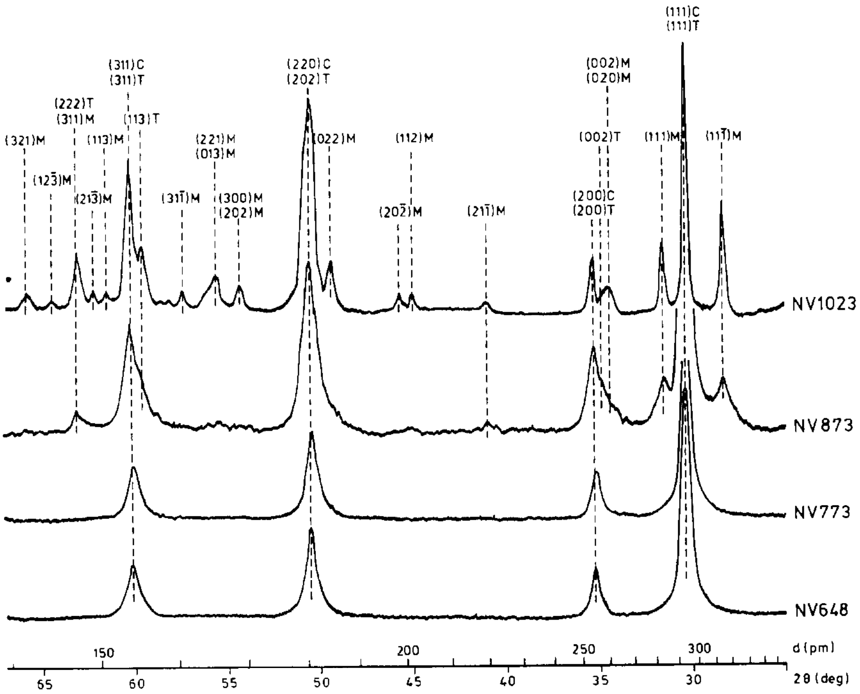

Fig. 2. X-ray diffraction patterns of samples of the NV-series.

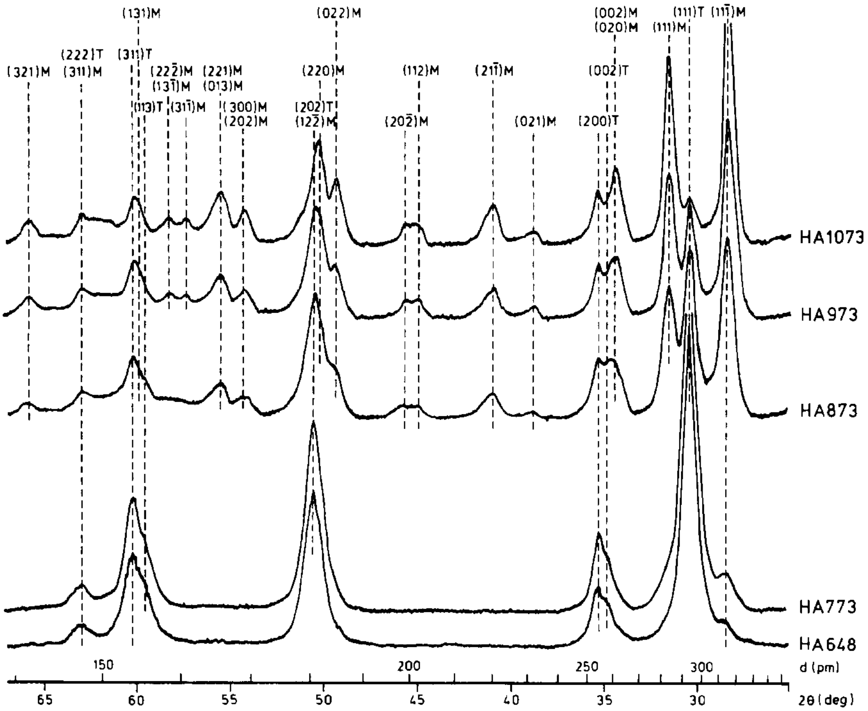

Fig. 3. X-ray diffraction patterns of samples of the HA-series.

Relevant portions of the diffractograms corresponding to the remaining samples are shown in Figs. 1 to 5. Broken vertical lines mark the position of the diffraction maxima corresponding to the cubic, tetragonal and monoclinic phases of pure ZrO_2. For the tetragonal and monoclinic phases, *d*-values were taken from the ASTM cards [20,21], which for tetragonal ZrO_2 corresponds to the high-temperature modification. For the cubic phase, *d*-values were taken from the work of Katz [13] who prepared cubic zirconium dioxide by dehydration of a zirconia gel at low temperature; they correspond to a cubic phase with $a_0 = 509$ pm, which is consistent with the values $a_0 = 510$ pm given by Boganov et al. [22] and $a_0 = 510$ (± 2) pm previously reported by Villa et al. [23]. The reference pattern for cubic ZrO_2 in the ASTM Powder Diffraction File [24] corresponds to an MgO-stabilized zirconia [25], and is likely to be less accurate.

Figures 1 and 3 show that, with the likely exception of NA648 (see below), the air-calcined samples consist of a mixture of the metastable tetragonal and the monoclinic phases of ZrO_2. For HA648 and HA773 (Fig. 3) presence of the monoclinic phase is revealed only by the $(11\bar{1})$ diffraction line, which is the most intense one [21]. The remaining samples of the HA-series show a progressive growth of the monoclinic phase (at the expense of the tetragonal) with increasing temperature. The NA-series (Fig.

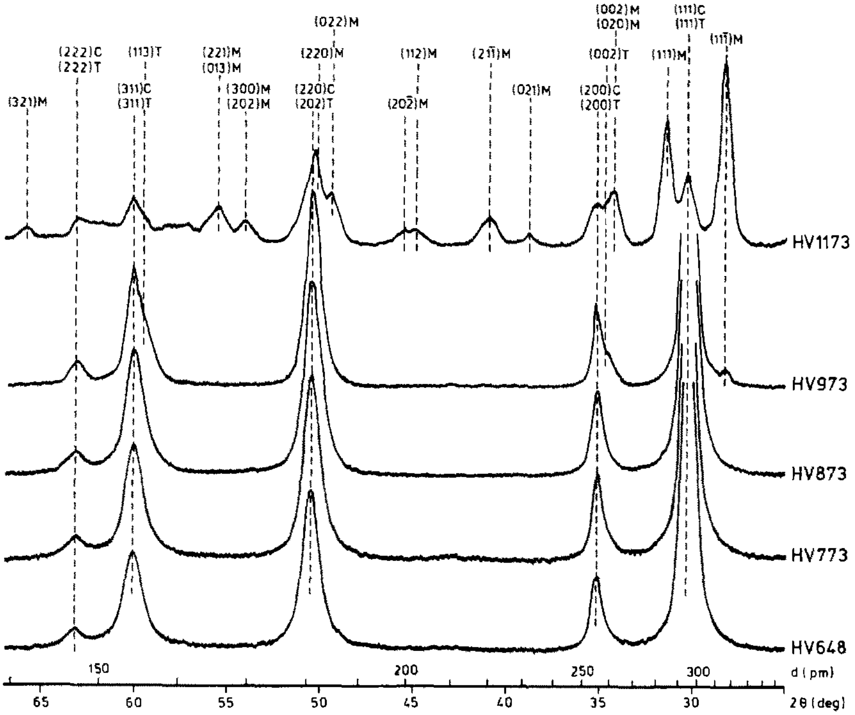

Fig. 4. X-ray diffraction patterns of samples of the HV-series.

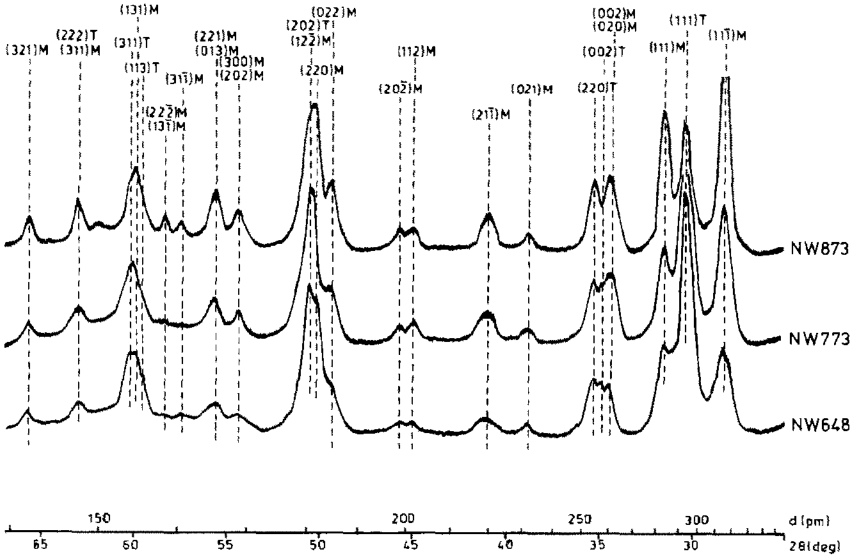

Fig. 5. X-ray diffraction patterns of samples of the NW-series.

TABLE 2

Crystallographic data for the metastable cubic phase of pure ZrO_2

hkl	$d_{obs.}$ (pm)		I/I_0	
	Present work	Katz [13]	Present work	Katz [13]
111	295	293	100	100
200	255	255	20	24
220	180.7	180.1	50	48
311	154	153.4	30	20
222	147	147.1	3	3
400	127	127.0	4	4
331	116	116.7	8	6

1) presents a more complex situation. NA648 shows lines of the monoclinic form along with those of a metastable phase which could either be cubic or tetragonal. Distinction between these two phases rests on the splitting of the (200, 002) and (311, 113) lines of the tetragonal modification, clearly seen in Fig. 3. This criterion is hard to apply to NA648 on account of the low crystallinity of the sample, and the simultaneous presence of diffraction lines from the monoclinic phase. On passing from NA648 to NA773 a pronounced increase of the tetragonal phase is observed, presumably growing from amorphous material present in NA648. For the remaining samples of the NA-series (NA873 and NA1023), Fig. 1 shows a progressive transformation of the tetragonal to the monoclinic modification, although both phases are still prominent in NA1023.

In the vacuum-calcined samples (Figs. 2 and 4) only the metastable cubic phase is observed up to 773 K in the NV-series and 873 K in the HV-series. Table 2 gives details of the crystallographic data for this cubic phase (sample NV648). The lattice parameter was found to be $a_0 = 510$ pm. Samples NV873 and HV973 show the splitting of the (200, 002) and (311, 113) diffraction lines, which reveals the onset of the transformation to the metastable tetragonal form. The corresponding diffractograms also show the simultaneous appearance of the monoclinic phase, which grows when temperature is increased. However, comparison of Figs. 1 and 2, and 3 and 4, shows that for equal temperature the monoclinic/tetragonal ratio is higher for the air-calcined samples.

Series NW (Fig. 5) shows a progressive conversion of the tetragonal into the monoclinic phase with increasing temperature. When comparing samples of this series with the corresponding analogues in the NA-series, the following points emerge: sample NW648 shows a higher degree of crystallinity than NA648, with a dominant tetragonal phase; and for samples calcined at 773 and 873 K, transformation of the tetragonal into the monoclinic phase is faster in the case of the NW-series.

The above crystalline phase analysis is briefly summarized in Table 1, which also shows the BET surface area of the different zirconia samples. Details of the corresponding nitrogen adsorption–desorption isotherms were given elsewhere [11,26,27]. Table 1 shows that, for equal calcination temperature, samples fired in vacuo have a higher surface area than the corresponding samples calcined in air, and those fired in a flow of water vapour saturated oxygen show the smallest surface area. Concomitantly, the presence of water vapour, from atmospheric air or humid oxygen, is seen to accelerate conversion of the tetragonal into the monoclinic phase. The role of water vapour in promoting sintering of metallic oxides has already been stressed by several researchers [28–30]. Increased sintering, and consequent crystallite growth, may be the main factor causing development of the monoclinic phase of zirconium dioxide. This is in agreement with the assumption made by Garvie [3] that the tetragonal phase has a lower surface free energy than the monoclinic phase so that the former stabilizes below a critical size. We may add that all zirconia samples described in the present work were white. This excludes non-stoichiometry effects, since non-stoichiometric zirconium dioxide is known to show a dark-grey or black colour [7,14].

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