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Effects of Mechanical Activation of Inorganic Gels on Their Thermal Behavior. 2. Comparison of Structure and Thermal Behavior between Zirconia and Titania Gels

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Changes in the temperature of crystallization, T_{crys}, due to mechanical pretreatment were entirely opposite between titania and zirconia hydrogels. The T_{crys} of the titania decreased by 18 and 44 K on rotation- and vibration-milling, respectively, while those for the zirconia increased by 14 and 18 K or 16 and 45 K, depending on the starting aqueous solutions, i.e., $ZrOCl_2$ or $ZrO(NO_3)_2$, respectively. These phenomena were discussed in terms of the microscopic phase transformation processes in noncrystalline gels during mechanical treatment. The difference between two hydrogels was concluded to be attributed to the differences in the geometry of the construction units, TiO_6 and ZrO_8, and the bond nature of metal–oxygen and metal–OH between TiO_2 and ZrO_2. © 1991 Academic Press, Inc.

Introduction

For the purpose of controlling the processes of crystallization and dehydration of amorphous inorganic hydrogels, we have studied previously the effect of mechanical activation on the structure and thermal behavior of TiO_2 hydrogels (*1*). The decrease in the temperature of crystallization, T_{crys}, determined from the DTA exothermic peak, was observed as a result of mechanical pretreatment. This was interpreted under an assumption of preordering from the apparently amorphous state to the defective metastable anatase.

We also concluded that the change in the property of the chemical bond between Ti^{4+} and OH^- after mechanical pretreatment significantly influenced the dehydration. Since the dehydration is highly dependent on the metal–hydroxyl interionic interaction, it seems necessary to compare the thermal behavior of TiO_2 gels with those of gels including cations other than Ti to obtain a more general understanding of the dehydration and crystallization processes. ZrO_2 gel seems appropriate for this purpose, for the reasons given below. The electron configurations of Ti^{4+} and Zr^{4+}, both belonging to the IV group of the periodic table, are very similar. However, the crystalline structures of TiO_2 are different from those of ZrO_2, so that the properties of the chemical bond between metal ions and hydroxyl groups are expected to be different between the two oxides, and accordingly between the two gels. It is possible to prepare the amorphous ZrO_2 gel by a method similar to that for TiO_2 gel.

In the present study, light is shed on the crystallographical factors and chemical properties of both hydrogels to elucidate the

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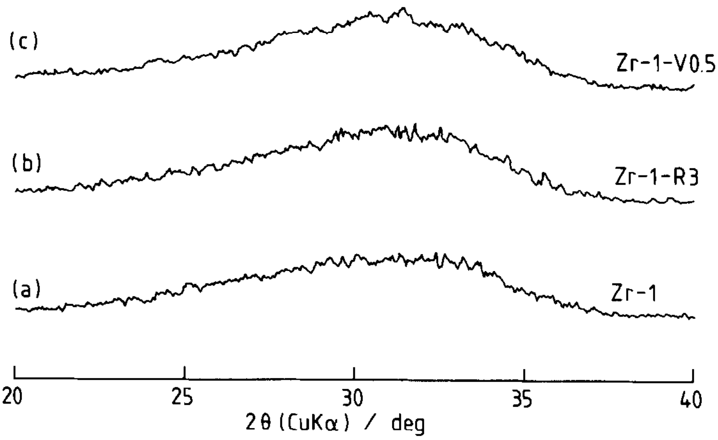

FIG. 1. X-ray diffraction patterns of zirconia gels. (a) Zr-1, (b) Zr-1-R3, (c) Zr-1-V0.5.

difference in the preordering and crystallization processes between TiO_2 and ZrO_2 hydrogels due to applied mechanical stresses.

Experimental

Zirconia sol was prepared by admixing 500 cm^3 of 0.5 M NH_4OH aqueous solution into 500 cm^3 of 0.1 M $ZrOCl_2$ aqueous solution at room temperature. The dialyzed sol was filtered and dried at 323 K for 15 hr. The gel ground with an agate mortar was dried again at 373 K and 1.3×10^3 Pa for 5 hr to obtain the sample Zr-1. The conditions of preparing Zr-1 were kept as similar as possible to those of preparing titania gel Ti-1 (*1*). No trace of NH_4^+ in Zr-1 was detected by the elementary analysis and FT–IR spectroscopy. According to X-ray fluorescence analysis, Zr-1 contained 2.1 wt% Cl, corresponding to 10.6% of the total weight loss by heating. The thermal behavior of the Cl-free zirconia gels, prepared by using $ZrO(NO_3)_2$ instead of $ZrOCl_2$, was also studied to check the influence of Cl. The Cl-free zirconia gels contained a small amount of 0.005 wt% nitrogen due to NO_3^- and NH_4^+ according to the elementary analysis.

The specimen X-1 (X = Zr or Ti) was ground by the rotation ball-mill or by the vibro-mill for m hr to obtain the sample X-1-Rm or X-1-Vm, respectively. Details of the preparation and mechanical pretreatments are given in the previous report (*1*). The amount of Cl decreased from 2.1 to 1.0 wt% after vibro-milling Zr-1 for 0.5 hr, while the weight ratio of Cl/H_2O was kept constant at 0.1. The amount of impurities NO_3^- and NH_4^+ in Cl-free gels prepared from $ZrO(NO_3)_2$ remained unchanged after mechanical treatment.

As reported previously (*1*), the gels were characterized by simultaneous thermogravimetry and differential thermal analysis (TG–DTA), differential scanning calorimetry (DSC), X-ray diffractometry (XRD), transmission electron microscope (TEM), selected area electron diffractometry (SAD), and FT–IR spectroscopy.

Results and Discussion

1. Comparison of the Thermal Behavior of ZrO_2 and TiO_2 Hydrogels after Mechanical Activation

The X-ray diffraction pattern of zirconia gel Zr-1 remained a halo even after rotation ball-milling for 3 hr or vibro-milling for 0.5

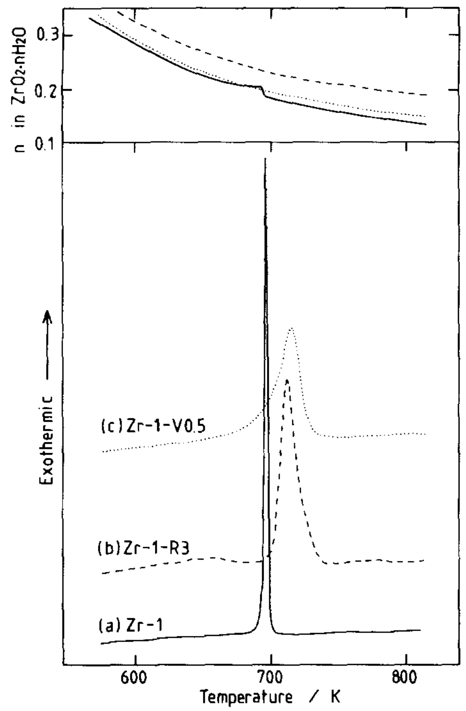

FIG. 2. DTA and TG thermograms of zirconia gels. (a) Zr-1, (b) Zr-1-R3, (c) Zr-1-V0.5.

hr, as shown in Fig. 1. DTA thermograms of zirconia gels are shown in Fig. 2. The exothermic peaks in Fig. 2 are attributed to the crystallization of noncrystalline zirconia into a metastable tetragonal phase, as confirmed from the XRD patterns. The change in the XRD profile with temperature is shown in Fig. 3 for Zr-1.

The peak temperature of crystallization, T_{crys}, increased by 14 K on rotation ball-milling for 3 hr. T_{crys} also increased by 18 and 28 K on vibro-milling for 0.5 and 3 hr, respectively. The T_{crys} of zirconia gels, together with some other properties, is summarized in Table I. The shift of T_{crys} of zirconia gels on mechanical activation is opposite to that of titania gels (*1*).

According to the X-ray fluorescence method, the titania and zirconia gels vibro-milled for 3 hr, Ti-1-V3 and Zr-1-V3, contained 1.79 and 0.95 wt% SiO_2 as an impurity, respectively. The T_{crys} of the former decreased by 44 K, while the T_{crys} of the latter increased by 28 K. Therefore, the change in T_{crys} cannot be explained by assuming the SiO_2 debris from the agate container and balls to be a nucleation site.

The weight loss, expressed conveniently as the hypothetical water content, *n*, of ZrO_2nH_2O, is plotted against the temperature, as shown in Fig. 2. The change in *n* value of ground samples is almost the same as that of Zr-1, although the slightly discontinuous decrease at T_{crys} was detected for unground Zr-1. In contrast, a discontinuous weight loss was observed for ground samples in the case of titania gels (*1*). Thus, the change in the weight loss due to mechanical pretreatment was different between zirconia and titania gels.

A decrease in the specific surface area,

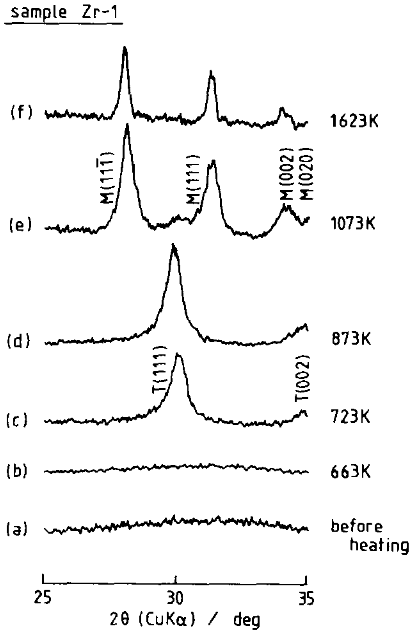

FIG. 3. Change in the XRD pattern of Zr-1 with heating. (a) Room temperature, (b) 663 K, (c) 723 K, (d) 873 K, (e) 1073 K, (f) 1623 K. T, tetragonal phase; M, monoclinic phase.

TABLE I

PROPERTIES OF ZIRCONIA GELS

Sample	S_{BET} ($m^2 g^{-1}$)	n^a	T_{crys} (K)	$T_E - T_S^b$ (K)	$-\Delta H_{crys}$ (kJ mole^{-1})
Zr-1	177	1.7	692 ± 1	5	21.1
Zr-1-R3	99.3	1.2	706	23	18.5
Zr-1-V0.5	24.5	0.8	710	33	15.6
Zr-1-V3	—	0.5	720	135	—

[a] n in ZrO_2nH_2O.

[b] The difference between the initial and the final temperatures of the exothermic peak.

S_{BET}, after grinding was common for ZrO_2 and TiO_2 gels, as shown in Table I and the previous report (*1*). The weight loss was slightly retarded for ZrO_2 gel after grinding, whereas that of TiO_2 gel was accelerated. Hence, the difference in the weight loss cannot mainly be attributed to the granulometrical properties. Instead, the difference in the coordination state of OH^- around cations and impurities between TiO_2 and ZrO_2 gels must have played a more important role.

2. *Color Change during Crystallization*

The color of zirconia gel turned from white to brownish just below T_{crys}, i.e., at 663 K. The brownish color of zirconia gel did not change when it was heated just above T_{crys}, i.e., to 723 K. Thus the color change of ZrO_2 due to heating was different from that of titania gel, the latter having turned suddenly from grayish to yellowish at T_{crys}. The above color changes seem to be related to the formation of the oxygen vacancies on dehydration (*2, 3*). The difference in the color change of two gels at T_{crys} is presumably attributed to the existence of the crystallographical shear (*CS*) in nonstoichiometric titania, which is to be relaxed on crystallization (*1*), while zirconia does not have such *CS* structure.

3. *Existence of a Locally Ordered Area in Apparently Amorphous Gels*

The selected area electron diffraction patterns of zirconia gel Zr-1, shown in Fig. 4a, were mostly halos, while spot patterns were detected locally as shown in Fig. 4b. The interplanar spacings calculated from the location of spots tallied well with those of tetragonal ZrO_2, as shown in Table II. Existence of such an ordered area was confirmed by the "lattice image" observed by the high resolution TEM. An example of such lattice images is shown for Zr-1 in Fig. 5. The distance between the two lines in Fig. 5, 0.291 nm, corresponds to the interplanar spacing of the tetragonal (111). Therefore, it is clear that the preliminary ordering of the tetragonal ZrO_2 exists in a small area in the apparently amorphous zirconia gels. Similar results on amorphous zirconia gels were also reported by other workers (*4, 5*). It seems well possible that the areas of locally ordered tetragonal phase in the XRD amorphous gel serve as embryos and later as nuclei capable of growing upon heating the gel above T_{crys}.

Two kinds of SAD patterns, i.e., one with a halo and the other with spots, were observed for the ground samples. The SAD spot patterns of Zr-1-R3 and Zr-1-V0.5 remained unchanged and identical to those of the tetragonal ZrO_2, as shown in Figs. 4c and 4d, respectively. The interplanar spacing of tetragonal (111) scattered between 0.284 and 0.306 nm for the former and between 0.287 and 0.312 nm for the latter. The fluctuation of the interplanar spacing, due to the scattering of the diffraction spots, was slightly larger than that of Zr-1, i.e., be-

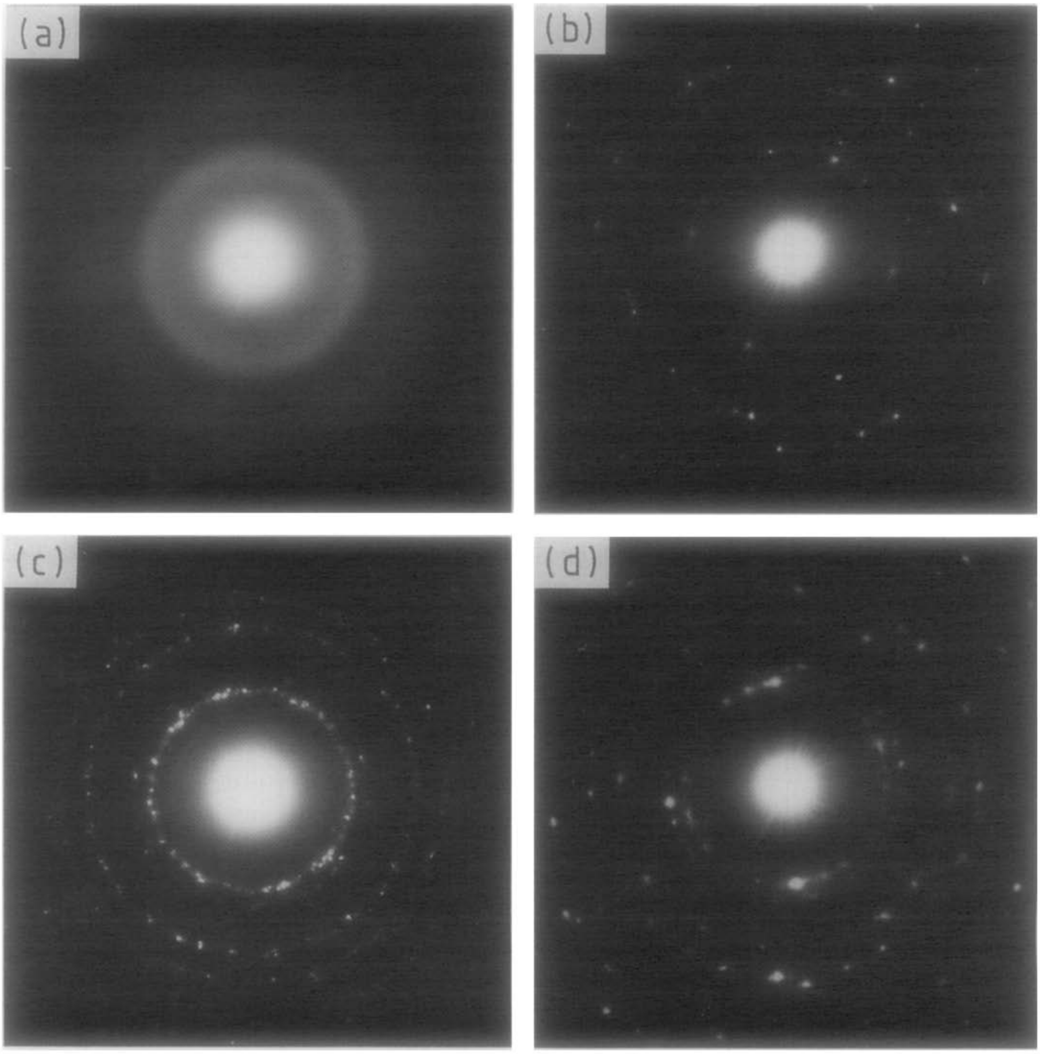

FIG. 4. SAD patterns of zirconia gels. (a), (b) Zr-1, (c) Zr-1-R3, (d) Zr-1-V0.5.

tween 0.287 and 0.294 nm. Apart from the experimental error, the variation here suggests the deviation of the construction unit from the tetragonal coordination state, as a result of deformation.

4. Change in the IR Spectra Due to Mechanical Activation

IR reflection spectra between 415 and 700 cm^{-1} are shown in Fig. 6 for Zr-1 heated up to various temperatures. No absorption band was observed for the zirconia gel Zr-1, as shown in Fig. 6a. The band at 495 cm^{-1} was observed for the well-developed tetragonal phase obtained by heating Zr-1 above 723 K, as shown in Figs. 6c and 6d. Five bands were detected at 429, 455, 546, 574, and 673 cm^{-1} for the monoclinic phase obtained by heating Zr-1 above 1623 K, as shown in Fig. 6f. The band at 546 cm^{-1} was not detected and two bands at 429 and 455

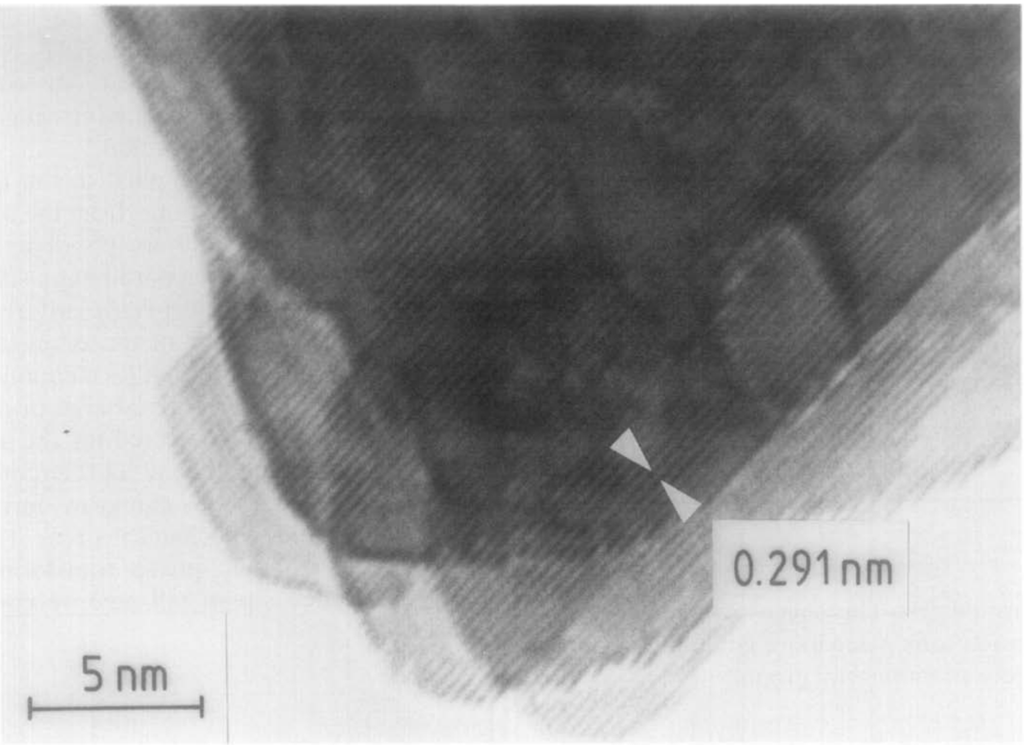

FIG. 5. Lattice image of partially ordered areas in Zr-1.

cm^{-1} were broader for the sample heated up to a temperature as low as 1073 K, as shown in Fig. 6e, although its XRD pattern (Fig. 3e) was already monoclinic. This broadening or absence of the bands due to lattice modes would suggest that the lattice vibrations are disturbed by the lattice distortion due to the oxygen vacancies and the small amount of hydroxyl groups that remains in the "unit cell" when the heating temperature is not high enough.

The broad band at 503 and 510 cm^{-1} was observed for the ground sample Zr-1-R3 and Zr-1-V0.5, as shown in Figs. 7b and 7c, respectively. The appearance of these IR absorption bands seems to be attributed to the ordering by mechanical stressing. These bands were not clear on the transmission spectra. From these observations, it is likely that the ordering due to mechanical stressing takes place preferentially at the gel surface, since the reflection specta are more sensitive to the states at the near-surface region than the transmission ones (*6*). However, the wavenumber of the observed broad band, 503 or 510 cm^{-1}, did not correspond to either tetragonal or monoclinic phase, presumably because of a highly distorted structure due to mechanical stress (*7*).

5. *Enthalpy of Crystallization*

The heat of crystallization, $-\Delta H_{crys}$, of zirconia gels decreased after grinding, as shown in Table I. This also favors the idea discussed in the previous section that the ordering in the apparently amorphous gels occurred during grinding, which should be combined with a partial stabilization. The breadth of the DTA exothermic peak, $T_E - T_S$, shown in Table I, was broader for

TABLE II

INTERPLANAR SPACINGS d_{hkl} CALCULATED FROM SAD SPOTS OF ZIRCONIA GEL ZR-1

d_{hkl} (nm)		
Gel	Tetragonal	(*hkl*)
0.30	0.30	(111)
0.25	0.26	(002)
	0.25	(200)
0.22	0.21	(112)
0.18	0.18	(202), (220)
	0.17	(221), (300)
0.15	0.16	(113)
	0.15	(131), (222)
0.13	0.14	(132), (123), (231)
	0.13	(004)

ground gels. This suggests that the crystallization took place more gradually when gels were preliminarily ground.

6. Ordering Processes of Hydrogels during Mechanical Pretreatment

The *stable* monoclinic phase crystallized for the sample ground by vibro-milling for 3 hr, Zr-1-V3, as shown in Fig. 8a. On the other hand, it was revealed by Raman spectroscopy and SAD (*1*) that the XRD amorphous titania gel ground under the same conditions, Ti-1-V3, had locally preordered states of *metastable* anatase. This difference in the mechanical ordering process between titania and zirconia gels should be related to the opposite shift of T_{crys}, as is discussed below.

It is generally accepted that the application of mechanial stress on the materials with a disordered structure increases the extent of disordering. But this increase cannot always proceed infinitely. Instead, some kind of recovery or relaxation may occur even during the continuation of mechanical stressing, leading, in most cases, to long-range ordering or crystallization. Since the hydrogels contain structural units characteristic of the respective oxides, i.e., TiO_2 and ZrO_2 in the present case, the process of crystallization by mechanical stressing could be understood as an apparent "microscopic structural transformation."

When shear stress is applied to the hydrogels, two relaxation routes from the mechanically activated state are possible: (i) the transformation of the coordination state of the structural unit (short-range order) itself, and (ii) the ordering of those units to form the long-range ordering. As mentioned previously, the locally ordered area of the metastable phase was detected for the apparently amorphous titania and zirconia gels. These ordered areas can grow during the relaxation under mechanical stress. The ease of "microscopic phase transformation" by applied stress will now be com-

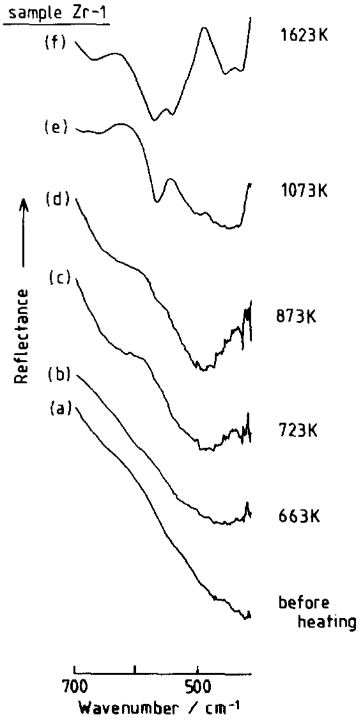

FIG. 6. Change in IR reflection spectrum of Zr-1 with heating. (a) Room Temperature, (b) 663 K, (c) 723 K, (d) 873 K, (e) 1073 K, (f) 1623 K.

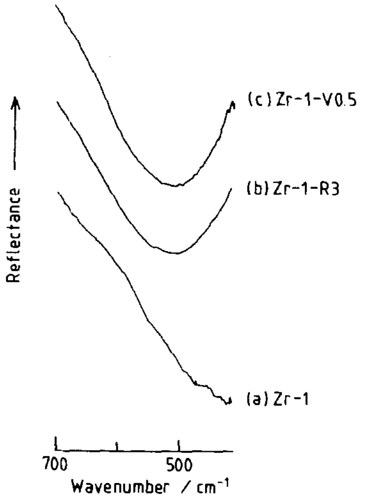

FIG. 7. IR reflection spectra of zirconia gels. (a) Zr-1, (b) Zr-1-R3, (c) Zr-1-V0.5.

pared between two kinds of gels on the basis of crystalline structure.

7. Difference in the Microscopic Phase Transformation Processes between ZrO_2 and TiO_2 Hydrogels

The electron configurations of Ti^{4+} and Zr^{4+} are the Ar and Kr closed shells, respectively. The coordination number of oxygen around Zr^{4+} for ZrO_2 is larger than that around Ti^{4+} for TiO_2. The former for the monoclinic and tetragonal phase is seven and eight, respectively, whereas the latter is six for anatase and rutile. The packing structure of oxygen is the distorted cubic closest packing (ccp) for anatase and the distorted hexagonal closest packing (hcp) for rutile (*8*), while that of ZrO_2 is not closest. The maximum cationic radius in the octahedral void of the closely packed oxygen is about 0.06 nm, being almost the same as that of Ti^{4+}, i.e., 0.0605 nm for sixfold coordination. This is smaller than that of Zr^{4+}, i.e., 0.078 and 0.084 nm for sevenfold and eightfold coordination, respectively (*9*). Because of this geometrical reason, the coordination number of oxygen around Zr^{4+} is larger than that of Ti^{4+}.

The maximum adsorbable amount of water on the surface of Zr-1 is 0.4 mole per 1 mole ZrO_2, being calculated by assuming the adsorption cross section of H_2O to be 10.8×10^{-20} m^2 (*10*). The amount of water, $n = 0.4$, is much smaller than experimentally found, $n = 1.5$, after correcting for Cl. In addition to that, the amount of water included in titania gel Ti-1 was smaller than that in zirconia gel Zr-1 in spite of larger S_{BET}. This remains valid even after the correction for the impurities; i.e., for titania, S_{BET} was 325 m^2 g^{-1}, where the net n value was 1.0, whereas for zirconia, S_{BET} was 177 m^2 g^{-1}, and the net n value was 1.5. The free volume in ZrO_2 is larger than that of TiO_2, since the oxygen packing of the former is not closest as mentioned above. Therefore, the lattice unit of ZrO_2 gel has a larger void to contain a larger number of hydroxyl groups, leading to the higher water content in the zirconia gel.

During the phase transformation of anatase to rutile, two Ti–O bonds in a TiO_6 polyhedron must be broken. Ti^{4+} and O^{2-} then move cooperatively; i.e., Ti^{4+} moves from an octahedral site to a new octahedral site and the packing structure of oxygen turns from ccp to hcp (*8*). On the other hand,

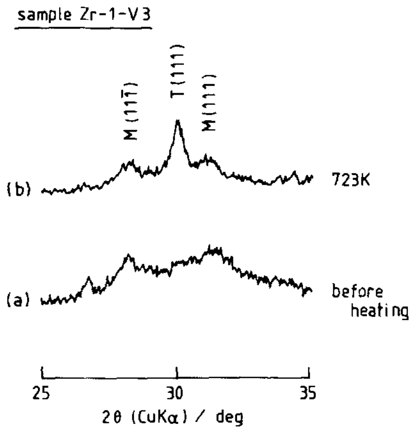

FIG. 8. Change in the XRD pattern of Zr-1-V3 with heating. (a) Room temperature, (b) 723 K. T, tetragonal phase; M, monoclinic phase.

the transformation of ZrO_2 from tetragonal phase to monoclinic phase occurs by gliding in the direction of the *c* axis through the breakage of one Zr–O bond in ZrO_8 (*11*). The dissociation energy of two Ti–O bonds, 13.8 eV, is larger than that of one Zr–O, 7.8 eV (*12*). Hence, it is expected that, under the mechanical stress, the phase transformation of tetragonal ZrO_2 into monoclinic ZrO_2 is easier than that of anatase into rutile for TiO_2.

8. Relation between Microscopic Transformation and Macroscopic Crystallization

The low crystalline monoclinic phase crystallized from the noncrystalline parts for the sample vibro-milled for 3 hr, Zr-1-V3, as shown in Fig. 8a. The temperature of the crystallization of Zr-1-V3 was 720 K, being larger than that of Zr-1, 692 K. By heating Zr-1-V3 up to 723 K, the XRD peak intensity of the monoclinic phase remained unchanged while that of the tetragonal phase increased, as shown in Fig. 8b. These results suggest that the tetragonal phase nucleated from the noncrystalline parts.

As mentioned above, the apparently noncrystalline ZrO_2 gel has a preliminary ordering of the tetragonal phase. Moreover, it is very likely that the area which gives a halo pattern in SAD analysis comprises the construction units of eightfold coordination as well, as inferred from the neutron diffraction analysis given in Ref. (*5*). Hence, the change in the coordination number of Zr from 8 to 7 should have occurred during the crystallization of the monoclinic phase via the mechanical route. At the same time, the rest of the eightfold coordination units were deformed during mechanical activation, as confirmed from the broader distribution of the (111) spots of SAD (Fig.4) and the shift of IR bands toward the higher energy side (Fig. 7). These changes in the construction units require extra energy for the rearrangement of the oxygen atoms around Zr in order for the tetragonal phase to crystallize on heating. This explains the shift of T_{crys} of ZrO_2 gels toward higher temperatures by mechanical activation.

The above-mentioned change in the coordination state may also bring about the stronger Zr–OH bonds in the ZrO_7 polyhedron, since the average Zr–O bond length, 0.2159 nm, of the monoclinic phase is smaller than that of the tetragonal phase, 0.2260 nm (*11*, *13*). In fact, the dehydration of ZrO_2 gel is delayed after grinding, as shown in Fig. 2.

The T_{crys}, 694 K, of Cl-free zirconia gel prepared from $ZrO(NO_3)_2$ also increased by 16 K on ball-milling for 3 hr or by 45 K on vibro-milling for 0.5 hr, respectively. In contrast, the T_{crys} of Zr-1, prepared by $ZrOCl_2$, increased by 14 or 18 K under the same grinding conditions, respectively. The difference in the shifts of T_{crys} by mechanical stress between two gels may be attributed to the difference in the species and amounts of impurities. The former contained 2.1 wt% Cl while the latter contained 0.005 wt% N. The role of impurities is to delay the rate of the transformation of tetragonal into monoclinic under the applied stress, leading to the decrease in the shift of T_{crys}. A similar phenomenon was observed in the case of phase transformation of $CaCO_3$ from aragonite into calcite, where the decrease in the rate of transformation was explained by the pinning effect of Pb^{2+} or Sr^{2+} substituting Ca^{2+} (*14*).

In contrast, the preliminary formation of the structural units of anatase favorably occurred during the grinding of TiO_2 gel (*1*). This may be interpreted as a kind of nucleation. Preformed nuclei could grow easily on subsequent heating. This should lead to the decrease in T_{crys}.

Conclusion

The tetragonal phase, already present microscopically in the apparently amorphous zirconia gel, transformed to the monoclinic phase by mechanical stressing. The rearrangement of oxygen ions in noncrystalline parts, from which the tetragonal nuclei are born, is necessary for the crystallization of the mechanically pretreated ZrO_2 hydrogel. This delays the growth of the tetragonal phase on subsequenty heating, leading to a higher T_{crys}. In contrast, the decrease in the T_{crys} of titania gels after grinding is attributed to the precursory ordering of anatase during mechanical stressing. The difference in the microscopic structural relaxation as well as the dehydration between TiO_2 and ZrO_2 gels is therefore attributed to the differences in the geometry of the construction units, TiO_6 and ZrO_8, and the bond nature of metal–oxygen and metal–OH between TiO_2 and ZrO_2.

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