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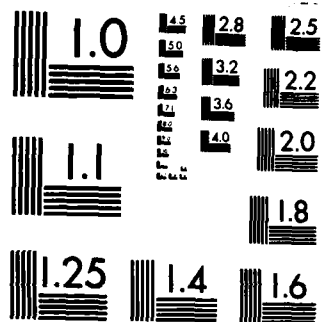
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INTRODUCTION OF STRUCTURAL VARIATIONS INTO OXIDE
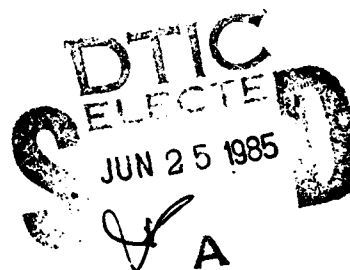POLYMERS AND THEIR EFFECT ON SINTERING AND
CRYSTALLIZATION

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FINAL REPORT

Bulent E. Yoldas

February 11, 1985

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CRYSTALLIZATION

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U.S. Army Research Office
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SOL,	SILANE,	SINTERING	CONDENSATION,	TITANIUM DIOXIDE,
GEL,	SILOXANES	SOLUTION,	CRYSTALLIZATION,	TITANIUM OXIDE,
POLYMERS,	HYDROLYSIS	TRANSFORMATION	POLYMERIZATION,	
SILICA,	ZIRCONIA	HYDROLYTIC	MORPHOLOGY	
ALKOXIDES,	ZIRCONIUM OXIDE	ORGANOMETALLIC	TITANIA	

Hydrolytic polycondensation of metal alkoxides produces polymeric units consisting of an oxide network framed by hydroxyl and organic groups. The morphology of the polymerization as well as the structure of these materials is determined by the kinetics of hydrolysis polymerization reactions. By controlling the kinetics of these reactions it is possible to produce modified ceramic materials with altered properties. In this work, by using three representative systems, i.e., silica, titania and zirconia, the effect of hydrolytic polycondensation parameters on the resultant materials was investigated. These parameters include:

20. ABSTRACT CONTINUED

molecular separation of species, their ratios, the reaction medium, the concentration of catalyst, the reaction time, the temperature and the type of alkyl group in the alkoxide.

In the silica system, the specific effects of these parameters on the polymeric make-up and molecular size distribution during the hydrolytic polycondensation of $Si(OC_2H_5)_4$ were investigated. There is strong evidence that the molecular size expansion occurs by two distinct processes: initially by a gradual "growth" process, and later by "recombination" of high-molecular weight species. The latter process often leads to a bi-modal distribution of molecular sizes. The effect of molecular variations in these polymers are also reflected in the behavior and properties of the oxide materials obtained by their thermal degradation.

In the titania system, the parameters that affect the hydrolytic polycondensation of titanium alkoxides $Ti(OR)_4$ were investigated. Titanium alkoxides vigorously hydrolyze with water, producing polycondensations whose equivalent oxide contents vary from 70 to over 90%, reflecting the average molecular size. The morphology of the resultant materials is also affected by the conditions of hydrolysis. The resultant morphologies, in turn, affect the sintering and crystallization behavior of the titanium oxides. The hydrolytic conditions that lead to the formation of clear polymer solutions under excess water is also presented. Investigations indicate that the long term stability is provided by the existence of a window in the acid concentration.

In the zirconia system, it has been shown that the alkyl groups and molecular separation during the hydrolytic condensation have particular significance in the modification of the monoclinic $\rightleftharpoons$ tetragonal transformation of the resultant ZrO_2. It has also been shown that the tetragonal phase produced by the hydrolysis of $Zr(OC_3H_7)_4$ can be stabilized by co-polymerization with silicon at room temperature.

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PART I

HYDROLYTIC POLYCONDENSATION OF Si(OC$_2$H$_5$)$_4$ AND EFFECT OF REACTION PARAMETERS ON POLYMERIZATION

1-1. INTRODUCTION

Investigation of hydrolysis reactions of alkoxysilanes goes

back as far as 1846.[1] Recently there has been a resurgence of interest

in this field, partly because the hydrolytic polycondensation reactions

construct an oxide network similar to that of quartz, thus suggesting

a possible way to form glass and ceramic materials by chemical

polymerization.[2-6] This intriguing possibility led to the investigation

of glass and ceramic formation by the so-called "sol-gel" process, and

comparison of these glasses to those formed by the traditional melting

process.[7-12] The initial interest in this field focused on the use

of the solution characteristics of these systems to attain a high degree

of homogeneity.[13] Later it was shown that large monoliths of SiO$_2$ could

be produced by the "sol-gel" process.[14-15]

Hydrolysis of tetraalkoxysilanes has been reviewed in many

excellent works.[16-20] In the work described here the effect of hydrolysis

conditions on the molecular make-up and size distribution, investigated

by size-exclusion liquid chromotography (SEC), as well as on the oxide

content of the resultant polymers have been studied. SEC separates molecules

according to their effective size in solution.[2] Separation occurs strictly on

the basis of a molecular size for molecules up to $\sim 10^8$, and can be

detected by a refractometer. Measurements were carried out at room

temperature with 1% solutions in alcohols.

1

Accurate molecular weights can be obtained only if exact calibration is available with standards of similar and known molecular weights. It is acceptable, however, to use sufficiently similar standards for comparison. Even though the exact molecular weights obtained in this fashion can be in error by a factor of two or three, the general shape of the size distribution curves and comparisons among them remain valid and provide useful information.[22]

One immediate effect of the polymer morphology and its size is reflected in the oxide contents of the polysiloxane polymers. The equivalent oxide content of dried polyorganosiloxanes, and that of the other polycondensed gels of metal alkoxides, gives a revealing insight into the average size and branching of these molecules. This simple and powerful tool has been dealt with in two previous papers.[23-24]

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1-2. HYDROLYTIC POLYCONDENSATION OF $Si(OC_2H_5)_4$

Silicon bonds with "OR" groups may be readily broken by water, causing partial hydrolysis:

$$(OR)_3 \equiv Si-OR + HOH \rightarrow (OR)_3 \equiv Si-OH + R(OH) \quad . \quad (1)$$
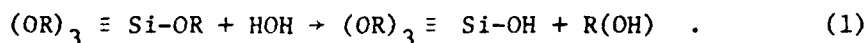
This reaction is normally carried out in a mutual solvent since $Si(OR)_4$ and H_2O are immiscible. The rate of reaction is significantly affected by the presence of catalysts--e.g., HNO_3 and HCl acids--and by temperature.

Subsequent reactions are process dependent, controlled not only by the basic chemistry but also by statistical probabilities and limitations induced by diffusion rates and concentrations. For example, total hydrolysis of the remaining bonds of $(OR)_3 \equiv Si-OH$ to a monomer $Si(OH)_4$ requires that interactions with any other species present during the hydrolysis process are precluded. Otherwise a polymerization reaction takes place:

$$\equiv Si-OH + RO-Si \equiv \rightarrow \equiv Si-O-Si \equiv + R(OH) \quad . \quad (2)$$
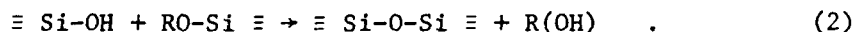
Since the infinite separation of polymeric species is not possible in practice, both reactions take place simultaneously creating not only a number of partially hydrolyzed species, but also a range of molecular-sizes. "OR" bonds are removed either by hydrolysis or by polymerization reactions. The mobility of the species in the reaction medium, the average diffusion distances, and the effect of the catalyst reaction temperature all play an important role in the selection of these reactions, and thus affect the morphology of the polymeric structures.

Parameters that introduce structural variations in polymer gel structures as listed in Ref. 25 are:

- Hydrolysis medium
- $H_2O/Si(OR)_4$ ratio
- Molecular separation by dilution
- Catalyst
- Temperature and time

The specific effects of each of these parameters on the hydrolytically polycondensed materials from $Si(OC_2H_5)_4$ and discussed in the following subsections.

1.2.1 Catalytic Effect

Both the hydrolysis (1) and polymerization (2) reactions are affected by the presence of a catalyst. Mineral acids such as HNO_3 and HCl are particularly effective catalysts for these reactions. Since these reactions are exothermic, increasing acid additions cause increased heating of the hydrolysis liquor as shown in Figure 1. In this experiment, 0.125, 0.375, 1.25, and 2.5 grams of HNO_3 acid were introduced into four freshly prepared identical liquors containing 208 g $Si(OC_2H_5)_4$ (1 mole), 36 g H_2O (2 moles), and 131 g dry ethyl alcohol, corresponding to a solution concentration of 16% wt. eq. SiO_2. As shown in Figure 1, the samples containing 1.25 and 2.5 g of HNO_3 reached their peak temperature just below 50°C within 15 minutes, whereas the sample containing 0.125 g of HNO_3 took over an hour to reach its peak temperature (~37°C). A diminishing difference between the 1.25 g and 2.5 g acid containing samples indicates that the catalytic effect of HNO_3 becomes saturated at about ~1.0 g HNO_3 per mole of $Si(OC_2H_5)_4$.
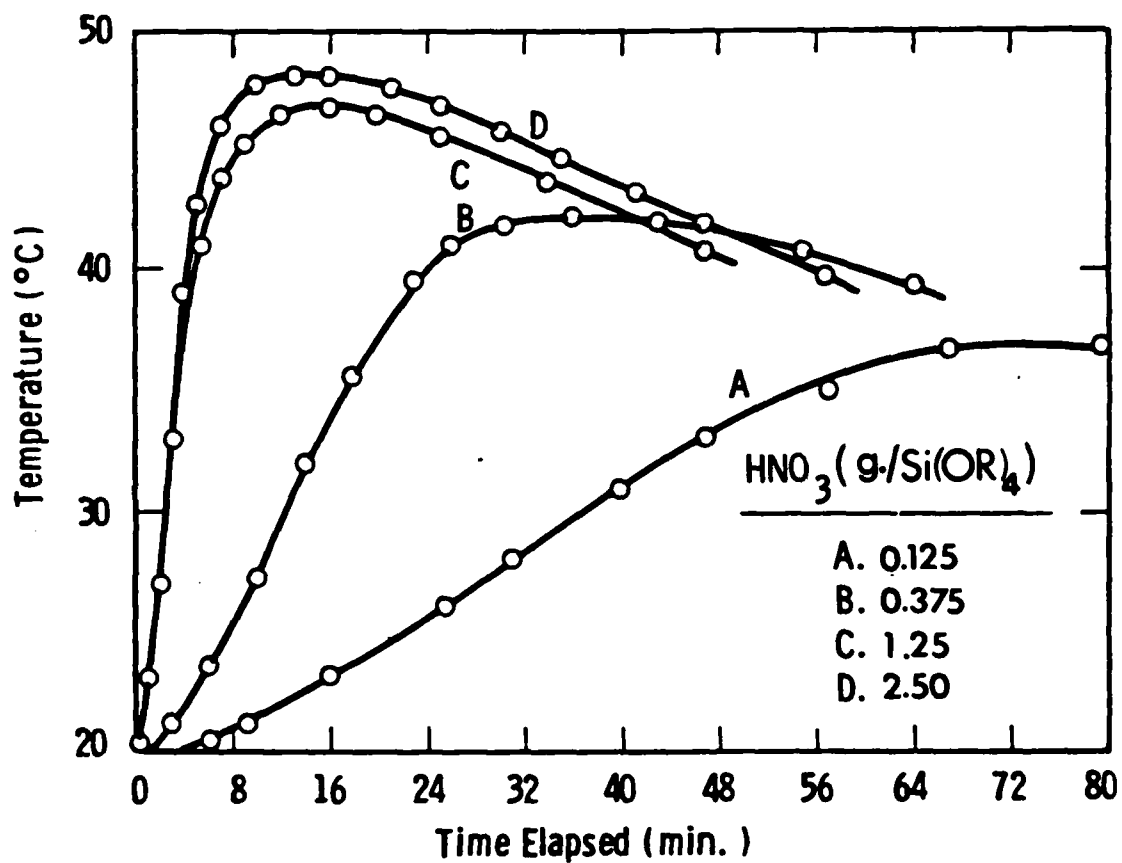
Figure 1. Effect of HNO_3 concentration on the heat generation of reactions during the 2 m H_2O hydrolysis of $Si(OC_2H_5)_4$ in ethanol at 15 % wt eq. SiO_2 solution concentration.

The rate of heating also gives an indication as to whether the hydrolysis or the polymerization reaction is favored. Hydrolysis reactions only require diffusion of relatively mobile water in the medium, whereas polymerization reactions require diffusion of larger and much slower organosiloxane molecules.

The long-term effect of acid catalysts on the molecular size distribution is also significant. Figure 2 shows the molecular weight distributions of two samples, prepared similarly to those described above, except that one contains 150 mg and the other 600 mg of HNO_3. After 24 hrs and after 7 days at 60°C, SEC fractionations were done in ethyl alcohol; points A, B, and C correspond to molecular weights of 400, 20,000, and 10^6 as calibrated by polyethylene glycols.

These molecular size distribution curves almost always show a bi-modal size distribution. The second peak occurs in later stages of the polymerization process. It appears that the initial hydrolysis-polymerization reactions create two types of high-molecular species, passive, P, and active P^*:

$$\text{Hydrolysis-polymerization} \rightarrow n_1 \, P + n_2 \, P^* \; . \tag{3}$$
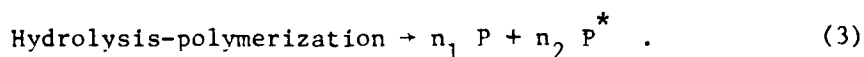
Active species are capable of combining with each other, creating even larger molecules:

$$P^* + P^* \rightarrow P_2^* \tag{4}$$

This gives rise to the second peak of the bi-modal distribution.

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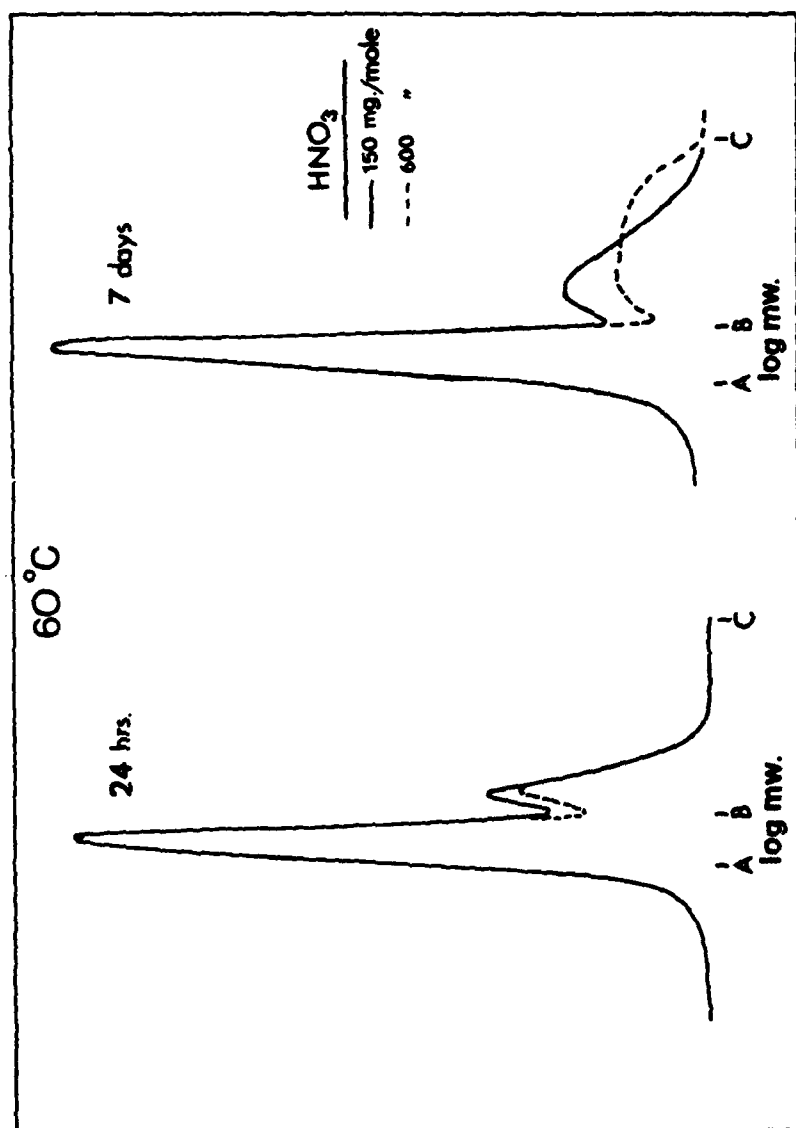
Figure 2. Effect of acid concentration on the molecular-weight distribution of polyorganosiloxanes formed by 2.2 mole H_2O hydrolysis of $Si(OC_2H_5)_4$ in ethanol after 24 hrs and 7 days at 60°C. (Solution concentration: 16% wt eq. SiO_2; points A, B and C would correspond to molecular weights of 400, 20,000 and 10^6 in polyethylene glycol standards.)

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In reaction (3) both polymeric species are created by an initial "growth" process involving monomers and small molecules as structural building blocks. In the course of statistical interactions during the construction of polymeric networks some high molecular species end up with essentially all "OH" terminal bonds. These are the relatively passive, "P", species. Some of the high molecular species, on the other hand, end up still containing a significant number of "OR" terminal bonds which can only be removed by further hydrolysis or polymerization. If the amount of water in the liquor is substantially exhausted, the hydrolysis reactions previously favored becomes unfeasible; thus this species enter into slow recombination reactions with each other. This causes a discontinuous jump on the molecular-weight distributions since "recombination" reactions multiply the molecular weight whereas the "growth" reactions contribute smooth continuous additions. This theory is supported by the fact that the size expansion of the second peak occurs at the expense of its population of species, and comes at a later stage. This recombination process is strongly affected by temperature as well as acid concentrations. It also causes organosiloxane gels to shrink within their liquor. Samples held at room temperature do not show the dramatic molecular-weight expansion shown at 60°C.

This effect of acid on polymer size is independently indicated by the increasing oxide content of the polymers for increasing concentration of acid (Table 1). The diminishing effect of acid concentration at a higher solution concentration is due to the effect of molecular spacing which is discussed later. In the experiments from this point on, unless otherwise specified, 150 mg HNO_3 per mole of $Si(OC_2H_5)_4$ is used.

Table 1

Effect of Acid Concentration at Various Molecular Separations
During the Hydrolysis of $Si(OC_2H_5)_4$ with 2 Moles of H_2O in Ethanol

Solution Concentration (% wt. eq. SiO2)	Oxide Content of Gel (% wt.)[*]		
	12 mg HNO3/m	360 mg HNO3/m	Δ(%)
2	--	∿63	--
4	∿61	∿68	7
8	∿69	∿71	2
16	∿73	∿74	1

[*]After 24 hrs at 60°C.

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1.2.2 Effects of Temperature and Time

Higher reaction temperatures and longer reaction times shift the molecular size distribution to higher values. Figure 3 shows the temperature and time effects on the molecular-weight distribution when $Si(OC_2H_5)_4$ is hydrolyzed with 2 m H_2O at 16% wt. eg. SiO_2 concentration. Seven days exposure at 20°C has approximately the same effect as 24 hrs at 60°C. This effect is more pronounced at higher solution concentrations and at higher $H_2O/Si(OC_2H_5)_4$ ratios (see Figures 1 and 3 in Reference 25).

One other significant effect of time and temperature is reflected by the tendency of these organosiloxane polymers to form carbon during the thermal degradation. Carbon formation tendency diminishes with increasing hydrolysis temperature and longer times.[2,6]

1.2.3 Effect of Hydrolysis Medium

Table 2 shows the oxide content of dried gels produced by 2 m H_2O hydrolysis of $Si(OC_2H_5)_4$ in methanol, ethanol, and 2-propanol. These solutions, after 24 hrs at 60°C, were gelled by rapid evaporation, then dried at 120°C for 24 hrs and calcined to 600°C to determine the oxide content. As can be seen from Table 2, the oxide content is strongly dependent on the solution concentration for all three alcohols. The fact that the oxide content of the polymers formed in methanol is higher may be explained by the fact that diffusion dependent polymer growth is less restricted in methanol (because of its low molecular weight), allowing higher mobility to the species. Higher solution concentrations have smaller molecular separations, which lessens the dependence on

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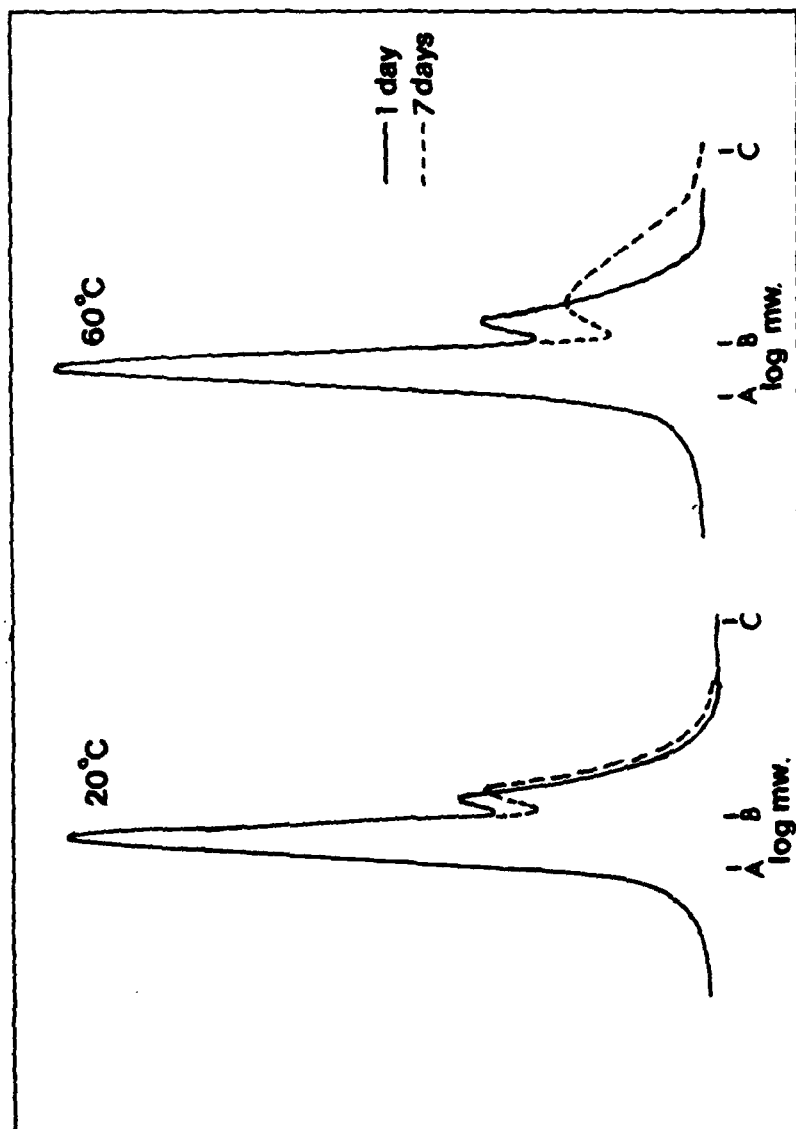
Figure 3. Effect of temperature and time on the molecular-weight distribution of polyorganosiloxanes produced by 2.2 m H_2O hydrolysis of $Si(OC_2H_5)_4$ in ethanol at 16% wt eq. SiO_2 concentration.

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Table 2

Effect of Solution Concentration During Hydrolysis on the Oxide Content of
Gels Formed by 2 Mole Water Hydrolysis of $Si(OC_2H_5)_4$ in Different Alcohols

Solution Concentration (% wt. eq. SiO_2)	Oxide Content of Gels (%wt.) formed in		
	Methanol	Ethanol	n-Propanol
1	83	64	–
4	81	66	46
16	78	75	83

diffusion; thus the differential effect of various alcohols tends to diminish at higher concentrations. The reverse effect of the solution concentration in methanol is not clearly understood, but may be due to the fact that hydrolysis is sufficiently complete. Thus no extensive "recombination", which requires "OR" bonds as discussed earlier, takes place.

The molecular-weight measurements in propanol give support to the oxide content data, showing low molecular weight species, incomplete hydrolysis, and even the presence of free water after 24 hrs. The hump on the left side of the molecular weight distribution curve of the solution formed in 2-propanol in Figure 4 is attributed to partially hydrolyzed species having very little if any polymerization. However, this condition changes drastically with increasing solution concentration in propanol, since higher concentration obviates the dependence on diffusion.

1.2.4 Effect of $H_2O/Si(OC_2H_5)_4$ Ratio

The effect of water concentration is one of the most important parameters in determining the chemical make-up, morphology and size distribution of polyorganosiloxane polymers. Unlike the other parameters (e.g., temperature, catalysts, concentrations, etc.), the water is directly involved in the chemical reactions that form the molecular structure. It must be emphasized, however, that the role of water concentration goes beyond the chemical requirements of hydrolysis. The molecular separation and concentration of the water determines the nature of the chemical reactions by influencing the statistical interactions.

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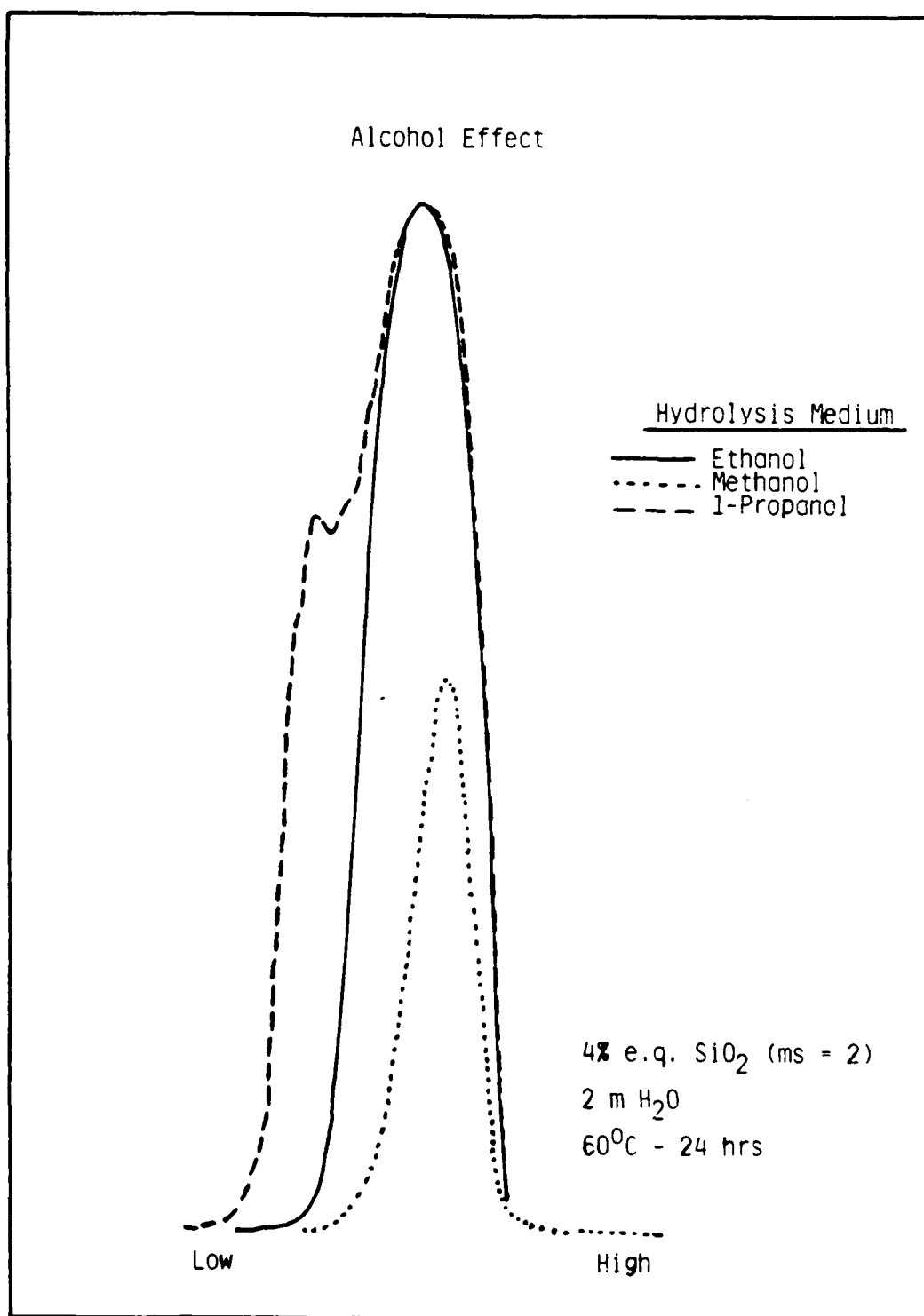
Figure 4. Molecular weight distribution curves of polyorganosiloxanes
produced by 2 m H_2O hydrolysis of $Si(OC_2H_5)_4$ in methanol,
ethanol, and 2-propanol after 24 hrs at 60°C. (Solution
concentration is 4% wt eq. SiO_2; 24 hrs at 60°C.)

The chemical requirement of water falls between 2 and 4 moles for a complete hydrolysis of the $Si(OR)_4$ specie in a monomer form; i.e., $Si(OH)_4$ would require 4 moles of water per mole of $Si(OR)_4$. However, this precludes any polymerization between species, and thus requires an infinite separation of the hydrolyzed species:

$$Si(OR)_4 + 4H_2O \rightarrow \overset{\displaystyle OH}{\underset{\displaystyle OH}{OH-\underset{|}{\overset{|}{Si}}-OH}} + 4R(OH) \quad . \tag{4}$$
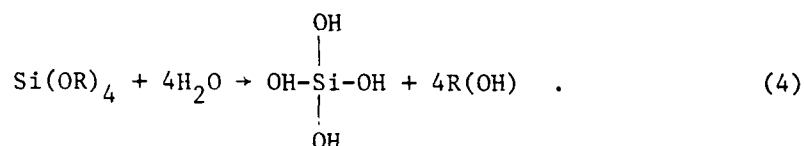
On the other hand, the chemical requirement of water would be 2 moles per mole $Si(OR)_4$ if an infinite polymerization takes place:

$$n\ Si(OR)_4 + 2\ nH_2O \rightarrow \left[\begin{matrix} & O & \\ | & | & | \\ O- & Si & -O \\ | & | & | \\ & O & \end{matrix} \right]_n + 4\ nROH \tag{5}$$
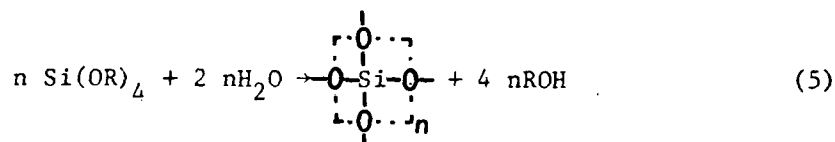
This reaction precludes the presence of any surface ($n \rightarrow \infty$) hydroxyl groups, since an ideal infinite polymer of SiO_2 is formed. Reality falls between these two extreme cases, but is much closer to the latter. The molecular weights of these polycondensed materials are generally in the thousands. The water requirement, from a purely chemical point of view, is slightly in excess of 2 moles, but its actual effect goes much beyond 4 moles of water.[23,25]

Table 3 shows the oxide content of polymers produced by hydrolysis of $Si(OC_2H_5)_4$ with 2 moles and 16 moles of water in methanol, ethanol, and 2-propanol. In all three reaction media , increasing amounts of water causes a significant increase in the oxide content. The effect of a high concentration of H_2O on the molecular weight distribution as determined by SEC is to broaden the distribution in high as well as low

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Table 3

Effect of Reaction Medium on the Oxide Content of Polymers Obtained by
2 and 16 Moles H_2O Hydrolysis of $Si(OC_2H_5)_4$

Water per $Si(OC_2H_5)_4$	Oxide Content of Gels (%wt) Formed in		
	Methanol	Ethanol	n-Propanol
2 moles	~81	~66	~46
16 moles	~93	~89	~83

molecular weight directions (compare the dotted and solid lines in Figure 5). Again, a higher water concentration causes a secondary peak of high molecular weight to occur in the late stages of polymerization.

1.2.5 Effect of Solution Concentration on Molecular Separation

Without changing all other parameters discussed earlier, one may change the molecular separation simply by diluting the system. Under diluted conditions, larger molecular separations result. Mobility of various species in that reaction medium becomes more important. Statistical probabilities of chemical interactions--which determine the size and shape of polymeric molecules--are altered. Diffusion rates often become the limiting factor.

As shown in Tables 1 and 2, higher solution concentrations generally yield polymers having a higher oxide content. Figure 6 shows the effect of solution concentration, expressed in terms of molecular spacing, on the oxide content of the polymer produced by 2 moles H_2O hydrolysis of $Si(OC_2H_5)_4$ in ethanol. Molecular spacing in pure $Si(OC_2H_5)_4$ is taken as unity, and separations in the hydrolysis medium are expressed in terms of multiples of this unit. Table 4 gives the relationship between the equivalent SiO_2 concentration of solution and the molecular spacing when $Si(OC_2H_5)_4$ is hydrolyzed by 2 m H_2O in ethanol. It should be noted that a critical amount of alcohol is necessary to make the mutually immiscible $Si(OC_2H_5)_4$ and H_2O a single-phase mixture. This requirement puts a limit on the maximum solution concentration, expressed in equivalent silica, of slightly over 17% by weight (ms $\sim$ 1.2). There is, of course, no limit to larger molecular separations.

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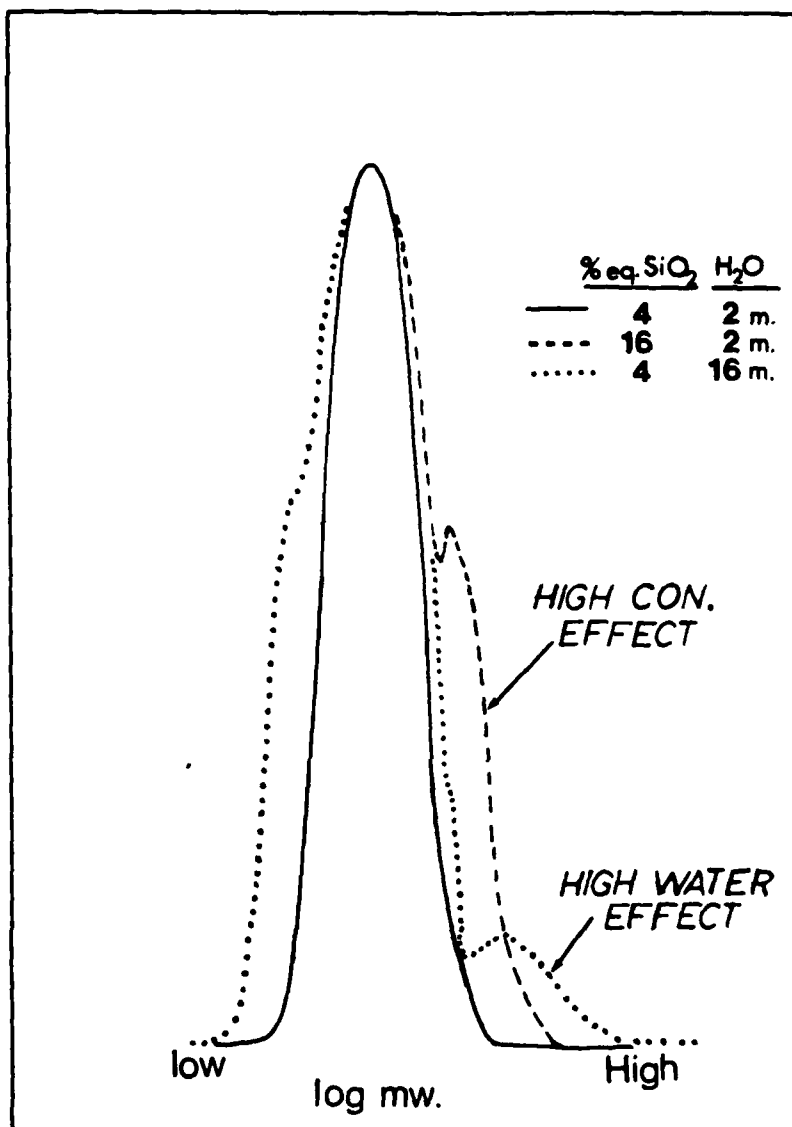
Figure 5. Effect of high solution concentration (dashed line vs solid line) and high water concentration (dotted line vs solid line) on the molecular-weight distribution of polyorganosiloxanes produced by hydrolysis of $Si(OC_2H_5)_4$ in ethanol (after 24 hrs at 60°C).

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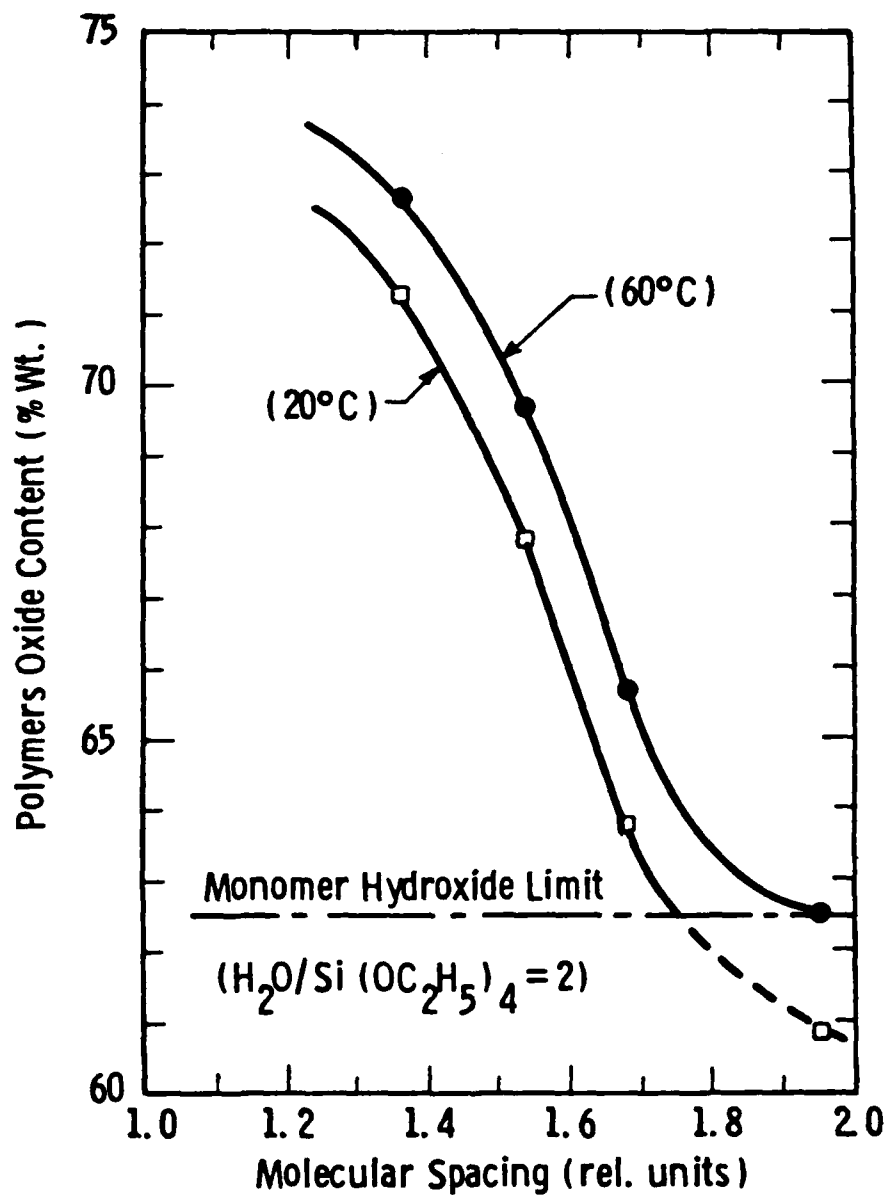
Figure 6. Effect of separation of $Si(OC_2H_5)_4$ molecules by dilution on
the oxide content of the organosiloxane polymers formed by
2 mole hydrolysis in ethanol. (Molecular spacing in diluted
solutions are expressed relative to the spacing of $Si(OC_2H_5)_4$
molecules in the undiluted state, which is taken as unity.)

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Table 4

Relationship Between Concentration (Expressed as Equivalent Weight Percent
SiO_2 in Solution) and Molecular Separation of $Si(OC_2H_5)_4$ when Hydrolyzed
with 2 Moles Water in Ethanol

Eq. SiO_2 (%wt)	Molecular Spacing	$Si(OC_2H_5)_4$	Make Up of Solution		Total Vol. (cc)
			H_2O	C_2H_5OH	
28.85	1.00[*]	208 g	–	–	∿229
24.6	1.05	208 g	36 g	–	∿265
16.0	1.23	208 g	36 g	131 g	∿430
8.0	1.58	208 g	36 g	506 g	∿905
4.0	2.01	208 g	36 g	1256 g	∿1855
2.0	2.54	208 g	36 g	2756 g	∿3753
1.0	3.21	208 g	36 g	5756 g	∿7551

[*]Molecular separation of $Si(OC_2H_5)_4$ in pure $Si(OC_2H_5)_4$ taken
as unity (corresponds to slightly over 7 Å). All other
molecular separations are expressed in terms of multiples
of this unit.

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Higher solution concentrations tend to shift the molecular-weight distributions towards higher values on a broad front (dashed line vs. solid line in Fig. 5). The secondary distribution peak differs from that of the high water effect in that somewhat smaller polymers are created in larger numbers in this case (compare dashed line with dotted line in Figure 5).

1-3. EFFECT OF MOLECULAR MODIFICATIONS ON SILICA

The molecular structure variations induced on the inorganic network of organosiloxane polymers by the parameters discussed here have a significant effect on the behavior and properties of the gel[27] as well as on the oxide obtained by thermal degradation of these gels. The crystallization, sintering, melting, and viscosity of the oxide material are modified by these variations in the polymeric structure. Figure 7 shows the effect of conditions during the hydrolytic polycondensation of $Si(OC_2H_5)_4$ on the sintering behavior of SiO_2 obtained by thermal degradation of organosiloxane polymers. In this experiment, two poly-condensation products were thermally decomposed in air at 600°C. The resultant oxide materials were then hot-pressed and the density was continuously monitored during the hot pressing through dimensional measurements. As a general rule, higher molecular weight is associated with easier sintering, crystallization, and melting behavior. These properties are related to stoichiometry and network connectivity.

The behavior of different size molecules is difficult to demon-strate, since a size distribution always exists, but the effect of molecular size on sintering is clearly indicated by Figure 8. In this experiment a 15% wt. eq. SiO_2 solution was prepared by 2 m H_2O hydrolysis of $Si(OC_2H_5)_4$ in ethanol with 600 mg HNO_3 addition per mole of $Si(OC_2H_5)_4$. A portion of the solution was taken out after 24 hrs at 60°C, gelled, and calcined to 600°C. The remaining portion

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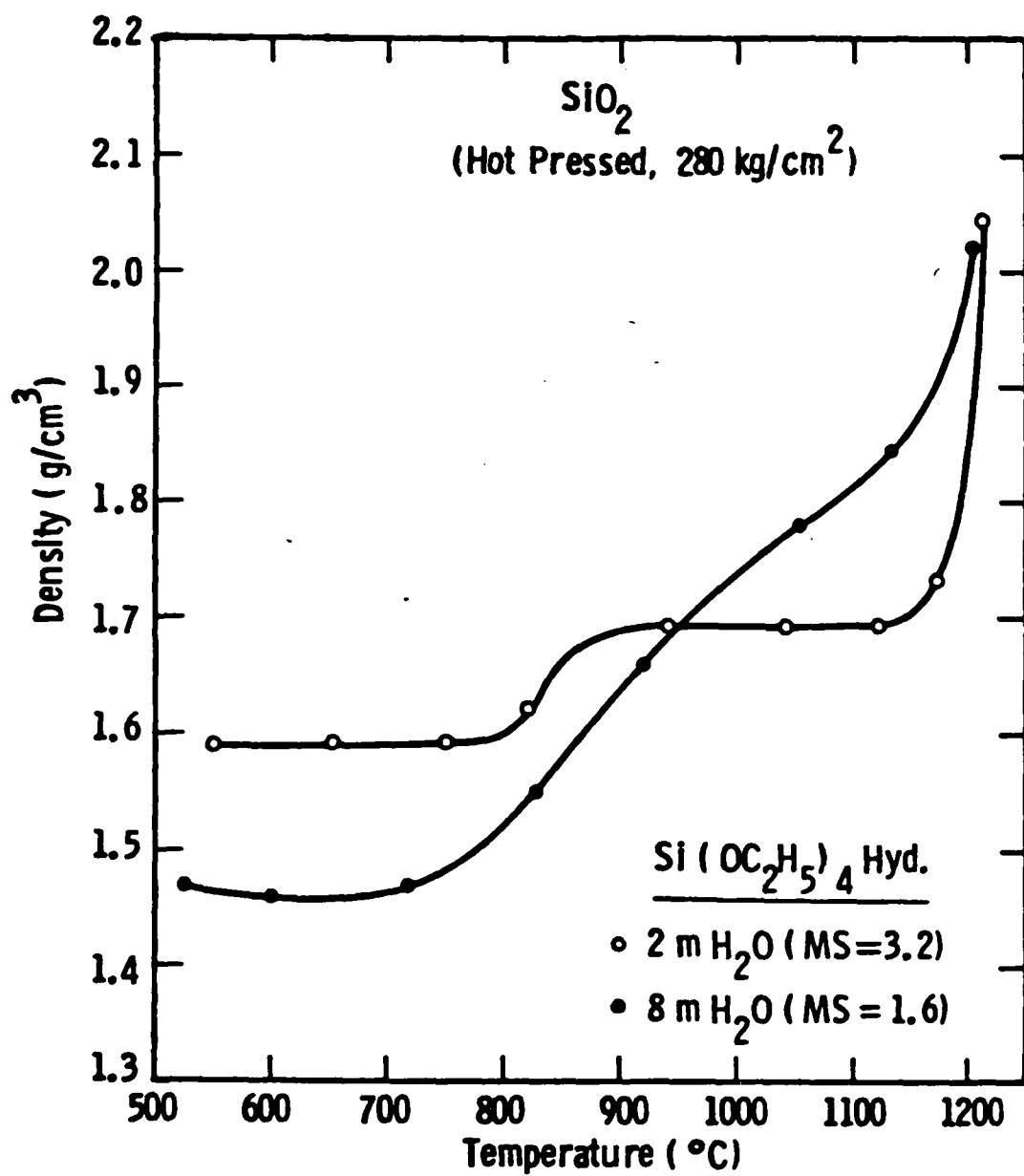
Figure 7. Silica samples derived by thermal degradation of poly-organosiloxanes formed under different conditions show different sintering behavior. (Thermal degradation was done at 600°C before hot pressing.)

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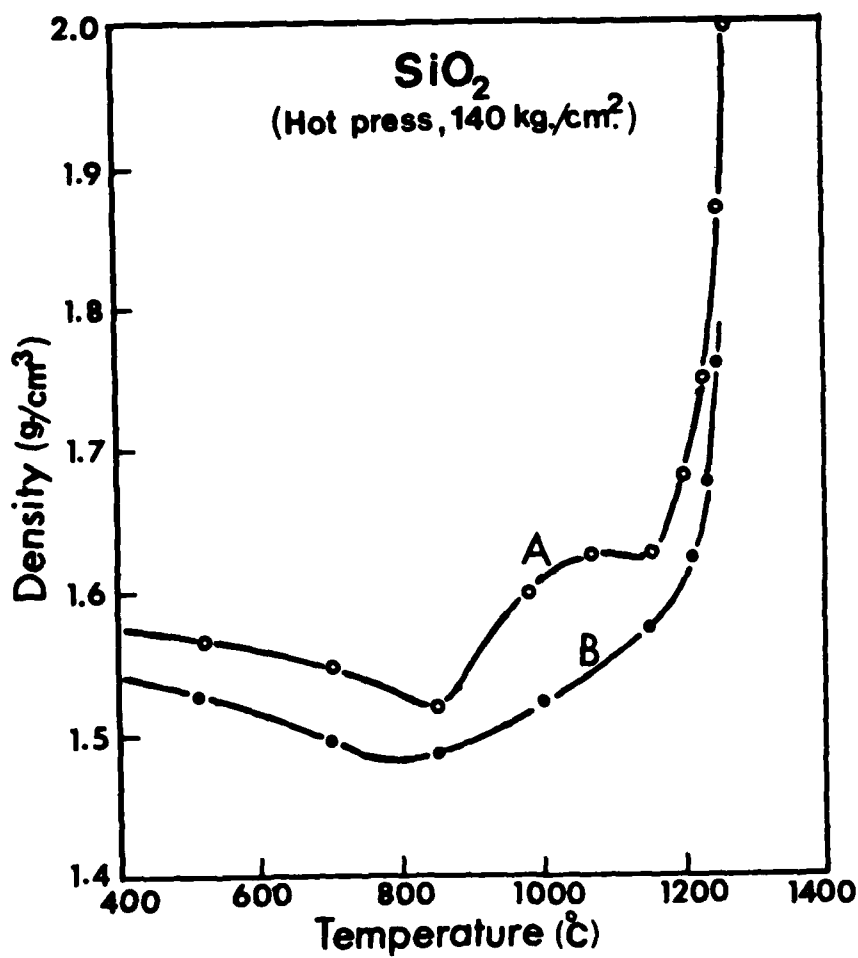
Figure 8. Densification curves of two silica samples which were produced
from the same solution at different aging times. A, 7 days
and B, 24 hours aging at 60°C (molecular-size distribution
of these samples are shown by dashed line in Fig. 2).

stayed at 60°C for seven days before gelling and calcining. The effect of the seven-day exposure on the molecular size distribution is shown as the dashed line in Figure 2. The hump in the sintering curve of the seven-day sample (curve A in Figure 8) appears to reflect the presence of very large molecules as indicated by the SEC curve in Figure 2.

We also observed a very significant phenomenon. Silicas obtained by thermal degradation of organopolysilixanes at low solution concentrations tended to lose a substantial portion of their weight by evaporation between 1700 and 1800°C when heated in vacuum: no corresponding weight loss occurred during air heating. Further discussion of this and other effects of molecular-structural variation on properties is beyond the scope of this paper and will be presented in another paper.

1-4. SUMMARY

The following general comments and conclusions can be made as a result of this investigation.

- The concentration of acid has a distinct effect, in both the short and long term, on the morphology and molecular-weight distribution of polymers produced by hydrolytic condensation of $Si(OC_2H_5)_4$. The short term effect favors hydrolysis reactions and the long term effect favors polymerization and recombination reactions.

- There is strong evidence that molecular size expansion occurs initially by a smooth "growth" process, and in a later stage by a "recombination" process. The "recombination" process takes place between high-molecular weight species and results in a bi-modal size distribution.

- Higher temperatures, longer times, and higher acid concentrations all tend to shift the molecular size to higher values. Higher $H_2O/Si(OR)_4$ ratios broaden the molecular size distribution in both high and low directions, and also give a bi-modal weight distribution in the later stages of polymerization.

- Hydrolysis-polymerization reactions of $Si(OC_2H_5)_4$ are much faster and proceed further in methanol than in ethanol and propanol. This hydrolysis medium effect diminishes at higher solution concentrations.

- Higher solution concentrations, i.e., smaller molecular separations, have the general effect of producing organosiloxane polymers having a higher oxide content. Higher solution concentrations shift the molecular weight distribution towards higher values, maintaining the population dispersion.

- Finally, the differences in the polymeric make-up and size distribution of organosiloxane polymers have an effect on the properties and behavior of oxide materials obtained from their thermal decomposition.

PART II

HYDROLYSIS OF TITANIUM ALKOXIDES AND EFFECTS OF HYDROLYTIC
POLYCONDENSATATION PARAMETERS

2-1. INTRODUCTION

The synthesis chemistry and structure of transition metal
alkoxides have been investigated systematically by chemists.[28-32] These
compounds react vigorously with water, producing metal hydroxides or
hydrated oxides. The reaction is often represented by the equation:

$$M(OR)_n + n\ H_2O \rightarrow M(OH)_n + n\ R(OH) \quad . \tag{6}$$
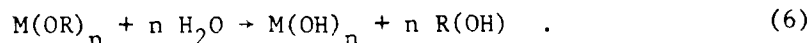
In reality, hydrolysis of titanium alkoxides and many other metal
alkoxides produces polycondensates whose chemical compositions are a function
of their physical size and polymeric morphology. This situation arises
from the fact that, during the hydrolytic condensation, an inorganic
network is formed by a chain of hydrolysis and polymerization reactions.

$$\equiv Ti-OR + H_2O \rightarrow \equiv Ti-OH + R(OH) \tag{7}$$

$$\equiv Ti-OH + RO-Ti\equiv \rightarrow \equiv Ti-O-Ti\equiv + R(OH) \tag{8}$$
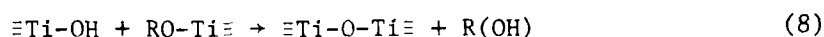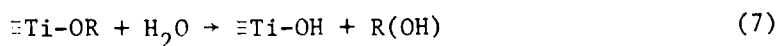
The oxide network extends as far as the hydrolysis conditions permit.
The terminating bonds of this otherwise expanding oxide polymer contain
(OH) and (OR) groups, which make the overall composition of the resultant
condensate dependent on the size and polymer morphology.[23]

As was discussed in earlier work,[33,25] certain parameters during
the hydrolytic condensation determine the average molecular size and
distribution. The polycondensed material from titanium alkoxides can never
be 100% oxide since this would require a polymer of infinite length with

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no terminal bonds involved. However, the concentration of (OH) and (OR) groups and their relative ratios can be altered by the hydrolysis conditions. These conditions include water/alkoxide ratio, molecular separation by dilution, hydrolysis medium, catalyst, reaction temperature, and alkyl groups in the alkoxide.[25] By varying these parameters one can change the kinetics of the reactions that form the molecular structure. Modifications of molecular size and morphology in turn modify the behavior and properties of oxide materials obtained by thermal degradation of these polycondensates, including crystallization and sintering.[34] For example, it has been observed that the monoclinic→tetragonal transformation of zirconias produced by hydrolytic condensation of zirconium alkoxides are affected by the nature of the alkyl group in the alkoxide.[34]

2-2. HYDROLYTIC POLYCONDENSATION OF Ti(OR)$_4$

2.2.1 Chemical Makeup and Oxide Content of Condensation

The equivalent oxide content of titanium alkoxide is given by the TiO$_2$/Ti(OR)$_4$ ratio. The molecular weights of the first three titanium alkoxides—Ti(OC$_2$H$_5$), Ti(OC$_3$H$_7$)$_4$, and Ti(OC$_4$H$_9$)$_4$—are 228, 284, and 340, respectively. Their oxide contents by weight are, therefore, $\sim$35%, 28.2%, and 23.5%, respectively. If a complete hydrolysis to tetrahydroxide, Ti(OH)$_4$, were to occur, the oxide content of that hydrolysis product would be 80/116 $\simeq$ 70% by weight.

Figure 9 shows the variation in the oxide content of the hydro-lytic condensates dried at 120°C as a function of hydrolysis water. As shown in the figure, when Ti(OC$_4$H$_9$)$_4$ was hydrolyzed in secondary butyl alcohol with various amounts of water under a constant solution concentration of 5% wt. eq., TiO$_2$, the oxide content of the dried, partially hydrolyzed material varies from less than 70 to more than 90%. When Ti(OC$_2$H$_5$)$_4$ was hydrolyzed in ethanol, the curve shown in Fig. 9 flattened out considerably, because of the higher diffusion rates in this system which control the polymerization.

The role of the water/alkoxide ratio during hydrolytic condensation goes beyond the chemical requirement; by affecting the statistical interactions of species, it becomes one of the parameters that determine the molecular size and polymer morphology.

A hydrolytic polycondensation equation which would take into account this variability of the oxide content and the polymeric nature
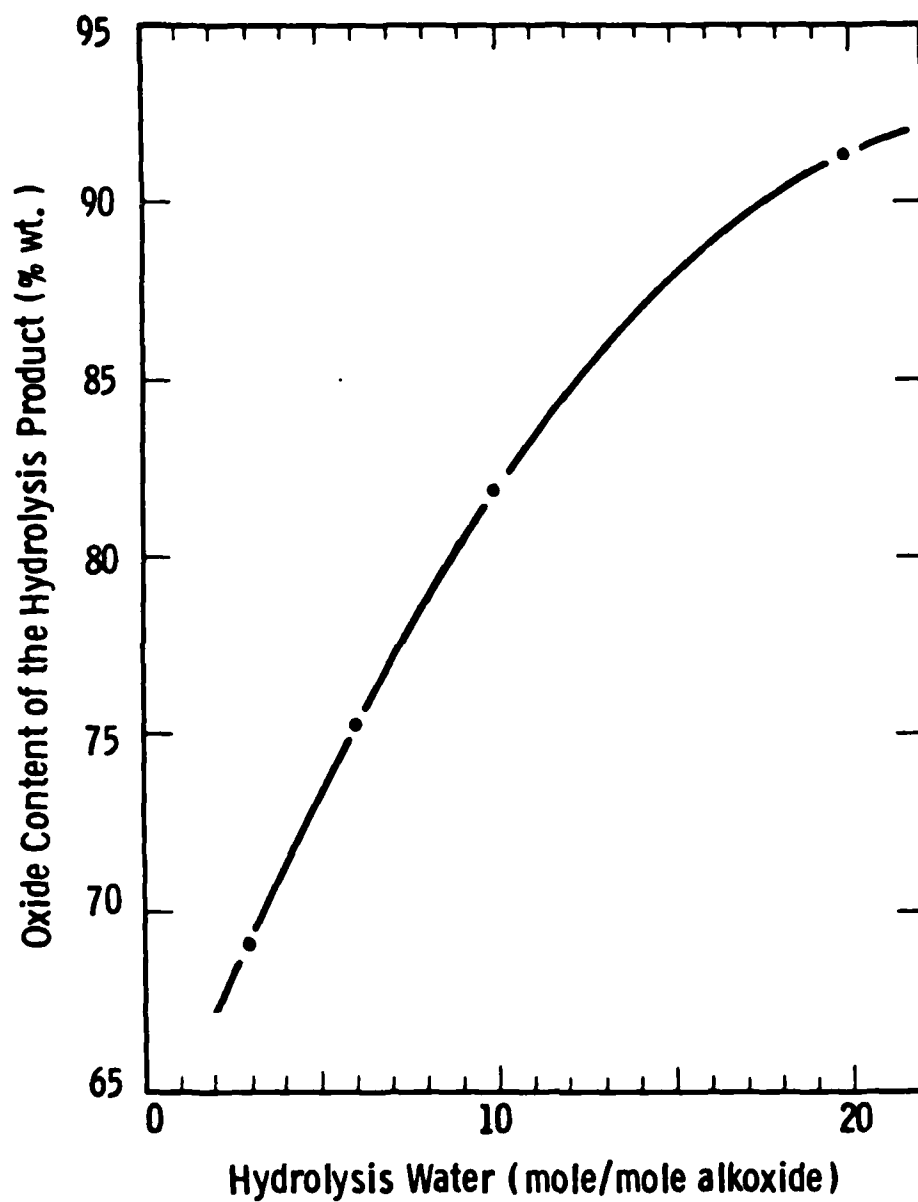
Figure 9. Effect of water/alkoxide ratio on the oxide content of hydrolytic polycondensation of $Ti(OC_4H_9)_4$ in butanol.

of the condensates can be written:

$$n \ Ti(OR)_4 + (4n + x-y) \ H_2O \rightarrow Ti_n O_{(2n - x+y/2)} (OH)_x (OR)_y + (4n-y)R(OH) \quad (9)$$
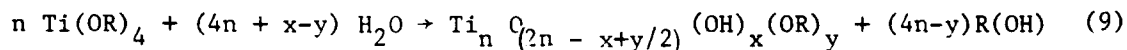
where n is the number of Ti ions polymerized in a given condensation, and x and y are the numbers of OH and OR groups in the molecule. The polymer size "n" in $Ti_n O_{(2n-x+y/2)} (OH)_x (OR)_y$ determines the oxide content when this compound is decomposed to the oxide:

$$TiO_{(2n-x+y/2)} (OH)_x (OR)_y \rightarrow n \ TiO_2 + x \ H_2O + y \ R(OH) \quad . \quad (10)$$
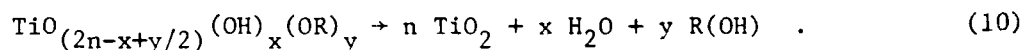
Analysis of the above equation shows an increase in the equivalent oxide content with increasing n. The initial increase in n occurs rapidly, then it levels off. (For a detailed discussion of the relationship between "n" and the oxide content of the polysiloxanes, see reference 23). The concentration of (OR) groups in the network structure decreases as the amount of water is increased in the hydrolysis medium. However, in the titania system, it was found that a certain concentration of OR groups always remains in the structure, regardless of the amount of water present. As the polycondensate is heated, a spontaneous burning of these residual organics takes place, often depositing carbon in the powder at around 185-190°C. Liberation of hydroxyl groups takes place more gradually, but the weight loss is almost complete at around 300°C for all practical purposes.[35]

2.2.2 Effect of Hydrolysis Conditions on Oxide Content and Morphology

Various factors in addition to the water/alkoxide ratio also affect the kinetics of network forming reactions. Such factors include the type of alkyl groups in the alkoxide, the host medium, molecular

separation of species, catalysts, and temperature. The alkoxides with higher alkyl groups are slower to hydrolyze and also slower to diffuse. Since polymerization requires partial hydrolysis and diffusion, these alkoxides tend to produce smaller polymeric condensates; as a consequence the oxide component of their molecules is smaller. The host medium of the condensation process also affects the diffusion rates. The hydrolytic condensation of titanium alkoxides carried out in lower alcohols yields material with a higher equivalent oxide content, reflecting a greater degree of polymerization. For example, while dried hydrolytic condensate of $Ti(OC_2H_5)_4$ formed in ethanol has an equivalent oxide content of $\sim$83-84% by weight, this figure drops to 73% when the hydrolysis is performed in butanol under the same conditions.

Table 5 gives the effect of some hydrolysis conditions on the oxide content of the condensate for $Ti(OC_2H_5)_4$ hydrolyzed with water and with H_2O_2. In this experiment undiluted $Ti(OC_2H_5)_4$ was mixed with water at two temperatures under either acidic or basic conditions. In one of the experiments, hydrolysis was performed by diluting 100 g of $Ti(OC_2H_5)_4$ with 1650 g of ethyl alcohol (thus the mixture contained 2% eq. TiO_2) before hydrolyzing with pure water. As shown in Table 5, the oxide content of the condensates varied from $\sim$75% for acidic conditions to more than 90 for neutral water (specifically, 91.7% for water at 25°C and 93.7% for water at 65°C). Interestingly, diluted hydrolysis produced the condensate having the highest oxide content ($\sim$96%).

The resultant morphologies were also very interesting. Figure 10 shows dramatic differences between the morphologies of titania samples formed via hydrolytic polycondensation of $Ti(OC_2H_5)_4$ under acidic and

Table 5

Effect of Hydrolysis Conditions on the Oxide Content and Sintering Behavior
of Hydrolytic Condensates of $Ti(OC_2H_5)_4$

	Hydrolysis Condition	Equivalent Oxide* Content (wt.%)	% Linear** Shrinkage at 1200°C
(1)	H_2O at 25°C	91.7	5
(2)	H_2O at 65°C	93.7	20
(3)	H_2O + NH_4OH	89.1	11
(4)	H_2O + HNO_3	75.6	32
(5)	H_2O_2 (30%)	83.3	12
(6)[†]	H_2O (25°C)	96.0	21

*Condensates dried at 120°C and calcined to 500°C to determine oxide
content.

**1" diameter samples pressed from thermally degraded TiO_2 powders,
sintered at 1200°C for 1 hr.

[†]Only in this sample was $Ti(OC_2H_5)_4$ diluted with ethanol to 5 times its
volume before reacting with water.
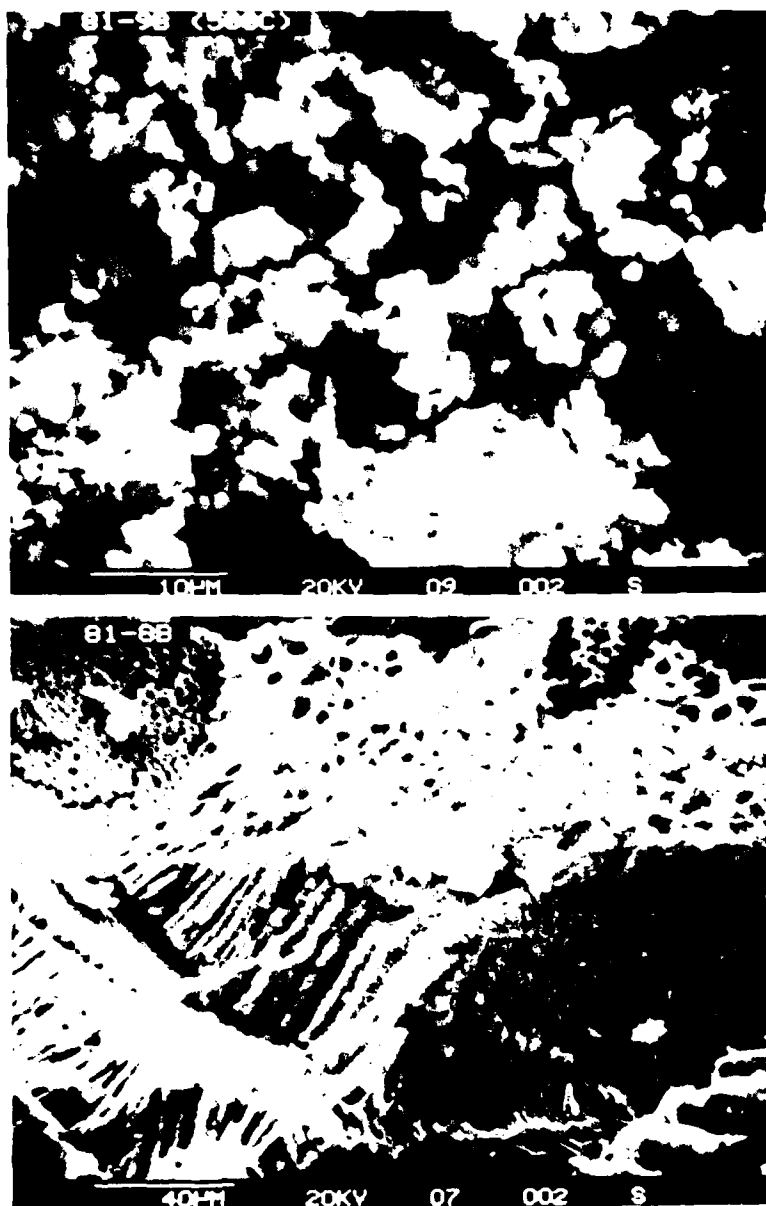
Figure 10. Morphologies of titanium oxides produced via hydrolytic poly-
condensation of $Ti(OC_2H_5)_4$ (A) with acidic water (5% HNO_3)
(B) with basic water (5% NH_4OH) heated to 500°C.

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basic conditions (samples 4 and 3 in Table 5). The honeycomb morphology of the material formed under basic conditions with ammonia is rather unusual and contrasts with the particulate granular morphologies which result from neutral and acidic conditions. (Acids have other effects, as described in Section 2-4).

The effect of H_2O_2 is also noteworthy. Hydrogen peroxide reacts vigorously with the condensation product, even when hydrolysis was completed earlier with water. Even more noteworthy is the fact that titania gels formed from clear solutions shrink rapidly without losing their shape when they are placed in H_2O_2 or when some H_2O_2 is introduced into their liquor. The mechanism of this phenomenon is not clearly understood, but the behavior is thought to be caused by the oxidation and removal of terminal alkyl groups. When these bonds are converted to hydroxyl bonds under the action of H_2O_2, they are able to react with the neighboring dangling bonds, creating bridging oxygens and causing the collapse of the previously open polymer network in a manner similar to the reaction shown in (8).

The effect of hydrolysis conditions discussed here is not limited merely to the particle morphology of the material. Infrared spectroscopy shows molecular structural modifications in the oxide network, and these modifications are stable even at high temperatures (Figure 11).
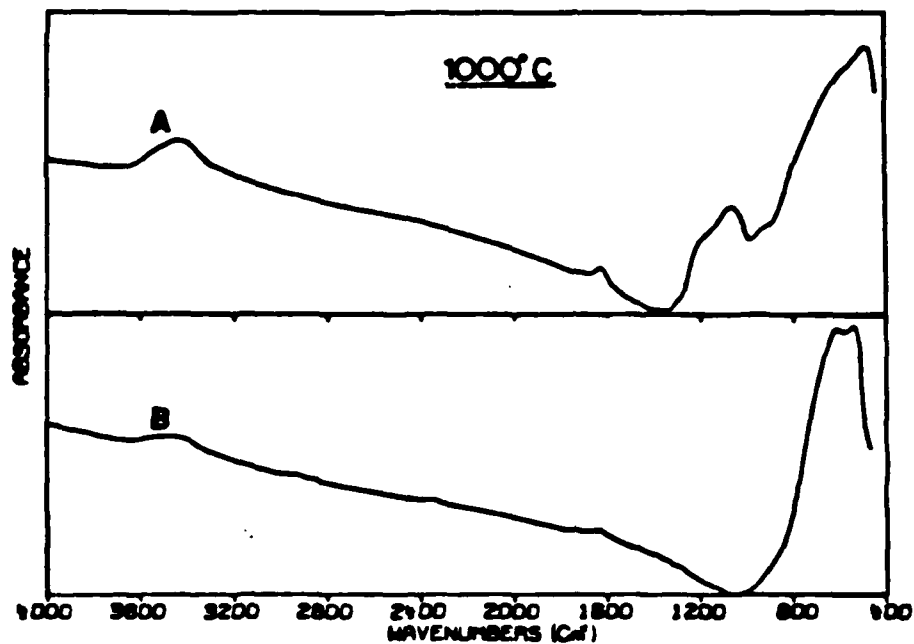
Figure 11. Spectral absorption curves of oxide materials produced after heating to 1000°C via hydrolytic polycondensation of $Ti(OC_2H_5)_4$ (A) with 2 mole and (B) 15 mole H_2O.

2-3.   EFFECT ON SINTERING AND CRYSTALLIZATION

Sintering of monodispersed alkoxide derived TiO_2 powders has been investigated by Barringer and Bowen.[36]   The molecular and morphological variations discussed in Section 2-2 have also an effect on sintering and crystallization behavior.   Table 5 shows the percent shrinkage of the pressed TiO_2 pellets obtained by thermal degradation of hydrolytic condensates formed under various hydrolysis conditions.   The condensation products of $Ti(OC_2H_5)_4$ were calcined at 500°C, pressed into pellets, and sintered at 1200°C for 1 hr.   Initial particle morphologies were considered part of the process and were not altered by grinding, etc. As shown in Table 5, a 5% shrinkage of the cold water hydrolyzed sample was improved to 20% when the water temperature was raised to 65°C and improved even further when acid was introduced into the liquor.   Although these dimensional shrinkages do not necessarily reflect differences between samples in the final densities, they do give a very good indication on the morphological effects on densification behavior.

Figure 12 shows the densification under hot pressing of three TiO_2 samples similarly prepared by hydrolytic condensation of $Ti(OC_2H_5)_4$ under neutral, basic, and acidic conditions.   Again it is clear that the initial compaction densities as well as the densification rates vary significantly for these three samples.

One other parameter--the molecular separation of species during the hydrolytic polycondensation by dilution--was found to affect the

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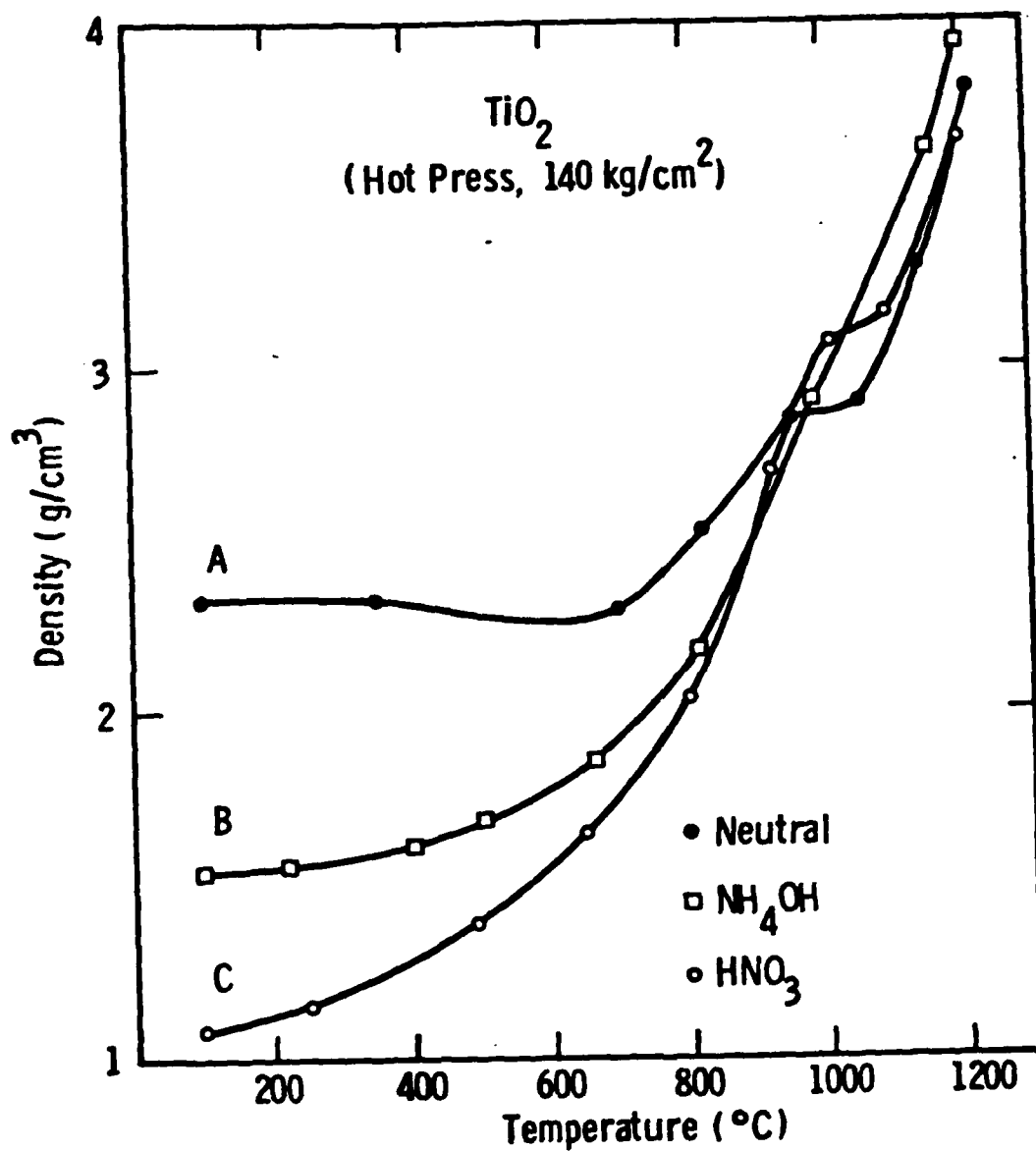
Figure 12. Densification curves of oxide materials formed by hydrolytic polycondensation of $Ti(OC_2H_5)_4$ (A) with pure water, (B) under basic conditions, (C) under acidic conditions.

densification rate as well as the crystallization of TiO_2 samples. The effect of molecular separation of species is a complex one and will be presented separately, but Fig. 13 shows this effect on the behavior of two titania samples. One of these samples was formed by hydrolysis of undiluted $Ti(OC_2H_5)_4$ (molecular separation was unity) with two moles of water; in the other case, $Ti(OC_2H_5)_4$ was diluted by ethanol to a volume where the molecular spacing was 1.7 times that in the undiluted form (five times the volume). Hot pressing tends to obviate the differences between these materials at high temperatures. When the same samples were fired in air, the density of the sample prepared via hydrolysis of undiluted $Ti(OC_2H_5)_4$ (ms=1) changed only 0.04 g/cm^3 (from 2.58 to 2.62 g/cm^3) between 800°C and 1200°C; however, the density of the TiO_2 samples obtained via hydrolysis of diluted $Ti(OC_2H_5)_4$ (ms=1.7) changed 0.9 g/cm^3 (from 2.08 to 2.98 g/cm^3) between the same temperatures. Molecular separation also affected crystallization. The hydrolytic polycondensation products of titanium alkoxides, even those of 96% oxide, were initially amorphous. But they tended to crystallize to the anastase structure at temperatures as low as 150-190°C. (This temperature may correspond to the release of residual organics at 185°C.) This crystalline phase later converted to rutile. This conversion temperature was also affected by the molecular spacing during the hydrolytic polycondensation. Figure 14 shows that, when the molecular spacing was 1, no rutile phase formed at 500°C. However, when the molecular spacing was 3, traces of rutile began to appear at 500°C.
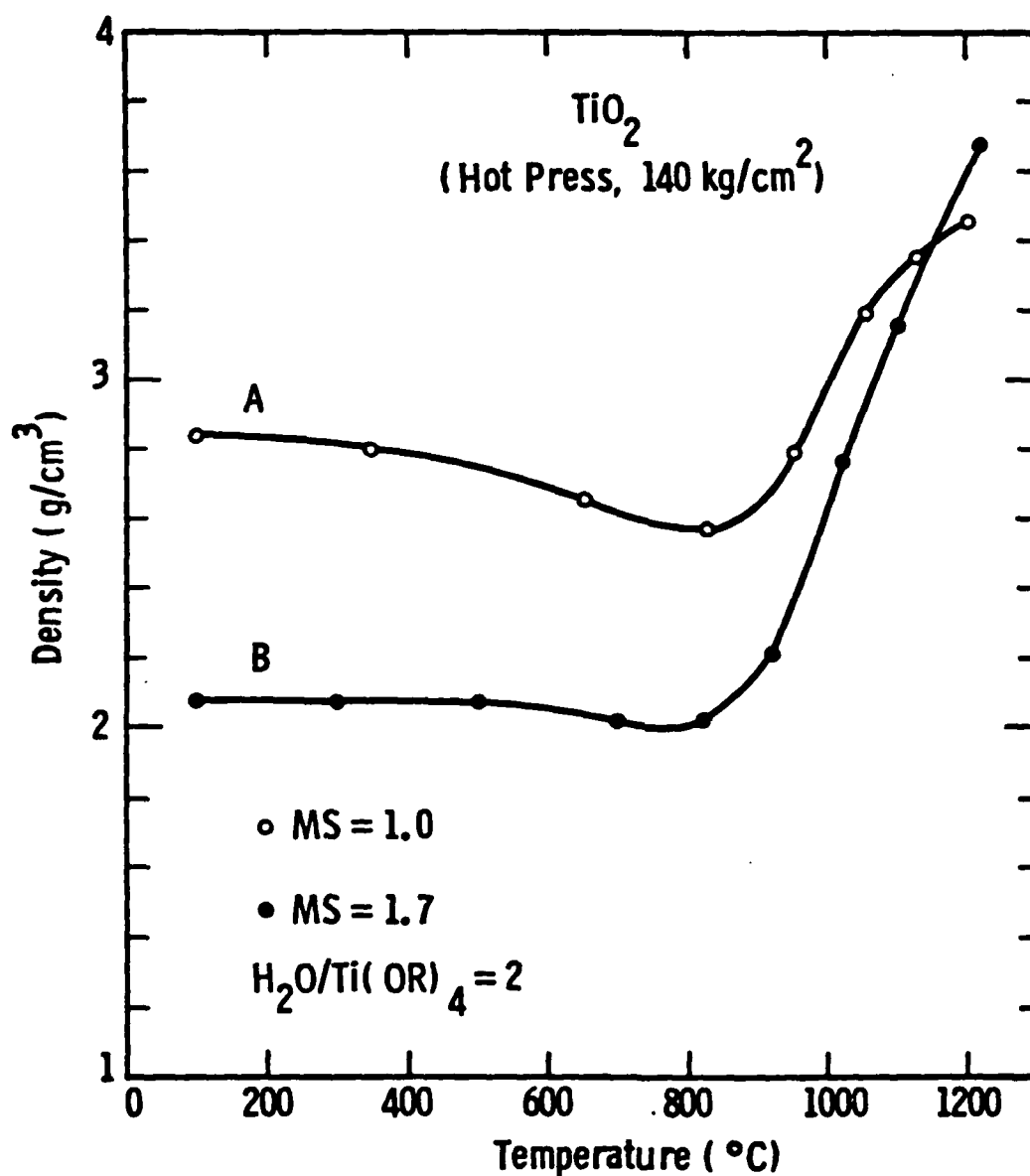
Figure 13. Changing the molecular spacing of species during hydrolytic polycondensation of $Ti(OC_2H_5)_4$ affects the compaction and sintering behavior of resultant titanias. (Separation of $Ti(OC_2H_5)_4$ molecules when diluted with ethanol is expressed relative to spacing of the molecules in undiluted $Ti(OC_2H_5)_4$ which is taken as unity.)

41
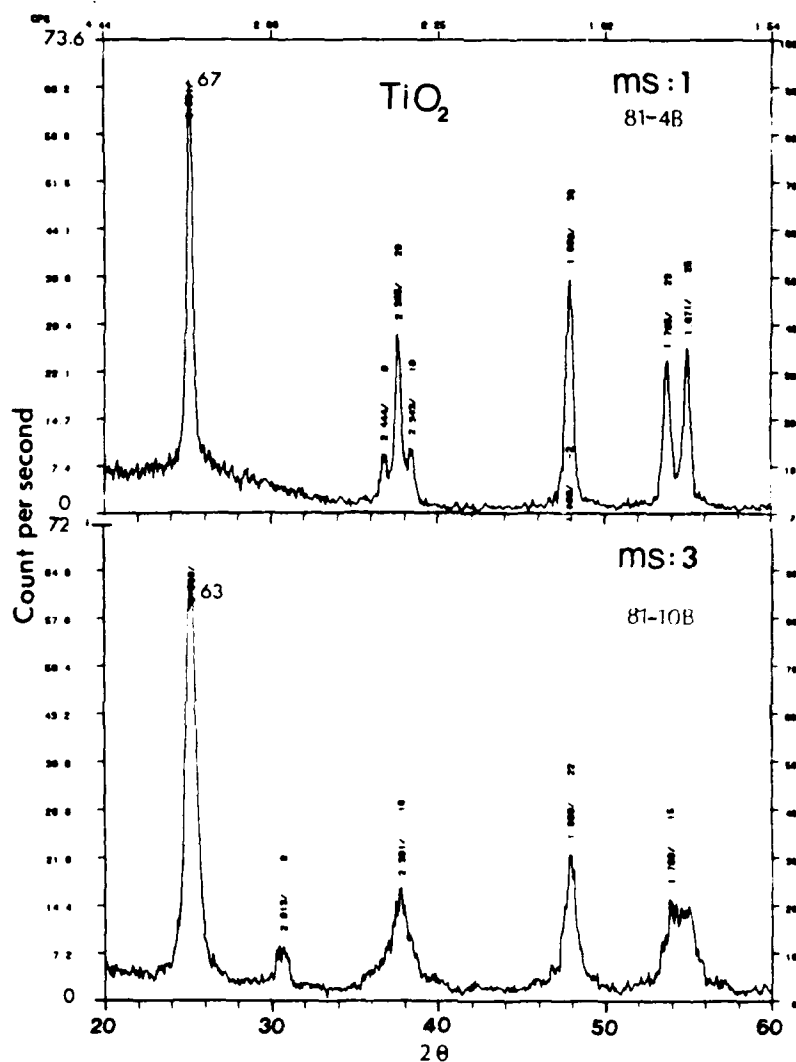
Figure 14. Molecular separation of alkoxide species during the hydrolysis also affects the crystallization behavior of the resultant oxides. Titanium oxide obtained via hydrolytic polycondensation of undiluted $Ti(OC_2H_5)_4$ (ms=1) shows only the anastase phase (top), whereas that produced via highly diluted alkoxide (ms=3) shows some rutile phase as well (bottom) at 500°C.

2-4. FORMATION OF CLEAR POLYMER SOLUTIONS

The hydrolytic polycondensation of titanium alkoxides under normal conditions leads to the formation and precipitation of particulate materials. Such precipitate formation and self-condensation can be prevented by careful control of molecular interactions during the hydrolysis such that certain amounts of (OR) groups are left in the molecular structure. This is done first by controlling the amount of water and dilution of the system, and second, by the presence of a critical amount of certain acids.[37] These solutions are useful in depositing optical titania coatings of precise thickness as well as forming titania-based glass and ceramic materials.[35,37,38]

Localized condensation particulates are avoided by introducing at least 0.014 moles of either HNO_3 or HCl acid. If the acid is introduced into the water-alcohol solution before mixing with the alkoxide, no cloudiness ever occurs; therefore this is the preferred method of introducing the acid. Acid can be added anytime after the mixing occurs and will cause the cloudy slurry to turn into a clear solution. However, if more than 0.3 moles of acid are used per mole of alkoxide, the stability of the solution is reduced and it will turn cloudy after several days to several months, depending on the acid concentration (see Fig. 15). So far, no organic acids have been found which work, and the only inorganic mineral acids which have been found to work are hydrochloric acid and nitric acid, although not all acids have been tried.

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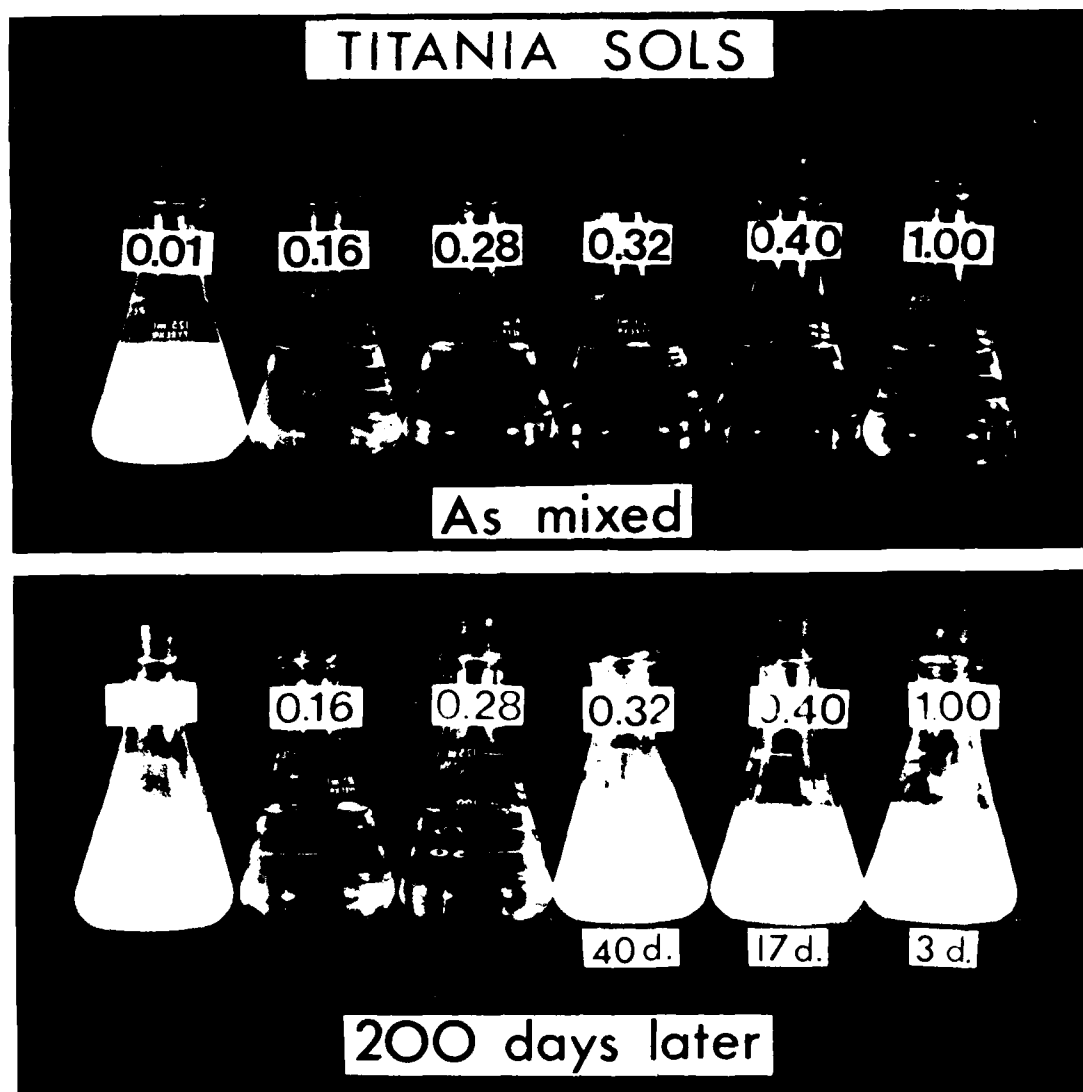
Figure 15. Clear polymer solutions are produced via two mole water hydrolysis of $Ti(OC_2H_5)_4$ in ethanol when more than 0.15 moles of HNO_3 acid per mole of alkoxide are introduced (top photo). However, solutions with acid/alkoxide ratios 0.32, 0.40, and 1.00 turn cloudy in 40, 17 and 3 days, respectively. The solutions with acid/alkoxide ratio 0.16 and 0.28 were still clear after 200 days (bottom photo).

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One must also consider the concentration and water/alkoxide ratio criteria in these clear solutions. If the water/alkoxide ratio is less than 1.7, the solution will not deposit clear continuous films. If the water/alkoxide ratio is much above 2, the solution tends to get to a clear single phase within hours or days, depending on the concentration. For example, if the equivalent TiO_2 concentration of the solution is 5% by weight, 5 moles H_2O per mole of alkoxide will cause gelling in about an hour. At higher water/alkoxide ratios, gelling occurs immediately at this concentration. Solutions with a concentration of 2% will gel in 24 hrs, while 1% concentrations will not gel at all.

These titania gels will shrink in their liquor (see Figure 16). The shrinkage occurs as a result of the formation of bridging oxygens by the reaction of dangling bonds with each other

$$\equiv Ti-OH + RO-Ti\equiv \rightarrow \equiv Ti-O-Ti\equiv + R(OH) \qquad (11)$$

$$\equiv Ti-OH + OH-Ti\equiv \rightarrow \equiv Ti-O-Ti\equiv + H_2O \qquad (12)$$
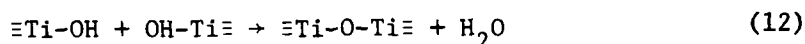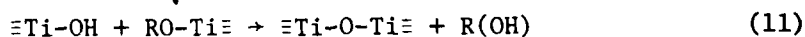
which collapses the gel network. Reaction 6 appears to be the dominant one, since addition of water in the liquor accelerates the shrinkage, presumably by creating more hydroxyl bonds which can then react with neighboring alkoxy bonds. Slight heating also accelerates the shrinkage. Creation of more bridging oxygens during the shrinkage is confirmed by chemical analysis. Gels initially containing 70-82% equivalent titania contained as much as 96% equivalent oxide after shrinkage ceased in their liquor. This could only happen by expulsion of (OR) and (OH) groups through the reactions shown in equations (11) and (12). (The oxide

Figure 16. Titania gel from a clear solution shrinks in its liquor to a fraction of its original size. This shrinkage is accelerated by introduction of H_2O or H_2O_2 into the liquor and slight heating. (The original volume of the gel was where the liquor level is now. The gel was tipped over later.)

content of the gels is measured by removing a portion of the gel at various stages, drying it at 120°C, and thermally degrading it to the oxide form at 500°C.)

Introduction of H_2O_2 into the liquor causes vigorous gel shrinkage.

2-5. SUMMARY

The parameters that affect the molecular makeup and structural
morphology of the titanias obtained by hydrolytic condensation of
titanium alkoxides were investigated. The effect of these structural
and morphological modifications extends to the sintering and crystalliza-
tion behavior of the oxide materials.

The requirements for the formation of clear stable solutions
in titania systems have been determined. The stability of these
solutions is a function of the acid/alkoxide ratio, and there is a
window for the most stable solutions at 0.15 to 0.30 moles of acid per
mole of alkoxide. Gelling time of these solutions is a function of
solution concentration and water/alkoxide ratio.

The clear titania gels formed from clear polymer solutions
shrink in their liquor by reaction of the dangling bonds of the molecules,
forming bridging oxygens. The oxide content of these gels increases as
they shrink. The shrinkage is accelerated by introducing water into
the liquor and by heating.

Vigorous shrinkage of the gels occurs when hydrogen peroxide
is introduced into the liquor .

PART III

ZIRCONIUM OXIDES FORMED BY HYDROLYTIC CONDENSATION OF ALKOXIDES
AND PARAMETERS THAT AFFECT THEIR MORPHOLOGY

3-1. INTRODUCTION

Zirconium alkoxides were synthesized and investigated in detail

by Bradley and his co-workers.[28,39,40] Later Mazdiyazni and his co-workers

investigated the formation of ZrO_2 from these compounds.[41,42]

The hydrolytic condensation of zirconium alkoxides differs

fundamentally from that of Si, Al, Ti, etc. The hydrolysis reactions

in this system lead to the formation of oxo- and aqua-groups rather than

true hydroxides. This is reflected in the fact that, while the equivalent

oxide content of hydrolytic polymer condensation products of Ti, Si, and

Al alkoxides vary in a broad range of values, depending, for example,

on the water/alkoxide ratio, the oxide content of zirconium alkoxide

remains constant.[24]

Hydrolytic polycondensation reactions are complex multiple

reactions. Mazdiyazni, et al., for example, observed that hydrolysis of

zirconium iso-propoxide follows at least two steps:[41]

$$Zr(OR)_4 + H_2O \rightarrow ZrO(OR)_2 + 2R(OH) \tag{13}$$

$$2ZrO(OR)_2 \rightarrow ZrO_2 + Zr(OR)_4 \tag{14}$$
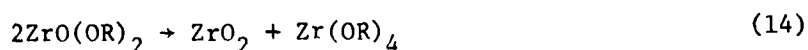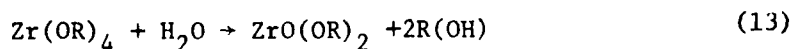
These reactions differ from the hydrolysis polymerization

reactions described for silicon, for example.[23] Nevertheless, it is

clear that any hydrolytic condensation reaction involves multiple reactions,

in which first water must alter some of the bonds of the alkoxide mole-

cules, and these altered species must react with each other or with

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Figure 17. Surface morphology of a ZrO_2 sample produced via hydrolytic polycondensation of $Zr(OC_4H_9)_4^n$.

unaltered species to form large molecules. In these reactions diffu-
sion and statistical interactions play significant roles in determining
molecular-weight distributions,[34] particle and surface morphologies
(see Figure 17), even in modifying certain materials properties.[25,33]
In a previous work[24] it was shown that the water/alkoxide ratio, in the
hydrolysis medium, even beyond the chemical requirements, strongly
influences the sintering and crystallization behavior of zirconia. In
the work described here the effects of alkyl in the alkoxide, molecular
separation during the hydrolysis, and hydrolysis water temperature on the
resultant zirconia are also investigated. These parameters are in addition
to, and somewhat more basic than, the processing parameters involved in
the production of mono-size particles from metal alkoxides.[43]

3-2. EFFECT OF ALKYL GROUPS

3.2.1 Effect on the Morphology

To check the effect of alkyl groups, R, in the zirconium alkoxides, $Zr(OR)_4$, 0.2 molar solutions of zirconium alkoxides were prepared by dissolving 1 mole each of $Zr(OC_2H_5)_4$, $Zr(OC_3H_7)_4^i$, $Zr(OC_3H_7)_4^n$, $Zr(OC_4H_9)_4^n$ in 5 l of alcohol of the same alkyl group. The first two compounds are solids and their dissolution in certain alcohols required the addition of acids, e.g., acetic acid. These solutions were then combined with mixtures containing 10 moles of water in 5 liters of the same alcohol. Thus, in effect, 1 mole of each alkoxide was hydrolytically condensed with 10 moles of water in its alcohol in a total volume of 10 liters.

Figure 18 shows scanning electron micrographs of the condensed materials after they were dried at 100°C. As is seen from Figure 2, the higher the alkyl group of the alkoxide the coarser the texture of the material tends to be. Zirconium ethoxide, $Zr(OC_2H_5)_4$, produced yellow transparent grains or films having no discernible texture (top photograph in Figure 18), where the particulate matrix of material produced from $Zr(OC_4H_9)_4^n$ is clearly visible (bottom photograph in Figure 18). The fine texture and continuous nature of material produced from zirconium ethoxide remained unchanged when the hydrolysis of this alkoxide was carried out in other alcohols, thus eliminating the possibility that ethanol was the cause of it. However, when $Zr(OC_2H_5)_4$ was used, it was necessary to add acetic acid for dissolution, so the effect of acetic acid on the

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Figure 18.   Textures of dried gels obtained via 10 mole water hydrolysis
of $Zr(OC_2H_5)_4$, $Zr(OC_3H_7)_4^n$, $Zr(OC_4H_9)_4^n$ in their alcohols (10
liter volume).

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microstructure remains undetermined. Nevertheless, the gradual coarsening of the matrix from $Zr(OC_3H_7)_4^n$ to $Zr(OC_3H_7)_4^i$ to $Zr(OC_4H_9)_4^n$ must be attributed to the alkyl groups, since no acid was present in these solutions.

3.2.2 Effects on Sintering and Crystallization

Figure 19 shows the sintering behavior of ZrO_2 obtained by hydrolysis of the four alkoxides mentioned in the previous section. The hydrolytic condensation products were calcined to 500°C and then hot pressed under 280 kg/cm^2 (4000 psi) pressure. The resultant particle size and morphology were considered part of the process, and no attempts were made to control or alter them. Figure 19 has several noteworthy features: First, it appears that a significant rate of sintering in these zirconias begins ∿800°C. Second, the unsintered compaction of zirconia obtained from $Zr(OC_2H_5)_4$ is twice as high as that observed for all others. Other zirconias, when pressed under 280 kg/cm^2 pressure, had a compaction density of around 2.25 g/cm^3, whereas that of zirconia obtained from $Zr(OC_2H_5)_4$ was around 4.5 g/cm^3. This is clearly due to the different polymerization characteristics of this alkoxide under acidic conditions giving a non-particulate, continuous, and apparently rather dense matrix as shown in Figure 18.

Probably the most important feature of the densification curves shown in Figure 19 is that, in three out of four materials, the density first increases, obtains a peak value at somewhere around 1300-1400°C, and then decreases with increasing temperature. This behavior has been observed by T. K. Gupta in non-alkoxide derived ZrO_2's and has been attributed to crystalline transformation.[44]
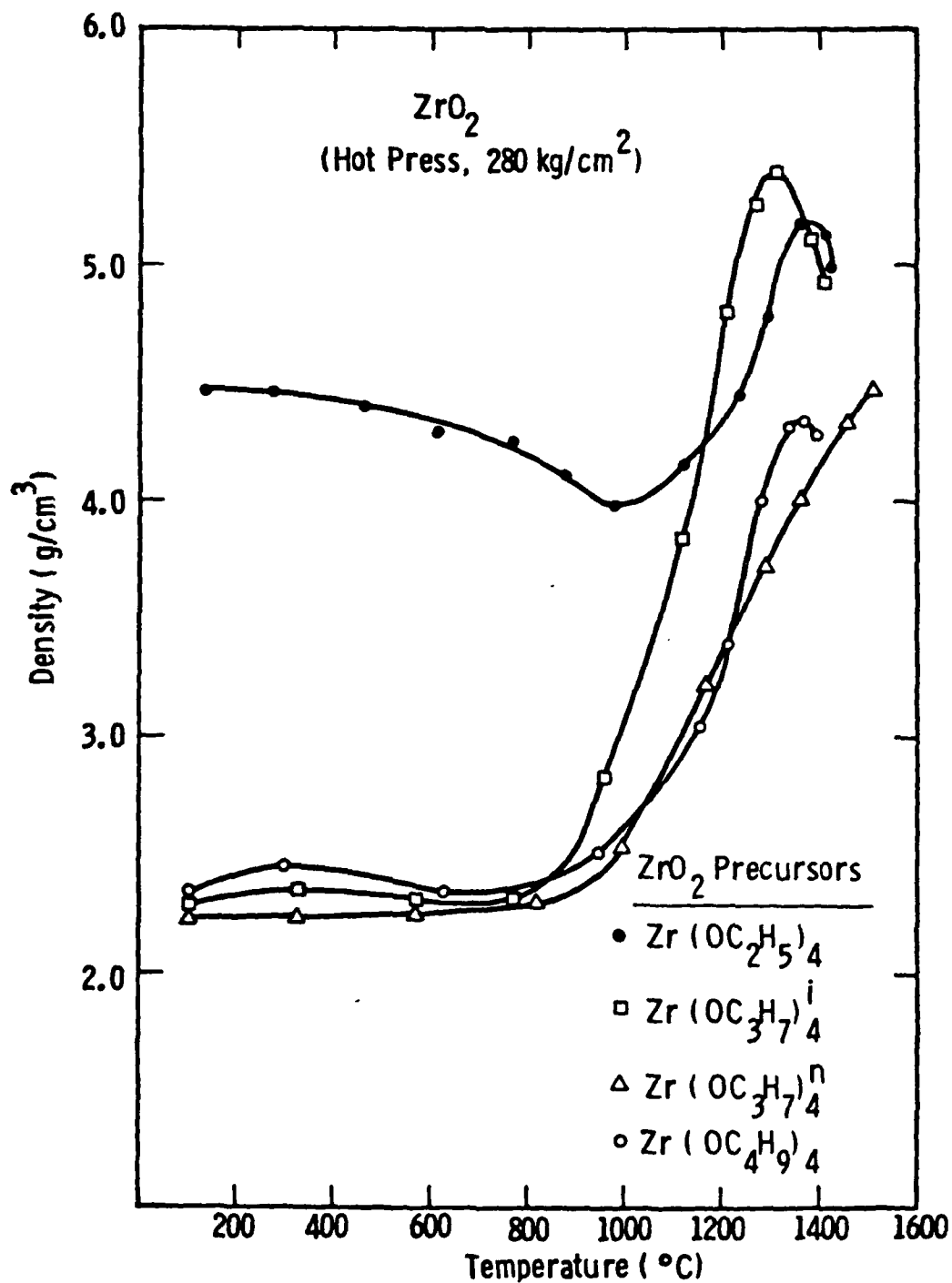
54

Figure 19. Densification behavior of ZrO_2 samples produced via hydrolysis of four different zirconium alkoxides. (Note that the temperature of the peak density varies and one of the samples does not exhibit the peak in the density curve.)

In our investigations it has been shown that this behavior is due to the monoclinic-to-tetragonal transformation. When ZrO_2 is produced by hydrolytic polycondensation of zirconium alkoxides, the initial phase is cubic.[45,23] This initial cubic phase starts to convert to the monoclinic phase upon heating; at a temperature as low as 500°C, trace amounts of the monoclinic phase are observed (Figure 20). The amount of monoclinic phase becomes as high as 87% at 1000°C[6] and the phase may be considered entirely monoclinic just below the temperatures at which the peak in the density curves occurs. As the temperature is increased, the monoclinic phase becomes unstable and converts to the tetragonal phase around 1300-1400°C. This conversion involves a volume change:[46] thus the peaks in the density curves are observed. It is interesting that not only do these peaks occur at somewhat different temperatures for differently prepared zirconias, but also that one of them, the $Zr(OC_3H_7)_4^n$ prepared material in Figure 19, does not go through this density reversal within the temperature range to 1400°C. This clearly indicates that the alkyl groups affect the particle size and morphology during the hydrolytic condensation, consequently also affecting the transformation behavior of the resultant zirconias. The effect of size on the transformation has been discussed previously by other workers,[47-49] and it is clear that the stabilization of phases can occur in ZrO_2 without any alloying agent. In the next section it is shown that molecular spacing during the hydrolytic polycondensation also affects this transformation.
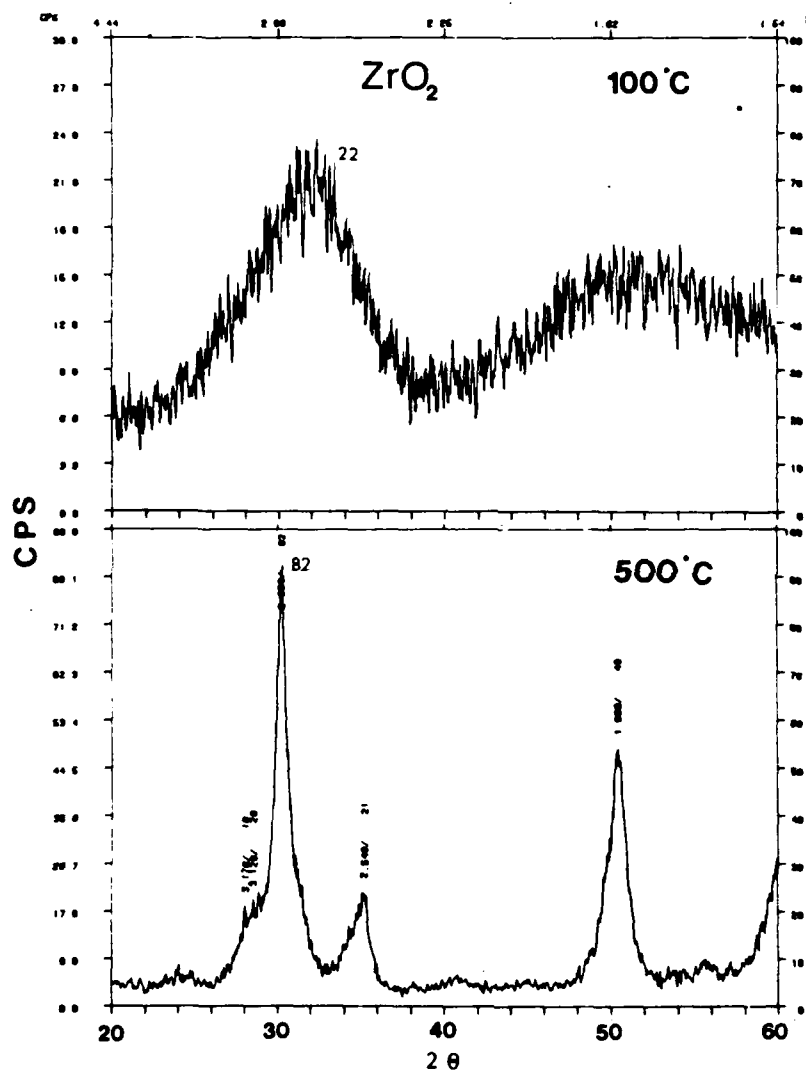
Figure 20. Diffuse x-ray diffraction pattern of hydrolytic condensation product of $Zr(OC_3H_7)_n$ at 100°C indicates cubic phase structure (top); the same material develops traces of monoclinic structure when heated to 500°C (bottom).

3-3. EFFECT OF MOLECULAR SEPARATION DURING HYDROLYTIC CONDENSATION

The size of condensed particles in various systems ranges from 10 $\overset{\circ}{A}$ up to 1 μm involving thousands of atoms. The size, i.e., extent of polymerization, is determined by the nucleation and diffusion rates of these atoms in the reaction medium.

Under diluted conditions, larger molecular separations result. The mobilities of those atoms that comprise the higher-molecular units become more important. Prediction of the effect of solution concentration on particle size is not a simple task, however, and although higher concentration favors larger molecules, it also causes more extensive nucleation, which restricts the growth. This effect of molecular separation will be addressed in another paper. For the present purposes, it is sufficient to show that altering the molecular separation has been found to modify the sintering and monoclinic-tetragonal transformation of the resultant ZrO_2. It has been reported that alkoxides of zirconia have an average degree of polymerization of 3.5 and that some form dimers in solvate.[29] Molecular separation of these units, even though they are not monomers, by an inert solvent alters the condensation process.

When the ZrO_2 derived from $Zr(OC_3H_7)_4^n$ was formed under more concentrated conditions (both the alkoxide and water were diluted in 0.7 liters of alcohol before mixing instead of 5 liters each as in the previous case), this did not affect the absence of the peak in the density curve exhibited previously (Figure 21). It appears that among the zirconium alkoxides studied, hydrolytic condensation of zirconium
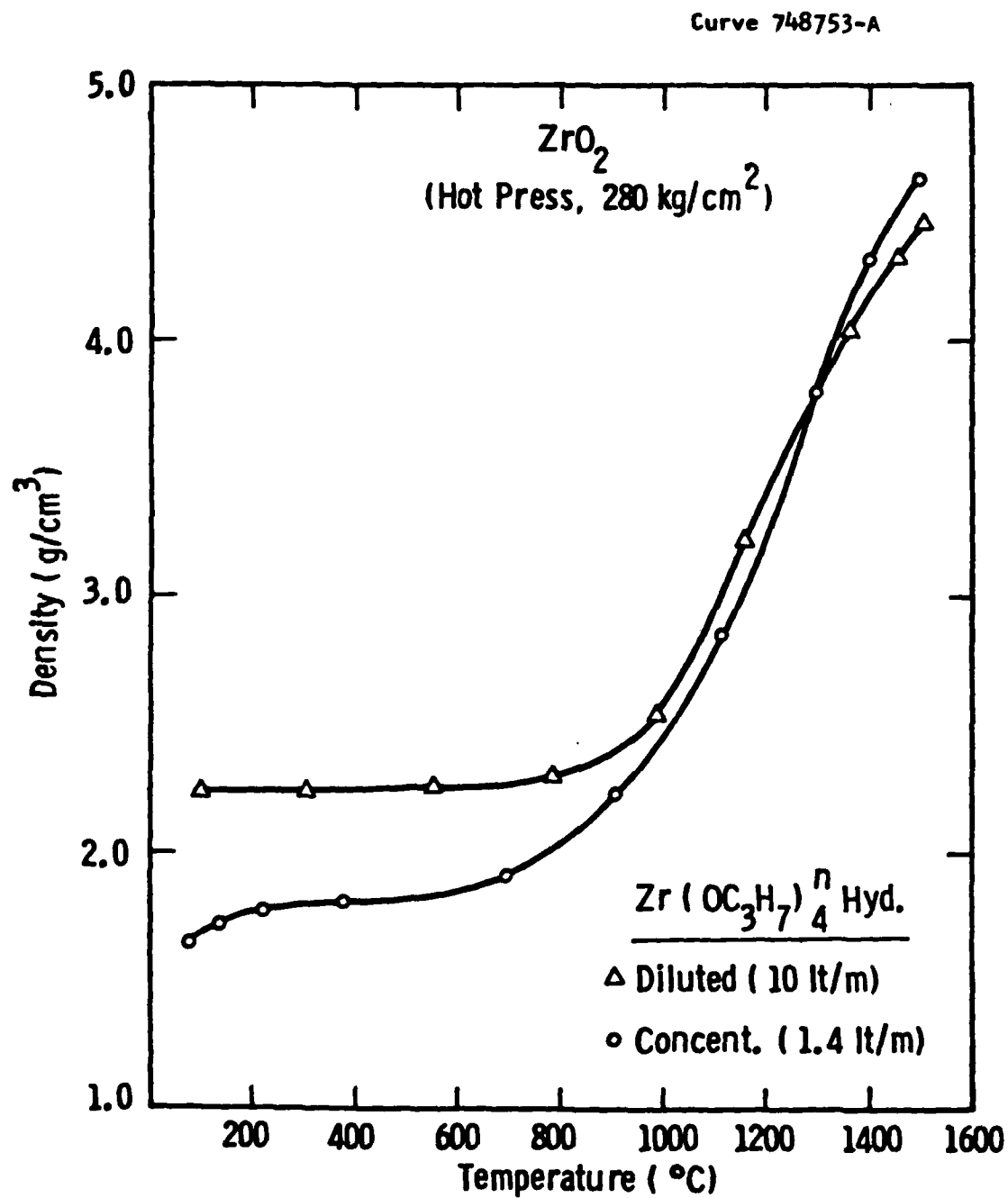
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Figure 21. The absence of a peak in the density curve is not affected when ZrO_2 is formed via hydrolytic polycondensation of $Zr(OC_3H_7)_4^n$ at two different solution concentrations.

n-propoxide, $Zr(OC_3H_7)_4^n$, results in zirconium oxides with a high resistance to monoclinic-tetragonal transformation.

In another experiment the density reversal associated with the transformation was eliminated (or retarded within the temperature range studied) by changing the molecular spacing of hydrolysis water in alcohol. In this experiment, instead of reacting a 0.2 molar solution of $Zr(OC_2H_5)_4$ (1 mole $Zr(OC_2H_5)_4$ in 5 liters of ethanol) with alcohol diluted water as described in Section 1, it was reacted with undiluted water (the molecular spacing, ms, of water in the diluted mixtures was 3 times that in pure water; thus ms=1 vs ms=3 for water). The zirconia obtained under this hydrolytic polycondensation of $Zr(OC_2H_5)_4$ did not show a peak in the densification curve within the temperature range (Figure 22) studied.

Formation of zirconias from metal-organic compounds also permits room temperature doping or alloying of these oxides leading to the stabilization of cubic or tetragonal phases. Table 6 shows the result of an interesting experiment in which zirconia was doped with various amounts of silica by reacting zirconium n-propoxide with partially hydrolyzed tetraethoxysilane in butanol. The silica doping stabilizes the tetragonal phase; near 100% stabilization seems to require about 22% SiO_2 doping by weight.
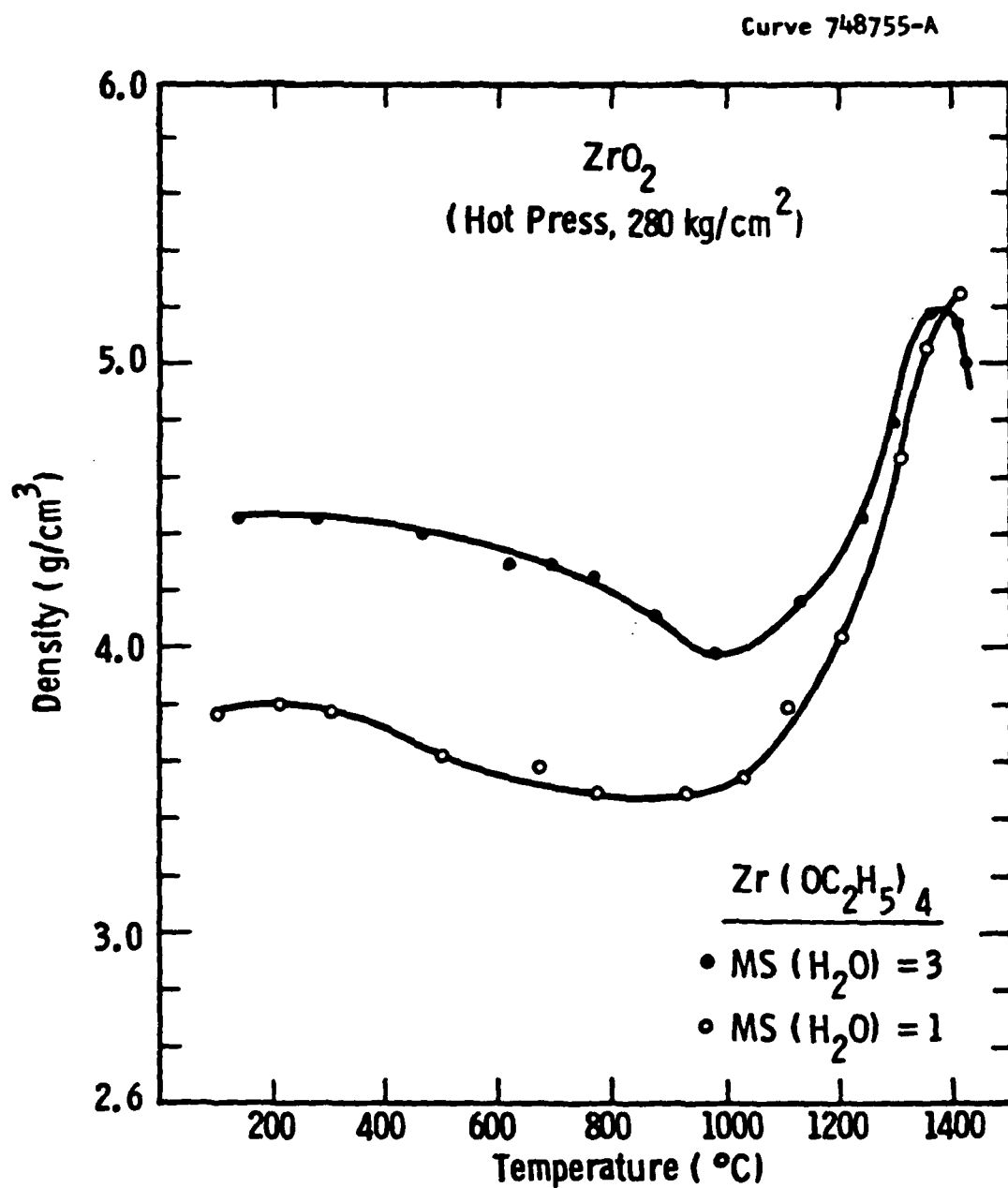
Figure 22. Changing the molecular spacing of water during the hydrolytic polycondensation of $Zr(OC_2H_5)_4$ affects the compaction rate and the monoclinic-tetragonal transformation, as indicated by the peak in the density curve. (Spacing of water molecules in undiluted water is taken as unity, and separation of water molecules when diluted by ethanol is expressed as a multiple of that unit.)

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Table 6

Effect of Silica Doping on the Crystalline Structure of ZrO_2[*]

| % wt. SiO_2 | 1100°C - 2 hrs. | |
	~% Monoclinic	~% Tetragonal
0	100	0
5	88	12
10	68	32
15	42	58
20	13	87

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[*]Prepared from zirconium n-propoxide and partially hydrolyzed tetra-ethoxysilane in butyl alcohol.

3-4. EFFECT OF WATER/ALKOXIDE RATIO AND PREVENTION OF PARTICULATE CONDENSATION

The effect of the water/alkoxide ratio during the hydrolytic condensation of metal alkoxides on the behavior of the resultant oxides is considerable. For example, Figure 23 shows the effect of water on the morphology of the condensate when $Zr(OC_3H_7)_4^n$ is hydrolyzed in 1.4 liters of isopropanol with 2 and 10 moles of water. These morphologies are also strongly affected by solution concentration.

Use of higher water/alkoxide ratios generally results in the formation of materials having superior sintering properties due to stoichiometry and particle morphology.[24] Sintering studies on zirconia samples produced at different water/alkoxide ratios show that the higher the hydrolysis water, the finer the texture of the matrix (see Figure 24). Samples produced with less than two moles of hydrolysis water consist of large angular particles showing no consolidation after 2 hrs of heat treatment at 1350°C (top photo in Figure 24), whereas the 15 mole water-hydrolyzed sample was sintered to a relatively high density of 5.4 g/cm^3.

This brings us to another aspect of the hydrolysis. When the zirconium alkoxide is hydrolyzed in alcohol with less than 2 moles of water per mole of alkoxide, the solution generally remains clear. When these clear solutions are gelled and thermally decomposed, they yield granular, transparent ZrO_2 particulates. When the water/alkoxide ratio exceeds 2, extensive localized hydrolytic condensation of particles
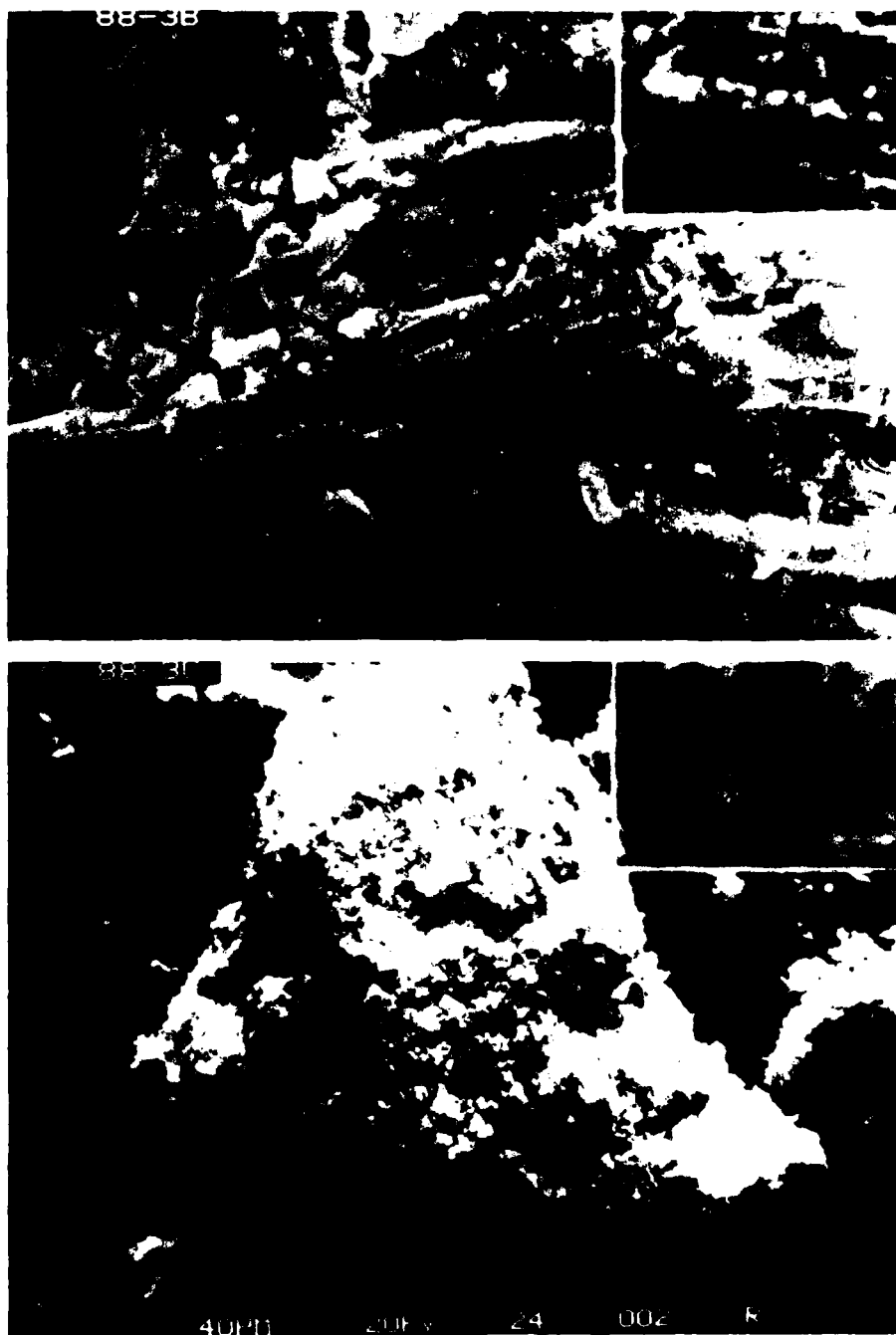
Figure 23. Changing the water/alkoxide ratio from 10 (top) to 2 (bottom) affects the morphology of the condensate. In the experiment 1 mole of $Zr(OC_3H_7)_4^n$ was hydrolyzed with 10 and 2 moles of H_2O in 1.4 liter of n-propanol.

Figure 24. Fracture surfaces of sintered ZrO_2 samples formed by hydrolytic condensation of $Zr(OC_4H_9)_4^n$ with different amounts of water in n-butyl alcohol at 5% eq. ZrO_2 concentration. (There was no consolidation in the 1 mole hydrolyzed sample shown in the top photograph during sintering.)

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occurs. The solution turns milky, reflecting the fact that it has become a two-phase suspension. When these materials are dried and thermally decomposed, they yield the ZrO_2 powders whose sinterin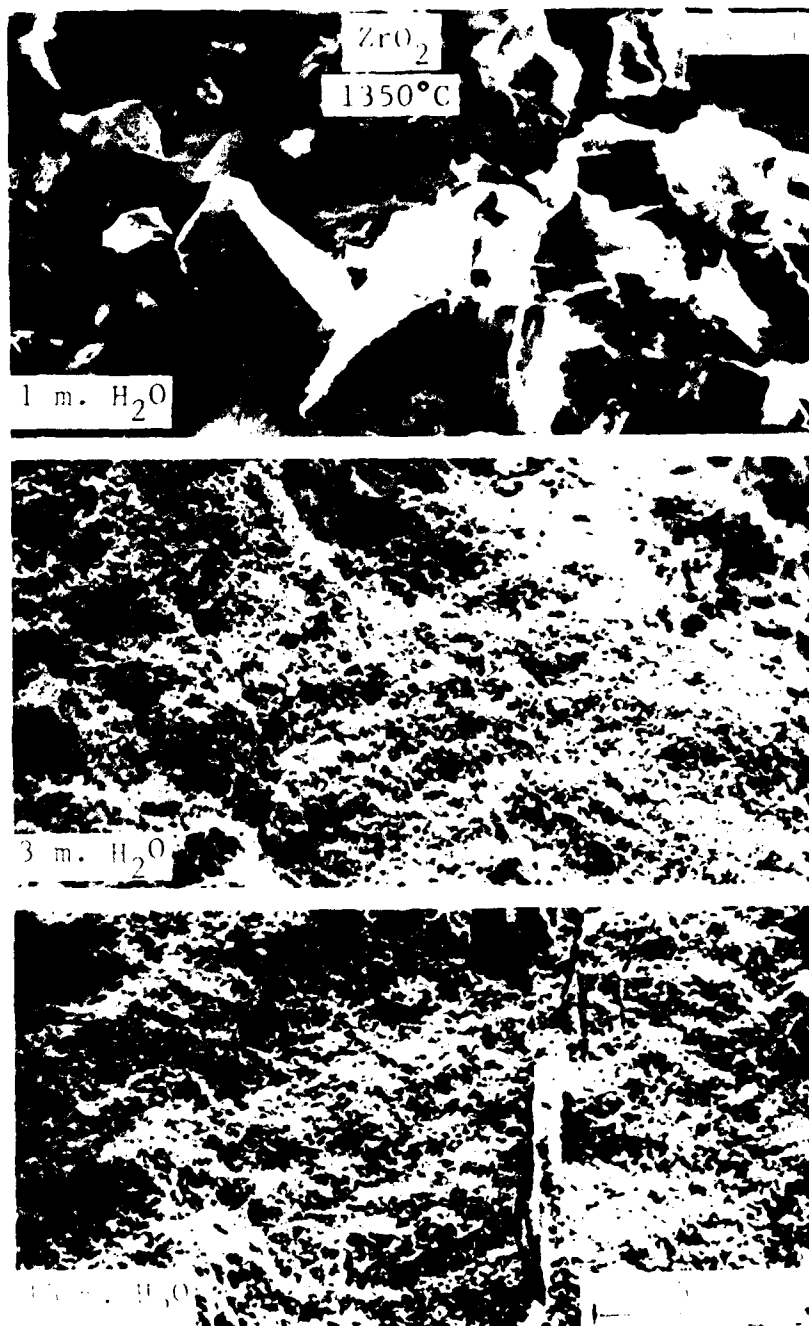g and crystalline transformation is being discussed here. One of the reasons for the localized condensation of particulates in these systems is the near-complete removal of "OR" groups from the molecular structure. The presence of a critical concentration of "OR" groups in the molecular structure is required for these molecules to be soluble in alcohols, $R(OH)$.[4]

It is, however, possible to prevent precipitate formation and to maintain the clarity of these solutions under large water concentration by introducing acids into the system. The amount of acid required to prevent localized condensations is a function of the solution concentration and the water/alkoxide ratio. Figure 25 shows the acetic acid and nitric acid requirements as a function of water/alkoxide ratio when $Zr(OC_4H_9)_4^n$ is hydrolyzed at concentrations corresponding to 2.5 and 5% equivalent ZrO_2 by weight in n-butanol.

Finally, the hydrolysis temperature has a bearing on the morphology and the particle size. Figure 26 shows the effect of hydrolysis water temperature on the morphology of the condensation. In this experiment a portion of 0.2 molar $Zr(OC_3H_7)_4^n$ in n-propanol was poured into water at 20°C; another portion was poured into water at 65°C. The coarse granular appearance of the cold-water-hydrolyzed material (top photo in Figure 26) is clearly different from the fine and fluffy structure of the hot-water-hydrolyzed material (bottom photo) even though the magnifications are somewhat different.

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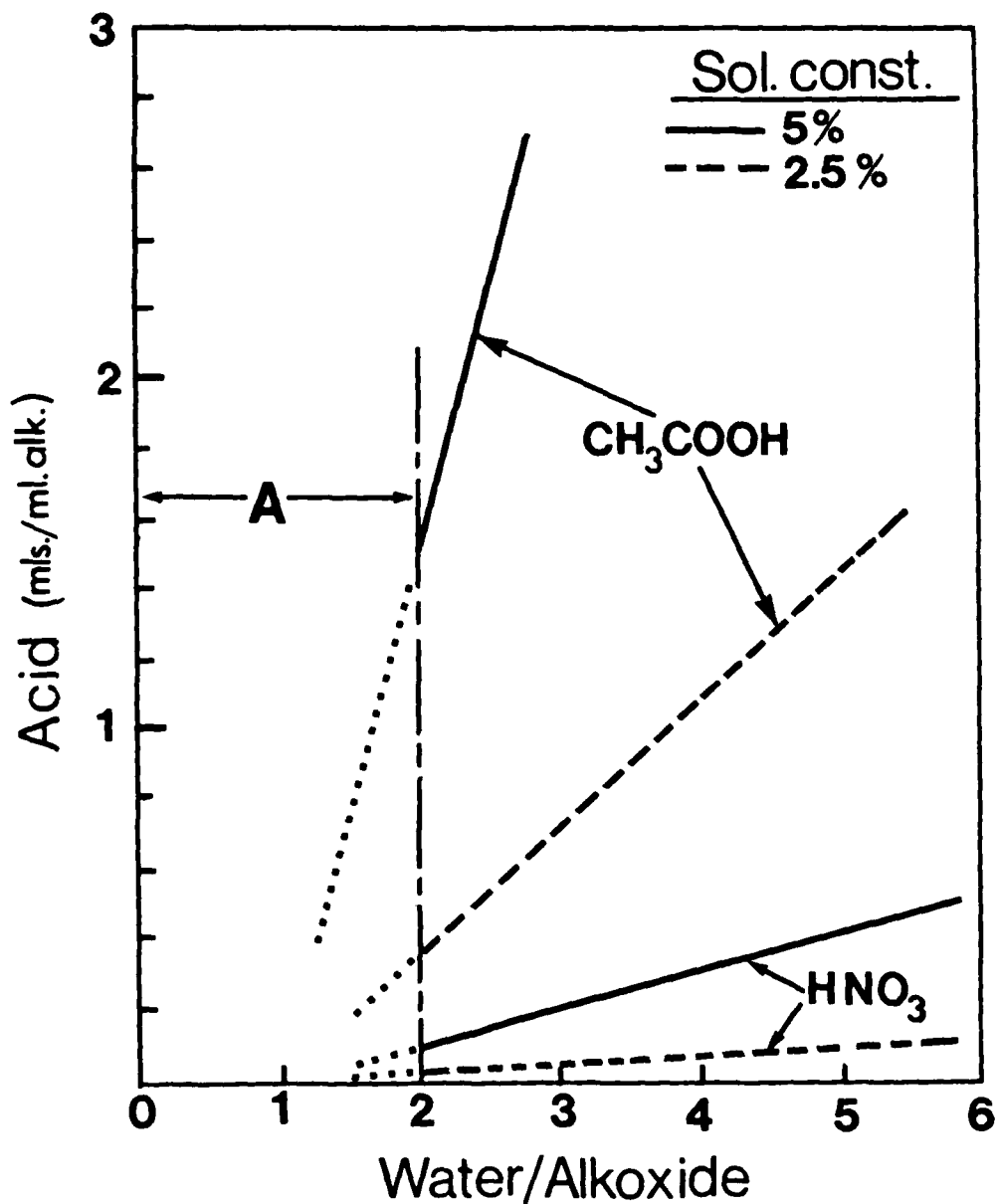
Figure 25. Acid requirement for the formation of clear zirconia solutions
as a function of water/alkoxide ratio at two different solution
concentrations when $Zr(OC_4H_9)_4^n$ is hydrolyzed in n-butanol.
Region A represents the area where no particulate condensation
occurs due to unsufficient water; thus no acid is required.
(Solution concentrations are expressed in terms of weight
equivalent ZrO_2.)

Figure 26. Effect of hydrolysis water temperature on the particle morphology. Top photograph shows $Zr(OC_3H_7)_4^n$ hydrolyzed with water at 20°C and the bottom photograph shows the hydrolysis with a water temperature of 65°C.

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3-5. SUMMARY
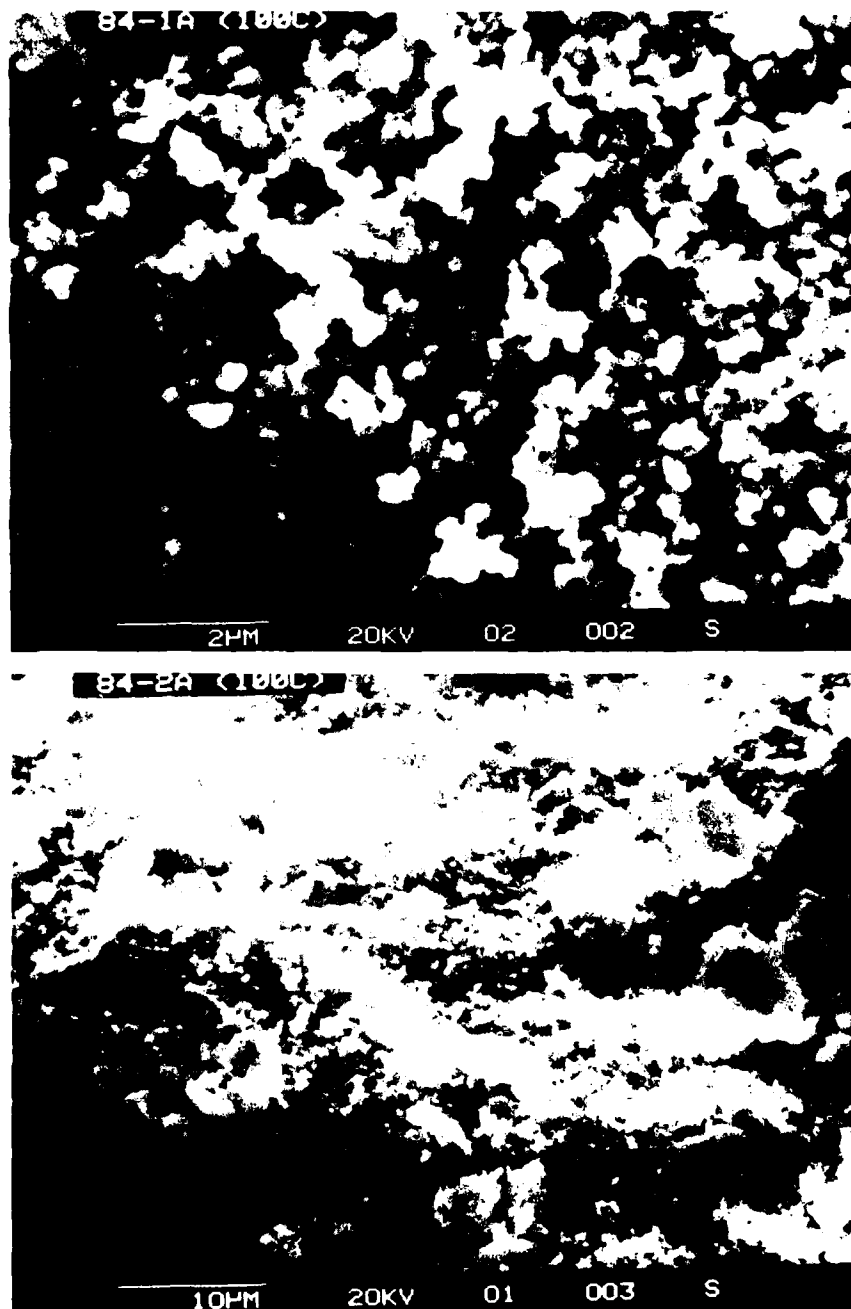
In the hydrolytic condensation of zirconium alkoxides, the alkyl groups of the alkoxides play an important role, affecting the morphology and particle size of the resultant materials. These in turn affect the sintering and monoclinic→tetragonal transformation of the ZrO_2 derived from these materials. Zirconium ethoxide, $Zr(OC_2H_5)_4$, tends to give the finest texture and highest compaction density before sintering. Zirconium n-propoxide $Zr(OC_3H_7)^n$, on the other hand, shows a unique property in producing a ZrO_2 that is resistant to the monoclinic→tetragonal transformation.

It has also been shown that the water/alkoxide ratio, the molecular separation of the reacting species, the reaction medium and the hydrolysis temperature all play important roles in determining the morphological make-up of the condensed materials. These morphological differences affect the thermal properties of the resultant ZrO_2 by modifying sintering behaviors and the phase transformation temperatures.

Localized condensations occurring at higher water concentrations can also be prevented by the introduction of acid. The acid requirement is found to be a function of the molecular spacing and the water/alkoxide ratio.

ACKNOWLEDGMENT

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