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Agglomerate control in the complexing sol-gel process①

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Abstract: Nanometer $ZrO_2 - 8\%\ Y_2O_3$(mole fraction, %) powders were prepared by the EDTA (ethylenediaminetetraacetic acid) sol-gel process. Effects of the addition of ethylene glycol on agglomerate control was investigated. The results showed that because of the replacement of hydrogen bonds with ethylene glycol in the polymerized gel, gel stabilization and homogeneity were improved and close approach of gel particles was prevented, which led to reduction of hard agglomerates to some extent. Calcined at 400 ℃ for 2 h and 700 ℃ for 2 h, the powders had a specific surface area of 35 m^2/g, average particle size of 28 nm, and median particle size (d_{50}) of 0.44μm with very sharp distribution, mostly being soft agglomerates.

Key words: complexing; EDTA; sol-gel process; $ZrO_2(Y_2O_3)$; agglomeration **Document code:** A

1 INTRODUCTION

Classified in terms of formation mechanisms of sol and gel, the sol-gel process includes three types: conventional colloidal sol-gel, inorganic polymeric sol-gel (i. e., hydrolysis of metal alkoxides), and complexing sol-gel[1]. For the inorganic polymeric sol-gel process, difference of hydrolysis rate among different alkoxides usually leads to poor homogeneity, so one problem with this process is the higher cost as a result of expensive chemicals and inconvenient preparation conditions[2]. This problem can be solved by using the complexing sol-gel process which has a number of advantages, including cheaper starting materials, simpler preparation conditions, and more homogeneous compositions[1]. For example, superconductors such as Y-Ba-Cu-O[3] and Pb-Sr-Y-Ca-Cu-O[4] have been prepared by citric acid; and Bi-Pb-Sr-Ca-Cu-O[5] and PZT[2] have also been synthesized by EDTA (ethylenediaminetetraacetic acid). Pechini[6] and Chen *et al*[5] found that the as-formed EDTA metal complexes could be further polymerized by ethylene glycol, as a result, cation segregation could be inhibited and a homogeneous precursor was easily obtained. Matsumoto *et al*[7] also reported that the presence of ethylene glycol in citrate complexes improved the synthesis process. However, agglomeration after thermal decomposition of the organic gel is a common problem of this method. Wang *et al*[2] discovered that the sinterability of calcined powders from the organic-gel route was affected by agglomeration and ball-milling was required for a higher sintered density. Although the complexing sol-gel method is commonly used, little work has been reported on the mechanisms involved in reduction or prevention of hard agglomerates. In this paper, we report an EDTA sol-gel process by which nanometer ZrO_2-8% Y_2O_3 powders are prepared, and discuss the effects of ethylene glycol on the agglomerate control and the average particle size.

2 EXPERIMENTAL PROCEDURE

The starting materials were $ZrOCl_2 \cdot 8H_2O$ (CP) and Y_2O_3(99.999%). $Zr(OH)_4$ precipitates (washed with distilled water until free of chloric ions examined by $AgNO_3$ solution) and Y_2O_3 powders were dissolved separately in nitric acid to produce $ZrO(NO_3)_2$ and $Y(NO_3)_3$ solutions, see reaction equations (1)～(3):

$$ZrOCl_2 + 2NH_4OH + H_2O \longrightarrow Zr(OH)_4 +$$

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$$2NH_4Cl \quad (1)$$

$$Zr(OH)_4 + 2HNO_3 \longrightarrow ZrO(NO_3)_2 + 3H_2O \quad (2)$$

$$Y_2O_3 + 6HNO_3 \xrightarrow{\triangle} 2Y(NO_3)_3 + 3H_2O \quad (3)$$

A second solution was prepared by dissolving EDTA acid in ammonium hydroxide to reach a pH value between 5~6. According to a nominal composition of ZrO_2-8% Y_2O_3, the mixed solutions of $ZrO(NO_3)_2$ and $Y(NO_3)_3$ were slowly added into vigorously stirred mixtures of EDTA and ethylene glycol solutions. The pH value was maintained at about 5 by adding NH_4OH. The final clear solutions was held at room temperature for 1h to equilibrate. The water in the solutions was then evaporated until a viscous gel was obtained, care should be taken at this step to avoid precipitation. The gel was subsequently pre-fired at 400 ℃ for 2 h to produce the soft precursor, which were readily ground and calcined at 700 ℃ for 2 h.

Simultaneous thermal anlysis (DTA/TG) was carried out from room temperature to 1 000 ℃ at a heating rate of 10 ℃/min to study decomposition of the precursor. The resulting phases with increasing temperatures were identified by XRD techniques, and the crystalline size of the powders was calculated from the half-width of a diffraction peak (111) using Scherrer's equation ($D = 0.89\lambda/\beta\cos\theta$). Infrared absorption (IR) spectra of the precursor and the calcined powders were also measured. The average particle size were determined with both BET method for nitrogen absorption ($d = 6/\rho Sw$) and TEM techniques. The median particle size (d_{50}) was measured by the gravitational subsidence methed.

3 RESULTS AND DISCUSSION

3.1 Characterization of precursor and calcined powders

Fig. 1 shows the DTA/TG curves of the precursor. From 42 ℃ to 217 ℃, three endothermic peaks were attributed to the dehydration of absorbed water, with the considerable weight loss. Two sharp exothermic peaks at 245 ℃ and 364 ℃ accompanied with great weight loss were indicative of bond breaking, carbonization, and oxidation of organic components in the precursor, after self-combustion with exhausting gases such as H_2O, CO_2, and NO_x. A distinct exothermic peak at 448 ℃ resulted from the crystallization of ZrO_2. It was found that the precursor decomposed almost completely at about 500 ℃.

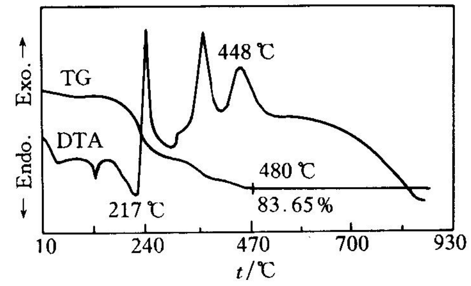


Fig.1 DTA/TG curves of the precursor

The corresponding XRD patterns are shown in Fig. 2. Apparently, the basic gel was amorphous but contained NH_4NO_3 as a minor phase. NH_4NO_3 decomposed completely and a ZrO_2 microcrystalline formed easily when heated to 300 ℃. Facilitated by the nitrate ions, further decomposition and oxidation of the organic components evolved a great amount of heat which increased the local temperature in the precursor. So burning of residual carbon and crystallization of ZrO_2 phase could happen at a very low temperature. It was seen that complete and pure cubic ZrO_2 formed at 500 ℃, in agreement with the anlysis results of DTA.

With the wavenumbers decreasing in the IR spectras (as shown in Fig. 3), there were stretch peaks of O—H (also including N—H, 3 750 ~ 3 000 cm^{-1}), C—H (3 000 ~ 2 700 cm^{-1}), and C═O (1 900 ~ 1 650 cm^{-1}), and C—H (1 475 ~ 650 cm^{-1}) bend peak, and stretch peaks of C—C (1 240 ~ 980 cm^{-1}), C—O (1 280 ~ 1 100 cm^{-1}), and C—O—M (1 610 ~ 1 400 cm^{-1}) in the precursor, respectively. These peaks disappeared almost completely but only Zr—O peak at 466 cm^{-1} existed whencalcined at 700 ℃ for 2 h.

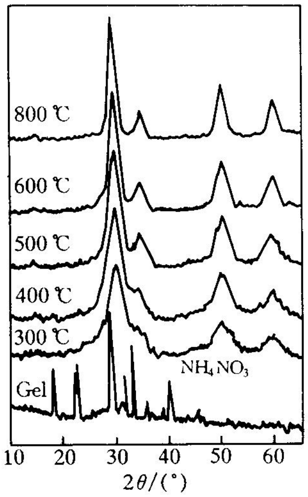


Fig.2 XRD patterns of the precursor and calcined powder

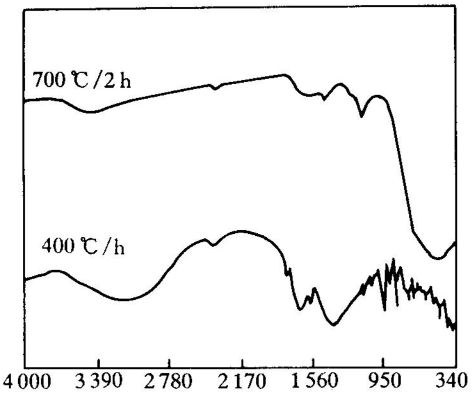


Fig.3 IR spectra of the precursor and calcined powder

3.2 Powder particle size and micrograph

Comparisons were made between the powders prepared without and with ethylene glycol, as listed in Table 1. Clearly, the addition of ethylene glycol to the initial gel led to larger specific surface area and smaller particle size, especially smaller median particle size (as seen in Fig.4) and lower agglomeration factor. It was also observed that powder particle size was greatly decreased by hand-grinding, indicating a reduction in the incidence of hard agglomerates. Fig.5 shows the TEM micrographs of the calcined powders. It was proved that the addition of ethylene glycol truely led to a reduction of hard agglomerates.

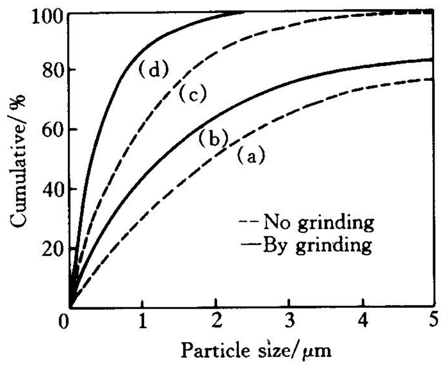


Fig.4 Particle size distributions of the powders
(a) (b)—Without ethylene glycol;
(c)(d)—With ethylene glycol

Table 1 Comparisons between the powders prepared without and with ethylene glycol

Powders	Without ethylene glycol	With ethylene glycol
Specific surface area, $S_w/(m^2 \cdot g^{-1})$	15.33	35.15
Average particle size, d_{BET}/nm	65	28
Scherrer crystallite size, D/nm	6.8	6.3
Median particle size, $d_{50}/\mu m$	1.88	0.44
Agglomeration factor, d_{50}/d_{BET}	29	16

3.3 Mechanisms of reduction of hard agglomerates

For the chemical coprecipitation method, it was well known that when gel was washed with ethanol, interparticle free water was removed and hydroxo groups were replaced by ethoxy groups. Combining with the steric effects of ethanol, close approach of gel particles and Zr-O-Zr chemical bond formation (Eqn. (4)):

$$\text{Zr-OH} + \text{HO-Zr} \xrightarrow{\text{calcination}} \text{Zr-O-Zr} + H_2O \qquad (4)$$

were prevented. Consequently, ethanol washing of hydrous zirconia produced soft rather than hard agglomerates[8].

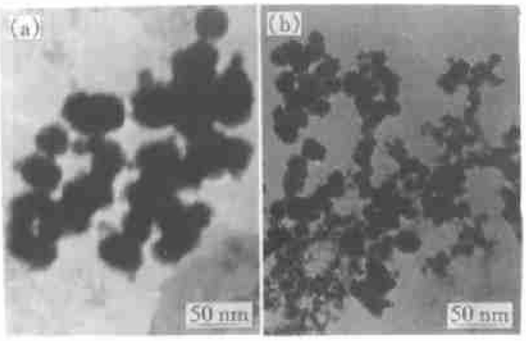
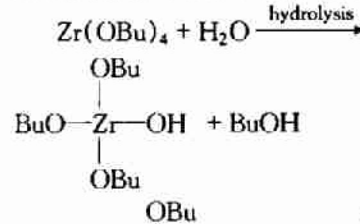
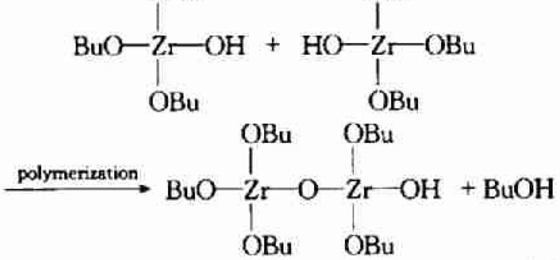


Fig.5 TEM micrographs of the calcined powders
(a)—Without ethylene glycol;
(b)—With ethylene glycol

For the inorganic ploymeric sol-gel process, because of lower surface tension and uneasier to form hydrogen bonds as a result of methanol medium used, hard agglomerates were nearly eliminated[9]. Hydrolysates from the metal alkoxides contained active hydroxo groups by which polymerization reaction took place to form high polymer with M-O-M chemical bonds, taking $Zr(OC_4H_9)_4$ as an example (Eqns. 5 and 6):



$$Zr(OBu)_4 + H_2O \xrightarrow{\text{hydrolysis}} BuO-\underset{OBu}{\overset{OBu}{Zr}}-OH + BuOH \qquad (5)$$



$$BuO-\underset{OBu}{\overset{OBu}{Zr}}-OH + HO-\underset{OBu}{\overset{OBu}{Zr}}-OBu \xrightarrow{\text{polymerization}} BuO-\underset{OBu}{\overset{OBu}{Zr}}-O-\underset{OBu}{\overset{OBu}{Zr}}-OH + BuOH \qquad (6)$$

However, for the complexing sol-gel process, the EDTA metal complexes were very stable without active hydroxo groups, so gel formation was achieved by evaporation to force complex moleculae to apporach each other by hydrogen bonds rather than by polymerization reaction similar to Eqn.6[10]. The sudden increase in the viscosity promoted a homogeneous distribution of cations throughout the resulting gel. Unfortunately, such hydrogen bonds were too unstable to resist heating or moisture, so the complex gel was soluable in water and moisture-retentive in air. On the other hand, the xerogel usually contained a great deal of physically and chemically bound water, it would have a bad dehydration effect if dehydration similar to ethanol washing in the coprecipitation method was conducted. The direct decompsoition of the gel without washing certainly led to the formation of hard agglomerates as a result of surface tension of water. Moreover, the gel without filtering contained a great number of troublesome impurity such as NH_4^+, OH^- and NO_3^- (or Cl^-), which acted as solid bridging during calcination and increased the incidence of hard agglomerates[9].

Previous studies of a relative simple sol-gel process, with citrate or EDTA precursor gels to synthesize some ceramic powders, didn't discuss the problem of hard agglomerate formation. The addition of ethylene glycol in the initial gel could produce more homogeneous gel as a result of prevention of cation segregation, as reported by a few researchers such as Pechini[6], Chen *et al*[5], and Matsumoto *et al*[7]. The EDTA metal complexes could be further polymerized by ethylene glycol[5], as indicated in Fig.6. In this work, proper concentration of ethylene ghycol was also found to be good for preparing homogeneous and limpid gel, especially for reducing hard agglomerates to some extent. This resulted from replacement of hydrogen bonds with ethylene glycol which prevented close approach of gel particles in the polymerized gel.

4 CONCLUSIONS

(1) Because of replacement of hydrogen bonds with ethylene glycol in the polymerized gel, gel stabilization and homogeneity are improved and close approach of gel particles is prevented, which lead to a reduction of hard

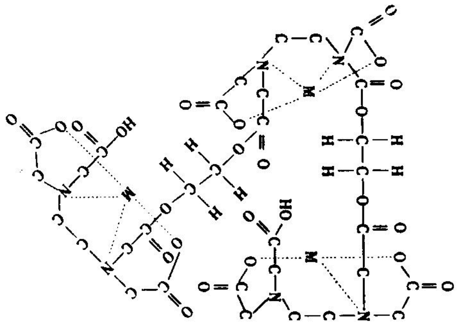


Fig. 6 Chemistry of polymerization of EDTA metal complexes induced by ethylene glycol

agglomerates.

(2) Calcined at 400℃ for 2 h and 700℃ for 2 h, the powders have an average particle size of 28 nm and median particle size (d_{50}) of 0.44 μm with very sharp distribution, mostly being soft agglomerates.

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