Journal of Thermal Analysis, Vol. 40 (1993) 1095-1102

THERMAL EVOLUTION OF $(Zr,Ti)O_2$ GELS SYNTHESIZED AT DIFFERENT BASIC *pH*

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$(Zr,Ti)O_2$ gels as precursors of zirconium titanate (ZT) powders were prepared by the sol–gel method, which involves hydrolysis of $ZrClO_2$ + $TiCl_4$ in the presence or absence of hydrogen peroxide, in two *pH* ranges, 8–9 or 11–12. Thermal evolution of these precursors has been studied by DTA, BET surface area, XRD and SEM. Differences in DTA curves, surface area and morphology were observed. In particular, ZT prepared at $pH = 8–9$ with hydrogen peroxide was purer, more homogeneous and presented a different morphology compared to ZT processed at $pH = 11–12$; hydrated/hydroxylated Zr-Ti species were formed to a greater extent in the latter case. Addition of hydrogen peroxide during chemical processing of these gels plays a key role in controlling the crystallization temperature of ZT.

Keywords: DTA, sol–gel method

Introduction

In the conventional synthetic route of zirconium titanate (ZT) materials, calcination of oxide mixtures leads to formation of this compound by solid-state reaction between ZrO_2 and TiO_2 at elevated temperatures (1200°–1600°C) which requires long heating times [1–5]. By this route, expensive treatments and post-treatments are generally required to obtain well-formed ZT materials with good properties. Recently, alternative chemical methods such as sol–gel and alcoxide synthesis routes have attracted much attention [6–11]. The chemical preparation

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of reactive precursors, especially by the coprecipitation and sol–gel methods offers advantages over traditional processing methods: high purity, better homogeneity, lower processing temperatures and improved material properties. Pure materials are thus obtained by a thermal process after hydrolysis, polycondensation reactions, dehydration and crystallization of gels as reactive ZT precursors [6–11]. The homogeneity of a gel depends mainly on the following parameters: solubility and chemistry of the reactants, temperature of the reactions and *pH*. Navío *et al.* [12] have recently reviewed the literature on the influence of chemical processing in the crystallization behaviour of ZT materials.

In this work, $(Zr,Ti)O_2$ gels were prepared by the sol–gel method. The method involves hydrolysis of $ZrClO_2$ and $TiCl_4$ solutions in the presence or absence of hydrogen peroxide, in two *pH* ranges, 8–9 or 11–12. The method we propose allows one to obtain different hydroxylated $(Zr,Ti)O_2$ gel precursors because of the change in *pH*.

In reported chemical preparation of powder materials based on Ti and Zr [6–12], small amounts of hydrogen peroxide were added. However, little attention has been paid until now to the effect of hydrogen peroxide on sol–gel processing of the $(Zr,Ti)O_2$ system, although Murata *et al.* [7] reported that addition of this chemical seems to improve coprecipitation. In this paper, a preliminary study of the effect of hydrogen peroxide on chemical processing of ZT materials is presented.

Experimental procedure

Materials

Amorphous $(Zr,Ti)O_2$ gels can be processed according to a general sol–gel method proposed by the authors in a previous paper [11]. The starting powdered precursor was obtained from an anhydrous methanol solution which contained equimolecular amounts of $ZrClO_2$ (Fluka AG, 43–44 wt% Zr), and $TiCl_4$ (Merck, 99.99%). Hydrogen peroxide (Merck, 30–32 wt% solution in water) was added in excess and mixed by constant stirring at 0°C. The hydrolysis was carried out by controlled and slow addition of 28 wt% aqueous ammonia within the *pH* ranges 8–9 or 11–12. The gelled mass was allowed to settle as a precipitate, and the supernatant liquid decanted after several washings with distilled water. The solid was filtered and repeatedly washed with distilled water until the filtrate showed negative reaction for Cl^- ions. Acetone was used for the final washing. The resulting solid was allowed to dry for several days under an infrared lamp, and finally powdered in an agate mortar.

Techniques

Differential thermal analysis (DTA) curves were obtained in static air with a Rigaku PTC-10 A Thermoflex instrument) at a heating rate of 8 deg·min^{-1}, using calcined alumina as the reference. X-ray diffraction (XRD) patterns were obtained at room temperature with a Phillips PW 1060 diffractometer using Ni-filtered CuK_α radiation. Specific surface areas (S_{BET}) were obtained with an automatic system (Micromeritics 2200 A) using nitrogen gas as the adsorbate at –195°C. Thermally treated products were examined with a scanning electron microscope (ISI model SS-40).

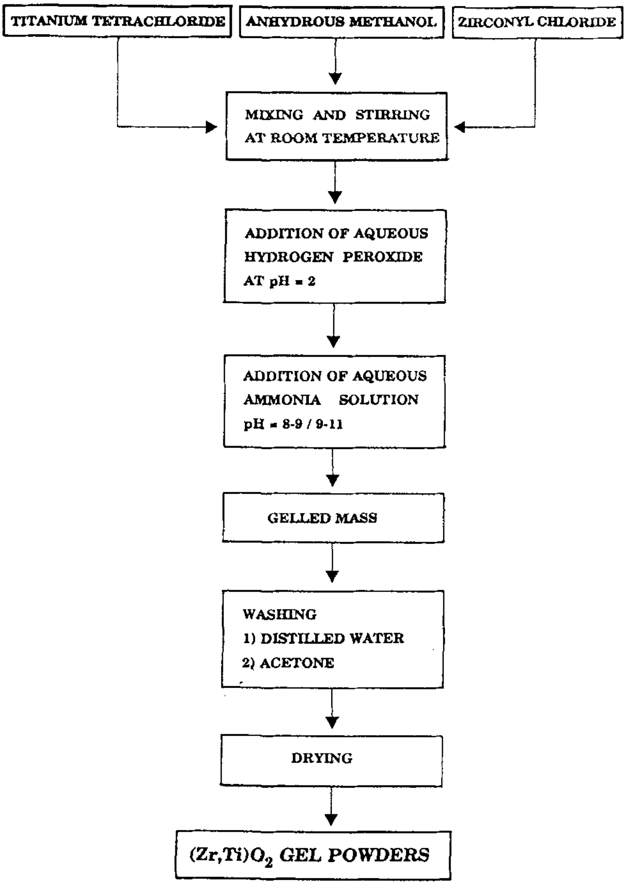

Fig. 1 Processing flow chart of (Zr,Ti)O_2 gel powders

Results and discussion

Processing of (Zr,Ti)O_2 gels

Reactive (Zr,Ti)O_2 powdered gel prepared by the above-mentioned method at *pH* 8–9 (Fig. 1), named hereafter gel A, was found to be amorphous by XRD. It was a yellow solid, and by chemical analysis, we found ca. 0.8 peroxo species per metal ion. The chemical formula was found to be $ZrTiO_{3.43}(OH)_{1.13}xH_2O$. The presence of peroxo species was not surprising because there is evidence in the literature that hydrated peroxides such as $MO(O_2)(H_2O)$ with M = Ti,Zr and $x \geq 2$ are formed by precipitation of Ti and/or Zr solution with ammonia in the presence of hydrogen peroxide [13–14].

Another type of gel precursor was prepared according to the same processing method used for gel A, but without addition of hydrogen peroxide. This powdered white gel (gel B) contained only hydrated and hydroxylated Zr and Ti oxides.

In another experiment, a sample termed gel C was prepared in a similar way as that employed for gel A, but the *pH* was increased to 11–12 with ammonia. Gel C contained hydrated/hydroxylated and hydroxoperoxo species of Zr and Ti oxides, as confirmed by chemical analysis.

Differential thermal analysis

Figure 2 shows DTA curves of gels A, B and C. Intense endothermic peaks at ca. 100°C are ascribed principally to elimination of organics and water trapped in or bonded to the porous amorphous solids. They are more intense for gel A. As temperature increases, the remaining water is eliminated. The exothermic effect at ca. 300°C has been linked to elimination of residual ammonia [11]. In addition, sharp exothermic DTA peaks at 640°C (gel A), 725°C (gel B) and 670°C and 700°C (gel C) are observed.

Below 500°C, XRD patterns indicated that the samples were amorphous. The product formed after heating gels A, B, and C at 1000°C was pure zirconium titanate. Figure 3 shows the XRD patterns for gel A and ZT generated from this gel. Consequently, the exothermic DTA peaks are associated with crystallization. ZT prepared from gel A was purer and more homogeneous than ZT prepared from gel B or gel C. The formation of peroxo species of Ti and Zr enhances crystallization of ZT materials at lower temperatures, possibly because the peroxobondings are easily broken by the thermal treatment. Indeed, it has been reported [14] that oxo-, hydroxo- and peroxo-(Zr,Ti) bonds can be formed in the (Zr,Ti)O_2 gel system, and therefore it is reasonable to assume that they are simultaneously present in gels A and C. Also, processing of (Zr,Ti)O_2 gels at lower *pH* is advantageous, because the formation of more hydrated/hydroxylated species of Zr and Ti is avoided. XRD results for gel C heated between the two exothermic peaks showed that ZT was formed.

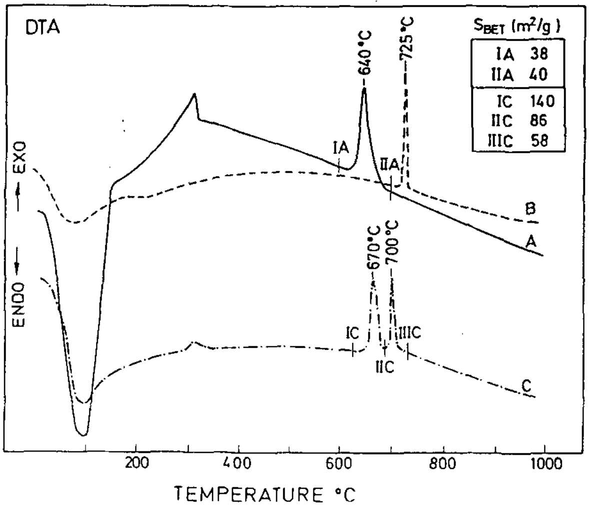

Fig. 2 DTA curves of gels A, B and C (see text.). Specific surface area data are included

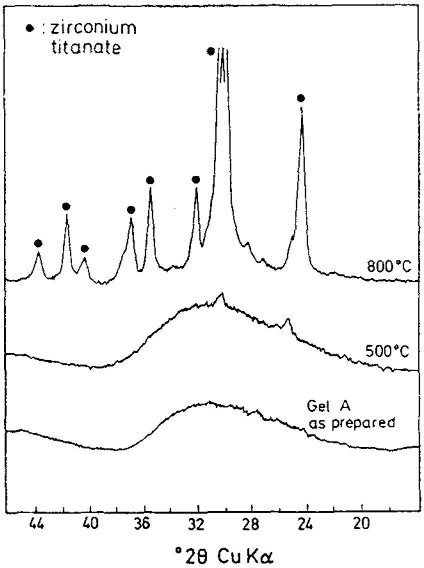

Fig. 3 X-ray diffraction patterns of gel A after heating at indicated temperatures

It is worth noting that gel A slowly lost its original yellow colour on ageing. The DTA curve of the aged material showed two exothermic peaks analogous to those observed in gel C. Gel C was processed at *pH* values at which hydrogen peroxide is unstable, so that the formation of hydroxyl bonds between Zr and Ti is more favoured than that of peroxo bonds. Indeed, the loss of the yellow colour in aged gel A has been recently attributed to atomic rearrangement due to oxygen loss from the peroxidic bonds [12].

SEM study

ZT materials formed by heating gels A and B at 800°C presented different morphologies (Fig. 4). Gel A produced regular and spherical particles (Fig. 4a), but this was not the case when gel B was the precursor (Fig. 4b). On heating gel C at 800°C, ZT was also formed and its morphology was very similar to that shown in Fig. 4b. However, two types of ZT particles were observed after heating gel C between the two exothermic DTA peaks at 684°C, as shown in Fig. 5. This is not

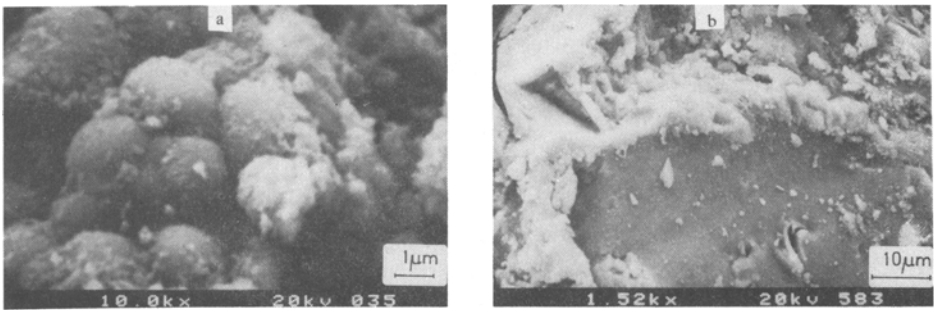

Fig. 4 SEM micrographs after heating at 800°C: (a) gel A, (b) gel B

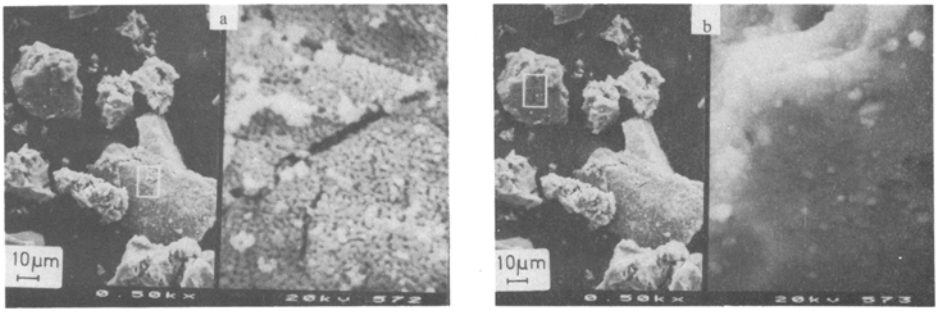

Fig. 5 SEM micrographs after heating gel C between the two exothermic DTA peaks (684°C) showing details of the two types of morphologies observed, (a) and (b)

is not surprising because gel C was processed within a *pH* range that produced partial decomposition of hydrogen peroxide, so that a situation not too different from that employed to process gel B (without hydrogen peroxide) occurred. This also corresponds with the thermal features observed for the three kinds of gels (Fig. 2).

Surface area

Surface area development during the thermal treatment of gels A and C is shown in the insert to Fig. 2. Higher surface area values for gel C is again and indication of the presence of higher amounts of hydrated and hydroxylated Zr,Ti species. The development of surface area before and after the exothermic DTA peak is in accordance with the crystallization process of ZT from gel C. Surface area values for gel A showed very little change in the temperature range in which the crystallization process was observed. This can be explained by assuming a compensation between two opposite effects: formation of small spherical particles and the beginning of sintering [11].

Conclusions

Addition of hydrogen peroxide in the chemical processing of $(Zr,Ti)O_2$ amorphous gels as reactive precursors of ZT materials plays a key role in controlling the crystallization temperature of this compound. Crystallization can occur as low as 640°C by use of hydrogen peroxide and processing at $pH = 8$–9. Formation of peroxo species of Zr and Ti causes crystallization to occur at low temperature probably because peroxo bondings are easily broken by thermal treatment.

Reactive precursors prepared by chemical processing at $pH = 8$–9 using ammonia lead to ZT of higher purity, lower surface area and better chemical homogeneity than those processed at $pH = 11$–12, where hydrated and hydroxylated species are formed to a greater extent. This illustrates the strong effect of *pH* in the synthesis of ZT by chemical methods.

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Financial support by Junta de Andalucia (research groups 1991) and the Ministerio de Educacion y Ciencia (Accion Integrada Grant HF-048, 1992) are greatfully acknowledged.

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Zusammenfassung – $(Zr,Ti)O_2$ Gele als Präkursoren von Zirkoniumtitanat (ZT) Pulvern werden mittels der Sol-Gel-Methode hergestellt, welche eine Hydrolyse von $ZrClO_2$ + $TiCl_4$ in Gegenwart oder Abwesenheit von Wasserstoffperoxid, in zwei *pH*-Bereichen (8–9 oder 11–12) umfaßt. Mittels DTA, BET spezifischer Oberfläche, Röntgendiffraktion und SEM wurde die thermische Entwicklung dieser Präkursoren untersucht. Dabei stieß man auf Unterschiede der DTA-Kurven, der spezifischen Oberfläche und der Morphologie. Insbesondere zeigte bei *pH* = 8–9 und mit Wasserstoffperoxid dargestelltes ZT eine größere Reinheit bzw. Homogenität sowie eine Morphologie, die sich von der desjenigen ZT unterschied, welches bei *pH* = 11–12 dargestellt wurde; in letzterem Falle werden hydratierte/hydroxylierte Zr-Ti-Spezies in größerem Maße gebildet. Der Zusatz von Wasserstoffperoxid während der chemischen Umsetzung dieser Gele spielt eine Schlüsselrolle bei der Festlegung der Kristallisationstemperatur von ZT.