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Ceramics International 32 (2006) 235–239

CERAMICS
INTERNATIONAL

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Preparation of a highly thermally stable titania anatase phase by addition of mixed zirconia and silica dopants

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Received 12 January 2005; received in revised form 24 January 2005; accepted 7 February 2005

Abstract

Sol–gel methods using a titanium isopropoxide precursor were employed in the synthesis of titania and the conversion of the amorphous product to anatase and then rutile by high temperature thermal treatment was followed by powder X-ray diffraction (PXRD), differential thermal analysis (DTA) and electron microscopy (EM). The thermal stability of the anatase phase was limited when pure materials were prepared. However, addition of 4+ dopants such as Zr^{4+} and Si^{4+} showed higher transition temperatures for the anatase to rutile phase change. The highest stability of the anatase phase was found for tertiary materials containing both Zr^{4+} and Si^{4+}. The mechanism for the anatase to rutile phase transition in these materials appears to be largely related to the attainment of a critical particle size above which the phase change becomes energetically favourable. The role of silicon and zirconium ions appears to reduce mass transport in the system thereby preventing the materials reaching the critical particle size until higher temperatures compared to undoped materials.

Keywords: D. TiO_2; Phase transformation; XRD; Critical particle size

1. Introduction

Titania is an important ceramic finding use as pigments, refractories, catalysts/photocatalysts, electronic materials and in thin film applications such as self-cleaning windows [1]. Titania has an unusually rich structural chemistry. Three principal structural phases exist; brookite, anatase and rutile with the first two being metastable with rutile the thermodynamically stable phase [2]. Titania also shows a number of shear plane structures or Magnéli-phases of stoichiometry Ti_nO_{2n-1} [3]. Anatase and rutile are the principal phases used in commercial applications. Anatase is the most widely used phase in catalysis and photocatalysis because it is the high surface area form of the material and is metastable at lower temperatures. Rutile is preferred in the pigments industry because of its brightness and durability [4]. The phase change to rutile requires movement of cations and anions and this leads to high mass transport rates during conversion and rapid loss of surface area by sintering.

Inclusion of dopants can be used to both elevate and depress the anatase to rutile transformation (ART) temperature (see, for example [5]). Most notably, the addition of silicon has been found to very significantly raise the ART temperature [6]. Inclusion of more than one dopant into titania has been shown to have beneficial effects compared to single element doping [7]. During the course of recent studies in UCC, we have studied inclusion of very many metal dopant ions and these are detailed elsewhere [8]. The highest ART temperatures were noted by the combined addition of Zr^{4+} and Si^{4+} into the titania structure. These results are presented here.

2. Experimental

PXRD data were collected on a Panalytical X'Pert diffractometer, equipped with an Accelerator detector. A Ni filtered Cu Kα X-ray source with 0.2° entrance and exit

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doi:10.1016/j.ceramint.2005.02.009

Stöller slits and a programmable divergent slit were used for data collection. Scherrer formulism was used to estimate particle sizes. A reference for the instrumental resolution was taken from a titania sample calcined at 1200 °C for 120 h. In all cases, at least three reflections were used and the particle size calculated as the average value. The relative weight fractions of anatase (W_A) and rutile (W_R) were calculated using the relative intensity of the anatase (1 0 1) peak (I_A) and the rutile (1 1 0) peak (I_R) and the relationships $W_A = 1/[1 + 0.8I_A/I_R]$ and $W_R = 1/[1 + 1.26I_R/I_A]$ as used by Spurr and Myers [9]. Physical mixing showed this relationship to be followed on our set-up and this is probably because of the similarity in position of these reflections which limits any instrumental contribution. A JOEL JSM 5510 secondary electron microscope (SEM) operating with a 15 kV accelerating voltage was used for collection of micrographs. Powder samples were blown onto a sample stub with double sided graphitic tape. Particles were sputter coated with gold to avoid charging. Differential thermal analysis (DTA) data were collected on a Stanton Redcroft STA 1640 at a heating rate of 10 °C min^{-1}.

A true sol–gel method was used for the synthesis of TiO_2 powders. Only catalytic amounts of water were used in the preparation. Around 35 ml of titanium(IV) isopropoxide (TIP) was dissolved in 50 ml of butan-1-ol. The required amount of metal precursor (as detailed below) were then added and the mixture magnetically stirred for 10 min. Separately, 0.56 ml of ~36% (w/w) HCl was dissolved in 30 ml of butan-1-ol and mixed for 10 min. The second solution was then added to the first and the whole was stirred for a further 15 min. This solution was then left to stand at room temperature for 4–5 days at which point a clear and transparent glass-like gel was formed. These gels were then dried at 60 °C for 5–7 days. The dried products were ground to a fine powder and divided into several lots, placed in quartz crucibles and calcined in air for 2 h at 50 °C intervals in the temperature range of 200–1100 °C. Dopant concentrations are given as wt.% as metal content and are written as, e.g. 5%Si5%Zr.

3. Results and discussion

In a series of experiments a number of doped materials were prepared by addition of the required amount of precursor into the synthesis procedure. The precursors used were: zirconium isopropoxide, aluminium-sec-butoxide, tetraethoxysilane, manganese(II) acetylacetonate, cobalt(II) acetylacetonate and vanadium(III) acetylacetonate. These were chosen because they maintained a good clear gel synthesis. PXRD data were collected through the temperature range. Typical data are shown in Fig. 1 for a 1% V doped material. No brookite was observed in these experiments and the PXRD profiles can be characterised as representative of anatase and/or rutile as indicated in Fig. 1. These data can be used to construct plots of the relative concentration of rutile versus temperature using the Spurr and Myer Formulism described above [9]. The ART temperature is taken as that required to transform 50% of the anatase to rutile (T_{50}) and calculated ART temperatures for various 1% doped samples and pure TiO_2 are described in Table 1. Also shown are T_{75} values (i.e. temperature for 75% conversion) because the T_{50} of Si doped materials cannot be accurately determined because of a plateau in the weight fraction versus temperature plot. There is a mixed effects of dopants used here increase and decreasing the transition temperature. This is expected as the addition of different cations can assist as well as hinder the transformation depending on the dopant mechanism and the defects formed [10]. However, from the results presented here, it can be reasonably concluded that for the tetravalent cation doping and alumina addition that the phase transition is largely hindered by strain effects in the lattice (caused by doping) which limit mass transport required in this phase transition. If this was not the primary mechanism, some of these dopants might be expected to create grain boundary and phase separation related defects, which would lead to preferential phases change and so lower the ART temperature. The hindrance of phase development by internal strain effects has been discussed elsewhere (see, for instance [11]).

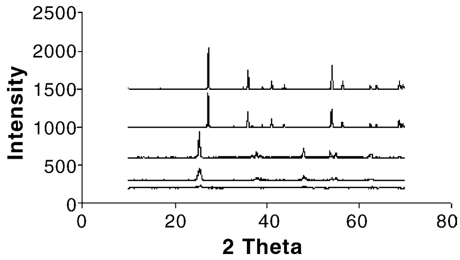

Fig. 1. PXRD profiles (intensity in arbitrary units against 2θ angle) as function of temperature from 200 °C (bottom) to 1000 °C (top) at 200 °C intervals for a 1% V doped TiO_2. The anatase structure is seen in the lower three traces and rutile in the top two.

Table 1
Estimated temperatures for the anatase to rutile transition from PXRD data for the 1% doped samples and pure titania

	Sample						
	1% Mn	1% Co	1% V	TiO_2	1% Zr	1% Al	1% Si
T_{50} (°C)	640	679	724	751	791	832	787
T_{75} (°C)	651	687	760	782	823	855	863

ART temperatures are given as a T_{50} and T_{75}, the temperatures for 50 and 75% conversion of anatase to rutile.

The conclusion can also be reached that the most effective dopants to increase the transition temperature are Al^{3+}, Zr^{4+} and Si^{4+}. It was decided that a series of materials should be prepared as a combination of these to increase the ART temperature. It was found that combinations involving aluminium doping gave disappointing results. Al–Zr and Al–Zr combinations provided no difference in the ART temperature to that measured with aluminium. Optimum combinations were found with Si–Zr dopant combinations and the best of these was a 5%Si5%Zr dopant mixture which

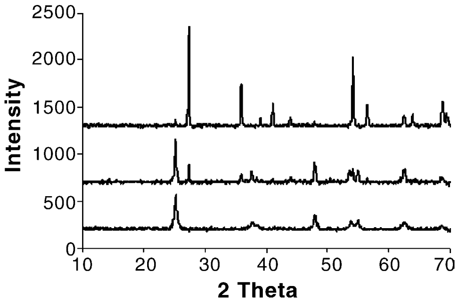

Fig. 2. PXRD profiles as function of temperature. Data shown are at 700 °C (bottom), 900 °C (centre) and 1100 °C (top) for a 5%Zr5%Si doped TiO_2. The anatase structure is seen in the lower trace and rutile in the top. The centre shows a mixture of phases.

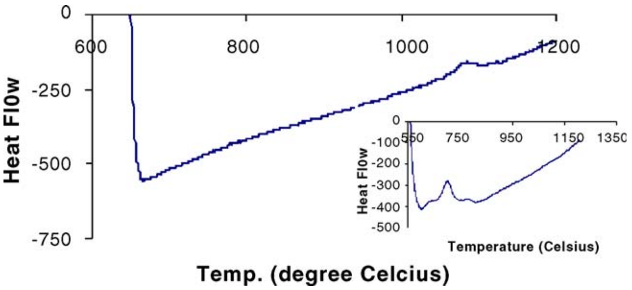

Fig. 4. DTA data of a 5%Zr5%Si sample showing a weak feature due to the anatase to rutile phase transition. Inset shows data recorded in identical manner for a TiO_2 only sample.

had a very high phase transition temperature. Typical PXRD results for a 5%Si5%Zr doped titania are shown in Fig. 2. It can be seen immediately that the phase transition occurs around 900 °C as both phases coexist at this temperature. All the XRD data are represented in Fig. 3 as the weight fractions plot calculated using the equations for W_A and W_R detailed above. The phase transition temperature (T_{50}) can be estimated as about 936 °C. This is one of the highest values recorded for the anatase to rutile transition. It is similar to data for a 10% Si doped TiO_2 sample which showed some coexistence of the two phases at 1100 °C but the phase transition commenced at a lower temperature than observed in the work reported herein [12].

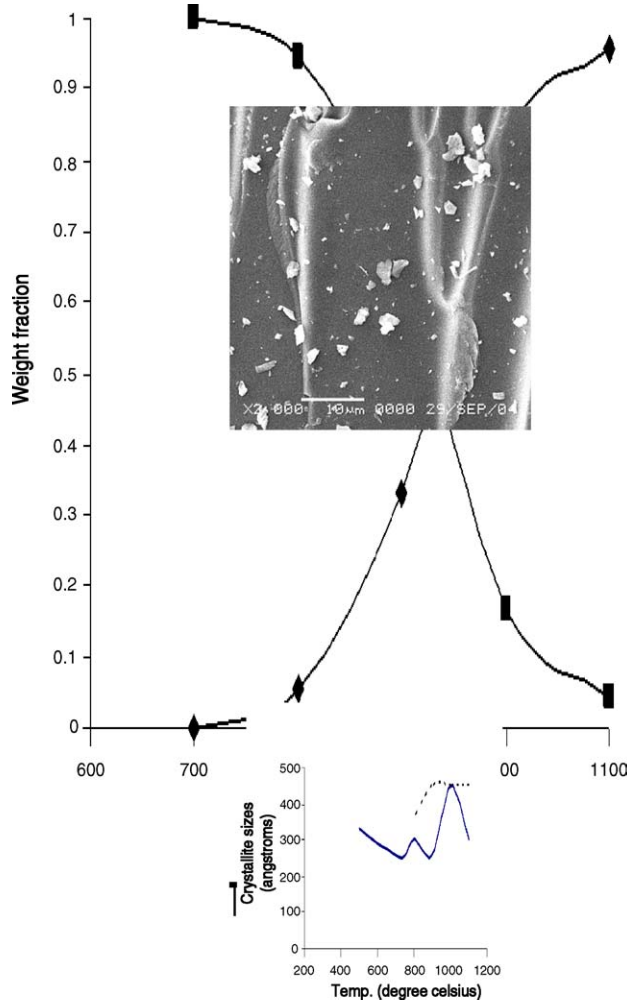

Fig. 3. 5%Zr5%Si doped TiO_2 data. Weight fractions of anatase (W_A, ■) rutile (W_R, ◆) as a function of temperature (°C), as derived by PXRD. The left inset shows an SEM image of the sample following heating to 1100 °C. The right inset is the particle sizes as a function of temperature for both rutile and anatase phases.

Direct and exact comparison of phase transition temperatures with previous literature data is difficult because the reaction is kinetically slow and sample heating times are long. The transition temperature was measured more directly by DTA. It is rare that the anatase to rutile phase transition has been observed directly by DTA. This is because of the very similar free energy of the two phases [13] which ensures the peaks are small and normally on quite high signal backgrounds. The low energy phase transition could be observed relatively easily here and typical data for a 5%Si5%Zr doped titania sample and non-doped TiO_2 are shown in Fig. 4. In these experiments, the phase transition temperature was measured as 1084 °C. This is somewhat higher than the ART temperature measured by PXRD (932 °C) as a result of the rapid heating rate. More importantly, the DTA measured value for the doped samples is some 359 °C greater than that of a pure TiO_2 sample prepared in the same way. This difference value is close to the difference in temperature noted by PXRD for the ART temperature calculated by PXRD; i.e. 932–846 °C (from Table 1) or 369 °C. The similarity of the values does suggest that the DTA method is indicative of the rate of change of the transformation and the high temperature peak observed has been correctly assigned to the weakly exothermic anatase to rutile phase transition. The similarity in PXRD and DTA values further suggests that the reaction follows the expected rate laws of a simple reaction and complex mechanisms around, e.g. autocatalytic processes can be ignored.

Information on the mechanism by which the phase transition temperature is increased by this doping can be gained from measurements of the particles size through the transition. Standard Scherrer formulism was used to calculate particle sizes from the width of the rutile (1 1 0) and anatase (1 0 1) reflection and data is shown in Fig. 3. At 700 °C, the anatase particles begin to grow and between 800

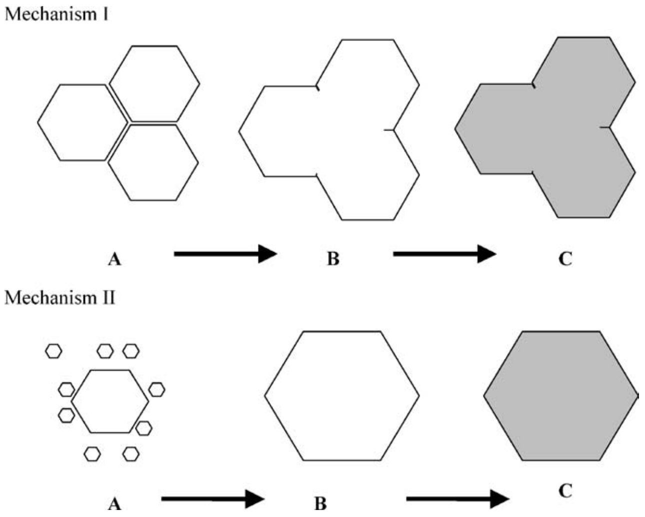

Fig. 5. Mechanisms for phase transformation. Mechanism I is particle agglomeration and mechanism II is the ripening process. In each case, (A) shows how particles grow to reach the critical size (B) when spontaneous phase change occurs (C).

and 900 °C, around 30% of the material has been converted to rutile. This is accompanied by a dramatic growth of the rutile particles and corresponding size decrease of the particle size of anatase measured. The rapid growth of rutile particle size during this process suggests that the mechanism consists of particle agglomeration or grain coalescence by grain boundary diffusion or diffusion at/to grain boundaries [14] so that a critical particle size for spontaneous phase transformation is attained. The critical size is defined when the energy cost of forming new surfaces is balanced by the stabilisation of the bulk energy when moving to the more thermodynamically stable rutile phase [15]. This critical size where this grain boundary process becomes important is determined at around 277 Å in this temperature range. Fig. 5 shows a simple schematic of the process and is described as mechanism I. Note that the actual critical size for phase transition might be actually larger than 300 Å as once agglomerated the transformation would be very rapid in comparison to the calcination period of hours. The apparent size of anatase particles decreases because the larger particles have been converted to rutile.

At temperatures between 900 and 1000 °C, the anatase particles apparently increase in size beyond the 300 Å value measured at lower temperature and to maximum value of 541 Å. Between 1000 and 1100 °C, the anatase particles remaining begin to decrease in size for the same reason as given above. We believe that the size of rutile particles does not grow very quickly at these higher temperatures because the mechanism is quite different to the smaller particle process and does not involve particle agglomeration but, rather, particle growth occurs by a ripening process involving consumption of smaller grains and is limited by mass transport and not grain boundary movement [16]. Again, the process is shown schematically in Fig. 5 as mechanism II.

We suggest the lower temperature process occurring via particle agglomeration occurs as a result of dopant material not dissolved into the titania structure and that exists at the grain boundaries. The mechanism is dominated by surface sponsored processes. Indeed, the particle size where this occurs (~300 Å) is significantly less than that observed for titania (and low concentration doped titania materials) which was measured at around 450 Å [8]. The possible effect of dopants on grain coalescence has been described elsewhere in depth [17]. The second larger particle related phase transformation process occurs at about this size (i.e. similar that of pure TiO_2) but at a much higher temperature. We argue that in this case, the dopant is well-dissolved in the anatase structure and particle agglomeration is not favoured and the particles grow by a process of 'ripening' via mass transport to the surface. Once individual particles reach the critical size a spontaneous phase change occurs. This occurs at higher temperatures than in pure titania because the dopants introduce stain in the anatase lattice which then limits mass transport and thus raises the temperature when the critical particle size is reached [18]. It should be noted that no significant amount of phase separation appears to occur through the phase transition and no new phases related to SiO_2, ZrO_2 or silicates could be resolved by PXRD. SEM data does provide further evidence for only very limited phase separation. Data collected following 1100 °C calcination shows large crystallites of one phase. There are a small amount of brighter particles but these may simply be damaged material or the excess dopant phases that sponsored low temperature small particle agglomeration. The lack of phase separation is surprising as we [8] and other authors have noted extensive segregation of zirconium containing phases during the ART in zirconia doped materials [19]. These observations suggest extensive collaborative interactions between zirconia and silica in the tertiary doping used here.

4. Summary

It was observed that doping of titania by a mixture of silica and zirconia can result in the effective stabilisation of the anatase phase and elevation of the temperature at which phase transformation to rutile occurs. The transformation to rutile appears to involve a low temperature process where small anatase particle agglomerate to reach a critical size when spontaneous transformation occurs. It is suggested that this occurs from the mediation of dopant material at the grain boundaries. In the higher temperature process, single anatase particles appear to grow by a ripening mechanism to reach the critical size for phase transformation. Both PXRD and DTA can be used to estimate the increased thermal stability of the anatase structure. This suggests that the anatase to rutile phase transition occurs via simple reaction kinetics.

Acknowledgements

The authors would like to thank the Enterprise Ireland Basic Research Grant Scheme and the HEA (Ireland) PRTL II Scheme for student support. The University of Limerick are thanked for access to DTA equipment and R. Farrell is thanked for SEM assistance.

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