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# Preparation of composite $Al_2O_3$–$TiO_2$ particles from organometallic precursors and transformations during heating

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Equimolar $Al_2O_3$–$TiO_2$ composite powders were prepared via controlled hydrolysis of organometallic precursors, sometimes in the presence of submicrometre commercial $\gamma$–$Al_2O_3$ or anatase-$TiO_2$ particles. Variations in the chemical procedures were used aimed at different submicrostructures within the resulting powders. Heating such powders in air shows that structural behaviour is influenced by the micromorphology of the composite particle. Transformation temperatures of the titania phases seem to depend upon some size parameter which would represent their morphology within the powders. Studies performed on a series of non-equimolar $Al_2O_3$–$TiO_2$ composite powders showed that the temperature of $\alpha$-$Al_2O_3$ formation may be decreased by $\sim 210°$ C possibly due to a seeding effect of rutile. Pseudobrookite $Al_2TiO_5$ was never detected at $\lesssim 1300°$ C in air.

## 1. Introduction

It is well recognized that high quality sinterable powders are an essential prerequisite for the successful development of a whole range of new high technology ceramic materials. Quality factors of particular importance include chemical purity and homogeneity as well as a fine non-agglomerated possibly monodispersed particle population. The sol–gel [1] and the hydrolysis of organometallic compounds [2] are among the widely explored chemical methods of powder synthesis. Such procedures which are not new in principle, are currently attracting much interest as potentially delivering composite, e.g. two-phase particles, which would be structurally controlled, both chemically and morphologically. Ceramics sintered from such powders can be expected to display very fine regular composite microstructures when the starting phases are non-reactive with one another. Or when reacting, such as for example to produce mixed oxide compounds, they may also give rise to highly dense fine-grained and single-phase polycrystals, more readily and reproducibly so than when conventional mixing procedures of the base compounds are resorted to.

Several papers have recently described the preparation of multiphasic powders or gels from sols or liquid suspensions (e.g. [3–5]) for a number of ceramic–ceramic and/or ceramic–metal combinations. However, except for a few reports [6–10] some of which are either not very recent or not very widely circulated, relatively little attention seems to have been devoted so far to the $Al_2O_3$–$TiO_2$ system. It is thus the object of this paper to present preliminary results on the preparation and characterization of $Al_2O_3$–$TiO_2$ particles from organometallic precursors. Such powders may find applications for example in the fabrication of aluminium titanate ceramics which are highly resistant to thermal fatigue. But it is not our purpose here either to experimentally assess their ceramic potential or to identify and devise an optimal route for their synthesis and subsequent handling. Rather we wish to focus our attention on exploring variations of the basic chemical approach, and to qualitatively illustrate some similarities and differences between the resulting composite particles of distinct micromorphologies and their structural changes upon heating.

## 2. Experimental procedures

Commercially available (Ventron or Fluka, best available grade) $Al(OR)_3$ and $Ti(OR)_4$ organometallics have been used in alcoholic media which were desiccated with a 0.3 nm molecular sieve prior to use. Hydrolyses of the precursors were performed either in the presence or absence of a dispersed $\gamma$-$Al_2O_3$ or anatase, respectively, also available commercially (Alumina C and $TiO_2$ P25, Degussa AG; D-6000 Frankfurt 11), aimed to serve as substrates for the products of the hydrolysis reactions. These commercial powders were aggregates of primary particles of size $\lesssim 30$ nm. The relative hydrolysis rates of aluminium and titanium alkoxides were adjusted by varying the nature of the alkoxide substituant and/or varying the reaction temperature between $-15$ and $+25°$ C. Equimolar amounts of the commercial $\gamma$-$Al_2O_3$ and $TiO_2$ (0.1 mol each) were also ultrasonically dispersed and mixed in 200 ml ethanol containing 1 mol deionized $H_2O$. This sample, "Powder C", was

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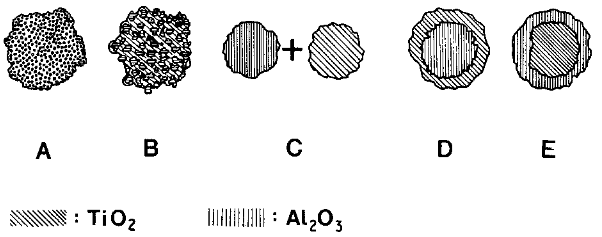


*Figure 1* Schematic illustrations of composite powder structures aimed at in the present work.

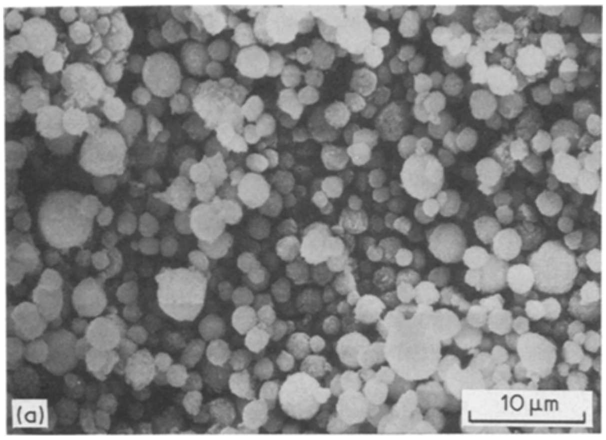
to serve as reference for subsequent characterizations during heating, and hence was spray-dried at 130° C (mini spray-drier type B-190, Büchi Laboratorium-Technik AG, CH-9230 Flawil).

After completion of the reactions, the suspensions also were spray-dried at 130° C for convenience reasons, with subsequent characterization experiments. The overall morphology of the dried products was observed in a scanning electron microscope. Differential thermal analysis (DTA) runs were performed in air on ~ 50 to 70 mg samples at constant heating rates of $10° C\,min^{-1}$ from 25 to 1200° C (Mettler system TA 2000). Phase compositions were determined by powder X-ray diffraction using Ni-filtered $CuK\alpha$ radiation on samples which had been heated for 1 h in air at temperatures chosen in relation to the DTA results.

## 3. Results and discussion

### 3.1. Particle preparation and morphology

Fig. 1 shows a schematic of the various ideal composite particle structures that were aimed at in this work.

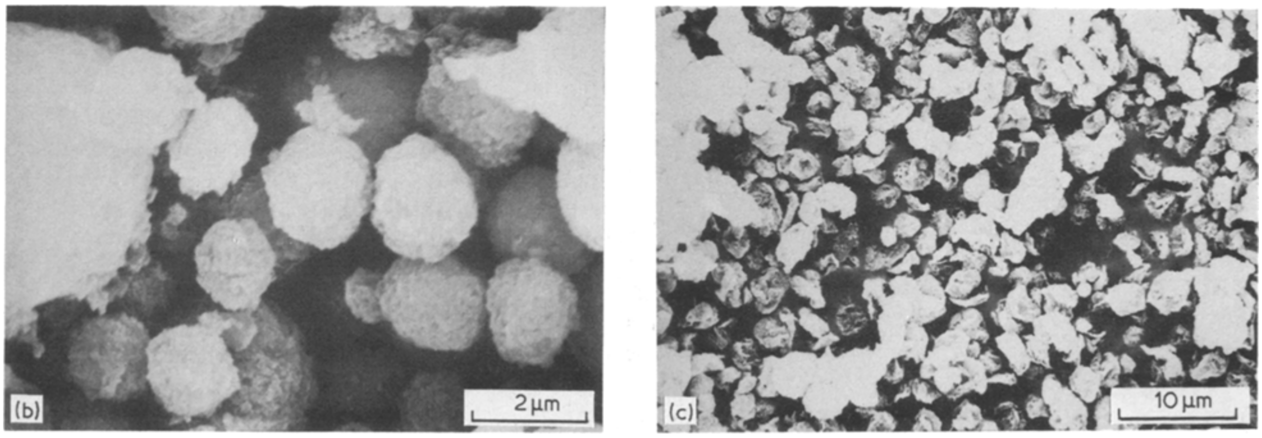


Case C in Fig. 1 represents the reference mixture of both commercial powders. Particles A and B were prepared by co-hydrolysis of aluminium and titanium precursors whereas D and E were the result of single hydrolyses in the presence of $\gamma$-$Al_2O_3$ and $TiO_2$ particles, respectively. More precisely the procedures were as follows.

For powder A, 75 mmol Al(iso-butoxide)$_3$ was added under nitrogen to a solution of 37.5 mmol Ti(ethoxide)$_4$ in 280 ml ethanol and heated in an ultrasonic bath until solubilization. 0.56 mol deionized $H_2O$ in 280 ml ethanol is then added at − 7° C to the mixture of precursors. Under these conditions, the hydrolysis occurred after about 30 sec. For powder B, the same procedure as just described was followed, except Al(sec-butoxide)$_3$ was used instead of the iso-butoxide. Different co-hydrolysis rates were noted: 3 to 5 sec for the Al-alkoxide compared to 30 to 40 sec for the titanium precursor. The appearance of both A and B powders after sedimentation and spray-drying is shown in Fig. 2. Sizes typically equal to ~ 1 to 4 µm are the result of the agglomeration of much smaller (~ 50 to 100 nm) particles during drying (Fig. 2b). Also to be noted (Fig. 2c) are the much greater size and irregular non-spherical shape, and probably chemical heterogeneity of powder B. This structural behaviour results from the different rates of hydrolysis which emphasizes the critical role played by the nature of the alkoxide precursor.

The core–shell structure of powder D was aimed at via a slow hydrolysis of the titanium precursor in the presence of $\gamma$-$Al_2O_3$ particles. In order to favour heterogeneous precipitation on alumina rather than formation of $TiO_2$ nuclei, hydrolysis was carried out at low temperature. More precisely: 0.15 mol Ti(ethoxide)$_4$ is added to 0.15 mol $\gamma$-$Al_2O_3$ ultrasonically dispersed in 800 ml ethanol. Separately 1.5 mol $H_2O$ is dissolved in 0.2 litre ethanol. Both solutions are cooled down and quickly mixed at low temperature to initiate $TiO_2$ nucleation. Temperature is then adjusted to ~ 7° C to allow hydrolysis to be completed in ~ 20 sec. The larger excess water needed to compensate the adsorption of the support was determined experimentally. In the case of powder E, it is worth noting that no simple procedure is known for

*Figure 2* SEM of $Al_2O_3$–$TiO_2$ particles obtained by co-hydrolysis and spray-dried. (a) Powder A, (b) powder A, (c) powder B.



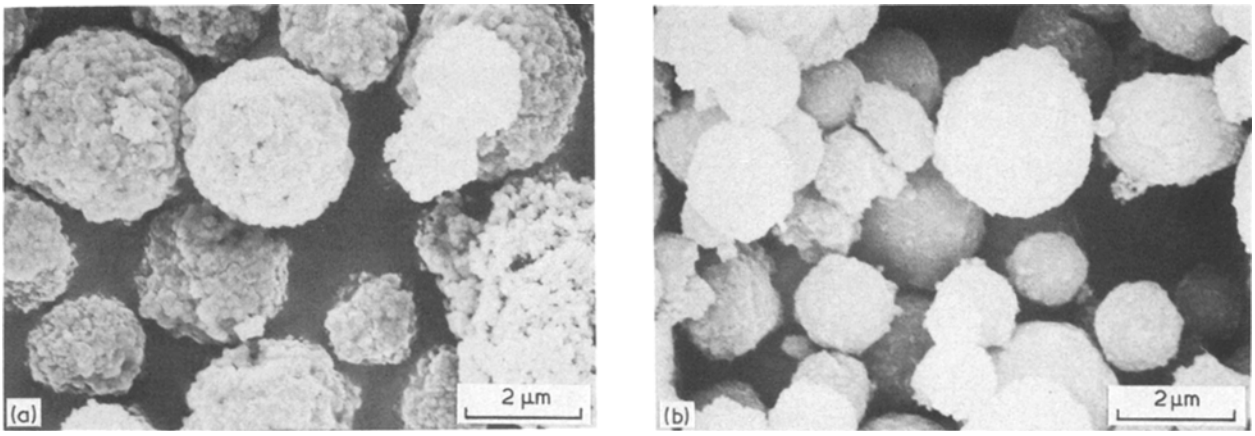


*Figure 3* SEM of $Al_2O_3$–$TiO_2$ powders obtained by single hydrolysis in the presence of inert particles. (a) Titanium precursor with inert $\gamma$-$Al_2O_3$. (b) Aluminium precursor with inert anatase.

producing submicrometre $Al_2O_3$ particles via hydrolysis within a bulk liquid. The gel route followed by spray drying was therefore chosen here: 100 mmol Al(sec-butoxide)$_3$ is added under stirring to 50 mmol $TiO_2$ ultrasonically dispersed in 0.2 litre isopropanol containing 5 mmol 65% $HNO_3$. This solution is hydrolysed by the quick addition of 0.5 mol $H_2O$ in 50 ml isopropanol. Within seconds at $-7$° C a gel is produced which is aged 7 days at 75° C, then redispersed in 0.2 litre ethanol and 50 ml $H_2O$ to be spray-dried. Fig. 3 shows that both dried D and E powders are similar looking spheres ~ 2 μm diameter again with a fine surface substructure. Considering the small sizes of either type of seed particles on the one hand, and the even smaller theoretical thicknesses (~ 2 nm for $TiO_2$ coatings on $Al_2O_3$ particles to yield an equimolar composition) of the deposited outer shells on the other, it does not appear easy to prove directly that powders D and E are indeed agglomerates of smaller particles which would have the composite structures sketched in Fig. 1. Other evidence now to be discussed, however, does show that significant differences exist between them both.

## 3.2. Transformations upon heating of equimolar powders

The DTA results recorded on all powders up to ~ 1200° C are shown in Fig. 4 which also illustrates the behaviour of the reference mixture C. Similarly, other DTA runs, not represented here, have been carried out on samples of pure titanium oxide and aluminium oxide, respectively, prepared via hydrolysis according to the above described methods. The overall downward drift of all DTA spectra is due to that of the base line as checked with a blank run.

It is to be noted first that by and large powders A and B follow a similar behaviour upon heating, except that peak maxima are shifted ~ 10° C toward higher temperatures in the latter case. Their structural evolutions are thus believed roughly identical. The main exotherms at ~ 770 and 970° C are thought to correspond to the rutile and $\alpha$-$Al_2O_3$ phase formations, respectively. Such an interpretation is at variance with a previously suggested one [6] which invoked the crystallization of metastable $Al_2TiO_5$ and its decomposition at ~ 750 and ~ 1000° C, respectively, without further substantiation. In fact, our X-ray diffraction evidence shows that after 1 h heat-treatments no crystalline phase is visible at 700° C, only rutile is detected at 800° C and both rutile and $\alpha$-$Al_2O_3$ are present at 1000° C. The formation of $\alpha$-$Al_2O_3$ in the same relatively low temperature range has been reported previously in similar compositions [7]. It also appears consistent with recent work [11–13] showing that seeding gels with appropriate particles are capable of lowering the $\alpha$-$Al_2O_3$ crystallization temperature by as much as ~ 150 to 170° C. It would be interesting to check whether precrystallized rutile could play such a role in powders A and B.

In powder C (Fig. 4c), only one exothermic peak is recorded at ~ 1015° C which again corresponds to $\alpha$-$Al_2O_3$ formation evidence for which is given by X-ray diffraction. In such a mixture, however, some rutile is present at all temperatures, together with anatase which is the main structural modification of the initial commercial $TiO_2$ particles. The relative proportion of rutile increases with temperature at the expense of anatase which has almost disappeared after 1 h at 1000° C. Interestingly, no evidence for a particular anatase → rutile transformation temperature

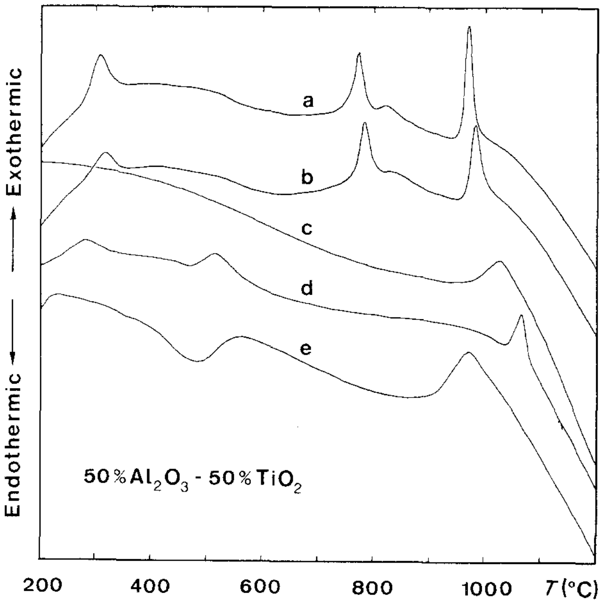


*Figure 4* Differential thermograms recorded in air. (a) Powder A. (b) Powder B. (c) Reference powder C. (d) Powder D. (d) Powder E.

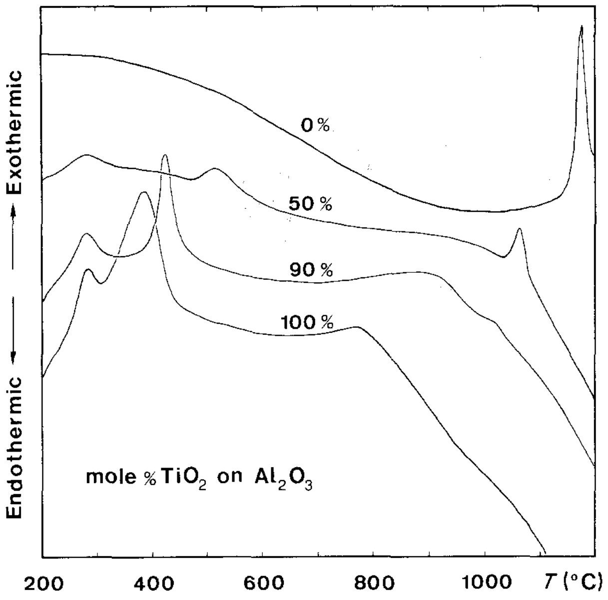


*Figure 5* Differential thermograms recorded in air: various $TiO_2$ mol % from Ti(ethoxide)$_4$ on $\gamma$-$Al_2O_3$ support.

was detected by DTA, presumably because some rutile already is present in the starting commercial $TiO_2$ powder. In the pure commercial alumina, however, DTA showed the characteristic $\alpha$-$Al_2O_3$ formation peak at ~ 1180° C as expected (Fig. 5a).

In powder D (Fig. 4d) two exotherms are recorded at ~ 515 and ~ 1065° C, respectively. The latter is clearly identified with the formation of $\alpha$-$Al_2O_3$ by X-ray diffraction. No $\alpha$ but anatase and some rutile are detected after 1 h at 1000° C, whereas only rutile and corundum are observed after 1 h at 1100° C. Here again then it appears that the $\alpha$-$Al_2O_3$ phase transformation temperature was lowered in the presence of rutile. The 515° C exotherm is due to the anatase crystallization from amorphous $TiO_2$. This rather high temperature is likely related to the characteristic size or thickness of the titania phase in the as-prepared particles.

Finally, in powder E (Fig. 4e), the 475° C endotherm is attributed to the $\gamma$-$Al_2O_3$ formation whereas the 970° C exotherm is due to the appearance of $\alpha$-$Al_2O_3$ as was the case in powders A and B. And again no evidence of transformations of the titania phases is seen with the DTA, as already noted with powders C and D.

## 3.3. Transformations upon heating of non-equimolar powders

The results of DTA experiments in which the relative amounts of hydrolysed Ti(ethoxide)$_4$ in the presence of $\gamma$-$Al_2O_3$ (structure D, Fig. 1) have been increased from 0 to 100 mol % $TiO_2$ are shown in Fig. 5. The peak corresponding to the anatase crystallization from amorphous $TiO_2$ is shifted to lower temperature (515° C → 420° C → 380° C) with an increase of the $TiO_2$ content (50 → 90 → 100 mol %, Figs 5b, c, d). A similar effect was observed with the broad low-amplitude bump around 750 to 950° C which X-ray diffraction showed to be the anatase → rutile transformation. This behaviour can be understood as arising from varying contributions of the surface energy to the overall free energy change of the system in the phase transformation. In fact, the estimated $TiO_2$ shell thickness on the support, as calculated from the latter's, B.E.T. surface area* should range from approximately 2 to 19 nm for 50 to 90 mol % $TiO_2$, respectively.

As far as the $\gamma \rightarrow \alpha$-$Al_2O_3$ phase transition is concerned, the opposite behaviour is observed. An increase of the $Al_2O_3$ content (10 → 50 → 100 mol %) within the composite powders led to the increase of the $\alpha$-$Al_2O_3$ nucleation temperature (1015° C → 1065° C → 1180° C). As outlined before, the presence of rutile appears to have a seeding effect, in lowering the crystallization temperature of $\alpha$-$Al_2O_3$.

## 4. Conclusion

In this work, equimolar and non-equimolar $Al_2O_3$ – $TiO_2$ composite powders have been prepared via controlled hydrolysis of organometallic precursors in alcoholic media. Ti(ethoxide)$_4$, Al(isobutoxide)$_3$ and Al(sec-butoxide)$_3$ have been used, sometimes in the presence of submicrometre commercial $\gamma$-$Al_2O_3$ or $TiO_2$ particles. Such powders were found to exhibit structural behaviour upon heating in air rather different to each other. In particular:

1. transformations of the titania phases are not always observable in DTA whereas they are readily seen from *a posteriori* recorded X-ray diffraction patterns;
2. temperatures at which these take place appear to depend upon some structural and size parameter which would be characteristic of the $TiO_2$ phase distribution within the powders;
3. the temperature of first $\alpha$-$Al_2O_3$ formation from transition aluminas also varies with the type of powder investigated. It may be decreased by as much as ~ 210° C possibly due to a seeding effect of rutile.

Finally, in no case was the $Al_2TiO_5$ pseudobrookite phase found until the heat-treatment temperatures reached the 1300° C level. The degree of corundum + rutile conversion into aluminium titanate again was qualitatively found to vary from one powder to the other, everything else being equal.

## Acknowledgements

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*100 ± 15 $m^2 g^{-1}$ according to the manufacturer.

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