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# AGEING OF WET-SYNTHESIZED OXIDE POWDERS
## Role of surface carbonation, effect on sintering, restoration

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Wet chemical synthesis of precursor oxide ceramics is a method to obtain small particulate powders. Such powders are far more prone to ageing in air than more traditional precursors. Thermogravimetric analysis is used to highlight the species responsible for the ageing of ceramic precursors. Indeed water and carbon dioxide are observed to evolve from aged powders. Ceramics obtained from aged precursors can reach a very low final density with respect to the theoretical value. A large degree of the original sintering properties can be recovered after washing the aged powders with ethanol in a basic medium.

**Keywords:** *ageing, alumina–YAG composites, ceramic precursors, high-res thermal analysis*

## Introduction

Wet chemical syntheses of ceramic powders can assure high purity products, chemical homogeneity in complex compositions as well as good sinterability (see for instance, the cycle of International Conferences entitled Better Ceramics through Chemistry). In many cases, partially crystallised powders having a still relevant specific surface area are used during firing for achieving high final densities of the ceramic bodies. However, the high surface reactivity of such powders can induce ageing phenomena when powder batches are stored in air even for few days, as recently evidenced in the framework of a research devoted to alumina/YAG ($Y_3Al_5O_{12}$) composite powders prepared by a reverse-strike co-precipitation method. The amorphous precipitate was stored just after drying in oven at 105°C and a relevant ageing was observed leading to a dramatic decrease in powder sinterability.

In order to avoid such detrimental evolution of the powder performances and to go deeper in the comprehension of such ageing phenomenon, a systematic investigation as a function of ageing time and atmosphere has been performed by means of various thermoanalytical procedures. To obtain optimal separation of thermal decomposition steps, a sample controlled thermal analysis (SCTA) procedure was used. The various decomposition products were elucidated using thermogravimetry coupled with evolved gas analysis.

## Experimental

An alumina–YAG composite powder having a 50 vol% composition (AY50) has been synthesised at 25°C by inverse co-precipitation, using the so-called reverse-strike method [1–3], that is adding the aqueous solution of the two metal chlorides ($AlCl_3 \cdot 6H_2O$ and $YCl_3 \cdot 6H_2O$) to an ammonia solution, kept at a constant pH of 9 (±0.2) during precipitation by extra-ammonia solution addition. The gelatinous precipitate was filtered and washed four times by dispersing in dilute ammonia, for eliminating the precipitation by-products, and then twice with absolute ethanol, for limiting hard agglomeration during drying in static air in an oven at 105°C. The dried powder was wet-planetary milled in absolute ethanol for 4 h and then characterised by simultaneous DTA-TG (Netzsch STA 409C). The phase evolution as a function of temperature was studied by X-ray diffraction (XRD, Philips PW 1710). On the ground of the previous characterisations the powder was pre-treated at 900°C for 30 min prior to uniaxial pressing at 300 MPa and sintering up to 1600°C for 3 h (heating and cooling rate of 10°C $min^{-1}$) in a dilatometer (Netzsch 402E). The final microstructures were investigated by Scanning electron microscopy (SEM, Hitachi…). This 'fresh' powder obtained just after drying and calcination at 900°C was characterised by adsorption manometry of nitrogen at 77 K

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and laser granulometry (Malvern) after dispersion in absolute ethanol.

A fraction of this fresh powder was stored under vacuum over a 13X zeolite to avoid both water and carbon dioxide uptake. Several other fractions of this fresh powder were left to age at room temperature for 30 days under various conditions: in ambient air, in a 50% relative humidity (RH) water atmosphere, in pure carbon dioxide and in a mixed 50% RH water-carbon dioxide atmosphere. These aged powders were used in the following thermal analysis studies.

The thermogravimetric analyses (Q500, TA Instruments) were carried out under inert gas flow (100 $cm^3$ $min^{-1}$) and up to a final temperature of 900°C followed by a 30 min plateau. Two heating modes were used. The first consisted of using SCTA in the form of the instruments Hi-Res mode under argon atmosphere in which the heating rate of 5°C $min^{-1}$ is modified with respect to the mass loss. The second heating mode used a 20°C $min^{-1}$ heating ramp under helium flow in which case the evolved species were analysed using a mass analyser (Thermostar, Pfeiffer Vacuum).

## Results and discussion

The as-precipitated 'fresh' powder after drying is mostly amorphous as detected by XRD. A dried powder sample was immediately calcined at 900°C for 30 min in static air, then wet-milled for 4 h in a planetary mill in absolute ethanol and finally submitted to a densification cycle (this sample will be called 'fresh' from now on). After calcination the AY50 powder is poorly crystallised and made of small crystallites (about 20 nm) of the metastable, hexagonal phase ($\eta$-$YAlO_3$) [4]. In fact, the final phases, YAG and $\alpha$-alumina, crystallise at higher temperatures, respectively at about 1100 and 1200°C.

Particle size distributions ranged between few microns and few tens of microns with a mean particle size of about 10 μm.

The BET surface areas obtained from the nitrogen adsorption isotherms at 77 K indicate a decrease in surface area from 50 $m^2$ $g^{-1}$ for the dried material to 40 $m^2$ $g^{-1}$ for the material calcined at 900°C.

After uniaxial pressing of the powder calcined at 900°C, the green body presented a low density (about 1.5 g $cm^{-3}$). However, during densification in dilatometer up to 1600°C, the 'fresh' material underwent a relevant linear shrinkage (about 30%) and a limited residual mass loss (about 4.5%), leading to a final density higher than 99% of the theoretical value (4.25 g $cm^{-3}$) (structure shown in Fig. 1).

More details on the chemical-physical characterisation of the powder and on their sintering behaviour are reported elsewhere [5]. On the contrary, a dried amorphous powder was stored in air or even in desiccator for 15 days (this material will be called 'aged' from now on). After that the aged powder was submitted to the same procedure described above (calcination at 900°C, milling and sintering up to 1600°C). However, in this case, the sintered material reached a very poor final density of about 65% of the theoretical value. From SEM observations of the polished and thermal etched sintered body, also a dramatic change of the microstructure of the aged material (Fig. 2) was observed if compared with the fresh one (Fig. 1a).

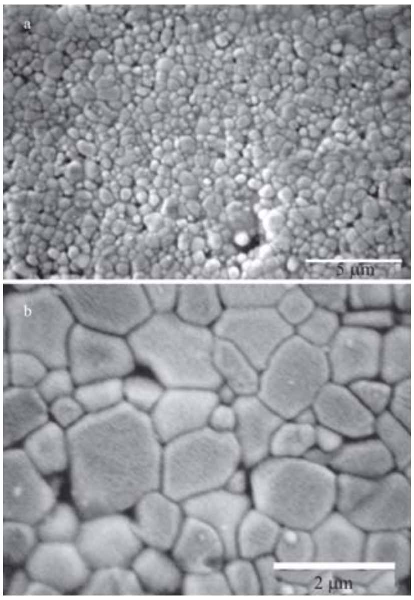

**Fig. 1** SEM a – low and b – high magnification image of the fresh AY50 material sintered at 1600°C for 3 h

In Fig. 2 more dense regions (some of them are evidenced by circles on the image) near highly porous ones (see for instance the arrows in the image) can be clearly recognised, as usually obtained by hard agglomerates compaction and densification. Therefore ageing of the powder has led to a lowering in its sinterability probably imputable to hard agglomeration during storage. Thermogravimetric analysis was used to characterise both the fresh sample and a number of aged materials (Figs 3–6).

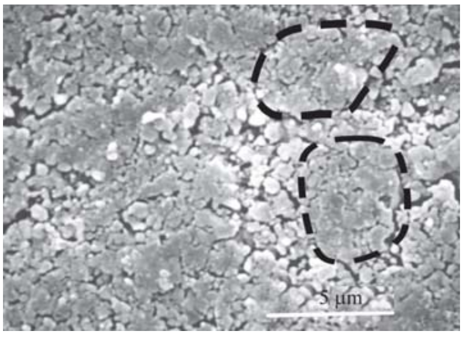

**Fig. 2** SEM micrograph of the aged AY50 sintered at 1600°C for 3 h

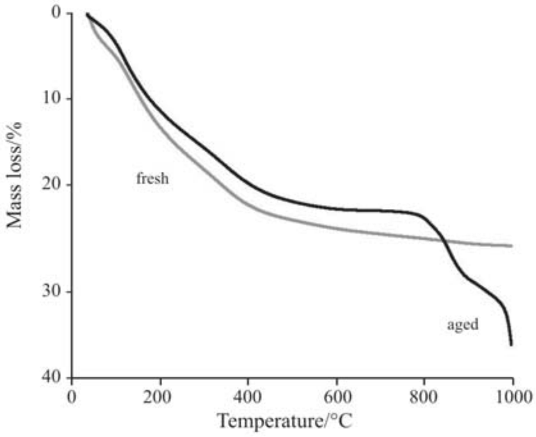

**Fig. 3** Hi-Res TG curves obtained with the ‘fresh’ and ‘aged’ samples

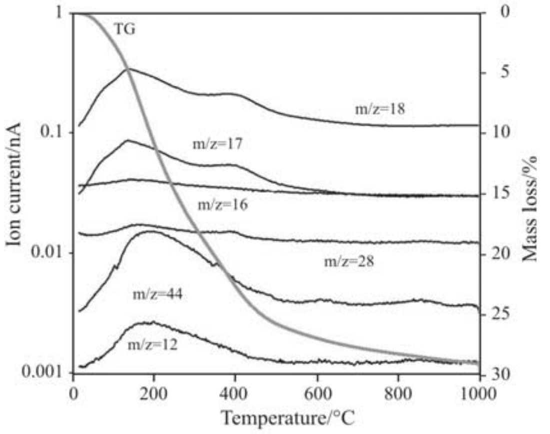

**Fig. 4** TG/MS curves obtained with the ‘fresh’ sample

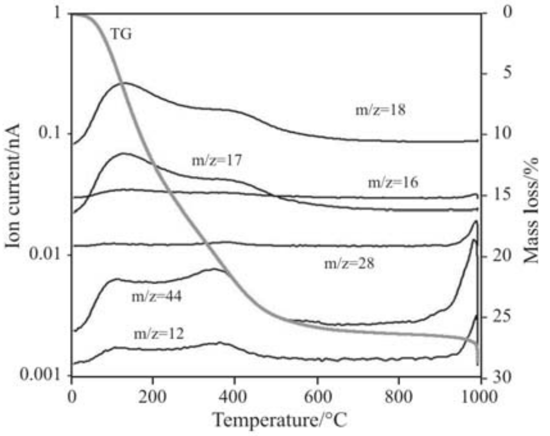

**Fig. 5** TG/MS curves obtained with the ‘aged’ sample

Figure 3 shows the thermogravimetric curves obtained for the initial ‘fresh’ and ‘aged’ samples, respectively. This curve was obtained under argon flow using the SCTA, Hi-Res Mode of the apparatus. The percentage mass loss with respect to initial mass is given as a function of temperature.

It can be noted that up to 100°C, a small mass loss is observed for fresh sample that is visible in the aged sample. This loss is most probably due to weakly adsorbed physisorbed water. Curves for both samples then have similar shape up to around 750°C at which point the aged sample shows two supplementary mass losses.

In an attempt to understand the differences between these two curves, a second series of experiments were carried out in which the evolved gases are followed. These experiments are shown in Figs 4 and 5. The mass loss curves are given as well as the main species detected by the mass analyser. For such experiments a rapid linear increase in temperature is required (20°C min$^{-1}$) which explains the shifts in temperatures with respect to Fig. 3.

Figure 4, obtained with the ‘fresh’ sample seems to show a continual loss of water up to 600°C as well as a small amount of carbon dioxide up to 300–400°C. Figure 5 however, obtained with the ‘aged’ sample also shows a loss of water vapour up to 600°C. It would seem that two steps of carbon dioxide loss are observed, centred at around 150 and 400°C. Finally at 1000°C, again an evolution of carbon dioxide is observed. The difference in nature of each experiment (Hi-Res and linear heating) means that it was impossible to observe the last step (Fig. 3) in the MS analysis (Fig. 4).

In an attempt to understand the ageing process, three samples were aged for one month in a 50% relative humidity water vapour atmosphere, under an atmospheric pressure carbon dioxide atmosphere and in a mixed water vapour/carbon dioxide atmosphere. The SCTA-Hi-Res TGA curves for these samples (Fig. 6) are compared with that obtained with the ‘fresh’ sample (Fig. 3).

It can be seen that in each of the atmospheres, an additional mass loss is observed. In the case of the sample treated under carbon dioxide, this mass loss would seem to occur in the region from 300 to 400°C. In the case of the sample treated under water vapour, this additional mass loss would seem to occur in the region prior to 300°C. It is only in the case where the sample is treated in the mixed atmosphere, that steps in the region from 800°C are observed.

These thermogravimetric results show that both water and carbon dioxide adsorb on the sample and probably do have an effect on the ageing process. However, it is only in the case of ageing in the combined $CO_2/H_2O$ atmosphere that a thermogravimetric curve is obtained that is comparable to that observed in the initial ‘aged’ sample (Fig. 3).

On the ground of the previous results it is possible to suppose the following mechanism related to the ageing phenomenon. During storage ethoxy groups which should limit hard agglomeration during firing [6] are stripped from the powder surface and dis-

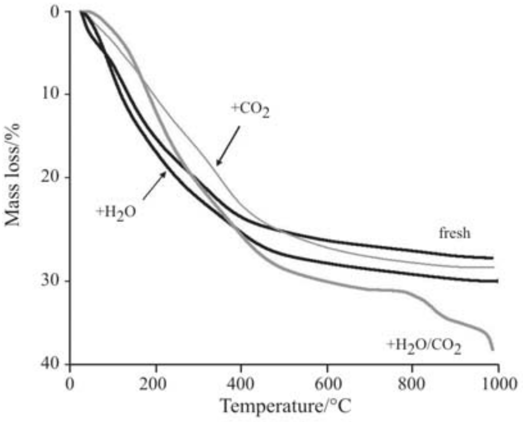

**Fig. 6** Hi-Res TG curves obtained with the 'fresh' and samples left for 1 month in water vapour, carbon dioxide or mixed water vapour/carbon dioxide atmospheres

placed by OH groups coming from water vapour. The elimination of the ethoxy groups makes easier carbon dioxide to adsorb on the powder surface. As a consequence, $CO_2$ can give rise to a classic acid-base reaction involving the surface OH groups of the amorphous precipitate of mixed Al and Y hydroxides. The related, local pH decrease with respect to the precipitation value of 9 can lead to a surface dissolution of the hydroxides in the carbonated layer. When the aged powder is calcined, this dissolved portion precipitates again between the powder particles giving rise to strong chemical links and therefore to hard agglomeration, since the beneficial effect of the ethanol washings [7–10] have been almost completely lost.

Therefore, a possibility to avoid such ageing effect could be immediately performed a thermal treatment of the amorphous powder to high temperature. However, at the pre-treatment temperature chosen (that is, 900°C), the material is still partially amorphous and it undergoes ageing due to the presence of residual surface OH groups. On the other hand, if the powder is treated at higher temperature and fully crystallised to avoid this problem (for instance, up to 1200°C), it reveals a dramatic decrease in sinterability.

To support the above proposed mechanism it was decided to wash the aged amorphous powder. However, ethanol washings alone are not able to induce any recovery effect. On the contrary a sample, which will be called 'washed' from now on, underwent washings in a basic solution (by using an aqueous or an alcoholic solution of ammonia at pH of 9) for 4 h. If an aqueous solution was used, after that also pure ethanol washings were performed, as previously described.

Basic washings induced an increase of the surface pH up to the value of 9, corresponding to the complete re-precipitation of the previously dissolved hydroxides and ethanol presence recreated the surface conditions to avoid hard agglomerate formation during firing. Then the washed samples were calcined at 900°C and sintered up to 1600°C, following the same procedure previously described for the fresh and aged samples. The washed AY50 yielded again an almost fully dense material (>98% of the theoretical value) (structure shown in Fig. 7).

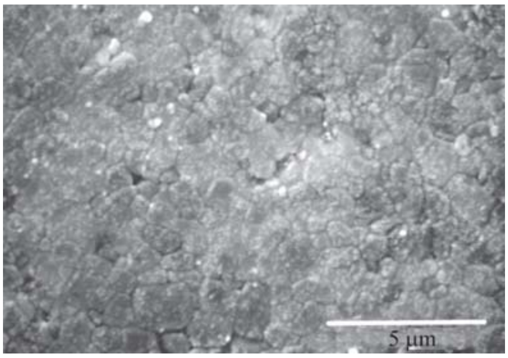

**Fig. 7** SEM micrograph of the washed AY50 material sintered at 1600°C for 3 h

Another indirect demonstration of the above proposed mechanism can be obtained by performing a qualitative comparison among the ageing behaviour of the above composition and that of two other alumina–YAG composites having different YAG volume content, that is 90 vol% alumina–10 vol% YAG (AY90) and 10 vol% alumina–90 vol% YAG (AY10).

After ageing in the same conditions of AY50, aged AY90 was able to sinter up to a very high final density (>95% of the theoretical value) without needing any post-washing procedure; on the contrary, aged AY10 reached a very poor final density, comparable to that of aged AY50, and requires the previously described washing procedure to only partially recover its sinterability; in fact, just after washing it was able to reach a density higher than 90% of the theoretical value.

This differential behaviour can be easily explained on the ground of the proposed model: in fact, whereas aluminium hydroxide presents a wide precipitation pH range, between 5 to 9.5 [1, 11], yttrium hydroxide is characterised by higher precipitation pH values, from 8 up to 9.5 [1]. This difference in the precipitation pH range can induce a differential re-dissolution process due to the surface acidification by $CO_2$ adsorption. This re-dissolution effect should affect the alumina–YAG materials in a different way as a function of the yttrium content, whose hydroxide can dissolve at a pH higher than aluminium one. As a consequence, higher the yttrium amount, higher the re-dissolution at the surface, higher the subsequent re-precipitation, hard agglomeration and lowering of sinterability.

## Conclusions

This paper shows the detrimental effect of ageing in water and carbon dioxide forming surface groups that detrimentally affect the sinterability of the precipitated powder. Importantly, it is possible to almost fully recover the initial sintering properties of an aged powder by washing in a basic solution.

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