

# PREPARATION OF POWDERS FOR ZIRCONIA CERAMICS FROM AQUEOUS SOLUTIONS OF FLUORIDES

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Received 10. 4. 1992

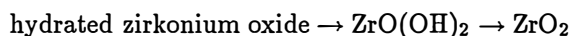
*Preparation of powdered zirconia with monodisperse, submicron and spherical particles is based on precipitation of hydrated zirconium oxide from aqueous solutions of zirconate salts. Investigation of the effects of concentration of hexafluorozirconic acid, the pH, temperature and type of the basic component employed in the precipitation of hydrated oxides has revealed the optimum conditions for the formation of the types of particles of zirconium oxide, mentioned above, from solutions of hexafluorozirconic acid. The best results were obtained with precipitating hydrated zirconium oxide from 0.1M solution of  $H_2ZrF_6$  with ammonium hydroxide at 20°C and pH 11.*

## INTRODUCTION

In the course of the last decade, ceramic materials based on zirconium oxide have been becoming increasingly popular on the market of new materials, mainly owing to their thermal and mechanical properties. This type of ceramics finds application at high temperatures, resists well temperature fluctuations as well as abrasion, and exhibits high strength. These properties predetermine the materials for application in internal combustion engines, medicine, and last but not least also in electronics.

As is the case of all ceramic materials, their strength is achieved by sintering during their manufacture. The final product of the sintering process is determined among others also by the character of the powdered raw materials. If these are adequately pure, monodisperse, have a spherical particle shape and are of submicron size, such powders with controlled characteristics, particle size and suppressed agglomeration, allow high mechanical strength to be achieved even at relatively low firing temperatures.

Precipitation of aqueous solutions of zirconium salts with bases yields zirconium oxide hydrated to various degrees, which depend on a number of factors [1]. The most important ones are temperature, pH and concentration of the initial solution. A highly dispersed hydrated zirconium oxide is formed at lower temperatures, while slow hydrolysis in a weakly acidic medium at elevated temperature yields low-hydrated  $ZrO(OH)_2$ . This is formed after one week standing of the solution at room temperature according to the following schematic reaction:



In dependence on pH, the following zirconium ions can be assumed to exist in the solutions [2].

| pH  | Type of ion  |
|-----|--|
| 0   | $Zr^{4+}$ , $Zr(OH)^{3+}$                                  |
| 0–1 | $Zr^{4+}$ , $Zr(OH)^{3+}$ , $Zr(OH)_2^{2+}$ , $Zr(OH)_3^+$ |

|       |  |
|-------|--|
| 1–1.5 | $Zr(OH)_3^+$   |
| 1.5–4 | $Zr(OH)_4^0$ , $Zr(OH)_x^{4-x}$ – polymers, pseudocolloids |
| 4–12  | $(Zr(OH)_4)_n$ – true crystals                             |
| 12    | zirconates.  |

The above table indicates that precipitation of strongly acid solutions, in which a significant proportion of zirconium is in the form of  $Zr^{4+}$ , yields hydrated zirconium oxide, and on the other hand, precipitation of weakly acid solutions containing type  $-Zr(OH)_2 - O - Zr(OH)_2 -$  polymers, produces  $ZrO(OH)_2$ .

The preparation of  $ZrO_2$  powders has been intensively studied [3]. Heistand et al. and other authors have succeeded in preparing monodispersed  $ZrO_2$  and YSZ by controlled hydrolysis of metal alkoxides. Ramamurthi and co-workers [4] reported on the combination of sol-gel and emulsion [5] processing for the preparation of  $ZrO_2$  powders. A zirconia gel was precipitated from solution of  $ZrOCl_2$  using a solution of  $NH_4OH$  [6].

In the next part of the paper we shall deal with the way of preparing such fine powders from zirconium fluoride. The latter was chosen basically because its preparation (compared to that of sulphates or chlorides of zirconyl) is simpler and more economical on industrial scale.

## EXPERIMENTAL

Having studied the available literature (mainly the patents, [8–13]), the authors decided to concentrate their attention, in the preparation of zirconium oxide of the properties mentioned above, on the following:

- 1) Decomposition of ammonium zirconyl carbonate;
- 2) Precipitation of hydrated zirconium oxide from solution with organic compounds containing the  $-NH_2$  functional group;
- 3) Precipitation with ammonia.

In addition to these ways of precipitating hydrated zirconium oxide from the solution of hexafluorozir-

conic acid, also other methods were tested, such as precipitation with tri-*n*-butylamine, pyridine in ethyl alcohol, urotropine and urea, and finally also precipitation of dipyrindine zirconium thiocyanate with ethyl alcohol. Tabular crystals of hydrated zirconium oxides were produced in all instances. The zirconium oxide has retained the same morphology after firing, as shown by Figs. 1 and 2.

#### Preparation of the $\text{H}_2\text{ZrF}_6$ basic solution

Zirconium oxide (grade S – MEL, Great Britain) was dissolved at 70°C in a polyethylene vessel in an equivalent amount of hydrofluoric acid (40%, A.R. grade – Spolek Ústí nad Labem). Following evaporation of the solution obtained, the crystals of  $\text{H}_2\text{ZrF}_6 \cdot x\text{HF}$  were removed from the mother liquor and dissolved in distilled water. The concentration of the solution was established by gravimetric determination of the  $\text{ZrO}_2$  content.

#### 1) Decomposition of ammonium zirconyl carbonate

In this method of preparing zirconium oxide, use was made of the principle of precipitating the basic zirconyl carbonate, as described in patent [11]. The preparation according to this patent is based on  $\text{K}_2\text{ZrF}_6$ , whose aqueous solution is mixed with an equivalent amount of  $(\text{NH}_4)_2\text{CO}_3$ . Zirconium ammonium fluorocarbonate of the approximate composition  $(\text{NH}_4)_2\text{ZrF}_2(\text{CO}_3)_2$  is formed when the pH is carefully controlled. Following addition of  $\text{CaCO}_3$  suspension, the complex is decomposed,  $\text{CaF}_2$  is precipitated and duly separated, and the complex of ammonium zirconyl carbonate (AZC), dissolved in the filtrate, is decomposed by an addition of nitric acid. Zirconium oxide is then prepared by annealing the precipitated basic zirconyl carbonate.

Because the preparation of  $\text{K}_2\text{ZrF}_6$  (and also filtration of the very fine  $\text{CaF}_2$ ) is difficult, the process was modified and the original procedure is described below.

A 1.42 M solution of  $\text{H}_2\text{ZrF}_6$  was precipitated with ammonia up to pH 10. The precipitate was separated by centrifugation and dissolved in cold oversaturated solution of  $\text{NH}_4\text{HCO}_3$ . From the ammonium zirconyl carbonate solution, hydrated zirconium oxide was precipitated in two ways:

a) By thermal decomposition in the presence of hydrogen peroxide and ethanol.

b) By decomposing the AZC with acetic acid in ethyl alcohol.

ad a):

Concentrated solution of hydrogen peroxide was added to the AZC solution until the precipitate

ceased to form. The suspension was diluted with the same volume of ethanol. The separated precipitate was then heated with 175 ml of ethanol while stirring, up to the boiling point of ethanol, and then centrifugated. In order to determine the effect of the number of washings with ethyl alcohol, a sample was taken after each centrifugation and dried freely in air.

Already the first boil with ethyl alcohol produced polydisperse, mostly spherical particles. Firing at 700°C for 60 minutes converted them to platelets, as shown in Fig. 3.

It may be assumed that the original spherical particles are probably hollow and this is why the platelets are formed by calcination.

ad b):

A solution of acetic acid in ethyl alcohol (1:1) was added to AZC solution up to pH of approx. 7. Firing the separated hydrated zirconium oxide yielded the oxide crystals shown in Fig. 4.

#### 2) Precipitation with organic compounds containing the $-\text{NH}_2$ functional group

These organic compounds show strong buffering effects and the precipitation thus takes place in a homogeneous medium. Moreover, the amino groups are capable of binding the fluoride ion so that better defined compounds are formed, and the fluoride ions can be readily removed by washing.

Ethylene diamine (EDA) was selected from a series of these compounds. The actual precipitation was arranged by preparing an EDA solution in ethyl alcohol (1:10) and adding to it, with a capillary, a 3.13 M solution of  $\text{H}_2\text{ZrF}_6$  solution up to pH 11. The resulting precipitate was digested twice with hot ethyl alcohol and centrifugated each time. Following free drying in air, the hydrated oxide was fired in two stages: at 500°C for 45 minutes and then at 900°C for 50 minutes. After the first firing, the zirconium oxide had a specific surface area of  $27.5 \text{ m}^2\text{g}^{-1}$ , and after the second,  $17.4 \text{ m}^2\text{g}^{-1}$ . The structure of the oxide after the second firing is shown in Fig. 5.

#### 3) Precipitation with ammonia

Precipitation with ammonia requires the optimum limits of pH and the concentration of the initial  $\text{H}_2\text{ZrF}_6$  solution to be established. The pH limits were determined by measuring the rate of settling and the settling volume of the zirconium oxide formed, in 100 ml graduated cylinders. On adding dilute ammonia to 3.14 M  $\text{H}_2\text{ZrF}_6$  solution and measuring pH it was found that the first turbidity was produced at pH 6.8 and quantitative precipitation took place in the region above pH 9.

The effect of concentration of the initial  $\text{H}_2\text{ZrF}_6$  solution and that of pH on the specific surface of dried hydrated zirconium oxide is illustrated by Table I.

Table I

The effect of concentration of  $\text{H}_2\text{ZrF}_6$  solution on the specific surface area  $S_0$  of hydrated zirconium oxide

| pH 10  |  | pH 11  |  |
|--|--|--|--|
| $c(\text{H}_2\text{ZrF}_6)$<br>[mol dm <sup>-3</sup> ] | $S_0$<br>[m <sup>2</sup> g <sup>-1</sup> ] | $c(\text{H}_2\text{ZrF}_6)$<br>[mol dm <sup>-3</sup> ] | $S_0$<br>[m <sup>2</sup> g <sup>-1</sup> ] |
| 0.742  | 2  | 0.523  | 1.4  |
| 0.405  | 3.5  | 0.285  | 1.3  |
| 0.212  | 3  | 0.157  | 9.6  |
| 0.111  | 6  | 0.078  | 14.5                                       |
| 0.045  | 28.9                                       | 0.031  | 19.3                                       |

The data in the Table indicate that at both pH values it is possible to precipitate solutions having the maximum concentration of 0.1 M  $\text{H}_2\text{ZrF}_6$  if the hydrated zirconium oxide is to have a specific surface area of at least 10 m<sup>2</sup>g<sup>-1</sup>.

On the basis of these findings, zirconium oxides were next prepared by precipitating from a 0.111 M solution of  $\text{H}_2\text{ZrF}_6$  by first adding an aqueous ammonia solution (1:1) till the first turbidity appeared, and concluding the precipitation with concentrated aqueous ammonia solution up to pH 10 or 11. After centrifugation, the precipitates were digested twice with hot ethyl alcohol and dried freely in air after the last centrifugation. The specific surface area of the hydrated oxides was 238 m<sup>2</sup>g<sup>-1</sup> for precipitation up to pH 10, and 209 m<sup>2</sup>g<sup>-1</sup> for precipitation up to pH 11. Firing of both samples at 900°C for 60 minutes yielded oxides with specific surface areas of 30 and 55 m<sup>2</sup>g<sup>-1</sup> respectively. The particle shape of the two types of oxides is shown in Figs. 6 and 7. X-ray analysis showed the zirconia to be monoclinic.

#### DISCUSSION OF RESULTS AND CONCLUSION

The study of the preparation of precursor powders for oxide ceramics based on zirconia was started with the aim to prepare particles of monoclinic zirconia, preferably of monodisperse particle size of less than 1 μm, and of spherical shape.

In the first stage, hexafluorozirconic acid was chosen as the initial material for precipitation of hydrated zirconium oxide. There were essentially two reasons for this choice: ready preparation from zirconium oxide, and ready elimination of fluoride ions. On assessing from this respect the powders of zirconium oxide obtained by the individual methods, that of precipitating the hydrated oxides with ammonia

appears to be the best one. If the concentration of the initial hexafluorozirconic acid is closely watched, the zirconium oxide obtained by firing the precipitated hydrated oxide is monodisperse, the particles are spherical in shape, and their size varies around 0.1 μm. The powder is loose, non-sticking and does not form agglomerates.

If homogeneous precipitation with an alcoholic solution of ethylene diamine is used, firing yields agglomerates of small particles of zirconium oxide. The character of these agglomerates strongly resembles the shape of crystals of the primary precipitated hydrated zirconium oxide.

Hydrated zirconium oxides obtained by decomposition of ammonium zirconyl carbonate (modified by a procedure according to patent [11], which appeared very promising) and after triple digestion in boiling ethyl alcohol, are composed of spherical particles. However, these are converted to small crystals by firing. For this reason, the method is unviable for the preparation of spherical particles according to the original goal.

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Translated by K. Němeček

## PŘÍPRAVA PRÁŠKŮ PRO ZIRKONIČITOU KERAMIKU Z VODNÝCH ROZTOKŮ FLUORIDŮ

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Při výrobě zirkoničité keramiky se vychází z prášků, které mají monodisperzní, kulové a podmikronové částice. Obvykle se takové suroviny připravují srážením z vodných roztoků zirkoničitých solí. Cílem této práce bylo připravit výše definovaný prášek z roztoku kyseliny hexafluorozirkoničité srážením různými typy zásadotvorných látek. Byly studovány vlivy pH, teploty a koncentrace výchozích roztoků na strukturu primárního hydratovaného oxidu zirkoničitého a z něj vypáleného oxidu. Nejlepších výsledků bylo dosaženo srážením hydratovaného oxidu zirkoničitého z 0.1 M vodného roztoku kyseliny hexafluorozirkoničité hydroxidem amonným při teplotě 20°C a pH 11.

Obr. 1. Morfologie  $ZrO_2$  připraveného z krystalického hydratovaného oxidu vyloučeného z roztoku  $H_2ZrF_6$  pyridinem v ethylalkoholu.

Obr. 2.  $ZrO_2$  po výpalu hydratovaného oxidu vyloučeného alkoholickým roztokem tri-n-butylaminu.

Obr. 3. Destičky  $ZrO_2$  vypáleného z hydratovaného oxidu, vyloučeného z roztoku  $(NH_4)_2ZrF_2(CO_3)_2$  tepelným rozkladem v přítomnosti peroxidu vodíku.

Obr. 4. Morfologie  $ZrO_2$  vypáleného z hydratovaného oxidu vyloučeného z  $(NH_4)_2ZrF_2(CO_3)_2$  kyselinou octovou v ethylalkoholu (1+1).

Obr. 5.  $ZrO_2$  vypálený z hydratovaného oxidu vyloučeného ethylendiaminem.

Obr. 6. Kulový tvar částic  $ZrO_2$  vypáleného z hydratovaného oxidu a vysráženého hydroxidem amonným do pH 10.

Obr. 7. Kulový tvar částic  $ZrO_2$  vypáleného z hydratovaného oxidu vysráženého hydroxidem amonným do pH 11.

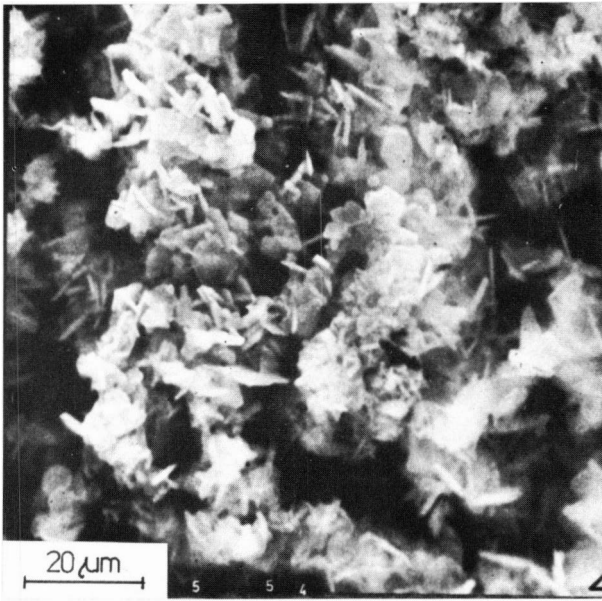


Fig. 1. The morphology of  $ZrO_2$  prepared from crystalline of hydrated zirconium oxide, precipitated from solution of  $H_2ZrF_6$  with pyridine in ethyl alcohol.

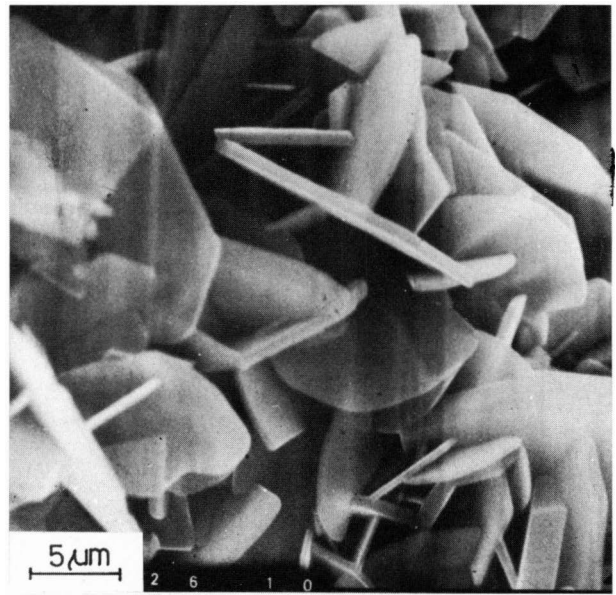


Fig. 3. Plates of  $ZrO_2$  fired from hydrated oxides precipitated from  $(NH_4)_2ZrF_2(CO_3)_2$  with acetic acid in presence of hydrogen peroxide.

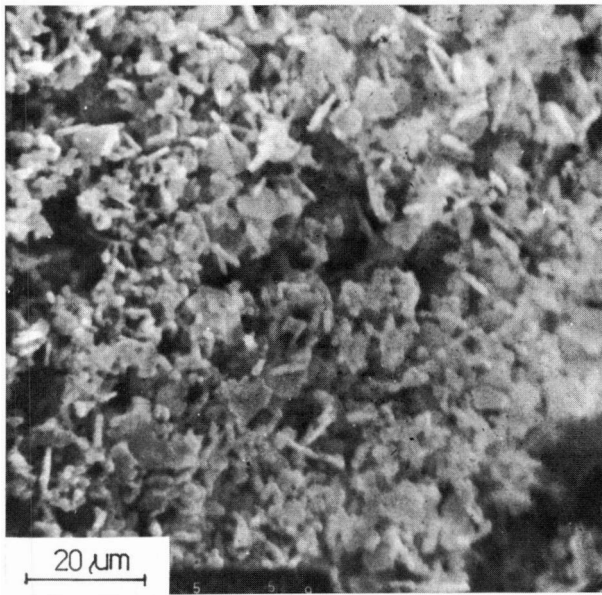


Fig. 2.  $ZrO_2$  produced by firing hydrated oxides precipitated with tri-n-butylamine in ethyl alcohol

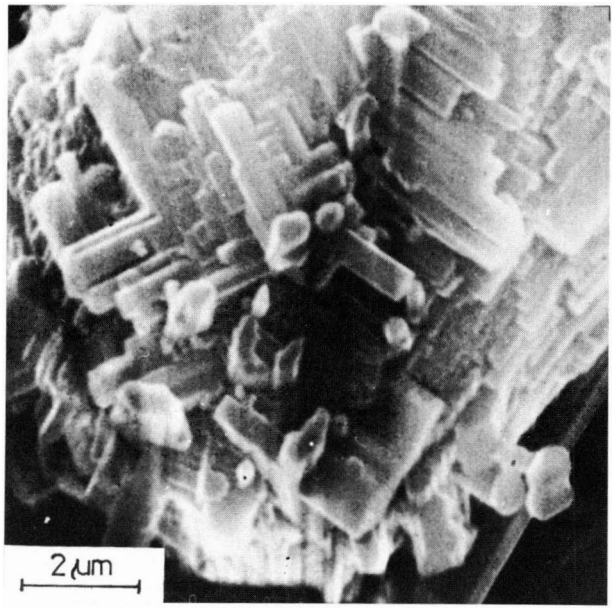


Fig. 4. The morphology of  $ZrO_2$  fired from hydrated zirconium oxide, precipitated from solution of  $(NH_4)_2ZrF_2(CO_3)_2$  with acetic acid in ethyl alcohol.

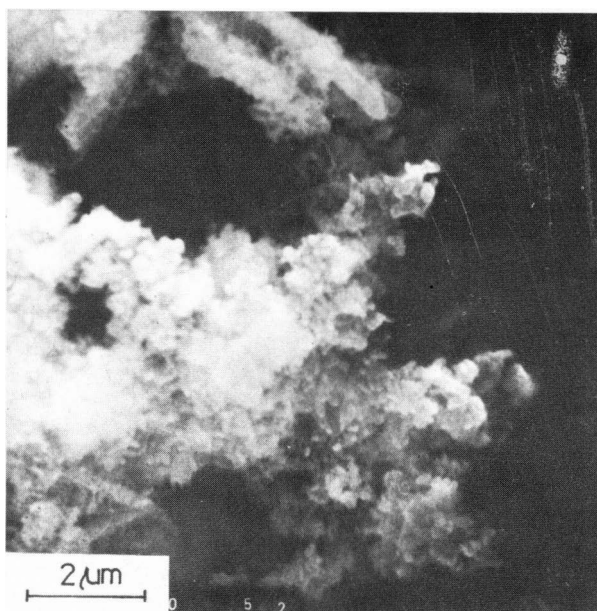


Fig. 5. ZrO<sub>2</sub> obtained by firing hydrated zirconium oxide precipitated with ethylen diamin.

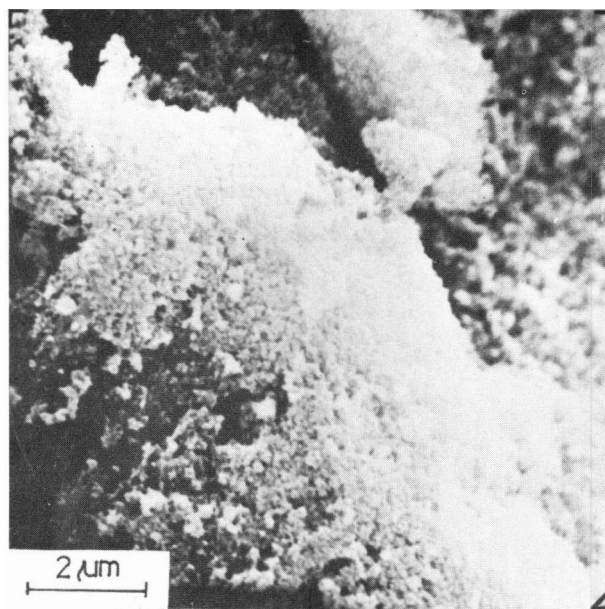


Fig. 7. Spherical shape of ZrO<sub>2</sub> particles obtained by firing hydrated zirconium oxide precipitated with ammonia up to pH 11.

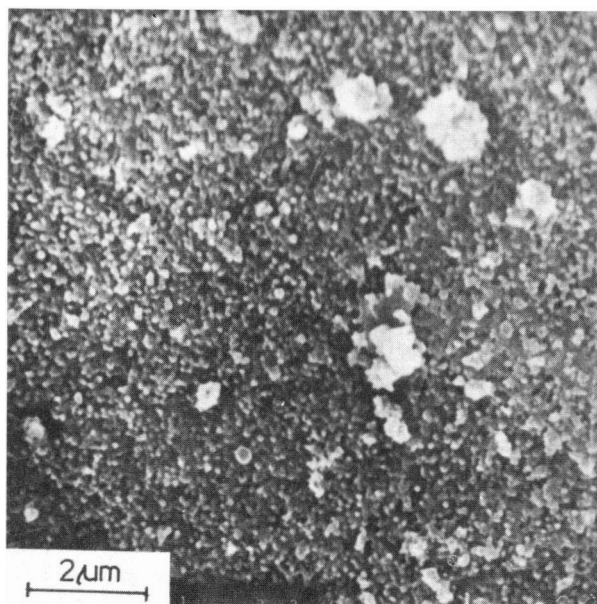


Fig. 6. Spherical shape of ZrO<sub>2</sub> particles produced by firing hydrated zirconium oxide precipitated with ammonia up to pH 10.