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Preparation of Pure and Doped Zirconia Powders and Their Characterisation

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Abstract: High purity zirconia is prepared either by crystallization of zirconium oxychloride via the basic sulphate, or by double crystallization of the oxychloride, followed by dissolution and hydroxide precipitation. A method is described here to prepare pure zirconia having transition metal impurities between 5 and 8 ppm starting from crude zirconia/zircon frit obtained from Indian zircon sand. In this method purification is done by keeping zirconium in the solution in the form of a double carbonate complex, whereas the impurity metals are precipitated as sulphides using H_2S gas. Excess carbonate and hydrochloric acid are recovered and recycled to make the process environment friendly and cost effective. X-ray diffraction analysis indicated a mixture of monoclinic and orthorhombic phases of zirconia incinerated at 825 °C, while only monoclinic at 1450 °C. But by doping with calcia, the orthorhombic phase became predominant even at higher temperatures, whereas monoclinic phase became insignificant. Median particle size after deagglomeration was found to be only 0.56 μm and distributed in a range of 0.11–7.7 μm as against 1.73–7.7 μm of the incinerated oxide after ultrasonic treatment and without grinding. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

The source of zirconium in India is zircon sand, the chemical form of which is zirconium silicate ($ZrSiO_4$). For decomposition, zircon is sintered with soda ash[1] at a temperature of 1050 °C for 4 h in order to convert it into sodium zirconate, silica and carbon dioxide or zircon frit, as it is usually called, as per the following equation:

$$ZrSiO_4 + Na_2CO_3 \xrightarrow[4h]{1050\,^{\circ}C} Na_2ZrO_3 + SiO_2 + CO_2$$

To prepare crude zirconia, zircon sand is fused with sodium hydroxide at 750 °C when sodium zirconate and sodium silicate are formed. The silicate is removed by leaching with water and the zirconate is converted to zirconium nitrate by treating with nitric acid. The nitrate, on treatment with ammonium hydroxide, forms hydrous zirconia. This on calcination at about 500 °C forms crude zirconia. Purification process to produce high purity zirconia starts from zircon frit by converting the zirconium part of it into a well defined compound like potassium zirconium fluoride, K_2ZrF_6, or zirconium oxychloride, $ZrOCl_2, 8H_2O$. Though Blumenthal[2] has referred to the absence of an integrated system of zirconium chemistry, a number of methods of purification have been developed later and reported in the literature.[3] These methods are as follows:

1. Basic sulphate precipitation.
2. Oxychloride crystallization.
3. Precipitation with sulphur dioxide or sodium thiosulphate.
4. Precipitation as phosphate and subsequent treatment.
5. Purification by reprecipitation of hydrated sulphate.
6. Preparation of double fluorides.
7. Thermal decomposition of alkali chlorozirconates.
8. Sublimation of zirconium tetrafluoride.

The oxychloride crystallization method has been very good, though Marden and Rich assumed this method to be too expensive.[4] However, this method has been used to produce pure oxychloride on a large scale.[5] In a very recent study, Chatterjee *et al.*[6] have compared the relative superiority of one wet chemical process to the other with respect to the purity of the product. They showed that two routes were found to be effective to get the highest purity zirconia having oxide impurities of 2–15 ppm. These are crystallization of the oxychloride via the basic sulphate and double crystallization of the oxychloride, followed by dissolution and hydroxide precipitation.

A method of preparation of pure zirconia is discussed in this article where the theory behind purification is different and based on complexing zirconium in the form of a double carbonate in order to keep it in the solution, whereas other metals are removed either by precipitating as hydroxide or as sulphide with the help of hydrogen sulphide gas in alkaline medium. The crystal phase, particle size distribution and median particle size are also determined for characterizing the product with a view to facilitate ceramic application.

2 EXPERIMENTAL PROCEDURE

2.1 Preparation of pure zirconia from its crude form

Crude zirconia powder was heated with concentrated sulphuric acid in a beaker to dryness by fuming. Distilled water was added to the residue with stirring. The undissolved matter was filtered out by a filter paper. To the filtrate, ammonium carbonate powder was added slowly with stirring till the white precipitate, which was formed initially, redissolved. It was again filtered using filter paper. To this filtrate hydrogen sulphide (H_2S) gas was passed for 45 min. The resulting solution was allowed to stand for 20 min. after which it was centrifuged to separate the black precipitate formed. The supernatant liquid was decanted out and H_2S was passed into it for 45 min. again. The resulting liquor was allowed to stand overnight and then filtered through the filter paper to separate the slight amount of black precipitate formed. H_2S was passed for the third time again for 45 min. when no more black precipitate was found. It was filtered again and the filtrate was boiled for 1 h 45 min. The white precipitate formed this time was centrifuged out. The precipitate was washed with distilled water and again centrifuged. The washed precipitate was dried and incinerated at 850 °C for 3 h. The zirconia powder obtained after incineration was washed with concentrated HCl by boiling for 30 min. The acid washing was decanted and the zirconia was further washed with distilled water. Acid washing was done three times in the same manner. The final acid washing was tested with 15.6% ammonium thiocyanate solution to ensure removal of iron. After the final wash the zirconia was heated at 500 °C for 1 h.

In a typical experiment, 6.5249 g of pure zirconia was obtained after starting with 9.9916 g of crude zirconia, a yield of 65.3%.

2.2 Preparation of pure zirconia from zircon frit

Zircon frit in powder form was taken in a beaker and concentrated hydrochloric acid was added to it with stirring by a glass rod. Distilled water was also added to it and stirred. The undissolved matter was separated out by centrifuging. The residue was dried in an infrared lamp and weighed. Ammonium carbonate was added to the solution in the form of powder when white precipitate was formed. Addition of the carbonate was continued until the white precipitate redissolved. Some undissolved part present at this stage was removed by centrifuging. To the clear solution hydrogen sulphide gas was passed for 45 min. and it was allowed to stand overnight. The black precipitate formed was removed by centrifuging followed by filtration of the last part of the supernatant liquid which could not be decanted out. Hydrogen sulphide gas was passed again for 45 min. to the solution and kept overnight. No precipitate was observed this time. The liquid was filtered through a filter paper to remove any fine precipitate present in it. This solution was taken in a conical flask. The flask was assembled with a heater and a condenser system as shown in Fig. 1. It was boiled for 1.5 h when white precipitate was formed with simultaneous evolution of a gas which was condensed/dissolved back in the distilled water kept in the receiver, as shown in Fig. 1. The precipitate was separated by centrifuging, washed with distilled water, dried and incinerated at 850 °C with 3 h soaking. The powder obtained was washed with concentrated LR grade hydrochloric acid by boiling for 1.5 h in three steps of 30 min. each. The supernatant acid after each leaching was decanted and fresh acid was added for further washing by boiling. The final washing was tested with 15.6% ammonium thiocyanate solution. After the HCl wash the mass was finally washed with distilled water, dried and incinerated at 500 °C for 1 h. While washing by boiling, the concentrated hydrochloric acid evolved was directed through the condenser system and dissolved back in water as shown in the schematic diagram, Fig. 1.

In a typical experiment, 200.44 g of zircon frit was treated with 400 ml conc. HCl followed by the addition of 2 litres of distilled water. The weight of undissolved matter at this stage was 51.2 g. A total of 749.63 g of ammonium carbonate was added and 71.82 g of pure zirconia was obtained. The yield was 72.4%.

2.3 Preparation of zirconia with calcia doping

Zirconium oxychloride solution obtained from zircon frit by treating with hydrochloric acid, as mentioned above, was taken in a beaker. Ammonium carbonate in powder form was added to it when a white precipitate was formed. Addition of the carbonate was continued till the white precipitate redissolved. Some brown precipitate which remained undissolved was discarded by centrifuging. The pH of the solution was 8.95. H_2S gas was passed through this solution for 50 min. when a black precipitate was found to appear. This precipitate, which settled on overnight keeping, was removed by centrifuging. Again H_2S was passed into the solution and the process was repeated again until no further black precipitate was obtained. The solution, which was yellow in colour, was boiled. When a white precipitate started forming a solution of calcium chloride was added to it. The pH of the resulting solution got reduced to 7.5. It was raised to 10 by adding NH_4OH and then boiling was continued till precipitation was complete. The precipitate was separated by centrifuging, washed with distilled water, dried and incinerated at 850 °C for 3 h.

Legend

1	Magnetic stirrer cum heater	5	ϕ 10 mm transparent PVC tube
2	Reaction vessel containing solution of double carbonate or HCl washings	6	Pressure relief device
3	Leibig condenser	7	Rubber cork
4	Receiver	8	ϕ 10 mm glass tube
		9	Teflon stirring paddle
		10	Trap

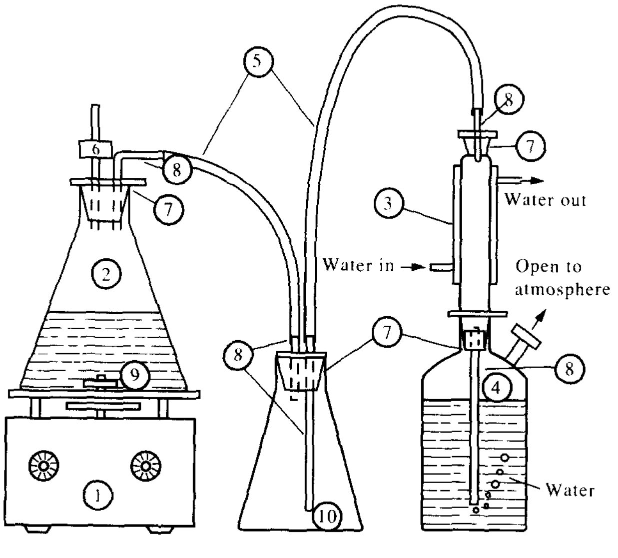

Fig. 1. Schematic of $HCl/(NH_4)_2CO_3$ recovery system.

In a typical experiment, $ZrOCl_2$ solution equivalent to 7.7757 g ZrO_2 was treated with 92.8192 g of ammonium carbonate and 2.2 g $CaCl_2$ was used for doping when finally 9.9852 g mixed oxide of zirconia and calcia was obtained. The yield appears to be above 100% because of some undecomposed hydrous zirconia.

X-ray diffraction and particle size analysis were done using a diffractometer, Diano Series 2000, USA and Horiba LA-500 model of Japan, respectively.

3 RESULTS AND DISCUSSION

3.1 Pure zirconia from its crude form and zircon frit

The principle of purification adopted here is to convert zirconium to a soluble double carbonate complex, whereas other metal impurities are precipitated as sulphides and hydroxides by passing H_2S gas in alkaline medium. Crude zirconia reacted with sulphuric acid to form zirconium sulphate.

$$ZrO_2 + 2H_2SO_4 = Zr(SO_4)_2 + 2H_2O \qquad (1)$$

Sodium zirconate formed oxychloride on treatment with hydrochloric acid.

$$Na_2ZrO_3 + 4HCl = ZrOCl_2 + 2NaCl + 2H_2O \qquad (2)$$

The reactions of ammonium carbonate with zirconium sulphate or zirconium oxychloride are as follows:

$$\begin{aligned} &4Zr(SO_4)_2 + 11(NH_4)_2CO_3 + 3H_2O \\ &\quad = 2(NH_4)_3[Zr_2O(OH)_3(CO_3)_3] \qquad (3) \\ &\quad +8(NH_4)_2SO_4 + 5CO_2 \end{aligned}$$

$$\begin{aligned} &4ZrOCl_2 + 7(NH_4)_2CO_3 + 3H_2O \\ &\quad = 2(NH_4)_3[Zr_2O(OH)_3(CO_3)_3] \qquad (4) \\ &\quad +8NH_4Cl + CO_2 \end{aligned}$$

The soluble carbonate complex breaks down into hydrous zirconia, by boiling the solution, as indicated below:

$$\begin{aligned} &(NH_4)_3[Zr_2O(OH)_3(CO_3)_3] + H_2O \\ &\quad = 2Zr(OH)_4 + 3NH_3 + 3CO_2 \end{aligned} \qquad (5)$$

Hydrous zirconia on calcination forms zirconia.

$$Zr(OH)_4 = ZrO_2 + 2H_2O \qquad (6)$$

The chemical analysis of some impurities present in purified zirconia, as obtained from crude zirconia and zircon frit, are shown in Table 1. It may be noted that the original source of crude zirconia and zircon frit used here was the same, zircon sand from India. So it is clear from this table that the purification process was incomplete in the case of zirconia prepared from zircon frit. This is because although the method of purification adopted for both cases was the same, the concentrations of the impurities were much less in the purified zirconia obtained from its crude form. This is probably because of the higher initial concentrations of impurities in zircon frit as compared to those in crude zirconia. Even though one step purification takes place when crude zirconia is prepared from the zircon sand, the iron concentration in it still remains quite high, 1100 μg/g. However, a two step purification process proved to be more effective in purifying the oxide. Since removal of the impurities as sulphide precipitates, which is employed here, is based on solubility product principle, it appears that a favourable equilibrium having very low impurities in dissolved form has been possible to reach while starting with lower initial concentrations of the multicomponent impurities. In other words, the precipitation of sulphides of impurity metals will be more and more complete if their individual solubilities are not interfered with by the presence of large enough concentrations of other ions. In an earlier article,[7] it has been shown how in the case of beryllium oxide the same method was so effectively used that after the removal of metal sulphides with the help of H_2S gas, no further washing of beryllia with hydrochloric acid was necessary. This is again due to the fact that a better equilibrium could have been reached in that case. So, there is definitely a possibility to tune the present process further in order to optimize the parameters for the better result. Table 1 also indicates that the impurity concentrations are possible to be brought down to very low levels by this method, making it appropriate for high purity zirconia preparation.

Table 1. Chemical analysis of impurities in pure zirconia prepared from its crude form and zircon frit

Impurities	From crude zirconia (μg/g)	From zircon frit (μg/g)
Fe	8	126
Co	<5	7.3
Ni	<5	18.6
Mn	5	17.4
Ti	<18	—
B	5	—
Hf	<37	—

3.2 *Economic aspects of the process*

Basic zirconium carbonate is normally $2ZrO_2$. CO_2. xH_2O, but the ZrO_2: CO_2 ratio may range from 4:1 to 1:1 depending on the methods and techniques of preparation.[8]

In the present process, consumption of ammonium carbonate has been the main item to contribute to the cost of purification of zirconia. But by choosing the right technique to minimise ammonium carbonate consumption and recovering the ammonium carbonate which is evolved while reprecipitating hydrous zirconia by boiling, the cost due to ammonium carbonate can be reduced substantially. Similarly, loss of hydrochloric acid during washing can be nullified by trapping back the acid by the system shown in Fig. 1 and using it again along with the washings for treating zircon frit in order to convert it into oxychloride. These recoveries also help the purification process to become environmentally benign.

In the experiment with zircon frit, 51.2 g undissolved matter was found in 200.44 g zircon frit. This is nothing but silica. So the actual quantity of sodium zirconate was 149.24 g in the frit, which corresponds to 99.22 g of ZrO_2. But the weight of pure zirconia obtained from this was 71.82 g, which means that the recovery was 72.45%. The overall recovery of the process shall be much better if the loss of ZrO_2 in HCl washings is taken into account, which as such is supposed to be recycled with HCl to the next batch.

Table 2. XRD data of purified zirconia from frit heated at 825 °C and 1450 °C

Peak no.	825 °C		1450 °C	
	d-value (Å)	*I*/*I* max (%)	*d*-value (Å)	*I*/*I* max. (%)
1	3.6718	24.05	3.7287	17.62
2	3.1401	100.00	3.6658	10.70
3	2.9489	63.69	3.1880	100.00
4	2.8413	76.56	2.8617	46.95
5	2.8217	68.38	2.6392	22.59
6	2.6227	25.00	2.5577	9.91
7	2.5353	25.97	2.2311	9.15
8	2.4837	7.25	2.1932	4.15
9	2.2655	6.74	2.0328	4.40
10	2.2094	14.79	2.0005	7.38
11	2.0251	9.47	1.8581	12.38
12	1.9880	8.32	1.8534	13.72
13	1.8436	25.00	1.8235	11.53
14	1.8171	34.40	1.8113	9.91
15	1.6943	10.07	1.7891	4.40
16	1.6818	5.33	1.7017	6.41
17	1.6557	11.98	1.6649	9.91
18	1.5564	5.78	1.6158	4.67
19	1.5369	14.06	1.5489	6.41
20	1.4757	9.47	1.5142	4.40
21	1.4196	5.33	1.5018	4.67
22	—	—	1.4818	4.94

Between crystallization and precipitation techniques for separation of impurities, the latter is known to be a cheaper one. The present method belongs to this category. Whereas other known purification methods, like crystallization of zirconium oxychloride via the basic sulphate or double crystallization of the oxychloride followed by dissolution and hydroxide precipitation, are quite costly processes. Further, when adopting these processes, acetone is used finally for washing the product. Acetone is very volatile, so loss is very high. It is a highly inflammable solvent. Hydrogen sulphide, in contrast, though hazardous, is known to be used industrially.

3.3 Characterization of zirconia powders produced

The XRD data of pure zirconia produced from zircon frit are shown in Table 2. It can be seen from the table that zirconia that has been heated up to 825 °C possesses both the monoclinic and orthorhombic phases. This is because the *d*-values 3.1401 and 2.9489 which are present in Table 2 correspond to monoclinic and orthorhombic phases, respectively. But in the same zirconia heated up to 1450 °C the main characteristic *d*-value, 2.96 (100%), of the orthorhombic phase disappeared, as can be seen in Table 2. The comparison between these two phases is made

Table 3. XRD data of doped zirconia heated up to 850 °C, 1100 °C and 1550 °C

	850 °C		1100 °C		1550 °C	
Peak no.	*d*-value (Å)	*I*/*I*max (%)	*d*-value (Å)	*I*/*I*max (%)	*d*-value (Å)	*I*/*I*max (%)
1	4.4681	8.62	4.6696	5.38	6.1143	4.21
2	3.1059	8.62	3.4550	5.38	4.8297	4.21
3	2.9603	100.00	2.9622	100.00	4.6941	4.21
4	2.8703	8.62	2.8182	5.38	3.6356	4.21
5	2.5585	25.46	2.5641	20.18	3.1791	4.21
6	1.9056	8.62	2.4122	5.38	2.9574	100.00
7	1.8092	55.22	1.8149	45.42	2.9323	4.21
8	1.5425	29.30	1.7810	5.38	2.8391	4.21
9	1.4790	8.62	1.7726	5.38	2.6317	4.21
10	1.4514	8.62	1.5466	27.98	2.5620	31.82
11	1.4448	8.62	1.4809	5.72	2.4712	4.21
12	1.3495	8.62	1.4221	5.38	1.8120	82.86
13	—	—	1.3909	5.38	1.8035	7.96
14	—	—	1.3524	5.38	1.7875	4.21
15	—	—	—	—	1.5820	4.21
16	—	—	—	—	1.5447	44.44
17	—	—	—	—	1.5370	4.21
18	—	—	—	—	1.5033	4.21
19	—	—	—	—	1.4796	14.30
20	—	—	—	—	1.3742	4.21
21	—	—	—	—	1.3661	4.21

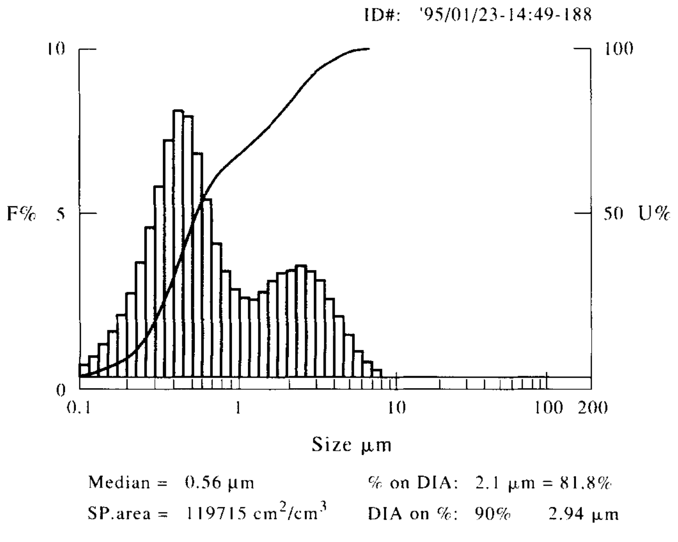

Fig. 2. Particle size distribution after grinding with an agate mortar.

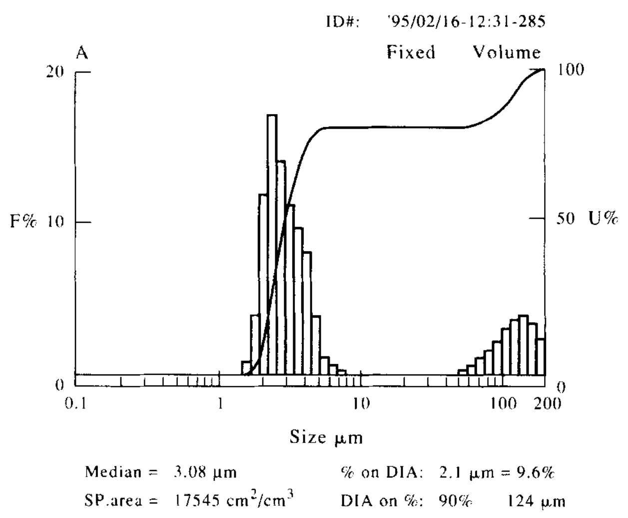

Fig. 3. Particle size distribution without grinding.

using the *d*-values of 100% intensity only because some of the other peaks are common to both the phases. This observation resembles the report[9] that the orthorhombic phase is metastable at atmospheric pressure and reverts back to the monoclinic phase on heating.

From Table 3 it is seen that the strong lines having *d*-values corresponding to the orthorhombic phase are distinctly present at all temperatures, whereas the characteristic peak *d*-values of the monoclinic phase are not distinct at lower temperatures but distinct at the highest temperature of 1550 °C. But the peak intensities indicate that orthorhombic is the main phase at all three temperatures, whereas the presence of monoclinic phase appears to be very feeble. The weight percent of calcia present in the doped zirconia produced from frit was 11.1%. All the *d*-values indicated in Table 3 belong to this doped zirconia.

Figures 2 and 3 show the particle size distributions of zirconia obtained from frit after grinding with agate mortar and pestle and without grinding but only by dispersing the particles with the help of ultrasonic treatment for 15 min., respectively. From Fig. 3 it is seen that the range of particle size is between 1.73 and 7.7 μm, whereas the fraction of size between 67.52 μm and 200 μm is actually agglomerates which did not disperse fully after the ultrasonic treatment. This was confirmed by increasing ultrasonic treatment time when the fraction between 67.52 μm and 200 μm reduced further to an insignificant quantity. The median particle size of this zirconia powder as obtained by decomposition of hydrous zirconia is 3.08 μm, as seen in Fig. 3. The particle size distribution is narrow here. But it widened in the range 0.11–7.7 μm after grinding when median particle size reduced to 0.56 μm only.

4 CONCLUSIONS

1. The method of purification of zirconia by converting it into a soluble double carbonate complex and precipitating the impurities as sulphides and hydroxides has been proved to be very good at obtaining high purity zirconia.
2. As it is based on precipitation technique which is cheaper and by the recovery of the carbonate and hydrochloric acid, this method has been found to be attractive and environment friendly.
3. Monoclinic phase is found in the purified zirconia at the elevated temperature of 1450 °C, whereas with 11.1% (W/W) calcia doping, the orthorhombic phase becomes predominant at temperatures from 850 to 1550 °C.
4. Particle size distribution of pure zirconia has been found to be in the narrow range 1.73–7.7 μm. The powder, however, could be ground further, reducing the median particle size from 3.08 μm to 0.56 μm.

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