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Preparation and Characterization of Yttria-Stabilized Zirconia Powders by Solvent Extraction Process

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Abstract: This study demonstrates that zirconium and yttrium can quantitatively be coextracted with di-(2-ethylhexyl) phosphoric acid or 2-ethylhexyl-phosphonic acid mono-2-ethylhexylester from commercial grade of starting materials under suitable conditions, and that both zirconium and yttrium can be stripped completely with oxalic acid from the extractants under some specific conditions. The resulting oxalates, after careful washing with absolute ethanol, may be calcined to both ultrafine and pure yttria-stabilized zirconia powders, while the stripped extractants can be recycled to extract zirconium and yttrium. The present process, therefore, is a more economical technique than the metal alkoxide process — one of the most popular chemical processing routes for the preparation of advanced ceramic powder, yet it is a very efficient technique for controlling the purity, particle size, and crystalline phase composition of the powders. © 1997 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

The superior mechanical, thermal, electrical and chemical properties of yttria-stabilized zirconia have recently become the focus of growing scientific and technological interest. The potential of the material has given rise to numerous synthetic approaches to obtain the material with the excellent properties. These approaches include mechanical ceramic processing, the coprecipitation of zirconium and yttrium ions in aqueous solution or ethanol solution, the hydrolysis and spray pyrolysis of metal alkoxides, hydrothermal processing, gas phase technique;[1–8] nevertheless, there is an urgent need for economic, high-purity and nanoscale powder preparation.

Recently solvent extraction has been a very important industrial technique for the extraction and purification of metals in hydrometallurgy. Some similarities in the solvent extraction behaviours of zirconium and yttrium brought about by those in the chemical properties of them led us to make an attempt at preparing YSZ powders by solvent extraction. Some puzzling problems, however, will be encountered in preparing YSZ powders by solvent extraction. First, zirconium and yttrium must quantitatively be coextracted with an extractant from a commercial grade zirconium oxychloride solution containing yttrium, while separating them from other impurities present in the solution. Second, zirconium and yttrium have to be completely stripped from the extractant loaded with them. This article describes how to circumvent these difficulties and develop successfully a solvent extraction process for preparing YSZ powders with high purity, ultrafine particle size and low cost.

2 EXPERIMENTAL SECTION

Preparation of Stock Solution. A commercial grade zirconium oxychloride containing about 34% zirconia was dissolved in distilled water and then filtered. To the resulting filtrate a 99.9% pure yttria was added and dissolved by heating. The stock solution contained about 185 g/litre ZrO_2 and 9 g/litre Y_2O_3, and was diluted with distilled water to the desired concentrations of zirconium and yttrium for extraction.

Extraction and Stripping. The organic phase used in the present work consisted of an extractant, a modifier and a diluent. The extractant chosen was a commercial grade di-(2-ethylhexyl) phosphoric acid or 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, and used as received. The modifier was a chemically pure *sec*-octylalcohol. The diluent was a commercial grade kerosene washed successively with aqueous sulphuric acid solution (concentrated H_2SO_4: distilled water = 1:1) and distilled water. The three reagents were mixed according to the desired concentration of the extractant and washed with 4 M HCl once. Extraction was conducted in a separatory funnel at a 1:1 volume ratio of organic phase to aqueous phase at 10 °C for 5 min, since preliminary experiments showed that extraction equilibrium was very closely approached in 5 min.

The organic phase loaded with zirconium and yttrium after extraction was scrubbed with 4 M HCl to remove some impurities. Zirconium and yttrium were stripped from the scrubbed organic phase with aqueous oxalic acid solution or ethanolic solution of oxalic acid. The stripped organic phase can be recycled to extract zirconium and yttrium.

2.1 Powder preparation

If an aqueous oxalic acid solution was used as a stripping agent, it was necessary to add dropwise aqueous ammonia to the resultant strip liquor with constant stirring until the pH value of the liquor was 9 in order to coprecipitate zirconium and yttrium quantitatively. The need, however, could be eliminated when an ethanolic solution of oxalic acid was used as a stripping agent. The resultant oxalates of zirconium and yttrium were filtrated, washed with absolute ethanol thoroughly, and dried under an infrared lamp overnight. The dried product, i.e. precursor, was calcined in air at 650 °C for 2.5 h to yield YSZ powders. The present process does away with the need for milling the calcined powder for a long time. The characteristics of the calcined powder were examined by the following techniques.

2.2 Characterization technique

The total concentration of zirconium and yttrium in stock solution or in the raffinate after extraction was assayed by EDTA-complexometric titration using xylenol orange indicator. The respective concentration of zirconium and yttrium was analysed by inductively coupled plasma emission spectroscopy. The chemical composition of the powder was confirmed by X-ray fluorescence analysis.

The crystalline phase composition of the powder was determined by X-ray diffraction using CuK_α-radiation. A scanning rate of 4 °/min was used to obtain the X-ray diffraction pattern of the powder. The amount of monoclinic phase (M) present in the powder was calculated from the following relationship:[9]

$$M = \frac{Im(111)}{Im(111) + It(111) + 1/8Ic(111)} \quad (1)$$

where $Im(111)$ denotes the intensity of the monoclinic peak(111), $Ic(111)$ represents the intensity of the cubic peak (111), and $It(111)$ refers to the intensity of the tetragonal peak (111). The amount of tetragonal phase (T) present in the powder was estimated from

$$T = \frac{1/4It(200)}{1/4I_t(200) + 1/6I_c(200)} \quad (2)$$

where $I_t(200)$ is the intensity of the tetragonal peak (200) and I_c (200) indicates the intensity of the cubic peak (200).

Transmission electron microscopy (TEM) was used to estimate the particle size of the powder and observe the agglomeration state of the powder.

The specific surface area measurement of the powder was made by the BET method using nitrogen adsorption at −193 °C. The particle size distribution analysis was performed for the powder by dynamic laser scattering.

3 RESULTS AND DISCUSSION

Although various types of solvent extraction systems have been suggested for zirconium and yttrium in the literature, respectively, there is no previous work dealing with the quantitative coextraction of zirconium and yttrium from an identical acid medium with the same extractant under some specific conditions. Since zirconium oxychloride is a very important and frequently used starting material in the preparation of various zirconium products and since di-(2-ethylhexyl) phosphoric acid and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (symbolized as D2EHPA and PC-88A, respectively) are the most important acidic extractants available commercially now, we have explored the extraction conditions under which zirconium and yttrium can quantitatively be coextracted with the two extractants from HCl medium, and found oxalic acid with which both zirconium and yttrium can be stripped completely from the two extractants under some specific conditions.

3.1 Effect of acidity

The percentage coextraction of zirconium and yttrium with D2EHPA and PC-88A was determined as a function of pH value, as shown in Fig. 1. It can be seen from Fig. 1 that the coextraction behaviour of zirconium and yttrium with respect to D2EHPA and PC-88A seems to make little difference, i.e. the coextraction of zirconium and yttrium with both D2EHPA and PC-88A follows an increasing trend as pH value increases, and that at pH 2.2 the quantitative coextraction of zirconium and yttrium occurs. This is because zirconium and yttrium are extracted with D2EHPA or PC-88A at low acidity according to the cation exchange reaction in which hydrogen ion is liberated from the acidic extractants.

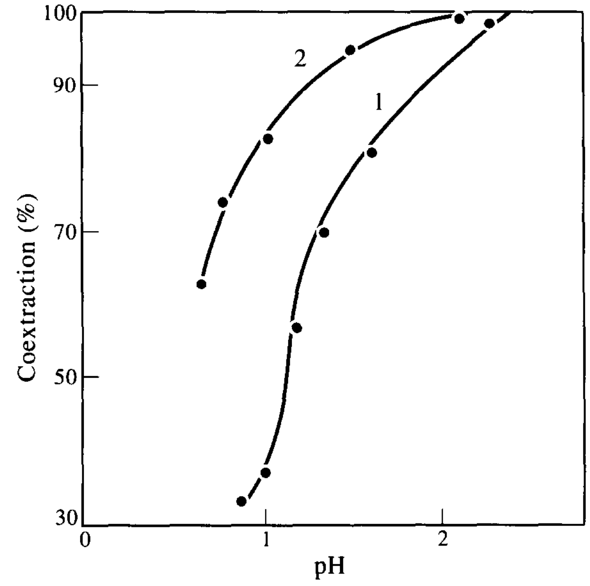

Fig. 1. Percentage coextraction of Zr and Y as a function of pH value. Curve 1, 0.371 M PC-88A; Curve 2, 0.302 M D2EHPA; Feed solution, 14.7 g/litre of Zr and Y oxides.

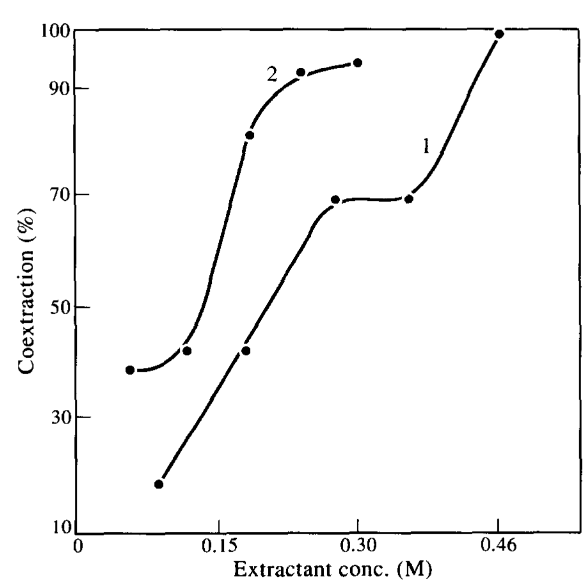

Fig. 2. Coextraction dependence of Zr and Y on extractant concentration. Curve 1, PC-88A; Curve 2, D2EHPA.

3.2 Effect of extractant concentration

Figure 2 presents the effect of extractant concentration on the coextraction of zirconium and yttrium from an aqueous solution containing 14.7 g/litre of zirconium and yttrium oxides at pH 1.4. It may be noted from Fig. 2 that the two extractants, D2EHPA and PC-88A, exhibit the same tendency towards an improvement in the percentage coextraction of zirconium and yttrium with increasing extractant concentration, and that at a level of 0.302 M D2EHPA and 0.464 M PC-88A the percentage coextraction of zirconium and yttrium can approach its maximum value.

3.3 Effect of metal concentration

Figure 3 shows the coextraction dependence of zirconium and yttrium on their concentration in feed solution. The experiments were performed under the following conditions: 0.302 M D2EHPA and 0.464 M PC-88A, an equilibrated aqueous phase pH 1.4. It is clear that the percentage coextraction of zirconium and yttrium with a given concentration of the extractant decreases with an increase in the concentration of zirconium and yttrium oxides in feed solution. This result is associated with the loading capacity of the extractant at the given concentration.

3.4 Scrubbing and stripping

During extraction, some undesirable impurities such as hafnium, iron(III), calcium, silicon were more or less coextracted with zirconium and

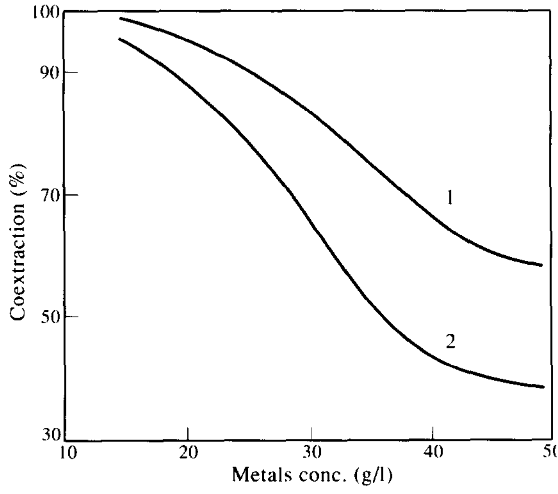

Fig. 3. Effect of metals concentration on their percentage coextraction. Curve 1, PC-88A; Curve 2, D2EHPA.

Table 1. Major impurities in yttria-stabilized zirconia powders prepared by different processes

Process	Major impurities (ppm)							Ref.
	Hf ×10^4	Fe	Si	Al	Ti	Na	Ca	
Metal alkoxides	1.3	100–200	60–400	<160	350	<50	—	2
Hydroxide coprecip.	—	10	50	500	—	50	—	12
Oxalate coprecip. in ethanol	2.1	100	<47	<53	—	—	1000	Present work
Solvent extraction	0.09	38	45	—	—	—	73	Present work

* Data except Hf.

yttrium into D2EHPA or PC-88A. However, it may be inferred from the aforementioned coextraction dependence of zirconium and yttrium on acidity that it is difficult to strip zirconium and yttrium with a concentrated hydrochloric acid solution (4 M HCl) from the D2EHPA or PC-88A loaded with them, while some of the coextracted impurities can, to a certain extent, be removed in the scrubbing operation.

Zirconium ion is amenable to direct hydrolysis, and zirconium and yttrium ions can be precipitated as the insoluble oxalates which may be calcined to yttria-stabilized zirconia powder, and zirconium and yttrium can, therefore, be stripped with aqueous oxalic acid solution or ethanolic solution of oxalic acid from D2EHPA or PC-88A loaded with them. Our earlier work demonstrated that zirconium and yttrium ions could more homogeneously and completely be coprecipitated with ethanolic solution of oxalic acid than with aqueous oxalic acid solution.[3,10] The precipitation of yttrium oxalate from D2EHPA could be induced and accelerated by increasing oxalic acid concentration and total acidity.[11] The yield of zirconium and yttrium from feedstock to YSZ powder by the present process has reached 90%. In addition, since oxalic acid is used as a stripping agent, the further separation of zirconium and yttrium from impurities may be accomplished in the precipitation stripping operation in favour of obtaining high-purity YSZ powder.

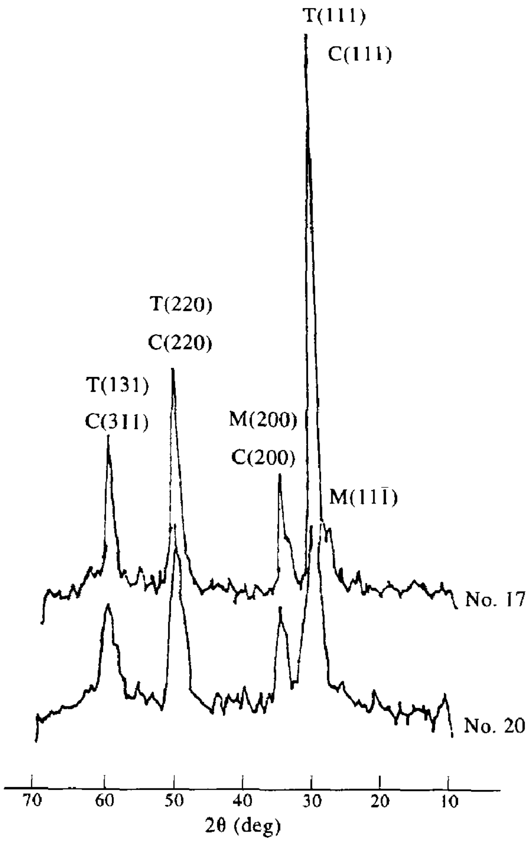

Fig. 4. X-ray diffraction patterns of powders.

3.5 Purity of powder

Mechanical and functional properties of ceramic materials are very sensitive to slight changes in chemical composition, crystalline phase fraction and grain size.

A high-purity yttria-stabilized zirconia powder has been prepared by the present process from a commercial grade zirconium oxychloride. The major impurities in the powder are shown in Table 1. Included for comparison are the data for other processes. It is evident from Table 1 that the purity of the powder prepared by the solvent extraction process seems to be higher than by other processes. The selective extraction, scrubbing and oxalic acid stripping operation, as mentioned previously, should be responsible for the high-purity of the yttria-stabilized zirconia powder prepared by the solvent extraction process.

3.6 Crystallinity of powder

The fraction of the tetragonal phase in yttria-stabilized zirconia can be a crucial variable which will influence its numerous properties. Therefore, the phase identification and phase fraction determination are of great importance. This can be accomplished by X-ray diffraction.

Figure 4 presents the X-ray diffraction patterns of the 2.3 mol% yttria-stabilized zirconia powders prepared by the solvent extraction process. The crystalline phase composition of powders (No. 17 and 20) may be calculated from Fig. 4 according to

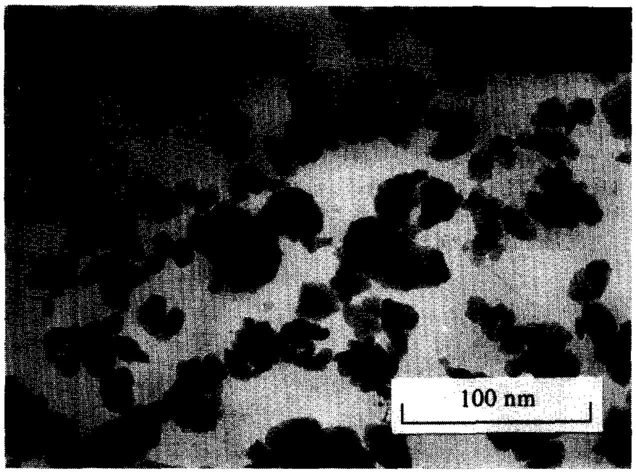

Fig. 5. Transmission electron micrograph of powder.

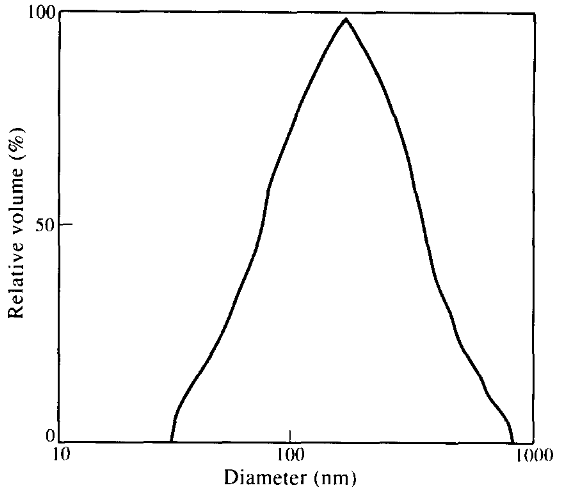

Fig. 6. Particle size distribution of powder.

eqns (1) and (2), monoclinic (M), tetragonal (T) and cubic (C) phases being 10%, 70% and 20% for powder No. 17, and 0, 20% and 80% for powder No. 20, respectively. It is clear that both powder (No. 20) free of monoclinic phase and powder (No. 17) in which the prevailing phase was tetragonal could be obtained by the present process. This might be associated with the preparation conditions of the precursor, which can play an important role in controlling the formation of various crystalline phases in the resultant powder. This will be subject to a more detailed discussion in a future publication.

3.7 Particle size of powder

The microstructure of the powder prepared by the present process was examined by transmission electron microscopy (TEM), as shown in Fig. 5. It is clear from the transmission electron micrograph that the powder is composed of near-spheroidal and less-agglomerated particles. Because the precursor is produced from organic solvents, aged in ethanol solution, and calcined at a relatively low temperature, the calcined powder is soft and less-agglomerated. This can also be demonstrated by the fact that the present process eliminates the need for milling the calcined powder for a long time to obtain the nanoscale powder. The particle size estimated from TEM is about 40 nm, which is in approximate agreement with the particle size calculated from the specific surface area 22.5 m^2/g of the powder.

In addition, the particle size distribution analysis, as shown in Fig. 6, indicates that the powder has a volume median diameter of 405 nm. The difference in the particle size obtained by the two kinds of measurements may be attributed to the presence of particle agglomeration. Even according to the particle size distribution analysis, Fig. 6 shows the cumulative volume percentage of the particles below 1000 nm is 100%. In other words, all the particles of the powder fall in the range of nanometre.

4 CONCLUSIONS

The present work demonstrates that the solvent extraction process developed may successfully be used to prepare high-purity and nanometre yttria-stabilized zirconia powders. In addition, the thought that spawned the work described in this article can also be applied to the preparation of other advanced ceramic powders.

By the present process, zirconium and yttrium can quantitatively be coextracted with 0.302 M D2EHPA or 0.371 M PC-88A in kerosene from a commercial grade zirconium oxychloride solution containing about 15 g/litre of zirconium and yttrium oxides at pH 2.2 or so in a single extraction stage, and zirconium and yttrium may be completely stripped with aqueous oxalic acid solution or ethanolic solution of oxalic acid from the acidic organophosphoric extractants loaded with them.

The amounts (ppm) of major impurities in the resultant powder are 9×10^2, 38, 45 and 73 for hafnium, iron, silicon and calcium, respectively. The powder free of monoclinic phase can be obtained by the present process. In addition, all the particles of the powder fall in the range of nanometre.

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