Sintering Nanodisperse Zirconium Powders with Various Stabilizing Additives

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Abstract:
Effect of various stabilizing additives on sintering kinetics of nanodisperse powders was studied by thermomechanical analysis. Temperature ranges of the most intense shrinking, characteristic points of shrinking rate changes were established. Peaks characterizing the most intense shrinking of nanodisperse zirconium powder samples were shown to allow to arrange the stabilizing additives as follows: \( \text{Y}_2\text{O}_3 \rightarrow \text{CeO}_2 \rightarrow \text{TiO}_2 \).

Keywords: Zirconium; Stabilizing additives; Nanopowders; Sintering kinetics.

1. Introduction

High-quality powders are necessary to obtain up-to-date ceramic materials. The Scientific Centre (SC) of Power Materials Science conducts research in synthesis of nanodisperse zirconium powders stabilized with various oxides. Zirconium powders which are produced commercially in Russia at the time, include a limited number of stabilizing additives and may not be exactly classified among nanodisperse powders [1-3]. Meanwhile, zirconia (mainly as stabilized forms) is considered by many researchers [4-6] as an extremely promising base for obtaining a new generation of filtering and catalytically active materials with specific surface properties. Stabilized zirconia is of interest due to the possibility of formation of solid solutions with high lattice oxygen mobility, high oxygen capacity, mechanical strength and thermal stability [7]. SC of Powder Materials Science has developed techniques for obtaining tetragonal zirconium doped with individual and mixed yttrium, ceria, titanium.

The work deals with the effect of various stabilizing additives on sintering kinetics of nanodisperse zirconium powders.

2. Experimental

Stabilized zirconium powders were obtained in laboratory by precipitating from aqueous-ethanol solutions of zirconium hydroxychloride and required nitrates or chlorides by ammonia solution [8]. Cerium was also introduced as nitric acid solution of rare-earth carbonate concentration containing mainly cerium carbonate by Solikamsky Magnievy Zavod OJSC (Perm Territory, Russia). The powders were sintered at 520 to 550 °C. Conditioning was carried out at temperatures of characteristic points at the differential thermal analysis.
The specific surface area of sintered powders was determined by thermal nitrogen desorption using Sorbi 4.1 and average particle size was calculated. Average size and size distribution of particles were studied immediately using DC-24000 particle size analyzer (CPS Instruments).

The phase composition was determined using XRD-6000, Shimadzu diffractometer in Cu kα radiation. The diffraction patterns were processed using Shimadzu XRD-6000/7000 V5.21 software package for data collection and processing. Raman spectra were obtained using «SENTERRA» multifunctional Raman spectrometer (Bruker) at radiating laser wavelength of 532 nm and radiation intensity of 5 mV.

Sintering kinetics of the synthesized powders were examined by means of “SENTSYS Evolution 24” thermomechanical analyzer/dilatometer (Setaram), on samples obtained by uniaxial compaction at 200 MPa. All measurements were performed in argon medium at temperature of up to 1500 °C, heating rate of 10 to 15 °C/min, cooling rate of 15 to 20 °C/min.

3. Results and Discussion

Table I gives the marking, composition and average particle size of the powders examined. The additive content is in wt %. Cerium added as rare-earth concentrate is given as CeO2 and designated as CeO2(k).

<table>
<thead>
<tr>
<th>Nos.</th>
<th>Composition</th>
<th>Thermal nitrogen desorption method (BET)</th>
<th>Average particle size from DC-24000, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZrO2−5Y2O3</td>
<td>60</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>ZrO2−8Y2O3</td>
<td>67</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>ZrO2−19CeO2</td>
<td>68</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>ZrO2−18CeO2(k)</td>
<td>58</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>ZrO2−13,7CeO2−3,2TiO2</td>
<td>44</td>
<td>23</td>
</tr>
</tbody>
</table>

Close values of average particle sizes obtained by various methods indicate that agglomerates of particles formed while obtaining the powder, are broken relatively easily under mechanical actions. The exception is ZrO2−13,7CeO2−3,2TiO2, the largest of the powders obtained. Individual powder particles are close to spherical shape.

Fig. 1 gives distribution diagrams of total particle percent versus their size for powders Nos. 4 and 5 based on data obtained using DC-24000 particle analyzer.

In ZrO2−18% CeO2(k) powder, 90% of particles are smaller than 40 nm. In ZrO2−13,7CeO2−3,2TiO2 powder, 60% of particles are smaller than 80 nm. The diagrams for powders Nos. 1 to 3 essentially coincide with distribution diagram in Fig. 1a. Thus, the powders obtained have a narrow particle size distribution in nanoscale range. Essential differences in particle size distribution of ZrO2−13,7CeO2−3,2TiO2 powder whose synthesis conditions were the same as powders Nos. 1 to 4 appear to be due to the fact that yttrium and cerium were added as ethanol nitrate solutions while titanium came from titanium chloride solution with high content of hydrochloric acid.
Fig. 1. Total Content of Particles versus Their Size: a – powder ZrO$_2$–18% CeO$_2$(k); b – powder ZrO$_2$–13,7CeO$_2$–3,2TiO$_2$.

Fig. 2. Raman Spectra of Zirconium Powders with Various Stabilizing Additives: 1 – ZrO$_2$–8% Y$_2$O$_3$; 2 – ZrO$_2$–19%CeO$_2$; 3 – ZrO$_2$–13,7CeO$_2$–3,2TiO$_2$

All powders examined had the same phase composition. According to X-ray diffraction analysis and Raman spectroscopy, the powders consist of tetragonal zirconium. Fig. 2 represents Raman spectra of as-sintered materials. Tab. II gives the characteristics of Raman spectra. As-fired powders have similar composition but the intensity of the spectra depends considerably on a stabilizing additive.
Tab. II. General Description of Raman Spectra

<table>
<thead>
<tr>
<th>Nos</th>
<th>Composition</th>
<th>Location of peaks, cm(^{-1})</th>
<th>(I_{260}/I_{315})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZrO(_2)−5%Y(_2)O(_3)</td>
<td>146 260 315 464 640</td>
<td>1.56</td>
</tr>
<tr>
<td>2</td>
<td>ZrO(_2)−8%Y(_2)O(_3)</td>
<td>146 262 318 464 640</td>
<td>2.45</td>
</tr>
<tr>
<td>3</td>
<td>ZrO(_2)−19%CeO(_2)</td>
<td>144 260 314 459 629</td>
<td>1.24</td>
</tr>
<tr>
<td>4</td>
<td>ZrO(_2)−18%CeO(_3)(k)</td>
<td>* 255 314 457 633</td>
<td>1.30</td>
</tr>
<tr>
<td>5</td>
<td>ZrO(_2)−13.7CeO(_2)−3.2TiO(_2)</td>
<td>144 270 315 455 640</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Note: * - powder with cerium concentrate has an intense peak at 85 cm\(^{-1}\) which could not be identified and probably pertains to impurities in cerium concentrate.

Various sources attribute 4 to 5 peaks to tetragonal zirconium [9, 10] because the peak at 315-316 cm\(^{-1}\) is not isolated in some cases. This peak was fixed in the powders examined but the intensity ratios \(I_{260}/I_{315}\) differ significantly (see Tab. 2). The peak has the minimum relative value in ZrO\(_2\)−8%Y\(_2\)O\(_3\), the powder closest to cubic zirconium.

Fig. 3 and Tab. III represent the examination results for shrinking rate of zirconium with various stabilizing additives. 3 peaks were fixed on shrinking rate curves for powders containing 5 and 8 wt % of yttrium which is associated in modern literature with presence of agglomerated particles in the powder. The first, the most intense peak at heat treatment temperature of 1000 to 1050 °C does not depend on yttrium content and heating rate. The second peak (1200 °C) shifts towards temperature increase as yttrium increases and towards temperature decrease as heating rate decreases. The position of the third peak (1400 °C) does not depend on yttrium content and heating rate. This peak is the most intense in commercial super dispersed partially stabilized zirconium powders (ДЦИ5, ДЦИ11).

Peaks at 1120 and 1300 °C were noted on the shrinking rate curve for nanodisperse zirconium powder stabilized with 15 mol % (19 wt %) of ceria. The most intense peak is at 1120 °C. If ceria is partially substituted by titanium (15 mol % CeO\(_2\)→10 mol % CeO\(_2\)+5 mol % TiO\(_2\)), stabilized zirconium sintering kinetics changed considerably. Three peaks are observed at the shrinking rate curve: 1150, 1260 and 1500 °C. The most intense peak is at 1500 °C.
Tab. III. Effect of Temperature and Stabilizing Additives on Shrinking Kinetics of Samples

<table>
<thead>
<tr>
<th>Additives</th>
<th>5%Y$_2$O$_3$</th>
<th>8%Y$_2$O$_3$</th>
<th>19%CeO$_2$</th>
<th>18%CeO$_2$(k)</th>
<th>13,7CeO$_2$–3,2TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of peaks</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Start of shrinking, °C</td>
<td>900</td>
<td>900</td>
<td>850</td>
<td>1050</td>
<td>1050</td>
</tr>
<tr>
<td>Most intense shrinking, °C</td>
<td>1050</td>
<td>1050</td>
<td>1120</td>
<td>1480</td>
<td>1500</td>
</tr>
<tr>
<td>Location of other peaks, °C</td>
<td>1200, 1400</td>
<td>1280, 1400</td>
<td>1300, 1500</td>
<td>1300</td>
<td>1150, 1260</td>
</tr>
</tbody>
</table>

Thus, peaks characteristic of the most intense shrinking of nanodisperse stabilized zirconium powder samples allow to arrange the stabilizing additives as follows: Y$_2$O$_3$ (1000-1050°C) → CeO$_2$ (1150°C) → TiO$_2$ (1500°C). It is of considerable interest that the most intense shrinking at high temperature was noted in presence of additives (ZrO$_2$–18% CeO$_2$(k)) or when supplementary components were introduced in the stabilizing additive (ZrO$_2$–13,7CeO$_2$–3,2TiO$_2$). ZrO$_2$–13,7CeO$_2$–3,2TiO$_2$.

Increase in powder particle size results in shift of maximum shrinking rate. Thus, commercial powder ZrO$_2$–5 wt. % Y$_2$O$_3$ (ДЦИ5) with as-supplied specific surface area of 3.5 to 6.5 m$^2$/g and <500 nm particle content of 27% (optical microscopy data) has maximum shrinking rate at 1400 °C, i.e. 300 deg higher than in nanodisperse powder.

4. Conclusions

Zirconium powders with various stabilizing additives obtained by precipitation from aqueous-ethanolic solutions of corresponding salts were examined. Agglomerates of particles formed while obtaining powder were shown to be broken relatively easily under mechanical actions. According to various methods, the powders obtained may be classified as nanodisperse.

Effect of various stabilizing additives on sintering kinetics of nanodisperse zirconium powders was studied by thermomechanical analysis. Temperature ranges of the most intense shrinking, characteristic points of shrinking rate changes were established.

The peaks characteristic of the most intense shrinking of nanodisperse stabilized zirconium powder samples were shown to allow to arrange the stabilizing additives as follows: Y$_2$O$_3$→CeO$_2$→TiO$_2$.

The most intense shrinking at high temperature was noted in presence of additives (ZrO$_2$–18% CeO$_2$(k)) or when supplementary components were introduced in the stabilizing additive (ZrO$_2$–13,7CeO$_2$–3,2TiO$_2$). ZrO$_2$–13,7CeO$_2$–3,2TiO$_2$.

When optimizing the sintering mode, intense shrinking processes at temperatures of less than 1200 °C are of particular interest.

Acknowledgment

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5. References


Садржај: Термомеханичком анализом проучаван је утицај стабилизирајућих адитива на кинетику синтеровања наноодисперзних прахова. Одређени су температурни опсези најинтензивнијег скупљања и карактеристичне тачке на којима долази до промена у брзини скупљања. Карактеристични пикови најинтензивнијег скупљања наноодисперзног цириконијумског праха указују на могућност формирања низа стабилизирајућих адитива по следећој шеми: Y$_2$O$_3$→CeO$_2$→TiO$_2$.

Кључне речи: цирконијум; стабилизирајући адитиви; нанопрахови; кинетика синтеровања