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EFFECT OF DEWATERING OF AMORPHOUS HYDROUS ZIRCONIA PRECIPITATES ON TETRAGONAL ZIRCONIA CONTENT IN CALCINED POWDERS

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Résumé - Des précipités d’hydroxydes de zircone amorphes ont été lavés avec différents liquides organiques avant calcination. Des différences significatives dans la stabilité de la phase ZrO₂ ont été observées et sont discutées en fonction de la morphologie, de la taille des cristallites et des contraintes dans les poudres calcinées.

Abstract - Amorphous hydrous zirconia precipitates were washed with different organic liquids prior to calcination. Significant differences in ZrO₂ phase stability were observed and discussed in terms of morphology, crystallite size and strains.

I - INTRODUCTION

Thermal decomposition of hydrous zirconia has been widely used for obtaining fine sinteractive ZrO₂ powders. The occurrence of the metastable tetragonal phase in these powders at room temperature was reported by several authors [1,2,3,4,5]. Different explanations for the stabilization were proposed, for example: the critical grain size effect [2,6,7,8], the influence of OH⁻ and other anion impurities [9,10], structural similarities between the amorphous phase and the tetragonal ZrO₂ lattice [1,11], strains [4,6] and non-stoichiometry [1,12]. It was recently shown that the pH during precipitation influences the tetragonal ZrO₂ content as well [13]. Hence, it seems that both the morphology and the chemistry of the powders influence the stability of the tetragonal phase.

The removal of water from hydrous zirconia precipitates prior to thermal decomposition can be promoted by organic liquid washing and the morphology of the resultant powder after calcination depends on the nature of the washing medium [14,15,16]. However, no studies have been reported regarding the influence of the washing medium on the nature of the amorphous precipitates and their relation to the properties of the calcined products. In the present paper we report on the attempt to explain the evolution of different crystal phases of ZrO₂ and their stability in terms of the influence of the washing procedure on the morphology of the amorphous precipitates.

II - EXPERIMENTAL PROCEDURE

Hydrous zirconia precipitates were prepared by pouring dilute zirconyl acetate or zirconyl chloride solutions at a constant rate into ammonia solution, maintaining a constant pH (10.5) throughout the precipitation. After several washings with distilled water, different portions of the precipitates were washed with an acetone–toluene–acetone (ATA) sequence, methyl alcohol, ethyl alcohol and iso-propyl alcohol, respectively, dried and subsequently calcined.
Amorphous precipitates and calcined powders were examined by X-ray diffraction (XRD), transmission electron microscopy (TEM) and electron diffraction (ED). Previously reported methods were used for the calculation of the phase content [17], strains and crystallite size [4].

No substantial differences in the morphology of amorphous precipitates washed with different alcohols were observed. The results of the samples washed with methyl alcohol are used in the present discussion.

III - RESULTS AND DISCUSSION

All the hydrous precipitates were found to be amorphous by XRD and ED. Different washings of precipitates resulted in significant differences in the morphology of the powders. In general individual particles are stacked together to form aggregates which in turn compose larger agglomerates. All alcohols and ATA treated powders formed weak agglomerates, which could be easily disintegrated by ultrasonic treatment. TEM of these two series of powders revealed that aggregates of alcohol washed samples are closely packed and rather large (100 nm and more), whereas ATA washing resulted in smaller (20 - 50 nm) and virtually loosely packed aggregates. The agglomerates of water washed samples were larger in size when compared with ATA and alcohol washed samples. The size and shape of the aggregates could however not be determined since the agglomerates were rather strong and could not be disintegrated by ultrasonic treatment. These observations are in agreement with the results of previous investigations [14,15].

TEM of calcined powders showed that during calcination the morphology of amorphous powders was retained (Figs. 1 - 2). Selected area ED patterns taken from several hundred nm regions consisted of rings with strong spots. However, SAED patterns obtained from smaller regions showed “single crystal” patterns (Fig. 4). Careful inspection of these spots revealed that they consisted of finer reflections scattered around a particular angular and $d_{hkl}$ mean value, which coincides with the value of the cubic zirconia. Dark field image formed using such a complex spot showed bright region of more or less homogeneous contrast (Fig. 3). Lattice image of such a region showed that it consisted of many crystallites of about 10 nm in size with slight differences in their orientation and also with small differences in their lattice spacings which corresponds to the observed splitting of the spots. These results indicate that the bright region observed in DF consisted of many crystallites which are nearly in the same orientation. Here—after, such regions are termed as domains. They seem to originate from the aggregates in the amorphous powders. This suggests the pre—existence of preferential orientation of the basic amorphous particles in aggregates. TEM studies also showed that the alcohol washed samples had larger domains than ATA washed samples. This indicates that alcohol washing resulted in larger regions of preferentially oriented amorphous units than ATA washing.

XRD of samples calcined for one hour at 450°C showed broad peaks centered around the expected positions of the cubic phase. However, the indications of splitting of the 113 peak suggested that the crystal structure could be tetragonal. For our further discussions we consider this phase as "metastable". No indications of the monoclinic phase were observed. Crystallite size and strains measured from the half widths of XRD peaks are shown in Table 1. It is evident that the water washed samples have higher strains and larger crystallite sizes than ATA and alcohol washed samples. However, at the present time the values of strains and crystallite sizes can not be considered unambiguously, since the contribution of different $d_{hkl}$ values of crystallites to line broadening could not be resolved. In any case, the crystallite size as estimated from TEM analysis was of the order of 10 nm which is close to the values obtained from XRD.

Prolonged calcination at 450°C up to 20 hours resulted in a 30 % m-ZrO$_2$ content in ATA washed samples, whereas alcohol washed samples were retained in metastable form. As given in Table 1, the average crystallite size of the monoclinic phase in ATA samples is smaller than that of the metastable phase. This implies that the crystallite size is not the only factor determining the metastable — stable monoclinic ZrO$_2$ transformation. The tentative explanation could be that the crystallites in the domains are constrained, which may explain the rather high stability of the metastable phase in alcohol washed samples when compared to ATA samples.
Fig. 1: Bright field image of ATA washed sample calcined at 450°C, 7 hr

Fig. 2: Bright field image of alcohol washed sample calcined at 450°C, 1 hr

Fig. 3: Dark field image of a domain in the alcohol washed sample

Fig. 4: Diffraction pattern of a domain
Table 1: Phase composition, average crystallite size and strains in calcined powders

<table>
<thead>
<tr>
<th>Wash medium</th>
<th>Calcination</th>
<th>% metastable phase</th>
<th>Average crystallite size (nm)</th>
<th>Strain x 10^-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>450°C, 1 hr</td>
<td>100</td>
<td>10.50</td>
<td>2.00</td>
</tr>
<tr>
<td>Methyl alcohol</td>
<td>450°C, 1 hr</td>
<td>100</td>
<td>11.60</td>
<td>0.30</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>450°C, 1 hr</td>
<td>100</td>
<td>11.60</td>
<td>0.30</td>
</tr>
<tr>
<td>Iso-propyl alcohol</td>
<td>450°C, 1 hr</td>
<td>100</td>
<td>13.00</td>
<td>0.30</td>
</tr>
<tr>
<td>ATA</td>
<td>450°C, 3 hr</td>
<td>70</td>
<td>37.00</td>
<td>2.50</td>
</tr>
<tr>
<td>ATA</td>
<td>450°C, 20 hr</td>
<td>d(1)</td>
<td>d(2)</td>
<td>10.50</td>
</tr>
<tr>
<td>Methyl alcohol</td>
<td>450°C, 3 hr</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methyl alcohol</td>
<td>450°C, 20 hr</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

d(1) average crystallite size of the metastable phase

d(2) average crystallite size of the monoclinic phase calculated from (111) peak

Table 2: Phase composition of samples calcined in oxidizing and reducing atmospheres for 1 hour at 600°C

<table>
<thead>
<tr>
<th>Wash medium</th>
<th>% metastable phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reducing atmosphere</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
</tr>
<tr>
<td>ATA</td>
<td>55</td>
</tr>
<tr>
<td>Methyl alcohol</td>
<td>35</td>
</tr>
</tbody>
</table>

Precipitates obtained from zirconyl chloride solution were calcined at 600°C for 1 hr in flowing oxygen and in vacuum (10 N/m²) respectively. Table 2 shows that the samples calcined in a reducing atmosphere contained larger amounts of the metastable phase than those calcined in an oxidizing atmosphere. It has also been observed that water washed samples calcined in reducing atmosphere were darker in color when compared with alcohol and ATA washed samples. This indicates in a qualitative way that the former samples were reduced to a larger extent [12]. By TEM analysis it was also found that the domains in all the samples calcined in reducing atmosphere were larger in size than those calcined in an oxidizing atmosphere. The reason is not clear at the present time. It seems that in this case one has to consider the influence of domain size along with non-stoichiometry on the stability of the metastable phase.

IV – SUMMARY

The rearrangement of the amorphous structural units of hydrous zirconia precipitates during washing with different organic liquids results in different sized aggregates. During calcination distinct domains are formed which consist of highly oriented crystallites. The domain size depends on washing medium and influences the transformation of the metastable ZrO₂ phase to the monoclinic phase.

The larger domain size along with the non-stoichiometry seem to prevent the transformation of the metastable phase in the samples calcined in a reducing atmosphere.
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REFERENCES: