Production of Zirconia from Zircon by Thermal Reaction with Calcium Oxide

Kamilia A. El-Barawy, Samir Z. El-Tawil and Adel A. Francis

Pyrometallurgy Division, Central Metallurgical Research and Development Institute (CMRDI), P. O. Box, 87 Helwan, Cairo, Egypt

Thermal reaction of Zircon with lime is studied within the temperature range 1200-1500°C for periods up to 4 h. The heating products are examined physically, chemically and mineralogically. The extent of reaction is determined from the solubilized silica obtained by leaching the sintered products in hydrochloric acid. A product assaying 91% ZrO₂ in monoclinic form is obtained by HCl acid leaching of the product fired at 1400°C for 2 h in presence of 1.2 stoichiometry calcium oxide. The thermal reaction of decomposition at the aforementioned temperature seems to follow a diffusion kinetic model in the form of \( x + (1-x) \ln (1-x) = kt \), where \( x \) is the extent of solubilized silica in time \( t \) and \( k \) is the rate constant. The apparent activation energy of the process was calculated and found to be 205 kJ/mole.

Key-words: Zircon, Sintering, Calcium oxide, Recovery, Zirconia, Kinetics and mechanism, Structure

1. Introduction

The future holds considerable promise for zirconia ceramics in engineering and electronic applications. Zirconium oxide can be prepared by the pyrochemical decomposition of zircon by alkaline earth oxides. The thermal reaction between lime and zircon has been the subject of investigations by research workers. It was essentially based on the selective attack of silica in zircon by calcium oxide within the temperature range 1100-1600°C, to form soluble calcium silicate and zirconia, followed by leaching with acid and alkali to remove the solubilized silica. Owing to the refractoriness of zircon as well as the sequence of reactions and accompanying phase transformation during the thermal reaction process, the rate controlling step in the overall reaction has not been clearly determined.

This paper is one of a series of investigations carried out by the authors aiming to produce zirconia from local zircon sand by reactions with alkaline earth metal oxide (CaO/MgO), alkali (Na₂CO₃ and NaOH), and also by direct chlorination of zircon with Cl₂ gas in presence of calcium zirconium silicate. The purpose of the present work is to study in detail the reaction of zircon with CaO in the high temperature range of 1200-1500°C in order to obtain sufficient information on the kinetics and mechanism of the reaction process.

2. Experimental

2.1 Raw material

Zircon concentrate sample of purity ~98% and grain size (125 μm) is obtained as a by-product from the beneficiation of Egyptian black sands (El Bardaweel lake) which are present in different localities along Egypt’s Mediterranean sea coast and Nile delta. Analysis of zircon concentrate is found to contain 66% ZrO₂, 32.13% SiO₂, 0.29% Fe₂O₃, 0.17% TiO₂, 0.23% Al₂O₃, 0.25% moisture and (RE)₂O₃. The other materials used are Analar grade of HCl and CaO of mean particle size (63 μm) prepared from thermal decomposition of pure CaCO₃ at ~900°C till constant weight.

2.2 Experimental procedure

Mixtures of zircon (mean particle size 63 μm) and calcium oxide ranging from \( x = 1 \) to 2.5 (\( x \) = molar ratio in CaO/ZrSiO₄) are blended and mixed thoroughly, charged in a platinum crucible and inserted in an electric tube furnace at fixed temperature. The stoichiometry (\( x \)) is the theoretical amount of CaO required to achieve a complete disintegration of zircon to produce zirconia and calcium silicate.

\[
\text{ZrSiO}_4 + \text{CaO} \rightarrow \text{CaSiO}_3 + \text{ZrO}_2 \quad (1)
\]

The heat treatment experiments are carried out in the temperature range 1200-1500°C for various times up to 4 h. The temperature of the furnace was controlled within ±5°C. At the end of each experiments, the crucible containing the charge was left inside the furnace to cool down, and then it was taken out for grinding and analyzing. Leaching of the fired ground products with dilute HCl acid (solid/liquid ratio=1 g/50 ml of 0.72 M HCl at 50°C for 1 h) is performed to separate the solubilized silica (CaSiO₃ or Ca₂SiO₄) and leaving behind an expected product of m-ZrO₂ containing a moderate amount of CaO. It should be noted that higher conc. of HCl than 0.72 M has no effect on the improvement in the recovery of silicate in the fired products.

3. Results and discussion

3.1 Effect of calcium oxide

The parameters affecting the recovery of zirconia and the formation of any probable intermediate compounds such as calcium zirconium silicate are studied. Mixtures of zircon and calcium oxide, containing variable amounts of lime ranging from \( x = 1 \) to 2.5 are heated in an electric furnace at 1400°C for 2 h. The fired products are evaluated primarily by X-ray diffraction analysis to specify the suitable condition to produce mainly CaSiO₃ and ZrO₂. Figure 1 reveal that the addition of 1.2 × CaO to zircon during heat treatment at 1400°C for 2 h leads to the maximum formation of mainly zirconia phase besides other phases with low intensity lines such as CaSiO₃ and Ca₂ZrO₄. Noting that Ca₃Zr₂Si₄O₁₂ was not observed within the overall range of temperature, while the other Ca₅ZrSi₄O₁₄ was only observed, the other phase constituents such as ZrO₂, CaSiO₃, Ca₂SiO₄ and Ca₂ZrO₄ were observed depending on
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Based on this result, the fired products are subjected to leaching process by HCl solution (s/1 ratio = 1 g/50 ml of 0.72 M HCl at 50°C for 1 h) to solubilize CaSiO₃. The results obtained in Table 1 reveal the maximum removal of solubilized silica ~94% and the remaining residue contains mainly ZrO₂ ~91%. At higher CaO, x > 1.2, the percentage of silica removal is lower and this is due to its capturing as calcium zirconium silicate which is apparently difficult to be leached.

Table 1. Extent of Solubilized Silica Removal for Sample Heated for 2 h at 1400°C

<table>
<thead>
<tr>
<th>Lime stoichiometry</th>
<th>Extent of silica removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>71.8</td>
</tr>
<tr>
<td>1.2</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>79.42</td>
</tr>
<tr>
<td>2.5</td>
<td>40.5</td>
</tr>
</tbody>
</table>

Fig. 1. XRD of zircon fired with different CaO stoichiometry at 1400°C for 2 h.

3.2 Effect of temperature and time

A series of thermal treatment are conducted using a mixture of zircon and CaO in x = 1.2 within the temperature range of 1200–1500°C for different periods up to 4 h. The effect of temperature and time on the extent of solubilized silica at constant x = 1.2 is shown in Fig. 2.

Fig. 2. Effect of temperature and time on the extent of solubilized silica at constant x = 1.2.

Fig. 3. XRD of fired specimens with a composition of x = 1.2 CaO within the temperature range 1200–1500°C for 2 h.
fired products are evaluated by XRD and leached by HCl acid to separate the solubilized silica, under the before-mentioned conditions. The results in Fig. 2 show generally an increase of the solubilized silica in the fired products (extent of reaction) with an increase in reaction temperature up to 1400°C and time up to 2 h.

About 30% of SiO<sub>2</sub> is separated after firing at 1200°C for 2 h, after which a slight increase is observed for periods up to 4 h. At 1300°C removal of ~70% SiO<sub>2</sub> is obtained after a reaction time of 4 h. However, by heating to a temperature up to 1400°C, an abrupt increase in the extent of solubilized silica ~91% is achieved after heating for 1 h. Heating for longer period than 1 h has a slight effect on the reaction extent and a value of ~94% is achieved for a period more than 2 h. At this optimum condition, the remaining analyzed residue contains mainly ZrO<sub>2</sub> ~91% and SiO<sub>2</sub> ~6.3%. Alternatively, by increasing the temperature up to 1500°C, the extent of silica removal decreases than that obtained after firing at 1400°C, reaching a maximum value of ~80% for ≥1 h.

XRD pattern of the fired products obtained at the temperature range 1200–1500°C for 2 h is given in Fig. 3. It indicates that zircon phase is mainly identified at 1200°C, besides the presence of ZrO<sub>2</sub>, Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub> and CaZrO<sub>3</sub> in low intensities. This result shows the incomplete formation of both zirconia and calcium silicates. The presence of unreacted zircon at 1200°C is due to the inadequate reaction rate. Microscopic photographs in Fig. 4 a and b show the presence of mainly zircon phase besides some ZrO<sub>2</sub> (black) dispersed in the glassy matrix. At higher temperatures 1300–1400°C, the zircon phase decreases and disappears at 1400°C. However, the phases of m-ZrO<sub>2</sub>, CaSiO<sub>3</sub> and CaZrO<sub>3</sub> increase at 1400°C. This result proves that the higher extent of reaction between zircon and CaO is achieved at 1400°C, which corresponds to a higher silica removal in Fig. 2. This is ascribed to the increased amount of CaSiO<sub>3</sub> in the reaction products as observed in Fig. 5. Microscopic investigation also reveals agglomerate of ZrO<sub>2</sub> crystals embedded in a calcium silicate matrix which show that the size of ZrO<sub>2</sub> grain is very thick in Fig. 6. It should be noted that the samples are mounted on a glass slide with a permanent cementing Canada balsam and observed using a polarizing microscope (transmitted light).

X-ray diffraction analysis of the residue remaining after HCl acid leaching of the fired product obtained at optimum conditions (1400°C for 2 h in Fig. 7) reveals the presence of m-ZrO<sub>2</sub> beside small amount of insoluble compounds Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub> and CaZrO<sub>3</sub>. Microscopic investigation of the residue in Fig. 8 shows the presence of m-ZrO<sub>2</sub> phase (subhedral grain) dispersed in the same zirconia matrix. Alternatively at 1500°C, the main phases identified in the fired products by XRD (Fig. 3) is m-ZrO<sub>2</sub> besides the presence of CaSiO<sub>3</sub> and Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub> in low intensities. The presence of Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub> which is insoluble in HCl leads to the decrease in the extent of reaction ~80% as shown in Fig. 2. Microscopic investigation at this higher temperature in Fig. 9 a and b shows mainly the presence of ZrO<sub>2</sub>, CaSiO<sub>3</sub> besides the formation of Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub>. It is also noted
that ZrO₂ grain is not enlarged and agglomerated as that revealed at 1400°C which may be ascribed to the reaction of ZrO₂ at this higher temperature 1500°C with silica and CaO to form Ca₃ZrSi₂O₉. At such temperature, the possibility of the presence of pores is very small. Therefore, the white lines observed inside the ZrO₂ grains indicate that some kind of melting occurs and reaction between ZrO₂, Ca₂SiO₄ and CaSiO₃ takes place to give Ca₃ZrSi₂O₉.

### 3.3 Reaction kinetics and mechanism

Different kinetic models²¹-²⁴ including phase boundary reaction (3 models), diffusion (5 models) and nucleation (1 model) are applied for the result of thermal reaction of zircon and lime within the temperature range 1200-1500°C for different periods up to 4 h. It was found that the result in Fig. 2 satisfy the following two-dimensional diffusion model up to 80% reaction extent.

\[ x + (1-x) \ln(1-x) = kt \]

In this model, the rate of reaction of particles rely on the grain shape factor which is intermediate between a slab and a sphere, where \( k \) is the rate constant and \( x \) is the extent of solubilized silica.

Bearing in mind that the reaction rate constant in the solid state kinetic models should be constant at each reaction extent. Hence, the reaction rate constant at each reaction extent is calculated and represented in Fig. 10. Arrhenius equation is applied to calculate the apparent activation energy of the reaction process by plotting log \( k \) against \( 1/T \) K⁻¹ in Fig. 11. The activation energy is calculated from the slope of the straight line and equals to ~205 kJ/mol. This higher activation energy value confirms the solid state diffusion process. Noting that the activation energy for the reaction of zircon with Na₂CO₃, NaOH, CaO/MgO and chlorination have been calculated and equal to 250, 62 and 120, and 36 kJ/mol, respectively.²⁶-²⁸
3.4 Mechanism of reaction

It is reported by De Keyser et al.\textsuperscript{25) that} Ca\textsuperscript{2+} diffuse toward the zircon phase while Si\textsuperscript{4+} and Zr\textsuperscript{4+} diffuse toward the calcium oxide phase which result in the formation of different compounds depending on the reaction condition. Based on the results obtained and the phases identified in the fired products within the temperature range 1100-1500°C, the sequence of the probable thermal reaction of zircon and CaO taking place can be considered as follows:

\begin{equation}
1100°C \quad \text{Ca}_2\text{ZrSi}_2\text{O}_8 + 4\text{CaO} \xrightarrow{1100°C} \text{Ca}_3\text{ZrSi}_2\text{O}_9 + \text{CaZrO}_3 \quad (2)
\end{equation}

The reaction products are identified by XRD in Fig. 12. At $\geq 1200°C$

\begin{equation}
\text{Ca}_2\text{ZrSi}_2\text{O}_9 \xrightarrow{} \text{CaSiO}_3 + \text{Ca}_2\text{SiO}_4 + \text{ZrO}_2 \quad (3)
\end{equation}

This dissociation reaction is in accordance with that reported in the phase diagram of CaO-ZrO\textsubscript{2}-SiO\textsubscript{2}\textsuperscript{26)-29) The remaining amounts of zircon react with excess of CaO according to the following reaction.

\begin{equation}
3\text{ZrSiO}_4 + 3\text{CaO} \xrightarrow{} 3\text{CaSiO}_3 + 3\text{ZrO}_2 \quad (4)
\end{equation}

The overall reaction at this temperature range

\begin{equation}
3\text{ZrSiO}_4 + 7\text{CaO} \xrightarrow{} \text{Ca}_3\text{ZrSi}_2\text{O}_9 + 4\text{CaSiO}_3 + 4\text{ZrO}_2 \quad (5)
\end{equation}

At 1500°C

A reaction between CaSiO\textsubscript{3} and Ca\textsubscript{3}Si\textsubscript{2}O\textsubscript{7} takes place, forming the compound Ca\textsubscript{9}Si\textsubscript{5}O\textsubscript{13} (melting point of 1464°C) as reported by Phillips and Muan\textsuperscript{30) CaSiO\textsubscript{3} + Ca\textsubscript{3}Si\textsubscript{2}O\textsubscript{7} \xrightarrow{} Ca\textsubscript{9}Si\textsubscript{5}O\textsubscript{13} (m.p. 1464°C) (6)

This compound is further reacted with the present ZrO\textsubscript{2} forming Ca\textsubscript{3}ZrSi\textsubscript{2}O\textsubscript{9} as approved by XRD.

\begin{equation}
\text{Ca}_3\text{Si}_2\text{O}_7 + \text{ZrO}_2 \xrightarrow{} \text{Ca}_3\text{ZrSi}_2\text{O}_9 \quad (7)
\end{equation}

The disappearance of CaZrO\textsubscript{3} at 1500°C may be attributed to its reaction with CaSiO\textsubscript{3} and form Ca\textsubscript{3}ZrSi\textsubscript{2}O\textsubscript{9} as identified by XRD.

\begin{equation}
2\text{CaSiO}_3 + \text{CaZrO}_3 \xrightarrow{} \text{Ca}_3\text{ZrSi}_2\text{O}_9 \quad (8)
\end{equation}

Therefore, the overall reaction at 1500°C may be suggested as follows

\begin{equation}
5\text{ZrSiO}_4 + 7\text{CaO} \xrightarrow{} \text{CaSiO}_3 + \text{4ZrO}_2 + 2\text{Ca}_3\text{ZrSi}_2\text{O}_9 \quad (9)
\end{equation}

It is noticed that the molar ratio of zircon : CaO (1 : 1.2) used in the present study is in agreement with the proposed overall reaction (1.4 × CaO)

4. Conclusion

The fired products obtained from the reaction of zircon and CaO mixture (1:1.2 stoichiometry) at 1400°C for 2 h proved to be the suitable condition for the preparation of ZrO\textsubscript{2}. Leaching of the product at this optimum condition with HCl leads to the removal of 94% soluble silicate. The remaining residue after leaching produce a commercial grade of ~91%ZrO\textsubscript{2}, 6.3%SiO\textsubscript{2} and 2.7%CaO. This product can be commercially applied in foundry and other allied industries. Also this product can be further processed to produce pure ZrO\textsubscript{2} or its valuable compounds.

Appendix

Symbols of Compounds Revealed by XRD Analysis

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Compound</th>
<th>ASTM. Card No.</th>
</tr>
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<tbody>
<tr>
<td>a</td>
<td>ZrSiO\textsubscript{4}</td>
<td>6-0266</td>
</tr>
<tr>
<td>b</td>
<td>m-ZrO\textsubscript{2}</td>
<td>13-307</td>
</tr>
<tr>
<td>c</td>
<td>c-ZrO\textsubscript{2}</td>
<td>27-997</td>
</tr>
<tr>
<td>d</td>
<td>CaZrSi\textsubscript{3}O\textsubscript{6}</td>
<td>16-155</td>
</tr>
<tr>
<td>G</td>
<td>CaZrO\textsubscript{3}</td>
<td>9-364</td>
</tr>
<tr>
<td>H</td>
<td>CaSiO\textsubscript{3}</td>
<td>19-248</td>
</tr>
<tr>
<td>K</td>
<td>Ca\textsubscript{2}SiO\textsubscript{4}</td>
<td>20-238</td>
</tr>
<tr>
<td>O</td>
<td>$\beta$-CaSiO\textsubscript{3}</td>
<td>19-249</td>
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References

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