Cubic Zirconia from Zircon Sand by Firing with CaO/MgO Mixture

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The effects of firing temperature and molar ratio of CaO/MgO on the formation of cubic ZrO₂ from zircon were determined. Experimental results indicate that a thermal reaction completed by firing at 1500°C for 2 h using a charge of zircon and 0.4CaO/0.6MgO molar ratio is favorable for the production of mainly pure cubic ZrO₂ as containing 1.29%MgO and 0.22%CaO after separating the silica by acid leaching. Different kinetic models have been tried, but the mechanism of the overall firing reaction obeys the diffusion 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 decomposition process is calculated and found to be 120 kJ/mol.

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**Key-words**: Zircon, Sintering, CaO/MgO mixture, Recovery, Zirconia, Kinetics and mechanism, Structure

1. Introduction

Zirconia is one of the important materials which find wide usage depending on its purity and crystal structure in several scope of applications such as ceramics, refractories, electronics and others. Cubic zirconia forms also the nucleus of a new class of ceramic materials which has great potential engineering future for structural applications. A little number of investigations\(^{12-12}\) have been reported in the literature on the decomposition of zircon using CaO/MgO mixture.

This paper is one of a series of investigations carried out by the authors aiming to produce zirconia by reactions of local zircon sand with alkaline earth metal oxides (CaO), alkali (Na₂CO₃ & NaOH) and with Cl₂ gas in presence of carbon.\(^{7-8}\) It deals with the preparation of cubic zirconia by the pyrochemical displacement of zirconia from local zircon by CaO/MgO mixture. The final product is evaluated physically, chemically and microscopically. The sequence of reaction mechanism and kinetics for the decomposition process of zircon by CaO/MgO mixture is also considered.

2. Experimental

2.1 Raw material

Zircon concentrate sample of 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, alkali (Na₂CO₃ & NaOH) and with Cl₂ gas in presence of carbon.\(^{7-8}\) Charges containing different percentage of CaO/MgO (1:1) ranging from 20.78%, 28.2% and 34.43% to zircon concentrate are fired at 1400°C for 2 h. They correspond to \( x=0.5, 0.75 \) and 1.0, in case of \( x=1.0 \)

\[ \text{ZrSiO}_4 + \text{CaO} + \text{MgO} \rightarrow \text{ZrO}_2 + \text{CaMgSiO}_4 \]

The results in Fig. 1 demonstrate that the intensities of lines representing the cubic structure of zirconium oxide in the fired products at 1500°C for 2 h increase as CaO/MgO percentage increases tending to be predominant at 34.43% (1x). The monoclinic zirconia tends to be minority as CaO/MgO percentage increases. Hence, it is pointed out that one molar ratio (\( x=1.0 \)) CaO/MgO (equivalent to 34.43% by weight to zircon) is the proper percentage of basic oxides added to obtain cubic zirconia (other percentages such as 38.6% and 42.3% have been applied, which are equivalent to \( x=1.2 \) and \( x=1.4 \)).

Regarding to the formation of orthosilicate during firing, the compound CaMgSi₂O₆ is identified in the fired products containing 0.5x CaO/MgO mixture (20.78%), while both CaMgSi₂O₆ and Ca₂MgSi₂O₇ are identified at 0.75x CaO/MgO mixture (28.2% and 34.43%). Leaching of the fired product with HCl acid (0.72 M at 50°C for 1 h, \( s/l=1 \)) gives solubilized SiO₂ of 70%, 75% and 96% for zircon samples containing CaO/MgO mixture of 20.78%, 28.2% and 34.43%, respectively.

2.2 Experimental techniques

Mixtures of zircon (mean particle size : 63 μm) and CaO/MgO ranging from \( x=0.5 \) to 1 (\( x=\text{molar ratio of (CaO+MgO)/zircon} \)) are blended and mixed thoroughly, charged in a platinum crucible and inserted in an electric tube furnace at a fixed temperature. The molar ratio (\( x \)) is the theoretical amount of CaO/MgO required to achieve a complete disintegration of zircon to produce ZrO₂ and calcium magnesium silicate. The firing experiments are carried out in the temperature range 1200°-1500°C for various periods up to 4 h. The temperature of the furnace was controlled within ±5°C. At the end of each experiment, the fired charge was drawn gradually and left inside the furnace to cool down, and then it was taken out for grinding and analyzing. Leaching of the powdered specimens with dilute HCl acid (\( s/l \) ratio = 1 g/50 ml, 0.72 M at 50°C for 1 h) is performed to separate the solubilized silica (calcium magnesium silicate) and leaving behind ZrO₂ as the main product in the residue. After leaching, the residues were calcined at 900°C for 1 h and the extent of the solid-state reaction is determined from the amount of solubilized silica by atomic absorption spectrometry\(^{13}\) with respect to the initial SiO₂ content in the zircon sample. To confirm the results, the remnant silica in the zirconia residues of some samples has been analyzed by HF. X-ray diffraction (XRD) using Cu radiation is used to identify the phases present and selected specimens are investigated microscopically.

3. Results and discussion

3.1 Effect of CaO/MgO mixture

Charges containing different percentage of CaO/MgO (1:1) ranging from 20.78%, 28.2% and 34.43% to zircon concentrate are fired at 1400°C for 2 h. They correspond to \( x=0.5, 0.75 \) and 1.0, in case of \( x=1.0 \)

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Leaching of the fired product with HCl acid (0.72 M at 50°C for 1 h, \( s/l=1 \)) gives solubilized SiO₂ of 70%, 75% and 96% for zircon samples containing CaO/MgO mixture of 20.78%, 28.2% and 34.43%, respectively.

3.2 Effect of temperature and time

Zircon sample containing CaO/MgO (1:1) mixture of percentage 34.43% (\( x=1 \)) by weight to zircon are fired at

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different temperature (1200–1500°C) for various periods up to 4 h. The fired products are subjected to XRD and microscopic investigation to identify the produced phases. In Fig. 2, the highest peak of cubic zirconia is observed in the fired product at 1200°C, along with a low intensity line of m-ZrO₂, zircon and CaMgSi₂O₆. At 1400°C and 1500°C, the c-ZrO₂ is the principal phase identified besides CaMgSi₂O₆ and Ca₂MgSi₂O₇.

Microscopic photograph of the fired sample at 1200°C in Fig. 3 reveals that the grains consist mainly of c-ZrO₂ black phase (proved by XRD and under crossed nicol the grains are isotropic), besides relics of zircon phase. At higher temperature of 1500°C, in Fig. 4, the main phases consist of cubic ZrO₂ (black) and a granular minute crystals of calcium magnesium silicate. Leaching of the fired products with HCl under the afore-mentioned conditions is carried out to determine the solubilized silica, which represents the reaction extent in the leachant solution.

Figure 5 illustrates the plot of the silica separated by HCl acid leaching of the fired product obtained at different temperature versus time of the firing. It is shown that the extent of solubilized silica increases gradually with rise in the firing temperature up to 1500°C and time up to 2 h after which the reaction is stopped. The maximum extent of solubilized silica increases at 1500°C for 2 h amounts to ~96%. Chemical analysis of the remaining residue after leaching at optimum condition shows the presence of 96% ZrO₂ and ~4% SiO₂ as well as traces of CaO and MgO. XRD of the dried residue in Fig. 6 reveals the presence of c-ZrO₂ as the main phase identified besides low intensity line of m-ZrO₂ phase. Microscopic investigation of this residue fired at 1500°C for 2 h in Fig. 7 advocate the presence of mainly c-ZrO₂ phase (proved by XRD).

It is important to notice that the maximum recovery of c-ZrO₂ ~96% by using CaO/MgO mixture is higher than that achieved by using only CaO or MgO where about ~91% in m-ZrO₂ form is obtained at 1400°C after firing for 2 h. In
the case of CaO and 93% of m-ZrO₂ in the case of MgO at a firing temperature of 1500°C for 2 h as shown in Fig. 8.

Also, by replacing the synthetic mixture CaO/MgO (34.43%) by natural dolomite in the sintering process, no significant difference in the removal of silica ~96.84% is observed and the remaining ZrO₂ is in the form of cubic structure besides little intensities of monoclinic zirconia in Fig. 9 in order to produce only a cubic zirconia structure, further sintering experiments were performed at 1500°C for 2 h. This can be accomplished by using the optimum percentage of mixed oxides/zircon of 34.43%(1 molar ratio) and varying the CaO/MgO molar ratio in the range of 0.67CaO/0.33MgO, 0.5/0.5, 0.4/0.6 and 0.33/0.67 which correspond to 2, 1, 0.67 and 0.5 molar ratio. Figures 10 and 11(a) show the complete disappearance of m-ZrO₂ and the predominance of cubic zirconia in the fired products by using 0.4CaO/0.6MgO molar ratio.

In Fig. 11(b), leaching of the reaction products show a complete removal of solubilized silica upon using the above CaO/MgO molar ratio of 0.4/0.6. Chemical analysis of the residue obtained at this optimum condition reveal the presence of pure c-ZrO₂ containing 1.29%MgO and 0.22%CaO and only c-ZrO₂ was detected as a crystalline phase.
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Accordingly, the optimum experimental firing condition for 0.4CaO/0.6MgO molar ratio mixture (34.43% by weight to zircon) at 1500°C for 2h is the preferable conditions to produce cubic ZrO$_2$. These conditions can be efficiently applied in commercial scale for the production of fully stabilized c-ZrO$_2$ which find many applications in various engineering industries and in the production of solid oxide fuel cells.

3.3 Kinetics and mechanism of the reaction

Different kinetic models, including phase boundary reaction (3 models), diffusion (5 models) and nucleation (1 model) are applied for the results of thermal reaction of zircon and CaO/MgO mixture within the temperature range 1200-1500°C for different periods up to 4h in Fig. 5. It was found that the result satisfies the two-dimensional diffusion model up to 70% reaction extent and till the firing temperature 1400°C.

$$X + (1-X)\ln(1-X) = kt$$

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. 13. By plotting $\log k$ against $1/T$ ($^\circ K^{-1}$) according to Arrhenius equation in Fig. 14, the activation energy is calculated from the slope of the obtained straight line and equals to 120 kJ/mol. This activation energy value is lower than that obtained upon using only CaO~205 kJ/mol in the charge mixture.7)

3.4 Mechanism of reaction

Based on the different phases identified by X-ray analysis in the fired products at 1200°-1500°C and according to the quaternary phase diagram of MgO–CaO–ZrO$_2$–SiO$_2$, the simple chemical reaction between zircon and CaO or MgO is taking place as follows:

Fig. 9. XRD of zircon with dolomite ore fired at 1500°C for 2 h.

Fig. 10. XRD of zircon with different molar ratio of CaO/MgO mixtures fired at 1500°C for 2 h.

Fig. 11. Effect of the variation of CaO/MgO molar ratio on the relative intensity of ZrO$_2$ structure formation fired at 1500°C for 2 h and (b) on the extent of solubilized silica.
In presence of a mixture of CaO and MgO the thermal reaction may be expressed by:

\[ 3\text{ZrSiO}_4 + 2\text{CaO} + \text{MgO} \rightarrow 2\text{CaSiO}_3 + \text{MgSiO}_3 + 3\text{ZrO}_2 \quad (4) \]

\[ \text{ZrSiO}_4 + \text{CaO} + \text{MgO} \rightarrow \text{CaMgSiO}_4 + \text{ZrO}_2 \quad (5) \]

Thereby, calcium silicate may react in two different way to give calcium magnesium silicate.

\[ \text{CaSiO}_3 + \text{MgSiO}_3 \rightarrow \text{CaMgSi}_2\text{O}_6 \quad (6) \]

\[ \text{CaMgSiO}_3 + \text{CaSiO}_3 \rightarrow \text{Ca}_3\text{MgSi}_2\text{O}_7 \quad (7) \]

Hence, the overall reaction proceeds as follows:

\[ 4\text{ZrSiO}_4 + 3\text{CaO} + 2\text{MgO} \rightarrow \text{CaMgSi}_2\text{O}_6 + \text{Ca}_3\text{MgSi}_2\text{O}_7 + 4\text{ZrO}_2 \quad (8) \]

4. Conclusion

The fired products obtained from the reaction of zircon and CaO/MgO mixture (34.43%) of a molar ratio 0.4CaO/0.6MgO at a temperature of 1500°C for 2 h proved to be the best condition for the preparation of a completely cubic ZrO2. Leaching of the fired product at this optimum condition with HCl (0.72 M, solid/liquid = 1/50 at 50°C for 1 h) leads to the complete removal of soluble silicate. The remaining residue after leaching and calcination at 900°C for 1 h contains mainly ZrO2 of cubic structure besides 1.29% MgO and 0.22% CaO. This product can be used successfully in many fields of engineering applications.

Fig. 12. XRD of zircon with 0.4CaO/0.6MgO molar ratio (a) fired at 1500°C for 2 h and (b) of the leached product.

Fig. 13. Applicability of solid-state models on CaO/MgO firing process.

The produced c-ZrO2 ss contains a considerable amount of MgO and CaO.

Appendix

Symbols of Compounds Revealed by XRD Analysis

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<th>Symbol</th>
<th>Compound</th>
<th>ASTM Card No.</th>
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<td>a</td>
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<tr>
<td>b</td>
<td>m-ZrO2</td>
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<tr>
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<td>F</td>
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References