Calciothermic Reduction of Zirconium Oxide in Molten CaCl₂

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The reduction of zirconium dioxide using liquid calcium and molten calcium chloride was investigated. The study focusing on the influence of reductant amount, reaction time, CaCl₂ amount, and temperature on the reduction process. Zirconium powder with oxygen content less than 800 ppm was obtained at 1 100°C after 3 h and by using two times the theoretical amount of Ca and four times that of CaCl₂. The reduction reaction of ZrO₂ was found to be multi steps process through the formation of intermediate phase CaZrO₃. The morphology of the obtained zirconium was observed to be highly affected by the reaction temperature.

KEY WORDS: zirconium; calciothermic reduction; calcium; calcium chloride.

1. Introduction

Superior corrosion properties of zirconium make it ideal as a structural material in the chemical processing industry. Some important areas where zirconium is used include reboilers, evaporators, tanks, packing, trays, reactor vessels, pumps, valves and piping. However, the major interest of zirconium comes from nuclear reactor applications because of its low thermal neutron absorption cross-section and of good strength. Zirconium finds also some application as an alloying addition to many ferrous alloys. Based on high deoxidizing power, zirconium is added to killed steel in the form of zirconium–iron–silicon alloys to produce ultra low oxygen content steel. Zirconium improves the mechanical properties of steel by inhibiting the grain growth. Like aluminum and titanium, zirconium increases the tensile properties of fully killed steels by raising its grain coarsening temperature and by forming zirconium sulfides.⁵⁻⁷

The current commercial production method of zirconium is the Kroll process.⁵⁻⁷ This process is classified into two main stages; zircon sand is firstly converted to zirconium dioxide, which subsequently treated by many hydrometallurgical processes in order to obtain pure zirconium oxide. In the second stage, the later is reconverted to zirconium tetrachloride and then reduced by liquid magnesium to form zirconium metal. In industrial operation, this process is one batch that consists of large number of individual steps. It takes 10 days to produce 10 tons of sponge zirconium from zircon sand due to its large number of steps. Compared with the modern production method for the common metal, the Kroll process is extremely intensive in the term of equipments, labor, energy, and maintenance. With this background, the development of an alternative to the Kroll process becomes an essential industrial requirement.

The production of pure zirconium dioxide through zircon fusion with alkali at temperatures between 600 and 850°C, followed by wet chemical treatments can solve many problems at the first stage. The authors have studied these pyro- and hydro-metallurgical steps. The problems encountered in the second stage of the Kroll process can be minimized if the reduction of zirconium dioxide is achieved in a single step process.

Aluminum, alkaline earth metals such as Ca and Mg and rare earth elements can be selected as the candidates for direct reduction of ZrO₂, because the stability of their oxides is higher than that of the zirconium oxide.¹¹ The reduction reaction can be representing as:

\[ \text{ZrO}_2 + 2R \rightarrow 2RO + \text{Zr} \] ①

where R is the reducing agent.

There are other several requirements in the reducing agent.¹²⁻¹⁵ Firstly, a reductant with wide solubility in Zr or with a strong affinity to form intermetallic compounds with Zr is not suitable. For example, α zirconium dissolves 10 mol% Al and β Zr dissolves 25% Al. Since the formation of the intermetallic compounds such as ZrAl₃ by reaction (2) is more favorable than the reduction to pure metal from the free energy point of view \((\Delta G_R = -13.6 \text{ kcal and } -4 \text{ kcal at } 298 \text{ K respectively})\),¹⁶⁻¹⁸ Al cannot be applied as a reductant for Zr preparation.

\[ \text{ZrO}_2 + 13/2 \text{Al} \rightarrow \text{ZrAl}_3 + 2/3 \text{Al}_2\text{O}_3 \] ②

Carbon, which is a common reducing agent in the metallurgical industry, has also a higher tendency to form carbides ZrCₓ or carbonitrides ZrCₓNᵧ than the producing of pure metal when it reacts with zirconium oxide.¹⁹⁻²⁰

The second requirement in the reductant is the deoxidation capacity. Kubaschewski and Bench²¹ reported that the equilibrium concentration of oxygen in Zr–O system were 0.05, 1.55 and 2 mol% where zirconium oxide was reduced with calcium, magnesium and barium, respectively. The free energy of dissociation in Zr–O system as shown in Fig. 1, together with the free energies of oxidation at 1 273 K for
common reductant, was reported in their work. It is clearly seen that only calcium may be expected to produce pure zirconium from oxides.

The third criterion is the ability to separate the pure metal from other reduction byproducts. For example, if magnesium used as a reductant the removal of the ignited magnesia (MgO) by acid leaching without attacking the formed zirconium would be a difficult task.\(^{22,23}\) The fourth important requirement in the reducing agent is that it must be cheap and available commercially and that it must satisfy the environmental requirements. Rare earths are expensive and cannot be used as economic reductant. Radioactive or noxious elements are excluded as zirconium reductants.

Calcium is the only candidate that satisfies all the above requirements. At 400°C, \(\Delta G^°\) of formation for ZrO2 is \(-970.92\) kJ/mol corresponding to an oxygen partial pressure \(P_{O2}=5\times10^{-7}\) atm at the equilibrium of the reaction, \(Zr+O_2\leftrightarrow ZrO_2\). The \(\Delta G^°\) of formation for 2CaO is \(-1062.6\) kJ/mol. At the equilibrium of the reaction 2Ca+O\(_2\)\(\leftrightarrow\)2CaO, \(P_{O2}\) is lowered to \(3\times10^{-8}\) atm i.e. by a factor of \(2\times10^7\) less than its value with zirconium.\(^{24,25}\)

From the O–Zr phase diagram, the solubility of O in Zr at equilibrium with ZrO2 is 5 wt%\(^{26,27}\). Reducing the oxygen partial pressure by a factor of \(2\times10^7\) brings the dissolved oxygen below the ppm level. Calcium has no recognized intermetallic compounds with zirconium, and it has low solubility in \(\beta\)-Zr and \(\alpha\)-Zr. Also it may be produced commercially through direct electrolysis of calcium chloride.

Practically, Kroll\(^{22,23}\) reported the presence of thousands ppm oxygen remained in the produced Zr after reducing with calcium. The slow mass transfer through the by-product CaO attached to the surface of Zr particles and hindered further reduction. Also, CaO that precipitated on the metal surface was trapped inside the particles when sintering took place. This CaO could not be eliminated during leaching by HCl and as a result, calcium and oxygen contents in the Ti powders could not be lowered to sufficient degree.

### 2. Experimental Work

#### 2.1. Materials

Pure zirconium dioxide obtained from Egyptian zircon sand via alkali fusion followed by the basic sulfate treatment was used at the present experiments. The powder was grained to increase the surface area of the particles that will be exposed to the reductant. Typical composition of this material is shown in Table 1 as analyzed by the X-ray fluorescence (XRF). Granules of high pure calcium metal (Aldrich 99.5%) with average size \((=9\) mesh\) have been used as reducing agent. The anhydrous calcium chloride used was in the analytical grade (Adwic 98% purity). The salt pellets were heated for 8h under argon atmosphere to ensure that no moisture was introduced to the reaction chamber.

#### 2.2. Equipment

The assembly used in these experiments is schematically illustrated in Fig. 2. The reactant mixture as well as the fluxing salt set in a glassy silica boat and charged into gas tight glassy alumina tube (I.D. 50 mm). Using such amorphous materials will reduce the contamination of the obtained zirconium with silica or alumina from the apparatus. The tube was placed inside the electrical furnace having a horizontal cylindrical heating chamber. The tube was evac-

<table>
<thead>
<tr>
<th>Component</th>
<th>XRF analysis, ppm</th>
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<tr>
<td>Fe</td>
<td>260</td>
</tr>
<tr>
<td>Ti</td>
<td>734</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;50</td>
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<tr>
<td>Ca</td>
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<td>Th</td>
<td>95</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1230</td>
</tr>
<tr>
<td>ZrO(_2)+</td>
<td></td>
</tr>
<tr>
<td>HIO(_2)+</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.** XRF analysis for the zirconia used in the reduction experiments.

Molten CaCl\(_2\) can dissolve about 20% mole CaO.\(^{28-30}\) Threadgill\(^{30}\) used this principle to precipitate electrolytically calcium metal from calcium oxide dissolved in molten calcium chloride bath. He also reported that the presence of CaO decrease the freezing point of CaCl\(_2\) and eutectic mixture with freezing point of 593°C could form at 16.9 wt% CaO.

This principle is used by many workers in the halide flux de-oxidation for many reactive metals and alloys.\(^{31-34}\) The oxygen residual in these metals or alloys could be extracted as CaO, which dissolved in molten CaCl\(_2\). Ono and Suzuki\(^{35}\) applied this dissolution mechanism in the reduction process of Ti from TiO\(_2\) and then enlarged their work to include many other metals and alloys.\(^{13,15}\) They observed that the by-product CaO can be removed in-situ from the reaction place, and that this dissolution enhances the reduction and subsequent de-oxidation more effectively. Until now, no published data are available for the same work with ZrO\(_2\). In the present work, the various factors affecting the reduction of ZrO\(_2\) by calcium in CaCl\(_2\) will be studied.
uated from one end by vacuum pump, and argon gas was supplied at the other end from the gas tank through stainless steel valve “A”.

2.3. Experimental Procedure

Zirconium powders were obtained by the following procedure:
1. About 12.7 g of ZrO$_2$ powders were put on the glassy silica boot as thin layer.
2. The required amount of Ca and CaCl$_2$ was then added before the boot packed in the alumina tube.
3. The alumina tube was evacuated through the valve “B” and the valve “A” was then opened allowing argon gas to fill the tube.
4. The tube was then evacuated and refilled with argon to ensure minimum moisture and oxygen content in the tube.
5. The tube was then heated to the required temperature and kept at this temperature until the end of reaction time.
6. The reaction product was allowed to cool in the furnace under argon atmosphere.
7. The product was then removed from the furnace and leached with hot distilled water to remove CaCl$_2$ and any excess amount of calcium (sometimes the whole silica boot is placed in the leaching tank due to the consolidation of the product and its adhering to the boot).
8. The obtained black powder was dried under argon atmosphere and then its calcium and oxygen contents were analyzed using ICP-AES and fusion-infrared absorption method respectively.

The stoichiometric amount of Ca was determined from reaction (3) while the stoichiometric amount of CaCl$_2$ was defined as the amount that can dissolve the entire amount of CaO formed through the reduction reaction.

\[
\text{ZrO}_2 + 2\text{Ca} \rightarrow \text{Zr} + 2\text{CaO} \quad \text{.........(3)}
\]

For example, 12.7 g of zirconia need 8 g of Ca to produce 9.1 g Zr and 11.2 g CaO. To dissolve this amount of CaO, the stoichiometric amount of CaCl$_2$ will be 33.5 g. To study the effect of Ca charge; the amount of Ca was changed from just stoichiometry to 250-mol% of it. In addition, the present work will study effect of CaCl$_2$ amount by changing it from the theoretical amount to 400%.

3. Results and Discussions

3.1. Effect of Calcium Amount

The charge of Ca was changed from just stoichiometry to 250 mol% of it as deduced from Eq. (3). The amount of CaCl$_2$ was evaluated to just dissolve the entire amount of CaO formed through the reduction reaction. The temperature was set at 900°C for 2 h under argon atmosphere. The products were allowed to cool in the furnace under argon and then leached with hot distilled water to remove CaCl$_2$ and any excess amount of calcium. The obtained black powder was dried under argon atmosphere and the calcium and oxygen contents were analyzed using ICP-AES and fusion-infrared absorption method respectively.

An interesting observation during water leaching step is the evolving of gas bubbles immediately formed after water addition. The intensity of these bubbles was increased with the increase in calcium content in the initial reactant mixture. Also, when the calcium content in the initial reactant was 200% that determined from reaction (3) (1:4 zirconia to calcium mole ratio), the pH of the leaching water increased from 7 to nearly 8. This gas bubbling and the increase in the pH value were due to the evaluation of hydrogen gas and the formation of calcium hydroxide according to the following reactions between the residual Ca and the byproduct CaO with water:

\[
\text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}_2 \quad \text{.........(4)}
\]
\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad \text{.........(5)}
\]

Figure 3 shows the change in the oxygen and calcium concentration in the obtained zirconium relative to the amount of calcium in the initial reactants. The calcium and oxygen content reached their lowest value when 200 mol% of the theoretical calcium was used in the initial charge. The increase in oxygen content after its minimum value may be attributed to the oxidation of the formed zirconium by the large dissolution heat that proceeds from reactions (3). This heat increased with increasing the amount of Ca dissolved in water and hence with the increase in Ca amount in the reactants. On the other hand, there is no specific reason for such increase in the calcium content after its
Calcium analyzed in zirconium is in one of the following forms: metallic calcium leftover after the reaction, the byproduct calcium oxide, calcium chloride and any form of intermetallic compounds such as CaZrO₃. Since the first three substances are not dissolved in zirconium, the analyzed calcium will be at the grain surface if it was in one of such forms. In spite of the fact that all these substances are soluble in water, the calcium content after water leaching is still at high level and need to be explained.

The SEM image demonstrated in Fig. 4 shows many primary fine particles congregated together to form the larger secondary grains. The exothermic reaction represented in Eq. (3) caused a local exothermic heat at the grain boundaries, sintered the metallic zirconium particles together and caught Ca, CaO, CaCl₂, beside the unreacted zirconia in the secondary grains. Hence the removing of such undesired phases through the convention processes become difficult without attack the zirconium powder and consequently the calcium content will be high. This conclusion from SEM image may introduce a reasonable explanation for the high calcium content but the dominant source of Ca contamination was still not specified because the intermetallic compound was not distinguished and Cl was not analyzed in the present work.

Similarly, the residual oxygen in the zirconium powder may be divided into five categories:
1. Oxygen dissolved in zirconium lattice interstitially and forms Zr–O solid solution.
2. CaO captured in the secondary metallic zirconium grains.
3. Unreacted ZrO₂ or the lower oxide of zirconium trapped also at the secondary zirconium grains.
4. Oxygen in the intermetallic compounds such as CaZrO₃ or its similar, and
5. Oxygen, which is adsorbed and chemisorbed on the surface of zirconium particles.

It is so difficult to distinguish between these classes through the chemical analysis applied in the present work as mentioned before.

3.2. Effect of Reaction Time

To study the effect of reaction time, the holding time was changed from 1 to 5 h. The charged mixture contained 200% of the theoretical amount of Ca plus the exact amount of CaCl₂ that can dissolve the produced CaO. The temperature was held at 900°C. Oxygen and calcium content in the obtained powder were analyzed as described previously and the phases after 1 h and 5 h were identified using XRD.

Figure 5 shows the variation in the oxygen and calcium concentration with time. The oxygen content was reduced to 960 ppm at 3 h and then risen to 1 590 ppm after 5 h, and calcium concentration was reduced to 1 020 ppm before it risen again to 1 320 ppm.

There are two reasons for this increase in the oxygen content. The first one is the evaporation of significant amount of CaCl₂ after prolonged time, and the simultaneous increase in the amount of the byproduct CaO, which increases the activity of CaO in the molten salt and the deoxidation process becomes slower. Another possible reason may be explained from the fact that the amount of CaO captured between zirconium grains will increase due to insufficient amount of CaCl₂ to dissolve entire CaO. The latter reason gives a reasonable explanation for increasing oxygen concentration as well as for the increase in Ca content.

The XRD patterns for samples obtained after 1 h and 5 h are illustrated in Figs. 6(a) and 6(b). Beside the α-Zr phase in the sample obtained after 1 h, the additional impurities phases CaZrO₃ and ZrO₂₋ₓ are found and hence the higher
O and Ca content in the obtained Zr is referred to such compound. The disappearance of the CaO phase indicates the complete dissolution of the formed CaO in the molten CaCl₂. For the sample obtained after 5 h reaction, all the XRD peaks observed is identified only by the α-Zr and CaO. The calcium zirconate and the lower oxides of zirconium were not detected. These results support the supposition of incomplete dissolution of CaO in the molten salt after prolonged reaction time. The appearance of the phases CaZrO₃ and ZrO₂₋ₓ at short reaction time and their disappearance for prolonged reaction lead to the conclusion that zirconium dioxide was reduced through the formation of intermediate phase CaZrO₃ and through consequence reduction steps of the lower zirconium oxides, as can be represented by the following reactions:

\[
\text{ZrO}_2 + \text{CaO} \rightarrow \text{CaZrO}_3 \quad \text{(6)}
\]

\[
\text{CaZrO}_3 + x\text{Ca} \rightarrow \text{ZrO}_{2-x} + (1+x)\text{CaO} \quad \text{(7)}
\]

\[
\text{ZrO}_{2-x} + (2-x)\text{Ca} \rightarrow \text{Zr} + (2-x)\text{CaO} \quad \text{(8)}
\]

All the above reactions are exothermic, and hence the heat evolved from the overall reaction (3) causes the gradual sintering of the reduced particles. Therefore, these intermediate phases can be captured between zirconium grains even for prolonged reaction.

The XRD intensity of the α-Zr peaks increased and the lines became higher and narrower for the prolonged reaction. Since the width of the XRD peaks reflects the crystals lines became higher and narrower for the prolonged reaction time. The appearance of the phases CaZrO₃ and ZrO₂₋ₓ at short reaction time and their disappearance for prolonged reaction lead to the conclusion that zirconium dioxide was reduced through the formation of intermediate phase CaZrO₃ and through consequence reduction steps of the lower zirconium oxides, as can be represented by the following reactions:

Also the large salt amount overcame the evaporating amount of it especially at high temperatures and for long time reactions. The oxygen amount was reduced to 670 ppm when 400% of the theoretical amount of CaCl₂ was used. It seems that if the amount of CaCl₂ rises above 400%, then the oxygen concentration will be lowered but such extensive salt amounts were not studied in the present work.

Calcium content also decreased sharply from 4 870 to 1 020 ppm when CaCl₂ was used. This result companied with that of oxygen content indicate the presence of CaO phase after reduction without CaCl₁ and most of the measured calcium content will refer to such form. However, the large oxygen content cannot be contributed to the oxygen in CaO only. Because, the sample after reduction without CaCl₂ contained 4 870 ppm Ca, supposing that the oxygen content is due CaO only, the oxygen content will be numerically evaluated as 1 950 ppm, which is much lower than the measured value (29 940 ppm). Certainly, this drastic difference indicates incomplete reduction, and ZrO₂ or other zirconium oxides will present in the produced powder.

3.4. Effect of Temperature

To study the effect of temperature on the reduction process, the other factors were set constant at its optimum values as determined from the above three sections, i.e., Ca amount was kept at 200 mol% of its theoretical amount, CaCl₂ was set at 400 mol% from its stoichiometry, and reaction time was set as 3 h. The oxygen and calcium content in the final produced powder was shown in Fig. 8. It is clear that the calcium content decreased with increasing the reaction temperature while the oxygen content decreased to reach a bottom value of 560 ppm at 1 100°C.

High reaction temperature leads to increase the solubility of CaO in molten CaCl₂ which enhances the insitu removal of the by-product, and the deoxidation process. The slight increase in the oxygen content above 1 100°C will refer to the higher evaporation rate of the reductant, which may cause insufficient amount of calcium for deoxidation. This calcium evaporation also explains the decrease of the residual calcium content at all test temperatures. The decrease in the calcium amount in the reduction product will decrease the exothermic heat evolved from reaction (4) and that will decrease the back oxidation of the obtained zirconium pow-
The SEM images for the zirconium obtained at 1 000 and 1 300°C are shown in Figs. 9(a) and 9(b). The morphology of the obtained powder at 1 000°C is similar to that obtained by the conventional Kroll process. These factors included the amount of calcium charged, reaction time, the amount of CaCl₂ and the reaction temperature. The produced powder was characterized using XRD, SEM scanning and the elemental chemical analysis. The results shown clearly that using 200% of the theoretical Ca, 3 h of reaction, 400% of the theoretical amount of CaCl₂ and temperature of 1 100°C were the optimal reaction conditions to obtain the lower oxygen content in metallic zirconium. The investigation suggested the reduction of zirconium dioxide through the formation of intermediate phases CaZrO₃ and the lower oxides of zirconium.

\[
\begin{align*}
\text{ZrO}_2 + \text{CaO} & \rightarrow \text{CaZrO}_3 \\
\text{CaZrO}_3 + x\text{Ca} & \rightarrow \text{ZrO}_{2-x} + (1+x)\text{CaO} \\
\text{ZrO}_{2-x} + (2-x)\text{Ca} & \rightarrow \text{Zr} + (2-x)\text{CaO}
\end{align*}
\]

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REFERENCES