Preparation of aluminium-zirconium master alloys

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Preparation of Al-Zr master alloys was investigated by aluminothermic reduction of zirconium oxide (ZrO₂) using sulphur (S)-based slags. The influences of process variables such as requirement of heat energiser (KClO₃ + Al), amount of aluminium (Al) reductant, slag compositions, etc. were investigated to establish conditions for good slag-alloy separation and also to get optimum recoveries of the alloy. A maximum recovery of 92.8% Al-Zr alloy was obtained for a charge containing 20% excess aluminium over stoichiometric requirement, 50 g KClO₃, and 99 g S per 100 g ZrO₂. The alloy, on chemical analysis, was found to contain 33.74 wt% Zr, 0.4 wt% oxygen, 0.0035 wt% nitrogen and 0.5 wt% S.

A fine-grained structure in cast aluminium is desirable as it imparts superior mechanical properties, better homogeneity and reduced porosity. The grain refinement in aluminium and its alloys is usually brought about by the addition of grain refiners. The grain refiners most commonly used for Al and Al based alloys are the transition metals¹, such as Ti, Zr, V, Cr, etc., all of which show peritectic formation of aluminides. Among these, Ti is the most effective. However, in Al based alloys, the effectiveness of TiAl₃ as a nucleant decreases markedly in the presence of elements such as Cu and Zn¹. In such cases, the grain refining function is effectively accomplished only by the use of zirconium. Koves Elemer⁴ has used Zr for grain refining of Al-Mg-Zn type of alloys, which find widespread applications in aerospace and defence industry. Zirconium is required to the extent of 0.28 wt% in aluminium to give very fine equiaxed grains. Zirconium can be introduced into molten aluminium before casting by addition of K₂ZrF₆ salt, which reacts in-situ to produce zirconium metal. However, use of such chemicals leads to inconsistent performance and detrimental side-effects like generation of toxic fluoride fumes, corrosion of refractories, risk of halide inclusions, cross formation leading to high metal loss etc. In view of these difficulties, direct addition of these chemicals inside the production furnace has now been abandoned by leading aluminium manufacturers. The above difficulties can however be overcome if Al-Zr master alloy containing = 5 wt% Zr is used.

The Al-Zr master alloys can usually be prepared by direct melting of constituent metals. However, because of the large differences in the densities (ρ) and melting points (T) of aluminium (ρ=2.7 g/cc; T=933 K) and zirconium (ρ=6.49 g/cc; T=2125 K), it is normally difficult to prepare a homogeneous alloy. Further, the process involves use of costly zirconium metal, which is prepared by an energy intensive route involving conversion of ZrO₂ into ZrCl₄ and reduction of ZrCl₄ with magnesium at high temperature under inert gas atmosphere⁵. Not much information is available in literature on the preparation of Al-Zr master alloys by other processes. Hermann Kessler⁶ suggested a production method involving addition of ZrO₂ to molten Al under flow of Cl₂ gas. Krishnan and Rajagopalan⁷ prepared Al-Zr alloys containing up to 10wt% Zr by in-situ reduction of ZrO₂ with aluminium using cryolite as flux for removing Al₂O₃. In a recent study from this laboratory⁸, Al-Zr alloys were prepared by aluminothermic reduction of ZrO₂ using lime-based slags. In these investigations, Al-Zr alloy containing 30.3 wt% Zr was obtained at an alloy recovery of 82.8% and Zr extraction of 47.5% under optimum conditions. However in the presence of lime, ZrO₂ has a tendency to form a compound like CaO.ZrO₂, which passes into the slag and thus affects the overall recovery of the alloy and the extraction of zirconium into the alloy. In order to avoid such complications and to improve the recovery of Al-Zr alloys, an alternative process was studied in the present investigation where lime was replaced with sulphur so that a low melting slag having a composition of Al₂O₃-16.7 wt%Al₂S₃ with a melting point of 1373 K⁹ was formed during reduction. The reaction involved separation of the alloy from the slag via liquid-liquid, slag-metal separation. The influences of various process variables such as requirement of heat energiser (KClO₃ + Al), amount of slags, compositions, etc. were investigated to establish conditions for good slag-alloy separation and also to get optimum recoveries of the alloy. A maximum recovery of 92.8% Al-Zr alloy was obtained for a charge containing 20% excess aluminium over stoichiometric requirement, 50 g KClO₃, and 99 g S per 100 g ZrO₂. The alloy, on chemical analysis, was found to contain 33.74 wt% Zr, 0.4 wt% oxygen, 0.0035 wt% nitrogen and 0.5 wt% S.
variables such as (i) requirement of heat booster, (ii) amount of reductant in the charge, (iii) slag compositions etc. were investigated to establish conditions for good slag-alloy separation and to achieve optimum recoveries of Al-Zr alloys.

**Physico-chemical Aspects of Aluminothermic Reduction of ZrO₂**

The reduction of ZrO₂ with stoichiometric amount of aluminium proceeds via reaction (1):

\[ \text{ZrO}_2 + 4/3 \text{Al} = \text{Zr} + 2/3 \text{Al}_2\text{O}_3 \]  

... (1)

The reaction (1) is feasible thermodynamically at 298 K but becomes unfavourable at 2000 K as indicated by the free energy data² presented in Table 1. The free energy change for such a reaction is given by the equation:

\[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{(z_2)(z_{ZrO3})(a_{Al})^{4/3}}{(z_{Zr})(z_{Al})(a_{Zr})} \right) \]

where \( \Delta G^\circ \) and \( \Delta G \) are the free energy changes for the reaction under standard and non-standard (actual) conditions. The free energy change (\( \Delta G \)) for such a reaction is positive at 2000 K. However, it can be made negative by lowering the activities of Zr and \( \text{Al}_2\text{O}_3 \) by alloying with an appropriate element or with the reductant itself, and dissolving slag in a suitable flux. This has been attempted in the present work by using a large excess of Al to serve the dual function of reductant and alloying agent as per reaction (2) shown below:

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

... (2)

where ZrAl₃ is the aluminium rich intermediate phase in the AI-Zr system. Because of the lowering of the activity of Zr due to formation of ZrAl₃ phase, the free energy change for reaction (2) becomes negative even at 2000 K (Table 1). The driving force for the above reaction is further improved by reducing the activity of \( \text{Al}_2\text{O}_3 \) by forming a low melting slag

\[ \text{Al}_2\text{O}_3 -16.7 \text{ wt}\% \text{Al}_2\text{S}_3 \text{ (m. pt. 1373 K)} \]

The specific heat for reaction (2), defined as the amount of heat released in kcal per kg of the reacting charge, is rather low (61 kcal/kg) and is much less than the minimum (600 kcal/kg) required for a successful thermit reduction. Hence, it is necessary to incorporate thermal boosters in the charge to provide sufficient heat for the reaction. The formation of ZrAl₃ intermetallic phase in fact reduces the heat requirement for the reaction because of its lower melting point (1853 K) as compared to that of pure zirconium metal (2125 K). The overall heat requirement for the slag-metal separation can be further reduced by forming lower melting slag for removing \( \text{Al}_2\text{O}_3 \) from ZrAl₃. This was done by forming sulphur-based slag. The reaction of sulphur with aluminium results in the formation of \( \text{Al}_2\text{S}_3 \) via reaction (3):

\[ 2\text{Al} + 3 \text{S} = \text{Al}_2\text{S}_3 \]  

... (3)

Such a reaction is accompanied by a release of 173 kcal of heat per mole of \( \text{Al}_2\text{S}_3 \) formed. The \( \text{Al}_2\text{S}_3 \) combines with \( \text{Al}_2\text{O}_3 \) forming a slag with a melting point of 1373 K corresponding to the composition \( \text{Al}_2\text{O}_3 - 16.7 \text{ wt}\% \text{Al}_2\text{S}_3 \). So the heat requirement for melting such a slag is considerably reduced as compared to that for \( \text{Al}_2\text{O}_3 \) which has a melting point of 2323 K. Such a slag is more fluid and helps in slag-metal separation. Additional heat necessary for the reaction was provided by incorporating required amount of (KClO₃ + Al) or (NaNO₃ + Al) as heat booster.

**Experimental Procedure**

ZrO₂ of 99% purity was supplied by Indian Rare Earths Ltd. Aluminium powder (Grade C, -120 mesh) used as reductant was obtained from the Indian Aluminium Company. Sulphur (S) and potassium chlorate (KClO₃) or sodium nitrate (NaNO₃) were of technical grade and procured from local suppliers.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Reaction</th>
<th>( \Delta G^\circ ) (kcal/moleZrO₂) at 298 K</th>
<th>( \Delta G^\circ ) (kcal/moleZrO₂) at 2000 K</th>
<th>( \Delta H^\circ_{\text{max}} ) (kcal)</th>
<th>Sp.Heat of charge (kcal/kg)</th>
<th>Melting point of phase (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \text{ZrO}_2 + 4/3 \text{Al} \rightarrow \text{Zr} + 2/3 \text{Al}_2\text{O}_3 )</td>
<td>-3.5</td>
<td>+8.0</td>
<td>-4.7</td>
<td>29.6</td>
<td>2125</td>
</tr>
<tr>
<td>2.</td>
<td>( \text{ZrO}_2 + 13/3 \text{Al} \rightarrow \text{ZrAl}_3 + 2/3 \text{Al}_2\text{O}_3 )</td>
<td>-13.6</td>
<td>-2.6</td>
<td>-14.6</td>
<td>61</td>
<td>1853</td>
</tr>
<tr>
<td>3.</td>
<td>( \text{ZrO}_2 + 11/9 \text{Al} + 1/3 \text{S} \rightarrow \text{ZrAl}_3 + 2/3[AI_2\text{O}_3 + 1/6\text{Al}_2\text{S}_3] )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1853</td>
</tr>
</tbody>
</table>
The reaction was carried out in clay bonded graphite or mild steel reactors (15 cm \( \Phi \times 75 \) cm height \( \times 0.3 \) cm thick plate) lined with calcined magnesia to a thickness of 5 cm on the sides and 7.5 cm at the bottom. The experiments were carried out in batches of a charge containing 100 g ZrO\(_2\). The charge consisting of ZrO\(_2\), Al, KClO\(_3\) and S was mixed intimately in required proportions and compacted into pellets of 18-mm dia under a pressure of 755 kg/cm\(^2\). It was then loaded into the lined reactor. A trigger mixture consisting of Al+KClO\(_3\) (1:1) was placed on the top surface of the charge and the reaction was initiated by igniting the trigger mixture with a burning magnesium ribbon. The reaction was found to proceed briskly to completion after it was allowed to cool for sufficient time.

Results and Discussion

The preparation of Al-Zr master alloy was studied by aluminothermic reduction of ZrO\(_2\) via reaction (2) where Al acted as both a reductant as well as alloying agent. The separation of ZrAl\(_3\) alloy from Al\(_2\)O\(_3\) was achieved via slag-metal separation by carrying out the thermit reaction in presence of sulphur and a heat booster. In order to provide sufficient heat for the reaction, the amount of KClO\(_3\) in the charge varied from 30 to 50 g per 100 g ZrO\(_2\). However, even with 50 g KClO\(_3\) in the loose charge, there was no proper slag-alloy separation. The reaction was then studied using a compacted charge. The use of compacted charge helped to bring about a good slag-alloy separation yielding a consolidated alloy well-separated from the slag. Thus, compaction of the charge was found to be necessary to affect good slag-alloy separation. Studies carried out on the requirement of heat energiser for the compacted charge showed that the use of KClO\(_3\) up to 40 g per 100 g ZrO\(_2\) yielded an alloy, which was entrapped with some slag particles. However when the amount of KClO\(_3\) was increased to 50 g per 100 g ZrO\(_2\), there was a clear slag-alloy separation indicating availability of sufficient heat for the reaction. The use of KClO\(_3\) beyond 50 g however resulted in a violent reaction affecting the alloy recovery adversely. The results of these studies are presented in Table 2. An alloy yield of 60.7% was obtained when the reaction was carried out with 50 g KClO\(_3\) and 10% excess Al in the charge. Use of NaNO\(_3\) in place of KClO\(_3\) yielded similar results.

Table 2 also presents the results of studies on the influence of variation of amount of aluminium in the charge on the yield of Al-Zr alloys. The alloy recovery improved from 48 to 92.8% as the aluminium content in the charge was increased from 0 to 20% excess over stoichiometric requirement. Further increase in aluminium content to 30% excess over stoichiometric requirement however decreased the alloy yield to 71.4%. Hence, for maximum yield of the alloy, the reductant should be around 20% in excess of the stoichiometric amount. Investigations were also carried out to study the influence of the amount of S in the charge. Use of sulphur to the extent of 99 g per 100 g ZrO\(_2\) was found to be the optimum requirement. Such a composition gave a sufficiently fluid slag with good slag-alloy separation.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Thermit Charge Composition (g)</th>
<th>Al Excess (%)</th>
<th>Alloy Yield (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>ZrO(_2) 100, Al 174, KClO(_3) 30, S 99</td>
<td>10</td>
<td>-</td>
<td>No slag-metal separation</td>
</tr>
<tr>
<td>2.</td>
<td>ZrO(_2) 100, Al 178, KClO(_3) 40, S 99</td>
<td>10</td>
<td>60.7</td>
<td>Slag entrapped in the alloy</td>
</tr>
<tr>
<td>3.</td>
<td>ZrO(_2) 100, Al 183, KClO(_3) 50, S 99</td>
<td>10</td>
<td>55.0</td>
<td>Good slag-alloy separation</td>
</tr>
<tr>
<td>4.</td>
<td>ZrO(_2) 100, Al 187, KClO(_3) 60, S 99</td>
<td>0</td>
<td>48.0</td>
<td>Violent reaction</td>
</tr>
<tr>
<td>5.</td>
<td>ZrO(_2) 100, Al 173, KClO(_3) 70, S 99</td>
<td>0</td>
<td>48.0</td>
<td>Good slag-alloy separation</td>
</tr>
<tr>
<td>6.</td>
<td>ZrO(_2) 100, Al 183, KClO(_3) 80, S 99</td>
<td>10</td>
<td>60.7</td>
<td>-do-</td>
</tr>
<tr>
<td>7.</td>
<td>ZrO(_2) 100, Al 192, KClO(_3) 90, S 99</td>
<td>20</td>
<td>92.8</td>
<td>-do-</td>
</tr>
<tr>
<td>8.</td>
<td>ZrO(_2) 100, Al 203, KClO(_3) 100, S 99</td>
<td>30</td>
<td>71.4</td>
<td>-do-</td>
</tr>
<tr>
<td>9.</td>
<td>ZrO(_2) 100, Al 171, KClO(_3) 110, S 99</td>
<td>20</td>
<td>61.4</td>
<td>-do-</td>
</tr>
<tr>
<td>10.</td>
<td>ZrO(_2) 100, Al 185, KClO(_3) 120, S 99</td>
<td>20</td>
<td>85.7</td>
<td>-do-</td>
</tr>
<tr>
<td>11.</td>
<td>ZrO(_2) 100, Al 192, KClO(_3) 130, S 99</td>
<td>20</td>
<td>92.8</td>
<td>-do-</td>
</tr>
</tbody>
</table>
Thus, a maximum recovery of 92.8% of Al-Zr alloy was obtained when ZrO₂ was reduced with 20% excess aluminium in presence of 50 g KClO₃ and 99 g S per 100 g ZrO₂ in the charge. Under these conditions, it was possible to achieve good slag-alloy separation. The alloy obtained under optimum conditions was found to analyse 33.74 wt% Zr, 0.4 wt% oxygen, 0.0035 wt% nitrogen and 0.5 wt% S (Table 3). The percentage zirconium extraction for such an alloy was 59.3%. It was thus possible to obtain an alloy containing 0.4 wt% oxygen and 0.0035 wt% nitrogen in spite of the facts that zirconium oxide was used as the starting material and also the reaction was carried out in the open atmosphere. This shows that the slag used in the present study provided effective protection to the molten alloy during the reaction as well as subsequent cooling.

In an earlier investigation from this laboratory, preparation of Al-Zr alloys was investigated by aluminothermic reduction of ZrO₂ using lime-based slags. In the presence of lime-based slags, Al-Zr alloy containing a maximum of 30.3 wt% Zr was obtained at an alloy recovery of 82.8% and zirconium extraction of 47.5%. Compared to these results, the present investigation has resulted in an improved alloy recovery of 92.8% and zirconium extraction of 59.3% by the use of sulphur-based slag in place of lime-based slag.

### Process Economics

The process detailed above gives an overall recovery of 92.8% of Al-Zr alloy containing 33.74 wt% Zr. The economics of the process is evident from a comparison of the cost of materials required for preparation of Al-Zr alloy containing 34 wt% Zr by aluminothermic reduction of ZrO₂ as well as direct alloying processes in Table 4. The cost of production per kg of the alloy by the aluminothermic reduction route is Rs. 395 as against Rs. 1086 for the direct melting process. Whereas in the former case the reaction is self-sustaining and does not need any external source of energy, the latter process, however, requires electrical energy for melting and hence the cost of energy required has to be added to the cost of the materials. The present process, therefore, offers substantial savings in the cost of production of Al-Zr alloys.

### Conclusions

The Al-Zr master alloys can be prepared by aluminothermic reduction of ZrO₂ in air in presence of sulphur as the slaging agent. A maximum alloy yield of 92.8% with a zirconium extraction of 59.3% is possible when reduction is carried out in presence of 20% excess aluminium over stoichiometric requirement. The reaction of ZrO₂ with Al, which is otherwise unfavourable, has been made feasible by using heat energiser like KClO₃ + Al. It has been possible to achieve good slag-alloy separation by using sulphur-based slags and the required amount of heat energiser. The Al-Zr alloys obtained by this route contain around 34 wt% Zr and low interstitial impurities. These alloys can be diluted to prepare Al-5% Zr master alloys for use in the grain refinement of Al and Al alloys.

### References