ABSTRACT

In view of the high chemical affinity of zirconium to oxygen, the reduction of zirconium dioxide is usually done by calcium. Metallic calcium is comparatively costlier among other metallic reducing agents (Ca, Mg, Al) and magnesium due to its lower affinity to oxygen. than calcium, is able to reduce ZrO_2 only to a solid solution of O in Zr. However, it is possible to suppose that in the atmosphere of the active gases like nitrogen and hydrogen magnesium will be able to reduce ZrO_2 further than in an inert atmosphere due to the formation of nitride and hydride of zirconium with the additional liberation of free energy.

The conditions of reduction of ZrO_2 with magnesium in different gases argon, nitrogen and hydrogen resulting in the direct formation of zirconium nitride and zirconium hydride from ZrO_2, have been investigated and correlated.

It is shown from thermodynamical considerations that for determining the conditions to obtain products practically devoid of oxygen from the reduction of ZrO_2, the change of free energy of the

reaction of ZrO_2 with Magnesium e.g. $ZrO_2 + 2\,Mg = Zr + 2MgO$ or $ZrO_2 + 2Mg + \frac{1}{2}N_2 = ZrN + 2MgO$ can not be taken as a base. In such a calculation the formation of solid solution of oxygen in zirconium during the last stage of reduction is not taken into account. In this solid solution as the concentration of oxygen decreases the value of free energy of the formation of the bond between Zr - O substantially increases.

The change of standard free energy for the reaction

$$\underset{\substack{\text{(solid solution with}\\ \text{minimum concentration}\\ \text{of oxygen in equilibrium}\\ \text{with } CaO + Ca)}}{Zr(O)} + Mg = Zr + MgO$$

was calculated for temperature 800°C and 1000°C and found to have a positive value + 9 K cal which shows that the reduction of ZrO_2 by Mg can not proceed to the end but can continue till the small concentration of oxygen in zirconium but higher than that obtained by reduction by Ca.

At the same time, the reactions $Zr(O) + Mg + \frac{1}{2}N_2 = ZrN + MgO$ and $Zr(O) + Mg + \frac{x}{2}H_2 = ZrH_x + MgO$ having the change of standard free energy values

ΔF^0 at $1000^\circ C$ equal to -49.5 K cal and -23 K cal respectively must proceed much further than the reaction of ZrO_2 with Mg in an inert atmosphere.

However, the following optimum conditions for reduction of briquetted mixture of ZrO_2 with magnesium are established :-

(a) In inert atmosphere of argon at $900^\circ C$ with soaking time 4 hours; magnesium excess 25 - 50 % the purity of the metallic zirconium obtained is 97.2 %.

(b) In nitrogen atmosphere at $1100^\circ C$ with soaking time 2 - 4 hours and excess magnesium 25 % zirconium nitride saturated with nitrogen having the composition close to ZrN and a face centered cubic structure with lattice constant a = 4.575 A° is obtained.

(c) In hydrogen atmosphere at 700 - $750^\circ C$ with soaking time 2 hours and excess Mg 25 - 50 % products obtained containing 1.9 - 2 % H in solid solution with Zr compared to the theoretical amount 2.15 % of hydrogen in ZrH_2. (Zr + H) content may reach a value of 99 - 99.5 % in the atmosphere of hydrogen during a period of 2 to 4 hours at $900^\circ C$. X-ray analysis for best samples showed a body centered tetragonal phase with lattice constants a = 3.527 A°, and c = 4.449 A°.

In the range of temperatures upto 1000°C the highest velocity of reduction of ZrO_2 with magnesium is observed in the atmosphere of hydrogen and the lowest in nitrogen. At 1100°C in the atmosphere of nitrogen the velocity sharply rises and the reduction with the formation of a compound close to the saturated ZrN is reached.

The measurements of particle sizes and their size distribution as well as of specific surface of powders reduced, showed that the coarseness of their particles increases in the order $Zr \longrightarrow ZrH_2 \longrightarrow ZrN$.

The procedures outlined and the results obtained in the present exploratory investigation show the possibility of direct obtaining from ZrO_2 the products rich in hydrogen and nitrogen with crystal structures and lattice constants corresponding to those for pure and fully saturated ZrH_2 and ZrN.