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EFFECT OF THE ADDITION OF CARBON ON THE CALCIOTHERMIC REDUCTION OF ZrO₂ AND TiO₂ UNDER NITROGEN PRESSURE

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The calciothermic reduction of metal oxides under nitrogen pressure is used to obtain refractory nitride powders, such as titanium and zirconium [1]. Carbonitrides of these metals are of interest for industrial applications and can be prepared by adding carbon to the $TiO_2/ZrO_2 - Ca - N_2$ system. The purpose of this work is to study the effect of carbon addition on the calciothermic reduction of ZrO_2 and TiO_2 under nitrogen pressure.

The important parameters of this process are the adiabatic temperature and the equilibrium composition of products. The TERRA software was used to calculate these parameters [2]. The objects of the study are systems $TiO_2+X\cdot C+N+Ca$ and $ZrO_2+X\cdot C+N+Ca$ where X is a dimensionless parameter expressing the ratio of the current and stoichiometric carbon content required for the synthesis of ZrC and TiC in the absence of nitrogen. The amount of calcium and N_2 pressure was also varied. Carbonitrides were identified by the possible formation of ZrC-ZrN and TiC-TiN solid solutions in the products. Figure 1 shows the calculated adiabatic combustion temperature of compositions as a function of the carbon content.

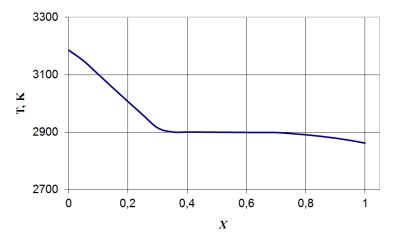


Fig. 1. Adiabatic combustion temperature (T) of the $TiO_2+X\cdot C+N+Ca$ system as a function of carbon content (parameter X) at nitrogen pressure of 2 MPa and calcium excess of 10%.

Compositions without carbon have the maximum combustion temperature. The addition of carbon lowers the temperature. The plateau at $T=2900~\rm K$ is due to the phase transition of CaO from liquid to solid state. Carbonitrides are formed in the products with any amount of carbon added. The formation of TiC and ZrC under equilibrium conditions is impossible. The resulting excess carbon interacts with excess calcium, forming CaC_2 carbide. Some carbon interacts with oxygen to produce CO. Increasing the pressure decreases the equilibrium CO content.

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