EFFECT OF PRESSURE ON THE JOINT REDUCTION OF ZrO2 AND B2O3 WITH CALCIUM*

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Calcium has found application as a reducing agent to obtain f-elements (rare-earth metals, their alloys, uranium, etc.) [1]. Calcium hydride is used [2] to obtain powders of metals, intermetallic compounds, refractory compounds and composite materials from oxides, where calcium is a reducing agent. The obtaining of refractory nitrides from oxides under nitrogen pressure using calcium as a reducing agent was implemented at the Tomsk Scientific Center of SB RAS [3]. The previous studies showed that the pressure of the gaseous medium ambiguously affected the temperature and combustion rate of calciothermal systems [4]. The goal of this work is to study the effect of pressure on the joint reduction of ZrO_2 and B_2O_3 with calcium.

The adiabatic combustion temperature (T_{ad}) and the equilibrium composition of the products were calculated using the TERRA software package [5]. The experiments were conducted in a constant pressure reactor under the argon atmosphere. High-purity titanium TiO_2 and zirconium ZrO_2 oxides, granulated calcium with a diameter of granules of 0.5-2 mm manufactured by Chepetsk Mechanical Plant, calcium iodate $Ca(IO_3)_2$ manufactured by Almerdale Assets Ltd, ultra-high-purity boron oxide B_2O_3 , high-purity nitrogen gas (GOST 9293-74, Russia) were used as starting materials. The prepared mixtures were placed in a paper crucible with a diameter of 23 mm. The temperature was measured with thermocouples W-5%Re/W-20%Re welded from \emptyset 0.2 mm wire. B_2O_3 oxide was added to the mixture, based on the formation of ZrB_2 and Zr in the products. The studies were conducted on 4 samples shown in Table.

Sample #	Ca(IO ₃) ₂ , g	ZrO ₂ , g	B_2O_3 , g	Ca, g
1	0	18.48	7.18	28.35
2	1.8	18.48	7.18	29.68
3	3.0	15.4	5.98	25.85
4	5.7	15.4	5.98	27.86

Calculations showed that for P=0.1 MPa, with an increase in the amount of $Ca(IO_3)_2$ additive, T_{ad} increases from 2283 K (sample 1) to 2703 K (sample 4), which reflects an increase in the thermality of the mixtures. An increase in pressure from 0.1 to 8.1 MPa leads to an increase in the T_{ad} of all compositions to the melting temperature of CaO - 2900 K. Despite the differences in the thermality of these mixtures, the latent heat of CaO melting restricts the growth of T_{ad} to 2900 K. In the pressure range p=0.1 - 1.5 MPa, the reduction of ZrO_2 is not complete, resulting in the formation of $CaZrO_3$. The composition of condensed products is represented by the phases: CaO, ZrB_2 , $CaZrO_3$, Zr. For pressures P>5 MPa, the oxides are completely reduced. The composition of the products in this case is represented by the phases: CaO, ZrB_2 , Zr. An increase in temperature with increasing pressure occurs mainly due to a shift in the equilibrium $CaZrO_3 + Ca \leftrightarrow Zr + CaO$ to the right. The increase in pressure was shown to favorably affect the joint reduction of ZrO_2 and B_2O_3 with calcium.

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