SHS Metallurgy of Titanium–Chromium Carbide from CaCrO₄ / TiO₂ / Al / C System

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Abstract

Regularities of combustion and autowave chemical transformation of highly exothermic mixtures CaCrO₄ / Al / C and CaCrO₄ / TiO₂ / Al / Ca / C were studied. It was shown that the mixture could burn over a wide range of concentrations of carbon contained in it; the variation of the mixture composition made it possible to produce cast refractory chromium compounds with different composition and structure. The addition of titanium oxide led to a decrease in the combustion temperature and, accordingly, adversely affected the synthesis parameters and quality of the target product. Highly exothermic additive CaO₂ + Al significantly increased the combustion temperature of the mixture and expanded the limits of combustion and phase separation. The product consisting predominantly of the target phase Ti₀.₈Cr₀.₂C and inclusions of Cr₂AlC MAX phase and Cr₇C₃ was obtained.

Keywords

Calcium chromate; carbides; cast materials; combustion synthesis; SHS metallurgy; titanium–chromium carbide.

The creation of new materials with a high level of properties is a key problem of modern technology. In this paper, we study the possibility of obtaining carbide ceramics from mixtures based on calcium chromate CaCrO₄ by the SHS metallurgy method. Refractory chromium compounds Cr₂₃C₆, Cr₇C₃, and Cr₃C₂ possess useful properties for solving technical problems (high hardness, strength, and resistance to corrosion and wear) and are widely used in practice to create protective coating. Composite materials based on titanium chromium carbide possess higher characteristics than on the basis of individual carbides. The solubility of Cr₃C₂ in TiC at 1700 °C is 30 %. At the chromium carbide content of 30 %, the microhardness of titanium carbide (3000 kg/mm²) increases to 4000 kg/mm² [1–3].

We studied two green mixtures. The overall reaction schemes can be represented in the forms:

\[
\begin{align*}
\text{CaCrO}_4 + \text{Al} + n\text{C} &= \text{Cr}_x\text{C}_y + \text{Al}_2\text{O}_3 + \text{CaO}; \\
\text{TiO}_2 + (70 \% \text{Al} / 30 \% \text{Ca}) + \text{C} &= \text{TiC} + \text{Al}_2\text{O}_3 + \text{CaO}. 
\end{align*}
\]

Earlier, we showed in [4] that calcium chromate has the capability to replace chromium oxides (Cr₂O₃ and CrO₃) in mixtures to obtain chromium borides. In the present paper, we used calcium chromate to obtain chromium carbides and titanium–chromium carbide. In the mixture (2), a part of aluminum was replaced by calcium for more complete reduction of TiO₂ [5].

A thermodynamic analysis was carried out using the THERMO program [6]. In the system (1), the carbon content was varied to produce various chromium carbides: Cr₂₃C₆, Cr₇C₃ and Cr₃C₂. The analysis showed that the adiabatic temperature of the chemical transformation of the mixture \( T_{ad} \) exceeds 3000 K, and the products of the chemical transformation of CaCrO₄ + 2Al + nC mixture at this temperature consist of Cr–Al–C melts (“metallic” phase, the desired product) and \( \text{Al}_2\text{O}_3–\text{CaO} \) (oxide phase, slag product), as well as the gas mixture of metal vapors (Al, Cr, Ca), suboxide (\( \text{Al}_2\text{O}_1 \), \( \text{Al}_2\text{O}_2 \)), and CO. An increase in the carbon content in the mixture \( n \) from 0 to 3.7 % leads to a decrease in \( T_{ad} \) and weight fraction...
Fig. 1. Influence of the carbon content in the initial mixture on the calculated adiabatic temperature \( T_{ad} \) and mass fractions of metallic \( a_1 \) and gaseous \( a_2 \) chemical conversion products of the oxide phase and an increase in the content of the metallic and gas phases (Fig. 1).

The experiments on this system showed that within the range \( n = 0–3.7 \% \), the mixture retained the ability to burn. Combustion proceeded in the frontal mode with a constant velocity. Combustion products had a molded appearance and were easily divided into two layers: metal (target) and oxide (slag). With an increase in the carbon content in the initial mixture, the burning velocity and relative mass loss decreased during combustion, while the yield of the target product in the ingot increased (Fig. 2).

Fig. 2. Burning velocity \( U \), yield of metallic phase \( \eta_1 \), and spread of combustion products (dispersion) \( \eta_2 \) as a function of \( n \) \((U = l/t_1\), where \( l \) is the height of the mixture, \( t \) is the time of burning; \( \eta_1 = m/M_1, \eta_2 = [(M_1 - M_2)/M_1] \times 100 \%, M_1 \) is the mass of the initial mixture, \( M_2 \) is the mass of the final combustion products and \( m \) is the mass of the metal ingot).

The results of the analysis show that the target products consist of different chromium carbides including MAX phase \( \text{Cr}_2\text{AlC} \). At \( n = 2.4 \% \) (calculated carbon content to prepare \( \text{Cr}_7\text{C}_3 \)), \( \text{Cr}_2\text{AlC} \) MAX phase dominates in the product structure that is confirmed by the data of the X-ray diffraction pattern presented in Fig. 3.

To produce titanium–chromium carbide \( \text{TiC–Cr}_3\text{C}_2 \), the content of the mixture (2) \( \alpha \) was varied in the mixture (1):

\[
\alpha = \left[ \frac{M_2}{(M_1 + M_2)} \right] \times 100 \%
\]

where \( M_1 \) is the mass of the mixture (1), \( M_2 \) is the mass of the mixture (2).

The results of the thermodynamic analysis of mixtures, which were calculated from different ratios of mixtures (1) and (2), are shown in Fig. 4. As can be seen, an increase in \( \alpha \) to 70 \% led to a smooth decrease in the combustion temperature. Within the range \( \alpha = 70–100 \% \), the combustion temperature...
The XRD analysis of the products showed that an increase in the fraction of mixture (2) in the charge led to a decrease in the amount of the Cr$_2$AlC phase and an increase in the amount of the Ti$_{0.8}$Cr$_{0.2}$C phase in the combustion product (Fig. 6).

Conclusions

The regularities of combustion and autowave chemical transformation of the highly exothermic composition CaCrO$_4$ / Al / C at various carbon contents are studied. It is shown that the mixtures are capable to burn in a wide range of carbon content.

The study of the CaCrO$_4$ / TiO$_2$ / Al / Ca / C system showed that the mixture burns in a wide range of $\alpha$. The combustion temperature of the mixture at $\alpha > 10$ % is insufficient to produce cast product.

The high-exothermic additive CaO$_2$ + Al allows to expand the combustion limits to $\alpha = 40$ % and the phase separation to $\alpha = 30$ %.

X-ray diffraction analysis of the samples showed that with increasing $\alpha$ (TiO$_2$), the content of the target product Ti$_{0.8}$Cr$_{0.2}$C increases, the content of Cr$_2$AlC MAX phase decreases.

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References