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SHS Metallurgy of Titanium–Chromium Carbide from $CaCrO_4$ / TiO_2 / Al / C System

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Abstract

Regularities of combustion and autowave chemical transformation of highly exothermic mixtures $CaCrO_4$ / Al / C and $CaCrO_4$ / TiO_2 / 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 CaO_2 + 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 $Ti_{0.8}Cr_{0.2}C$ and inclusions of Cr_2AlC MAX phase and Cr_7C_3 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 $CaCrO_4$ by the SHS metallurgy method. Refractory chromium compounds $Cr_{23}C_6$, Cr_7C_3, and Cr_3C_2 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 Cr_3C_2 in TiC at 1700 °C is 30 %. At the chromium carbide content of 30 %, the microhardness of titanium carbide (3000 kg/mm^2) increases to 4000 kg/mm^2 [1–3].

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

$$CaCrO_4 + Al + nC = Cr_xC_y + Al_2O_3 + CaO; \quad (1)$$

$$TiO_2 + (70\ \%\ Al / 30\ \%\ Ca) + C = $$
$$= TiC + Al_2O_3 + CaO. \quad (2)$$

Earlier, we showed in [4] that calcium chromate has the capability to replace chromium oxides (Cr_2O_3 and CrO_3) 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 TiO_2 [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: $Cr_{23}C_6$, Cr_7C_3 and Cr_3C_2. 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 $CaCrO_4 + 2Al + nC$ mixture at this temperature consist of Cr–Al–C melts ("metallic" phase, the desired product) and Al_2O_3–CaO (oxide phase, slag product), as well as the gas mixture of metal vapors (Al, Cr, Ca), suboxide (Al_2O, Al_2O_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

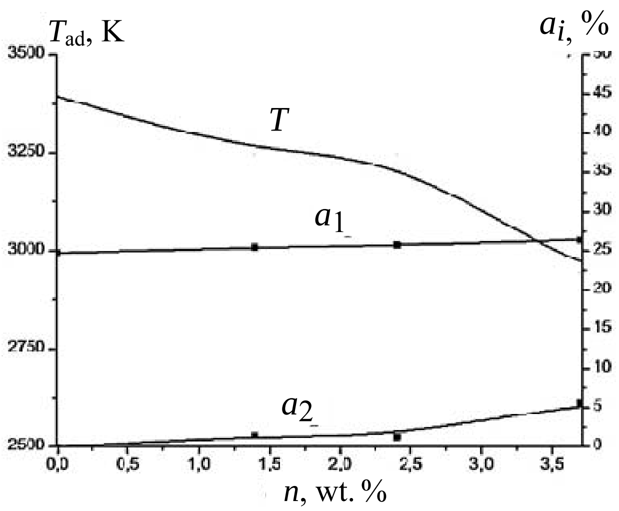

Fig. 1. Influence of the carbon content in the initial mixture on the calculated adiabatic temperature T_{ad} and mass fractions of metallic a_1 and gaseous a_2 chemical conversion products

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).

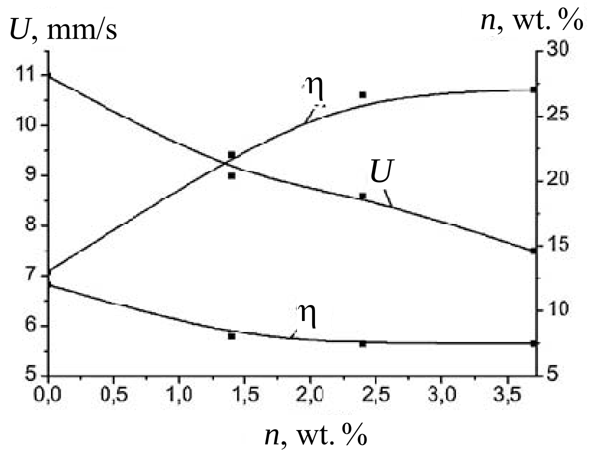

Fig. 2. Burning velocity U, yield of metallic phase η_1, and spread of combustion products (dispersion) η_2 as a function of n
($U = l/t$, where l is the height of the mixture, t is the time of burning; $\eta_1 = m/M_1$, $\eta_2 = [(M_1 - M_2)/M_1]\times 100$ %, M_1 is the mass of the initial mixture, M_2 is the mass of the final combustion products and m is the mass of the metal ingot)

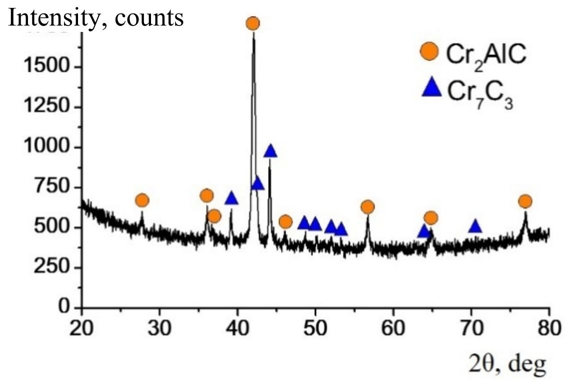

Fig. 3. X-ray diffraction pattern of the product obtained at n = 2.4 %

The results of the analysis show that the target products consist of different chromium carbides including MAX phase Cr_2AlC. At n = 2.4 % (calculated carbon content to prepare Cr_7C_3), Cr_2AlC 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 $TiC–Cr_3C_2$, the content of the mixture (2) α was varied in the mixture (1):

$$\alpha = [M_2/(M_1 + M_2)] \cdot 100\ \%,$$

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 (α) to 70 % led to a smooth decrease in the combustion temperature. Within the range α = 70–100 %, the combustion temperature

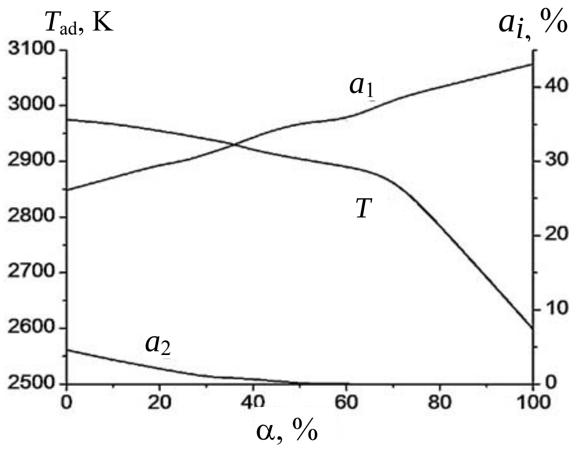

Fig. 4. Effect of α on the calculated adiabatic temperature T_{ad}, mass fractions of metallic a_1 and gaseous a_2 chemical conversion products

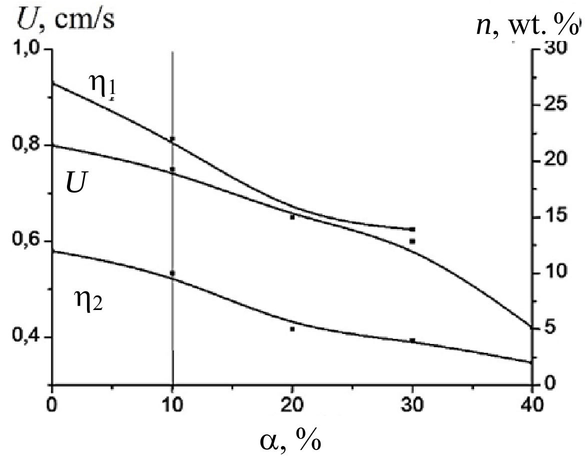

Fig. 5. Burning velocity *U*, yield of metallic phase η_1, and spread of combustion products (dispersion) η_2 as a function of *n*
$U = l/t$, where *l* is the height of the mixture, *t* is the time of burning; $\eta_1 = m/M_1$, $\eta_2 = [(M_1 - M_2)/M_1]\times 100$ %, M_1 is the mass of the initial mixture, M_2 is the mass of the final combustion products and *m* is the mass of the metal ingot

dropped to 2600 K. The quantity of gaseous combustion products decreased to zero at α = 50 %. The yield of the desired product a_1 increased with increasing α.

According to the experimental data, the mixtures burned within the range α = 0–40 % (Fig. 5). With increasing α, the burning velocity *U*, yield of metallic phase η_1, and spread of combustion products η_2 decreased. At α = 10 %, the limit of phase separation takes place. The introduction of highly exothermic additive CaO_2 + Al led to an increase in the phase-separation limit to 30 %.

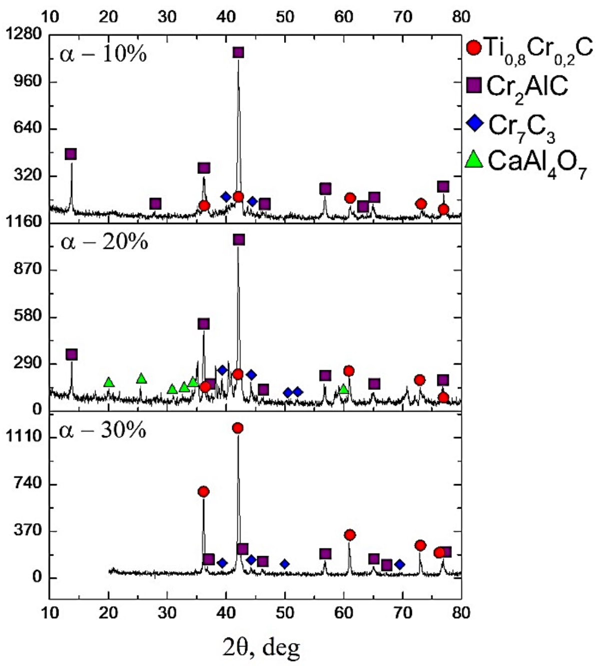

Fig. 6. X-ray diffraction pattern of the product obtained at α = 30 %

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_2AlC 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 α. The combustion temperature of the mixture at α > 10 % is insufficient to produce cast product.

The high-exothermic additive CaO_2 + Al allows to expand the combustion limits to α = 40 % and the phase separation to α = 30%.

X-ray diffraction analysis of the samples showed that with increasing α (TiO_2), the content of the target product $Ti_{0.8}Cr_{0.2}C$ increases, the content of Cr_2AlC MAX phase decreases.

Acknowledgements

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