Synthesis of Ti–Cr–C composite materials from $CaCrO_4$based mixtures

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Synthesis of Ti–Cr–C composite materials from $CaCrO_4$ based mixtures

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Abstract. Regularities of combustion and autowave chemical transformation of $CaCrO_4$/Al/C, $CaCrO_4/TiO_2$/Al/Ca/C, and $CaCrO_4$/NiO/TiO_2/Al/Ca/C highly exothermic mixtures was studied. It was shown that the mixtures can burn in a wide range of carbon content. The variation in mixture composition makes it possible to prepare cast refractory chromium compounds with different composition and microstructure. The addition of titanium oxide leads to a decrease in the combustion temperature and, accordingly, adversely affects the synthesis parameters and quality of target product. Highly exothermic CaO_2/Al additive significantly increases the combustion temperature of mixture, expands the limits of combustion and phase separation. The introduction of nickel oxide into mixture positive effects on synthesis parameters. Reduced nickel reacts with free aluminum and in doing so inhibits the formation of Cr_2AlC MAX phase. The product consisting of Cr_3C_2 and $Ti_{0.8}Cr_{0.2}C$ carbides and Ni_3Al intermetallic binder was prepared.

1. Introduction

Chromium and chromium–titanium carbides possessing high hardness and resistance to aggressive environment at elevated temperatures are widely used for producing composite materials and applying protective coatings on the working surfaces of parts operating under extreme conditions. As the matrix, nickel aluminides characterized by high heat resistance and hardness and increasing the adhesion strength of coatings with steel base and their resistance to impact, as well as reducing their porosity are most often used [1]. As a rule, carbide ceramics is produced by powder metallurgy methods using high-temperature set ups. The most effective approach to produce such materials in the cast form is the metallothermic SHS process using mixtures of chromium and titanium oxides with aluminum and carbon as a raw material. The temperature released during the redox reaction is sufficient to produce a high-temperature melt used for obtaining cast synthesized products. Refractory chromium compounds $Cr_{23}C_6$, Cr_7C_3, and Cr_3C_2 possess properties necessary for solving technical problems (high hardness, strength, and resistance to wear, heat, and corrosion) [2] and are widely used to create protective coatings [3, 4]. In the Ti–Cr–C system, TiC and Cr_3C_2 phases are the most important for practical application. 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].

2. Results and discussion

In the present paper, we studied the possibility of using $CaCrO_4$ calcium chromate as a chromium-containing agent instead of chemically unstable chromium oxide (VI) CrO_3.

The overall reaction schemes can be represented in the forms:

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

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

$$NiO + 2Al \Rightarrow Ni + Al_2O_3 \quad (3)$$

The content of mixtures (2) and (3) was varied in the basic mixture (1). In the mixture (2), a part of aluminum was replaced with calcium for more complete reduction of TiO_2 [5]. Thermodynamic analysis was carried out using a THERMO program [6].

In the system (1), the carbon content was varied to prepare various chromium carbides: $Cr_{23}C_6$, Cr_7C_3, and Cr_3C_2. The analysis showed that the adiabatic temperature of chemical transformation of the mixture (T_{ad}) exceeds 3000 K. The increase in the carbon content in the mixture (nC) from 0 to 3.7% leads to a decrease in T_{ad} and an increase in the content of metallic and gas phases (figure 1a).

Experiments on this system showed that within the range nC = 0–3.7%, the mixture retains the ability to burn. Combustion products have a cast form and are easily divided into two layers: metal (target) and oxide (slag). As the carbon content in the green mixture increases, the burning velocity and relative mass loss during combustion decrease, and the yield of the target product in the ingot increases (figure 1b).

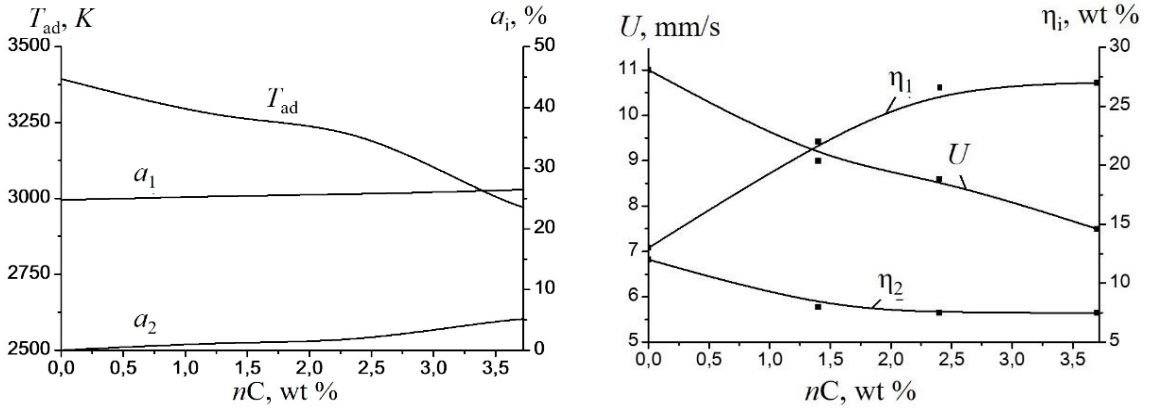


Figure 1. (a) Calculated adiabatic temperature T_{ad} and mass fractions of metallic (a_1) и gaseous (a_2) chemical conversion products as a function of nC; (b) burning velocity U, yield of metallic phase η_1, and spread of combustion products (dispersion) η_2 as a function of nC. $U = l/t$, where l 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 green mixture, M_2 is the mass of the final combustion products, and m is the mass of the metal ingot.

The XRD results show that target products consist of different chromium carbides including Cr_2AlC MAX phase. At nC = 2.4% (calculated carbon content to prepare Cr_7C_3), the final product is seen in figure 2 to contain mainly Cr_2AlC MAX phase.

Figure 3 shows the results of the thermodynamic analysis of mixtures, which were calculated from different ratios of mixtures (1) and (2) to produce titanium–chromium carbide. It can be seen that an increase in the fraction of mixture (2) (α) to 70% leads to a smooth decrease in the combustion temperature. Within the range α = 70–100%, the combustion temperature drops to 2600 K. The

quantity of gaseous combustion products decreases to zero at α = 50%. The yield of the desired product (a_1) increases with increasing α. Experiments revealed that the mixture burns within the range α = 0–40%. With increasing α, the burning velocity U, yield of metallic phase η_1, and spread of combustion products η_2 decrease. At α = 10%, there is no phase separation. The introduction of highly exothermic additive CaO_2/Al made it possible to increase the phase-separation limit to 30% (figure 3b).

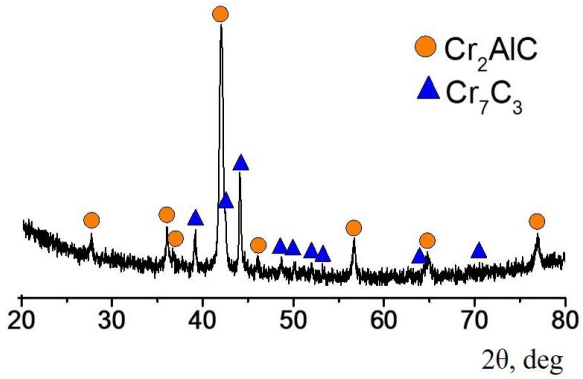


Figure 2. X-ray diffraction pattern of the product prepared at nC = 2.4%.

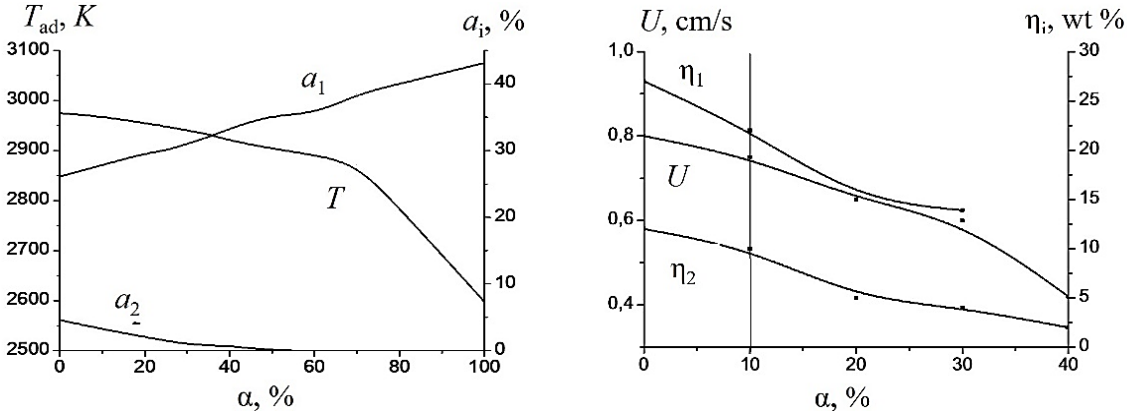


Figure 3. (a) Calculated adiabatic temperature T_{ad} and mass fractions of metallic (a_1) и gaseous (a_2) chemical conversion products as a function of α; (b) burning velocity U, yield of metallic phase η_1, and spread of combustion products (dispersion) η_2 as a function of α. $\alpha = [m_2/(m_1 + m_2)]\times100\%$, where m_1 is the mass of mixture (1) and m_2 is the mass of mixture (2); $U = l/t$, where l is the height of the mixture, t is the time of burning; $\eta_1 = m/M_1$, $\eta_2 = [(M_1–M_2)/M_1]\times100\%$, M_1 is the mass of the green mixture, M_2 is the mass of the final combustion products, and m is the mass of the metal ingot.

The XRD data of prepared products show that an increase in the fraction of mixture (2) in the charge contributes to a decrease in the amount of the Cr_2AlC phase in the final product while $Ti_{0.8}Cr_{0.2}C$ phase content grows (figure 4).

In order to produce composite materials, a charge with α = 30% and mixture (3), the content of which was calculated to obtain 30% nickel in the final product, was chosen. The addition of a given amount of the mixture based on nickel oxide into the mixture makes it possible to increase the calculated combustion temperature to 2900 K that positively affects the synthesis parameters: overall yield of target phase and its phase composition. The microstructure and X-ray diffraction pattern of this composite material are presented in figure 5. As can be seen, the synthesized product consists of Cr_3C_2, intermetallic binder Ni_3Al, and $Ti_{0.8}Cr_{0.2}C$.

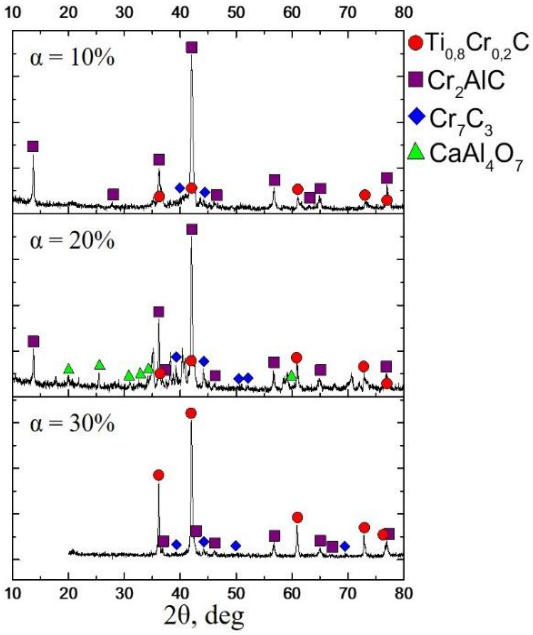
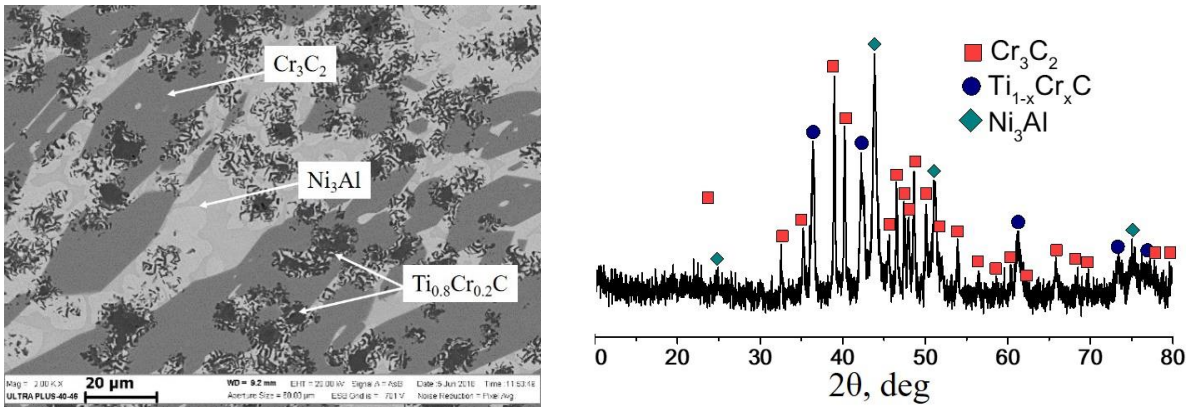


Figure 4. X-ray diffraction patterns of products prepared at different ratio of mixtures (1) and (2).



(a) (b)

Figure 5. (a) Microstructure and (b) X-ray diffraction patter of the composite material.

Conclusions

1) The regularities of combustion and autowave chemical transformation of highly exothermic mixtures $CaCrO_4$/Al/C, $CaCrO_4$/TiO_2/Al/Ca/C and $CaCrO_4$/NiO/TiO_2/Al/Ca/C are studied.
2) The introduction of TiO_2 leads to a decrease in the combustion temperature and adversely effects on synthesis parameters and quality of target product. The highly exothermic CaO_2/Al additive significantly increases the combustion temperature of the mixture and expands the limits of combustion and phase separation.
3) Composite material consisting of Cr_3C_2 and $Ti_{0.8}Cr_{0.2}C$ carbides and intermetallic binder Ni_3Al are obtained.

Acknowledgements

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References

[1] Kiffer R and Benezovskii F 1968 *Solid materials* (Moscow: Metallurgiya) 384 p
[2] Rudneva V V and Galevskii G V 2007 *Izv. vuzov. Cvetnaja Metal*. **2** 67–70

[3] Guilemagy J M, Espallargas N, Suegama P H and Benedetti A V 2006 *Corros. Sci.* **48** 2998–3013
[4] Korzhik V N, Borisova A L, Popov V V, Kolomytsev M V, Chaika A A, Tkachuk V I and Vigilyanskaya N V 2014 *Avtomat. Smarak* **12**
[5] Andreev D E, Yukhvid V I, Ikornikov D M and Sanin V N 2017 *Eng. Mater.* **746** 262–266
[6] Shiryaev A 1995 *Int. J. Self-Propag. High-Temp. Synth.* **4** 351–362