Advanced structural materials based on the Ti-Cr-Al-C system

A M Shulpekov, O K Lepakova, V G Salamatov and N I Afanasyev
Tomsk Scientific Center, SB RAS, 10/4 Akademichesky Ave., Tomsk 634055, Russia

E-mail: shulp@yandex.ru

Abstract. The SHS process of the Ti-Cr-Al-C powder mixture is studied in the paper. The increase in the content of chromium in the mixture is shown to decrease the maximum temperature of the front of combustion wave. If the content of chromium in the mixture is above 20 wt.%, the process proceeds in the nonstationary combustion mode. Nanolaminate phases Ti2AlC and Ti3AlC2 or their mixtures are found to be formed when the content of chromium is not more than 20 wt. %. The addition of chromium increases the oxidation resistance of materials which can be recommended for use under extreme operating conditions, as an example for electrical contacts, bearings, heating elements, heat exchangers, and high-temperature ceramics.

1. Introduction
The structure of the crystal lattice of nanolaminates possess a unique combination of the properties of both metals and ceramics: high electrical and thermal conductivity, easily cutting, crack resistance, plasticity at high temperatures, resistance to high temperature oxidation and thermal shocks, excellent corrosion resistance in corrosive liquid, low density, high elasticity, and stability at temperatures above 1000°C. MAX-phase-based materials are promising for use under extreme operating conditions, as an example for electrical contacts, bearings, heating elements, heat exchangers, and high-temperature ceramics [1].

For example, materials based on the Ti-Si-C system are used by the authors to create electrically conductive polymer compounds for electric heaters with improved performance characteristics [2]. Obtaining the materials based on the Ti-Cr-Al-C system by the self-propagating high-temperature synthesis (SHS) has been studied by many authors [3, 4]. These materials are shown to be promising for use as high-temperature ceramics. Experiments have revealed that single-phase materials based on Ti3AlC2, Cr2AlC phases possess the best properties. However, due to the complexity and multistage nature of the processes occurring during SHS, the phase composition largely depends on the initial components, their ratio, the methods for preparation of green mixtures, and the conditions of the process. This fact demonstrates the relevance of research aimed at the further study of processes in the Ti-Cr-Al-C system, the structure and properties of the synthesis products.

The goals of this work are to obtain materials on the basis of the Ti-Cr-Al-C system by the SHS method and to study the physical and chemical properties of materials and the mechanism of phase and structure formation.
2. Procedure
The initial components of reactions were metal powders that were no less than 99.5 wt.% of the main substance: Ti (average particle size \(d = 1.0 \times 10^{-4} \text{ m}\)), Cr (\(d = 1.5 \times 10^{-4} \text{ m}\)), Al (\(d = 5 \times 10^{-6} \text{ m}\)) and C, carbon (\(d = 11.3 \times 10^{-7} \text{ m}\)). The powders were mixed in the ratio given in table 1. The prepared mixtures were used to form cylindrical samples with a diameter of \(2 \times 10^{-2} \text{ m}\) and a relative density of 0.4÷0.6. The combustion of the samples was initiated from the upper end by a heated electrospiral and an ignition composition (Ti+2B) in an experimental setup under argon (purity is not less than 99.9%) at a pressure \(5 \times 10^5 \text{ Pa}\). The setup was a sealed reaction chamber equipped with optical glass and electrical inputs to initiate combustion and record electrical signals.

After the initiation of combustion, a self-sustaining reaction wave propagated along the samples. Synthesis was recorded by a MotionPro x-3 high-speed video camera (frame rate is up to 10000 s\(^{-1}\), spatial resolution is \(1 \times 10^{-5} \text{ m}\)) that was used for direct monitoring the velocity and structural characteristics of the surface combustion wave of mixtures. Temperature was controlled with a BP-5/20 \(1 \times 10^{-4} \text{ m}\) thick thermocouple that was placed inside the sample in its lower end. EMF was recorded by an analog-to-digital converter (sampling frequency rate is up to 1 MHz) and analyzed on a computer. In certain experiments, the temperature of the combustion wave was measured by the method of spectral pyrometry [5]. The main point of this method is that the optical spectrum of thermal radiation of objects contains a region in which the distribution of radiation intensities is similar to Planck radiation. It is assumed that in the similarity region the emitter is a «gray» body and its emissivity does not depend on the wavelength, \(\varepsilon(\lambda)\approx\text{const}\). The distribution of the spectral radiation intensity in the found region as a function of temperature can be described by the Wien approximation (Planck function for short wavelengths).

The radiation from the section (\(5 \times 10^{-3} \text{ m}\)) of the reaction wave through the optical fiber placed into the reaction chamber was recorded by a CCD spectrometer (HR 4000, OceanOptics) that records radiation in the range of 200÷1100 nm with a frequency of 220 Hz and the duration of signal accumulation in a single spectrum of \(4.5 \times 10^{-3} \text{ s}\). The spectra obtained were constructed in the Wien coordinate plane: \(x=\lambda^{-1}\), \(y=\ln(\lambda^3I)\) (where \(\lambda\) is the wavelength and \(I\) is the spectral intensity of radiation). The linear dependence of the spectral data in the wavelength range of 500-580 nm indicates the fulfillment of the similarity conditions, which can be used to find the temperature corresponding to each spectrum from the slope angle. The equation of the straight line was found by the method of least squares.

The error in determining the temperature due to the root-mean-square deviation from the linearity of the experimental points did not exceed 1%.

Table 1. Composition of the initial mixture for the synthesis of materials

| No(sample) | composition   | Ti, wt.% | Cr, wt.% | Al, wt.% | C, wt.% |
|------------|---------------|----------|----------|----------|---------|
| 1          | Ti\(_2\)AlC   | 71       | 0        | 20       | 9       |
| 2          | Ti\(_{1.9}\)Cr\(_{0.1}\)AlC | 67       | 4        | 20       | 9       |
| 3          | Ti\(_{1.5}\)Cr\(_{0.5}\)AlC | 52       | 19       | 20       | 9       |
| 4          | Ti\(_{1.1}\)Cr\(_{0.9}\)AlC | 38       | 33       | 20       | 9       |

The phase composition of the synthesis products was determined using a portable desktop X-ray device (RIKOR, radiation Co\(_{60}\)) provided by Tomsk Common Use Center SB RAS. Microstructural studies were conducted using an optical microscope (Axiovert 200M, KarlZeiss).

3. Discussion
Phenomena occurring in the combustion wave of a powder mixture of titanium, aluminum and soot have been investigated by many authors. The main stage of the process is shown to be the reaction between titanium and carbon, and the interaction proceeds through the aluminum melt which in this case is a diffusion accelerator. MAX phases, in the opinion of the authors, are formed during the interaction of titanium carbide and titanium aluminides at the stage of primary or secondary structure.
formation. According to the thermocouple measurements, the addition of chromium to the Ti-Al-C mixture leads to a decrease in the temperature of the wave front (figure 1a). In addition, when the chromium content in the mixture is up to 20 wt.% the change in temperature is small, and with increasing the chromium content the temperature drops sharply to 1450 K.

![Figure 1](image1.png)

**Figure 1.** Maximum temperature in the combustion wave (a) and the dynamics of the spectrometric temperature in the reaction combustion wave of the mixture for sample No. 4.

The data of high-speed video camera showed that the combustion of powder mixtures with a chromium content of more than 20 wt. % occurs in the nonstationary mode. After ignition, a plane decaying reaction wave propagates from the end of the sample at a velocity monotonically decreasing along its axis from 6.5 mm/s to zero for 0.04 s. Then, in the low-temperature zone of wave ($T=1380$ K, according to the data of dynamic spectrometry) the reactions are initiated and start developing across the sample with a temperature of up to 1860 K and a rate of up to 12.9 mm/s, initiating the next decaying wave (figure 1b). A similar combustion mode was observed earlier in the Ti-B system [7]. The sample after synthesis consists of titanium carbide and AlCr$_2$, has a layered structure, is fragile and does not represent any interest as a structural material.

When the chromium content in the mixture is up to 20 wt. %, the phases Ti$_2$AlC, Ti$_3$AlC$_2$ and TiC are detected as an impurity. The sample without the addition of chromium consists of the MAX phase of Ti$_2$AlC with a small impurity of titanium carbide (figure 2). The addition of chromium leads to the appearance of a Ti$_3$AlC$_2$ phase that is additional for the Ti$_2$AlC phase.

![Figure 2](image2.png)

**Figure 2.** X-ray diffraction pattern of synthesis products (a) sample No. 1, stoichiometry of Ti$_2$AlC, (b) sample No. 2, Ti$_{1.9}$Cr$_{0.1}$AlC, (c) sample No. 3 Ti$_{1.5}$Cr$_{0.5}$AlC. Phases: 1 – Ti$_2$AlC, 2 – Ti$_3$AlC$_2$, 3 – TiC.
Sample No. 3 consists of the Ti₃AlC₂ phase and an impurity of titanium carbide. Thus, the addition of chromium stabilizes the Ti₃AlC₂ phase. The presence of chromium as any compounds on the X-ray diffraction patterns is not detected. According to the authors of the paper in [8], chromium can replace titanium in the MAX phase lattice, which can explain the absence of chromium compounds in the samples.

The study of the microstructure of the samples also indicates the presence of crystals of MAX phases and titanium carbide in the form of small rounded particles (figure 3).

![Figure 3. Microstructure of the synthesis products: (a) sample No. 1, (b) sample No. 3.](image)

Thermal oxidation resistance of the material was studied by heating the obtained samples in a muffle furnace under air at a temperature of 1175 K. The resistance criterion was the change in the mass of the sample after annealing (Figure 4). It can be seen that samples No. 2 and No. 3 containing (Ti₁₋ₓCrₓ)₂AlC and (Ti₁₋ₓCrₓ)₃AlC₂ as the main MAX phase have the lowest weight. After annealing, an off-white loose film with a weak adhesion to the surface is formed on the surface of sample No. 1. The surface of samples No. 2-4 is covered with a gray-green dense film. The authors of the work [9] showed that the MAX phases of the Ti-Al-C system were oxidized due to the diffusion of oxygen into the sample and the removal of carbon in the form of its oxides. The process can be presented by the scheme:

\[
4\text{Ti}_3\text{AlC}_2 + (2y+3)\text{O}_2 = 4\text{Ti}_3\text{C}_2\text{O}_y + 2\text{Al}_2\text{O}_3
\]

\[
4\text{Ti}_3\text{C}_2\text{O}_y + (20-2y)\text{O}_2 = 12\text{TiO}_2 + 8\text{CO}_2\ (g).
\]

Or as a sum:

\[
4\text{Ti}_3\text{AlC}_2 + 23\text{O}_2 = 12\text{TiO}_2 + 2\text{Al}_2\text{O}_3 + 8\text{CO}_2\ (g)
\]

Thus, the film on the surface of the sample probably consists of a mixture of titanium and aluminum oxides. The film of titanium oxide, in contrast to Al₂O₃, is loose, porous and does not have protective properties. The increased thermal oxidation resistance of samples No. 2 and 3 can be explained by the following facts. The structure of the MAX phases of Ti-Cr-Al-C can be represented by carbide nanolayers (Ti₁₋ₓCrₓ)₂C (Ti₁₋ₓCrₓ)₃C₂ separated by the layers of aluminum atoms. Thus, the process of oxidation can be considered to be an interaction of air oxygen with titanium and chromium carbides. Chromium carbide is known to be oxidized not so fast due to the high strength of the Cr-C bond compared to the strength of the Ti-C bond. In addition, the film of Cr₂O₃ is more hard and dense compared to that of TiO₂. The low thermal oxidation resistance of sample No. 4 is due to the fact that
the material contains a large amount of titanium carbide that has a low oxidation resistance. In addition, the sample has a high porosity.

Figure 4. Oxidation kinetics of the samples under air at a temperature of 1173 K (the number of the curve corresponds to the sample number).

Thus, the material based on the Ti-Cr-Al-C system was obtained by the SHS method. The processes occurring during the SH-synthesis were investigated. Metallographic studies and X-ray phase analysis revealed the $(\text{Ti}_{1-x}\text{Cr}_x)_2\text{AlC}$, $(\text{Ti}_{1-x}\text{Cr}_x)_3\text{AlC}_2$, TiC phases. The addition of chromium from 5 to 20 wt. % to the initial mixture is shown to significantly increase the oxidation resistance of material. The materials obtained are promising for use as heat-resistant structural materials.

References
[1] Zhimou L, Erdong W and Jiemin W 2014 Acta Materialia73 186
[2] Shulpekov A M, Lepakova O K, Golobokov N N and Dyukarev M A 2017 Russian Physics Journal 60 5
[3] Levashev E A, Pogozhev Yu S, Shtansky D V and Petrzhik M I 2009 Russ. J. Non-Ferrous Metals 50 151
[4] Zhimei S, Rajeev A and Jochen M 2003 Phys. Rev. B. 68 4
[5] Magunov A N 2009 Prib.Tekh. Ekspl. 4 5
[6] Fedotov A F, Amosov A P, Latukhin E I, Ermoshkin A A and Davydov D M 2014 Izvestiya Vuzov. Tsvetnaya Metallurgiya 16 50
[7] Kirdyashkin A I, Kitler V D, Salamatov V G, Yusupov R A and Maksimov Yu M 2007 Combustion, Explosion, and Shock Waves 43 645
[8] Zhimou L, Erdong W, Jiemin W, Yuhai Q, Huimin X, Xichao L, Qianqian J, Guangai S, Xiping C, Jingyang W and Meishuan L 2014 Acta Materialia 73 186
[9] Song G M, Pei Y T, Sloof W G, Li S B, De Hosson J Th M and van der Zwaag S 2008 Scripta Materialia 58 13