SHS-synthesis of nanolaminate materials of the system Ti-Cr-Al-C and their term-oxidative stability

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Abstract. The features of SHS processes in the powder mixture Ti-Cr-Al-C are studied. It is shown that an increase in the chromium content in the mixture lowers the maximum temperature of the combustion wave front. When the chromium content in the mixture is above 20 wt. % process goes into non-stationary combustion mode. The nanolaminate phases Ti2AlC, Ti3AlC2, or their mixture are formed when the chromium content is up to 20 wt. %. Chromium is embedded in the crystal lattice of MAX phases, replacing titanium in the crystal lattice. The introduction of chromium increases the resistance of the material to oxidation. Samples of composition Ti1.1Cr0.9AlC are not inferior in oxidation resistance to materials based on Cr2AlC. However, their synthesis, in contrast to Cr2AlC, is possible in the autowave mode of SHS at room temperature. This allows them to be recommended for use in parts operating under extreme operating conditions, such as electrical contacts, bearings, heating elements, heat exchangers, as high-temperature ceramics.

1. Introduction
The structural features of the crystal lattices of nanolaminates cause a unique combination of properties of both metals and ceramics: high electrical and thermal conductivity, easily processed by cutting, crack-resistant, resistant to high-temperature oxidation and thermal shock, plastic at high temperatures, have excellent corrosion resistance in aggressive liquid media and at the same time low density, high elasticity, stable at temperatures above 1000 °C. Materials based on MAX phases are promising for use in parts operating under extreme operating conditions, such as electrical contacts, bearings, heating elements, heat exchangers, as high-temperature ceramics [1]. For example, materials based on the Ti-Si-C system were used by the authors to create electrically conductive polymer compounds for electric heaters with enhanced performance characteristics [2].

The production of materials of the Ti-Cr-Al-C system by the SHS method was studied by many authors [3-12]. The prospects of using the materials of this system as high-temperature ceramics are shown. It was established experimentally that single-phase materials based on the phases Ti3AlC2, Cr2AlC have the best properties. However, due to the complexity and multistage nature of the processes that occur during SHS, the phase composition largely depends on the initial components, their ratio, methods of preparation of the charge, and the conditions of the process. This makes relevant research aimed at further studying the processes in the Ti-Cr-Al-C system, the structure and properties of synthesis products.

The aim of the work is to obtain materials based on the Ti-Cr-Al-C system using the SHS method, to study the physicochemical properties of the materials and the mechanism of phase and structure formation.
The paper is structured as follows: the Section 2 describes the process of obtaining samples for research, the experimental methods, and the instruments used to obtain and analyze the results. The results obtained are discussed in the Section 3, in particular, the effect of the amount of chromium in the sample on the maximum temperature in the combustion wave, the phase composition of the products, their microstructure, and thermal oxidative stability. Section 4 presented the conclusions derived from the results of the study.

2. Procedure
The starting components of the reactions were powders of metals not less than 99.5 wt.% Of the main substance: Ti of grade PTS-1 (average particle size $d \approx 1.0 \times 10^{-4}$ m), Cr - HRP-1C (d $\approx 1.5 \times 10^{-4}$ m), Al - ASD-4 (d $\approx 5 \times 10^{-4}$ m) and C – carbon black PM-15 (d $\approx 1.3 \times 10^{-7}$ m). The powders were mixed in ratios according to table 1. The prepared mixtures were molded in the form of cylindrical samples with a diameter of $20 \times 10^{-3}$ m with a relative density of $0.4 \div 0.6$. Combustion by samples was initiated from the upper end of a heated electric coil and igniting composition (Ti + 2B) in an experimental setup in argon (purity not less than 99.9%) at a pressure of $5 \times 10^{3}$ Pa.

Table 1. The composition of the initial mixture for the synthesis of materials.

| № sample | The composition of the initial mixture | 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         |
| 5        | Cr$_2$AlC                             | 0         | 58        | 27        | 13        |

The installation was a sealed reaction chamber equipped with optical glass and electrical inputs for initiating combustion and removal of electrical signals. After initiation, a self-sustaining reaction wave propagated along the samples. The synthesis processes were recorded with a WRe-5/20 thermocouple with a thickness of $1 \times 10^{-4}$ m, which was placed inside the sample from its lower end. The EMF recording was carried out by an analog-digital converter (sampling frequency up to 1 MHz) and analyzed on a computer. The phase composition of the synthesis products was determined on a portable tabletop X-ray device RIKOR ($CoK\alpha$ radiation) provided by Tomsk Common Use Center SB RAS. Microstructural studies were performed on an optical microscope (Axiovert 200M, Karl Zeiss) and a scanning electron microscope (SEM 515, Philips) equipped with an EDAX energy dispersive attachment with a surface resolution of $\approx 1 \mu$m.

3. Discussion
The phenomena occurring in the wave of combustion of a mixture of powders of titanium, aluminium, and carbon black have been investigated by many authors [13]. It is shown that the leading stage of the process is the reaction between titanium and carbon, and the interaction proceeds through an aluminium melt, which in this case is a diffusion accelerator. According to the authors, the formation of MAX phases occurs during the interaction of titanium carbide and titanium aluminides at the stage of primary or secondary structure formation. According to the thermocouple measurements, the introduction of chromium into the Ti – Al – C mixture leads to a decrease in the temperature of the wave front (figure 1).
Moreover, when the content of chromium in the mixture is up to 20 wt. % temperature change is small, and with its higher content, the temperature sharply decreases to 1450 K. The burning of powder mixtures, with a chromium content of more than 20 wt. % flows in non-stationary mode.

The sample after synthesis consists of titanium carbide and AlCr₂, has a layered structure, is brittle and is of no interest as a structural material. When the chromium content in the mixture to 20 wt. % detected phase Ti₂AlC, Ti₃AlC₂ and TiC is present as an impurity.

Moreover, the sample without the addition of chromium consists of the MAX phase of Ti₂AlC with a small admixture of titanium carbide (figure 2). The addition of chromium leads to the addition of the Ti₃AlC₂ phase to Ti₂AlC. Sample No. 3 consists of the Ti₃AlC₂ phase and an admixture of titanium carbide. Thus, the introduction of chromium stabilizes the phase of Ti₃AlC₂. The presence of chromium as any compounds on radiographs is not detected. According to the authors [14-16], chromium can replace titanium in the MAX-lattice, which can explain the absence of chromium compounds in the samples.

**Figure 1.** Maximum temperature in the combustion wave with different chromium content.

**Figure 2.** XRD patterns of synthesis products a) sample No. 1, b) sample No. 2, c) sample No. 3. Phases: 1 - Ti₂AlC, 2 - Ti₃AlC₂, 3 - TiC.
Figure 3. X-ray diffraction pattern of Cr$_2$AlC. Phase: 1 - Cr$_2$AlC.

Figure 4. The microstructure of the products of synthesis: a) sample No. 1, b) sample No. 3.

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.

The data of energy dispersive microanalysis of the sample of composition Ti$_{1.9}$Cr$_{0.1}$AlC (4 wt.% Cr) confirmed that chromium is contained in the MAX phases Ti$_3$AlC$_2$ (point 1) and Ti$_2$AlC (point 2) (Figure 5). The content of chemical elements in the phases are given in table 2. The concentration of titanium, aluminum, and carbon in the sample at point 1 coincides with the theoretical content for the Ti$_3$AlC$_2$ phase, and at point 2 for the Ti$_2$AlC phase.

Figure 5. SEM - micrographs of a sample of Ti$_{1.9}$Cr$_{0.1}$AlC composition of MAX - phases present in the product: a - MAX phase Ti$_3$AlC$_2$, b - MAX phase Ti$_2$AlC.

Table 2. The elemental composition of the samples Ti$_{1.9}$Cr$_{0.1}$AlC in points 1, 2 on Figure 5.

| Point No | Phase       | Ti, Wt. % | Cr, Wt. % | Al, Wt. % | C, Wt. % |
|----------|-------------|-----------|-----------|-----------|-----------|
| 1        | Ti$_3$AlC$_2$ | 70,50     | 0,61      | 15,29     | 13,60     |
| 2        | Ti$_2$AlC    | 68,07     | 2,40      | 20,55     | 8,99      |
Thermal-oxidative stability of the material was studied by heating the obtained samples, as well as powder with particles with a diameter of 3-80 10^{-6} m in a muffle furnace in air at 1198 and 1298 K. The stability criterion was the change in the mass of the sample after firing (figure 4). It is seen that samples No. 3 and No. 4, containing as the main MAX phase (TiCr)$_2$AlC and (TiCr)$_3$AlC$_2$, have the smallest mass change. After firing, a loose film of white color with a yellowish tinge forms on the surface of sample No. 1. The surface of samples No. 2-4 is covered with a dense film of gray-green color.

On the radiograph obtained directly from the surface of the oxidized sample (No. 1), phases of titanium oxide (IV) and aluminum oxide are observed, which are products of the interaction of the MAX phase with atmospheric oxygen (Figure 7). In addition, the Ti$_3$AlC$_2$ phase was detected on the radiograph. However, the initial sample consists of phases Ti$_2$AlC and TiC. It can be assumed that the formation of Ti$_3$AlC$_2$ occurs during the interaction of Ti$_2$AlC with TiC during heat treatment.

Burning the powders at a temperature of 1198 for 4 h showed that the main phases during thermal decomposition of the material are TiO$_2$, Al$_2$O$_3$, as well as additional Cr$_2$O$_3$ for sample No. 3 and TiC for sample No. 4.

**Figure 6.** The kinetics of oxidation of samples in air at a temperature of 1198 K (the number of the curve corresponds to the number of the sample).

**Figure 7.** XRD pattern of the surface of sample No. 1 after heat treatment in air at 1298 K. Phases: 1 - TiO$_2$, 2 - Al$_2$O$_3$, 3 - Ti$_3$AlC$_2$.

The authors of [6] showed that the oxidation of MAX phases of the Ti – Al – C system proceeds due to the diffusion of oxygen into the sample and the removal of carbon in the form of its oxides. The process can be represented as a diagram:

\[
4Ti_3AlC_2 + (2y + 3)O_2 = 4Ti_3C_2O_y + 2Al_2O_3 \\
4Ti_3C_2O_y + (20 - 2y)O_2 = 12TiO_2 + 8CO_2 (g).
\]

Summary:

\[
4Ti_3AlC_2 + 23O_2 = 12TiO_2 + 2Al_2O_3 + 8CO_2 (g)
\]
Thus, the film on the sample surface consists of a mixture of titanium and aluminum oxides. The film of titanium oxide, unlike Al₂O₃, is loose, porous and does not possess protective properties. The increased thermo-oxidative stability of samples No. 2 and No. 3 can be explained if we consider the following. The structure of the MAX phases of Ti – Cr – Al – C can be represented as nanolayers of (TiCr)₂C, (TiCr)₃C₂ carbides separated by layers of aluminum atoms. Thus, the oxidation process can be represented as interaction with titanium carbide and chromium with air oxygen. It is known that chromium carbide oxidation is more difficult due to the higher strength of the Cr-C bond compared to the strength of the Ti-C bond. In addition, the Cr₂O₃ film is stronger and denser than TiO₂.

4. Conclusion
Thus, a material based on the Ti-Cr-Al-C system was obtained by the SHS method. The processes occurring in the process of SHS are investigated. Metallographic studies and X-ray phase analysis revealed the phases (TiCr)₂AlC, (TiCr)₃AlC₂, TiC. It is shown that the introduction of chromium from 5 to 20 wt. % in the initial mixture can significantly increase the resistance of the material to oxidation. Materials promising for use as heat-resistant structural materials.

Appendices
SHS – Self-Propagating High-Temperature synthesis.
MAX-phase - a triple layered compound with formal stoichiometry Mn+1AXn (n = 1, 2, 3 ...), where M is a transition d-metal; A is a p-element (for example, Si, Ge, Al, S, Sn, etc.); WRe5/20 thermocouple - tungsten-rhenium thermocouple.

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References
[1] Eklund P, Rosen J and Persson P O Å 2017 J. Phys. D: Appl. Phys. 50 113001
[2] Shulpekov A M, Lepakova O K, Golobokov N N and Dyuakarev M A 2017 Russian Physics Journal 60 5
[3] Aslamazashvili Z, Tavadze G, Chikhradze M, Namicheishvili T and Melashvili Z 2017 IOP Conf. Ser.: Earth Environ. Sci. 95 042036
[4] Amosov A P, Luts A R, Latukhin E I, Rybakov A D, Novikov V A and Shipilov S I 2018 IOP Conf. Ser. 1115 042002
[5] Shehegolev A V, Aulov V F, Ishkov A V, Ivanayskiy V V and Krivochurov N T 2018 IOP Conf. Ser.: Mater. Sci. Eng. 441 012047
[6] Latukhin E I, Amosov A P, Borisov D V, Ryabov A M, Illarionov A Yu 2017 Bulletin of the Samara State Technical University. Ser. Technical science. 53 1
[7] Amosov A P, Latukhin E I, Ryabov A M, Umerov E R, Novikov V A 2018 IOP Conf. Ser. 1115
[8] Arman S, Arman S, Vahed R Iranian Journal of Materials Science and Engineering 2014 11 4
[9] Cabioc’h T J. of the European Ceramic Society 2012 32
[10] Du Yu-Lei Chin. Phys. Lett 2009 26 11
[11] Wang X H J. Mater. Sci. Technol. 2010 26 5
[12] Song G M 2007 Proc. of the First Internat. conf. on Self-Healing Materials, Noordwijk aan Zee (Netherlands) p 96
[13] Fedotov A F, Amosov A P, Latukhin E I, Yermoshkin A A and Davydov D M 2014 Proceedings of the Samara Scientific Center of the Russian Academy of Sciences 16 6
[14] 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
[15] Wang X H Corros. Sci. 2003 45
[16] Chlubny L, Lis J, Chabior K, Chachlowska P, Kapusta C 2015 Archives of Metallurgy and Materials 2015 60