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Patterns of SHS processes in multilayer Ti/Al/C powder systems

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Abstract. The relevance of the work is associated with the widespread use of high-temperature heaters in industry. A promising method for producing such heaters is self-propagating high-temperature synthesis (SHS). Max-phases, combining the properties of metals and ceramics, are resistant to oxidation in air at high temperatures, are not afraid of thermal shocks and are promising for the production of high-temperature heaters. The purpose of this work was to study the possibility of obtaining electrically conductive coatings based on the MAX phase of Ti_2AlC by the SHS method in the “thermal explosion” mode. To do this, layers of Ti, Al, C powders and Ti + C, 2Ti + Al mixtures in various combinations were deposited on the substrate. The samples were subjected to a linear change in oven temperature, and the temperature of the powder layers was documented. Anomalously low reaction initiation temperatures were recorded. It has been suggested that this may be due to the oxidation of the mixture components in air and the transition of the process from the thermal explosion mode to the ignition mode. Samples with high electrical conductivity were obtained that can be used as electric heaters.

Keywords: self-propagating high-temperature synthesis, MAX-phase, heater.

1. Introduction

High-temperature electric heaters are used in the firing and sintering of cermets, ceramics, glass, ferrites, etc. Basically, such heaters are made from molybdenum disilicide and silicon carbide. The operating temperature of such heaters is 1000–1800 °C. At temperatures up to 1000 °C, tubular heaters made of nichrome wire (TEN) are very widely used. Heating elements, despite their relative cheapness and ease of manufacture, have a significant drawback. For electrical insulation of a nichrome spiral, ceramics, which has low thermal conductivity, are used. As a result, a significant part of the energy is lost, and such heaters have low efficiency. However, the advantage of heating elements is their high resistance to thermal shock, which simplifies their operation and increases reliability. Heaters made of $MoSi_2$ and SiC allow one to achieve higher temperatures, but are extremely fragile and require special operating conditions.

Nanolaminant MAX-phases combine the properties of both ceramics and metals. They have high electrical conductivity, at the level of many metals, are resistant to high temperatures, and withstand thermal shocks. This makes them suitable candidates for high temperature electric heaters. One of the most interesting MAX phases are Ti_3AlC_2 and Ti_2AlC, which have high Young’s modulus, degree of fracture toughness and bending strength [1–4]. The reaction between the starting components is exothermic, as a result of which the method of self-propagating high-temperature synthesis is widely used to obtain these materials.

Therefore, one of the goals of this work was to develop a method for producing conductive materials based on the MAX phase of Ti_2AlC for electric heaters with high operating temperatures. Since heaters made of $MoSi_2$ and SiC are manufactured in a protective atmosphere (nitrogen, argon), the technology is quite complex and requires special equipment. Therefore, one of the tasks was to develop a method for producing heaters in an air environment. In addition, the purpose of the work was to study the interaction of individual components with each other and clarify the mechanism of formation of the Ti_2AlC phase.

2. Materials and Methods

To prepare the mixtures, we used PTX titanium powders (99.2 wt.% Ti, $d < 40$ μm), PM 15 carbon black (90 wt.% C, $d < 0.015$ μm), and ASD 4 aluminum ($d < 10$ μm). A suspension in isopropyl alcohol was prepared from a mixture of powders (Ti + C, Ti + Al) or Ti, Al, and C separately. The suspension was applied to ceramic plates (VK 1, 98 wt.% Al_2O_3, 6 mm × 50 mm × 2 mm) through a stencil with a thickness of 0.5 to 1.7 mm. The layers were applied sequentially on top of each other in various combinations. In addition, individual samples were pressed in a mold with a rectangular cross-section of 50 × 14 mm. The samples were placed on the surface of a flat electric oven. The heating rate of the furnace was controlled using an autotransformer. To measure the temperature in the lower layer, a chromel-alumel thermocouple was used. The thermocouple was connected to an LA20USB ADC (ZAO Rudnev-Shilyaev) (12 bit, $f = 50$ kHz), which was connected to a personal computer (Fig. 1).

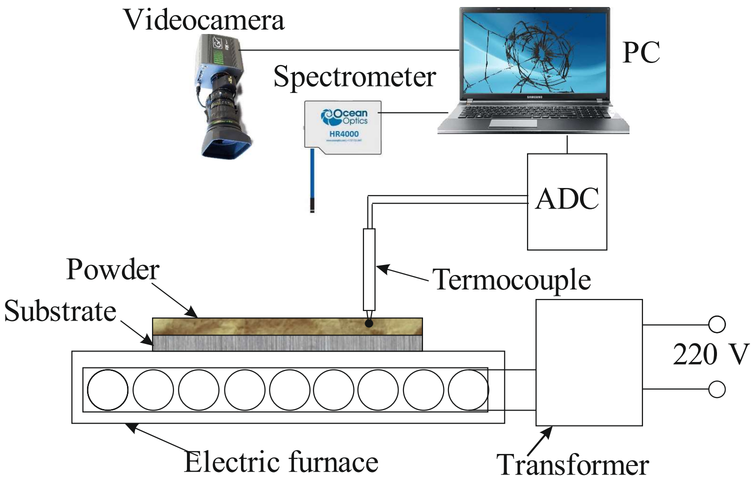


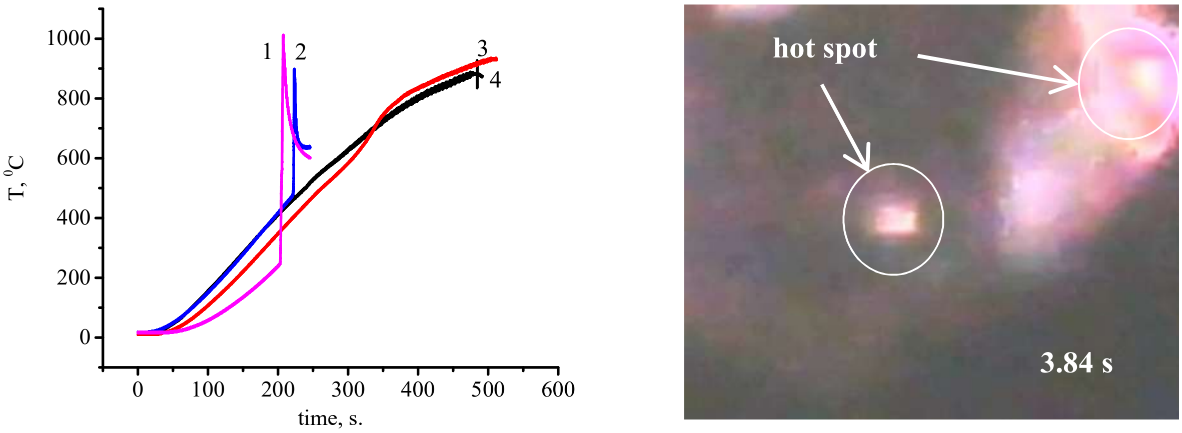
Fig. 1. Experimental setup for studying SHS processes in the thermal explosion mode.

Video recording of the process was carried out using a high-speed video camera “Motion ProX-3” (Imaging Solutions GmbH, Germany). The temperature in the upper layer was measured by spectral pyrometry using a spectrometer (HR 4000, Ocean Optics) ($0.2–1.1\times10^{-6}$ m., frequency 220 Hz, signal accumulation time in one spectrum – 4.5×10^{3} s.). The microstructure of the coating was studied using an Axiovert optical microscope (Karl Zeiss, Germany). Electrical resistance was measured using a two-probe method. To do this, copper contacts were applied to the ends of the sample using an electrochemical method, through which an electric current was passed. The potential difference between the metal needles was measured using a microvoltmeter.

3. Results and Discussions

The synthesis of materials in the frontal mode of combustion wave propagation leads to partial oxidation of the coating by air oxygen. As a result, the material is not electrically conductive. Therefore, experiments were carried out to study the possibility of producing electrically conductive materials in a thermal explosion mode. To do this, the substrate with the deposited layers was placed on an electric furnace and heated at a linear speed from 70 to 170 degrees/min. Fig. 2a shows thermograms, and Table 1 shows thermal explosion parameters for single-layer samples: carbon black, titanium, Ti + C and two-layer Ti / C samples.

It can be seen that no peak is observed for soot. For the Ti + C layer, a slight increase in temperature is observed in the range of 650–750 °C. It should be noted that for pressed samples and the process carried out in argon, the temperature of initiation of a thermal explosion for a Ti + C mixture exceeds 1000 °C [5]. This temperature was not achieved in the experiment. The peak for the titanium layer is explained by its oxidation by atmospheric oxygen, which is typical for fine powders (450–550 °C) [6]. The initiation temperature for two-layer samples (about 250 °C) is abnormally low. The following facts should be taken into account here. Firstly, at these temperatures, soot begins to oxidize intensively, which heats up the layers.



(a)

(б)

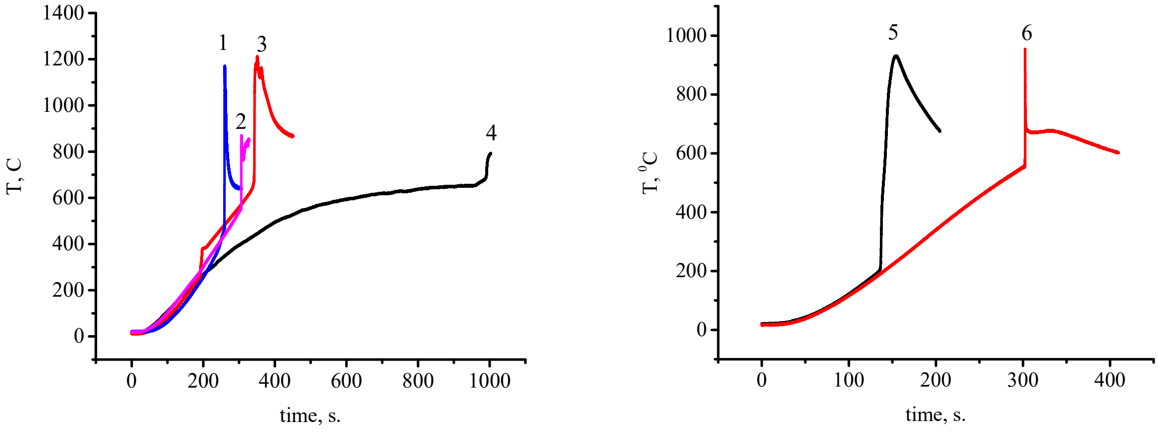
Fig. 2. Thermograms of samples (a): 1 – Ti/C, 2 – Ti, 3 – TiC, 4 – C and video frames for the Ti/C sample (b).

This leads to a disruption of the thermal balance and an avalanche-like development of the process of interaction between soot and titanium. Secondly, the process often occurs in the ignition mode, rather than a thermal explosion. Many foci appear on the surface of the layer, which move chaotically across the surface (Fig. 2b). In this case, the measured temperature will depend on the distance that the source has traveled to the thermocouple.

Table 1. Thermal explosion parameters for Ti/C, Ti, TiC samples.

Sample	V_{heat}, degr./min.	T_{ing}, °C	T_{max}, °C
Ti/C	114	225	950
Ti	161	465	860
TiC	143	610	795

Similar results were obtained for single-layer Ti_2Al and two-layer Ti/Al and TiC/Al samples (Fig. 3a). The authors' data show that the initiation temperature of the mixture (Ti + Al) is 600-700 °C. [7]. In the experiment, a temperature of about 450 °C was obtained (Table 2).



(a)

(b)

Fig. 3. Thermograms of samples: 1 – Ti_2Al, 2 – TiC/Al, 3 – Ti/Al, 4 – Al (a), 5 – Al/Ti/C, 6 – Ti_2AlC (b).

Perhaps, as shown above, this may be due to the onset of oxidation of the titanium powder. However, the initiation temperature of the Ti/Al layer is much higher and coincides with the oxidation temperature of aluminum powder (about 650 °C). However, according to the authors, this temperature is much higher [8]. The initiation temperature for a two-layer TiC/Al sample (about 650 °C) also coincides with the oxidation temperature of aluminum.

Table 2. Thermal explosion parameters for Ti_2Al, TiC/Al, Ti/Al, Al samples.

Sample	V_{head}, degr./min.	T_{ing}, °C	T_{max}, °C
Ti_2Al	157	430	1150
TiC/Al	147	640	780
Ti/Al	113	620	1195
Al	56	650	760

Fig. 3b shows thermograms for a single-layer sample from a mixture (2Ti + Al) and a three-layer sample (Al/Ti/C). And in Table 3 are the thermal explosion parameters for these samples. It can be seen that for a single-layer sample the initiation temperature is close to the ignition temperature of titanium. However, for a three-layer sample, an abnormally low temperature was obtained (about 200 °C), lower even than the oxidation temperature of soot. What causes this effect requires further study. A three-layer sample (Al/Ti/C) with a total thickness of about 7 mm was pressed into a flat rectangular shape. Initiation was carried out from the end of the sample; the initiating mixture (Ti + B) captured all layers. The combustion wave front propagated along the boundary between the Al/Ti and Ti/C layers. Moreover, the speed along the Ti/C boundary is significantly greater than the speed along the Al/Ti boundary. The sample consists of three layers: TiC at the boundary of the Ti/C layers, intermetallic compounds based on Ti and Al (middle layer) and an aluminum layer (Fig. 4). Thus, it can be assumed that during SHS in a mixture (Ti + Al + C), parallel reactions of both titanium with aluminum and titanium with carbon are possible.

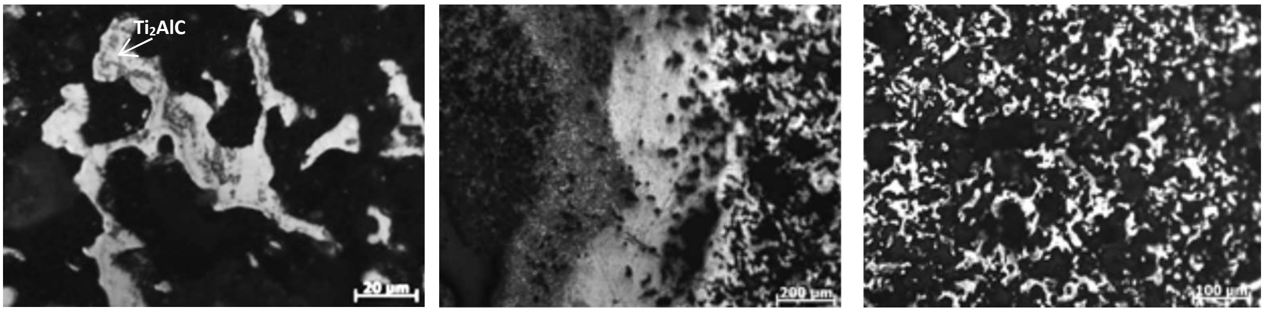


Fig. 4. Micrographs of different areas of the Al/Ti/C sample.

Table 3. Thermal explosion parameters for Al/Ti/C, Ti_2AlC samples.

Sample	V_{head}, degr./min.	T_{ing}, °C	T_{max}, °C
Al/Ti/C	127	185	895
Ti_2AlC	128	530	925

The electrical resistance of the obtained samples was measured. All obtained samples have good electrical conductivity (except Al/Ti/C), within the range of 4–25 Ohm×mm (Table 4). This allows them to be used as conductive coatings and electric heaters. The Ti_2Al sample has electrical conductivity comparable to metals, which makes it possible to use this composition to obtain electrical contacts for electric heaters.

Table 4. Specific electrical resistance of samples.

Sample	ρ, Ohm×mm
Al/Ti/C	3333
Ti	24
Ti/C	25
Ti_2Al	0.7
Ti_2Al/C	6
Ti_2AlC	4
TiAl	4
TiC/Al	18

4. Conclusions

The initiation temperature and maximum temperature of the thermal explosion process in layered powder systems Ti, Al, C, TiC Ti_2Al for various combinations of layers, and the electrical conductivity of the synthesized materials were measured. Anomalously low reaction initiation temperatures were recorded during linear heating of the samples. It has been suggested that this may be due to the oxidation of the mixture components in air and the transition of the process from the thermal explosion mode to the ignition mode. The practical possibility of obtaining thin layers based on the studied systems with high electrical conductivity by the SHS method in air is shown. The obtained results are the basis for developing a method for obtaining flat thin-layer electric heaters.

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