Formation of phase composition of aluminum matrix composites during mechanical activation and self-propagating high-temperature synthesis

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Abstract. The authors investigated the effect of mechanical activation and self-propagating high-temperature synthesis (SHS) on the phase composition of composite materials of Al-TiO$_2$-B system. It has been shown that with increasing the duration of mechanical activation of initial powders the amount of crystalline boron-containing phases in the mixture increases. X-ray diffraction analysis of powder mixtures after SHS allows making conclusion about necessity of activation for at least 45 min to obtain a target compounds. Experimental results allow reasonably choosing the modes of mechanical activation for production of aluminium matrix composites with specified composition and controllable properties.

1. Introduction

The method of self-propagating high-temperature synthesis (SHS), discovered by A.G. Merzhanov and his colleagues, are now widely used in the production of various refractory inorganic compounds and composite materials [1-3]. The essence of the SHS process is that, after local initiation of the reaction interaction in the mixture of the initial powdery precursors, the combustion front spontaneously spreads over the entire volume of the system due to heat transfer from hot products to unheated initial materials in which the reaction is also initiated [4-6].

Aluminum matrix composites obtained by the aluminothermic SHS reaction in the system of initial Al-TiO$_2$-B components contain Al$_2$O$_3$ and TiB$_2$ particles as in-situ reinforcing phases [7]. These endogenous particles form pure interfacial boundaries with the matrix, characterized by strong adhesive bond [8]. Depending on the ratio of the initial components, their fractional and morphological characteristics, the composition of the interaction products can vary significantly, as well as the properties of the resulting composites. In particular, it was found [9] that at a molecular ratio of B:TiO$_2$ = 2:1, the Al$_3$Ti phase in the composite can be completely eliminated, and TiB$_2$ and Al$_2$O$_3$ particles with an average size of 0.31 μm are uniformly distributed in the aluminum matrix. Thus, the addition of boron to the Al-TiO$_2$ system eliminates the negative effect of large needle-like inclusions of the Al$_3$Ti phase on the strength and ductility of aluminum matrix composites.

The synthesis of an aluminum matrix composite reinforced with Al$_2$O$_3$ and TiB$_2$ phases during the reaction sintering of a three-component powder mixture Al + TiO$_2$ + B allowed to conclude that the TiO$_2$ reduction reaction with aluminum melt is a step-by-step process [10] with the formation of various unstable phases of titanium oxide, the main of which is Ti$_3$O$_7$. Along with this, several
transition phases, such as AlB₂, γ-Al₂O₃ and Al₃Ti, were detected. In the work [11] it was shown that the properties of Al/(TiB₂ + Al₂O₃) composites can be controlled by changing the relative amounts of components in the system.

In the manufacturing of composite materials based on the Al-TiO₂-B system by the SHS method, intense reactions of interfacial interaction between the components of powder mixtures can occur. It was shown [12] that in this system the thermodynamic equilibrium is strongly biased towards the formation of the products of SHS reaction. The leading reaction is the aluminothermic reduction of titanium from its oxide, accompanied by the greatest decrease in Gibbs free energy and a significant exothermic effect. The released heat quickly raises the temperature of the system and presumably initiates the formation of titanium boride.

However, the interaction in the Al-TiO₂-B system during self-propagating high-temperature synthesis does not always go through to completion, which leads to the appearance of unreacted initial components in the synthesized composites [13]. Preliminary mechanical activation of powder reagents allows significantly expand the functionality of the SHS-process and increase the depth of interaction. In the process of mechanical activation of powders in high-energy ball mills, the total number and area of contacts between components increases, particles are crushed and various defects accumulate in them, and hard non-metallic particles are embedded into plastic metal particles, which increases the reactivity of the powder mixture [14]. This approach allows one to lower the temperature necessary for initiating the SHS reaction and to increase the conversion degree of the initial materials into reaction products.

The aim of this work is to experimentally establish the peculiarities of change in the phase composition of composite materials based on the Al-TiO₂-B system under the influence of mechanical activation and in the conditions of SHS-process proceeding according to the generalized equation of chemical reaction:

\[ 4\text{Al} + 3\text{TiO}_2 + 6\text{B} \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{TiB}_2 \]

2. Materials and methods
Powders of aluminum (50-200 μm), titanium dioxide (50-100 μm) and amorphous boron (≤63 μm) were used as initial materials. The mechanical activation of mixtures of powder precursors in stoichiometric proportions was carried out in a planetary ball mill Fritsch Pulverisette 6 (Germany) at a rotation speed of 600 rpm and a variable processing time (5, 25 and 45 minutes). Balls made of 100Cr6 bearing steel were used as grinding bodies. The ratio of the mass of the powder mixture to the mass of the balls was 1:20. To conduct SHS, powder mixtures were pressed on a Carver 3664 laboratory hydraulic press into cylindrical compacts with a diameter of 10 mm and a height of 8–10 mm, which were placed in a muffle electric resistance furnace heated to 750 °C for initiation of the SHS reaction.

The phase analysis of composite compacts in the initial state and after the SHS process was carried out using a D8 ADVANCE X-ray diffractometer (Bruker AXS, Germany) in CuKα radiation with a wavelength of 1.5406 Å at a scan step of 0.05 ° (2θ) by Bragg-Brentano method. The interpretation of the X-ray diffraction patterns was carried out in the Diffrac.Suite software package using the ICDD PDF-2 database.

3. Results and discussion
X-ray diffraction patterns of the Al-TiO₂-B powder mixture before and after the SHS reaction at different mechanical activation times are shown at Fig. 1 and Fig. 2, correspondingly. The results of the interpretation of the diffraction patterns in the form of the percentage of different phases in the resulting mixtures are presented in tables 1 and 2.
Figure 1. X-ray diffraction patterns of the Al-TiO$_2$-B powder mixture before the SHS reaction at different mechanical activation times

Figure 2. X-ray diffraction patterns of the Al-TiO$_2$-B powder mixture after the SHS reaction at different mechanical activation times
Table 1. Amount of crystalline phases in the Al-TiO$_2$-B powder mixture before the SHS reaction at different mechanical activation times

| $\tau_{ma}$, min | Amount of crystalline phases, % | Al | TiO$_2$ | AlB$_{10}$ | TiB$_{0.02}$O$_2$ |
|------------------|-------------------------------|-----|---------|------------|------------------|
| 5                |                               | 50.89 | 49.11  | -          | -                |
| 25               |                               | 33.09 | 34.15  | 32.76      | -                |
| 45               |                               | 19.96 | 23.88  | 35.63      | 20.53            |

Table 2. Amount of crystalline phases in the Al-TiO$_2$-B powder mixture after the SHS reaction at different mechanical activation times

| $\tau_{ma}$, min | Amount of crystalline phases, % | Al | TiO$_2$ | TiO | Al$_2$O$_3$ | Al$_2$O$_4$ | TiB$_2$ | TiB$_{0.02}$O$_2$ | Fe |
|------------------|-------------------------------|-----|---------|-----|-------------|-------------|---------|------------------|----|
| 5                |                               | 17.0 | 4.12   | 35.58 | 16.49       | 12.0        | -       | -                | -  |
| 25               |                               | -    | -      | 22.35 | 20.24       | 23.06       | -       | 12.63            | 0.59|
| 45               |                               | 19.96 | 23.88  | 35.63 | 36.38       | -           | 31.27   | 2.57             | 1.75|

The results show that during short-term mechanical activation of a mixture of powder precursors, the components are mixed without the appearance of new phases. After 25 minutes of activation, amorphous boron reacts with aluminum to form the AlB$_{10}$ compound. In a powder mixture activated for 45 min, along with aluminum boride, interaction products of titanium dioxide with boron which have complex stoichiometry (TiB$_{0.02}$O$_2$) are found.

After SHS in an Al-TiO$_2$-B powder mixture activated for 5 and 25 min, titanium diboride in the reaction products was not detected by X-ray phase analysis. The amount of formed alumina in SHS products gradually increases with increasing mechanical activation time from 5 to 45 minutes. A significant number of target phases Al$_2$O$_3$ and TiB$_2$ after SHS is detected only in samples subject to mechanical activation for at least 45 minutes. At this activation time, there is a sharp decrease in the amount of titanium oxyboride phase. In addition, there is a small amount of iron, apparently representing a milling yield from steel balls. It was noted that in all cases the Al$_3$Ti phase was not detected in the reaction products. It can be assumed that a further increase in the time of mechanical activation can contribute to an increase in the SHS interaction depth, however, it can lead to additional saturation of the mixtures with the milling products of steel balls. One way to prevent this may be the application of harder grinding bodies.

The results obtained allow us to reasonably approach the choice of modes of mechanical activation of precursors to obtain composite materials of the Al-TiO$_2$-B system with a targeted phase composition and controllable properties.

4. Conclusions

With an increase in the mechanical activation time in the initial Al-TiO$_2$-B powder mixture, the amount of crystalline boron-containing phases increases. Phase analysis of powder mixtures after SHS allows us to conclude that mechanical activation for at least 45 minutes is necessary to obtain the target phases. At this activation time, a significant amount of Al$_2$O$_3$ and TiB$_2$ is observed in SHS products. This confirms the advisability of using mechanical activation of powder precursors to increase the yield of SHS reaction products.

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