Al-Ti-B₄C materials obtained by high-temperature synthesis and used as a master-alloy for aluminum

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Abstract. The paper presents microstructure, composition, and burning rate of Al alloy produced by high-temperature synthesis (SHS) from powder mixture Al-Ti-B₄C with different concentration of Al powder. It has been established that the phase composition of materials obtained at gas-free combustion includes TiB₂, Al, and TiC. It is shown that Al content growth powder in initial Al-Ti-B₄C mixture from 7.5 to 40 wt.% reduces the burning rate of the powder from $9 \cdot 10^{-3}$ to $1.8 \cdot 10^{-3}$ m/s. For the system consisting of 60 wt.% of (Ti + B₄C) and 40 wt.% of Al there is the increase in the porosity of the compacted initial powder mixture from 30 to 51 and reduction in the burning rate from $1.8 \cdot 10^{-3}$ to $1 \cdot 10^{-3}$ m/s. The introduction of 0.2 wt.% of the obtained SHS materials into the melt of pure aluminum causes reduction of the grain size of the resulting alloy from 1200 to 410 μm .

1 Introduction

Due to the wide use of aluminum alloys in mechanical engineering and aircraft building, there is a great concern about increasing the strength and ductility of aluminum alloys. Traditionally, modifiers of aluminum alloys are titanium diboride and titanium carbide [1-4]. In the composition of the modifying mixture, these materials play the role of nuclei of crystallization in aluminum-based alloys. It is known that the size of the injected refractory particles affects the grain size in aluminum alloys [2, 3]. However, the direct introduction of refractory compounds into the aluminum melt is very difficult due to flotation and poor wettability of the particles. One approach to solving this problem is the use of a master alloys based on a metal matrix containing various micro or nanoparticles of refractory compounds like TiB₂, TiC, etc. [5-7], produced mostly by self-propagating high-temperature synthesis (SHS).

The SHS technology is based on an exothermic reaction between the initial components in a powder system with the evolution of heat necessary to initiate the combustion process in the next layer [8]. The formation of the structure of materials occurs during the interaction of the components of the initial mixture (in situ), which allows to control the phase composition and morphology of the reaction product by changing the synthesis parameters, such as the burning rate and the reaction temperature. It is possible to adjust the synthesis parameters both at the stage of preparation of the initial mixtures and during the synthesis process [5].

The aim of the paper is to show the effect of Al content in SHS-obtained Al-Ti-B₄C powder on thermal properties, composition and structure of aluminum alloys.

2 Materials and methods

This work consisted of two parts. First part was to obtain and research SHS-material. The second part was producing aluminum alloy using SHS-material as a master-alloy followed by the study of obtained alloy structure.

The initial powder mixture used for alloy production included titanium powder (Ti, purity 99.5%, average particle size – 100 μm), aluminum powder (AlP, purity of 99.5%, 80 μm), and boron carbide powder (B₄C, purity 99.0%, 8 μm). The weight ratio of the initial components in initial powder mixture Al-Ti-B₄C was selected on the basis of the conditions of the synthesis reaction (in the stationary mode, layer-by-layer burning, without attenuation, with the initial temperature of the sample 25°C). The exothermic reaction occurring during the synthesis process was characterized by the following formula:

The powders Ti and B₄C were mixed in a stoichiometric ratio of 72 wt.% Ti + 28 wt.% B₄C. The weight content of Al powder in the initial initial powder mixture varied from 5 to 40 wt.%. Mixtures were

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pressed at 120 MPa. The SHS was carried out in a steel reactor with a volume of $3 \cdot 10^{-3} \text{ m}^3$ and initiated by local heating of the upper surface of the samples with a nichrome spiral. The propagation processes of the synthesis wave were recorded on a high-speed video camera.

To obtain alloy we used pure aluminum (99.5%). The introduction of the SHS-obtained materials into the aluminum melt was carried out at 750°C in a mechanical mixer [9] prior to stirring for 30 s, followed by pouring into a steel chill mold. The amount of added SHS material in aluminum was 0.2 wt.%.

The study of the structure of the obtained materials was carried out using scanning electron (SEM, Philips SEM-515) and optical (Olympus GX-71) microscopy. X-ray phase analysis was performed using a Shimadzu XRD 6000 diffractometer. The burning rate of compositions was determined using high-speed digital video camera Citius Centurio C100 (Citius Imaging Ltd, Finland). The porosity of the final materials was determined by hydrostatic weighing.

3 Results and discussion

Figure 1 shows the process of SH-synthesis from the moment of initiation of the reaction to its full course. It can be seen from the figure that the process is close to layer-by-layer burning in the stationary mode [7]. At the same time, from the works [10, 11] it is known that the formation of ceramic particles (carbide boride and titanium diboride) in the material is carried out by the mechanism of solid-phase diffusion of B_4C particles and Ti particles.

Fig.1. The process of SHS in a sample of the Al-Ti- B_4C powder system: combustion initiation (a), the middle of the process (b), the end of burning (c).

Figure 2 shows the dependence of the burning rate of the Al-Ti- B_4C system on the content of aluminum powder in the initial dry mix. It should be noted that with the addition of aluminum powder in the initial dry mix more than 40 wt.% there is under-burning of samples or it is not possible at all to initiate the process of synthesis of components.

It can be seen from the Figure 2 that the growth of Al content the initial powder mixture from 7.5 to 40 wt.% cause decrease of the burning rate of samples from

$9 \cdot 10^{-3}$ to $1.8 \cdot 10^{-3} \text{ m/s}$. This is due to the fact that aluminum powder contained in the initial dry mix acts as an inert diluent, which reduces the rate and adiabatic temperature of the charge reaction by absorbing the heat released during synthesis [12]. A decrease in the burning rate in turn leads to a slowdown in the growth of ceramic particles TiB_2 and TiC , which is caused by a slower process of their recrystallization [13]. At the same time, the addition of aluminum powder to the Ti- B_4C system in an amount of up to 7.5 wt.% leads to an increase in the burning rate of the charge. The burning rate of the Ti- B_4C system without aluminum is $9.5 \cdot 10^{-3} \text{ m/s}$, and the maximum burning rate is achieved with the addition of 2.5 wt.% Al. This is caused by additional convective heat transfer that occurs during the propagation of molten al through the sample, since the propagation of the combustion wave from SHS systems occurs due to the initiation of the reaction from one layer to another through conductive heat transfer [8, 12].

Fig. 2. Burning rate of the Al-Ti- B_4C powder system on the content of aluminum powder.

Also, based on the data [2, 3] and the obtained dependences of the burning rate on the content of al, it can be assumed that the particle size of titanium carbide and diboride in SHS materials obtained from a powder system is 60 wt.% (Ti + B_4C) + 40 wt.% Al, will be the smallest relative to other systems. In addition, studies have shown that with a decrease in porosity in the initial powder mixture and 51 to 30% leads to an increase in the burning rate of the samples from $1 \cdot 10^{-3}$ to $1.8 \cdot 10^{-3} \text{ m/s}$. This is primarily due to an increase in the number of contacts between particles, and this leads to more intensive growth of TiB_2 and TiC particles in the resulting SHS materials due to their recrystallization process [12-14]

Fig.3. SEM images of material obtained from the mixture 60 wt.% (Ti + B₄C) + 40 wt.% Al at the initial porosity of the initial powder mixture 51%.

Fig. 4. XRD pattern of the sample obtained from the powder of the system Al-Ti-B₄C.

According to XRD data the material composed of a metal Al matrix and distributed ceramic particles TiB₂ and TiC (Figure 4). According to XRD data phases content is 42 wt.%, 36 wt.% and 22 wt.% for TiB₂, Al and TiC respectively (Table 1). The electron microscopy data shown that the size of the ceramic particles was 2 μm (Figure 3).

Table 1. The results of X-ray diffraction SHS materials prepared from powder mixtures 60 wt.% (Ti + B₄C) + 40 wt.% Al at the initial porosity of the compact 51%.

Phase detection	Phases content, wt. %	lattice parameters Å	OCD Size, nm	$\Delta d/d \cdot 10^{-3}$
TiB ₂	42	a = 3.0238 c = 3.2208	41	1.7
Al	36	a = 4.0472	46	0.5
TiC	22	a = 4.3184	64	0.4

It has been revealed that with the introduction of 0.2 wt.% in the melt of the SHS material in the aluminum melt it was found that the grain structure of the ingots obtained is crushed. It was found that the grain size of

the starting material that does not contain the master alloy, was 1200 μm (Figure 5a), and with the introduction of 0.2 wt.% of SHS materials, the average grain size of the resulting alloy was ~ 410 μm (Figure 5b).

Fig. 5. Optical image of aluminum ingots obtained for, alloy without articles of the obtained SHS-material (a) and with 0.1 wt.% TiB₂ and TiC particles (b).

4 Conclusion

The conducted studies show the prospect of manufacturing master alloys by the SHS method intended for modifying the structure of aluminum. At the same time, the controlled SHS process allows to obtain master alloys with a given phase and particle size distribution.

It was found that the aluminum powder contained in the initial raw mix acts as an inert diluent, which decreases the burning rate and adiabatic temperature of the reaction of the raw mixtures due to the absorption of heat released during synthesis. The rate of combustion of the Ti-B₄C system without the addition of aluminum is

$9.5 \cdot 10^{-3}$ m/s, and the maximum burning rate is achieved with the addition of 2.5 wt.% Al.

Using the X-ray phase analysis method, it was found that the phase composition of the material obtained from the mixture is 60 wt.% (Ti + B₄C) + 40 wt.% Al is represented by Al, TiB₂ and TiC.

It is shown that with the introduction of 0.2 wt.% SHS materials obtained from the powder system 60 wt.% (Ti + B₄C) + 40 wt.% Al in the melt of pure aluminum the grain size of the obtained ingots decreases from 1200 μm to 410 μm.

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References

1. W.H. Sillekens, D.J. Jarvis, A. Vorozhtsov, V. Bojarevics, C.F. Badini, M. Pavese, H. Dieringa, *Metall. Mater. Trans. A* **45**(8), 3349 (2014)
2. C. Suryanarayana *Progress in Materials Science*, **46**(1-2), 184 (2001)
3. E. Hacha *Aluminum: Properties and Physical Metallurgy: A Handbook*. (Trans. with English. Metallurgy, 1989)
4. G.V. Sakovich, A.B. Vorozhtsov, S.A. Vorozhtsov, A.I. Potekaev, S.N. Kulkov, *Russ. Phys. J.* **59**(3), 435 (2016)
5. S.A. Vorozhtsov, A.P. Khrustalev, D.G. Eskin, S.N. Kulkov, N. Alba-Baena, *Russ. Phys. J.* **57**(11), 31 (2015)
6. I.A. Zhukov, V.V. Promakhov, A.E. Matveev, V.V. Platov, A.P. Khrustalev, Ya.A. Dubkov, A.I. Potekaev, *Russ. Phys. J.* **60**(11), 2025 (2018)
7. Z. Fan, Y. Wang, Y. Zhang, T. Qin, X.R. Zhou, G.E. Thompson, T. Hashimoto, *Acta Materialia*, **84**, 292 (2015)
8. A.G. Merzhanov, A.S. Mukosyan *Solid Flame Combustion* (Torus Press, Moscow, 2007)
9. S. Vorozhtsov, L. Minkov, V. Dammer, A. Khrustalyov, I. Zhukov, V. Promakhov, M. Khmeleva, *JOM*, **69**, 2653 (2017)
10. Ye.A. Levashov, M.I. Petrzhik, M. Ya. Tyurina (Bychkova), F.V. Kiryukhantsev-Korneyev, P.A. Tsygankov, A.S. Rogachev, *Metallurg*, **5**, 27 (2010)
11. A. I. Gusev, A.A. Rempel, *Nanocrystalline materials* (Cambridge Int Science Publishing, 2004)
12. A.E. Matveev, *Proc. XIV Int. Conf. of Students and Young Scientists "Prospects of fundamental sciences development"*, **2**, 193 (2017)
13. I.P. Borovinskaya, T.I. Ignat'eva, O.M. Emel'yanova, V.I. Vershinnikov, V.N. Semenova, *Inorganic Materials*, **43**(11), 1206 (2007)
14. I.P. Borovinskaya, A.G. Merzhanov, N.P. Novikov and A.K. Filonenko, *Combustion, Explosion and Shock Waves*, **10**(1), 2 (1974)