

## The Impact of Fractional Difference of Components on the Properties of Hard Alloys Produced by the SHS Method

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**ABSTRACT.** By changing the fractional ratio of titanium and boron powders the phase composition of the end combustion product in the process of self-propagating high-temperature synthesis (SHS) is regulated. As a result, hard alloys of titanium with boron exceeding by their performance attributes the widely used alloys of this type are produced. © 2010 Bull. Georg. Natl. Acad. Sci.

**Key words:** hard alloy, powder, titanium, titanium boride, SHS, dispersivity.

In the process of self-propagating high-temperature synthesis (SHS), the reaction proceeds in a burning wave mode in a narrow zone which in the form of a combustion wave spontaneously moves at a definite speed along the bulk of the compacted charge and separates initial reagents from the warmed-up reaction products [1]. High combustion temperature is achieved in the course of the reaction at the expense of release of the chemical energy of the initial system and does not require heat application from the outside.

Hard alloys produced by the SHS method possess high mechanical properties and by their high mechanical properties are not inferior to the known commercial hard alloys. However, their synthesis in the SHS mode is associated with a number of problems being generally caused by the multiphase character of combustion products.

In the present work, based on the Ti-B alloys system, a possibility of regulation of the phase composition and quality of the end product – hard alloy – is being investigated through changing the dispersivity of the initial powder-like components in the charge.

In general, the powder-like charge used for synthesis consists of A, B and C components. The A component assumes the function of a fuel, the B component – that

of an oxidant, and the C component – of a binder composition. Between components A and B, a chemical interaction in the condensed phase with the production of refractory compounds takes place, and the C elements, weakly interacting with the combustion products, fill up the interparticle pores playing concurrently the role of a binder.

Let us consider an idealized picture of the powders used in the SHS process. In the case of the Ti-B alloys system, the initial charge consists of titanium and boron particles. If these particles are equal in size, then upon their mixing a monofractional (homogeneous) two-component statistical mixture is formed. Contacts of three types can be observed in such a mixture: the particles contact with like particles forming bonds, 1-1 and 2-2, as well as forming unlike (heterogeneous) contacts 1-2. According to the laws of statistical physics, the entropy of such a chaotic system equals:

$$\Delta S = -R(N_1 \ln N_1 + N_2 \ln N_2), \quad (1)$$

the probability of occurrence of like contacts is proportional to the numerical value of the component ( $N_i$ )

$$\frac{P_{1-1}}{ZN_0} = N_1; \quad \frac{P_{2-2}}{ZN_0} = N_2, \quad (2)$$

and the concentration dependence of the number of unlike contacts ( $P_{1-2}$ ) is described by the symmetric parabola

$$\frac{P_{1-2}}{ZN_0} = N_1N_2. \quad (3)$$

Here  $N_0$  is the total number of particles in the system, and  $Z$  is the coordination number of the particle which, owing to the homogeneity of the system, is a constant value within the whole concentration range. The maximum value of the packing factor or space population estimated as the ratio of the total volume of particles to the volume occupied thereby for uniform granular media runs up to  $K=0.64$  [2].

However, upon mixing of unequal particles, these regularities do not apply. A difference in the sizes of mixable couples leads to an increase of  $K$ , changes the internal structure of the mixture and results in an increase of the number of unlike bonds in comparison with the monofractional system. This is easy to understand if one assumes that in an unordered system of like particles some of their number is substituted in one case with the same number of particles of the same size but different colour, and in the other case – with particles of a bigger size. In the former case, the number of “colored” or unlike contacts can be calculated from the statistics of ideal mixtures (3), and in the latter – from the data of [3], in which the phenomenological theory of statistics of two-fractional systems is given:

$$\frac{P_{1-2}}{ZN_0} = \frac{1}{4}N(1-N)[\alpha(1-N) + \beta N], \quad (4)$$

where  $\alpha = \left(1 + \frac{d_2}{d_1}\right)^2$ ,  $\beta = \left(1 + \frac{d_1}{d_2}\right)^2$ ,  $d_1$  and  $d_2$  are the diameters of the mixable particles (at that  $d_2 > d_1$ ), and  $N$  is the part of big-size particles.

The function (4) describes a family of non-symmetric parabolic curves, the more shifted towards the components of a smaller size, the more is the ratio  $d_2/d_1$ . In the case of significant grain-size difference of the mixable powders, the coefficient  $\beta$  in formula (4) becomes negligible and therefore it can be assumed that the number of unlike contacts and, consequently, the heat released in the course of synthesis will increase proportionally  $(1+d_2/d_1)^2$ .

The assumption seems physically justified that burning in the course of SHS depends upon the number of unlike contacts – the more is their number, the more

effectively will the fusion reaction apparently proceed. On the other hand, however, with an increase of  $d_2/d_1$  the volume of big particles will also increase under cubic dependence. Therefore, it can be expected that at definite critical values of  $d_2/d_1$ , the reaction heat will not be sufficient for melting big-size particles; the threshold state will occur and the SHS process will be gradually inhibited until its complete termination. Attention should be also given to the circumstance that with an increase in the fractional difference of components, micro areas with a great number of small particles devoid of heterogeneous contacts and therefore weakly participating or generally not participating in the fusion process will be formed. At a definite ratio of grain-size characteristics of the initial powders, this factor will also inhibit the further development of the synthesis process. Consequently, by changing the fractional composition of titanium and boron powders within reasonable limits, the phase composition of the end combustion product can be controlled. The experimental data given below are a graphic example of the above.

The Figure presents the results of an X-ray phase analysis of the Ti-B system fusion products, depending on the titanium concentration under conditions of its dispersivity variation in the initial charge. Used were powders of dispersivity:  $\delta=40-100$ ;  $100-140$ ;  $140-200$ ;  $200-300$  and  $300-500$   $\mu\text{m}$  and boron powder of dispersivity in the order of  $\delta=1$   $\mu\text{m}$ .

It follows from these data that at average dispersivity of a binder metal, 70- $\mu\text{m}$  combustion product will be two-phased. At that, with an increase of the binder metal's content in the initial charge, the number of Ti-B<sub>2</sub> reduces, while Ti-B – increases. An increase in the size of particles of the binder metal in the initial charge leads to an increase in the content of titanium diboride. At an average dispersivity of the binder metal 120  $\mu\text{m}$ , the availability of a free metal will be observable in the end synthesis product, the quantity of which will increase with an increase of the dispersivity in the binder metal. Upon availability of a binder metal 250  $\mu\text{m}$  dispersivity, the end product will represent titanium diboride and free titanium. The phase Ti-B<sub>2</sub> has the appearance of well-faceted white-color rounded crystals. The titanium boride grains are bordered with a phase of pure titanium. This proves that the SHS process in the Ti-B system proceeds with formation of an intermediate molten area. The reaction is excited at the places of contact of the unlike particles with the formation of solid combustion products, and the heat released at that melts the titanium particles. Liquid titanium, while wetting the solid combustion products, penetrates through the mechanism

of capillary seepage [4] to the next layer of unreacted boron particles and reacts with them.

Thus, the combustion wave spontaneously moves along the specimen. The participation of the liquid phase facilitates contact between the reagents and intensifies the combustion process. Concurrently with the change of grain-size composition of the charge, the conditions of heat and mass transfer, the interaction mechanisms, the flow conditions also change, and the content and volume of the combustion products are self-regulated as individual phases.

Further increase in the dispersivity of the binder metal in the initial charge ( $>300 \mu\text{m}$ ) results in the deterioration of the end product's quality. In particular, the produced specimens are characterized by excessive porosity, low strength and are prone, in certain cases, to destruct. Apparently, the threshold effect, of which we spoke above, bound with the critical fractional ratio of the dispersivities of components sets in here.

The described model distorts the actual situation under conditions of averaging the fractional composition of titanium powder; nevertheless, it satisfactorily outlines the trends observable in the experiment and allows estimating the limits of the fractional difference of components in the initial charge, ensuring the production of the desired phase composition and quality.

In conclusion, let us briefly characterize the pro-

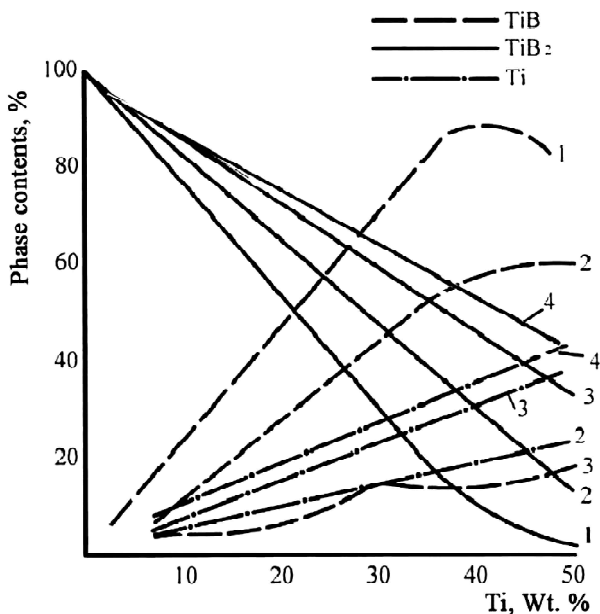


Fig. Change of phase composition of combustion products of Ti-B system, depending upon the content of binder metal content (Ti) at average dispersivity of titanium in the initial charge 1 –  $70 \mu\text{m}$ ; 2 –  $120 \mu\text{m}$ ; 3 –  $160 \mu\text{m}$ ; 4 –  $250 \mu\text{m}$

erties of titanium diboride-based hard alloys produced by the SHS method:

- The upper bound of the flexural strength (850 MPa) of  $\text{TiB}_2$ -Ti system alloys is observable at titanium content  $\sim 30 \text{ mass } \%$  and its dispersivity in the order of  $\delta = 250 \mu\text{m}$ . The upper bound of flexural strength (3500 MPa) is attainable at titanium concentration  $\sim 25 \text{ mass } \%$ ;

- The strength of titanium alloys (30-50 mass %) at average dispersivity of  $250 \mu\text{m}$  does not practically change and totals 92-93 units, exceeding the strength of widespread WC-Co alloys.

- The concentration-fractional dependence of the coefficient of thermal expansion (CTE) of Ti- $\text{B}_2$  alloys has a tendency to CTE growth at an increase of the content of titanium and its dispersivity. The average CTE of Ti- $\text{B}_2$  system 30%Ti alloy having dispersivity of  $250 \mu\text{m}$  at the temperature range of  $20\text{-}700 \text{ C}^0$  totals  $8.3 \cdot 10^{-6} \text{ degrees}^{-1}$ .

- The heat resistance studies conducted under cyclic heating to  $1000 \text{ C}^0$  with subsequent cooling in water demonstrated that the general standard of heat resistance of  $\text{TiB}_2$ -Ti alloys (45 cycles of heat changes until the specimen destruction) is higher in comparison with the commercial hard alloys of TiC-Ni and WC-Co (19-22 cycles respectively). Such a difference in heat resistance is accounted for by proximity of the CTE phase component of the  $\text{TiB}_2$ -Ti system.

- The heat-resistance of  $\text{TiB}_2$ -Ti alloys was judged by the weight increment in time at various temperatures ( $500, 700, 1000 \text{ C}^0$ ). The most intensive oxidation is observable in the initial period ( $\sim 8$  hours), when an oxide coating is being formed. The higher the content of the binder, the speedier grows the weight increment. The oxide coating/film consists basically of rutile flaking. In the course of further oxidation, the flaking is caked, the pores are closed up, and the thin vitreous oxide film immunizes the surfaces, fully covering the specimen.

The given results show that by selecting the fractional composition of the dispersivity components of the charge the phase composition of the end SHS product can be changed and hard alloys of the system Ti-B, whose performance characteristics are not inferior to commercial alloys (BK and TK), and even outperform them by some properties.

Hard  $\text{TiB}_2$ -Ti alloys can be successfully used as a wear-proof tool with the working temperature below the polymorphous transformation of titanium ( $883 \text{ C}^0$ ), above which titanium, converting into the plastic state, loses its resilient properties.

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მასალათმცოდნეობა

## კომპონენტთა ფრაქციული განსხვავების გავლენა თმს მეთოდით მიღებულ სალ შენადნობთა თვისებებზე

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ტიტანისა და ბორის შენადნობების მაგალითზე ნაჩვენებია საკაზმე ფხვნილების გრანულომეტრიული თანაფარდობის ( $d_2/d_1$ ) გავლენა თმს-ით მიღებული პროდუქტების ფაზურ შემადგენლობაზე. რეკომენდებულია  $d_2/d_1$  ისეთი მნიშვნელობა, რომელიც უზრუნველყოფს Ti-B სისტემაში მაღალი სისაღის მქონე შენადნობის მიღებას. მიღებული შენადნობი საექსპლუატაციო თვისებებებით საგრძნობლად გამოირჩევა ამ ტიპის ცნობილი შენადნობებისაგან.

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