

Self-propagating high-temperature synthesis of composite material TiB₂-Fe

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Results of an investigation of the microstructure and phase composition of materials of the Ti-B-Fe system, obtained by self-propagating high-temperature synthesis (SHS) are presented.

Investigations were conducted for two types of powder mixtures; the first was a mixture of elemental powders Ti, B, Fe and the second was a mixture of ferroboration alloys, FeB_n, with titanium. The possibility of using commercial ferroalloys to obtain of boron-containing MMC_s is shown. The combination of SHS with force effect rolling leads to a dense product with high operational properties. More efficient fields of the application of SHS composite to produce TiB₂-Fe are shown. © 2004 Kluwer Academic Publishers

1. Introduction

Borides and their alloys based on them find the use in industry since they have high temperature strength, heat resistance, wear resistance and resistance to oxidation. In the nuclear industry borides are used as absorbers of thermal neutrons. Some borides are used in resistors, cathodes and electronic components.

Self-propagating high-temperature synthesis (SHS) is one of the most progressive methods for obtaining TiB₂ and TiB₂-reinforced materials [1]. The Ti-2B system has drawn the attention of many investigators from the moment of its discovery [2–6]. Due to the high exothermicity of this system, it has been used as a model in the study of combustion processes and owing to its attractive high physical and mechanical properties it is of interest for its practical use SHS of the Ti-2B system was frequently the object of investigation. But one of the more prospective variants of the wide use of titanium diboride in technology is the development of composite materials based on it, consisting of finely dispersed particles of titanium diboride, bonded with a more viscous binder.

The aim of this work is the study of phase composition and the microstructure of combustion products of the three-component system Ti-B-Fe and the search for optimum technological processes for the manufacture of articles and coatings based on them.

2. Materials and investigation methods

Commercial powders of titanium (a particle size range—15–400 μm, purity—99.0 mass%), iron (particle size range—10–350 μm, purity—99.8 mass%), amorphous boron (a particle size range is 0.1–1.0 μm,

purity is 98.0 mass%); FeB alloy (21.0 mass% of B) and FeTi (60 mass% of Ti) were used to obtain reaction mixtures. Table I shows the SHS systems considered here and the compositions of the starting mixtures.

Cylindrical samples with porosity of 35–40% were made from powder mixtures by cold pressing and reacted by SHS at constant pressure of 0.5 MPa in inert argon. The ignition of the pressed samples was monitored with the help of a radiant heat colour tungsten coil. Synthesis products were investigated by light (MIM-8M) and electron scanning (REM-200) and transmission (UEMV-100 K) microscopy. X-ray diffraction investigations were carried out using a DRON-2 calorimeter with Cu K_α and Co K_α radiation. The mechanical characteristics of sintered materials were determined according to standard methods. The composition of the structural components in synthesized and sintered samples was defined with a “Cameca” microanalyzer.

Some methods of investigation are described in the corresponding sections of the article.

3. Investigation of SH-synthesis products of the Ti-B-Fe system

As shown previously in our work [7], the phase composition and SH-synthesis product structure of MMC_s of the Ti-B-Fe system are defined by a mechanism of component interaction in the SHS wave. Contact eutectics play an important role in this mechanism, on the basis of which solid-liquid melts, different in viscosity and element concentration, are formed in a combustion wave. The degree of diffusion-convective mixing of these melts in the combustion wave determines the phase composition and the structure of end products.

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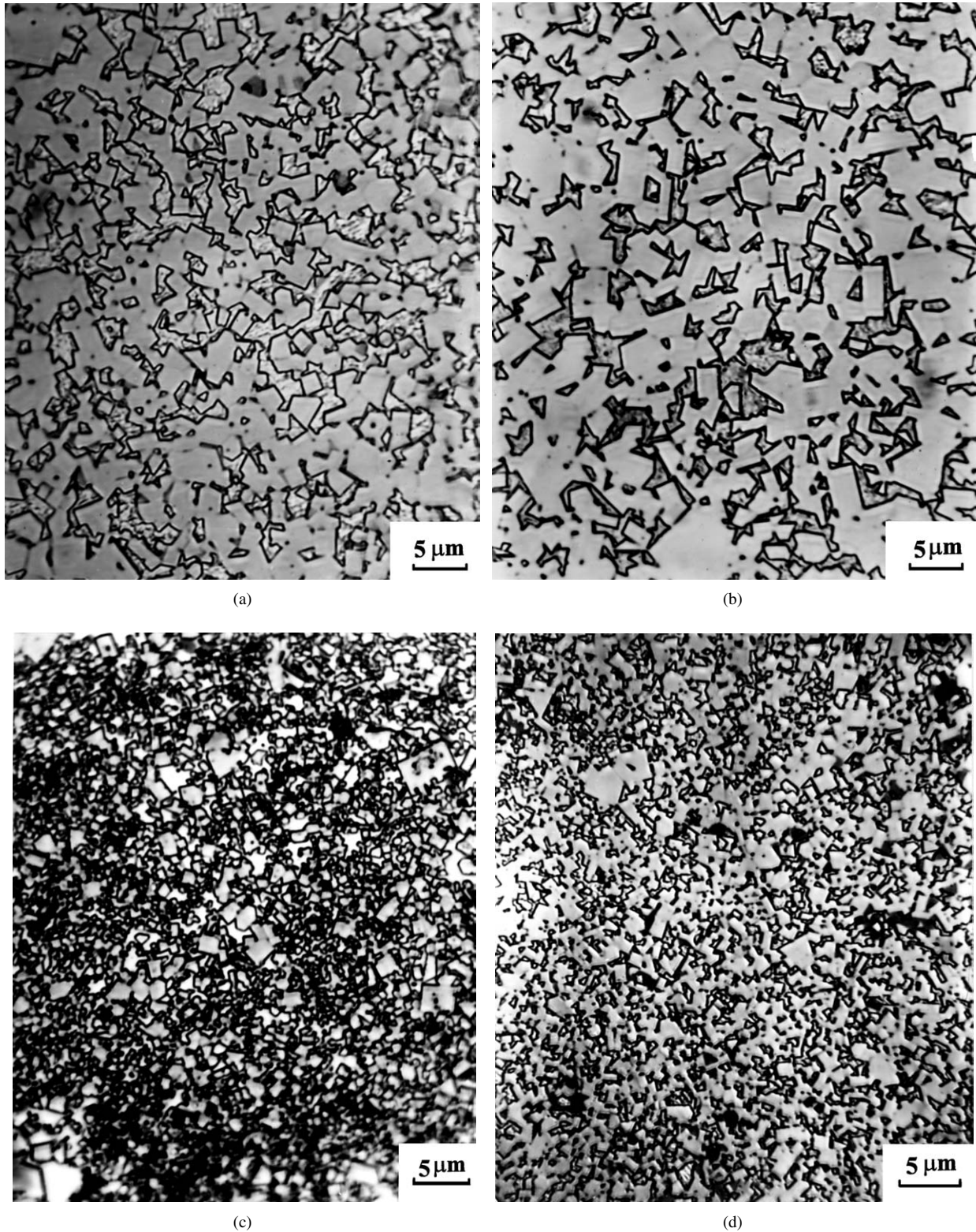


Figure 2 Microstructures of end products of the system titanium-boron-iron for two types of powders mixtures: (a) Fe + 2B + Ti, (b) Fe + 4B + 2Ti, (c) FeB₂ + Ti and (d) FeB₄ + 2Ti.

composition of the synthesis products when the charge is a mixture of elemental powders is analyzed below.

Fig. 4a shows the microstructure of combustion products of mixtures of Fe + Ti + 2B composition, composed of finely dispersed starting powders (Ti \approx 15 μ m; Fe \approx 10 μ m). The microstructure consists of TiB₂ crystals with sharp edges with a size not more than 5 μ m, uniformly distributed in the matrix consisting mainly of iron and small amounts of titanium, according to the data of micro-X-ray spectrum analysis.

Electron-microscopic investigations of the end products indicate the eutectic character of intergrain spacings. On the basis of the data obtained, we consider that the matrix consists of quasibinary eutectic TiB₂-Fe (92% of mass Fe). The microstructure in Fig. 4a is the result of the crystallization of the unified, homogeneous, solid-liquid melt, being formed behind the combustion front at a temperature, close to the liquidus temperature of the quasibinary vertical section of the TiB₂-Fe phase diagram [8].

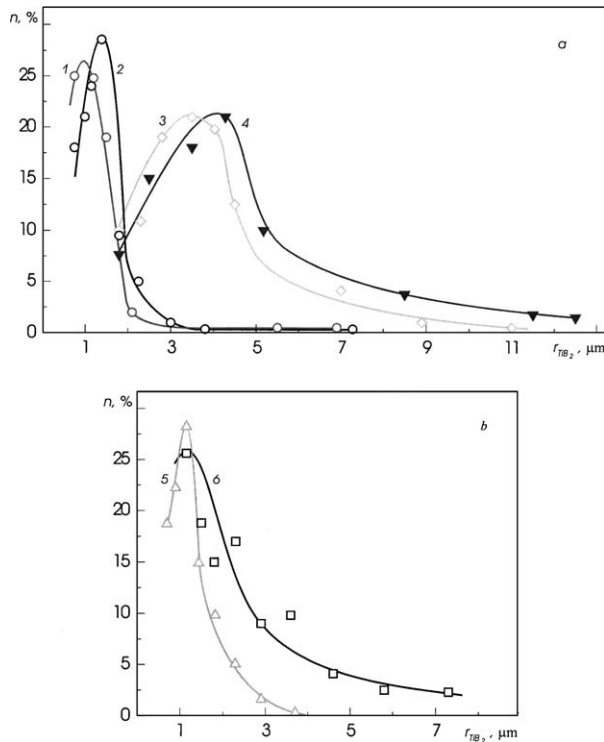


Figure 3 Distribution of sizes of TiB_2 particles in end products for two types of powders mixture: (a) mixture of Ti, B, Fe powders: 1—Fe + B + 0.5Ti; 2—Fe + 2B + Ti; 3—Fe + 4B + 2Ti; 4—Fe + 6B + 3Ti and (b) mixture of FeB_n , Ti powders: 5— FeB_2 + Ti; 6— FeB_6 + 3Ti.

Increasing the average size of the titanium and iron particles in the starting mixtures leads to the formation of microareas with microstructures, different from equilibrium (Fig. 4b and c). Fig. 4a shows a microsection with a eutectic FeTi-Ti, and Fig. 4c—with eutectic Fe_2B -Fe. The first eutectic is characteristic of samples, synthesised from mixtures of powders with coarsely dispersed titanium, the second one—with coarsely dispersed iron.

Comparison of the end products for two types of charge shows that large amount of non-equilibrium phases are obtained in samples, produced by SHS of ferroboron alloys and Ti. At the same time, the microstructure of such samples is characterized by a homogeneity in the TiB_2 grains distribution according to sizes and smaller grains.

One of the important challenges of SHS is to obtain fully dense products.

The maximum combustion temperatures for all investigated Ti-B-Fe reaction systems lie inside the “L-S” region of quasibinary vertical section of the TiB_2 -Fe phase diagram [9]. Consequently, solid-liquid mass: iron-boron-titanium melt with TiB_2 , TiB, FeB etc. refractory particles, suspended in it, is formed behind the combustion front of all compositions being investigated. More specifically, behind the front there are several solid-liquid melts, which are formed in successive interaction of two elements in contact [7]. At any time, the equalization of the concentration composition as well as the coalescence of individual solid-liquid melts takes place as the result of diffusion-convective processes. It follows that the porosity of the end SHS product will depend upon many factors: component dispersion, maximum temperature, development of the

combustion wave, viscosity of solid-liquid melts, temperature holding time, cooling rate, amount of gases adsorbed on the surface of particles, etc.

The composition and relationship between components, size of titanium particles and the temperature of mixtures preheating were varied in experiments.

Comprehensive investigations showed that the porosity of end products is lesser when ferroboron alloys (FeB_n) were used as starting reagents. Except for the temperature factor this is due to the fact, that the amount of adsorbed gases is much less on particles of ferroboron alloys in comparison with particles of amorphous boron. Preliminary thermal treatment of the starting mixtures results in a reduction in porosity of the end products.

As a whole, the investigations conducted showed, that it is not possible to obtain products of the TiB_2 -Fe system with a porosity less than 10% in combustion without supplementary physical-mechanical exposures.

4. Production of dense product in Ti-B-Fe system with SHS + rolling

The phase composition and microhardness ($H_\mu = 1500 \text{ kg/mm}^2$) of the obtained SHS materials of Ti-B-Fe system predetermine their high operation properties. But the presence of pores (up to 10–15%) in the end products reduces their strength characteristics. To obtain non-porous material it is necessary to combine SHS with additional physical-mechanical exposures (ultrasonic vibrations, pressure, rolling, etc.) or to obtain the powder from the SHS material and then densify using powder metallurgy methods.

Some characteristics of the material, obtained with rolling of combustion products of the Ti-B-Fe system are cited in this work. In this case the mixture of the third composition consisting from powders of conventional ferroalloys: Fe-B ferroboron (21.6 mass% of boron) and Fe-Ti ferrotitanium (60.0 mass% of Ti) was used to realize the SHS process.

The analysis of product the microstructure, conducted with light and transmission electron microscopy showed, that almost all particles of titanium diboride are of a size equal to 1–2 μm . The rolling has destroyed large intergrown TiB_2 crystallites, that led to the increase in the extent of grains boundaries (Fig. 5a). Fig. 5b shows a TiB_2 particle with slip bands. Evidently, under these conditions of the SHS product treatment, plastic deformation of TiB_2 took place.

The product density after rolling was $\approx 98\%$ of the limiting value, hardness HRA ≈ 91 , and the wear resistance at the level of the WC-Co (15.0 mass% of Co) alloy. Data presented and their comparison with characteristics of materials, obtained with the use of model alloys from mixtures of elemental powders, show, that the replacement of the latter with commercial ferroalloys does not lead to the essential decrease in physical-mechanical properties of finite products. At the same time, the cost of the SHS materials production of the Ti-B-Fe system with the use of commercial ferroalloys

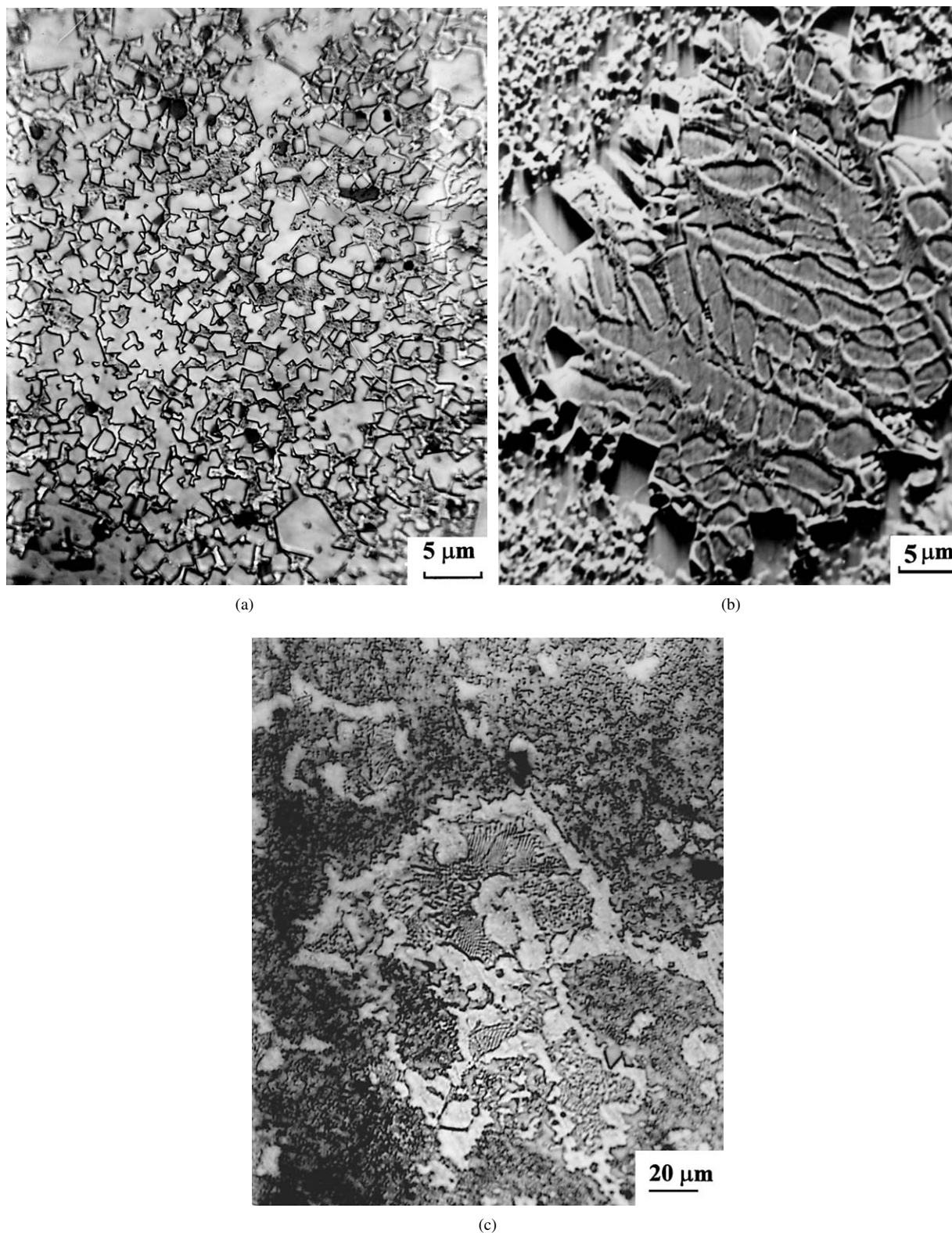


Figure 4 Microstructures of end products of Ti, B, Fe powders mixture of Fe+2B+Ti composition: (a) $r_{Ti} \approx 15 \mu m$; $r_{Fe} \approx 10 \mu m$, (b) $r_{Ti} \approx 400 \mu m$, $r_{Fe} \approx 10 \mu m$ and (c) $r_{Ti} \approx 15 \mu m$; $r_{Fe} \approx 350 \mu m$.

will be much less compared to the use of expensive elemental powders.

5. Sintering of SHS composite powders of Ti-B-Fe system

As shown composite TiB_2 -Fe and composite powder based on this material may be obtained from different mixtures: ferroboron alloys (FeB_n) with titanium or ferrotitanium alloys (Fe-Ti); elemental powders Ti, B

and Fe or Fe-Ti alloys with boron. The technology for the production of SHS composite TiB_2 -Fe powder consists of four successive operations: 1—preparation of exothermic mixture of the required composition; 2—mixing of starting reagents; 3—SH synthesis of composite material and 4—production of powder through grinding the composite.

Fig. 6a shows the morphology of the powder after grinding of the reaction product in pneumo-pulse grinding device, while the microstructure of this powder is

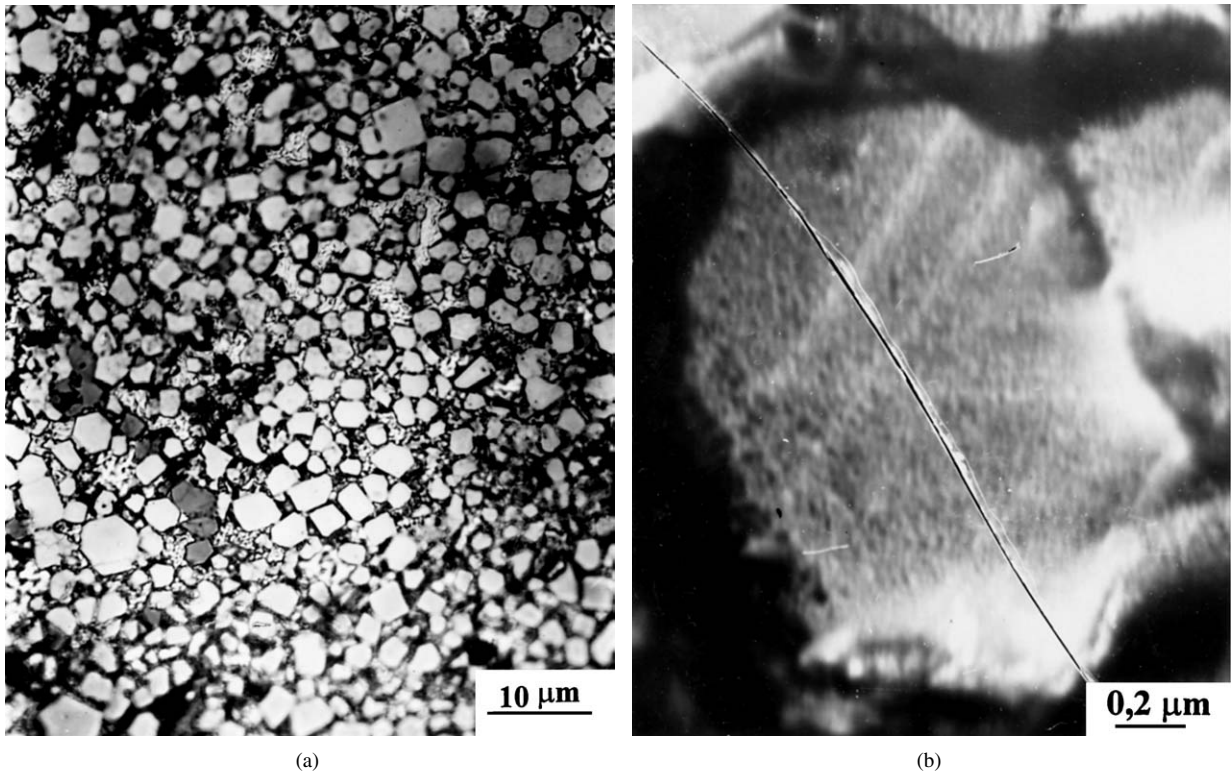


Figure 5 Microstructure of rolled alloy of FeB + FeTi composition: (a) optical microscopy and (b) TiB₂ particle.

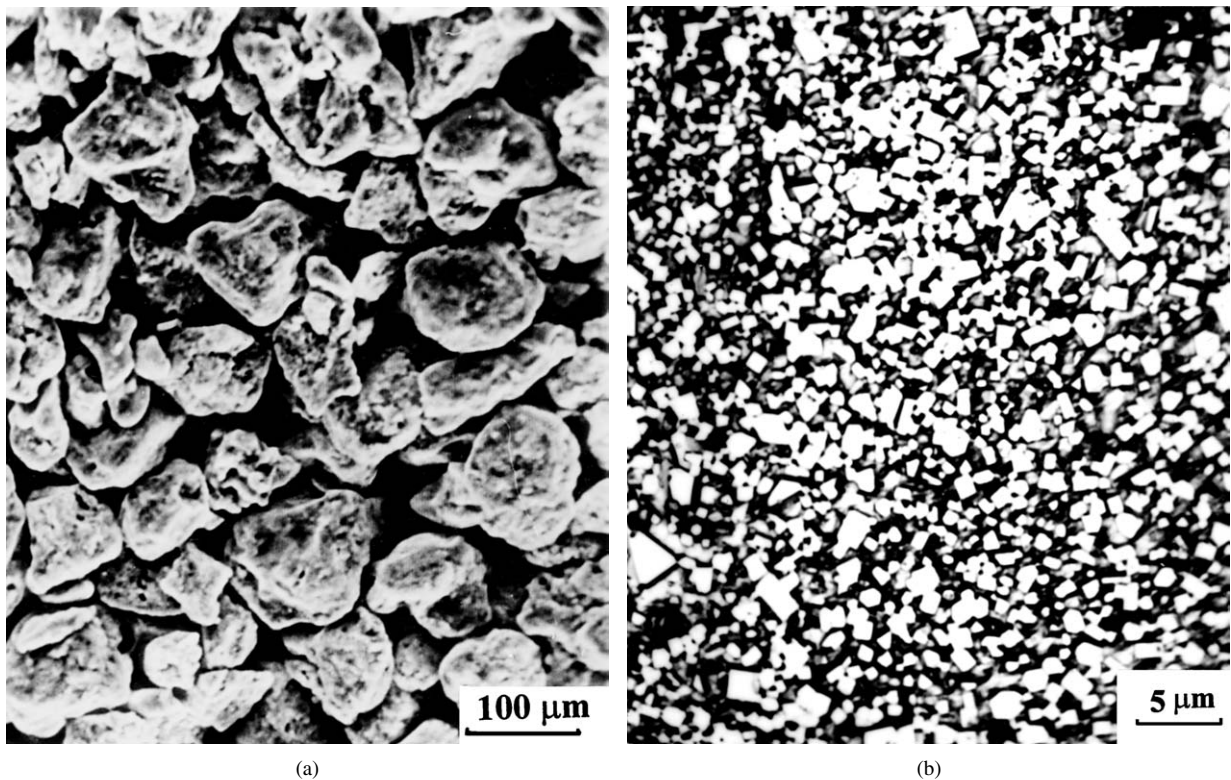


Figure 6 External view (a) and microstructure (b) of SHS composite TiB₂ + Fe powder.

shown in Fig. 6b. The peculiarity of the microstructure of this powder is that each individual grain of powder is a ready-made composite, consisting of finely dispersed titanium diboride particles, that were formed directly during SHS and distributed in the metal-matrix of eutectic TiB₂-Fe, consisting of 7.8 mass% of TiB₂.

Compared to conventional powder metallurgy, two main problems are solved; there is no need to obtain

submicron TiB₂ particles and a strong adhesion bond between the refractory particle and the metal-matrix is promoted.

The properties of sintered hard alloys are defined not only by composition, but also by the structure character (grain size, porosity, mutual phase arrangement, value of intergrain spacings), the formation of which is determined, to a large extent, by the temperature and

sintering time. Since SHS composite TiB_2 -Fe powder is a new powder material, it was necessary to determine the optimum sintering conditions for evaluation of the possibility of its use for the production of hard alloyed articles.

In the work two types of powders were studied: composite powders, obtained with SH synthesis of mixtures of ferroboron alloys (FeB_n) with titanium (CP-1) and those, obtained from mixtures of elemental powders Ti, B, and Fe (CP-2).

The investigations showed that it is possible to obtain dense sintered material only at a temperature exceeding the melting temperature of composite powder matrix by 30–50°C. The matrix is mainly quasibinary TiB_2 -Fe eutectic (≈ 92.0 mass% of Fe) with a melting temperature $T_m \approx 1340^\circ\text{C}$. Thus, the compaction of TiB_2 -Fe composite powders occurs with participation of a liquid phase, i.e., it proceeds under conditions of liquid-phase sintering.

Investigations of sintering also showed, that the sintering conditions for obtaining of dense hard alloys with comparable properties from CP-1 and CP-2 differ in temperature and holding time. Thus, in order to obtain CP-2 material with maximum density and hardness higher temperatures and longer holding times in comparison with powders of the first type CP-1 (~ 1450 and 1600°C , 40 and 60 min, respectively) are necessary.

Distinctions between conditions of CP-1 and CP-2 sintering are, perhaps, embedded in the nature of the products, obtained during SHS. As already noted, the main phases in SH-synthesized products of Ti-B-Fe system are TiB_2 and α -Fe for both types of charge. However, FeB, Fe_2B , FeTi, etc. are present in some products. The amount of these phases is usually larger in products, obtained from SHS using ferroboron alloys with titanium. These phases form low-temperature eutectics, which make a contribution to the process of liquid-phase sintering of SHS composite TiB_2 -Fe powders. Comparison of microstructures of the SHS powders and the sintered samples shows that the morphology of TiB_2 crystals changes on sintering, becoming more oval. Such change in the morphology of TiB_2 crystals is the result of recrystallization of refractory particles from the molten matrix (Fig. 7).

Physico-mechanical characteristics of sintered compacts from TiB_2 -Fe SHS powders are mainly determined by the degree of compaction. Investigations showed, that samples, sintered from the composite powder of composition TiB_2 :Fe = 52:48 mass% at 1450°C and a holding time of 60 min, have the best properties. In further investigations, connected with practical use of the developed SHS powder, the powder of mentioned composition was selected as basic one. Hard alloy, sintered according to the mentioned conditions had the following properties: HRA ≈ 85 , strength limit on bending = 1200 MPa, relative density $P_{\text{rel}} \sim 98\%$ of theoretical density.

The effect of Cr and Ni additives as well as Ni-Cr (20 Ni, 80 Cr) alloy on the sintering of composite powders of the Ti-B-Fe system and their properties was also studied in the work. Nickel in amounts up to 5.0 mass%

exerts an activating effect on sintering allowing a reduction of the sintering temperature to 1400°C . More hard double boride $(\text{TiCr})\text{B}_2$ forms in sintered products on addition of chromium. In this case higher sintering temperatures— 1550 – 1600°C are necessary to obtain dense material.

Experiments using the NiCr (20 Ni, 80 Cr) alloy powder showed a similar effect to nickel.

6. The effect of mechanical activation on phase composition and structure of sintered composite material on the base of SHS titanium diboride

Mechanical activation (MA) of the composite TiB_2 -Fe powder was conducted in order to reduce the temperature and the time of sintering of SHS composite TiB_2 -Fe powder and also to enhance the operation properties of sintered materials together with chemical activation (introducing of minor amounts of additives of various substances).

SHS composite powder of the composition of 52 mass% TiB_2 + 48.0 mass% Fe with average grain size of 200 μm was subjected to mechanoactivation. MA was carried out in a planetary mill MPV (centrifugal acceleration $g = 65 \text{ m}^2/\text{sec}$) with water cooling. Volume of the steel drums was 1000 cm^3 , the diameter of steel balls was 0.3–0.4 sm. Interrelation of balls mass to the powder mass was 20:1. The medium of activation was argon, alcohol, gasoline. Grinding time was 15, 30 and 60 min.

Investigations conducted showed, that intense mechanical treatment of TiB_2 + Fe SHS powder increases their activity during sintering. The powders, activated through grinding are easily pressed without a binder and the sintering temperature is reduced by 70– 100°C .

Mechanical activation of TiB_2 -Fe SHS powder in gasoline led to the change of phase composition in sintered samples. According to X-ray phase analysis in sintered samples, titanium carbide TiC and iron boride Fe_2B are present apart from TiB_2 and α -Fe.

The microstructure of samples, sintered from starting TiB_2 -Fe SHS powder with a particle size less than 100 μm (Fig. 8a) and activated for 30 min in gasoline (Fig. 8b) are presented in Fig. 8. Both samples were sintered for 60 min at 1300°C . The sample, sintered from the starting SHS powder is porous consisting of starting grains of powder, sintered at contacts. According to X-ray phase analysis only TiB_2 and α -Fe are present. In the microstructure of the sample, sintered from the powder activated in gasoline, a grey-coloured phase appeared, the size of which is not more than 2 μm and the volume portion is $\approx 20\%$. According to the X-ray and micro X-ray spectral analyses data the grey-coloured phase is titanium carbide.

The experimental data speak about complex physical-chemical phenomena, proceeding during MA of TiB_2 -Fe SHS powder in gasoline. The formation of new TiC and Fe_2B phases in sintered products; high density ($\approx 99\%$ of theoretical one) and hardness (HRA ≈ 85 – 90) are the result of these phenomena.

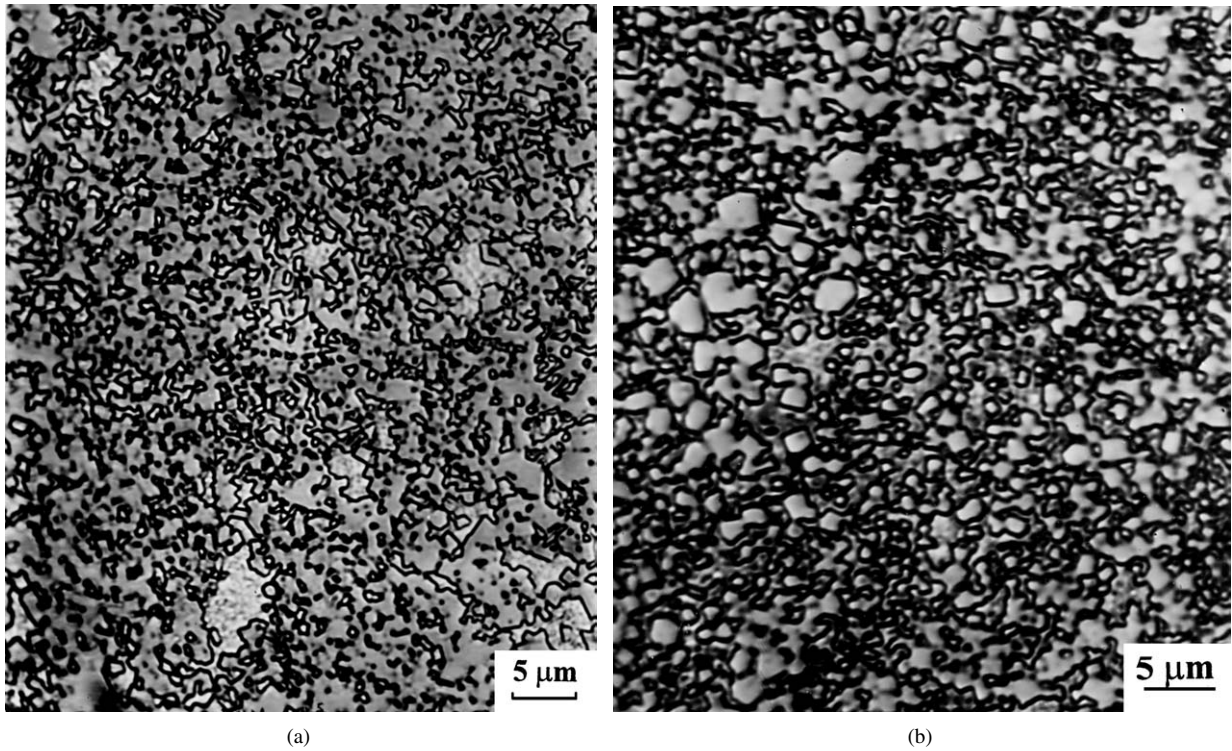


Figure 7 Microstructure of SHS composite TiB₂-Fe powder (a) and sintered alloy (b).

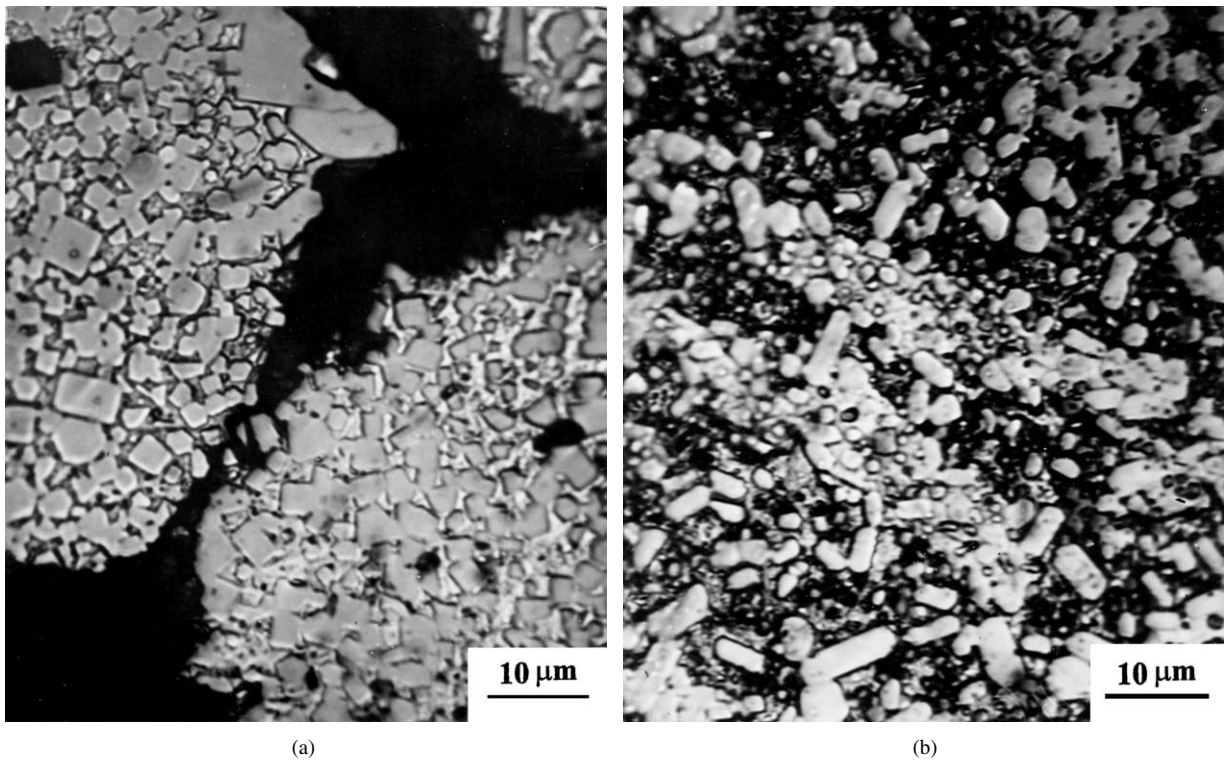


Figure 8 Microstructures of sintered samples from SHS composite TiB₂ + Fe powder before (a) and after mechanical activation in gasoline (b).

7. The possibility of using TiB₂-Fe SHS composite material as hard facing material

The method of electron beam surfacing (EBS) was used to evaluate the possibilities of the developed powder as hard facing material. Structures of coatings from SHS composite powder TiB₂-Fe, deposited on a substrate of steel 3 (0.14–0.22 mass% C) with EBS [10] are presented in Fig. 9. The transition area between the substrate and the coating is shown in Fig. 9a. The

transition area includes the part of the base material with changed microstructure, a very narrow layer directly separating the substrate and the coating, which smoothly passes into the coating. Under selected conditions of coating deposition, the formation of the latter occurs as a result of intense interaction between composite TiB₂-Fe particles with a bath melt under action of electron beam. In the area, adjacent to the coated material, the dissolution of composite particles in the

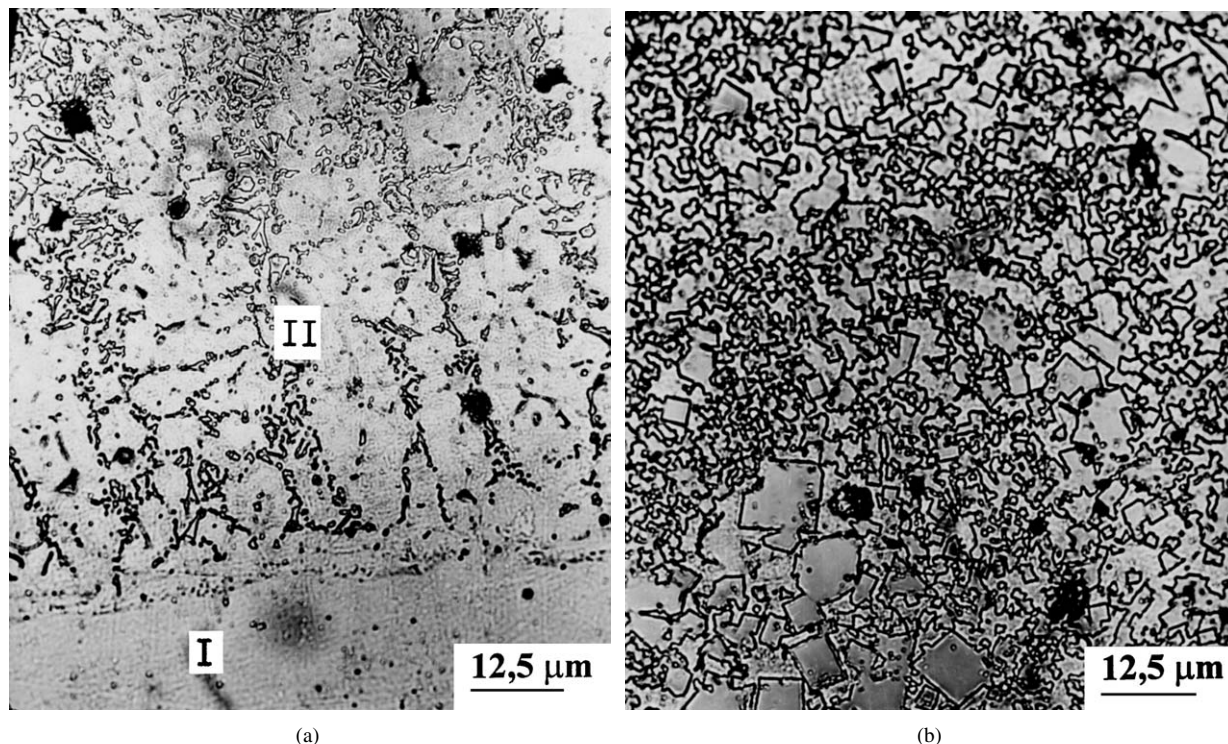


Figure 9 Microstructure of hard facing from SHS composite powder on steel 3: (a) at the interface and (b) hard faced layer. I—support steel 3; II—hard facing.

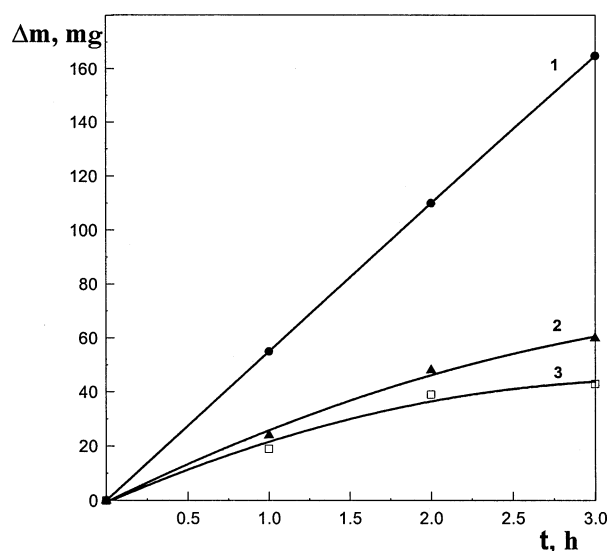


Figure 10 Wear of SHS composite coatings, deposited with electron beam hard facing method: 1—steel 45; 2—TiB₂-Fe; 3—TiB₂ + Ni.

metallic melt and its saturation with titanium and boron occurred. The degree of the dissolution of hard-facing material with the coated material decreases with increase in distance from the base to the coating surface. Micrographs of coating microstructures testify this fact.

TABLE II Relative wear resistance and hardness of coatings, faced with electron beam method

	Coating material	Hardness	K_w
1.	Standard steel 45	130 (HV)	1.0
2.	TiB ₂ -Fe	60 HRC	3.75
3.	TiB ₂ -Ni	64 HRC	8.50
4.	PG-US-25	59 HRC	3.20

Thus, in the region, adjacent to the coated material the coating microstructure corresponds to a solidified pre-eutectic melt of quasibinary cut of the binary phase diagram of Ti-B-Fe system. This area gradually passes into the area, the microstructure of which corresponds to crystallization of the eutectic melt TiB₂-Fe (7.8 mass% of TiB₂). As the distance from the steel substrate to the coating surface increases the coating microstructure consists of titanium diboride crystals, arranged in a eutectic matrix (Fig. 9b). The hardness, measured on the surface of the deposited layer was ~9.5–10.0 GPa.

Data on the wear behaviour of the hard-faced SHS material TiB₂-Fe in comparison with the standard (steel 45) are presented in Fig. 10.

Higher indexes of hardness and wear resistance were obtained when SHS composite powder TiB₂-Ni, which was made similar to TiB₂-Fe, was used as hard-faced material. In this case Ni-B alloy (17 mass% of boron) was used as one of the starting components. Experimental data on the wear behaviour of the coating from this powder are also given in Fig. 10.

Relative wear resistance (K_w) and hardness of coatings of the base of titanium diboride are presented in Table II. Thus, investigations conducted showed the possibility of preparing wear resistant coatings with electron beam hard facing using SHS powder mixtures based on titanium diboride.

8. Conclusion

The structure and phase composition of products of Ti-B-Fe system for two types of charge (1—the mixture of elemental Ti, B, and Fe powder; 2—the mixture of ferrobore alloys FeB with titanium) dependence on various SHS parameters were studied in

the work. Dense hard alloy with good properties: HRA ~83–90, strength limit on bending \approx 1200 MPa; wear resistance—at the bend level of tungsten-coating hard alloy WC-Co (15.0 mass% Co)—may be obtained by combination SHS with rolling (pressure).

Commercial ferrous alloys may be used to obtain SHS materials of Ti-B-Fe system. Their use does not lead to deterioration of the physical and mechanical properties of the finished products. At the same time the cost for production of SHS materials of the Ti-B-Fe system will be much less in comparison with the cost when using expensive elemental powders as starting materials.

Composite TiB₂-Fe powder, obtained with SHS may be recommended for production of parts of machines for construction and instrumental purpose by powder metallurgy methods as well as for deposition of protective coatings with methods of hard facing and deposition. By introducing minor amounts of nickel or Ni-Cr alloy one may influence the sintering conditions and obtain hard alloys with improved operation characteristics.

Preliminary mechanoactivation of SHS powder TiB₂-Fe results in the reduction of the sintering temperature by 30–70°C and decreases the isothermal holding time from 60 to 40 min. It was also found, that

mechanoactivation in gasoline leads to the change in phase composition of the sintered products.

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