

Chapter 2

Hard Titanium and Zirconium Boride Alloys and Items Manufactured from Them by SHS Compaction

2.1 Items Produced from Borides as an Alternative to Tungsten-Based Alloys

An area for the application of boride-based hard alloys has not yet been definitively established. These alloys seem to possess tremendous potential, however, for use in a number of industry sectors [1] and, in particular, for production of metal-working industry tools because of such important properties as high wear-resistance, chemical stability in many aggressive media, ability to retain mechanical strength at high temperatures, and high resistance to high-temperature oxidation.

One of the important R&D directions of materials science is the development of new effective methods for the production of tungsten-free hard alloys whose performance is comparable to or even exceeds that of tungsten-containing alloys. From this standpoint, transition metal borides can be considered quite promising candidates as components for production of desired tungsten-free hard alloys.

To date, the SHS method has been used to obtain over 200 different compounds (carbides, borides, nitrides, silicides, chalcogenides, intermetallides, and others) used for the manufacture of heat resistant refractory construction, tooling, electrotechnical, and other materials and parts capable of operation under extreme conditions [2, 3]. Additionally, some powders manufactured by the SHS method have been used as abrasive materials. One of the primary advantages of SHS is the potential it offers for direct production of items of a desired shape and size. In Refs. [4–10], an SHS-based method in conjunction with compaction of the combustion products for production of tungsten-free hard alloys from multicomponent mixtures of metal and nonmetal powders was proposed and developed. This method was used to manufacture tungsten-free hard alloys consisting of Ti (30) and TiB (70 %) known as STIM—a Russian acronym for “synthetic hard tool materials.” A number of new STIM alloys, SHS manufactured from titanium and

Table 2.1 Physical–mechanical properties of STIMs

Alloy grade	Composition	Density, g/cm ³	Mean particle size, μm	Hardness, HPA	Bending strength, kg/mm ²	Impact strength kg cm ²
STIM-1B/3	TiC; TiB ₂ ; Ni	4.94	5–7	93.5	70–80	0.09
STIM-2	TiC; Ni	5.5	5–7	90	100–110	0.15
STIM-2A/3	TiC; Ni	6.4	1–2	87	170–180	0.12
STIM-VB	TiC; Cr ₃ C ₂ ; Ni	5.37	3–5	92.5	90–100	0.09

carbon and binder metal (Ni, Mo, Cu, and some others, exclusive of the expensive Co), were developed. For some systems, additional reagents (B and Cr) were used.

The physical–mechanical properties of a number of STIMs are provided in Table 2.1 [10]. The SHS method can be used to produce both very hard (STIM-1B/3, 93–94 HRA) and high-strength (STIM-2A) hard alloys. In the case of liquid SHS products (melts), castings techniques are used to produce the desired items. The manufacture of cast items from refractory materials with melting points as high as 3000–3500 K is a unique challenge met by the advantages afforded by the SHS method [11].

The obtained results propelled further R&D work in the area of production of tungsten-free boron-containing hard alloys. Our team focused on the manufacture of systems based on titanium and zirconium borides and containing Ti or Zr as a binder, respectively [12–17].

The studied systems were selected on the basis of the following factors:

1. Borides of Ti and Zr are characterized by high hardness, a high melting point, and high heat resistance;
2. Borides of Ti and Zr are characterized by a narrow region of homogeneity and slight solubility in Ti and Zr. In other words, the components meet compatibility requirements;
3. Due to close thermal expansion coefficients (TEC) for Ti and Zr and their borides, the corresponding hard alloys should be characterized by a minimum value of “deformation-induced mosaicity potential” ($\Delta\alpha\Delta T$) [18] that is inversely proportional to the degree of thermal cycling stability of the material;
4. SHS reactions in the Ti–B and Zr–B systems are characterized by high temperatures and rates, and the released heat is sufficient to melt the metal binder; this ensures the conditions required for effective compaction of the hard alloy.
5. Our primary objectives were to study the potential of the SHS-compaction method for the production of large-size items from materials based on Ti and Zr borides and to determine their areas of application.

2.2 Transition Metal Borides

One overall disadvantage of boride-based hard alloys is their brittleness and insufficient thermal stability which is generally explained by certain features of transition metal borides [19]. Typically, intermetallic (electronic) phases exhibiting rather narrow homogeneity regions are characteristic for B–transition metal systems. Moreover, B and transition metals can form interstitial phases having rather wide homogeneity regions. The tendency for formation of boride phases increases from Ti (Zr) to Mo (W). Ti and Zr borides are similar to electronic phases while Mo and W borides exhibit a number of properties characteristic of interstitial phases.

Hägg found that if the atomic radius ratio of nonmetal (R_x) and metal (R_m) meets the condition $R_x/R_m < 0.59$ in transition metal and nonmetal alloys (C, B, N), the nonmetal atoms will occupy interstitial sites in the metal sublattice. If the radius ratio exceeds 0.59, interstitial phases with more complex structures will form [20].

Hägg phases (interstitial phases) belong to a small group of systems whose structural type depends on relative atomic sizes. Regular valent ratios are not characteristic for these phases. According to the results of an analysis of energy band structure, some p -electrons are transferred to the transition metal atoms. This accounts for the high binding energy and melting points of boron compounds [20].

Since the B atomic radius is 0.87 Å, zirconium ($R_x/R_m = 0.54$) and titanium ($R_x/R_m = 0.59$) alloys satisfy Hägg's condition.

Transition metal borides have various structures in which the bonds between B atoms play an important role. An increase in boron content in the boride phase results in an increase in B–B bond strength. The poor thermal stability of transition metal borides seems to be associated with the rigidity of their structure. An analysis of data on the thermal stability and physical–mechanical properties of refractory compounds allows one to conclude that the majority of boride-containing composites exhibit poor performance under thermocycling conditions. In this connection, an assessment of the potential of SHS for the manufacture of new boride-containing composite materials exhibiting high stability under cyclic thermal loading was of interest.

SHS yields products in various forms: one can synthesize powders, cakes, or melts depending on the ratio of combustion temperature to product melting point. In some instances, the temperature and heating rate in the combustion wave are extremely high, in which case SHS can be regarded as an extreme chemical process requiring the imposition of constraints on its application in industry [21, 22].

Depending on the aggregate state of SHS reagents, combustion processes can be divided into three types: solid–solid, solid–gas, and solid–liquid. Solid–solid systems include metal powder mixtures containing B, C, Si, S, and others. Mechanisms and patterns of gasless combustion in the Ti–B and Zr–B systems were studied in Refs. [23–31].

It was found that Ti interacts with B in the combustion mode in a wide range of B content in the charge mixture—from 8.3 to 56 wt%—which corresponds to the $\text{Ti} + 0.4\text{B}$ and $\text{Ti} + 5.7\text{B}$ systems. Two boride phases were observed for this system: TiB and TiB_2 —with orthorhombic and hexagonal structures, respectively. In Ref. [30], detection of an additional phase in the combustion product— Ti_3B_4 (with an orthorhombic structure)—is described. According to [27], the combustion product for $\text{TiB}_{0.4}$ – $\text{TiB}_{0.8}$ compositions consists largely of monoboride and free Ti. For $\text{TiB}_{0.9}$ – $\text{TiB}_{1.2}$ compositions, in addition to monoboride and free Ti, two new phases appear: Ti_3B_4 and TiB_2 . As boron content grows, monoboride disappears while the content of the diboride phase increases (due to a decrease in Ti_3B_4 content) until ultimately only the diboride phase can be found in the combustion products (Fig. 2.1 [32]). Additionally, phases Ti_2B and Ti_2B_5 have been described. The first of the two is an unstable high-temperature phase forming at 2200 °C as a result of a peritectic reaction and decomposing to yield TiB and Ti at $T > 1800$ °C. The second (Ti_2B_5) is stable only at $T > 2500$ °C.

In Ref. [30], it was demonstrated that the Ti–B system can be classified as a gasless combustion system and its combustion mechanism was proposed. In this system, the vapor tension of the reagents is quite low ($P_{\text{Ti}} = 8$ kPa, $P_{\text{B}} = 0.4$ kPa) even at the maximum combustion temperature (3190 K, which corresponds to SHS of TiB_2). The reagents melt in the warming-up zone where reactions do not occur. Most important for an understanding of the combustion mechanism is the occurrence of processes in a heated subzone characterized by a temperature ranging from 1950 to 2450 K. Ti melt wets hard particles of B and, due to surface tension force, spreads over their surface (effect of capillary spreading [31]). When the B melting point is attained, its particles are thus covered with a Ti melt layer.

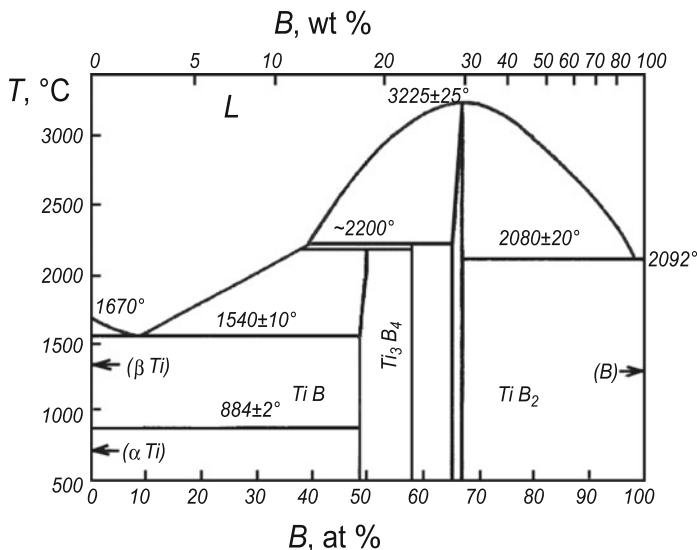
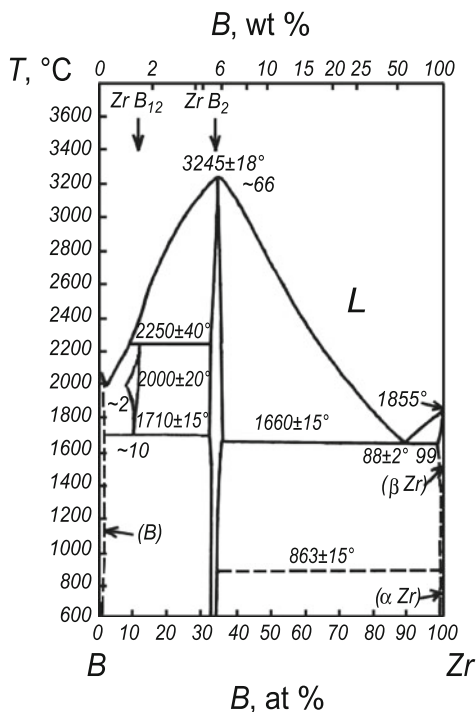


Fig. 2.1 Phase diagram for the Ti–B system

Fig. 2.2 Phase diagram for the Zr–B system



Accordingly, the diffusion process time is determined not by the Ti particle size but by the B particle size ($\leq 1 \mu\text{m}$ in the experiments under discussion [24]).

Zr reacts with B in the combustion mode where B content ranges from 6.5 to 37 wt%, which corresponds to $Zr + 0.6B$ and $Zr + 5B$, respectively. Three intermediate phases were found to exist in the Zr–B system: ZrB (10.60 % of B), ZrB_2 (19.18 % of B), and ZrB_{12} (58.74 % of B) [33–35]. Figure 2.2 is a phase diagram for the Zr–B system [34]. ZrB was not detected in the combustion products under normal conditions or during quenching of the product in liquid Ar [24]. A ZrB_2 phase was found in the combustion product for the samples used in the experiments. Where the amount of B in the initial reagent mixture is not sufficient for the formation of ZrB_2 , unreacted Zr is detected in the combustion product. In Ref. [24], the effect of the reagent ratio on the combustion rate in the Zr–B system was studied.

2.3 Structure of Powders

Reagent mixtures for SHS are composed of metal and nonmetal powders manufactured by various methods of powder metallurgy. These powders belong to a class of bulk (granular) materials that also includes constructional materials (cement, sand, gravel) and bulk produce (wheat, barley, rice, sugar, etc.).

Properties of these types of systems are studied within the framework of a special area of applied mechanics known as mechanics of granular materials [36].

The most obvious macroscopic characteristic describing the spatial arrangement of particles in granular material is the packing factor K , represented mathematically as the ratio of total particle volume (for one particle, v_i) to the volume of the entire system (V_0):

$$K = \frac{\sum v_i}{V_0}. \quad (2.1)$$

Various aspects of granular medium packing have been studied since ancient times. It is commonly known that when filling a volume with uniform granular material (all particles having the same size), the resultant porosity equals $\Pi = 1 - K = 0.36$, whereas mixtures comprising particles of significantly different sizes result in a marked increase of K in the system. Packing of granular materials cannot be described using an exact analytical approach. An analytical expression for the packing factor was not obtained even in the case of an equigranular system although its value was found and confirmed experimentally [37, 38]. Computer simulation widely used for the solution of this problem is also unable to provide a clear answer [39, 40]. One solid fact remains: the minimum porosity (Π) of a large-volume body irregularly and densely packed with identical spherical particles is not dependent on particle size and equals 0.36 %.

The structure (or spatial arrangement) of particles significantly influences the properties of the materials they comprise. Let us consider the structure of granular medium in greater detail.

The simplest structural model of granular medium is based on an assumption that all particles which comprise it are spheres (a spherical approximation). In a system model composed of spheres of the same size, one considers an ensemble of randomly packed hard spheres (steel balls, for example). The purpose of the model is to create a geometric image of a random structure and analyze the statistical patterns characteristic of its creation. As a perfect crystal is modeled by connecting sphere centers, so the obtained model provides an illustration of the spatial arrangement of the particle centers.

According to Bernal [41], there are two mutually exclusive ways to fill a space with materially identical spheres: ordered (regular) filling—which is characteristic for crystals—and disordered (irregular or random) filling—which is characteristic for granular materials.

A crystal model demonstrates the spatial arrangement pattern for atom centers, sets up distances between them, and determines corresponding volumes. The atom packing factor K uniquely determines the type and geometry of the crystal structure. For example, at $K = 0.68$, the atom centers are uniquely arranged in a body-centered cubic (bcc) structure, at $K = 0.74$, the most dense, close-packed hexagonal (hcp), and face-centered cubic (fcc) structures are formed, $K = 0.52$ corresponds to a simple cube, etc.

Similarly, a model of granular material composed of identical particles is supposed to describe an irregular spatial “network” of particle centers. In contrast to

the discretely changing K for regular structures, K for granular materials changes monotonously. The structure of bulk material is loose due to the presence of bridges and arch clusters. Determined experimentally, the lower limit of K for irregular random packing equals 0.59 [37, 42]. In this case, the medium is in an unstable equilibrium; any disturbance (shaking or vibration, for example) results in diminishing of interparticle pores and densification of the system. This can be explained by the tendency of the system to arrive at a state characterized by minimum potential energy attained at the minimum volume of the system (we often use this effect in our everyday lives). As mentioned previously, the upper limit of K (for a system composed of a number of identical spheres) is constant and equals 0.64.

Regular arrangement of particles corresponds to crystal structures possessing symmetry axes of orders II, III, IV, and VI. The most compact arrangement ($K = \frac{\pi}{\sqrt{18}} \approx 0.74$) corresponds to hcp or fcc structures. In the most compact packing, each sphere contacts two spheres. This type of arrangement, however, is not unique; 12 spheres can be in contact with a central sphere if they are located in the vertices of an icosahedron. These polyhedra are characterized by the fifth order of symmetry and cannot fill space in a regular manner (as regular polygons cannot cover a plane without creating overlaps or gaps, see Sect. 1.4). In the statistical sense, however, icosahedra can participate in the formation of irregular systems composed of uniform-sized particles.

Symmetry of the fifth order is characteristic for a dense irregular spatial arrangement of spheres. Bernal's statement can thus be rephrased as follows: two states—irregular and crystalline (regular)—represent types of the most compact spatial arrangement of uniform-sized particles.

In a regular crystal lattice, one is always able to identify a primitive cell with full Bravais lattice symmetry. This type of cell includes, for example, the Wigner–Seitz cell built by placing perpendicularly oriented planes across the midpoints of vectors connecting a randomly selected lattice point with the closest vicinal points. With its center in one of the lattice points, the obtained Wigner–Seitz polyhedron occupies a spatial domain such that the distance between any point of the domain and the central point is smaller than the distance between that point and any other point of the lattice.

The translation of this type of polyhedron results in the filling of an entire available space without leaving gaps or causing overlaps. A crystal can be treated as a regular ensemble of Wigner–Seitz cells. Obviously, the number of cell faces equals the coordination number which, in the regular crystal lattice, is constant for any point. In the case of an irregular structure, the concept of the coordination number has no strict physical meaning.

For a random close-packed system of particles, an ensemble of Voronoi polyhedra can be used to describe its structure. Voronoi polyhedra are irregular and nonidentical; they do not possess Bravais lattice symmetry. The coordination number for a regular structure is constant and determined by the number of adjacent physical structural elements while for an irregular structure, the coordination number cannot be constant and is determined by the number of surrounding physical and geometrical elements. This approach was used to describe

coordination polyhedra of Laves-type metal phases [43] and subsequently developed to describe the structure of irregular systems [44].

Voronoi polyhedra (ranging in number of faces from 13.3 [45] to 14 [46]) are thus the basic structural unit of a randomly close-packed medium. In this case, the majority of p -angular faces are pentagons. For a close-packed regular structure, a Voronoi polyhedron degenerates into a Wigner–Seitz cell in the form of a cub-octahedron with 12 faces, each sphere having 12 “neighbors,” whereas the number of “neighbors” for an irregular structure has a statistical meaning and changes within a considerably wide range [41]. The maximum of the corresponding function obtained by means of both mechanical modeling and analysis, however, yields the most probable coordination number—equal to 13.5—which suggests the predominance of the polygon face for the polyhedra.

In contrast to crystalline structures, whose coordination polyhedra are represented by regular (or Archimedean polyhedra), granular medium is characterized by irregularity of adjacent polyhedra. In granular medium, long-range order and symmetry do not exist. However, quasi-identical polyhedra fill the space. The tendency for statistically arranged particles to make up Voronoi polyhedra in the form of irregular convex polyhedra with 13 pentagonal faces indicates a trend for formation of particles into icosahedral groups. This stems from the fact that the dodecahedron and the icosahedron form a dual pair. For the icosahedral arrangement of points in space, the dodecahedron thus plays the role of a Voronoi cell for the central point. Points of contact between a dodecahedron and a sphere inscribed in it form an icosahedron and vice versa.

Mechanical modeling using steel balls of various sizes to study the properties of mixtures is commonly used to describe properties of granular materials. It is known that mixing spheres of different sizes results in an increase in packing density [47, 48] (Figs. 2.3, 2.4).

For two-component mixtures, K increases monotonously from $K = 0.64$ at $D = d$ (where D and d represent the diameters of the mixed spheres) tending to $K = 0.87$ at $\frac{D}{d} \rightarrow \infty$ (Fig. 2.5). The porosity of a two-component granular mixture composed of particles of significantly different sizes attains its minimum value when all pores between the large particles are occupied by small particles. In this case, small particles occupy 64 % of the total void volume between the large particles (spheres), and the porosity of the system in the $\frac{D}{d} \rightarrow \infty$ limit decreases to $\Pi = 0.13$ in the small sphere content of 26 vol %.

Obviously, not all varieties of behavior of real powder systems can be exhaustively described using spherical model patterns. This is due to the wide distribution of the real powder system particle size (10–20 %) and a significant morphological diversity of powders. As a result, their properties (size and shape of the particles, specific surface, flowability, packed density, compressibility, etc.) are quite unique for a specific system and can hardly be generalized. However, it was found that powders composed of spherical particles are less prone to the formation of bridges (bonds), have relatively high flowability and fill a volume to a rather high density. The packed density (i.e., weight of a unit of volume) for a real

Fig. 2.3 Packing factor for two-component mixtures with various ratios of component particle diameters as a function of component content with a larger particle [47]

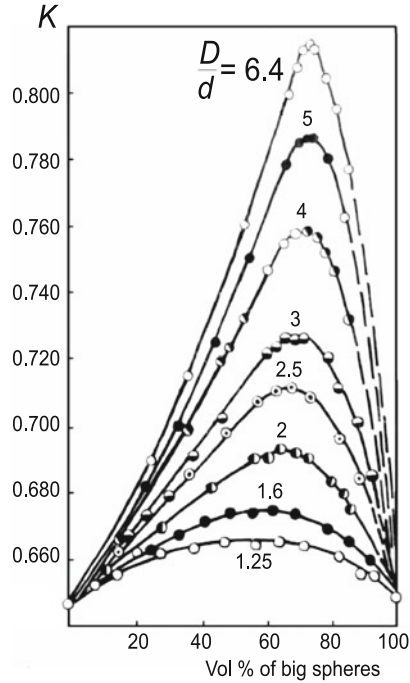
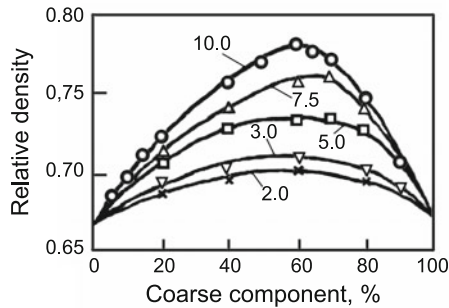


Fig. 2.4 The effect of particle size ratio (numbers along the curves) on relative tap density [48]

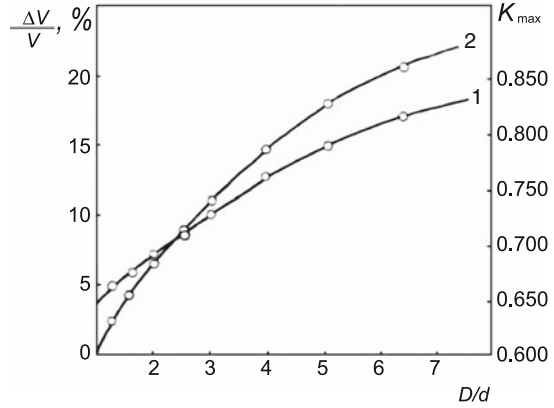


powder composed of spherical particles is higher than that of powder consisting of angular particles (which can be as low as 50 % of the density of the corresponding solid material). Flaky powders are characterized by especially low packed density, in some cases as low as 10 % of that of the corresponding solid.

Particle size does not significantly influence the packed density of powders composed of spherical particles, while the density of flaky powders markedly decreases with a decrease in particle size. This is explained by the fact that diminishing particle size produces an increase in the specific surface area, which in turn produces increased friction between particles (Table 2.2 [48]).

In Ref. [49], as a result of studying the statistical properties of Voronoi polyhedra formed in dissolved mixtures composed of two types of particles differing in

Fig. 2.5 Maximum packing factor (1) and relative compression (2) as functions of the ratio of the sphere diameter



size, the following expression was obtained for estimation of the coordination number in a system of spheres of different sizes:

$$Z = \frac{Z_0}{4} \left(\frac{D}{d} + 1 \right)^2, \quad (2.2)$$

where $Z_0 = 14$ is the coordination number of a mixture composed of identical particles ($D = d$).

These findings allow one to estimate the number of d -type particles participating in the formation of the local coordination of a D -type particle and imply that for mixtures including particles of different sizes, the number of dissimilar bonds is different at the beginning and end of the concentration interval.

Properties of real disordered systems are closely related to the number of dissimilar bonds Z_{1-2} (in other words, to the number of contacts between large and small particles). In Refs. [50, 51], the following expression was proposed for its calculation:

$$\frac{Z_{1-2}}{ZN_0} = \frac{1}{4} N(1-N)[\alpha^*(1-N) + \beta^*N] \quad (2.3)$$

where $\alpha^* = \left(1 + \frac{D}{d}\right)^2$, $\beta^* = \left(1 + \frac{d}{D}\right)^2$, D and d are the diameters of the mixed particles ($D > d$) and N is the fraction of the large particles.

Table 2.2 Dependence of the packed density of powders on particle size

Particle size, μm	150–100	100–75	75–50	50–40	<40
Packed density, g/cm^3					
Chromium–nickel steel (spherical particles)	4.5	4.5	4.5	4.5	4.3
Electrolytic iron	3.6	3.4	3.1	2.8	2.4
Reduced iron	2.15			2.08	1.87

The obtained results seem useful for the structural theory of granular media, particularly for explanation of some of the phenomena occurring in SHS considered below.

2.4 Effect of the Charge Particle Size on SHS

Phase composition and the quality of combustion product are determined by main parameters of SHS—combustion temperature and velocity and rate of hot product cooling. Combustion velocity and rate of cooling are influenced by many factors, among which the ratio of metal and nonmetal particle sizes may be one of the most important.

Let us consider the thermochemical grounds for the effect of reagent particle size on SHS for systems whose combustion can be described in terms of a classical model of solid flame [52].

If the metal and nonmetal particles are identical, their mixing results in the formation of a two-component uniform statistical mixture. In this case, interparticle contacts Z_{i-j} can be divided into three types: contacts between particles of the same nature: 1–1 and 2–2, and contacts between particles of a different nature: 1–2. In accordance with the laws of statistical physics, the entropy of such an irregular system can be expressed as

$$\Delta S = -R(N_1 \ln N_1 + N_2 \ln N_2), \quad (2.4)$$

and the probability of formation of bonds between identical particles is proportional to the component fraction N_i :

$$\frac{Z_{1-1}}{ZN_0} = N_1, \quad \frac{Z_{2-2}}{ZN_0} = N_2, \quad (2.5)$$

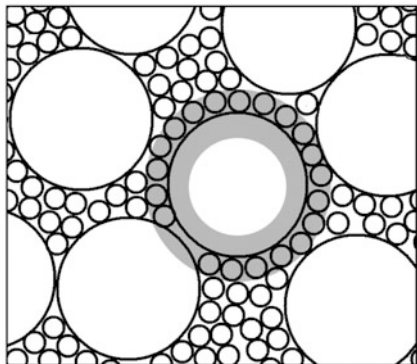
and the concentration dependence of the number of contacts between different particles Z_{1-2} is described by a symmetric parabola

$$\frac{Z_{1-2}}{ZN_0} = N_1 N_2, \quad (2.6)$$

where N_0 is the total number of particles in the system and Z is the coordination number for a particle. Z is constant in the entire concentration interval since all particles composing the system are the same size. As mentioned above, the maximum packing factor for uniform granular systems $K = 0.64$.

When mixing particles of different sizes, however, these patterns and relationships do not hold. As pointed out previously, a difference in the sizes of mixed particles produces an increase in K (Fig. 2.3), a change in the internal structure of the mixture (2.2), and an increase in the number of bonds between different particles (2.3) as compared with those of a uniform system. For better

Fig. 2.6 Schematic for powder structure model. $D > d$, layer thickness is $2d$, reaction layer thickness/small particle diameter ratio $n = 2$



visualization, let us imagine that a certain quantity of particles in an irregular system composed of identical particles is replaced by, in one case, the same quantity of particles of identical size though of a different “color” and in the other, by the same quantity of larger particles. In the first case, the number of “bicolor” contacts (or contacts between different particles) can be calculated by using statistical methods for ideal mixtures (2.6). In the second case, one can use formula (2.3), which describes the statistics of two-fraction systems.

Function (2.3) describes a set of asymmetrical parabola-like curves whose shift toward the component characterized by a smaller particle size is more pronounced for higher D/d ratios. If the difference in particle size of the mixed powders is quite significant, coefficient β^* in formula (2.3) becomes negligible. One can, therefore, assume that the number of “bicolor” contacts decreases in proportion to $(1 + \frac{D}{d})^2$.

It would be reasonable to assume that the SHS pattern may be influenced by the number of “bicolor” contacts. Let us consider an ideal close-packed set of metal and nonmetal particles (Fig. 2.6). For such systems, the particle size of metal powder (D) is usually one to two orders of magnitude higher than that of nonmetal powder (d), i.e., $D \gg d$. SHS can be imagined as follows: in an elementary volume of the reaction zone, a reaction resulting in combustion products (boride, carbide, and silicide) is initiated in “bicolor” particle contacts. The released reaction heat melts the metal particle and is transferred further, warming adjacent charge layers. The molten metal wets the newly formed solid combustion products and penetrates (according to the mechanism of capillary spreading [31]) to the next layers of warmed-up reagents, reacting with them. The combustion wave thus spontaneously propagates along the sample. The liquid phase ensures effective contacts between the reagents and facilitates heat and mass transfer, resulting in activation of combustion.

The combustion mechanism we have considered, implies the influence of the number of heterogeneous (metal–nonmetal) contacts on the progress of combustion; an increase in the number of heterogeneous contacts seems to result in an increase in the intensity of SHS. As mentioned above, the number of heterogeneous

contacts increases in proportion to $(1 + \frac{D}{d})^2$ while at the same time, the volume of the metal particle increases in proportion to $(\frac{D}{d})^3$, resulting in an increase of the heat required to melt it. Thus, the ratio of the reaction thermal effect (Q_r) to the heat necessary to melt the metal particle (Q_m) determines the SHS route.

The reaction is initiated on the surface of a metal particle at its contact with smaller nonmetal particles. Let us assume that the reaction propagates through n layers where the thickness of each layer is equal to a small particle diameter d . Reaction thermal effect can then be represented by

$$Q_r = \pi D^2 n d \gamma_p \Delta H_r^*. \quad (2.7)$$

This heat is consumed when the metal particle is melted and the surrounding area is warmed.

The heat required to melt the metal particle is

$$Q_m = \frac{\pi}{6} D^3 \gamma_m \left[C_p^*(T_m - 298) + L_m^* \right], \quad (2.8)$$

where γ_p and γ_m are densities of the product and pure metal, respectively, ΔH_r^* is the specific thermal effect of reaction $nM + mN = MnNm$, C_p^* is the mean specific isobar heat of the metal at a temperature ranging from 298 K to T_m , and L_m^* is the specific heat of metal fusion. Rewriting Eqs. (2.7) and (2.8) as

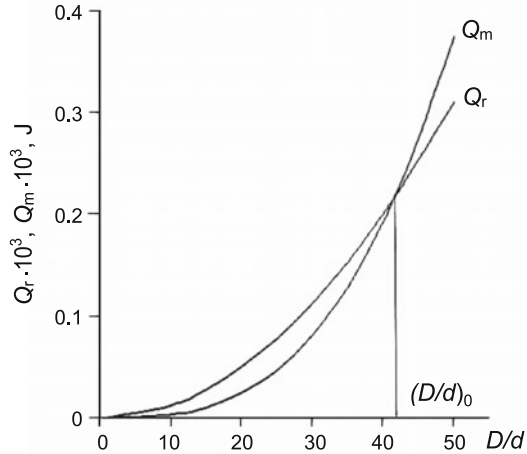
$$Q_r = \pi n \gamma_p \Delta H_r^* \left(\frac{D}{d} \right)^2 d^3, \quad Q_m = \frac{\pi}{6} \gamma_m \left[C_p^*(T_m - 298) + L_m^* \right] \left(\frac{D}{d} \right)^3 d^3, \quad (2.9)$$

one obtains expressions defining the relationship between Q_r and Q_m and D/d for the reagent mixture. Constants $A_1 = \pi n \gamma_p \Delta H_r^*$ and $A_2 = \frac{\pi}{6} \gamma_m \left[C_p^*(T_m - 298) + L_m^* \right]$ are uniquely determined by the thermochemical parameters and properties of a given metal–nonmetal couple. In a general case, function (2.9) is determined by constants A_1 and A_2 . If $A_1 \leq A_2$, then Q_r , as a quadratic function of D/d , is always lower than Q_m , which is a cubic function of D/d . In other words, the heat required to melt a metal particle exceeds the reaction thermal effect at any values of D/d and, SHS cannot occur. At $A_1 > A_2$, Q_r becomes greater than Q_m in a certain interval of D/d and SHS can occur. The larger the A_1/A_2 ratio, the wider the D/d interval.

Obviously, the condition $Q_r > Q_m$ (given the invariability of all other factors—mixture composition, pressure, relative density, etc.) determines the threshold state of combustion. Equating (2.7) and (2.8), one determines the upper limit ratio of the charge component particle size at which combustion can propagate in the form of a wave (for values exceeding the limiting value, combustion self-propagation does not take place):

$$\left(\frac{D}{d} \right)_0 = \frac{6n\gamma_p \Delta H_r^*}{\gamma_m \left[C_p^*(T_m - 298) + L_m^* \right]} = \frac{A_1}{A_2}. \quad (2.10)$$

Fig. 2.7 Dependence of Q_r and Q_m on the charge component particle size for the Ti–B system



A_1/A_2 determines the limiting value of $(D/d)_0$. Assuming that the reaction occurs in two layers ($n = 2$) (Fig. 2.6), this is illustrated in Fig. 2.7 for the Ti–B system. In this case, still preserving a generalized approach, one can assume $d = 1 \mu\text{m}$. For $d \neq 1 \mu\text{m}$, one arrives at similar expressions in the d^3 scale.

Specific heat for the reaction $\text{Ti} + \text{B} \rightarrow \text{TiB}_2$ is $\Delta H_r^* = 4.65 \cdot 10^3 \text{ J/g}$, mean specific isobar thermal capacity of Ti $C_p^* = 0.61 \text{ J/gK}$ and specific melting heat $L_m^* = 305 \text{ J/g}$ [53]. Taking into account that $\gamma_{\text{Ti}} \approx \gamma_{\text{TiB}_2} = 4.5 \text{ g/cm}^3$ and using Eq. (2.10), one obtains $D/d = 43$.

The interval $1 < D/d < (D/d)_0$ increases with an increase in A_1/A_2 . Absolute values of A_1 and A_2 determine the absolute difference $Q_r - Q_m$. When D/d is small or in the vicinity of the threshold value, the difference $Q_r - Q_m$ decreases and synthesis efficiency decreases. This explains the experimentally determined rule according to which the particle size of metal powders (D) used in successful SHS should be significantly lower than that of the nonmetal components (d). In the case of the opposite particle size ratio, SHS does not take place despite the fact that the concept of heterogeneous contacts remains valid.

The thermochemical parameters of some systems [53] and the threshold value of $(D/d)_0$ calculated using (2.10) are presented in Table 2.3.

Data obtained using the approach described above are approximate given that the model used for this method significantly simplifies the structure of a real powder; a real powder is characterized by a more complex morphology and greater particle diversity. In reality, the particle size of a powder of a certain brand is characterized by 20–30 % variation. In addition, powder particles have a well-developed rough surface as compared with the smooth surface of the spherical model particle. The surface area of a real particle can therefore be significantly greater than that of a sphere of the same volume. This implies an increase in the number of heterogeneous contacts (and hence an increase of Q_r).

Table 2.3 Calculation of parameters characteristic for threshold state for some systems

Synthesis product	$\Delta H_f, \text{kJ/g}$	$L_m^*, \text{kJ/g}$	$C_p^*, \text{J/gK}$ at 298– T_m	Metal melting point, T_m, K	Density, g/cm^3		$A_1 \cdot 10^3, \text{J/cm}^3$	$A_2 \cdot 10^3, \text{J/cm}^3$	$A_1/A_2 = (D/d)_0$
					Metal	Compound			
1	2	3	4	5	6	7	8	9	10
TiB ₂	4.65	0.305	0.611	1941	4.51	4.50	126	2.95	43
ZrB ₂	2.87	0.211	0.309	2130	6.49	6.10	105	2.52	42
CrB ₂	125	0.402	0.643	2148	7.14	5.60	42	5.65	7
NiB	1.44	0.292	0.541	1726	8.90	7.39	64	4.73	14
TiC	3.06	0.305	0.611	1941	4.51	4.25	78	2.95	26
ZrC _{0.96}	1.96	0.211	0.309	2130	6.49	6.40	75	2.52	30
VC	1.59	0.328	0.656	2173	6.10	5.36	51	4.75	11
Ti ₅ Si ₃	1.78	0.305	0.611	1941	4.51	4.32	46	2.95	16

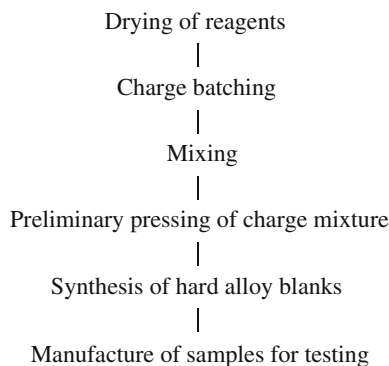
If the nonsphericity of particles is taken into account using the method of the equivalent sphere [54], for example, calculated values of $(D/d)_0$ are higher than those estimated when using expression (2.10). The threshold ratios of component particle sizes for real powders, thus always exceed those estimated by using formula (2.10).

2.5 Reagents and Manufacturing Process for Production of Hard Alloys Based on Titanium and Zirconium Borides

Experimental data for SHS in the Ti–B and Zr–B systems were analyzed using the “solid flame” model considered in the previous section. The following reagents were used in the experiments:

- Amorphous B, brown, particle size $\leq 1 \mu\text{m}$, B content $\geq 94.0 \text{ wt\%}$, elemental B $\geq 92.5 \text{ wt\%}$;
- Ti powder (PTM brand), particle size $40 \mu\text{m}$, main component content $\geq 99.1 \text{ wt\%}$;
- Ti powder (PTK brand), particle size $100 \mu\text{m}$, main component content $\geq 99.1 \text{ wt\%}$;
- Zr powder (PTsRK brand), particle size $\sim 90 \mu\text{m}$, active Zr content $98.6 \text{ wt\%}$;
- Steel St45 powder (sifted waste product of bar steel milling), particle size $100 \mu\text{m}$;
- Cu powders (particle size $\sim 50 \mu\text{m}$, main component content $\geq 99.3 \text{ wt\%}$), Mo (particle size $\sim 40 \mu\text{m}$, main component content $98.89 \text{ wt\%}$), and Al (particle size $50 \mu\text{m}$, main component content $99.2 \text{ wt\%}$).

General flow chart for the production of hard alloys by SHS compaction



Ti, Zr, Al, Mo, and Cu powders were dried in a vacuum drying chamber at 60–70 °C at a maximum residual pressure of 1 mm Hg for 10–12 h. The B powder was dried at 150–180 °C for 24 h. The components were placed into a steel cylindrical-hard alloy ball mill and mixed for 40 h (rate of roller rotation was 43 rpm). The charge was pressed in a press-die (68 mm in diameter) using a hydraulic press (press tonnage 98 kN).

Hard alloy blanks were synthesized using an installation consisting of a reaction press-die, a hydraulic press (1500 kN), and an automatic control panel. The reaction press mold (105 mm in diameter) (Fig. 2.8) was placed on the press work surface. Its base was filled with quartz sand. The initiating coil was inserted through the side power points.

Process parameters (initiation duration, pressing delay, and pressing duration) were set on the control panel. Pressure values for preliminary pressing and compaction of the still hot porous SHS product were set on the press contact pressure gauge. Process parameters for the Ti–B and Zr–B systems are presented in Table 2.4.

Fig. 2.8 Reaction press mold for the manufacture of hard alloys by SHS compaction: 1 W initiation coil, 2 charge tablet, 3 heat insulator, 4 press mold tray, 5 guide cylinder, 6 puncheon with gas flues, 7 gas flues

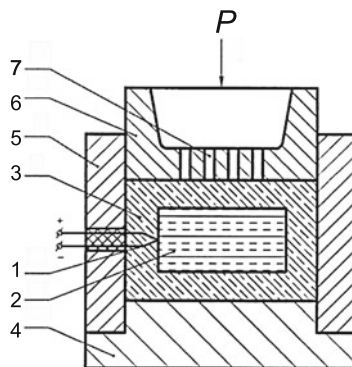


Table 2.4 Parameters for synthesis of hard alloys for systems Ti–B and Zr–B

	Stage	System	
		Ti–B	Zr–B
1.	Initiation duration, s	0.5	0.5
2.	Compaction delay duration, s	1–14	0.5–8
3.	Compaction duration, s	1.0–15	0.5–10
4.	Prepressing pressure, kg/cm ²	60–80	60–80
5.	Compaction pressure, kg/cm ²	200–1000	150–1400
6.	Initiation voltage, V	20–25	20–25

**Fig. 2.9** Blanks manufactured by SHS compaction

Photographs of the blanks produced by SHS compaction are presented in Fig. 2.9. To eliminate internal stress, the blanks were annealed in an electric oven at 800 °C for 2 h.

The annealed blanks were mechanically processed, i.e., polished using diamond polishing wheels on a high-precision plain grinder and cut to obtain samples for physical–mechanical analysis and parts for production of final product.

2.6 Pattern Formation of Final Combustion Product for the Zr–B and Ti–B Systems

When used for direct one-stage production of hard alloys, the SHS compaction method completely eliminates from the production process such energy-intensive intermediate stages as the crushing and grinding of synthesis products. To ensure optimal characteristics and performance parameters, SHS hard alloys should have

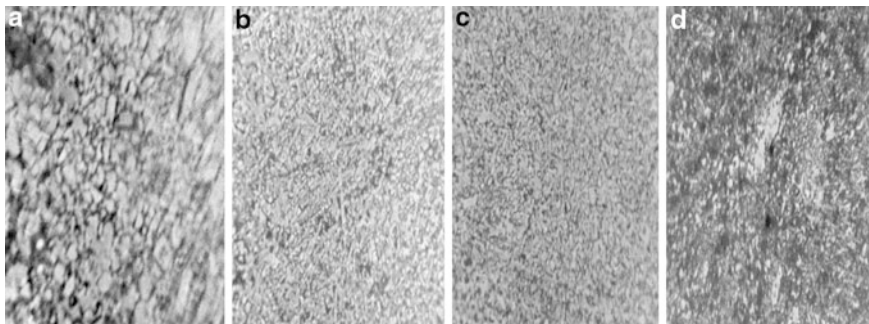


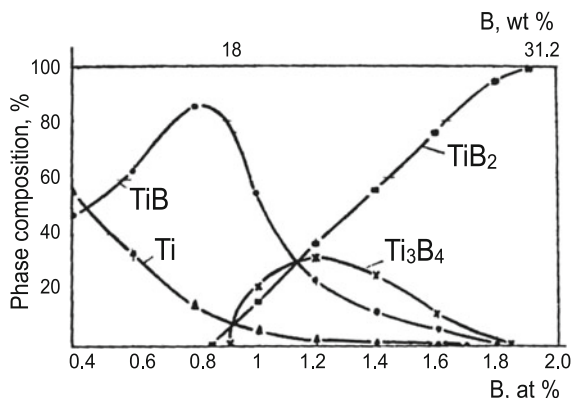
Fig. 2.10 Microstructure of ZrB_2 (a) and alloys— $\text{ZrB}_2 + 20\% \text{ Zr}$ (b) $\text{ZrB}_2 + 30\% \text{ Zr}$ (c) and $\text{ZrB}_2 + 50\% \text{ Zr}$ (d) (Magnification 700x)

not only the desired chemical and phase composition, but also a highly dispersed and uniform structure. For this reason, the study of phase formation in systems used for the manufacture of SHS hard alloys is of particular interest.

X-ray phase analysis revealed that combustion in the Zr–B system (B content ranging from 6.5 to 19.5 wt%) yields zirconium diboride and solid solution of boron in zirconium [13, 14]. Formation of the solid solution was confirmed by a measurement of zirconium microhardness equaling 950 kg/mm^2 , which agrees with the literature data. According to [55], the microhardness of zirconium increases from 120 to 1150 kg/mm^2 with the dissolution of up to 2.81 wt% boron. Combustion of the stoichiometric $\text{Zr} + 2\text{B}$ mixture yields a single-phase product— ZrB_2 . The microstructure of pure zirconium diboride is shown in Fig. 2.10a. ZrB_2 grains are round in shape, particle size ranges between 12 and 15 μm . An increase in Zr content (binder) results in decreased particle size. With excess Zr content as high as 20 wt%, the grains of the boride phase become needle-shaped and range in length from 6 to 8 μm (Fig. 2.10b); this is characteristic for well-formed crystals of B-transition metal compounds. A further increase in excess Zr content produces rounding of the grain and a significant decrease in mean particle size to 1–3 μm (Fig. 2.10c, d).

Change observed in the shape of the boride phase grains can be explained as follows: combustion of the stoichiometric Zr–B mixture at 3300 K [23] yields a single product— ZrB_2 . One might assume on the basis of thermodynamic analysis of the system [23] that the liquid phase fraction is approximately 20 % at adiabatic combustion of the stoichiometric Zr–B system. In reality, this fraction is much lower due to significant heat loss and crystallization of ZrB_2 grains occurs under conditions of liquid phase deficiency, which results in the formation of round grains. In the presence of excess Zr melt, the mechanism of growth of ZrB_2 grains changes. Due to the hexagonal crystal lattice, the growth rate of a ZrB_2 grain depends on a direction which leads to formation of needle-shaped crystals.

Fig. 2.11 Phase composition of Ti + B combustion product as a function of B content in the reagent mixture



A further increase in Zr content results in smaller grains and a transition from needle-shaped to round crystals. This seems to be associated with a decrease in the sample temperature which in turn reduces the grain growth rate.

Phase formation in the multiphase Ti–B system is far more complex [12]. Ti + B combustion product phase composition as a function of B content in the charge (8.5–31.2 %) is presented in Fig. 2.11. Near the lower concentration limit, the combustion product contains TiB and Ti phases which form a eutectic. The formation of the eutectic is confirmed by the characteristic microstructure for alloys of this type (Fig. 2.12a). As the B content in the reagent mixture increases (within a given concentration range), the alloy microstructure changes, and the formation of TiB grains (particle size ranging from 1 to 50 μm depending on the product composition) is observed (Fig. 2.12b). The maximum particle size for this phase corresponds to its maximum content in the final product.

In addition to single-phase TiB, combustion of the Ti + B (18 wt%) mixture yields phases Ti₃B₄, TiB₂, and a certain amount of unreacted Ti. The TiB content in the combustion product is 55 wt%. Formation of the aforementioned phases would seem to be associated with sample quenching via fast cooling since TiB₂ exists only at a high temperature in accordance with the corresponding region of the phase diagram for the Ti–B system (Fig. 2.1); the literature provides no information about Ti₃B₄.

A further increase in the B content of the charge (>18 wt%) results in an increase of Ti₃B₄ and TiB₂ phase content. Ti₃B₄ content reaches its maximum value at the initial B content of 24 wt% and then decreases. Single-phase product TiB₂ forms in the stoichiometric B content of the mixture. The TiB₂ particle size ranges between 1 and 10 μm (Fig. 2.12c).

It is worth mentioning that the TiB₂ phase forms not only on the interface but also inside TiB grains (Fig. 2.12d). Due to a high crystallization temperature, TiB₂ crystals precipitate from the liquid phase first and become crystallization centers

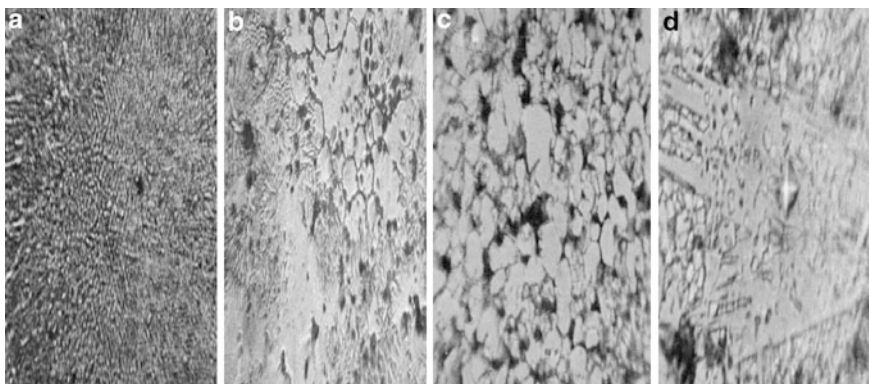


Fig. 2.12 Microstructure of hard alloys TiB + 40 % Ti (a) TiB + 15 % Ti (b) titanium diboride (c) and monophase Ti–B material (d) (Magnification 700x)

for TiB characterized by a lower melting point. As a result of this two-stage crystallization, TiB₂ grains are enveloped in the TiB phase.

Study of the formation of final combustion products in the Ti–B and Zr–B systems led to the discovery that a desired hard alloy final product can be obtained by varying the metal/B ratio in the reagent mixture. This is easier in the case of the Zr–B system, which always produces a two-phase combustion product: Zr diboride and solid solution of B in Zr. The situation is more complex for the Ti–B system. Combustion in this system yields several boride phases—TiB, TiB₂, and Ti₃B₄—which imposes constraints on the production of compact hard alloys. The binding metal content of a material is sufficient for effective compaction only if the process results only in the formation of titanium monoboride (initial B content is 8.5–15.2 wt%). At B content exceeding 15.2 wt%, the Ti binder content is not sufficient for the production of a hard alloy with a very low porosity (<1 %) due to the formation of a multiphase combustion product. From microhardness measurements it was concluded that the binding metal (Zr) in the ZrB₂–Zr system has a microhardness of 950 kg/mm² and the microhardness of the binder (Ti) for the TiB–Ti system is 200 kg/mm². This indicates the presence of a significant amount of dissolved B in Zr, which increases the microhardness of Zr. The solubility of B in Ti is apparently insignificant, which results in a negligible change in its ductility.

Metallographic analysis revealed that the size and shape of SHS-produced TiB–Ti and ZrB₂–Zr hard alloys are strongly dependent upon metal binder content. At a low content of metal binder, the material contains round grains (10–15 μm in diameter), while at higher binder contents the shape and size of crystalline grains change (Fig. 2.10). At a metal binder content ranging from 30 to 50 wt%, the material is characterized by a fine-grained structure (2–3 μm). It is therefore possible to obtain materials with hard phase grains of a desired shape and size by varying the metal binder content.

2.7 Physical–Chemical and Mechanical Properties of Hard Alloys Based on Titanium and Zirconium Borides

The main properties of hard alloys which determine the areas of their application are hardness, strength, ductility, thermal stability, and wear resistance. Additional important properties include corrosion stability, thermal conductivity, and electrical conductance. Determination of these properties is an important aspect of the characterization of developed and synthesized materials.

2.7.1 Bending Strength and Ultimate Compression Strength

Bending strength and ultimate compression strength of the synthesized materials were determined using $5 \times 5 \times 35$ and $3 \times 3 \times 5$ mm samples, respectively, and a universal Instron-1195 testing machine. Bending strength was calculated as an average of 10 independent measurements for 10 samples.

Bending strength and ultimate compression strength as functions of binding metal (Ti or Zr) content are presented in Fig. 2.13 [14, 56]. The dependencies exhibit pronounced maxima. The TiB–Ti-based material exhibits its maximum strength ($\sigma_b = 1200$ MPa, $\sigma_c = 3100$ MPa) at a Ti content of 45 wt%. For the ZrB₂–Zr-based material, maximum strength parameters ($\sigma_b = 540$ MPa, $\sigma_c = 2200$ MPa) are reached at a Zr content of 30 wt%. The unusual behavior of these systems as compared with the standard correlation between composition and strength properties characteristic of hard alloys—a decrease in both σ_b and σ_c with increased binding metal content (>45 wt%)—is accounted for by the decrease in combustion velocity for these systems (Table 2.5). As a result, isothermal conditions of the compaction process are violated; this prevents the synthesis of alloys with minimal residual porosity (<1 %).

Fig. 2.13 Bending strength (dotted lines) and ultimate compression strength (solid line) of ZrB₂–Zr 1 and TiB–Ti 2 as functions of metal binder content in the charge

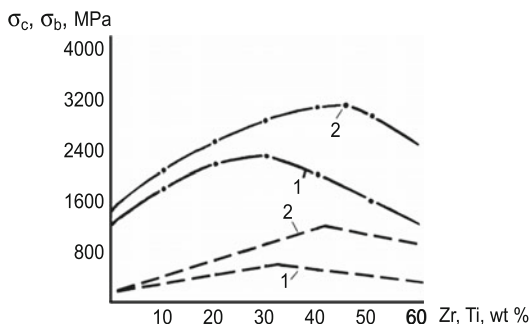


Table 2.5 Combustion temperature and velocity for the $\text{ZrB}_2\text{-Zr}$ and TiB-Ti systems

System	Combustion temperature, T_c , K	Combustion velocity, U_c , cm/s
$\text{TiB} + \text{Ti}$ (10–50 wt%)	2400–2000	3–1
$\text{ZrB}_2 + \text{Zr}$ (10–50 wt%)	3100–2800	11–6

2.7.2 Hardness

Sample hardness was measured using a Rockwell hardness tester with a pyramid-shaped diamond indenter at a load of 60 kg (Five indentations were made on each sample).

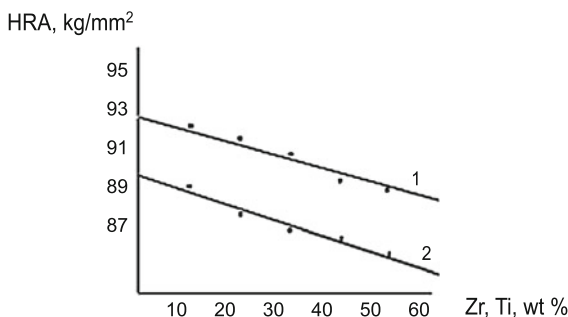
The hardness of TiB-Ti and $\text{ZrB}_2\text{-Zr}$ alloys with various contents of the metal binder was measured in a manner similar to that used for carbide-based hard alloys such as WC-Co . The hardness of the $\text{ZrB}_2\text{-Zr}$ alloys exceeds that of the TiB-Ti alloys (Fig. 2.14) although microhardness values for their components are quite similar (2250 kg/mm^2 for ZrB_2 and 2200 kg/mm^2 for TiB). The difference in the hardness of these alloys is explained by the higher solubility of B in Zr compared to that in Ti. The role of the binder in the $\text{ZrB}_2\text{-Zr}$ alloys is played by a solid B solution in Zr (rather than by pure Zr) whose microhardness (950 kg/mm^2) significantly exceeds that of a solid B solution in Ti. Due to the negligible solubility of B in Ti (0.5 wt%), the microhardness of the latter barely changes.

2.7.3 Thermal Stability

Thermal stability was studied using $12 \times 12 \times 5 \text{ mm}$ samples heated to 1000°C which were maintained at this temperature for 5 min and then cooled in water to room temperature. Thermal stability was determined as the number of heating–cooling cycles (ξ) performed prior to sample destruction. Five plates were tested for each composition.

For the manufacture of hard alloys exhibiting good resistance to thermal shock, the following requirements should be met:

Fig. 2.14 Hardness of the $\text{ZrB}_2\text{-Zr}$ 1 and TiB-Ti 2 alloys as a function of the binder content



- coefficients of thermal expansion for the hard phase and ductile binder should be quite close;
- components of the synthesized material (particularly the metal binder) should be characterized by high strength.

Taking into account these requirements, we selected the TiB–Ti, ZrB₂–Zr, and TiB–Ti–ZrB₂ systems. The resultant synthesized materials exhibited a high thermal stability which confirms the correctness of the component selection criteria.

In the simplest case, thermal stability of hard alloys (ξ) can be estimated as a ratio of metal binder strength to the amplitude of stress resulting from thermal cycling;

$$\xi = \frac{\sigma_b}{E_b(\alpha_1 - \alpha_2)\Delta T}, \quad (2.11)$$

where σ_b is the ultimate tensile strength of the metal binder, E_b is the elasticity coefficient of the metal binder, α_1 and α_2 are thermal expansion coefficients of the binder and hard phase, respectively, and ΔT is the amplitude of temperature fluctuations.

Thermal stability data on thermal stability calculated using formula (2.11) and experimental data on the number of thermal cycles prior to sample destruction (ξ) for a number of hard alloys containing 30 wt% metal binder are given in Table 2.6.

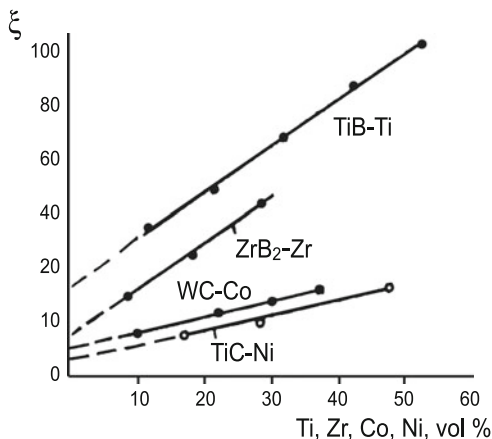
Both the experimental and calculated data demonstrate that thermal stability for the TiB–Ti, ZrB₂–Zr hard alloys is higher than that of traditional commercially available hard alloys based on the TiC–Ti and WC–Co systems. This provides additional confirmation of the assertion that an alloy’s strength is strongly dependent upon the closeness of the thermal expansion coefficients of its components—the ductile metal binder and hard phase.

Experimental data illustrating the effect of metal binder content on the thermal stability of TiB–Ti, ZrB₂–Zr, TiC–Ni, and WC–Co hard alloys are presented in Fig. 2.15. An increase in the concentration of the metal binder results in the growth of thermal stability of the alloys. This indicates the significant influence of strength (all other factors held equal) on resistance to thermal shock since the strength of hard alloys normally increases with an increase of metal binder concentration. The use of a boride-forming metal as a binder was found to ensure high thermal stability in the synthesized hard alloy material.

Table 2.6 Experimental and calculated data on the thermal stability of various hard alloys containing 30 wt% metal binder

Hard alloy	Calculated thermal stability	Experimental thermal stability
TiC–Ni	10	19
WC–CO	10	22
ZrB ₂ –Zr	20	54
TiB–Ti	40	72

Fig. 2.15 Thermal stability of hard alloys as a function of metal binder content



2.7.4 Heat Resistance

Heat resistance of the obtained materials was determined for $40 \times 40 \times 6$ mm samples which were heated to 500, 700, 900, and 1000 °C and maintained at these temperatures for some time in a muffle furnace and subsequently cooled in a desiccator. Heat resistance was determined from the sample weight increment (average of five experiments).

Oxidation of borides involves two processes: evaporation of boric oxide and formation of borates [57]. Boric oxide is characterized by a high volatility playing a significant role at low temperatures. At 1100–1300 °C, the formation of pyroborates of refractory metals which enhance the protective properties of the oxide film begins to dominate. This explains the exceptionally high heat resistance (oxidation resistance) of borides which exceeds that of carbides and nitrides in a number of cases. As a rule, borides of transition refractory metals are resistant to various aggressive media including acids, metal and salt melts, and hot gases. Because of these properties, borides of transition metals are considered quite promising for the manufacture of hard alloys.

The study of heat resistance-related behavior and patterns of hard alloys is quite interesting from both a theoretical and practical point of view in that it can result in the development of materials exhibiting exceptional performance.

Thermostating of the TiB–Ti, ZrB₂–Zr, and TiB–Ti–ZrB₂ hard alloy samples at 500–1000 °C for 50 h showed that their oxidation kinetics generally depends on alloy composition and temperature. The process is characterized by pronounced inhibition [13].

The weight increments for TiB–Ti system samples containing various amounts of Ti as functions of time exposure at different temperatures are presented in Fig. 2.16. At 500–700 °C, active oxidation is observed for the first 10 h, after which the dependencies reach plateaus. This behavior is explained by the formation of a protective oxide film on the surface of the samples. At 900 and

Fig. 2.16 Weight increment of the TiB–Ti alloy samples as a function of exposure time at different temperatures for TiB + 10 % Ti 1, TiB + 20 % Ti 2, and TiB + 30 % Ti 3

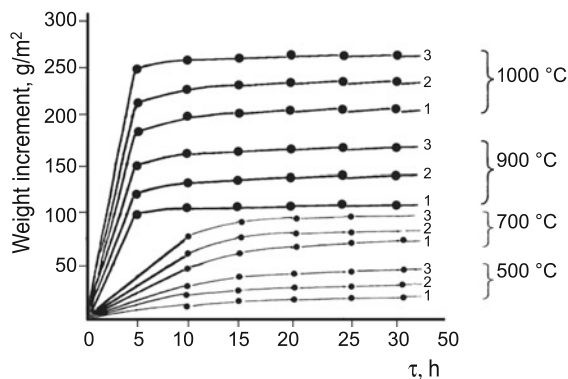
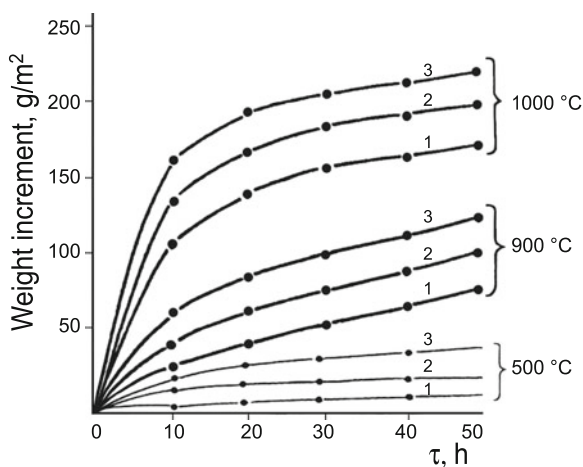


Fig. 2.17 Weight increments of the ZrB₂–Zr alloy samples as a function of exposure time at different temperatures for ZrB₂ + 10 % Zr 1, ZrB₂ + 20 % Zr 2, and ZrB₂ + 30 % Zr 3



1000 °C the film forms much faster—in 5 h, with no sample weight change observed thereafter. At lower temperatures (500–700 °C), it thus takes more time for the protective film to form and consolidate (approximately 20 h) while at high temperatures (900–100 °C), completion of the process takes much less time (5 h).

X-ray structural analysis revealed that the oxide film consists of TiO₂. An increase in Ti content in the analyzed alloys was observed to produce an increase in the TiO₂ content of the oxide film.

Weight increments for ZrB₂–Zr system samples containing various amounts of Zr as functions of exposure time at different temperatures are presented in Fig. 2.17. The active oxidation time of the sample surface for these alloys was found to be much longer than that of the TiB–Ti alloys and the effect of autoinhibition is less pronounced. This is explained by the loose and porous structure of the oxide film forming on the surface of zirconium-containing samples, and thus by the more active diffusion of oxygen through it.

As the content of the Zr binder in the ZrB₂–Zr alloys grows, their resistance to oxidation decreases.

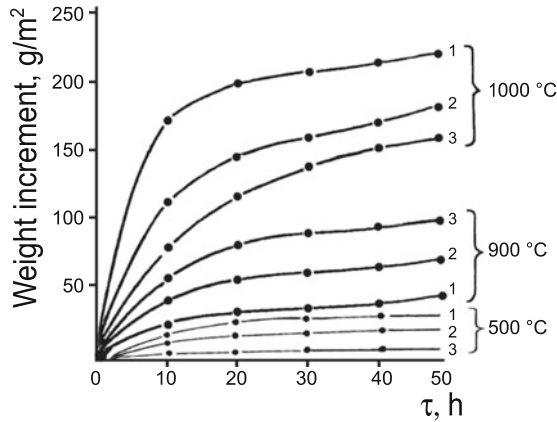


Fig. 2.18 Weight increments of the TiB–Ti–ZrB₂ alloy samples as a function of exposure time at different temperatures for (TiB–40 % Ti) + 10 % ZrB₂ 1 (TiB–40 % Ti) + 20 % ZrB₂ 2 and (TiB–30 % Ti) + 30 % ZrB₂ 3

Thus, it was found that a high-strength oxide film protecting the material surface from further oxidation does not form on the ZrB₂–Zr alloys. Their ability to resist oxidation is greater than that of the TiB–Ti alloys, however, which makes the ZrB₂–Zr alloys good candidates as a base for heat resistant materials.

Heat resistance of alloy consisting of TiB, 40 % Ti, and ZrB₂ additive was also studied (Fig. 2.18). The heat resistance of this material was observed to increase with an increase of ZrB₂ content.

For better understanding of the oxidation mechanism, a comparison of the oxidation kinetic curves of the studied alloys and pure metals was performed [58]. The sample weight increment was found to be proportional to metal binder content, which means that formation of the metal binder oxide significantly contributes to the sample weight increase. This conclusion is in strong agreement with the literature data on heat resistance of Ti and Zr borides [59].

Moreover, the oxidation processes of these three alloys were found to have rather close values of effective activation energy (≈ 42 kJ/mol), which correspond with activation energy for the diffusion-assisted mass transfer occurring at

Table 2.7 Heat resistance of industrial alloys and alloys under study

Composition	Weight increment for time of oxidation at 900 °C, %		
	5 h	10 h	15 h
66 % WC, 25 % TiC, 6 % Co	10	17.5	22
35 % WC, 60 % Ti, 5 % Co	8	14	17
94 % W, 6 % Co	17	–	–
TiB + 20 % Ti	10	12	12.5
ZrB ₂ + 30 % Zr	6	8	10
(TiB + 40 % Ti) + 20 % ZrB ₂	9	11	11

oxidation of composite materials. Heat resistance values for industrial alloys and the alloys under study (TiB–Ti, ZrB₂–Zr, and TiB–Ti–ZrB₂) are presented in Table 2.7.

Heat resistance values for the alloys under study approximate those of commonly used industrial alloys, and in some cases, even exceed them. The results of the studies prove the tremendous potential of hard alloys based on Ti and Zr borides for the manufacture of heat resistant materials.

2.7.5 Corrosion Resistance

For the study of corrosion resistance, 20 × 20 × 5 mm samples were exposed to sulfuric acid at 200 °C and to lithium vapor and melt. The degree of corrosion was estimated by the gravimetric method [60]. After mechanical removal of the corrosion products from their surface, the samples were washed in running water. Corrosion rate (g/m²) was calculated from the difference of the sample weight before and after the experiments.

The corrosion rate of the hard alloys in sulfuric acid at 200 °C increases with time (Table 2.8), which would seem to be associated with an increase in the material–medium interface area. The Ti–B alloys (containing various amounts of the Ti binder) exhibit a higher corrosion resistance in comparison with the ZrB₂–Zr and TiB–Ti–ZrB₂ alloys. As the content of the metal binder increases, the corrosion resistance of all studied alloys decreases. This indicates poor corrosion

Table 2.8 Corrosion resistance of hard alloys TiB–Ti, ZrB₂–Zr, and TiB–Ti–ZrB₂ in 10 % H₂SO₄ at 200 °C

Hard alloy composition	Corrosion resistance, g/m ² h	
	20 h	40 h
TiB + 20 % Ti	0.43	0.65
TiB + 30 % Ti	0.38	0.55
TiB + 40 % Ti	0.54	1.2
TiB + 50 % Ti	0.52	1.5
TiB + 60 % Ti	0.6	1.4
ZrB ₂ + 10 % Zr	1.2	1.6
ZrB ₂ + 10 % Zr	1.4	1.5
ZrB ₂ + 30 % Zr	0.8	1.2
ZrB ₂ + 40 % Zr	1.1	2.2
ZrB ₂ + 50 % Zr	1.8	2.8
ZrB ₂ + 60 % Zr	1.6	3.2
(TiB + 40 % Ti) + 10 % ZrB ₂	0.65	1.6
(TiB + 40 % Ti) + 20 % ZrB ₂	0.95	2.5
(TiB + 40 % Ti) + 30 % ZrB ₂	1.4	2.2
(TiB + 40 % Ti) + 40 % ZrB ₂	1.3	2.8
(TiB + 40 % Ti) + 50 % ZrB ₂	1.4	2.6

stability for the metal binders (Ti and Zr) in sulfuric acid solutions [61]. This is confirmed by selective dissolution of the metal phase in the $\text{ZrB}_2\text{-Zr}$ alloys found during X-ray diffraction analysis of the corrosion product formed on the alloy surface. It is known that selective dissolution of one phase can catalyze dissolution of the other. The corrosion resistance of $\text{TiB} + 40\% \text{ Ti}$ was found to decrease as a certain amount of ZrB_2 was added to the system.

Analysis of the obtained data allowed one to conclude that the corrosion resistance of the TiB-Ti , $\text{ZrB}_2\text{-Zr}$, and TiB-Ti-ZrB_2 alloys surpasses that of the traditional hard alloys used in industry.

2.7.6 Electroconductivity

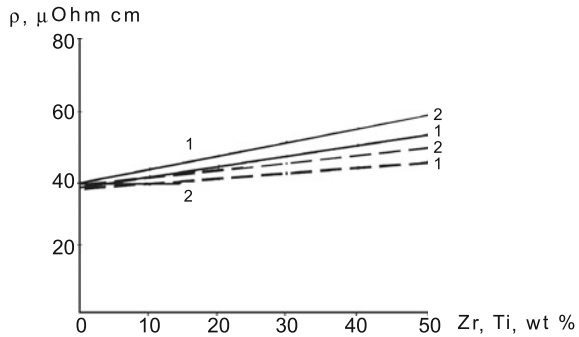
Electroconductivity and thermal conductivity were measured simultaneously using a standard laboratory device under stationary temperature conditions (20–1000 °C) in a protective medium. The precision of the thermal conductivity measurements was 3–5 % and the precision of the electroconductivity measurement was 1–1.5 %.

The resistivity of the TiB-Ti , $\text{ZrB}_2\text{-Zr}$, and TiB-Ti-ZrB_2 alloys was found to increase with an increase in metal binder content (Table 2.9). The resistivity of the TiB-Ti-ZrB_2 alloys decreases with an increase of ZrB_2 concentration and increases with an increase in temperature. Comparative analysis of the temperature dependencies of the studied alloys and their components allows one to conclude that the electroconductivity of these alloys at low contents of the metal binder

Table 2.9 Resistivity of the TiB-Ti , $\text{ZrB}_2\text{-Zr}$, and TiB-Ti-ZrB_2 hard alloys at 20–1000 °C as a function of metal binder content

Hard alloy composition, wt%	Resistivity, $\mu\text{Ohm cm}$					
	20	200	400	600	800	1000
$\text{TiB} + 10\% \text{ Ti}$	46	55	65	72	80	88
$\text{TiB} + 20\% \text{ Ti}$	50	60	68	74	79	90
$\text{TiB} + 30\% \text{ Ti}$	52	70	76	82	88	94
$\text{TiB} + 40\% \text{ Ti}$	56	72	78	84	98	104
$\text{TiB} + 50\% \text{ Ti}$	61	78	88	96	100	108
$\text{ZrB}_2 + 10\% \text{ Zr}$	42	50	56	64	70	78
$\text{ZrB}_2 + 20\% \text{ Zr}$	45	58	66	72	79	84
$\text{ZrB}_2 + 30\% \text{ Zr}$	48	64	70	76	82	88
$\text{ZrB}_2 + 40\% \text{ Zr}$	50	74	80	86	92	98
$\text{ZrB}_2 + 50\% \text{ Zr}$	52	77	83	88	94	100
$(\text{TiB} + 40\% \text{ Ti}) + 10\% \text{ ZrB}_2$	54	70	82	88	92	98
$(\text{TiB} + 40\% \text{ Ti}) + 20\% \text{ ZrB}_2$	51	64	76	82	88	94
$(\text{TiB} + 40\% \text{ Ti}) + 30\% \text{ ZrB}_2$	48	56	74	78	84	90
$(\text{TiB} + 50\% \text{ Ti}) + 40\% \text{ ZrB}_2$	44	54	70	76	82	88
$(\text{TiB} + 40\% \text{ Ti}) + 50\% \text{ ZrB}_2$	41	50	60	70	78	85

Fig. 2.19 Experimental (solid line) and theoretical (dotted line) resistivities of the $\text{ZrB}_2\text{–Zr}$ 1 and TiB–Ti 2 systems as functions of Zr content at 20 °C



(<30 wt%) is mainly determined by the electroconductivity of the boride phase, whereas at high contents of the metal binder (>30 wt%) it is determined by the electroconductivity of the binder [62, 63]. Experimental and theoretical values of resistivity for the TiB–Ti and $\text{ZrB}_2\text{–Zr}$ hard alloys with various contents of metal binder are given in Fig. 2.19. Calculations were performed using the generalized theory of conductivity [64, 65]. According to the used model, the boride phase (TiB or ZrB_2) is assumed homogeneous and the binder (Ti or Zr) distribution along the sample is homogeneous and isotropic. The binder domains can be represented by isolated (without electrical contacts between them) small spheres. The effective resistivity of such a system can be found from the equation

$$\frac{\rho_0 - \rho}{\rho_0 + 2\rho} = \zeta \frac{\rho_0 - \rho_1}{\rho_0 + 2\rho_1}, \quad (2.12)$$

where ρ represents the effective resistivity of the hard alloys, ρ_1 represents the resistivity of the metal binder, ρ_0 represents the resistivity of the boride phase, and ζ represents the volume fraction of the metal binder.

According to the data presented in Fig. 2.19, experimental and calculated resistivity dependencies at low contents of the binder can be described by the Clausius–Mossotti model. This implies that metal binder particles are separated from each other and there are no electrical contacts between them. The resistivity of such alloys should be determined by the electroconductivity of the boride phase (TiB , ZrB_2). As the binder content grows, the structure of the alloy changes, resulting in the formation of electrical contacts between the metal binder particles; the difference between the experimental and calculated data becomes more pronounced.

The change of the TiB–Ti alloy structure is confirmed by metallographic analysis. At low contents of the metal binder, the metal particles are isolated (Fig. 2.12) while at a higher Ti concentration the formation of a continuous metal matrix containing boride phase grains is observed.

Patterns for resistivity change of the TiB–Ti , $\text{ZrB}_2\text{–Zr}$, and TiB–Ti–ZrB_2 systems resulting from temperature and composition changes are similar to those of other alloys.

2.7.7 Thermal Conductivity

Thermal conductivity of the TiB–Ti and ZrB₂–Zr hard alloys was found to increase with an increase in temperature, whereas the opposite trend was noted for TiB–Ti–ZrB₂ (Table 2.10). As the metal binder content grows, the thermal conductivity of the TiB–Ti and ZrB₂–Zr systems decreases while increasing for the TiB–Ti–ZrB₂ system. Comparative analysis of temperature dependencies of these alloys and their components allows one to conclude that their thermal conductivity is mainly determined by that of the boride phase. For a qualitative explanation of thermal conductivity patterns, experimental data were compared with calculated data. Calculations were performed under the assumption that at low contents of the metal binder, its particles are isolated from each other. In this case, the following expression can be used [64]:

$$\lambda = \lambda_1 \left(1 - \frac{\zeta}{\frac{1}{1 - \lambda_1/\lambda_2} - \frac{1 - \zeta}{3}} \right), \quad (2.13)$$

where λ is the thermal conductivity of the hard alloy, λ_1 and λ_2 are the thermal conductivities of the hard phase and metal binder, respectively, and ζ is the volume content of the binder.

In Fig. 2.20, experimental results on the thermal conductivity of the TiB–Ti and ZrB₂–Zr hard alloys are compared with calculated results. As binder content grows, the difference between the calculated and experimental data increases.

Table 2.10 Temperature dependencies of thermal conductivity of the TiB–Ti, ZrB₂–Zr, and TiB–Ti–ZrB₂ hard alloys at 20–1000 °C

Hard alloy composition, wt%	Thermal conductivity (λ), cal/cm s grad						
	20	200	400	600	800	900	1000
TiB + 10 % Ti	0.054	0.056	0.057	0.059	0.060	0.061	0.063
TiB + 20 % Ti	0.052	0.054	0.055	0.056	0.057	0.059	0.061
TiB + 30 % Ti	0.049	0.051	0.052	0.054	0.055	0.055	0.058
TiB + 40 % Ti	0.046	0.049	0.051	0.052	0.052	0.054	0.055
TiB + 50 % Ti	0.043	0.045	0.045	0.046	0.047	0.049	0.052
ZrB ₂ + 10 % Zr	0.058	0.059	0.059	0.061	0.062	0.062	0.064
ZrB ₂ + 20 % Zr	0.057	0.058	0.061	0.062	0.063	0.064	0.065
ZrB ₂ + 30 % Zr	0.055	0.054	0.056	0.057	0.058	0.059	0.063
ZrB ₂ + 40 % Zr	0.054	0.055	0.057	0.058	0.059	0.061	0.062
ZrB ₂ + 50 % Zr	0.052	0.055	0.056	0.057	0.058	0.060	0.061
(TiB + 40 % Ti) + 10 % ZrB ₂	0.050	0.048	0.049	0.047	0.046	0.045	0.044
(TiB + 40 % Ti) + 20 % ZrB ₂	0.052	0.049	0.048	0.046	0.044	0.043	0.044
(TiB + 40 % Ti) + 30 % ZrB ₂	0.054	0.049	0.047	0.045	0.045	0.046	0.047
(TiB + 50 % Ti) + 40 % ZrB ₂	0.056	0.054	0.053	0.052	0.049	0.049	0.047
(TiB + 40 % Ti) + 50 % ZrB ₂	0.057	0.056	0.055	0.052	0.051	0.050	0.049

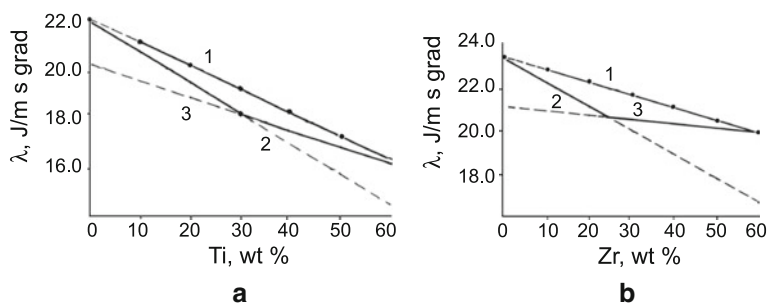


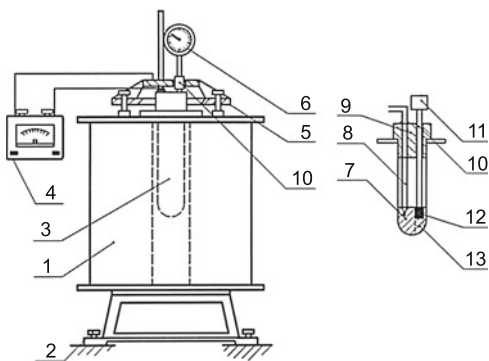
Fig. 2.20 Experimental 1 and calculated 2, 3 thermal conductivities of the TiB–Ti (a) and ZrB₂–Zr (b) hard alloys as functions of metal binder content

Characteristics of the studied hard alloys were thus found to approximate those of traditional hard alloys, and in some cases, to exceed them.

2.7.8 Temperature Dependence of STIM-4 and TiB Thermal Expansion Coefficients

The coefficient of thermal expansion was measured at a temperature ranging from 20 to 1000 °C using an original sintered quartz dilatometric cell (Fig. 2.21) consisting of a tube and a push bar. The analyzed sample (4 mm in diameter, 30 mm long) was fastened between a flange at the lower end of the tube and the push bar. The assembled cell was placed into a furnace equipped with a temperature controller and PP-1 thermocouple. Change in sample length as a function of temperature was transferred via the push bar to an indicator (1 MGM-type, division value 0.001 mm). Sample length was recorded for every 100 °C increment, while taking into account the thermal expansion of quartz and natural movement of the device.

Fig. 2.21 Schematic of quartz dilatometer: 1 furnace, 2 furnace setting screws, 3 quartz tube, 4 galvanometer, 5 fixture for indicator, 6 indicator, 7 graphite cylinder, 8 thermocouple, 9 centering bush, 10 quartz push bar, 11 head, 12 sample, and 13 quartz support



Thermal stability (i.e. the ability of material to effectively operate under conditions of significant temperature gradients) is one of the most important characteristics of hard alloys to ensure their effective performance at high temperatures. The coefficient of thermal expansion (α) is an important parameter determining the thermal stability of a material. For example, hard alloy VK8 possessing high thermal conductivity and strength exhibits rather low thermal stability, which is explained by a significant difference (three times) between the thermal expansion coefficients of the hard phase and ductile binder. Consequently, the use of this hard alloy under conditions involving drops in temperature produces a thermal stress that reduces the thermal stability of the material.

It is known that as thermal expansion and density coefficients decrease, the thermal stability of hard alloys increases. In addition, thermal stability depends on thermal conductivity, grain size, strength, and ductility.

STIM-4 hard alloys were found to exhibit rather high thermal stability [14]. This is explained by the closeness of the hard phase and metal binder thermal expansion coefficients since the former was synthesized from the latter.

Modest service life of hard alloy instruments is associated with a high level of residual stress due to poor compatibility of the instrument and its casing materials. It is also important to study temperature dependence of the STIM-4 coefficient of thermal expansion for its effective use in the manufacture of various instruments in combination with other materials (used for production of metal ferrules or bands, for example). Data on the thermal expansion coefficient of STIM alloys (including STIM-4) are present in the literature [66], while data on the influence of metal binder content on the thermal expansion coefficient are absent. We therefore studied temperature dependence of the thermal expansion coefficient of STIM-4 alloys with different metal binder contents.

Temperature dependencies of the coefficient of thermal expansion for Ti (1), STIM-4 alloys (2, 3, and 4), and TiB (5) are presented in Fig. 2.22. The temperature dependence of the Ti coefficient of thermal expansion is quite complex,

Fig. 2.22 The thermal expansion coefficient of Ti 1 TiB + 50 % Ti 2 TiB + 30 % Ti 3, TiB + 10 % Ti 4, and TiB 5 as a function of temperature

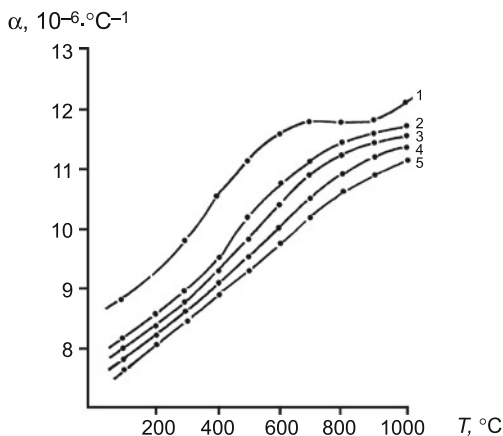
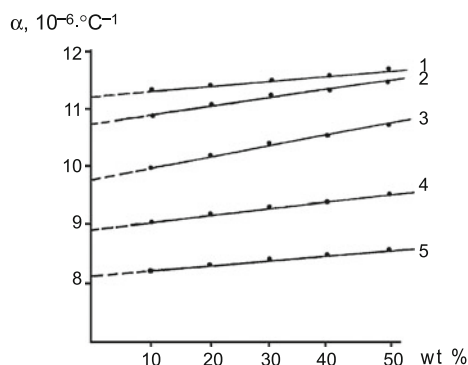


Fig. 2.23 Coefficient of thermal expansion as a function of metal binder content for STIM alloys at 1000 1 800 2 600 3 400 4, and 200 °C 5



while the thermal expansion coefficients of STIM-4 alloys increase with an increase in temperature.

Data on the coefficient of TiB thermal expansion are not available in the literature. These data can be obtained by linear extrapolation of temperature dependencies of thermal expansion coefficients for various STIM-4 alloys to their interception with the Y-axis, which corresponds to zero content of the metal binder (Fig. 2.23). The extrapolated temperature dependence of the TiB coefficient of thermal expansion is presented in Fig. 2.22 (curve 5).

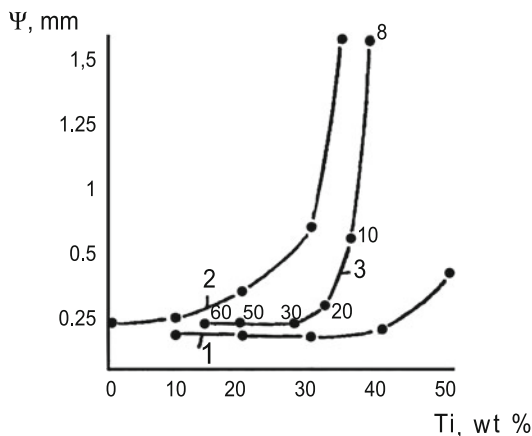
Mean coefficients of thermal expansion for Ti and TiB in the 20–1000 °C temperature range were found to be 10.3 and $9.8 \cdot 10^{-6} \text{ T}^{-1}$, respectively. The coefficient of thermal expansion for TiB_2 is $8.1 \cdot 10^{-6} \text{ T}^{-1}$ [67]. The difference between coefficients of thermal expansion for the TiB–Ti pair is thus lower than that of the TiB_2 –Ti pair.

In conclusion, we would like to emphasize that the use of Ti and Zr as metal binders for hard alloys based on their borides results in the production of materials exhibiting a high thermal stability that significantly exceeds that of commercially available hard alloys. Thermal stability was observed to be determined by the strength of the metal binder and the closeness of the coefficients of thermal expansion for the ductile metal binder and hard phase. For hard alloys based on the TiB–Ti, ZrB_2 –Zr systems, these characteristics are rather close, thus ensuring their high thermal stability.

2.8 Laboratory and Factory Tests for Wear Resistance of Hard Alloys

Cutting properties of materials were studied using samples of standard disposable inserts ($12.7 \times 12.7 \times 4.76 \text{ mm}$). Wear-resistance tests were performed using a screw-cutting lathe to cut constructional carbon steel, employing a procedure with the following parameters:

Fig. 2.24 Dependence of ψ on metal binder content for $\text{ZrB}_2\text{-Zr}$ 1 TiB 2 and TiB-Ti-ZrB_2 3. Small numbers near curve 3 indicate the content of ZrB_2 (wt%) in the TiB-Ti-ZrB_2 alloys



- Cutting speed: 200 ± 10 m/min
- Feed: 0.074 mm/rotation
- Cutting depth: 0.5 mm
- Cutting time: 8 min.

Magnitude of the wedge wear (l) was measured using a laboratory microscope. Wear resistance was calculated using the formula

$$\psi = 0.014l.$$

Wear resistance of hard alloys strongly depends on hardness, bending, and compression strength, and in some cases, heat, corrosion, and oxidation resistance. Wear resistance of the TiB-Ti , $\text{ZrB}_2\text{-Zr}$, and TiB-Ti-ZrB_2 hard alloys was determined from the degree of wear of the clearance face of cutting plates manufactured from hard alloys with optimal mechanical characteristics. The experimental data on wear resistance of hard alloys (Fig. 2.24) indicate a strong dependence on their composition. The $\text{ZrB}_2\text{-Zr}$ (curve 1) hard alloys are characterized by relatively high wear-resistance and their cutting performance remains rather strong even at high contents of the metal binder (30–40 wt%). This is explained by the fact that the role of metal binder in this case is played by solid solution B in Zr, which exhibits a high microhardness, rather than by pure Zr.

For the TiB-Ti hard alloys, wear resistance drops when the content of the metal binder reaches 20 wt% (curve 2). This may be associated with high cutting edge working temperatures (850–950 °C [68]), which exceed the temperature of the polymorphous transformation of Ti binder (883 °C). After its polymorphous transformation, Ti loses its ability to elastic deformation and turns into a ductile state [69]. This is not the only reason, however, for reduction in wear resistance of the Ti-B hard alloys. Wear resistance of hard alloy is affected not only by polymorphous transformation of metal binder but also by the microstructure (shape and size) of the hard phase grain. The dependence of wear resistance of the $\text{TiB} + 40\%$ Ti alloy on the binder content at the partial replacement of TiB by

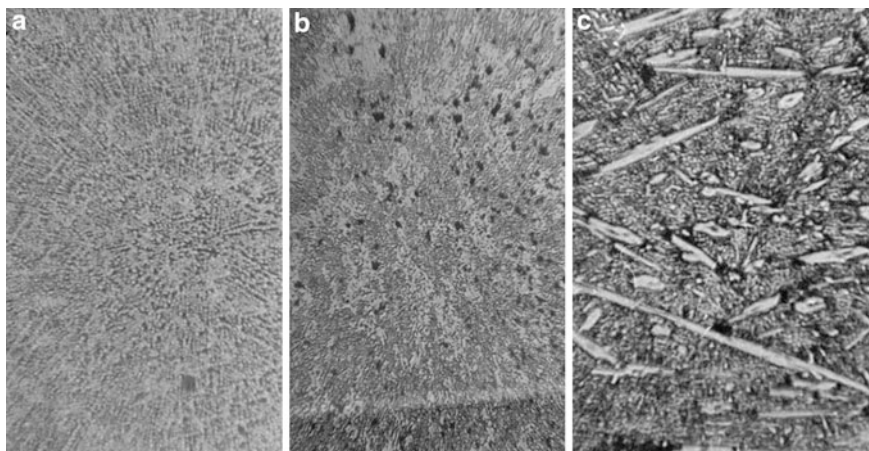


Fig. 2.25 Microstructure of alloys TiB + 40 % Ti (a) (TiB + 40 % Ti) + 10 % ZrB₂ (b) and (TiB + 40 % Ti) + 30 % ZrB₂ (c) (magnification $\times 1000$)

ZrB₂ is presented in Fig. 2.24 (curve 3). Wear resistance of the TiB + 40 % Ti alloy containing ZrB₂ significantly increases. This increase cannot be explained by the effect of polymorphous transformation of the metal binder since it is the same in both materials. In this case, the main role seems to be played by the structure. Indeed, as the ZrB₂ content grows, the TiB round grains become acicular (Fig. 2.25). As a result, a rigid skeleton made of refractory material forms; this ensures a strong resistance to wear associated with tearing of individual grains and clusters from the alloy.

It would be interesting to determine wear resistance of the studied alloys operating at a temperature lower than that of the polymorphous transformation of the metal binder, as at steel drawing. The heating temperature of large drawing dies depends on the area of passage: the larger the area, the lower the heating temperature (normal range is 200–400 °C [70]). Due to the high thermal stability (90–100 thermal cycles in the range of 20–1000 °C) and strength ($\sigma_b = 900$ –1200 MPa) exhibited by the TiB–Ti hard alloys [14, 15], they can be used for the manufacture of large hard alloy blanks (>100 mm in diameter and >70 mm long) and parts using SHS compaction. It is worth noting that production of high-quality large items from hard alloys based on other systems (for example, TiC–Ni) is quite problematic.

A photo of a hard-alloy blank produced from the TiB–Ti hard alloy by SHS compaction is presented in Fig. 2.26. Blanks were used for the manufacture of drawing dies which were tested at Izhtal' factory. Tests were performed using a linear draw bench for drawing 40X and St45 steels from $\varnothing 35$ to $\varnothing 32$. Characteristics of the produced blanks are given in Table 2.11.

The results of factory tests of the dies are presented in Table 2.12. The performance of the TiB–Ti hard alloy dies with respect to their working capacity (5.0 t) and wear resistance exceeds that of the traditional commercially available

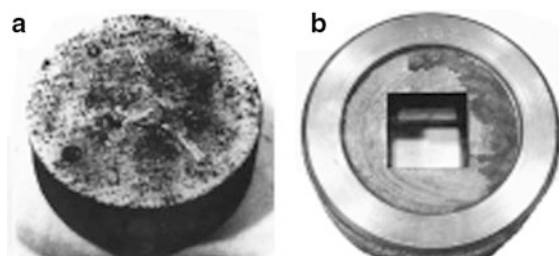


Fig. 2.26 Hard alloy (TiB + 40 % Ti) blank (a) and a drawing die composed of it (b)

Table 2.11 Characteristics of blanks for drawing dies

Composition of hard alloy	Hardness HPA, kg/mm ²	Bending strength, MPa
TiB + 30 % Ti	88	800
TiB + 40 % Ti	87.5	1000

Table 2.12 Results of factory tests of drawing dies

Die number	Composition	Processed material	Weight of the processed material before measurement of the wear, t	Wear, mm
1	TiB + 30 % Ti	40X	1	0.03
2	TiB + 40 % Ti	St 45	1	0.03
			2	0.03
			3	0.06
			5	0.09
3	VK-8	St 45	4	0.1

tungsten-containing hard alloy VK-8. Thus the TiB–Ti hard alloy with various contents of metal binder can be successfully used for the manufacture of wear-resistant tools operating at temperatures lower than 800 °C.

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2013, XIX, 156 p. 106 illus., Softcover

ISBN: 978-3-642-35204-1