July 3, 1956 C. G. GOETZEL ET AL 2,752,666

HEAT RESISTANT TITANIUM CARBIDE CONTAINING BODY AND METHOD OF MAKING SAME

Filed July 12, 1954

3 Sheets-Sheet 1

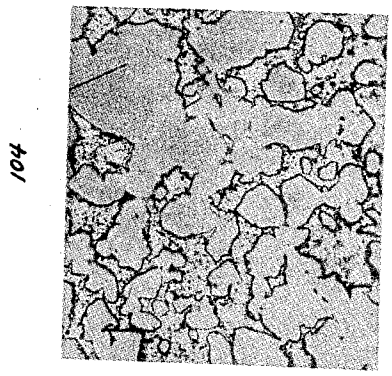

Fig. 7



Fig. 8

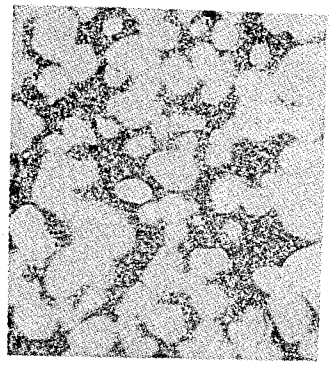

Fig. 5



Fig. 6

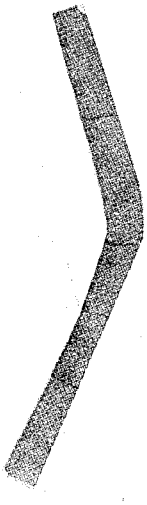

Fig. 1



Fig. 2



Fig. 3

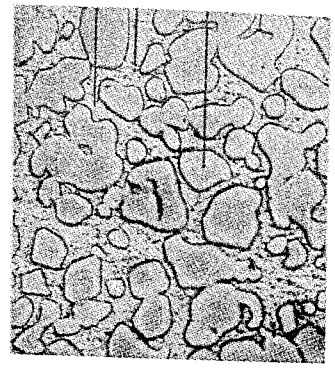

Fig. 4

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3 Sheets-Sheet 2

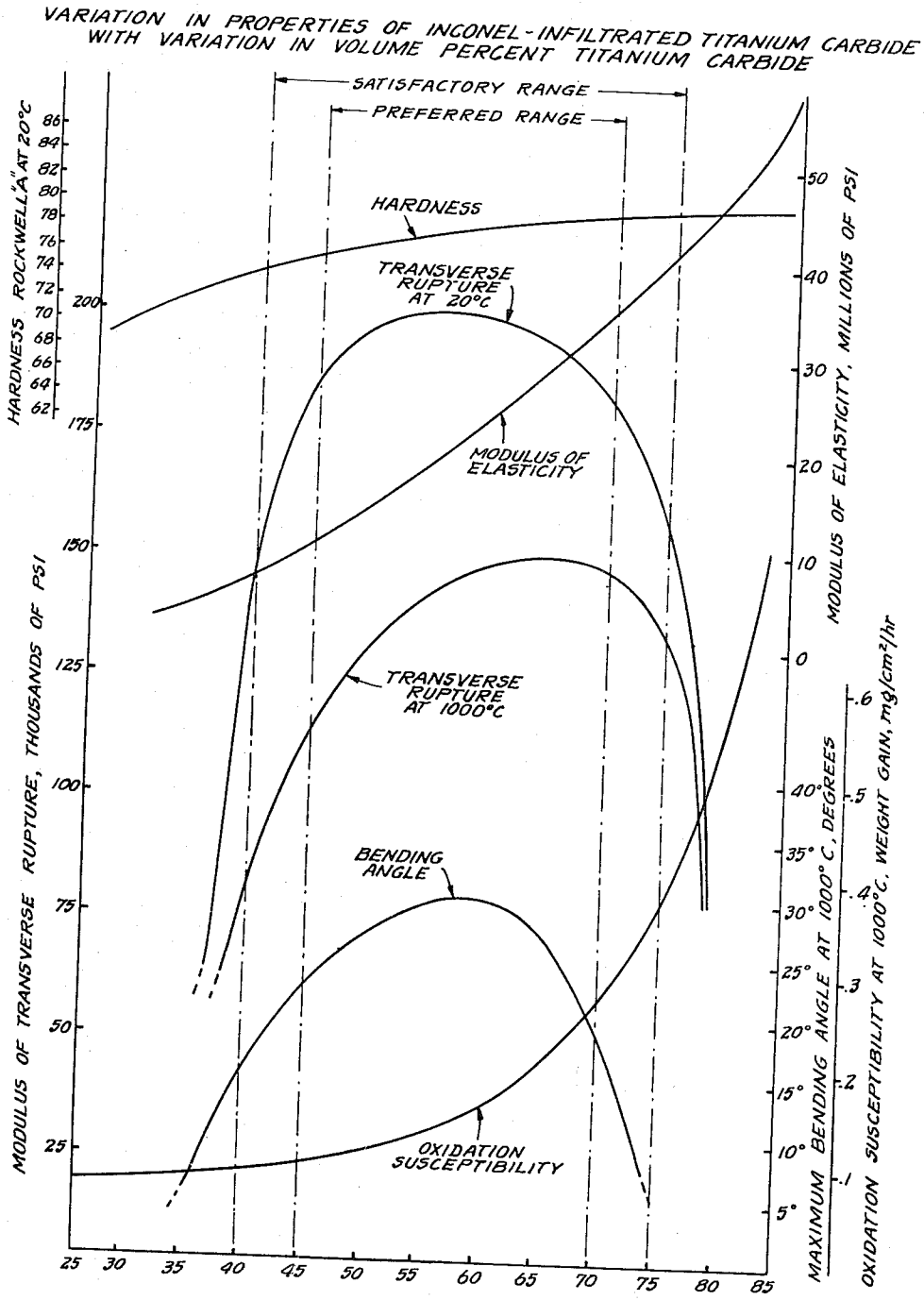

FIG. 9.

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3 Sheets-Sheet 3

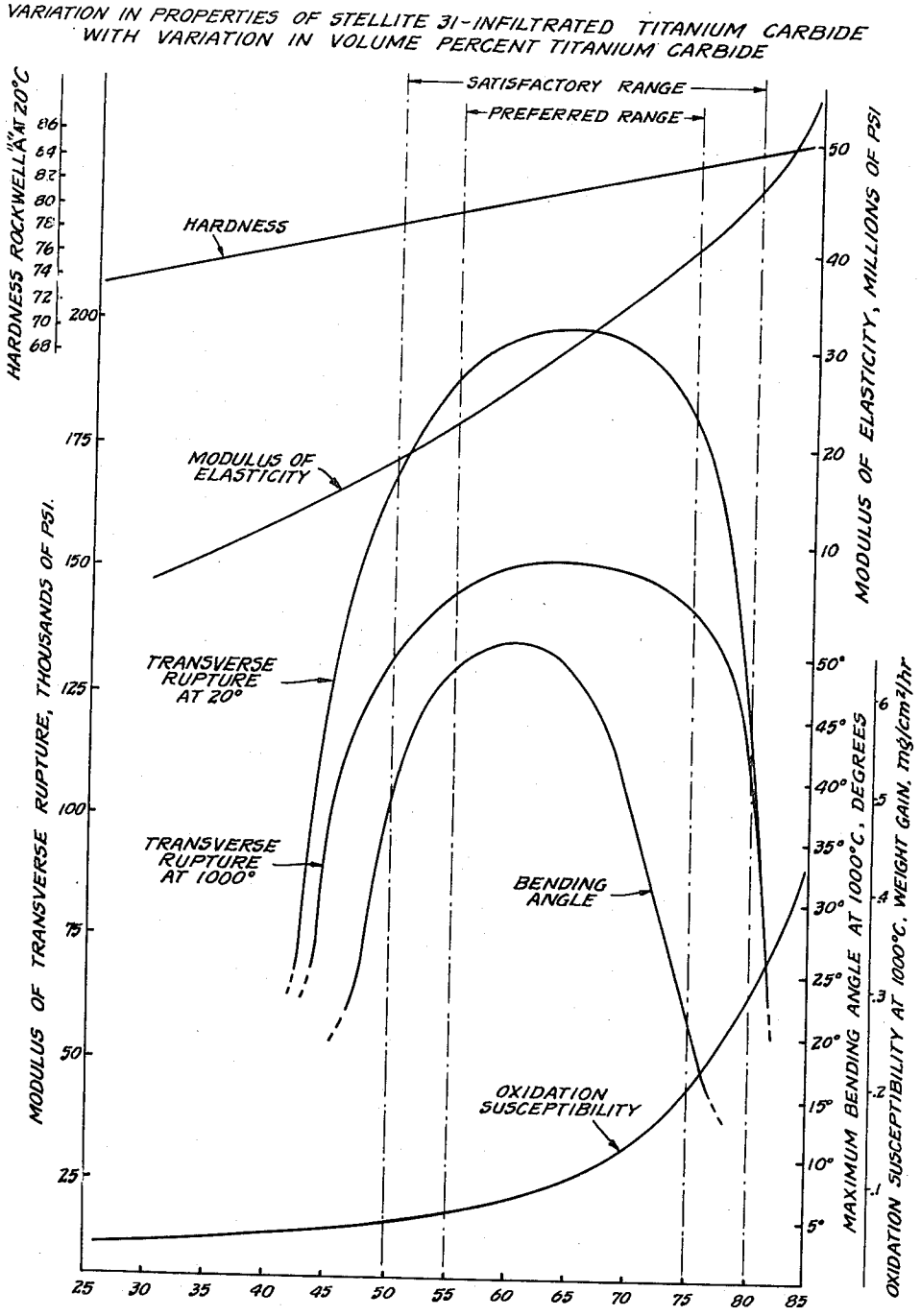

FIG. 10.

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HEAT RESISTANT TITANIUM CARBIDE CONTAINING BODY AND METHOD OF MAKING SAME

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Application July 12, 1954, Serial No. 442,564

11 Claims. (Cl. 29—182.8)

The present invention relates to high heat resistant composite refractory carbide bodies or so called "Cermets" and more particularly to structural elements comprising titanium carbide which in use are subjected to high static and/or dynamic stresses and to thermal shock at elevated temperatures of up to about 1000° C. and higher. This application is a continuation-in-part of U. S. application Ser. No. 312,334, filed September 30, 1952.

Increased operating temperatures and efficiencies of jet engines and other high powered thermal engines have necessitated the development of materials with ceramic-like properties for use at elevated temperatures to replace metallic materials such as heat-resistant iron-base alloys, e. g. stainless steels, and heat resistant chromium-containing alloys based on nickel or cobalt or both. While heat resistant alloys have added measurably to the development of jet engines, such alloys were found to have limited use at temperatures of the order of about 1000° C. and higher because of their tendency to soften and creep at such high temperatures under the high static and/or dynamic stresses which usually prevail during service. This is generally true of structural elements of jet engines and like power plants, particularly fluid guiding members such as turbine buckets, nozzle vanes, etc. Because structural elements had to have high melting points and adequate stability at high temperatures, work was centered upon very high melting point, substantially chemically stable ceramic-like materials such as the carbides, nitrides, borides, silicides, etc., of tungsten, molybdenum, chromium, tantalum, columbium, zirconium, titanium and other high melting point metals. These ceramic-like materials could not be used by themselves as they were brittle and friable and lacked toughness. Moreover, they could not be processed by ordinary melting techniques and, thus, special powder metallurgy methods had to be employed.

Generally, in producing composite shapes from the ceramic-like material, the material in powder form is mixed with a small amount of a ductile binder metal powder of the iron group or similar metals, pressed into the desired shape and then sintered at an elevated temperature under controlled conditions below the melting point of the ceramic-like material and generally just below, at, or just above the melting point of the binding metal material, much as the well-known tungsten carbide cutting tools are manufactured with cobalt-binder. Another method employed in producing composite shapes comprises forming a coherent, porous skeleton body from the ceramic-like material and then filling the pores by infiltration with a molten iron group metal or heat resistant alloys based on these metals. It was found that composite shapes produced in this manner retained to a certain extent much of the high temperature attributes of the ceramic-like material and to a lesser extent some of the attributes of the ductile metallic binder material. The composite ceramic-like material generally exhibited satisfactory resistance to oxidation at elevated temperatures up to 1000° C. and higher but did not always have

good resistance to high dynamic stresses (mechanical shock) and to thermal shock when employed, for example, as blades in jet engines, rocket engines and the like. In other words the composite ceramic-like material tended to be brittle compared to alloy metal materials and was subject to failure at ordinary and elevated temperatures due to mechanical and/or thermal shock, despite the fact that the material had adequate chemical resistance to hot corrosive gases, particularly to hot oxidizing gases. Thus, blades made of the material would fail prematurely by cracking due to mechanical and/or thermal shock long before the blades would show significant signs of adverse chemical attack by the environment. It was found through certain evaluation tests that these composite materials were not prone to have good resistance to impact and that generally the impact resistance at room temperature of such materials comprising titanium carbide was of the order of about 3 to 4 inch pounds and less as measured by the standard Micro-Charpy or drop impact test, on unnotched test bars having a cross section of three-sixteenths of an inch square.

Although many attempts were made to overcome the aforementioned difficulties and disadvantages, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It is the object of the invention to provide a method for producing heat resistant bodies comprised substantially of a refractory carbide, for example titanium carbide, said bodies having improved resistance to mechanical and/or thermal shock.

It is also the object to provide a heat resistant structural element, such as a fluid guiding member, for jet engines and the like, said element being characterized by improved strength and toughness at ordinary and elevated temperatures of up to about 1000° C. and higher.

In the parent case, U. S. Ser. No. 312,334, it was shown that in the production of hot shaping dies or die nibs from refractory metal carbide material comprised of titanium-base carbide, dies with markedly improved die life could be produced capable of withstanding the combined effect of thermal and mechanical stresses provided the die had a special and particular kind of microstructure. It was found that when an extrusion die had the special microstructure, the die was capable of working under very high loads of compression, while in contact with hot metal being worked for prolonged periods of time, without cracking, deforming or otherwise becoming defective as compared to prior carbide dies which had shorter operating lives. It was also found that the die material had a markedly improved resistance to impact and thermal shock as a consequence of the special microstructure and was not brittle in the sense that prior carbide materials were brittle. Additional investigational work has indicated that the special microstructure is important in the production of structural elements for jet engines, particularly fluid guiding members which in use are subjected to complex flexing or vibrational stresses under conditions involving high fluctuating temperatures.

The advantage of the present invention will become apparent from the following description taken in conjunction with the accompanying drawing in which:

Fig. 1 is a reproduction of a photograph of a bend-test specimen made of an infiltrated titanium-base carbide body produced in accordance with the invention showing its good hot-bending property.

Fig. 2 is a reproduction of a photograph of a bend-test specimen of an infiltrated titanium-base carbide of similar composition to the body of Fig. 1 but outside the invention showing its inferior hot-bending property.

Fig. 3 is a reproduction of a photograph of a bend-test specimen of a cemented prior art titanium carbide body showing its poor hot-bending property.

Figs. 4 and 5 are reproductions of photomicrographs of infiltrated titanium carbide bodies produced in accordance with the invention;

Fig. 6 is a reproduction of a photomicrograph taken of a nozzle vane produced in accordance with the invention after being tested under conditions simulating most severe service for 96 hours in an actual jet engine turbine.

Figs. 7 and 8 are reproductions of photomicrographs of similar titanium carbide bodies outside the scope of the invention.

Figs. 9 and 10 depict curves showing the physical and mechanical properties of titanium carbide bodies of the invention correlated with the composition of bodies (percent by volume titanium carbide) infiltrated with a heat-resistant nickel-base alloy and with a heat-resistant cobalt-base alloy, respectively.

The present invention is based on the discovery that hard heat resistant articles comprising a composite body containing titanium carbide can be produced having an improved combination of mechanical and chemical properties such as wear resistance, oxidation and corrosion resistance, heat and stress resistance, high hot hardness, toughness, ductility, resistance to mechanical and/or thermal shock, resistance to vibration, to fatigue, etc. In producing heat resistant articles, particularly structural elements such as fluid guiding members, in accordance with the invention, a material is employed containing about 40% to 80% by volume of a refractory carbide such as titanium carbide, substantially the balance by volume being a matrix-forming metal comprising at least one iron group metal as an essential element, e. g. a heat resistant metal comprising a metal selected from the group consisting of chromium, molybdenum and tungsten in an amount ranging up to about 30% by weight, the total amounts of the metals of said group not exceeding about 40%, a metal selected from the group consisting of up to about 8% total of columbium, tantalum and vanadium, substantially the balance of the matrix-forming metal being at least one metal selected from the iron group consisting of iron, cobalt, and nickel, the sum of the iron group metals making up at least about 40% by weight and preferably about 50% of the matrix-forming metal. It will be understood that the expression "substantially the balance" or "balance" when directed to the composition of the infiltrant metal does not exclude the presence of other alloying elements, such as titanium, zirconium, aluminum, etc., nor does it exclude the presence of residual elements, such as carbon, nitrogen, silicon, manganese, copper, etc. which may be present incidentally or as impurities or which may be intentionally added in amounts which do not deleteriously affect the properties of the infiltrant metal.

In producing structural elements, it is essential that refractory carbide powder (e. g. titanium carbide) be subjected to a high temperature heating in the presence of the matrix-forming metal in a liquid state at a temperature at least above the liquidus temperature of said matrix metal but substantially below the melting point of the refractory carbide, in a technical vacuum or a controlled atmosphere of sub-atmospheric pressure of less than 2500 microns of mercury column, and for a time sufficient to allow the liquid matrix-forming metal of the high temperature metal to wet completely the refractory carbide and to form a continuous matrix surrounding individual and aggregated carbide grains. The treatment may be carried out in the presence of a stationary or a moving liquid phase comprised essentially of the matrix-forming metal. Although the liquid phase at the beginning of the treating cycle may comprise the original matrix-forming metal, it will be understood that as the liquid phase treatment progresses, the matrix-forming metal will undergo a modification in composition and in certain physical and mechanical properties by phase reactions involving essentially the matrix-forming metal and the carbide. Upon completion of the treating cycle, the thus-formed composite body is cooled in vacuum to substantially below the solidus or freezing temperature of the prevailing liquid phase whereby a hard metal carbide body is produced having a micro-structure comprising a substantially continuous ductile matrix of the matrix-forming metal with fine particles of a precipitate evenly dispersed therethrough and larger isolated refractory carbide grains and grain aggregates having substantially rounded or partially spheroidized polyhedral or polygonal shape (as best shown in Fig. 4). When the refractory or titanium carbide body is produced with the aforementioned microstructure, an outstanding combination of mechanical properties obtains, particularly a marked improvement in toughness and in resistance to mechanical and thermal shock at elevated temperatures.

In carrying out the invention, many types of proven high temperature or heat resistant metals can be employed as the matrix-forming metal. The following list of approximate alloy compositions are given as examples of matrix-forming metals which can be used:

Percent Ni	Percent Co	Percent Fe	Percent Cr	Percent Mo	Percent W	Percent Al	Percent Mn	Percent V
80	----	----	20	----	--	--	--	----
80	----	6	14	----	--	--	--	----
58	----	5	15	17	5	--	--	----
95	----	----	----	----	--	4.5	0.5	----
----	69	----	25	6	--	--	--	----
10	56	----	26	----	7.5	--	--	----
10	51.5	2	20	----	15	--	1.5	----
25	----	53	16	6	--	--	--	----
8	----	74	18	----	--	--	--	----
----	----	77	4	----	18	--	--	1
----	----	86	14	----	--	--	--	----
----	----	82	18	----	--	--	--	----
----	----	73	27	----	--	--	--	----

As will be understood, the aforementioned alloys may contain small amounts of other elements such as carbon, nitrogen, boron, etc.

It will be appreciated that the foregoing alloys are merely illustrative of the types of matrix-forming metals that can be employed and that modifications of these alloys are contemplated within the scope of the invention. In other words, the matrix-forming infiltrant metal may be comprised of a heat and oxidation resistant iron group base alloy, for example nickel-base, cobalt-base, and iron-base alloys. Such alloys generally contain at least about 40% preferably at least about 50% of the iron group metal. Alloys of the aforementioned types containing effective amounts of the so-called well-known strengthening or age hardening elements, such as zirconium, titanium, aluminum, etc., are also contemplated within the scope of the invention.

In carrying the invention into practice, it is preferred to produce structural elements by the powder metallurgy method of infiltration. In this method, the high temperature heating is accomplished by employing a moving liquid phase of the matrix-forming metal. By employing the preferred embodiment, the product can be closely controlled and optimum results can be consistently obtained. In producing hard heat resistant articles by the preferred method, a porous refractory metal carbide skeleton body, for example one comprising titanium carbide, is prepared and shaped into the structural element desired, such as a fluid guiding member, and is then infiltrated or impregnated in a vacuum at an elevated temperature with a molten infiltrant metal.

The composition of the infiltrated body comprises about 40% to 80% by volume of the refractory carbide, a carbide based on titanium, and about 60% to 20% by volume of the matrix-forming metal. For consistent results, it is preferred that about 45% to 75% by volume of the carbide be employed, substantially the balance comprising about 55% to 25% of the matrix former. A satisfactory composition range is one comprising about 50% to 80% by volume of titanium carbide and about

50% to 20% by volume of a heat resistant cobalt-base alloy. Another satisfactory composition range comprises about 40% to 75% by volume of titanium carbide and about 60% to 25% by volume of a heat resistant nickel-base alloy. Still another satisfactory composition range comprises about 40% to 70% by volume of titanium carbide and about 60% to 30% of a heat-resistant iron-base alloy. Of course, small amounts of other metal carbides, preferably in solid solution with titanium carbide, may be employed without departing from the scope of the invention. For example, a heat resistant ceramic-like body may be comprised of a titanium-base carbide containing up to about 5% each of such metal carbides as silicon carbide, boron carbide, and up to about 10% each of chromium carbide, vanadium carbide, molybdenum carbide, tungsten carbide, zirconium carbide, or hafnium carbide, the total amounts of these carbides not exceeding 25% by volume of the body. The titanium-base carbide may be employed over the same ranges set forth hereinabove for the refractory metal carbide in carrying out the invention. By titanium-base carbide is meant a carbide comprising substantially titanium and includes titanium carbide per se.

In making the body by the preferred method, a porous carbide skeleton body is prepared by first admixing with the powdered carbide a metallic auxiliary binder component, such as nickel, cobalt or iron in minor proportions up to about 10% by weight of the carbide. A titanium carbide powder which has been found suitable in carrying out the invention is one containing approximately 18% combined carbon and about 2.5% of graphitic carbon. Other grades of titanium carbide powder containing free carbon in amounts from about 0.1% to about 3.5% have also been found suitable. The powders with substantial amounts of free carbon are preferably treated by heating to a high temperature under a reducing atmosphere, e. g. hydrogen or carbon monoxide. After pulverizing the thus-treated titanium carbide powder to pass through a 140 mesh screen, it was found to give exceptionally good and reproducible results when employed in producing heat resistant ceramic-like bodies in accordance with the invention.

The skeleton body, having intercommunicating pores therethrough, is produced either by hot pressing or by cold pressing a mixture of the titanium carbide and the metallic cementing component. If the powder mixture is cold-pressed into a porous body, it is given a pre-sintering treatment in a reducing atmosphere of ordinary or sub-atmospheric pressure below 2500 microns of mercury column, preferably at a temperature ranging from about 1100° C. to 1300° C. for a time sufficient to produce a coherent skeleton body capable of withstanding handling in subsequent operations, e. g. for a time equivalent to at least about 10 minutes per cubic inch of the body.

In the event the powder mixture is hot pressed, a pre-sintering treatment is not required provided the hot pressing temperature is above the liquefaction temperature of the cementing component. After the skeleton body is produced, it may be machined to a size close to the final specifications if necessary, but cutting with cemented carbide tools, or by refractory wheel grinding, diamond chipping, or other methods commonly employed in the fabrication of hard carbide products. In machining the body, an over-size shrinkage allowance of about 2% to 10% is generally made in order to compensate for the shrinkage which occurs in subsequent heating operations.

The thus-prepared skeleton body is then subjected to a high temperature sintering treatment in order to effect additional bonding of the carbide particles into a porous skeleton of sufficient strength to enable the body to retain its shape during subsequent infiltration treatment. In carrying out the high temperature sintering operation, it is preferred to sinter the skeleton body at a temperature between 50° C. and 250° C. above the temperature used in the subsequent infiltration operation in a technical vacuum corresponding to a sub-atmospheric pressure ranging from an initial pressure of preferably not more than 1000 microns down to a final or finishing pressure of 50 microns of mercury and preferably down to 10 microns. The surrounding gas at such sub-atmospheric pressure must be non-oxidizing to the body, i. e. reducing or inert, to prevent substantial decarburization and oxidation of the titanium-base carbide during the treatment. After the titanium-base carbide skeleton body has been sintered, it is then cooled in the vacuum prevailing.

In carrying out the infiltration step, an amount of infiltrant metal sufficient to fill completely the open spaces or pores in the skeleton is placed in contact with the skeleton, for example on top of it so that the force of gravity can be utilized to supplement the capillary forces which draw the molten metal into the pores of the skeleton. Generally, it is desirable to prepare the skeleton body for infiltration by embedding it in a supporting mass of inert powdered granular material so that the absorption of the molten infiltrant can be controlled and confined to the interior of the body. One material which has been found especially effective is powdered granular aluminum oxide of high chemical purity as described in a co-pending application U. S. Ser. No. 292,498, filed June 9, 1952, in the names of the applicants. Another effective material is one comprising beryllium oxide as described in U. S. patent application Ser. No. 413,258, filed March 1, 1954.

In carrying out the infiltration, the skeleton body and the properly positioned infiltrant alloy are heated to a temperature from about 25° C. to 250° C. above the liquidus temperature of the infiltrant alloy. A controlled non-oxidizing atmosphere of sub-atmospheric pressure is preferred, i. e. a technical vacuum ranging from a maximum pressure of not more than 2500 microns at the instant of melting of the infiltrant, preferably not more than 1000 microns, down to a final or finishing pressure of 50 and preferably 10 microns of mercury. The non-oxidizing atmosphere may be reducing or inert to the carbide material and infiltrant metal. The time of infiltration temperature is dependent on the cross section of the skeleton body, the characteristics of the infiltrant alloy in the liquid state, and also on the rate of evacuation of gaseous impurities at the infiltration temperature. As will be shown hereinafter, the time must be sufficient to complete the penetration of the liquid infiltrant alloy throughout the entire porous structure of the skeleton body and also to allow for the solidus-liquidus system to approach equilibrium conditions by diffusion and other chemical and metallurgical reactions that take place between the titanium-base carbide skeleton and the liquid infiltrant so as to obtain a substantially stable matrix structure. In other words it is essential that the infiltrated body be subjected to additional heating after infiltration.

The aforementioned additional heating following infiltration is important and is referred to as the matrix-stabilizing treatment. This treatment is mainly responsible for obtaining the improved results of the invention. Thus by subjecting the infiltrated body in situ to additional heating at substantially the infiltration temperature for a time sufficient to complete substantially the diffusion, solution, and alloying reactions which occur between the matrix-forming infiltrant metal and the carbide, the matrix resulting from the treatment is metallurgically stabilized. It is only by employing the matrix-stabilizing treatment that it is possible to obtain the fullest cooperating effect between the refractory carbide, particularly titanium carbide, and the matrix-forming infiltrant metal so as to achieve the new and vastly improved results provided by the invention.

If no time is allowed for the matrix-stabilizing treatment subsequent to infiltration or if such time is insuffi-

cient the original skeleton structure of the titanium-base carbide maintains and the body, for example a fluid guiding member, having such a structure will not have the desired combination of physical and mechanical properties, and in particular will have poor hot strength, poor hot ductility, poor toughness, and poor resistance to mechanical and thermal shock. On the other hand, when the matrix-stabilizing time following the complete penetration of the pore system by the molten infiltrant is adequate, the original skeleton network of angular-like polygonal titanium-base carbide particles is physically modified so that the carbide particles forming the original continuous skeleton become partially rounded or substantially spheroidized and become isolated either singly or in clusters or aggregates. The microstructure resulting from the foregoing matrix-stabilizing treatment constitutes a dominant, continuous phase comprising substantially the matrix-forming infiltrant metal having dispersed evenly therethrough fine particles of a precipitate and isolated titanium-containing carbide grains and grain aggregates, the grains having substantially spheroidized and/or partially spheroidized polyhedral shapes.

The exact mechanism by which the modification of the carbide skeleton structure is effected is not clearly understood. However, it is believed that as the infiltration process progresses, the infiltrant metal, in addition to filling up the pores in the carbide skeleton, also penetrates the skeleton body along the carbide interfaces, thereby dissolving and/or dislodging the original cohesive bonds at the contact areas between adjacent carbide particles. As a result, the original skeleton structure becomes disrupted and discontinuous, resulting in isolated carbide grains or grain aggregates, while the matrix-forming infiltrant phase becomes a dominant and continuous matrix-structure. Since the overall volume changes of the composite body are only of a small order of magnitude, it is apparent that at least part of the skeleton material at the carbide interfaces is dissolved into the infiltrant alloy matrix rather than being merely physically displaced. This appears to be borne out further by the observation under the microscope of an evenly dispersed minute hard precipitate in the solidified infiltrant alloy matrix. It is believed that this precipitate is produced as a result of the solution by the infiltrant metal of part of the skeleton material at the interface of the original carbide particles which after cooling is precipitated throughout the matrix as very fine particles. This also seems to be borne out by microhardness tests which have disclosed unusually high hardness numbers for the matrix material which are far above the hardness of the original infiltrant alloy. To illustrate this point, a typical microhardness number of a precipitate-containing matrix of a titanium carbide body infiltrated with a nickel alloy containing 14% chromium, 6% iron, the balance substantially nickel, known by the trademark of "Inconel," was found to be equivalent to about 350 to 400 Vickers as compared to a hardness number equivalent to about 120 to 240 Vickers of the original Inconel alloy prior to infiltration.

Whatever the explanation, it is important that the correct microstructure be obtained if the results of the invention are to be achieved. During the matrix-stabilizing treatment subsequent to the complete absorption of the infiltrant metal in the pore system of the skeleton, the liquid phase gradually becomes a continuous matrix while the body retains substantially its shape despite the substitution of a liquid matrix for the solid carbide network as a dominant and possibly the predominant phase. It has been found that the nearer the stabilizing temperature is to the liquidus temperature of the liquid phase metal prevailing after infiltration, the longer is the time required for stabilizing the matrix and vice versa. Upon termination of the matrix-stabilizing treatment, the infiltrated body is cooled in vacuum to below the freezing point of the liquid matrix, preferably at a slow rate of at most about 25° to 50° C. per minute. As a result of the foregoing treatment, the ceramic-like body has the microstructure mentioned hereinbefore comprising a matrix containing the infiltrant metal having dispersed therethrough fine particles of a precipitate, and the larger, substantially or partially spheroidized polyhedral-like or polygonal-like grains of the titanium-base carbide from the original skeleton. If the body is not matrix-stabilized, subsequent to completion of infiltration, the original titanium carbide skeleton structure comprising angular grains maintains and the body will not have the desired combination of physical and mechanical properties, particularly adequate toughness and resistance to mechanical and/or thermal shock.

As illustrative of the foregoing, attention is directed to Figs. 1 and 2. Fig. 1 illustrates a titanium-base carbide test bar produced in accordance with the invention and given the proper matrix-stabilizing treatment showing its ability to markedly deform under stress at an elevated temperature. Fig. 2 depicts a similar titanium carbide body which was not given the proper stabilizing treatment subsequent to completion of infiltration and shows its inferior hot deforming property. For comparative purposes, a cemented titanium carbide body containing 20% by weight of nickel was similarly tested (see Fig. 3) and was found to have extremely poor deforming properties. All of the foregoing specimens illustrated in Figs. 1, 2 and 3 had been subjected to a bend test at a temperature of 1000° C. by centrally loading up to the breaking load a 3-inch long test bar supported by two knife edges over a span of 2¾ inches.

The test specimens illustrated in Figs. 1 and 2 were prepared by completely infiltrating a carbide skeleton comprising about 63% by volume of titanium carbide with a nickel-base alloy containing 14% chromium, 6% iron, and the balance substantially nickel. Subsequent to completion of infiltration, the specimen depicted in Fig. 1 was then subjected to a matrix-stabilizing treatment in situ at substantially the infiltration temperature for 50 minutes. The specimen depicted in Fig. 2 was not given the matrix-stabilizing treatment. Thus, while both specimens had virtually the same composition and virtually the same density of 6.2 grams per cubic centimeter, the test specimen which was matrix-stabilized in accordance with the invention (Fig. 1) exhibited a hot-bending angle of over 30° under a bending stress of 125,000 p. s. i. without fracturing, while the specimen which was not matrix-stabilized in accordance with the invention exhibited a hot-bending angle of only 15° for virtually the same composition under a low breaking stress of 85,000 p. s. i. The titanium carbide cemented with 20% weight of nickel (Fig. 3) which exhibited practically no bending angle at 1000° C. had a low breaking stress of 63,000 p. s. i. and was markedly inferior to the test specimen produced in accordance with the invention (Fig. 1).

The necessity for subjecting the titanium carbide body to the proper matrix-stabilizing treatment subsequent to infiltration is also illustrated by referring to Figs. 4 to 6 which show the microstructure which is obtained when practicing the invention. Fig. 4 shows the microstructure at 1000 times magnification of an unetched infiltrated body within the invention which comprises a matrix containing the infiltrant metal **101** having dispersed therethrough fine particles of a precipitate **102** and essentially isolated larger titanium carbide grains and grain aggregates having a substantially rounded or spheroidized polyhedral shape **103**. Fig. 5 is similar to Fig. 4 but shows a microstructure in the etched condition at 1000 times magnification after etching with Marble's reagent and illustrates more clearly the profuse fine precipitate disturbed throughout the matrix surrounding the isolated titanium carbite grains. Fig. 6 illustrates the microstructure of an actual nozzle vane which withstood about 96 hours of actual testing in an engine under aggravating high temperature conditions. Normally a nozzle vane under

the same test conditions is considered acceptable if it withstands about 50 hours of testing. When a nozzle vane of titanium carbide does not have the aforementioned microstructure, it has poor resistance to thermal and mechanical shock and fails prematurely. Figs. 7 and 8 are illustrative of microstructures outside the scope of the invention. Thus, Fig. 7 shows the microstructure of a titanium carbide body of the same composition as the body of Fig. 4 comprising titanium carbide grains 104 having relatively sharp corners and edges in substantially the close-packed position of the original skeleton. Fig. 8 shows a microstructure of a similar product produced by a prior method comprising a close-packed arrangement of titanium carbide grains. It has been found that such microstructures outside the invention are indicative of poor ductility, poor strength, inadequate toughness and poor resistance to mechanical and/or thermal shock.

It is believed that the poor resistance to mechanical shock is due to an internal notch effect caused by local stress concentrations which are set up internally at or near the corners of the closely packed carbide grains during periods of applied dynamic stresses, such as centrifugal and/or vibrational stresses, etc. It is not uncommon for prior art titanium carbide bodies with this type of structure to exhibit low resistance to impact (drop or Micro-Charpy unnoticed bar test) of the order of about 3 inch pounds, the impact values hardly ever exceeding 4 inch pounds in value.

While the rounding of the corners of the angular-shape carbide grains has been found to minimize the so-called internal notch effect, this is not the only criterion. The matrix surrounding the rounded or partially spheroidized carbide grains must in itself be in a substantially stabilized condition with respect to the carbide grains. In other words, time should be given for the matrix to become enriched in the carbide which is expelled from solution as a fine precipitate when the material is cooled to below the solidus temperature. When this metallurgical stabilization is achieved and the carbide grains are substantially or partially spheroidized and surrounded by a continuous matrix containing a finely dispersed precipitate, improved results are assured.

Contrary to the prior art, it has been found that optimum resistance to impact is obtained when the stabilized matrix is not too soft but rather has a relatively high hardness and especially a high degree of toughness. The increase in toughness and hardness is attributed to the appearance of the fine precipitate resulting from the stabilization treatment. When the matrix is on the soft side, e. g. of the order of about 340 Vickers average or lower as determined by the microhardness test for a skeleton body containing about 60% by volume of TiC and infiltrated with a nickel base alloy, it is usually indicative of a matrix not sufficiently stabilized and generally the impact resistance of the body is low (drop impact of notched bar ¼ inch square cross section), for example of the order of about 4 inch pounds. When the matrix is harder and tougher (e. g. about 370 Vickers average or higher) and contains an even and profuse distribution of a fine precipitate together with the spheroidized larger grains of titanium-base carbide, the drop impact resistance of the body (¼ inch square, notched bar) is generally high and of the order of about 12 inch pounds. For purposes of control, the appearance of the fine precipitate in the matrix is considered indicative of an adequately stabilized matrix. It has been observed that the high impact values appear to be correlated to the mean spacing distance between the carbide grains after stabilization, with particularly high values being obtained at a mean spacing distance of the order of about 4 or 5 microns, preferably at least about 3 microns, and higher, for a carbide grain size ranging from about 2 to 20 microns, and averaging about 6 microns. For finer carbide grain sizes, it will be understood that the mean distance between the grains should be proportionately smaller.

The matrix stabilization time will vary according to the particle characteristics of the titanium carbide powder employed in producing the skeleton. For example, if the carbide powder is partially rounded or spheroidal to start with, less time is required to produce the desired microstructure, the controlling factor then being whether the matrix is sufficiently enriched in titanium carbide so that an even dispersion of fine precipitate is obtained in the matrix after cooling below the solidus temperature. Likewise, the finer the particle size of the starting carbide powder, the shorter will be the matrix stabilizing period. Infiltrated skeletons produced from carbide powder of 5 microns and less in size will stabilize faster than if the starting carbide powder is 10 microns or larger in size. The stabilizing time can be determined easily for each type of powder since the appearance under the microscope of the fine precipitate in the matrix is a good indicator of matrix stabilization after rounding of the large carbide grains occurs.

In producing refractory carbide bodies in accordance with the invention, it is not necessary to infiltrate the porous carbide skeleton and matrix stabilize it in a one furnace operation. For example, the carbide skeleton can be infiltrated with the matrix-forming metal in the manner described hereinbefore up to the point the skeleton is completely infiltrated but short of the point of matrix stabilization, followed by cooling to ordinary temperatures. The thus infiltrated skeleton may be shaped to specified form or dimensions and then placed back into the furnace and subjected to a matrix-stabilization treatment at a temperature above the liquidus temperature of the matrix-forming metal for a time sufficient to modify the skeleton structure and produce the novel microstructure described hereinbefore. The matrix-stabilizing treatment may be carried out either in vacuum or at sub-atmospheric pressure or at ordinary atmospheric pressure in a reducing or inert atmosphere.

In addition to having excellent toughness and improved resistance to impact, the titanium carbide bodies provided by the invention also exhibit remarkable resistance to thermal shock. A test which is employed in evaluating the resistance of metals to thermal shock is as follows:

A rectangular test specimen measuring one-quarter (¼) inch thick by three-eighths (⅜) inch wide by two (2) inches long is heated in a gas flame to a temperature of about 1100° C. and then quenched in water. The number of repeated heating and quenching cycles that the specimen can withstand without cracking is taken as a measure of resistance to thermal shock. An infiltrated titanium carbide body of the invention when subjected to the foregoing test showed excellent resistance to thermal shock in that it withstood as many as 21 heating and quenching cycles before cracking and shattering. However, when a cemented titanium carbide body containing 30% by weight of nickel was subjected to the same test, the body withstood only 10 heating and quenching cycles before fragmenting. A tungsten carbide body cemented with 13% by weight of cobalt cracked, shattered, and spalled during the first quenching cycle.

The improved combination of properties which can be obtained by the present invention are shown by referring to the table below, which gives various physical and mechanical properties of a typical infiltrated titanium carbide body. This body was produced by infiltrating a porous titanium carbide skeleton comprising about 60% by volume of the body with a matrix-forming heat and oxidation resistant alloy containing about 80% nickel, 14% chromium and 6% iron.

TABLE

Specific gravity	6.0–6.4.
Transverse rupture strength, at:	
Room temperature	190,000–250,000 p. s. i.
870° C.	150,000–190,000 p. s. i.
1000° C.	115,000–150,000 p. s. i.
Tensile strength, at 1000° C.	50,000 p. s. i.
Stress rupture strength, at:	
870° C. for 100 hours	38,000 p. s. i.
1000° C. for 100 hours	15,000 p. s. i.
Elongation, at 1000° C. for 100 hours and 15,000 p. s. i.	5%.
Modulus of elasticity, at 1000° C.	40,000,000 p. s. i.
Hardness, Rockwell "C" scale	55–58.
Charpy impact strength, unnotched specimen	10 ft. lbs.
Thermal expansion per ° C. over range from:	
20° C. to 650° C.	9.9×10^{-6} (in./in.).
20° C. to 1000° C.	10.8×10^{-6} (in./in.).
Thermal conductivity	0.063 cal./sec./° C./cm.
Electrical resistivity	$1.37–1.43\times10^{-4}$ 52/cm.
Weight gain, upon 100 hr. exposure to still air at 1000° C.	20–30 mg./cm.^{2}.

As has been mentioned hereinbefore, in producing infiltrated refractory carbide bodies such as titanium carbide bodies in accordance with the invention, it is preferred that a matrix-forming, heat resistant alloy be employed as the infiltrant metal, such as heat resistant nickel-base, cobalt-base, and iron-base heat resistant alloys. The improved results which can be obtained by employing a nickel-base alloy as the infiltrant metal is shown in Fig. 9 which depicts a set of curves illustrating the improved physical and mechanical properties exhibited by various compositions of titanium carbide composites infiltrated with an alloy containing 14% chromium, 6% iron and the balance substantially nickel (known by the trademark Inconel).

Likewise, the improved properties which are obtained by employing a cobalt-base alloy as the infiltrant metal are shown in Fig. 10 which depicts a set of curves showing the improved physical and mechanical properties exhibited by various compositions of titanium carbide composites infiltrated with an alloy containing 26% chromium, 10% nickel, 7.5% tungsten, 0.5% carbon, and the balance substantially cobalt (known by the trademark Stellite alloy No. 31).

Iron-base, heat resistant alloys have also been employed as infiltrant metal in producing heat resistant refractory carbide bodies within the scope of the invention. One iron-base alloy which may be employed in the invention as an infiltrant metal is a high-chromium stainless steel referred to as No. 446 alloy containing about 25% chromium, substantially the balance being iron containing the usual residual elements, such as carbon, silicon, manganese, etc. Tests conducted using the aforementioned high chromium steel as the infiltrant have indicated that satisfactory results can be obtained for titanium carbide composites comprising about 40% to 70% by volume of titanium carbide and about 60% to 30% by volume of the steel infiltrant. High modulus of rupture strength properties of over 100,000 p. s. i. were obtained at 1000° C. when the infiltrated composite contained about 61% to 67% by volume of titanium carbide with values running as high as about 123,000 p. s. i., and with bending angles as high as about 38 degrees.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given:

Example 1

A titanium carbide powder of a minus 325 mesh size containing approximately 75% titanium, 18% combined carbon and 3.0% free carbon was charged into a graphite crucible and heat treated in a reducing atmosphere at a temperature of 1900° C. for a period of one hour. The resulting agglomerated mass, after cooling, was crushed, pulverized and passed through a 140 mesh screen. About 5% by weight of carbonyl-nickel powder all passing through a 325 mesh sieve was mixed with the titanium carbide powder by milling in a stainless steel ball mill for 24 hours. The titanium carbide-nickel mixture was then blended dry with 1% by weight of phenolformaldehyde resin moistened with acetone and mixed thoroughly, followed by drying, pulverizing and screening through a 100 mesh sieve.

About 330 grams of the powder mixture was compacted in a carbide lined steel die at a pressure of about 10 t. s. i. into a block 2.5" x 5.0" x 0.60" high, of approximately 60% density of full. The pressed block was presintered at 1200° C. for one-half hour in a reducing atmosphere in a vacuum furnace. After cooling, a nozzle vane shape having a weight of approximately 190 grams was machined from the block.

The machined nozzle vane skeleton was sintered in a carbon tube furnace at 1600–1700° C. for approximately two hours under a vacuum ranging from about 500 microns to 50 microns Hg pressure. After cooling under vacuum, the sintered nozzle vane skeleton was placed in an alumina boat and about 250 grams of a nickel alloy sheet comprising 14% chromium, 6% iron and the balance substantially nickel was placed on top.

The assembly was heated in a carbon tube vacuum furnace to about 1480° C. for approximately 12 hours. During this treatment, the nickel alloy melted and infiltrated the vane shaped skeleton completely within 3 hours and during the additional 9 hours dissolved the amount of titanium carbide necessary to attain equilibrium and to stabilize the matrix to give optimum properties. The infiltrated and heat treated nozzle vane body was cooled under vacuum.

The resulting nozzle vane body had a weight of 444 grams and a density of about 6.31 g./cc. It was machined and lapped to the final nozzle vane dimensions.

Nozzle vanes produced in the above manner were mounted between shroud rings in the stationary section of a jet engine turbine and guided the hot combustion gases against the turbine buckets in a cycling test simulating an accelerated sequence of actual flight conditions. The vanes withstood this test without signs of damage or failure for more than 96 hours. The novel microstructure of an actual vane tested in the foregoing manner is illustrated by Fig. 6.

Example 2

A nozzle vane shaped skeleton was prepared as in Example 1 except that the titanium carbide powder was of 325 mesh size and comprised about 75% titanium, 18% combined carbon and 0.3% free carbon. The skeleton was machined into the shape of a nozzle vane and then sintered at 1400° C. for 1 hour under vacuum. After cooling under vacuum, the sintered nozzle vane was placed on a beryllia boat and about 300 grams of the nickel alloy sheet placed on top.

The assembly was heated in a carbon tube vacuum furnace to about 1430° C. for approximately 4 hours. During this treatment, the nickel alloy melted and completely infiltrated the vane skeleton within 1½ hours, and during the additional 2½ hours, dissolved the amount of titanium carbide necessary to attain equilibrium and to stabilize the matrix to give optimum properties. The subsequent operations were the same as Example 1, yielding a body weighing approximately 390 grams and having a density of about 6.65 g./cc.

Example 3

A skeleton test bar was fabricated in accordance with the procedure of Example 1. The skeleton bar measured 3" x ⅜" x ¼" and weighed approximately 17 grams. The infiltration of the bar with 20 grams of nickel

alloy took a total time of 70 minutes, 15 minutes being required to completely infiltrate the skeleton body, and the additional 55 minutes for the matrix stabilizing treatment.

Example 4

The procedure followed in Example 3 was employed except that titanium carbide powder was mixed with 5% by weight of cobalt. The skeleton bar in this case was infiltrated with 20 grams of an alloy containing 26% chromium, 10% nickel, 7.5% tungsten, 0.5% carbon, and the balance substantially cobalt. The infiltration of the bar took a total time of 1½ hours at 1430° C., 30 minutes being required to completely infiltrate the skeleton body, and the additional 60 minutes for the matrix stabilizing treatment.

The bars produced in Examples 3 and 4 had good bending properties and behaved similarly to the bar illustrated in Fig. 1 of the drawing.

Example 5

The procedure described in Example 1 was employed with the exception that a large body was hot pressed from a titanium carbide-metal powder mixture containing 10% cobalt powder of minus 325 mesh size. An approximately 70% dense, ring-shaped hollow cylinder skeleton body was produced by pouring 194 grams of the carbide-metal powder mixture into an annular cavity of 2.5 inch outside diameter of a graphite mold having a thickness of 3 inches and an outside diameter of 6 inches, and a 1 inch diameter core. Two tubular graphite punches acting in opposite directions were used to form a cavity having a depth of 13/16 inch when pressed flat with the facings of the mold. After filling the cavity with the powder, the punches projected approximately one-quarter inch on each facing of the mold.

The filled mold was inserted into a carbon-lined vertical induction furnace kept at 1100° C. The furnace was closed and the mold was then heated to 1600° C. in the absence of oxygen and nitrogen for over a period of 90 minutes, the induction current being shut off for five minutes each at 1300° C. and 1500° C. to permit thorough penetration of the heat throughout the mold and powder mass. The mold was kept at 1600° C. for 75 minutes and a pressure of 2000 p. s. i. exerted, until the punches were pressed flush with the mold body. Carefully controlled cooling followed, the temperature being reduced 100° C. every five minutes until 1200° C. was reached. At 1200° C. the mold was removed from the furnace and cooled.

The skeleton body was then removed, reheated in a carbon tube vacuum furnace and first sintered to a density of about 72% of full, and then, in a second operation, infiltrated with an alloy containing 25% chromium, 6% tungsten and the balance being substantially cobalt, followed by the matrix-stabilization treatment, as described in Example 1. The weight of the cobalt alloy charge was 201 grams. The total time required to complete the infiltration and the matrix-stabilizing treatments at 1525° C. was about 195 minutes, of which about 45 minutes was required to complete the infiltration.

The final weight of the infiltrated body was 395 grams, and the final density of the body was 6.44 grams per cubic centimeter. The titanium carbide content was about 69% by volume.

The ring was finish-machined and ground on all outside faces and the center bore hole, and finally cased in a steel block.

Although the foregoing examples are concerned with the fabrication of titanium carbide articles, it will be appreciated that articles of other types of refractory carbide articles, e. g. of tungsten carbide or tungsten-base carbide articles can be similarly fabricated. By tungsten-base carbide is meant a carbide comprising substantially tungsten and containing up to about 30% of such other carbides as titanium and tantalum carbide or up to about 20% of molybdenum, columbium, chromium or vanadium carbides. Thus, in producing tungsten-base carbide articles by the infiltration method, the body would be similarly matrix-stabilized after infiltration to produce a microstructure comprising a substantially ductile matrix having dispersed therethrough fine particles of a precipitate and isolated tungsten-containing carbide grains and grain aggregates of substantially spheroidized and/or partially spheroidized polyhedral or polygonal shapes.

While infiltration is the most desired method for producing the heat resistant bodies provided by the invention, the bodies may also be prepared by pressing a powdered mixture of the different ingredients in the proper proportions at room temperature into the desired shape, followed by sintering at a temperature above the liquidus of the matrix-forming heat resistant alloy phase but below the melting point of the carbide, the sintering being carried out in the presence of a substantially stationary liquid phase of the heat resistant alloy. While the liquid phase in the above method is considered to be essentially stationary as compared to the infiltration method which works on the principle of a mass capillary action, nevertheless the liquid phase may move slightly during part of the sintering cycle due to microscopic capillary action induced by the minute pores in the compressed powder body, and also due to plastic flow caused by shrinkage forces. In employing the foregoing method, the usual precautions must be taken in pressing oversize bodies so as to allow for shrinkage in subsequent heating operations. Likewise, great care in the selection of the powdered ingredients and in the sintering cycle and atmosphere, as well as in the supports and forms used for the articles during sintering must be exercised.

The present invention is applicable not only to heat resistant structural elements such as fluid guiding members in power plants but also to the production of other types of structural elements such as high temperature wear and erosion resistant parts and components, as well as hot shaping dies and tools including dies which are used to hot deform metals and alloys into complicated shapes.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

We claim:

1. A heat resistant article of high strength and high resistance to impact and creep at elevated temperatures of up to about 1000° C. and higher comprising a composite body containing about 40% to 80% by volume of titanium-base carbide and about 60% to 20% by volume of a ductile heat resistant matrix-forming metal comprising up to about 30% by weight of at least one metal selected from the group chromium, molybdenum and tungsten, the sum of these metals not exceeding about 40%, substantially the balance of the matrix-forming metal being at least one metal selected from the group consisting of iron, cobalt and nickel, the sum of these metals comprising at least about 40% by weight of the matrix-forming metal, said composite characterized by a microstructure comprising a substantially ductile matrix of said matrix-forming metal having dispersed therethrough fine particles of a precipitate and essentially isolated larger titanium-base carbide grains and grain aggregates having a substantially spheroidal polyhedral-like shape, the mean spacing distance between the grains and grain aggregates being at least about 3 microns for carbide grain sizes ranging substantially from about 2 to 20 microns and averaging about 6 microns in size, the minimum mean distance being proportionately smaller for finer average grain sizes.

2. The heat resistant article in accordance with claim 1,

characterized in that the composite comprises about 45% to 75% by volume of titanium-base carbide and about 55% to 25% by volume of the heat-resistant matrix-forming metal.

3. The heat resistant article in accordance with claim 1, characterized in that the composite comprises about 40% to 70% by volume of titanium-base carbide and about 60% to 30% by volume of said matrix-forming metal containing iron as the major element constituting at least 40% by weight of the matrix-forming metal.

4. The heat resistant article in accordance with claim 1, characterized in that the composite comprises about 50% to 80% by volume of titanium-base carbide and about 50% to 20% by volume of said matrix-forming metal containing cobalt as the major element constituting at least about 40% by weight of the matrix-forming metal.

5. The heat resistant article in accordance with claim 1, characterised in that the composite comprises about 40% to 75% by volume of titanium-base carbide and about 60% to 25% by volume of said matrix-forming metal containing nickel as the major element constituting at least about 40% by weight of the matrix-forming metal.

6. In a method of producing heat resistant articles of high strength and high resistance to impact and creep at elevated temperatures of up to about 1000° C. and higher comprising titanium-base carbide grains dispersed in a substantially ductile matrix of a heat resistant matrix-forming metal, the improvement which comprises heating to an elevated temperature a porous body of compacted particles of said carbide making up about 40% to 80% by volume of the compact and subjecting it to infiltration in the presence of a liquid phase infiltrant metal comprising said matrix-forming metal at a temperature ranging from about 25° C. to 250° C. above the liquidus temperature of said matrix-forming metal at a sub-atmospheric pressure of less than about 1000 microns of mercury for a time sufficient to allow the liquid matrix-forming metal to wet substantially completely the carbide and infiltrate the body, said matrix-forming metal comprising up to about 30% by weight of at least one metal from the group consisting of chromium, molybdenum and tungsten, the sum of these metals not exceeding about 40%, substantially the balance of the metal being at least one metal selected from the group consisting of iron, cobalt and nickel, the sum of these metals comprising at least 40% by weight of the matrix-forming metal composition, then subjecting said infiltrated carbide to a matrix-stabilizing treatment comprising further heating it in situ at substantially said infiltration temperature in the presence of said liquid phase for a time sufficient to round off the particles of said carbide and to enrich the matrix-forming metal in dissolved carbide, cooling the thus treated compacted carbide to ordinary temperatures thereby producing a heat resistant article having a microstructure comprising a continuous matrix of substantially ductile matrix comprising said matrix-forming metal having dispersed therethrough fine particles of a precipitate and isolated larger titanium-base carbide grains and grain aggregates having substantially spheroidal polyhedral-like shape, the mean spacing distance between the carbide grains and grain aggregates being at least about 3 microns for carbide grain sizes ranging substantially from about 2 to 20 microns and averaging about 6 microns in size, the minimum spacing distance being proportionately smaller for finer average grain sizes.

7. The method of claim 6, wherein the porous body comprises about 45% to 75% by volume of the titanium-base carbide.

8. The method of claim 6, wherein the porous skeleton body comprises about 40% to 70% by volume of titanium-base carbide and wherein the heat-resistant matrix-forming metal contains iron as the major element constituting at least about 40% by weight of the metal.

9. The method of claim 6, wherein the porous skeleton comprises about 50% to 80% by volume of titanium-base carbide and wherein the heat resistant matrix-forming metal contains cobalt as the major element constituting at least about 40% by weight of the metal.

10. The method of claim 6, wherein the porous skeleton comprises about 40% to 75% by volume of titanium-base carbide and wherein the heat resistant matrix-forming metal contains nickel as the major element constituting at least about 40% by weight of the metal.

11. The method of claim 6, wherein after the titanium-base carbide body has been substantially completely infiltrated, the infiltrated body is cooled to ordinary temperatures, shaped into a desired form and then subjected to the matrix-stabilizing treatment comprising heating it to a temperature ranging from about 25° C. to 250 C. above the liquidus temperature of the matrix metal for a time sufficient to modify and obtain said desired microstructure.

References Cited in the file of this patent

UNITED STATES PATENTS

2,612,443 Goetzel ---------- Sept. 30, 1952

OTHER REFERENCES

Trent et al.: Metallurgia, August 1950, pgs. 111–115.