METHOD OF INTERSTITIALLY CASTING METAL IN HIGH MELTING SKELETON BODIES

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The present invention relates to a method of producing heat resistant, refractory metal compound articles of improved surface quality. The invention also relates to a refractory support for use in the production of such articles characterized by improved resistance at elevated temperatures to metalfurferous systems involving reactive solid and/or liquid phases.

Examples of heat resistant articles which may be produced by the invention include thermal elements, e. g. turbine blades, nozzle vanes, nozzle vane guides, partitions, etc., for jet engines and the like, valves, valve parts, tools and wear resistant parts, and generally articles subjected to use in stress and/or to corrosion, erosion, abraision, etc., at ordinary and elevated temperatures. The present invention is a continuation-in-part of U. S. patent application Ser. No. 413,258, filed March 1, 1954, in the names of Claus G. Goetzel and Leonard P. Skolnick.

It is well known to produce heat resistant refractory metal compound articles comprising refractory metal compound grains dispersed through a metal matrix containing one or more matrix-forming metals of the iron group metals (iron, nickel, cobalt) with or without alloying ingredients, for example chromium, tungsten, molybdenum, tantalum, columbium, titanium, zirconium, etc. Generally, the matrix metal carbide in the presence of a stationary or moving liquid phase of a matrix-forming metal. In the method involving heating in the presence of a stationary liquid phase, the carbide metal in powder form is commingled with a matrix-forming or binder metal or alloy powders pressed into a desired shape and then sintered at an elevated temperature above the melting point of the matrix metal and below the melting point of the refractory metal carbide, much as the well-known tungsten carbide cutting tools are manufactured using cobalt as a binder. In the method involving a moving liquid phase, a porous and coherent carbide skeleton is produced and then infiltrated with a molten matrix-forming metal.

The heating temperatures employed in producing the articles are high and may range up to about 250° C. above the melting point of the matrix produced by the matrix-forming metal. Such liquid phase heating methods may range from about 1100° C. to 1700° C. Because of the high heating temperatures and the materials employed, the liquid and solid phases prevailing during the heating are chemically active and tend to react with the environment in which the liquid phase heating is conducted, with the result that the product is in many instances adversely affected. This holds true for the prevailing atmosphere, if any, as well as the refractory supports or containers contacting the article. Thus, it is important that the environment be maintained as inert as possible. In the case of the atmosphere, inert conditions may be achieved by utilizing inert gases, such as argon, helium, etc., or by utilizing a reducing gas such as carbon monoxide or hydrogen which may be considered inert for the purpose. Inert conditions may also be obtained by employing sub-atmospheric pressure ranging down to high vacuum.

Generally the most troublesome variable is the refractory support whose behavior at elevated temperatures cannot be predicted with any certainty, especially in metalfurferous systems involving a reactive molten metal phase. This problem is particularly acute in the production of heat resistant articles by infiltration involving a mass movement of infiltrant metal through a porous carbide skeleton while in contact with a refractory support, be it a crucible, a container, a mold, a flat base, or other supporting structure, etc.

In the co-pending case (U. S. Ser. No. 413,258), beryllia was found to make an excellent support material for the production of titanium carbide articles from powdered titanium carbide of special composition containing free carbon in amounts ranging from about 0.1% and up to about 1% or 1.2%. However, beryllia was limited in its application as a support to only a few materials and also was disadvantageous in that it presented health hazards due to its toxicity and, therefore, considerable care had to be exercised in using it. It was pointed out in the co-pending case that attempts had been made to utilize commercially available zirconia because of its reputed inertness but that this material was unsatisfactory as a support for metalfurferous systems involving the infiltration of a refractory carbide skeleton such as titanium carbide, with a heat resistant alloy, e. g. nickel, cobalt or iron. The molten metal phases in such systems were particularly reactive and were generally incompatible with the zirconia supports. The products produced from the use of zirconia as a support had inferior physical properties and exhibited mottled surfaces and in many instances completely lost their shape. Several types of so-called "stabilized" zirconia were tried and even these were found not satisfactory. In other words what had heretofore been known as stabilized zirconia was not satisfactory for the purposes of the invention. Although many attempts were made to overcome the foregoing disadvantages, none, as far as we are aware, was entirely successful.

A zirconia refractory of special composition has now been discovered that may be employed as a support in the production of heat resistant materials involving the presence of a reactive molten metal phase. The support is particularly applicable to the production of titanium carbide articles and generally to articles comprising high melting point refractory metal systems, such as refractory metal and/or refractory metal compound.

It is an object of the present invention to provide a method for producing heat resistant articles involving liquid phase heating at an elevated temperature.

It is another object of the present invention to provide a liquid phase heating method for producing heat resisting articles from refractory metal compound materials and matrix-forming metals, particularly heat resistant articles comprising refractory metal carbides, such as titanium carbide.

It is also within the scope of the invention to provide a refractory support comprising zirconia of special composition. The invention further provides a mold assembly for use in the production of heat resistant articles by the infiltration of a matrix-forming metal into a porous skeleton body.

A still further object of the invention is to provide a support or container for reactive molten metals, such as molten infiltrants employed in the production of heat resistant titanium carbide articles by infiltration.

Other objects will be apparent from the following description taken in conjunction with the accompanying drawings, wherein:

Fig. 1 is an embodiment of a zirconia support or mold assembly employed in carrying out the process of the invention involving the production of an infiltrated element of titanium carbide;
Figs. 2 and 3 illustrate a zirconia support or mold assembly utilized in the production of a plurality of infiltrated elements comprising titanium carbide, Fig. 3 being a cross section taken along the line 3—3 of Fig. 2; and

Fig. 4 is a three-dimensional representation of a zirconia mold assembly partially cut away utilized in the precision production of a turbine bucket and the like.

The present invention contemplates a method of producing heat resistant articles of improved internal and external metallurgical quality, particularly articles comprising substantially titanium carbide, by utilizing zirconia of special composition as a support during the liquid phase heating cycle, for example, as employed in the infiltration process. It has been discovered that when the zirconia comprising the support has a crystallographic structure, substantially cubic in form, the support remains, for all practical purposes, inert and does not adversely affect the resulting product to any great extent. A support comprising the special zirconia has given particularly good results in the production of heat resistant articles involving a system comprising a porous skeleton of titanium carbide and a refractive melt infiltrate nickel-base alloy. The results of the invention are obtained when the zirconia making up the support is crystallographically substantially cubic, i.e. has a structure at least three-quarters cubic.

Best results are obtained when the crystallographic structure of the zirconia is at least about 95% cubic and preferably at least about 98%. Generally, zirconia exists in the monoclinic form which is unsuitable for the purposes of the invention.

In order to insure zirconia of substantially cubic structure, it is important that the zirconia contains in solid solution crystallographic modifiers in amounts up to about 20% by weight of the zirconia and preferably not exceeding about 10% by weight, the amounts generally ranging from about 2% to 10%. For a structure of at least about 95% cubic, up to 10% of the modifiers may be employed while at least 98% cubic structure may be obtained with modifiers ranging from about 2% to 10% by weight. Examples of crystallographic modifiers which are effective in maintaining a cubic structure are calcium, magnesium, beryllia, stronbia, baria, ceria, and the like.

In order to insure the desired properties of cubic zirconia, impurities should not exceed 5% by weight and preferably should be kept below 2%.

A typical zirconia analysis which has proven very satisfactory is one consisting of about 5.2% calcium, 1% magnesium, and the balance zirconia, including the presence of such impurities as 0.16% SiO2, 0.1% TiO2, 0.11% Fe2O3, 0.05% Al2O3, 0.001% K2O, 0.003% Na2O and 0.001% B2O3.

As has been stated hereinbefore, the special zirconia is particularly useful as a support in the production of titanium carbide articles by infiltration. The infiltration temperatures involved are above 1100°C and generally above 1300°C. The infiltration temperatures are usually selected in accordance with the melting point of the infiltrant or matrix-forming metal or alloy and may range up to about 250°C above the melting point of the metal.

The zirconia support material may be employed in various forms. For example, it may be employed as a powder pack surrounding a skeleton in a mold, as a coating on a refractory support, in a compacted, or sintered form, or a hot pressed or slip cast form, etc. The support may be a simple flat structure, a container such as a boat, a crucible, a mold, or may comprise predetermined sintered shapes which may be fitted or assembled together to define a cavity having an internal configuration conforming to the shape and dimension of the article to be produced. Thus, for example, the zirconia in powder form can be shaped by compaction and firing into a plurality of refractory components which when fitted or assembled together will receive snugly and support a porous skeleton shape, such as a turbine blade, for infiltration.

The remarkable properties of crystallographically modified (i.e., cubic zirconia) powder enables it to be utilized as a dry investment for the vertical infiltration of porous skeleton shapes. Its use in this regard is akin to a precision casting mold with the exception that binder materials are not necessarily used to maintain the rigidity of the investment. The heat resistant articles produced by this method of infiltrations which in effect is a type of precision investment casting, exhibit a high degree of dimensional fidelity, improved surface quality, and generally are substantially free from areas of porosity normally found when other types of zirconia are employed as a dry investment or support.

The cubic zirconia powder is utilized as a dry investment by ram-packing it around a vertical or otherwise disposed porous skeleton body within a refractory container. The ram-packing may be effected on a conventional foundry compressed air jetting table. The ram-packing of zirconia powder in a mold provides a dense zirconia support or investment with a minimum of shrinkage after firing at a high temperature or during its use under high temperature infiltration conditions. The density of ram-packed zirconia powder and consequently its shrinkage properties may be controlled by controlling its particle size distribution. Examples of approximate particle size distributions which have enabled the production of dry zirconia investment of relatively high densities and low shrinkages are given as follows:

<table>
<thead>
<tr>
<th>Particle Diameter</th>
<th>No. 1 Percent</th>
<th>No. 2 Percent</th>
</tr>
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<tbody>
<tr>
<td>Less than 200 microns</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Less than 150 microns</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Less than 100 microns</td>
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<tr>
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<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Less than 25 microns</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Less than 10 microns</td>
<td>5</td>
<td>5</td>
</tr>
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</table>

Examples of dry investment molds utilizing ram-packed zirconia powder are illustrated by Figs. 1 to 4. Fig. 1 shows a refractory metal flask 1 of molybdenum having a vent hole 2 at its bottom the hole being traversed just above it with the flask by a stopper 3 of refractory material. The flask contains a packing of zirconia powder 4 in which is vertically disposed a porous skeleton of titanium carbide in the shape of a bar 5 which is in contact with a porous disc 6 of titanium carbide at its upper extremity which is utilized to meter and control the flow of infiltrant metal into and through the skeleton. The titanium carbide disc 6 is snugly fitted within a retainer ring 7 of fired cubic zirconia which holds and retains the infiltrant stock 8 which usually comprises a heat resistant alloy, such as a nickel-base alloy containing about 6% to 7% iron, 13% to 15% chromium and the balance substantially nickel.

In preparing such a support or mold, a refractory oxide or refractory metal flask of high softening point above the liquid phase heating temperature, preferably above about 1700°C is partially filled with loose zirconium oxide powder of substantially cubic form. Next a porous skeleton bar of titanium carbide or other high melting point material is inserted gently into the loosely packed powder and the entire assembly vibrated on a jolting table. Additional zirconia is added until the level is just below the top of the skeleton. A retaining ring of fired cubic zirconia is placed around the top of the bar and a porous titanium carbide filter disc inserted therein. The infiltrant metal is then placed inside the retainer ring on top of the porous titanium carbide disc and the whole made ready for infiltration which is conducted under inert conditions such as in a vacuum.
The skeleton is infiltrated in the usual manner and then cooled. Removing the infiltrated article from the flask presents practically no difficulties. On account of the special properties of cubic zirconia, the molten infiltrant metal does not react adversely with it and consequently the infiltrated article separates from the packed zirconia powder (which is usually moderately sintered) rather cleanly with a minimum of surface imperfections.

The porous disc placed on top of the skeleton functions as a filter to meter the infiltrant metal at a substantially uniform rate throughout the skeleton. The porous disc serves to prevent a fluctuation of the infiltrant metal in contact with the components of the skeleton, whereby the infiltrant metal in flowing interstitially throughout the skeleton does not substantially attack or dissolve it. In other words the infiltrant metal is brought as close as possible into chemical equilibrium with the skeleton before it enters it interstitially.

Observations have shown that cubic zirconia is remarkably resistant to the infiltrant metal itself even when the infiltrant metal is saturated with titanium and carbon or other skeleton forming materials during the initial stage of infiltration. Molten infiltrant metal saturated with the skeleton ingredients of the filter disc is usually quite reactive. Yet such a reactive liquid phase does not react substantially with the zirconia retaining ring in which it is contained and is not adversely affected by the material of the ring. Thus, the zirconia support material may be utilized for infiltrating systems involving reactive liquid phases at elevated temperatures and may be employed as a melting crucible.

Figs. 2 and 3 show the top and side elevation views of a multiple vertical infiltration mold utilizing a zirconia pack as in Fig. 1 and enabling the simultaneous production of four infiltrated elements or bars of titanium carbide. Fig. 3 which is a cross section of the multiple mold taken along line 3—3 of Fig. 2 shows a graphite crucible 10 into which is fitted a tungsten flask 11 closed at its bottom end by a tungsten plug or plate 12. The tungsten flask contains a packing of zirconia powder 13 into which is vertically disposed in spaced relation four bars 14 of porous titanium carbide each in contact with a porous filter disc 15 of the same material as the bar lying snugly within retaining ring 16 of fired cubic zirconia containing infiltrant metal stock 17.

Fig. 4 shows a cut-away view in three dimensions of a mold assembly utilizing a zirconia pack in the vertical infiltration of a titanium carbide skeleton turbine bucket. The assembly comprises a graphite crucible 20 into which is fitted a refractory metal flask or tube 21, e.g. tungsten, having a refractory metal bottom or plug 22. The refractory metal flask contains a packing of zirconia powder 23 into which is vertically disposed a porous skeleton of titanium carbide in the shape of a turbine bucket 24 which is integral or in contact with a porous filter disc 25 of titanium carbide utilized to meter and control the flow of infiltrant metal. The filter disc is snugly fitted into a retaining ring 26 of fired cubic zirconia which holds and retains infiltrant metal stock 27. This technique of infiltrating skeleton blades enables the production of an article with a high degree of dimensional fidelity similar to that obtained in precision casting.

In order to achieve the results of the invention, it is important that the liquid phase heating be conducted under substantially inert conditions which may be obtained in an inert atmosphere of argon, helium, etc., or of carbon monoxide, hydrogen or other reducing gases which do not react adversely with the materials employed in the process. It is preferred that the heating be conducted in a technical vacuum of less than 500 microns of mercury column down to about 5 microns or lower for efficient infiltration, the lowest possible attainable vacuum being preferable.

One of the advantages of cubic zirconia molds which are inert to reactive metalliferous systems is that such molds enable the production of infiltrated articles by means of centrifugal pressure. This may be achieved by disposing the mold containing the skeleton radially to the axis of spinning of a centrifugal casting machine. Under an appropriate elevated temperature and inert conditions, preferably a vacuum, the molten infiltrant metal causes the molten infiltrant metal to flow into it. This type of infiltration has the advantage of not only filling substantially all of the interstices of the skeleton with metal but also of enriching the surface of the skeleton with a layer of infiltrant metal which is desirable for protection and for increasing the density of the layer. This may be accomplished, if desired, by making a small allowance for a space between the surface of the skeleton and the surface of the investment adjacent it. The advantages of infiltration by centrifugal pressure is that it enables the production of a turbine blade with a foot of ductile infiltrant metal which can subsequently be machined into a fir tree root. By making an allowance in the mold for a space or cavity to be occupied by the blade root, this space is filled with excess infiltrant metal during centrifugal infiltration as an integral part of the blade. The foregoing method involving the use of a cubic zirconia mold may also be employed in casting a foot section of good metallurgical quality onto a previously infiltrated or sintered turbine blade or, if desired, the foot section may be gravity cast as root onto the blade. This may be accomplished by under-casting the root-forming metal about the lower end portion of the blade which may be provided with slots or other means to effect an under-cast joint of the metal to it after solidification. By controlling the temperature of the blade and the casting conditions, adequate diffusion bonding of the root-forming metal to the blade can be achieved. Thus, the investment of cubic zirconia finds wide and varied uses in the production of articles from metalliferous systems containing a reactive molten metal phase.

As illustrative of the invention, the following examples are given:

**Example 1**

In producing a turbine bucket in accordance with the liquid phase heating technique of the invention, a batch of titanium carbide powder of substantially less than 10 microns in particle size and containing approximately 79.1% titanium, about 19.2% combined carbon and about .14% free carbon (the balance free titanium, iron, oxygen, nitrogen, zirconium, etc.) was blended dry with about 1% by weight of a thermosetting phenolformaldehyde type resin. The mixture was then moistened with acetone, wet mixed thoroughly, and the powder mass finally dried, pulverized and passed through a 100 mesh screen (U. S. Standard). Approximately 320 grams of the powder were pressed into a rectangular block to a density of about 60% of full density (i.e., 40% porosity by volume). The block was then sintered for one hour at 1500° C. in a vacuum ranging from 32 to 25 microns of mercury column. The sintered block was cooled under vacuum, removed and then accurately machined to the contours of the bucket shape comprising a root-section and a foil section. The total weight of the skeleton body was approximately 170 grams after machining.

The skeleton body was then placed into a tungsten flask and surrounded with zirconia powder (at least 93% cubic) having the following approximate size distribution:

<table>
<thead>
<tr>
<th>Size (microns)</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 200</td>
<td>5</td>
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<tr>
<td>Less than 100</td>
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<td>Less than 50</td>
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<td>Less than 20</td>
<td>5</td>
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<tr>
<td>Less than 10</td>
<td>5</td>
</tr>
<tr>
<td>Less than 5</td>
<td>5</td>
</tr>
</tbody>
</table>

The entire assembly was vibrated on a conventional factory jolting table. Additional zirconia was added until it completely surrounded the bucket skeleton shape, leav-
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ing the end surface of the root-section exposed. A porous titanium carbide top plug which had been pressed from a minus 325 mesh titanium carbide powder and sintered in vacuum at 1400 °C. was placed on the exposed end surface of the bucket as shown in Figure 4. A pressed ring of cubic zirconia fitting this top plug was now placed over it and the infiltrant allotment placed into the container. The infiltrant metal in this case consisted of approximately 250 grams of a nickel alloy of the type comprising about 13% to 15% chromium, about 6% to 8% iron, and the balance substantially nickel. The entire assembly was then placed into a graphite outer container as shown in Figure 4, and lowered into a carbon tube induction heated vacuum furnace. The interstitial penetration or infiltration of the alloy into the pores of the skeleton was conducted at 1400 °C. for one hour at a vacuum of 30 microns of mercury column at the infiltration temperature. The infiltrant metal penetrated the pores of the skeleton vertically, filling the body completely through its entire length. After cooling in a vacuum to the solidification of the lowest melting phase, the assembly was removed in a reducing or neutral atmosphere at substantially atmospheric pressure. The cooled assembly was then removed from the furnace. The removal of the infiltrated bucket shape from the zirconia mass could be readily effected since substantially no reaction occurred between any of the metallic/organic phases and the inert support mass. Some mechanical bonding occurred since some sintering of the inert support mass did occur, converting it from a loose powder into a hard, friable mass which could be broken away easily from the infiltrated body. The infiltrated body was substantially free from surface imperfections and adherences and the excess metal which had not infiltrated the skeleton body remained above it in the pressed zirconia ring. The highly reactive metal phase in this ring was also clean and did not exhibit any adverse reaction with the zirconia in contact with it.

The bucket produced in this manner had an average density of about 6.2 grams per cubic centimeter and could be separated from the excess metal along its length by slicing. The concave and convex facings of the airfoil section required only polishing before use, whereas the root section required machining of serrations needed for attaching to the turbine wheel.

Example II

In producing a stator guide or nozzle vane, a sintered block of titanium carbide as prepared in Example I was accurately machined to the contours of the nozzle vane shape.

A zirconia mold for holding the body during the infiltration process was pressed from cubic zirconia powder (at least 95% cubic) of less than 30 microns in particle size. To aid in pressing approximately 1% of methyl cellulose was added as a binder and 1% of stearic acid as a die lubricant. Two halves were pressed, one containing the concave contour and one the convex contour of the nozzle vane, with provisions made for shrinkage of the mold during firing. Each half also contained a cavity at one end which would provide space in the completed assembly for containing the infiltrant metal above one end of the skeleton body. The mold was subsequently fired in air at 2500 °F. for 3 to 4 hours. The slowly cooled mold was now assembled with the blade positioned in it. The two halves of the mold were held by means of side plates of zirconia which were manufactured similarly to the mold halves.

The infiltrant metal consisted in this case of a cobalt base alloy comprising about 25% chromium, 10% nickel, 7.5% tungsten, 1% iron and the balance substantially cobalt which was placed in the container provided for it by the two mold halves. The entire assembly was now placed into a carbon tube induction heated vacuum furnace. The infiltration was conducted at 1400 °C. for one hour at a vacuum of 20 microns of mercury column at the infiltration temperature. The infiltrant metal melted, flowed through the orifice provided by the two halves of the mold and penetrated substantially the pores of the skeleton vertically, filling the body completely through its entire length. After cooling as in Example I and removal from the furnace, the two halves of the mold could be separated and the infiltrated nozzle vane freed from the support. No adverse reaction appeared to occur between either the infiltrant metal and the support or the liquid metal phase above the body and the support. The blade produced in this manner had an average density of about 6.3 grams per cubic centimeter and could be separated from the excess metal at one end by slicing. The concave and the convex facings of the airfoil section required only polishing before use.

Example III

A wear-resistant ring shaped thermal element was produced in accordance with the invention by pressing a skeleton body of the required shape from a mixture of titanium carbide powder and 5% chromium carbide powder. The titanium carbide powder was of finer than 325 mesh (U. S. Standard) and contained approximately 75% titanium, 18% combined carbon and 7.5% free carbon (the balance free titanium, iron, oxygen, titanium carbide, iron carbide, and carbon). The titanium carbide powder was passed through 325 mesh and contained approximately 11.3% combined carbon, no free carbon, with the balance substantially chromium.

The pressed body was sintered at 1550 °C. in a vacuum corresponding to 50 microns of mercury column. After cooling in vacuum the porous titanium carbide-chromium carbide body consisted of about 63% carbide by volume. This body was now joined to the infiltrant metal by means of a titanium carbide liner 1/8 inch long and 1/8 inch in diameter. The infiltrant comprised in this case of SAE 1080 steel. The porous titanium carbide body weighed approximately 150 grams and the infiltrant allotment was approximately 250 grams.

The skeleton body with the infiltrant joined to it was now placed into a packing of cubic zirconia powder similar to that used in Example I inside of an aluminum oxide refractory flask. The entire assembly was ram-packed. The infiltration was conducted in a carbon tube induction heated vacuum furnace at a temperature of 1550 °C. for one hour at a vacuum of 60 microns of mercury column at melting. After cooling in vacuum the assembly could be removed from the furnace and the infiltrated body with the connecting gate and excess infiltrant removed from the hard friable powder mass. The surface of both the infiltrated body and excess infiltrant mass was clean, smooth and apparently free from reaction products. The infiltrated body could be removed from the excess metal infiltrant by cutting at the connecting gate. It had an ultimate density of approximately 6.1 grams per cubic centimeter, and after polishing the working surface was ready for use as a wear part at elevated temperatures.

Example IV

In preparing an alloy to be used for infiltrating a titanium carbide body so as to produce a blade shape for aircraft component, the alloy of interest had a nominal analysis of 0.9% carbon, 1.6% aluminum, 8.3% iron, 5.7% iron, 13.6% chromium, with the balance essentially nickel. To prepare this alloy homogeneously it was melted in vacuum from a charge comprising 92% of a nickel-base alloy containing about 13% to 15% chromium, 6% to 8% iron and the balance substantially nickel and 8% of titanium carbide powder, all passing through 325 mesh with an analysis of about 80% titanium and 20% carbon.

The melting was conducted in a mold consisting of the
cubic zirconia of the invention. The melting period was 30 minutes at a temperature of 1500°C.

After cooling in vacuum the alloy was removed from the furnace and was apparently free from any reaction products with the mold material. Its chemical analysis was close to that of the desired nominal composition.

Example V

To prepare a percussion tool shaped as a triangular prism, a mixture of tungsten carbide containing 30% cobalt binder by weight was pressed conventionally and sintered in a vacuum chamber at a temperature of about 1800°C. The sintering chamber was evacuated by a vacuum pump. The sintered component was then removed from the mold and the mold was reused. The component was then polished and ground to the desired shape. The component was then heat treated in a furnace at a temperature of about 1500°C for about 30 minutes.

Sintering was conducted in a molybdenum wound hydrocarbon atmosphere furnace at a temperature of approximately 1530°C for 1/2 hour.

After cooling the zirconia could be broken open to remove the percussion tool. No substantial adverse reaction was evidenced between the carbide composition and the zirconia mass. Furthermore the product was free of distortion and its surface clean and free from imperfections.

While the illustrative examples given hereinbefore are concerned with liquid phase sintering in metalloferrous systems comprising titanium carbide and a liquid matrix-forming metal, it will be apparent that other refractory compounds may be employed. Such refractory metal compounds include the carbides, borides, nitrides, silicides, etc., of titanium, zirconium, chromium, molybdenum, tungsten, vanadium, columbium, tantalum, etc., and mixtures of two or more of these compounds.

The invention is preferably applicable to refractory metal carbides, particularly titanium carbide or a carbide based on titanium. Thus, titanium-base carbide may comprise up to about 5% by volume of each of such metal carbides as silicon carbide, boron carbide, and up to about 10% by volume each of chromium carbide, columbium carbide, tantalum carbide, vanadium carbide, molybdenum carbide, tungsten carbide, zirconium carbide or hafnium carbide, the total amounts of these carbides generally not exceeding 25% by volume of the titanium-base carbide. By titanium-base carbide is meant a carbide comprising substantially titanium and includes titanium carbide as such.

The matrix-forming metals which may be employed in the metalloferrous systems referred to herein include the iron group metals iron, nickel and cobalt, mixtures thereof, and heat-resistant alloys based on these metals, i.e., heat resistant nickel-base, cobalt-base and iron-base.

Examples of nickel-base matrix-forming alloys include: 80% nickel and 20% chromium; 80% nickel, 14% chromium and 6% iron; 15% chromium, 7% iron, 1% cobalt, 2.5% titanium, 0.7% aluminum and the balance nickel; 58% nickel, 15% chromium, 17% molybdenum, 5% tungsten and 3% iron; 95% nickel, 4.5% aluminum and 0.5% manganese, etc.

Examples of carbon-base matrix alloys which may be employed as matrix-forming include: 69% cobalt, 25% chromium and 6% molybdenum; 65% cobalt, 25% chromium, 6% tungsten, 2% nickel, 1% iron and other elements making up the balance of 1%: 56% cobalt, 10% nickel, 26% chromium and 7.5% tungsten; and 51.5% cobalt, 10% nickel, 20% chromium, 15% tungsten, 2% iron and 1.5% manganese, etc.

Some of the iron-base matrix-forming alloys include: 53% iron, 25% nickel, 16% chromium, and 6% molybdenum; 74% iron, 18% chromium and 8% nickel; 86% iron, 14% chromium; 82% iron and 18% chromium; 73% iron and 27% chromium, etc.

The matrix-forming metal or alloy may contain up to about 30% by weight of a metal selected from the group consisting of chromium, molybdenum and tungsten, the sum of the metals of said group preferably not exceeding 40%, substantially the balance being at least one iron group metal selected from the group consisting of iron, cobalt and nickel, the sum of the iron group metals being preferably at least about 40% by weight of the matrix-forming alloy. If desired, the matrix-forming alloy may also contain up to about 8% total of at least one metal from the group comprising tantalum, columbium and vanadium.

Alloys of the aforementioned types containing effective amounts of so-called well-known strengthening or age-hardening elements, such as zirconium, titanium, aluminum, etc., may be also employed in matrix-forming metals or alloys.

Metalloferrous systems based on refractory metal compounds (e.g., titanium-base carbide) and matrix-forming metals, may be produced over a wide range of compositions. In producing grades by liquid phase sintering or by infiltration, the refractory metal compound may range from about 40% to 80% by volume (preferably about 45% to 75%) and the matrix-forming metal range from about 60% to 20% by volume (preferably about 55% to 25%).

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 appended claims.

We claim:

1. In a method of producing a heat resistant refractory metal compound body in which grains of at least one said metal compound selected from the group consisting of carbides, borides, nitrides and silicides of titanium, zirconium, chromium, molybdenum, tungsten, vanadium, columbium and tantalum are dispersed through a metal matrix, said body being produced by heating the refractory metal compound at an elevated temperature in the presence of a liquid phase of the matrix metal, the improvement wherein the liquid phase heating is conducted while said liquid phase is in contact with said metal compound and with a zirconia support whose crystallographic structure is substantially cubic.

2. In a method of producing a heat resistant titanium-base carbide body comprising grains of said carbide dispersed through a metal matrix, said body being produced by heating the carbide at an elevated temperature in the presence of a liquid phase of the matrix metal, the improvement wherein the liquid phase heating is conducted while said liquid phase is in contact with said carbide and having a zirconia support in which the zirconia contains up to about 20% by weight of at least one crystallographic modifier selected from the group consisting of calcia, magnesia, beryllia, strontia, baria and ceria effective to maintain the crystallographic structure of said zirconia substantially cubic.

3. In a method of producing heat resistant articles of improved internal and external quality wherein the production thereof is concerned with reactive solid and liquid phases involving the infiltration of a matrix-forming metal into a porous skeleton body comprising at least one high melting point refractory metal compound selected from the group consisting of carbides, borides, nitrides and silicides of titanium, zirconium, chromium, molybdenum, tungsten, vanadium, columbium and tantalum, the improvement wherein the infiltration is conducted while said molten matrix-forming metal is in contact with said skeleton body and with a refractory support of zirconia whose crystallographic structure is substantially cubic.

4. In a method of producing heat resistant articles of improved internal and external quality wherein the production thereof is concerned with reactive solid and liquid phases involving the infiltration of a matrix-forming metal into a porous skeleton body comprising at least one high melting point refractory metal compound selected from the group consisting of carbides, borides, nitrides and silicides of titanium, zirconium, chromium, molybdenum, tungsten, vanadium, columbium and tantalum, the improvement wherein the infiltration is conducted while said molten matrix-forming metal is in contact with said skeleton body and with a refractory support of zirconia whose crystallographic structure is substantially cubic.
ing metal into a porous skeleton body comprising at least one high melting point refractory metal carbide, the improvement wherein the infiltration is conducted while said molten matrix-forming metal is in contact with said carbide skeleton body and with a refractory support of zirconia whose crystallographic structure is at least about 95% cubic.

5. In a method of producing heat resistant articles of improved internal and external quality wherein the production thereof is concerned with reactive solid and liquid phases involving the infiltration of a matrix-forming metal into a porous skeleton body comprising at least one high melting point refractory metal carbide with a molten matrix-forming metal, the improvement wherein the infiltration is conducted while said molten matrix-forming metal is in contact with said carbide skeleton body and with a refractory support of zirconia whose crystallographic structure is at least 98% cubic.

6. In a method of producing heat resistant articles of improved internal and external quality wherein the production thereof is concerned with reactive solid and liquid phases involving the infiltration of a matrix-forming metal into a porous skeleton body comprising titanium-base carbide, the improvement wherein the infiltration is conducted while said molten matrix-forming metal is in contact with said skeleton body and with a refractory support of zirconia containing up to about 20% by weight of at least one crystallographic modifier selected from the group consisting of calcia, magnesia, beryllia, strontia, baria and ceria effective to maintain the crystallographic structure of said zirconia at least about 98% cubic.

7. In a method of producing heat resistant articles of improved internal and external quality wherein the production thereof is concerned with reactive solid and liquid phases involving the infiltration of a matrix-forming metal into a porous skeleton body comprising a titanium-base carbide, the improvement wherein the infiltration is conducted while said molten matrix-forming metal is in contact with said refractory body and with a refractory support of zirconia containing up to about 10% by weight of at least one crystallographic modifier selected from the group consisting of calcia, magnesia, beryllia, strontia, baria and ceria effective to maintain the crystallographic structure of said zirconia at least about 95% cubic.

8. In a method of producing heat resistant articles of improved internal and external quality wherein the production thereof is concerned with reactive solid and liquid phases involving the infiltration of a matrix-forming metal into a porous skeleton body comprising titanium-base carbide, the improvement wherein the infiltration is conducted while said molten matrix-forming metal is in contact with said skeleton body and with a refractory support of zirconia containing about 2% to 10% of at least one crystallographic modifier selected from the group consisting of calcia, magnesia, beryllia, strontia, baria and ceria effective to maintain the crystallographic structure of said zirconia at least about 98% cubic.

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