July 9, 1957 C. G. GOETZEL ET AL 2,798,810

METHOD OF MAKING A SINTERED, HIGH TEMPERATURE ARTICLE

Filed Dec. 27, 1952 2 Sheets-Sheet 1

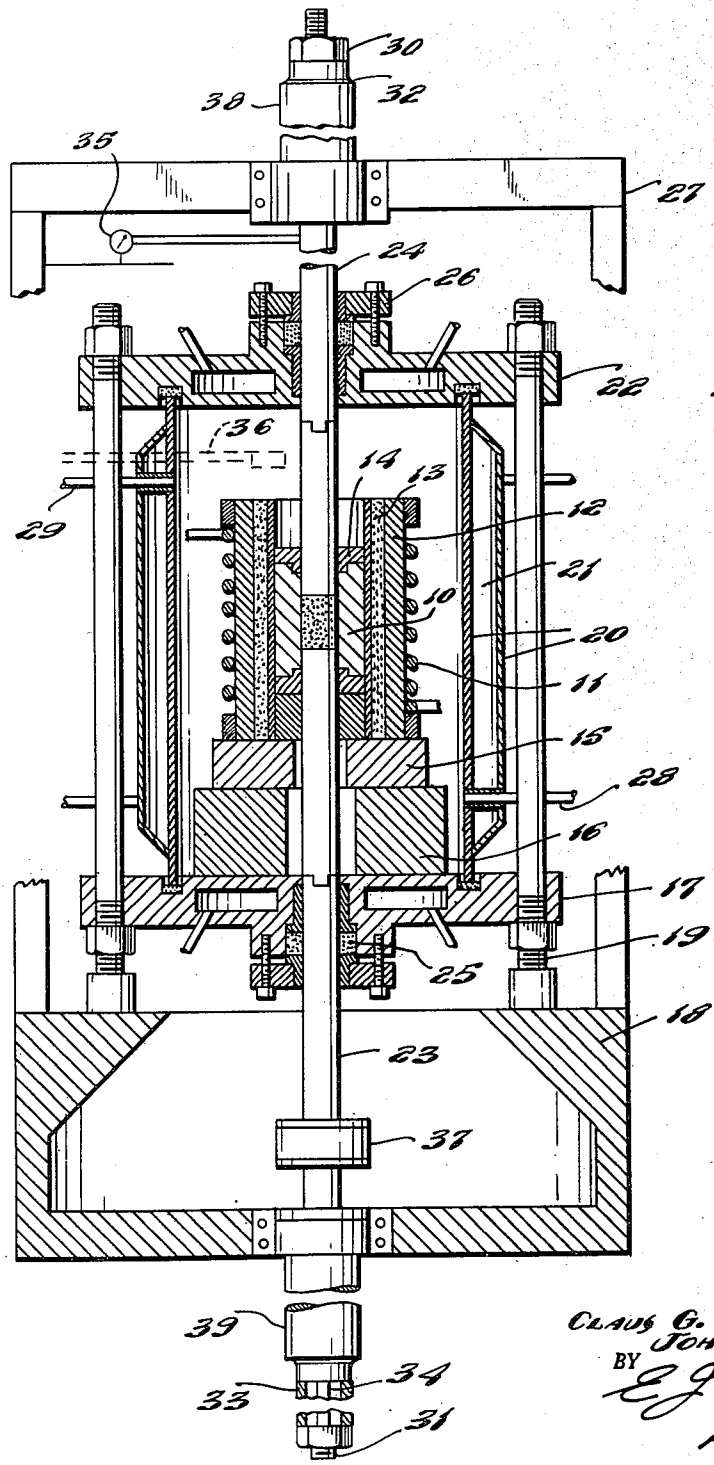


Fig. 1.

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Filed Dec. 27, 1952 2 Sheets-Sheet 2

Fig. 2.

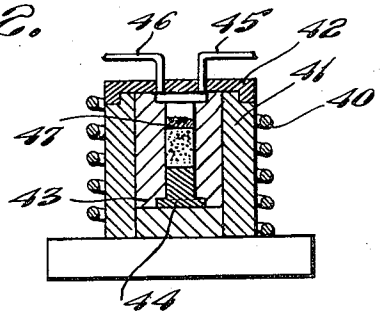


Fig. 3.

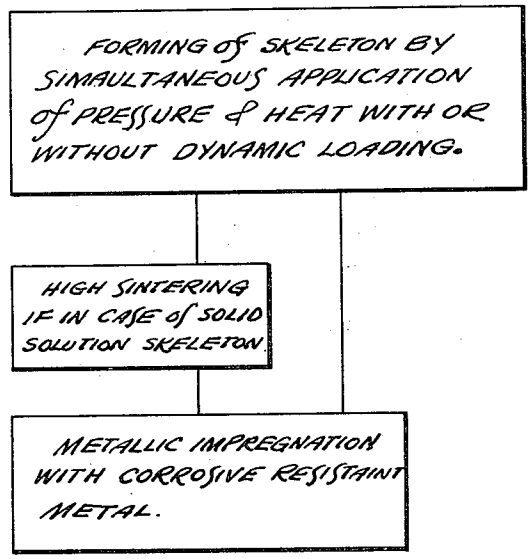
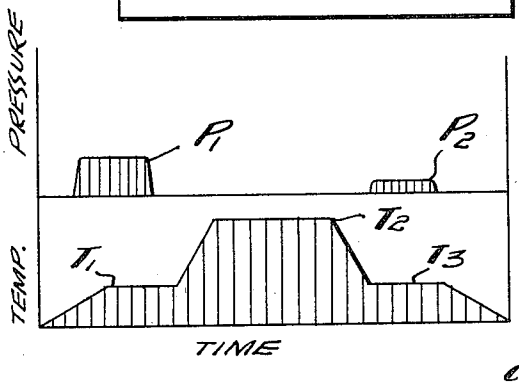


Fig. 4.



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METHOD OF MAKING A SINTERED, HIGH TEMPERATURE ARTICLE

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Application December 27, 1952, Serial No. 328,184

6 Claims. (Cl. 75—201)

The present invention relates to a method of producing from high melting point refractory compounds composite articles which are resistant to mechanical stresses and gaseous corrosion at a high temperature. This application is a continuation-in-part of our copending U. S. application, Ser. No. 795,101, filed December 31, 1947, now abandoned.

In recent years there has been a considerable demand for high temperature materials capable of withstanding high loads at elevated temperatures and also capable of resisting the corrosive effects of hot combustion gases at high operating temperatures. The demand for such materials has been particularly heavy since the commercial development by the aircraft industry of jet engines which have been continually improved in design to operate at higher and higher temperatures in order to obtain increased power output, high speeds, etc. Many high temperature materials, including wrought alloys, have been proposed for use as turbine blades, buckets, vanes, nozzles for jet engines, gas turbines, rockets, and the like, but these materials have not been too satisfactory in view of the increased high temperature requirements imposed on these materials. While wrought alloys have been partially satisfactory in fulfilling the needs of industry, these alloys present high temperature limitations in that they tend to soften at high operating temperatures and also in that their melting points are close to the proposed high operating temperatures around which power plant units of new engines are being designed. Precision cast alloys have likewise been proposed but like the wrought alloys were also limited for high temperature use because of their melting and softening points.

Considerable attempts have been made to solve the foregoing problem by employing powder metallurgy techniques. It was natural to turn to this field for a solution to the problem since it offered the possibility of fabricating heat resistant articles from refractory metal compounds of very high melting points without having to resort to the actual melting of these compounds. Thus, heat resistant articles were produced by employing the method developed for the fabrication of carbide cutting tools. In this method a refractory metal carbide (e. g. titanium carbide) is mixed with a small amount of cementing binding agent (e. g. cobalt) and pressed (by either cold or hot pressing) in a die into the desired shape which is then followed by sintering (the sintering not being required for hot pressed powders) at a relatively high temperature with the aim of producing a dense, coherent article of high hot strength. However, heat resistant articles produced by this method were likewise not too satisfactory due to inherent porosity, fine grain size and weak grain boundaries, all of which contributed to unfavorable hot tensile strength, unfavorable hot fatigue strength, and unfavorable long-time-to-rupture strength (stress to rupture) at elevated temperature. These articles were also limited in their use in that they tended to be brittle and thus were subject to mechanical failure due to mechanical vibration, fatigue, heat shock, etc.

In another attempt to solve the foregoing problem, a method was proposed to produce heat resistant articles by combining the powder metallurgy technique with infiltration. In other words this method differed from the aforementioned powder metallurgy cementing method in that the refractory metal compound (e. g. titanium carbide) was mixed with a small amount of a binder metal (e. g. cobalt or nickel) and then cold pressed to a porous skeleton structure followed by sintering to produce a fairly coherent porous skeleton which was then contacted with a molten infiltrant metal (e. g. a metal of the iron group or their base alloys) which was thereafter absorbed by the porous skeleton by capillary action. While this method was found to be a marked improvement over the conventional cementing method with regard to such important properties as hot tensile strength, stress to rupture, hot ductility, hot fatigue strength, thermal shock resistance, etc., it was found wanting in certain aspects. In forming skeletons of complex and irregular shapes by cold pressing involving conventional pressing techniques, it was found difficult to obtain consistently a uniform product. For example, in cold pressing an article such as porous turbine blade skeleton from a mixture of refractory metal carbide and a binder metal, it was found difficult to effect a uniform translation of the pressure throughout the blade body during pressing because of the high hardness, the angularity and the high contact friction of the carbide particles, unless complicated pressing techniques, e. g., multiple punches, were resorted to. In the case of the turbine blade, a high concentration of the carbide particles would tend to build up in the thin sections of the blade (e. g. the leading and trailing edges of the blade) while the thicker portions of the blade, particularly near the center of the blade, would develop a high degree of porosity and thus be lower in carbide particle concentration. Thus, the skeleton would have a marked degree of non-uniformity throughout the cross-section. Such a condition in the finally produced blade would adversely affect the performance of the blade in that the leading and trailing edges of the blade with the high concentration of refractory metal carbide body would tend to be brittle and to fail by vibration fatigue and thermal shock or mechanical impact during service.

The aforementioned adverse condition was found to be even further aggravated by the solvent action of the infiltrant metal on the carbide particles which it contacted during infiltration of the skeleton body. Thus, in the region of the leading and trailing edges of the blade where the carbide particles would tend to be highly concentrated, very little of the infiltrant metal would be absorbed and as a result very little of the carbide particles would dissolve. However, in the more porous areas in the thicker portions of the blade, e. g. near the center, a comparatively large amount of infiltrant metal would be absorbed which, because of its high concentration, would tend to dissolve considerably more of the carbide particles in the carbide-deficient areas which would result in further adversely increasing the non-uniform characteristics of the blade throughout its cross section. Thus, the effect of the non-uniform distribution of carbide particles brought about initially by the cold pressing of the powder was found to be further aggravated by the infiltration process. This adverse condition usually resulted in the final product having directional properties rather than uniform properties in all directions which uniformity is especially desired in turbine blades which in use are subjected to complex, multi-directional stresses.

While it will be appreciated that both hot and cold pressing are well known techniques in powder metallurgy, the available knowledge was found inadequate in solving the instant problem of providing satisfactory products

entirely by the infiltration method suitable for high temperature applications referred to hereinbefore. For example, in the production of bearings, hot pressing has been employed to produce skeleton bodies from soft, low melting point metals such as silver powder as an equivalent of cold pressing. The porous skeleton bodies produced by either method were infiltrated with molten lead or thallium. In such processes, it has also been suggested as an equivalent alternative that silver admixed with a small amount of lead be pressed into a porous skeleton body, sintered into a porous coherent mass and thereafter infiltrated with molten lead. While on first blush this might be taken to mean that both cold and hot pressing can be used for the instant purpose, we have found that such equivalence does not hold for the production of high temperature resistant articles from hard, very high melting point and relatively stable refractory compound materials such as titanium carbide, tungsten carbide, chromium carbide, etc. Although both hot and cold pressing can be employed to produce heat resistant articles from such materials, we have found that unobvious results of a very high order of magnitude will be obtained if one of the methods, i. e. hot pressing, is employed, provided that the operations are carried out under properly controlled conditions.

Other features and advantages of the invention will become apparent from the following description and drawing which are merely exemplary, in which:

Fig. 1 is a sectional view of one type of press that can be used in performing the present invention;

Fig. 2 is a schematic view of an apparatus for impregnation of the skeleton;

Fig. 3 is a flow diagram showing the sequence of operations; and

Fig. 4 is a chart showing relationship of temperature, pressure and time when a single operation is used.

In general the invention comprises a hot pressing and infiltration method in which the skeleton-forming process prior to infiltration is carried out under special conditions conductive to imparting certain plastic properties to hard refractory compounds (e. g. titanium carbide) thereby enabling the skeleton-forming pressure to equalize itself throughout the skeleton body. The results will be a porous skeleton body having uniform porosity throughout which after infiltration will give an end product having a uniform distribution of the infiltrant metal and uniform properties throughout its cross section. This is achieved by hot pressing the hard, high melting point refractory compound powder (e. g. titanium carbide) into a skeleton body of controlled uniform porosity at an elevated temperature above about 1150° C. at least for a sufficient time to impart to the carbide particles an effective degree of desired plasticity which results in pressure equalization throughout the body during pressing. This effect is even further enhanced and benefited by carrying out the hot pressing in the presence of a liquid metal phase and is achieved by employing small amounts of binder metal addition agent evenly dispersed throughout the refractory powder, the binder metal being maintained in the liquid state during compaction. Thus, the liquid phase serves as a sort of hydraulic cushion in further equalizing the stresses throughout the body despite the fact that the body at the same time is maintained in a state of controlled porosity. By properly manipulating, during hot pressing, the time of pressing in relation to the heating, holding and cooling cycle, the skeleton body can be maintained in its as-pressed porous condition with a uniform distribution of the refractory compound particles throughout the porous body, regardless of the complexity of the shape of the body. If the heating and hot pressing cycles are not controlled in the manner illustrated in the examples hereinafter with particular reference to the time of pressure application, it is difficult to control the final porosity of the skeleton because of the pressure

and temperature gradients which develop during the hot pressing. Thus, without such control, the natural tendency of the liquid binder to cause shrinkage of the body as a result of interfacial tension forces cannot be effectively prevented with the result that the requisite uniform porosity cannot be maintained. If the shrinkage forces that occur during hot pressing are allowed to be excessive, certain sections of the body are apt to become over-densified which renders the skeleton body unusable for the subsequent infiltration step.

The foregoing method differs in many respects from the ordinary hot pressing method employed for cemented carbides. In producing articles by the cementing process, the carbide particles containing the cementing agent in admixture therewith are heated while under a steady static pressure (amounting in the order of 25% of the final pressure employed) until the binder metal is molten after which the pressure is fully applied (e. g. about 1000 pounds per square inch) and maintained during the holding and cooling cycle in order to obtain complete densification.

In accordance with the invention, the loose powder is heated to a plastic range of the refractory compound (e. g. to 1600° C. in the case of TiC) and the pressure applied for a short period of time (e. g. up to about two minutes) after which the pressure is released and the heating continued, depending upon the mass, until the heat has penetrated throughout the body, which step is then followed by cooling without applied pressure. A skeleton body of controlled and uniform porosity is obtained.

The desired porosity of the skeleton body is determined by calculation beforehand and depends upon the theoretical density of the powder mixture, the weight of the powder employed in producing the porous skeleton, the final size of the porous skeleton, and its apparent density. If a mixture of titanium carbide powder and nickel powder is employed for producing a skeleton comprising about 90% titanium carbide and 10% nickel, such a mixture would have a theoretical density of about 5.3 grams/cm.^{3} (based on the density for titanium carbide of about 4.9 grams/cm.^{3}, and the density for nickel of about 8.9 grams/cm.^{3}). Thus, for the purpose of illustration, if a porous skeleton of the aforementioned powder mixture weighing 5.3 grams is desired having a porosity of about 50% by volume, this weight of powder would be hot pressed in a mold to a predetermined volume of about two cubic centimeters or to an apparent density of about 2.65 grams/cm.^{3}. If a porosity of 10% is desired, this same weight of powder would be hot pressed in a mold to a predetermined volume of about 1.11 cubic centimeters or to an apparent density of about 4.78 grams/cm.^{3}. If an intermediate porosity of 30% is desired, the 5.3 grams of powder mixture would be hot pressed in a mold to a predetermined volume of about 1.43 cubic centimeters or to an apparent density of about 3.77 grams/cm.^{3}. The desired volume of the hot pressed skeleton body is determined by mechanical stops positioned in such a manner that the stroke of the press is limited or the movement of the plunger is arrested. In producing the desired porosities in this manner, the absolute value of the ultimate pressure is not critical as long as it is great enough to overcome the resistance to packing by the interparticle friction of the powder in the mold and until the mechanical stops are reached. A practical working pressure of about 1000 to 1500 p. s. i. has been found adequate for the refractory compounds described herein.

The invention is particularly well adapted for use in producing objects of intricate or complex shapes, wherein the cavity of the mold is so shaped that, under ordinary and prior procedures, non-uniform phase distribution, densities and physical or chemical properties will occur in the skeleton and the finished article. Merely by way of example, the invention is illustrated in conjunction

with the manufacture of a turbine blade, but it is to be understood that many types of articles, such as turbine buckets, nozzles, vanes, valves, etc., may be successfully produced in accordance with the invention. A turbine blade to be made in accordance with the invention may have a feather or trailing edge, a leading edge, a curved body portion and a base of the desired shape.

In carrying the invention into practice, refractory compound powders, or mixtures thereof, with about 0.5 to 15 percent by weight of a metal powder selected from the group consisting of nickel, cobalt, iron and chromium powder is used for the production of the skeleton bodies and these powder mixtures are heated during their compaction and sintering in a mold to within a temperature range of between 1150 and 1750 degrees C. The amount of binder metal employed is dependent upon the refractory compound from which the skeleton is produced. For example, too much binder metal employed with some refractory materials leads to abnormal shrinkage during hot pressing while too little tends to result in a product of high fragility. It has been found that as a general rule the refractory compounds of high specific gravity tend to require low amounts of binder metal while refractory compounds of low specific gravity tend to require higher amounts of the binder metal in order to maintain proper volumetric relationship necessary to produce optimum bonding.

The refractory compounds which can be processed in accordance with the invention include the stable and high melting point carbides, borides particularly the di-borides), silicides (particularly the di-silicides), and nitrides of such refractory metals as titanium, zirconium, chromium, tungsten, columbium, molybdenum, vanadium, and tantalum, and also such other stable refractory compounds as beryllium oxide, magnesium oxide, aluminum oxide, zirconium oxide, silicon carbide and boron carbide. By refractory compounds are meant such stable materials having melting points in excess of the melting point of iron, i. e. in excess of about 1535° C. These compounds are also characterized by having hardnesses in excess of 750 kgs./mm.^{2} as measured by Vickers diamond pyramid indenter.

By way of example, a typical composition of a homogeneous skeleton material to be used for the purpose of this invention consists of 70% by weight of tungsten carbide (WC), 25% titanium carbide (TiC), and 5% cobalt (Co), the tungsten carbide (WC) and titanium carbide (TiC) components being preferably combined as a solid solution. Another typical composition of a homogeneous skeleton material as employed by this invention consists of 45 percent by weight tungsten (WC), 25 percent titanium carbide (TiC), 25% chromium carbide (Cr_3C_2), and 5% cobalt (Co), the tungsten carbide, titanium carbide and chromium carbide being preferably combined as a solid solution. Still another composition is one containing 95% titanium carbide (TiC) and 5% chromium carbide (Cr_3C_2) the titanium carbide and chromium carbide being preferably combined as a solid solution to the combined total of which is added 10% nickel. Another composition is one containing about 100% titanium carbide (TiC) to which is added about 10% nickel.

A titanium carbide powder containing finely dispersed free carbon in amounts of about 1 to 3 percent is preferred. Also, mixtures of free carbon-containing titanium carbide powder and about 5 to about 15 percent chromium powder to produce by diffusion heat treatment titanium carbide-chromium carbide solid solutions may be used successfully for the purpose of this invention after pulverization.

The first step in carrying out the process provided by the invention is to select the desired powdered material to be used for the skeleton and to feed this into the mold prior to its being placed in the compacting apparatus, although the powdered material can also be fed into the mold after the mold is in the compacting arrangement. It is preferable to so select the particle size distribution of the material as to obtain the desired density. An example of a suitable particle size analysis for the material would be 50 percent, ranging between 30 and 40 microns average particle diameter, 30 percent between 20 and 30 microns, and 20 percent between 10 and 20 microns. Still another example would be one wherein 50 percent of the particles are between 5 and 10 microns, 30 percent between 2 and 5 microns, and 20% between ½ and 2 microns.

Of course, the selection of the density depends upon the material, mold shape, pressure used, etc. The density attained must not be more than 90 percent of theoretical density because a pore volume of less than about 10 percent will, as stated before, cause the skeleton to lose the intercommunicating character of the pores thereof.

The unexpected results of the invention are believed to be achieved at least in part by controlling the heating and the compaction of the refractory compound and binder metal powder mixture so that the porosity by volume be not less than 10% nor more than 50%. It is preferred, however, that the porosity be controlled between 20% to 45%, by volume. Contrary to all customary practice and experience, such porous bodies can be satisfactorily produced by hot pressing in spite of the powerful and contractive shrinkage action of the liquid phase.

The desired density of skeletons for intricately shaped bodies may best be formed by a hydraulic press having a controlled stroke limit and means to heat the powder charge in the mold under pressure to a temperature sufficient to cause plastic flow and creation of sinter bonds.

In order to insure uniform density of the skeletons, means should be employed to impart to the filled mold pressing, heating and vibratory or dynamic loading actions. Dynamic loading may be effected by impact or the sudden application of force.

Dynamic loading may, for instance, be produced by providing the hydraulic press with pulsating pressure devices or the like so as to impart the desired flow to the powder, or a vibrating table may be connected so as to give the desired motion to the powder.

When a complex or intricately shaped mold is employed, the powder is placed in it and formed into a uniform dense shape by the combination of pressing, heating and vibration, dynamic or impact type loading superposed thereon or associated therewith in the desired relationship. The material in the mold will be uniformly distributed and the density will be uniform, which are necessary for the obtainment of satisfactory articles.

In accordance with the present invention, the skeleton body may be removed from the hot press and transferred to a device to be subjected to infiltration.

If desired, a separate sintering heat treatment following hot pressing and prior to infiltration may be applied to the skeleton, which produces a degree of alloying, since the skeleton is composed of two or more substances (i. e. the refractory compound and binder metal). Preferably the sintering is carried out in a protective or reducing atmosphere (e. g. CO or H_2) of subatmospheric pressure if carbides constitute the refractory compound. Other refractory compounds are preferably resintered in a protective or inert atmophere (e. g. argon or helium) at subatmospheric pressure.

The production of a porous skeleton of optimum combination of strength and corrosion resistance at elevated temperature may be achieved by forming solid solutions of two or more refractory metal compounds by a diffusion heat treatment at high temperatures in a controlled atmosphere. The compounds may be titanium carbide and tungsten carbide; or tantalum carbide, columbium carbide and titanium carbide; or titanium carbide and chromium carbide.

The hot pressed compact which may undergo a sub-

sequent heat or sintering treatment is in the form of a skeleton and ready for infiltration with a high temperature heat resistant metal or metal alloy. This metal may be placed in contact with the skeleton and the temperature increased to slightly above the melting point of the impregnating metal, i. e., at least 1100° C., so as to cause the flow of the molten infiltrant into the pores of the skeleton by capillary action.

According to the invention, the impregnating metal may be caused to fill the pores of the skeleton by a pressure differential apparatus such as a pressure applying device, especially when the compacting, the hot pressing heat treatment, and the infiltration are performed in a single apparatus.

If desired, the impregnated skeleton may be subjected to heat treatment for the purpose of producing an equilibrium structure to form an alloy and thus eliminate the liquid phase at the infiltration temperature or modify its composition so that it contains some of the skeleton material in solution. Upon cooling, a new phase may then precipitate within the infiltrant base matrix.

In Fig. 1 is shown one type of a hydraulic hot press arrangement which can besuccessfully used for the purposes of the present invention, the press being arranged so that the heating, pressing and infiltration can be performed within an enclosure in a protective atmosphere. The mold **10** containing the powdered charge may be placed in the press and the powdered material may be heated by means of the high frequency heating coil **11** surrounding the quartz tube **12** and the graphite sleeve **13**. Mold covers **14** may be employed as desired. The mold, schematically illustrated in the drawing, may be made of a ceramic or graphite.

The heating arrangement and mold holder are located on a support **15** carried on a base **16**. The base **16** is supported on a water cooled bottom cover **17**, which in turn is adjustably mounted on a stand **18** by means of bolts **19**. Side wall **20** of the press is arranged to be in sealing engagement with the bottom cover **16** and to have a water cooling jacket wall **21** thereon. An upper cover **22** may be arranged to be removably mounted upon the side wall **20** in sealing engagement therewith, said upper cover **22** having a suitable water cooling arrangement.

A pair of hydraulic or suitably operated plungers or rams **23** and **24** are provided to pass through stuffing boxes **25** and **26** located on the covers. The plungers are operated by any suitable types of hydraulic cylinders **38**, **39** or other mechanism as desired, the upper hydraulic or air cylinder **38** being carried on the frame **27** of the machine. The loose powder in the mold may be subjected to a constant pressure by means of the two opposing rams or may have a superimposed pulsating, jolting or vibrating action thereon so as to compact uniformly the powdered material.

One exemplification of dynamic loading is indicated at **37** in Fig. 1 in the form of a device in or connected to the lower ram **23**. Of course, it is possible to design the arrangement so that only one plunger is used.

The space within the wall **20** preferably has a protective atmosphere (inert or reducing atmosphere), or is evacuated. The atmosphere can be supplied through pipes **28** and **29**. Other means of heating the powder skeleton in the mold may be used, such as direct resistance heating by passing low voltage high amperage electrical currents through the mold, high frequency induction heating, etc. The skeleton can be heated to the desired temperature and hot pressed by the rams of the press.

It is desirable to stop the rams the correct distance apart to obtain the desired porosity of the compact. Means must be provided for stopping the movement of the rams relative to each other to avoid overcompressing of the compact. The movement of rams may be by adjustable nuts **30** and **31**. The upper nut **30** and ram **24** will be stopped by an abutment **32**, and the lower nut **31** will be stopped by the removable spacer member **33**. The spacer member may be bifurcated so as to straddle the lower ram **23**. If the spacer member **33** is removed then the lower ram **23** can be given an extra stroke following the hot pressing, after upper ram **24** has been withdrawn thus serving as a knock-out mechanism for the compact and/or mold. A gauge **35** may be provided accurately to indicate the distance of travel of the upper ram and to assist setting off the stops. This helps to insure the desired density or porosity of the skeleton.

In certain instances, it may be desirable to preform the skeleton in a suitable press, and then transfer the precompressed skeleton in the same mold to a sintering zone or apparatus where the hot pressing can be accomplished.

The intricate shape of an article being molded, like the turbine blade illustrated, prevents its removal from the mold without destroying it, unless a multi-piece mold is provided to which, however, the article, once removed, cannot be returned.

Upon completion of the sintering operation, the compacted and sintered skeleton in the mold is ready for impregnation with a high-temperature, heat-resistant metal. The impregnating material may comprise such metals as iron, nickel, cobalt, their alloys with each other and with chromium, molybdenum, tungsten, and vanadium as well as columbium and tantalum. The metals and alloys employed as infiltrants may contain such residual elements as carbon, nitrogen, silicon, manganese, copper, etc., which may be present as impurities or intentionally added without deleteriously affecting the alloy. In general the alloys employed as infiltrants may comprise heat-and oxidation-resistant nickel-base, cobalt-base, and iron-base alloys. For example, alloys of the aforementioned types containing effective amounts of the so-called well-known age hardening and strengthening elements, such as zirconium, titanium, aluminum, etc., are also contemplated within the scope of the invention.

A typical alloy composition of an infiltrant material employed successfully according to this invention comprises an alloy containing 69% by weight of cobalt, 25% chromium and 6% molybdenum; another one contains 50 percent by weight of cobalt, 29 percent chromium, 15 percent nickel and 6 percent molybdenum. Other examples are: 52 percent by weight of cobalt, 28 percent chromium, 11 percent nickel and 9 percent tungsten; 60 percent by weight of nickel, 16 percent molybdenum, 14 percent chromium, 5 percent tungsten and 5 percent iron; 60 percent by weight of chromium, 25 percent molybdenum and 15 percent iron; 80 percent nickel, 13 percent chromium, 7 percent iron; and 70 percent iron and 30 percent chromium.

The invention may be practiced with the apparatus of Fig. 1 by placing the powdered material into the mold **10** while the lower ram **23** is in position in the bottom of the mold. The upper cover **22** is then put in place and properly sealed on the side wall **20**. After sealing, the space within the wall **20** can be subjected to a desired atmosphere. Following this, heating is started to bring the powdered material to the desired temperature for the hot pressing operation, the temperature depending upon the materials used for the skeleton. The rams are then operated to compress the powdered material to the desired porosity, the stops of the press having been suitably set. The upper ram may be moved into the mold cavity so as to close the same, the lower ram being already in place to close off the bottom of the mold. After the upper ram has entered the mold cavity, pressure is applied so as to cause the rams to move towards each other and thus complete the desired compression of the powdered materials.

If diffusion alloying heat treatment is desired in the same apparatus of a skeleton containing two or more diffusion alloyable materials, then the temperature of the skeleton after hot pressing is raised to the desired level. The rams can be maintained in the stopped position following the hot pressing operation, or they may be separated.

Following the hot pressing, or the hot pressing and diffusion heat treatment, the mold and skeleton, or the skeleton itself may be taken to a suitable location for infiltration with the infiltrant alloy, or for further sintering prior to the infiltration step.

Fig. 2 exemplifies an infiltration apparatus having a suitable heating element **40**, a receptacle **41**, and a cover **42**. The mold **43** may have a bottom plug **44** placed therein to fill the cavity provided in the mold for accommodating the lower ram in the press arrangement of Fig. 1. Pipes **45** and **46** may be placed in the cover **42** for leading a suitable inert or reducing atmosphere to the interior of the infiltration apparatus. The infiltrant metal is placed at **47** on top of the compacted skeleton and brought to the desired temperature for infiltration of the compact by capillary action.

Alternatively, the infiltrant metal may be placed on top of the compacted skeleton, while the compact is still in the apparatus of Fig. 1. One method of accomplishing this would be by means of a ladle **36** having elements thereof extending through the walls of the apparatus for manipulation from the exterior of the press. After the upper ram **24** has been withdrawn, the ladle **36** can be operated so as to cause the infiltrant metal to come into contact with the upper face of the skeleton in mold **14**. The infiltrant metal shall be brought to the proper temperature, unless it is already at the correct temperature, to infiltrate properly the compact by capillary action.

It is evident that, if desired, the ram **25** may be employed to assist the infiltration of the skeleton with the infiltrant metal by the application of a mechanical driving force thereto.

The flow diagram of Fig. 3 shows the sequence of operations when the skeleton is formed by simultaneous application of heat and pressure. The pressure applied to the powder material may be a constant or may have dynamic loading superimposed. Following compaction, the skeleton may be subjected to a high sintering operation or heat treatment at a temperature within the range of 1600° C. to 2000° C. for the purpose of diffusion alloying if the skeleton is composed of material which can be combined by alloying, such as in a solid solution. After the formation of the skeleton is completed, either with or without the diffusion heat treatment as the case might be, the skeleton is infiltrated with a high-temperature, heat-resistant alloy.

When the skeleton is composed of materials to be combined in a solid solution, the process can be carried out in one apparatus, such as that of Fig. 1, by utilizing the information of Fig. 4, wherein the relationship between temperature, pressure and time is indicated.

After the powdered skeleton material is placed in the mold, it is brought to a suitable sintering temperature T_1, at which time a pressure P_1 is exerted on the heated powdered material for a suitable length of time. The pressure is then released and the heating of the skeleton continued to a diffusion alloying temperature T_2, which is maintained for the required time. The skeleton then is permitted to cool to a temperature T_3 suitable for the infiltration. Of course, the infiltrant metal should be introduced into the skeleton or brought into contact with it after temperature T_3 has been reached. The skeleton must be permitted to cool because if the infiltrant metal is entered at a high temperature there may be serious gas eruptions. The infiltration can be carried out by the capillary action of all the pores of the skeleton.

In the preferred form of the invention, the infiltration is carried out with the skeleton in a mold which may or may not be the mold previously employed in the hot pressing operation. The infiltration may also be carried out in a reducing or an inert atmosphere of sub-atmospheric pressure, or in a technical vacuum of 1000 to 25 microns mercury column. Moreover, it may be desirable to perform any sintering operation prior to infiltration under the above mentioned atmospheric conditions.

The following table which compares the properties of infiltrated hot pressed skeletons produced in accordance with the invention to optimum properties obtained with infiltrated skeletons produced by cold pressing shows the unexpectedly superior results of the improvement:

Comparison of properties of Inconel-infiltrated titanium carbide of similar composition produced from hot pressed and from cold pressed skeleton bodies

Properties	Hot Pressed Skeleton	Cold Pressed Skeleton
TiC Content (Vol. Percent)	63-65	64-66.
Final Density, gm./cm.^{3}	6. 08-6. 26	6. 10-6. 22.
Hardness, Ra	80	82.
Modulus of Rupture, p. s. i.:		
at room temp	250, 000-266, 000	186, 000-216, 000.
at 1,600° F	245, 000-262, 000	185, 000-195, 000.
at 1,800° F	129, 000-148, 000	120, 000-130, 000.
Deflection Under Maximum Load in inches:		
at 1,600° F	0. 100-0. 174	0. 103-0. 163.
at 1,800° F	0. 104-0. 269	0. 105-0. 240.
Bending Angle Under Maximum Load, Degrees:		
at 1,600° F	4°-7. 5°	4°-8°.
at 1,800° F	13°-27°	15°-21. 5°.
Ballistics Impact at 1,800° F	Withstood 333 and 600 ft./sec.	Withstood 333 and 600 ft./sec.
Thermal Shock Cycles To Fail in Water Quench from 2,000° F	15	5.

In producing the foregoing data, titanium carbide skeletons were infiltrated with a nickel-base alloy known by the trade-mark of Inconel (comprising about 80% nickel, about 14% chromium and about 6% iron). The modulus of rupture at room temperature for the infiltrated hot pressed body produced in accordance with the invention ranges from about 250,000 to 266,000 pounds per square inch (p. s. i.) while the infiltrated cold pressed body exhibited a lower value ranging from about 186,800 to 216,000 p. s. i. The modulus of rupture at 1600° F. of the infiltrated hot pressed body is superior to the infiltrated cold pressed body in that value of 245,000 to 262,000 p. s. i. was obtained for the hot pressed body as compared to a lower value of 165,000 to 195,000 p. s. i. for the cold pressed body. Similarly, the values for the modulus of rupture at 1800° F. also points to the superiority of the infiltrated hot pressed body over the lower modulus of rupture of the cold pressed body. The infiltrated hot pressed body is considerably more resistant to thermal shock having withstood a total of 15 drastic water quenching cooling cycles from a temperature of about 2000° F. before showing the first sign of failure, as compared to the cold pressed body which withstood only 5 such heating and cooling cycles.

Furthermore, infiltrated products produced in accordance with the invention have also demonstrated a high and superior load-carrying capacity at elevated temperatures. A hot body infiltrated with Inconel and comprising about 66% by volume of a cemented titanium carbide skeleton exhibited the extraordinarily high rupture life of 382 hours when subjected to a rupture stress of 35,000 p. s. i. at 1600° F. An infiltrated cold pressed body of similar composition exhibited less than half the life (153 hours) at the same temperature under a lower rupture stress of 32,500 p. s. i. One of the best cobalt base alloys now in use for turbine blades in jet engines and known in the trade as X-40 or "Stellite 31" (23% chromium, 10% nickel, 7% tungsten, 0.4% carbon and the balance substantially cobalt) exhibits a rupture life of less than 10 hours at a temperature of 1600° F. under a rupture stress of only 25,000 p. s. i., or a rupture life of 35 hours at a temperature of 1500° F. under a rupture stress of about 30,000 p. s. i.

Those skilled in the art will gain a better understanding of the invention from the following illustrative examples:

EXAMPLE 1

A powder mixture containing 900 grams tungsten car-

bide powder, 500 grams titanium carbide powder, 500 grams chromium carbide powder and 100 grams cobalt binder metal powder was prepared, placed in a stainless ball mill, and milled for forty-eight hours. The mixture was dried and pulverized.

A skeleton body test-bar having a density of 70% of theoretical density was produced by pouring 89 grams of the carbide-binder metal powder mixture into a rectangular cavity or mold opening of 3 inches in length, and one-half inch width and 1½ inches in thickness. Two graphite punches, one half inch thick, and each snug fitted into the mold opening from opposite directions and forming a cavity having a depth of one-half inch when pressed flush with the facings of the mold were used. After filling the mold cavity with the powder, the punches projected approximately one-sixteenth of an inch from each side of the top and bottom facing of the mold, thereby limiting the maximum pressing stroke to approximately one-eighth of an inch.

The filled mold was inserted into a carbon-lined vertical induction furnace maintained at 1100° C. The furnace was sealed and purged with hydrogen. The mold was then heated for a period of 45 minutes up to 1600° C., the induction current being shut off for three 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 thirty minutes and pressure exerted through two graphite pressure plates each placed on the top and bottom mold facing to overlap each of the projecting punches, the pressure being applied for one and one-half minutes at 1500 p. s. i. until the punches were pressed flush with the top and bottom faces of the mold. The cooling was carefully controlled, the temperature being reduced 100° C. every five minutes until 1200° C. was reached, by gradually reducing the power input of the high frequency induction furnace. At 1200° C. the mold was removed from the furnace and naturally cooled in air.

The hot pressed skeleton body was then ejected from the graphite mold and heated 30 to 60 minutes in a hydrogen furnace at 1800° C. at a subatmospheric pressure of 50 to 150 microns mercury to reduce surface oxides and remove graphite surface films from contact with the mold by formation of volatile hydrocarbon compounds. The skeleton body was then cooled in hydrogen, placed in contact with 35 grams of a cobalt alloy known as Vitallium (69% cobalt, 25% chrominum, and 6% molybdenum) inside an Alundum boat located in a graphite carrier. The body was infiltrated with Vitallium for a period of 40 minutes at 1525° C. An atmosphere of dessiciated hydrogen was maintained during this operation.

The density of the final bar was 9.73 g./cc. and the total weight was 124 grams.

EXAMPLE 2

The procedure of Example 1 was changed in that turbine nozzle vane blade was hot pressed from the carbide metal powder mixture. A 70 percent dense skeleton blade body was produced by pouring 218 grams of the carbide-binder metal powder mixture into a rectangular cavity or mold opening 4½ inches in length and 2½ inches in width, in a graphite mold having an outside diameter of 6 inches and a thickness of 3½ inches. The shape of the vane was determined by two graphite punches each snug fitted into the mold opening or cavity from opposite directions. The working face of one punch simulated a negative profile of the concave face of the nozzle vane while the working face of the other punch simulated the negative profile of the convex face of the vane. When the punches were pressed into the mold opening flush with the top and bottom facings of the mold, the space remaining between the working faces of the two punches corresponded to the shape of the nozzle vane having the desired air foil shape.

The filled mold was inserted into a carbon-lined induction furnace maintained at 1100° C. The furnace was closed and purged with hydrogen. The mold was then heated for a period of 75 minutes up to 1600° C., the induction current being shut off for four minutes at 1300° C. and 1500° C. to permit penetration of the heat throughout the mold and powder mass. The mold was kept at 1600° C. for sixty minutes and pressure exerted through two graphite plates of sufficient size each placed on the top and bottom mold facing to overlap each of the projecting punches, the pressure being applied for two minutes at 2,000 p. s. i. 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° was reached. At 1200° C. the mold was removed from the furnace and cooled.

The skeleton body was then ejected, reheated in a hydrogen furnace and infiltrated with Vitallium, as in Example 1. The weight of the Vitallium charge was 74 grams; the time for infiltration at 1525° C. was seventy-five minutes.

The final weight of the infiltrated body was 292 grams, and the final density was 9.73 g./cc.

EXAMPLE 3

A titanium carbide powder of minus 325 mesh size containing approximately 75% Ti, 18% combined carbon, and 2.5% free carbon was mixed with 5% by weight of minus 325 mesh electrolytic chromium powder. The mixture was then charged into a graphite crucible and heat treated in a reducing atmosphere by bringing the mixed powders to a temperature of about 2000° C. and holding at temperature for a period of one hour. The chromium was allowed to react with the available free carbon to form chromium carbide which subsequently formed a solid solution with the titanium carbide. The agglomerated mass resulting therefrom was cooled, crushed, pulverized and then passed through a 140 mesh sieve.

The solid solution carbide powder was then mixed with 10% by weight of carbonyl nickel powder binder of minus 325 mesh and the mixture dry milled in a stainless steel ball-mill for twenty-four hours.

A bar shaped skeleton body of 60% density was produced from the solid solution carbide-binder metal powder mixture by pouring it into a rectangular cavity or opening of three inches in length and three eighths of an inch in width in a graphite mold measuring five inches in length, two and one half inches in width, and one and one-half inches in thickness. Two graphite punches, five-eighths of an inch thick and each snug fitted into the mold opening from opposite directions, are used to form a cavity having a depth of one-quarter inch when they are pressed into the opening flush with the top and bottom facings of the mold. After filling the cavity with powder, the punches projected approximately one thirty-second of an inch from each side of the top and bottom facing of the mold, thereby limiting the total maximum pressing stroke to approximately one-sixteenth of an inch.

The filled mold was inserted into a carbon-lined vertical induction furnace kept at about 1150° C. The furnace was sealed and the mold heated in the absence of oxygen and nitrogen for a period of about forty-five minutes up to 1600° C., the induction current being shut off for three 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 eight minutes and a pressure of 1000 p. s. i. exerted through two graphite pressure plates of sufficient size each placed on the top and bottom mold facing to overlap each of the projecting punches. Pressing was carried out for approximately one minute until the punches were pressed flush with the mold body. The cooling was carefully controlled by steadily reducing the power input of the high frequency induction furnace, 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 allowed to cool naturally in the open space. The hot pressed skeleton bar was then ejected from the graphite mold and heated in a carbon tube furnace at 1400° C. in a hydrogen atmosphere for one hour. The skeleton bar was then cooled, placed in contact with 30 grams of a nickel alloy known as Nichrome-V (80 percent nickel and 20 percent chromium), and infiltrated in a carbon tube furnace at 1500° C. in a hydrogen atmosphere for twenty minutes. The amount of Nichrome-V infiltrant was in excess of the calculated theoretical amount to give an adequate supply of molten metal during the infiltration process and to compensate for any errors made in calculation.

The density of the final bar was 6.71 gm./cc. and the total weight after machining off the excess infiltrant metal was 24.5 grams. The final specimen had an approximate composition as follows: Ti—36%, C—8%, Ni—39%, Cr—14%, Fe—2%. The specimen had a modulus of rupture of about 190,000 p. s. i. at room temperature, 116,000 p. s. i. at 190° C., and a bending angle deflection of 20° at 985° C.

EXAMPLE 4

A titanium carbide powder of minus 325 mesh size containing approximately 75% Ti, 18% combined carbon and 2.5% free carbon was charged into a graphite crucible and heat-treated in a reducing atmosphere to a temperature of 1900° C. for a period of about one hour. The agglomerated mass resulting therefrom was cooled, crushed, pulverized, and passed through a 140 mesh sieve. To the powder was added and mixed 10% by weight of carbonyl nickel powder binder of minus 325 mesh size, the mixture being thereafter dry milled in a stainless steel ball-mill for twenty-four hours.

In the production of a 63% dense nozzle vane skeleton, 400 grams of the titanium carbide binder metal powder mixture was poured into a rectangular cavity or opening of four inches in length and two and one-fourth inches in width in the graphite mold measuring six inches in diameter and three and one half inches in thickness. Two graphite punches, one and one half inches thick and each snug fitted into the mold opening from opposite directions, are used to form a cavity having a depth of one-half inch when they are pressed into the opening flush with the top and bottom facings of the mold. After filling the cavity with powder, the punches projected approximately one-sixteenth of an inch from each side of the top and bottom facing of the mold, thereby limiting the total maximum pressing stroke to approximately one-eighth of an inch.

The filled mold was inserted into a carbon-lined vertical induction furnace kept at 1100° C. The furnace was sealed and the mold heated in the absence of oxygen and nitrogen for a period of ninety minutes up to 1600° C., the induction current having been 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 ninety minutes and a pressure of 2000 p. s. i. exerted through two graphite pressure plates of sufficient size each placed on the top and bottom mold facing to overlap each of the projecting punches. The pressing was carried out for approximately two minutes, until the punches were pressed flush with the mold body. The cooling was carefully controlled by steadily reducing the power input of the high frequency induction furnace, 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 allowed to cool naturally in the open space.

The hot pressed rectangular skeleton block was then ejected from the graphite mold and ground to the contours of a nozzle vane. The resulting 140 gram nozzle vane skeleton was heated in a carbon tube vacuum furnace at 1600–1700° C. for two hours. At temperature, the sub-atmospheric pressure in the furnace was reduced from about 400 microns to about 150 microns. The skeleton nozzle vane was then cooled in vacuum, placed in contact with 190 grams of a nickel alloy known as Inconel (80% nickel, 14% chromium, and 6% iron), and infiltrated in a carbon tube vacuum furnace at 1500° C. for approximately two hours. As in Example 3, the amount of infiltrant metal used was in excess of the calculated theoretical amount.

The density of the final, machined nozzle vane was 6.40 gm./cc. and the total weight was 294 grams.

EXAMPLE 5

The procedure of Example 4 was changed in that, after hot pressing, the 63% density skeleton block was ejected from the mold and cut into strips three-eights inch wide by one-fourth inch thick and by three inches long for processing into test bars. The cut strips were heated in a carbon tube vacuum furnace at 1600–1700° C. for one hour. At temperature, the sub-atmospheric pressure in the furnace was reduced from about 400 microns to about 50 microns. The skeleton bar which weighed eleven grams was cooled in vacuum, placed in contact with fifteen grams of the nickel alloy Inconel, and infiltrated in a carbon tube vacuum furnace at 1500° C. for seventy minutes. The amount of Inconel infiltrant was in excess of the calculated theoretical amount.

The density of the final test bar was 6.4 gm./cc. and the total weight after machining off the excess infiltrant was 22 grams.

The final material had an approximate composition as follows: Ti—38%, C—8½%, Ni—38½, Cr—7½, Fe—6%. The test specimens had an average modulus of rupture strength of 258,000 p. s. i. at room temperature, of 253,000 p. s. i. at 870° C., and of 125,000 p s. i. at 985° C. with an average bending angle deflection of 17° at that temperature. One of the test specimens when subjected to a stress-rupture test at about 870° C. had a rupture life of 382 hours at a stress of 35,000 p. s. i., with a corresponding elongation of 1½%.

EXAMPLE 6

The procedure of Example 4 was changed in that a nozzle vane skeleton body was produced by hot pressing the titanium carbide-metal powder mixture directly into the contour shape of a nozzle vane.

The hot pressing mold in this case consisted of a graphite mold body of eight inches in diameter and four inch thickness with a rectangular hole four inches long and two and one-fourth inches wide into which fit two graphite punches acting in opposite directions from the top and bottom faces of the mold. The working face of one punch comprised the negative profile of the concave face of a nozzle vane while the working face of the other punch comprised the negative profile of the convex face of the vane. When pressed flush to the facings of the mold, the space remaining between the two punches in the mold formed a cavity having, as cross section, the desired air foil shape of the nozzle vane.

In the production of a 63% dense nozzle vane skeleton 140 grams of titanium carbide-metal mixture was carefully placed in the mold so as to approximate the distribution of the mass in the final hot pressed nozzle vane shape.

The hot pressing, sintering and subsequent infiltration of the nozzle vane were in accordance with the procedure described in Example 4.

The density of the final nozzle vane was 640 gm./cc. and the total weight about 295 grams.

Since certain changes in carrying out the above process could be made without departing from the scope thereof, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

Having thus described the invention, what we claim

as new and desire to be secured by Letters Patent is as follows:

1. In a method for the production of high temperature resistant articles comprised substantially of a refractory material having a Vickers hardness of at least 750 kgs./mm.^{2} and a melting point higher than 1535° C., said articles having improved resistance to corrosive gases and high deforming stresses at elevated temperatures and being suitable for use as blades, buckets, nozzles, vanes, etc., in jet engines, gas turbines, rockets, and the like, the steps comprising intimately mixing said refractory compound material selected from the group consisting of carbides, borides, silicides, and nitrides of titanium, zirconium, chromium, tungsten, molybdenum, columbium and vanadium and including the compounds berillium oxide, magnesium oxide, aluminum oxide, zirconium oxide, silicon carbide, and boron carbide in powder form with 0.5% to 15% by weight of at least one binder metal powder selected from the group consisting of nickel, cobalt, iron and chromium, charging said intimately mixed powders into a mold, subjecting said intimately mixed powders to a skeleton forming treatment comprising heating said powder mixture to a temperature above the melting point of said metal binder and hot pressing said heated mixture at a pressure of about 1000 to 2000 p. s. i. in the presence of the liquid binder metal while maintaining a uniform and interconnected pore volume of said pressed skeleton within the range of about 10% to 50% by volume of the skeleton, maintaining said pressure for a short period of time ranging up to about two minutes after which it is released while continuing the heating, and thereafter infiltrating said porous skeleton body with a molten heat-resistant alloy infiltrant having a melting point higher than 1100° C.

2. The method according to claim 1, wherein the steps of producing and infiltrating the skeleton body are carried out in the same mold.

3. In a method for the production of high temperature resistant articles comprised substantially of a refractory compound material having Vickers hardness of at least 750 kgs./mm.^{2} and a melting point higher than 1535° C., said articles having improved resistance to corrosive gases and high deforming stresses at elevated temperatures and being suitable for use as blades, buckets, nozzles, vanes, etc., in jet engines, gas turbines, rockets, and the like, the steps comprising intimately mixing said refractory compound material selected from the group consisting of carbides, borides, silicides, and nitrides of titanium, zirconium, chromium, tungsten, molybdenum, columbium and vanadium and including the compounds beryllium oxide, magnesium oxide, aluminum oxide, zirconium oxide, silicon carbide and boron carbide in powder form with 0.5% to 15% by weight of at least one binder metal selected from the group consisting of nickel, cobalt, iron and chromium, charging said intimately mixed powders into a mold, subjecting said intimately mixed powders to a skeleton-forming treatment comprising heating said powder mixture to a temperature ranging from above the melting point of the binder metal to about 1750° C., and hot pressing said heated mixture in the presence of the liquid binder metal at a pressure of about 1000 to 2000 p. s. i. while maintaining a uniform and interconnected pore volume of about 20% to 45% by volume in said pressed skeleton, maintaining said pressure for a short period of time ranging up to about two minutes, releasing the pressure while continuing the heating, and subjecting the compacted porous skeleton to sintering at a temperature within the range of 1600° C. to 2000° C. in a protective atmosphere, cooling said skeleton and thereafter infiltrating it at an elevated temperature with a molten heat resistant alloy infiltrant having a melting point above 1100° C.

4. The method according to claim 3, wherein the refractory compound material comprises titanium carbide.

5. The method according to claim 3, wherein the refractory compound material comprises about 95% titanium carbide and about 5% chromium carbide with nickel being the binder metal in an amount comprising 10% of the titanium carbide and chromium carbide mixture.

6. The method according to claim 3, wherein the refractory compound material comprises about 45% tungsten carbide, 25% titanium carbide, and 25% of chromium carbide, the binder metal comprising about 5% cobalt.

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