July 26, 1960 W. R. RAYMONT 2,946,680

POWDER METALLURGY

Filed Aug. 10, 1955

Fig. 1

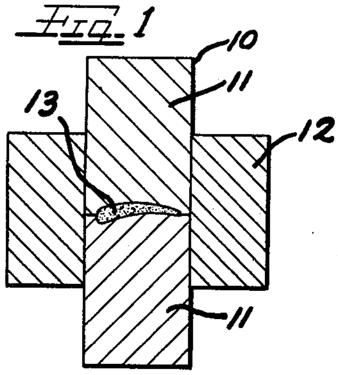


Fig. 2

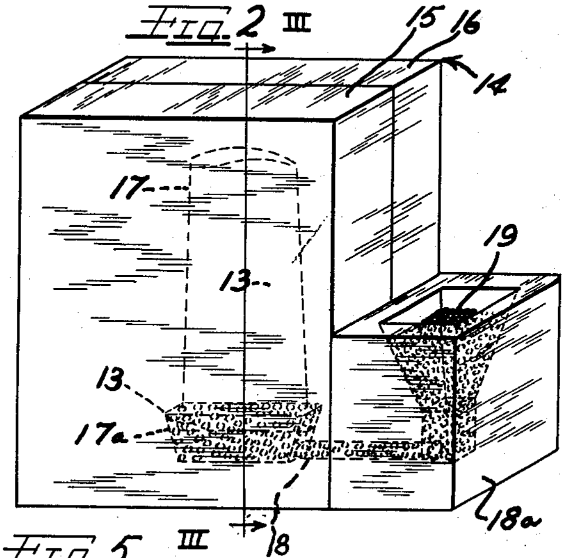


Fig. 3

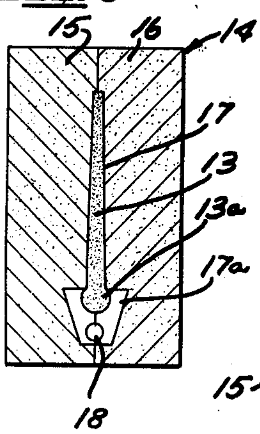


Fig. 5

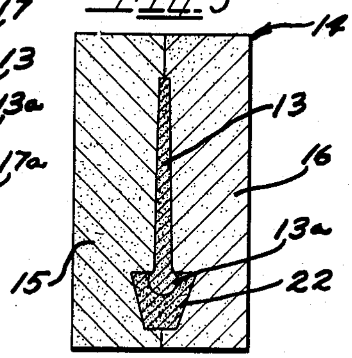


Fig. 6

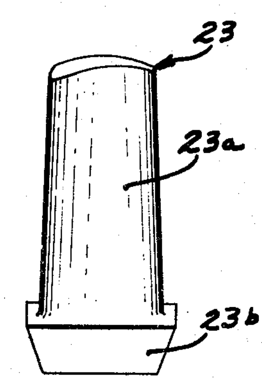
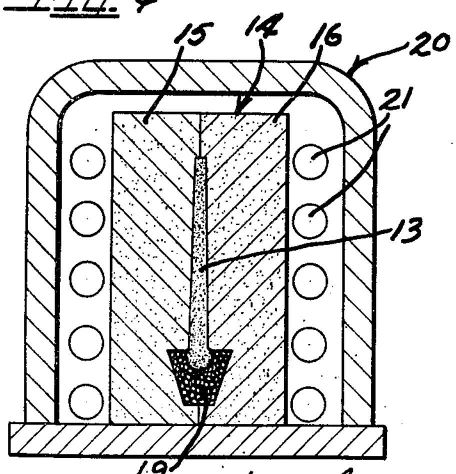


Fig. 4



Inventor
WILLIAM R. RAYMONT

By Hill, Sherman, Meroni, Gross & Simpson
Attys

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POWDER METALLURGY

William Roger Raymont, University Heights, Ohio, assignor to Thompson Ramo Wooldridge Inc., a corporation of Ohio

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5 Claims. (Cl. 75—200)

This invention relates to the production of highly refractory powdered metal articles with smooth finished surfaces. Particularly this invention deals with the production of powdered metal fluid directing members such as turbine buckets, compressor blades, nozzle diaphragm vanes, and the like jet engine parts wherein a powdered metal compact is infiltrated in an inert mold which will produce finished surfaces on the member while being penetrated by the infiltrant material.

While the invention will hereinafter be specifically described in connection with the production of ceramic-metallic compositions commonly known as "cermets," it should be understood that the principles of this invention are generally applicable to powder metallurgy methods and the invention, therefore, is not limited to the preferred specifically illustrated and described embodiments. Typical "cermet" compositions included in the preferred embodiments of this invention are refractory compounds such as titanium carbide, tungsten carbide, zirconium boride and aluminum oxide (alumina) in combination with refractory metals such as nickel, cobalt and chromium. Various mixtures of the metal compounds and the metals can be used.

Cermet compositions of the type indicated, because of their ability to withstand high temperatures and corrosive atmospheres, are well adapted for the manufacture of fluid directing members for gas turbine engines. However, heretofore known processes for making the cermet fluid directing members have been complex, time consuming, expensive and did not always provide a smooth surface finish which is highly desirable for such members.

A typical known process for fabricating turbine blading from cermet compositions involved the formation of a compact from powdered compositions, a pre-sintering of the compact, a shaping of the compact into desired airfoil contour either by coining or by means of a contour duplicating machine, sintering of the shaped compact to achieve desired density and strength, and finishing of the sintered blade by grinding and polishing operations. The finishing operations were particularly difficult because of hardness of the material and at best, only produced a mechanical finish.

In accordance with the present invention, turbine blading and the like is produced by forming a preform of the powdered metal compound or mixture of compounds, pre-sintering the preform if desired, confining the preform in a porous inert mold having a smooth mold cavity surface and infiltrating the preform while in the mold to fill the pores of the preform with the infiltrant and to build up any surfaces on the preform which are spaced from the mold cavity. If desired, the sintering and infiltrating steps can be carried out simultaneously in the mold. Further, if desired, the preform can be formed in the mold as, for example, by slip casting from a slurry, by centrifuging the powder directly into the mold, or the like. The infiltrated preform while still confined within the mold, can then be heat treated if desired, to

alloy the infiltrant and preform the ingredients. The mold finish is imparted to the surfaces of the member and the heretofore required expensive finishing operations are minimized or eliminated entirely.

A preferred mold material is zirconium oxide which is stabilized with calcium oxide to prevent crystallographic changes during heating. Other inert refractory materials including beryllium oxide, chromium oxide and porous clays, earth and the like, can be used provided that they will not react with the preform or wet the infiltrant metal.

A feature of the invention includes the formation of an infiltrant metal portion on the preform simultaneously with the infiltration of the preform. For example, an integral root end of the infiltrant metal can be formed on the preform to the exact shape of the surrounding die cavity walls while the infiltrant is filling the pores of the preform.

Another feature of the invention includes the simultaneous firing of the mold and sintering of the preform in the mold so that the mold will not restrain the preform against shrinkage.

A still further feature includes a pre-sintering of the preform and a separate pre-firing of the mold to shrink the preform and mold down to a common point where further sintering and firing will only produce substantially equal rates of shrinkage for both the preform and the mold.

A still further feature of the invention is to control the shrinkage rate of the mold to match the shrinkage rate of the preform by regulating the particle size of the mold powder in shaping the mold.

A still further feature of the invention is the conducting of the infiltrating operation in the mold under vacuum or in an inert atmosphere to eliminate oxidation complications.

It is then an object of this invention to provide a powder metallurgy process which imparts desired finishes to articles.

Another object of this invention is to provide a method of simultaneously infiltrating and finishing the surface of a powdered metal body.

A specific object of the invention is to provide a method of making cermet compositions of improved surface finish characteristics by the use of porous inert molds.

Another specific object of this invention is to provide a method of making turbine blades with a root end of one composition suurrounding and firmly bonded to the end of a vane portion of another composition.

Another specific object of this invention is to provide a method of making infiltrated powdered metal turbine blading which minimizes surface finishing operations and produces a smooth surface superior to heretofore available mechanically polished surfaces.

Another object of this invention is to provide an inexpensive method of making cermet articles including the formation of a preform and the formation of an inert refractory mold for receiving the preform wherein the preform and mold are simultaneously sintered and fired and the preform is then infiltrated with a metal that will pass through the mold without wetting the same and will impart to the preform the surface finish of the mold.

Other and further objects of this invention will be apparent to those skilled in the art from the following detailed description of the annexed sheet of drawings which, by way of a preferred example only, illustrates one method of this invention.

On the drawings:

Figure 1 is a vertical cross-sectional somewhat diagrammatic view of a die forming apparatus for producing preforms.

Figure 2 is an isometric view of a porous refractory mold assembly for the preform of Figure 1 showing infiltrant metal particles for the infiltration operation of this invention.

Figure 3 is a vertical cross-sectional view along the line III—III of Figure 2 with the particles omitted from the mold cavity.

Figure 4 is a vertical cross-sectional somewhat diagrammatic view of the mold of Figure 2 mounted in a vacuum furnace for the heat treating operations.

Figure 5 is a view similar to Figure 3 and illustrating the assembly after the heat treatment in the furnace of Figure 3.

Figure 6 is a perspective view of a finished turbine bucket produced by the method of this invention.

As shown on the drawings:

In Figure 1 the die assembly **10** includes a pair of opposed punches or dies **11** slidably guided in a fixture **12** and having active faces cooperating to produce a preform **13** of the desired airfoil contours of fluid directing members.

The material used to form the preform **13** may be a powder of any of a variety of ceramic, intermetallic or other refractory compositions such as for example, alumina, titanium carbide, zirconium boride, tungsten carbide and the like. It is preferred that particle size of these powders be relatively small and distributed more or less uniformly over a desired particle size range. A particularly effective particle size distribution pattern for titanium carbide includes about 35 parts by weight having a maximum dimension of 3 microns, about 32 parts by weight having a dimension in the range of from 3 to 6 microns, about 30 parts by weight having a dimension in the range of from 6 to 12 microns, and a maximum of about 3 parts by weight having a particle size in excess of 12 microns.

While it is not absolutely essential that the refractory particles be pure, better results will be obtained if certain contaminants are held within reasonable limits. For example, the specifications for the titanium carbide which are employed in this process are substantially as follows:

Table I

Ingredient:		Percent by weight
Combined carbon	minimum	19
Free carbon	maximum	0.3
Iron	do	0.1
Oxygen	do	1.2
Nitrogen	do	0.25
Hydrogen	do	0.03
Other impurities	do	0.75

The procedure for producing the preform may vary. One preferred procedure consists in mixing the refractory particles with a thermally depolymerizable binder such as polybutene, the binder constituting from about 5 to 35% by volume of the compact. Normally, the binder is added in solution in a suitable solvent such as xylene. The preform is then shaped cold in the dies **11** at pressures of about 0.5 to 25 tons per square inch and heated to a temperature sufficient to depolymerize the binder, and drive off the solvent. Processes of this type are fully described in U.S. Patent No. 2,593,507 to Eugene Wainer.

Another technique includes formation of a press block of the powder in the dies **11** at die pressures in the range of 0.5 to 50 tons per square inch followed by pre-sintering of the block in a vacuum furnace having a pressure of from 0.1 to 500 microns of mercury. The pre-sintering is conducted at temperatures of from 2000 to 2650° F. for a period varying from 5 minutes to 5 hours. The die block is then machined to the desired contour or alternately, of course, could be die shaped as accurately as possible.

According to this invention the preform **13** is to be infiltrated and heat treated in an inert porous mold which will impart finished surface characteristics to the blade. While a number of mold materials are useful, zirconium oxide, stabilized against crystallographic changes, is preferred. A heat stabilizer such as calcium oxide which reacts with zirconium oxide to form a stabilized crystallographic material, is used. Normally, about 1% or less of calcium oxide will be sufficient to stabilize the zirconium oxide at any temperatures reached during the heat treatment and infiltration of the preform.

It is preferred to have the zirconium oxide particles more or less uniformly distributed in the range of from between 5 and 44 microns. To aid in shaping the mold, a lubricant such as calcium stearate or lead stearate in an amount of 1 to 5% of the total composition can be used together with a binder such as methyl cellulose. About 1 to 2% by weight of a methyl cellulose solution having a 5% concentration in water will normally be sufficient.

Pressures employed in shaping the mold in metal dies (not shown) may vary widely but usually pressures of about 1 to 5 tons per square inch will be satisfactory.

The "green" mold is fired at temperatures of from 2000 to 3000° F. for a period of from 30 minutes to 5 hours. Usually a 2-hour firing treatment at 2500° F. is preferred. As explained above, the firing can occur simultaneously with the sintering of the preform in the mold.

As shown in Figures 2 and 3, the refractory mold is illustrated as a vertically split mold **14** composed of halves or sections **15** and **16** together cooperating to define a mold cavity **17** which snugly receives the vane portion of the preform **13** while a rounded head **13*a*** of the preform projects into an enlarged cavity portion **17*a***. This cavity portion **17*a*** communicates with a gate passage **18** projecting laterally from an end of the cavity **17*a*** to a sprue cup **18*a*** alongside the mold and having a cavity feeding the gate passage. The mold sections **15** and **16** are held together in any suitable manner as by means of clamps, insertion in a sheath, or the like.

If desired, the preform **13** can be made directly in the mold. Thus the powder can be incorporated in a suitable slurry which is then slip cast into the porous mold which will drain off the liquid components of the slurry and confine the solids in the shape of the mold cavity. Alternately, the powder can be centrifuged in the mold to form the preform.

As shown in Figures 2 and 4, the mold **14** with the preform **13** therein has infiltrant metal particles **19** deposited in the sprue cup **18*a*** and surrounding the preform end **13*a***. The mold assembly is now ready for the infiltration step and is placed in a sealed furnace **20** which can be evacuated or flooded with an inert gas such as argon or helium to maintain an inert atmosphere around the mold. The furnace is heated as by means of electrical heating elements **21** which surround the mold **14**.

The infiltration is carried out at temperatures ranging from about melting point of the infiltrant metal to about 200° above that melting point. The infiltration step will be completed in a time period from as little as 5 minutes to as much as 2 hours or more.

In addition to providing a sufficient amount of the corrosion resistant metal to impregnate completely the pores of the porous preform **13**, additional amounts of the infiltrant metal are provided to form a cast root **22** (Fig. 5) for the turbine blade, the root completely enveloping and bonded to the anchoring end **13*a*** formed on the preform **13**. The metal of the root **22** and the infiltrant of the pores of the preform **13** thereby provide a continuous, mono-metallic single phase system which not only provides the strength and corrosion resistance required in turbine blading or the like but also provides for a permanent bond between the vane portion and the root portion of the turbine blading.

Numerous different infiltration metals can be employed to advantage in the present invention. The corrosion resistant nickel-chromium alloys and the cobalt base alloys are particularly valuable for this purpose. The commercial heat resistant alloys such as those of the "Inconel" and heat resistant nitrided steels (Nitralloy) may also be employed. A typical "Inconel" alloy ("Inconel X") has the following composition:

Table II

Element:	Percent by weight
C	.08 maximum
Mn	.05 to 1
Si	.06 maximum
Cr	14–16
Al	0.5–1.0
Ti	2.0–2.6
Co	0.8–1.2
Fe	6–8
Ni	Balance

After the infiltration has been completed, the infiltrated compact can be further heat treated in the mold. For example, this can be accomplished by merely dropping the temperature of the assembly from the infiltration temperature to a temperature which will normally be on the order of 200° F. or so below the melting point of the infiltrant. Again, the heat treatment time will vary considerably depending upon the materials employed, the strength desired, the porosity, and similar factors, but ordinarily periods ranging from 5 minutes to 2 hours will be employed. The heat treatment, like the infiltration, is carried out under non-oxidizing conditions, and preferably under vacuum conditions in which the absolute pressure is in the range from about 0.5 to 500 microns of mercury.

As shown in Figure 6, a turbine bucket **23** formed according to this invention has a vane portion **23*a*** of airfoil shape and an enlarged massive anchoring root end portion **23*b***. The vane portion **23*a*** is composed of a skeleton network or matrix of the refractory compounds with the pores of the network or spaces between the particles filled with the infiltrant metal in firmly bonded relation thereto. The root end **23*b*** is composed of the infiltrant metal although it also has a core of the refractory compound surrounded by the infiltrant metal. All surfaces of the bucket **23** are smooth and have imparted thereto a finish of the walls defining the mold cavity. Since the mold material is not wet by the infiltrant metal and since the mold is quite porous, the metal can freely flow to all surfaces of the bucket without causing the bucket to stick to the mold.

According to this invention it is also practical to form the mold in one piece around the preform and to simultaneously pre-sinter the preform and fire the mold. This will prevent relative shrinkage between the preform and mold so that stresses are minimized. In this modification the preform can be completely enveloped by the mold. This modification has the advantage of eliminating separate firing and sintering steps and also eliminating the necessity for machining the end of the root which would otherwise be exposed in the sprue.

In order to further control the shrinkage, the particle sizes and relative densities of the preform and mold can be regulated. For example, suitable shrinkage conditions are obtained by making a preform of titanium carbide powder of less than 5 micron particle size under a pressure of 1 ton per square inch at room temperatures. The powder can contain about 1% lubricant or plasticizer such as "Sterotex" or paraffin wax. The preform thus formed has a density of about 50%.

The mold is formed from zirconium oxide powder of about 20 to 40 micron size, is pressed at room temperature at pressures of about 1 ton per square inch and may have a lubricant and a binder added. A suitable lubricant is about 3% by weight "Sterotex." A suitable binder is about 2% by weight of a 5% solution of methyl

cellulose. The preform is sintered and the mold is fired at a temperature of 2600° F. for about ½ hour. This causes a simultaneous shrinkage of the mold and preform in amounts of 7 to 8% by volume and the resulting parts will have a density of about 62 to 64%. The sintering and firing can occur simultaneously with the preform in the mold or separated from the mold.

If the mold is formed around the preform, provision must be made to contact the preform with the infiltrant metal. The infiltration can then occur at temperatures of about 2600° F.

If shrinkage of the mold and preform are not correlated, the mold cavity should be shaped so that it will permit relative shrinkage without stressing the preform to a rupture point. The pre-sintering and pre-firing of the mold will bring the parts down to a common remaining shrinkage factor where they will shrink at substantially equal rates when heated during the subsequent infiltrating and sintering operations.

Carrying out the infiltration under vacuum conditions takes advantage of the improved properties of alloys melted under vacuum conditions as compared with air melted alloys. For example, a typical corrosion resistant alloy has a ductility about four times as great when melted in vacuum as compared to its ductility when melted in air.

The following physical properties were obtained by the process of the present invention employing titanium carbide particles as the matrix and "Inconel X" as the infiltrant metal:

Table III

Density	6.2 gms./cc.
Tensile strength, room temperature	50,000 p.s.i.
Modulus of elasticity at 1800° F.	40,000 p.s.i.
Stress rupture strength:	
100 hr. life at 1600° F.	40,000 p.s.i.
100 hr. life at 1800° F.	15,000 p.s.i.
Thermal expansion, per ° F.:	
From 70° to 1200° F.	5.5×10^{-6} in./in.
From 70° to 1800° F.	6.0×10^{-6} in./in.
Thermal conductivity	0.063 cal./sec./cm.^{2}/° C./cm.
Electrical resistivity	$1.37\text{–}1.43\times10^{-4}$ ohm/cm.
Impact strength, unnotched Izod	8–10 ft. lbs.
Hardness	55–58 Rc.
Weight gain, after 100 hrs. in still air at 1800° F.	20–30 mg./cm.^{2}.
Transverse strength:	
Room temperature	190,000–250,000 p.s.i.
1600° F.	150,000–190,000 p.s.i.
1800° F.	115,000–150,000 p.s.i.

It will be evident that various modifications can be made to the described embodiments without departing from the scope of the present invention.

I claim as my invention:

1. The method of making corrosion resistant shapes from refractory compositions which comprises forming a refractory powder into a self-sustaining shaped preform, supporting said preform in a porous ceramic mold which has a thermal shrinkage rate substantially the same as that of said preform, infiltrating said preform while in said mold with a molten corrosion resistant composition under non-oxidizing conditions, and heat treating the infiltrated preform while the same is still confined in said mold.

2. A method of making corrosion resistant shapes from refractory compositions which comprises forming refractory powder into a self-sustaining shaped preform, supporting said preform in a tight fitting complementary ceramic mold having a thermal shrinkage rate substantially the same as that of said preform, infiltrating said preform while in said mold with a molten corrosion resistant composition under vacuum conditions, and heat treat-

ing the infiltrated preform while the same is still confined in said mold.

3. The method of making improved corrosion resistant shapes from refractory compositions which comprises forming a refractory powder into a self-sustaining shaped preform, confining said preform in a tightly fitting ceramic mold having a thermal shrinkage rate substantially the same as that of said preform, infiltrating said preform in said mold with a molten corrosion resistant infiltrant composition under non-oxidizing conditions, reducing the temperature after completion of infiltration to a temperature below the melting point of the infiltrant composition but high enough to heat treat the infiltrated mass, and heat treating said infiltrated mass at said temperature.

4. The method of making an infiltrated article having controlled surface characteristics which comprises compacting a powder to provide a self-sustaining preform of desired shape, forming a complementary preform mold having a shrinkage rate substantially the same as the shrinkage rate of the preform at the infiltration temperature, assembling the preform in the mold, and infiltrating the preform at an elevated infiltration temperature with a material that will not wet the mold but which is compatible with the preform, allowing the preform and mold to shrink at substantially the same rate, and continually supporting the preform in the mold whereby the mold finish will be imparted to the preform and the surface characteristics of the infiltrant material will be controlled by the mold finish.

5. The method of making an infiltrated powdered metal article which comprises compacting a powdered metal to form a self-sustaining preform of desired shape, forming a preform mold for said preform, regulating the particle sizes and relative densities of the preform and mold to provide substantially the same shrinkage rate for the preform and mold, assembling the preform in the mold, contacting the preform with an infiltrant metal which is compatible with the preform but which will not wet the mold, heating the assembly above the melting point of the infiltrant metal to infiltrate the preform with the metal, allowing the preform and mold to shrink at substantially the same rate, and continually supporting the preform in the mold to thereby control the surface characteristics of the resulting article.

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