United States Patent [15] **3,701,379**
Fassler et al. [45] **Oct. 31, 1972**

[54] **PROCESS OF CASTING UTILIZING MAGNESIUM OXIDE CORES**

[72] Inventors: **Michael H. Fassler**, Middletown, Conn.; **Norman E. Brinker**, Gardena, Calif.

[73] Assignee: **United Aircraft Corporation**, East Hartford, Conn.

[22] Filed: **July 6, 1971**

[21] Appl. No.: **160,184**

[52] **U.S. Cl.** **164/132,** 164/43
[51] **Int. Cl.** **B22d 29/00**
[58] **Field of Search** 164/41, 43, 132

[56] **References Cited**

UNITED STATES PATENTS

3,407,864	10/1968	Anderko et al.	164/41
3,473,599	10/1969	Rose	164/41
3,645,491	2/1972	Brown et al.	164/43

Primary Examiner—J. Spencer Overholser
Assistant Examiner—John E. Roethel
Attorney—Richard N. James

[57] **ABSTRACT**

A metal casting having internal passages and apertures can be formed by pouring molten metal into a mold having a magnesium oxide core disposed therein. The core can be made by forming a mixture of magnesium oxide and an evanescent resin and shaping this mixture by suitable molding techniques. The evanescent resin is then slowly volatilized to leave a core of substantially pure MgO which can be sintered to form a carbonaceous material-free, self-supporting body. After a casting is made around the core, it can be removed by washing the casting in a non-corrosive media such as water or dilute acetic acid.

9 Claims, No Drawings

PROCESS OF CASTING UTILIZING MAGNESIUM OXIDE CORES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the manufacture of metal castings having internal passages and apertures disposed therein. Specifically, the present invention relates to the manufacture of superalloy metal castings by investment casting techniques in which small and narrow passages and apertures are internally disposed.

2. Description of the Prior Art

In investment casting, a disposable pattern, which is a replica of the part to be cast and which includes any necessary gates and risers, is usually dipped in a refractory slurry which hardens to form a smooth coating that serves as the mold face. The precoating or dipcoating of the pattern usually is carried out by immersing the pattern in a suspension of a fine refractory powder in a suitable liquid binder that is capable of hardening during drying at room conditions. Following dipping, the excess slurry is drained from the pattern and the coating is stuccoed while wet with coarser refractory particles which help to set the coating.

A ceramic shell-mold is usually prepared by repeating the dipping and stuccoing operations described above until a shell having a sufficient thickness to resist the stresses occurring in subsequent operations is built up around the pattern. The usual thickness range is from one-eighth of an inch to one-half of an inch, although thinner or heavier shells may be formed for special situations. After forming the refractory shell-mold, the disposable pattern is removed from the shell-mold which is then prepared for the casting operation. The typical pattern materials used in the process have been either wax blends or plastics such as polystyrene and, occasionally, polyethylene.

It is sometimes desirable to form hollow articles and particularly ones with very small and narrow passages by these investment casting techniques. Commonly, to make such articles, a ceramic core, usually formed of pressed silica as the major constituent, is disposed within the mold at an appropriate location. While these silica cores are quite useful, they are difficult to remove with a non-corrosive leaching media after the casting has been made. It can be appreciated that when very small or fine apertures or interstices are filled with an insoluble core material that difficulty can be encountered when attempting to totally remove the material with a non-corrosive leaching medium.

Other cores used for forming hollow cast articles have included soluble metal halide salts mixed with borax, magnesium oxide or talc. Such compositions have been disclosed in the U.S. Pat. to Anderko, No. 3,407,864. Disclosed in the U.S. Pat. to Rose, No. 3,473,599, is the use of a mixture of magnesium oxide and calcium phosphate. In the case of the halide-containing core, we have found that the halogen can react undesirably with the superalloy during casting. In the case of the magnesium oxide-calcium phosphate core, we have found that is is gassy, brittle and difficult to use when making castings of superalloys.

SUMMARY OF THE INVENTION

We have found that cores of essentially pure magnesium oxide are quite advantageous in investment

casting, especially in the so-called directionally solidified casting of superalloys. Alloys which can be cast and used with our magnesium oxide cores are disclosed in the Ver Snyder U. S. Pat., No. 3,260,505. Because magnesium oxide dissolves in hot water and is readily soluble in organic acids, we have found that a core of this material is easily dissolved from even the most narrow and small crevices inside of a casting. Moreover, the thermal expansion rate for magnesium oxide is quite close to that of the superalloys which are used in directionally solidified casting processes. Thus, much of the stresses due to gross mismatches in thermal expansion rates which could cause cracking is eliminated and castings having extremely complicated configurations with re-entrant features can be easily made.

In the practice of the present invention, a mixture is made of essentially pure magnesium oxide and an evanescent resinous binder. The mixture is then poured or injected into a mold and allowed to harden according to conventional techniques. The core is then removed from the mold and slowly heated in air to burn off the carbonaceous material from the binder and form a carbonaceous material-free structure. Generally, temperatures in the range of 1,000° F. are sufficient to remove the resin and form the "green" structure of essentially pure magnesium oxide. The "-green" core is then heated to above about 2,000° F. to sinter the magnesium oxide particles and form a rigid, self-supporting structure which can subsequently be used in investment casting. Because the core is heated slowly during the early stages of firing, generally less than about 10° F./hour, no significant shrinkage occurs. With this process, cores have been made which have exceedingly complex shapes and cross sections as thin as 0.015 to 0.25 inch. These molded and fired cores can sustain the rigors of casting temperatures as high as 2,800° to 3,000° F.

In the present process, 40 to 70 w/o magnesium oxide is mixed in a solution of an evanescent, resinous binder to form a thick slurry. Suitable thermosetting and thermoplastic resins, for example, include polyethylene, polystyrene, carbowax, phenolformaldehyde and polyvinyl alcohols. The magnesium oxide-resin mixture is transferred into a die having the configuration that is desired and the binder dries to form a solid body having the shape of the core, The body is then removed from the die and transferred to a furnace for slow heating to burn off and volatilize the evanescent, resinous binder. The heating should be sufficiently slow to remove the carbonaceous material without disrupting the integrity of the core while the gas is leaving. Preferably, the magnesium oxide has a particle size between about 25 and 150 microns since below about 25 microns the magnesium oxide wets only with great difficulty while above about 150 microns the particles are too coarse to produce a quality casting.

The method by which the core is formed will depend upon the configuration which is required. However, the methods of forming which may be used include extrusion, injection molding, transfer molding, compression molding, ramming, isostatic pressing, and slip casting or pouring. To form a core, the preferred process involves mixing a thermoplastic resin dissolved in a solvent, with magnesium oxide and conventional die lubricants. The solvent is volatilized and an appropriate quantity of the resulting resin-MgO paste is placed in a transfer cavity of a transfer press. Heat and pressure, in the order of 10,000 to 20,000 p.s.i., is applied to the resin-MgO paste to inject the material (while hot) into the die and fill it. The die is then split apart and a core is removed.

We have found that it is quite important to use essentially pure magnesium oxide, since contamination with other materials can lead to deterioration of the casting. For demonstration, a core was made of 5 percent calcium phosphate and 95 percent magnesium oxide. This core was compared to a core made of 100 percent magnesium oxide. When a casting was made and tested using the impure core, matrix oxidation of the surface of the casting occurred to a depth of 0.0,007 inch and alloy depletion occurred to 0.0,005 inch. With the essentially pure magnesium oxide core, matrix oxidation only occurred to a depth of 0.0,002 inch and alloy depletion only occurred to 0.0,003 inch. While the microsections indicated a reaction between the core and the casting with both the magnesium oxide core and the magnesium oxide-calcium phosphate core, the extent of the reaction in the first mentioned core was less than with the latter.

In general, the process further includes the conventional casting steps of pouring a molten metal or alloy into a shell-mold of the desired shape in which the magnesium oxide core of the present invention is disposed so as to form the apertures and internal passages when the casting cools. When the magnesium oxide core is washed out from the casting, apertures and passageways remain in the casting.

According to the preferred practice of the present invention, the alloy to be cast is melted in a vacuum furnace with a vacuum of 50μ or better, and after having been held at a temperature of from 100° to 250° F. above its melting point for a short period of time, it is cast in a mold. Generally the shell-mold has the shape of a gas turbine or gas-contacting blade and is preferably formed of ceramic or siliceous material, such as a shell-mold formed of alternate layers of finely divided siliceous material, such as silicates, zirconia, or other argillaceous or refractory material and finely divided sand or like material, there usually being several layers of each of the two materials. Such shell-molds are usually formed on a wax pattern, and after drying, the shell-mold is fired to remove the wax as is customary in the "lost wax" molding method.

The magnesium oxide core of the present invention is conventionally mounted within the wax assembly and becomes permanently fixed in the shell-mold after the wax has been removed. It is disposed so as to allow the molten metal to flow around it, whereby the hollow portions can be formed when the metal cools.

In the vacuum casting furnace apparatus, the shell-mold is provided with the electrical heating means so that its upper portion can be heated to a temperature, preferably at least 100° F. above the melting point of the alloy, prior to the pouring of the metal into the mold. When in casting position, the mold is supported with its open bottom end on a support member which can be chilled and will remain substantially colder than the body of the shell-mold during the casting operation, thereby chilling the cast metal in the shell-mold at its lower end.

The chilling of the cast metal at one end causes the casting to crystallize in a columnar structure having unidirectionally oriented crystals aligned substantially parallel to the axis of the casting and with almost complete avoidance of grain boundaries normal to the stress axis.

When the casting has cooled to room temperature, or sufficiently so that it does not react with the atmosphere, the vacuum may be destroyed and the casting and its shell-mold are removed from the apparatus, after which the shell-mold is removed, usually destructively, from the casting, and the core is then ready to be removed.

To remove the core, the part is dipped in water or preferably an organic acid solution, such as acetic acid less than about 10 normal. Agitating the solution around the casting will quickly dissolve the magnesium oxide and provide a casting which is then suitable for finish-machining.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples of the present invention are presented to show several ways that the core can be prepared and a variety of alloy and casting techniques can be cast around the core.

EXAMPLE I

70 grams of polystryrene are dissolved in 200 grams of methylethylkeytone. To the solution, add 30 grams of stearic acid and 50 grams of mineral oil as mold releasing and lubricating agents. To the solution is added 400 grams of MgO having a particle size between about 40 and 150 microns to form a slurry. This slurry is then thoroughly mixed so that all of the MgO is wetted and then the solvent, methylethylkeytone, is volatilized preferably by subjecting it to a vacuum.

The mixture then becomes rather thick and putty-like in consistency. It is broken up and weighed into appropriate units, in the present case 115 gram samples, for use in a transfer molding press. The sample is then placed in a transfer cavity of a transfer molding press and subjected to pressures of 20,000 p.s.i. to transfer it into the die and form the core. The core which was produced by the process was smooth and well formed without significant amounts of flashing.

When removed, the core was placed in a ceramic die, generally corresponding in shape to the shape of the core, and fired in air slowly according to the following schedule:

15 hrs. at 350° F.
8 hrs. at 400° F.
15 hrs. at 500° F.
8 hrs. at 550° F.
64 hrs. at 700° F.
8 hrs. at 750° F.
2 hrs. at 850° F.

During this firing schedule, the carbonaceous materials from the lubricants and the evanescent resin are volatilized to leave a green MgO core. The rate of raising the temperature is not critical so long as the gases which are produced, such as CO, CO_2 and other products of thermal decomposition of the resin and lubricant do not disturb the integrity of the core. If the temperature was raised rapidly, the escaping gases could dislodge pieces of the MgO and ruin the core.

When the above schedule is completed, the temperature is rapidly raised to about 2,400° F. ± 300° F. for up to 11 hours to sinter the particles of MgO together and form a solid body. Generally the degree of sintering is that which is sufficient to join the particles together but insufficient to cause appreciable shrinking, generally less than about 5 percent. It will be recognized that when the core was heated very slowly as described above, many voids were left in the body due to the elimination of the carbonaceous material. The sintering can cause a realignment of the MgO particles, relative to each other, if the heating is too drastic. Appreciable realignment and hence shrinkage, can be avoided by heating the core to a point where the particles are joined together and this stage can be readily determined by visually observing the core during various stages of heating.

When the core cools from the sintering, it can be used for any conventional investment casting operation or in directional and single crystal solidification processes. The following are other blends and compositions which have been used to form the core. The firing conditions were similar to those which were described above.

EXAMPLE II

A mixture of the following is formed:
240 gms xylene
84 gms polystyrene
36 gms stearic acid
7.2 gms lithium fluoride
400 gms magnesium oxide

The polystyrene is dissolved in the xylene and then the balance of the ingredients is added, the last being the magnesium oxide which is thoroughly wetted to form a slurry. The lithium fluoride is added as a lubricant for the molding operation and its use is also beneficial in picking up trace quantities of iron which may be present in the magnesium oxide. It is believed that much of the resulting lithium compounds are volatilized during subsequent firings. Following the formation of the slurry, the remaining steps to form the core are similar to those which had been described in Example I. The core which was produced had smooth sides and was acceptable for use in casting techniques.

EXAMPLE III

A mixture of the following is formed:
400 gms xylene
200 gms mineral oil
20 gms carbowax
160 gms polystyrene

The mixture is formed and 200 gms of MgO are blended into 100 gms of the mixture. A core of good quality was formed according to the steps described in Example I above.

EXAMPLE IV

A mixture of the following is formed:
400 gms magnesium oxide
200 gms methylethyl keytone
100 gms polystyrene
70 gms stearic acid
3.6 gms magnesium fluoride

The steps are similar to that which was described previously and a high quality, MgO core is formed. The magnesium fluoride is used as a fluxing agent to lower the sintering temperature and as a scavenger to remove traces of iron and silicon which may be present.

When the magnesium oxide cores have been prepared, they are preferably used in conjunction with casting of nickel or cobalt base alloys. The nickel base alloys are those having the following weight percentage range of composition of ingredients:

	Percent
Chromium	2 to 25
Cobalt	4 to 30
Molybdenum or tungsten	2 to 14
Aluminum	0 to 9
Titanium	0 to 6
Aluminum and titanium, at least	3.5
Carbon	0.1 to 0.5
Boron	0.005 to 0.1
Zirconium	0.05 to 0.2
Hafnium	0.5 to 3.0

Balance essentially nickel in a quantity of at least 35 percent and preferably and usually more than 50 percent by weight, although, in addition to the foregoing constituents, the alloy may include the following elements within the following percentage ranges:

	Percent, max.
Vanadium	1.5
Iron	5.0
Manganese	1.0
Silicon	1.0

with trivial amounts of sulfur, phosphorus, copper, etc., which do not deleteriously affect the novel advantageous characteristics of the casting.

Certain cobalt alloys are also useful in conjunction with the present invention and these include the alloys comprised within the following analyses:

	Percent, by weight
Chromium	15 to 27
Nickel	0 to 12
Tungsten	5 to 12
Titanium, maximum	1
Carbon	0.40 to 1.2
Zirconium	0.05 to 2.5
Hafnium	0.5 to 3.0

with optional additions of the following elements:

	Percent
Tantalum	0 to 10
Columbium	0 to 3
Boron, maximum	0.01
Iron, maximum	1.5
Manganese, maximum	0.2
Silicon, maximum	0.2

The balance of the alloy being essentially cobalt preferably and usually more than 50 percent by weight and being not less than 35 percent by weight of the total alloy and as indicated, a portion of the cobalt may be replaced by nickel. As with the nickel alloys, the cobalt alloys may include trivial amounts of impurities such as sulfur, phosphorous, copper, and the like.

The magnesium oxide cores of the present invention are particularly useful in conjunction with the casting of nickel-base alloys such as B-1900 and MarM200 or cobalt-base alloys such as MarM509. In the cases of B-

1900 and MarM200, 0.5 to 3.0 w/o hafnium has been added to the alloy to improve its elevated temperature ductility. The cores can be used in either the conventional casting processes or the above described process for directionally solidifying the alloy to form the casting.

It is apparent that modifications and changes can be made within the spirit and scope of the present invention, but is is our intention only to be limited by the following claims.

As our invention, we claim:

1. A method of producing a casting of metallic material, the steps which comprise: forming a mixture including magnesium oxide and an evanescent resin; forming a body from said mixture; said body corresponding to the shape of predetermined internal passages to be formed within said casting; heating said body to remove substantially all of the volatilizable material contained therein and to produce a core consisting essentially of magnesium oxide; disposing said core within a shell-mold to form a mold assembly; filling said shell-mold assembly with a molten metallic material and allowing said material to solidify and form a casting; dissolving said core from the inside of said casting.

2. The process according to claim 1 wherein said heating is divided into two stages, the first stage including slowly heating said body at a rate sufficient to volatilize substantially all of the carbonaceous material but insufficient to generate quantities of gases which would dislodge particles of said magnesium oxide, the second stage including heating the body sufficiently to sinter the magnesium oxide particles together and form a core, but insufficient to cause appreciable shrinkage.

3. The process according to claim 1 wherein the magnesium oxide has a particle size between about 25 to 150 μ.

4. The process according to claim 1 wherein said mixture is prepared by dissolving said resin in an organic solvent and said magnesium oxide is slurried in the solution, said solvent then being volatilized to produce a putty-like mass.

5. The process according to claim 4 wherein at least a portion of the putty-like mass is placed in a transfer cavity of a transfer molding press and subjected to pressure in the order of 10,000 to 20,000 p.s.i. to force the mass into an associated die having said predetermined shape.

6. The process according to claim 4 wherein said mixture further includes stearic acid as a lubricant and lithium fluoride as a flux.

7. The process according to claim 4 wherein said resin is polystyrene.

8. The process according to claim 1 wherein the dissolving step involves contacting said core with an organic acid.

9. The process according to claim 8 wherein the acid is acetic.

* * * * *