United States Patent Office 3,259,948 Patented July 12, 1966

3,259,948

MAKING FINE GRAINED CASTINGS

Roy C. Feagin, Mountain Lakes, N.J., assignor to Howe Sound Company, a corporation of Delaware

No Drawing. Filed Apr. 9, 1962, Ser. No. 185,882
17 Claims. (Cl. 22—196)

This invention relates to making fine grained metal castings. More particularly it relates to a method for making such castings wherein a cobalt aluminate or cobalt silicate compound is applied to the surface of the mold in which the casting is made to effect catalyzed nucleation of the alloy being cast during initial solidification of the alloy melt in order to insure that the casting will have a fine grained structure.

It has long been known that the grain size of a metal has an important bearing on such of its physical properties as tensile strength, hardness and ductility. Fine grained metal usually is stronger, harder and less ductile than the same metal in coarse grained form. Grain size of metals is generally controlled by the extent of working and the heat treatment to which the metal is subjected in the course of being fabricated to desired form. However refractory alloys which cannot readily be worked, that is, which are hard and lacking in ductility or malleability, cannot be produced in fine grained form by such conventional procedures. The most practical method for making desired articles of such alloys is by casting, and cast articles ordinarily have a coarse grain structure.

It has been recognized for a considerable time that the grain size of metals and other polycrystalline materials in the as-cast condition can be refined by suitable use of nucleation catalysts, that is substances which promote growth of crystals from the melt. An alloy melt, upon cooling to the temperature at which it becomes molten, may not solidify at once, but instead may subcool considerably before solidification begins. This is due to the fact that solidification proceeds from tiny particles, called nuclei, which form or are present in the melt. Immediately below the melting point is a metastable temperature zone in which the alloy melt will not nucleate spontaneously. In the absence of suitable foreign particles (heterogeneous nucleation), or particles of the same substance which might be added (homogeneous nucleation), solidification will not occur until the melt has cooled to a temperature below the metastable zone, whereupon nucleation will occur spontaneously. The final grain size obtained will depend on the relative rates of spontaneous nucleation and crystal growth. If nucleation is rapid compared to crystal growth, a fine grain size will result. If crystal growth is rapid compared to nucleation, large grains will be formed.

Particles which provide foci for initiation of the growth of crystals from the melt before the melt has subcooled through its metastable zone are called *nucleation catalysts*. The term "catalyst" often is used in the chemical art to refer to a substance which promotes or accelerates a reaction without entering into it, or at least without being consumed by it. A nucleation catalyst differs in that the particles of such catalyst may become embodied in ("consumed" by) the crystals whose growth they initiate. A nucleation catalyst does, however, accelerate crystallization of a polycrystalline material from the melt by providing nuclei on which the crystals may start to grow before the melt would, in the absence of such catalyst, spontaneously crystallize; and probably for this reason the term "catalyst" has come to be applied to them.

The present invention provides an improved method for the production of fine grained castings and is based on the finding that remarkably effective results have been realized by using a cobalt aluminate or cobalt silicate compound for catalyzing nucleation of alloys. It is impractical to incorporate this compound into the alloy and the invention thus contemplates applying the compound to the surface of the mold in which the casting is to be made. Then a melt of the alloy is introduced into the mold and is cooled in the mold to below its freezing temperature. The casting produced is characterized by having a notably fine grain size, much finer than could be obtained under the same casting conditions in a mold to which no nucleation of the catalyst had been applied and even finer than would be realized if one of the many nucleating catalysts presently in use were thus applied. Thus, a principal and decided advantage that cobalt aluminate and cobalt silicate compounds have over other nucleating catalysts is found in the consistency in grain refinement which metallic castings made according to the method of the invention are found to possess.

The method of the invention lends itself particularly well to making fine grained castings by the techniques of modern precision casting, involving forming a refractory mold about an expendable patern and then, after the mold has hardened, eliminating the pattern from within it. While it is possible to apply the cobalt aluminate or cobalt silicate nucleation catalyst to the mold surface after the pattern has been removed or otherwise eliminated from the mold, it is generally easier, and productive of better results, to apply it to the surface of the pattern before the mold is formed about it. Then when the pattern is removed from the mold, at least a portion of the catalyst remains to define (in part at least) the surface of the mold. For example, in making precision metal castings in molds by building up a mold shell of refractory composition on a fusible pattern of wax, plastic, frozen mercury, or the like, the cobalt aluminate or cobalt silicate compound is suspended in a liquid vehicle which can be applide as a first or prime coat on the pattern by painting it on or by dipping the pattern in it, after which a refractory mold shell is formed about the thus-coated pattern; or the catalyst may with advantage be incorporated in a hardenable refractory composition which is coated on the pattern (for example by dipping) and allowed to harden on the pattern to form a refractory mold shell in which the casting subsequently is made.

The concentration of the cobalt aluminate or cobalt silicate compound need not be high in order to achieve excellent reduction in grain size. Effective reduction in grain size has been achieved by incorporating as little as 10 grams per liter and as much as 300 grams per liter or more in a liquid coating or refractory composition. Ordinarily however, the most satisfactory range is between 20 to 50 grams per liter. This is particularly true for high nickel alloys.

By use of the term "mold shell," we do not mean to imply that such shell necessarily forms the complete mold. It may of course do so, but it may equally well be only one component of the completed mold assembly. The term "mold shell" is used mainly to denote the layer of refractory applied directly to the pattern, which forms that portion of the mold with which the melt comes in contact when it is poured into the mold cavity to form the casting. Such shell, if thick enough and strong enough, may form the complete mold; or it may be thickened by the application of additional refractory to make a thick strong shell mold; or it may serve only as the inner component of a bulky mold assembly which has been built up in a flask with either tightly packed dry unbonded granular refractory or well-bonded cementitious refractory to form a sturdy mold capable of withstanding rough handling and great stresses. The "shell" may also be but half, or some other fraction, of a complete mold shell, which when joined to one or more other fractional shells makes up a complete mold shell. Furthermore, the terms "mold" and "mold shell" are used throughout this specifi-

cation to include cores which are inserted into molds to form cavities in the castings.

It is theorized that the use of cobalt aluminate and cobalt silicate as a nucleation catalyst for promoting grain growth is very effective because the cobalt is fully reacted during nucleation and cannot be oxidized further. Thus, the full benefit of the oxidation producing effect of cobalt is used and corresponding finer grain structure is realized. This is in contrast to oxides of cobalt wherein total reaction of the cobalt is never fully realized and the resultant grain structure is not as fine.

The invention is described below in detail with respect to a preferred embodiment for the production of fine grained precision metal castings. In general the procedure employed for making such castings entails forming an expandable pattern of the casting, then coating the pattern with a hardenable refractory slurry to form a refractory shell about the pattern, then reinforcing such shell sufficiently to enable it to withstand the stresses of pattern elimination and casting, then eliminating the pattern by melting and pouring it from the refractory shell, then pouring a molten metal into the shell, and then cooling the molten metal in the shell until it has solidified. The method of the invention involves applying the cobalt aluminate or cobalt silicate compound nucleation catalyst to the pattern preparatory to, or in the course of, applying the hardenable refractory to the pattern to form the refractory shell (although such catalyst may be applied directly to the mold surface after elimination of the pattern without departing from the invention). Except insofar as application of such a nucleation catalyst is concerned, the steps of the procedure outlined are those heretofore commonly used in the precision casting art, and all the various forms and modifications of such steps may be employed in carrying out the method of the invention.

In the production of a large number of identical precision castings it is common practice to make one or a few master patterns from which one or a few master molds are prepared. Expendable production patterns, usually of wax or other thermoplastic material or of frozen mercury or other readily fusible metal, are made in these master molds.

The preferred method of the invention entails applying a nucleation catalyst to the surface of the production pattern. A particularly advantageous procedure for doing so is to incorporate the cobalt aluminate or cobalt silicate catalyst in the hardenable liquid refractory slurry composition which is coated on the pattern and allowed to harden thereon in forming the refractory mold shell. Such refractory compositions generally comprise mainly a suspension of finely divided refractory such as zircon, alumina or silica in an aqueous vehicle such as an aqueous solution of ethyl silicate, or an aqueous colloidal silica dispersion, or other substance which is capable of hardening by gelation or otherwise as the water evaporates after a coating of the composition has been applied to the pattern. When the pattern is of frozen mercury, the composition is of course non-aqueous, but is instead a suspension of finely divided refractory in an organic vehicle containing agents that cause it to harden after being coated on the pattern at very low temperature. For purposes of carrying out the method of this invention, the cobalt aluminate or cobalt silicate compound, in finely divided form, is dispersed in such refractory composition. The composition is applied to the pattern by the procedure of coating the composition on the pattern. Such may be done by brushing or spraying, but preferably the composition is applied by the dipcoating technique, involving dipping the pattern in a body of the liquid composition, which is common practice in the precision casting art.

Advantageously the cobalt aluminate or cobalt silicate catalyst incorporated in a composition is capable of functioning as a priming coat for the pattern if it is not incorporated directly in the refractory coating composition. For this purpose it may be incorporated as the sole finely divided solid in a solution of ethyl silicate or an aqueous silica sol, especially if one of these substances is used as the vehicle for the subsequently applied refractory composition.

If the cobalt aluminate or cobalt silicate compound does not tend to remain in suspension in the refractory composition or other vehicle in which it is dispersed, any suitable dispersing agent may be employed to hold it in suspension. If such composition or vehicle does not wet or otherwise adequately adhere to the pattern, a wetting agent may be incorporated in it. Other additions also may be made to the composition to facilitate its preparation or to improve it for application to particular patterns or for use under particular conditions.

Quantities of cobalt aluminate have been prepared by reacting aluminum oxide with a technical grade of cobalt oxide (CO_3O_4) thereby obtaining a composition containing a predominant amount of cobaltous aluminate, some cobaltic aluminate and a minor amount of corundum (Al_2O_3). Thus, a majority of the aluminum oxide has reacted to form a theoretical cobaltous-cobaltic aluminate. Other cobalt aluminate pigments used analyzed strong cobaltous aluminate, weak corundum, and still others analyzed approximately 40% cobalt. The cobalt silicate used analyzes approximately 55% cobalt.

The amount of cobalt aluminate incorporated in the composition coated on the pattern need not be large. Significant grain refinement is attained when 20 grams and less of cobalt aluminate per liter of pattern-coating composition is incorporated therein, and near maximum grain refinement results when the oxide concentration is 50 grams per liter. This excellent grain refinement is achieved at up to 200 grams per liter after which the increase in effectiveness of the composition for promoting grain refinement becomes relatively less marked; but concentrations higher than 200 grams per liter may nonetheless be used to advantage as may concentrations containing less than 20 grams per liter. These same concentrations apply equally as well to cobalt silicate, and similar results are achieved.

It is noteworthy that the above concentrations are particularly effective when used with a high nickel alloy. When a melt such as a high cobalt alloy is used in the method of the invention, the cobalt aluminate and cobalt silicate compounds function most effectively as nucleation catalysts at concentrations of 50 grams per liter and above, with excellent reduction in grain size at concentrations of 200 grams per liter and above. In all these instances however, higher contents have been utilized up to 20% of the refractory component.

It is possible to employ the method of the invention to control grain size on various parts of the same casting. To do so, the cobalt aluminate or cobalt silicate catalyst is applied only to selected portions of the pattern. For example, if it is desired to produce a casting having one portion fine grained and another portion relatively coarse grained, the portion of the pattern corresponding to the fine grained part of the casting is coated with a composition containing one or more of the specified compounds, and the portion of the pattern corresponding to the relatively coarse grained part of the casting receives a coating of a composition containing little or none of such compound. A similar procedure may be used to insure production of a uniformly fine grained casting under conditions that ordinarily would result in different sections of the casting having grains of markedly different size. For example when a casting having sections differing substantially in thickness is cast in accordance with heretofore customary practices, and particularly when the casting conditions enable the thin section to cool rapidly, the grain size of the thin section may be notably finer than that of the thick section. Uniform fine grain size may be achieved in such castings by coating the thick section of the pattern with a composition containing a substantial concentration of the cobalt aluminate or sili-

cate catalyst, and coating the thin section with a composition containing little or none of it.

When, as is generally preferred, the cobalt aluminate or cobalt silicate is dispersed in the refractory composition, applied to and hardened on the pattern to form the refractory shell, only the first-applied composition will contain such compound. Usually a number of coats of a hardenable refractory composition are applied successively, one over the other, to the pattern, to build up a mechanically strong refractory shell; but the cobalt aluminate and silicate catalysts are effective only where they can come in contact with the molten metal. Consequently there is no advantage to be gained from incorporating it in the compositions that are used to form the second and subsequent coats of refractory. As a matter of fact, it is common practice to employ a different composition for the first coat applied to the pattern than for the subsequent coats. The first coating composition generally contains a finer refractory, better suited to form a good mold surface, than the second and subsequent coating compositions. No departure from conventional practice is entailed, therefore, in using a different coating composition for the first coat than for the second and subsequent coats.

After the first hardenable refractory composition has been applied to the pattern (whether or not it contains a dispersed cobalt aluminate or cobalt silicate catalyst) and before it has hardened, it is preferably "sanded" or sprinkled with relatively coarse refractory particles. These particles become embedded in the refractory and help to bond the second refractory coat to the first. Preferably each successive coat of refractory composition, except the last, is similarly sanded.

Formation of the refractory mold and production of a casting therein, after the nucleation catalyst has been applied to the pattern, may follow the practices customarily used in making precision castings. After the refractory shell has been built up to desired thickness, it may be reinforced if it is not itself sufficiently strong to withstand the stresses to which it is subjected. To this end it may be mounted in a flask and be surrounded by a densely packed cementitious refractory (secondary investment) or by a tightly packed but unbonded filling or refractory particles (unbonded back-up). Thick strong shells, or shells which are not to be subjected to substantial stresses, may not need to be reinforced.

Next the pattern is eliminated from the mold. Usually this is accomplished by heating the mold with pattern therein to above the fusion temperature of the pattern while the mold is inverted to facilitate out-flow of the pattern material. When the pattern is of wax or other thermoplastic material, heating of the mold is continued sufficiently to insure elimination by oxidation or volatilization or both of the residual pattern material adhering to its surface. Instead of fusion and volatilization, solvent extraction may be used to eliminate the pattern. The pattern may be thus extracted using either a liquid or vapor solvent extraction process.

However the pattern is eliminated, it is necessary that the cobalt aluminate or cobalt silicate compound remains on and defines at least in part the mold surface. No special step need be taken to insure this result, however. If, as is preferred, the catalyst was applied by incorporating it in the refractory composition forming the inner coat of the shell, or in a prime coat comprising a hardenable composition, then of course it remains there when the pattern is eliminated. It is only necessary to use reasonable caution in eliminating the pattern from the mold to insure that the catalyst will transfer from the pattern and remain behind on the surface of the mold.

The mold is preferably heated to an elevated temperature preparatory to making the casting. Then the molten alloy is run into the mold and allowed to cool until it has solidified. The resulting casting usually is allowed to cool in the mold until it has reached a low enough temperature for handling, after which the refractory shell is broken away and the desired cast shapes are separated from the gates and risers.

The cobalt aluminate compounds particularly, and also the cobalt silicate compounds have been especially effective as a nucleation catalyst for fine grade castings made of high nickel or high cobalt alloys; thus the invention particularly contemplates the use of aluminate and silicate compounds of cobalt for making castings of such alloys. The invention is not limited to making fine grained castings of any special alloy compositions, however.

Table I lists by way of example the nominal compositions (in percent by weight) of several alloys which have been successfully cast in fine grain form by the method of the invention.

TABLE I

	Alloy A, percent	Alloy B, percent
Carbon	0.10 max	0.50
Manganese	0.15 max	
Silicon	0.20 max	
Sulfur	0.015 max	
Chromium	15.0	25.5
Titanium	3.25	
Boron	0.030	
Aluminum	4.25	
Tungsten		7.5
Molybdenum	5.0	
Iron	4.00 max	2.00 max.
Copper	0.10 max	
Zirconium	0.06 max	
Nickel	balance	10.5
Cobalt	18.5	balance

Castings made in accordance with the invention are characterized by having a grain size notably smaller in those sections corresponding to the parts of the mold surface to which the nucleating catalyst has been applied, than similar castings made in the same manner but in a mold not similarly treated. Metal castings produced by the method of the invention are characterized by having grains too small to be seen with the naked eye (for example having grains less than one one-hundredth inch across) when identical shapes cast under the same condition but without use of nucleation catalysts have grains averaging from one-quarter inch to one-half inch across.

It is interesting and of significant importance that the grain refinement achieved by the method of the invention penetrates quite deep into the casting. Although nucleation catalysts applied by this method is primarily a surface phenomenon, its effect extends to a substantial distance beneath the surface. Grains are often elongated in a direction normal to the surface of the casting due to the fact that solidification starts at numerous foci at the surface and proceeds inwardly with less interference from other grains than laterally. The effect does not appear to be entirely a surface phenomenon, however, since many more grains which clearly did not originate at the surface are seen in sections cut through untreated castings.

Following are specific examples of the production of a fine grained casting by the method of this invention:

A hardenable refractory slurry composition was prepared by suspending finely milled zircon in a water-base dipcoat refractory containing 20% silicon dioxide. Cobalt aluminate which analyzed strong cobaltous aluminate and weak corundum was added to the resulting slurry in the concentration of 50 grams per liter. A wax pattern of a cluster of turbine blades was dipped in the resulting composition, and the coating thus applied to the pattern was sanded in the usual manner. Three additional dipcoats of a similar hardenable refractory containing no cobalt aluminate or equivalent were then applied, each coat being sanded with ground fused fireclay and allowed to harden before the next

was applied. The coated pattern was mounted in a flask and backed up with a cementitious secondary investment. After the secondary investment had hardened, the resulting mold was inverted and heated to melt the wax pattern and burn out the residue of wax which adhered to the surface of the mold cavity. Heating was continued until the mold temperature attained 1800° F. A melt of alloy A as set forth in Table I above, at a temperature of 2800° F. was then poured into the mold. The casting thus formed was allowed to solidify and cool to a convenient handling temperature in the mold, after which the mold was broken away and the turbine blades were separated from the gates and risers to which they were joined. These castings were found to have had their grain structure reduced to less than one one-hundredth inch across. Thus the individual grains were so small as to be practically indiscernible to the naked eye. In contrast, like turbine blades cast under identical conditions at the same time in molds in which no cobalt aluminate or equivalent material had been incorporated were characterized by having grains up to one-quarter inch across.

In another specific example, cobalt silicate was added to the slurry in the concentration of 100 grams per liter. Alloy B was heated to 2800° F. and was poured into the heated mold as above. After cooling the castings were noted to have a fine grain structure and in this case were characterized by having grains about one thirty-second inch across.

In general fine grain structures were achieved in all instances. Excellent reduction in grain size was achieved with alloy A with only a minor amount of cobalt aluminate or cobalt silicate added. However with alloy B excellent reduction in grain size was achieved only at the higher concentrations of nucleating catalyst per liter of slurry.

I claim:

1. The method of making a fine grained casting of an alloy which comprises:
   (a) forming the surface of the mold in which such casting is made with a surface layer comprising a compound of the group consisting of cobalt aluminate and cobalt silicate,
   (b) introducing a melt of the alloy into the mold, and
   (c) cooling the alloy in the mold to below its freezing temperature to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

2. The method of making a fine grained casting of an alloy which comprises:
   (a) forming the surface of the mold in which such casting is made with a surface layer comprising cobalt aluminate,
   (b) introducing a melt of the alloy into the mold, and
   (c) cooling the alloy in the mold to below its freezing temperature to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

3. The method of making a fine grained casting of an alloy which comprises:
   (a) forming the surface of the mold in which such casting is made with a surface layer comprising cobalt silicate,
   (b) introducing a melt of the alloy into the mold, and
   (c) cooling the alloy in the mold to below its freezing temperature to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

4. The method of making a fine grained casting of an alloy containing a high proportion of at least one of the metals nickel and cobalt which comprises:
   (a) forming the surface of the mold in which such casting is made with a surface layer comprising a compound of the group consisting of cobalt aluminate and cobalt silicate,
   (b) introducing a melt of the alloy into the mold, and
   (c) cooling the alloy in the mold to below its freezing temperature to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

5. The method of making a fine grained casting of an alloy which comprises:
   (a) forming the surface of the mold in which such casting is made with a surface layer comprising a compound of the group consisting of cobalt aluminate and cobalt silicate,
   (b) heating the mold,
   (c) introducing a melt of the alloy into such heated mold, and
   (d) cooling the alloy in the mold to below its freezing temperature to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

6. The method of making a fine grained casting of an alloy which comprises:
   (a) applying to the surface of a pattern of the desired casting a compound of the group consisting of cobalt aluminate and cobalt silicate,
   (b) forming a mold about the pattern to which such compound has been applied,
   (c) removing the pattern from the mold while leaving at least a portion of such compound to define at least a part of the mold surface,
   (d) heating the mold,
   (e) introducing a melt of the alloy into said heated mold, and
   (f) cooling the alloy in the mold to below its freezing temperature to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

7. The method of making a fine grained casting of an alloy which comprises:
   (a) coating the surface of an expendable pattern of the desired casting with a compound of the group consisting of a cobalt aluminate and a cobalt silicate,
   (b) forming a mold by applying a hardenable refractory composition to the coated pattern,
   (c) eliminating the pattern from within the mold after said refractory composition has hardened while leaving such compound to define the mold surface at least in part,
   (d) heating the mold,
   (e) introducing a melt of the alloy into said heated mold, and
   (f) cooling the alloy in the mold to below its freezing temperature to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

8. The method of making a fine grained casting of an alloy which comprises:
   (a) coating the surface of a fusible pattern with a substance comprising a compound of the group consisting of cobalt aluminate and cobalt silicate,
   (b) forming a mold by applying a hardenable refractory composition to the coated pattern,
   (c) heating the pattern to above its fusion temperature to eliminate it from the mold after said refractory composition has hardened, whereby such compound remains to define at least in part the surface of the mold cavity,
   (d) heating the mold,
   (e) introducing a melt of the alloy into said heated mold, and
   (f) cooling the alloy in the mold to below its freezing temperature to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

9. The method of making a fine grained casting of an alloy which comprises:

(a) dispersing a compound of the group consisting of cobalt aluminate and cobalt silicate in a hardenable refractory composition,
(b) applying a coating of said composition to a pattern of the desired casting,
(c) allowing the coating to harden on the pattern,
(d) subsequently removing the pattern from within said hardened coating to form a mold cavity,
(e) heating the mold,
(f) thereafter introducing a melt of the alloy into said heated mold cavity, and
(g) cooling the alloy therein to below its freezing temperature to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

10. The method of making a fine grained casting of an alloy which comprises:
(a) coating a thin film of a liquid composition containing at least about 10 grams per liter of a compound of the group consisting of cobalt aluminate and cobalt silicate on the surface of an expendable pattern,
(b) forming a mold by applying a hardenable refractory composition to the coated pattern,
(c) eliminating the pattern from within the mold after said refractory composition has hardened while leaving such compound to define the mold surface at least in part,
(d) heating the mold,
(e) introducing a melt of the alloy into contact with the thus-defined heated mold surface, and
(f) cooling the alloy to below its freezing temperature while it remains in contact with said mold surface to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

11. A method according to claim **10** wherein said liquid composition contains 20 grams to 50 grams per liter of cobalt aluminate.

12. A method according to claim **10** wherein said liquid composition contains 20 grams to 50 grams per liter of cobalt silicate.

13. A method according to claim **10** wherein said alloy contains a high proportion of nickel and said liquid composition contains from 20 grams to 50 grams per liter of said compound.

14. A method according to claim **10** wherein said alloy contains a high proportion of cobalt and said liquid composition contains at least about 50 grams per liter of said compound.

15. The method of making a fine grained casting of an alloy containing a major proportion of cobalt which comprises:
(a) coating a thin film of a liquid composition in which there is suspended from about 20–200 grams per liter of a compound of the group consisting of cobalt aluminate and cobalt silicate on the surface of an expendable pattern,
(b) forming a mold by applying a hardenable refractory composition to the coated pattern,
(c) eliminating the pattern from within the mold after said refractory composition has hardened while leaving such compound to define the mold surface at least in part,
(d) heating the mold,
(e) introducing a melt of the alloy into contact with the thus-defined heated mold surface, and
(f) cooling the alloy to below its freezing temperature while it remains in contact with said mold surface, to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

16. The method of making a fine grained casting of an alloy which comprises:
(a) coating on the surface of a fusible pattern a thin film of a liquid composition in which there is suspended from about 20–200 grams per liter of a compound of the group consisting of cobalt aluminate and cobalt silicate,
(b) forming a mold by applying a hardenable refractory composition to the resulting coated pattern,
(c) heating the pattern to above its fusion temperature to eliminate it from the mold after said refractory composition has hardened whereby said compound remains to define at least in part the surface of the mold cavity,
(d) heating the mold,
(e) introducing a melt of the alloy into contact with the thus-defined heated mold surface, and
(f) cooling the alloy to below its freezing temperature while it remains in contact with such mold surface to effect catalyzed nucleation of said alloy by said compound during initial solidification of the melt.

17. A process for making castings having a fine grain structure which comprises forming a mold; providing a nucleation catalyst in the form of cobalt aluminate on the casting surface of the mold; introducing molten metal into the mold to form a casting therein and removing the casting from the mold.

References Cited by the Examiner

UNITED STATES PATENTS

2,778,079	1/1957	Carney et al.	22—215
3,019,497	2/1962	Horton et al.	22—196

J. SPENCER OVERHOLSER, *Primary Examiner.*

WILLIAM J. STEPHENSON, MARCUS U. LYONS, M. V. BRINDISI, *Examiners.*