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MAKING FINE GRAINED CASTINGS

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This invention relates to making fine grained castings of metal or other polycrystalline material. It is particularly directed to a procedure for making precision castings of which the whole, or selected portions, are characterized by having a notably fine grained structure. Basically the method of the invention entails applying a nucleation catalyst to the surface of the pattern of the article to be cast, and forming the mold in which the casting is to be made about such pattern.

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. While grain size of metals is generally controlled by the extent of working and the heat treatment it is subjected to, 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 controlled by suitable use of nucleation catalysts, that is, substances which promote growth of crystals from the melt.

A pure substance, heated at constant pressure, melts at a definite temperature. Upon cooling to this same temperature, the substance may not solidify, and may subcool considerably before solidification begins. This is due to the fact that solidification proceeds from tiny particles of the parent phase, called nuclei, which form or are present in the melt. Immediately below the melting point is a metastable temperature zone in which the substance will not nucleate spontaneously. However solidification can still occur in this zone on suitable foreign particles (heterogeneous nucleation), or on particles of the same substance which might be added (homogeneous nucleation). Upon further cooling a temperature is reached at which nucleation will proceed spontaneously, even in the absence of foreign particles.

The probable reason for the existence of this metastable zone is the fact that extremely fine particles actually melt at a lower temperature than the same material in bulk. The temperature in the metastable zone, while below the normal melting point, is still above the melting point of the tiny nuclei, which are thereby prevented from forming. As an example of this metastable zone, one investigator prepared a melt of phenyl salicylate (melting point, 42° C.) under special dust-free conditions, which did not solidify for six months at 25° C. Similar conditions apply to crystallization from saturated solutions, due to the higher solubility of extremely fine particles compared to that of large particles.

The grain size of a casting will depend on the number of sites at which solidification can start. If only a few sites are available, the grains will grow relatively large before their growth is hindered by the presence of other grains. On the other hand, if solidification and crystal growth start at a large number of points, the grains will have grown only slightly before their mutual interference prevents further growth.

A melt containing no foreign particles capable of catalyzing nucleation will have to subcool through the metastable zone before solidification can occur. 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.

Two procedures have been devised heretofore for catalyzing nucleation of metal castings. One is to incorporate a nucleation catalyst in the melt prior to casting, and the other is to apply a nucleation catalyst to the surface of the mold in which the molten metal is cast. The former procedure requires the use of a catalyst that can be effectively disseminated through the melt; and moreover it requires use of a rather large quantity of the catalyst and some modification of the composition of the melt due to the addition of the catalyst. The latter procedure may require great manipulation skill, depending on the nature of the mold, and in any event results in altering the surface character of the mold and sometimes in significantly altering its dimension.

The present invention provides an improved procedure for producing fine grained castings with the aid of a nucleation catalyst, which is characterized by applying such catalyst to the pattern about which the mold is formed. This procedure is generally easy from the manipulation standpoint because the surface to which the catalyst is applied in general is an easily accessible exterior surface. It also has the advantage of requiring a minimum amount of the catalyst, and does not result in any deformation, dimensional or otherwise, of the mold.

The invention therefore provides a method of making a fine grained casting which comprises applying a nucleation catalyst to the surface of a pattern, forming a mold about the pattern to which such catalyst has been applied, removing the pattern from the mold while leaving at least a portion of the catalyst to define the surface of the mold, and forming a casting in such mold.

The method is particularly suitable for use in making precision metal castings in molds formed by building up a mold shell of refractory composition on an expendable pattern, for example a fusible pattern of wax, plastic, frozen mercury, or the like. The nucleation catalyst most conveniently is incorporated in a liquid vehicle which can be coated on the pattern by painting or by dipping the pattern in it, after which a refractory mold shell is formed about catalyst-coated pattern; or the catalyst may with advantage be incorporated in a hardenable refractory composition which then is coated on the pattern (for example by dipping) and allowed to harden on the pattern to form a refractory mold shell.

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

The catalyst may if desired be applied to the pattern in the form of a compound which by subsequent treatment of the mold just prior to casting is converted to the desired most actively catalytic form. For example, a metallic catalyst may be coated on the pattern in the form of a reducible compound of the metal, and then after or in the course of eliminating the pattern from the mold the mold may be treated to reduce such compound to metallic form.

A particularly advantageous embodiment of the invention for making a fine grained precision casting therefor comprises dispersing a nucleation catalyst in a hardenable liquid refractory composition, applying a coating of such composition to a fusible pattern and allowing it to harden thereon, building up a relatively thick layer of refractory material about such coating, thereafter heating the pattern to above its fusion temperature to eliminate it from within said shell and form a mold cavity the surface of which is defined by said catalyst-containing refractory composition, and forming a metal casting in such mold cavity.

The method of the invention lends itself particularly to making castings having only selected portions subjected to nucleation catalysis. Such may be desired, for example, when one portion only of the casting is to be fine grained and the remainder is to be coarse grained; or it may be a desirable procedure to promote a uniform fine grained structure when the shape and dimensions of the casting are such that one portion thereof tends normally to be rather fine grained because of rapid cooling while another portion tends normally to be coarse grained. In utilizing the method of the invention for such purpose, the nucleation catalyst is applied to selected portions only of the surface of the pattern, leaving other portions of its surface free of such catalyst. A mold is formed about the pattern to which the catalyst has been thus applied, and the pattern then is removed, leaving catalyst to define the portion of the mold surface corresponding to the portion of the pattern to which it had been applied. A casting then is formed in the mold. The resulting casting has relatively fine grained portions corresponding to the portions of the pattern to which the catalyst had been applied, and relatively coarse grained portions corresponding to the other portions of the pattern.

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 expendable 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 or 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 a nucleation catalyst to the pattern preparatory to, or in the course of, applying the hardenable refractory to the pattern to form the refractory shell. Except insofar as such application of 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 method of the invention entails applying a nucleation catalyst to the surface of the production pattern. As indicated above, a nucleation catalyst is a substance which promotes nucleation, or initiates formation, of a solid crystal from the melt. Numerous substances are capable of functioning in this fashion. In the case of metals, finely divided crystals of a substance having the same basic crystal structure as, and lattice constants which do not differ greatly from, the crystal of the metal have in general been found to be the most satisfactory nucleation catalysts. Such materials should of course have a melting point high enough so as not to be themselves melted when heated to the extent necessary for the casting operation; and they should not be volatile or converted by chemical reaction to volatile or gaseous compounds when so heated. They may, however, be of the same or generally the same composition as the melt to be nucleated, or they may be of a wholly different composition. So far as this invention is concerned, the particular nucleation catalyst employed is not consequential. Any substance which catalyzes nucleation of the melt to be cast may be employed in carrying out the method of the invention.

The nucleation catalyst may be applied to the pattern in any manner suited to its nature and to the character of the particular process. A dry very finely divided catalyst may be dusted on the pattern surface, though it may be difficult by this procedure to insure retention of the full desired amount of catalyst on the pattern surface. A preferable procedure is to form a liquid composition containing the catalyst, and to apply such composition to the pattern. For example, when the catalyst is metallic, an aqueous colloidal sol of the catalyst metal may be prepared, and such sol may be applied to the pattern by dipping the pattern in the sol or by brushing or spraying the sol on the pattern. If the catalyst is an oxide or other non-metallic compound, it may be suspended in very finely divided form in an aqueous or other liquid vehicle and the resulting suspension may be applied by the dipping, brushing or spraying technique.

The catalyst may be applied to the pattern directly in active form, or in the form of a chemical compound or other substance which by subsequent treatment can be converted to the desired active form. For example, if a noble metal is the desired catalyst, a compound of such metal which decomposes at the temperature to which the mold is heated preparatory to making the casting may be coated on the pattern. If a non-noble metal is the desired catalyst, it may be applied to the pattern in the form of reducible compound, and the mold may be treated with a reducing agent such as a reducing gas or a volatile hydrocarbon to reduce such compound to metallic form just prior to making the casting.

A particularly advantageous procedure for applying the catalyst to the pattern is to incorporate the 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 nucleation catalyst, in finely divided solid form, is dispersed in such refractory composition, and is applied to the pattern by the procedure of coating such composition on the pattern. As with the suspensions or sols of the catalyst alone, the refractory catalyst-containing composition may be applied by brushing or spraying on the pattern; but preferably it 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 catalyst is incorporated in a composition 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 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 catalyst 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 other 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 modify its preparation or otherwise improve it for application to particular patterns or for use under particular conditions.

The quantity of catalyst incorporated in the composition depends upon a combination of factors such as its effectiveness in catalyzing nucleation, the fineness of grain size desired, and the effectiveness with which it is applied. With some strong catalysts, very fine grained castings can be produced from patterns coated with compositions containing 0.01% by weight of the catalyst. In other cases, especially where inexpensive catalysts are dispersed in a hardenable refractory composition, concentrations up to 30% by weight may be used with success. While in general the concentrations of catalyst in the composition applied to the pattern will fall between these limits, the method of the invention may be employed successfully in appropriate cases with compositions containing more or less of the catalyst.

As noted above, 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 nucleation catalyst is applied only to selected portions of the pattern, or compositions containing different concentrations of the catalyst may be applied to different 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, then in accordance with the invention the portion of the pattern corresponding to the fine grained part of the casting is coated with a nucleation catalyst, and the portion of the pattern corresponding to the relatively coarse grained part of the casting has no nucleation catalyst applied to it at all, or receives a coating of a composition containing a lower concentration of the catalyst. 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 the method of the invention, by coating only the thick section of the pattern with the nucleation catalyst, or by coating the thick section with a composition containing a relatively high concentration of such catalyst and coating the thin section with a composition containing a relatively low concentration of catalyst.

Instead of using coating compositions having different concentrations of catalyst to control differently the degree of nucleation of different parts of the casting, catalysts of different degrees of effectiveness may be used for this purpose. For example, when a different degree of nucleation is desired to be promoted on different parts of the same casting, the portion of the pattern corresponding to the part of the casting where the greatest degree of nucleation is to be promoted may be coated with a composition containing a strong nucleation catalyst, and portions of the pattern corresponding to parts of the casting where a lesser degree of nucleation is to be catalyzed may be coated with a composition containing a relatively weak nucleation catalyst.

When, as is generally preferred, the nucleation catalyst is dispersed in the refractory composition applied to and hardened on the pattern to form the refractory shell, only the first-applied such composition will contain the catalyst. 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 nucleation catalyst is effective only where it can come in contact with the molten metal. Consequently there is no advantage to be gained from incorporating such catalysts 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. Consequently no departure from conventional practice is entailed in using, according to the method of the invention, a different coating composition for the first coat than for the second and subsequent coats.

If the nucleation catalyst is applied otherwise than by inclusion in the refractory composition used to form the first coat of the refractory shell, then such shell is formed about the pattern, after applying the nucleation catalyst, in accordance with customary practices. This involves applying successive coats of hardenable refractory composition to the pattern, each coat being allowed to harden before the next is applied. The first coat generally is of such composition, and contains a refractory of suitable nature and fineness, so as to form a good mold surface in contact with the pattern.

After the first hardenable refractory composition has been applied to the pattern, whether or not it contains a dispersed nucleation 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 of 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 nucleation catalyst remains on the mold surface. No special step need be taken to insure this result, however. If the catalyst was applied by incorporating it in the refractory composition forming the inner coat of the shell, then of course it remains there when the pattern is eliminated. If the catalyst was applied by coating the pattern with it in dry form or with a sol or other liquid dispersion of it, it tends normally to become bonded to the refractory composition when the first coat of such composition is applied. Hence 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 cavity.

After elimination of the pattern, the mold is heated to a suitable casting temperature or left unheated, as desired.

If the nucleation catalyst was applied to the pattern in a form requiring reduction or other chemical treatment to convert it to the desired active form, such treatment generally is administered at this time. Then molten metal is poured into the mold and is allowed to solidify. The resulting casting is cooled in the mold to 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 castings thus made are characterized by having a grain size notably smaller, in those sections corresponding to the parts of the pattern to which the nucleation catalyst had been applied, than similar castings made in the same manner but without use of a nucleation catalyst. The actual grain size depends of course on the effectiveness of the catalyst used, the concentration of the catalyst composition applied to the pattern, the particular metal cast, and the casting condition. It is easily possible, however, by the method of the invention to produce metal castings having grains too small to be seen with the naked eye, when identical shapes cast under the same condition but without use of a nucleation catalyst 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 catalysis applied by this method is a surface phenomenon, its effect extends to a substantial distance beneath the surface. However, it does not extend laterally very far, as evidenced by the fact that when the edge of the coating containing the nucleation catalyst is sharply defined along the surface of the pattern, the line of demarcation between fine grained and coarse grained structure in the casting is also sharp and coincides with the line on the pattern.

Castings can be made by the method of the invention with the same high precision and fineness of surface that have been achieved heretofore, and with a degree of grain refinement not heretofore possible in such castings. It is a marked advantage of the method of the invention that the mold is formed with the nucleation catalyst on its surface, without in any way altering its surface or dimensions once it has been formed on the pattern.

Following are specific examples of the new method:

Example 1.—Platinum was selected as a satisfactory nucleation catalyst for a refractory cobalt alloy containing substantial proportions of nickel and chromium. A platinum-containing coating composition was prepared by precipitating platinum hydroxide from 5 ml. of a 5% $PtCl_4$ solution, and the precipitate was suspended in 5 ml. of a silica sol to which a wetting agent had been added. The resulting composition was brushed on the surface of a wax pattern of a disc 2 inches in diameter by ⅛ inch thick. After the composition had dried on the pattern, a shell mold was formed by dipping the pattern in a composition of finely milled zircon suspended in a colloidal silica sol. This coat of refractory composition while still wet was sanded with fused alumina of minus 80 mesh, plus 100 mesh particle size. After the first coat had hardened, three successive coats of a refractory composition comprising a mixture of finely ground zircon and finely ground fused fireclay suspended in aqueous colloidal silica sol was applied. Each such coat was applied by dipping the pattern in the composition, sanding it while still wet with fused fireclay particles, and then allowing it to harden before applying the next coat. The last coat was not sanded. The shell thus produced was reinforced by placing it in a flask and vibrating particles of fused fireclay about it in the flask until such particles had packed down to substantially their maximum bulk density. The flask was then placed inverted in a furnace and heated until the wax had melted and run out. Heating was continued until such residue of wax as remained in the shell had volatilized or burned away. Finally the mold was heated to 1800° F., and a molten alloy composed nominally of about 25.5% chromium, 10.5% nickel, 7.5% tungsten, 0.5% carbon, and the balance cobalt at a temperature of 2850° F. was poured into it. The resulting casting was allowed to cool in the mold to near room temperature. Then the mold was taken from the flask and the refractory shell was broken away. Upon inspection the casting was found to have grains about 1/32 inch to ⅛ inch in diameter. Identical castings made in the same manner but without applying any nucleation catalyst to the pattern had grains averaging about ½ inch in diameter.

Example 2.—An aqueous sol containing colloidal platinum was prepared by mixing 1 ml. of a 2% colloidal platinum sol with 4 ml. of an aqueous silica sol containing a wetting agent. The resulting sol was brushed on a wax pattern and a mold was prepared about the thus-coated pattern as described in Example 1. A casting of the same cobalt-base alloy was then made as described in Example 1. The resulting casting was found to have grains averaging only 1/32 to 1/16 inch in diameter.

Example 3.—An aqueous colloidal sol of cobaltous hydroxide of undetermined concentration but probably at least 10 g./l. was prepared and mixed in equal proportions with a colloidal silica sol (30% SiO_2). The resulting solution was brushed on one half of a wax pattern of a disc 2 inches in diameter by ⅛ inch thick, the other half of the pattern being left uncoated. A refractory mold was then formed on the pattern as described in Example 1. After eliminating the wax pattern, about 1 cc. of n-heptane was introduced into the mold while it was still hot, and the mold was loosely capped, to insure reduction of the cobaltous hydroxide to metallic form, the form deemed most effective as a nucleation catalyst. A casting of the cobalt-base alloy described in Example 1 was then made in the mold, in the same manner as described in Example 1. The casting thus made was found to have the half corresponding to the half of the pattern which had been coated with the cobaltous hydroxide sol to have grains too small to be seen with the naked eye, whereas the grains of the other half of the casting were about ⅛ inch to ¼ inch in diameter. The line of demarcation between the coarse grained and fine grained halves of the casting was very sharp.

Example 4.—Cobaltic oxide was dispersed in a liquid refractory dipcoat composition in the proportion of 200 g./l. The basic dipcoat composition was a suspension of finely milled zircon in an aqueous sol of colloidal silica, containing also a small proportion of a wetting agent to insure satisfactory coating on a wax pattern. A wax pattern of a disc 2 inches in diameter by 1/8 inch thick was coated with this composition by dipping it therein. The coating was sanded with alumina and a mold shell was built up and reinforced as described in Example 1. After the mold had been formed and the pattern eliminated, about 1 cc. of trichlorethylene was introduced into the mold cavity and the mold was loosely capped for one-half minute to insure reduction of the cobaltic oxide to metallic form, metallic cobalt being the chosen nucleation catalyst for this example. A casting was then made of the alloy described in Example 1. The resulting casting had a very fine grain structure, the grain size being for the most part just discernible with the naked eye.

Example 5.—A mold was prepared and a casting made with the same materials and in the same manner as in Example 4, except that the mold after elimination of the pattern was not treated to reduce the cobaltic oxide. In this example the cobaltic oxide introduced into the first dipcoat composition was itself the nucleation catalyst. The casting made had an extremely fine grained texture, the individual grains being barely discernible with the naked eye.

We claim:

1. The method of making a fine grained casting which comprises applying a nucleation catalyst to the surface of a pattern, forming a mold about the pattern to which such catalyst has been applied, removing the pattern from the mold while leaving at least a portion of the nucleation catalyst to define at least in part the surface of the mold, said portion of the nucleation catalyst being securely bonded to the mold, introducing a melt into said mold to form a casting therein without incorporating any substantial amount of catalyst from the mold into the casting, whereby the casting consists essentially of the original melt material, and removing the casting from the mold without there being any essential transfer of catalyst material from the mold wall into the casting.

2. The method of making a fine grained casting which comprises coating the surface of an expendable pattern with a substance comprising a nucleation catalyst, forming a mold by applying a hardenable refractory composition to the coated pattern, eliminating the pattern from within the mold after said refractory composition has hardened while leaving said catalyst to define the mold surface at least in part, said catalyst being securely bonded to the refractory mold composition, introducing molten metal into said mold to form a casting therein without incorporating any substantial amount of catalyst from the mold into the casting, whereby the casting consists essentially of original metal of the melt, and removing the casting from the mold without there being any essential transfer of catalyst material from the mold wall into the casting.

3. The method of making a fine grained casting which comprises applying to the surface of a fusible pattern a thin film of a liquid composition comprising a relatively infusible nucleation catalyst, forming a mold by applying a hardenable refractory composition to the resulting catalyst-coated pattern, heating the pattern to above its fusion temperature to eliminate it from the mold after said refractory composition has hardened, whereby said catalyst remains to define at least in part the surface of the mold cavity, said catalyst being securely bonded to the refractory mold composition, introducing molten metal into said mold to form a casting therein without incorporating any substantial amount of catalyst from the mold into the casting, whereby the casting consists essentially of original metal of the melt, and removing the casting from the mold without there being any essential transfer of catalyst material from the mold wall into the casting.

4. The method of making a fine grained casting which comprises dispersing a nucleation catalyst in a hardenable refractory composition, applying a coating of said composition to a pattern, allowing the coating to harden on the pattern, subsequently removing the pattern from within said hardened coating to form a mold cavity, said nucleation catalyst being securely bonded to the refractory composition defining the surface of such cavity, introducing molten metal into said mold cavity to form a casting therein without incorporating any substantial amount of catalyst from the mold composition into the casting, whereby the casting consists essentially of original metal of the melt, and removing the casting from the mold without there being any essential transfer of catalyst material from the mold wall into the casting.

5. The method of making a fine grained casting which comprises dispersing a nucleation catalyst in a hardenable refractory composition, applying a thin coating of such composition to an expendable pattern and allowing it to harden on the pattern, then applying additional coats of a hardenable refractory composition about the thus-coated pattern and allowing said additional coats to harden to form a refractory shell of substantial thickness, thereafter eliminating the pattern from within said shell to form a mold cavity, said nucleation catalyst being securely bonded to the refractory composition defining the surface of such cavity, introducing molten metal into said mold cavity to form a casting therein without incorporating any substantial amount of catalyst from the mold composition into the casting, whereby the casting consists essentially of original metal of the melt, and removing the casting from the mold without there being any essential transfer of catalyst material from the mold wall into the casting.

6. The method of making a casting which comprises applying a nucleation catalyst to selected portions of the surface of a pattern while leaving other portions of its surface free of such catalyst, forming a mold about the pattern to which such catalyst has thus been applied, removing the pattern from the mold while leaving catalyst to define the portions of the mold surface corresponding to the portions of the pattern to which it had been applied, such catalyst being securely bonded to the mold, introducing molten metal into said mold to form a casting therein without incorporating any substantial amount of catalyst from the mold into the casting, whereby the casting consists essentially of original metal of the melt, and removing the casting from the mold without there being any essential transfer of catalyst material from the mold wall into the casting whereby a casting is formed having relatively fine grained portions corresponding to the portions of the pattern to which catalyst had been applied and relatively coarse grained portions corresponding to the other portions of the pattern.

7. The method of making a casting which comprises dispersing a nucleation catalyst in a hardenable refractory composition, applying a thin coating of such composition to selected portions of the surface of a fusible pattern while leaving other portions of its surface free of such composition, then building up a refractory mold about the thus-coated pattern, thereafter heating the pattern to above its fusion temperature to eliminate it from within the mold and to form a mold cavity having selected portions of its surface defined by refractory composition in which catalyst is securely bonded as an integral part thereof and other portions free of such catalyst, and introducing molten metal into said mold to form a casting therein without incorporating any substantial amount of catalyst from the mold into the casting, whereby the casting consists essentially of original metal of the melt, and removing the casting from the mold without there being any essential transfer of catalyst material from the mold wall into the casting whereby a casting is produced having fine grained portions corresponding to the portions of the pattern to which the catalyst-containing composition had been applied.

8. The method of making a fine grained casting which comprises applying a reducible compound of a metallic

nucleation catalyst to the surface of a pattern, forming a mold about the pattern to which such compound has been applied, removing the pattern from the mold while leaving at least a portion of the compound securely bonded to the mold composition to define at least in part the surface of the mold, reducing said compound at least in part to metallic form, introducing molten metal into said mold to form a casting therein without incorporating any substantial amount of catalyst from the mold into the casting, whereby the casting consists essentially of original metal of the melt, and removing the casting from the mold without there being any essential transfer of catalyst material from the mold wall into the casting.

9. The method of making a fine grained casting which comprises applying a reducible compound of a metallic nucleation catalyst to the surface of a fusible pattern, forming a mold about the pattern to which such compound has been applied, heating the mold and pattern to above the fusion temperature of the pattern to eliminate it from the mold while leaving at least a portion of said reducible compound securely bonded to the mold composition to define at least in part the surface of the mold, introducing a reducing agent into the mold cavity and heating the mold in the presence of such agent to reduce said compound to metallic catalyst form, introducing molten metal into said mold to form a casting therein without incorporating any substantial amount of catalyst from the mold into the casting, whereby the casting consists essentially of original metal of the melt, and removing the casting from the mold without there being any essential transfer of catalyst material from the mold wall into the casting.

References Cited in the file of this patent

UNITED STATES PATENTS

1,033,489	Tatham	July 23, 1912
2,042,735	Scheil	June 2, 1936
2,728,124	Sofield	Dec. 27, 1955
2,743,495	Eklund	May 1, 1956
2,836,867	Bean	July 3, 1958
2,880,486	Wallace	Apr. 7, 1959
2,951,272	Kiesler	Sept. 6, 1960

FOREIGN PATENTS

755,073	France	Sept. 4, 1933
789,769	Great Britain	Jan. 29, 1958

Disclaimer

3,019,497.—*Robert A. Horton*, Dover, N.J., *Richard L. Ashbrook*, La Porte, Ind., and *Roy C. Feagin*, Mountain Lakes, N.J. MAKING FINE GRAINED CASTINGS. Patent dated Feb. 6, 1962. Disclaimer filed Oct. 24, 1972, by the assignee, *Howmet Corporation*.

Hereby enters this disclaimer to claims 1 through 7 of said patent.

[*Official Gazette March 13, 1973.*]