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Matter et al.

[11] **3,789,910**

[45] **Feb. 5, 1974**

[54] **DIP CASTING METHOD USING TRANSPIRATIONALLY COOLED MOLD CAVITY**

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[52] **U.S. Cl.** **164/121,** 425/DIG. 119, 164/255, 164/DIG. 1, 164/64, 164/62, 164/130, 164/122, 164/276, 425/271

[51] **Int. Cl.** **B22d 23/04,** B22d 25/04

[58] **Field of Search** ..... 164/61, 124, 348, 278, 255, 164/77, 154, 155, 151, 156, 283 R, 283 MS, 283 MT, 282 US, 82 US, 88, 87, 281 US, 64, 63, 62, 122, 121, 276 US, 277 US, DIG. 1; 425/271, 269, 275, 272, 237, 405 US, DIG. 119

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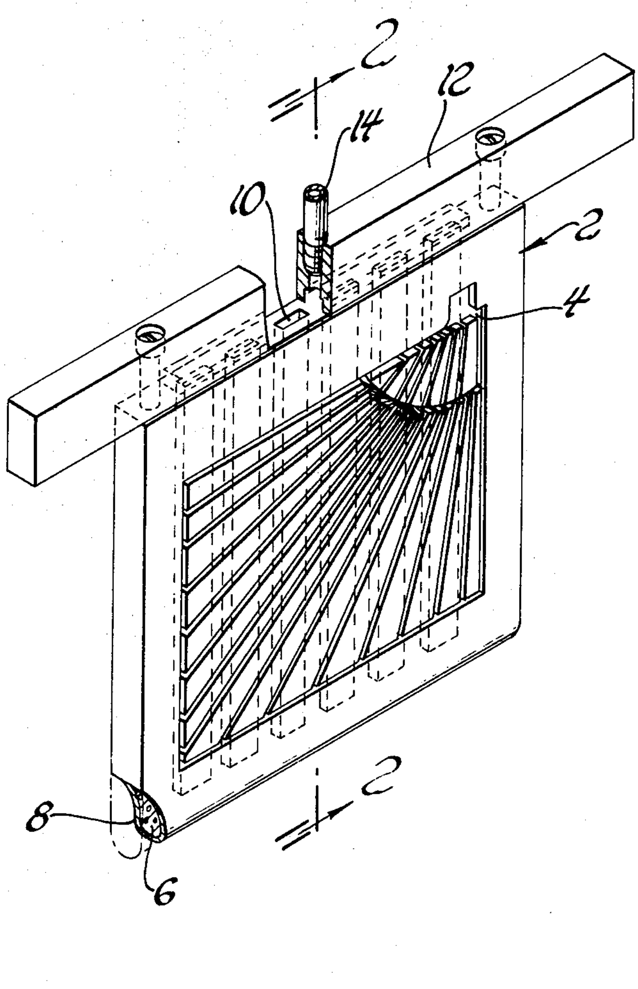
[57] **ABSTRACT**

A method and die for forming intricate, thin-sectioned castings. A die is provided having a porous metal body, an impervious surface and a mold cavity through the surface and in the porous body. The impervious surface is heated to a melt-metal-shedding temperature at which the casting metal does not adhere to the surface upon its removal from the melt. Air is introduced behind the mold cavity and exits through the cavity's porous walls thereby transpirationally cooling the cavity without substantially cooling the surface. The die is immersed in the casting metal where it is quickly solidified in the cool mold cavity. The process is particularly useful for casting low alloy lead battery grids.

5 Claims, 9 Drawing Figures



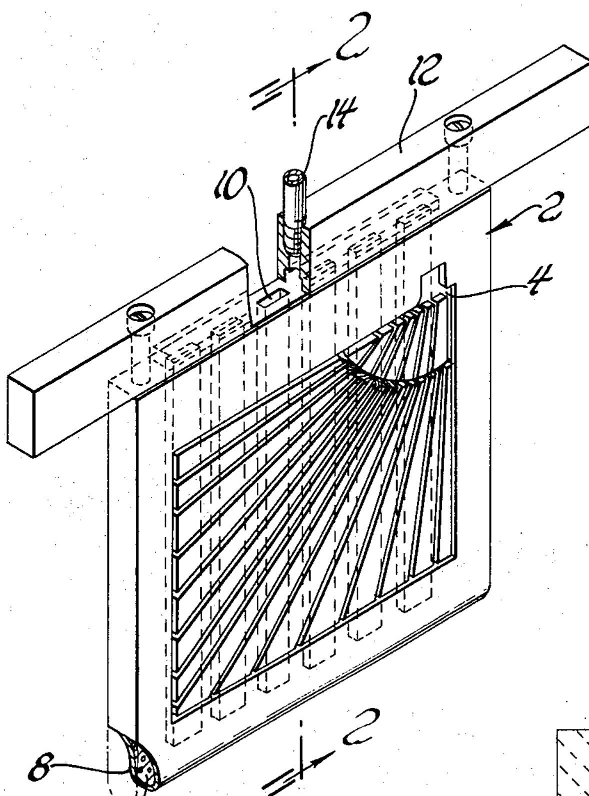


Fig. 1

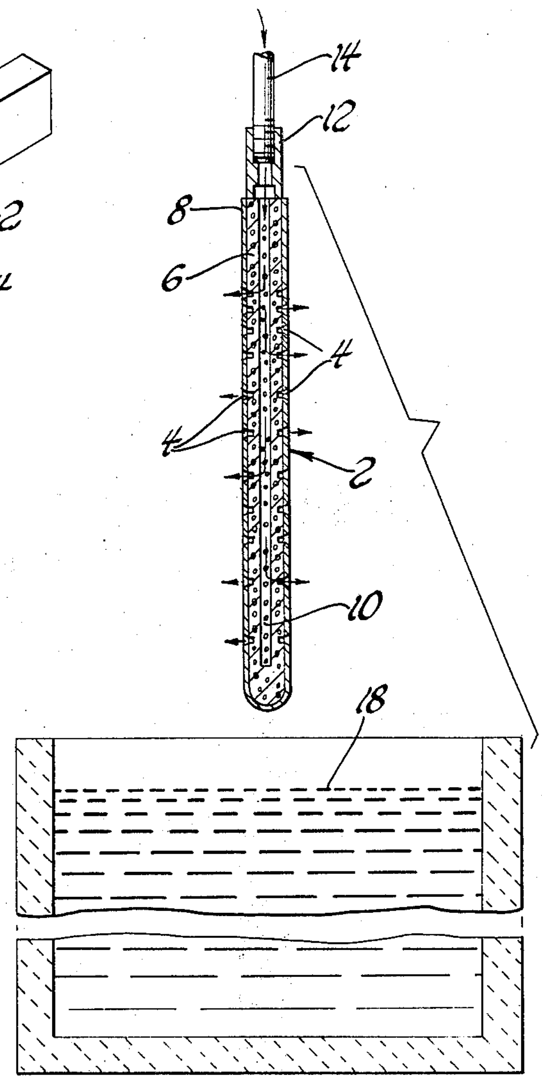


Fig. 4

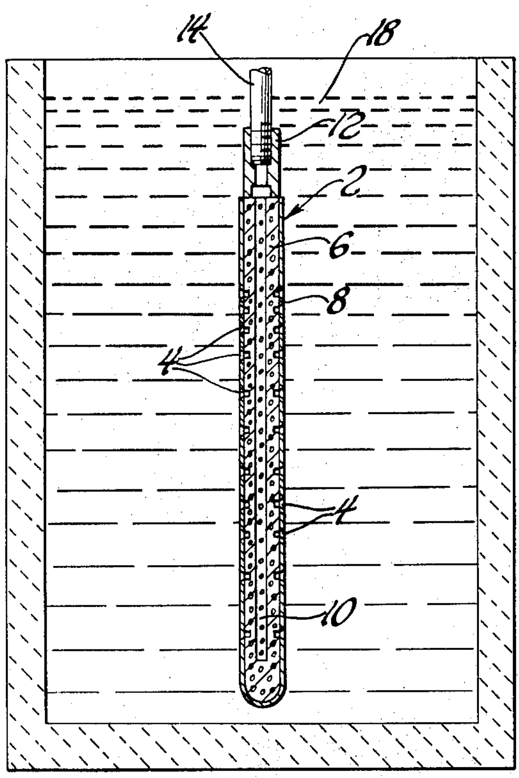


Fig. 3

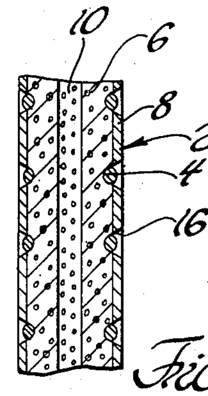


Fig. 2

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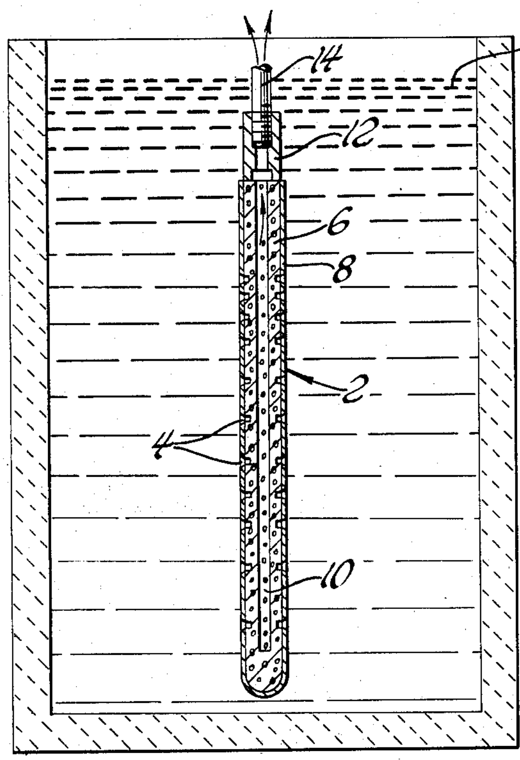

Fig. 5

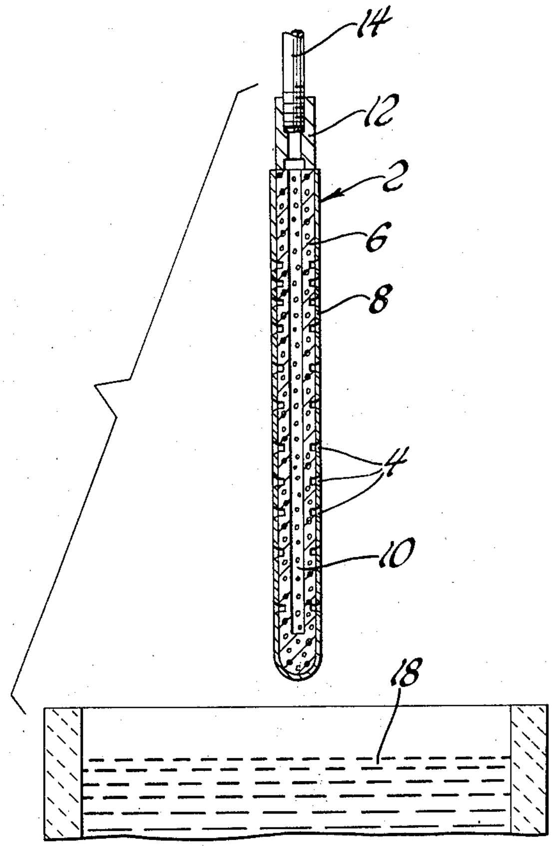

Fig. 6

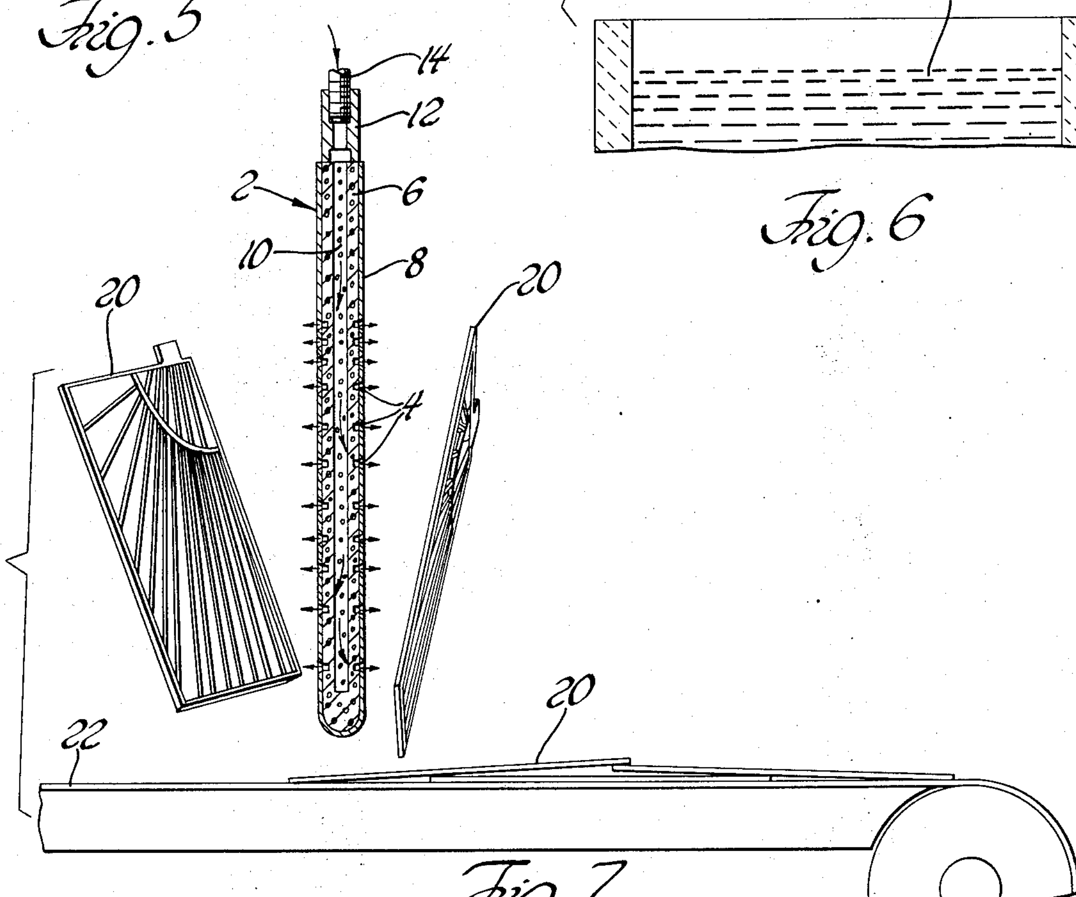

Fig. 7

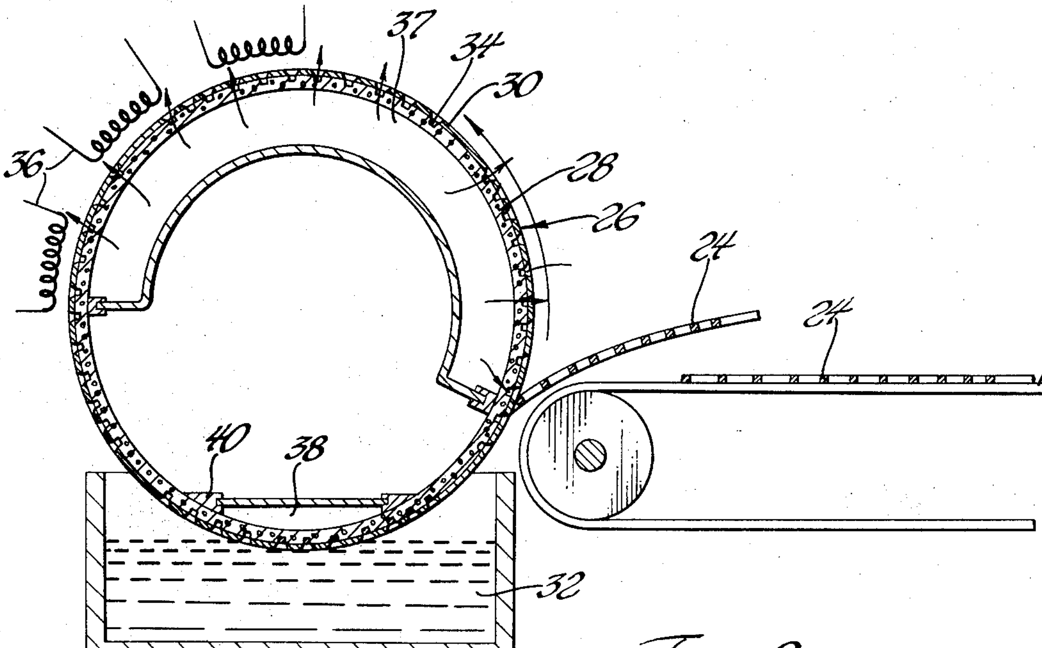

Fig. 8

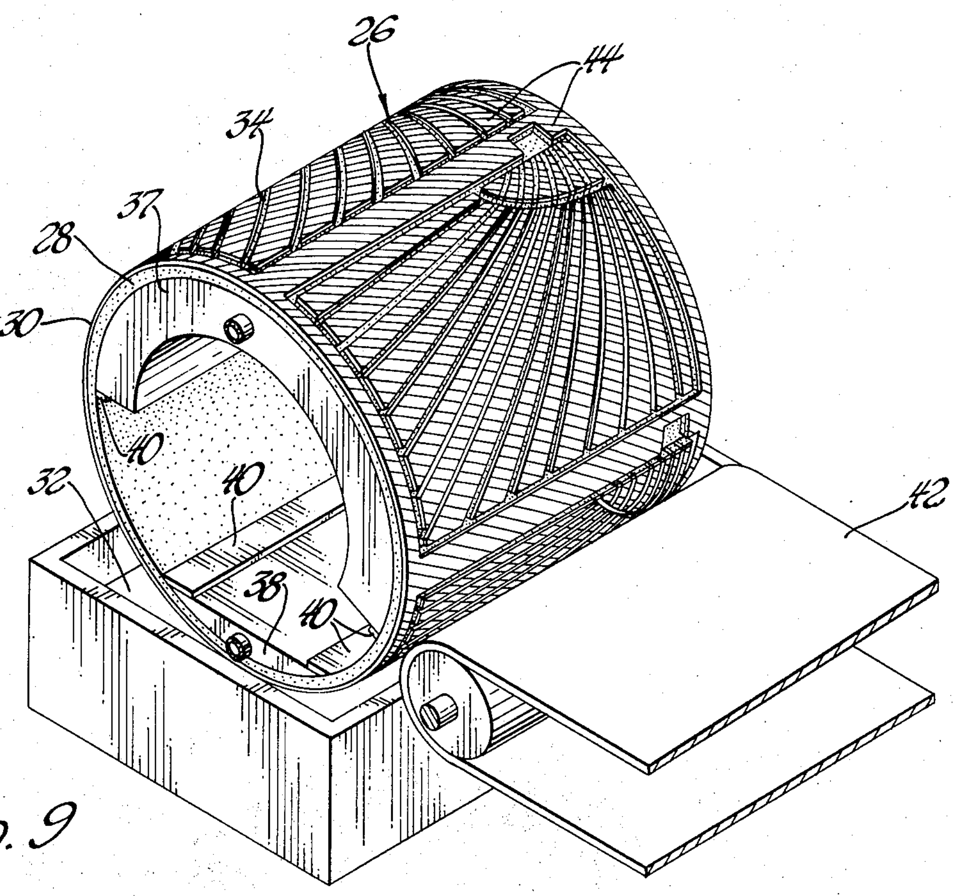

Fig. 9

DIP CASTING METHOD USING TRANSPIRATIONALLY COOLED MOLD CAVITY

This invention relates to an improved method for casting intricate, thin-sectioned articles requiring close tolerances, and particularly for casting lead-acid storage battery grids from low alloy lead. Grids cast according to this process have no further need for a sizing or trimming follow-up operation.

Dip casting machines and methods in which a cool die contacts a metal melt and solidifies metal from the melt thereon are known. None of these machines or methods has been completely suitable for consistently casting intricate articles to close tolerances where small dimensions are involved. In casting articles of this type, and particularly lead-acid storage battery grids, presently available machines do not reliably provide good reproduction of the mold configuration. A number of solutions have been proposed. For example, Nichols et al. U.S. Pat. No. 3,455,371, issued July 15, 1969, and assigned to the assignee of the present invention has a die with a mold cavity formed in part by a low thermal conductivity material and in part (i.e., at the bottom) by a high thermally conductive material. The latter conducts heat out of melt in the mold cavity. A belt acts as a temporary closure for the cavity and, if also cool, further aids in cooling the metal in the cavity. Cool belts, however, tend to cause flash to form between the wires. When hotter belts are used, belt life is short and cooling time long.

It is an object of the present invention to provide a process for quickly casting intricate, thin-sectioned, articles to close tolerances, without the need for a sizing or trimming follow-up operation, which process readily lends itself to automated production techniques. This and other objects of the present invention will become more readily apparent from the detailed description which follows and which is discussed in conjunction with the several figures in which:

FIG. 1, is a perspective view of one embodiment of a die used in the present invention;

FIG. 2 is an enlarged side elevational view of the die of FIG. 1 taken along the section line 2—2;

FIGS. 3 – 7 depict the several steps involved in the inventive process;

FIG. 8 illustrates a continuous casting process using the invention; and

FIG. 9 shows another embodiment of the invention.

According to the present invention, a die is provided which has a porous metal body and an impervious surface layer which acts as a thermal barrier between the porous metal and the melt being cast. In a preferred embodiment, this surface layer comprises a relatively low thermal conductivity material which, after heating, does not rapidly lose heat by conduction. In another embodiment, the surface layer is an insulator, and in still a third embodiment the surface comprises a high thermally conductive material having a relieved surface which limits contact with the melt and thereby effectively acts like a low thermal conductor. The thickness of the layer varies from about 0.0005 inch to about 0.06 inch depending on its actual or effective thermal conductivity. During the casting cycle, the surface is maintained at a melt-metal-shedding temperature. By melt-metal-shedding temperature is meant a temperature to which the surface layer of the die is heated and at which metal from the melt, even if slightly solidified, will not cling or adhere to the surface for any appreciable distance above the melt immediately after leaving the melt. This temperature will vary with the chemical and physical composition of the surface layer as well as the chemical composition and temperature of the melt and the depth of immersion. Shallow immersed surfaces, for example, do not have to be as hot before entry as deeply immersed surfaces. For lead grid casting the surface temperature will vary from 150° F. to about 400° F. A preferred surface layer has a low, or effectively low, thermal conductivity so that it acts as a thermal barrier between the high temperature melt and the cooled porous body during the short time interval in which the die contacts the melt. Materials for this purpose include low thermal conductivity metals (e.g., stainless steel), insulators (e.g., cork), and high thermal conductivity metals which have a relieved surface in limited contact with the melt. In the latter instance, the high surface tension of the melt precludes penetration of the melt into the valleys between the relieved peaks and limits melt-surface contact to the peaks. Such a relieved surface may be formed by scribing or etching (e.g., half-toning) a given pattern onto the surface to a depth where the melt will not normally reach unless actually forced into the valleys. The degree of contact between the melt and surface is readily controlled by the depth to which the die is immersed. In this regard, shallow immersion (i.e., about one eighth inch or less) results in a low melt head and a correspondingly low pressure forcing the melt between the relieved peaks. Surface layers employing this feature can be significantly cooler than smoother surfaces without there being a significant chilling affect on the melt. The porous metal body contains a mold cavity which opens through the impervious surface to receive the melt-metal. The walls of the mold cavity are porous like the main body of the die. The remainder of the surface of the die is covered or sealed by the impervious surface layer described. Means are provided in the die to introduce air, or other gas, into the die behind the mold cavity. At the beginning of the process, the impervious surface layer of the die is heated to the melt-metal-shedding temperature. Preferably, this is a temperature where no solidification of the casting melt occurs at the surface. Air is then blown into the die, through the porous metal body and out through the porous walls of the cavity to cool the cavity walls substantially below the temperature of the surface layer. In the case of low alloy lead battery grids, particular advantages result from lowering the temperature of the walls substantially below the solidus temperature of the lead alloy melt. When the cavity walls are cooled sufficiently, the air is shut-off and the die quickly immersed in the casting melt. In a preferred form, a vacuum is drawn through the porous metal to suck melt into the cavity, but, with a deep immersion, vacuum may be eliminated since the head of the melt will force it into the cavity. For shallow immersion such as shown by FIG. 8, vacuum is always preferred especially when a relieved surface die is used. After the melt is forced into the cavity, quick local solidification therein begins, with no substantial solidification on the surface of the die. The die is then removed from the melt and air again forced into the die to eject the casting and commence the porous body cooling cycle.

The porous metal body and surface of the die may comprise the same material chemical compositionwise. For example, in casting lead alloy grids, sintered particles of stainless steel are used as the porous body and are provided with a surface layer of stainless steel. With stainless surface layers 1/16th inch thick, the transpirational cooling of the walls of the mold cavity is so efficient that a large thermal gradient (i.e., as much as 300° F.) between the cavity and the surface layer can be achieved in a matter of seconds and maintained for short durations which are sufficiently long for the short casting cycles (i.e., about ½ second) involved. More specifically, a die is made by sintering 10 micron 316 stainless steel powders into a porous block 2 in. × 4 in. × ½ in. The surface of the block is then mechanically ground in a manner which causes particles on the surface to flow together and seal off the many pores and form an impervious surface layer about 0.002 inch thick. If a thicker surface layer is desired, additional stainless steel can be hot sprayed onto the machine-sealed surface followed by heating in an oven to fuse the sprayed stainless steel together. An appropriate grid-forming pattern is then mechanically cut through the impervious surface layer. This is followed by cutting into the porous body to form the mold cavity using any convenient cutting technique which will not close-off or seal the pores in the walls of the cavity. Among the techniques available for this purpose are electrochemical machining, chemical milling, electrical discharge machining and any of a variety of photoetching techniques. Electrical discharge machining is preferred since it requires the least control for the cutting medium/coolant.

Dies comprising a composite of thermally different materials can also be made and be quite effective. For example, a porous body (e.g., sintered brass) has a mold cavity cut into it using one of the non pore closing techniques mentioned. The mold cavity is then masked-off as by coating or filling with a readily removable substance (e.g., wax). The unmasked portion of the die is then coated with an appropriate, dissimilar (e.g., low thermal conductivity) material as by electroforming (e.g., with chromium or Fe-Ni alloys), flame or plasma spraying etc., to form the impervious surface of the die. Among the materials available for such coatings are other metals, metal oxides, carbon and cork. The masking is then removed, as by chemical or thermal means, leaving the desired porous cavity wall and impervious die surface. If aluminum is used, a thermally dissimilar layer may be formed by anodizing.

In casting lead-acid storage battery grids using a low antimony content lead, the process produces grids having fine detail and strengths comparable to grids with much higher antimony content but cast conventionally. Alloys cast from less than 1% antimony had the attributes of grids conventionally cast with 3% or more antimony, and alloys cast hereby with about 3% antimony had the attributes of grids conventionally cast with 6% or more antimony. Such alloys, of course, also contain other ingredients in various combinations as is well known in the art. Among such other ingredients are calcium, arsenic, tellurium, tin, cadmium and lithium. The process is likewise applicable to antimony-free alloys. The ability of this process to eliminate substantial amounts of antimony without practicably affecting strength and structure quality of the grid is significant. In this regard, cast battery grids used for automobile batteries are usually about 0.060 inch thick at the border and are usually gravity die cast with much larger amounts of antimony and other alloying agents which increase the flowability of the casting alloy and impart mechanical strength to the cast grids. Unfortunately, high antimony concentrations have a detrimental affect on battery performance to the extent that, during cycling, the antimony corrodes away from the positive grids and deposits on the negative grids, where it lowers the hydrogen overvoltage and promotes gassing. Moreover, high amounts of antimony contribute to the tendency of the battery towards self-discharge. As a result, the industry has sought to reduce, and if possible eliminate, the antimony content of the grid alloy without losing the benefits thereof. The process of this invention permits the use of very low antimony content lead alloys as well as antimony-free alloys without any appreciable loss in grid strength. The precise mechanism involved is not known, but it is believed that the alloy is quenched so fast in the chilled mold cavity that the alloy agents are trapped in supersaturated solid solution with the lead thus producing a casting which is quickly age hardenable at room temperature. Age hardening is observed as early as 5 minutes after casting and increases with time. In the alternative, the rapid cooling could disperse the alloy additions in a more finely divided form and more homogenously throughout the lead than heretofore available processes and thereby create a situation akin to age hardening.

The following more detailed description of the invention is given in conjunction with FIGS. 1 – 9 which show a die **2** having a mold cavity **4**, here shown to have a battery grid configuration. The die **2** comprises a porous metal body **6** and an impervious surface layer **8** best shown in FIG. **2.** A plurality of channels **10** are provided to admit pressurzied air and vacuum into the porous metal body **6** behind the mold cavity **4.** Manifold **12** communicates the several channels **10** and is connected to an appropriate air pressure or vacuum source (not shown) via conduit **14.**

The sectioned enlargement, FIG. **2,** shows the impervious layer **8** contiguous the porous body **6.** An intermediate layer, such as an insulator (not shown), could be employed. The impervious layer **8** about 0.060 inch covers all of the die except the mold cavity **4.** At one end of the block, channels **10** are discharge machined into the block and covered with air manifold **12.** A grid pattern having a 30 degree relief angle or draft is cut into the impervious layer down to the porous block. The relief angle, which may vary substantially, affects the shape of the solidified grid wire and facilitates stripping of the grid from the die. Smaller relief angles cause the shape of the melt meniscus to be flatter and vice versa. At the bottom of this machined pattern, the block is discharge machined to an appropriate depth to give the desired border and grid wire shape.

In the practice of the process, the die **2** is heated, by any convenient means such as flames, radiation, immersion, etc., to a melt-metal-shedding temperature. A convenient way to heat the surface layer is shown in FIG. **3** in which the die **2** is dipped into a melt **18** of the same material which is to be cast. This may be done in the casting pot itself or in a separate pot used only for treating the die. In either event, the die **2** is heated for a sufficient time to bring the surface **8** of the die **2** to the requisite temperature which, as indicated, varies with the materials involved. When flame or radiation heating means are used, the cooling air can be flowing at the same time that the surface layer is being heated.

The cooling air is forced (see FIG. 4) into the manifold 12 and out only through the porous walls of the mold cavity 4. The remainder of the die block is sealed by the impervious surface layer 8. This causes local cooling of the cavity walls by one of the most efficient cooling methods known, i.e., transpirational cooling. The heated impervious surface layer 8 tries to heat the cooled areas by conduction, but cannot do so as long as the air flow continues. The impervious surface layer 8 then has no way to cool, except by conduction into the porous body 6 which, owing to its voids, is a very poor conductor. Hence the surface layer 8 remains hot while the porous walls of the cavity 4 remain cool. Temperature differentials of as much as 300° F. are possible between the cavity 4 and the surface 8. Depending on the composition, thickness and surface condition, the layer 8 can vary in temperature from about 150° F. to above the melting temperature of the melt. For lead antimony alloys and smooth stainless surface layers, temperatures of about 400° – 600° F. are preferred.

When the walls of the cavity 4 cool, which takes only a few seconds, the pressure in the manifold 12 is reduced to a vacuum and the die 2 dipped into the melt 18. A deep immersion technique is shown in FIG. 5 and a shallow immersion technique is shown in FIG. 8. In the case of lead, the surface of the melt is flame fluxed, covered with a protective atmosphere or, preferably, continuously flowed over a weir to present a clean melt surface to the die surface 8. Vacuum exhausts all air from the cavity 4 and sucks the melt 18 into contact with the cold walls thereof. Metal cannot enter the pores of the stainless as it freezes upon immediate contact. The melt freezes in the cavity 4 as illustrated in FIG. 2. The shape of the meniscus extending into the impervious layer 8 varies somewhat with the draft angle 16. Battery grids have been cast to 0.060 inch in about ½ second using this method. After solidification in the cavity 4, the die 2 is withdrawn from the melt 18 (See FIG. 6). Due to the initial temperature of the surface layer 8, its temperature rise in the melt 18 and its brief sojourn in the melt 18 little, if any, solidification occurs against the surface 8. When some solidification does occur, it is non adherent and the film formed falls from the surface 8 immediately after the die is removed from the melt. Hence, for all intents and purposes, the only metal effectively leaving the melt 18 is the metal solidified and held to the cavity 4 by the vacuum. Positive pressure is again fed into the air manifold 12 to eject the casting 20 (FIG. 7) and commence cooling of the cavity walls for the next cycle. The castings 20 are caught by any convenient means e.g., belt 22. Castings made by this process have no entrapped air and require no substantial further processing before they are ready for pasting, etc.

FIG. 8 depicts an embodiment of the invention in which a die in the form of a drum 26 produces a continuous strip of castings 24. A drum shaped die, of course, may also produce individual castings by not providing interconnecting mold cavities. The drum 26 has an inner porous body 28 and an outer impervious surface layer 30 having essentially the same properties discussed above. An additional thin coating (e.g., about 0.010) of an insulator such as cork may be provided for shallow immersion (i.e., about ⅛ inch) and cooler drum surfaces. Mold cavities 34 are provided on the face of the drum 26. The drum 26 rotates through a melt 32 at a speed commensurate with the solidification time required. Preferably, the melt 32, which is externally heated, is the sole supply of the heat required to bring the surface layer 30 to the melt-metal-shedding temperature. Auxiliary heater means such as radiators 36 may be employed to supplement the heat supplied by the melt 32. The drum 26 may be closed at both ends so that cooling and ejecting air pressure can be maintained in the portion of the drum which is not submerged in the melt 32. Alternatively, a pressure chamber 37 may be provided. A vacuum chamber 38 is provided behind the melt-immersed portion of the drum 26 for evacuation of air from the cavities 34. Appropriate sealing means 40 are provided to prevent loss of pressure or vacuum in the appropriate chambers 37 or 38. The casting strip 24 is blown from the drum 26 and collected on belt 42.

In one specific example of this process, a die is made by pressing and sintering 10 micron, 316 stainless steel powders into a 2 in × 4 in × ½ in block. The block is then surface ground using a Norton alumina grinding wheel No. 38A46-18VBE to seal the surface to a depth of about 0.002 inch. One of the 2 in × ½ in ends of the block is drilled and a ¼-inch stainless steel tube inserted and welded into the bore in the block. The block is then hot sprayed to a thickness of about 0.08 inch with a stainless steel brazing alloy known as Nicrobraze 160 manufactured and sold by the Wall Colmonoy Corporation. The block is next heated in a hydrogen atmosphere at a point midway between the solidus and liquidus lines of the Nicrobraze (i.e., about 1,930° F.) for 1 hour to sinter the hot sprayed stainless into an impervious layer approximately 0.06 inch thick. A grid pattern, such as shown in FIG. 1, is machined into the impervious stainless steel brazing alloy surface layer down to the porous stainless and in a manner which provides a relief angle of about 30° and a width of about 0.06 inch at the porous metal — impervious layer interface. A mold cavity is discharge machined to form a hemispherical trough grid wire cavity having a radius of about 0.03 inch. The die is then heated in a gas flame to a uniform temperature of about 650° F. During heating room temperature, 60 psi air is introduced through the stainless steel tube into block for about 15 seconds to cool the mold cavity to about 150° F. The pressure in the die is next reduced to a vacuum of about 5 in. to about 10 in. of water. The die is then dipped for about ½ second in a 650° F. melt comprising principally 3% antimony, about 0.3% tin, about 0.1% arsenic and the balance lead. The die is then removed from the mold, the casting blown from it and the cycle started over again. The grids thusly produced have a wire width of 0.06 inch and thickness of about 0.045 in. including about 0.015 in. of meniscus metal solidified in the impervious layer above the mold cavity. Immediately after casting, the grid is quite soft but within about one minute hardens to a tensile strength of about 4,700 psi and within 30 minutes to a tensile strength of about 8,000 psi, based on a subjective comparison to lead alloys having known tensile strengths.

FIG. 9 depicts another embodiment of a continuous dip casting process similar to that shown in FIG. 8 except that the impervious layer 30 comprises a highly thermally conductive material (e.g., copper) having a plurality of grooves/striations 44 cut into it. Otherwise the several elements of the drum die and their functions are the same as described in conjunction with FIG. **8.** The layer **30** is about 0.04 inch thick over a porous sintered bronze body **28.** The grooves/striations are 0.015 inch wide and 0.007 inch deep and spaced to have a density of 16 striations per inch. When coupled with immersions into the melt of less than ⅛ inch and preferably about 1/16th inch, only the ridges between the striations contact the melt. Trapped air in the valleys between the ridges effectively maintain the thermal barrier character of the layer regardless of the thermal conductivity of the material making up the layer. When using this technique supplemental heating of the layer can often be eliminated since the ridges are quickly heated to a melt-metal-shedding temperature simply on contacting the melt **32** without extracting so much heat from the melt to cause excessive solidification against the surface layer. This is so even when the melt is only about 50° above its melting point or in its melting range for broad melting alloys, which is the preferred melt temperature useful for this invention.

While we have disclosed our invention in terms of specific embodiments thereof we do not intend to be limited thereto except to the extent hereinafter set forth in the claims which follow.

We claim:

1. A process for forming intricate, thin-sectioned castings from a metal melt comprising the steps of:

a. providing a die comprising a porous metal body, an impervious, low thermally conductive layer on the body sealing off the surface of the body and a mold cavity in said body opening through said layer;
b. heating said layer to a temperature where the melt-metal is readily shed from the outer surface of the layer after leaving the melt;
c. passing a cooling gas through said porous metal body and out the walls of said cavity to cool the cavity walls below the solidification temperature of said melt-metal;
d. immersing said die into said melt to fill said cavity with melt;
e. removing the die from the melt and shedding any melt-metal from said outer surface of the layer thereby carrying away from the melt only the metal solidified in said cavity; and
f. stripping the casting from the cavity.

2. A process for forming intricate, thin-sectioned, age-hardenable, lead-acid storage battery grids from a lead alloy melt comprising the steps of:

a. providing a die comprising a porous metal body, an impervious, low thermally conductive layer on the body sealing off the surface of the body and a grid-forming mold cavity in said body opening through said layer;
b. heating said layer to a temperature where the lead alloy is readily shed from the outer surface of the layer after leaving the melt;
c. while maintaining said layer at such a temperature, passing a cooling gas through said porous metal body and out the porous walls of said cavity to cool the cavity walls below the solidus temperature of said lead alloy;
d. immersing the thusly prepared die into a lead alloy melt containing less than about three percent antimony to a sufficient depth for said melt to fill said cavity;
e. quenching said lead alloy in said cool cavity at a sufficiently rapid rate to obtain a supersaturated solid solution of the alloy ingredients in the lead;
f. removing the die from the melt and shedding any melt-metal from said outer surface of the layer thereby carrying away from the melt only the metal solidified in said cavity;
g. stripping the thusly formed grid from the cavity; and
h. allowing the thusly formed grid to age and strengthen.

3. The process according to claim **2** wherein said alloy contains less than 1 percent antimony.

4. A process for forming intricate, thin-sectioned, age-hardenable, lead-acid storage battery grids from a lead alloy melt comprising the steps of:

a. providing a die comprising a porous metal body, an impervious, low thermally conductive layer on the body sealing off the surface of the body and a grid-forming mold cavity in said body opening through said layer;
b. heating said layer to a temperature where the lead alloy is readily shed from the outer surface of the layer after leaving the melt;
c. passing a cooling gas through said porous metal body and out the walls of said cavity to cool the cavity walls below the solidus temperature of said lead alloy;
d. immersing said die into a lead alloy melt containing less than about 1 percent antimony while drawing a vacuum behind said porous metal body to suck said melt into said cavity;
e. quenching said lead alloy in said cool cavity at a sufficiently rapid rate to obtain a supersaturated solid solution of the alloy ingredients in the lead;
f. removing the die from the melt and shedding any melt-metal from said outer surface of the layer thereby carrying away from the melt only the metal solidified in said cavity;
g. blowing a cooling gas through said porous metal body and out the walls of said cavity to strip the thusly formed grid from the cavity and commence cooling of the cavity walls; and
h. allowing the thusly formed grid to age and strengthen.

5. A dip casting die comprising:

a. a porous metal body adapted to be transpirationally cooled;
b. an impervious, low thermally conductive layer on the body sealing off the surface of the body;
c. a mold cavity having porous walls in said body opening through said layer; and
d. means for introducing cooling gas into said porous metal body for exiting through and transpirationally cooling the porous walls of said cavity.

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