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MELTING AND CASTING OF TITANIUM

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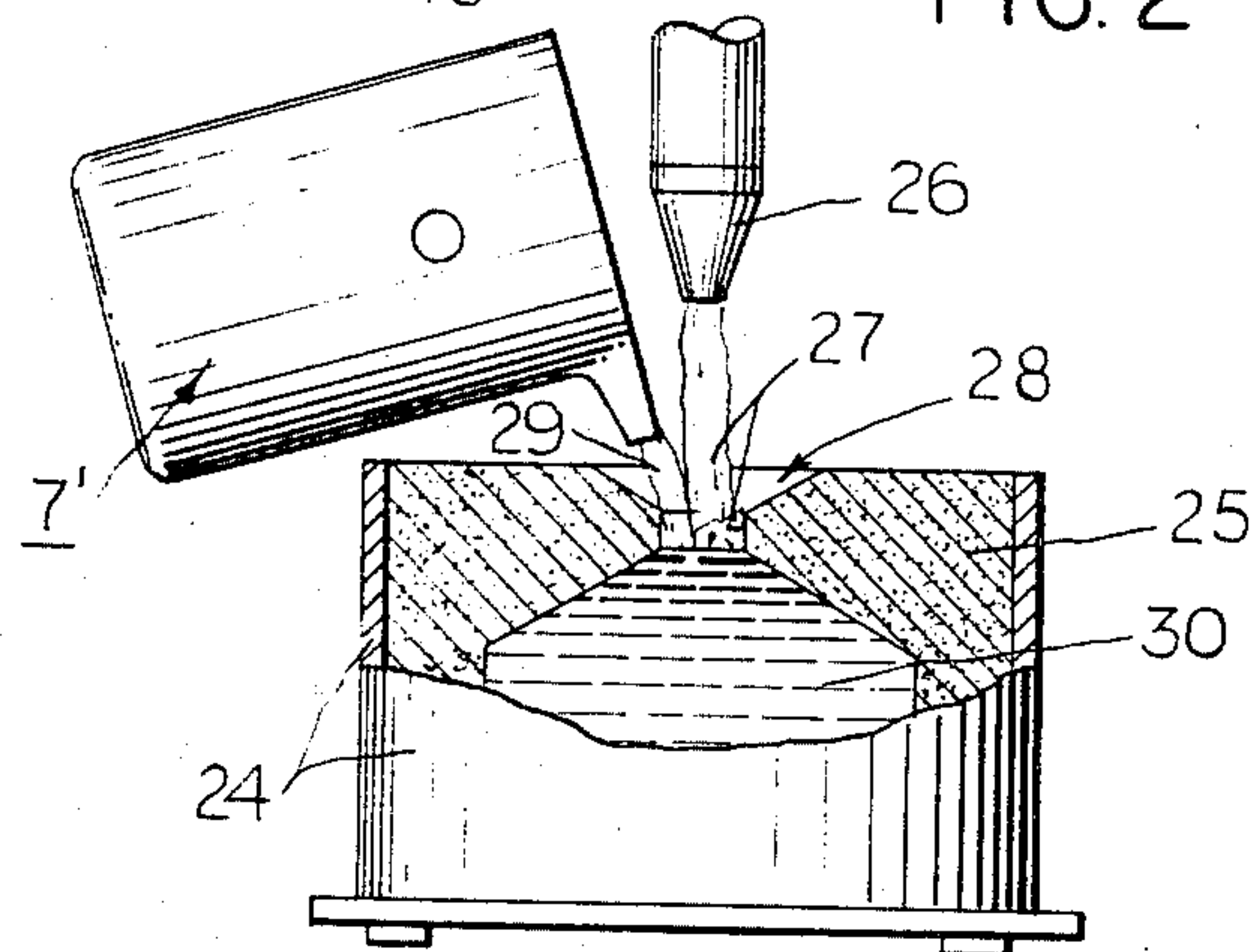
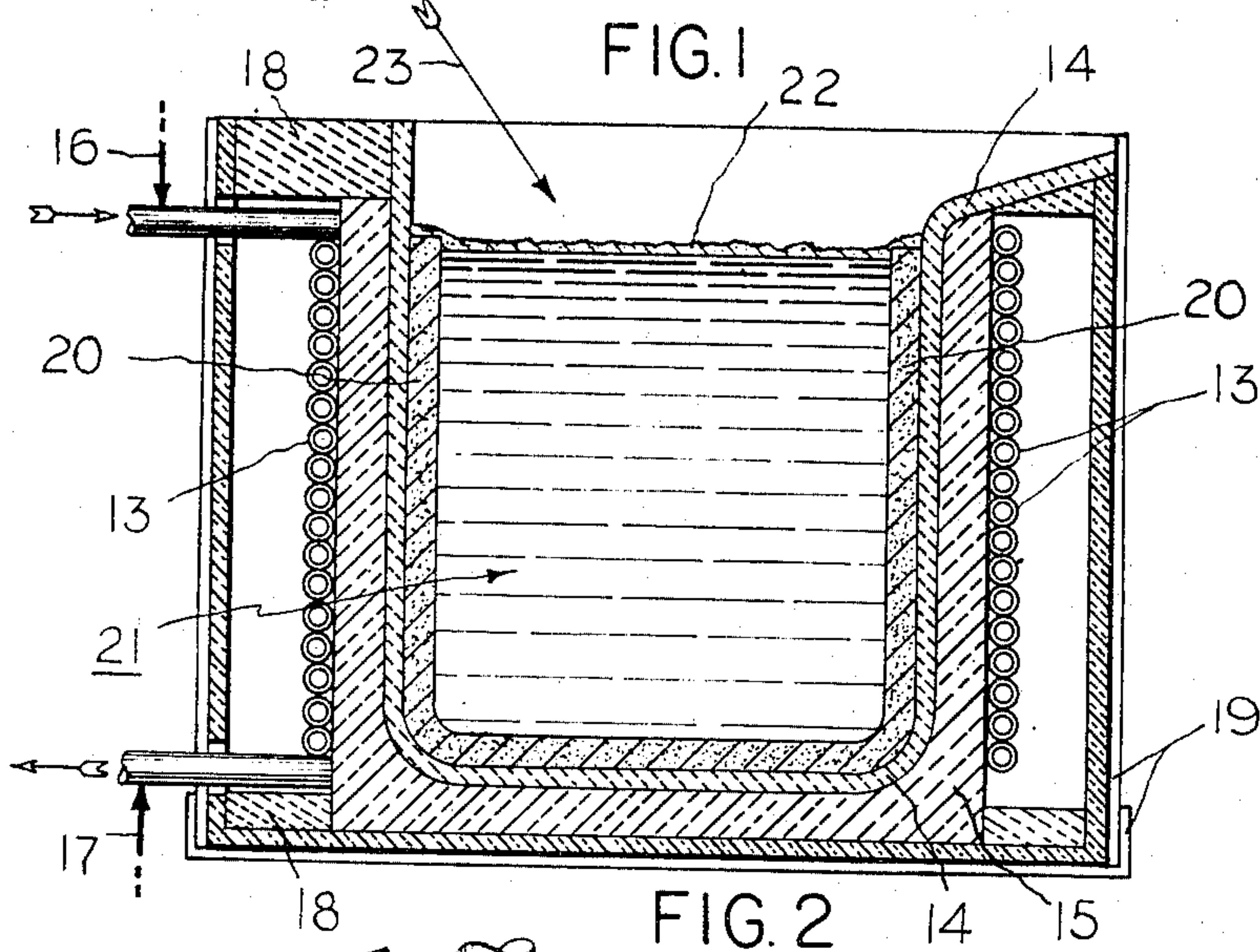
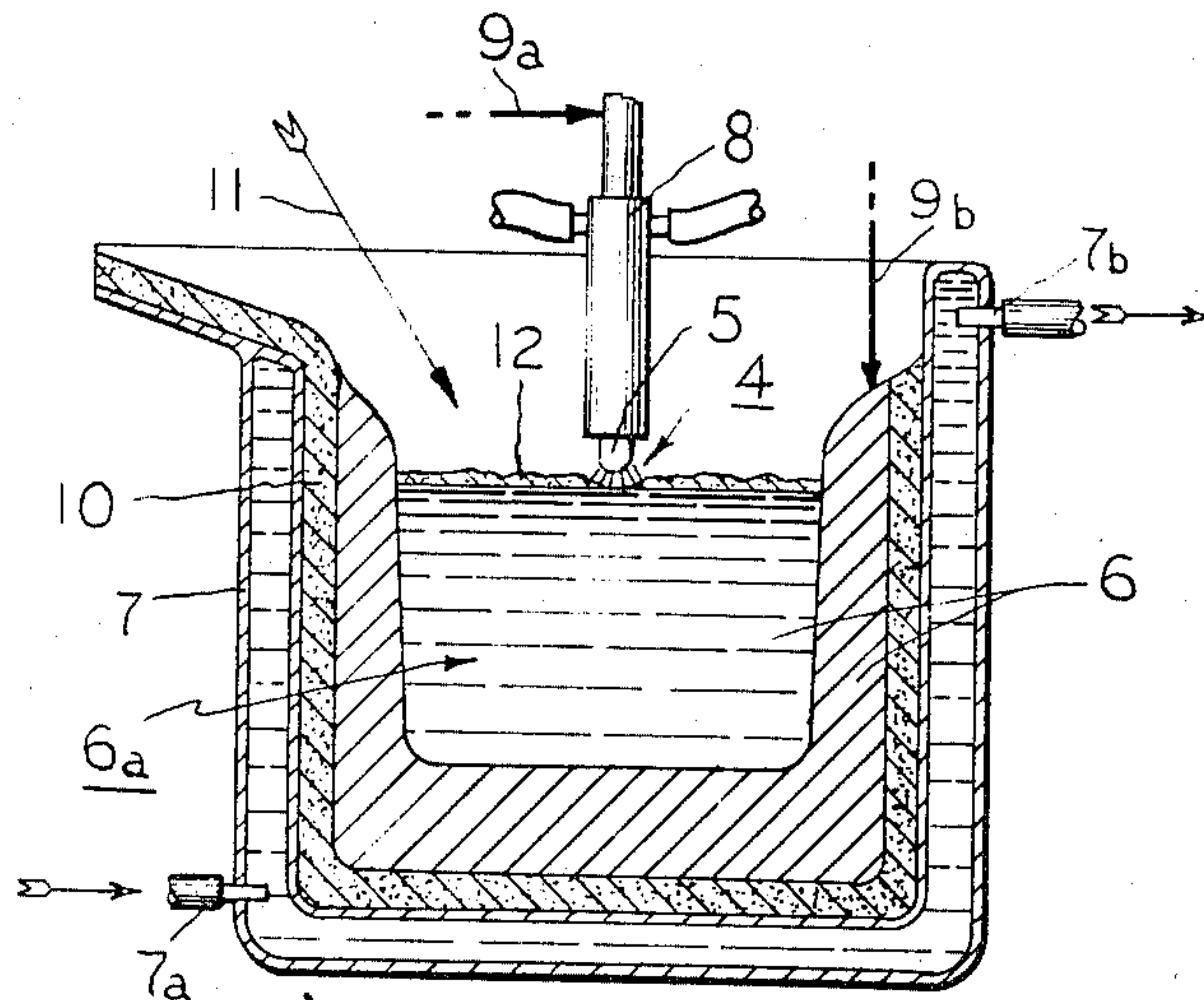


FIG. 3

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MELTING AND CASTING OF TITANIUM

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Continuation of application Ser. No. 507,611, Oct. 22, 1965, which is a continuation of application Ser. No. 325,067, Nov. 20, 1963. This application Feb. 23, 1967, Ser. No. 632,127

5 Claims. (Cl. 164—68)

ABSTRACT OF THE DISCLOSURE

A quantity of molten titanium is protected against embrittling contamination by containing all of the molten titanium within a receptacle and releasing along all titanium surfaces which are in contact with the receptacle the liquid and gaseous halide products of melting and decomposition (caused by heat of the molten titanium) of non-reactive flux consisting essentially of at least one halide which generates these protective products on exposure to temperatures of molten titanium.

This application is a continuation of my copending application Ser. No. 507,611, filed Oct. 22, 1965, which latter application was a continuation of a copending application Ser. No. 325,067, filed Nov. 20, 1963, both now abandoned.

The present invention relates to improvements useful in the foundry processing of titanium and, in one particular aspect, to novel and improved melting and casting practices whereby titanium masses substantially free of the common embrittling impurities are produced conveniently and at relatively low cost.

Titanium is a highly attractive metal to the engineering designer because it exhibits unusually favorable strength-to-weight ratios, good ductility, and extraordinary immunity corrosion. Certain alloys of titanium are also known to offer excellent ductility, high endurance ratios and desirable fatigue resistance; moreover their tensile strengths, fatigue limits and hardness tend to increase at very low temperatures. Unfortunately, this metal is seriously vulnerable to contamination while in the molten state, inasmuch as it acts as a nearly universal solvent which either dissolves or is polluted by atmospheric gases and about every known refractory. Heated titanium (above about 1100° F.) reacts so swiftly and deleteriously with these other substances that protective measures must be rigorously enforced to prevent atmospheric air and moisture from contaminating the molten material either in the furnace where it is being prepared or in the mold where it is being cast to a desired form. Evacuated or inert gas environments have been relied upon to inhibit the unwanted reactions, but, for optimum results, these environments must be rigorously controlled by skilled personnel and they tend to involve cumbersome and costly equipment. Drastic losses of ductility can result from improper protection of titanium while it is in a molten state, examples of excessive contaminations being the very low values of about 0.5% of oxygen and 0.25% of nitrogen. Hydrogen likewise has embrittling effects, while carbon adversely affects machinability and welding, and both are to be scrupulously avoided. Inert atmosphere and high-vacuum techniques require uncommon laboratory-oriented skills, equipment, and care, and they are thus not readily integrated into the usual foundry operations.

In accordance with the present teachings, the needed protections of the highly reactive molten titanium within furnace and mold can be realized without evacuation and

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either without substitution of an inert gas atmosphere or merely with a very simple auxiliary blanketing of inert gas. Heat-affected surfaces of the titanium are preserved free of contaminants principally by non-reactive flux which liberates a protective gas, such as a gaseous chloride, and at the same time serves as part of the container or vessel for the molten metal. In addition, the container thus formed is constructed to permit exhaust of generated gases from the flux, and, in certain practices, the exposed upper surfaces of the molten titanium are also covered with gas-liberating molten or finely-divided amounts of a similar flux which provides more complete isolation from troublesome gases of the ambient atmosphere while yet being pervious and non-rigid to accommodate release of generated gases and the like.

It is one of the objects of the present invention, therefore, to provide novel and improved techniques and associated apparatus for the production of masses of high-purity titanium and its alloys in molten and cast forms.

A further object is to provide improved and economic processing of titanium sponge which yields substantially uncontaminated melts, ingots and castings of titanium.

Another object is to provide improved methods and apparatus for the furnace melting of relatively large amounts of high-purity titanium which avoids the use of complex and costly evacuation or inert-gas chambers.

Still further it is an object to provide improvements in the expensive and simple casting of ductile titanium masses by relatively unskilled personnel.

By way of a summary account of practice of this invention in one of its aspects, a quantity of low-cost titanium sponge and/or clean scrap titanium is heated to the molten state by its electrical resistance to flow of secondary currents induced by a surrounding high-frequency induction coil. For this purpose, the titanium charge is disposed within an electrically non-conductive open-topped crucible which, in turn, has been coated internally with a thick substantially solid lining of a special non-reactive and substantially non-conductive flux composition. Preferably, this flux composition includes halogen compounds such as sodium chloride and potassium chloride, and the interior lining of the crucible may be formed either by applying the flux, and permitting it to solidify, or by separately casting a suitable hollow liner and inserting it into the crucible. The cavity within the lined crucible is charged with the metal, and/or titanium sponge, and appropriate excitation of the high-frequency coil then results in melting of the charge within the lining. At the high temperatures of the melting titanium charge, the flux composition decomposes and liberates gaseous halides which rise through the charge and are exhausted from its upper surface, thereby shielding and isolating all exposed titanium surfaces from reactions with ambient atmospheric gaseous contaminants. Preferably, fresh amounts of the finely-divided flux are added atop the charge as melting continues, and additional amounts of the charge may also be added to accumulate a large molten volume. When the melting has been accomplished, ingots and other castings are conveniently formed using a mold prepared from sand molding material which has been well mulled, or mixed, with a finely-divided flux like that employed in the furnace. Pouring from crucible to mold is performed swiftly, to avoid substantial contact with the air, and finely-divided flux is added atop the cast metal to produce a shielding halide gas layer which supplants the atmospheric gases at that site.

Although the features and aspects of this invention which are considered novel are set forth in the appended claims, further details as to preferred practices of the invention, as well as the further objects and advantages

thereof, may be most readily comprehended through reference to the following description taken in connection with the accompanying drawings, wherein:

FIGURE 1 portrays, in cross-section, an improved arc furnace arrangement for producing uncontaminated melts of titanium;

FIGURE 2 depicts induction furnace melting of titanium having low impurity content, the equipment being shown in section; and

FIGURE 3 represents the operation of sand casting high-quality ductile titanium in accordance with the present teachings, a portion of the illustrated special sand-type mold being broken away to expose its interior.

The metal-melting furnace arrangement characterized in the FIGURE 1 illustration is of the direct-arc type, wherein an electric arc 4 is drawn directly between an electrode 5 and a titanium charge 6 beneath it within a crucible 7. For purposes of preparing highly ductile titanium, it is important that those materials which are embrittling contaminants of titanium be avoided, and the electrode 4 is thus preferably formed of a metal such as tungsten or, in the case of consumable electrodes, of titanium sponge which has been prepared in a suitable length for feeding. The crucible 7 is preferably made of copper, which possesses good thermal conductivity, and this is of a force-cooled jacketed construction involving the circulation of a coolant such as water through the couplings 7a and 7b and in heat-exchange relationship with the inner walls of the jacketing. Electrode 5 is also preferably cooled, particularly in those instances when a non-consumable electrode is employed, and a water-cooled electrode holder 8 is shown for this purpose. An electrical power source (not shown) of a conventional form provides excitation of the electrode, as designated by the coupling 9a and of the metal charge and molten pool within the crucible, the latter by way of the conductive crucible and coupling 9b. Arc 4 is responsible for generation of heat which rapidly melts the charge and forms a pool 6a of titanium which may be tilt-poured into a mold via the crucible spout; in another known type of furnace construction, the molten metal may instead be tapped from below, through a drain at or near the bottom of the furnace.

Before melting is commenced, those interior surfaces of the copper crucible which are expected to come in contact with molten titanium are heavily lined with a special non-reactive flux composition. Thick lining 10 in FIGURE 1 is illustrative, and this may for example be formed either as a separately-cast solid part or as a liquid material applied to the cool interior surfaces and allowed to solidify there until the desired thicknesses of flux composition have been attained. The materials used in the flux compositions are of pronounced importance, inasmuch as they should not so react with the solid or molten titanium as to embrittle it and, moreover, they should release non-reactive gas which can supplant or flush out any potentially contaminating gases in the air near surfaces of the titanium charge. These requirements are satisfied by certain halide salts which do not react appreciably with titanium up to the highest temperatures expected in the melting operation. Relatively plentiful and inexpensive salts such as potassium and sodium chlorides (KCl and NaCl) may be used, with typical percentages running from about 55-65% NaCl and 35-45% KCl, by weight. In another example, stannous chloride, SnCl_2 , may also be added advantageously, preferably in small amounts, such as about 1-2%, by weight. This chloride starts melting at a relatively low temperature (of the order of 500° F., and, more specifically, about 475° F.; the boiling point being about 1153° F.) and it thus affords the desired type of shielding protection before the titanium charge has actually begun to melt but while it is hot enough to be highly susceptible to contamination. The other chlorides melt and are principally effective at much higher temperatures; KCl melts at about 1040° K. and vaporizes at about 1680° K. Thermodynamic calculations of the free ener-

gies of reaction between KCl, for example, and titanium to form the possible chlorides of titanium (TiCl_2 , TiCl_3 and TiCl_4) provide evidence of the relative inertness of the compound for the present purposes (i.e., the free energy of formation of TiCl_4 in reaction with KCl is but about 112 kilogram calories per mole, at 2,500° K.; of TiCl_3 but about 69 kcal./mole; and of TiCl_2 but about 40 kcal./mole. Magnesium chloride (MgCl_2) is found to be a very desirable material for these purposes also. Similar conditions of non-reactivity with titanium can be found in the case of the other halides of interest, the characterizing free energy of reaction, Fr, at 2,500° K. being as follows (in kcal./mole) in selected instances:

Reaction product produced	TiCl_4	TiCl_3	TiCl_2
(a) ΔFr , titanium in reaction with NaCl	90	52.5	29
(b) ΔFr , titanium in reaction with CaCl_2	124	78	46
(c) ΔFr , titanium in reaction with BaCl_2	144	93	56
(d) ΔFr , titanium in reaction with MgCl_2	32	9	0
	TiF_4	TiF_3	TiF_2
(a) ΔFr , titanium in reaction with NaF	12	9	30
(b) ΔFr , titanium in reaction with KF	12	9	30
(c) ΔFr , titanium in reaction with CaF_2	84	63	66
(d) ΔFr , titanium in reaction with BaF_2	92	69	70

In addition to the chlorides and fluorides, bromides and iodides are suitable agents, the latter having the greater atomic weights and, thus, decreased reactivity. The hypogroscopic nature of the halides may in some cases make it desirable that the heated or molten titanium be protected from the contaminating effects of the water from that source. For this purpose, a small quantity of a hydroxide-forming oxide, such as Na_2O , Li_2O or K_2O is included in the flux composition; up to 5% of this material by weight of the entire flux composition serves this need. These oxides react readily with any moisture which may be present, especially at elevated temperatures, to form hydroxides (such as NaOH, LiOH and KOH) which do not decompose and which therefore provide the desired protective isolation from such moisture. In addition to the halides and hydroxide-forming oxides, the non-reactive flux composition may include finely-divided titanium sponge. To the extent that such sponge may melt, it introduces no significant impurities and merely becomes part of the molten titanium pool in the furnace, and, to the extent that it does not, it serves as an essentially non-reactive filler and binder for the halide-containing flux composition.

As the molten titanium pool 6a is developed in response to the intense heating which attends the generation of the arc 4, additional amounts of titanium sponge and/or clean titanium scrap may be introduced, together with quantities of the non-reactive flux material, the latter preferably in a finely-divided form. Arrow 11 in FIGURE 1 suggests this, and indicates the path through which both materials may be dumped into the open-topped crucible 7 as needed. Titanium sponge which may be added to the crucible in this manner may also advantageously be in a finely-divided state. Enough of the halide fluxing agent must be present to insure that the top surfaces of the molten titanium pool 6a do not become contaminated by the troublesome gases from the ambient atmosphere; preferably, this agent forms a substantially full protective layer 12 atop the molten titanium, some of which layer may comprise melted flux while the balance includes partially-melted or unmelted flux which has not decomposed and which may be of the finely-divided form. Depending upon the temperatures which are experienced by the flux composition, it will produce a non-reactive liquid or gaseous film, or both, atop the molten titanium and will thereby effectively screen out possible contaminants which could seriously deteriorate the resulting ductility characteristics of the cast product. As the melting progresses, layer 12 may at least in part be formed by amounts of the lining 10 which may have melted under furnace heat and which have surfaced through the molten titanium pool. However, this lining does not become com-

pletely melted away or decomposed, because of the inhibiting cooling effects of the circulated coolant in the water-cooled copper crucible 7, and because of the lining thickness selected. Preferably, a substantially continuous cover "skull" or "skin" of molten flux is maintained over the exposed top surface of the molten titanium throughout the melting process, although this way in some instances require that only relatively small quantities of the finely-divided or hot liquid flux material be added during the melting operation, the balance being supplied automatically upon gradual melting of the flux liner 10. Additional protection, if desired, can also be developed cooperatively by blanketing the top surfaces of the charge with inert gas, such as argon. This may be accomplished by at least partially covering the crucible and feeding the inert gas into the space below the cover. Finely-divided titanium, preferably in the form of titanium sponge, may be included in admixture with the flux material of the liner, to vary the thermal conductivity characteristics of that liner without introducing any impurity which would adversely affect the resultant melt. Thicknesses of the liner walls are selected, empirically, for example, to insure that it, the liner, is not completely decomposed at any position about the molten pool during any one melting operation. A full charge of molten titanium may be built up within a crucible, starting with a large unmelted mass therein, or by adding more and more titanium to the crucible as smaller quantities are melted. Alternatively, molten amounts may be tapped or poured off soon after they appear.

The FIGURE 2 furnace arrangement for induction melting of titanium in accordance with these teachings includes the usual conductive induction coils 13 in surrounding relationship to a ceramic crucible 14 and the packed refractory cement enclosure 15. Alternating current excitation of a suitable frequency is applied to the coil via leads 16 and 17, and, preferably, a coolant such as water is forced through the hollow coils 13 to suppress their thermal deterioration. Blocks 18 of refractory material complete a conventional structure holding the coil and crucible arrangement within a sturdy metal framework 19 which preserves mechanical integrity enabling the assembly to be tilted in a stand (not shown) for pouring. Within crucible 14 there may be nested a solid lining 20 of the special flux composition, of formulation as disclosed hereinabove, except that preferably there is no significant amount of titanium sponge within the flux composition. This lining serves to protect the molten titanium from contaminants, melting and decomposing to yield a protective liquid and gaseous blanketing atop the melt 21. In addition, this blanketing 22, is preferably augmented by the addition of either hot liquid or finely-divided flux deposited from above, as needed, and as designated by the arrow 23. Alternatively, all of the protective flux composition may be applied to the top of the charge or melt, in the liquid finely-divided form. The titanium charge being melted (titanium sponge, scrap, or the like) offers resistance to the flow of secondary electrical currents induced in it by electromagnetic induction, thereby developing intense heat which causes the desired melting, in a manner well known in the art. This process can be carried on without using any protective enclosures. However, in some instances it can also be helpful to maintain an artificially-created protective gaseous atmosphere, such as one of argon, either with or without adding the flux atop the charge. In the latter event, a convenient technique involves introducing the inert gas below a simple cover (not illustrated) which has openings permitting the gases to escape while at the same time preserving a blanket of gas below it to screen out the ambient atmosphere.

The extraordinarily troublesome contamination problems which are encountered in the furnace-melting of titanium are also present in connection with the casting which follows, and it is important that these be minimized

if the full benefits of the improved melting practices are to be realized. Gases from the ambient air can be of insignificant contaminating effect if the pouring or drainage from furnaces like those of FIGURES 1 and 2 is accomplished swiftly. However, these gases can readily cause contamination as the molten titanium is taking shape and solidifying within the mold. Oxygen in the sand molding material of the parts of a mold is of serious consequence. To overcome these difficulties, one or both of two practices should be adopted. One of these involves the treatment (as by mixing or "mulling") of the sand material used in the mold with a quantity of the aforementioned flux composition, the latter in one case being in a granular form for uniform admixture with and distribution throughout the mold sand material and, in another case, being in fluid form for brushing, spraying or the like. The other practice involves the application of a quantity of the special flux composition to the top surfaces of the metal in the mold, either in liquid or finely-divided form. In FIGURE 3, for example, the mold box 24 contains a simple type of core-less mold 25 having both the sand mold material and flux granules in an admixture which includes sand material in quantity needed to develop the customary integrity of mold shape and which includes the granular flux in quantity sufficient to protect the case titanium from contaminants by melting and releasing the protective gas when the molten titanium is introduced and solidifies. The heat of the titanium poured into the mold from a crucible, 7", causes the desired flux decompositions to occur, without more being done. A discharge tube 26 from a suitable reservoir of the flux composition (not shown) releases, the melted and/or finely-divided flux composition 27 downwardly into the sprue cup 28 and onto the top of the titanium 29 after it is poured from the crucible. Preferably, the same flux composition is also introduced into any vents or risers, to protect the molten titanium mass 30 there also. Importantly, the melted and/or finely-divided flux composition permits gases and other surfacing material to escape or float at the top, while at the same time maintaining a substantially full protective cover until the molded ingot or other molded product has become fully solidified and substantially immune to embrittling contamination. Another useful technique involves the coating of the exposed surfaces of molded parts, such as the interior surfaces of the mold 25, with a liquid form of the flux by spraying, brushing, or the like. In certain instances, this may be done in addition to mixing the mold material with the flux in powdered or granular form, to further promote the protective effects which can be obtained. The mold material (or "sand," as it is known in the art) which may be used with the flux in making the usual mold parts, including sub-sections and cores, include the customary refractory materials such as silica, alumina, zirconia, zircon, graphite, and others such as are listed by Taylor, Flemings and Wulff on page 40 of their text "Foundry Engineering," published by John Wiley & Sons, Inc., New York, 1959.

Certain of the techniques, structures and formulations selected for discussion here for purposes of adequate disclosure are intended to be representative, rather than limiting, in character. The furnace and mold constructions may obviously be of forms different from those illustrated, while yet lending themselves to exploitations of the protective concepts. The halide fluxing agents may in appropriate instances include fine titanium sponge, such as about 2% by weight, or may be made more fluid or paste-like by the addition of a liquid binder such as titanium tetrachloride and silicon tetrachloride, which does not release harmful hydrogen or carbon. Additive oxides such as Na_2O , Li_2O or K_2O , which react with any water present in the hygroscopic halides to form hydroxides which will not decompose during the melting or casting, may also be introduced in typical amounts up to about 5% by weight. The halide cover for the titanium, while

being fluid or porous to permit escape of gases and the like, also advantageously restrains the escape of heat in the case of furnaces and molded products which should be cooled slowly.

Therefore, although specific practices have been described and preferred embodiments and materials have been discussed, it should be understood that various changes, modifications, additions and substitutions may be effected by those skilled in the art without departure from these teachings, and it is aimed in the appended claims to embrace all such variations as fall within the true spirit and scope of this invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The foundry process of maintaining a quantity of titanium including molten titanium protected against embrittling contamination by hydrogen, nitrogen, oxygen and carbon which comprises containing all of the molten titanium within a receptacle having a composition which includes a solid non-reactive flux distributed substantially uniformly therethrough along surfaces in contact with the quantity of titanium therein, said non-reactive flux consisting essentially of at least one halide which at temperatures near the melting temperature of titanium generates molten and gaseous halide products which protect the adjoining titanium from contaminants and said surfaces and which rise to the surface of the molten titanium to protect the upper surfaces thereof against contaminants, said non-reactive flux including at least one halide selected from the group of sodium chloride, potassium chloride, barium chloride, calcium chloride, magnesium chloride, barium fluoride and calcium fluoride, together with at least one percent, by weight, of stannous chloride.

2. The foundry process of melting titanium while protecting it against embrittling contaminations which comprises containing all of a charge from which titanium is to be melted within a furnace lined fully about all surfaces which contact the charge with a non-reactive protective flux consisting essentially of at least one halide which at temperatures near the melting temperature of titanium generates molten and gaseous halide products which protect the molten titanium against said contaminations, said furnace having a crucible lined with solid flux to thicknesses which fully protect the charge from contacting the crucible while melting and decomposing gradually during the melting operation, melting the charge only so long as the lining protects the molten titanium from contacting the crucible, and removing the molten titanium from the crucible before the surfaces of the crucible are exposed through the lining.

3. The foundry process of arc melting titanium while protecting it against embrittling contaminations which comprises containing all of a charge from which titanium is to be melted within a furnace lined fully about all surfaces which contact the charge with a non-reactive protective flux consisting essentially of at least one halide which at temperatures near the melting temperature of titanium generates molten and gaseous halide products which protect the molten titanium against said contaminations, said lining of non-reactive flux further including finely-divided titanium sponge, covering the exposed upper

surfaces of the charge with a substantially continuous and flowable coating of non-reactive protective flux consisting essentially of at least one halide which generates molten and gaseous halide products which protect the molten titanium against contamination from the ambient environmental atmosphere, and drawing an electric arc between the charge and an electrode through said coating to melt the charge while it is contained within the furnace lining and covered by the coating.

4. The foundry process of melting titanium while protecting it against embrittling contaminations which comprises containing all of a charge from which titanium is to be melted within a furnace lined fully about all surfaces which contact the charge with a solid non-reactive protective flux consisting essentially of at least one halide which at temperatures near the melting temperature of titanium generates molten and gaseous halide products which protect the molten titanium against said contaminations, covering the exposed upper surfaces of the charge with a substantially continuous and flowable coating of nonreactive protective flux, said coating of flux consisting essentially of at least one halide which generates molten and gaseous halide products which protect the molten titanium against contaminants from the ambient environmental atmosphere, and melting the charge while it is contained within the furnace lining and covered by the coating.

5. The foundry process of melting titanium as set forth in claim 4 wherein said charge is contained within an electrically non-conductive crucible opened to an ambient environmental atmosphere and lined with a solid non-reactive protective flux consisting essentially of at least one halide selected from the group of sodium chloride, potassium chloride, barium chloride, calcium chloride, magnesium chloride, barium fluoride and calcium fluoride, and wherein said melting is brought about by inducing secondary alternating electrical currents in the charge from coils outside said crucible and lining.

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