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Rasmussen

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[54] **PROCESS, STRUCTURE AND COMPOSITION RELATING TO MASTER ALLOYS IN WIRE OR ROD FORM**

[76] Inventor: **Robert T. C. Rasmussen,** 1296 Randy Drive, Pottstown, Pa. 19464

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[58] **Field of Search** ..... 75/53, 57, 27, 129, 93 G; 148/26; 29/197, 420

[56] **References Cited**

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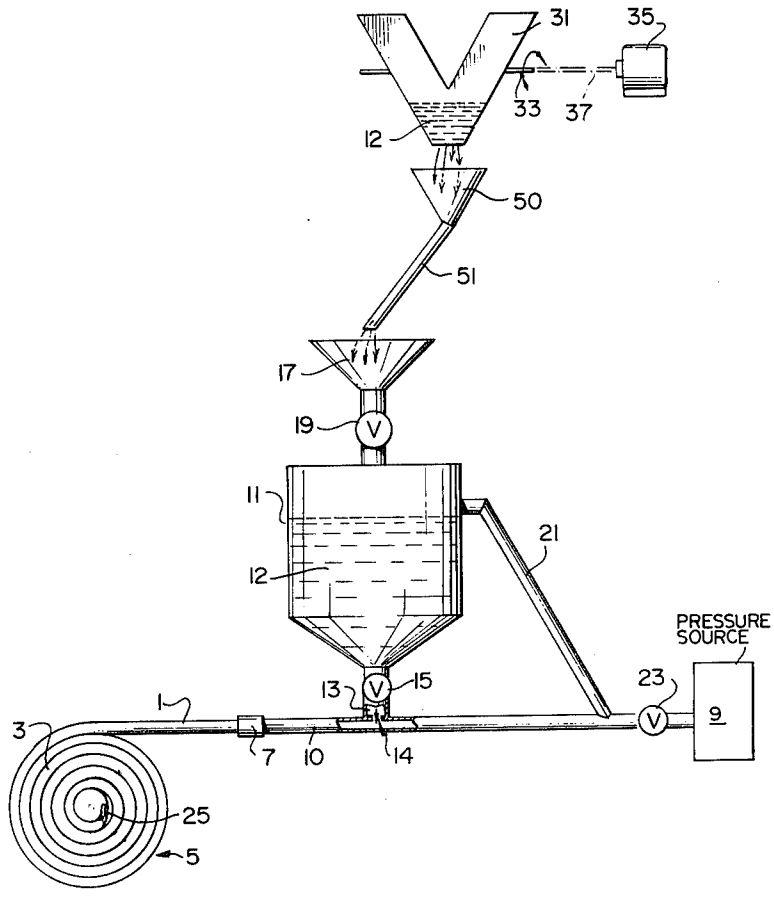
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Primary Examiner—P. D. Rosenberg
Attorney, Agent, or Firm—Watson, Cole, Grindle & Watson

[57] **ABSTRACT**

Process, structure and composition relating to master alloys in wire or rod form consisting of a hollow tube (which may itself be one of the alloy constituents) containing as granular filler one or more other alloy constituents and/or other substance as substances useful in the master alloy in question. The invention contemplates a filled tube master alloy wire or rod, where the desired alloy element or elements may typically comprise the tube material itself as all or part of a desired alloy element, and granular filler material in the form of a pure metal or suitable alloy, or a blend of pure metals or suitable alloys. The master alloys in wire or rod form may contain or enclose all or part of the desired grain refining, inoculating, deoxidizing or alloy constituent or constituents as pulverized metal or alloy within a tube of aluminum, mild steel, or other suitable metal or alloy.

15 Claims, 4 Drawing Figures



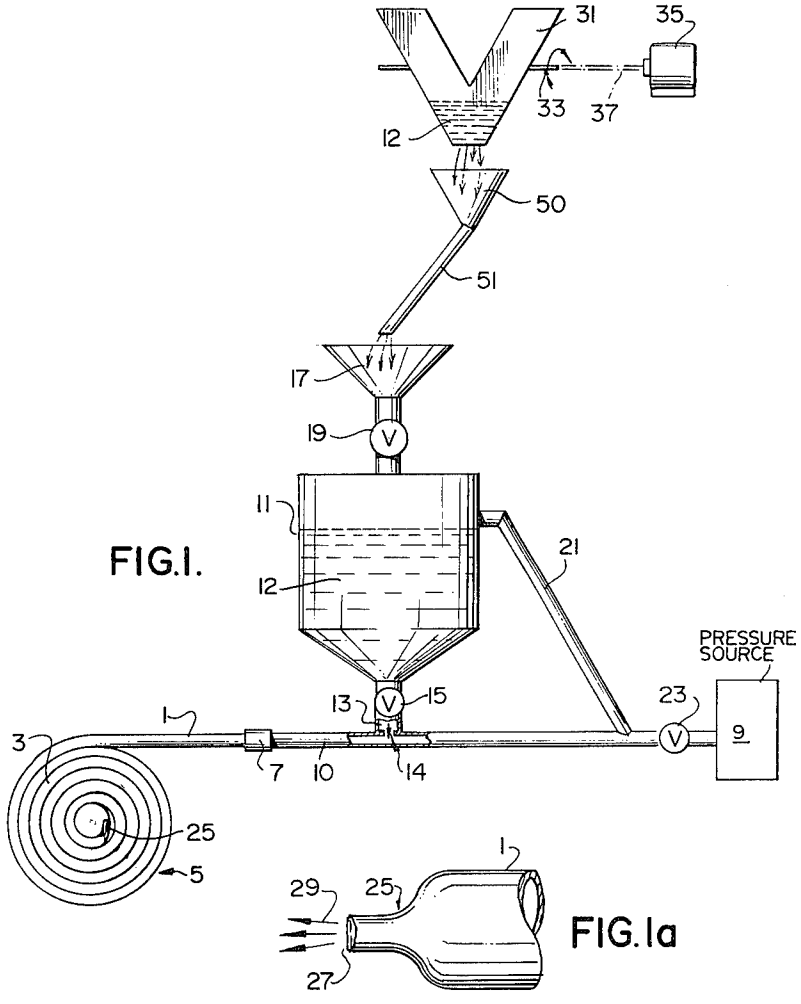


FIG.1.

FIG.1a

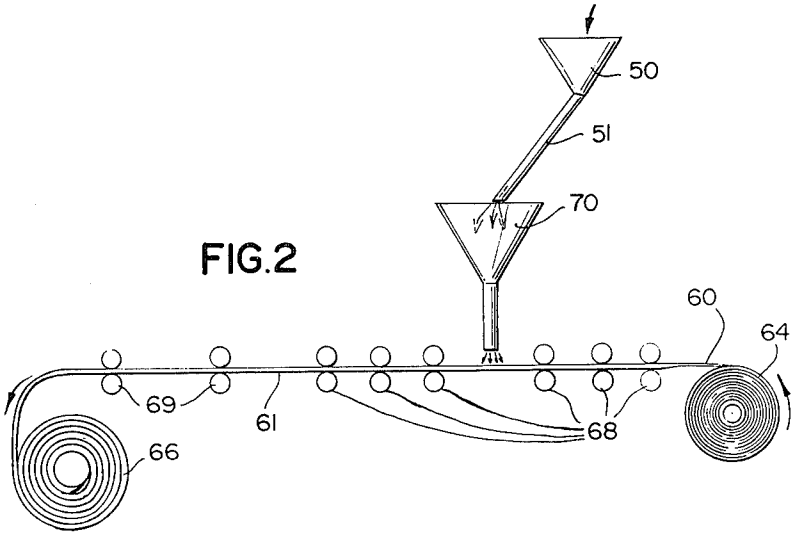


FIG.2

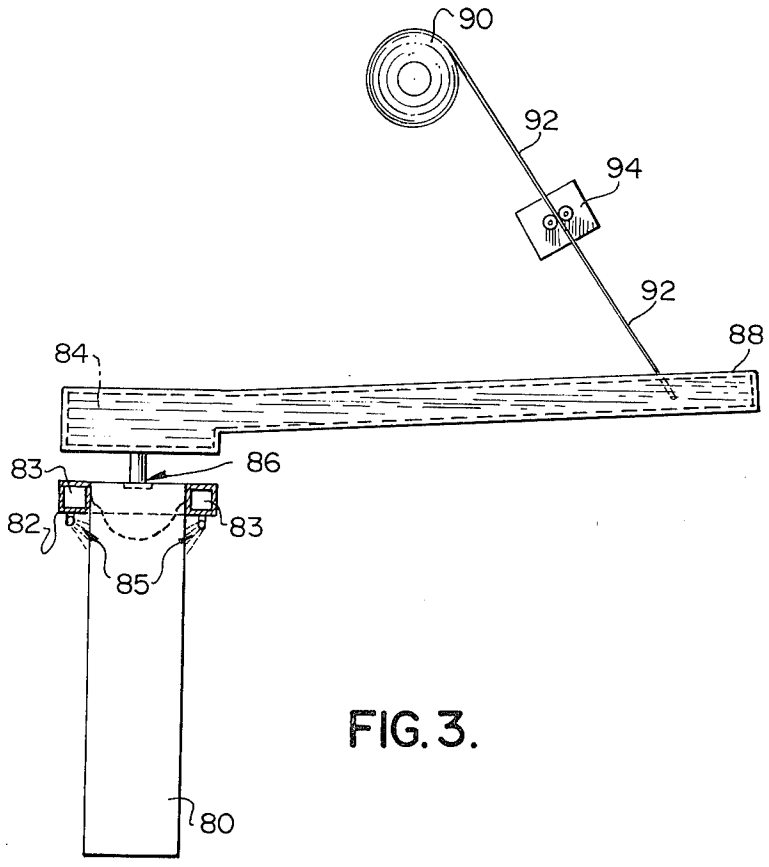


FIG. 3.

PROCESS, STRUCTURE AND COMPOSITION RELATING TO MASTER ALLOYS IN WIRE OR ROD FORM

This invention relates to master alloys in wire or rod form and to the method of making the same.

In particular the present invention relates to master alloys in wire or rod form consisting of a hollow tube (which may itself be one of the alloy constituents) containing as granular filler one or more other alloy constituents and/or other substance as substances useful in the master alloy in question.

The term "master alloy," often referred to as "hardener" in the aluminum industry, may be defined as a "preliminary" alloy, of composition high in one or more alloying elements, which is added in making a melt of the desired final alloy composition and which permits closer control of the final alloy composition than is possible with the addition of the pure metals. Other benefits often derived from adding desired metals as master alloys include lower cost, more uniform distribution of the metal or metals added and faster solution rate of the additive.

Detailed examples of the master alloys of the present invention will be given below, but to aid in understanding the present invention, two very simple examples of embodiments of the present invention will be given. One example is a hollow tube of aluminum filled with pulverized manganese, where Al and Mn are intended to be the constituents comprising the master alloy. A second simple example is a hollow tube of steel filled with pulverized calcium-silicon and aluminum powder where the Ca and Si are intended to be deoxidizers and the Al is intended to be a grain refiner for steel.

As will be described in greater detail, the present invention contemplates a filled tube master alloy wire or rod, where the desired alloy element or elements may typically comprise the tube material itself as all or part of a desired alloy element, and granular filler material in the form of a pure metal or suitable alloy, or a blend of pure metals or suitable alloys.

Master alloys in wire or rod form as contemplated by the present invention are particularly advantageous for use in direct chill casting of aluminum alloys and steels. In such processes the master alloys in wire or rod form may contain or enclose all or part of the desired grain refining, inoculating, deoxidizing or alloy constituent or constituents as pulverized metal or alloy within a tube of aluminum, mild steel, or other suitable metal or alloy.

As will be described more fully below, the enclosing material is in tubular form, either already made in such form or formed from a strip of the proper material as part of the manufacturing process of the making of master alloys of the present invention, and the substance or substances held within the tube are enclosed therein by one of the methods to be described.

It may be useful to discuss direct chill casting in which process master alloy wire or rod made according to the present invention is particularly useful.

Direct chill casting has been described as "gravity extrusion" to indicate in a simplified way how it is carried out. Briefly, with respect to semi-continuous direct chill casting of aluminum alloys, the molten metal is poured into a horizontally-disposed open-bottom mold which is cooled by a water jacket contained therein. Before starting a cast, a stool or bottom block carried by a hydraulic cylinder is raised into the mold to provide a starting mold bottom. As metal flows into the mold, the cylinder begins its downward travel lowering the billet out of the mold. The metal commences to solidify in the mold but complete solidification is achieved by water sprays on the cast billet below the mold, and final cooling is accomplished by immersion of the billet in a tank of water. Various shapes and sizes of billets and slabs are cast in this manner. Modifications of the above procedure are employed in the continuous direct chill casting of aluminum alloys, steels and copper base alloys.

It is accepted practice in the direct chill casting of aluminum ingots to add master alloys to the molten aluminum for grain refining purposes. Previously, the master alloys in their traditional slab form were introduced into the aluminum in the holding furnace prior to casting. A recent improvement in the manner of adding the master alloy involves continuous feeding of master alloy rod or wire into the launder or distributor that feeds the molten aluminum or aluminum alloy to the direct chill casting machine. Presently available master alloy wires comprise aluminum base alloys that are compositioned by melting in induction furnaces and cast by direct chill casting into billet logs that are subsequently cut to proper billet length for extrusion or rolling to wire. The method of manufacturing master alloy wire or rod just referred to is costly and is limited to alloy compositions that can be direct chill cast and that are formable by hot or cold working.

Aluminum base master alloys now available as wire, usually ⅜-inch diameter, include **5** to **6** percent titanium alloys and **5** percent titanium alloys containing from about **0.1** to **1.0** percent boron. These master alloys in wire form are intended exclusively for grain refining or modifying purposes in the direct chill casting of aluminum alloys. Master alloy wire or rod produced in accordance with the method of the present invention also include master alloys for innoculation, deoxidation and addition of alloy constituents to direct chill cast aluminum alloys and steels.

Direct chill casting of steel has in recent years become common. Continuously direct chill cast steels are rapidly gaining acceptability, even in critical applications. Much of the improvement in the quality of direct chill cast steels is due to improved pouring practices and addition of deoxidizers and grain refiners to the pouring stream. The improved pouring practice comprises prevention of oxidation by protecting the stream falling from the pouring vessel just above the mold (commonly referred to as the tundish) into the mold with a shroud of an inert gas for small ingots; streams for casting larger sections are often protected by tubes of refractory material extending from the tundish nozzle into the mold metal. Grain refiners such as vanadium, columbium or aluminum are added to the pouring stream or in the tundish; addition of calcium-bearing deoxidizers to the stream in conjunction with any of these grain refiners has markedly improved the type of resulting non-metallic inclusions.

It is obvious that in direct chill casting of steel, the continuous addition of master alloy grain refiners and deoxidizers in wire form to either the tundish or, particularly, to the pouring stream or mold metal would greatly facilitate precise control and convenience of making the additions. Continuous feeding of aluminum base master alloy wire formed from the compositioned

master alloy (say 3 percent B, balance A1) to the tundish or pouring stream in the direct chill casting of steel has the disadvantage that the master alloy wire has so low a melting temperature in comparison with the pouring temperature of steel that the wire will melt before entering the molten steel, requiring a faster feeding rate than that which will give the desired alloy addition or use of wire of smaller diameter than it is practical or economical to produce. Another disadvantage of such aluminum base master alloy wire is the fact that the concentration of the alloy constituent is limited by the maximum percentage that it is practical to produce (say 6% Ti, 5 to 6% Ti and 1.3% B, or 4% B alone with the balance essentially A1). This also means that the ratio of aluminum to other alloy constituent or constituents such as titanium and/or boron is very high and much higher than desired for addition to direct chill cast steels. A further disadvantage is the fact that the unit cost of the alloy constituent or constituents of the aluminum base master alloy is much higher than need be the case for addition to steel where iron in the master alloy is not objectionable. For instance, the cost of boron in ferroboron is only a fraction of the cost of boron in 4% boron-aluminum alloy. Since the boron addition to wrought aluminum alloys is small, say 0.004 to 0.02 percent, use of ferroboron as the boron additive would not introduce an objectionable percentage of iron into many wrought aluminum alloys. Likewise, since the titanium addition to wrought aluminum alloys is small, about 0.02 percent, use of ferrotitanium as the titanium additive would not introduce an objectionable percentage of iron into many wrought aluminum alloys.

The process of the present invention comprises manufacture of master alloy wire or rod for continuous feeding to direct chill cast aluminum alloys and steels by enclosing all or part of the desired alloy constituent or constituents as pulverized metal or alloy (typically about minus 24 mesh, with or without a limit as to the percentage of extreme fines) within a tube of aluminum, mild steel, stainless steel or other formable metal or alloy obtainable either as an already manufactured tube or else in strip form suitable to be formed into a tube in the process of making the master alloy wire or rod.

The present invention contemplates three alternative methods of enclosing all or part of the desired alloy constituent or constituents within a tube. According to one method contemplated by the present invention, the pulverized filler material may be forced into a coiled tube and the ends of the tube crimped or otherwise closed to prevent the escape of the enclosed material. It will normally be easier to force pulverized material into a large tube than a small tube, but where a tube of relatively small size is desired, the pulverized material may be forced into a tube of, say, one inch diameter. The thus formed one inch diameter filled tube may be reduced to rod or wire of the desired diameter by conventional rolling, swaging or drawing methods whereby the length of the filled tube is increased while decreasing the thickness of the tube wall and the diameter of the tube and filler.

In another method, a variant of the first, a coiled tube may be evacuated of gas and permitted to fill with pulverized filler material by suction. In the carrying out of this method, instead of crimping an end of the tube, such end would be attached to an evacuating device, and the pulverized material could be readily fed into the tube.

A further alternative method is to form the wire or rod master alloy from a flat strip of metal enclosing the selected pulverized material. In such a case, the tube material will be in the form of a strip of proper thickness and width for the particular master alloy wire or rod and it is also contemplated by the present invention that the strip will be formed into a trough, the pulverized filler material fed to the trough as the trough is formed, and the edges of the filled trough are folded over and crimped or otherwise sealed to form a tube. The filled tube thus formed is swaged, rolled, drawn or otherwise worked down to the desired diameter of wire or rod. The foregoing operations are done automatically with precise control of the rates at which the strip is shaped and the filler material is added to give filled tube wire or rod having uniform crosssectional composition, i.e., uniform proportions of tube material and filler material.

With any of the aforesaid methods of forming master alloy wire or rod, the tube material can supply part of the desired addition constituent or constituents, but it should not be a material that will introduce an objectional quantity of an undesired impurity into the direct chill cast alloy to which the master alloy wire is fed. The filler material can be a blend of two or more desired additive materials or of such additive material and tube material in powder form. For instance, the aluminum strip tube material for manganese-aluminum master alloy wire may supply all of the aluminum in the wire, or alternatively, aluminum powder can be blended with the manganese powder to provide part of the desired aluminum content in the filler material. Flux that may be desired in the use of the master alloy wire may be blended into the filler material, or it may be applied as a coating on the surface of the master alloy wire.

As a practical manufacturing method it may be desirable to produce master alloy rod or wire of predetermined lengths as in coils of predetermined size. In such event, the pre-formed tube can be of pre-determined length to produce filled tube of proper length to produce the resulting master alloy rod or wire in coils of desired length or weight, say a coil of ⅜-inch rod weighing 250 pounds. Likewise, filled tube in which the tube is formed from strip material can be sheared to proper length to produce the master alloy rod or wire in coils of desired size, or the filled tube can be fed continuously to reduction rolls and the resulting master alloy rod or wire will be sheared to produce coils of desired size.

A preferred embodiment of the present invention will now be described with the assistance of the accompanying drawings wherein like parts are denoted by the same reference numerals.

In the drawings,

FIG. 1 illustrates a method whereby rod or wire master alloy may be produced by forcing pulverized material into a tube;

FIG. 1*a* shows a fragmentary enlarged portion of what is shown in FIG. 1 to better illustrate the end of the tube denoted by 1;

FIG. 2 illustrates a method alternative to the method of FIG. 1, wherein rod or wire master alloy is produced by forming a strip into a tube and enclosing pulverized material therein; and,

FIG. 3 illustrates a typical method of making use of master alloy wire in direct chill casting.

Referring first to FIG. 1 where there is illustrated one form of the method herein described for producing rod or wire master alloy, the tube intended to be filled is shown at 1. Tube 1 will be typically an aluminum or mild steel tube of approximately one inch outside diameter with a wall thickness 0.009 to 0.040 inch. As shown in FIG. 1, tube 1 is formed into a coil denoted by 3. Coil 3 would normally be supplied to the process as a working reel denoted by 5 with the tube 1 being coiled layer on layer.

The outer end of the tubing on the working reel 5 is connected by a pressure-tight coupling denoted by 7 to the discharge tube or nozzle from a pressure source denoted by 9. The discharge tube or nozzle is denoted by 10. Pressure source 9 may be any of several types of pressure feeders such as a totally enclosed screw feeder, a reciprocating ram, a pump or, preferably, means for the entrainment of pressurized air or suitable gas such as nitrogen or argon. It is the latter preferred form which is illustrated in FIG. 1.

It is contemplated that pulverized material denoted by 12 (sometimes referred to as granular filler material) will be supplied to a bin denoted by 11 from which the pulverized material 12 will be fed into tube 1 in a manner to be outlined in greater detail below. The pulverized material 12 will be of a size of the order of minus 24 mesh. The pulverized material 12 reaches bin 11 through a hopper denoted by 17, the details of which will also be referred to below.

The pulverized material 12 is preferably supplied to and passed through a blender shown at 31. Blender 31 is of a conventional kind where there is a hollow V-shaped container capable of being rotated about a shaft, denoted by 37, the rotation being indicated by the arrow at 33. The driving motor for blender 31 is denoted by 35. After the required number of revolutions of the blender 31 the pulverized material 12 is completely blended.

After being blended in blender 31, the pulverized material 12 is fed to hopper 17, thence to bin 11 and to tube 1 as already described. Any suitable transfer system may be provided between blender 31 and hopper 17, such as belts or tubes, but the details thereof are not important to the present invention. A funnel denoted by 50 with a spout denoted by 51 are shown as an example of a suitable transfer system.

Bin 11 is connected to discharge tube 10 by means of a connecting tube denoted by 13 which is in turn connected to discharge tube 10 and thence to tube 1 through coupling 7. Tube 13 has therein a valve denoted by 15 for turning on and shutting off the supply of pulverized material 12 to discharge tube 10. An orifice denoted by 14 permits the pulverized material 12 to enter discharge tube 10 in a smooth stream.

The hopper 17 is connected to bin 11. One of the features to maintain proper pressure in bin 11 is a valve shown at 19. Another feature to keep bin 11 under pressure is a tube denoted by 21 connected to pressure source 9 and to bin 11. A valve denoted by 23 turns on and off the pressure available from pressure source 9.

It will be apparent that if there is pulverized material 12 in bin 11 and valve 15 is open, valve 19 closed, and valve 23 open, pulverized material 12 will drop down into the discharge tube 10 and be carried into tube 1 and around through the various turns of coil 3.

To facilitate the filling of tube 1, it is desirable if the end of tube 1 at the interior of coil 3, such end being denoted by 25, is crimped, as particularly shown in FIG. 1A at 27. The crimping at 27 is not sufficient to completely close off tube 1 but it restricts the flow of gas out of tube 1 at end 25 and the gas escapes, as shown at 29, allowing relatively high pressure to be maintained in tube 1 without excess loss of pulverized material 12 when tube 1 is filled. While the filling is taking place, air in tube 1 will be expelled from partly crimped end 25 as shown by the arrows at 29 and where the tube 1 is almost full the crimping can be completed, effecting a tight seal at the end 25 of tube 1 remote from discharge tube 10 and coupling 7.

When tube 1 is filled, the end of tube 1 at nozzle and coupling 7 will also be crimped or pinched shut while being disengaged from the coupling to the nozzle 7.

The filled tube 1 will then be fed from the "working" reel 5 to suitable diameter-reducing and length-increasing means, such as reduction rolls, a swaging machine or dies for reduction to the desired master alloy rod diameter, say ⅜-inch, and the master alloy rod will be coiled on a finished rod reel as it emerges from the reduction mechanism to provide a coil of master alloy rod.

It will be apparent that a variant of the method just described is the provision of vacuum means at the end 25 of tube 1 to draw the pulverized material 12 into tube 1. In such a case, the remainder of the apparatus could be relatively unchanged, with valves 15 and 19 open and valve 23 closed.

It may be found helpful to discuss the practical aspects of the reels of master alloy rod or wire as suitably used industrially. The practical size of the working reel 5 would not likely correspond to a practical size of a typical supply reel of tube 1.

Starting with a supply of tube 1 a size of the order of one inch o.d. is a practical size. Such tubing is readily available in supply reels (not shown). It would take about 246 feet (about 39 turns on a 2-foot diameter coil) of 1-inch diameter tubing to make about 1,755 feet of ⅜-inch diameter filled tube master alloy rod (about 279 turns in a 2-foot diameter coil), which would be a normal coil of aluminum-base master alloy rod weighing about 250 pounds.

The available or free end of the tube 1 on the supply reel (not shown) would be crimped or pinched almost shut as particularly described in connection with FIG. 1A, after which sufficient length of tubing for one coil of ⅜-inch master alloy rod (say 246 feet as above) would be recoiled on the working reel 5, this length of tubing being cut off in such manner that the available end of the tubing on the working reel 5 would be a fully open circular section. As coiled in working reel 5, the crimped end 25 is the inner end of working reel 5, as already noted.

After tube 1 is filled it will, as already indicated, be fed from the working reel 5 to reduction rolls, a swaging machine or dies for reduction to the desired master alloy rod diameter, say ⅜-inch, and the master alloy rod will be coiled on a finished rod reel as it emerges from the reduction mechanism to provide a coil of master alloy rod.

The length of such finished master alloy wire or rod would be 1,755 feet, according to the given example, ready for shipment to the customer.

In FIG. 2 is illustrated an alternative method for making master alloy wire or rod. In FIG. 2 a blender like blender 31 in FIG. 1 will usually be used but is not shown in this Figure. Instead of the hopper 17 of FIG. 1, there is provided a hopper denoted by 70 in the apparatus of FIG. 2. Again, any suitable transfer system to hopper 70 may be provided and the aforesaid example structure is again shown. In the form of apparatus of FIG. 2 there will be a flat strip of metal denoted by 60 which will be formed into a tube denoted by 61 and at the same time filled with pulverized material. Obviously, the strip 60 will be made of whatever material it is desired to constitute the encasing tube of the wire or rod master alloy.

The strip 60 may be fed from a reel denoted by 64 and the filled tube in finished form of wire or rod master alloy may be coiled on a spool denoted by 66.

Forming rolls are denoted by 68. The forming rolls 68 first form the strip 60 into a trough, it is filled with pulverized material 12 from hopper 70, and the forming rolls 68 then complete the forming into a tube. Reduction rolls 69 then reduce the filled tube to the desired rod diameter, say ⅜ inch.

FIG. 3 indicates the manner in which master alloy wire or rod of the present invention is used in a direct chill casting process. The direct chill mold is shown at 82, cut away to show the water jacket 83, water circulation means (not shown) and sprays denoted by 85 are directed onto the ingot as it descends from the mold. The direct chill cast ingot is shown at 80. Molten metal is fed to the mold 82 from a tundish denoted by 84 through a nozzle and float valve denoted by 86. Molten metal is fed to the tundish from launder denoted by 88. A coil of master alloy wire or rod in accordance with the present invention is shown at 90, from which emerges a wire or rod denoted by 92. Proper feed speed is controlled by a variable speed feeder denoted by 94.

The launder 88 receives metal from the melting or holding furnace (not shown) or from a ladle and delivers the metal to the direct chill casting machine. The rate at which the wire is fed is co-ordinated with the rate at which the molten metal is delivered to introduce the desired percentage of master alloy constituent or constituents into the molten metal being cast. The master alloy wire may be fed to the molten metal in the launder 88 as shown, in the tundish 84, in the stream from the tundish nozzle 86 or in the molten metal in the water cooled mold 82 of the direct chill casting machine; introduction of master alloy as wire in this manner is particularly convenient and advantageous in the direct chill casting of steel wherein the molten metal in the tundish or water cooled mold is kept under vacuum or an inert atmosphere to prevent oxidation.

The applicant feels it is necessary to discuss direct chill casting in some detail in order to show the advantage of the present invention in its proper light. However, it will be obvious that the present applicant does not make any claim to invention in this application in connection with the direct chill casting.

Examples of master alloys for continuous feeding as wire or rod to direct chill cast aluminum alloys that can be produced by the process of this invention are shown in the following, but the application of the process is not confined to the examples shown.

EXAMPLE 1.

Manganese-Aluminum Master Alloy Wire.

Many engineering alloys of aluminum contain from about 0.40 to 1.50% Mn. The practice has been to add the required manganese to the holding furnace prior to casting in the form of manganese-aluminum master alloy analyzing from about 25 to 65% manganese or of briquettes analyzing about 75% Mn that are made from a blend of manganese and aluminum powders. It is advantageous in the direct chill casting of such aluminum alloys to add the manganese as Mn-Al master alloy wire to the launder or distributor that feeds the direct chill casting machine. Besides being costly to produce Mn-Al master alloy wire by present conventional practice, the cast Mn-Al master alloys are too brittle to form by hot or cold working. According to my invention, Mn-Al master alloy wire would be made by the filled tube method in which the tube would be aluminum (either pre-formed and filled in accordance with the method of FIG. 1 or formed from strip and filled in accordance with the method of FIG. 2) and the filler material (nominally minus 24 mesh size) would be electrolytic manganese, alone or blended with aluminum powder depending upon the overall analysis of tube plus filler desired. Overall wire compositions contemplated range from about 25 to 75% Mn, preferably 50 to 75% Mn. Where higher iron contents can be tolerated, all or part of the manganese filler can be supplied as a cheaper form of manganese such as standard or medium carbon ferromanganese or low or intermediate iron ferromanganese.

EXAMPLE 2.

Silicon-Aluminum Master Alloy Wire.

Silicon is a common constituent of many wrought aluminum alloys that are direct chill cast. Its content ranges from about 0.30 to 1.20 percent in such alloys. It would be advantageous in many cases to add the silicon as Si-Al master alloy wire to the launder or distributor that feeds the direct chill casting machine, but Si-Al alloys generally have a low-melting phase that bleeds during freezing of the cast alloy and they are not formable by hot or cold working. These difficulties can be overcome by manufacturing the master alloy wire in accordance with the method of my invention. The tube would be aluminum (pre-formed or formed from strip in the process) and the filler would be silicon metal, alone or blended with aluminum powder depending upon the overall composition desired. Overall wire compositions contemplated range from about 25 to 75% Si, preferably in the upper part of the range, 50 to 75% Si.

EXAMPLE 3.

Manganese-Silicon-Aluminum Master Alloy Wire.

Many wrought aluminum alloys that are direct chill cast contain both manganese and silicon as minor alloy constituents, and it would be advantageous to have master alloy wire containing both Mn and Si in the desired proportions. Such a master alloy wire can be produced according to my invention by providing or forming a tube of aluminum and filler of either silicomanganese or ferromanganese silicon to supply all of the manganese and all or part of the silicon required as very low cost Mn and Si units. Depending upon the pro-

portions of Mn and Si desired, additional Si can be provided in the filler by blending silicon metal with the manganese-silicon alloy. Electrolytic manganese can be blended with the manganese-silicon filler material to provide part of the manganese if required to lower the proportion of Fe in the master alloy wire. Overall master alloy wire composition with silicomanganese alone as filler would be about **45%** Mn, **30%** Al, **14%** Si, **10%** Fe and **1%** C. Higher Si content can be achieved by adding silicon metal to the filler at the expense of Mn. Lower Fe content can be achieved by using electrolytic manganese as part of the filler material; this also would lower the overall Si content of the wire.

EXAMPLE 4.

Magnesium-Silicon-Aluminum Master Alloy Wire.

A number of wrought aluminum alloys contain from about **0.6** to **1.3%** Mg and **0.6** to **1.0%** Si. It would be advantageous to add all of the Mg and all or part of the Si as master alloy wire in the direct chill casting of the wrought aluminum alloys. The Mg and Si would be incorporated in the master alloy wire as filler comprising magnesium silicide analyzing about **50** percent each of Mg and Si or magnesium and silicon metals in the desired proportions. Aluminum powder may also be blended with the Mg and Si filler materials to obtain the desired overall wire composition with aluminum as the tube material. Overall wire compositions contemplated range from about **10** to **35** percent each of Mg and Si, with the balance essentially aluminum.

EXAMPLE 5.

Titanium-Aluminum Master Alloy Wire.

This master alloy wire would be produced by the method of this invention by blending titanium chips (usually **4%** V, **6%** Al, balance Ti), low carbon ferrotitanium (say **42%** Ti, **5%** Si max., **9%** Al max., balance Fe) or titanium sponge pulverized to about minus **24** mesh with aluminum powder to provide the filler material, with aluminum serving as the tube material. Overall wire compositions contemplated range from about **3** to **50%** Ti, with the balance essentially aluminum.

EXAMPLE 6.

Titanium-Boron-Aluminum Master Alloy Wire.

This master alloy wire would be made by the method of this invention by blending pulverized titanium as in Example **5** with ferroboron (approximately **17** to **24%** B, balance mainly Fe) also pulverized to about minus **24** mesh and aluminum powder to provide the filler material, with aluminum serving as the tube material. Overall wire compositions contemplated range from about **5** to **50%** Ti, **0.1** to **10%** B, Fe about five times the B content, balance essentially aluminum.

EXAMPLE 7.

Boron-Aluminum Master Alloy Wire.

This master alloy wire would be made by the method of this invention by blending ferroboron, manganese-boron, silicon-boron or other suitable boron alloy pulverized to about minus **24** mesh with aluminum powder to provide the filler material, with aluminim serving as the tube material. Overall wire compositions contemplated range from about **1** to **12%** B, balance essentially aluminum after allowing for any other constituent of the boron alloy used.

EXAMPLE 8.

Miscellaneous Aluminum Base Master Alloy Wires.

These master alloy wires would be made by the method of this invention by blending with aluminum powder to provide the filler material one or more of the following pulverized metals, as metal or suitable alloy: Fe, Pb, Bi, Sr, P, Be, Ca, Ce or rare earth alloys or mischmetal, Cr, Co, Cb, Cu, Ga, Fe, Li, Mg, Mo, Ti, Ni, Ta, V and Zr. Tube material would be aluminum.

EXAMPLE 9.

Aluminum Base Master Alloy Rod or Wire Sheared to Short Lengths for Addition to Aluminum Holding Furnace.

The filled tube method of manufacturing master alloy rod or wire may also be used to produce slugs of master alloy, comprising pulverized filler material encapsulated in an aluminum sheath, suitable for charging to the aluminum holding furnace. What is contemplated is production of filled tube master alloy rod or wire of desired diameter, say ¼ to **1** inch, and shearing the rod or wire to the desired slug length, say **2** to **6** inches, the degree of compaction of the filler material and the manner of shearing being such that the aluminum tube is pinched together to close the sheared ends of the slugs.

It will be found convenient to use the process of FIGS. **1** or **2** to carry out this example and its variants to be referred to below although this is by no means essential.

Several master alloys in slug form are contemplated by this example and its variants, as follows:

a. Phosphorus-Silicon-Iron-Aluminum Master Alloy. Phosphorus, particularly as a P-Si alloy, has proved to be a superior refiner of primary silicon in hypereutectic silicon-aluminum casting alloys when added to the casting alloy to give about **0.025** to **0.05%** P. Ferrophosphorus, nominally **25%** P and balance mainly Fe, and silicon metal, both pulverized to about minus **24** mesh, would be blended in proportions to give filler material analyzing from about **10** to **20%** P, **28** to **56%** Fe and **60** to **22%** Si. Aluminum tube material would comprise from about **20** to **30%** of the overall rod or wire composition. Or, ferrophosphorus might comprise the entire filler material.

b. Strontium-Silicon-Aluminum Master Alloy. Strontium also is an effective refiner or modifier in hypereutectic silicon-aluminum casting alloys. Filler material in this case would comprise strontium-silicon alloy, nominally **45%** Sr, **45%** Si and balance impurities, pulverized to about minus **24** mesh, blended with aluminum powder and enclosed in aluminum tube. Overall slug or rod compositions contemplated range from about **5** to **30%** each of Sr and Si, and the balance essentially aluminum.

c. Silicon-Aluminum Master Alloy. In some cases for both wrought and particularly cast aluminum alloys the required silicon content may exceed the quantity that it is practical to add as rod or wire in the casting operation. In such cases Si-Al master alloy slugs could be produced as in Example **2** for addition to the aluminum holding furnace.

d. Manganese-Aluminum Master Alloy. Mn-Al master alloy slugs could be produced as in Example 1 for addition to the aluminum holding furnace.

e. Silicon-Manganese-Aluminum Master Alloy. Si-Mn-Al master alloy slugs could be produced as in Example 3 for addition to the aluminum holding furnace.

Examples of master alloys for continuous feeding as wire or rod to direct chill cast steels, including stainless and other alloy steels, that can be produced by the process of this invention are shown in the following, but the application of the process is not confined to the examples shown.

EXAMPLE 10.

Calcium-Silicon-Aluminum-Iron Master Alloy Wire.

This master alloy wire for deoxidation would be manufactured by the process of this invention by using calcium-silicon (30 to 33% Ca, 60 to 65% Si) as the usual filler material, with low carbon steel serving as the tube material. The filler material may comprise from about 25 to 75 percent of the overall wire composition, depending upon the rate at which it is desired to feed the master alloy wire to the tundish or mold metal during direct chill casting to add the required percentage of Ca and Si to the resulting steel ingot. It may be advantageous to incorporate aluminum in the master alloy wire for grain refinement; this can be done by blending aluminum powder in the desired proportion with the Ca-Si filler material, or aluminum might serve as the tube material instead of low carbon steel.

EXAMPLE 11.

Columbium-Iron Master Alloy Wire.

Columbium, usually as ferrocolumbium (50 to 70% Cb, balance essentially Fe) has long been required as a small addition to alloy steels to stabilize carbon. A new development with great promise is in "I-F" steels, essentially low-carbon deepdrawing steels to which Cb is added at a level of $10 \times (C + N)$. This master alloy wire would be manufactured by the method of this invention by using ferrocolumbium as the filler material, with low carbon steel serving as the tube material. Overall master alloy wire compositions might range from about 20 to 55% Cb, balance essentially Fe. Deoxidizer or grain refiner, such as aluminum powder, might be blended with the ferrocolumbium filler material in any desired proportion, but probably at a weight ratio of Al to Cb no higher than 2 to 1. Filler material might comprise up to about 80 percent by weight of the overall wire.

EXAMPLE 12.

Synergistic Grain Refining Master Alloy Wire for Steel.

According to U.S. Pat. No. 3,383,202 to Dunstan W. P. Lynch, a complex silicon base grain refining alloy containing 30 to 60% Si, 5 to 15% Mn, 5 to 20% Ce plus La, up to 15% Ca plus Ba, 1 to 6% each of Cb plus Ta, V, Zr, and Ti, 1 to 3% Al, 0.04 to 0.15% B and balance Fe (about 21 to 27%) is a superior grain refining alloy for cast or wrought steels. I propose to introduce such a grain refining alloy in wire or rod form by using the grain refining elements as filler, with low carbon steel serving as the tube material. The filler material may be the compositioned grain refining master alloy pulverized to about minus 24 mesh, or it might be a blend of the individual elements in the form of metals or suitable alloys.

EXAMPLE 13.

Miscellaneous Master Alloy Wires for Addition of Grain Refiners, Deoxidizers and Alloy Additions to Direct Chill Cast Steels.

Aluminum, vanadium, columbium, titanium and zirconium are well known grain refining elements for the production of fine grained steels when added in small amounts to the steel prior to casting. Columbium and titanium also are well known carbon stabilizers to prevent intergranular corrosion. Calcium, silicon, manganese, chromium, vanadium, molybdenum, boron and the rare earth metals often are added in small percentages, alone or in various combinations, to impart desired properties to the steel ingot. One or a combination of two or more of these additives would comprise the filler material as pulverized metal or suitable alloy with low carbon steel serving as the tube material in the manufacture of filled-tube master alloy wires in accordance with my invention.

It may be desirable or necessary in some cases of continuous feeding of master alloy wire in the direct chill casting of aluminum alloys and of steels to provide supplemental localized heating to assure quick melting and dissolution in the host metal of the ingredients of the master alloy wire. I propose that such supplemental heating be provided by applying direct or alternating current to the wire in such manner that arc or resistance heating is achieved at the point of introduction of the wire into the casting metal or alloy, as in the case of welding. This procedure might be particularly useful with respect to feeding of titanium-aluminum, titanium-boron-aluminum or boron-aluminum wire produced by the process of this invention in the direct chill casting of aluminum alloy ingots to assure prompt melting and dissolution of the titanium and boron filler materials. It would also be useful where the weight percentage of the master alloy wire that it is desired to add to either aluminum alloy or steel direct chill cast ingot is large enough to require supplemental heating to assure complete melting of the master alloy wire and its dissolution in the host metal or alloy to which it is added. Such supplemental arc or resistance heating would in any case cause turbulence and mixing of the melted master alloy wire and the host metal or alloy to assure complete and homogeneous mixing of the wire and host constituents.

It will be found that the present invention greatly broadens the usefulness of master alloys by providing improved and new master alloys in wire or rod form and improved method of making the same.

I claim:

1. A composite structure of a synergistic grain-refining master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of low carbon steel and the filler material of substantially 30 to 60% Si, 5 to 15% Mn, 5 to 20% Ce plus La, 0 to 15% Ca plus Ba, 1 to 6% of Cb plus Ta, 1 to 6% of V, 1 to 6% Zr, 1 to 6% of Ti, 1 to 3% Al, 0.04 to 0.15% B and balance Fe.

2. A composite structure of material for grain refining, deoxidizing, inoculating and alloy additions for use in a direct chill cast process, the structure being com-

prised of a tube containing pulverized filler material, the tube material made of a low carbon steel and the filler material at least two of Al, V, Cb, Ti, Zr, Ca, Si, Mn, Cr, Mo, B and rare earths.

3. A composite structure of a manganesealuminum master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of aluminum and the filler material of **0** to **10%** aluminum and at least one of the group of electrolytic manganese, standard ferromanganese, medium carbon ferromanganese, low iron ferromanganese and intermediate iron ferromanganese, the overall composition ranging from **50** to **75%** Mn, the balance consisting of Al and other constituents of the manganese material used.

4. A composite structure of a silicon-aluminum master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of aluminum and the filler material of **0** to **10%** aluminum and silicon, the overall composition ranging from **50** to **75%** Si, the balance consisting of Al and minor impurities.

5. A composite structure of a manganese-silicon-aluminum master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of aluminum and the filler material of at least one of the group of silicomanganese and ferromanganese-silicon to give a desired overall composition of about **45** to **50%** Mn, **15** to **25%** Si and **4** to **10%** Fe, the balance consisting of Al and minor impurities.

6. A composite structure of a magnesium-silicon-aluminum master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of aluminum and the filler material of **0** to **10%** aluminum and magnesium silicide, the overall composition ranging from about **10** to **35%** each of Mg and Si, the balance essentially Al.

7. A composite structure of a titanium-aluminum master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of aluminum and the filler material of titanium sponge and aluminum to give an overall composition of about **3** to **50%** Ti, the balance essentially Al.

8. A composite structure of a titanium-boron-aluminum master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of aluminum and the filler material of titanium sponge, ferroboron and aluminum to give overall composition of **5** to **50%** Ti, **0.1** to **10%** B, Fe about five times the B content, balance essentially Al.

9. A composite structure of a boron-aluminum master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of aluminum and the filler material of aluminum and one of the group of ferroboron, manganese-boron and silicon-boron to give overall composition of **1** to **12%** B, the balance essentially Al after allowing for any other constituents of the boron alloy used.

10. A composite structure of an aluminum base master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of aluminum and the filler material of at least one of the group of Fe, Pb, Bi, Sr, P, Be, Ca, Ce, rare earths, mischmetal, Cr, Co, Cb, Cu, Ga, Ge, Li, Mg, Mo, Ti, Ni, Ta, V and Zr, or alloys thereof.

11. A composite structure in accordance with claim **10** wherein there is additionally aluminum as part of the filler material.

12. A composite structure of a deoxidation material for use in a direct chill cast process, the structure being calcium-silicon-iron master alloy and comprised of a tube containing pulverized filler material, the tube material made of low carbon steel and the filler material of calcium-silicon, the overall composition ranging from about **8** to **16%** Ca, **16** to **34%** Si and **50** to **75%** Fe by weight at **50%** volume compaction of the filler material.

13. A composite structure of a grain refining and deoxidizing master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of one of the group of low carbon steel and aluminum and the filler of calcium-silicon and **0** to **10%** aluminum.

14. A composite structure of a columbium-iron master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of low carbon steel and the filler material of ferrocolumbium, so that the overall composition is about **20** to **55%** Cb, the balance essentially Fe.

15. A composite structure of a columbium-aluminum-iron master alloy for use in a direct chill cast process, the structure being comprised of a tube containing pulverized filler material, the tube material made of low carbon steel and the filler material of ferrocolumbium and aluminum, the filler material comprising up to about **80** percent by weight of the overall composition.

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