Jan. 9, 1973 D. A. CORRIGAN ET AL 3,709,722

PROCESS FOR ACCRETING MOLTEN COPPER ON A MOVING CORE MEMBER

Original Filed April 6, 1970 2 Sheets-Sheet 1

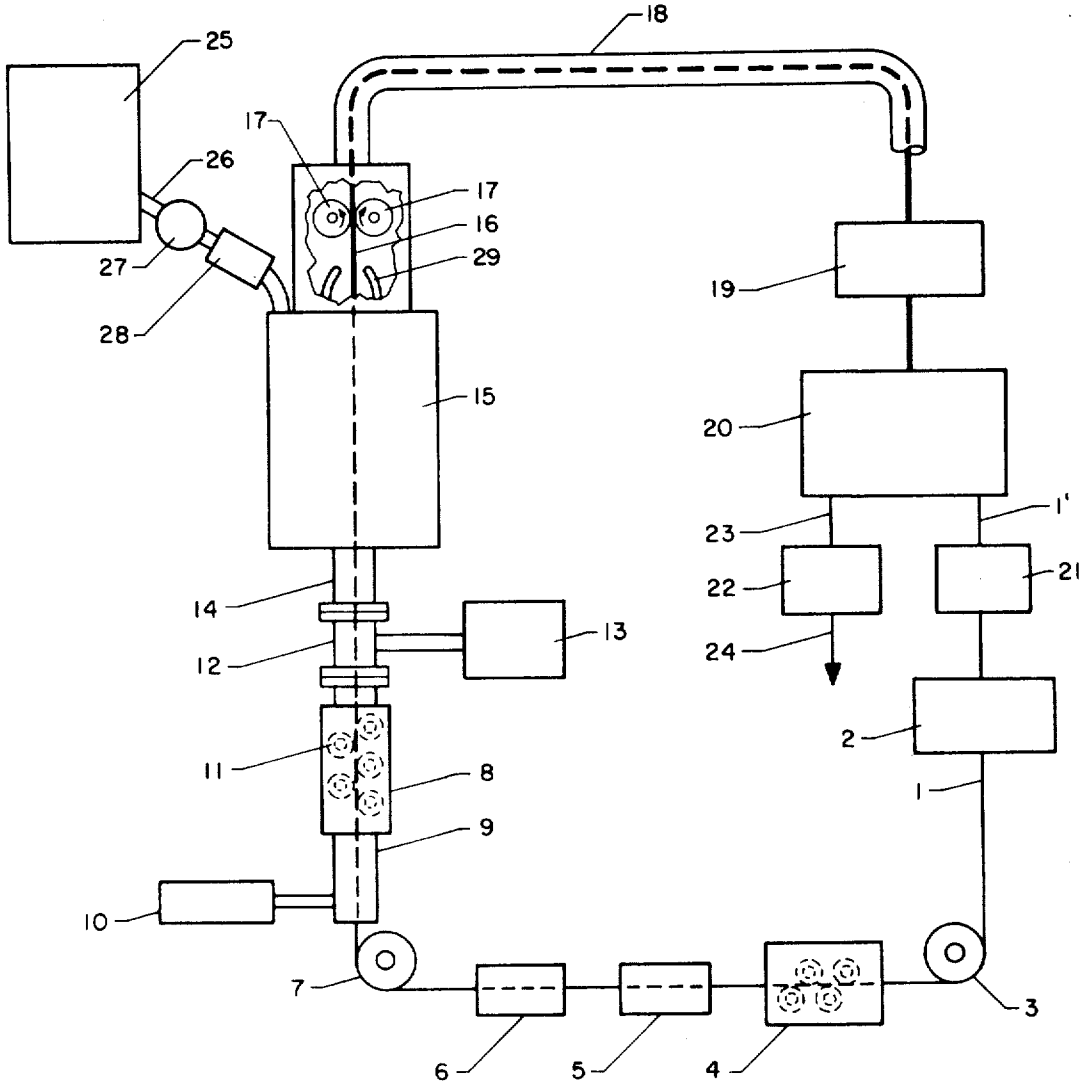


FIGURE 1

PROCESS FOR ACCRETING MOLTEN COPPER ON A MOVING CORE MEMBER

Original Filed April 6, 1970 2 Sheets-Sheet 2

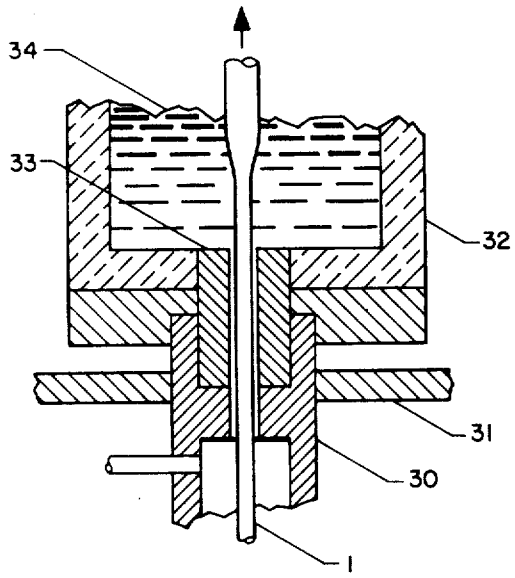


FIGURE 2A

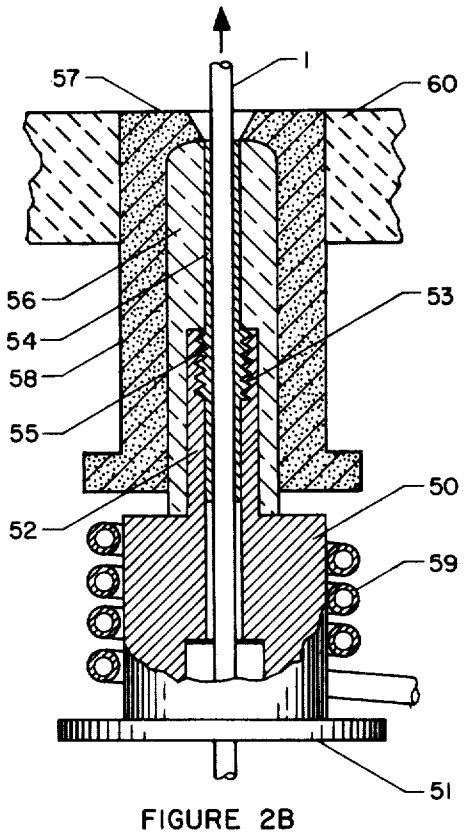


FIGURE 2B

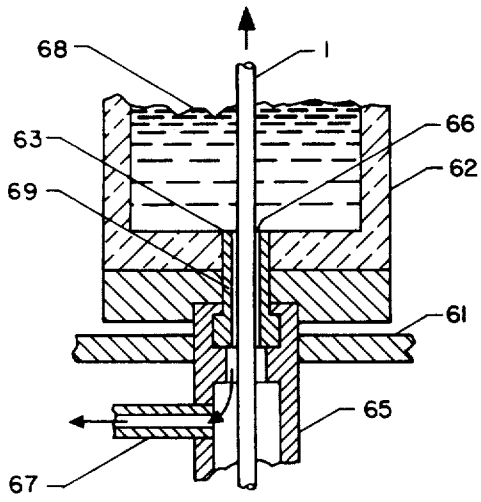


FIGURE 2C

United States Patent Office 3,709,722 Patented Jan. 9, 1973

3,709,722

PROCESS FOR ACCRETING MOLTEN COPPER ON A MOVING CORE MEMBER

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Original application Apr. 6, 1970, Ser. No. 25,770, now Patent No. 3,610,204. Divided and this application Apr. 7, 1971, Ser. No. 132,227

Int. Cl. C23c 1/00

U.S. Cl. 117—114 R 2 Claims

ABSTRACT OF THE DISCLOSURE

This patent relates to an improvement in the continuous casting dip forming process. In the dip forming process for making wire rod a core member is passed upwardly through a crucible containing a molten metal. The crucible contains a nozzle or bushing through which the core member passes at a relatively high rate. Construction materials for this nozzle or bushing element are critical in obtaining high quality wire rod.

This is a division of application Ser. No. 25,770 filed Apr. 6, 1970 and now Pat. No. 3,610,204.

BACKGROUND OF THE INVENTION

The dip-forming process, such as used in continuous casting of metal, is now well known in the art. According to this process, an elongated body or core material such as a metal rod is typically pretreated by passing it through a straightener, a surface cleaning apparatus and a shaving die which also serves as a vacuum seal for a vacuum entrance chamber positioned below or at the bottom of a crucible containing a bath of molten material. The continuous elongated core or body is passed upwardly through the molten bath, which bath may have the same chemical composition as that of the core or a different composition. The molten material in the crucible accretes or deposits upon the outer surface of the core thereby increasing its cross sectional area appreciably. After emerging from the crucible the resulting casting member is cooled as by a water spray from one or more jet nozzles at least sufficiently so that the cast member may be rolled or worked. From there the cast member may be passed through a suitable roller mechanism where it is reduced in cross-sectional area and then passed to a suitable receiving means such as a take-up reel.

The dip-forming process briefly described above is fully set out in one or more of the following patents:

Patent No.	Inventor	Issue date
3,008,201	R. P. Carreker, Jr.	11/14/61
3,060,053	R. P. Carreker, Jr. et al.	10/23/62
3,060,054	J. A. Russell et al.	10/23/62
3,060,055	H. H. Bixler	10/23/62
3,060,056	B. B. Scott	10/23/62
3,235,960	R. P. Carreker, Jr.	2/22/66
3,466,186	R. P. Carreker, Jr.	9/9/69

To the extent necessary the disclosures of the above cited patents are incorporated by reference herein.

A metallurgical investigation of wire breaks led to our discovery that a problem in the dip formed rod was caused by molybdenum inclusions. A study of the dip forming process reveals that the only location in the system where molybdenum is known to be present is the bushing or nozzle in the entrance port. Thus we deducted that the molybdenum inclusions in the wire were the results of the

use of a molybdenum bushing or nozzle through which the core material passed into the molten copper bath.

Two alternate causes of molybdenum inclusion in the copper rod appear to contribute to the problem. Mechanical removal of molybdenum particles from the bushing or nozzle may be due to spalling, welding, and/or galling. In combination with the mechanical removal, or by itself, there may be intergranular attack of molybdenum by molten copper and/or atmosphere in the molten metal crucible. It is theorized that the molybdenum particles embedded in the core material as it passes through the molybdenum bushing are those particles dislodged from the molybdenum bushing after the grain boundary is weakened by a combination of impurities and high temperatures. Certain impurities in the molten copper probably change the wetting characteristic at the molybdenum grain boundaries and the grain boundaries thus become weakened and particles of molybdenum become susceptible of mechanical removal by the core passing through the bushing. The fact that molybdenum is not insoluble in liquid copper may also contribute to the difficulty experienced.

Three patents cited above, Pats. 3,008,201; 3,325,960 and 3,466,186, refer to the use of a refractory metal bushing or nozzle in the dip forming system. In these cited patents the only refractory metal specifically named is molybdenum. Our investigation shows that two of the three refractory metals generally commercially available, i.e. molybdenum and tantalum, are not suitable for use in the dip forming system. The third commercially available refractory metal, tungsten, according to our investigation, finds marginal use in the dip forming system but is not as effective as other metals such as rhenium or rhenium based alloys. Thus it is clear that the teaching in the cited patents cannot be relied upon by one skilled in the art.

SUMMARY AND OBJECTS

The invention therefore relates to a method for accreting molten material, i.e. copper, on a continuously moving rod wherein the rod passes through an entrance bushing whose physical characteristics are such that no material will be removed from the bushing and deposited on the moving rod to cause inclusions in the accreted rod or the wire products made therefrom. The chief object of the present invention is to provide an improved method and process for accreting molten material on a moving rod to form a rod having greater thickness and being substantially uniform in character and free of detrimental inclusions, welded particles, tears, scrapes, gouges, and scratches experienced in the prior art process. Still another object of the invention is to provide an entrance bushing to the molten metal crucible having physical properties that will not result in mechanical removal of particles from the bushing due to spalling, galling, welding, and/or tearing.

DESCRIPTION OF THE INVENTION

The attached drawings illustrate a preferred embodiment of the invention.

FIG. 1 is a schematic flow diagram of the elements required to practice a method of accreting molten material on a moving member.

FIGS. 2A, 2B and 2C are sectional views of a portion of the crucible illustrating the area through which the core member is introduced into the crucible and illustrating three types of bushings or nozzles.

As shown in FIG. 1, which is a schematic representation of the overall dip-forming process, an elongated body 1 of a length of material in the solid state having a first cross sectional configuration and area is continuously withdrawn from a storage means 2 such as a reel or the like and is guided by an appropriate means such as a pulley 3 through

preliminary treatment apparatus which may consist of a conventional straightener **4**, a conventional surface cleaning apparatus **5**, for example an electrolytic bath, and a rinsing or washing bath **6**. The straightened, cleaned and wet body **1** is guided by means **7** into and through an elongated or tubular conduit **8** comprising a drying means **9** which may be supplied with a neutral atmosphere from a source **10**, conventional power driven feeder rolls **11** which frictionally engage and drive body **1** into a vacuum entrance chamber **12** provided with a vacuum source **13**, which permits the body to pass therethrough while subject to vacuum but which prevents the passage of atmosphere therewith, and an entrance port **14** provided in the bottom of a crucible **15**. The body **1** is then passed through a bath of molten material contained in crucible **15**, the bath suitably but not necessarily having the same chemical composition as body **1**.

Molten material in crucible **15** accretes or deposits and solidifies upon the outer surface of the body **1** increasing its cross-sectional area appreciably into a body **16** which may be of substantially homogeneous composition. After emerging from crucible **15**, the body **16** may be subjected to water sprays from jet nozzles **29** and thereby cooled and then passed between sizing apparatus, such as a pair of sizing rolls **17** which function to remove or correct minor surface irregularities. The body **16** is then guided by means of a cooling duct or conveyor **18** to any suitable receiving means such as a reel **19** where it may be allowed to accumulate. From the reel or receiving means **19** the body is passed through conventional reducing apparatus **20** such as wire drawing apparatus or rolling equipment where the body **16** is reduced to a body **1'** having any desired reduced cross-sectional area.

Body **1'** may be allowed to accumulate at a storage means **21** such as a reel or the like. When a sufficient length of body **1'** has accumulated in the storage means **21**, body **1'** may be cut and the remainder of the body diverted to storage means **22** as product **23**. Product **23**, as indicated by arrow **24**, may be substantially continuously fed to other fabricating apparatus or may be packaged at this point as a final product.

The portions of the body **1'** stored at **21** may be used to replenish body **1** in storage means **2** and permit continuous operation of the apparatus.

Since body **1** is continuously passed through the crucible **15** molten material is continuously removed from the crucible. The depth of the molten material in the crucible should be preferably maintained at a substantially constant depth and this may be continually accomplished by providing a melting apparatus such as furnace **25**. Material having the appropriate composition is melted in furnace **25** and permitted to flow into the crucible through a conduit **26**, a regulating valve **27** and a heating launder or conduit **28** into the bath contained in the crucible **15**.

Referring now to FIGS. 2A, 2B and 2C, there is shown various designs of the entrance bushing or nozzle through which the core or wire rod passes into the molten metal bath. In FIG. 2A there is shown a tube **30** defining an evacuated passage through which the core rod **1** passes into the crucible **31**. Between the crucible **31** and the crucible liner **32** there is a nozzle **33** through which the core rod **1** passes into the molten bath **34**. The nozzle **33** is a cylindrical member to be constructed from the materials as herein described.

In FIG. 2B there is shown another nozzle and entrance port design. The entrance port comprises a centrally apertured cylindrical bushing element **50** of a thermally conductive material such as copper having a flange **51** at one end and a reduced cylindrical extension **52** at its other end. The centrally disposed aperture at the outer end of extension **52** is enlarged and internally threaded as shown at **53**. A thin wall tubular element or bushing **54** constructed of the materials as described in this application is provided with a threaded collar **55** at about its midpoint and is threadedly secured to extension **52** with a portion of its length, forming a liner for extension **52** as shown. A substantially cylindrical bushing **56** of a ceramic material such as fired alumina or the like, is provided with a central aperture which receives extension **52** and that portion of tubular element **54** which extends beyond the terminal portion of extension **52**. A bottom wall of crucible **60** is provided with an aperture **57** within which is secured a substantially cylindrical centrally apertured bushing **58** of a refractory material such as graphite which retains within its aperture ceramic bushing **56** as shown. Cooling means such as coil **59** through which coolant may be circulated is in heat exchange relationship with element **50** as shown and serves to extract heat from element **50** and tubular element **54**.

In operation, body **1** passes through the central aperture of element **50** and through the tubular member or element **54** and emerges in the bath of molten material contained in crucible **60**. The internal dimensions and configurations of tubular member **54** is such that body **1** may freely pass therethrough but molten material may not leak downwardly along body **1**.

FIG. 2C illustrates yet another design for the entrance port to the molten metal crucible. Crucible liner **62** containing molten metal **68** is enclosed in a crucible **61**. Tube **65**, adapted to be evacuated, is connected to a vacuum source through tube **67**. As rod **1** passes through the opening of tube **65** and is introduced into nozzle **69** suitable clearance space **66** is provided between rod **1** and the nozzle surface. At the discharge end **63** of nozzle **69** hydraulic pressure of the molten metal in the crucible liner **62** combined with the vacuum in the opening brings the solidified material into the clearance **66**. Continuous solidification of molten material at discharge end **63** of the nozzle substantially prevents molten material flowing into nozzle to impede the successful operation of this continuous accretion.

Having discovered the major cause for the wire breakage in copper wire made from the dip formed rod, the applicants devised an accelerated test to determine the characteristics of materials that would meet the requirements of not spalling, galling, welding or tearing when a rod or core member was passed through a member made from the test materials at a speed equal to or greater than that used in the copper dip forming process. A series of simulated tests were carried out by rotating a copper surface in contact with the surface of a test material, at such a speed that the outer portion of the copper surface traveled at least about 200 feet per minute which is the approximate velocity at which the core or wire rod travels during a typical dip forming operation. The experiments were carried out using a $\frac{5}{16}$ diameter copper wire rod actually produced by the dip forming process. A cross section of this copper rod was polished and the rod was inserted in a drill press. The candidate test materials were mounted in plastic and polished. A 200 gram force was applied between the copper wire rod and the candidate material surfaces. A drill press was rotated at about 3600 r.p.m. for 10 minutes. After the test the two meeting surfaces, that is the surface of the copper rod and the candidate test materials, were observed with a microscope. The copper rod surfaces were also analyzed by the electron microprobe for the major elements contained in the test material.

The first test was carried out using molybdenum as test material. After the test, the molybdenum surface was severely scored, and these grooves were partially filled with copper mixed with molybdenum particles. The copper surface was severely roughened and several molybdenum inclusions were clearly visible. These inclusions were positively identified by the electron microprobe as pure molybdenum. This test confirmed the earlier findings of molybdenum inclusion in the broken wire.

Other tests were carried out using tantalum, tungsten, tungsten-25% rhenium, molybdenum-50% rhenium, soft

rhenium, hard rhenium, alumina, and sintered tungsten carbide as candidate materials with the following results:

TABLE I

Test material	Condition of— Copper surface	Test material surface
Molybdenum, 50% rhenium.	A few scratches, dark material deposited on surface (not embedded). This material contains molybdenum and rhenium.	A few scratches and a small amount of dark material deposited on surface.
Soft rhenium	A few scratches, no embedded rhenium, some tarnishing.	Surface scratched and deformed. No foreign material on surface.
Hard rhenium	Some tarnishing, no embedded rhenium.	Excellent surface.
Tungsten	Several scratches, severe deformation, some tearing but no embedded tungsten.	Very few scratches, light stain, otherwise excellent surface.
Tungsten, 25% rhenium.	Some tarnishing, no embedded rhenium nor tungsten.	Excellent surface.
Tantalum	Severely eroded, but no tantalum particles present.	Copper welded to surface, but tantalum maintained integrity.
Sintered tungsten carbide.	Some tarnishing, no embedded tungsten nor cobalt.	Excellent surface integrity.
Alumina	Very little tarnishing, otherwise excellent surface.	Excellent surface.

relatively expensive. Alloying rhenium with molybdenum indicated that a suitable rhenium-molybdenum alloy for nozzle material contains at least 50% rhenium. Although tungsten alone is a reasonably satisfactory bushing material it may be advantageously alloyed with rhenium. Any tungsten-rhenium alloy may be used within the scope of this invention. For economic considerations tungsten-rhenium alloys containing about 25% or less rhenium are preferred. It appears that tungsten carbide and alumina may be acceptable construction materials except that their well known low impact resistance and thermal shock sensitivity may cause these materials to shatter in service.

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

1. In a method for accreting molten copper on a continuously moving core rod, the steps which consist in passing the core rod from the atmosphere into an evacuated passage, introducing the moving rod from the passage into a nozzle located in the lower portion of a crucible containing molten copper, passing the moving core rod through the molten copper causing accretion of molten copper on the moving rod and passing the rod from the crucible; the improvement wherein the moving rod is introduced into a nozzle constructed from a hard non-

TABLE II

	Test materials							
	Molybdenum	Tantalum	Tungsten	Rhenium	Molybdenum, 50% rhenium alloy	Tungsten, 25% rhenium alloy	Tungsten carbide	Alumina
Relative hardness	Soft	Soft	Hard	Hard	Somewhere between hard and soft.	Hard	Very hard	Very hard.
Solubility of test material in liquid copper.	1,400 p.p.m.[1]	250 p.p.m.	<1 p.p.m.	<1 p.p.m.	Unknown	Unknown	Unknown	Unknown.
Observed "cold" welding [2]	Yes	Yes	No	No	No	No	No	No.
Test material known to be prone to spalling.	Yes	No	Yes	No	No	No	Yes	Yes.
Test rod surfaces [2]	Very poor	Very poor	Good	Excellent	Excellent	Excellent	Excellent	Excellent.
Test rod surfaces [2] contains test material particles.	Yes	No	No	No	No	No	No	No.
Test material useful as bushing material.	No	No	Yes	Yes [3]	Yes	Yes	Probably no.[4]	Probably no.[4]

[1] Wlodek, S. T., and Wulff, J., Trans. AIME 218 (1960) 716.
[2] Visual and microscopic observation of surfaces of test materials and copper rod.
[3] Best material but very expensive.
[4] Material very hard and brittle, probably would shatter in service.

Table II lists some known physical properties and observed characteristics of the test materials.

As can be observed from a study of Table II the refractory metals, molybdenum and tantalum, would not be satisfactory materials for construction of the nozzle or bushing.

Several observations can be made from Table II with regard to the physical characteristics of materials from which entrance bushings or nozzles may be made. Relatively hard materials, i.e., tungsten, rhenium, and rhenium based alloys should be used to make the nozzles rather than the relatively soft refractory metals—molybdenum and tantalum. Solubility of the nozzle construction material in molten copper should be less than approximately 250 parts per million. Cold welding should not occur between the core rod and the bushing or nozzle construction material. The core rod surface should be relatively unaffected by its unavoidable contact with the interior walls of the bushing while moving at speeds of about 200 or more feet per minute.

From our tests and observations rhenium would be the most ideal material for the bushing. However it is cold welding metal selected from rhenium, rhenium based alloys, tungsten and tungsten-rhenium alloys.

2. The method of claim 1 wherein the nozzle is constructed from a metal selected from a rhenium-molybdenum alloy containing at least 50% rhenium, and a tungsten-rhenium alloy containing at least 75% tungsten.

References Cited

UNITED STATES PATENTS

3,008,201	11/1961	Carreker, Jr.	164—254
3,160,517	12/1964	Jenkin	118—49.5 UX
3,227,577	1/1966	Baessler et al.	117—102 M
3,235,960	2/1966	Carreker, Jr.	117—61
3,424,130	1/1969	Byrnes et al.	118—405
3,466,186	9/1969	Carreker, Jr.	117—114 R

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U.S. Cl. X.R.

117—119, 128, 131; 164—138