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PROCESS FOR HOT WORKING OF COPPER

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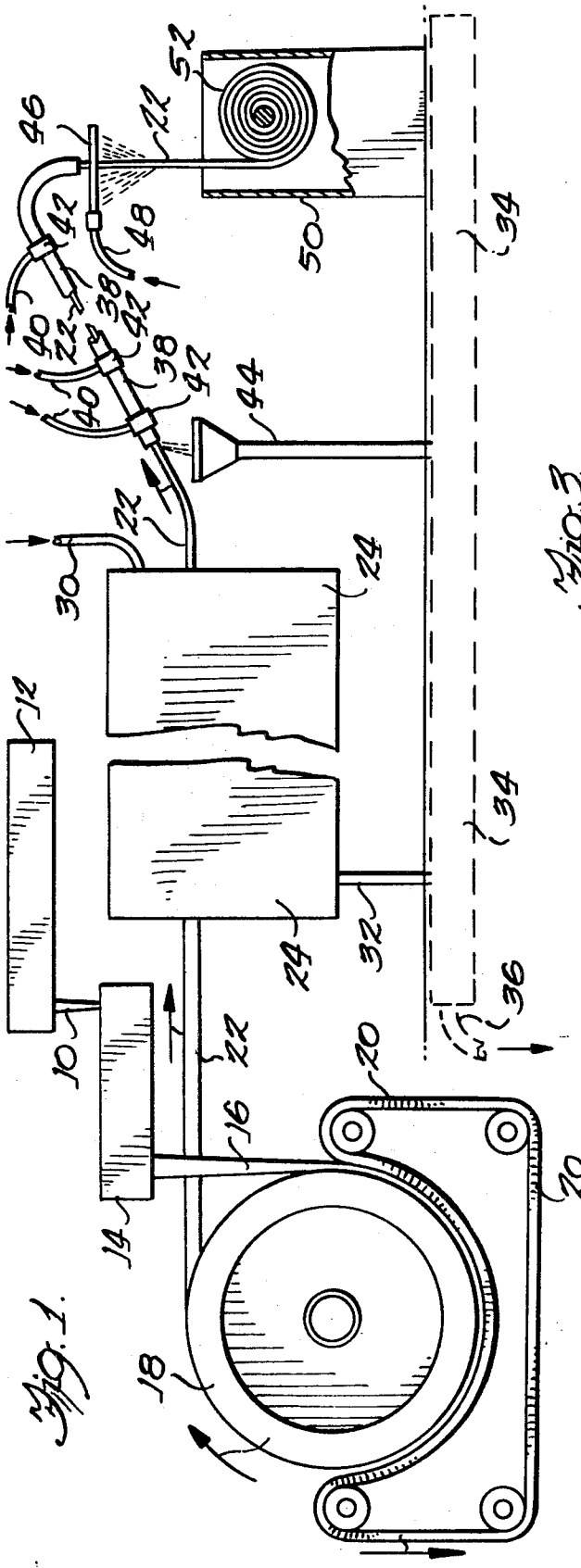


Fig. 1.

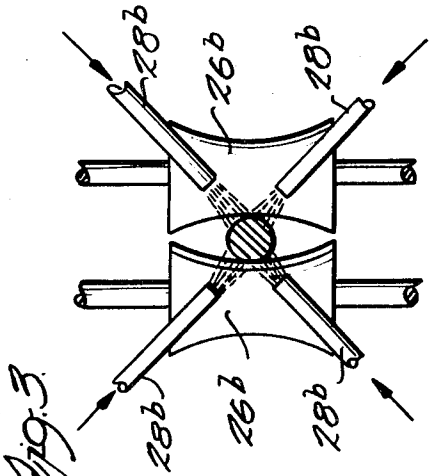


Fig. 3.

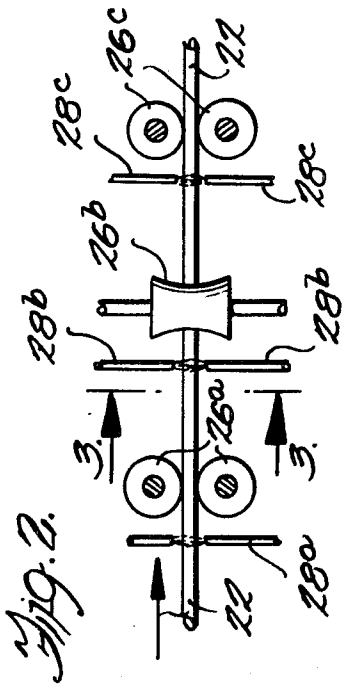


Fig. 2.

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PROCESS FOR HOT WORKING OF COPPER

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ABSTRACT OF THE DISCLOSURE

This improvement in the art of hot working copper and copper alloys in the presence of an oxygen-containing environment to minimize or eliminate the problems associated with oxide formation on the surface thereof at elevated temperatures comprises contacting the stock substantially continuously during the hot working thereof with an aqueous solution containing ammonium chloride.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a method of coping with the problem of undesired oxide formation on the surface of copper during the hot working thereof. More specifically, it relates to an improved and less costly process for hot working copper and copper alloys which results in a product having bright surfaces and eliminates or minimizes production and related problems associated with prior art techniques.

While the invention is described and claimed herein with particular reference to copper, it should be understood that this term encompasses alloys containing about 50% or more of copper and which are subject to the formation of copper oxides when exposed to an oxygen-containing environment at elevated temperatures. Such term would thus include the various brasses and bronzes and other copper alloys subject to oxide formation, as set forth in, for example, the "Metals Handbook," eighth edition vol. 1, pages 959–1052 (Copyright 1961 by the American Society for Metals).

While a specific embodiment is described herein in connection with the production of copper rod or wire from molten copper, it should be understood that the invention is not limited thereto. It has general application in the hot working of copper wherein the copper is mechanically worked at temperatures above about 400° F. in an oxygen-containing environment, as more fully set forth hereinafter.

In the various processes by which copper and copper-base alloys are shaped, it is sometimes advantageous to work the metal at temperatures in the range from about 400° F. to about 1800° F. Such processes are termed hot working processes and are to be distinguished from cold working processes in which the metal being shaped is at or near the ambient temperature. In general, hot working processes are employed to reduce the force required to achieve the desired dimensional changes, to eliminate the need for annealing between the various stages of the forming process, to increase the rate at which the process can be operated, to reduce the size, strength or complexity of the machinery used for forming, and to achieve more control of metallurgical transforations.

Any process for hot working copper or copper-base alloys must take congnizance of the ability of oxygen to readily react with copper in the aforementioned hot working temperature range. This reaction results in the development of either a red (Cu_2O) or black (CuO) coating on all surfaces exposed to oxygen. Above a temperature of about 1100° F., the black cupric oxide will predominate. From about 400° F. to about 1100° F., the red cuprous form is most apparent. Below about 400° F. to

500° F., oxide formation is not sufficient to constitute a problem.

The presence of these oxides is detrimental for several reasons. They increase the rate of abrasive wear of tooling surfaces, they can lead to undesired oxide buildup on tooling and forming surfaces, and they interfere with the production of smooth surfaces and close tolerance dimensions. They also constitute an undesired impurity which can detract from the physical and chemical properties of the metal, particularly if imbedded below the surface by the mechanical working, and they detract from the electrical and decorative utility of the finished shape.

DESCRIPTION OF THE PRIOR ART

Attempts have been made to eliminate the problems related to copper oxide formation in hot working processes by operating the processes in an oxygen-free atmosphere or by making the time of exposure to elevated temperatures extremely short. These methods of operation have not been generally adapted because of the increased complexity of the required equipment, the lack of operational flexibility and excessive cost.

Instead, the oxide layer is conventionally removed from copper subsequent to the hot working operation by either acid pickling or a mechanical process such as shaving or grinding. These measures are not completely satisfactory. They do not inhibit oxide formation in the first instance. They do not remove oxides which are "buried" within the copper as the result of mechanical working of the copper after initial oxide formation. They introduce additional handling and processing steps into the manufacturing scheme. They are non-selective and result in an appreciable loss of sound non-oxidized metal.

It is therefore an object of the present invention to advance the art of hot working copper by economically and effectively coping with the problems associated with oxide formation on the surface of the workpiece. It is a specific object of the present invention to cope with the problem of oxide formation without being forced to use oxygen-free environments and extremely short exposure times with attendant complexity and loss of operational flexibility. It is an other object to cope with the problem of oxide formation without resorting to subsequent acid pickling or mechanical processes such as shaving or grinding.

It is another object to inhibit oxide formation in the first instance and/or to remove what oxides are formed without appreciable loss of non-oxidized copper and without additional handling and processing steps. It is further object of the present invention to provide a method for coping with oxide formation without "burying" the oxides within the copper and without oxide buildup on the hot working tools, e.g., forming rolls and the like. These and other objects of the present invention will become apparent as the description of the invention proceeds.

SUMMARY OF INVENTION

The improvement consists of the application of an aqueous solution containing about 0.1% to about 20% by weight of ammonium chloride (NH_4Cl) to the exposed surfaces of the workpiece while it is being worked, said application being essentially continuous both in time and in coverage at least during the actual working of the metal. Thereafter, further application of the solution is desirable until the temperature of the workpiece has dropped to about 400° F. or lower. The aqueous solution is then removed by, for example, an air wipe, leaving substantially no residue.

The concentration of ammonium chloride to be used is not critical within the ranges indicated and is dependent on the amount of oxidation which has occurred before application of the solution, the temperature levels

at various points in the metalworking process, the configuration and composition of the workpiece and the relation between the surface being treated and the volume of solution being applied. The volume of solution must, of course, be sufficient to maintain itself substantially in liquid condition when in "contact" with the workpiece. Actually a vaporous film or interface may exist immediately adjacent the workpiece surface.

Other considerations involve the permissible flow velocity over the workpiece, the movement, if any, of the workpiece during the hot working thereof, and permissible or desired concentration levels as dictated by corrosion considerations. Concentration and flow rates also depend in part upon pumping, cooling, reservoir facilities and the like. Because of the many variables, concentration and flow rates are best and most readily selected for a given situation empirically in the light of the specific examples hereinafter set forth. For such purposes, initial concentrations in the range of about 0.25% to 10% by weight, preferably about 0.5% to 5% by weight, are suggested.

The treating solution may, and usually will, contain other ingredients than ammonium chloride, although they are not required in order to practice the present invention. For example, a typical aqueous treating medium may contain, in addition to ammonium chloride, surface active agents, corrosion and bacterial inhibitors, friction-reducing agents, defoamers, emulsifiers, coupling agents and the like. These and other ingredients and desirable proportions thereof are known to those skilled in the art of hot working of metals. An advantage of the ammonium chloride system is that it doesn't burn or otherwise leave any substantial residue.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be more clearly understood from the following detailed description of a specific embodiment, read in conjunction with the accompanying drawings, wherein:

FIG. 1 is a schematic plan view of the process of the present invention as applied to the production of copper wire from molten copper;

FIG. 2 is a schematic view of a portion of the form rolling mill employed in the process of FIG. 1 to progressively achieve the desired cross-sectional configuration for the wire; and

FIG. 3 is a section view taken along the line 3—3 of FIG. 2.

DESCRIPTION OF A PREFERRED EMBODIMENT

Referring to FIG. 1, substantially pure molten copper **10** passes from copper melting furnace **12** to holding ladle **14**, where it is held at about 2000° F. A continuous and rapidly solidifying stream of copper **16** is charged to a peripheral channel (not shown) in the rim of casting wheel **18** where it is held in place on the down side for about 150–180° of rotation by overlying moving steel strap **20**. The peripheral channel in the rim of casting wheel **18** may have any desired cross section, e.g., semicircular, curvilinear or rectilinear, so long as it permits the ready release of the resulting solidified copper rod **22**.

Rod **22** leaves the periphery of casting wheel **18** tangentially in a slightly offset direction to clear stream **16** and at about 1600°–1700° F. It enters the enclosed chamber of form rolling mill **24**, which contains a series of rolling stands or form rolls **26**, as illustrated in FIGS. 2 and 3.

Each of the form roll sets **26***a*, **26***b*, **26***c*, etc., which may be spaced about one to four feet apart, is configured to progressively reshape and reduce the cross-sectional area of the copper rod as it proceeds from roll stand to roll stand. For example, area reduction may approximate 25% at each stand. As shown in FIG. 2, the axes of the rolls are alternated between horizontal and vertical, although they may be otherwise disposed. In the illustrated embodiment, the final product is intended to have a circular cross section. Each roll is configured to progressively achieve the same, a total of six to twelve roll stands being typically employed.

Before entering the first set of rolls, rod **22** is effectively immersed in an aqueous solution containing about 0.1% to 20%, e.g., about 0.25% to 10%, preferably about 0.5% to 5%, by weight of ammonium chloride, specific examples of preferred solutions being set forth hereinafter in the examples. The solution is applied to the rod before entering each of the roll stands by means of a series of spray pipes **28** which in the present embodiment are radially disposed at about 90° intervals around rod **22**.

Spray pipes **28** receive the treating solution from a manifold which, in turn, is connected to a treating solution supply reservoir by means of inlet pipe **30**. The treating solution leaves mill **24** via drain pipe **32**, whence it is returned to the supply reservoir via collector **34** and return pipe **36**.

As previously indicated, the concentration of ammonium chloride and flow rate of the solution is sufficient to maintain bar **22** substantially free of copper oxides which may be formed thereon by exposure to oxygen-containing ambient conditions. Not only are the copper oxides removed by the solution but the envelopment of the rod substantially continuously with the solution during the hot working and cooling thereof tends to decrease the exposure of the rod to oxygen and thus reduces the amount of oxide formation.

The effective immersion of the rod in treating solution prior to each roll stand eliminates any copper oxide before it can be mechanically worked into the rod subsurface. The flow rates are, of course, sufficient to maintain the treating solution in liquid state, except possibly for a transient gaseous interface at the surface of the copper. As a practical effect, the retention of a portion of the treating solution on much of the surface of the rod between sprays results in almost substantially continuous contact.

After leaving the last rolling stand in mill **24**, rod **22**, which might more aptly now be described as a wire, leaves the mill at about 700°–800° F. and enters tubular cooling chamber **38**.

In a typical installation, cooling chamber **38** may be anywhere from ten to eighty feet in length and is supplied with treating solution from the reservoir by inlet pipes **40** which feed annular distributors **42**. The treating solution is drained gravitationally from chamber **38** into funnel-mouth collector pipe **44** and is returned to the reservoir via collector **34** and return pipe **36**.

Wire **22** leaves chamber **38** at substantially less than 400° F., e.g., about 150°–350° F. Residual treating solution is removed therefrom by means of an air blast introduced via annular air wipe distributor **46** which receives compressed air via inlet line **48**. Wire **22** then enters coiling apparatus **50** and is collected in the form of a coil **52**.

In a specific embodiment, rod **22** has a cross section of approximately two to three square inches when it leaves casting wheel **18** and is reduced to a wire having a cross-sectional area of approximately 0.1 to 0.3 square inch by the time it leaves mill **24**. In the practice of a specific embodiment, a reservoir having a capacity of 15,000 to 20,000 gallons is used to charge a treating solution having about 1.5% by weight of ammonium chloride to both mill **24** and chamber **38** in sufficient volume to keep the rod covered with fluid at least during contact with the rolls and during at least a substantial portion of the travel in cooling chamber **38**. The capacity of the reservoir is sufficient that substantial temperature rises of the treating solution are avoided and frequent makeup additions of ammonium chloride are unnecessary.

Several suitable treating solutions are typified by the specific compositions set forth in the following examples.

EXAMPLE I

To demonstrate the effectiveness of the present process, duplicate runs are made. In the first run, a prior-art treat-

ing solution is employed. In the second run, the process of the present invention is practiced as now further detailed.

A bar of copper having essentially a square cross section two inches on a side and a temperature of 1600° F. is shaped into a rod having a circular cross section one-half inch in diameter by passing the bar through an eight stand form rolling mill with appropriately shaped rolls, as already described. Throughout this process, a fluid is sprayed on the surface of the bar for cooling and lubrication and to prevent welding to the rolls. The fluid normally used for such an operation is an emulsion of petroleum oil in water which contains about 2% by volume of mineral oil and emulsifiers.

The rod leaves the eighth stand of rolls at a temperature of 900° F. and is cooled to 120° F. by continued application of the same fluid. The rod which is produced by using such a fluid has its surface covered with an oxide film which varies in color from reddish-brown to black.

A comparison run was made wherein 2% by weight of ammonium chloride was added to the previously described emulsion. The resulting rod had the characteristic salmon-pink color of a fresh clean copper surface.

EXAMPLE II

In the metalworking process described above, a fluid having the following composition was sprayed on the rod during the forming process and subsequent cooling step.

Ingredients:	Parts by wt.
Water	1000
Ammonium chloride	20
100 SUS mineral oil	15.8
Petroleum sulfonate (av. MW=455)	1.3
Sulfonated sperm oil	1.2
Ethylene glycol mono butyl ether	0.3
Hexadecyl alcohol	0.3
2,3,4,6-tetrachlorophenol	0.2
Ethoxylated fatty alcohol	0.9

The finished rod was clean and bright and was essentially free of surface oxidation.

EXAMPLE III

In the metalworking process described above, a fluid having the following composition was sprayed on the rod during the forming process and subsequent cooling step.

Ingredients:	Parts by wt.
Water	1000
Ammonium chloride	6.7
Sodium acid pyrophosphate	4.7
Oleyl imidazoline	1.3
Octylphenol polyethoxy ethanol (30 mol ETO)	1.2
Dehydroabietylamine	0.2
Dehydroabietylamine ethoxylate (5 mol ETO)	0.8
Propylene glycol	1.1

The resulting rod was clean and bright and was essentially free of surface oxidation.

From the above description it is apparent that the objects of the present invention have been achieved. While only certain embodiments have been illustrated, many alternative modifications will be apparent from the above description to those skilled in the art. These and other alternatives are considered within the spirit and scope of the present invention, and coverage thereof is intended by this application.

Having described the invention, what is claimed is:

1. In the process of mechanically working copper at elevated temperatures above about 400° F. in the presence of oxygen-containing gases, the improvement which comprises contacting exposed surfaces of the copper substantially continuously while being mechanically worked in the oxygen-containing environment at such elevated temperatures and while being cooled in said environment to a temperature below such elevated temperatures with an aqueous solution containing about 0.1% to 20% by weight of ammonium chloride, whereby the exposed surfaces of the copper are maintained substantially free of copper oxides.

2. The process of claim 1 including the further step of purging residual aqueous solution from the exposed surfaces after cooling the copper below such elevated temperatures by subjecting the surfaces to high velocity air.

3. The process of claim 1 wherein the concentration of ammonium chloride in the solution is in the range of 0.5% to 5% by weight.

4. The process of claim 1 wherein said solution is brought in contact with said copper by a plurality of sprays.

5. The process of claim 4 wherein the copper is mechanically worked in a plurality of progressive steps and said solution is sprayed on the copper prior to each step by said plurality of sprays.

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U.S. Cl. X.R.

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