The present invention relates to a new and improved process for degassing copper base alloys. It is highly desirable to develop effective means for degassing copper base alloys since this is a serious problem which has long confronted the industry. For example, a number of the major difficulties encountered in the fabrication of copper base alloy strip can be directly traced to defects in the starting process ingot produced by evolution of gases from the melt during solidification. Gas filled voids create in this manner prevail through the rolling and thermal treatment operation and eventually produce such gross defects as center plane separation or blistering in the finished copper or brass strip.

In this area two types of gases are significant in copper base alloys. These are as follows:

1. Gases that dissolve atomically in the molten metal and precipitate as discrete bubbles during solidification because of reduced solubility. Hydrogen is the only gas of importance in this category and is known to produce unsoundness in the form of porosity.

2. Gases formed by reaction of compounds or elements in liquid solution in the melt during the latter stages of solidification when equilibrium conditions are upset. Gases of this category include water vapor, carbon monoxide, carbon dioxide and sulfur dioxide. Typical reactions that occur in the melt during solidification which result in the formation of these gases are:

\[
\begin{align*}
2H_2 + Cu_2O &= H_2O + 2Cu \\
C_2H_2 + Cu_2O &= CO_2 + 2Cu \\
CO &= Cu_2O + CO_2 \\
Cu_2S &= 2CuO + SO_2 + \text{Cu}
\end{align*}
\]

Of the gases mentioned above, hydrogen, water vapor, carbon monoxide and carbon dioxide are considered to be most responsible for producing unsoundness in the bulk of copper base alloys.

In order to minimize gaseous unsoundness in copper base alloys, it is necessary to reduce the hydrogen content of the melt close to or below the equilibrium solid solubility level at the melting point or solidus temperature and either substantially eliminate oxygen or the gas formers such as carbon and cuprous sulfide from the melt. Unfortunately, presently used degassing practices cannot accomplish this effectively. These practices generally involve an oxidation reduction type treatment of the melt. The melt is first oxidized by either percolating dry air through it or by the addition of a glassy flux containing an oxidizing agent, such as manganese dioxide or cuprous oxide. This serves to reduce the hydrogen content of the melt to the desired level, by the reaction

\[
\begin{align*}
2H_2 + Cu_2O &= H_2O + 2Cu
\end{align*}
\]

Subsequently, the melt is deoxidized using materials such as metallic phosphorous and lithium or calcium boride to reduce the oxygen content to a satisfactory level. The oxidation-reduction degassing method is very time consuming and can only be used with reasonable success on virgin metal charges. In scrap charges, oxidation must be carried out until all residual reducing elements, e.g., tin and phosphorous are burned out before the melt can be effectively oxidized. This results in the loss of expensive alloying additions such as tin, from the melt. Also, this method is not always effective as evidenced by fairly frequent epidemics of blistering and center plane separation in finished strip. A further problem is that the procedure cannot be used in the production of low oxygen copper of high electrical conductivity since the addition of either oxidizing (e.g., cuprous oxide) or reducing agents (e.g., phosphorous) will substantially reduce the electrical conductivity of this alloy. Further, the presence of cuprous oxide renders the alloy susceptible to hydrogen embrittlement.

Accordingly, it is the principal object of the present invention to provide an improved process for degassing copper base alloys.

It is a further object of the present invention to provide a simple, convenient and effective method for degassing copper base alloys.

It is a still further object of the present invention to provide a method as above which overcomes the difficulties heretofore encountered, which does not result in the loss of expensive alloying additions from the melt, which is effective as evidenced by the lack of blistering in the finished strip and which is otherwise convenient and effective.

Further objects and advantages of the present invention will appear hereinafter.

In accordance with the process of the present invention it has now been found that the foregoing objects and advantages may be readily accomplished and an improved process for degassing copper base alloys may be provided by adding a halide selected from the group consisting of a metal, a metalloid and carbon to the molten copper base alloy, said halide being such that it will react with cuprous oxide in liquid solution in the alloy to form insoluble reaction products separable from the melt by gravity and recovering the resultant degassed alloy. Preferably the halide should also volatilize in the molten alloy.

In accordance with the process of the present invention as discussed above, a halide is added to a molten copper base alloy, at a temperature above the solidus or melting point. Naturally, this temperature will vary depending on the particular alloy. The halide which is added is characterized by reacting with the available cuprous oxide in liquid solution in the alloy to form insoluble reaction products separable from the melt. The insoluble compounds may be either solid, liquid or gas and they separate from the melt by gravity.

The amount of halide which is employed is dependent upon the amount of cuprous oxide and hydrogen in solution in the melt. It is preferred to use an excess of the halide in order to assure maximum effectiveness. Naturally, any lesser amount may be employed with the effectiveness of the degassing varying accordingly. As a general rule, the amount of halide used is at least sufficient to theoretically remove all oxygen in solid solution in the melt, preferably in excess, and optimally from 50 to 150 percent in excess.

The particular halide which is employed is not critical with the exception that the halide must satisfy the aforementioned requirements and preferably will volatilize in the melt. It is preferred to use anhydrous chlorides in view of their particular effectiveness. Representative compounds which may be conveniently employed include, but are not limited to, the following: aluminum bromide, aluminum chloride, aluminum fluoride, carbon tetrabromide, carbon tetrachloride, hexachloroethane, dichlorodifluoromethane, dichlorotetrafluoroethane, silicon tetrachloride, titanium tetrachloride, silicon tetrabromide, silicon tetrachloride, disilicon hexafluoride, titanium tetrafluoride, boron trifluoride, boron trifluoride, boron trifluoride, beryllium dibromide, beryllium dichloride, beryllium fluoride, magnesium dibromide, zinc tetrachloride, and calcium iodide.

The particular copper base alloy which is employed is not especially critical. Any of the conventional copper...
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base alloys may be effectively degassed in accordance with the process of the present invention. By copper base alloys it is intended to signify any alloy containing at least 50 percent copper. Conventional alloying additions which may be included in varying quantities in the copper base alloy include, for example, zinc, tin, iron, zincium, titanium, silicon, aluminum, manganese, nickel, and beryllium.

By reducing the oxygen content of the melt to a sufficiently low level, the formation of reaction gases can be prevented even when substantial quantities of gas formers such as carbon, cuprous oxide and hydrogen are present. Degassing agents of this type will also minimize the occurrence of hydrogen porosity. By using an excess of the agent and allowing the vapors to percolate through the melt, hydrogen will diffuse to, and disport in the vapor bubbles, and be swept from the melt. In other words, for hydrogen removal it is essential that the reagent be in the gaseous state in the melt, and preferably also that one of the reaction products be in the gaseous state in the melt.

The process of the present invention attains numerous advantages over the art. Some of the more important of these include the fact that only one operation is required to remove both oxygen and hydrogen from the molten alloy, the reaction between the halide and cuprous oxide proceeds rapidly; therefore, the total time required to treat the melt is relatively short. Furthermore, melts prepared from both virgin metal and scrap metal charges can be effectively treated in accordance with the process of the present invention without fear of burning out costly alloying additions, such as tin. Also hydrogen can be effectively removed from the molten alloy prepared from the scrap charges without removing residual phosphorus present. Alloys used in applications where electrical conductivity properties of the alloy are important can be adequately and effectively degassed in the molten state in accordance with the process of the present invention without contamination of the melt. Heretofore, this has not been possible since degassing processes require the use of reducing agents, such as phosphorus and lithium, which remain as an alloying ingredient and thus adversely affect the electrical conductivity properties.

A further application of the present invention is the control of oxygen level in copper, high purity copper and dilute copper alloys. Present practices require the use of costly low oxygen, electrolytic, tough pitch copper as a starting material. In accordance with the present invention the oxygen content can be continuously to the desired level, thus allowing the use of high-grade copper scrap and other cheaper starting materials.

Several methods are available for treating copper base alloy melts with the degassing agents disclosed herein. In the case of reagents such as aluminum chloride which are solids at room temperature and sublime or volatilize at a temperature below melt temperature, the reagent may be added in either solid or gaseous form. Solid addition may be carried out by placing a charge of the reagent (for example anhydrous aluminum chloride) in a graphite phosphorizer and subsequently plunging the phosphorus to the bottom of the melt in the furnace. The reagent would then vaporize and allow a stream of bubbles to percolate through the melt. The rate of sublimation or evolution can be controlled by, for example, mixing inert materials with the degassing agent or feeding the degassing agent in an inert stream of gas and percolating said stream through the melt. Gaseous additions of reagents may be made at room temperature and which volatize or sublime below melt temperature, require the use of a still. Once in the vapor state, the reagent itself can be percolated through the melt in the furnace using a graphite fluxing wand or a carrier gas can be employed to sweep the volatilized reagent from the still through the melt in the above prescribed manner.

It should be also noted that melt treatment with the type of reagent described herein can be carried out during transfer of the melt from the furnace to the casting station in a special chamber.

A particularly effective reagent is anhydrous aluminum chloride. This material sublimes at about 330° F. It rapidly converts to a vapor when added to a melt and forms bubbles that would percolate through the molten metal. Hydrogen is removed by the diffusion desorption mechanism previously described. In addition, the AlCl₃ vapor would react with cuprous oxide in solution in the melt according to the following reaction, thus removing available oxygen:

$$\text{2AlCl}_3(\text{gas}) + 3\text{Cu}_2\text{O}(\text{liquid}) \rightarrow 2\text{Al}_2\text{O}_3(\text{solid}) + 6\text{CuCl}(\text{liquid})$$

The aluminum oxide formed is insoluble in copper base alloys and has a relatively low specific gravity, therefore, it would separate readily from the melt by gravity. The CuCl formed would be in the liquid state. Since it also has a specific gravity considerably lower than that of copper, it too should also separate readily from the melt by gravity.

The above reaction, which has a ΔF (free energy of reaction) of -70 kcal. per mole will go substantially to completion. Furthermore the reaction is self initiating at melt temperatures since the aluminum chloride is present as a gas and the cuprous oxide as a liquid.

Another particularly effective reagent is carbon tetrachloride which boils at 76° C. When this reagent is percolated through the melt in gaseous form, hydrogen is removed by aforementioned diffusion desorption mechanism. In addition, available oxygen is removed according to the following reaction:

$$\text{CCl}_4(\text{gas}) + 2\text{Cu}_2\text{O}(\text{liquid}) \rightarrow \text{Cu}_2\text{O}_2(\text{gas}) + 4\text{CuCl}(\text{liquid})$$

The gaseous carbon dioxide is insoluble in copper base alloys, readily separates from the melt and if present in excess removal of the melt removes dissolved hydrogen. The CuCl formed is in the liquid state and would separate as previously discussed. The above reaction has a ΔF of -170 kcal. per mole and will go substantially to completion.

Other preferred reagents which operate by similar mechanisms include: hexachloroethane and titanium tetrachloride.

The process of the present invention and the improvements resulting therefrom will be more readily apparent from a consideration of the following illustrative examples.

Example 1

Fifty pounds of electrolytic, tough pitch copper was melted down in a clay-graphite-mold and brought to a temperature of 2200° F. A charcoal cover was added to protect the melt. The starting oxygen content of the melt was 0.22 percent by weight and the starting density of a chill cast sample taken from the melt was 8.838 g./cc. The melt was then treated with 0.6105 pounds of anhydrous AlCl₃ by bubbling the gaseous AlCl₃ through the melt. Immediately after treatment the oxygen content was 0.07 percent and the density of a chill cast sample was 8.911 g./cc. Fifteen minutes after treatment the oxygen content of the melt was 0.03 percent and the density of a chill cast sample was 8.935 g./cc. No aluminum was detectable in the melt after treatment with the AlCl₃.

Example 2

In a manner after Example 1, molten copper was treated with carbon tetrachloride with the following results: the starting oxygen content of the melt was 0.20 percent by weight and the starting density was 8.849 g./cc. Immediately after treatment with 0.444 pound of carbon tetrachloride the oxygen content was 0.07 percent and the density was 8.888 g./cc. Fifteen minutes after treatment the oxygen content was 0.03 percent and the density was 8.902 g./cc. No change in carbon content of the melt could be detected immediately after treatment.
Example 3

In a manner after Example 1, molten copper was treated with AlBr₃ with the following results: The starting oxygen content of the melt was 0.11 percent by weight and the starting density was 8.875 g/cc. Immediately after treatment with 0.6248 pound of anhydrous AlBr₃, the oxygen content was 0.02 percent and the density was 8.901 g/cc. No aluminum was detectable in the melt after treatment with AlBr₃.

Example 4

In a manner after Example 1, molten copper was treated with TiCl₄ with the following results: the starting oxygen content of the melt was 0.13 percent by weight and the starting density was 8.855 g/cc. Immediately after treatment with 0.3561 pound of TiCl₄, the oxygen content was 0.07 percent and the density was 8.902 g/cc. Fifteen minutes after treatment the oxygen content was 0.04 percent and the density was 8.904 g/cc. No titanium was detachable in the melt after treatment with TiCl₄.

Example 5

In a manner after Example 1, molten copper was treated with CBr₃ with the following results: the starting oxygen content of the melt was 0.34 percent by weight and the starting density was 8.777 g/cc. Immediately after treatment with 1.76 pounds of CBr₃, the oxygen content was 0.07 percent and the density was 8.869 g/cc. Fifteen minutes after treatment the oxygen content was 0.07 percent and the density was 8.834 g/cc. No change in the carbon content of the melt could be detected immediately after treatment.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claim, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:
A process for degassing copper base alloys which comprises: providing molten copper base alloy and bubbling gaseous aluminum chloride through said molten alloy, said aluminum chloride being such that it will volatilize in the molten alloy and react with cuprous oxide in liquid solution in the alloy to form insoluble reaction products separable from the melt by gravity.

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