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METHOD OF MAKING COPPER-TITANIUM ALLOYS

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My invention relates to improved methods in the production of copper-titanium alloys in which copper is the predominant constituent, and more particularly to novel methods by which the molten copper may be alloyed with titanium or its compounds with the use of different flux materials that afford a coating for the metals in the molten state to protect same from oxidation which becomes excessive where the molten metals are exposed directly to the atmosphere.

Difficulties have long been experienced in casting copper, since perfectly pure copper when melted in contact with air absorbs oxygen which produces a somewhat porous condition in the ingot; in like manner titanium rapidly absorbs nitrogen and oxygen from the air, and alloys with higher amounts of titanium tend to form surface films that greatly increase casting difficulties.

The objects of my invention are, among other things, to provide new and simplified methods of producing these copper-titanium alloys economically, without loss of copper and titanium, particularly of titanium, so as to obtain pure alloys free from oxides, nitrides or carbides that readily form when the molten metals are in contact with the atmosphere or carbonaceous gases.

Titanium is useful for the production of age-hardening copper alloys of good electrical conductivity and strength, but when the addition of pure titanium in the metallic form to a bath of molten copper is attempted, it is very difficult to secure good recoveries of titanium in a clean alloy. Since titanium is of much lower specific gravity and higher melting point than copper, it floats on the latter, and a large portion of the titanium burns in the air forming a refractory dross before it dissolves in the copper. Such method may of course be carried out under vacuum, but this is impractical commercially since no foundries at present are equipped to melt the constituent metals in that way.

The amount of titanium used for age-hardening copper is usually less than 2%, and never more than 3 or 4%, so that the use of a master-alloy containing 25 to 30% titanium and the balance copper is practical for the production of the age-hardening alloys under normal foundry conditions.

For example, for making 100 pounds of a 2% titanium alloy, it would be necessary to add only about 10 pounds of a 25% master alloy to 92 pounds of molten copper including an allowance for oxidation losses, and this addition is not too large to be absorbed by the melt within a reasonable time before pouring. The master alloy containing 70 to 75% copper is much heavier than pure titanium, and its melting point is about 1200° C., as compared to 1800° C. for titanium, so that it is much more readily stirred into the copper than the pure metal and dissolves faster; hence the loss by oxidation and drossing is not particularly serious.

Copper-titanium master alloys have heretofore been made by reducing titanium from its oxide with aluminum either by a thermit reaction or in a bath of copper in an electric furnace. Alloys made by such methods always suffer from the objection of a residual aluminum content that is not desired in age-hardening copper alloys. An appreciable proportion of the titanium in copper-titanium alloys made by electric or alumino-thermic methods is nearly always in the form of nitride that is also objectionable, since titanium so combined is not effective for age-hardening, and the nitride is infusible thereby causing dirtiness and slow solubility of the master alloy in a copper melt. Hence titanium alloys of this nature have not been used successfully for the manufacture of age-hardening copper alloys.

Very good copper-titanium master alloys may be made by melting the two pure metals together under vacuum, but this process is expensive and difficult to carry out on a large or industrial scale. The process is much simplified if a controlled atmosphere is substituted for a vacuum, but atmospheres of carbonaceous gases or nitrogen are impractical on account of the affinity of titanium for nitrogen and carbon; hydrogen and helium both dissolve in the copper, thereby producing a master alloy from which sound copper alloy castings cannot be made; and the use of argon or other rare gases is too expensive.

I have discovered improved methods for the production of copper-titanium master alloys of high purity by mixing and melting the two pure metals that involves the use of a thick layer of a novel suitable slag or flux on top of the molten copper in order to protect the titanium metal floating on the copper from the action of the atmosphere, while it is dissolving in the copper bath below.

My methods are cheap and require no expensive equipment or materials, and may be easily carried out on any scale desired. If certain essential precautions hereinafter described are carefully observed, the production of a clean, high-grade copper-titanium master alloy containing no titanium-nitride, aluminum, hydrogen, or other objectionable impurities is attained and the recovery of the titanium metal used is excellent.

For the successful working of my improved methods the slag used must be very fluid at the fusion temperature of copper and the copper-titanium alloys to be made (about 2000 to 2200° F.), and yet it must not decompose or volatilize rapidly at those temperatures. Also it must of

course not react chemically with titanium or carry oxygen or nitrogen to the metal beneath.

Owing to the high reactivity of titanium with oxides such as silica at temperatures of 2000° F. or over, it is necessary that no silicates or other oxides should be present in this slag, and it is equally important that no easily reduced metals should be present, since such metals would be reduced by the titanium and contaminate the copper-titanium alloy. I have found that chlorides and fluorides of the alkali and alkaline-earth metals are most suitable, and I have tested a number of mixtures of these salts as to their fluidity and volatilization at 2000 to 2300° F. Calcium fluoride was found to have too high a melting point, and most of the inexpensive chlorides, such as calcium chloride, sodium chloride, potassium chloride, and strontium chloride, volatilized too rapidly above 2000° F. Sodium fluoride also volatilized like the chlorides.

Mixtures of some of the latter with 80% to 90% of calcium fluoride, however, I found to have satisfactory properties, the following being among the best (percentages being parts by weight):—

(1) 80% CaF_2+10% NaF+10% $CaCl_2$
(2) 90% CaF_2+10% $SrCl_2$
(3) 85% CaF_2+15% $BaCl_2$
(4) 90% CaF_2+10% NaCl

Mixture No. 1 I found to be somewhat preferable to the others in fluidity and stability, and was most used, but was generally modified to the extent of decreasing the proportion of calcium fluoride to equal four (4) parts to one part (1) of each of the other ingredients. As the sodium fluoride and calcium chloride tend to be lost from the slag during use, they should be replenished duration an operation if the slag seems to be losing fluidity.

Since these slags at 2000° F. and above were extremely corrosive on all kinds of refractories that include clay and magnesia, I found it quite necessary to practice my methods with a pure Acheson graphite crucible. With other kinds of crucibles, such as those known as "Plumbago" containing a clay bond, the slag absorbed oxides from the crucible and became viscous, so that the titanium metal was held in the slag. The titanium then oxidized and instead of dissolving cleanly in the alloy beneath, it formed an infusible crust under the slag thereby causing a very low recovery of titanium in the fluid alloy.

To prevent any such trouble from oxidation I found it advisable to keep the pure Acheson graphite crucible covered, preferably with a flat piece of graphite, although the cover might be removed temporarily in order to add the titanium and for stirring, etc. In this way a reducing atmosphere was maintained most of the time in the crucible. I also found it of advantage to use a narrow, deep, crucible rather than a shallow broad one so that there would be less surface of the melt exposed to the air.

During the operation the temperature of the furnace should be maintained sufficiently high to keep the slag and alloy beneath in a fluid condition, but not so high as to cause the slag to fume very strongly.

As illustrative examples of successful operations in making high-grade copper-titanium alloys according to my methods, the following descriptions are given:—

Example 1.—A piece of an Acheson graphite electrode about 4 in. in diameter was first hollowed out in the form of a crucible about 6 inches deep with walls about ⅜ inch thick, and placed inside a silicon-carbide tube, which in turn was set in a gas-fired furnace. About 400 grams of pure scrap copper were then placed in the bottom of this crucible and covered with about 7 ounces of a mixture of 80% calcium fluoride, 10% sodium fluoride, and 10% calcium chloride (Mixture No. 1).

The gas fire was lit, and in about 1½ hours the copper and slag were molten at a temperature of about 2200° F. More slag was then added, making a total quantity of 10 ounces used. When this slag became fluid, small solid lumps of metallic titanium, together with pieces of pure copper scrap were added gradually to the crucible. These additions were made every 10 to 15 minutes extending over a period of about 1½ hours, the total quantity of titanium added being 261 grams, and the total copper used being 870 grams. The final addition was of copper only.

The metals sank readily through the slag except in a few instances when a lump had to be poked in with a copper rod. The same rod was also used for stirring. The crucible was kept covered with a brick between additions, and the temperature was maintained between 2200 and 2360° F. After the last addition had been stirred in, the fire was shut off, and the alloy allowed to solidify in the crucible. When cold, a clean button was easily separated from the slag. It weighed 1081 grams, and I found it contained 24.54% titanium at the top, and 16.50% at the bottom.

Taking the average titanium content as 20.52%, this indicated a recovery of 85% of the titanium added; or assuming that the 50 gram loss of metal used was all titanium, the average analysis would be 19.5% titanium, and the recovery 81%.

Example 2.—A piece of an Acheson graphite electrode about 6 inches in diameter and 16 inches long was first machined into the form of a crucible 14 inches tall, 4 inches inside diameter at the bottom and 4½ inches at the top, and with walls about ½ inch thick. This crucible was thoroughly coated on the outside with a plastic refractory held in place with wire mesh, and after drying it was heated slowly in a gas-fired furnace.

Ten pounds of pure copper scrap were charged into the crucible, and before this was melted about ten ounces of a slag mixture, composed of 4 parts calcium fluoride, 1 part calcium chloride, and 1 part sodium fluoride were thrown in to cover the copper. About two hours after starting the furnace the copper and slag were melted at a temperature of about 2000° F., and another addition of 10 ounces of slag was made, and the crucible was covered with a flat piece of graphite. About half an hour later, when the slag was thoroughly fluid again, metallic titanium in solid rough lumps of about ¾ to 1½ inches size was added. Every ten minutes about ½ pound of titanium was dropped through the slag, and about every half hour the slag was replenished. On one occasion the slag addition consisted of ¼ pound NaF and ¼ pound $CaCl_2$, to increase the fluidity. Before adding a batch of titanium the bath was stirred with a pure graphite rod to make sure that the previous batch had dissolved.

When 3 pounds had been added, the subsequent additions were accompanied by copper, to the extent of about 11 ounces copper to 8 ounces titanium, and these additions were spaced 15 minutes apart. The total amount of copper used was 14 pounds, and the total of titanium was 6 pounds, with 3 pounds of slag. About 25 minutes after

the last addition, the contents of the crucible were poured out into iron ingot molds, the alloy and slag being all very fluid and separating cleanly from each other. The alloy recovered weighed 19 pounds, and the first ingot was found to contain 28.62% titanium while the last one contained 29.16%. The recovery of titanium therefore was 92%, indicating a reasonably low oxidation loss in the slag.

Example 3.—When the titanium available for use in making this alloy is too finely divided to sink rapidly through the slag used, it may be packed in sections of copper tubing of convenient size with both ends closed. These capsules may then be added through a deep bath of slag just as lumps of titanium were added in the previous examples. In one instance tubing of 1 inch outside diameter and 0.042 inch wall thickness was used, 22 capsules about 4½ inches long being prepared and filled with 1782 grams of fine metallic titanium globules. The copper charge consisted of 2486 grams of scrap, and 1672 grams in the form of tubing.

The same crucible and furnace were used as described in Example 2, and the same kind of slag, namely 4 parts calcium fluoride, 1 part sodium fluoride and 1 part calcium chloride. A little of the slag was placed in each capsule to displace some of the air within.

The operation of melting was carried out in the same way as has been heretofore described, two capsules being added about every five minutes with occasional slag additions. The total amount of slag used was four pounds. The alloy produced weight 5330 grams after cleaning and contained 26.5% titanium, which represents a recovery of about 79% of the titanium added.

The loss is naturally higher in this method than in Examples 1 and 2 because of oxidation of the fine titanium by the air unavoidably entrapped between the particles inside the capsules.

When fine titanium metal was added directly to the slag, without being packed in copper capsules, it failed to sink through the slag with sufficient rapidity and became oxidized thereby making the slag pasty and interfering with the proper alloying action. Likewise when a crucible containing a clay binder was used without being carefully covered, the same pastiness of the slag resulted so that titanium was held in it and oxidized before alloying. In both instances a large proportion of the titanium was lost in the form of a dirty infusible product, that gave recoveries of only 10 to 25% of the titanium in a form that could be used for treating copper.

Example 4.—Another method of utilizing finely-divided titanium metal for making high-grade copper-titanium is to place the titanium in a pure graphite crucible in layers alternating with layers of finely divided copper, such as shot or turnings, and then cover the charge with sufficient non-oxidizing slag so that on heating the interstices between the metal particles may be filled with slag replacing the air with still enough slag left to form an effective cover on top.

Following this method, 4585 grams of copper shot and 1965 grams of titanium globules were charged in alternate layers in the same kind of crucible described in Example 2, the top and bottom layers being copper. The slag used was 4 pounds of the same mixture of 4 parts calcium fluoride, 1 part sodium fluoride, and 1 part calcium chloride. The crucible was covered with a graphite block, and heated about 2½ hours. The charge was then found to be fluid and was then poured into molds.

The alloy product weighed 5439 grams and contained 26.74% titanium, indicating a recovery of 74% of the titanium added. On account of the cost of the finely divided copper, and the low yield due to oxidation by air unavoidably entrapped with the metal under the slag, this method is not considered to be as desirable as the method given in the description of Example 2.

As has been hereinbefore described, my invention is not to be confined to the particular slag formulae mentioned in the examples, nor to any definite composition of copper-titanium alloy. Any halogen salts of alkali or alkaline-earth metals free from oxygen may be employed in my methods, although I believe that a mixture composed of at least 50% calcium fluoride would be most convenient to use for reasons of economy and resistance to volatilization.

To obtain proper fluidity in the slag without using excessively high temperatures, there should be at least 10% of a lower-melting salt added to the calcium fluoride; and probably 20 to 35% of such a common and cheap salt, such as sodium chloride, or of a mixture of calcium chloride and sodium fluoride, added to 65 to 80% of calcium fluoride, would form the most appropriate mixture for protection of the titanium in making high-grade copper-titanium alloys.

Other modes of applying the principles of my invention may be used in place of these described, and various changes may be made in the ingredients of the slag formulae and the methods disclosed that maintain the protective non-oxidizing coating for the titanium in the production of copper alloys of high titanium content provided the ingredients or steps stated in the appended claims, or their equivalents be employed.

I claim as my invention:—

1. In a method of making copper-titanium alloys by melting together the pure metals, the step which consists in immersing the titanium in a flux comprising a fluid fused halogen salt of an alkaline-earth metal to prevent oxidation of the titanium.

2. In a method of making copper-titanium alloys by melting together the pure metals, the step which consists in immersing the titanium in a fluid fused mixture of halogen salts of alkali and alkaline-earth metals to prevent oxidation of the titanium.

3. In a method of making copper-titanium alloys by melting together the pure metals, the step which consists in immersing the titanium to prevent oxidation thereof in a fused mixture comprising calcium fluoride and a relatively smaller amount of an alkali-metal chloride.

4. In a method of making copper-titanium alloys by melting together the pure metals, the step which consists in immersing the titanium to prevent oxidation thereof in a fused mixture comprising calcium fluoride and relatively smaller amounts of an alkali-metal fluoride and an alkaline earth-metal chloride.

5. In a method of making copper-titanium alloys by melting together the pure metals, the step which consists in immersing the titanium to prevent oxidation thereof in a fused mixture comprising calcium fluoride not less than 50% and relatively smaller amounts of an alkali-metal fluoride and an alkaline-earth metal chloride.

6. In a method of making copper-titanium alloys by melting together the pure metals, the step which consists in immersing the titanium to

prevent oxidation thereof in a fused mixture comprising calcium fluoride from 65 to 80% and sodium chloride from 20 to 35%.

7. In a method of making copper-titanium alloys by melting together the pure metals, the step which consists in immersing the titanium to prevent oxidation thereof in a fused mixture comprising calcium fluoride from 65 to 80% and a mixture of calcium chloride and sodium fluoride from 20 to 35%.

8. A method of making alloys containing from 10 to 40% titanium with the balance substantially copper, which comprises immersing the metallic titanium with the copper in a non-oxidizing flux consisting of a mixture of halogen salts of alkali and alkaline-earth metals, and then heating the metallic charge out of contact with the atmosphere to a temperature sufficiently high to effect the solution of the titanium in the copper.

9. A method of making alloys containing from 10 to 40% titanium with the balance substantially copper, which comprises superimposing a non-oxidizing flux composed of halogen salts of alkaline-earth metals above the copper and melting same, then immersing metallic titanium in the molten slag formed, and then heating the charge sufficiently high to dissolve the titanium below the molten slag to alloy with the subjacent molten copper.

10. A method of making alloys containing from 10 to 40% titanium with the balance substantially copper, which comprises superimposing a non-oxidizing flux composed of a mixture of calcium fluoride not less than 50% and relatively smaller amounts of an alkali-metal fluoride and an alkaline earth-metal chloride above the copper and melting same, then immersing metallic titanium in the molten slag formed, and then heating the charge sufficiently high to dissolve the titanium below the molten slag to alloy with the subjacent molten copper.

11. A method of making alloys containing from 10 to 40% titanium with the balance substantially copper, which comprises superimposing a non-oxidizing flux composed of a mixture of calcium fluoride from 65 to 80% and sodium chloride from 20 to 35% above the copper and melting same, then immersing metallic titanium in the molten slag formed, and then heating the charge sufficiently high to dissolve the titanium below the molten slag to alloy with the subjacent molten copper.

12. A method of making copper-titanium alloys which comprises melting a quantity of copper in a crucible of pure graphite, maintaining a superimposed fluid non-oxidizing slag composed of fused halogen salts of alkali and alkaline-earth metals on the molten copper, and then immersing metallic titanium in the slag to dissolve in the molten copper through said fluid slag.

13. A method of making copper-titanium alloys which comprises melting a quantity of copper in a covered crucible of pure graphite, maintaining a superimposed fluid non-oxidizing slag composed of fused halogen salts of alkali and alkaline-earth metals in a reducing atmosphere on the molten copper, and then immersing metallic titanium in the slag to dissolve in the molten copper through said fluid slag.

14. A method of making high-grade copper-titanium alloys which comprises maintaining a fluid non-oxidizing slag composed of fused halogen salts of alkali and alkaline-earth metals in a covered crucible of pure graphite at a temperature above the melting point of copper, adding thereto solid pieces of the metals copper and titanium, and then melting said metals together below the slag.

15. A flux for use in making copper-titanium alloys in which copper is the major constituent, which consists in a fluid fused mixture of calcium fluoride as the major ingredient and a smaller amount of an alkali-metal chloride.

16. A flux to be used in contact with molten copper-titanium alloys in which copper is the major constituent, comprising a fused mixture of calcium fluoride as the major ingredient and relatively smaller amounts of an alkali-metal fluoride and calcium chloride, said flux being fluid at temperatures from 2000° to 2300° F.

17. A flux for use in making copper-titanium alloys in which copper is the major contituent, which consists in a fluid fused mixture of calcium fluoride from 65 to 80% and sodium chloride from 20 to 35%.

18. A flux to be used in contact with molten copper-titanium alloys in which copper is the major constituent, comprising a fluid fused mixture of calcium fluoride from 65 to 80% and calcium chloride and sodium fluoride from 20 to 35%.

19. In a method of making copper-titanium alloys by melting together the pure metals, the step which consist in immersing the titanium to prevent oxidation thereof in a fused mixture comprising calcium fluoride and a relatively smaller amount of an alkaline-earth metal chloride.

20. In a method of making copper-titanium alloys by melting together the pure metals, the step which consists in immersing the titanium to prevent oxidation thereof in a fused mixture comprising calcium fluoride and relatively smaller amounts of an alkli-metal fluoride and an alkaline-earth metal chloride.

21. A method of making alloys containing from 10 to 40% titanium with the balance substantially copper, which comprises superimposing a non-oxidizing flux composed of a mixture of calcium fluoride not less than 50% and relatively smaller amounts of an alkali-metal fluoride and an alkaline-earth metal chloride above the copper and melting same, then immersing metallic titanium in the molten slag formed, and then heating the charge sufficiently high to dissolve the titanium below the molten slag to alloy with the subjacent molten copper.

22. A flux to be used in contact with molten copper-titanium alloys in which copper is the major constituent comprising a fused mixture of calcium fluoride as the major ingredient and relatively small amounts of an alkali-metal fluoride and an alkaline-earth metal chloride, said flux being fluid at temperatures from 2000° to 2300° F.

23. A flux to be used in contact with molten copper-titanium alloys in which copper is the main constituent comprising a fused mixture of calcium fluoride and relatively small amounts of an alkali-metal fluoride and an alkaline earth-metal chloride.

24. A flux to be used in contact with molten copper-titanium alloys in which copper is the main constituent comprising a fused mixture of calcium fluoride from 65 to 80% and sodium chloride from 20 to 35%, said flux being fluid at temperatures from 2000° to 2300° F.

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