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COPPER-BORON ALLOYS AND METHOD OF MAKING SAME

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This invention relates to alloy-like compositions of copper and boron and to new and improved methods of producing them.

Many attempts have been made in recent years to alloy substantial amounts of boron with copper. Heretofore, small amounts of boron have been alloyed with copper by reaction between various materials containing copper and boron either chemically or physically combined therein. These methods were not commercially successful, since only small amounts of boron could be introduced into the alloy, and also because the resulting composition contained sizeable amounts of undesirable impurities and exhibited low yields of boron.

More recently, however, a process was developed and is set forth by Cooper in Patent No. 2,964,397 wherein useful alloys of boron and copper containing up to 10% by weight of boron are produced by reacting particulate, elemental boron and copper in an inert atmosphere at a temperature above 1450° C. While this method produced commercially successful alloys of copper and boron, the method was not adapted to produce useful homogeneous alloys containing over 10% boron.

When copper-boron alloys are to be utilized as master alloys to produce alloys containing lesser amounts of boron, it is desirable to provide relatively large amounts of soluble boron in the master alloy, not only for economic reasons but also for ease of handling. Furthermore, when smaller amounts of a copper-boron master alloy are added to produce a desired amount of boron in the finished alloy, there is less chance of adding relatively large amounts of impurities to the melt. It is also highly desirable to provide a master alloy having relatively large amounts of "free" available boron which can be dissolved in the melt substantially instantaneously.

The principal objects of the present invention are to provide a new and improved method of making homogeneous, high purity alloys of copper and boron; to produce novel, homogeneous, high purity alloys of copper and boron containing between about 10% and 99% boron; to produce novel, homogeneous, high purity alloys of copper and boron containing between about 67% and 99% boron which are particularly useful as master alloys; and to produce novel, homogeneous, high purity alloys of copper and boron which may be utilized in high temperature conductivity applications.

The foregoing and other objects of the invention will be more fully appreciated from the following detailed description and from the specific examples of the invention given for illustrative purposes.

In general, copper-boron alloy compositions according to the present invention may be produced by mixing particulate boron and particulate or pelletized copper and heating the mixture to above 2000° C. in a pressurized, inert atmosphere. For ease of handling during charging, the boron and copper may be compressed and/or sintered

into a coherent mass. It is not necessary to form the starting materials into an intimate mixture, nor is it necessary to reduce the particle size of the starting materials for intimate contact. Alloys of boron and copper have been produced according to the present invention by compacting some of the boron into a briquetted shell or cup, placing the desired amount of copper, which is in the shape of relatively large globules or pellets, in the boron cup, adding the remaining required boron to the cup to envelop the copper, and then pressing the sample so formed into a coherent mass.

Temperatures of over 2000° C. and pressures ranging from 2 to 5 atmospheres absolute are necessary to produce copper-boron alloys having over 10% boron. While it is possible to produce homogeneous copper boron alloys containing less than 10% boron at temperatures less than 2000° C. and at atmospheric pressure, it has been found that if the boron content of the alloy is to be any value over 10%, the utilization of temperatures of less than 2000° C. and atmospheric pressure will produce non-homogeneous masses wherein there exist copper flow and segregation of undissolved boron. However, it is to be understood that the process according to the present invention will produce alloy-like compositions of copper and boron containing less than 10% boron. Since industry requires master alloys having a uniform and homogeneous distribution of boron and copper and also a high percentage of available boron, the non-homogeneous masses discussed above are totally unacceptable.

It has further been found that temperatures ranging from 2300° C. to 2600° C. are particularly advantageous in the present process since these temperatures produce a more pure product. In the temperature range of from 2000° C. to 2300° C. boron dissolves slowly into the melt and necessitates a longer time at temperature. If the alloying constituents are held at these temperatures for extended lengths of time, however, the finished product contains furnace contaminants, such as tungsten from the electrode, if an arc furnace is employed, or carbon if a resistance furnace is utilized. At temperatures in excess of 2300° C., boron enters into solution with the copper substantially instantaneously and tungsten and carbon pick-up are not serious problems. Temperatures over 2600° C. are operable to carry out the present method, depending upon the particular heating means available, and an upper temperature of 2600° C. is set forth herein merely for purposes of illustrating an economical temperature limit.

The present invention is preferably carried out by using elemental boron of relatively high purity (e.g., about 99%), although, if desired, various presently available grades of so-called "elemental boron" containing substantial amounts of boron oxides and small amounts of metallic impurities may be employed. The use of lower grade boron results in a concomitant lower yield of available boron in the resulting master alloy.

The relatively high temperatures utilized in the process according to the present invention may be produced by arc, induction, or resistance furnaces. These furnaces also induce a desirable stirring effect in the alloy as it is being melted.

Various aspects of the invention will be more fully understood from the following examples and the accompanying discussions. In the examples all of the percentages given are by weight.

EXAMPLE I

A series of copper-boron alloys were prepared by mixing boron powder and copper powder of approximately 30 mesh in the following ratios:

Mixture	Percent Boron	Percent Copper
1	4.00	96.00
2	10.03	89.97
3	15.00	85.00
4	30.00	70.00
5	50.00	50.00
6	67.00	33.00
7	74.00	26.00
8	80.00	20.00
9	95.00	5.00

The copper-boron mixtures were pressed into disks. Each disk, in turn, was placed on a water cooled hearth of an arc furnace. A tungsten electrode having a diameter of ½ inch and a length of 2½ inches was positioned above the crucible with the tip of the electrode extending to within about ½ inch of the disk. The upper portion of the tungsten electrode was also water cooled.

After a disk had been placed in the furnace, the door was closed tightly, and a supply of argon gas was fed into the furnace. With the outlet port at its maximum opening, the flow of argon was continued for about ten minutes to purge the air in the furnace. The size of the outlet port was then adjusted so that the flow of argon gas from the furnace was reduced to permit the build up of gas pressure within the furnace of from about two to five atmospheres absolute pressure.

Switches were then closed to start the flow of electrical current from the tungsten cathode to the copper hearth anode and form an arc therebetween. When the arc had reached a temperature ranging from 2000° C. to 2600° C. and had become stable, the position of the tungsten cathode in the furnace was shifted so that the arc passed between the tungsten cathode and the disk on the copper hearth. The temperature was maintained between 2000° C. and 2600° C. during the entire heating cycle. The melt was made homogeneous by manipulation of the tungsten cathode which moved the position of the arc on the melt causing the melt to roll around the hearth. After about five minutes the current was turned off and the material on the hearth was permitted to cool and was then removed from the furnace.

The resulting products were hard, clean, semi-lustrous, alloy-like buttons, each containing boron in amounts greater than 95% of the boron content of its original mixture. The alloy-like buttons were found to be homogeneous, solid solutions of boron and copper or, in some instances, solid solutions of boron or copper with compounds of boron and copper chemically combined in stoichiometric proportions, and consisted of small crystals of uniform size. The buttons prepared from mixtures 6, 7, 8, and 9, however, exhibited an oxidized surface upon exposure to the atmosphere and, upon examination, it was found that this oxidation indicated the desirable presence of free boron in the alloy.

EXAMPLE II

The procedure of this example was the same as Example I except that the boron was added to a cylindrical die, and copper in the form of globules or pellets was placed in the center of the boron. Additional boron was then added to envelop the boron and the mixture was pressed to form a coherent mass. In this example, the boron and copper were mixed in the following ratios:

Mixture No.	Percent Boron	Percent Copper
10	80.00	20.00
11	74.00	26.00
12	67.00	33.00

After being heated in the arc furnace for five minutes at 2600° C. under a pressurized argon atmosphere of from about two to five atmospheres absolute pressure, the current was turned off and the material was permitted to cool.

Similar to the results achieved in Example I, the resulting products were alloy-like buttons, each containing substantially the same relative copper-boron percentages found in its original mixture. The surface of the buttons formed an oxide coating upon exposure to the atmosphere, indicating the desirable presence of free or undissolved boron homogeneously distributed therein.

EXAMPLE III

The copper-boron alloys produced in accordance with the procedure set forth in Example I were subjected to resistivity tests to determine their resistivity and the resistivity of graphite and arc melted boron as compared with pure, high electrical conductivity copper. All measurements were made at spacings of ½ inch and the ohm meter was set at zero by using pure conductivity copper. Table I shows the results of these tests.

Table I

Material:	Resistivity in ohms
Copper bar	0
Graphite slab	0.1
Arc melted boron	200
4.00% boron–96% copper alloy	0.1
10.03% boron–89.97% copper alloy	0.1
15% boron–85% copper alloy	0.1
30% boron–70% copper alloy	0.1
50% boron–50% copper alloy	0.1
67% boron–33% copper alloy	0.5
74% boron–26% copper alloy	0.7
80% boron–20% copper alloy	1.4
95% boron–5% copper alloy	0.3

The above results show that the resistivity of copper-boron alloys compares favorably with the resistivity of pure, high conductivity copper, even at relatively high boron contents. The copper-boron alloys according to this invention are suitable for use as conductors in applications requiring operating temperatures that are higher than the melting point of pure conductivity copper, e.g., as lead-in conductors in a high temperature resistance furnace between externally located copper bus bars and internally located graphite resistance elements.

In contrast with the results achieved in the above examples, the following examples show some of the difficulties encountered in attempts to produce copper-boron alloys having over 10% boron when atmospheric pressure and temperatures under 2000° C. are utilized during the melting procedure.

EXAMPLE IV

37.5 grams of boron particles containing 99+% boron were mixed in a ball mill with 265.5 grams of copper particles containing 99+% copper. 303 grams of this mixture were placed in a graphite crucible in a resistance furnace containing a hydrogen atmosphere which had previously been heated to a temperature of about 1450° C. The hydrogen atmosphere was maintained at atmospheric pressure and the heating was continued for 12 hours at 1650°–1700° C. The ingot produced was cooled in hydrogen and removed from the furnace. Upon weighing the ingot, it was found that 8.0 grams of the starting materials had been lost in the furnace. Macroscopic examination of cross sections of the ingot revealed gas pockets and segregation. A slice of the ingot was cleaned at its outer edges to remove the graphite that had adhered thereto from the furnace wall. Analysis of this slice showed that 12.74% boron was found as compared to a calculated yield of 12.50%, showing that the boron was not uniformly distributed throughout the ingot. Of this 12.74%, however, only 6.18% acid soluble boron was found to have entered the alloy. The rest of the boron was present as insoluble oxides.

Another slice of ingot was inserted in an Alundum

crucible and the crucible was placed in a vacuum resistance furnace. The sample was heated at about 1420° C. for three hours at a reduced pressure of between about 150 and 100 microns of mercury to distill off as much of the copper as possible to determine the boron distribution in the alloy.

Examination of the resulting product showed a heterogeneous structure having heavy segregations of boron throughout.

EXAMPLE V

150 grams of boron particles containing 99+% boron and 150 grams of copper particles containing 99+% copper were prepared and heated according to the procedure of Example IV. The resultant product was an incoherent powdery mass, brown in color with some beads of copper having a diameter of about 5/16 inch. Analysis of this material showed that it contained an acid soluble boron content of only 3.52% as compared to a calculated theoretical yield of 50%.

EXAMPLE VI

A copper-boron product was prepared, having a calculated yield of 10.06% boron, according to the procedure of Example IV. Another product was prepared, having a calculated yield of 15% boron, according to the procedure of Example I. In order to determine the relative distribution of boron in the resulting products, the copper contained therein was removed in the following manner. Each product was placed in an Alundum crucible and these crucibles were in turn, placed in a graphite crucible. The graphite crucible was then placed in a vacuum resistance furnace and the products were heated to a temperature of 1425° C. for one hour and twenty-five minutes under a reduced pressure of 190 microns of mercury. Upon examination of the product resulting from the procedure of Example IV, it was found that there were signs of copper flow and boron segregation. The product resulting from the procedure of Example I, on the other hand, exhibited a homogeneous structure having a uniform boron crystal distribution throughout.

As shown in the foregoing description and examples, the present invention provides a new and useful process for the production of homogeneous, alloy-like, copper-boron compositions, the process being of particular value for producing such compositions containing over 10% boron. These alloy-like compositions are useful as master alloys to produce alloys containing lesser amounts of boron, and for other purposes. The compositions containing over 67% boron are particularly useful as master alloys because they contain free boron entrained therein which is immediately available and will quickly dissolve in the melt to which the master alloy is to be added. The alloy-like compositions produced in accordance with the present invention may be used as high temperature conductors.

It is apparent from the above description of the invention that various modifications can be made within the scope of the present invention. Therefore, the invention is not intended to be limited to the details as disclosed herein, except as may be required by the appended claims.

What is claimed is:

1. A method of making homogeneous, alloy-like, copper-boron compositions comprising preparing a mixture of copper and boron and heating said mixture to above about 2000° C. in an inert atmosphere and under a pressure between about 2 and 5 atmospheres absolute pressure.

2. A method of making homogeneous, alloy-like, copper-boron compositions comprising preparing a mixture of copper and between about 10% and 99% by weight boron and heating said mixture to above about 2000° C. in an inert atmosphere and under a pressure between about 2 and 5 atmospheres absolute pressure.

3. A method of making homogeneous, alloy-like, copper-boron compositions comprising preparing an intimate mixture of particulate copper and between about 10% and 99% by weight particulate boron and heating said mixture to above about 2000° C. in an inert atmosphere and under a pressure between about 2 and 5 atmospheres absolute pressure.

4. A method of making homogeneous, alloy-like, copper-boron compositions comprising preparing a mixture of copper and between about 10% and 99% by weight boron and heating said mixture to between about 2000° and 2600° C. in an inert atmosphere and under a pressure between about 2 and 5 atmospheres absolute pressure.

5. A method of making homogeneous, alloy-like, copper-boron compositions comprising preparing a mixture of copper and between about 10% and 99% by weight boron and heating said mixture to between about 2300° and 2600° C. in an inert atmosphere and under a pressure between about 2 and 5 atmospheres absolute pressure.

6. A method of making homogeneous, alloy-like, copper-boron compositions comprising preparing a mixture of copper pellets and between about 10% and 99% by weight particulate boron and heating said mixture to about 2600° C. in an inert atmosphere and under a pressure between about 2 and 5 atmospheres absolute pressure.

7. A method of making homogeneous, alloy-like, copper-boron compositions comprising preparing a mixture of particulate copper and between about 10% and 99% by weight particulate boron, compressing said mixture into a coherent mass, and heating said mass to between about 2000° and 2600° C. in an inert atmosphere and under a pressure of between about 2 and 5 atmospheres absolute pressure.

8. A homogeneous, alloy-like composition consisting of copper and between about 10% and 99% by weight boron.

9. A homogeneous, alloy-like composition consisting of copper and between about 67% and 99% by weight boron, and wherein at least some of said boron is present as free boron.

References Cited in the file of this patent

Lihl et al.: "Herstellung und Konstitution von Kuper-Bor-Legierungen," Metall., Band 8, 1954, pp. 11–19.