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PROCESS FOR PRODUCING BORON-COPPER ALLOYS

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My invention relates to processes for producing copper alloys which include the reduction of metalloids from their compounds, and more particularly to processes for the reduction of boron from its compounds under conditions which permit the boron to alloy with copper.

The primary object of my invention is to provide boron-copper alloys and a method of producing them.

Many attempts have been made to introduce substantial amounts of boron into copper alloys but hitherto none has been successful from a commercial standpoint. Boron can be produced by several methods at a present cost of approximately \$300.00 per pound. Such material is always more or less contaminated with oxides, carbides, borides and metals, and can be alloyed with copper only with great difficulty, if at all. As a matter of fact, several processes for deoxidizing copper have been proposed with the assumption that boron does not alloy with copper. The melting point of boron is approximately 2300° C. The customary range of temperatures used in copper alloying practice is from about 1000° C. to about 1350° C. The literature and previous experience does not reveal any method by which metallic boron can be alloyed with copper by melting. The impurities contained in boron apparently form a coating on the surface, thus preventing the molten copper from coming in contact with the boron so that it dissolves only with great difficulty.

Alloys of boron with iron, boron with manganese, and boron with nickel are available commercially. These also dissolve in molten copper with great difficulty because of their high melting points and the presence of impurities, especially carbides. Furthermore, these alloys are objectionable as a means of introducing boron into copper alloys because they introduce fixed amounts of iron, manganese, or nickel, if they dissolve at all.

In the deoxidation of copper with calcium boride the reaction is a reduction of the cuprous oxide while the calcium boride is oxidized but no boron is set free to alloy with the copper.

In the process which I have developed a magnesium-copper alloy and a compound containing boron are heated in intimate contact with one another to a high temperature. Under these conditions the boron is liberated in a nascent state and alloys immediately with the copper while the magnesium passes off into the slag.

The composition of the magnesium-copper alloy used will be determined by the amount of boron desired in the finished product. The boron

content of the final alloy is approximately one-fifth of the magnesium content of the original magnesium-copper alloy. I consider it within the scope of this invention to use any proportions of magnesium and copper in the original alloy that will give me any desired boron content in the finished product. The other alkaline earth metals, calcium, strontium, and barium, or the alkali metals, for example lithium, sodium, and potassium may be substituted for all or part of the magnesium, if economic conditions permit. One alloy which gives good results is:

	Per cent
Copper-----	84
Magnesium-----	8 15
Lithium-----	4
Calcium-----	4

At present I prefer to use mostly magnesium because it is least costly.

Another condition under which additional elements may be present is when it is desired to produce a copper base alloy containing other elements besides copper and boron. For this purpose I may add one or more of the following elements: beryllium, aluminum, silicon, phosphorus, sulphur, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zinc, arsenic, selenium, zirconium, molybdenum, silver, cadmium, indium, tin, tellurium, tungsten, palladium, tantalum, platinum, gold, or lead.

It is considered within the scope of this invention to divide the magnesium-copper to any desired degree of fineness.

The compounds most suitable for use in my process contain oxygen in addition to the boron. Among these are boric anhydride, boric acid, metallic borates and perborates. Boric acid, boric anhydride and borax are most easily obtained at the present time. The borate minerals, some of the more common of which are boracite, borax, bechilite, colemanite, pandermite, sassolite, and ulexite and boron-bearing silicate minerals, such as tourmaline, datolite, danburite and axinite can be used directly if desired. If there are large amounts of halides associated with the minerals it usually pays to remove them because the chloride, bromide, iodide and fluoride of boron are volatile and therefore carry away some of the boron during the process. Fused boric anhydride is the most satisfactory compound in many ways but it is not always the most economical.

The boric anhydride which I use is the fused and ground commercial product. Boric acid also may be used, but the frothing due to the release

of the combined water which it contains makes it necessary to employ a much larger container for the reduction. The same applies to borates and the minerals. I sometimes mix borax and the other salts to obtain certain values of density, viscosity, and melting point in the slag but chlorides, bromides, and fluorides generally should be avoided.

There are several methods of bringing the magnesium-copper alloy into intimate contact with the boron compound. For example, I may melt the magnesium-copper and the boron compound separately and then pour them one into the other. I also may melt either the boron compound or the magnesium-copper and add the other to it as a solid. I prefer, however, to pulverize the magnesium-copper, mix it with the powdered boron compound, and heat this mixture.

The reducing action of the magnesium on the boron compounds begins near 600° C. and will take place at any temperature above approximately 600° C. up to 1500° C. and higher. The best temperature is determined by the melting point and viscosity of the metal and of the slag, the boiling point of the magnesium or other equivalent metal named above, and the limitations imposed by the properties of the refractories and by the objectionable formation of borides at the higher temperatures. As an example, for 20% magnesium-80% copper alloy and pure boric anhydride 1200° C. to 1350° C. is the best reaction temperature.

The time required for the reaction to go to completion appears to be comparatively short, but since this is affected by so many variables it cannot be predicted exactly for any given set of conditions. Therefore, a few trials are necessary to determine the time required for any particular run. In one set of experiments I obtained good results by holding the furnace at 1300° C. for 15 minutes.

In making up the charge I have found that the ratio of boric anhydride to magnesium may be about six to one by weight. Thus for each pound of alloy consisting of 30 parts magnesium and 70 parts copper by weight about 1.8 pounds of boric anhydride will be required. In these proportions the magnesium is all used without leaving any great excess of unattacked boric anhydride. When I add other metals to the magnesium-copper alloy, or use other compounds of boron, as mentioned above, the proportions naturally will be different. I do not wish to be limited to any particular ratio of magnesium to boron compound.

It is not definitely known what takes place but it appears that as the reaction progresses the boric anhydride is reduced to boron by the magnesium vapor liberated from the molten magnesium-copper. It is apparently reduction of the boron to the nascent condition in contact with the copper which makes the process possible. The temperature of the liquid boric anhydride is above the temperature at which magnesium exerts an appreciable vapor pressure with the probable result that the constant evolution of magnesium vapor stirs the interior of the droplets and thus makes possible the reduction and alloying. The magnesium oxide produced, combines with the excess of boric anhydride to form magnesium borate, a compound which flows at the temperature of the process. According to the law of mass action the collection and retention of the reaction products at the surface of

the metal must be prevented for the completion of the reaction. In the present process the magnesium oxide is removed by chemical combination, and the boron is absorbed by alloying and diffusing into the copper or copper alloy. It also is essential that the slag remain fluid until the reduction is complete.

Toward the end of the reaction the boron-copper alloy tends to collect on the bottom of the crucible or furnace with the slag floating on the top of it. The collection of the metal into a pool is hastened by raising the temperature toward the end of the reaction. The metal and the slag may then be poured into a convenient receptacle or mold, or be drawn off together or separately from the furnace by means of spouts, or other convenient arrangements, or both may be allowed to solidify in the crucible or furnace.

If it is desired to retain the boron-copper in the form of droplets or shot for convenience in adding to other metals and alloys, the slag may be thickened by adding appropriate salts or inert materials and holding the temperature as low as practicable so the droplets of metal remain dispersed. The mass of slag and metal then may be allowed to solidify in the furnace or crucible, or it may be poured into a convenient receptacle and subsequently may be broken up. It is sometimes convenient to pour the mass of slag and metal into water. The boron-copper shot is separated by crushing the slag, treating it with sulphuric or hydrochloric acid and washing the decomposed slag away by decantation. The sulphuric or hydrochloric acid does not attack the copper-boron alloy unless oxidizing substances are present.

Simple treatments of the slag permit the recovery of boric acid, borax, and other useful compounds. For example, if the crushed and ground slag be treated with sulphuric or hydrochloric acid, and the liquor be concentrated by evaporation and cooled, most of the boric acid may be filtered off. The filtrate from the boric acid may be made alkaline with caustic soda, whereupon the magnesium precipitates as hydroxide. The small quantity of boric acid not precipitated by the acid treatment is converted to borax by the alkali treatment so that when the magnesium hydroxide has been filtered off there remains a solution of sodium sulphate or sodium chloride and borax. These compounds may be recovered from the filtrate by fractional crystallization.

I am aware that a process for producing boron by heating together boric anhydride and magnesium filings is well known. In this process the reaction takes place with almost explosive violence. The product is a fused mass of boron, magnesium boride, magnesium borate and unattacked boric anhydride. The boron which finally can be separated from this mass by a long series of chemical treatments is in the form of a fine powder contaminated with impurities. As was mentioned previously it is difficult, if not impossible, to alloy this form of boron with copper.

In my process the reaction proceeds quietly at a rate which can be controlled at will by varying the amount of heat applied externally. My process provides for the separation of the boron-copper alloy from the slag either as an ingot or as pellets or shot without extensive chemical treatment. The product obtained from my process is by the act itself alloyed with copper and can be rolled or forged without any further

remelting, or it may be melted with other metals and alloys in any desired proportions.

Aluminum also has been used to produce boron by heating filings or turnings in contact with boric anhydride. This has the same disadvantages as the reduction with pure magnesium.

In my process, if a certain aluminum content is desired in the final product, I may use aluminum-copper alloy instead of magnesium-copper alloy. If, however, a binary boron-copper alloy free from aluminum is desired, I prefer not to use aluminum-copper alloy as a reducing agent because the temperature of 1400° C. to 1900° C. required to eliminate the aluminum completely from the final product is higher than with the alkali and alkaline earth metals.

I have discovered that beryllium, which is similar to aluminum in its chemical properties, also will reduce boron from its compounds, either alone or when alloyed with copper. The temperature required to complete the reaction in my process is not as high with beryllium as with aluminum but the present high price of beryllium limits its use to production of alloys comprising beryllium, boron and copper. My experiments have shown that silicon alloyed with copper has a reducing action on boron compounds but this also has no advantages over the alkali and alkaline earth metals except in the production of alloys in which it is desired to have a silicon content.

I have proved by chemical analysis and by spectrographical and microscopical examination that the alloy produced by my process is boron-copper.

As an example, Heat No. 746 in my experiments was found to contain:

	Percent
Copper -----	94.96
Iron -----	0.20
Silicon -----	0.37
Boron -----	4.27
Magnesium -----	0.12

Thus the process as described above, makes available a useful product, boron-copper alloy, and other copper base alloys containing boron, which hitherto have not been produced commercially. The difficulties of making boron-copper alloys have been so great previously that enough apparently has not been available even to determine their diagram of thermal equilibrium. With the metal from my process available, it will be possible not only to study the equilibria but to investigate all of the other properties of these alloys.

My process depends upon a peculiar and fortunate set of circumstances which I have discovered as described above.

One valuable use for my process which I have already found is in the manufacture of high-conductivity deoxidized copper. In deoxidizing copper by adding to it metals which combine with oxygen it is customary, and considered necessary to leave a small residue of the deoxidizing agent in the alloy in order to obtain and maintain complete oxidation. Unless this excess is used, more oxygen is picked up from the air while the copper is being poured into molds.

Since the oxygen pick-up from the air varies considerably with the speed of pouring, size of stream, temperature and velocity of the air, and many other factors it is necessary to use an excess of deoxidant to make certain that the wire bar, cake, billet, etc., finally taken from the mold will be completely deoxidized. This excess of deoxidant, as is well known, usually phosphorus,

silicon, manganese or beryllium reduces the conductivity of copper markedly even if present only in traces. I have found that boron is a good deoxidizing agent and that it does not reduce the conductivity of copper as strongly as phosphorus, silicon, manganese and beryllium. The following table shows the properties of copper deoxidized with boron produced by my process.

Properties of annealed boron-deoxidized copper wire

Percent boron found by analysis	Tensile strength, lbs./sq. in.	Elongation percent in 2"	Conductivity percent I. A. C. S.	Bends after annealing 30 min. in hydrogen at temp. of 850° C.
.000 -----	35,300	51.0	100.69	1
.011 -----	35,500	49.5	100.32	11
.022 -----	36,500	48.5	97.85	12
.055 -----	36,000	45.0	95.99	11
.113 -----	37,300	46.5	92.32	13

In the above table the column headed "Bends after annealing 30 min. in hydrogen at temp. of 850° C." shows the number of 180° bends over an 8 mm. radius which could be given without fracture occurring, to the 0.128" diameter wires that had been subjected to a pure hydrogen atmosphere for ½ hour at 850° C. It is well known that copper which contains oxygen is embrittled by annealing in hydrogen. Therefore, the large number of bends obtained in this test on all of the samples with the boron additions as compared to the sample without the boron additions prove that the boron deoxidized the copper. In current material specifications, 10 bends in this test are required for copper to be considered deoxidized while the minimum number of bends found in my tests on boron deoxidized copper was 11.

The principle of this invention may be applied to the deoxidation of copper by boron in many ways. For example, the copper could be first alloyed with a very small percentage of magnesium and then treated with boric anhydride with suitable agitation. Another way of carrying out the process would be to mix pulverized magnesium-copper and boric anhydride, for example, and stir them into molten copper. I consider it within the scope of this invention to use any apparatus or procedure which will bring nascent boron, reduced from boric anhydride or compounds of boron with oxygen, and other elements according to my process in contact with a molten copper. At present, however, to produce boron deoxidized copper, I prefer to make up a suitable boron-copper alloy beforehand containing, for example, 5% boron, and add a sufficient quantity to the molten copper to deoxidize it and protect the copper from oxidation during pouring.

My procedure for preparing deoxidized copper is distinguished from other processes for accomplishing the same result and which involve boron, by the use of metallic boron contained in a copper alloy rather than by the use of a boride such as calcium boride or an unsaturated oxide such as boron suboxide.

Having thus set forth the nature of my invention, what I claim is:

1. The process for introducing boron into copper-base alloys in which a copper alloy containing magnesium is heated in intimate contact with a compound comprising boron and oxygen to a sufficient temperature to release boron in the nascent state in contact with copper.

2. A process for producing copper-base-boron

alloys which consists in heating an alloy comprising a reducing agent and copper, in contact with a compound comprising boron and oxygen to a sufficient temperature that the boron compound is reduced and the boron alloys with the copper.

3. The process for producing boron-copper alloys which consists in heating a mixture of a compound comprising boron and oxygen and a copper base alloy comprising copper and a metal of the alkaline earth and alkali metal groups to a sufficient temperature to release boron in the nascent state in contact with copper.

4. A process of producing a copper-base alloy containing boron consisting in bringing together 15 boric anhydride and a magnesium-copper alloy at a sufficiently elevated temperature to decompose the magnesium-copper and liberate nascent boron in contact with the copper.

5. A process of producing a copper-base alloy 20 containing boron consisting in bringing together in intimate contact copper alloyed with a metal of the alkaline earth and alkali metal groups and a compound comprising boron and oxygen, at a sufficiently elevated temperature to decompose 25 the copper alloy and free nascent boron in contact with copper so that the nascent boron combines with the freed copper.

6. The process of producing a copper-base alloy containing boron consisting in heating a copper alloy containing magnesium in contact with a quantity of boric anhydride in weight equal to about six times the weight of the magnesium in the copper alloy to a sufficient temperature to free nascent boron in contact with the copper alloy. 5

7. A process of producing an oxygen free copper-base-boron alloy of high electrical conductivity which consists in melting the copper or a copper alloy under a slag containing boron-oxygen compounds and adding a magnesium-copper alloy to the melt. 10

8. A process for producing copper-base alloys 15 containing boron which consists in bringing calcium borate into intimate contact with a magnesium-copper alloy at a sufficiently elevated temperature to melt the borate and the copper alloy. 20

9. A process for producing boron-copper alloys which consists in bringing borax into intimate contact with a copper base alloy comprising copper and magnesium at a sufficiently elevated temperature to melt the borax and the copper alloy. 25

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