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PREVENTION OF HYDROGEN-EMBRITTLEMENT IN OXYGEN-BEARING COPPER

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This invention relates to the prevention of hydrogen embrittlement in oxygen-bearing metals, and more particularly to the production of copper which contains minor amounts of refractory metal oxides but which contains substantially no oxygen in a form available for reaction with diffused hydrogen.

It is well known that in some metals there is a tendency toward hydrogen embrittlement when the metal is exposed to a hydrogen-containing atmosphere or other hydrogen-containing environment at elevated temperatures. Hydrogen embrittlement may be described as the formation of water vapor within an oxygen-containing metal as a result of the inward diffusion of hydrogen gas into the metal structure, the oxygen being in solid solution in the metal or in the form of precipitated nodules of metal oxides (e.g. cuprous oxide) which are readily reducible by the diffused hydrogen. The hydrogen diffusing into the metal combines with the oxygen therein to form steam, and the expanding steam weakens the metal structure at the grain boundaries thereof which causes brittle failure of the metal when subjected to stress. This can be a serious problem. For example, tough pitch copper is a high grade electrolytically or pyrometallurgically refined copper containing very few metallic impurities and usually between about 0.02 and 0.07% by weight of oxygen predominantly in the form of cuprous oxide. Tough pitch copper has good electrical conductivity and is relatively easy to fabricate into finished products. However, due to the slight but significant free oxygen content (that is, oxygen in a form available for reaction with diffused hydrogen) of this material it is subject to hydrogen embrittlement when heated in the presence of a hydrogen-containing environment (for example, when being brazed with the aid of a conventional acetylene torch or in a hydrogen atmosphere furnace), and therefore the use of tough pitch copper is restricted in practice by the need to avoid hydrogen embrittlement of this material.

Hydrogen embrittlement of metals, and in particular copper, may be prevented by eliminating as completely as possible the oxygen present in the copper or other metal that is available for reaction with hydrogen. The production of copper that is virtually oxygen-free is an expensive and difficult procedure requiring the use of elaborate melting furnaces and casting machines specifically designed to permit deoxidation and prevent reoxidation of the copper. Oxygen-free copper of high purity has excellent electrical conductivity and can be fabricated by conventional techniques in hydrogen-containing atmospheres without danger of hydrogen embrittlement of the resulting fabricated structure. However, OFHC copper, as this oxygen-free high conductivity product is called, is a soft and malleable material and has little mechanical strength when heated, and therefore it is not suitable for products requiring reasonable strength and good dimensional stability at elevated temperatures—such for example as required by high power vacuum tubes and other electronic equipment in which high temperatures are generated by the electrical energy used by the equipment.

It is known that the physical strength of high purity copper (e.g. OFHC copper) can be dramatically increased by a process known as dispersion hardening, and the increase in strength and hardness of dispersion hardened copper is retained even at the elevated temperatures at

which such coppers as tough pitch, OFHC, precipitation hardened and other similar coppers would become relatively soft and lacking in mechanical strength. In this process a very small but significant quantity of certain metal oxides such as aluminum oxide, chromium oxide, zirconium oxide, beryllium oxide and other refractory metal oxides is dispersed throughout the otherwise relatively pure solid copper matrix. The presence of these metal oxides hardens and strengthens the copper, and the thus strengthened copper retains its strength and hardness at temperatures at which other copper and copper alloys soften and lose their strength.

The actual treatment of the copper required to obtain the desired dispersion of hardening metal oxides therein is complicated and difficult and may be accomplished in a number of ways. In the most convenient process substantially pure copper is alloyed with a small but significant quantity of a metal which will form a hardening oxide. The alloy is then cast, extruded or otherwise formed into a suitable ingot or other shape, and the solid copper alloy is exposed to a source of oxygen at an elevated temperature in a manner which results in the diffusion of oxygen into the interior of the metal ingot where it reacts with the alloying metal to form the desired refractory metal oxide dispersed through copper matrix. The resulting oxygenated metal ingot contains refractory oxides which harden the metal and also a small but significant quantity of free oxygen predominantly in the form of cuprous oxide that is precipitated and elemental oxygen that is dissolved in the metal. As a consequence, although the dispersion hardened copper has vastly improved strength, stiffness and hardness even at elevated temperatures, it is nonetheless subject to hydrogen embrittlement if exposed to hydrogen at an elevated temperature due to the presence of the free oxygen therein, and in this respect dispersion hardened copper suffers from the same restrictions as to its use as does tough pitch and other oxygen-containing coppers.

We have now discovered that hydrogen embrittlement of tough pitch, dispersion-hardened and other free oxygen-containing coppers and copper alloys may be substantially completely prevented by treating the copper in the solid state with elemental boron in such a manner that effectively sequesters the free oxygen present in the copper so that subsequent exposure to hydrogen at an elevated temperature has no deleterious effect. More specifically, we have found that if free oxygen-containing copper (and by that we mean copper or copper alloys which contain oxygen in a form that is available for reaction with diffused hydrogen) is exposed to boron vapor at an elevated temperature, the boron will diffuse into the solid copper matrix and react with the free oxygen present therein to form precipitated particles of boron oxide dispersed throughout the copper matrix. The boronated copper contains, in addition, elemental boron dissolved in the solid copper matrix to the extent that boron is soluble in this metal. Accordingly, our new process for preventing hydrogen embrittlement of free oxygen-containing copper comprises subjecting the solid oxygen-containing copper to the vapors of elemental boron at a temperature of at least about 800° C. and below the melting point of the copper for a sufficient time to allow the boron to diffuse into the solid copper lattice and react with the free oxygen therein and further to substantially saturate the copper matrix with elemental boron. The resulting boronated copper contains boron oxide, substantially no free oxygen and dissolved elemental boron up to limit of solubility of boron in solid copper, or up to about 0.06% by weight of dissolved elemental boron.

Our new process may be employed to sequester the free oxygen content of any metal such as copper or copper base alloys that is subject to hydrogen-embrittlement,

and as previously noted it is particularly useful in the treatment of tough pitch copper and dispersion hardened cooper to reduce the free oxygen content of these materials to levels at least as low as that of oxygen-free or OFHC copper. Elemental boron readily diffuses into the solid copper matrix of high purity copper or copper alloys at elevated temperatures despite the fact that the solubility of boron in solid copper is not more than about 0.06% boron by weight. Moreover, boron reacts readily with free oxygen present in the solid metal matrix (that is oxygen present in the metal in a form that will react with elemental hydrogen that diffuses into the solid metal) to form a stable refractory metal oxide (B_2O_3) that is not subsequently reducible by diffused hydrogen. As a result, when free oxygen-containing copper is exposed to the vapors of elemental boron at an elevated temperature, boron will diffuse rapidly into the heated copper matrix and will react with the free oxygen present therein to form precipitated particles of boron oxide, and the diffusion of elemental boron into the copper will continue until all of the available oxygen has been sequestered by conversion to boron oxide and until the copper becomes substantially saturated with dissolved elemental boron. The precipitated particles of boron oxide dispersed throughout the copper matrix have no deleterious effect on the desirable properties of copper, and in fact the boron oxide particles may serve to strengthen and harden the copper in the same manner that the dispersed particles of refractory metal oxides (such as aluminum oxide, zirconium oxide and the like) serve to strengthen and harden dispersion hardened copper.

The free oxygen-containing copper to be boronated may be exposed to the vapors of elemental boron in any suitable manner. For example, the solid, oxygen-containing copper part may be heated in an atmosphere of boron gas at a temperature of, say, 950° C. for approximately one hour. Or, the copper part may be packed in boron powder and the thus packed part placed in an oven or other suitable heating chamber where it is maintained at a temperature of, say, between about 800° and 950° C. for a sufficient length of time to insure complete reaction of the free oxygen with boron. Or, the copper part may be painted with a mixture of boron powder and a suitable binder (such as nitrocellulose) and the thus painted part heated at a temperature of between 800° C. and 950° C. for a sufficient period of time to insure that the free oxygen content of the copper is substantially completely sequestered by reaction with boron. The copper part being boronated should be maintained at a temperature of at least about 800° C. and below the temperature at which copper becomes excessively soft, and preferably it should be maintained at a temperature between about 800° and 950° C., during the boron treatment. The length of time required to insure substantially complete reaction between the diffused boron and the free oxygen content of the copper part will depend upon the boronation temperature and upon the size and composition of the copper part. In general, the time of exposure to boron vapors should be sufficient to allow the copper part to become substantially completely saturated with element boron, and this is a matter that may be determined in each case by observation and determination of the elemental boron content of the copper being treated.

Tough pitch copper ordinarily contains between about 0.02 and 0.07% by weight of oxygen predominantly in the form of cuprous oxide, a form of oxygen with which diffused hydrogen will react and which would result in hydrogen embrittlement of the copper unless sequestered in accordance with our invention. When tough pitch copper is treated with elemental boron in accordance with our invention, the resulting "oxygen-free" product contains between about 0.02 and 0.08% by weight of boron oxide, up to about 0.06% by weight of elemental boron and substantially no free oxygen available for reaction with elemental hydrogen. Similarly, dispersion hardened copper typically may contain up to 0.5 or 0.6% by weight of oxygen predominantly in the form of cuprous oxide. When dispersion hardened copper is boronated in accordance with our invention, the product obtained contains substantially no free oxygen, up to about 0.8 or 0.9% by weight of boron oxide and up to about 0.06% of elemental boron dissolved in the copper, in addition to the hardening refractory metal oxides present therein. The "oxygen free" product of our process is not subject to hydrogen embrittlement, and in the case of dispersion hardened copper it retains its high strength and hardness at elevated temperatures.

The following examples are illustrative but not limitative of the practice of our invention:

Example I

A test strip of electrolytic tough pitch copper containing approximately 0.04% by weight of oxygen predominantly in the form of cuprous oxide was packed in boron powder and the thus packed strip was placed in an oven maintained at a temperature of 800° C. for a period of 2 hours. The resulting boronated copper test strip contained 0.05% by weight of boron oxide and 0.06% by weight of elemental boron dissolved in the copper matrix. The test strip was then placed in a hydrogen-containing atmosphere at a temperature of 850° C. for a period of 1 hour. The test strip was then subjected to repeated bending operations without fracture or failure due to hydrogen-embrittlement after a dozen 180° reverse bendings.

A second test strip of electrolytic tough pitch copper containing the same amount of free oxygen as that of the first test strip was placed in the same hydrogen-containing atmosphere at the same temperature and for the same length of time as the first test strip. On removal of the second test strip from the hydrogen atmosphere, it was subjected to a bending operation. The test strip failed as a result of brittle fracture due to hydrogen embrittlement after a 45° bend in one direction.

Example II

A test strip of dispersion-hardened copper containing about 0.2% by weight of zirconium oxide and about 0.04% by weight of oxygen predominantly in the form of cuprous oxide was packed in powdered boron and the thus packed copper test strip was placed in an oven at a temperature of 800° C. for a period of 2 hours. On completion of the boron treatment, the boronated copper test strip contained 0.05% by weight of boron oxide, about 0.06% by weight of elemental boron and substantially no free oxygen available for reaction with elemental hydrogen. The boronated test strip was then placed in a hydrogen-containing atmosphere at a temperature of 900° C. for a period of 1 hour. The test strip was then subjected to repeated bending operations without failure due to hydrogen embrittlement.

A second test strip of dispersion-hardened copper identical with the first test strip was placed in the same hydrogen-containing atmosphere at the same temperature and for the same length of time as the first test strip. The resulting hydrogen-treated, dispersion hardened test strip was then subjected to a bending operation. The test strip failed, due to hydrogen embrittlement, after less than one bending operation.

Example III

A test strip of dispersion-hardened copper containing 0.8% by weight of aluminum oxide in finely divided form dispersed uniformly throughout the solid copper matrix and about 0.04% by weight of free oxygen predominantly in the form of cuprous oxide was packed in boron powder, and the thus packed test strip was placed in an oven at a temperature of 800° C. for 2 hours. The boronated test strip contained 0.05% by weight of boron oxide, about 0.06% by weight of elemental boron and substantially no oxygen in a form available for reaction with hydrogen. The boronated, dispersion-hardened test strip

was then placed in a hydrogen-containing atmosphere at a temperature of 900° C. at a period of 1 hour. The test strip was then subjected to repeated bending operations without failure due to hydrogen embrittlement.

A second test strip of dispersion-hardened copper of identical composition with the first test strip was placed in the same hydrogen-containing atmosphere at the same temperature and for the same length of time as the first test strip, and the resulting hydrogen-treated dispersion-hardened copper strip was subjected to a bending operation. The test strip failed, due to hydrogen-embrittlement, after less than one complete bending operation.

From the foregoing description of our new procedure for the prevention of hydrogen embrittlement of copper and other such metals it will be seen that we have made an important contribution to the art to which our invention relates.

We claim:

1. Process for preventing hydrogen embrittlement of oxygen-containing copper which comprises

subjecting solid oxygen-containing copper to elemental boron at a temperature of at least about 800° C. and below the melting point of the metal for a sufficient time to allow boron to diffuse into the solid metal lattice and react with the oxygen therein, and

recovering a boronated metal product containing boron oxide, dissolved elemental boron and substantially no oxygen.

2. Process for preventing hydrogen embrittlement of oxygen-containing copper which comprises

subjecting the solid oxygen-containing copper to elemental boron at a temperature of at least about 800° C. and below the melting point of the metal for a sufficient time to allow boron to diffuse into the solid copper lattice and react with the oxygen therein and further to substantially saturate the copper matrix with elemental boron, and

recovering a boronated copper product containing boron oxide, up to about 0.06% by weight of dissolved

elemental boron and substantially no oxygen in a form available for reaction with diffused hydrogen.

3. Process according to claim 2 in which the oxygen-containing copper is boronated at a temperature of between about 800° and 950° C.

4. Process according to claim 2 in which the oxygen-containing copper is subjected to an atmosphere containing boron vapor.

5. Process according to claim 2 in which the oxygen-containing copper is packed in elemental boron powder.

6. Process according to claim 2 in which the oxygen-containing copper is painted with a mixture of boron powder and an inert binder.

7. Dispersion-hardened copper containing boron oxide dispersed throughout the copper matrix, said boron oxide being present in an amount up to about 0.9%, up to about 0.06% elemental boron in solid solution in the copper, and substantially no oxygen in a form available for reaction with hydrogen.

8. Dispersion-hardened copper according to claim 7 containing fine particles of a refractory metal oxide dispersed throughout the solid copper matrix.

9. Dispersion-hardened copper according to claim 8 in which the refractory metal oxide is selected from the group consisting of aluminum oxide, beryllium oxide, chromium oxide and zirconium oxide.

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