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METHOD OF MAKING INTERNALLY OXIDIZED DISPERSION HARDENED COPPER PRODUCT

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ABSTRACT OF THE DISCLOSURE

A wrought, ductile, product comprising a copper matrix through which particles of a metal oxide are intimately dispersed is made by internally oxidizing at a high temperature (preferably 1400° F. to 1700° F.) an alloy of copper and one or more readily oxidized metals having oxides of high heats of formation. The oxidation converts the metal alloyed with the copper to oxide and saturates the copper matrix with oxygen. The oxidized metal is heated (preferably at 1400° F. to 1700° F.) in hydrogen until the oxygen dissolved in the copper matrix (but not the oxide of the metal alloyed initially with the copper) is reduced, resulting in severe embrittlement of the metal. The resulting copper product is broken up mechanically to granular form, and then is formed into an extrusion billet which is extruded hot (at say 1700° F. to 1900° F.) into a ductile, workable shape of suitable cross section. The extruded shape may be cold worked to final form.

This invention relates to the production of an internally oxidized dispersion hardened copper product comprising a matrix of metallic copper having particles of a metal oxide intimately dispersed therethrough. The invention is particularly directed to an improved method for making such a product.

It is not practical to produce dispersion hardened copper by conventional melting and casting procedures. Such products have, however, been made by the methods of powder metallurgy, involving mixing powders of copper and the metal oxide, compacting and sintering the mixed powders, and working the sintered compact to the desired fabricated shape.

More recently the process of the McDonald, Spooner, and Coxe U.S. Pat. No. 3,296,695 has been developed for internally oxidizing an alloy of copper (or similar metal) with a minor portion of the metal of the oxide. Briefly, this procedure involves exposing a rolled relatively thin strip of such alloy to an oxidizing environment under conditions such that oxygen diffuses through the strip and oxidizes the metal alloyed with the copper. The resulting internally oxidized strip is coiled to form a cylindrical billet which is then extruded hot into a shape of desired cross section.

The present invention provides an improvement on the process of the McDonald, Spooner and Coxe patent, in which an alloy of copper and readily oxidized metal such as beryllium, aluminum, magnesium, zirconium, or silica, after being internally oxidized, is subjected to a reducing operation in a hydrogen-containing atmosphere to eliminate excess oxygen dissolved in the copper matrix. Such reduction severely embrittles the copper. This brittle product is readily broken up into small particles which are canned or compacted to form an extrusion billet.

According to the invention, therefore, a method is provided for making a wrought, ductile, dispersion hardened copper product composed essentially of a copper matrix through which is dispersed a relatively small

amount of oxide of a readily oxidized metal the oxide of which has a high heat of formation, which comprises heating to an elevated temperature a thin shape of an alloy of copper and said readily oxidized metal in the presence of an amount of oxygen sufficient to oxidize all of said readily oxidized metal and to saturate the residual copper matrix with oxygen, and continuing such heating until said readily oxidized metal is substantially completely converted to oxide and the copper matrix is substantially saturated with oxygen. The resulting oxidized metal then is heated to an elevated temperature in a hydrogen-containing atmosphere until the oxygen dissolved in the copper matrix is substantially completely reduced and the copper matrix has become severely embrittled. The resulting hydrogen-reduced product is comminuted, the comminuted metal is formed into an extrusion billet, and said billet is coalesced by extrusion at an elevated temperature into a shape of desired cross section.

The alloy of copper and readily oxidized metal is preferably in thin sheet or strip form when subjected to oxidation, so that diffusion of oxygen completely through it may occur in a reasonably short period of time.

It is desirable to avoid over-oxidizing the copper alloy, and accordingly it is preferable to limit the amount of oxygen available during the oxidation treatment. This can be accomplished, for example, by supplying the oxygen in the form of a controlled amount of copper oxide, with which the alloy is in intimate contact while it is being heated during the oxidation step. During such heating, the copper oxide dissociates and the oxygen thereof diffuses through the copper. The amount of copper oxide present should of course supply the amount of oxygen required for internally oxidizing the readily oxidized metal component of the alloy and substantially saturating the copper matrix with dissolved oxygen.

The copper oxide can be provided separately from the alloy, or it can be provided by surface-oxidizing the alloy in air until a scale of copper oxide has formed thereon to the requisite extent. The resulting surface-oxidized metal is then further heated in an inert atmosphere until the readily oxidized metal has become substantially completely oxidized and the copper matrix has become substantially saturated with dissolved oxygen.

Alternatively, the amount of oxygen supplied may be limited by conducting the internal oxidation operation in a closed chamber in which the atmosphere initially contains about the right amount of free oxygen to oxidize the readily oxidized component of the alloy and to saturate the copper matrix.

The oxidation operation is preferably carried out at a temperature in the range of 1400° F. to 1700° F. Lower temperatures can be used, but the time required to complete the oxidation treatment is then greatly increased.

Higher temperatures also may be used, with some reduction in the time required for to complete formation of the oxide, but close temperature control is then necessary to avoid local overheating which might result in partial or incipient fusion of the metal.

The hydrogen reduction of the metal after it has been subjected to the oxidation step may be carried out in any conventional heat-treatment furnace designed for maintaining a controlled atmosphere in contact with the metal. The hydrogen content of the atmosphere may be supplied in the form of commercially pure hydrogen, or it may be supplied in the form of any hydrogen-containing reducing gas, such as cracked ammonia, reformed natural gas, or producer or water gas. Preferably a faily high hydogen content is desirable in the furnace atmosphere dur-

ing the reduction operation, so that elimination of the excess oxygen proceeds rapidly.

The hydrogen reduction, like the oxidation operation, is preferably carried out at a temperature in the range from 1400° F. to 1700° F. Temperatures below 1400° F. may be used successfully, but the time required for the reduction operation to be completed increases rapidly as the temperature is decreased. Also, higher temperatures than 1700° F. may be used, but necessitate close temperature controlled to avoid localized melting or incipent fusion of the copper.

Hydrogen diffuses rapidly through hot metallic copper, and rapidly eliminates oxygen dissolved therein. However, it does not readily reduce metal oxides having high heat of formation, such as are produced by internal oxidation of the initial alloy, at temperatures below the melting point of copper. Consequently no great difficulty is encountered in eliminating the dissolved oxygen from the copper matrix while retaining the dispersed metal oxide that has been formed by the preceding internal oxidation of the starting alloy.

It has been long known that when copper containing dissolved oxygen is reduced with hydrogen, the metal becomes embrittled. Various explanations of this phenomenon have been advanced; but whatever the reason may be, the degree of embrittlement becomes generally more severe the greater is the oxygen content prior to reduction. In the process of the present invention, advantage is taken of this embrittlement. In fact, it is desirable that the copper be substantially saturated with dissolved oxygen prior to hydrogen reduction, so as to effect substantially maximum embrittlement of the metal as a result of such reduction.

The reduced embrittled metal, in accordance with the invention, is mechanically broken up into pieces small enough to be handled as a granular material. Such comminution may be effected in various ways, for example, it can be accomplished in a hammer mill, or by subjecting the embrittled strip to a rolling operation. Any other procedure for subjecting the metal to mechanical stress can also be used for reducing it to small particles.

The comminuted metal is next formed into a billet for hot extrusion. It is possible to form such billet by compacting and sintering the granular metal at a temperature approximating 1500° F. to 1800° F.; but a generally simpler and preferred procedure is to can the granular metal in a sheet copper container of the correct size for charging into an extrusion press.

The resulting billet, however formed, is subjected to hot extrusion in a conventional extrusion press, at conventional copper extrusion temperatures (for example, from 1700° F. to 1900° F.). The hot extrusion operation converts the granular copper of the billet into a dense, homogeneous, extruded copper shape of whatever cross section has been selected. For example, the billet may be extruded in the form of a copper rod, bar, tube or other conventional shape. The hot extrusion operation has the effect of converting the embrittled metal to ductile and workable form, without, however, altering its character as a two-phase product comprising a copper matrix through which particles of the metal oxide are dispersed. It thus retains its character as a dispersion hardened material; yet it is free from embrittlement and may be worked mechanically to a smaller cross sectional area or may be otherwise formed by a plastic deformation operation. In fact, such cold working of the extruded shape to finished form is generally preferred. The metal may be subjected to intermediate anneals during such working to restore workability lost by work hardening of the copper matrix; and it may be subjected to a final anneal to relieve work hardening stresses.

Various readily oxidized metals having oxides of high heats of formation may be used in preparing the alloy from which the internally oxidized copper product of this invention is made. Among such metals are, for example,

beryllium, aluminum, magnesium, zirconium and silicon. Combinations of such metals also may be used. The amount of such metal or metals present in the alloy is generally in the range from 0.01 percent to 1 percent by weight of the alloy. A particularly advantageous alloy to be treated in accordance with the invention is composed essentially of 0.05 percent to 0.10 percent by weight beryllium and the balance commercially pure copper. The beryllium of such alloy is substantially entirely converted to a beryllium oxide (beryllia) by the internal oxidation treatment described above.

The invention is exemplified below:

EXAMPLE 1

A solid solution alloy composed of 0.1 percent by weight beryllium and the balance commercially pure copper in the form of a rolled sheet 0.02 inch thick, was packed in a closed heating chamber in intimate contact with cuprous oxide in sufficient amount to supply enough oxygen by dissociation to completely oxidize the beryllium content of the alloy and to saturate the copper matrix. The pack was heated for six hours at 16000° F. The pack was then cooled to room temperature, the oxidized strip was removed from the pack, and the surface of the strip was cleaned mechanically. The oxidized strip was then introduced into a controlled-atmosphere heat-treatment furnace wherein it was heated in an atmosphere of commercial hydrogen at 1600° F. for six hours. At the conclusion of the treatment the strip was cooled to room temperature (under non-oxidizing conditions) and was found to be very brittle. The brittle strip was comminuted in a hammer mill to the form of small granular particles. These particles were utilized to fill a cylindrical container made of thin sheet copper, 3¼ inches in diameter, to form an extrusion billet. This billet was heated to 1800° F., and at such temperature was extruded into the form of a round rod 0.875 inch in diameter. The resulting rod was found to be free from brittleness and capable of being plastically deformed without physical injury. The extruded rod was cold drawn, without intermediate anneals, to a wire 0.100 inch in diameter. The drawn wire was stress relieved at 1300° F. for 1½ hours, and its physical properties were then determined at 68° F. and at 1600° F. with the following results:

	At 68° F.	At 1,600° F.
Ultimate tensile strength, p.s.i.	80,000	23,000
Yield strength (0.2% offset), p.s.i.	63,000	22,000
Elongation in 2", percent	12	2
Electrical conductivity, percent I.A.C.S.	85	21

EXAMPLE 2

A strip of the alloy of Example 1 was formed into an open coil, with space between the turns, and the coil was heated in air at 1300° F. for 2 hours in order to form a light copper oxide scale on the surface of the sheet. The resulting surface-oxidized coil was further heated in a nitrogen atmosphere at 1600° F. for 6 hours. As a result of this treatment, the oxygen of the surface scale diffused through the metal, saturating the copper matrix and internally oxidizing the beryllium to beryllium oxide. The thus-oxidized strip was then reduced in a hydrogen atmosphere and further treated as described in Example 1, with similar results.

EXAMPLE 3

A strip of the alloy of Example 1 was formed into an open coil as in Example 2 and was heated for 6 hours at 1600° F. in a closed chamber containing a measured amount of oxygen gas sufficient to convert the beryllium of the alloy to beryllium oxide and to saturate the copper matrix with oxygen. Following such oxidation treatment, the coil was reduced in a hydrogen atmosphere and further processed as described in Example 1, with similar results.

The coalesced extruded products of Examples 1, 2, and 3 are not then susceptible to hydrogen embrittlement since all dissolved oxygen in the matrix has already been gettered.

What is claimed is:

1. A method of making a wrought, ductile· internally oxidized, dispersion hardened copper product composed essentially of a copper matrix through which is dispersed a relatively small amount of oxide of a readily oxidized metal the oxide of which has a high heat of formation, which comprises

(a) heating to an elevated temperature a thin shape of an alloy of copper and said readily oxidized metal in the presence of an amount of oxygen sufficient to oxidize all of said readily oxidized metal and substantially to saturate the residual copper matrix with oxygen.

(b) continuing such heating until said readily oxidized metal is substantially completely converted to oxide and the copper matrix is substantially saturated with oxygen,

(c) heating the resulting oxidized metal to an elevated temperature in a hydrogen-containing atmosphere until the oxygen dissolved in the copper matrix is substantially completely reduced and the copper matrix has become severely embrittled,

(d) comminuting the resulting hydrogen-reduced product,

(e) forming the comminuted metal into an extrusion billet, and

(f) coalescing said billet by extrusion at an elevated temperature.

2. The method according to claim 1, in which the alloy of copper and readily oxidized metal is subjected to oxidation in sheet form.

3. The method according to claim 1, in which the alloy of copper and readily oxidized metal is oxidized by heating it in a closed chamber on contact with a sufficient quantity of copper oxide to furnish by dissociation the amount of oxygen required by the oxidation operation.

4. The method according to claim 1 in which the alloy of copper and readily oxidized metal is heated in air until a scale of copper oxide has formed on the surface thereof, and the resulting surface-oxidized metal is then further heated in an inert atmosphere until the readily oxidized metal has become substantially completely oxidized and the copper matrix has become substantially saturated with dissolved oxygen.

5. The method according to claim 1, in which the alloy of copper and readily oxidized metal is oxidized by heating in a closed chamber in an atmosphere initially containing just sufficient free oxygen to oxidize all the readily oxidized metal and substantially to saturate the residual copper matrix with oxygen.

6. The method according to claim1 in which the oxidation of the alloy is carried out at a temperature in the range from 1400° F. to 1700° F.

7. The method according to claim 1 in which the hydrogen reduction of the oxidized metal is carried out at a temperature in the range from 1400° F. to 1700° F.

8. The method according to claim 1 in which the hydrogen-reduced and comminuted metal is compacted and sintered to form a cohesive extrusion billet.

9. The methd aoccording to claim 1 in which the hydrogen-reduced and comminuted metal is packed in a copper can to form an extrusion billet.

10. The method according to claim 1 in which the initial alloy is composed of 0.01% to 1% by weight of readily oxidized metal and the balance commercially pure copper.

11. The method according to claim 1 in which the readily oxidized metal of the initial alloy is selected from the group consisting of beryllium, aluminum, magnesium, zirconium and silicon.

12. The method according to claim 1 in which the billet of comminuted embrittled metal is extruded at a temperature in a range from 1700° F. to 1900° F.

13. The method according to claim 1, in which the coalesced extruded metal is cold worked to finished shape.

14. The method of making a wrought, ductile dispersion hardened copper product composed essentially of a copper matrix through which is dispersed a relatively small amount of beryllia, which comprises

(a) heating to temperature in the range from 1400° F. to 1700° F. a thin shape of a beryllium-copper alloy composed essentially of 0.05% to 0.25% beryllium and the balance commercially pure copper in the presence of an amount of oxygen sufficient to oxidize substantially the entire beryllium content of said alloy and substantially to saturate the residual copper matrix with oxygen,

(b) continuing such heating until substantially all the beryllium of the alloy is oxidized to beryllium oxide and the copper matrix is substantially saturated with oxygen,

(c) heating the resulting internally oxidized metal to a temperature between 1400° F. and 1700° F. in a hydrogen-containing atmosphere until the oxygen dissolved in the copper matrix is substantially completely reduced and the reduced metal product has become severely embrittled,

(d) comminuting the resulting embrittled product,

(e) forming the comminuted product into an extrusion billet, and

(f) coalescing said billet by extrusion at a temperature in the range from 1700° F. to 1900° F.

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