METHOD OF MAKING ALLOYED COPPER

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18 Claims

ABSTRACT OF THE DISCLOSURE

Deoxidized copper having near-trace amounts of iron and possibly also chromium is alloyed in a non-reactive environment with zirconium and aluminum. The resulting alloyed metal experiences a significantly delayed onset of embrittlement when stressed at elevated temperatures.

SUMMARY OF THE INVENTION

Copper, such as deoxidized electrolytic copper or oxygen-free high-conductivity (OFHC) copper and having an iron content in a near-trace (approximately 50 parts per million by weight) amount, possibly a chromium content as much as 10 parts per million by weight, and other elements in amounts considered to be impurities, is alloyed with zirconium in the approximate range from 0.005% by weight of 0.03% by weight in combination with aluminum in a like or even greater amount. When alloyed properly under vacuum conditions or in a metallographically inert gaseous environment, the resulting alloyed metal develops improved resistance to embrittlement at grain boundary regions, especially under conditions of approximately 900° F. to 1,000° F., and 4,000 p.s.i. tensile stress to 5,000 p.s.i. tensile stress.

Detailed Description

Metallurgical examination of failed cast copper parts and failed forged copper parts, each type having been subjected to temperatures of at least 700° F. to 1,000° F. under tensile conditions estimated to involve at least 4,000 p.s.i. to 5,000 p.s.i. stress over prolonged periods of time, suggests that the principal phenomenon causing cracking or flaking and erosion of surface metal failures in the parts is a form of embrittlement. Such embrittlement apparently involves the preferential precipitation of iron-rich and also possibly chromium-rich material at grain boundary regions of the copper in the form of near-continuous films either alone or with subsequent preferential oxidation or sulfidation attack on such iron and/or chromium enriched zones.

It has been discovered that the onset of such failure by embrittlement can be significantly delayed in the stressed and heated copper parts, particularly at elevated temperatures where the iron-rich (and chromium-rich) materials diffuse more rapidly, by the controlled combining of zirconium and also aluminum into the copper in minimum amounts that are stoichiometrically related to the iron (and possibly chromium, if any) content of the copper. Although additions of the specified zirconium and aluminum alloying elements to the copper in amounts greater than the preferred range may not reduce the embrittlement delay that is otherwise obtained, and sometimes may even somewhat enhance the improvement, the increased amounts may have an adverse effect on other properties such as reducing electrical conductivity.

For the purpose of this invention it is preferred that the amount of zirconium added be in the range of 0.005% to 0.03% by weight of the total alloy. In many instances the amount of zirconium alloyed into the copper to obtain the advantages associated with this invention is in the narrower range of approximately 0.01% to 0.02% by weight of the total alloy.

The amount of aluminum to be alloyed into the same copper in the practice of this invention is essentially like the amount of zirconium although proportionally larger amounts of aluminum, within limits, do not appear to adversely affect the delay in onset of embrittlement that otherwise is obtained. Thus, the invention also preferably involves the addition of the corresponding amount of aluminum in the range of approximately from 0.005% to 0.03% by weight to the copper and often an amount in the range from 0.01% to 0.02% is utilized. No clear upper limit for the aluminum content is known and in at least one instance a total of 0.3% aluminum has been employed with a 0.02% zirconium addition.

It is also important in the practice of the instant invention that the alloying elements be combined with the copper in a controlled manner. In one such acceptable method of alloying the copper is vacuum melted, deoxidized by hydrogen-bubbling in a partial vacuum, combined with the alloying elements under a vacuum condition, thoroughly mixed by argon bubbling in a partial vacuum, and afterwards also cast and solidified under vacuum. In an alternate acceptable method deoxidized copper is melted, alloyed, mixed, and cast and solidified entirely in a non-reactive gaseous environment such as in essentially pure argon. Exposure of the alloying elements to oxygen at metal melting temperatures must be avoided. Also, alloying conditions should be such that the zirconium and aluminum additions not be in an oxide, nitride, or carbide form or their effectiveness will not be realized. Accordingly, it is preferred that the specified alloying ingredient be combined in their metallic form. Although not presently known, it is conjectured that homologues of the alloying elements, particularly chromium, are operative to obtain the advantages of the instant invention.

The comparative data in the following Tables I and II illustrates the significance of the instant invention with respect to effecting a delay in the onset of embrittlement under conditions of tensile stress and elevated temperatures. Table I provides information regarding the improved alloys; Table II, on the other hand, relates to copppers alloyed in a conventional manner. In each case, however, the alloyed metal tested was prepared in a manner involving deoxidation and was subjected in tensile bar form, to a tensile stress of at least 4,000 p.s.i. and a temperature of approximately 950° F. The time to embrittlement (rupture) under the specified test conditions is given for each of the representative melt alloy compositions indicated.

**TABLE I**

<table>
<thead>
<tr>
<th>Melt number</th>
<th>Condition</th>
<th>Zirconium</th>
<th>Aluminum</th>
<th>Copper</th>
<th>Hours to rupture</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>As cast</td>
<td>0.005</td>
<td>0.01</td>
<td>99.95</td>
<td>226</td>
</tr>
<tr>
<td>94</td>
<td>.0.0</td>
<td>0.01</td>
<td>0.02</td>
<td>99.95</td>
<td>179</td>
</tr>
<tr>
<td>89</td>
<td>.0.0</td>
<td>0.02</td>
<td>0.20</td>
<td>99.79</td>
<td>179</td>
</tr>
<tr>
<td>92</td>
<td>.0.0</td>
<td>0.02</td>
<td>0.20</td>
<td>99.69</td>
<td>138</td>
</tr>
</tbody>
</table>

1. Treated at 5,000 p.s.i. tensile stress; subsequent loading of bar to 7,000 p.s.i. tensile stress resulted in nearly immediate rupture.
In the foregoing tables, amounts given as zero or nil were unmeasurable and are essentially considered to be less than trace amounts (less than approximately 50 parts per million). The iron content of each alloy in each instance was determined to be less than 30 parts per million (less than 0.003%) by weight, such amount being derived from spectrographic analyses.

From the accomplished alloying improvements it has also been determined that the method of alloying copper with the specified amounts of zirconium and aluminum is effective to significantly reduce the iron content of the copper. In one instance it was determined that a starting copper having approximately 50 parts per million of iron by weight exhibited an iron content of 10 parts per million by weight (approximately) after the alloying with zirconium and aluminum had been completed.

I claim:

1. The method of alloying of copper with approximately from 0.005% to 0.03% zirconium on a weight basis and approximately from 0.005% to 0.3% aluminum comprising the steps of melting basically de-oxidized copper, and combining with the copper the said alloying elements of aluminum and zirconium in an oxygen-free environment, mixing of said such ingredients, and casting and solidifying the ingredients in an oxygen-free, non-reactive environment.

2. The method defined by claim 1, wherein the zirconium and aluminum are each combined in an amount of approximately from 0.005% to 0.01%.

3. The method defined by claim 1, wherein the zirconium is combined in an amount of approximately 0.01%.

4. The method defined by claim 1, wherein the zirconium is combined in an amount of approximately 0.02% and the aluminum is combined in an amount of approximately 0.3%.

5. The invention according to claim 1, and said environment being essentially gaseous.

6. The invention according to claim 1, and said environment being essentially gaseous pure argon.

7. The invention according to claim 1, and said ingredients of aluminum and zirconium being in metallic form.

<table>
<thead>
<tr>
<th>Melt number:</th>
<th>Condition</th>
<th>Zirconium</th>
<th>Aluminum</th>
<th>Copper rupture</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>As cast</td>
<td>0</td>
<td>0.01</td>
<td>99.97</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>0</td>
<td>0</td>
<td>99.88</td>
</tr>
<tr>
<td>36</td>
<td></td>
<td>0.002</td>
<td>0.001</td>
<td>99.99</td>
</tr>
<tr>
<td>ETP</td>
<td>Wrought</td>
<td>0</td>
<td>0</td>
<td>99.88</td>
</tr>
<tr>
<td>OFHC</td>
<td></td>
<td>0</td>
<td>0</td>
<td>99.99</td>
</tr>
</tbody>
</table>

The invention according to claim 1, and the de-oxidizing of said copper occurring by bubbling hydrogen gas through the copper in a partial vacuum.

The invention according to claim 1, and the combining of the alloying elements of aluminum and zirconium with the copper occurring under a vacuum condition.

The invention according to claim 1, and the mixing of the alloying elements of aluminum and zirconium with copper occurring by bubbling argon gas in a partial vacuum.

The invention according to claim 1, and the casting and solidifying of the alloyed ingredients occurring under a vacuum condition.

The invention according to claim 1, and the zirconium and aluminum being in oxide-free and nitride-free and carbide-free forms.

The invention according to claim 1, and the melting of the copper occurring in substantially a vacuum.

The invention according to claim 13, and the de-oxidizing of said copper occurring by bubbling hydrogen gas through the copper in a partial vacuum.

The invention according to claim 14, and the combining of the alloying elements of aluminum and zirconium with the copper occurring under a vacuum condition.

The invention according to claim 15, and the mixing of the alloying elements of aluminum and zirconium with copper occurring by bubbling argon gas in a partial vacuum.

The invention according to claim 16, and the casting and solidifying of the alloyed ingredients occurring under a vacuum condition.

The method defined by claim 1, wherein the zirconium and aluminum are each combined in an amount of approximately from 0.005 to 0.03%.

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