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COPPER-ZIRCONIUM ALLOY

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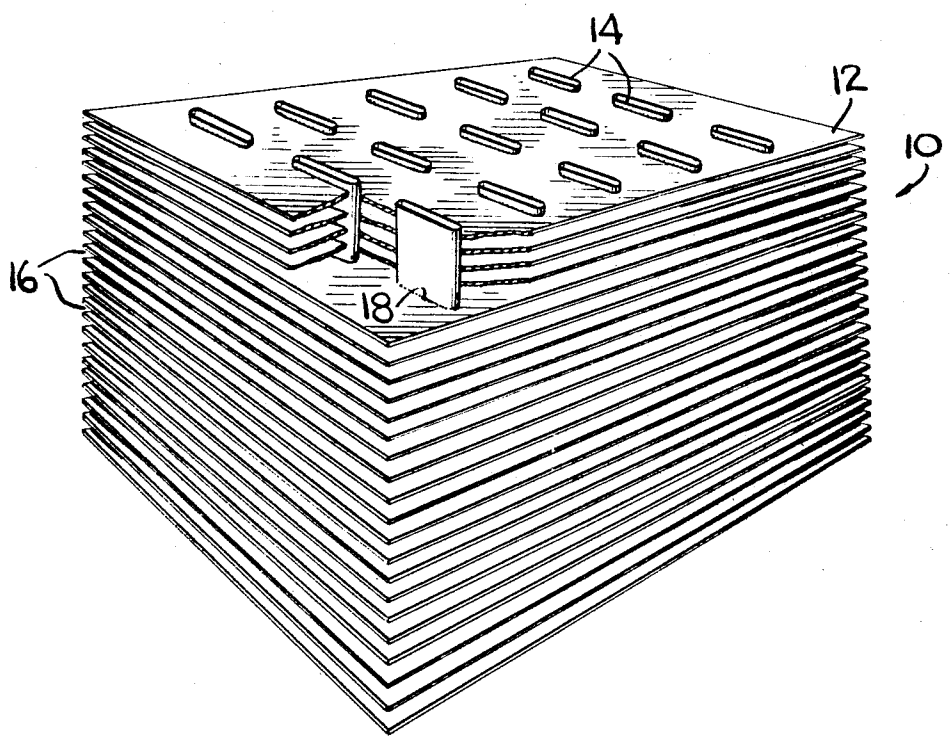


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# COPPER-ZIRCONIUM ALLOY

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7 Claims. (Cl. 75—153)

## ABSTRACT OF THE DISCLOSURE

Copper-zirconium alloys containing, by weight, 0.01% to 0.3% zirconium, 0.01% to 0.04% magnesium, up to 1.2% chromium, with the balance essentially copper, wherein the copper is initially a copper containing less than 600 parts per million of oxygen and less than 0.015% residual phosphorus. Also disclosed are copper-zirconium alloys as aforesaid, except that the maximum magnesium content is 0.06% and there is a minimum chromium content of 0.03%. In addition, there is disclosed a process for minimizing zirconium and chromium losses in the aforementioned alloys by adding magnesium no later than the said zirconium and any chromium to be included therein.

The present application is a continuation-in-part of our co-pending application Ser. No. 496,291, filed Oct. 15, 1965, now abandoned.

The present invention relates to copper-base alloys and, more particularly, to the copper-zirconium family of alloys.

As is well known, the copper-zirconium family of alloys arose out of a need in the art for high thermal and electrical conductivity alloys having good mechanical properties and/or characteristics over a rather wide range of temperatures. Exemplary of this family are the alloys disclosed in United States Patents Nos. 2,842,438, 2,847,303, 3,019,102, 3,107,998 and 3,194,655. Each of these alloys was developed for a specific purpose and, in general, each of them has performed satisfactorily when used for its intended purpose. However, each of them, like most other materials, has certain shortcomings and these shortcomings militate against their use for some high-volume commercial applications, e.g., automotive radiators, particularly where cost is an important consideration. For example, with the exception of the alloys disclosed in United States Patent No. 2,847,303, each of the other alloys is advantageously prepared from copper which is substantially devoid of oxygen, e.g., OFHC brand copper or copper prepared in an inert atmosphere or a vacuum. Alloys prepared from such high-purity coppers are relatively expensive which seriously inhibits their use for many applications.

The alloys disclosed in United States Patent No 2,847,303 are similarly disadvantageous. For example, the copper-zirconium alloys containing phosphorus which are described therein do not have consistently good conductivity when produced in accordance with the usual commercial practices since the amount of phosphorus added to the melt must be stoichiometrically related to the amount of oxygen present. If too much is used, the strength of the alloy is reduced. If too little is used, complete deoxidation is not achieved. Consequently, industry, when melting phosphorus-containing copper-zirconium alloys, has been faced with the difficult problem of carefully controlling the oxygen content of the charge. These controls are clearly objectionable from a practical or economic standpoint.

Of course it has been possible to produce high-strength copper-zirconium alloys without using high-purity starting materials or without purging the oxygen from impure starting materials with phosphorus but the resultant alloys gain their increased strength only at the expense of their conductivity. Consequently, what is needed is an inexpensive alloy having good mechanical properties at room and elevated temperatures together with good conductivity.

Although attempts have been made to provide such an alloy, none, as far as we are aware, has been entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that inexpensive copper-zirconium alloys having good mechanical properties in combination with surprisingly high conductivities may now be economically produced.

It is an object of the present invention to provide new copper-zirconium alloys having a unique combination of properties and/or characteristics.

It is another object of the present invention to provide inexpensive copper-zirconium alloys having good mechanical properties and/or characteristics together with good conductivities over a wide range of temperatures.

Another object of the present invention is to provide new radiator assemblies for use in automobiles and other vehicles which assemblies comprise especially good heat-transfer components.

The invention also contemplates the provision of copper-zirconium alloys having a unique combination of ingredients in special proportions, which alloys are characterized by being resistant to softening after being exposed to temperatures in excess of 400° C., e.g., 425° C.

Still another object of the instant invention is the provision of copper-zirconium alloys having good casting characteristics.

Among other objects is the provision of a novel process for producing high-conductivity copper-zirconium alloys having good mechanical properties and characteristics, which process minimizes losses of alloying ingredients.

It is a further object of this invention to provide a special process for making heat-transfer apparatus having components capable of retaining their strength and conductivity after being subjected to an elevated-temperature joining operation.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing which is a perspective view of a typical tube and fin type radiator assembly in which a portion of the view is broken to more clearly show the relationship of the fins to the tubes.

Generally speaking, the present invention contemplates the production of unique low-cost copper-zirconium alloys. Each of the alloys of this invention, after being subjected to appropriate cold working and heat treating operations, has good electrical and thermal conductivity together with high mechanical strength, e.g., an ultimate tensile strength (UTS) in excess of 50,000 pounds per square inch (p.s.i.) after exposure to elevated temperatures of 400° C. or higher for about 5 minutes. Alloys within the contemplated scope of the present invention having the foregoing desirable properties and/or characteristics contain, in weight percentages, 0.01% to 0.3%, e.g., 0.15%, zirconium, 0.01% to 0.06%, e.g., 0.04%, magnesium, up to 1.2%, e.g., up to 0.8%, chromium with the balance, apart from the usual impurities and residual elements, essentially all copper.

When the alloys of this invention are substantially devoid of chromium, they are characterized by having an electrical and thermal conductivity in relation to the International Annealed Copper Standard (IACS) in excess of 85% although these chromium-free alloys have somewhat lesser strengths than those alloys within the scope

of this invention that do have chromium therein. On the other hand, when chromium is included in the copper-zirconium-magnesium alloys contemplated herein, higher strengths are realized particularly at elevated temperatures. Even though the chromium-containing alloys of this invention have lower conductivities when compared to chromium-free alloys, the chromium-containing alloys contemplated herein still achieve conductivities of at least 75% after appropriate processing. Such conductivities are more than just acceptable for many important applications especially since greater strengths are attained with the addition of chromium to the alloys of this invention.

Unlike comparable prior art alloys, the copper-base alloys of this invention can be produced from coppers containing, by weight, as much as 600 parts per million (p.p.m.), i.e., 0.06%, of oxygen without materially and detrimentally altering the advantageous properties and/or characteristics of these alloys. This is a very desirable economic advantage since it permits the use of the less expensive grades of copper in the manufacture of these alloys. Accordingly, tough pitch copper, which is a copper containing 0.02% to 0.05% oxygen and which is obtained electrolytically or by refining copper in a reverberatory furnace, can be successfully used in producing the alloys of the present invention. Of course, it is to be appreciated that high-purity, substantially oxygen-free coppers may also be employed in the manufacture of the alloys of the present invention if cost is not an important consideration. Thus, cathode copper is a suitable starting material as is copper which has been produced in a reducing atmosphere such as OFHC brand copper (which is 99.99% or more pure), copper prepared in an inert atmosphere, under a charcoal cover or in a vacuum and chemically deoxidized coppers such as lithium-deoxidized copper. Even phosphorus-deoxidized copper is acceptable. However, where the conductivity and strength of the alloy is to be maximized, the amount of any residual phosphorus present in the final copper composition should be held below 0.015% by weight.

The alloys of this invention containing the aforementioned ingredients, i.e., copper, zirconium, magnesium and optionally chromium, in the aforementioned specially proportioned amounts are characterized by being cold-workable at stresses in excess of 60,000 p.s.i. These alloys are further characterized by having good castability. In addition, even in the as-cast condition, these alloys exhibit an evenly distributed fine-grained structure.

As was previously mentioned, the alloys according to this invention always contain copper together with zirconium and magnesium and each of these metallic elements in combination with each of the other two ingredients contributes significantly in obtaining the properties and/or characteristics of the alloys. For example, the zirconium content is in the range of 0.01% to 0.3%, e.g., 0.01% to 0.15%, by weight of the alloy including the weight percentages of copper and magnesium. The inclusion of zirconium in the amounts specified in the alloys of this invention has an important bearing on the tensile strength when appropriate amounts of magnesium are copresent. Consequently, if less than 0.01% zirconium is present, even though the appropriate amounts of magnesium are included in the alloy, the strength of the alloy detrimentally decreases. Advantageously, at least 0.02% zirconium is present since the larger amounts enhance the strength of the alloy. Zirconium appears to have at least one other important role in the magnesium-containing copper alloys of this invention. It seems that zirconium forms a solid solution with the magnesium so that any deteriorating effects which could be attributable to magnesium are substantially obviated. In addition, when chromium is present in the alloys of this invention in amounts of up to 1.2%, e.g., 0.5%, zirconium has the function of decreasing the notch sensitivity of the chromium-containing alloys of this invention. While zirconium has the foregoing attributes, the maximum amounts of zirconium should be also controlled in order to attain a better combination of properties such as fabricability, strength and conductivity. Thus, even though increasing amounts of zirconium increase the strength, these higher amounts decrease workability or fabricability and increase the cost of producing the alloy. A good balance which tends to optimize these competing factors is attained whenever the zirconium does not exceed 0.3% and, where conductivity is an important design factor, the amount present should not be more than about 0.15%. Moreover, since many of the installed or commercially available continuous annealing lines operate at temperatures of about 600° C., it is useful to maintain the zirconium content toward the lower part of the range, i.e., 0.03% or 0.02%. At these lower amounts, the alloys of this invention can be solution annealed in the readily available continuous annealings lines.

As is well known, a relatively small amount of hafnium is commonly associated with zirconium in the forms in which zirconium is commercially available. For example, zirconium is available as an alloy sponge nominally consisting of, by weight, up to 4% hafnium, e.g., 0.5%, with the balance essentially zirconium. Accordingly, the copper-zirconium-magnesium alloys of this invention can also contain such hafnium introduced into them with the zirconium, and any such hafnium up to 20% of the zirconium is deemed to be zirconium for the purposes of this invention.

Magnesium, when present in the amounts hereinbefore set forth, i.e., 0.01% to 0.06%, together with the proper amounts of zirconium (whether chromium is present or not) as previously mentioned, has a number of beneficial effects, including alloying as well as deoxidizing effects. Firstly, magnesium improves the recovery of zirconium probably because of its deoxidizing effect together with its apparent ability to form a solid solution with zirconium. Secondly, unlike any other known alloying addition to copper-zirconium alloys, magnesium has the remarkable synergistic effect with zirconium of increasing the strength of the alloy without decreasing the conductivity as much as any of the other alloying additions known to the art. Thirdly, magnesium improves the casting characteristics of copper-zirconium and copper-zirconium-chromium alloys. For example, it has been observed that magnesium inhibits grain growth at the solution annealing temperature. Furthermore, magnesium improves the fluidity as well as probably lowering the oxidation rate as evidenced by differences in scale formation. That is, copper-zirconium alloys and copper-zirconium-chromium without magnesium form a thick black oxide while the same alloys with appropriate amounts of magnesium copresent, as hereinbefore set forth, form the much thinner and more desirable red oxide. Fourthly, magnesium, when used in the aforestated ranges, permits the use of the inexpensive grades of copper, e.g., tough pitch copper, when making the alloys of the present inventions, and these less pure grades of copper can be used without substantially sacrificing such desirable properties and/or characteristics as conductivity. And fifthly, magnesium in combination with zirconium (whether chromium is present or not) in the alloys of the present invention may permit alloy producers to use shaft furnace copper as it comes from the cathode melting furnaces as the starting material. In general, such copper is not usable as it comes from the furnace since it will not get a level set. In order to obtain a level set, shaft furnace copper (which contains about 50 p.p.m. of oxygen) is usually oxidized up to 200 to 400 p.p.m. of oxygen by running it through air. With magnesium, it is unnecessary to oxidize the shaft furnace copper prior to use.

Failure to adhere to the aforementioned magnesium ranges in the copper-zirconium and copper-zirconium-chromium alloys of the present invention results in poorer alloys. For example, if too much magnesium is used, e.g., more than about 0.06%, the conductivity and the ductility of the alloy fall off. On the other hand, if too little is used,

e.g., less than about 0.01%, the foregoing attributes of magnesium will not be realized. For example, the recovery of zirconium and chromium, if present, in the final alloy composition will materially decrease unless a high purity copper, e.g., OFHC brand copper, is used in making the alloy.

As was pointed out hereinbefore, the alloys of this invention may contain up to 1.2% chromium by weight. The addition of chromium to the copper-zirconium-magnesium alloys of the invention results in higher strengths, particularly at elevated temperatures, without detrimentally decreasing the conductivity for many important commercial applications. For example, the cold-worked and heat-treated alloys of this invention containing as little as 0.03% chromium have strengths which are at least 10%, e.g., 25%, higher than similar chromium-free alloys which have been subjected to the identical treatments. Furthermore, as the chromium is increased within the aforementioned range, still higher strengths are obtainable. Another important feature of the chromium-containing alloys of this invention is that they resist softening even after exposure to temperatures as high as 600° C. and higher. On the other hand, increasing the chromium content above 1.2% results in only slight or no appreciable improvement in the strength properties and/or characteristics of the alloys within the contemplation of this invention. Instead, alloys containing more than 1.2% chromium are expensive and tend to be more brittle and are characterized by having poorer fabricability and castability than those alloys containing less than 1.2% chromium. Advantageously, when chromium is present, it is present in amounts of 0.03% to 0.5% by weight of the alloy.

In carrying the invention into practice, particularly unexpected results are obtained when the alloys contain, in weight percentages, 0.01% to 0.03% zirconium, 0.02% to 0.04% magnesium, up to 0.5%, e.g., 0.03% to 0.5%, chromium with the balance, apart from the usual impurities and residual elements, copper provided that said copper initially contained less than 600 p.p.m., e.g., 500 p.p.m., of oxygen. Such alloys have a superior combination of physical, mechanical and/or metallurgical properties and/or characteristics in combination with being inexpensively producible. For example, at room temperature the alloys have an UTS of at least 60,000 p.s.i., a 0.1% offset yield strength (YS) of at least 58,000 p.s.i., a conductivity of at least 85% IACS together with adequate ductility in the 90% cold-worked condition. In addition, these alloys when subjected to a heat treatment for one hour at 400° C. exhibit a conductivity of at least 90% IACS which conductivity is not detrimentally affected even after submission of the alloy to a further heating to 450° C. for 5 minutes.

Alloys within the broad and advantageous ranges are resistant to softening whenever they are first subjected to cold-working operations. Advantageously, the alloys are cold-worked at least 40%, e.g., at least 50%, to obtain greater resistance to softening. More advantageously, they are cold-worked at least 75%. As those skilled in the art will readily appreciate, the softening temperature is a function of the amount of cold work, to wit, the lower the amount of cold work, the higher the softening temperature, and conversely. In any event, the softening temperature of the chromium-free alloys of this invention lies between 325° C. and 475° C. When chromium is present in the amounts heretofore mentioned, the sof ening temperature is between about 500° C. and 550° C.

The processing of the unique copper-zirconium-magnesium and copper-zirconium-magnesium-chromium alloys of this invention should be carried out using the special sequence of steps, under controlled conditions, as hereinafter more fully set forth. This novel process comprises melting copper containing, by weight, less than 600 p.p.m. of oxygen, e.g., electrolytic tough pitch (ETP) copper, and then adding the alloying ingredients zirconium and magnesium. The melting of the copper can be carried out in air, under a protective cover or in a vacuum. It is advantageous, particularly when using tough pitch or other relatively high-oxygen containing coppers, to add the magnesium before or simultaneously with the zirconium and any chromium to be added in order to minimize zirconium and chromium losses. If the zirconium or zirconium and chromium are added prior to the magnesium, the zirconium and/or chromium losses can be as high as 70%. On the other hand, the simultaneous or earlier addition of magnesium to the melt can lower the zirconium and/or chromium losses to only 20% or less. The melt, in which the proper sequencing of magnesium and zirconium or zirconium plus chromium has been carried out, is hereby estabilshed, i.e., all losses of alloying ingredients are accounted for, and the established melt contains, in weight percentages, 0.01% to 0.3%, e.g., 0.01% to 0.15%, zirconium, 0.01% to 0.06%, e.g., 0.01% to 0.04%, magnesium, up to 1.2% chromium with the balance initially copper containing less than 600 p.p.m. of oxygen. Advantageously, the established melt contains, by weight, 0.01% to 0.03% zirconium, 0.02% to 0.04% magnesium, up to 0.5% chromium with the balance being essentially all copper initially containing less than 600 p.p.m. of oxygen. The established melt is then cast in air. As those skilled in the art will readily appreciate, whenever superior properties and/or characteristics are desired, the established melt may be cast through a flame curtain or in other non-oxidizing atmospheres such as an argon atmosphere.

It is advantageous, particularly because of the small amounts used, to add the magnesium and zirconium in their elemental form to the melt, e.g., as a sponge. Chromium, when included in the allow, is also added in elemental form. The disadvantage with master alloys is that they may be depleted somewhat or rich in alloying constituent from portion to portion and any such variance in alloying constituent could markedly upset the careful balance of ingredients needed in the alloys of the present invention. However, it is to be understood that master alloys can be used, e.g., the zirconium can be added as a copper-zirconium alloy nominally containing, by weight, 30% zirconium.

For the purpose of giving those skilled in the art a better understanding and a better appreciation of the invention the following illustrative examples are set forth:

## EXAMPLE I

Two alloys within the scope of the present invention were made by preparing melts of ETP copper in a graphite crucible and adding the alloying ingredients magnesium and zirconium at 1250° C. Both alloying ingredients were in the elemental form and the zirconium addition nominally contained about 0.5% hafnium by weight. The melts were held at 1250° C. for about 5 minutes before casting them into 1" diameter rods. Each casting was examined visually and the surfaces were found to be good. One of the castings (hereinafter preferred to as "Alloy A") was made from ETP copper containing, by weight, 0.05% oxygen and 0.0017% sulfur. The Alloy A casting contained, by weight, 0.014% zirconium and 0.02% magnesium with the balance substantially all copper. In the preparation of Alloy A, the magnesium was added prior to the zirconium.

The other casting (hereinafter referred to as "Alloy B") was made from ETP copper containing, by weight, 0.04% oxygen and 0.0018% sulfur. Alloy B contained, by weight, 0.015% zirconium, 0.04% magnesium with the balance substantially all copper. In the preparation of this alloy, the magnesium and the zirconium were added together.

Specimens of each alloy were then preheated in the ambient atmosphere to a temperature of about 982° C. and held at the temperature for about one hour. Subsequently, the preheated alloy specimens were hot rolled to 0.25" rods. The rods were then solution annealed at about 649° C. in the ambient atmosphere for 30 minutes. It is to be appreciated that the solution annealing temperature can

be varied from 600° C. to 950° C. and the time at temperature can be varied from a few minutes for wire to a few hours, e.g., 2 hours, for thicker sections as those skilled in the art will understand. The specimens were then water quenched and cold drawn to 0.079" diameter wire (90% cold work).

These specimens were tested to rupture and Alloy A was found to have an UTS of 65,500 p.s.i. and 0.1% offset YS of 63,000 while Alloy B had an UTS of 68,000 p.s.i. and a 0.1% offset YS of 65,000 p.s.i. The conductivity of each alloy was also measured and Alloy A had a conductivity of 89% IACS. The conductivity of Alloy B was found to be 86% IACS. Accordingly, it is clear that the alloys of this invention have useful mechanical properties and/or characteristics in the cold-worked condition. Furthermore, the foregoing tests clearly demonstrate that good conductivities are obtainable with the unique alloys of this invention even though a relatively impure copper, i.e., electrolytic tough pitch copper, was used in the making of the alloys.

## EXAMPLE II

In order to show the effects of exposure to elevated temperatures upon the alloys of the present invention, specimens of Alloy A and Alloy B were mechanically tested to rupture after heating the specimens for one hour under a charcoal blanket and quenching in water. In addition to the mechanical testing, specimens of each alloy were given conductivity tests. The results of these tests on specimens heated at different temperatures, i.e., 350°, 400° and 450° C., are set forth in Table I.

TABLE I

| Alloy Designation | Heating Temp., ° C. | U.T.S. (p.s.i.) | 0.1% Offset Y.S. (p.s.i.) | Conductivity (percent IACS) |
|---|---|---|---|---|
| A | 350 | 57,000 | 51,000 | 91 |
| B | 350 | 60,000 | 53,000 | 87 |
| A | 400 | 52,000 | 45,000 | 94 |
| B | 400 | 56,500 | 49,000 | 92 |
| A | 450 | 47,000 | 40,500 | 95 |
| B | 450 | 53,500 | 45,500 | 91 |

It is clear from Table I that the alloys of this invention have excellent properties and/or characteristics including conductivity after heating to various temperatures. As a comparison, an alloy (hereinafter referred to as Alloy Z) outside of the invention with regard to the zirconium content was prepared, hot and cold worked and tested in a manner identical to that for Alloys A and B. Alloy Z was prepared from ETP copper containing, by weight, 0.04% oxygen and 0.0015% sulfur and the final composition of the alloy, in weight percentages, was 0.056% magnesium with the balance essentially copper. This alloy after heating at 450° C. for one hour had an UTS of only 36,000 p.s.i. and a very low 0.1% offset YS of 10,500 p.s.i. Another copper alloy (Alloy Y) outside the scope of the invention, i.e., one containing 0.008% chromium, was similarly prepared from ETP copper and it was tested in the same manner as Alloys A, B and Z. Alloy Y, which was heated for one hour at 450° C., exhibited an UTS of only 12,000 even though it had strengths, in the 90% cold-worked condition, comparable to Alloys A and B in the cold-worked condition. Additionally, Alloys Y and Z exhibited conductivities substantially equivalent to the conductivities exhibited by Alloys A and B. Accordingly, it is clear that efforts to improve prior art copper-base alloys by certain additions were not entirely successful. For example, while Alloys Y and Z have good mechanical properties and/or characteristics in the as-worked condition and good conductivities, their strengths after exposure to elevated temperatures are considerably less than the alloys coming within the scope of the present invention.

## EXAMPLE III

To demonstrate the resultant effects of varying the sequencing of inoculating with zirconium and magnesium, a casting was prepared from ETP copper containing, by weight, 0.044% oxygen and 0.0017% sulfur in the same manner as for Alloys A and B except that zirconium was added to the copper melt prior to the magnesium addition. 0.079" specimens (90% cold worked) of this alloy containing, by weight, 0.012% zirconium, 0.02% magnesium with the balance essentially all copper were processed and hot rolled in the same manner as for Alloys A and B. All of the specimens that were heated were heated for one hour and water-quenched. The results of testing this alloy (hereinafter referred to as "Alloy X") are shown in Table II.

TABLE II

| Alloy Condition | U.T.S. (p.s.i.) | 0.1% Offset Y.S. (p.s.i.) | Conductivity (percent IACS) |
|---|---|---|---|
| Cold-Worked (C.W.) | 65,000 | 63,000 | 89 |
| C.W. and Heated at 350° C. | 55,000 | 49,000 | 91 |
| C.W. and Heated at 400° C. | 46,000 | 36,000 | 94 |
| C.W. and Heated at 450° C. | 37,500 | 20,500 | 92 |

It is manifest from Table II that the properties of Alloy X, having the zirconium added prior to the magnesium, had a substantial deterioration in its mechanical properties at the higher temperatures. As a matter of fact, after heating at 450° C. for one hour, Alloy X had a YS which was only about 50% of the YS of either Alloy A or B which alloys were heated at the same temperature and for the same length of time.

As was pointed out hereinbefore, there is a demand for a low cost copper alloy which will retain an UTS of 50,000 to 60,000 p.s.i. and a conductivity of at least 80% IACS after exposure to a temperature of 425° C. for 3 minutes. One use for such an alloy is its employment as the structural material for heat transfer fins for automobile and other vehicle radiators as exemplified by the radiator assembly depicted in the drawing. Referring now thereto, the drawing is a perspective view, partially broken, of a typical fin and tube type radiator assembly **10** having a plurality of fins or heat transfer surfaces **12** and tubes or water passages **14**. Between the fins are cooling air passages **16**. The fins **12** are joined to the tubes **14** by soldering, e.g., in a furnace, at the junctures **18**. As those skilled in the art will readily understand, the radiator assembly **10** is also provided with a head sheet and a bottom sheet as well as tank covers (not shown).

The reason for the strength requirements stems from the amount of handling, particularly during assembly and installation, to which the apparatus is subjected coupled with a requirement that the fins be quite thin. Being so thin, they must be strong enough to resist the multiple stresses to which they are subjected during fabrication and installation. In addition, the strength as well as the conductivity requirement take into effect the temperature at which the soldering operation is conducted.

To illustrate the utility of the alloys of the present invention for such heat transfer surfaces, the following example is set forth:

## EXAMPLE IV

Specimens of Alloys A and B were mechanically tested to rupture in the (a) cold-worked condition and (b) cold-worked and heated conditions as hereinbefore set forth. All heating was conducted at the temperature hereinafter indicated for one hour followed by a water quench. In each case, the specimens were in the 90% cold-worked condition prior to heating. All specimens, including those only cold-worked, were then subjected to a temperature of 450° C. for 5 minutes before testing. In addition to the mechanical tests, conductivity tests were also conducted. The results of this testing are set forth in Table III.

TABLE III

| Alloy Designation | Alloy Condition | U.T.S. (p.s.i.) | 0.1% Offset Y.S. (p.s.i.) | Conductivity (percent IACS) |
|---|---|---|---|---|
| A | Cold-Worked (C.W.) | 56,000 | 50,500 | 93 |
| B | C.W. | 58,000 | 53,000 | 87 |
| A | C.W. and Heated at 350° C. | 55,000 | 48,000 | 92 |
| B | C.W. and Heated at 350° C. | 58,500 | 51,000 | 90 |
| A | C.W. and Heated at 400° C. | 51,500 | 43,500 | 94 |
| B | C.W. and Heated at 400° C. | 56,500 | 49,500 | 94 |
| A | C.W. and Heated at 450° C. | 49,000 | 40,000 | 94 |
| B | C.W. and Heated at 450° C. | 54,000 | 46,000 | 93 |

As noted from Table III, the alloys of these inventions have exceptional strengths and conductivities even when subjected to a heating and/or reheating step in excess of that demanded or desired. Thus, they are admirably suited for radiator fin applications. Alloys X, Y and Z, on the other hand, after exposure to a temperature of 400° C., for one hour, water quenching and reheating to 425° C. for 5 minutes, had strengths as measured by their UTS of 44,500, 35,500 and 36,500 p.s.i. and strengths, as measured by their YS, of only 34,000, 11,000 and 11,000 p.s.i., respectively.

## EXAMPLE V

In order to show the novel and desirable effects of additions of chromium to the alloys of this invention, three copper-zirconium-magnesium alloys containing chromium, i.e., Alloys C, D and E, were prepared in the same manner as Alloys A and B. All alloying ingredients were in elemental form and the chromium and zirconium additions were added after the magnesium inoculation of the copper melt. The chromium and zirconium losses are found to be less than 20%.

Alloy E was made from ETP copper containing 0.053% oxygen while Alloys C and D were prepared from high-purity copper containing less than 0.01% oxygen. These alloys had the compositions set forth in Table IV.

TABLE IV

| Alloy Designation | Copper, Percent | Zirconium, Percent | Magnesium, Percent | Chromium, Percent |
|---|---|---|---|---|
| C | Balance | 0.012 | 0.058 | 0.046 |
| D | do | 0.15 | 0.06 | 0.42 |
| E | do | 0.07 | 0.035 | 0.5 |

Each alloy was cast in air into 1" diameter rods and each was visually examined and the surfaces were found to be good. After a heat treatment as set forth in Example I, specimens of each alloy were hot rolled to 0.25" rod and solution annealed at about 649° C. for 30 minutes, water quenched and cold drawn to 0.079" wire (90% cold-worked). These specimens were tested to rupture in the cold-worked condition with the results set forth in Table V.

TABLE V

| | U.T.S. (p.s.i.) | 0.1% Offset Y.S. (p.s.i.) | Elongation in 2", percent |
|---|---|---|---|
| Alloy Designation: | | | |
| C | 67,000 | 64,000 | 5 |
| D | 73,000 | 69,000 | 4 |
| E | 67,000 | 65,000 | 4 |

Alloys C, D and E, each of which had been cold-worked 90%, were also subjected to heating at various temperatures for one hour and then tested to rupture with the results set forth in Table VI. In addition, Table VI also contains the results of measuring the conductivity of these alloys.

TABLE VI

| Alloy Designation | Heating Temp., ° C. | U.T.S. (p.s.i.) | 0.1% Offset Y.S. (p.s.i.) | Elongation in 2", percent | Conductivity, percent IACS |
|---|---|---|---|---|---|
| C | 500 | 65,000 | 57,000 | 9 | 83 |
| C | 600 | 48,000 | 35,000 | 19 | 88 |
| D | 500 | 82,000 | 75,000 | 12 | 76 |
| D | 600 | 65,000 | 55,000 | 12 | 84 |
| E | 500 | 79,000 | 73,000 | 11 | 80 |
| E | 600 | 64,000 | 55,000 | 12 | 86 |

From the foregoing Table VI, it is clear that, when chromium is added in amounts up to 1.2% to the copper-zirconium-magnesium alloys within the scope of the present invention, the alloys have greater retention of strength (better resistance to softening) accompanied by higher ductility after exposure to elevated temperatures, such as are encountered in brazing operations, than do the chromium-free alloys of this invention. In addition, the resistance to softening is achieved with very little sacrifice in conductivity.

The alloys of the present invention, by virtue of their excellent properties and/or characteristics are suitable for use in a number of important applications where high-strength coupled with good conductivity is a requirement as is the case for radiator fins. They may also be successfully employed in other heat-transfer applications, e.g., condensers, requiring good strength and conductivity after a high temperature joining operation particularly where costs are to be minimized. Another reason these high strength copper-zirconium-magnesium alloys are attractive is that they contain relatively small amounts of alloying ingredients, e.g., as low as 0.02 weight percent total. Even when chromium is present, the amounts of alloying ingredients may be as low as 0.05% total.

Although the present invention has been described in conjunction with preferred or advantageous embodiments, it is to be appreciated that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

What is claimed is:

1. A copper-zirconium alloy containing, by weight, 0.01% to 0.3% zirconium, 0.01% to 0.06% magnesium, 0.03% to 1.2% chromium with the balance essentially copper.

2. A copper-zirconium alloy containing, by weight, 0.01% to 0.3% zirconium, 0.01% to 0.04% magnesium, up to 1.2% chromium, with the balance essentially copper, wherein the copper is initially a copper containing less than 600 parts per million of oxygen and less than 0.015% residual phosphorus.

3. A copper-zirconium alloy as claimed in claim 2 wherein the zirconium content is 0.01% to 0.15%.

4. A copper-zirconium alloy as claimed in claim 2 wherein the chromium content is up to 0.8%.

5. A copper-zirconium alloy as claimed in claim 2 wherein the copper is initially tough pitch copper.

6. A copper-zirconium alloy as claimed in claim 2 wherein the chromium content is 0.03% to 0.5%.

7. A copper-zirconium alloy as claimed in claim 2 wherein the zirconium content is 0.01% to 0.03% and the magnesium content is 0.02% to 0.04%.

**References Cited**

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