United States Patent Office

3,330,653

Patented July 11, 1967

3,330,653

COPPER-ZIRCONIUM-VANADIUM ALLOYS

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No Drawing. Filed Feb. 12, 1965, Ser. No. 432,383
7 Claims. (Cl. 75—153)

ABSTRACT OF THE DISCLOSURE

High conductivity copper-base alloys having high strength at elevated temperatures, which alloys contain 0.003% to 1% zirconium, 0.005% to 0.1% vanadium with the balance substantially all copper.

The present invention relates to alloys and, more particularly, to copper base alloys having a unique combination of properties and characteristics.

Heretofore the art has endeavored to produce high conductivity materials having improved mechanical properties and characteristics at both room and elevated temperatures. As is well known, the materials having high electrical and thermal conductivity contain copper. However, as is also well known, alloying ingredients added to strengthen or harden copper or its alloys ordinarily cause a detrimental decrease in conductivity. Furthermore, while increasing quantities of alloying ingredients tend to increase strength, they also tend to worsen the electrical and thermal conductivity. Hence the art has been faced with very difficult and anomalous problems.

One of the better solutions to the aforementioned problems has been the development of the copper-zirconium family of alloys as described in U.S. Patent Nos. 2,842,438, 3,019,102 and 3,107,998. Each of these alloys presented a distinct, useful advance in an art where even small improvements are extremely difficult to achieve. For example, the copper-zirconium alloy has high electrical and thermal conductivity together with good strength and hardness at temperatures as high as 500° C.

An arsenic addition, e.g., 0.1% to 0.5%, to the copper-zirconium alloy system provided the art with an alloy having improved room temperature properties and characteristics which were attained without disadvantageously affecting the other useful properties and characteristics. On the other hand, a hafnium addition, e.g., 0.1% to 1.2%, to the copper-zirconium system proved to be an advance in a still different direction. For instance, the hafnium-containing alloys have better mechanical properties and characteristics at 400° C. than do either the copper-zirconium or coper-zirconium-arsenic alloys.

Despite the foregoing advances and improvements, the need for materials possessing still better physical and mechanical properties and characteristics, particularly at elevated temperatures, has persisted. This is due to the progressively increasing requirements being imposed upon structural components for various electrical and electronic applications. Although attempts have been made to provide such a material, 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 copper-base alloys having high elevated-temperature strength together with excellent thermal and electrical conductivity may now be economically produced.

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

Another object of this invention is to provide novel copper alloys having improved age-hardening characteristics.

The invention also contemplates new, high conductivity copper alloys having good elevated temperature properties and/or characteristics.

It is a further object of the invention to provide improved copper alloys having relatively small amounts of alloying ingredients.

Still another object contemplated by this invention is the provision of electrical and electronic components having useful strengths at elevated temperatures.

One of the other objects of this invention contemplates the provision of copper alloys having a unique combination of ingredients in special proportions, which alloys are characterized by markedly improved elevated temperature properties and/or characteristics.

It is another object of the invention to provide high conductivity, high strength copper-base alloys having good casting characteristics.

A further object of the present invention is to provide a special process for hardening copper-base alloys without materially diminishing other valuable properties and/or characteristics of such alloys.

A still further object is the provision of a novel process for making the copper-base alloys of this invention.

Other objects and advantages will become apparent from the following description:

Generally speaking, the present invention contemplates the production of unique copper-zirconium alloys having high electrical and thermal conductivity together with unexpectedly good strengths and hardnesses at temperatures in excess of 500° C., e.g., 600° C. The copper alloys of this invention contain, in weight percentages, 0.005% to 0.1% vanadium and 0.003% to 1%, e.g., 0.01% to 0.3%, zirconium. 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. Thus, the 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. In addition to vanadium and zirconium in the amounts heretofore set forth, the alloys of this invention also contain copper which makes up the balance of the alloys aside from the usual impurities and residual deoxidizers.

It is essential that the copper employed in this invention be of high purity and be substantially oxygen-free. Although any chemically deoxidized copper such as phosphorus or lithium-deoxidized copper is generally satisfactory for use in making the alloy, it is advantageous to use copper which is substantially oxygen-free without requiring treatment with any of the conventional deoxidants. Cathode copper is accordingly particularly suitable as is copper which has been produced in a reducing atmosphere such as OFHC brand copper (which is 99.99% pure), copper prepared in an inert atmosphere, under a charcoal cover, or in a vacuum.

The alloys of this invention containing the aforementioned ingredients (copper, zirconium and vanadium) in the aforementioned proportioned amounts are characterized by a high recrystallization temperature and resistance to grain growth at elevated temperatures. In this connection, it appears that incipient grain growth occurs between about 550° C. and 600° C. These alloys are further beneficially characterized by having good castability and fabricability under usual operating procedures.

As was stated hereinbefore, the alloys according to this invention contain copper, zirconium and vanadium in specially related and controlled amounts and each of these elements in combination with each of the other two ingredients plays an important role in controlling the properties and/or characteristics of the alloys. For example, the zirconium content is in the range of 0.003% to 1%, e.g., 0.01% to 0.3%, by weight of the alloy. The inclusion of zirconium in the amounts specified in the copper alloys of this invention contributes significantly to the tensile strength when appropriate amounts of vanadium are copresent. Accordingly, if too little zirconium is present (less than 0.003%), the strength of the alloy detrimentally decreases. Advantageously, at least 0.01% zirconium is present since its contribution to the strength of the alloy is greatly enhanced. Zirconium appears to have at least one other important function, i.e., it appears that zirconium affords some assistance in increasing the solubility of vanadium in the copper alloys of this invention. Despite its attributes, the maximum amounts of zirconium must also be controlled in order to attain a better combination of properties and characteristics such as workability, strength, conductivity, etc. Thus, the amount of zirconium present should not exceed about 1%, and, where maximum conductivity is an important design factor, the amount present should be less than about 0.3% and, advantageously, less than about 0.15%.

Vanadium should be present in amounts of 0.005% to 0.1%, e.g., 0.01% to 0.1%, by weight of the alloy, since it has a synergistic effect with zirconium and copper in producing high conductivity alloys having excellent elevated temperature strengths and hardnesses. If less than 0.005% is present, there is little or no perceptible improvement in the elevated temperature properties of the copper-zirconium alloys. If more than 0.1% vanadium is present, inclusions (which may possibly be vanadium carbide or some copper-zirconium-vanadium complex) are formed which substantially impair the workability of the alloy. Advantageously, the upper portion of the vanadium range is 0.05% since only minimal improvement can be expected with further vanadium additions. More advantageously, the vanadium added is at least 99.5% pure with the remainder predominately iron. However, as those skilled in the art will appreciate, a ferro-vanadium alloy nominally containing 90% vanadium and 10% iron may be used in producing the alloys of this invention adapted to be used in less stringent applications.

In carrying the invention into practice, particularly unexpected results are obtained when the alloys contain, in weight percentages, 0.01% to 0.15% zirconium, 0.01% to 0.05% vanadium and the balance, apart from less than 0.001% of impurities and residual deoxidizers, initially oxygen-free copper. Such alloys have a superior combination of physical, mechanical and/or metallurgical properties and/or characteristics. For example, at room temperature the alloys have an ultimate tensile strengths (UTS) of at least 60,000 pounds per square inch (p.s.i.) and a 0.1% offset yield strength (YS) of at least 55,000 p.s.i. in the 90% cold-worked condition. In addition, after subjecting to a working and heat-treating process, including an ageing treatment at 600° C., which process is more fully described hereinafter, the 90% cold-worked alloys have a room-temperature UTS of at least 48,000 p.s.i. and a conductivity in relation to the International Annealed Copper Standard (IACS) of at least 92%.

Alloys within the broad and advantageous ranges are age-hardenable whenever they are first subjected to cold-working. Advantageously, the alloys are cold-worked at least 40%, i.e., at least 50%, to obtain greater age-hardening response. The alloys so prepared have a strain-lattice structure which apparently contributes to the useful elevated temperature properties and characteristics of the alloys. The ageing temperatures lie between 350° C. and 650° C. The ageing time is about 30 minutes to 3 hours and, advantageously, one hour. Better results are achieved when the age-hardening heat treatment is conducted at temperatures between 450° C. and 600° C. and, more advantageously, between 500° C. and 600° C. and held at that temperature for one hour. When heat-treated in this

manner, the alloys of this invention have conductivities as high as 94% IACS at room temperature and strengths (UTS) as high as 27,000 p.s.i. when tested at the high temperature of 600° C. after holding at that temperature for about one hour.

In order to efficiently produce the alloys within the scope of the invention and to minimize zirconium and vanadium losses due to their reactivity, a special sequence of steps requiring specially controlled process conditions is used. This novel process comprises melting high-purity copper and then adding vanadium to the melt (before adding zirconium) at a temperature between 1450° C. and 1600° C. If, on the other hand, zirconium is added prior to, or at the same time as, vanadium, there are considerable losses. Accordingly, when zirconium is added prior to the vanadium, zirconium losses may be as high as 40%. In contradistinction thereto, when vanadium is added prior to zirconium under appropriate conditions, there are substantially no losses. In order to insure complete alloying of the vanadium, the melt is held at that temperature for at least 5 minutes but preferably not more than 30 minutes, e.g., 10 minutes, in order to minimize vanadium losses. Before adding zirconium (which is advantageously in the form of zirconium sponge although other forms may be used such as a copper-zirconium addition alloy nominally containing 30% zirconium), the temperature of the melt is reduced to between 1200° C. and 1325° C. The melt is thereby established, i.e., all losses of alloying ingredients are accounted for, and the established melt contains, by weight, 0.003% to 1% zirconium, 0.005% to 0.1% vanadium and the balance copper. Advantageously, the established melt contains, by weight, 0.01% to 0.15% zirconium, 0.01% to 0.05% vanadium and the balance being essentially copper. The temperature is then raised to approximately 1350° to 1400° C. and held thereat for about 5 minutes to 30 minutes before casting at a temperature between 1250° and 1350° C. in oder to insure substantially complete alloying without unnecessary losses. Castings produced in accordance with the aforedescribed process are sound and have good surfaces.

For the purpose of giving those skilled in the art a better understanding of the invention and a better appreciation of its advantages the following examples are set forth. In these examples, a series of copper castings having varying zirconium and vanadium contents were prepared. OFHC brand copper of 99.99% purity was melted in a crucible and the temperature of melt was brought to 1500° C. Vanadium rods of 99.5% purity (balance mostly iron) were then added to the melt. The temperature of the melt was maintained at 1500° C. for seven minutes before lowering to 1300° C. Zirconium sponge, nominally containing 0.5% hafnium, was then added and the temperature of the melt was raised 50° C. to 1350° C. and held at the temperature for seven minutes. After lowering the melt temperature to 1300° C., the alloys were cost into 1" diameter rods. The compositions of these alloys in weight percentages are set forth in Table I.

TABLE I

Alloy Designation	Zirconium (percent)	Vanadium (percent)	Copper (percent)
1	0.04	0.03	Balance.
2	0.08	0.05	Do.
3	0.13	0.05	Do.
4	0.16	0.028	Do.
5	0.16	0.037	Do.
6	0.42	0.05	Do.
7	0.69	0.04	Do.

The castings were hot-rolled to 0.25" diameter rods at 950° C. and then solution annealed at 1000° C. for one hour under charcoal. As those skilled in the art will readily appreciate, the solution annealing temperatures can be varied between 900° C. and 1000° C. and the time at temperature can be varied between 20 minutes and 2 hours. The solution-annealed 0.25″-rods were then quenched in water. After quenching, the rods were cold-worked 90% to 0.079″ diameter rods and mechanically tested to rupture at room temperature. The results of these tests are set forth in Table II.

TABLE II

Alloy Designation	UTS (p.s.i.)	0.1% Offset YS (p.s.i.)	Elongation in 2″ (percent)
1	61,000	56,000	4
2	63,000	58,000	3
3	66,000	61,000	3
4	66,000	(1)	3
5	69,000	(1)	3
6	73,000	68,000	3
7	74,000	69,000	2

[1] Not tested.

From the foregoing Table II, it is clear that the alloys of this invention have useful mechanical properties and/or characteristics in the unaged but cold-worked condition.

To illustrate the effects of ageing, alloys 1, 2, 3, 6 and 7 were aged at various temperatures for one hour under charcoal, water quenched and then tested. The results of these tests are set forth in Table III.

TABLE III

Alloy Designation	Aging Temp. (° C.)	UTS (p.s.i.)	0.1% Offset YS (p.s.i.)	Elongation in 2″ (percent)	Conductivity (percent IACS)
1	350	61,000	54,000	7	73
2	350	68,000	59,000	9	69
3	350	71,000	62,000	8	65
6	350	77,000	69,000	8	64
7	350	79,000	71,000	5	64
1	450	62,000	55,000	6	85
2	450	67,000	58,000	8	83
3	450	71,000	62,000	7	80
6	450	76,000	68,000	9	78
7	450	77,000	69,000	9	77
1	550	59,000	51,000	6	93
2	550	62,000	54,000	7	93
3	550	63,000	56,000	8	93
6	550	67,000	59,000	7	91
7	550	67,000	59,000	6	90
1	600	54,000	46,000	8	94
2	600	57,000	48,000	8	94
3	600	58,000	49,000	9	92
6	600	54,000	41,000	14	92
7	600	49,000	32,000	20	92

It is clear from Table III that the alloys of this invention have excellent properties including conductivity after ageing particularly at the higher ageing temperatures. As a comparison, an alloy outside of the invention with regard to the zirconium content was prepared and tested in a manner identical to that for alloys 1 through 7. This alloy contained 0.027% vanadium, less than 0.001% zirconium with the balance essentially all copper. After ageing at 550° C. for one hour, it was tested and found to have a UTS of only 55,000 p.s.i. and a YS of only 47,000 p.s.i. Another copper alloy outside the scope of the invention, i.e., one containing 0.2% titanium, balance copper, was similarly tested. This alloy was cold-worked 84% and aged at 600° C. in the manner heretofore set forth for alloys 1 through 7. While it had fair room-temperature strength a UTS of 38,000 p.s.i.), its conductivity was only 38% IACS. Thus, it is clear that efforts to improve prior art copper-base alloys by certain additions were not entirely successful. Indeed, if such a prior art alloy were improved as to strength, it was improved only at the expense of another desirable property, e.g., conductivity, which is in direct contradistinction to the alloys coming within the teachings of this invention.

To demonstrate the unexpected elevated temperature properties of the alloys of this invention, specimens of certain of the designated alloy compositions having a diameter of one inch within the scope of the invention were reduced in area by different amounts of cold work and aged at 400° C. one hour under charcoal and water quenched. These specimens were brought to different elevated temperatures and were mechanically tested to rupture after holding at the elevated temperature for one hour. These results are set forth in Table IV.

TABLE IV

Alloy Designation	Cold-Work (percent)	Test Temperature (° C.)	UTS (p.s.i.)	0.1% Offset YS (p.s.i.)	Elongation in 2″ (percent)
2	85	400	50,000	42,000	7
2	85	450	42,000	38,000	6
2	85	500	42,000	38,000	6
2	85	600	27,000	24,000	5
4	90	600	25,000	20,000	8
5	90	600	31,000	23,000	6
5	54	500	38,000	37,000	6
4	54	600	26,000	26,000	5
5	54	600	27,000	27,000	5

These data of Table IV manifestly indicate the exceptional elevated temperature properties and characteristics of the alloys of this invention even at temperatures as high as 600° C. at which temperature most of the prior art high conductivity alloys are dead soft. Of particular interest is alloy 2 which had no decrease in properties whatsoever even though the temperature was raised from 450° C. to 500° C.

The alloys of the present invention, by virtue of their excellent properties and/or characteristics at temperatures up to 600° C. in conjunction with conductivities up to 94% IACS, find use in a variety of important applications. For example, the wrought alloys can be used in electric and electronic structural applications e.g., for the manufacture of klystron tubes, requiring retention of strength at temperatures in excess of 500° C. In many such cases, the structural component has to be brazed or otherwise joined to another structural component using a joining method or alloy that causes a weakness in the overall system. With the advent of the alloys of this invention, it is now possible to use brazing alloys having higher melting temperatures (and consequently higher strengths) without deteriorating the properties and/or characteristics of the high conductivity, structural copper-zirconium-vanadium alloy. In addition, the alloys of the present invention can be used in structural applications where high thermal conductivity in combination with good strength at temperatures up to 600° C. is an important design factor. One important application of this type is using the alloy in rocket nozzles. The alloys contemplated herein are also commercially attractive since they contain relatively small amounts of alloying ingredients, e.g., as low as 0.01 weight percent total or even less.

Although the present invention has been described in conjunction with preferred 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 base alloy having high conductivity in combination with excellent strengths at temperatures up to 600° C. which alloy contains, by weight, 0.003% to 1% zirconium, 0.005% to 0.1% vanadium and the balance, aside from impurities and residual deoxidizers, substantially all copper.

2. A copper base alloy having high conductivity in combination with excellent strengths at temperatures up to 600° C. which alloy contains, by weight, 0.01% to 0.3% zirconium, 0.01% to 0.1% vanadium and the balance, aside from impurities and residual deoxidizers in amounts of less than 0.001%, substantially all copper.

3. A copper base alloy having high conductivitiy in combination with excellent strengths at temperatures up to 600° C. which alloy contains, by weight, 0.003% to

1% zirconium, 0.01% to 0.1% vanadium and the balance initially-oxygen-free copper.

4. A copper base alloy having high conductivity in combination with excellent strengths at temperatures up to 600° C. which alloy contains, by weight, 0.01% to 0.3% zirconium, 0.005% to 0.1% vanadium and the balance initially-oxygen-free copper.

5. A copper base alloy containing, by weight, 0.01% to 0.3% zirconium, 0.01% to 0.05% vanadium with the balance high-purity copper.

6. A ternary copper base alloy containing, by weight, 0.01% to 0.15% zirconium, 0.01% to 0.05% vanadium and the balance high-purity copper.

7. An alloy according to claim 6 in which the vanadium has a purity of at least 99.5%.

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