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COPPER-ZIRCONIUM-HAFNIUM ALLOYS

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This invention relates to copper base alloys and more particularly to ternary alloys containing copper, zirconium and hafnium. The object of the invention is to provide an improved copper base alloy having superior strength and ductility properties at elevated temperatures.

Briefly stated, the alloys of the present invention are age hardenable and contain from 0.02 to 0.15% by weight of zirconium, 0.1 to 1.2% hafnium, the balance being copper which is preferably initially oxygen free though any deoxidized copper may be used in making the alloy. With appropriate processing as will be hereafter described, the alloys are suitable as electrical and thermal conductor material useful in a variety of applications as, for example, the making of commutator segments, contactor plates and wires, welding tips and wheels, and the like.

In making the alloys of the present invention, it is essential that oxygen-free copper be used. Although any chemically deoxidized copper such as phosphorus or lithium deoxidized copper is generally satisfactory for use in making the alloy, it is preferred to use copper which is substantially oxygen free without requiring treatment with any of the conventional chemical deoxidants. Cathode copper is accordingly particularly suitable as is copper which has been produced in a reducing atmosphere such as OFHC brand copper, copper prepared in an inert atmosphere, under charcoal cover, or in a vacuum.

The alloys are made following conventional alloying practices utilizing a protective gas cover during melting of the copper, alloying and casting operations. By way of illustration, the copper is first melted under argon or other suitable protective gas cover in an alloying furnace such as an Ajax induction furnace using a graphite crucible. With the copper melt at a temperature of from 1250 to 1300° C., the alloying ingredients are added either successively or simultaneously using appropriate amounts of zirconium and hafnium in any suitable form for alloying purposes. Zirconium and hafnium as metal, sponge and master alloys of the respective metals with copper are illustrative of some of the materials that may be used in making the ternary alloys of the present invention. After alloying, the melt is held at temperature for a few minutes following which the alloy is cast into graphite or any other suitable molds. No difficulty is experienced in producing sound castings.

Although alloys containing from 0.02 to 0.15% zirconium and from 0.1 to 1.2% hafnium, balance copper with its incidental impurities provide new and useful alloys possessing generally improved properties, it has been found that best results are obtained when the alloy contains from 0.10 to 0.15% zirconium and from 0.5 to 0.9% hafnium, balance copper.

After the casting has been prepared according to the alloying procedure as described above, the material is amendable to extensive hot working as by hot rolling, extruding or forging upon preheating the alloy to about 980° C. in a charcoal bed. Heat treatment thereof is carried out by solution annealing in a non-oxidizing atmosphere at a temperature of from about 900° to 980° C. and preferably at about 950 to 965° C. for a period of from a few minutes to about an hour depending upon the size of the casting. The solution annealed and quenched alloy may then be aged suitably at temperatures of from 300 to 600° C. and preferably between 400 and 550° C. with or without cold working of the material between the solution annealing and precipitation hardening or aging steps. In general, maximum properties are developed with an aging period of from one to two hours with best results being obtained by aging at from 500 to 550° C. when the material has not been cold worked and at temperatures of from 400 to 500 and preferably at about 450° C. when the alloy has been subjected to intermediate cold working.

Representative alloys of the present invention are listed in Table 1. The properties shown for the various alloys referred to therein were determined on unaged material after one inch diameter castings were hot rolled to 0.25 inch rods, said rods being solution annealed at 980° C. for one hour, quenched in water and then cold drawn to 0.081 inch diameter wire with 90% reduction.

TABLE 1

Room temperature properties of Cu-Zr-Hf *alloys (before aging)*

Casting No.	Composition		Tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elongation percent (in 2 inches)	Electrical conductivity (percent I.A.C.S.)
	Percent Zr	Percent Hf				
1	0.03	0.04	59,000	54,000	4.0	75.0
2	0.04	0.11	61,000	55,000	4.0	70.0
3	0.03	0.15	60,000	55,000	4.0	64.0
4	0.03	0.28	64,000	59,000	3.0	53.0
5	0.04	0.66	70,000	66,000	2.4	40.0
6	0.03	1.16	75,000	68,000	2.4	34.0
7	0.14	0.07	63,000	58,000	4.0	57.0
8	0.09	0.09	60,000	53,000	4.0	65.0
9	0.12	0.18	63,000	57,000	4.0	56.0
10	0.11	0.32	68,000	62,000	3.0	47.0
11	0.11	0.63	71,000	63,000	4.0	41.0
12	0.10	1.15	74,000	66,000	4.0	38.0

The same alloys upon being aged at 400° C. for one hour possessed the properties shown in Table 2.

TABLE 2

Room temperature properties of Cu-Zr-Hf *alloys (after aging)*

Casting No.	Composition		Tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elongation percent (in 2 inches)	Electrical conductivity (percent I.A.C.S.)
	Percent Zr	Percent Hf				
1	0.03	0.04	62,000	53,000	10.0	87.0
2	0.04	0.11	63,000	53,000	10.0	84.0
3	0.03	0.15	64,000	55,000	11.0	80.0
4	0.03	0.28	70,000	61,000	12.0	73.0
5	0.04	0.66	80,000	72,000	12.0	63.0
6	0.03	1.16	88,000	80,000	10.0	56.0
7	0.14	0.07	68,000	60,000	13.0	80.0
8	0.09	0.09	63,000	55,000	10.0	81.0
9	0.12	0.18	68,000	59,000	12.0	76.0
10	0.11	0.32	74,000	65,000	12.0	70.0
11	0.11	0.63	80,000	72,000	12.0	66.0
12	0.10	1.15	83,000	77,000	10.0	61.0

The effect of varying the aging temperature on the properties of two representative alloys is shown by the

data in Table 3. The alloys having the composition 0.04% Zr, 0.66% Hf, balance Cu (Alloy "A") and 0.11% Zr, 0.63% Hf, balance Cu (Alloy "B") were processed by solution annealing at 965° C. for one hour, quenching, cold drawing to 0.081 inch diameter wire with 90% reduction after which the material was aged as stated in Table 3.

TABLE 3

Effect of temperature on cold worked Cu-Zr-Hf *alloy wire*

Alloy	Treatment	Tensile Strength (p.s.i.)	Yield strength (p.s.i.)	Elongation percent (in 2 inches)
A	Cold worked condition	70,000	66,000	2.4
A	Heated at 300° C., 1 hour	71,000	65,000	8.0
A	Heated at 350° C., 1 hour	76,500	68,000	11.0
A	Heated at 400° C., 1 hour	80,000	72,000	9.0
A	Heated at 450° C., 1 hour	77,000	72,000	9.0
A	Heated at 500° C., 1 hour	71,000	64,000	9.0
A	Heated at 550° C., 1 hour	62,000	55,000	9.0
A	Heated at 600° C., 1 hour	53,400	42,000	15.0
A	Heated at 650° C., 1 hour	42,000	21,000	28.0
A	Heated at 700° C., 1 hour	38,500	14,000	34.0
B	Cold worked condition	71,000	63,000	4.0
B	Heated at 300° C., 1 hour	75.300	69,200	9.2
B	Heated at 350° C., 1 hour	78,800	72,000	13.0
B	Heated at 400° C., 1 hour	80,000	73,000	12.0
B	Heated at 450° C., 1 hour	79,000	73,000	8.8
B	Heated at 500° C., 1 hour	71,500	64,400	8.8
B	Heated at 550° C., 1 hour	63,500	54,800	11.0
B	Heated at 600° C., 1 hour	49,500	36,000	17.6
B	Heated at 650° C., 1 hour	40,500	18,000	33.0
B	Heated at 700° C., 1 hour	39,500	17,000	26.0

As will be noted from Table 1, the electrical conductivity of the alloy containing 0.11% Zr, 0.63% Hf in the cold worked and unaged condition is 41% I.A.C.S. After aging for 1 hour at temperatures of 450 and 500° C., however, the electrical conductivity of the same alloy rose to values of 80 and 84% I.A.C.S. respectively.

The effect of aging at different temperatures after solution annealing the alloy is seen from the data presented in Table 4. In these tests the alloys containing 0.04% Zr, 0.66% Hf, balance copper (Alloy "A") and 0.11% Zr, 0.63% Hf, balance copper (Alloy "B") were processed into 0.178 inch diameter cold drawn wire, solution annealed at 965° C. for one hour, quenched and then heated for one hour at the specified temperatures.

TABLE 4

Properties of solution annealed and aged Cu-Zr-Hf *alloys*

Treatment	Tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elongation percent (in 2 inches)	Electrical conductivity (percent I.A.C.S.)
ALLOY "A"				
Sol. anneal 1 hr. at 965° C. quench	34,000	5,600	40.0	41.7
Sol. anneal-age 1 hr. at 400° C.	35,000	7,000	40.0	43.0
Sol. anneal-age 1 hr. at 450° C.	33,000	7,000	40.0	44.0
Sol. anneal-age 1 hr. at 500° C.	33,000	8,000	43.0	43.0
Sol. anneal-age 1 hr. at 550° C.	39,000	19,000	34.0	83.0
Sol. anneal-age 1 hr. at 600° C.	35,000	15,000	35.0	82.0
ALLOY "B"				
Sol. anneal 1 hr. at 965° C. quench	35,000	6,000	40.0	45.0
Sol. anneal-age 1 hr. at 400° C.	35,000	8,000	30.0	48.0
Sol. anneal-age 1 hr. at 450° C.	38,000	8,000	38.0	47.0
Sol. anneal-age 1 hr. at 500° C.	34,000	11,000	38.0	47.0
Sol. anneal-age 1 hr. at 550° C.	41,000	20,000	40.0	86.0
Sol. anneal-age 1 hr. at 600° C.	38,000	14,000	38.0	85.0

It will be noted from the above data that maximum precipitation hardening occurs at 550° C. This is about 50° C. higher than other copper base alloys and indicates the superior high temperature properties of the present alloys. It will also be noted that the properties of the higher zirconium content alloy are slightly superior to the alloy containing 0.04% Zr.

The effect of variation in the extent of cold working of a representative alloy containing 0.11% Zr, 0.63% Hf, balance copper, is shown in Table 5. The processing steps comprised first solution annealing the alloy at 965° C., cold working by drawing to the reduction indicated and finally aging at 400° C.

TABLE 5

Properties of solution annealed, cold worked and aged Cu-Zr-Hf *alloy*

Treatment	Tensile strength (p.s.i.)	Yield strength (p.s.i.)	Elong. (percent in 2 inches)	Elec. cond. (percent, I.A.C.S.)
Sol. anneal 1 hr. at 965° C.	35,000	6,000	40.0	45.0
Sol. anneal-age 1 hr. at 550° C.	41,000	17,000	40.0	86.0
Sol. anneal cold work 25%	51,000	48,000	5.0	45.0
Sol. anneal cold work 55%	62,000	59,000	3.0	44.0
Sol. anneal cold work 75%	67,000	63,000	3.0	44.0
Sol. anneal cold work 90%	71,000	63,000	4.0	41.0
Sol. anneal-cold work 25%-age 2 hrs. at 400° C.	65,000	55,000	14.0	60.0
Sol. anneal-cold work 55%-age 2 hrs. at 400° C.	72,000	65,000	10.0	68.0
Sol. anneal-cold work 75%-age 2 hrs. at 400° C.	76,000	68,000	12.0	68.0
Sol. anneal-cold work 90%-age 2 hrs. at 400° C.	80,000	72,000	12.0	66.0

The alloy of maximum tensile strength of 80,000 p.s.i. with 12% elongation and 66% electrical conductivity is obtained upon cold drawing to a reduction of 90% prior to aging the cold worked material.

The superior high temperature properties of the alloys of the present invention are made readily apparent by comparison of the high temperature tensile and elongation properties thereof with other copper base alloys such as copper-zirconium and copper-chromium which materials are generally recognized as possessing superior high temperature tensile strength and ductility. The procedure used in making the comparison consisted of first aging the cold worked 0.081 inch diameter wire specimens of each of the alloys specified in Table 6 and allowing the specimens to cool to room temperature. The aged and cooled specimens were then reheated to 400° C., held at this temperature for one hour and tensile strength tests were run at a crosshead speed of 0.02 inch per minute. The results are summarized in Table 6.

TABLE 6

High temperature tensile properties

	Tensile strength (p.s.i.)	Elongation (percent in 10 inches)
Cu+0.04% Zr+0.66% Hf	60,800	6.0
Cu+0.11% Zr+0.63% Hf	61,400	10.0
Cu+0.65% Hf	57,600	4.0
Cu+0.15% Zr	50,000	2.0
Cu+0.31% Cr	44,000	1.0

It will be noted that both of the tested Cu-Zr-Hf alloys not only possess superior tensile strength and elongation properties at 400° C. compared with the designated Cu-Zr, Cu-Cr and Cu-Hf alloys but also that the significant improvement with respect to such high temperature properties is not obtainable with the use of either zirconium or hafnium as the sole alloying ingredient for copper.

It is apparent that many differing embodiments of this invention may be made without departing from the spirit and scope thereof and it is not intended to be limited thereby except as indicated in the appended claims.

What is claimed is:

1. An age hardenable copper base alloy containing from 0.02 to about 0.15% zirconium, from 0.1 to about 1.2% hafnium and the remainder oxygen-free copper.

2. An age hardenable copper base alloy containing from 0.04 to about 0.15% zirconium, 0.5 to about 1% hafnium, balance oxygen-free copper, said alloy being

characterized by superior high temperature tensile strength and ductility in the age hardened condition.

3. An homogeneous copper alloy consisting of from 0.1 to 0.15% zirconium, 0.5 to 0.9% hafnium, balance copper with incidental impurities normally associated therewith, said copper being oxygen-free prior to its being alloyed with said zirconium and hafnium.

4. An age hardenable copper-base alloy containing

from 0.02 to about 0.15% zirconium, 0.1 to about 1.2% hafnium and the remainder chemically deoxidized copper with incidental impurities normally associated therewith.

References Cited in the file of this patent

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