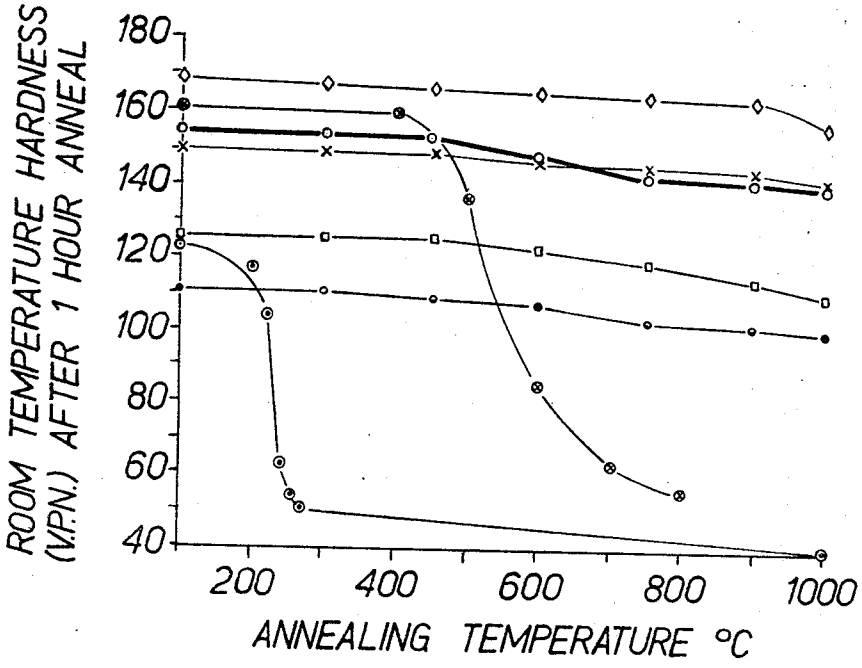
Aug. 25, 1970 D. H. ROBERTS 3,525,609

COPPER ALLOY MATERIAL

Filed Feb. 24, 1967



LEGEND

- D.S. Cu. – 0·25 w/o Ag 1·3 v/o Al_2O_3
- D.S. Cu. – 4 v/o Al_2O_3
- D.S. Cu. – 2·3 v/o Al_2O_3
- D.S. Cu. – 1·3 v/o Al_3O_3
- D.S. Cu. – 0·5 v/o Al_2O_3
- PURE Cu – FULLY HARDENED
- Cu. – 0·7 w/o Cr

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COPPER ALLOY MATERIAL

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U.S. Cl. 75—153 5 Claims

ABSTRACT OF THE DISCLOSURE

A dispersion strengthened copper alloy, and method of making same, comprising copper alloyed with silver, cadmium or zinc and strengthened by internally oxidized aluminium as dispersoid. The dispersion strengthened copper alloy consists of up to 1% by weight of a metal from the group consisting of silver, cadmium and zinc and copper constituting the balance of the free metal content together with 0.5% to 4.3% by volume of finely divided aluminium oxide dispersed throughout the alloy.

BACKGROUND OF THE INVENTION

Field of the invention

The importance of copper in the electrical field is acceepted without question because of its high electrical conductivity, relative abundance and favourable cost. However the pure metal is mechanically weak, particularly at elevated temperatures. Thus efforts have been made to develop copper materials which have improved strength compared with pure copper without significant loss of electrical conductivity.

DESCRIPTION OF THE PRIOR ART

One line of approach has been to seek copper alloys which exhibit this increased strength coupled with reasonable electrical conductivity. Two of the most successful copper alloys which have been developed are copper with 0.7% chromium and copper with 0.15% zirconium, which when fully heat treated can have electrical conductivities of 80% and 90% respectively as measured against the International Annealed Copper Standard (IACS). These alloys also have relatively high strength in the heat treated state, but they are limited in service to temperatures of about 400–450° C. because at higher temperatures rapid over-ageing of the structure tends to occur, with adverse effect on both physical and mechanical properties.

Another line of approach more recently examined has been to strengthen the copper by means of an inert refractory oxide, dispersed within it. Such material has been shown to possess high structural stability and strength at elevated temperatures together with good electrical conductivity.

Two main techniques have now become established for preparing these materials. The first involves the mechanical mixing of inert refractory oxide particles with copper powder, followed by compacting using standard powder metallurgical techniques and then extrusion. The second technique utilises the process known as internal oxidation. Here copper is alloyed with a small quantity of an easily oxidizable (solute) metal, for example, aluminium, silicon or beryllium, which forms an oxide with a much higher negative free energy of formation than that of the oxide of the solvent (copper). The powdered alloy is then treated under suitable conditions of time, temperature and partial pressure of oxygen to internally oxidize the

aluminium to alumina (Al_2O_3). The internally oxidized powder is compacted and extruded as for mechanically mixed powders.

Whereas both processes produce copper of increased strength particularly at elevated temperature, the internal oxidation process can produce copper containing a better dispersion of refractory oxide, which in turn results in greater thermal stability, strength and electrical conductivity.

It is also well known that increased strength at temperatures up to about 450° C., i.e. approximately one third of the absolute (° K.) melting point, is exhibited by many conventional copper alloys.

It would be expected however that the addition of a third metal to the starting alloy in the preparation of dispersion strengthened material using the internal oxidation process would be likely to adversely interfere with the oxidizing action, for example, by reducing the rate of diffusion of oxygen in copper, or that this action would adversely interfere with any beneficial results which the addition of such a third metal might otherwise have had in alloying with copper.

SUMMARY OF THE INVENTION

We have found, however, that by using aluminium as the internally oxidizable constituent and judiciously selecting the third metal with regard to its properties vis-a-vis those of copper and aluminium, it is possible to obtain by the internal oxidation technique a dispersion strengthened copper alloy (namely of copper and this third metal) which has significantly improved mechanical properties as compared to dispersion strengthened copper per se, while also having good electrical conductivity.

According to the present invention a dispersion strengthened copper alloy is obtained by internal oxidation of aluminium in a ternary alloy of copper with up to 1% by weight of aluminium and up to 1% by weight of one of the metals silver, cadmium and zinc.

These three metals, silver, cadmium and zinc, have relatively low (negative) free energies of oxide formation as compared with the aluminium, which therefore oxidizes preferentially. Moreover they do not form compounds with aluminium, so that the aluminium does not combine with them in a form unsuitable for oxidation. Consequently they have little or no effect on the internal oxidation process. Each of these three metals does, however, form a solid solution alloy with copper, with the result that the internally oxidized alloy exhibits the effects of both solid solution strengthening and dispersion strengthening of the copper, giving a resulting product which can have a higher strength at temperatures below one third of the absolute melting point (° K.) than a corresponding dispersion strengthened unalloyed copper matrix. Furthermore silver, cadmium and zinc have least effect on the electrical conductivity of copper when alloyed with it, so that the conductivity of the final product is good.

Silver is preferred as the third element of the initial ternary alloy, for the following reasons:

(1) Silver in copper (at least up to 1%) has the least effect of any metal in reducing the electrical conductivity below that of pure copper;

(2) Silver oxide has a very low (negative) free energy of formation, significantly lower than for cadmium and zinc: it is therefore least likely to oxidize with the aluminium during the oxidation treatment;

(3) Silver additions in copper not only have a solution strengthening effect but also increase the re-crystallisation temperature;

(4) It is well known that internally oxidized bulk metal displays intergranular brittleness due to the relatively high concentration of oxide that is formed in the

grain boundaries. In attempts to overcome this, internally oxidized binary alloy powder has been compacted and heavily deformed, usually by extrusion. While this has improved the overall dispersion of the oxide, the larger particles of oxide which now originate from the grain boundary regions of the polycrystalline powder often become aligned by the extrusion process in a way that can again result in low ductility, particularly at elevated temperature. With the present invention, it has been found that the presence of silver improves the dispersion of the aluminium oxide by reducing the concentration of aluminium atoms at the grain boundaries of the polycrystalline copper-silver alloy powder prior to internal oxidation. The reason for this is that, because the atomic radii of aluminium (1.43 A.) and silver (1.44 A.) are nearly the same, the aluminium and silver atoms compete almost equally in the copper for grain boundary sites, thereby reducing the natural concentration of aluminium atoms that would be found there and producing a more uniform dispersion of aluminium oxide within each powder particle during internal oxidation;

(5) Because of this improvement of oxide dispersion, the ductility of the internally oxidized alloy is also improved, particularly at elevated temperatures.

DESCRIPTION OF PREFERRED EMBODIMENTS

By way of example the following procedure was adopted for preparing a copper-silver (Cu-Ag) alloy dispersion strengthened (D.S.) with internally oxidized aluminium (Al_2O_3). The symbols $^w/_o$ and $^v/_o$ are used to indicate percentages by weight and volume respectively.

A ternary copper alloy of Cu-Al-Ag was prepared by melting a mixture of the three constituents in suitable proportions to give a Cu—0.25 $^w/_o$ Ag alloy containing 1.3 $^v/_o$ disseminated Al_2O_3 after internal oxidation. (1 $^w/_o$ Al in the ternary alloy would convert to about 4.3 $^v/_o$ Al_2O_3). Using available laboratory equipment, powder was formed from the melt by casting billets of the ternary alloy, heating them in hydrogen for 24 hours at 1000° C. for homogenisation, working them to wire, and then spraying the wire to powder using a metal spraying pistol. For commercial production of the powder other, more suitable, methods of powder formation would be used, various methods being well known in the art such for instance as atomisation of the molten ternary alloy directly to powder.

The powder was then subjected to an internal oxidation procedure involving in sequence:

(1) Surface oxidation of the powder to cuprous oxide (plus some solute aluminium oxide) by heating in oxygen for 2 hours at 300° C.;

(2) Diffusion of the oxygen from the cuprous oxide surface film into the underlying alloy by heating the powder at 700° C. in a sealed argon-filled container, the partial pressure of oxygen being sufficient, under these conditions to internally oxidize the aluminium to alumina;

(3) Chemical reduction of any excess of cuprous oxide to copper by heating the powder in hydrogen for one hour at 300° C.

The internally oxidized alloy powder was compacted hydrostatically at 30 ton/in.^{2} and sintered for 2 hours at 1000° C. in hydrogen. Finally the sintered compacts were extruded to rod at 750° C. using an extrusion ratio of 10:1.

By a similar procedure rods of internally oxidized D.S. copper were prepared starting from binary copper-aluminium alloys with such proportions of aluminium as to give final compositions of copper with 0.5, 1.3, 2.3 and 4 $^v/_o$ alumina respectively.

Table I shows the average room temperature properties of the internally oxidized Cu-Ag alloy with 1.3 $^v/_o$ Al_2O_3 as compared with internally oxidized copper having 1.3 and 2.3 $^v/_o$ Al_2O_3. Elongation was measured on a gauge length of 0.90 inches.

TABLE I

Property	Material: D.S.Cu 1.3$^v/_o$ Al_2O_3	D.S.Cu-0.25$^w/_o$ Ag 1.3$^v/_o$ Al_2O_3	D.S.Cu 2.3$^v/_o$ Al_2O_3
Tensile strength, lb./in.^{2}	55,000	65,000	67,700
0.2% proof stress, lb./in.^{2}	53,000	62,700	57,000
0.1% proof stress, lb./in.^{2}	50,000	59,000	50,100
Young's modulus $\times 10^6$, lb./in.^{2}	16.1	15.0	17.0
Elongation, percent	23	22	19
Area reduction, percent	67	60	35
Electrical conductivity, percent IACS	95	90	88

It will be seen that, relatively to D.S. Cu with 1.3 $^v/_o$ Al_2O_3, the addition of silver has raised the mechanical properties to compare favourably with D.S. Cu with 2.3 $^v/_o$ Al_2O_3. It is particularly noticeable that the ductility of the D.S. Cu-Ag alloy as measured by reduction of area and by elongation is substantially greater than that of D.S. Cu with 2.3 $^v/_o$ Al_2O_3, and furthermore that the Cu-Ag alloy retains very high electrical conductivity which is also greater than that of D.S. Cu with 2.3 $^v/_o$ Al_2O_3.

Table II shows the tensile strength and elongation properties of the internally oxidized Cu-Ag alloy with 1.3 $^v/_o$ Al_2O_3 at different elevated temperatures, as compared with these same properties of internally oxidized copper with various Al_2O_3 contents.

TABLE II

	D.S. Cu-0.25$^w/_o$Ag 1.3$^v/_o$$Al_2O_3$		D.S. Cu 1.3$^v/_o$ Al_2O_3		D.S. Cu 2.3$^v/_o$ Al_2O_3		D.S. Cu 4$^v/_o$ Al_2O_3	
Temp. (° C.)	Tensile strength, lb./in.^{2}	Elongation, percent	T.S.	El.	T.S.	El.	T.S.	El.
300	45,000	5.0	35,700	4.5	40,900	4.0	47,800	3.0
450	31,200	5.0	25,500	5.0	30,600	4.0	33,700	3.0
650	19,400	8.0	18,800	6.0	21,500	4.0	24,500	3.5
750	16,300	8.5	15,100	5.5	16,500	4.5	19,800	3.0
850	10,800	11.0	10,400	6.0	14,000	5.0	14,450	5.0
950	6,270	10.0	6,750	8.0	6,360	6.5	8,000	5.0

These results show that the D.S. Cu-Ag alloy with 1.3 $^v/_o$ Al_2O_3 has significantly improved elevated temperature strength at least up to approximately 450° C. (approximately one third of the (° K.) melting point of copper) as compared with D.S. Cu with the same alumina content (1.3 $^v/_o$ Al_2O_3). Furthermore the D.S. Cu-Ag alloy shows comparable strength to D.S. Cu with a higher alumina content (2.3 $^v/_o$ Al_2O_3) over the full temperature range. It is also seen that D.S. Cu-Ag has significantly higher ductility, particularly at 650° C. and above, as compared to the other D.S. Cu materials. It would appear that the increased strength up to 450° C. is due to solution strengthening, while beyond that the improvement in strength and ductility is due to finer dispersion of Al_2O_3 resulting from presence of the silver as mentioned previously.

The accompanying graph shows curves representing the hardness of various copper materials after heating for one hour at various elevated temperatures. The materials concerned, as shown by the legend given below the graph, are the internally oxidized copper and copper-silver alloy materials already referred to, together with, for comparison purposes, pure, fully hardened copper and the known copper—0.7% chromium alloy.

It can be seen from the graph that D.S. Cu-Ag alloy with 1.3 $^v/_o$ Al_2O_3 has a hardness and thermal stability

virtually equal to D.S. Cu with almost twice the alumina content throughout the temperature range. As compared with copper and copper-chromium the thermal stability above 200° C. and 400° C. will be particularly noticed.

While a specific procedure has been described for the manufacture of a dispersion strengthened copper-silver alloy by internal oxidation of a ternary copper-silver-aluminium alloy, it will be appreciated that similar procedures can be used for manufacturing the dispersion strengthened copper-cadmium and copper-zinc alloys of the invention, it being well within the ability of metallurgists to determine any modification of the process parameters that may be necessary.

I claim:

1. A dispersion strengthened copper base alloy consisting of a metal from the group consisting of silver, cadmium and zinc being present in an amount up to 1% by weight, said metal being present in an amount sufficient to form a solid solution alloy with copper, from about 0.1 to 1% by weight of aluminium; and copper constituting the balance of the free metal content, said aluminium being present as 0.5% to 4.3% by volume of finely divided aluminium oxide dispersed throughout said alloy formed by internal oxidation of aluminium initially alloyed with the copper and the metal of said group.

2. A dispersion strengthened alloy according to claim 1 consisting of 0.25% by weight of silver, and copper constituting the balance of the free metal content, together with, dispersed throughout said alloy, 1.3% by volume of finely divided aluminium oxide formed by internal oxidation of aluminium initially alloyed with the copper and silver.

3. A method of manufacturing a dispersion strengthened copper base alloy which includes the steps of forming a ternary alloy consisting of, by weight, at least 98% copper, a proportion not exceeding 1% of a metal which is a member of the group consisting of silver, cadmium and zinc, said metal being present in an amount sufficient to form a solid solution alloy with copper, and from 0.1% to 1% of aluminium, and internally oxidizing the aluminium in said alloy to form a dispersion of finely divided aluminium oxide throughout the residual alloy of copper and the metal of said group.

4. A method according to claim 3, which includes the steps of forming a ternary alloy consisting of 99.45% copper, 0.25% silver and 0.3% aluminium, by weight, and internally oxidizing the aluminium in said alloy to form a dispersion of aluminium oxide, in a proportion of 1.3% by volume, throughout the residual alloy of copper and silver.

5. A method according to claim 3 wherein the said internal oxidation of the aluminium is effected by heating powder particles of the said ternary alloy in oxygen to form surface films of cuprous oxide on the particles, and causing oxygen from said surface films to diffuse into the particles by heating in a sealed container filled with an inert gas.

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CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

29—182.5; 75—157.5, 162, 206, 212; 148—6.31, 32