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BERYLLIUM COPPER COMPOSITION AND METHOD OF PRODUCING GREEN COMPACTS AND SINTERED ARTICLES THEREFROM

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This invention relates generally to a new composition of matter for use in forming articles of copper based beryllium containing alloy and to a method of forming green compacts and sintered articles therefrom, and particularly to a powder composition for producing green compacts and articles wherein the beryllium content of the article is from about 1% to 3%, by weight, and cobalt may be present in an amount of about a trace to 0.5%, and other alloying ingredients may be present in minor proportions.

Heretofore, beryllium cooper alloy powders have been formed by sintering, cold pressing and sintering and hot pressing.

It is impossible in prior cold compacting operations to obtain the density desired in the green compacts or sintered articles, particularly if high densities approaching the theoretical density of the materials is required.

The sintering method before used is satisfactory for very large articles but is not satisfactory for smaller articles due to the great expense of repeatedly heating and cooling the equipment for each article formed.

On the other hand, while casting is satisfactory in some respects, a considerable amount of scrap results and, for economy, must be recovered, and its recovery and recasting involve considerable expense.

Again, the articles produced by prior powder metallurgy techniques are insufficiently bonded and fail to meet the tensile strength, transverse rupture strength, and density requirements desired for commercial applications.

Methods of cold compacting and sintering the alloy powders, while amenable to mass production operations, have previously been found incapable of providing articles having suitable mechanical properties and precision tolerance required for production of commercial parts.

Methods of cold compacting and sintering beryllium copper alloys to provide articles of satisfactory mechanical properties and precision tolerance without further machining operations are highly desirable as replacement techniques for precision casting methods which are time consuming and do not lend themselves nearly as well to mass production operations.

A major problem presented in the development of a cold press sintering method has been the inherent difficulty of compaction at room temperatures of beryllium copper alloy powder to high density and suitable green strength. The resistance of commercially available free alloy powder to compactability is its limited specific surface and particle size distribution and the resistance of such powder to plastic deformation, especially with alloys containing one or more percent by weight of beryllium.

Refractory beryllium oxide film which forms upon exposure of the alloy powder to the atmosphere is incapable of reduction by H_2, NH_3 or hydrocarbon gas and results in weak particle to particle bonding as compacted and as sintered. Likewise, because of the spherical shape of the beryllium copper alloy particles, direct compaction thereof, either cold or during sintering, is difficult. The manufacture of compactable and sinterable beryllium copper alloy powders is difficult if not impossible by the standard techniques of chemical or electro-chemical reduction, and other attritioning processes.

Other metal powders, for example, copper, nickel, cobalt powders, can be reproduced from their oxides and salts by chemical reduction of their salts or oxides or by electrolytic deposition from a suitable bath containing solutions of said metals. Such powders produced by such methods have extensive surface areas in the form of complex rough surfaces which interlock during cold compaction to give excellent grain strength. As they are soft and plastic, they can be compacted at from about 70% to about 90% theoretical density at room temperature at relatively low compacting pressures of from about 10 t.s.i. to about 50 t.s.i. The resultant compacts are then readily sinterable to substantially theoretical density bodies having desirable mechanical properties. The commercially available pre-alloyed beryllium copper alloy powders are, in contrast to readily compactable soft and plastic metal powders, resistant to compaction because of the above described characteristics of the beryllium copper alloy and consequently are not compactable, at relatively low pressure of 10 t.s.i. to 50 t.s.i., to bodies of high density and satisfactory mechanical properties.

Problems resulting from the application of the prior methods to beryllium copper alloy powder are overcome by the present invention. The present invention relates to the production of such articles by compacting, at temperatures below sintering, a mixture or blend of copper based beryllium containing alloy powder and copper powder, and then sintering the compacted blend.

In general, the prior powder metallurgy techniques for the production of articles from beryllium copper alloy powder have had limited application in the fabrication field because of the problems presented in the practice of such methods. The copper based beryllium containing alloy powder is mixed or blended with copper powder in predetermined proportions prior to compaction. The mixture is compactable at relatively low pressures of, for example, from 10 t.s.i. to 50 t.s.i., and at temperatures below sintering, preferably room temperature, into compacts capable of being handled without disintegration and of being subsequently sintered to provide articles and bodies which have mechanical properties superior to those heretofore obtainable from the compaction and sintering of beryllium copper alloys without the addition of the free copper powder, and of which, upon annealing and heat treatment, the properties can be further enhanced.

By the introduction of copper powder having the proper amount of particles of the desired fineness, resistance of beryllium copper alloy to compaction can be overcome and green compacts can be produced and sintered to form articles with the result that, at the end of the sintering operation, the beryllium content is diffused uniformly throughout the entire mass of copper and other ingredients forming the sintered article.

It is an object of the invention to provide a composition and method of forming green compacts of beryllium copper alloy capable of being handled without disintegration and which, upon subsequent sintering, form articles and bodies having excellent mechanical properties and high tensile strength.

It is a further object of the invention to provide mixtures of beryllium copper alloy powder and copper powder, which mixtures are capable of being compacted at a temperature below sintering so as to form green compacts which, in turn, are capable of being handled without disintegration and, upon subsequent sintering, or sintering followed by annealing and age hardening, are capable of providing articles and bodies of very high density and excellent mechanical properties.

A correlative object is to provide compositions comprising mixtures of beryllium copper alloy powder and fine copper powder which compositions can be compacted at pressures as low as 10 t.s.i. sufficiently to be handled without disintegration and which, upon compaction at higher pressures, such as 50 t.s.i. can be compacted at temperatures below sintering, to densities of from about 75% to almost 90% of theoretical density of the composition and which, upon sintering near or above the melting point of the beryllium copper alloy powder, but below the melting point of the copper powder, form beryllium copper alloy bodies and articles in which the beryllium copper alloy powder is diffused throughout the copper content of the article, and which have excellent mechanical properties.

A more specific object is to form initially bodies in the manner and of the type above described, and then, after sintering, to increase the density by further compacting the body followed by further sintering thereof, or by combined additional compaction and sintering, and particularly by further compacting or coining the initial body while it is heated to elevated temperatures.

Another object is to enhance or increase the mechanical properties of the sintered bodies by annealing and age hardening the bodies after either their initial formation and sintering, or their additional sintering following the original sintering and compaction.

Another specific object is to effect more accurate control over the high and low densities so that they may be consistently obtained in the finished product.

Another object is to produce, by the foregoing procedures, bodies of alloy which contain predetermined quantities of each of the essential metals present in the powders employed.

Another object is to produce beryllium copper alloy strip by rolling, below sintering temperature, a blend of beryllium copper alloy powder and copper powder and subsequently sintering the resultant compact.

Another object is to increase the density of the rolled, compacted and sintered strip by subsequent annealing and rerolling steps.

These and other objects and advantages will become apparent from the following description.

Beryllium copper alloy powders suitable for use as the starting alloy material of the present invention may be produced by atomization, crushing, grinding, pulverizing, and attritioning of prealloyed copper based beryllium containing material. As an alternative method, the powder can be produced by mixing predetermined portions of beryllium powder and copper powder and reacting the intimate mixture, in a solid state, in either inert, vacuum, or dry hydrogen atmosphere, at about 1200° F. to 1600° F. to form a friable compact. The compact is then crushed to form the desired beryllium copper alloy powder. The beryllium copper alloy powder preferably is one of which the particle size is 100 mesh or less, produced by atomization of the melts of the desired beryllium copper alloy composition. The beryllium copper alloy powder produced by any of these methods is satisfactory for use in the present invention.

The alloy powder is then mixed with the copper powder having low apparent density, excellent compactability, high green strength in compacted form.

The preferred copper powder is one produced by chemical reduction of a copper oxide or salt, or prepared by electrolytic deposition from a solution. Two types of fine, preferably pure, copper powders have been found to provide particularly desirable products in the practice of the invention. The copper powders have respective apparent densities of about 1.70 and 2.20 grams per cubic centimeter, and particle size of which 90% and 80% is finer than minus 325 mesh, respectively.

The mixtures of beryllium copper alloy powder and the pure copper powder consist essentially, by weight, of from about 10% to 90% of beryllium copper alloy powder, the balance pure copper powder. Preferably the beryllium copper alloy powder and the pure copper powder are used in equal proportions by weight. In order to achieve optimum properties of the bodies during subsequent sintering and optimum mechanical properties during subsequent impaction and sintering or subsequent heat treating and age hardening, cobalt or nickel may be optionally included in beryllium copper alloy powder in amounts of from a trace to about 0.5%, by weight, of the powder composition or mixture. Further, the metals customarily included in minor amounts, for example, less than 1%, in copper based beryllium containing alloys may be included for imparting the properties specific to each, as is well known in the art.

In forming articles, the intimately mixed powders are compacted at temperatures below sintering, and at pressures of from about 5 t.s.i. to about 100 t.s.i., preferably from about 40 t.s.i. to 50 t.s.i. When so compacted, the green compacts have densities of from about 70% to about 90% of their theoretical density. At the lower limit of the pressures, the compacts are adequate for handling without disintegration, but do not approach the theoretical density very closely. However, at the higher pressures, they do approach very closely to the theoretical density. The degree of compaction depends upon the particular characteristics desired in the green compact or in the finished article.

An advantage of the invention is that lower densities can be obtained with the same procedures and equipment as provided for the high densities, thus providing a more generally applicable method of forming the compacts and bodies.

Generally, the green compacts are sintered near or slightly above the melting point of the beryllium copper alloy, which is from about 1590° F. to about 1800° F., depending upon conditions, in an atmosphere of dry hydrogen, dry cracked ammonia, hydro-carbon gas, carbon monoxide gas, inert gases, or vacuum atmosphere. The sintering temperatures are preferably from about 1500° F. to about 1750° F. These are preferred because they cause rapid diffusion of the beryllium throughout the copper, and result in a dense, strong, homogeneous sintered body more rapidly than was heretofore possible.

Further, the article provided by the sintering operation can be used as sintered, or further processed, such as by coining and resintering, to provide articles having densities greater than 90% theoretical density, and higher tensile strength and hardness values than those of the initially sintered product. As mentioned, all of these properties of the originally sintered products can be enhanced by subsequent annealing and age hardening.

Generally, an increase in the beryllium copper alloy content does not seem to effect the density of the green compact, but it does reduce the transverse rupture strength. On the other hand, the transverse rupture strength of the sintered product increases with the increase of beryllium content, at least up to about 3% beryllium, by weight, of the total mixture.

The foregoing general statements are borne out by the following tables:

Table I

Example	Blend Mixture		Wt. Percent Be	Theo. Density, gms./cc.	Green Density, gms./cc.	Percent of Theo. Density	Green Transv. Rupture Strength, p.s.i.
	Be-Cu Alloy Powder	Copper Powder					
1	0	100	0	8.96	7.9	88	12,100
2	10	90	.40	8.85	7.6	86	7,500
3	20	80	.80	8.70	7.4	85	5,800
4	30	70	1.20	8.60	7.3	84	4,100
5	40	60	1.60	8.44	7.2	85	3,000
6	50	50	2.00	8.35	7.1	85	2,400
7	60	40	2.40	8.22	6.9	84	1,100
8	70	30	2.80	8.10	6.7	83	1,000
9	80	20	3.20	7.97	6.3	79	680
10	90	10	3.60	7.90	6.1	77	100

Table II

Example	Be-Cu Alloy Powder Compositions	Percent of Total Composition		Green Compacts				Sintered Compacts			Sintered Temp. (° F.)
		Be	Co	Theo. Density (g./cc.)	Actual Density (g./cc.)	Percent of Theo. Density	Transverse Rupture Strength (p.s.i.)	Actual Density (g./cc.)	Percent of Theo. Density	Transverse Rupture Strength (p.s.i.)[1]	
11	2.42% Be, 0.57 Co, Balance Cu.	0.5	0.13	8.79	7.60	86.5	8,000	7.83	89	45,200	1,700
12	2.42% Be, 0.57% Co, Balance Cu.	1.0	0.23	8.63	7.40	85.6	4,600	7.94	91	56,900	1,700
13	4% Be, Balance Cu	1.5	0	8.47	7.18	85	3,280	7.68	91	75,700	1,700
14	4% Be, Balance Cu	1.6	0	8.44	7.17	85	3,000	7.66	91	88,500	1,700
15	4% Be, Balance Cu	2.0	0	8.35	7.10	85	2,400	7.59	91	140,000	1,700
16	4% Be, Balance Cu	2.4	0	8.22	6.88	84	1,100	7.63	91	143,000	1,650
17	6% Be, 1% Co, Balance Cu.	3.0	0.5	8.05	6.60	82	2,900	7.47	93	102,000	1,625

[1] Sintered powder was water quenched from 1,450° F. and aged 3 hours at 600° F.

Table III

Example	Temperature, ° F.	Sintered Density, g./cc.	Percent Theoretical Density	Transverse Rupture Strength (p.s.i.)[1]
18	([2])	[2] 7.10	85	[2] 2,350
19	1,200	6.94	83	6,640
20	1,300	7.0	83.5	8,200
21	1,400	7.0	84	13,100
22	1,500	7.2	86	21,700
23	1,550	7.2	86.5	31,300
24	1,575	6.6	79	81,500
25	1,600	6.65	80	88,800
26	1,625	7.0	84	96,300
27	1,650	7.0	84	108,000
28	1,700	7.6	91	145,000
29	1,750	7.8	94	159,600

[1] Water quenched from 1,450° F. and aged three hours at 600° F.
[2] As briquetted.

NOTE.—All examples of Table III are green compacts, sintered at the temperatures noted and prepared by compacting a blend containing equal parts, by weight, of beryllium-copper alloy powder containing 4% beryllium having a particle size finer than minus 100 mesh and copper powder of the type used in the preceding Tables I and II.

Referring to the foregoing tables, Table I includes Examples 1 through 10 wherein the beryllium copper alloy powder is varied from 10 to 90%, by weight, of the total mixture. In order that these can readily be compared, the alloy powder of all of the mixtures and the resultant green compacts is atomized beryllium copper alloy powder of particle size finer than minus 100 mesh. This powder contains about 4% beryllium. The other powder is substantially pure copper powder of 2.2 grams per cc. apparent density in which 80% of the particles are finer than minus 325 mesh. They were compacted at 50 t.s.i. in a die of rectangular cross section having a length of about 1.250 inches and a width of 0.500 inch, the die being filled to approximately ⅝ inch. This table shows the variance in the green density and the green transverse rupture strength for various percentages of beryllium alloy powder content.

In Table II, the green and sintered properties of a number of different alloys, some of which contain cobalt, are shown. These powders were a blend of beryllium copper powder of particle size of minus 100 mesh and copper powder as set forth in connection with Table I. The blends, or mixtures, were compacted at 50 t.s.i. in the die described in connection with Table I. They were sintered in dry hydrogen gas for one hour.

From Table II, it appears that the transverse rupture strength of the green compacts decreases with an increase in beryllium alloy powder content. On the other hand, the transverse rupture strength of the sintered compacts increases with an increase in beryllium. Further, neither the green density nor the density of the sintered article changes radically with a change in beryllium within the range shown.

Table III shows the relation of the sintering temperature to the percentage of theoretical density and transverse rupture strength of the sintered products which have subsequently been age hardened for three hours at 600° F. In preparing these specimens, the material used was a blend of equal parts of beryllium copper alloy containing 4% beryllium with a particle size of minus 100 mesh or less, and pure copper powder of the type used in the preceding tables. In this connection, it is interesting to note that there is a sudden increase in transverse rupture strength from a temperature of 1550° F. to 1575° F., and that below this temperature the transverse rupture strength gradually increases, but at a lower level. It greatly increases at 1575° F., and continues to increase, at a higher level. At the same time, the percentage of theoretical density remains high throughout the range. Strangely enough, however, the percentage of theoretical density does drop suddenly at about 1575° F. It then consistently builds up as the temperature increases from 1575° F. Thus the percentage of theoretical density increases in the lower range of temperatures, up to about 1575° F., then drops off rapidly at about 1575° F., and then resumes an increase from the new starting level, reaching a greater percentage of theoretical density at about 1750° F. than was obtained at any of the lower temperatures.

Alloy strip may be formed by the present method. For example, equal parts of atomized beryllium copper alloy powder, of minus 100 mesh particle size, and containing 4% beryllium, by weight, and pure copper powder of 80% less than minus 325 mesh particle size, were employed. The blended powder or composition was roll compacted into green strip by a two high rolling mill with six inch diameter rolls which were 13 inches wide, operating at 10 to 12 surface feet per minute. The green strip was rolled approximately 1½ inches wide, 0.030 inch gauge, and approximately 70% of theoretical density of 8.35 grams per cc. Next, the strip was sintered for about 15 minutes at about 1700° F. in dry hydrogen gas during which operation the beryllium content became uniformly diffused. The resultant strip was 0.027 inch thick and about 75% of theoretical density. The sintered strip was cold rolled to a gauge of 0.016 inch and to about 95% theoretical density. Next, the cold rolled strip was annealed in dry hydrogen gas for one hour at about 1550° F. and water quenched, and subsequently was cold rolled to about 0.010 inch thickness. The mechanical properties of the cold rolled strip following this procedure had an ultimate tensile strength of 95,800 lbs. t.s.i., 0.8 percent elongation in one inch, and a Rockwell "C" hardness of 24. The same material, after aging two hours at 600° F., had an ultimate tensile strength of 134,000 lbs. t.s.i., a yield strength of 132,700 lbs. t.s.i. at 0.01 percent offset. The percent of elongation was about 0.9% in one inch. The Rockwell "C" hardness was about 35. This indicates a great increase in the desired mechanical properties as a result of the limited age hardening. From this example, it is apparent that green compacts of the composition of the present invention can be subsequently fabricated into various structural shapes such as are commonly used as starting materials and shapes in the manufacture of various fabricated articles.

Thus by the prior methods, a copper based alloy powder containing not more than about 3% beryllium could not be formed readily into green compacts of such density as to be sinterable into bodies of substantially theoretical density. However, by using the same quantity of the two metals, but with a predetermined part of them in the form of beryllium copper alloy powder and the remainder in the form of copper powder, such compacts can be formed. These compacts, when sintered, result in a product of substantial theoretical density and composed of an alloy in which all of the metal content of both powders has become alloyed. The alloy of which the bodies are composed contains a beryllium to copper ratio equal to that present in the mixture of the two powders.

Having thus described my invention, I claim:

1. A method of producing a green compact to be made into a sintered body of beryllium copper alloy and comprising intimately intermixing beryllium copper alloy powder and free copper powder, to form a mixture wherein the beryllium content ranges from about 0.4% to about 3.6%, by weight, of the total mixture, then compacting the mixture at temperatures below sintering to predetermined density.

2. The method according to claim 1 wherein the particle size of the alloy powders is finer than minus 100 mesh and the particle size of the copper powder is at least 80% less than minus 325 mesh.

3. The method according to claim 1 wherein the copper powder is substantially pure.

4. The method according to claim 1 wherein small amounts of powder or other metal from the class consisting of cobalt, nickel, and mixtures thereof, are added to the mixture before compacting.

5. The method according to claim 4 wherein the other metal is present in an amount up to about 0.5 percent, by weight, of the total mixture.

6. The method according to claim 1 wherein the compact is sintered in a reducing atmosphere.

7. The method according to claim 1 wherein the compact is sintered at from 1550° F. to 1750° F.

8. The method according to claim 1 wherein the compact is sintered and the sintered compact is subsequently subjected to additional compacting pressure sufficient to increase its density.

9. The method according to claim 8 wherein the sintered compact is heated prior to the application of the additional pressure and is maintained in heated condition during said application.

10. The method according to claim 1 wherein the two powders are present in substantially equal quantities, by weight.

11. The method according to claim 1 wherein the copper powder is from about 1.7 to about 2.2 g./cc. apparent density, and at least about 80% minus 325 mesh particle size.

12. A method of producing a beryllium copper alloy green compact in strip form, comprising compacting an intimate mixture of beryllium copper alloy powder and copper powder, wherein the beryllium content ranges from about 0.4% to about 3.6%, be weight, of the mixture by rolling the mixture, at a temperature below sintering, into a compact of strip shape and of a density such that the compact is capable of being handled without disintegration.

13. The method according to claim 12 wherein the compact is subsequently sintered, at from about 1550° F. to about 1750° F.

14. A green compact for subsequent sintering consisting essentially of an intimate mixture of beryllium copper alloy powder and copper powder, said mixture containing from about 0.4% to about 3.6%, by weight, of beryllium, and being compacted sufficiently to be handled without disintegration.

15. A composition for forming green compacts for subsequent sintering, and consisting essentially of an intimate mixture of beryllium copper alloy powder and copper powder, said mixture containing from about 0.4% to about 3.6%, by weight, of beryllium, and said powders being of fine particle size.

16. The composition according to claim 15 wherein the powders are present in about equal amounts, by weight, the beryllium copper alloy powder has a particle size of less than minus 100 mesh, and the copper powder has a particle size of at least about 80% minus 325 mesh and an apparent density of from about 1.7 to about 2.2 g./cc.

17. The method according to claim 1 wherein the compact is sintered in a non-oxydizing atmosphere.

18. The method according to claim 1 wherein the mixture is compacted at pressure in the range of from about 5 t.s.i. to about 100 t.s.i.

19. The method according to claim 18 wherein said pressure is about 50 t.s.i.

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