Feb. 29, 1944. V. O. ALLEN ET AL 2,343,038

ALLOYS FOR METAL TO GLASS SEALS, AND THE LIKE, AND METHOD OF PRODUCING SAME

Filed Dec. 19, 1941

Fig. 2.

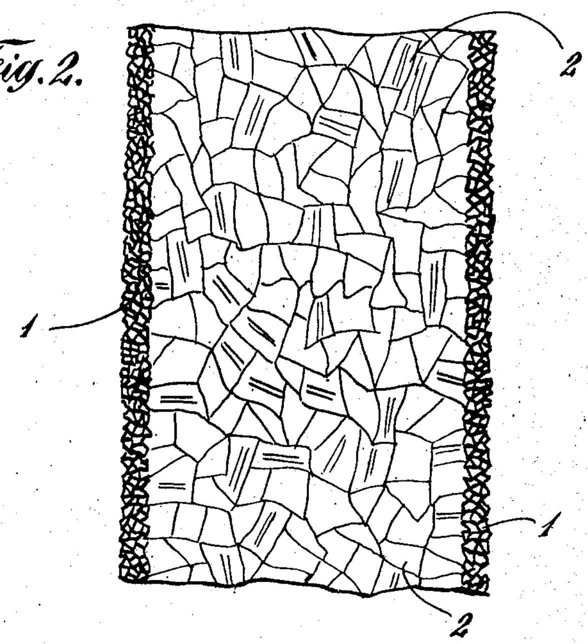


Fig. 1.

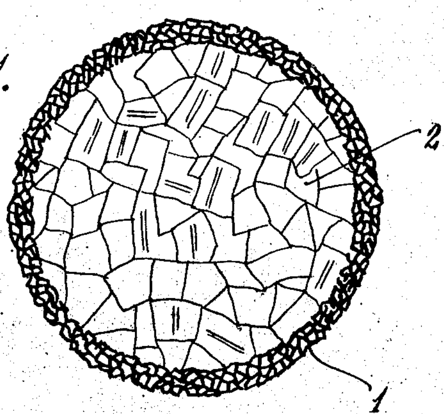
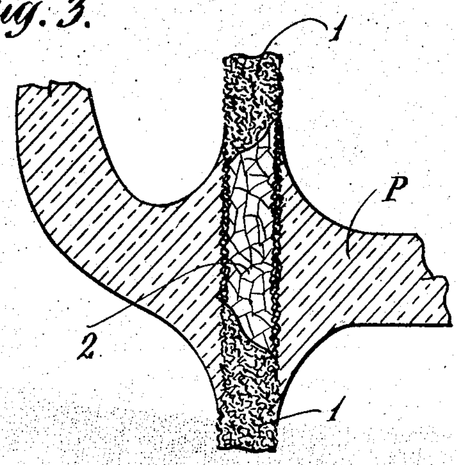


Fig. 3.



INVENTORS
Victor O. Allen
Joseph F. Polak
BY [signature]
ATTORNEY

UNITED STATES PATENT OFFICE

2,343,038

ALLOY FOR METAL TO GLASS SEALS AND THE LIKE AND METHOD OF PRODUCING SAME

Victor O. Allen, Madison, and Joseph F. Polak, Newark, N. J., assignors to Wilbur B. Driver Company, Newark, N. J., a corporation of New Jersey

Application December 19, 1941, Serial No. 423,566

7 Claims. (Cl. 148—6)

This invention relates to metallurgy and more particularly to the metallurgy of beryllium-containing alloys and to metallic material adapted for use in combination with non-metallic material, such as glass, enamel, porcelain, refractories, thermionically active metal oxides, organic plastics and the like material.

Heretofore in the art many different metals and metal alloys have been proposed for use in combination with glass, enamel, porcelain, thermionically active metal oxides, refractories, organic plastic materials and the like non-metallic compositions in the manufacture of metal to glass seals, electrically insulated wire, cathodes for electronic devices, and the like devices. In such field of use, the common problem involved is to obtain a relatively tight adherent bond between the metallic and non-metallic materials.

One of the objects of the present invention is to provide a metal base for use in combination with the above identified non-metallic materials in the forming of said devices and products which has a surface specifically adapted to provide for the mechanical securing of the said non-metallic material thereon, irrespective and independent of any other type of bond union therebetween.

Another object is to provide a metal base which has a surface adapted to provide a mechanical interlocking of non-metallic material therewith.

Still another object is to facilitate the securing together of metallic and non-metallic materials.

Other objects and advantages will be apparent as the invention is more fully hereinafter disclosed.

In accordance with these objects, we have discovered that beryllium additions in fractional percentages up to 1% to any of the base metals Cu, Ni, Co and Fe and alloys consisting principally of at least one of these metals, consistently produces a surface condition which in brief comprises an area extending inwardly from the surface for a relatively small distance as compared to the thickness or diameter of the base which area consists of metal grains or crystals of relatively small size as compared to the metal grains or crystals in the interior of the base and of relatively large grain boundaries as compared to the grain boundaries which boundaries are normally filled with an acid and alkali soluble and glass miscible constituent appearing to mainly consist of beryllium oxide or oxide compounds consisting predominately of beryllium oxide.

This characteristic structure of the beryllium-containing alloys above identified provides, on appropriate removal of the grain boundary material by acid or alkali pickling or by fusion of glass compounds thereon, a surface having a plurality of microscopic surface cracks and fissures extending inwardly in the fine grained area which provides key-ways for the mechanical interlocking and securing thereon of various non-metallic materials, such as glass, enamel, procelain, organic plastic materials and the like.

The particular structure obtained, the depth thereof and the size or width of the intergranular surface key-ways obtained, may be widely modified without essential departure from the present invention, and we have found that the most satisfactory types thereof are obtained by subjecting the metal while in the cold-worked condition to a recrystallization heat-treatment in an atmosphere reducing with respect to the oxide compounds of the base metal or metals of the alloy, but oxidizing with respect to the Be content thereof. Under these conditions we have found that with any given Be-containing alloy, by the proper selection of the heat-treating temperature and time, the grain size of the small grained surface area and the size of the grain boundary areas may be effectively controlled to obtain a grain size and grain boundary area best suited for the particular service use intended.

As a specific embodiment of the present invention, but not as a limitation thereof, the adaptation of the same to glass sealing-in alloys will be described. Before describing the same reference should be made to the accompanying drawing, wherein:

Fig. 1 is a diagrammatic cross-section of a wire formed in accordance with the present invention;

Fig. 2 is a diagrammatic longitudinal section of the same, and

Fig. 3 is a diagrammatic cross-sectional view of a glass to metal seal illustrating the nature of the improvement obtained therein by the practice of the present invention.

Referring to the drawing, the improved metal product of the present invention comprises a metal article, such as a metal wire, strip, sheet and the like article comprised of an alloy consisting of a metal of the group Cu, Fe, Ni and Co and alloys consisting predominantly of at least one of these metals and from small fractional percentages up to about 1% beryllium, said alloy being characterized by having a surface area 1 consisting of relatively fine grained metal having relatively large sized grain boundaries as contrasted to the grain size and grain boundary area in the central or core portion 2 of the article.

In the art of making metal to glass seals various metals and metal alloys have been proposed, such as copper, nickel, iron, nickel-iron, chromium-nickel-iron, nickel-cobalt-iron, nickel-cobalt-chromium-iron, copper-clad nickel-iron and the like alloys. In most of these prior art alloys the alloy composition, per se, is closely controlled to provide an alloy composition having a specific coefficient of expansion substantially equivalent to the glass with which it is to be employed. The alloy composition, per se, forms no part of the present invention except insofar as additions of beryllium metal thereto in fractional percentages below 1% are made for the purposes of the present invention and in accordance with the present invention. The specific method of manufacturing the beryllium-containing alloy, per se, also forms no part of the present invention and various methods are available in the art.

Copper, as one example of the present invention, is one of the most common of the metals employed in forming glass to metal seals and joints, either alone or as a surfacing metal for nickel and iron alloys and the most common such seal or joint is that known in the art and indicated in Fig. 3 as a leading-in wire W for conducting an electric current from the exterior to the interior of an incandescent filament lamp bulb or electronic device such as a radio tube through a press P.

In accordance with the present invention, we have found that by incorporating from small fractional percentages (as low as .025%) up to 1% of beryllium in the copper, the resultant copper-beryllium alloy may be bonded to glass without the necessity of oxidizing the surface of the copper as heretofore has been found necessary in the art. This result is obtained preferably by annealing the copper-beryllium alloy prior to use in the forming of a metal to glass seal or joint in an atmosphere reducing with respect to copper oxide, but oxidizing with respect to beryllium. Under such conditions it is found that the surface of the wire for an extended distance inwardly, varying in depth with respect to the beryllium content and with the time of exposure of the metal to the oxidizing action of the atmosphere, develops a relatively fine grain size, as compared to the metal of the central portion, with relatively large grain boundary areas as compared to the grain boundary areas of the metal of the central portion. This result is accentuated where the metal prior to heat-treatment is in the strain-hardened condition whereby beryllium oxidation occurs simultaneously with recrystallization.

In general, we have found that within rather wide limits the finer the grain size of the surface area the better the bond between the glass and metal surface, the said bond appearing to be directly dependent upon the total number of interlocks per unit of surface area between the glass and metal surface in the plurality of enlarged grain boundaries present in the metal surface. As the beryllium oxide normally present in the grain boundaries is of relatively high solubility in fused silicates, fusion of the glass onto the metal surface results in an opening of these grain boundaries for the flowing thereinto of the fluid silicate material comprising the glass.

Substantially the same result is obtained where the beryllium-containing copper is employed as a surfacing material on metals which are with more difficulty formed into metal to glass joints such as Ni and Fe or various Ni and Fe-base alloys heretofore proposed for similar use in the art and known generally under the name "dumet."

The addition of fractional percentages of beryllium to the Ni or Fe or to the various Ni and Fe-base alloys heretofore proposed for use in the forming of metal to glass seals or joints, also results in the formation of the surface condition hereinabove described with respect to copper, and schematically illustrated in the drawing.

As in copper, the effect is accentuated and made more predominate where the alloy is subjected to a recrystallizing heat-treatment in an atmosphere reducing with respect to the base metal oxides, but oxidizing with respect to beryllium. In general, with beryllium-containing alloys consisting predominately of one of the base metals Cu, Fe, Co and Ni, an atmosphere suitable for this purpose consists primarily of hydrogen for its reducing effect on Cu, Fe and Ni oxides and secondarily of one of the oxidizing gases O_2, H_2O, CO_2, together with various amounts of an inert gas such as nitrogen and various percentages of auxiliary metal oxide reducing gases such as CO and volatile hydrocarbons. In those Fe, Ni and Co alloys which in addition to beryllium also contain some chromium, the surface of the heat-treated article normally will be covered with an adherent film of chromium oxide, which for the purposes of sealing the wire to glass is desirable and of no detriment to the present invention.

As an example, beryllium-containing copper, preferably is annealed at about 800° C. in an atmosphere consisting of substantially pure hydrogen saturated with water vapor at atmospheric temperature. Nickel, iron and cobalt and the various alloys consisting predominately of one of these metals which contain from small fractional percentages up to 1% Be and those which also contain chromium may be annealed at 1200° C. in the same atmosphere. Alternatively we have found an atmosphere consisting of illuminating gas saturated with H_2O (water vapor) at atmospheric temperatures equally as satisfactory in the annealing of these alloys for the purposes of the present invention.

As specific examples of alloys of the iron group metals which heretofore have found wide utility in the art of forming metal to glass seals and which have been found to be responsive to the present invention, the following alloys well known in the art may be identified:

Main alloy constituents

Alloy No.	Cu	Ni	Cr	Co	Fe
1		42	5.5		Balance.
2			30		Do.
3		28		18	Do.
4		30	8	25	Do.
5	Surfaced	42			Do.

Each of the alloys 1 to 5 inclusive, identified above are specific alloys having coefficients of expansion particularly adapting the alloy for use with glass having the composition usually employed in the lamp and radio tube industry. In each of the alloys (1 to 4 inclusive) we have found that Be in fractional percentages up to about 1% characteristically produces in the wire on final annealing in an atmosphere reducing with respect to the base constituents but oxidizing with respect to the beryllium, a surface area extending inwardly an appreciable distance consisting of relatively small grains as compared to the grain size interiorly and having relatively large grain boundary areas as compared to the grain interior filled with oxidized material consisting mainly of beryllium oxide compounds. Alloy 5 is known in the art as "dumet" wire or "copper-clad nickel-iron" and in place of copper, in accordance with the present invention, Be-Cu alloys containing fractional percentages of Be not over about 1% are substituted for the copper surfacing the nickel-iron base thereof. More specifically, we have found that it is preferable to maintain the Be content as low as possible and at the minimum amount required to obtain the desired fine grained surface area on oxidation-reduction heat treatment, as amounts materially over this amount tend to alter the coefficient of expansion of the alloy. In general and with most of the alloys above identified this minimum amount appears to be approximately .50%.

Alternatively, substantially pure nickel and pure iron frequently have been employed as glass sealing in alloys. We have found that the addition of Be in from small fractional percentages up to 1% to substantially pure Ni and Fe materially improves the sealing in properties of the metals and moreover improves the utility of the nickel particularly as a base metal for thermionically active cathodes, for example, cathodes of the oxide coated type wherein the oxide coating is applied to the metal surface.

The oxidation-reduction annealing operation hereinabove described may be conducted as a continuous process known in the art as "strand annealing" or by the "batch" method without essential departure from the present invention. In general, in strand annealing higher temperatures and shorter time intervals may be employed than in batch annealing, as well as quicker cooling rates, as is well recognized in the art, particularly where recrystallization simultaneously with oxidation-reduction annealing is desired.

Having hereinabove described the present invention generically and specifically and given several specific embodiments thereof, it is believed apparent to one skilled in the art that the same is adapted for wide utility in the general field of forming seals and joints between a metal and a non-metallic material such as glass, enamel, porcelain, organic plastic and the like materials, by providing the metal surface with a plurality of interiorly extending microscopic key-ways for interlocking the metal and non-metallic material together.

Where the non-metallic surfacing material, per se, has a relatively low solubility for beryllium oxide or where the presence of beryllium oxide, per se, in the non-metallic surfacing material is undesired or detrimental, the heat-treated Be-containing alloy may be subjected to a pickling operation in either acid or alkaline solutions to dissolve out the grain boundary material in the fine grained surface area of the wire, sheet or strip prior to the application of the non-metallic material thereon.

The present invention offers particular utility in the art of forming tight, hermetic joints between a metal and non-metal such as an organic plastic which at the present time is difficult to obtain, such as, for example, in forming metal reinforced articles comprised of organic plastic. There are a large number of organic plastics known in the art, the most common of which are known generally by the trade names Lucite, Bakelite, etc., and chemically as cellulose acetate, phenol-resins, protein condensation products. Each of the organic plastics are characterized by being chemically inert and non-reactive with metals generally and substantially all metal to organic plastic unions are pressure unions. The interlocking joint obtained by the practice of the present invention provides not only for the mechanical bonding of the organic plastic to the metal surface, but for the maintaining of the bond therebetween over relatively wide temperature ranges.

The present invention also is particularly adapted for use in connection with forming electrically insulated enameled wire products, such as enameled copper wire, as one skilled in the art will readily perceive. In such use, it is preferable to maintain the beryllium copper to a very low fractional percentage approximating .025% in order to eliminate deleterious loss in electrical conductivity in the copper, especially where the wire is to be employed as coil windings in electrical devices.

Having hereinabove described the present invention generically and specifically, it is believed apparent that the same may be widely varied without essential departure therefrom and all such adaptations and modifications thereof are contemplated as may fall within the scope of the following claims.

What we claim is:

1. The method of treating an alloy consisting predominately of at least one of the base metals Fe, Co, Ni, and containing fractional percentages of Be to develop therein a crystal structure consisting of a fine grained surface area of appreciable depth having relatively wide boundaries overlying a larger grained core area having relatively small boundaries, which comprises cold working the alloy and heat-treating the cold worked alloy at a recrystallization temperature in an atmosphere reducing with respect to the metal oxides of the base metal but oxidizing with respect to the said beryllium for a time interval producing the desired depth of said fine grained surface area and to obtain the desired larger grain sized core.

2. The method of claim 1, wherein said atmosphere consists principally of hydrogen and one of the oxidizing gases oxygen, water vapor and carbon dioxide.

3. The method of claim 1, wherein said atmosphere consists of a mixture of reducing, inert and oxidizing gases, said reducing gases consisting at least of one of the gases hydrogen, carbon monoxide and volatile hydrocarbons, said oxidizing gases consisting of at least one of the gases oxygen, water vapor and carbon dioxide, and said inert gas consisting of nitrogen.

4. The method of treating an alloy consisting predominately of at least one of the base metals Fe, Co, Ni, and containing fractional percentages of Be to develop therein a crystal structure consisting of a fine grained surface area of appreciable depth having relatively wide boundaries overlying a larger grained core area having relatively small boundaries, which comprises cold working the alloy and heat-treating the cold worked alloy at a recrystallization temperature which approximates 1200° C. in an atmosphere reducing with respect to the metal oxides of the base metal but oxidizing with respect to the said beryllium for a time interval producing the de-

sired depth of said fine grained surface area and to obtain the desired larger grain sized core.

5. The method of claim 1, wherein the temperature of heating approximates 1200° C. and wherein said atmosphere consisting of hydrogen saturated with water vapor at atmospheric temperatures.

6. A metallic article of manufacture, said article consisting of an alloy produced by the process of claim 1.

7. A metallic article of manufacture, said article consisting of an alloy produced by the process of claim 4.

VICTOR O. ALLEN.
JOSEPH F. POLAK.