Patented Apr. 29, 1941 2,240,064

UNITED STATES PATENT OFFICE

2,240,064

ALLOY FOR METAL TO GLASS SEALS

Victor O. Allen, Madison, and Charles P. Marsden, Jr., Bloomfield, N. J., assignors to Wilbur B. Driver Company, Newark, N. J., a corporation of New Jersey

No Drawing. Original application September 6, 1940, Serial No. 355,668. Divided and this application February 6, 1941, Serial No. 377,654

6 Claims. (Cl. 75—128)

This invention relates to metallurgy and more particularly to the metallurgy of Cr-containing alloys of the iron group metals and to a method of degasifying the same without deleteriously affecting the adherence and the chemical and physical properties of the surface oxide film on said alloys thereby to better condition the same for use in the forming of metal to glass seals.

This application is a divisional application of prior filed application Serial No. 355,668 filed September 6, 1940, which application is assigned to the same assignee as the present application.

One of the objects of the present invention is to provide an improved method for degasifying said alloys. Another object is to provide a degasified alloy product having a surface oxide film that is firmly adherent to the metal surface and capable of forming a gas impervious seal with glass. Still another object is to provide a Cr-containing alloy of the iron group metals adapted for use in the forming of metal to glass seals. Another object is to provide an improved metal to glass seal. Other objects and advantages will be apparent as the invention is more fully hereinafter disclosed.

In the forming of metal to glass seals, such as, for example, in the manufacture of presses for use in the manufacture of electric lamps, electrical discharge devices, radio tubes and the like, the glass is fused onto the surface of leading-in or support wires passing therethrough and is usually pressure molded therearound. In addition to a favorable coefficient of expansion relative to that of the glass enclosing the wire, the surface of the wire must be provided with an adherent film of oxide to securely bind the glass and metal surfaces together and moreover the oxide film and the metal must be substantially free of gas and of compounds reactive with the glass to form gaseous products at the temperatures employed in the forming of the seal.

Heretofore in the art various chromium-containing alloys of the iron group metals have been proposed for use in the forming of metal to glass seals of the various types utilized in the lamp, radio tube, and gaseous conduction and electron discharge device industry, for the reason that chromium alloys are generally characterized by an adherent film of oxide. One of the most satisfactory of such alloys from a coefficient of expansion viewpoint for use with lead glass of the type known in the art by the code numbers G1 and G12, in the forming metal to glass seals is an alloy consisting of chromium 5–6%, Ni 42–43%, balance Fe.

Considerable difficulty however has been experienced in adapting these alloys to such use primarily because degasification of the alloy apparently deleteriously effects the sealing characteristics of the surface oxide film on the alloy and the adherence of the film to the metal surface.

We have discovered that degasification of the alloy while in the molten state by the use of metallic degasification agents requires generally the use of a sufficient excess of the agent to provide at least fractional alloyed percentages of the agent in the solidified metal to take care of dissolved gases liberated on solidification. The surface oxide film formed subsequently on the solidified degasified alloy prior to the forming of the metal to glass seal is comprised at least in part of the oxide compounds of the alloyed percentages of degasifier agents remaining in the alloy and we have found that the presence of these oxide compounds of the degasifier agent materially alters the adherence and the chemical and physical properties of the normal Cr.Ni.Fe oxide film present on the surface of the alloy and the sealing properties of the film to glass.

We have discovered that by using metallic beryllium as a degasifier agent for such alloys or by using aluminum and beryllium together as degasifier agents, residual alloyed percentages of the same as high as about 1% may be employed without detrimental effect to the sealing properties of the surface oxide film or to the adherence of this film to the metal surface and with certain positive benefits thereto. We have further found that the fractional percentages up to about 1% of alloyed beryllium are beneficial as a precipitation hardening agent in the alloy, permitting the use of smaller diameter wires or thinner sheet material than has heretofore been permissible with such type alloys.

In accordance with the above discoveries, to produce the improved alloy product of the present invention the chromium-containing alloy of the iron group metals, as for example, the iron-chromium-nickel alloy above noted as being comprised of Cr 5–6%, Ni 42–43%, balance Fe, is produced in the customary manner by first forming a molten substantially pure iron bath and adding the required percentages of nickel and chromium thereto. Considerable care must be taken to eliminate from the bath substantially all associated metal and metalloid impurities. In commercial practice, however, fractional percentages of the elements carbon, sulfur, phosphorus, manganese, boron, titanium and silicon will usually be present in the alloy, each in amounts not exceeding about .20%.

To the molten Cr.Ni.Fe alloy thus formed, beryllium is added in an amount at least sufficient to thoroughly degasify the molten metal and to provide Be in fractional percentages up to about 1% in the degasified and solidified metal. After allowing sufficient time for the degasification reaction to proceed to completion the Be-compounds formed thereby are removed from the bath by collecting the same in a flux such as

molten cryolyte or fluorspar which is then skimmed off from the molten metal and the degasified and scorified metal is cast into ingots. The cast metal then is worked down to desired wire sizes as heretofore practiced in the art, with the exception that prior to any cold mechanical deformation the metal must be annealed at temperatures approximating 700–900° C. for a time interval required to effect solution of the beryllium content and then rapidly cooled to atmospheric temperatures to retain the beryllium in solid solution. Extensive cold mechanical deformation may then be effected without difficulty.

As a modification of this practice, we have found that the molten alloy may be degasified with aluminum prior to the addition of the beryllium thereto, thereby effecting a material saving in the amount of the beryllium employed.

Other degasifying agents such as Mn, Si, Ti, Zr, B and the like are not to be considered substantial equivalents for Al in the present invention as they have been found to be detrimental to the adherence and glass sealing properties of the normal oxide film of these alloys when used either alone or in combination with beryllium.

As a specific embodiment of the practice of the present invention, we have found that in the Cr.Ni.Fe alloy containing 5–6% Cr, 42–43% Ni, balance substantially all iron except for fractional percentages up to about 1% of unavoidable metal and metalloid impurities, beryllium in fractional percentages up to about 1% may be incorporated without detriment to the glass sealing or film adherence properties of the normal oxide film of the alloy. As the beryllium content increases, the precipitation hardening advantage of this constituent increases and we have found that between .50–.75% is the most satisfactory range of beryllium for this result.

We have found it desirable to lower the chromium content of the alloy with increases in the beryllium content in order to maintain the thermal coefficient of expansion of the alloy substantially constant. For example, with Be as high as 1% the Cr content is preferably lowered to about 5% and with Be as low as .25% the Cr content may be as high as 5.75% but preferably is within the range 5.25–5.50%.

Where the alloy has been degasified with aluminum prior to the addition of beryllium thereto, the aluminum content of the degasified and solidified alloy should not exceed about .25% and preferably is within the range .10 to .20%. With this aluminum content, we have found that as low as .30% Be will produce substantially equivalent precipitation hardening results as .50% Be in the absence of aluminum.

Our preferred alloy composition for use in the forming of metal to glass seals comprises Cr 5.0–5.25%, Ni 42%, Be .50%, balance substantially pure Fe. Another preferred alloy composition comprises Cr 5.0–5.25%, Ni 42%, Al .20%, Be .30%, balance substantially pure Fe. In each of these alloys the total carbon, sulfur, phosphorus, manganese and silicon should be present in substantially residual amounts.

In the forming of a metal to glass seal utilizing this alloy and lime glass, the surface of the alloy is thoroughly cleaned, a relatively thin oxide film is formed thereon, preferably by heating under oxidizing conditions to elevated temperatures, and glass is fused and pressure molded onto the oxidized metal surface, as heretofore practiced in the art. The Be and Al oxides present in the oxide film will be found to be non-deleterious to the adherence of the film to the metal surface and to the sealing properties of the film with the glass. The presence of the Be in the metal inhibits the evolution of gas from the metal at the sealing temperatures employed and it will be found that the sealing temperature employed is sufficient to induce precipitation hardening of the metal by the formation of Ni and Cr beryllide compounds. To condition the alloy for the maximum beneficial effects incident to this precipitation hardening, the alloy prior to sealing into glass should be subjected to a Be-solutioning heat treatment at temperatures within the range 700–900° C. followed by quick cooling. Such heat treatment may be done under oxidizing conditions, if desired, to simultaneously produce on the surface of the metal the desired thickness and character of oxide film best adapted for sealing to glass.

Having hereinabove described the present invention generically and specifically, it is believed apparent that many modifications and departures may be made therein without departing essentially from the nature and scope thereof and all such are contemplated as may fall within the scope of the following claims:

What we claim is:

1. A metal part for a metal to glass seal, said part consisting of an alloy comprised of Cr 5–6%, Ni 42–43%, Be in fractional percentages below about 1%, balance Fe except for fractional percentages of other metal and metalloid impurities each in amounts not exceeding about .20%.

2. A metal part for a metal to glass seal, said part consisting of an alloy comprised of Cr 5–6%, Ni 42–43%, Be .50–.75%, balance Fe except for fractional percentages of other metal and metalloid impurities each in amounts not exceeding about .20%.

3. A metal part for a metal to glass seal, said part consisting of an alloy comprised of Cr 5%, Ni 42–43%, Be about 1%, balance Fe except for fractional percentages of other metal and metalloid impurities each in amounts not exceeding about .20%.

4. A metal part for a metal to glass seal, said part consisting of an alloy comprised of Cr 5.25–5.50%, Ni 42–43%, Be .25%, balance Fe except for fractional percentages of other metal and metalloid impurities each in amounts not exceeding about .20%.

5. A metal part for a metal to glass seal, said part consisting of an alloy comprised of Cr 5%, Ni 42%, Be .50%, balance Fe except for fractional percentages of other metal and metalloid impurities each in amounts not exceeding about .20%.

6. In a metal to glass seal, a metal part comprised of an alloy comprised of Cr 5–6%, Ni 42–43%, Be in fractional percentages below about 1%, balance Fe except for fractional percentages of other metal and metalloid impurities, each in amounts not exceeding about .20%.

VICTOR O. ALLEN.
CHARLES P. MARSDEN, JR.