

Nov. 28, 1967

S. BITKO

3,355,332

GLASS-METAL SEAL

Filed Oct. 28, 1963

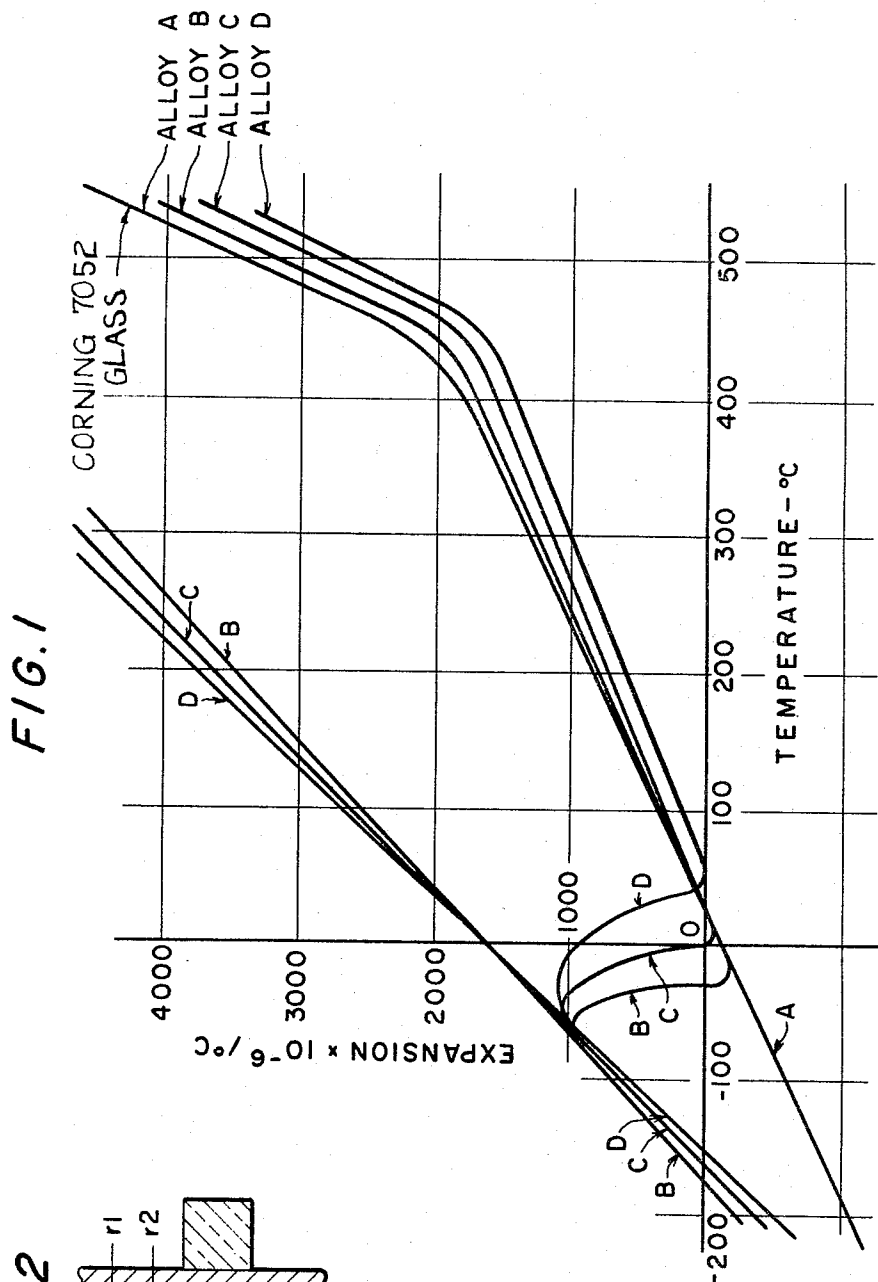
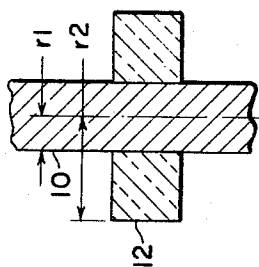


FIG. 2



INVENTOR:
SHELDON BITKO

BY Harry Ernest Rubens

ATTORNEY

1

3,355,332

GLASS-METAL SEAL

Sheldon Bitko, Stamford, Conn., assignor of one-half to
Harry Ernest Rubens, Greenwich, Conn.
Filed Oct. 28, 1963, Ser. No. 319,474
3 Claims. (Cl. 148—13)

This invention relates to a glass-metal seal of the type wherein the glass surrounds the metal conductor.

Glass to metal seals are divided into two groups, i.e. seals to hard glasses having coefficients of linear thermal expansion ranging from 3.2 to 5.0×10^{-6} per degree C., and seals to soft glasses with expansions above say 8.8 .

Searches for metals and glasses with matched coefficients of expansion over the range from room temperature to the upper annealing temperature of the glass have resulted in the general use of tungsten, molybdenum, and alloys containing these metals, or the nickel-iron-cobalt alloys, for sealing to hard glass; and platinum, platinum substitute alloys, nickel-iron alloys, and high expansion alloys containing a proportion of chromium, for sealing to the soft glasses.

A seal with matched coefficients of expansion should be understood to mean one in which the residual stresses whether tensile or compressive, are held to an acceptable minimum.

It is generally accepted that in such a seal, the stresses developed in the interface of a glass-metal junction should be compressive where the glass is strongest, rather than in tension where the glass is weakest.

One of the methods of reducing the strain is by lowering the expansion coefficients since the strains developed for a given temperature, will be less for the low expansion materials.

In using the iron alloys, the ratio of constituents are, in the prior art, optimized to obtain the lowest coefficients of expansion, the highest inflection point, and the lowest transformation temperature.

The inflection point is the temperature at which the rate of expansion increases with increasing temperature. The transformation point of a metal is that temperature at which the metal passes through a phase change. In nickel-cobalt-iron alloy seals, the gamma-alpha transformation point is of the utmost importance.

By obtaining a high inflection point and a low gamma-alpha transformation point, the maximum linearity exists between the expansion and contraction coefficients in the metal and glass.

In the prior art, the relationship between the constituents of the alloy is adjusted so that the gamma-alpha transformation cannot be induced, even by immersion in liquid air (-194° C.).

Substitution of cobalt for some of the nickel in the iron-nickel alloy will desirably lower the coefficient of expansion without affecting the inflection temperature thus providing alloys for sealing to hard glasses.

However increasing the cobalt content, will increase the temperature at which the transformation phase is initiated. Thus the cobalt content has been limited in the prior art to avoid transformation during the useful seal temperature range.

The optimum cobalt content is presently taken as the percentage of nickel and cobalt and of other elements which will cause transformation to take place below -100° C. See the Journal of Franklin Institute 1935, 220, 733-753.

Carbon has been recommended in order to prevent transformation. However it is accompanied by an undesirable alteration in the physical properties of the alloy. So too are manganese, chromium, and silicon.

2

One of the objects of the present invention is to provide a metal alloy in which the cobalt content of the conductor in a glass-metal seal may be increased resulting in a lower thermal expansion coefficient than the conductors now in use for similar seals.

Some of the other problems in glass-seal design are:

- (1) Lead fatigue failure (bending test)
- (2) Lead pull failure (pulling test)
- (3) Thermal shock failure (stain on heat up)
- (4) Glass climb (meniscus chips exposing wire)

In matched seals, items 2 and 3 are functions of the bond strength of the glass-to-metal seal. The greater the oxide generally, the greater the bond strength.

However, the greater the oxide coating, the lower is the lead fatigue strength and the higher the glass climb. The problem is presently resolved into balancing the requirements 2 and 3 against 1 and 4. This is difficult to do since the exact amount of oxide necessary varies with the coefficient of expansion of the metal and glass in each individual melt, and when paired with each other.

By placing the seal under increased compression items 2 and 3 would be improved and since less bond strength and penetration of the glass into the metal is necessary, the quantity of oxide may be reduced, improving items 1 and 4 proportionately.

Other objects of the invention accordingly are to provide a seal with higher lead fatigue strength, with increased pull-out values, with improved thermal shock characteristics and with less glass climb, all obtained by increasing the compressive stresses at the glass-metal interface.

These and other objects are obtained and the new results achieved as will be apparent from the seals, alloys, and the method of preparing the same as is fully disclosed in the following description, particularly pointed out in the appended claims and from a consideration of the drawing attached hereto in which:

FIG. 1 is a chart plotting expansion against temperature throughout the heating and cooling cycle of an improved glass-metal seal of the present invention, and

FIG. 2 shows the dimensional relationship between the glass and the conductor.

The present practice is to specify a metal alloy which has a slightly lower expansion characteristic than the glass. Upon cooling, this theoretically provides a slight compression. Unfortunately two factors intervene. First, manufacturing procedures preclude the possibility of uniformly matching batches of glass and metal, for in approximately 50% of the seals, the disparity in "matched" batches will cause seals to develop excessive tensile stresses at the interface during the cooling process. For example, it has been found that a change of only 0.33% in the silicon or aluminum impurity in the metal, is sufficient to produce tensile stresses in excess of 400% over the tensile strength of the glass.

Another factor is that metal has a higher thermal conductivity than the glass and will cool more rapidly putting the glass under tension which will result in a weakened seal.

I have discovered that by increasing the volume of the conductor during the cooling process by changing the alloy from a face centered cubic structure (gamma phase) to a body centered cubic structure (alpha phase), I can maintain compressive stresses in the glass-metal interface, despite the foregoing difficulties. When this transformation takes place, it can be shown that the body centered structure would have 1.4% greater volume than the face centered structure.

In linear dimensions then, the 1.4% increase in volume corresponds to a 0.5% increase in diameter of a wire.

This means that a seal made with terminal wire in the gamma phase, and the temperature of the seal is lowered to the point where the glass is rigid (i.e. below the strain point) that if the terminal wire metal is now induced to transform from the gamma to the alpha phase, an increase of approximately 0.5% in diameter of the wire will serve to put the glass-metal interface in definite compression constantly throughout the normal operating temperature range.

By using a nickel-cobalt-iron alloy with an increase in the cobalt content over that presently used, a transformation can be induced to take place during the normal operating temperature of the seal, which will compensate for the loss in compressive stresses that can otherwise take place. An additional advantage is the lower coefficient of expansion obtained by employing the higher cobalt content. A further advantage may be obtained by increasing the nickel content. This will increase the inflection temperature. Although it does this by also increasing the expansion coefficient, this increase can be suppressed by adding cobalt without loss of the increase in the inflection point.

Thus there is obtained a higher inflection point metal with a lower coefficient of expansion, which will permit the use of glass having a higher inflection point and a lower expansion characteristic. This adds even further to the maximum temperature limit of the seal, and to an increase in its thermal shock strength.

In accordance with the present invention therefore an alloy is provided for the conductor in a glass seal which will pass through the transformation point in the operating temperature range of the seals to obtain new and desirable results hitherto unforeseen.

Examples

I have found that an alloy containing by weight 28% nickel, 18% cobalt and the balance iron, has a transformation point about -30°C . An alloy containing 27% nickel, 19% cobalt, and the balance iron has a transformation point about 0°C . and an alloy having 26% nickel, 20% cobalt has a transformation point of about 30°C .

Tests

Using a known alloy containing 17% cobalt, 29% nickel, and the balance iron, which possesses a transformation point below -80°C ., sample seals were made up of this and the various alloys of the examples, and pull strength tests were conducted to determine the relative values. The glass used was Corning 7052, a borosilicate glass having the same nominal curve as the known 17% cobalt alloy as shown in the expansion chart of FIG. 1. The test results are as follows:

TEMPERATURES AT WHICH TRANSFORMATION WAS INDUCED

Alloy Lot	Percent Cobalt	Pull-out Values, Room Temp., pounds	Pull-out Values for 4°C . Temp., ¹ pounds	Pull-out Values for -60°C . Temp., ² pounds	Pull-out Values for -196°C . Temp., ³ pounds
D-----	20	30	30	30	30
C-----	19	17	18	28	30
B-----	18	17	17	25	28
A-----	17	15	15	15	15

¹ Ice water. ² Dry Ice. ³ Liquid nitrogen.

The seals were subjected to progressively lower temperatures to induce transformation. It can be seen that even though transformation was only partially obtained, that increased pull-out values resulted.

The D or 20% cobalt alloy maintained the highest pull-out values ranging from room temperature to -196°C ., indicating that transformation took place above room temperature, while the 19% and 18% cobalt content increased their pull-out values as the transformation was further induced. However, no change occurred in the

17% cobalt metal which could not be induced to transform at any temperature. The expansion and contraction curves for the various alloys are shown in FIG. 1. After transformation from the gamma to the alpha phase, the expansion coefficients increase when the temperatures are increased, as is evident by the upper curve of B, C, and D.

Seals made with alloys A, B, C, and D were tested using the helium mass spectrometer leak tester. It was found that when subject to increasing degrees of thermal shock, such as immersion into molten metal baths, glass seals made with lot A material showed leakers at 325°C ., but that in the transformed or partially transformed alloys, i.e. lots B, C, and D, temperatures in excess of 450°C . produced no terminal leak failures. It is worth noting that such tests were performed on seals that were manufactured simultaneously so that process variations could be eliminated from the results.

Further advantages

Other advantages of this technique are:

(1)(a) Oxide coating of conductors which is required for the A alloy, to insure bonding, may be reduced to a degree sufficient to promote wetting only and to eliminate signs of scratches or draw marks. (b) This will simplify the cleaning and if used the plating technique. (c) Also the lead fatigue value is considerably improved due to lesser oxide penetration.

(2) Conductors are stiffer due to higher hardness. This cuts down tangling and makes insertion into the sockets easier.

(3) Metal grain size is smaller making for easier and more reliable welds.

(4) In the usual seal, the pull-out strength is provided in part by the oxide placed on the metal. This causes considerable glass climb. By reducing the oxides to a minimum or by eliminating the oxides entirely, the glass climb can be reduced or avoided, thus providing glass less apt to crack.

The present seal is intended for a glass seal design wherein the glass is of sufficient volume to provide adequate resistance to the compression developed. Referring to FIG. 2 of the drawing, it is recommended that where r_1 is the radius of the conductor 10 and r_2 is the radius of the glass 12, that: $r_2=2r_1$ where K is a maximum.

A typical seal would have a K of 3, with a conductor diameter of .020". However, acceptable seals can be made where K is as low as 1.1 if r_1 is sufficiently small.

It is conceivable that a retransformation from the alpha to the gamma phase could take place at temperatures above 600°C . This is however about 100°C . above the maximum use temperature of this family of glass seals.

It is also true that if the seal is cooled sufficiently, the greater contraction of the alpha phase material could cross the glass seal cooling curve, and put the glass-metal interface under tension. However using the theoretical calculation for the expansion that takes place for complete transformation, it appears that such a cross over could exist on materials that start transformation at 0°C ., only by cooling the seal to a temperature of 100°C . below absolute zero. Consequently this condition is meaningless.

Nickel-cobalt-iron alloys having a composition by weight of from 20 to 50% nickel, 5 to 20% of cobalt, .1 to 1.0% of manganese and other metals except iron, and 74.9% to 24% of iron can be made to transform within the operating temperatures of glass seals which is from above -100°C . to about 300°C .

The transformation can take place without disturbing the inflection point which matches that of the glass or about 450°C . where the expansion coefficient starts to increase significantly.

In general the conductor of suitable diameter is cleaned and both conductors and glass is heated. The heated glass

5

is then flowed around the conductor and the temperature is allowed to cool below the transformation temperature. The process of oxidizing the conductor may be beneficially employed, but the seal must be operated below the annealing point of the glass once transformation takes place less loss of the compressive stresses occur.

In accordance with the present invention I have created a glass-metal seal employing metal capable of being transformed from a gamma to an alpha phase. The constituents of the alloy are preferably optimized to obtain a high inflection point and transformation point which may be completed at approximately room temperature. Increasing the cobalt content to obtain the beneficial lowering of the expansion coefficient may advantageously be used to increase the temperature at which the gamma phase will change to the alpha phase. The transformation of the alloy will allow the seal to operate thereafter with higher compressive stresses eliminating the danger of tensile stresses developing in the glass-metal interface. Additionally the pull-out values will increase, the danger of leaks developing from thermal shock will be lessened, less oxide will be needed with better lead-fatigue values, stiffer conductors will result, better cleaning, plating and welding techniques are possible, and with less glass climb and breakage.

I have thus described my invention, but I desire it understood that it is not confined to the particular forms and methods shown and described, the same being merely illustrative, and that the invention may be carried out in other ways without departing from the spirit of my invention, and, therefore I claim broadly the right to employ all equivalent instrumentalities coming within the scope of the appended claims, and by means of which objects of my invention are attained and new results accom-

6

plished, as it is obvious that the particular embodiments herein shown are examples given and described are only some of the many that can be employed to attain these objects and accomplish these results.

I claim:

1. In the method of heat treating a glass to metal composite wherein the glass surrounds the metal, and the metal consists substantially of an iron-nickel-cobalt alloy, the step of transforming the metal from the gamma to the alpha phase microstructure at temperatures between 0° C. to 300° C.

2. The method of claim 1 wherein the metal consists substantially of 19-20% cobalt, 27-26% nickel, and the balance iron.

3. A glass-metal composite wherein the glass surrounds the metal, and the metal consists substantially of 19-20% cobalt, 27-26% nickel, and the balance iron, said metal having a substantially alpha phase microstructure at temperatures of 0° C. up to 300° C.

References Cited

UNITED STATES PATENTS

2,062,335	12/1936	Scott	75—170 X
2,065,404	12/1936	Scott	161—196
2,071,196	2/1937	Burger et al.	75—170 X
2,334,020	11/1943	Muller	29—472.9
2,677,877	5/1954	Cox	29—472.9
2,743,553	5/1956	Armistead	161—196

HYLAND BIZOT, *Examiner*.

P. WEINSTEIN, *Assistant Examiner*.

DAVID L. RECK, *Primary Examiner*.