April 7, 1942. P. R. KALISCHER ET AL 2,279,168

PROCESS FOR KOVAR-GLASS SEALS

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Fig. 1.

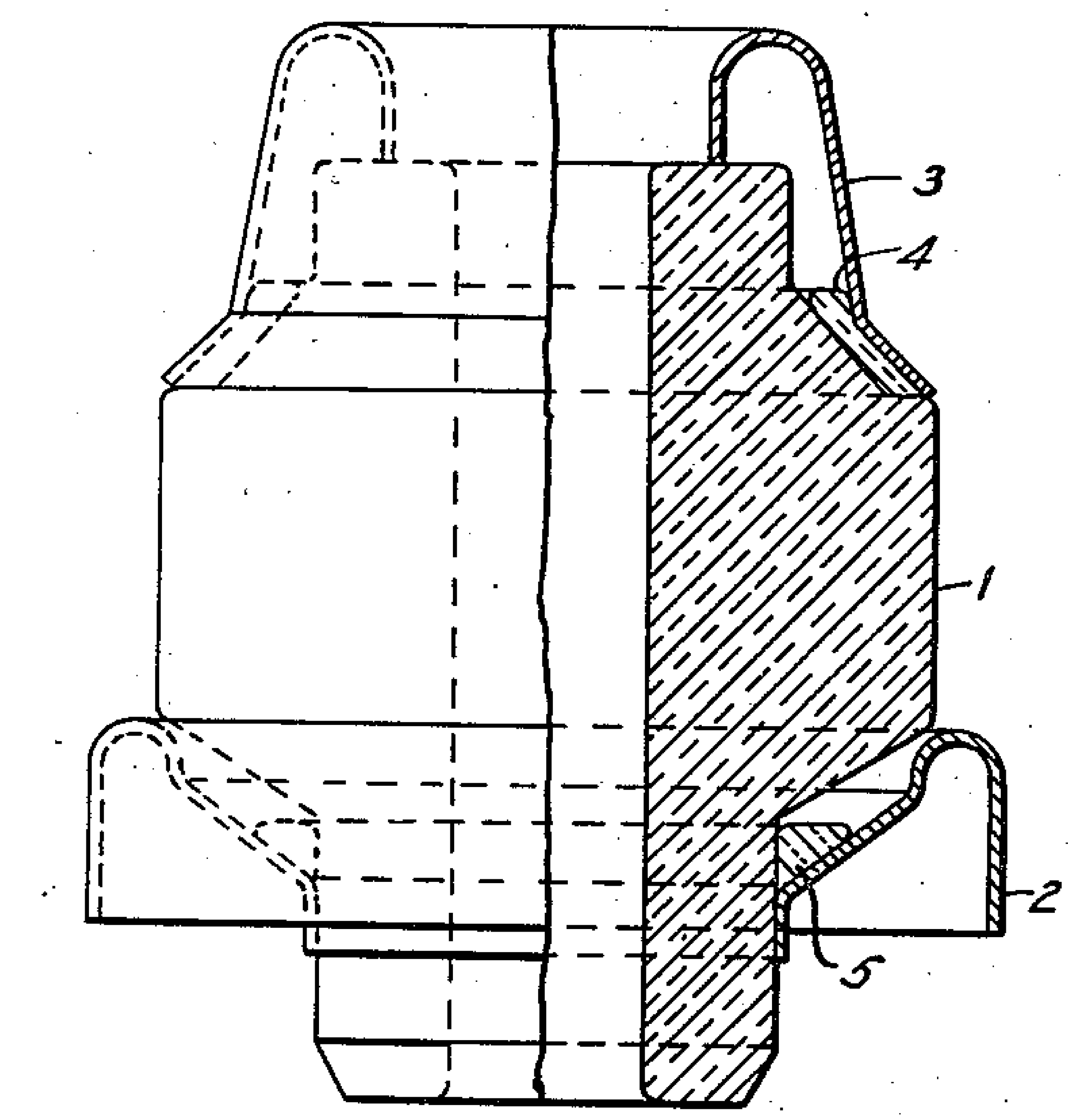


Fig. 2.

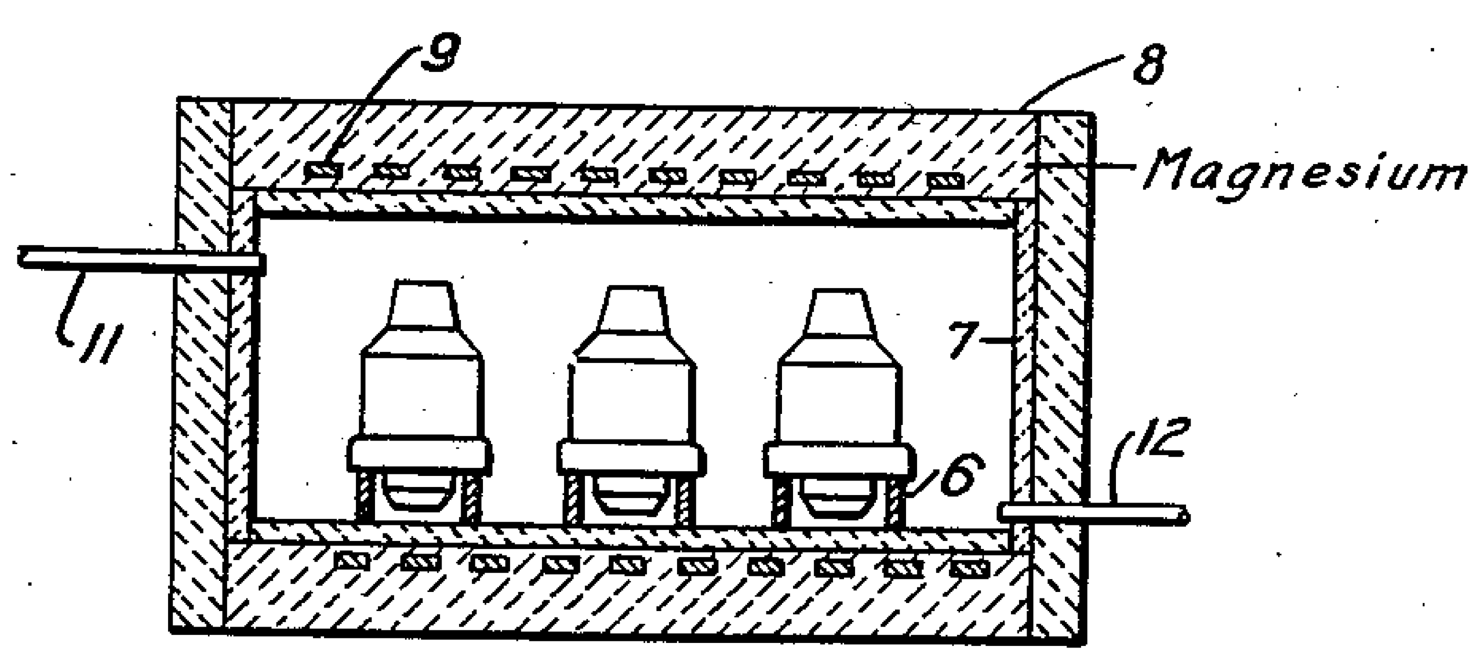
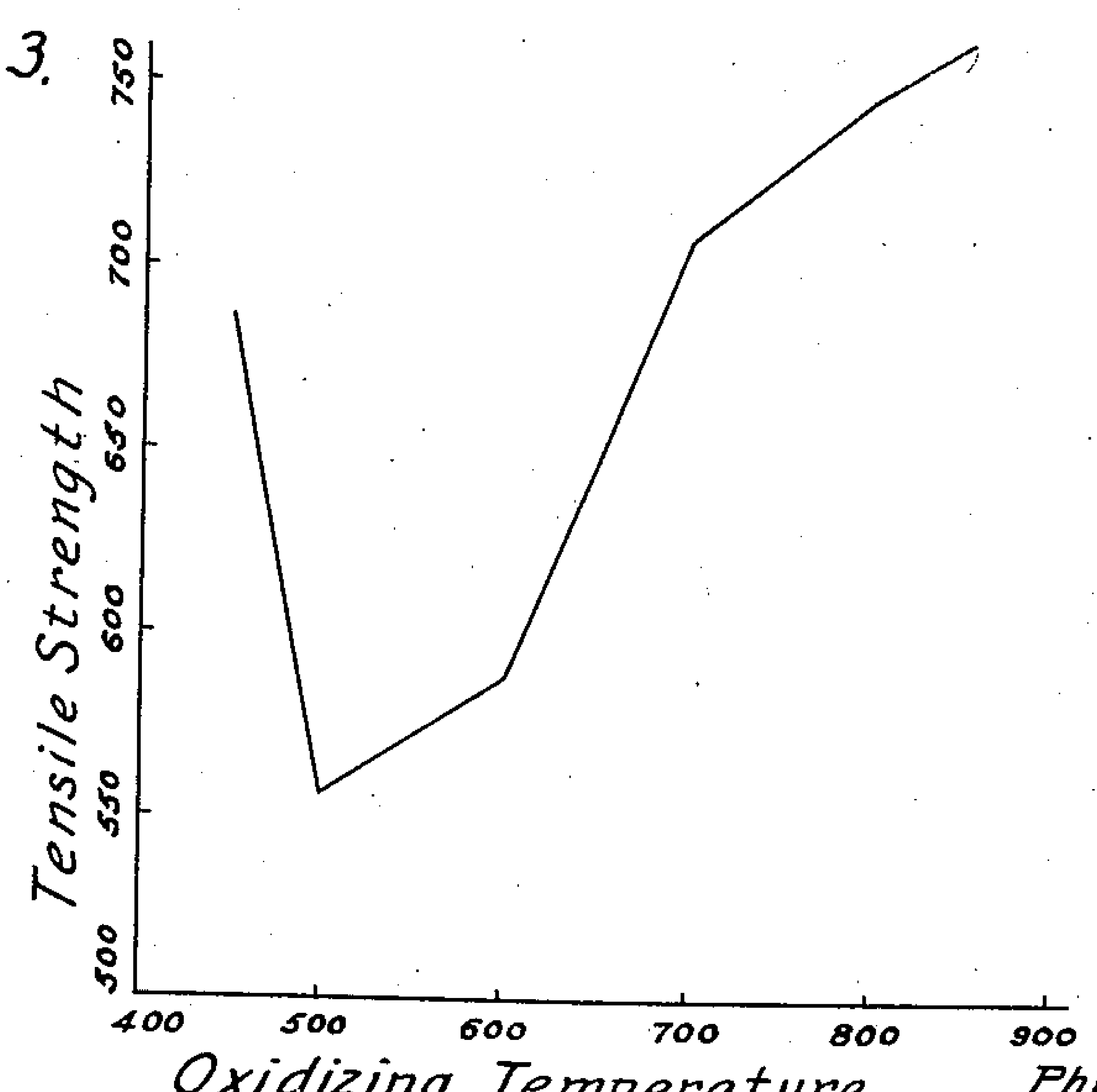


Fig. 3.



WITNESSES:

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PROCESS FOR KOVAR-GLASS SEALS

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Application February 29, 1940, Serial No. 321,456

4 Claims. (Cl. 49—81)

Our invention relates to a process of manufacturing seals between cobalt-nickel-iron alloys and glasses, and, in particular, relates to the process of making seals in which the glass is interposed between the aforesaid alloy and a porcelain member to form a vacuum-tight seal between the porcelain and the metal.

One object of our invention is to provide a method by which seals of the above-described character which are of uniform strength can be made by methods of quantity production.

Another object of our invention is to provide a process by which seals of the above-described character can be made by factory methods which will be uniformly vacuum-tight.

Still another object of our invention is to provide a factory process for making seals of the above-mentioned character which will insure a product which can be relied upon not to crack or leak after being put into commercial use.

A further object of our invention is to provide a process for making seals of the above-described character which shall be free from the uncertainties incident to the hand process of seal making previously employed.

The foregoing and other objects of our invention will be apparent upon reading the following specification in connection with the drawing, in which:

Figure 1 shows, partly in elevation and partly in section, a terminal-insulator embodying a seal made in accordance with our invention;

Fig. 2 is a cross-sectional view of a furnace containing terminal-insulators of the type illustrated in Fig. 1 while undergoing the manufacturing process in accordance with our invention; and

Fig. 3 is a graphical plot employed in explaining certain features of our invention.

For many types of electrical apparatus, it is desirable to employ a vacuum-tight envelope through which conductors pass through sleeves of insulating material. This requires, in general, that there shall be two interfaces or junction-surfaces between the insulating material and a metallic conductor; one such surface between the inleading-conductor and the insulator and the other such surface between the insulating material and a portion of the metallic envelope. The only method of joining insulators to metals which has proved really reliable in service is a fused junction between them. The problem of finding insulating materials and metals which had physical characteristics making it possible to form fused vacuum-tight junctions between them has been one on which an enormous amount of research has been expended over a period of more than fifty years, and it is only within the past few years that a really satisfactory solution to the problem has been found in the joints between borosilicate glass and the alloy Kovar, the principal constituents of which are cobalt, nickel and iron, which are described in Scott Patents Nos. 1,942,261 and 2,062,335, assigned to the assignee of the present application.

While seals in which a glass-insulating sleeve intervenes between a Kovar collar welded to a metallic envelope and a Kovar rod passing through an opening in the envelope are satisfactory for many purposes, a seal in which a porcelain ring is connected to the Kovar collar and the Kovar in-lead by intervening layers of glass has proved desirable for many purposes. Such a seal is described in the copending application of Dewey D. Knowles, Serial No. 97,976, filed August 26, 1936, and assigned to the assignee of the present application.

Fig. 1 illustrates a porcelain insulating member of the general type just mentioned. It comprises an annular member 1 made of porcelain, for example, comprising approximately

	Per cent
SiO_2	70.97
Al_2O_3	23.15
Fe_2O_3	0.39
TiO_2	0.76
CaO	0.12
MgO	0.14
Na_2O	1.09
K_2O	3.30

The surface is covered with a glaze comprising about

	Per cent
Feldspar	36.1
Whiting	11.0
Kentucky special ball clay	13.0
Flint	21.1
Barium carbonate	10.0
Iron oxide	3.8
Manganese dioxide	3.0
Chromium oxide	2.0

Surrounding the lower cylindrical end of the member 1 is a collar 2, preferably of sheet metal, consisting of the alloy Kovar, comprising preferably substantially the following proportions:

	Per cent
Nickel	30
Cobalt	18
Iron	52

A collar 3 of the same material surrounds the upper end of the insulator 1. The collar 3 may be welded or soldered to a flange on a metal rod projecting through the central hole in porcelain 1, and collar 2 may be soldered or welded to a metallic envelope or chamber. Between the collars 2 and 3 and the porcelain member 1 is fused a layer of glass which is preferably the material known to the trade as G705AJ glass, manufactured by the Corning Glass Company. An analysis of a specimen of this glass, which the applicants believe to be correct, showed the following major constituents:

	Per cent
SiO_2	67.3
Na_2O	4.5
K_2O	0.7
B_2O_3	24.3
Al_2O_3	2.2

It is customary in the glass blowing art to make seals between glass and metal by heating the glass in a gas flame in contact with the metal until the glass forms a fused junction with the latter. The two are then allowed to cool together, sometimes being held in a smoky gas flame to control the rate at which they cool down from their highest temperature a hundred degrees C. or so. This controlled cooling toward room temperature is called "annealing." Since most metals oxidize when heated in the atmosphere of the room, oxidation of the metal surface takes place when a glass blower makes seals as just described. It is possible for the glass blower to make seals of the type shown in Fig. 1 by this manual method, heating the porcelain slowly to a temperature at which the glass fuses, then coating its surface with a layer of glass at the two regions required, heating the collars 2 and 3 to roughly the same temperature, pressing them in place against the surface of molten glass, and then annealing the unit. However, when the attempt was made to carry out this process in quantity production, it was found that the resulting seals varied considerably in strength and durability. For many purposes, it was desirable to have seals which could withstand considerable mechanical forces tending to produce an axial displacement of the inleading conductor which passed through the central hole and was welded to the collar 3 and the metallic container which was welded to the collar 2. For this reason, it was necessary that seals produced at different times should be fairly uniform in mechanical strength, and, consequently, the lack of uniformity in the seals produced by hand methods caused considerable loss in commercial manufacture.

The applicants undertook the problem of overcoming these difficulties and providing a method of producing uniformly satisfactory seals in quantity production. One avenue of investigation which the applicants entered upon concerned the oxidation of the Kovar collars 2 and 3. They discovered that, while it was possible, by carrying out the heating of the seal-components in closed furnaces, to avoid any oxidation whatever of the Kovar surface, the seals resulting when this was done were much less satisfactory than those obtained with the ordinary methods of the glass blower. A certain amount of oxidation of the metal surface was found to be necessary in order to form a strong adherent and vacuum-tight junction of the glass to the metal, and too thin an oxide film may dissolve completely in the glass and make an unsatisfactory seal. On the other hand, it was found that, if the coating of oxide was made too thick, it tended to break off and make a seal which was both mechanically weak and liable to leakage between the glass and the metal. Leakage can occur in such cases due to porosity of the oxide.

In order to devise a method of insuring the proper thickness of oxide on the Kovar metal, the applicants carried out a series of experiments in which Kovar metal rods were heated in a furnace of the general type shown in Fig. 2, but in contact with the air at a series of different temperatures ranging from 400 degrees C. to 1000 degrees C. Two different sets of samples were made, one set being maintained at the desired temperature for three minutes and the other set for fifteen minutes. These tests showed that a uniform adherent film of oxide formed as long as the heating-temperature was not above 900 degrees C.; but that above this, the oxide tended to break and scale.

With this information available, a series of tests was made in which Kovar rods were placed for three minute periods in a furnace of the general type of Fig. 2 which was heated to various temperatures between 450 degrees C. and 900 degrees C. Upon removal from the furnace, a tightly fitting glass tube was slipped over the oxidized wire and rapidly sealed to the latter by heating the glass with a gas flame. The resulting seals were then tested for mechanical strength, applying tension between the Kovar rod and the glass in an axial direction. The results of these tests are shown in Fig. 3 in which the abscissae represent the temperature of the furnace in which the Kovar rod was oxidized for three minutes and the ordinates represent the tensile strength in pounds per square inch of the bond between the Kovar rod and the glass. As this curve showed, the oxidizing temperature which gave the greatest tensile strength was 850 degrees C. Some of the seals, when tested, failed because the metal pulled away from the glass and others failed because the glass itself broke in tension. The maximum permissible load in any seal is that overcoming the strength of the bond between the metal and its oxide.

The foregoing tests showed that, to obtain the best seals, it was necessary to accurately control the step of oxidizing the Kovar; and the manual process in which the glass blower oxidized the Kovar incidentally to make the seal proper would not permit such accurate control. It, therefore, seemed to be necessary to carry out the oxidation of the Kovar at a preliminary step, and to carry out the subsequent completion of the seal to glass and porcelain under conditions which would not alter the Kovar-oxidation. In other words, the oxidation of the Kovar should be carried out in a furnace having an oxygen-containing atmosphere; and the subsequent completion of the seal should be carried out in an atmosphere which neither produced further oxidation nor reduction of the Kovar surface. This required that the seal be completed inside a furnace with a controlled atmosphere.

While it would doubtless be possible to employ a number of chemically inert atmospheres, such as argon and helium, in the furnace in which the seals would be completed, nitrogen seemed to be the most desirable atmosphere to employ because of its greater cheapness and availability. It was found that any atmospheres containing hydrocarbons produced bubbles and other deleterious effects in the seals. Commercial nitrogen was found to contain, roughly, 0.05% oxygen, and the latter was sufficient to produce further oxidation of the Kovar. Also even slight traces of moisture caused oxidation of Kovar. Consequently, the above-mentioned remaining trace of oxygen in the commercial nitrogen had to be removed, and it was found that a satisfactory product was attained by passing the gas over hot copper and then over a drying agent, such, for example, as calcined lime or phosphorous pentoxide.

In order to carry out the completion of the seals in the atmosphere just described, a furnace of the general type shown in Fig. 2 could be employed. The collars 2 oxidized as already described, were supported on racks 6 inside a refractory container 7, which might, for instance, be of silica and which formed a completely enclosed chamber. The walls 7 were surrounded by a heat-insulating cover 8 which might, for instance, be a mixture of asbestos and magnesia, in which was imbedded a helical resistance heater 9. Through an inleading duct 11 and an outgoing duct 12, the inside of the container 7 could be flushed and washed out with the purified nitrogen above mentioned. It was also possible, when desired, during the heating or cooling process, to use the same ducts 11 and 12 to displace the nitrogen with hydrogen or any other desired gas. The collars 2 having been arranged in rows on the supports 6, annular members of glass 5 were placed in position within the collars 2 and the porcelain members 1 then inserted in position. Annular members of glass 4 were then supported on the shoulders near the top of the porcelain members 1 and the Kovar collars 3 placed in position resting on the glass rings 4. The furnace, with the seals in place on the member 6, was then closed tight from the atmosphere of the room and the air inside the furnace displaced with pure nitrogen.

Upon raising the temperature inside the furnace sufficiently, the glass rings 4 and 5 become soft and finally fused vacuum-tight to the oxidized surface of the Kovar members 2 and 3 and to the glazed surface of the porcelain member 1. Tests were made to determine the minimum temperature at which the glass would become sufficiently fluid to make vacuum-tight seals to the Kovar and to the porcelain, and this temperature was found to be in the neighborhood of 1050 degrees C. Experiments also showed that the porcelain had a region of transformation in the neighborhood of 575 degrees C. in which it underwent a marked volume change, and that, if it were heated or cooled rapidly through this region, strains were set up which were liable to cause cracking. Experiments had shown that there was practically no oxidation of the Kovar in an atmosphere of air below 600 degrees C., and this fact appeared to offer the possibility of beginning the heating of the furnace while the displacement of air by nitrogen was still in progress. A series of tests was accordingly made in which the complete replacement of the nitrogen occurred at various temperatures during the heating of the furnace and in which the time at which the seal was maintained at maximum temperature around 1050 degrees C. was varied from 8 minutes to 45 minutes. The resulting seals were then subjected to mechanical load tending to pull the porcelain member 1 away from the collar 2. Seals made in this way were also subjected to tests for vacuum tightness. The result of these tests showed that the only seals which could be relied upon to be mechanically strong and to be vacuum-tight were those in which the air had been displaced by nitrogen before beginning the heating of the furnace and in which the time at which the seal was maintained at a temperature of 1050 degrees C. was 45 minutes. The length of the oxidation period must be right, as too short a time fails to permit sufficient solution of the oxide in the glass while too long a time permits too complete a solution of the oxide.

As a result of all the foregoing considerations, the following program was evolved for making satisfactory seals:

1. Pre-heat the Kovar parts in air for three minutes at 850° C.
2. Assemble the component parts of the structure on a suitable jig and put in furnace.
3. Flush furnace with oxygen-free dry nitrogen.
4. Heat from room temperature to 500° C. rapidly, but in not less than 1 hour.
5. Heat from 500° C. to 600° C. at a rate of not more than 50° C. per hour.
6. Heat rapidly from 600° C. to 1050° C. but in not less than one hour.
7. Hold at 1050° C. to 1100° C. for 45 minutes.
8. Cool rapidly to 600° C., but in not less than one hour.
9. Hold for one hour at 600° C.
10. Cool from 600° C. to 450° C. slowly, not faster than 50° C.
11. Cool rapidly to 150° C. or lower, but in not less than two hours.
12. Remove sealed assemblies from furnace at 150° C. or lower.

For many purposes, it is desirable to be able to solder the Kovar members 2 and 3 to metal containers and the like, and for this purpose it is desirable to reduce the oxide on their surfaces after the seals have been made. This can be done by displacing the nitrogen atmosphere of the furnace with hydrogen when 600 degrees C. is reached during the cooling portion of the cycle. However, there is some tendency for certain furnace linings to absorb this hydrogen and retain it until the furnace is used again for manufacturing seals, at which time the hydrogen comes out and reduces the oxide on the Kovar to some extent. We, accordingly, consider it more desirable to permit the seals to cool to near room temperature in their nitrogen atmosphere and then to remove them to another furnace in which they may be heated to a temperature of 550 degrees C. to 600 degrees C. In so doing, the rates of heating indicated by items 4 and 5 in the foregoing tabulation and the rates of cooling indicated in items 10 to 12 must be observed.

While we have described our invention in connection with the making of seals between Kovar, G705AJ glass and porcelain, it would be recognized that the principles involved which apply to the glass and the Kovar are applicable to the making of seals in which no porcelain member is present. In such case, the items 5 and 8 to 10 in the steps enumerated above may be modified, as they relate primarily to heat-treatment of the porcelain, and it is also noted that they may be modified somewhat to suit different porcelains in a manner those skilled in the art can readily determine by experiment. Where no porcelain is used in the seal, items 1 to 3 of the above-enumerated program will be unchanged, the seal may then be heated to 1050° C. in about 2½ hours, then follow item 7; then cool to 500° C. in from 1 to 1½ hours; cooling from 500° C. to 450° C. takes place in 2 hours; and items 11 and 12 of the foregoing program be then followed. It will also be recognized that, while the specific glass has been described as G705AJ and the alloy as containing 30% and 18% cobalt, the general principles apply also to seals employing other glasses and nickel-cobalt-iron alloys of other compositions than those just mentioned, such, for example, as those described in Scott Patents Nos. 1,942,260 and 2,062,335 already mentioned. The methods of determining the duration, temperature and other characteristics of the various steps in the process are broadly applicable to seals generally between different glasses and/or different metals than those here described, and the application of those methods experimentally to determine proper magnitudes for such characteristics under altered conditions of operation or environment will be evident to those skilled in the art and are within the purview of our invention. We, therefore, desire that the terms of the following claims shall be given the broadest interpretation of which they are reasonably susceptible.

We claim as our invention:

1. The method of forming a seal between a cobalt-nickel-iron alloy and glass, which comprises the steps of first heating the alloy for a period of three minutes at 850 degrees C. in an atmosphere of air, permitting it to cool to substantially room temperature, placing the alloy in contact with glass in an enclosure having an atmosphere of substantially pure non-oxidizing and non-reducing gas, heating it to a temperature sufficient to thoroughly fuse said glass, and allowing the seal to cool slowly to room temperature.

2. The method of forming a seal between a cobalt-nickel-iron alloy and glass, which comprises the steps of first heating the alloy for a period of three minutes at 850 degrees C. in an atmosphere of air, permitting it to cool to substantially room temperature, placing the alloy in contact with 705AJ glass in an enclosure having an atmosphere of substantially pure non-oxidizing and non-reducing gas, heating it to a temperature sufficient to thoroughly fuse said glass, and allowing the seal to cool slowly to room temperature.

3. The method of forming a seal between a cobalt-nickel-iron alloy and glass, which comprises the steps of first heating the alloy for a period of three minutes at 850 degrees C. in an atmosphere of air, permitting it to cool to substantially room temperature, placing the alloy in contact with glass in an enclosure having an atmosphere of substantially pure nitrogen gas, heating it to a temperature sufficient to thoroughly fuse said glass, and allowing the seal to cool slowly to room temperature.

4. The method of forming a vacuum-tight joint between a cobalt-nickel alloy and a porcelain surface, which comprises oxidizing the alloy in air for approximately three minutes at 850 degrees C., permitting it to cool, placing the alloy in contact with a member comprising borosilicate glass, placing the porcelain surface in contact also with said member of borosilicate glass, heating the structure thus produced in an atmosphere which is neither oxidizing nor reducing at the rate of not over 500 degrees C. per hour up to a temperature of 500 degrees C., heating from 500 degrees C. to 600 degrees C. at 50 degrees C. per hour, heating in not less than one hour from 600 degrees C. to 1050 degrees C., holding the temperature between 1050 degrees C. and 1100 degrees C. for 45 minutes, cooling to 600 degrees C. in not less than one hour, cooling from 600 degrees C. to 450 degrees C. not faster than 50 degrees C. per hour, and cooling from 450 degrees C. to 150 degrees C. in not less than two hours.

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