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METHOD OF MAKING GLASS-TO-METAL SEALS

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Many alloys have been proposed and some are well known for making glass-to-metal seals. In general these alloys have been so selected as to composition that the thermal expansion characteristics of the alloy will match, or conform appropriately to, the corresponding characteristics of the glass. For many practical applications, it has been considered desirable that the alloy should have a slightly higher coefficient of thermal expansion than that of the glass to which it is to be sealed, so that when cold the glass will be in a controlled state of slight compressive stress. If, however, this difference is too great, cracking or stripping of the glass may occur.

The present invention is particularly (but not exclusively) concerned with the sealing of certain alloys to relatively soft glasses having coefficients of thermal expansion in the region of .0000080 to .000010 per degree centigrade over the range 20° to 500° C. Such glasses are common glass as used, for example, in the manufacture of plate glass having a coefficient of expansion of the order .00000895 per degree centigrade, or another with an expansion coefficient of .00000930 per degree centrigrade, or a special high expansion glass with an expansion coefficient of .00000972.

For the purpose of sealing to glasses of the above kind, it has hitherto been a general practice to employ chromium irons containing 16 to 30 per cent of chromium. A drawback to the use of such alloys with a chromium content in the higher part (say 26–30%) of the range, is the difficulty of producing the alloys in suitable forms for subsequent use, since they have poor hot and cold working properties, in particular, they are difficult to spin or deep press. Efforts have been made to overcome these difficulties by various alloy additions, but these are only partially successful. In consequence, attention has been given to the alloys within the lower part of the chromium range, say 16 to 22% chromium, which are much easier to work. These, however, have a slightly higher coefficient of expansion than the 26 to 30% alloys and can only be used with reasonable success for sealing to special glasses having high coefficients of expansion. They also tend to suffer from transformation changes which have a deleterious effect on the sealing characteristics. One way of dealing with these transformation changes is to add stabilizing elements such as titanium, niobium, tantalum, aluminium, molybdenum, vanadium and tungsten, which suppress the transformation changes, or by using an alloy with a very low

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carbon content. These modifications to the plain chromium iron alloys, however, do not materially affect the normal thermal expansion rate and unless glasses with a suitable rate of expansion are selected trouble still arises by cracking or stripping of the glass.

The present invention provides a method of making a glass-to-metal seal which is characterised by the step of applying a light coating of cobalt or cobalt-containing substance to the surface of the "metal" or the "glass" in the vicinity of the seal, prior to sealing. In making a seal by a method involving the coating step aforesaid, the cobalt of the coating will oxidise to form cobalt oxide which will be absorbed by the hot plastic glass in its vicinity, the thus modified glass being plastic at a much lower temperature than glass without cobalt oxide addition. In this way the method results in the production of a seal which is substantially stress-free and adherent.

While the invention may be applied to glass-to-metal seals in general, the principal application which is contemplated is to seals between chromium iron alloys and relatively soft glasses of the kind previously indicated.

In carrying out the invention any convenient method may be employed for applying the cobalt coating. Electroplating or metal spraying methods may for example be used. Alternatively the coating may be applied by dusting the metal or glass surfaces with powdered cobalt oxide or powdered cobalt-containing substances. Again, if desired, the coating may be applied by painting or spraying the metal or glass with a suspension in liquid (e. g. water, paraffin or oil) of cobalt oxide or cobalt-containing substances, in which case the liquid should be dried off before the seal is made in order to prevent bubble formation in the glass.

The above methods are equally suitable for both types of plate glass available in this country and with both 17% chromium iron and 20% chromium iron available as standard products. The invention has also proved satisfactory with chromium irons containing appreciable amounts of retained austenite when cooled from the sealing temperature. These materials would not otherwise give satisfactory seals.

The invention is particularly advantageous in the manufacture of spun cones of cathode-ray tubes used in the Television Industry, and in similar applications.

The invention is particulary applicable to the making of glass-to-metal seals using chromium

iron comprising carbon 0.2% maximum, chromium 10 to 30% and the remainder substantially all iron. The preferred range for the chromium iron is carbon 0.1% maximum, chromium 16–22% and the remainder substantially all iron. Stabilizing elements such as titanium, niobium, tantalum, aluminium, moylbdenum, vanadium and tungsten may also be present.

The invention includes glass-to-metal seals (e. g. for electric filament lamps, cathode-ray tubes and the like) when made by methods which include the characteristic step herein described.

I claim:

1. A method of making a glass-to-metal seal which consists in first applying a light coating consisting of metallic cobalt to at least one of the glass and metal surfaces at which the seal is to be formed, and then effecting heat sealing under conditions such that the cobalt of the coating will oxidise to form cobalt oxide which will be absorbed by hot plastic glass in the vicinity, the thus modified glass being plastic at a much lower temperature than glass without cobalt oxide addition.

2. A method of making a seal between glass and a chromium-iron alloy, which method consists in first applying, by the process of electro-plating, a light coating comprising cobalt to the metal surfaces at which the seal is to be formed, and then effecting heat sealing under conditions such that the cobalt of the coating will oxidise to form cobalt oxide which will be absorbed by the hot plastic glass in the vicinity of the seal, the thus modified glass being plastic at a much lower temperature than glass without cobalt oxide addition

3. A method of making a glass-to-metal seal between a chromium-iron alloy containing a portion of carbon 0.1% maximum, chromium 16–22% and the remainder substantially all iron, and a relatively soft glass having a coefficient of thermal expansion in the region of .0000080 to .000010 per degree centigrade over the range 20° to 500° C,. which method consists in first applying a light coating comprising a cobalt containing substance which will upon heating form cobalt oxide to at least one of the glass and chromium-iron surfaces at which the seal is to be formed, and then effecting heat sealing under conditions such that from the coating aforesaid there will be produced cobalt oxide which will be absorbed by hot plastic glass in the vicinity of the seal, the thus modified glass being plastic at a substantially lower temperature than the same glass without such modification.

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