New Techniques in Glass-to-Metal Sealing*

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Summary—The new techniques in glass-to-metal sealing described in the paper include accurate and controlled oxidation of the metal, and the powder-glassing method of making seals. The accompanying experimental data refer to Kovar, since most of the laboratory work has been on glass-to-Kovar seals.

Data are presented for Kovar oxidized at a number of controlled temperatures and varying times. Excellent adherence of glass to Kovar is obtained with a weight gain of about 0.0003 to 0.0007 grams per square centimeter regardless of temperature of oxidation. With preoxidation, any tendency for peeling or flaking shows up readily on cooling to room temperature. This condition is undesirable, since it indicates subsequent poor glass-to-metal adherence.

The powder-glassing method of making seals consists of grinding the glass, suspending the powdered glass in a suitable liquid, applying it to the prepared metal, and fusing to form a thin glass layer. The glass tube or bulb is subsequently joined to this layer as a glass-to-glass seal. Several examples of applications are given, one of them pertaining to multisection blanks employing butt seals.

Hypotheses on the function of H_2 baking of Kovar, the adherence of glass to Kovar, and the nature of the oxidation process of Kovar are presented.

Introduction

In MAKING glass-to-metal seals the usual technique consists of cleaning the metal, oxidizing it the proper amount in order to develop a strong, vacuum-tight seal, and sealing the glass to the metal while it is still hot. Consequently, in seals made on the glass lathe, success is entirely dependent upon the skill and judgment of the operator. This is especially true on large and intricate seals. He must decide whether he is oxidizing sufficiently and, also, whether a firmly adhering oxide layer has been obtained.

The development of the powder-glassing method at the Research Department of the Westinghouse Lamp division enables the making of seals on a controlled basis. The new techniques in glass-to-metal sealing to be described include accurate and controlled oxidation of the metal, and the application of the glass in a powdered state that is fused to form a thin glass layer to which the glass tube or bulb is subsequently joined as a glass-to-glass seal.

Oxidation of Metal

Since most of the laboratory work has been on glass-to-Kovar seals, references to specific data will be on Kovar, an iron-nickel-cobalt alloy developed at Westinghouse.

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Prior to oxidation the Kovar is baked in a wet hydrogen atmosphere at 1100°C. for 15 to 30 minutes, in order to eliminate possible bubbling at the glass-metal interface during sealing.

Experiments on oxidation were carried out in an electrically heated oven at controlled temperatures and varying times. Curves for weight gain per unit area versus time were thus obtained for a number of constant temperatures, as shown in Fig. 1. A range of values is indicated, since such variations occurred with changes in H_2 baking, cleanliness of pieces, standing prior to oxidation, etc.

The excellent adherence of the glass to Kovar is obtained with a weight gain of about 0.0003 to 0.0007 grams per square centimeter regardless of temperature of oxidation, i.e., approximately 17 minutes at 800°C., 3 minutes at 900°C., 1 minute at 1000°C., or $\frac{1}{4}$ minute at 1100°C.

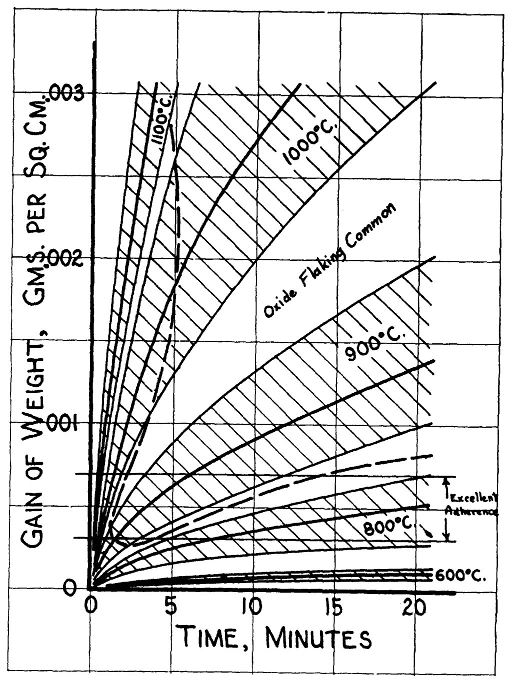

Fig. 1—Oxidation of Kovar. Time-rate curves are shown. Area inside V-shaped dotted curve indicates conditions under which greatest tendency for oxide flaking exists.

If the piece is underoxidized, the strength of the seal is poor but it is still vacuum tight. If it is overoxidized, the strength is good but the seal may be a leaker because the glass is unable to penetrate the oxide layer completely, thus leaving a continuous porous path through which gases can seep into the tube.

With the preoxidation of Kovar any tendency for peeling or flaking shows up on cooling to room temperature. Statistical recording has shown that this tendency exists more strongly under certain conditions of temperature and time, as indicated in Fig. 1 by the area inside the V-shaped dotted line. Flaking is emphasized by improper or lack of H_2 baking, dirty Kovar, and other factors.

Pieces with flaking or peeling oxide layers should be eliminated immediately, since poor oxide adherence also results in poor glass adherence. Such a tendency may be missed with the usual glassing technique, wherein the glass is sealed to the oxidized metal while the latter is still hot.

Powder-Glassing Method of Making Seals

Grinding of glass, in any form, to pass through a 200-mesh sieve constitutes the first step in the preparation of the glass for use in the powder-glassing method of making seals. A porcelain-ball mill is used to avoid contamination by iron. The composition of the ground glass is the same as normally used for sealing to a given metal; for instance, Corning 7052 or 704 for Kovar.

The powdered glass is suspended in a suitable liquid such as water or alcohol. With alcohol, which has been used most extensively at Westinghouse, a few drops of $LiNO_3$ solution or NH_4OH keep the glass particles from settling out into a hard mass, thus enabling the suspension to be easily dispersed after standing. The best ratio of liquid to solid is determined by careful experimentation.

The powdered-glass suspension is then applied to the oxidized Kovar surface by spraying. The pressure of the spray is controlled by the viscosity of the suspension and the shape of the piece. Pressures ranging from 10 to 40 pounds have been employed.

If the powdered glass is to be applied by dipping or slushing, the suspension is adjusted to the proper viscosity and mobility to obtain the necessary thickness of coating. In either case, the glass is restricted to the desired areas by proper masking prior to application, or by brushing afterwards.

The dried powdered-glass coating is then fused in an electrically heated oven. 7052 and 704 glasses produce a smooth coating by firing at 1000°C. for 6 minutes. The powdered glass can also be fused by fires or by induction heating of the metal. Kovar-glass seals are fired in air, since the rate of oxidation of the Kovar is slow in relation to the rate of fusion of the glass. For seals with copper, however, if oxidation during fusion is undesirable, the firing would have to be carried out in a neutral atmosphere, since the rate of oxidation of the metal is faster than the rate of fusion of the glass. The fired pieces are removed from the heat and allowed to cool in air without any annealing. These powder-glassed parts are now ready for tube assembly and can be stored indefinitely.

The thickness of the fused-glass coating is not critical but has ranged mostly from 4 to 6 mils. The thinner coatings are generally preferred, since there is less tendency for pulling away from edges. Considerable amounts of bubbles, seen with low-power magnification, are present. However, these can be ignored, since no detrimental effects have been noticed because of their presence.

Afterwards, the sealing of the tube or bulb to the powder-glassed parts becomes simply a glass-to-glass seal. Nothing is gained in temperature, since just as much heat and "working" are necessary to make the glass-to-glass seal. The advantage lies in the fact that the seals are now protected and extended heating will not affect them, allowing the operator to work on the seals without any time limitations, which is very important in some cases.

Hypotheses

Hydrogen Baking

Wet-hydrogen baking, for instance, in the time allotted should remove any carbon in the surface of the Kovar at either 900 or 1100°C., but the temperature also controls the grain size of the Kovar, as shown in Fig. 2. Variations in time also alter the grain size, but not as effectively. The whole temperature range is used in baking but the large-grain-size structure is desirable, since the oxide, and the glass in turn, then have been found on an average to adhere more firmly to the metal surface.

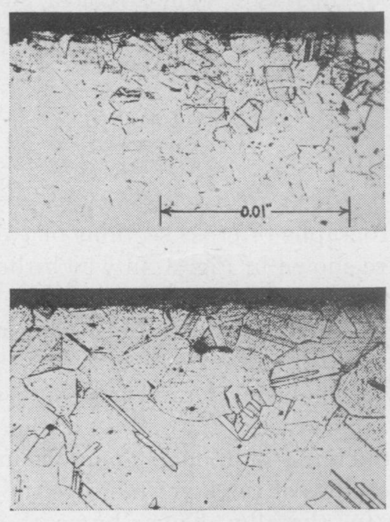

Fig. 2—Effect of wet-hydrogen baking at several temperatures on grain size of Kovar. Magnification, 85×.

Adherence

The adherence of glass to metal can be attributed to both ionic bonds and physical roughness of the metal. The ionic bond is the oxygen bond resulting in an affinity between the metal and glass, manifested as wetting of the former by the latter. Firing in air without any noticeable preoxidation is sufficient to cause this wetting action. Some adherence because of this wetting alone is evidenced by glassing untreated polished Kovar, but this adherence is weak.

The desirable function of oxidation is to roughen the metal surface by action on the grains, as well as along grain boundaries. The degree of roughness is related to the severity of oxidation, and hence the need for a minimum thickness of oxide to develop the adherence strength of the glass. The maximum thickness of this type of oxide is restricted by the ability of the molten glass to penetrate, but not necessarily dissolve completely, the oxide layer at sealing temperature, primarily because of vacuum-tightness considerations. Final adherence strength is thus realized because of the mechanical clinging of the glass or oxide to the roughened metal surface. A good finished seal, however, does not have nor does it need a continuous oxide layer at the interface.

The preference for large grain texture is due to the resulting decrease of grain boundaries. Oxide ridges are formed at boundaries because the volume of oxide is greater than the volume of a corresponding amount of metal, and more metal surface is available there for oxidation. These ridges are not as completely penetrated by the glass as the oxide on the grain surface, with a subsequent loss of some strength, since the glass develops its chief mechanical adherence by direct contact with the roughened metal surface.

Oxidations

Photomicrographs of cross sections of two Kovar-to-glass seals are shown in Fig. 3, in which the Kovar had been preoxidized at 1000°C. for 1 minute to produce the normal amount of oxidation, and also for 10 minutes.

An observation of considerable interest is the presence of a new metallic layer in the surface of the Kovar, with an average thickness of about 10 microns in the normal seal. X-ray studies of the layer indicate the same structure as that for the alloy Kovar but with a condensed crystal lattice because of less iron. In turn, X-ray examinations and chemical analyses of the oxide layer indicate that it is primarily Fe_3O_4. Therefore, in the oxidation of Kovar, iron diffuses preferentially, forming an oxide layer composed primarily of iron oxide and a new alloy layer at the surface consisting mostly of nickel and cobalt.

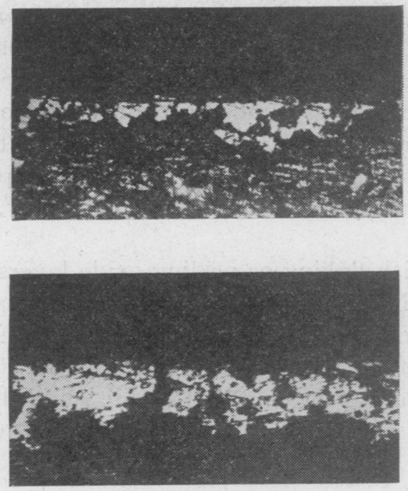

Fig. 3—Photomicrographs of cross sections of Kovar-to-glass seals showing presence of new alloy layer at Kovar surface. Magnification, 350×.

APPLICATIONS

The use of the powder-glassing techniques can be referred to several specific examples. Part of the liquid air trap in the mass spectrometer consists of a special Kovar cylinder brazed to a heavy copper tube. Glass-to-metal seals are required on each end of the part. Prior to the use of the new methods, usual sealing techniques resulted in a shrinkage of about 40 per cent. The powdered-glass method allowed the making of successful seals with no shrinkage. Fig. 4 shows the powder-glassed portions of the cylinder to which subsequent seals were made.

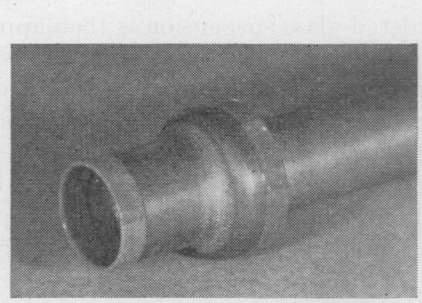

Fig. 4—Part of the liquid air trap in the mass spectrometer, showing the fused thin glass coating applied to the Kovar part. Magnification about 1/3×.

Similar experiences prevailed in the making of multisection blanks employing butt seals. Such butt seals were normally found impossible to make on a glass lathe, since the opposite side of a Kovar ring was oxidizing while the glass blower was making a seal. By first powder-glassing the rings on both sides this difficulty was eliminated, since the glass coating protected the seal interface during subsequent heat applications. Consequently, good multisection butt seals with controlled oxidation resulted, and such blanks became possible as shown in Fig. 5. The steps in the glassing of the Kovar rings are also indicated.

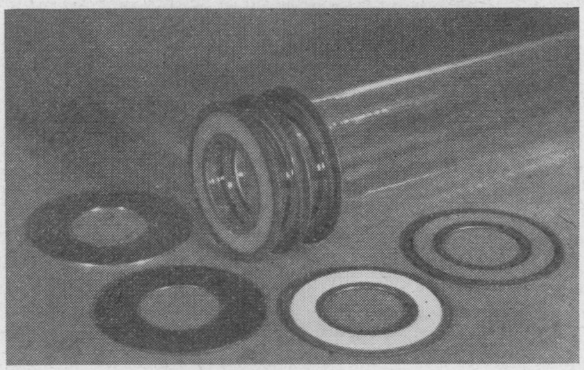

Fig. 5—Multisection blank employing butt seals. The following steps in the powder-glassing of the Kovar rings are shown: cleaning, oxidizing, spraying of powdered-glass suspension, and fusing of coating to form thin layer (on both sides). Magnification, 1/3×.

Conclusion

Although the techniques which have been described have been specifically referred to the use of Kovar, they can also be applied to other sealing metals. The processing steps are simple, but the introduction and development of new types of equipment are necessary for plant production.

The broad advantages of the techniques described are the resultant possibilities of making glass-to-metal seals on a controlled basis, developing mass-production methods, improving glass-blowers' efficiency, producing intricate seals that previously have been too difficult or too costly, and indefinite storing of powder-glassed parts without any special precautions. Lastly, the method of powder-glassing is a valuable research tool, since assembly of intricate designs now becomes possible.

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Sidney Bertram (A'36–SM'47) was born at Winnipeg, Canada, on July 7, 1913. He attended the Los Angeles City College from 1930 to 1933. From 1934 to 1936 he was an instructor at the Radio Institute of California, leaving to enter the California Institute of Technology where he received the B.S. degree in engineering in 1938. Later Mr. Bertram was employed as a research engineer by the International Geophysics Company. In 1939 he entered the Ohio State University, receiving the Master's degree in electrical engineering in 1941. From 1941 to 1942 he was engaged in war research under the O.S.U. Research Foundation. In 1942 he joined the staff of the University of California, Division of War Research, where he was engaged in the development of underwater-sound-ranging equipment. In 1945 Mr. Bertram joined the staff of the Physical Research Unit of the Boeing Aircraft Company and in 1946 he returned to the Ohio State University as an assistant professor in electrical engineering. He is a member of Sigma Xi, Tau Beta Pi, and Eta Kappa Nu.

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Dr. Dellinger was vice-president of The Institute of Radio Engineers in 1924, and president in 1925. He has been vice-president of the International Scientific Radio Union since 1934, and chairman of the Radio Technical Commission for Aeronautics since 1941.