May 1, 1951 J. M. BOOE 2,551,413

METHOD OF PRODUCING SILVER-THALLIUM-INDIUM ALLOYS

Filed Jan. 31, 1946

Fig. 1

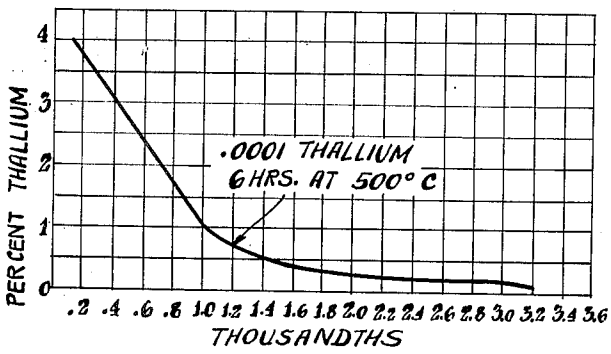


Fig. 2

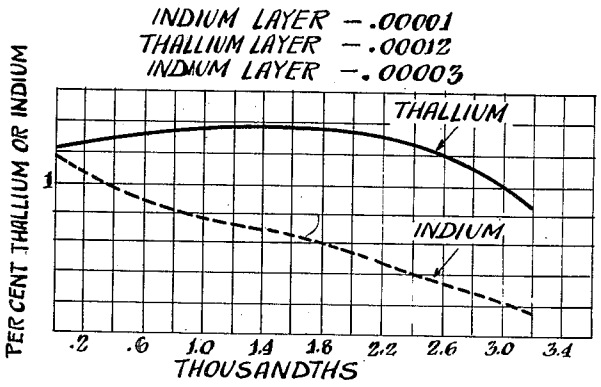


Fig. 3

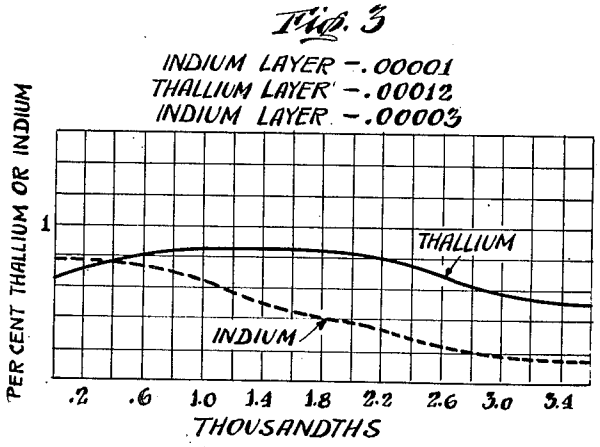


Fig. 4

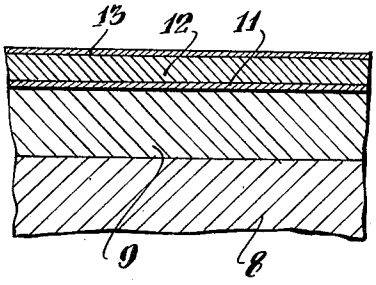
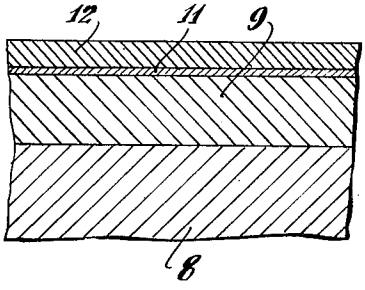


Fig. 5



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METHOD OF PRODUCING SILVER-THALLIUM-INDIUM ALLOYS

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5 Claims. (Cl. 204—37)

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This invention relates to new and improved silver-thallium-indium alloys, and, more particularly, to bearings formed from such alloys.

An object of the invention is the production of new silver-thallium-indium alloys having good anti-friction properties and high resistance to corrosion.

Another object of the invention is to provide a method of producing silver-thallium-indium alloys of the above-mentioned type.

Another object of the invention is to provide a method for diffusing thallium and indium into silver.

A further object is to provide a method of producing silver-thallium-indium alloys having desirable bearing properties and increased resistance to corrosion by means of a combination of electrodeposition and diffusion.

Other objects of the invention will be apparent from the following description taken in connection with the appended claims.

The present invention comprises the combination of elements, methods of manufacture, and the products thereof brought out and exemplified in the disclosure hereinafter set forth, the scope of the invention being indicated in the appended claims.

In the drawing:

Figures 1 to 3 inclusive are graph diagrams showing the distribution of thallium in silver as is obtained by diffusion treatments of various type.

Figures 4 and 5 are cross-sections of two forms of bearings electroplated with indium and thallium, before the diffusion treatment.

Silver-thallium alloys have various applications of which the most important is in bearings where generally a thin layer of the silver-thallium alloy is provided upon a suitable backing or base. Considerable difficulty has been experienced, however, in forming such layers on a practical and industrial scale. It has been already suggested to codeposit the silver-thallium alloy from a suitable electrolyte but this procedure was quite slow and cumbersome. Another suggestion involved electrodepositing thallium over the silver and subsequently heating the combination in order to diffuse the thallium into the silver. It was found, however, that the resulting penetration of the thallium into the silver was not deep enough to provide the most desirable bearing characteristics. As illustrated graphically in Figure 1, when a .0001'' film of thallium over silver was heated for six hours at 500° C. in a hydrogen atmosphere, starting the

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furnace at room temperature, the resultant diffusion gradient was quite steep. At the desired depth between 2 and 3 thousandths of an inch, the percentage of thallium in silver was less than one-fourth of one per cent. When thallium alone was diffused into silver a rather crystalline and mottled surface was left on the surface of the resulting alloy, thus producing an undesirable surface for bearings.

According to the present invention it has been found that a deeper and more uniform diffusion of the thallium into the silver can be accomplished by the use of indium in combination with the thallium. This novel method of diffusing thallium into the silver with the aid of indium leaves a very smooth surface on the silver, which is very desirable for bearing applications.

An alloy is obtained as shown in Figure 4 by electrodepositing indium 11 to a thickness of .00003'' upon a plated silver bearing layer 9, electrodeposited on a steel backing 8. Immediately thereafter thallium 12 is electroplated onto the indium surface to a thickness of .00012''. Then the thallium plated surface is immediately covered with electrodeposited indium 13 to a thickness of .00001''. The indium and thallium are then diffused into the underlying silver 9 by heat treatment in a suitable reducing atmosphere, such as hydrogen, for six hours at 600° C., starting the furnace from room temperature. As illustrated graphically in Figure 2, the percentage gradient of thallium in silver is flattened out considerably and now the percentage of thallium averages over one per cent at a depth between 2 and 3 thousandths of an inch. Thus, the resultant alloy contains four times as much thallium as was obtained without the use of indium.

The percentage gradient of thallium in silver may be flattened out still further by prolonging the heat treatment to 12 hours at 600° C. in a hydrogen atmosphere, starting the furnace at room temperature. Figure 3 illustrates graphically the results of such prolonged heat treating where the thallium content shows a somewhat smaller percentage deviation between a depth of 2 and 3 thousandths of an inch.

The diffusion of thallium and indium into silver may be accomplished without the second indium layer. A plate for diffusion treatment in accordance with this invention may be prepared as shown in Figure 5 where a steel backing 8 has successive electroplated layers of silver 9, indium 11 and thallium 12.

According to one preferred embodiment of this invention, it is desired to produce a bearing alloy

which shall consist of 2%—plus or minus ½%—thallium in silver, this percentage to persist to a depth of at least .002" below the unworn bearing surface. As shown in Figure 4, such an alloy is obtained by depositing thallium 12 to a thickness of .0002" on a silver plated bearing layer 9 upon which induim 11 has been electroplated to a thickness of .00002" immediately prior to the deposition of the thallium. The thallium plated surface is immediately covered with electrodeposited indium 13 to a thickness of .0002". The indium and thallium are then diffused into the underlying silver by heat treatment in a hydrogen atmosphere at about 500 to 600° C. for a period of about 6 to 12 hours, starting the furnace from room temperature.

By varying the thickness of the thallium and indium deposits upon the silver bearing layer and by varying the furnacing temperatures and time periods, silver alloys can be produced by the diffusion method of the present invention which contain up to about 10% thallium and up to about 10% of indium.

The preferred composition embodying the invention expressed in percentages by weight of the constituents comprises:

	Per cent
Thallium	About 2.5
Indium	About .5
Silver	Balance

In preparing the silver base upon which the thallium and indium are to be electrodeposited it is essential that the silver be strongly bonded to the steel so that the bond will not fail under the chisel test after having been subjected to a temperature of 600° C. for six hours. The steel backing is properly cleaned, after which it is subjected successively to a nickel strike and a silver strike, and then given a final silver plate. As silver plating methods and baths are well known to those skilled in the art no detailed description of such methods is believed to be necessary.

It is essential that the work be silver plated oversize enough that it may be machined to proper dimension after plating. The plated silver must be machined to .00024" under size of the final dimension since subsequent plating operations will add .00024" to the final thickness of the bearing material, these dimensions being applicable to the preferred embodiment outlined in the foregoing.

The silver plated work, machined to the proper size, is then thoroughly degreased in a suitable volatile solvent either by hand or in a suitable degreaser. After masking to prevent plating where not desired, the first indium layer is applied according to the procedures outlined in the Gray Patent 1,935,630 and in the Murray et al. Patent 1,965,251.

The thalium deposit must be immediately applied without delay. The work, having been rinsed from the indium plating bath, is immediately placed in the thallium bath before any water-break appears on the surface of the work.

The final indium deposit must be applied before the work shows any water-break after the final rinse following the thallium plating. The final indium plate is applied exactly like the first indium plate, and to the same thickness; however, the plating time may be different since indium apparently deposits from a cyanide bath at a different rate on thallium than it does on silver. Alternatively, as previously stated, the final indium plate may be only about one-third as thick as the first indium plate.

After the application of the final indium plate the work should be blown dry and the masking removed. The indium plate must not be touched and must be protected from scratches. The plated work is placed in a hydrogen furnace at room temperature and the temperature then raised to 600° C. and maintained for six hours, after which the work is removed to a cooling chamber, and allowed to cool before being removed.

A thallium electroplating bath may be made up in the following manner:

Thallium metal, 25 grams per liter (3.3 ounces per gallon)
Free perchloric acid, 10 grams per liter (1.3 ounces per gallon)
Peptone, 10 grams per liter (1.3 ounces per gallon)
Cresylic acid, 2 to 3 milliliters per liter (7.5 to 11 milliliters per gallon)

The bath is prepared by shaving up the thallium metal and dissolving it in a slight excess of perchloric acid and warming under a fume hood until the metal is all dissolved. After adding the peptone, the level is adjusted and the free perchloric acid is titrated with standard NaOH solution. The free perchloric acid is then adjusted and the cresylic acid is added.

The thallium plate rate needs to be checked only occasionally. The indium plating rate, however, should be checked frequently, and after each bath correction; and further, the plating rate of indium should be checked on thallium and on silver both, as the plating rate of indium will vary with the base metal. Plating rate tests should be made using a thin copper dummy cathode silver plated to about 0.002 inch and of the same size and shape as the work.

It is essential that the distribution of both indium and thallium be uniform over the surface of the work. Correct distribution is usually obtained only by cut and try methods. Distribution varies principally with anode size and location, and with agitation of the work or the bath.

In furnacing the bearings with the plated layers of indium and thallium, it is desirable to start the furnacing at room temperature so that diffusion of the plated metals will begin before their melting points are reached. This prevents sudden melting and running off of the thallium and indium coating as would be the case if the bearings were placed directly in the furnace at high temperature.

The present invention provides a uniform silver-thallium bearing surface and a method of producing the same which avoids the difficulties encountered in directly co-depositing silver and thallium. According to the present invention the powerful wetting effect of indium is utilized in successfully driving the thallium into the silver during the heat-treatment in a hydrogen atmosphere while previous attempts to diffuse thallium, without indium, into silver failed.

The resulting silver-indium-thallium bearing of this invention possesses a high fatigue resistance, excellent corrosion and wear resistance, a smooth surface with a low coefficient of friction and a comparatively high thermal conductivity. The method of the invention makes possible the formation of thallium-silver bearings in which the thallium is diffused in a fairly uniform per-

centage to the desired depth under the bearing surface.

While the present invention, as to its objects and advantages, has been described herein as carried out in specific embodiments thereof, variations and modifications may be resorted to by those skilled in the art without departing from the principles of the invention. Thus, it has been found that the method of the invention may be applied with equal or similar results to producing copper base bearings wherein thallium and indium are diffused into the copper much in the same way as with silver base bearings. All of these variations and modifications are considered to be within the true spirit and scope of the present invention, as disclosed in the foregoing description and defined by the appended claims.

What is claimed is:

1. The method of forming a bearing alloy which comprises electroplating successive layers of indium, thallium and indium over a silver base and subjecting the resulting combination to heat treatment for about 6 to 12 hours at a temperature of about 500 to 600° C. to cause diffusion of the thallium and indium into the silver and the formation of a thallium indium silver alloy.

2. The method diffusing thallium into silver which comprises electrodepositing successive layers of indium and thallium upon a silver base, and subjecting the resulting combination to heat treatment in a reducing atmosphere for about 6 to 12 hours at a temperature of about 500 to 600° C.

3. The method of diffusing thallium and indium into silver which comprises electrodepositing successive layers of indium, thallium and indium onto a silver base and subjecting the resulting combination to heat treatment in a hydrogen atmosphere at a temperature of about 600° C. for about 6 hours, starting the furnace at room temperature.

4. The method of forming a bearing alloy which comprises electroplating a layer of indium having a thickness of about .00002 inch to about .00003 inch upon a silver base, electroplating a layer of thallium having a thickness of about .00012 inch to about .0002 inch upon said indium layer, and heat treating the resulting plated silver base at a temperature of about 500 to 600° C. for about 6 to 12 hours.

5. The method of forming a bearing alloy which comprises electroplating a layer of indium having a thickness of about .00002 inch to about .00003 inch upon a silver base, electroplating a layer of thallium having a thickness of about .00012 inch to about .0002 inch upon said indium layer, electroplating a layer of indium having a thickness of about .00001 inch to about .00002 inch upon the thallium layer, and heat treating the resulting plated silver base at a temperature of about 500 to 600° C. for about 6 to 12 hours.

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