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ALLOY

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Fig. 2

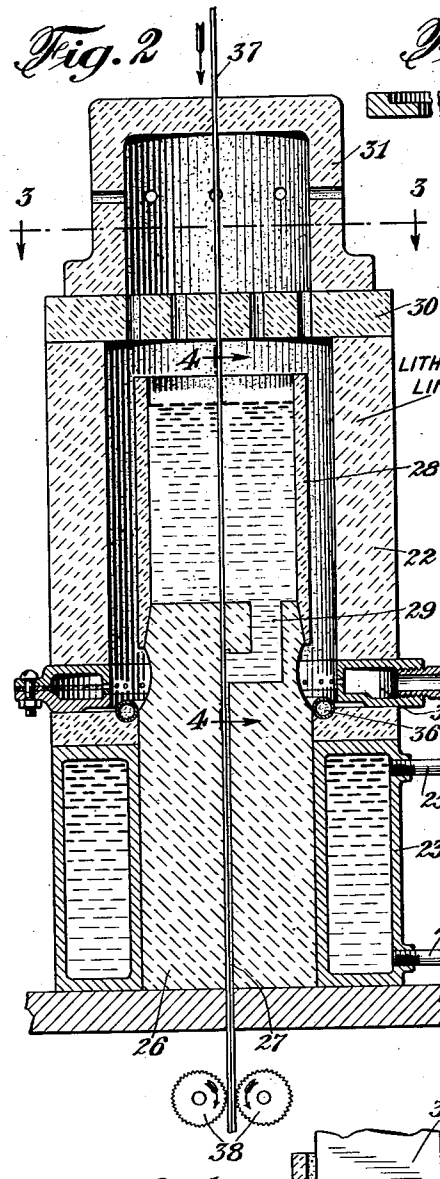


Fig. 1

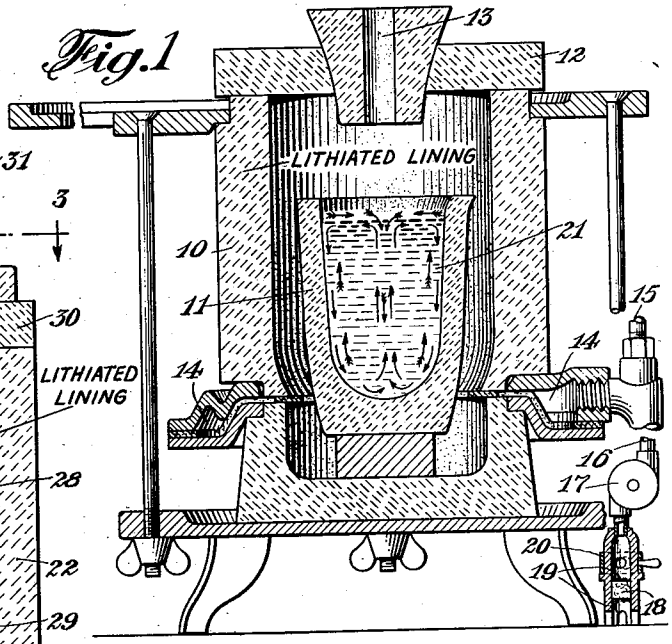


Fig. 3

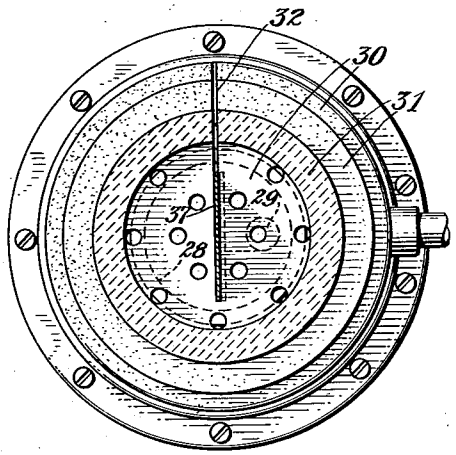
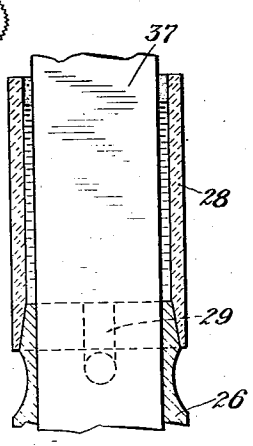


Fig. 4



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Fig. 5

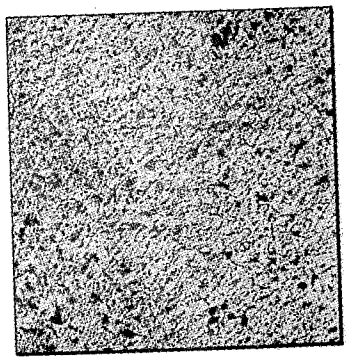


Fig. 6

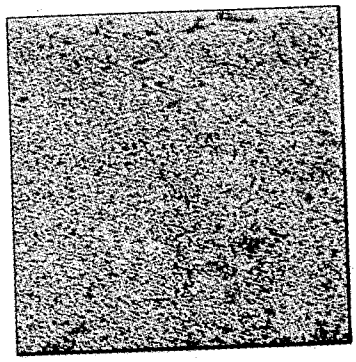


Fig. 7

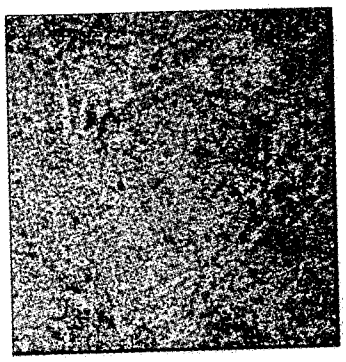


Fig. 8

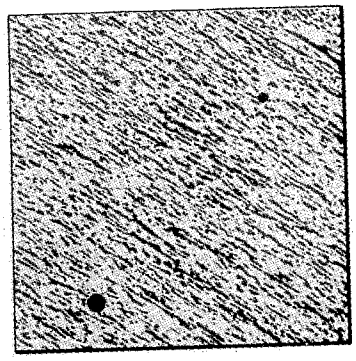


Fig. 9

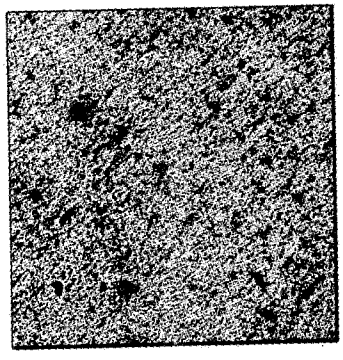
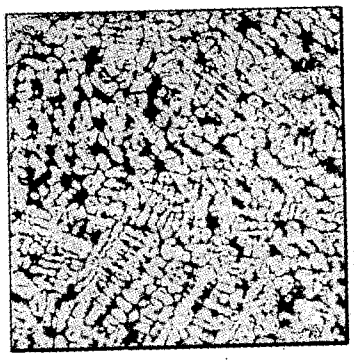


Fig. 10

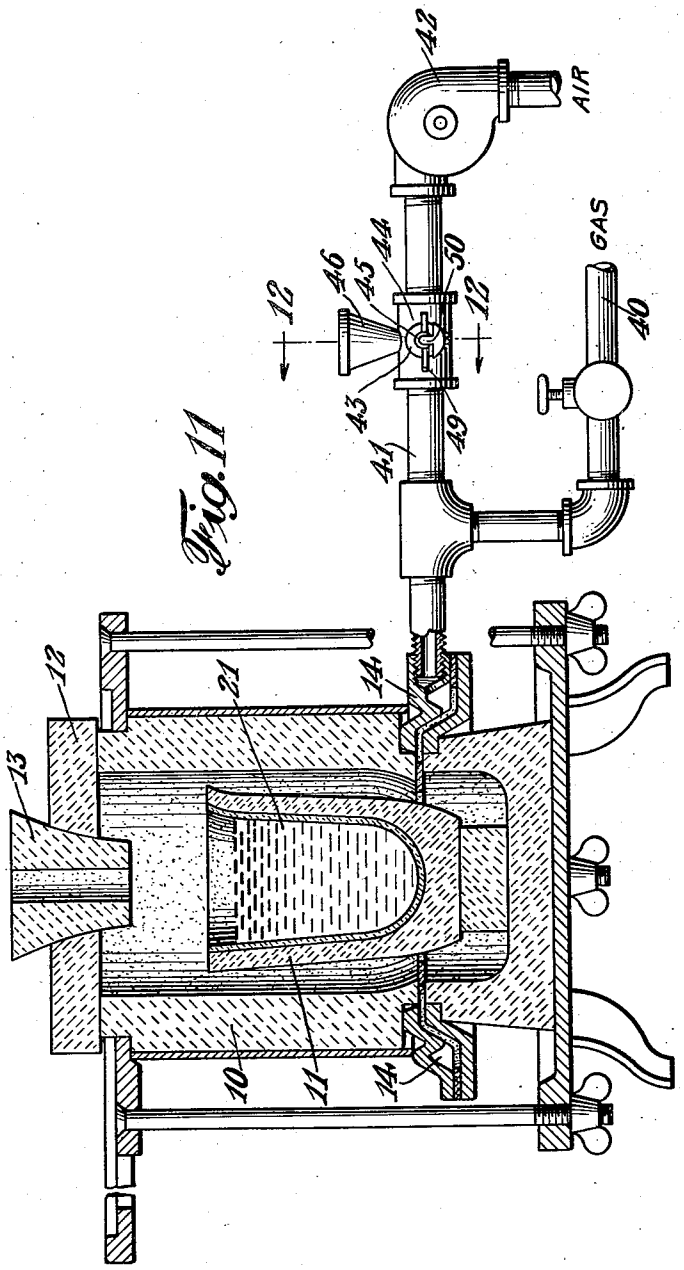


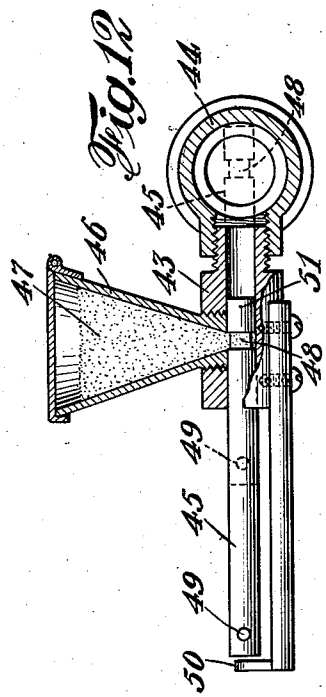
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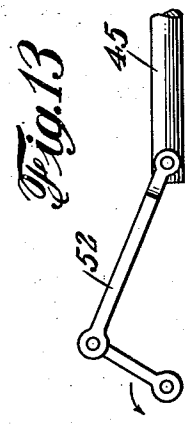
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ALLOY

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UNITED STATES PATENT OFFICE

2,229,117

ALLOY

Harold J. Ness, Bloomfield, N. J.

Application March 1, 1938, Serial No. 193,277

26 Claims. (Cl. 75—163)

This invention relates to alloys and to the method of producing the same. It is described hereinafter with reference to bearing metal alloys composed primarily of copper and lead but certain features of the process described are applicable to the production of alloys of other metals.

The present application is a continuation in part of my earlier applications Serial No. 27,712, filed June 21, 1935, and entitled "Alloys"; Serial No. 56,567, filed December 28, 1935, entitled "Alloys"; and Serial No. 79,968, filed May 15, 1936, entitled "Metallurgical Process."

In the development of greater power and higher speeds in internal combustion engines for automobile and aircraft and in other machines, it has been necessary to employ bearing alloys which, at the elevated temperatures obtained in such machines, have mechanical properties, such as compressive strength, tensile strength and resistance to pounding, exceeding those of the usual white-metal bearing alloys. Alloys of copper and lead have been employed to some extent to replace tin-base alloys for such service.

It has been shown by W. Claus (Zeit f. Metallkunde, vol. 29, No. 9, p. 264) that copper-lead mixtures containing 37 to 38 per cent lead are completely miscible above 950° C. (1742° F.). However, a melt of such composition when cooled slightly below this temperature consists of a solid phase containing over 95 per cent copper and a liquid phase which is relatively pure lead, and on cooling through the freezing range, the liquid phase of nearly pure lead coalesces into relatively large masses.

Since the solubility of lead in copper in the solid state is negligible, such alloys usually consist of a copper matrix containing lead in the interstices. Such copper-lead alloys have not been uniformly successful for anti-friction bearings, due to the low lead content which it has been possible to obtain in the alloy and to the segregation or coalescence of the lead into relatively large unevenly distributed masses in the copper matrix.

Mechanical stirring of the molten alloy above the casting temperature has been resorted to in order to reduce segregation in the crucible and chilling of the casting has been employed to reduce segregation in the mold. Mechanical stirring of the molten mass is troublesome, however, and it is difficult to obtain other than a mild agitation of the molten mass in this manner. Moreover, stirring must be stopped an appreciable time prior to the actual pouring so that a certain amount of settling-out of the lead will ordinarily occur before pouring is completed. After pouring the lead still further segregates in the mold, forming large lead particles non-uniformly distributed throughout the casting. Such segregation weakens the casting and under the high temperatures reached in the use of the copper-lead alloy for bearings, excessive sweating of the lead to the surface occurs. This renders the bearing porous, weakens the physical properties thereof, and the resulting unprotected copper surface may cause scoring of the rotating or sliding elements.

In spite of all the precautions observed heretofore in the production of copper-lead alloys, there has been an exceedingly large percentage of rejections in the commercial production of such alloys and uniform distribution of the lead in a finely divided form in the copper has not been commercially obtained.

One of the objects of the present invention is to eliminate the difficulties which have heretofore accompanied the production of such alloys.

Another object is to provide a method of producing alloys in which agitation of the molten mass is obtained without mechanical stirring.

Another object is to provide such a method in which the agitation of the mass continues in the mold and up to the time of solidification of the mass.

Another object is to provide a method of making copper-lead alloys in which the lead will be firmly bonded to the copper and either metal, as desired, retained in a finely divided state in a continuous network or matrix of the other metal.

Still another object is to provide such a method which will result in a more uniform dispersion and fine subdivision of either metal, as desired, in the other, than has been obtainable heretofore.

Another object is to provide a process of making copper-lead alloys of better physical properties than heretofore obtainable.

Still another object is to provide a method of producing copper-lead alloys free from segregation, having greater lead content than has heretofore been deemed commercially possible.

Another object is to provide a simple, economical and reliable method of producing copper-lead alloys.

A still further object is to produce a copper-lead alloy of strong physical properties and high anti-friction and anti-scoring properties at either low or elevated temperatures.

Another object is to produce a copper-lead alloy having uniform distribution of either metal, as desired, in finely divided form in the other metal.

Another object is to provide a bearing metal alloy in which sweating out of the lead at high operating temperatures and/or pressures will not occur.

Another object is to produce copper-lead alloys having lead contents up to 70%.

Another object is to produce an oxygen free alloy of copper and lead.

Another object is to provide a malleable alloy of copper and lead which may be rolled or otherwise mechanically worked.

Another object is to produce copper-lead alloys in which the lead is contained within the grains of the copper, or in which the copper is contained in a substantially continuous matrix of lead, as desired.

Other objects and advantages will hereinafter appear.

The present invention is based, in part, upon the discovery that when lithium is introduced into certain alloys, as for example, a copper-lead alloy, and precautions are observed to maintain some lithium in the alloy, a natural circulation or agitation of the molten mass occurs which enhances the intimate mixing of the alloying ingredients and that such agitation or automatic stirring action continues, after it has once started, until actual solidification of the alloy upon cooling. As a consequence, no opportunity is afforded for the ingredients to segregate. Moreover, the agitation is very rapid, apparently occurring simultaneously throughout the entire molten mass so that a thorough stirring of the molten mass results and, upon solidification thereof, the ingredients of the alloy are retained in an intimate, uniform and finely subdivided form.

The lithium, when maintained in a small proportion in the copper-lead mixture by regulated conditions of operation, the nature of which will hereinafter appear, produces in the molten mass as the temperature thereof is raised to above a certain "critical" temperature, a violent agitation which appears to proceed upwardly from the center of the mass, thence radially outwardly toward the sides of the containing crucible and down the sides of the crucible. This circulatory agitation proceeds in the direction indicated as long as the temperature is retained above the "critical" temperature, and it is accompanied by considerable surface turbulence and a crackling and simmering sound. As the mass is permitted to cool down to the "critical" temperature, the turbulence and the rate of circulation decreases until the "critical" temperature is reached, at which point a reversal in the direction of the circulatory agitation occurs, the movement at the surface then proceeding from the sides of the crucible towards the center thereof at an increasing rate approximating that of the previous surface movement, and thence apparently axially downward into the mass. This latter movement continues as the temperature is lowered below the "critical" temperature, and up to the point of solidification. Upon reheating, the movement of the mass continues in the radially inward direction at the surface until the "critical" temperature is again reached, at which point the direction of movement again changes to an outward radial movement at the surface.

The "critical" temperature varies with the proportion of the copper and lead in the mixture, lying approximately between the limits of 1700° and 1900° F. For a copper-lead-lithium alloy containing 35 per cent lead, it is believed to be about 1850° F. It is readily determined, for any particular mixture, from observation of the surface of the mass, since the transition from outward to inward movement of the mass at the surface thereof is pronounced and unmistakable.

The proportion of lithium required to effect this stirring or agitating action is very small, very definite and active agitation and uniform and fine dispersion of the lead having been obtained in the production of copper-lead alloys, which upon analysis showed as little as 0.00017% of lithium. Too great a percentage of lithium in the molten mass will, under certain conditions, react so violently as to cause spattering and for this reason it is preferable to maintain the lithium content of the charge not over about 1 per cent.

The lithium may be introduced into the mixture in a variety of ways, as for example, alloyed with the lead, alloyed with the copper, in a solid metallic state either alone or wrapped in other metals, such as copper, lead, nickel, etc., or as a vapor.

In introducing the lithium into the melt alloyed with lead, it is necessary, of course, to first produce a lead-lithium alloy of the desired proportions. This may be accomplished by packing the lithium metal into a small crucible which is then inverted and pushed down into a bath of molten lead. The lithium-lead alloy thus formed may be added in its molten condition, preferably slowly, to molten copper, but it is better practice and more convenient in some respects to permit this lithium-lead alloy to solidify in suitable ingots, which ingots are added to the molten copper. By either method the lithium is carried by the heavy lead to the bottom of the molten copper before it is released. Economy in the use of the lithium is thus obtained. The percentage of lithium in the lead-lithium alloy may vary somewhat, lead containing 0.5 per cent lithium being usable without difficulty and producing the desired agitation and fine uniform distribution of lead in the finished casting, whereas lead containing 1.85 per cent lithium, under certain conditions, reacts so violently as to cause spattering. Lithium-lead alloys of intermediate composition may be used more or less freely, depending upon the temperature of the molten copper, the amount of lithium-lead alloy added, and similar conditions. Additional pure lead may be added, of course, to regulate the lead content of the mixture, which as stated, may comprise as high as 70% of the composition without danger of lead segregation.

After the lithium-lead alloy and pure lead, if required, is added to the molten copper, the temperature of the charge is regulated to above the "critical" temperature at which agitation occurs.

In place of adding the lithium to the charge as an alloy with lead, it may be alloyed with copper in a similar manner and the lead added to the charge. In this latter case the lithium-copper alloy may be melted in the crucible and pure lead, either in solid or fuse state, added thereto, or the lead and lithium-copper alloy may both be introduced into the crucible in the solid state and heated together to above the critical temperature at which agitation occurs. Of course, a lithium-lead alloy may be added in place of pure lead, to the lithium-copper alloy, if desired.

While the method of introducing lithium into the molten mass as an alloy of either lead or copper is highly satisfactory, this is not necessary since the pure lithium may be added directly to the fused mixture of lead and copper, either by dropping solid pieces of lithium therein or by packing it in a crucible which is inverted and pushed down into the molten mass, in the manner described for producing the lithium-lead alloy. This results in a loss of some lithium from the mass. If desired, the lithium may be

wrapped in a protective metal such as iron, nickel or tin before introduction into the molten lead-copper mass. The addition of small amounts of these metals does not prevent the agitating and dispersing action of the lithium and for certain purposes adds desirable properties to the completed alloy.

Since the quantity of lithium required is extremely small, it may be added as a vapor, merely by creating a lithium vapor or atmosphere about the crucible, in any suitable manner, as for instance, by liberation of the lithium from the lining of the furnace, which has been previously treated with lithium, as will hereinafter appear, or by introducing lithium metal or a compound thereof into the furnace atmosphere. In whatever manner the lithium is introduced into the charge, thereafter the mass is heated to above the "critical" temperature at which agitation starts.

The pouring temperature should be above the so-called "critical" temperature. The pouring may be done as soon as the pouring temperature is reached, although the quality and fineness of dispersion is not affected by continued heating above the "critical" temperature for a substantial period, i. e., from half an hour to an hour or more, or the temperature may be alternately raised and lowered above and below the "critical" temperature, thereby alternating the direction of agitation. This reversal of direction of agitation may be produced at either relatively short intervals or at substantially longer intervals, without materially affecting the resulting castings, as long as the pouring is done above the "critical" temperature.

Due to the inherent agitation of the molten mass with continued heating thereof, it may be readily cast from holding furnaces, which are generally used when producing die or permanent mold castings.

The molten mass, as it cools in the molds, passes through the "critical" temperature, at which time a reversal of the direction of agitation occurs, the movement at the surface continuing in an inward direction from the sides of the mold, until stopped by solidification of the mass. There is, therefore, no opportunity for segregation of either the lead or copper to occur. The molten mass is very dense and therefore there is little or no shrinkage during solidification.

Pouring at temperatures below the critical temperature may result in segregation of the lead.

It has been found, however, that the mere addition of lithium to the charge in the proportions specified, does not result in the stirring action described nor in the production of a finely divided and uniformly distributed structure, but in addition it is necessary to prevent, at least in part, loss of lithium from the charge or to conduct the process under conditions which will supply additional lithium to the charge as the process continues. In practice it has been found that the linings of the furnaces used, which contain large proportions of silica, unless pretreated react with the lithium of the charge, as a result of which the lithium is very quickly and completely absorbed from the charge. In order to prevent the loss of the lithium from the charge in this manner and to provide continuously a lithium containing atmosphere about the crucible during heating of the charge, the lining of the furnace is treated with lithium vapor at a high temperature so that the lining will take up a portion of the lithium with which it is treated. The furnace linings thus treated will remain in a suitable lithiated condition for a considerable period, when not in use, and may be used for melting lithium containing copper alloys repeatedly without reconditioning. This conditioning of the furnace lining, it is believed, results in a saturation or near saturation of the lining by the lithium or a compound thereof whereby the lining, upon subsequent melting of a charge, is not free to readily absorb additional lithium from the charge, but on the contrary liberates lithium to produce a lithium atmosphere over and possibly through the crucible, which atmosphere retards the escape of lithium from the charge. If desired, this lithium containing atmosphere may comprise the sole means of introducing the lithium into the charge, excellent results being obtainable by merely heating a pure copper and lead mixture in a furnace having a lithium treated lining. Sufficient lithium is absorbed into the charge, from the lithium containing atmosphere produced from heating of the lining, to cause pronounced agitation of the molten mass and a fine and uniform distribution of the lead in the copper or of the copper in the lead, as desired, upon casting. This method of introducing the lithium into the melt is, in some respects, a preferred one since in the resulting castings the lead is extremely well distributed and finely divided.

The lithium may be maintained in the charge, however, in other ways, as for instance, when employing a coke or coal fired furnace, the reducing effect of the carbon-monoxide gas given off from the fuel and the absence of lithium absorbing substance adjacent the crucible prevent to some extent the escape of the lithium from the charge, as a result of which castings of good quality may be produced.

The amount of lead which may be combined with copper while one of the metals is retained in a uniformly dispersed and finely divided state in the other may vary up to about 70% lead. When copper, lead and lithium alone are employed or even if small amounts of such metals as tin, iron and silicon are added, the copper or copper and other alloying components, if present, form a continuous matrix or cellular network in which the lead is dispersed as discontinuous finely divided particles, firmly bonded to the copper, a condition which produces high tensile and compressive strength and resistance to pounding. The grain structure of the copper-lead alloys produced in accordance with the process herein described is entirely different from copper-lead alloys as heretofore produced, the latter comprising copper and lead in masses of heterogeneous sizes and shapes whereas the copper in the alloy of the present invention assumes the elongated grain structure of oxygen free copper with the lead finely divided and highly dispersed within the individual copper grains, each copper grain including a countless number of separate lead particles. The alloy being produced in a lithium containing atmosphere, it is completely oxygen free and has not only grain formation but physical properties comparable to oxygen free copper.

The number of lead particles appearing in a cross section of the copper-lead alloy of the present invention is enormous and for an alloy containing 40% lead, it may vary from, say, 50,000 to several hundred thousand per square inch and the average size of a lead particle may be of the order of magnitude of 10^{-6} square inches or

smaller although the present invention is not limited to such particle size or distribution range, the foregoing figures being given only by way of example. The tensile strength of a copper-lead alloy containing 65% copper and 35% lead is of the order of magnitude of 14,000 lbs. per square inch, the compressive strength of the same alloy being of the order of 48,000 lbs. per square inch and the elongation approximately 15%. The presence of lithium in the alloy in addition to its dispersing action, toughens and hardens both the copper and lead of the alloy and increases their tensile strength, thereby further enhancing the physical properties of the alloy. Moreover, due to the encasement of the individual lead particles within the copper grains, the lead will not sweat out under operating conditions and temperatures, a feature which is not present in copper-lead alloys of the prior art. The addition of iron, tin and/or silicon in small percentages serves to harden the alloy.

It has been found that the addition of small amounts, say up to 9% of nickel to the charge, produces a reversal of the position of the copper and lead in the alloy, causing the copper to be retained in finely divided and uniformly distributed condition in a lead matrix, the structure often being dendritic. The greater the amount of nickel employed, the greater the thickness of the lead sheath surrounding the individual copper particles. No explanation is offered for this effect of the nickel on the structure of the alloy. For most commercial purposes an alloy having a continuous matrix of copper is preferred for the additional strength obtained, the ability to roll or mechanically work the alloy, etc., but for some purposes an alloy having a lead matrix such as is obtained by adding nickel, may be desired.

One feature of the alloy of this invention is its capability of being remelted and recast without danger of segregation since a remelt thereof when conducted under the same controlled condition as an original melt evidences the same agitating effect as an original melt. Since remelting results in a continued internal working of the mass, it is possible to remelt and recast worn out bearings or to cast the original melts into ingots for subsequent recasting. The melt may be cast either as a homogeneous bearing element or as a bearing surface cast onto a supporting or backing metal such as steel, as desired, for such uses as bearings, brake-linings, clutch surfaces, piston surfaces, etc.

The dispersion of one metal in the other is extremely uniform and finely divided whether the casting is permitted to cool fast or slowly and therefore it may be readily cast in steel, iron or dry sand molds. The sand employed should be substantially chemically inert to lithium. However, I prefer to employ permanent molds and to heat the same to reduce the chilling effect of the molds on the castings. This results in a somewhat more even structure throughout the casting, due to a slower and more even cooling thereof and more even agitation of the mass during cooling. This is contrary to the usual practice of producing copper-lead alloys in which chilling of the casting is ordinarily resorted to in order to obtain a quick solidification, in an attempt to reduce lead segregation in the mold. With the present process the pouring can be conducted directly through the air without oxygen absorption due to the presence of the lithium in the melt, which appears to form a protective atmosphere about the molten stream.

In order that the invention may be more clearly understood reference will now be had to the accompanying drawings, in which:

Fig. 1 is a vertical section of a gas fired furnace suitable for the production of a copper-lead-lithium alloy;

Fig. 2 is a vertical section of a furnace and die for the coating of backing strips with a copper-lead-lithium alloy;

Fig. 3 is a sectional view on the line 3—3 of Fig. 2;

Fig. 4 is a sectional view on the line 4—4 of Fig. 2;

Fig. 5 is a photomicrograph of a copper-lead-lithium alloy containing substantially 25% lead and less than 1% of lithium, with the remainder copper. X100;

Fig. 6 is a photomicrograph of a copper-lead-lithium alloy containing substantially 50% lead and less than 1% of lithium, with the remainder copper. X100;

Fig. 7 is a photomicrograph of a copper-lead-lithium alloy containing substantially 70% lead and less than 1% of lithium, with the remainder copper. X100;

Fig. 8 is a photomicrograph of a copper-lead-lithium alloy containing substantially 35% lead and less than 1% of lithium, with the remainder copper. X250;

Fig. 9 is a photomicrograph of a copper-lead-lithium-silicon alloy containing substantially 35% lead, less than 1% lithium, ½% silicon and the remainder copper. X100;

Fig. 10 is a photomicrograph of a copper-lead-lithium-nickel alloy containing substantially 35% lead, less than 1% lithium, 2% nickel and the remainder copper. X100;

Fig. 11 shows means for introducing lithium compounds into the furnace of Fig. 1;

Fig. 12 is a vertical sectional view of the mechanism of Fig. 11, taken on the line 12—12 of Fig. 11; and

Fig. 13 is a fragmentary detail of an automatic intermittent feed, which may be employed with the mechanism of Fig. 12.

Referring to Fig. 1, I have shown a gas fired furnace of conventional construction having a refractory lining 10 within which is contained a crucible 11, which may be of graphite, preferably lined with a refractory cement such as sillimanite to prevent reaction of the lithium therewith. A refractory cover plate 12 having a suitable gas vent 13 is provided. Gas and air are admitted through a burner ring 14 surrounding the furnace, the gas being supplied through a conduit 15 and the air through a conduit 16. The blower 17, shown diagrammatically, and suitable valves (not shown) control the amount of air and gas supplied. In order to assist in maintaining an adequate supply of lithium vapor in the furnace above and around the crucible, the incoming air is caused to flow through a chamber 18 containing solid lithium particles or a powdered compound of lithium, contained between metal screens 19. A bypass sleeve 20 permits air to be introduced independently of the lithium chamber 18, if desired. Sufficient lithium either in elemental or compound form is carried into the furnace with the air and vaporized therein, to produce a strong lithium spectral line when the gases escaping from the furnace are viewed with a spectroscope, thus denoting the presence of lithium

in the furnace gases in an elemental form and in an ionized condition. Experimental data indicates that the presence of lithium in the elemental form is due at least in part to the reducing action of carbon monoxide gas in the furnace on lithium oxide, under the conditions prevailing in the furnace. A furnace lining which has been found suitable consists of silica 65%, alumina 25%, and the remainder ignition loss, i. e., moisture and other volatile material, and small percentages of iron, titanium, lime and magnesia.

The lining is treated by heating lithium in the furnace for a substantial period at a temperature sufficient to cause formation of a strong lithium vapor in the furnace as previously described. The lithium for treating the lining may be introduced into the furnace, as a charge, through the top thereof, although sufficient lithium can be carried into the furnace with the air flowing through the chamber 18, to effectively treat the lining. The sufficiency of the amount of lithium or lithium compound taken up by the lining can be determined by heating a charge of copper and lead therein. If upon heating of such a charge to a temperature of from about 1700 to 1900° F., an agitation of the mass occurs, the lining is sufficiently treated for a successful carrying out of the present process. If no agitation occurs, it is necessary to retreat the furnace lining in the same manner. The treatment can also be effected by applying to the lining a compound of lithium, such as lithium chloride. The compound may be applied as a water solution or suspended or dissolved in other volatile vehicles, as fully set forth in my copending application Serial No. 112,988, filed November 27, 1936, and entitled "Furnaces."

The direction of the agitation of a nickel free molten alloy in the crucible is indicated by arrows in Fig. 1, the plain arrows indicating the apparent direction of the agitation when the charge 21 is heated to above the "critical" temperature, and the feathered arrows indicating the direction of agitation when the charge is permitted to cool below the "critical" temperature. With nickel added to the charge in amounts up to the order of magnitude of 9%, the direction of agitation is always that shown by the plain arrows.

In the process of producing copper-lead-lithium alloys in which the lithium is introduced into the furnace atmosphere from the lining of the furnace, it is desirable to replace or add to the lithium given off by the walls, by permitting a small amount thereof to be carried in to the furnace by the air flowing through the lithium containing chamber 18, although this is not necessary since repeated heats can be made with a single treatment of the furnace lining.

As previously stated, the charge is heated in the lithium vapor containing atmosphere until circulation occurs in the direction of the plain arrows, after which it may be poured immediately or the heating may be continued for long periods either above or below the "critical" temperature until it is convenient or desirable to pour.

If the alloy is to be used for coating backing strips, such as steel, the molten alloy may be poured from the crucible 11 into a holding furnace such as shown in Fig. 2. This furnace has a lining 22 similar to the lining 10 of the melting furnace, which also has been treated with lithium. The lining 22 rests upon a water jacket 23 having a water inlet 24 and an outlet 25. Extending downwardly through the lower portion of the furnace and the water jacket 23 is a cylindrical die block 26 of refractory material having a rectangular opening 27 extending therethrough. A graphite receptacle 28 preferably having a lining of sillimanite or other refractory cement resistant to the disintegrating effect of lithium, extends upwardly from the die block, in which receptacle the molten metal is contained. A passageway 29 extends downwardly from the receptacle 28 to the slot 27. An apertured plate 30 closes the furnace and has resting thereon an apertured dome 31. The plate 30 and dome 31 are slotted in from one side, as indicated at 32 in Fig. 3. A burner ring 33 has inlets 34 and 35, through which gas and air are admitted to maintain the alloy in the receptacle 28 in a molten state. Lithium or a compound thereof may be contained in the air inlet 35, if desired, in the same manner as shown at 18 in Fig. 1, but as an alternative, I have provided a refractory tube 36 in the base of the furnace which is packed with lithium and which serves to liberate lithium vapor slowly throughout the coating process.

The strip 37 to be coated is passed downwardly through the slots 32 in the dome 31 and plate 30, thence through the receptacle 28 and die block 26, being drawn slowly through the molten alloy by a pair of feed rollers 38. The slot 27 in the die block, below the passageway 29, is somewhat wider than the strip 37, thereby permitting the alloy to flow from the passageway 29 and into the die block slot in contact with one face of the strip 37. The cooling jacket 23 causes the alloy to solidify as a coating on the strip.

The lithium vapor generated or released by the furnace lining passes over the receptacle 28, permitting an absorption of lithium into the charge, thereby to maintain the agitation of the mass and consequent high quality of the alloy coating. The lithium vapor also passes, with the gases, through the apertured plate 30 and dome 31 in contact with the upper portion of the strip 37, and due to its reducing action, prevents oxidation of the surface of the heated strip prior to its passage into the molten mass. Consequently, due to the extremely clean surface thus produced on the strip and the freedom of the alloy itself from impurities resulting from the clean-up effect of the lithium on the molten alloy, the coating material forms an alloy bond with the strip as it solidifies thereon. The coating has the pliable and malleable characteristics of copper combined with the bearing characteristics of lead and the coated strips may be stamped, bent, machined and otherwise worked into any desired form. Clad metal bearings produced as described above are claimed in my copending application Ser. No. 193,287, filed March 1, 1938, and entitled "Bearing."

Referring next to the Figs. 5 to 9 of the drawings, it will be noted that the lead, indicated by the dark areas, is dispersed very uniformly throughout the copper and is in an extremely fine state of subdivision, whether the lead is present in a low percentage (25% in Fig. 5) or a high percentage (70% in Fig. 7). The dark or lead particles, as observed under the microscope, are extremely fine, substantially uniformly distributed and entirely surrounded by the copper, thus indicating a continuous copper matrix with the lead particles dispersed directly in the copper grains. The tensile and compressive strength of these alloys are considerably in excess of that of the copper-lead alloys heretofore commercially available being of the order of oxygen free copper.

Moreover, as stated, they are malleable and may be readily rolled or otherwise mechanically worked without loss of lead from the copper matrix.

Fig. 9 shows a copper-lead-lithium alloy containing a small percentage of silicon. The silicon renders the alloy tough and hard with a high tensile strength. The copper-lead-lithium nickel alloy shown in Fig. 10 exhibits a reversal of the position of the lead and copper, the copper, indicated by light areas, being surrounded by lead, thus indicating a continuous lead matrix with copper dispersed therein.

As previously stated, the composition of the copper and lead content of the alloy may vary within wide limits while maintaining the advantages of fine structure and uniform dispersion. The relative amounts of lead and copper will be varied in accordance with the service to be performed by the alloy. For heavy work, as in railroad rolling stock, a bearing rich in copper is preferred, as for instance, an alloy containing in the original melt, lead 15%, lithium 0.01 to 0.1% and the remainder copper.

A still harder bearing metal alloy may consist, in the original metal, of lead 10%, tin 0.2 to 2.0%, lithium 0.1% and the remainder copper.

Iron may also be used to harden the alloy, as for instance, a composition consisting in the original melt of lead 30%, iron 0.5%, lithium 0.1% and the remainder copper.

A good bearing metal for general use may consist of an alloy having in the original melt lead 30%, lithium 0.15% and the remainder copper.

For high speed applications, an alloy of greater antiscoring properties is required, as for instance, one containing 50% or more of lead, such as shown in Fig. 6.

The amount of lithium added to the original melt is not critical, the values given above representing the quantity used in the particular batches referred to, greater or lesser amounts not materially affecting the resulting alloy. A portion of the lithium is lost during heating, the amount depending upon the length of heating and the temperatures attained. The upper limit of the lithium content added to the charge appears to be restricted to about 1%, by the violence of the agitation produced thereby. Finished alloys containing as low as 0.00017% of lithium have shown pronounced agitation in the furnace and extremely fine subdivision and uniform dispersion of the lead in the copper upon casting. Analysis of the lithium content of a number of very satisfactory copper-lead-lithium alloys, by the spectroscopic method, the proportions of lithium frequently being too small for accurate determination by ordinary chemical analysis methods, is given below, to indicate the range of lithium to be expected in such alloys:

	Lead	Lithium
	Percent	*Percent*
A	30	0.0033
B	30	0.0007
C	29.5	0.0002
D	16.25	0.00033
E	About 30	0.00017

The amount of lithium originally introduced into the charge in Examples A to D was from 0.5% to 1.0%. No lithium was introduced into the charge in Example E, the lithium being absorbed into the charge entirely from the lithium containing atmosphere created by the previously treated furnace lining. It is believed that the active portion of the furnace atmosphere consists of lithium in the metallic state and that the lithium in the copper-lead alloy is also in a metallic state although these facts are difficult of determination and it is possible that under the conditions prevailing in the furnace some active compound of lithium may be formed which effects the stirring action and imparts other beneficial characteristics to the alloy. The term "lithium" is employed in the claims, therefore, to include either metallic lithium or lithium in whatever other form it may occur in the furnace atmosphere and in the alloy.

In place of introducing metallic lithium into the furnace, a compound thereof, such as the chloride, fluoride, hydroxide, oxide, or carbonate of lithium or lithium containing ores such as spodumene or amblygonite, or mixtures thereof, may be used. The lithiated atmosphere may be provided in a gas fired furnace, for instance, by introducing a small quantity of a compound of lithium in powdered form; into the air or gas stream leading into the furnace or it may be injected or blown directly into the furnace through an aperture provided in one of the walls thereof. An apparatus for introducing the powdered lithium compounds directly into the furnace or into the air or gas conduit extending thereinto is fully disclosed in my copending application Serial No. 143,410, filed May 19, 1937, and entitled "Injecting apparatus." In an oil fired furnace the lithium compounds may be added directly to the oil, either as an oil soluble compound or in colloidal suspension. A process of treating fuel oil with lithium compounds is disclosed in my copending application Serial No. 154,203, filed July 17, 1937, and entitled "Promotion of combustion." In the case of electric furnaces the lithium compounds may be mixed with powdered carbon, such as graphite, and the mixture blown in a fine spray into the furnace in the manner set forth in my copending application Serial No. 143,411, filed May 19, 1937, and entitled "Metallurgical process."

The amount of lithium compound required to produce the requisite condition of the furnace atmosphere is very small but is not critical and may be readily determined by experiment for any particular furnace. The furnace should be operated on the reducing side so that the furnace gases will contain a small percentage of carbon monoxide, the purpose of which will hereinafter appear. The desired rate or frequency of introduction of the lithium compound may be determined by spectroscopic examination of the gases escaping from the furnace.

The use of the lithium compounds in place of metallic lithium simplifies the problem of introducing the lithium into the furnace, since the suitable compounds are more stable and more readily handled. Moreover, such compounds are normally in a pulverulent state and the amount to be introduced can be readily metered and introduced by simple, reliable and inexpensive apparatus. Lithium metal, moreover, is several times as expensive as the compounds for equivalent amounts of lithium, since the metal must be produced from the compound by an expensive and involved process. Also, it has been found, when using a salt, such as lithium carbonate, introduced either continuously or at intervals throughout the process, that suitable results may be obtained in a new or unseasoned furnace, although with continued use a finer subdivision of one metal within the other is obtained.

While I prefer to employ the apparatus shown

in my copending application Serial No. 143,410, referred to above, for introducing the powdered compounds into the furnace, I have, for ease of illustration, shown a simplified equipment for this purpose in Figs. 11 to 13 which will now be described.

Gas and air are admitted through the burner ring 14 surrounding the furnace, the gas being supplied through a conduit 40 and the air through a conduit 41. A blower 42, shown diagrammatically, and suitable valves (not shown) control the amount of air supplied.

Interposed in the air line 41 is means for introducing lithium compounds into the furnace. This means comprises a sleeve 43 threaded into a T 44 in the air line, a piston 45 slidable in the sleeve 43 and a hopper 46 for the lithium compound 47. The piston 45 is provided with an annular recess 48 adapted in the retracted position of the piston to be positioned beneath the hopper so as to receive a charge of the compound and to convey the same into the air line 41 when the piston is moved to the dotted line position. The compound thus introduced into the air stream is carried by this air into the furnace where it is highly heated. A cross bar 49 facilitates the manual reciprocating movement of the plunger 45 and a stop 50 limits the outer movement thereof. The end 51 of the piston fits closely in the bore of the cylinder and prevents the air under pressure in conduit 41 from blowing out through the hopper 46.

If desired, the plunger 45 may be reciprocated by a continuously operating crank 52, as shown in Fig. 13, so as to supply the lithium compound in definitely timed increments.

The desired frequency of operation of the plunger may be determined by spectroscopic inspection of the gases escaping from the vent 13, the lithium compound being supplied in such quantities and at such frequency as to maintain a strong lithium line in the spectrum when the furnace gases are viewed through a spectroscope.

The lithium compound so introduced is reduced to lithium metal in the furnace and produces in the copper-lead charge a natural circulation or agitation of the molten mass in the same manner as when metallic lithium is introduced into the furnace.

The furnace lining 10 may be composed largely of silicon oxide and if desired, the lithium compounds may be introduced into the furnace at spaced intervals since the lining serves as a storage and liberating medium whereby the desired atmosphere is maintained within the furnace between the periods of introduction of the lithium compound. It is not necessary, however, that the lining be of the particular composition specified heretofore, since linings have been found satisfactory having a silica content of about 31% with approximately 62% alumina and the remainder mainly iron oxide and titanium oxide. Linings of magnesium oxide, aluminum oxide and chromium oxide may also be employed or the furnace lining may be composed of hard burned brick of low permeability and low porosity containing approximately 50% silica and 44% alumina, having a bulk density of about 1.2 oz. per cu. inch and a fusion point of about 3200° F. A cement for bonding the bricks, such as sillimanite, cyanite, andulusite, and mullite, analyzing as follows: silica 38.07%, alumina 56.63%, titanium 1.14%, iron oxide .73%, ignition loss 2.78% and the remainder moisture and other impurities, has been found suitable. This cement may also be used as a coating for the bricks after their assembly in the furnace. In general, cellular insulating brick or moulded or tamped-in linings have not been as satisfactory as linings built up from hard burned refractories, apparently due to the high permeability thereof or the reaction of the lithium or one of its compounds with the binder employed in such moulded linings. Linings, hearths and other refractory parts of the furnace consisting of or containing silicon carbide have been found to react detrimentally with the lithium of the atmosphere, due possibly to the nature of the binder commonly employed, causing breakdown of the refractory and to some extent, reduction in the efficiency of the lithium containing atmosphere for its intended purpose.

I prefer to introduce the lithium metal or compound into the furnace mixed with the air or fuel since this insures that it will pass through the hottest part of the flame, which is at a temperature several hundred degrees above the average furnace temperature. Hence the lithium or its compound will be more readily converted into a vapor.

Under the conditions prevailing in the furnace the lithium compound, or at least a portion thereof, breaks down liberating free metallic lithium. The reaction is apparently first the formation of lithium oxide which reacts with carbon monoxide as follows:

$$2Li_2O+CO=Li_2CO_3+2Li$$

The lithium is thus freed to combine with the oxygen of the furnace or any oxygen that may be included in the metal being heated and the lithium carbonate of the above reaction is thermally broken down to lithium oxide liberating carbon dioxide. The reaction is then repeated with the lithium oxide so formed. As will be noted from the reactions set forth above each particle of lithium present in the furnace goes through the above cycle repeatedly, until it ultimately escapes with the furnace gases and it is necessary, therefore, to supply additional lithium or lithium compounds only to replace that so escaping and that absorbed by the material being heated or deposited on parts of the furnace.

In electric furnaces I add carbon monoxide to the furnace or a supply of carbon from which carbon monoxide may be generated, in order to obtain a reduction of the lithium oxide in accordance with the foregoing equation.

The lithium used in the alloys and in the process described was pure lithium such, for example, as that prepared by the Maywood Chemical Works of Maywood, N. J., but it is contemplated that less pure lithium or lithium alloyed with other permissible components of the alloy to be produced or other compounds of lithium, the components of which readily escape or are harmless, may be used.

The copper used has been oxygen free copper, known in the art as such, and the lead has been that known commercially as 99.9 plus per cent pure, but it is contemplated that less refined commercial grades of copper and lead are adapted for use in carrying out the invention.

It is to be understood that brasses or bronzes may be used in place of pure copper and that such elements as nickel, iron, tin, silicon and other suitable alloying elements, as previously indicated, may be included in minor amounts in the composition to produce desirable variations in the physical properties of the alloy and such al-

loys of copper are intended to be included under the term "copper" when used in the claims.

The term "alloy" is used throughout the specification and in the claims, in a broad sense, to include a solid solution, mechanical mixture or other form of combination of the various elements thereof.

It is to be understood that the particular examples given of copper-lead-lithium alloys and the procedure for producing the same are to be considered in an illustrative sense and not as defining the limits of the invention.

What I claim is:

1. The method of forming an alloy composed at least in part of copper and lead which comprises heating the constituents of the alloy together in a molten state in the presence of lithium until agitation of the molten metal occurs.

2. The method of forming an alloy composed at least in part of copper and lead which comprises heating the constituents of the alloy together in a molten state in the presence of lithium until agitation of the molten metal occurs and pouring the molten mass into molds while agitation is continuing.

3. The method of forming an alloy composed at least in part of copper and lead which comprises heating the constituents of the alloy together in a molten state in the presence of lithium until circulatory agitation of the molten mass occurs in a direction which at the surface of the mass is from the center towards the sides and pouring the molten mass into molds while the agitation is continuing in such direction.

4. The method of producing agitation in an alloy composed of copper and lead which comprises heating the metals together in a molten state with lithium and simultaneously providing a lithium containing atmosphere about the molten metal.

5. The method of producing agitation in an alloy composed at least in part of copper and lead which comprises alternately heating and cooling the metal, in the presence of lithium, to above and below the critical temperature at which the direction of agitation reverses.

6. The method of forming an alloy composed at least in part of copper and lead which comprises heating together copper and lead in a molten state in the presence of lithium vapor until agitation of the metal occurs.

7. The method of controlling the size of lead particles in a copper-lead alloy which comprises heating the copper and lead in the presence of lithium to a temperature at which agitation of the molten metal occurs, and retaining said mass in a state of agitation for a period depending on the minuteness of lead particles desired.

8. The method of producing alloys composed at least in part of copper and lead which comprises heating the metals together in a molten state, agitating the molten mass and continuing the agitation during cooling and up to the point of solidification of the alloy, the agitation being produced by the presence of lithium in contact with the melt.

9. The method of producing copper-lead-lithium alloys which comprises melting together copper, lead and lithium to a temperature at which agitation of the mass occurs and preventing escape of at least part of the lithium from the molten metal.

10. The method of producing copper-lead-lithium anti-friction articles comprising melting copper, lead and lithium together at a temperature sufficient to produce agitation of the molten metal, casting the metal into ingots, remelting the same as desired to a temperature sufficient to cause reagitation and recasting the same into said articles.

11. The method of producing copper-lead-lithium alloys which comprises incorporating lithium or lithium compounds in the lining of a furnace by maintaining a lithium containing atmosphere in the furnace for a sufficient length of time, and thereafter heating copper and lead therein to a temperature at which agitation of the molten metal occurs.

12. The method of producing anti-friction alloys, comprising heating copper and lead together in a molten state with a fractional per cent of lithium and minor proportions of iron, nickel, silicon or tin, until agitation of the molten metal occurs.

13. A copper-lead-lithium alloy containing 5% to 70% lead, not over about 1% of lithium and substantially all of the remainder copper, the lithium being present in sufficient amount to render the alloy substantially homogenous.

14. A copper-lead-lithium alloy having 5% to 70% lead in finely divided form, said alloy containing not over about 1% of lithium and substantially all the remainder copper, the lithium being present in sufficient amount to cause substantially uniform dispersion of the lead in the copper.

15. The method of producing copper-lead alloys comprising heating said copper and lead in a molten state in a furnace, and providing lithium in the furnace atmosphere during the heating of the alloy.

16. The method of producing agitation in an alloy composed of copper and lead which comprises heating the metals together in a molten state and providing an atmosphere about the molten metals which exhibits a lithium spectral line.

17. The method of forming an alloy composed at least in part of copper and lead which comprises heating together in a molten state copper and lead in an atmosphere which exhibits a lithium spectral line and maintaining such atmosphere substantially throughout the process.

18. The method of producing a copper lead alloy which comprises fusing together lead and lithium and fusing together the lead lithium alloy and copper.

19. The method of producing a copper lead alloy which comprises fusing together lead and lithium in a proportion of the order of 1000 parts of lead to 1 part of lithium and fusing together the lead lithium alloy and copper in a proportion of about 1 part of said alloy and 1 to 3 parts of copper.

20. The method of producing a copper lead alloy which comprises fusing together lead and lithium in a proportion of the order of 1000 parts of lead to 1 part of lithium by holding the lithium submerged in the molten lead, and fusing together the lead lithium alloy and copper in a proportion of the order of 1 part of said alloy and 3 parts of copper.

21. The method of producing a copper lead alloy which comprises fusing together lead and lithium and fusing together the lead lithium alloy and copper in a proportion of 2 parts of said alloy and 1 to 30 parts of copper.

22. The method of producing a copper-lead alloy which comprises fusing lead with lithium, fusing copper, adding the lead-lithium alloy to

the fused copper and regulating the temperature to a point at which agitation of the molten mass occurs.

23. The method of producing a copper-lead lithium alloy comprising heating copper and lead in a molten state in an atmosphere containing lithium produced by the decomposition of a lithium compound.

24. The method of producing a copper-lead lithium alloy comprising heating copper and lead in a molten state in an atmosphere containing lithium produced by the decomposition of a lithium halide.

25. The method of producing a copper-lead lithium alloy comprising heating copper and lead in a molten state in an atmosphere containing lithium produced by the decomposition of lithium carbonate.

26. A copper-lead-lithium alloy containing from 5% to 70% lead, detectable amounts up to 1% of lithium and substantially all of the remainder copper, the lead being finely distributed within the grains of the copper.

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