The present invention relating torollable alloys is particularly directed to the manufacture of copper alloys of two or more constituents such as copper and lead; or copper, lead and tin, capable of being rolled in what may be termed commercial rolling practice. Our process may be applied also to the manufacture of either copper alloys by the melting of the constituent materials on or to these alloys reinforced by a layer of steel. The essence of the invention, we believe to be, the discovery that when copper alloys, such as leaded bronze or copper-lead, are cast with certain structural characteristics, the alloys may be rolled by commercial rolling practices such as certain ones used and generally known in brass mills.

According to our information none of the brass mills furnishes rolled leaded materials containing more than about 4% lead. The reason for this is that even 4% lead in the alloy increases rolling difficulties. It is known that certain castings roll with comparative ease while others are almost, if not impossible, to work. The exact reason for this is not known beyond the fact that the difference lies in structural peculiarities. Attempts to roll copper alloys containing large amounts of lead have thus far been unsuccessful except by the methods herein described.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereafter fully described and particularly pointed out in the claims; the annexed drawings and the following description setting forth in detail certain structures embodying the invention, such disclosed means constituting, however, but one of various structural forms in which the principle of the invention may be used.

In said annexed drawings:

Figs. 1a, 1b, 1c and 1d are photomicrographs showing the appearance of an alloy which will be described, (1a) in the "as cast" condition in cross section, (1b) the structure after a 50% reduction in thickness by rolling, (1c) the "as cast" condition at the surface and (1d) the structure after a 50% reduction on an enlarged scale, respectively;

Figs. 2a, 2b, 2c and 2d are photomicrographs showing the condition of a second alloy, (2a) in the "as cast" condition in cross section, (2b) a structure after a 50% reduction, (2c) the "as cast" condition at the surface and (2d) the structure after a 50% reduction on an enlarged scale, respectively

Fig. 3 is a photomicrograph of another alloy, showing the appearance of the alloy in cross section, after a 50% reduction without crack-inducing effects.

Fig. 4 is a similar view of still another alloy;

Fig. 5 is a photomicrograph showing the structure of an alloy to be described in the "as cast" condition;

Fig. 6 is a similar view, but showing the structure of an alloy after annealing; and

Fig. 7 is a similar view showing the structure of the material after annealing but with a 50% reduction.

In general, the structure of the alloy in the "as cast" condition which renders the same capable of being commercially rolled is as follows:

In alloys consisting of two or more phases there will usually be differences between the various phases. These differences are both mechanical and chemical. By way of illustration, we will take a leaded bronze containing the constituents: lead 8–10%; tin 4–10%; zinc 2–0%; copper, remainder. In the "as cast" condition, there are three or more phases usually present: (1) the high lead or soft phase; (2) the alpha or copper-rich phase; (3) a pseudo-phase rich in copper but higher in tin (and zinc if present) than the alpha phase and solidifying at a lower temperature than the alpha. The last material (3) is also considerably harder than material (2).

Alloys of this general composition have been known to metallurgists for many years, but only in the cast condition. Repeated prior attempts to roll this alloy have been unsuccessful. In order to cold roll such alloys commercially, we have found that certain structural conditions are desirable.

1. The lead should be surrounded by a phase sufficiently resistant to deformation so that when subjected to the pressure incident to rolling, this phase will confine the lead and not allow it to form into stringers, that is, thin bands of lead elongated in the plane of rolling. It is well known that when more than small amounts of these stringers are present, the material is weak and tends to separate into fibres through the stringers. When most of the lead is surrounded by the pseudo-phase, mentioned above, the comparatively high deformation resistance of this phase is effective in preventing the formation of detrimental lead stringers. Where the layer of the pseudo-phase is quite thick, rolling has actually been accomplished wherein the lead particles were elongated less than the alpha phase.

Where only two phases are present, namely, a lead-rich and a copper phase, rolling is more
difficult but if conditions (2) and (4) named below are present, rolling may be effected.

2. During solidification, we have found it desirable that crystallization takes place in such a way that the dendritic crystal growth is substantially continuous through the thickness and normal to the direction of rolling.

To avoid a substantial amount of porosity in a cast article it is desirable to produce a cooling of the molten metal from one surface toward an opposite surface. Such cooling produces dendrites extending substantially parallel to each other from one surface. To secure these results it is necessary, as will be evident from the present description, to cause a controlled solidification of the metal at one surface and proceeding toward an opposite surface, and by the term "controlled" as herein used is meant a solidification which is not necessarily uniform as regards time, but which is uniform as regards the progress of the solidifying front of metal from one surface toward the opposite surface. For example, there might be uniform cooling in the usual sense for a short period of time and for, say, one-eighth of the distance from one surface to an opposite surface. The solidification might then progress rapidly toward the opposite surface, but the rate of solidification might change one or more times during such progress. This type of solidification is intended to be included in the term "controlled cooling" or "controlled solidification" as herein used.

3. The hard pseudo-phase should tend to form an interdendritic net work through the structure.

4. The lead phase should be dispersed through the structure in particles not too large. It will be apparent to those skilled in the art that such factors are obtained by controlling the cooling conditions in certain ways.

To illustrate the above, we may refer to the figures. Assume for example, that in the alloy consisting of three phases, shown as 1, 2 and 3, it is desired to effect the results secured by this invention to have the softest phase 3 dispersed throughout the material and in the form of small particles. Since this material is that which is most easily drawn out under a rolling pressure forming stringers, these particles should be enclosed in a harder material or phase and it is desirable that this phase (2) in turn be harder than the remainder (1) of the composition. The structure of the "as cast" material or phase is such that there is an orientation of the dendrites, as shown in Fig. 1, producing directional properties and the phase 1 is weak, which makes it easier for the phase 2 to prevent the excessive deformation of the lead. If these conditions exist, rolling of the material will produce a structure in which the particles 3 of the softest constituent may have been elongated, but as they are enclosed by the material or phase 2, which is the hardest of the three constituents, they have not produced stringers which might cause cracking of the material. If there is a proper dispersion of the softest particles and if these are properly enclosed within the hard phase, the entire material may be rolled without detrimental cracking since the soft particles are not allowed to form points of weakness or long drawn stringers in the material.

If you refer now to Figs. 1a, 1b, 1c and 1d, there are shown photomicrographs of an alloy consisting of approximately 8% lead, 4% tin, 3% zinc and the remainder copper. The specification for this alloy usually calls for 7 to 9% lead, 3.5 to 4.5% tin, .01 to .4% zinc, and the balance substantially copper. In Fig. 1a the material is shown in the "as cast" condition, in cross section, at one hundred magnifications. This material is cast against a steel backing strip or support and solidification is produced by the method described in our copending application, Serial No. 308,228, filed December 8, 1939. The result of this method of solidification will be obvious from the photomicrograph which shows a number of substantially parallel dendrites extending in a direction normal to the surface of the steel supporting member 5. In this figure, there appear particles of lead 3 dispersed throughout the material and surrounding a harder phase. The remainder of the material lying between the lead particles surrounded by their protective coating of the pseudo-phase is an alpha copper phase. Fig. 1b shows the same material after a reduction by rolling of 50% and at the same magnification. In this figure, the lead particles 3, at the left of the figure, can be distinctly shown and have been drawn out, but have not been allowed to form stringers or to flow together by reason of the harder protective pseudo-phase surrounding the lead particles. The extra large lead particles which can be clearly distinguished in this photomicrograph, but it will be noticed that the particles of lead are in the main, small and distributed through the metal. In Fig. 1c, there is shown the surface of the alloy referred to in the "as cast" condition and here again it will be noted that the lead particles are in the main, small and well distributed through the metal.

Fig. 1d is a photomicrograph showing the same material after a 50% reduction but under magnification of 350, which will, of course, magnify the differences in size of the lead particles. Even at such magnification, however, the bulk of the lead particles are small and well distributed throughout the material and have been protected against the formation of stringers by the harder coating of the pseudo-phase.

In Figs. 2a, 2b, 2c and 2d are shown micrographs of a second alloy, the photomicrographs corresponding to those of Figs. 1a, 1b, 1c and 1d. This second alloy consists of approximately 80% copper, 10% lead and 10% zinc. The specification for this alloy usually calls for 9 to 11% lead, 9 to 11% tin, .01 to .5% zinc, and the balance substantially copper. Fig. 2a shows the structure of the material in the "as cast" condition which corresponds closely to the structure of the material shown in Fig. 1a. Similarly, Fig. 2b shows the material after a 50% reduction and corresponds closely to material shown in Fig. 1a. Fig. 2c shows the structure of the material as cast at the surface with good distribution of the lead, and Fig. 2d shows the material after a 50% reduction under magnification of 350, and again we find the lead phase well distributed.

In Fig. 3 there is shown still another alloy of the same general character and containing a larger amount of lead and of approximately the following analysis:

<table>
<thead>
<tr>
<th>Element</th>
<th>Per-cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>72</td>
</tr>
<tr>
<td>Lead</td>
<td>3</td>
</tr>
<tr>
<td>Tin</td>
<td>8</td>
</tr>
</tbody>
</table>

This view shows the metal after a 50% reduction without cracking, at a magnification of 100 and there is to be noted a satisfactory distribution of
lead particles and the absence of serious stringers. Fig. 4 is a similar view showing still another alloy containing still more lead and having the approximate analysis as follows:

\[
\begin{align*}
\text{Per-cent} & \\
\text{Copper} & = 67 \text{ to } 74 \\
\text{Lead} & = 22\frac{1}{2} \text{ to } 27\frac{1}{2} \\
\text{Zn} & = 3 \text{ to } 4
\end{align*}
\]

A maximum of 3% zinc

In this view the metal is shown after a 50% reduction without cracking. Although some of the lead particles are definitely elongated, it is remarkable with so much lead present to find that the protective action of the hard phase has effectively prevented the formation of detrimental stringers.

While the above are illustrations of commercially rollable structures in particular alloy compositions, our invention is by no means limited to such alloys. For example, in certain systems of a cast-copper-zinc lead containing phase analogous to the two copper phases discussed above, may not form, but a single phase which is cored may replace them. Coring takes place by a change of composition during cooling such that the pseudo-phase crystallizes first and is in turn surrounded by a lower melting and harder but not crystallizing as a new and discrete. However, it is important that the soft phase be surrounded by a material of a relative greater hardness or resistance to deformation sufficient to prevent excessive elongation of the lead. It is also important that the dendrites be relatively uniform in size and extend substantially through the thickness of the work normal to rolling direction. While it is, of course, desirable that pockets caused by entrapped gas or precipitated gas be absent and that interdendritic shrink be absent, these defects are not as detrimental to our successful rolling as under the present commercial casting and rolling conditions.

As would be expected of those skilled in the art, once such material is rolled down and annealed at the usual annealing temperatures for copper alloys, or for steel, if it be steel backed, the recrystallized structure is quite different from the as cast structure. Dendrites are absent and the matrix is now composed of unstrained grains. The lead particles are more or less rounded and lie at the grain boundaries of the copper phase. Coring has disappeared as has the pseudo-phase. This new structure is workable by ordinary commercial practice such as that used for rolling low lead-copper alloys. This workability, we attribute to the substantial absence of flaws or discontinuities in the copper phase, and the favorable dispersion of the completely separated lead particles. During deformation the lead deforms to the same extent as the copper phase but only to the same extent, i.e. there are no cavities or cracks in the copper phase into which the lead can be internally extruded to form detrimental stringers.

When the casting has the preferred structure heretofore described, it may also be possible to roll the material after an annealing which destroys the pseudo-phase. Rolling cannot be accomplished, however, unless the cooling has approached the conditions described previously, that the dendrites are not continuous through the thickness normal to rolling. Should the dendrites not be continuous but segmented into two or more sections, then it will be found that the lead will segregate at these points which are points of weakness. During rolling, the structure will open up at these points and the lead will form into stringers which cannot be removed satisfactorily in later operations. If the dendrites are not substantially parallel, the structure will also be found to be weak and will not deform uniformly during rolling, resulting in cracks.

To illustrate the foregoing, we may refer to Figs. 5, 6, and 7 of which Fig. 5 shows the same composition as that already described in Figs. 2a, 2b, 2c and 2d. The metal of Fig. 5 is shown in the "as cast" condition. In Fig. 6 the same metal is shown after annealing, and we may here note the disappearance of the dendritic structure. After annealing, the material as shown in this figure presents the same favorable distribution of the lead but the pseudo-phase has disappeared, being replaced by equiaxed grains due to the recrystallization of the metal. This material is now conditioned for rolling, and in Fig. 7, the same material is shown after a 50% reduction. We here find the lead phase elongated in the direction of the rolling and the slip lines throughout the alpha copper phase, but no cracking appeared and no formation of detrimental lead stringers.

It has been found that lead containing alloys having the characteristics herein described and containing lead in amounts from 3% to 7% can be made and rolled with uniform satisfactory results. An alloy of this type, which we have successfully rolled, falls within the range of 3 to 7% lead, 3\% to 5\% tin, 0.1 to 5\% zinc, and the balance substantially copper. Copper-lead alloys containing lead in an amount up to as much as 4% of lead are, in some cases, now made and rolled but many mills refuse orders for such material and the mills which will accept such orders may experience heavy losses in rolling, and produce, in some cases, from 30% to 40% of scrap material due to the formation of stringers and cracks in the rolled material. The present invention contemplates the casting of a material in which, as already described, the soft particles, that is in the last case, the lead, is so enclosed in harder deformation resistant shells that it is not string out or produce cracks during rolling.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the structure herein disclosed, provided the means stated by any of the following claims or the equivalent of such stated means be employed.

We therefore particularly point out and distinctly claim as our invention:

1. A rolled copper alloy article resulting from a product which has been unidirectionally cooled during solidification and reduced at least 5% of its original thickness containing from about 5% to about 25% of lead substantially uniformly distributed throughout a matrix and elongated in a direction parallel to the direction of rolling, the article being substantially free from detrimental lead stringers.

2. A rolled copper alloy article resulting from a product which has been unidirectionally cooled during solidification and reduced at least 5% of its original thickness containing from about 3% to about 7% of lead substantially uniformly distributed throughout a matrix and elongated in a direction parallel to the direction of rolling.
the article being substantially free from detrimen-
tal lead stringers.

3. A composite strip comprising a strip of 
steel having bonded thereto a layer of a copper 
ally resulting from a product which has been 
unidirectionally cooled during solidification and 
reduced at least 5% of its original thickness and 
containing from about 5% to about 25% of lead 
substantially uniformly distributed throughout a 
matrix and elongated in a direction parallel to 
the direction of rolling, said layer of copper alloy 
being substantially free from detrimental lead 
stringers.

4. A rolled copper alloy article resulting from 
a product which has been unidirectionally cooled 
during solidification and reduced at least 5% of 
its original thickness containing about 5% to 
about 25% of lead evenly distributed throughout 
the article in the form of small particles con-
tained within surrounding shells of a harder de-
formation-resistant phase, the article being sub-
stantially free from detrimental lead stringers.

5. A rolled alloy article resulting from a prod-
uct which has been unidirectionally cooled dur-
ing solidification, said article consisting of 22½ 
to 27½% of lead, 3 to 4% of tin, .01 to 3% of 
copper, the lead being substantially uniformly 
distributed throughout a matrix and elongated 
in a direction parallel to the direction of rolling, 
the article being substantially free from deter-
mental lead stringers.

6. A rolled alloy article resulting from a prod-
uct which has been unidirectionally cooled dur-
ing solidification, said article consisting of 3½ 
to 5% of tin, .01 to 5% of zinc, 3 to 7% of lead, 
with the balance substantially copper, the lead 
being substantially uniformly distributed 
throughout a matrix and elongated in a direction 
parallel to the direction of rolling the article 
being substantially free from detrimental lead 
stringers.

7. A rolled alloy article resulting from a prod-
uct which has been unidirectionally cooled dur-
ing solidification, said article consisting of 7 to 
9% lead, 3½ to 4½% tin, .01 to 4% zinc, with 
the balance substantially copper, the lead being 
substantially uniformly distributed throughout 
a matrix and elongated in a direction parallel 
to the direction of rolling, the article being sub-
stantially free from detrimental lead stringers.

8. A rolled alloy article resulting from a product 
which has been unidirectionally cooled during solildi-
cation, said article consisting of 9 to 11% lead, 
9 to 11% tin, .01 to 5% zinc, and the balance 
substantially copper, the lead being substantially 
uniformly distributed throughout a matrix and 
elongated in a direction parallel to the direction 
of rolling, the article being substantially free 
from detrimental lead stringers.

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