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HARD LEAD ALLOYS AND METHODS OF MAKING SUCH ALLOYS

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This invention relates to hard lead alloys and methods of making such alloys, and more particularly to work hardened lead alloys.

It is a well known fact that most metals harden on cold working, while lead and practically all lead alloys either soften during cold working or acquire a temporary hardness which disappears in a short time, leaving the alloy substantially as soft or softer than it was prior to the cold working.

Objects of the invention are to provide hard lead alloys and effective methods of making such alloys.

In accordance with one embodiment of the invention, a calcium-lead alloy is cold worked to impart a permanent hardness thereto and increase its tensile strength.

Considerable work has been done on age-hardened or dispersion hardened lead alloys in which an alloy is quenched from a high temperature to obtain a supersaturated solution of the hardening constituents in the alloy which are subsequently precipitated out and dispersed in finely divided form by normal room temperature aging or by artificial aging at slightly elevated temperatures. Both antimony and calcium have been used as the age hardening constituents of lead alloys.

The present invention is based upon the discovery of the peculiar phenomenon that a lead-calcium alloy may be hardened and its tensile strength increased by cold working. This is not true of lead-antimony alloys and is contrary to the general phenomena in cold working lead and its alloys. In an article published in the Journal of the Institute of Metals, No. 2, 1931, vol. 41, entitled "The effects of cold rolling and of heat treatment of some lead alloys," the authors Waterhouse and Willows give some data showing that tin-lead, antimony-lead, cadmium-lead, tin-cadmium-lead, and cadmium-antimony lead alloys, either softened or developed a transient hardness after cold working which passed after a short aging period, leaving the alloys substantially as soft or softer than they were prior to the cold working.

Lead-calcium, however, may be cold worked to impart a permanent hardness and tensile strength thereto, and the increase in hardness and tensile strength may range as high as 70% or over.

As a specific example, a lead-calcium alloy having a calcium content of .043% was cold rolled to reduce its cross-sectional area 25% with a resultant increase in tensile strength from 4100 pounds per square inch to 5320 pounds per square inch, an increase of over 1200 pounds per square inch or 29%. Further, rolling to reduce its cross-sectional area 50% resulted in an increase in tensile strength of over 1700 pounds per square inch or 42% over its original state.

The effect of cold working is even more striking in lead-calcium alloys which have been previously age hardened. For instance, a lead-calcium alloy having a calcium content of .043% was quenched from a temperature in the region of its solid solubility temperature and aged at 100° C. for 16 hours. This alloy was cold rolled to reduce its cross-section 25% and showed an increase in tensile strength of 51% over its soft state and cold rolling to reduce its cross-section 50% resulted in an increase of 63% in tensile strength over its soft state. These increases are 23% and 35% greater, respectively, than obtained by quenching and aging alone.

The effect of aging lead-calcium alloys after cold working also results in an increase in the tensile strength. Thus a lead alloy having a .043% calcium content which had been cold worked to reduce its cross-section 25% was aged at a temperature of 100°C. for 16 hours which increased its tensile strength 17% over its tensile strength after cold working. It appears that the cold working and aging have in part a similar effect because a similar specimen cold worked to reduce its cross-section 50% and then aged showed an increase in tensile strength of only 14% over its tensile strength after cold working. The cold working may be carried to a point where subsequent aging will have practically no effect on the hardness of the alloy. However, cold working is in many respects quite dissimilar in effect from aging, as shown by the fact that a specimen having .043% calcium content annealed at 225°C. for one hour showed an increase of 66% in tensile strength after cold working, whereas aging has no appreciable effect in increasing the tensile strength of such a calcium alloy annealed at this temperature. Furthermore, cold working causes an increase in tensile strength of an alloy that has been fully hardened by heat treatment and aging but as pointed out above an alloy that has been sufficiently cold worked cannot be further hardened by aging.

From this it will be seen that lead-calcium alloys may be work hardened irrespective of whether or not they have been previously heat treated to produce a supersaturated solution suitable for age hardening and while the final hardness after work hardening is greater in a

previously age hardened specimen, the percentage of increase of hardness due to cold working is greater in a specimen that has not been previously age hardened.

While it is not desired to be limited to any particular theory, it appears that the increase in hardness upon cold rolling of a lead-calcium alloy is due at least in part to the deformation of the grains. The permanence of the increased hardness is probably due to the raising of the recrystallization temperature by the addition of calcium to prevent annealing at normal temperatures. The effectiveness of work hardening is limited to lead-calcium alloys having less than 1% of calcium, as the high calcium alloys are softened by cold work.

In the foregoing description the tensile strength of the alloys has been referred to for convenience since hardness and tensile strength vary proportionally in a particular lead alloy.

It will be understood that the nature and embodiments of the invention herein described are merely illustrative and that many changes and modifications may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A work hardened lead alloy containing less than 1% calcium, said alloy being characterized by its permanent hardness induced by said work hardening.

2. A work hardened lead alloy containing a less amount of calcium than the maximum solid solubility value of calcium in lead, said alloy being characterized by its permanent hardness induced by said work hardening.

3. A work hardened lead alloy containing from .01% to .10% of calcium, said alloy being characterized by its permanent hardness induced by said work hardening.

4. A work hardened lead-calcium alloy containing approximately .04% of calcium, said alloy being characterized by its permanent hardness induced by said work hardening.

5. A method of making a hard lead-calcium alloy containing on the order of .04% calcium which comprises cold working the alloy to impart thereto a permanent hardness induced by said cold working.

6. A method of hardening a lead-calcium alloy containing from .01% to .10% of calcium which comprises cold working the alloy to impart thereto a permanent hardness induced by said cold working.

7. A work-hardened and age-hardened lead base alloy containing calcium in amounts less than 1%, said alloy being characterized by its permanent hardness induced by the combined action of said work-hardening and age-hardening.

8. A work-hardened and age-hardened lead base alloy containing calcium in amounts from .01% to .10%, said alloy being characterized by its permanent hardness induced by the combined action of said work-hardening and age-hardening.

9. A work-hardened and age-hardened lead base alloy containing on the order of .04% calcium, said alloy being characterized by its permanent hardness induced by the combined action of said work-hardening and age-hardening.

10. A method of hardening a lead base alloy containing less than 1% of calcium which comprises heating the alloy to form a solution of the calcium in the lead, quenching the alloy to form a supersaturated solution, ageing the alloy to precipitate and disperse the age-hardening ingredient, and cold working the alloy to impart thereto a permanent hardness induced by the combined age-hardening and cold working.

11. A method of hardening a lead base alloy containing from .01% to .10% of calcium which comprises heating the alloy to form a solution of the calcium in the lead, quenching the alloy to form a supersaturated solution, ageing the alloy to precipitate and disperse the age-hardening ingredient, and cold working the alloy to impart thereto a permanent hardness induced by the combined age-hardening and cold working.

12. A method of hardening a lead base alloy containing approximately .04% of calcium which comprises heating the alloy to form a solution of the calcium in the lead, quenching the alloy to form a supersaturated solution, ageing the alloy to precipitate and disperse the age-hardening ingredient, and cold working the alloy to impart thereto a permanent hardness induced by the combined age-hardening and cold working.

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