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DISPERSION HARDENING OF LEAD

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This invention is concerned with the manufacture of lead sheeting, and extruded lead sections, and is particularly concerned with a method of producing a sheet material consisting of lead or lead alloy which has been specially hardened for certain industrial purposes.

The softness of unalloyed lead, although frequently considered an advantage, for example in the quick laying of small pipe-lines, can be a disadvantage in other ways, e.g. in the construction of accumulators. Some method of hardening the metal is therefore desirable, and the method known as dispersion-hardening has been discovered to be one that might give the desired result.

In a dispersion-hardened metal, particles of hard material which are inert to the matrix are well dispersed throughout the body of the metal. The particles, being situated inside the lead crystals and in the grain boundaries, inhibit slip thus increasing the tensile strength, creep strength and hardness of the metal, and its resistance to grain growth.

"Grain growth" can be described in general terms as follows:

A body of metal may be regarded as being composed of "grains" (i.e. crystals) very strongly bonded together. It is generally accepted that the grain boundary regions are stronger than the grains themselves. Neglecting the influence of other factors such as work hardening etc., the hardness and strength of a metal will depend upon the grain size. The larger the grain size the softer and weaker the metal and conversely. Thus, when the temperature of a piece of metal is raised sufficiently high it commonly happens that the metal grains coalesce (i.e. "grain growth" occurs) so that, after cooling, the said piece of metal is composed of a smaller number of larger grains and is accordingly softer and weaker than it was before.

Most metals have to be heated to well above room temperature to cause grain growth; 250° C. for copper for example and 400–450° for iron. In the case of lead, however, grain growth occurs at room temperature. In dispersion hardened lead the dispersed particles and, in particular, those particles located at or near the grain boundaries, prevent grain boundary movement and thus inhibit "grain growth."

The cold, plastic deformation (i.e. deformation without cracking) of a piece of metal, distorts and work hardens the crystals and thus the piece of metal as a whole is work hardened. Heating a work-hardened piece of metal to a sufficiently high temperature results in recrystallisation (i.e. the growth of new small crystals) and further heating to higher temperatures results it grain growth as described above. It is a pecularity of pure lead that recrystallisation and grain growth will occur at temperatures not much above room temperature (150° C.).

Powder metallurgy techniques are commonly used in the manufacture of dispersion-hardened metal objects, a uniform mixture of the powdered metal and hardening component in appropriate proportions being compacted to the required shape and then sintered. The hardening component may be in the form of the oxide of the same or another metal and is very finely divided, the size range being typically from 0.1 to 10 microns.

The present invention arose out of the necessity of producing dispersion-hardened lead for accumulator plates.

Conventional powder metallurgy methods were not suitable, principally for the following reasons:

The oxide film with which lead particles are normally covered is not broken down during the normal compacting process, so that there is no metal-to-metal contact to permit the particles to be sintered, and sintering in a reducing atmosphere will not effectively remove the oxide coating from the surfaces of the particles.

As a result of experiments in the cold working of lead, there has been discovered a method of treating lead particles so that a polycrystalline piece of lead is obtained with the lead oxide, with which the lead particles are initilally coated, distributed uniformly throughout it—the lead being thus dispersion-hardened.

The method of this invention consists in extruding lead particles through a die to form a piece of lead of circular or other cross section and then rolling the lead along and across the direction of extrusion to form a thin sheet.

A hardened lead alloy can be produced by the same method if the particles have been previously coated with another metal, as described later in this specification.

The process of extrusion breaks up the oxide film on some of the particles into fragments which become embedded in the lead particles. The lead particles then bond to each other and recrystallise as a result of the deformation to which they are subjected. If a cross-section through a piece of lead extruded in the manner described above is examined under a microscope, it will be seen that the oxide films on the original particles have been most effectively broken up near the surface of the extruded piece, i.e. in the region subjected to the greatest deformation whilst the lead was being forced through the die. Towards the centre of the extruded piece the break up of the oxide films into discrete fragments becomes progressively less pronounced until finally no break up can be seen.

When the extruded piece is rolled down to a thin sheet the oxide films and fragments are further broken up and dispersed throughout the metal and further recrystallisation of the metal occurs with the fragments of oxide located within and between the metal crystals. The fact that recrystallisation has occurred is evidenced by the ductility of the rolled sheet. The rigidity of the dispersion-hardened lead is increased and it is found to have a tensile strength of up to three times that of normal lead.

The preferred size range of the initial lead particles is determined by such considerations as thickness of oxide, or applied metal layer, packing density of the particles and the final grain size required, but the range would normally by from 1 to 100 microns.

The method is not necessarily limited to pure lead particles, but may be applied to lead alloy particles. Particles of lead containing, for instance, 1% tin to improve the corrosion resistance of the finished product, might be used.

It is also possible that the method could be applied to a mixture of lead particles and particles of some other compound, such as tungsten carbide, silicon carbide or finely ground glass.

It has been found that if the oxide on the lead particles, which are the starting material of the present process, is replaced by a substance which is more friable than lead oxide, then the fragmentation of the particle coatings will be observed at a greater depth in the cross-section of the extruded piece than is the case with an extruded piece formed under identical conditions from oxide coated particles. Similarly, the further fragmentation of the coatings and the dispersion of the fragments throughout the material by rolling can be accomplished with less deformation of the extruded piece than is necessary with a piece formed by the extrusion of oxide coated particles.

It has been found that coatings of copper of silver applied to the lead particles by chemical precipitation after the removal of the oxide layer, are more friable than the normal oxide layers and that, accordingly, particles so coated with copper or silver are particularly suitable for the production of dispersion-hardened lead by the methods of extrusion and rolling already described.

The methods used for coating the particles with these metals are as follows:

Copper

(1) Treatment with acetic acid.
(2) Treatment with copper acetate solution.
(3) Washing and drying.

Silver

(1) Treatment with nitric acid.
(2) Treatment with silver nitrate solution.
(3) Washing and drying.

The following description gives the methods in detail:

Copper

(1) 10% (by volume) acetic acid is added to 100 gm. of the lead powder until the mass of powder is just damp. The acetic acid readily attacks the oxide layer and if too much is used begins to dissolve the lead so that a large quantity of lead acetate is produced which is a nuisance later on.

(2) Saturated copper acetate solution is added dropwise to the "slurry" of lead powder, lead acetate and acetic acid resulting from (1). As a result of the reaction which proceeds, copper is deposited on the lead and lead acetate goes into solution. The reaction is seen to be complete when the blue colour of the copper acetate has disappeared.

The amount of copper acetate solution used depends upon the depth of copper coating required. Typically 5 ccs. of saturated copper acetate solution are added to the 100 gms. of treated lead.

(3) The product of (2) is thoroughly washed in demineralised and de-oxygenated water.

The washing is continued until the wash water comes away clear and stays clear.

It is found that the water comes away clear in the early stages of the washing. This is followed by a stage when it is milky, after which it again becomes clear. The washing is continued until this third stage is reached.

It is believed that the milky stage is due to the reduction in the concentration of acetic acid to the point

where basic lead acetate which is readily soluble in acetic acid is precipitated. The second clearing indicates that most of the basic lead acetate has been removed.

(4) The product of (3) is washed in methanol (methyl alcohol) until the effluent liquid is clear. The explanation of this seems to be that the methanol progressively reduces the amount of water present so that the small quantity of basic lead acetate present in solution is precipitated. When the liquid becomes clear it indicates that the acetate has been removed.

(5) The product of (4) is dried at about 50° C. in a stream of oxygen-free nitrogen.

Silver

As for copper except that in (1), 1% (by volume) nitric acid is used in place of acetic acid and in (2) saturated silver nitrate solution is used in place of copper acetate solution.

The copper or silver coated lead is preferably stored in air tight containers since the coating produced is not a homogeneous skin and if the lead is exposed to the air a layer of lead oxide forms underneath the coating. Measurements on the particles used have shown that a suitable coating thickness is from $\frac{1}{2}\mu$–2μ.

What I claim is:

1. A method of producing hardened lead alloy which comprises removing the lead oxide coating from a mass of lead particles by means of a solvent, coating the particles with one metal of the group consisting of copper and silver by chemical deposition, thereafter extruding the lead particles cold through a die to form a piece of lead alloy of predetermined cross-section, and then rolling this extruded piece of lead alloy along and across the direction of extrusion to form a thin sheet.

2. A method according to claim 1 wherein the solvent used to remove lead oxide comprises acetic acid and the chemical deposition produces a copper coating by deposition from a solution comprising copper acetate.

3. A method according to claim 1 wherein the solvent used to remove lead oxide comprises nitric acid and the chemical deposition produces a silver coating by deposition from a solution comprising silver nitrate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,148,040	Schwarzkopf	Feb. 21, 1939
2,294,895	Drapeau et al.	Sept. 8, 1942
2,483,075	Truesdale	Sept. 27, 1949