Patented Aug. 20, 1935.

2,011,987

UNITED STATES PATENT OFFICE

2,011,987

ZINC ALLOY

Urlyn C. Tainton and Frank W. Harris, Baltimore, Md.; said Harris assignor to said Tainton

No Drawing. Application April 29, 1932, Serial No. 608,348

7 Claims. (Cl. 75—1)

This invention relates to improved materials for the manufacture of metallic foil and similar products. Materials in question consist primarily of zinc of high purity which has been modified by the methods described below so as to render it capable of being cold-rolled into extremely thin sheets, having a brilliant surface even when a number of sheets are superimposed and rolled simultaneously as in the operation known as pack rolling.

Ordinary commercial grades of zinc contain substantial quantities of other metals as impurities. Using methods described in our Patent No. 1,759,493 we were the first to produce commercially zinc of very high purity, 99.99 per centum, or better. Ordinary zinc containing impurities possesses properties quite different from those of pure zinc and it is not suitable for the manufacture of thin foil. Not only is impure zinc less malleable but the impurities segregate and cause pinholes and perforations in the foil when the thickness is reduced to a point comparable with the size of these segregations. For example, zinc containing even small amounts, 0.1 per centum, or more, of cadmium, and lead, shows pinholes when rolled to a foil of a thickness of .0003″ or less. Even pure zinc itself is not well suited to the manufacture of foil especially when pack rolling is used because of its tendency to recrystallize at low temperatures which causes the foil to have a dull or matte surface and also in some cases causes pinholes or perforations of the foil.

For the reasons mentioned above, no considerable commercial use has been made of zinc as a material for the manufacture of metal foil. Practically all of the metal foil now used consists of tin, lead or aluminum. These metals are much more expensive than zinc so that the substitution of zinc in this field would be very advantageous provided that the disabilities mentioned above can be overcome.

The possibility of solving this problem was first brought to our attention by the discovery that certain types of cathode zinc deposits could be made to give extremely bright, thin foil by direct rolling, while the same metal melted and cast into a slab did not give bright foil. After considerable investigation, we traced this condition to the presence in the cathode deposit of occluded colloids which prevented the recrystallization which is characteristic of pure zinc even at room temperature. Further research showed that this result might be obtained even from cast metal by adding to it small quantities of certain elements which brought about the same effect as the occluded colloids. Methods of doing this are described in our co-pending application, "Improvements in metallic foil", Serial No. 531,610, to which this application is to be considered complementary, describing as it does, specific materials having characteristics suitable for the purposes desired.

At the time of the filing of the application above referred to, our knowledge of the subject was largely empirical. Further research has led to a clearer understanding of the principles involved and to the development of specific new materials having properties in many respects better than those mentioned in the former specification. We have found that for the best results in the manufacture of very thin foil, it is desirable that there shall be no segregation of impurities of a size comparable with the thickness of the finished foil. This calls for the use of very high grade metal in the first instance. The elements which are added to this high grade zinc to prevent recrystallization, should be added in amounts not greater than will form a solid solution or perhaps colloidal dispersion with the zinc under the conditions of casting, heating and working that are to be employed. It is also desirable that the modifying element should have certain specific physical characteristics which adapt it for the purpose of preventing recrystallization.

We find that the modifying element should be one having a low atomic volume and a low co-efficient of compressibility. It should also have a space lattice different from that of zinc. These characteristics appear to cause the metal to act as a sort of reinforcement in the zinc metal, resisting the molecular rearrangement which is involved in the recrystallization of cold worked pure zinc at ordinary temperatures.

If a curve be drawn showing the relation of atomic volume to atomic number, it will be found that the elements having atomic numbers 24, 25, 26, 27, 28 and 29 lie very close to the bottom, the atomic volumes being, respectively, 7.7, 7.7, 7.1, 6.8, 6.7 and 7.1 cubic centimeters. The atomic volume of this group averages 7.2 as against the average of all other commercial metals of 14.3. The average co-efficient of compressibility of the group is 0.68×10^{-6} for pressure measured in megabars. The corresponding co-efficient for the other commercial metals is 5.56×10^{-6}.

Of this group, i. e., chromium, manganese, iron, cobalt, nickel and copper, the metals which crystallize with a face-centered cubic space lattice; namely, nickel, copper and manganese, are especially suitable. The other metals of the group crystallize with either the hexagonal close-packed or body-centered cubic lattice form.

As an illustration of the way of carrying this invention into effect, we will describe the preparation of a manganese-zinc alloy suitable for the purpose. High grade zinc of a purity of 99.99 per centum or higher is melted in an appropriate furnace and there is stirred into it a quantity of zinc-manganese alloy previously prepared from pure zinc and pure manganese and containing about 4 per centum manganese. Sufficient of this high manganese alloy is added to the zinc to give a final manganese content of 0.075 per centum. After thorough mixing, the molten metal is poured into moulds and may then be subjected to the preliminary rolling treatment to produce sheets which can be reduced to foil by appropriate cold-rolling treatment.

Instead of manganese, other metals having the above described characteristics may be employed, nickel and copper being particularly effective in certain cases. The amount of metal added should be as small as possible, having regard to the necessity for preventing recrystallization and should be kept below the maximum amount which can be retained in solid solution or colloidal dispersion. Quantities which we have found most effective for our purposes are:

Manganese	up to 0.1%
Nickel	up to 0.1%

In order to obtain a better perspective of this invention and its relation to that of our prior filed application, Serial No. 531,610, we quote therefrom the following:

"This invention relates to metallic foil, and with regard to certain more specific features, to improved methods of producing metallic foil having smooth bright surfaces.

For the purposes of this invention, however, it is desirable that the plastic properties of the zinc metal be retained. It is also desirable to restrain or prevent the recrystallization which occurs in pure zinc even at room temperatures, which itself occasions a matte surface when zinc sheets are rolled in a pack.

We have discovered that certain substances if added to the zinc in proper amount will inhibit this recrystallization property while not substantially decreasing, and in some cases actually increasing, the plastic properties of the metal. It is important that the added substances be not present in such amounts as to produce a hard strong metal, which while useful for ordinary purposes, would be of little utility for the purposes herein considered. For example, any substantial amounts of iron, cadmium or magnesium would be detrimental to the purposes of this invention.

Our researches have shown that the desired effect may be produced by the addition to pure zinc of various elements in carefully graduated amounts. In the case of metals which form a brittle eutectic alloy with zinc, the amount of alloying metal added should be less than is required to form the eutectic. If aluminum be used, for example, the amount added should be less than 5.0%, this representing the corresponding eutectic mixtures. The following metals have been tried and found effective for our purposes:

Antimony in amounts up to 4%.
Copper and aluminum in amounts up to 2%.
Tin and silver in amounts up to 1%.
Mercury in amounts up to .1%.

Various combinations of these metals have proved effective and it is probable that other metals may also be used. On account of the large number of the elements, it is not possible to cover in this specification all of the combinations of zinc with other metals that may be effective." (End of quotation.)

Since the filing of said earlier application, Serial No. 531,610, our work has further developed how high grade zincs effectively respond to alloying with one or more of the following metals; namely, chromium, manganese, iron, cobalt, nickel and copper, in ~~order to~~ produce an alloy having malleable and ductile characteristics of pure zinc but without tendency to recrystallize at low temperatures.

Most of our work has been conducted with zinc having a purity of 99.99 per centum or better, but from the work it is ascertained that the desired effects may be realized by using other high grade zinc; namely, zinc having a purity of 99.93 per centum or better.

As previously indicated in this application, manganese up to 0.1 per centum, or nickel up to 0.1 per centum, when in an alloy containing at least 99.9 per centum of zinc—having a purity of 99.99 per centum or better—produces or ensures an exceedingly effective and desirable alloy. In fact, such an alloy having 0.075 per centum of either manganese or nickel, or a mixture of both, is one that effectively meets the rigid requirements essential to make a bright metal foil by compressive processes employing cold packed rolling of sheets into foil formation. Our work also demonstrates that the percentages or ratios mentioned can be somewhat extended or modified and still realize the desired commercial and practical ends. It is also demonstrated that besides manganese and/or nickel there can be used the other metals mentioned; namely, chromium, iron, cobalt and copper, the latter of which was mentioned in the prior filed application, Serial No. 531,610, as being effective in amounts up to 2 per centum, but in respect to iron it was indicated in said prior application that any substantial amounts thereof would be detrimental to the purposes of the invention thereof. Either one of the six metals just mentioned in this paragraph can be employed, or mixtures of any of said six mentioned metals can be employed, as the alloying metal, or metals, to produce the desired alloy.

When copper is used, a somewhat higher percentage is essential as compared with that for nickel or manganese. With a high percentage of zinc in the alloy, to wit, 99.85 per centum or better, we have ascertained that it is possible to attain the desired end by having the copper alloy content as low as 0.15 per centum or even slightly less. Generally, with copper alone as the alloy a higher percentage thereof is required than for the other metals mentioned. It will be possible to produce the desired alloy with the zinc content of 99.85 per centum or better, and with an alloy metal content of one or more of the metals just mentioned of as high as 0.15 per centum, but in general, with the exception of copper, it is advisable to keep the alloy percentage down, for example, to .075 per centum as in the case of nickel since that per centum in general for most of the metals will suffice to prevent or avoid, and is effective in preventing and avoiding, the tendency of the zinc to recrystallize at low temperatures, probably due to, and we believe due to, the alloying metals being held in solid solution or colloidal dispersion in or by the zinc of the alloy.

As a matter of fact, and as above indicated, some of the metals herein mentioned were investigated prior to our earlier application, Serial No. 531,610, but as herein outlined our subsequent investigations have given us a more intimate knowledge and understanding in respect thereto and in respect to their behavior in the alloying of zinc.

It should be mentioned that the heat treatment of these alloys should be such as will prevent the segregation of the alloying constituents. For example, it is found that if certain of the zinc-nickel alloys are heated for prolonged periods at temperatures around 250° C., the nickel tends to separate in the form of a nickel-zinc constituent along the boundaries of the crystals. Under these conditions, the inhibitory effect on the recrystallization is largely lost. It appears desirable to cool the ingots rather rapidly and not subject them to prolonged or unnecessary heating.

It will be found that the alloys so prepared have the remarkable property of giving a bright foil even when rolled in a pack which ordinarily will yield only dull surfaces on the inside sheets of the pack that do not touch the rolls.

In order to effect this, a slab is cast of an alloy such as the .075% manganese alloy above described. This slab may be, say, two inches thick and of a width similar to what is required in the finished foil. The slab is first rolled at a temperature of, say, 250° C. until the primary crystallization is broken down, after which further reductions may be made in the cold and without annealing. We find that reductions as high as 80 per centum may be made at each pass through the rolls. When the metal gets down to a thickness of, say, 0.01'', a number of sheets may be superimposed and passed through the rolls simultaneously. The rolling of the pack so formed is continued until the thickness of the foil reaches the point desired. It is preferable to arrange the rolling so that the sheets in the pack have a certain degree of movement relative to one another so that the surfaces do not touch always at the same point.

This may be accomplished by separating the sheets of the pack at intervals during the rolling operation or by bending or coiling the pack so that the sheets are made to slide over one another between passes through the rolls. By so doing, a very thin foil may be obtained with a brilliant surface. We have produced metal as thin as .0001'' and although the inside sheets of the pack did not touch the rolls from the time when they were about one hundred times as thick as this, yet the foil was found to have a surface even brighter than if it had been rolled entirely on polished rolls.

We are aware that a considerable amount of work has been done in the field of zinc alloys with the object of preventing what is known as "cold flow", i. e., the tendency of zinc metal to yield slowly under continuous stress. A number of alloys have been developed for this purpose which are claimed to be harder and stiffer than zinc itself, and more or less free from the property of plasticity which, from a structural standpoint where the material has to carry applied loads, is, of course, undesirable. Typical of such alloys is that described in the United States patent of Willis M. Peirce and Edmund A. Anderson, No. 1,832,733, which consists of an alloy of zinc with copper and lithium. Peirce, et al., state that copper alone, if present in solid solution in the zinc, produces only a slight increase in the resistance to the cold flow and his invention requires the addition of another element, in this case lithium, present in an amount greater than its solid solubility with zinc at ordinary temperatures. This second hardening constituent produces a very substantial increase in resistance to cold flow by hindering slip between the crystals.

The object of the present invention is directly opposite to this. It is essential for our purpose that the property of plasticity be retained and the presence of any hardening constituent is deleterious.

For purposes of this invention, it is important that the amount of alloying element should be kept down below the point at which it would tend to make the metal hard and stiff. We find it desirable that the cold-worked alloy should have an elongation under stress of at least 10 per centum. Some of the best alloys we have prepared show an elongation five times as great as this.

Instead of the compressive working and more specifically the rolling of the cast ingot or slabs as called herein into what may be termed sheets that are thereafter cold-rolled into foil, it is feasible and within the purview, scope and defines of this invention to work and reduce the cast ingot by any suitable compressive process and specifically, by rolling, and to cut the resulting rolled material into billets, slabs or the like and to further work the billets or slabs by compressive cold workings and more specifically, by cold-rolling into other forms as bars, sheets and the like, and to cut the same to form a blank of a desired shape to produce a final product, a semi-final product or a blank as the case may be and by further cold compressive operations as herein outlined produce a specific final product or article as by pack-rolling into foil formation or as by any other cold compressive operation typified by way of example as by extruding or drawing to form tubular or other shaped articles.

We find that the alloys described in this invention are well adapted to the production of brilliant metallic pigments or so-called "bronze powders" produced by stamping of the metal into flake or powder form. As the metal is not subject to recrystallization, the powder so produced possesses an unusually high co-efficient of reflectivity.

These alloys are also well adapted for drawing into fine wire for use in the manufacture of brake linings, etc. Their high percentage of elongation under stress makes them unusually well adapted for weaving and similar purposes.

What we claim is:

1. A ductile malleable metal alloy comprising at least 99.85 per centum of elemental zinc in the final alloy and of approximately 0.075 per centum of manganese as the alloying metal.

2. A ductile malleable metal alloy comprising at least 99.85 per centum of elemental zinc in the final alloy and of approximately 0.075 per centum of nickel as the alloying metal.

3. A ductile, malleable metal alloy composed of at least 99.9 per centum of zinc having a purity of 99.99 per centum or better and approximately 0.075 per centum of manganese as the alloying metal.

4. A ductile, malleable metal alloy composed of at least 99.9 per centum of zinc having a purity of 99.99 per centum or better and approximately 0.075 per centum of nickel as the alloying metal.

5. A ductile malleable metal alloy comprising at least 99.85 per centum of zinc and approximately 0.075 per centum of alloying material provided by either manganese or nickel or by both of said alloying metals.

6. A wrought product of ductile malleable metal alloy composed of at least 99.85 per centum of zinc and approximately 0.075 per centum of alloying material provided by manganese and nickel or by either of said alloying metals.

7. A homogeneous ductile malleable metal alloy having the malleable and ductile characteristics of pure zinc but without the tendency to crystallize at low temperatures, said alloy comprising at least 99.85 per centum of zinc that is substantially free from segregated impurities and approximately 0.075 per centum of alloy material that is in solid solution or colloidal dispersion in the zinc and which alloying material is provided by either manganese or nickel or by both, the alloying material at the approximate per centum limit specified being insufficient in amount to exist in the alloy in any form other than in solid solution or colloidal dispersion in the zinc.

URLYN C. TAINTON.
FRANK W. HARRIS.