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# COPPER BASE ALLOY

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2 Claims. (Cl. 75—162)

This invention relates to an improved zinc base alloy and a process for producing such an alloy. More particularly, the invention pertains to an alloy of this type which is characterized by outstanding wear resistance properties due to the presence of hard particles of an iron-titanium-aluminum alloy. The present application is a division of United States patent application Serial No. 520,147, which was filed on July 5, 1955.

Zinc base alloys commercially used today for drawing dies and similar purposes usually possess inadequate wear properties for many requirements. It is therefore a principal object of the present invention to overcome this deficiency by providing a zinc base alloy characterized by greatly increased wear properties, high resistance to fracture, good castability and homogeneity. It is a further object of this invention to provide a drawing die formed of an inexpensive zinc base alloy which possesses high wear resistance, a low melting point and uniform shrinkage.

These and other objects and adavantages are attained in accordance with the present invention with a zinc base alloy containing a small amount of dispersed particles of iron-titanium-aluminum alloy. The iron-titanium- aluminum particles contain hard intermetallic compounds or phases of aluminum-titanium which are primarily responsible for the outstanding wear resistance of the zinc base alloy.

In particular, we have found that a zinc base alloy which contains small amounts of copper and additional aluminum, as well as the aforementioned hard particles, is especially suitable for use as a drawing die. A small amount of magnesium also may be advantageously included in the alloy. In this type of zinc base alloy the aluminum and copper are added to increase the tensile strength and hardness and to reduce the solidification temperature of the alloy. Magnesium is preferably included in the alloy to overcome the corrosive influence of any impurities which may be present in the alloy. It therefore promotes dimensional stability and prevents a decrease in the strength of the alloy on aging. The resultant material is a long-wearing, generally homogeneous alloy having good castability properties.

As disclosed in United States Patent No. 2,720,459 entitled "Highly Wear Resistant Zinc Base Alloy," which issued October 11, 1955, in the name of James C. Holzwarth, the wear resistance of zinc base alloy may be improved by the inclusion of dispersed, hard particles of nickel-titanium in the alloy. However, iron-titanium-alloys do not contain any relatively critical nickel and hence are preferred in the event of a nickel shortage because of a national emergency or for other reasons. Furthermore, the average iron-titanium-aluminum alloy is appreciably less expensive than typical nickel-titanium alloys.

In accordance with the invention, therefore, the aforementioned beneficial properties are obtained to a particularly high degree in a zinc base alloy containing aluminum, copper and magnesium by the inclusion therein



of iron-titanium-aluminum in the form of small particles which are generally uniformly dispersed throughout the zinc base alloy. As hereinafter more fully explained, these particles may be advantageously introduced into the zinc-rich melt in the form of a copper base intermediate alloy.

The low melting point of the zinc base alloy eliminates the need for elaborate equipment in the alloying procedure, only a comparatively simple gas- or oil-fired melting kettle being required. The uniform shrinkage characteristic of this alloy permits the exact size of castings to be predetermined with precision, eliminating the necessity for extensive use of profiling machines. Accordingly, the subject alloy is ideally suited for use as drawing dies since the processing of dies formed of this alloy is comparatively simple, requiring a minimum of equipment and labor. Cost is further reduced by the fact that this alloy can be remelted many times, permitting the material in obsolete dies to be almost entirely recovered.

In addition, the facility with which this type of zinc base alloy can be cast and the diversity of forms into which the molten alloy will flow make it a very desirable material for a variety of purposes. Furthermore, finished castings of this alloy can be produced relatively quickly, making them available for production use within a relatively short time.

The high wear resistance of the final zinc base alloy is due to the presence of the dispersed, hard particles of iron-titanium-aluminum alloy. Hard compounds or phases are known to occur in the binary system of titanium-aluminum, but these hard materials alone are generally unsuitable for inclusion in a cast zinc base alloy since their densities are lower than the density of the zinc-rich melt to which they are added. Particles of titanium-aluminum therefore tend to float to the top of molten zinc base alloys and are of little value in applications where substantial homogeneity of the casting is required. Furthermore, certain of these phasee will decompose or dissolve in molten zinc and lose their identity. However, we have found that these hard titanium-aluminum compounds can be combined with iron and, with proper selection of compositions and alloying methods, the resultant iron-titanium-aluminum alloy can be made to remain in suspension in the molten zinc base alloy as discreet hard particles which provide the final cast alloy with greatly increased wear resistance. These hard particles do not readily float or settle out of the zinc-rich melt since they have a specific gravity which closely approximates that of the zinc-rich melt.

Regardless of the exact chemical composition of the iron-titanium-aluminum particles, their presence in the softer zinc matrix material is responsible for the marked increase in wear resistance, particularly with the type of wear experienced with dies used in drawing and forming operations. Hence the present invention provides an alloy which has proper particle distribution, as well as aptimum particle size, resulting in physical characteristics which satisfy all requirements for an outstanding tool alloy.

Commercially satisfactory results may be obtained in accordance with our invention with a final zinc base alloy containing approximately 1% *to* 3% by weight of hard particles of iron-titanium-aluminum alloy. However, the iron-titanium-aluminum particles may be present in amounts as large as about 4% by weight, and in some instances a noticeable improvement in wear resistance results when these particles constitute as little as about 0.5% of the zinc base alloy. If the alloy contains more than approximately 4% of these particles, the castability of the alloy is impaired and its cost becomes excessive. Hence, a desirable zinc base drawing die alloy which possesses exceptional wear resistance is one con-

sisting essentially of about 2% to 5% aluminum, 0.5% to 5% copper, 1% to 3% hard particles of iron-titanium-aluminum and the balance substantially all zinc. The inclusion of approximately 0.02% to 0.3% magnesium is beneficial to reduce the corrosive tendencies of impurities such as lead, cadmium and tin. It will be understood, of course, that the zinc base alloy also may contain small amounts of silicon and other elements as incidental impurities.

Thus it can be seen that in accordance with our invention a zinc base alloy containing at least approximately 85% zinc has its wear resistance appreciably improved by the presence of the aforementioned hard iron-titanium-aluminum particles. It will be understood, however, that the term "zinc base alloy," as used herein, is intended to encompass those alloys in which zinc is the major constituent and preferably constitutes at least 50% of the alloy.

More specifically, we have obtained oustanding wear characteristics in a cast alloy consisting essentially of 87% to 93% zinc, 3% to 5% aluminum, 2% to 3.5% copper, 0.05% to 0.2% magnesium, and 1% to 3% iron-titanium-aluminum alloy in the form of dispersed hard particles. An alloy consisting of approximately 4% aluminum, 0.15% magnesium, 3.25% copper, 1.5% iron-titanium-aluminum and the balance zinc plus incidental impurities appears to possess optimum castability and wear resistance properties.

Wear resistance, of course, is a function of both the size and distribution of the hard iron-titanium-aluminum particles. Since particle size and distribution are dependent on such factors as metal viscosity, solidification rates and methods of alloying, this invention also provides a preferred procedure for preparing the zinc base alloy. In the case of a drawing die it is desirable to produce maximum wear resistance without causing scoring of the part being drawn. The hard constituent or constituents of aluminum-titanium may be conveniently formed by initially alloying aluminum and titanium and thereafter dissolving this binary alloy in molten iron. Alternatively, the iron-titanium-aluminum alloy may be prepared by melting together the three individual constituents.

Inasmuch as the iron-titanium-aluminum pre-alloy does not readily dissolve in the zinc-rich melt, it is preferred to introduce these hard particles in the form of an intermediate alloy or hardener containing copper. When the iron-titanium-aluminum is added to molten copper, it is substantially transformed into the molten state. During solidification of the intermediate alloy, the solubility of the iron-titanium-aluminum is decreased and is therefore preferentially isolated as a network in the copper-rich matrix. In order to form long-wearing particles of suitable size, this hardener is preferably added to the zinc in the solid state. Since it is desirable to cast the copper base intermediate alloy in shapes which will dissolve most readily in the molten zinc-rich alloy, it is preferred to form castings having a high ratio of surface area to volume, such as flat plates or thin sheets. Generally the formed iron-titanium-aluminum particles have diameters in the order of about 0.001 inch. If the particles are much smaller than this, the wear resistance of the final zinc base alloy is not increased to the desired extent.

Upon introduction of the intermediate alloy to the zinc-rich melt, the copper or copper-rich matrix is dissolved, leaving the relatively insoluble network of iron-titanium-aluminum suspended in the zinc as wear-resistant particles of appropriate size. Agitation of the zinc-rich melt causes these particles to become generally uniformly dispersed through the melt, and the particles remain so dispersed in the solidified zinc base casting.

The desired drawing die alloy composition is preferably obtained by melting substantially pure zinc and, after elevating the temperature of the molten zinc to between about 950° F. and 1075° F., dissolving therein the aluminum to be added except that which is contained in the copper-iron-titanium-aluminum intermediate alloy. This addition of aluminum retards drossing of the zinc at higher temperatures and, if a cast iron melting pot is employed, it inhibits attack of the pot by the zinc-rich melt. After further raising the temperature of the melt to approximately 1100° F. to 1300° F., an appropriate amount of the copper-iron-titanium-aluminum hardening alloy is added in the solid state, as hereinbefore indicated. The elevated temperature should be maintained until the copper-rich matrix in this hardening alloy is dissolved, the solution rate being increased by periodic agitation. After this solution is accomplished, we have found it desirable to lower the temperature of the melt to approximately 900° F. to 950° F. A suitable flux, such as ammonium chloride, may then be added to remove dross from the melt. The magnesium is thereafter introduced, if it is to be included in the alloy, preferably by submerging it in the bath. The final alloy may then be cast to shape in suitable molds.

Although the aluminum not included in the iron-titanium-aluminum alloy can be added either before or after addition of the hardener, the above alloying sequence has been found to be most satisfactory. Alternatively, a portion of this aluminum may be added prior to the introduction of the hardener and the remaining aluminum added after the hardener addition.

As hereinbefore explained, it is desirable that the iron-titanium-alumium alloy have a density which approximates that of the zinc-rich melt in order to prevent flotation or segregation of the iron-titanium-aluminum particles. The density of zinc at its melting point is 6.92 grams per cc., and the addition of about 4% aluminum decreases the density of the resultant alloy to approximately 6.9 grams per cc. Therefore, in order to obtain proper distribution of the iron-titanium-aluminum particles, it is desirable to form these particles of an alloy having a specific gravity of about 6.5 to 7.5 grams per cc. Since the density of iron is 7.87 grams per cc. and the densities of aluminum and titanium are, respectively, 2.7 and 4.54 grams per cc., an iron-titanium-aluminum alloy consisting essentially of 78% iron, 14% titanium and 8% aluminum has been found to provide excellent results. Such an alloy has a calculated density of about 6.96 grams per cc., which is slightly higher than the specific gravity of the aforementioned zinc-rich melt. Based on density requirements, therefore, the iron should constitute about 65% to 90% of the iron-titanium-aluminum alloy. However, there appears to be a tendency for the particles of this alloy to dissolve in the zinc if the iron content is above approximately 85%.

We prefer to have a ratio of titanium to aluminum in the iron-titanium-aluminum alloy of about 1.56 to 1, but an appreciable variation in the relative amounts of these three constituents is permissible. Thus we have found that the wear resistance of a zinc base alloy may be substantially improved with an iron-titanium-aluminum pre-alloy comprising approximately 8% to 16% titanium, 5% to 13% aluminum and the balance iron. Such a pre-alloy produces particles of optimum size and density. In some instances, however, this pre-alloy may contain as little as 4% or as much as 24% titanium, and the aluminum content may vary from about 3% to 23%.

When the iron-titanium-aluminum pre-alloy is mixed with the molten copper, usually at a temperature of 2200° F. to 2700° F., it is preferred to form an intermediate alloy containing approximately 55% to 90% copper. If this alloy has a copper content less than 55%, it is difficult to place the copper-rich matrix of the copper-iron-titanium-aluminum intermediate alloy in solution in the zinc-rich melt. It will be seen from the above figures, therefore, that a copper base alloy comprising about 0.8% to 8% titanium, 0.5% to 6% aluminum, 6.5% to 40% iron and the balance copper is appropriate for use in carrying out the present invention. In order to pro-

vide a zinc base alloy with approximately 0.5% to 4% iron-titanium-aluminum particles, the intermediate alloy may constitute about 1% to 9% of the final alloy, although 3% to 6.5% is preferred. When such an intermediate alloy is added to a zinc-rich melt, it introduces into the final alloy approximately 0.4% to 3% iron, 0.06% to 0.6% titanium and 0.04% to 0.4% aluminum in the form iron-titanium-aluminum particles and about 0.5% to 5% copper which is not combined with these particles.

Since the hard particles result principally from the combination of aluminum and titanium and are formed during the preparation of the prealloy, the alloying procedue employe in forming the hardener is of considerable importance in achieving optimum results. Accordingly, the iron-titanium-aluminum pre-alloy may be compounded by melting together a metallurgical alloy of aluminum-titanium with the proper amount of iron, preferably at a temperature of approximately 2900° F. to 3100° F. Inasmuch as titanium is a readily oxidizable and nitridable element, it is desirable to use an insert gas as the melting atmosphere. We have otained most satisfactory melting and high titanium recovery using an induction furance under an argon atmosphere.

It has been found convenient to initially form a titanium-aluminum alloy by preparing a charge of the desired percentages of titanium sponge and aluminum pig, such as commercially available 2S aluminum. The intermediate alloy may also contain small amounts of other metals, such as manganese, silicon, chromium, magnesium and nickel. Normally the maximum quantity of these metals would not exceed approximately 6% manganese, 2% silicon, 1% chromium, 1% magnesium and 0.5% nickel. These percentages of the minor constituents are not critical in most instances, however, and are listed as examples only.

The titanium and aluminum are preferably placed in a magnesium oxide crucible, covered, and heated to a temperature between approximately 2700° F. and 2950° F., preferably under an inert gas atmosphere. The formed titanium-aluminum alloy, which solidifies at about 2400° F., may be poured from the crucible while the temperature of the alloy is between 2500° F. and 2700° F. The metal preferably is cast as pigs in chilled molds. As hereinbefore indicated, a titanium-aluminum alloy containing approximately 35% to 70% titanium and 30% to 65% aluminum appears to provide highly satisfactory results.

When the aforementioned percentages of aluminum and titanium are employed in the ferrous base pre-alloy, intermetallic compounds, such as TiAl and $TiAl_3$ are formed and combine with the iron as a hard ternary compound or compounds. These compounds are principally responsible for the substantial improvement in the wear resistance of the final zinc base alloy. Of course, commercial titanium-aluminum of the proper composition may be used rather than first preparing this alloy from titanium sponge and 2S aluminum, as described above.

It will be noted that it is necessary to form particles of iron-titanium-aluminum in order to obtain high wear and score resistance in accordance with the invention. Merely adding the iron, titanium and aluminum separately to the zinc-rich melt, even if these constituents are introduced in the aforementioned preferred proportions, does not form these hard particles or provide the necessary wear resistance. It is the alloy of iron, titanium and aluminum, rather than the individual elements, which contributes the desirable properties of wear and score resistance to the final zinc base alloy.

Wear tests were conducted to compare zinc base alloys formed in accordance with our invention with the same material devoid of iron-titanium-aluminum particles. Samples 1⅛ inch wide and ⅝ inch high were prepared from the cast zinc base alloys to be tested, and each specimen was machined at one edge to prepare a ⅛ inch by 1⅛ inch rubbing surface. The specimens were next successively locked in a fixture of a wear test machine and placed in contact with a rotating smooth-surfaced wheel of low carbon steel having a face width of one inch. Increased wear resistance was measured by decreased weight loss in grams.

A wear test using this apparatus was conducted in which the specimen load was increased during a five hour period from zero load and automatically adjusted to produce a constant frictional load rather than a constant load normal to the wheel. This test included a ten minute run-in period in which only the weight of the specimen being tested and its holder bore against the wheel, a period of 1¾ hours to load the specimen to 500 pounds, a 30 minute period at 500 pounds to establish the frictional characteristics, and the balance of the five hours run with the established value of friction maintained constant. After each test any loosely adhering, deformed metal and burrs were removed from the wear test sample, and loss in weight values were used in comparing the wear resistance of the specimens.

At the end of the test period the zinc base alloy specimens formed from a zinc base alloy consisting essentially of 3.25% copper, 4% aluminum, 0.1% magnesium and the balance zinc showed an average weight loss of 0.4764 gram. On the other hand, a zinc base die alloy specimen of similar composition but containing the aforementioned preferred amounts of the iron-titanium-aluminum particles lost an average of only approximately 0.0335 gram. The results of this test show how greatly the presence of dispersed particles of the hard iron-titanium-aluminum alloy increases the wear resistance of zinc base alloys.

Although the final alloy formed has been described as particularly suitable as a drawing die material, it also may be employed to considerable advantages in other applications in which high wear resistance, good castability, uniformity of properties throughout a cast section, good machinability, and anti-score properties are of importance.

While we have set forth herein specific examples of zinc base alloys possessing high wear resistance characteristics due to the presence of hard particles of iron-titanium-aluminum, it is not intended to restrict the invention to any specific zinc base alloy. We believe that we are the first to discover the value of adding these particles to zinc base alloys generally, and the invention is not to be restricted except as defined in the following claims.

We claim:

1. A copper base alloy comprising approximately 6.5% to 40% iron, 0.8% to 8% titanium, 0.5% to 6% aluminum and the balance substantially all copper.

2. A copper base alloy comprising about 55% to 90% copper, 6.5% to 40% iron, 0.8% to 8% titanium and 0.5% to 6% aluminum, a substantial proportion of said iron, titanium and aluminum being present in the form of a hard network of at least one iron-titanium-aluminum ternary compound in a copper-rich matrix of said alloy.

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# CERTIFICATE OF CORRECTION

Patent No. 2,907,653 October 6, 1959

James C. Holzwarth et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 51, after "zinc" insert -- base --; line 57, for "aptimum" read -- optimum --; column 5, line 14, for "due employe" read -- dure employed --; line 23, for "furance" read -- furnace --.

Signed and sealed this 28th day of June 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents