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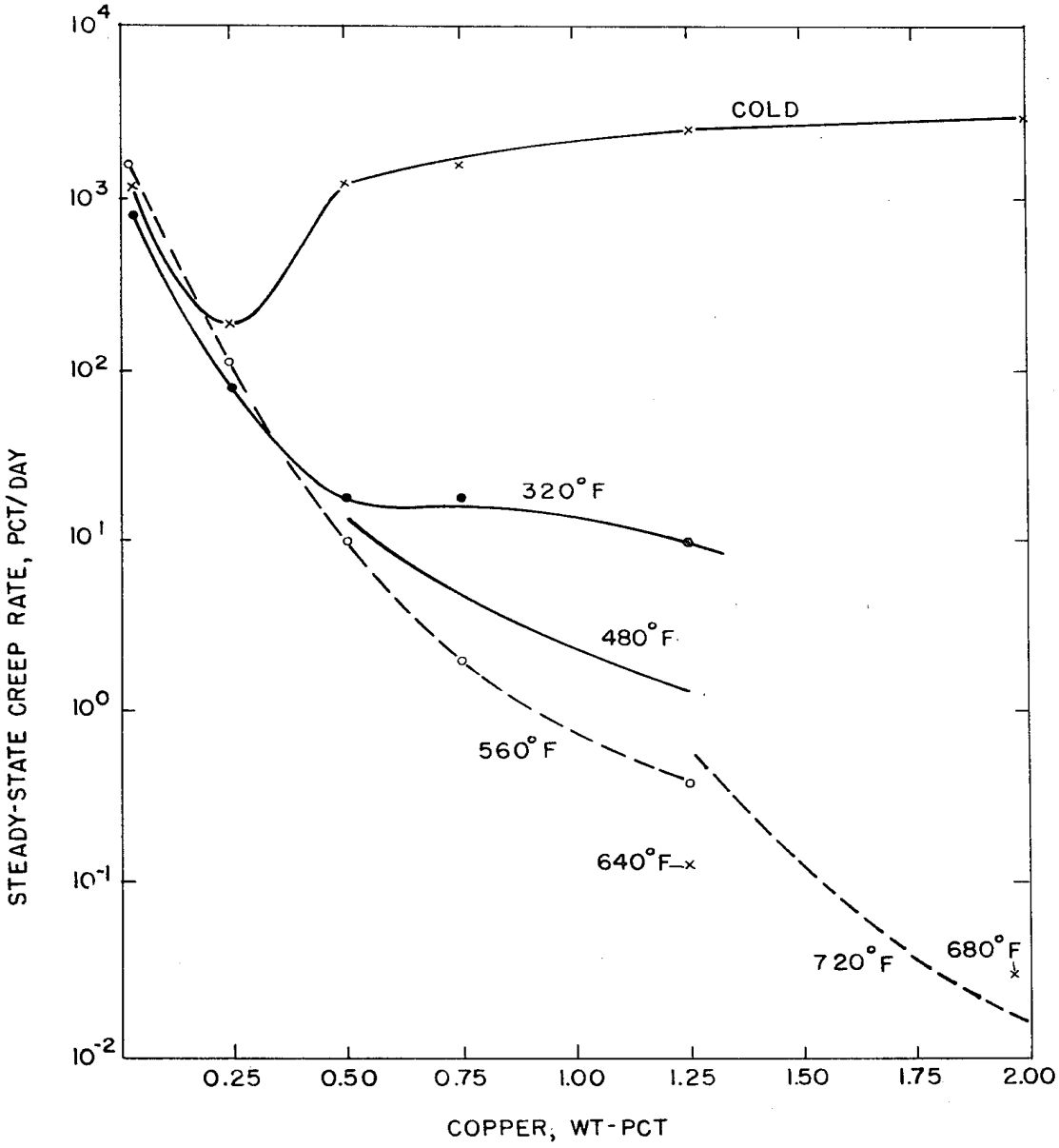

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PROCESS FOR IMPROVING CREEP RESISTANCE OF ZINC-COPPER ALLOYS

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ABSTRACT OF THE DISCLOSURE

Creep resistance of binary zinc-copper alloys containing up to about 2 weight percent copper is substantially increased by working the alloys within a temperature range correlated with copper content so as to control the degree to which copper is retained by the zinc matrix while simultaneously controlling the form and amount of zinc-copper ϵ-phase precipitated at grain boundaries.

BACKGROUND OF THE INVENTION

A major factor limiting the industrial application of wrought zinc alloys lies in their characteristically low creep resistance under sustained loads. Wrought zinc alloys often possess properties favorable, or highly desirable for a given application but are not selected because of a lack of adequate creep resistance or an uncertainty as to their creep behavior. Generally, the properties of wrought zinc alloys are extremely sensitive to their prior history as well as to their composition and minor impurities. Some factors recognized as strongly influencing the properties of rolled sheet and strip of given alloys include the type of starting ingot, rolling temperature, reduction per pass, total reduction, intermediate anneals and anneals subsequent to rolling.

Simple, essentially binary zinc alloys, such as those containing a small amount of copper, are greatly superior in most mechanical properties to unalloyed zinc. Typical of such commercially available alloys are Zilloy-40 and Zilloy-15. Both alloys are produced in sheet or strip form and are recommended for drawn or mildly formed parts requiring stiffness. However, these alloys deform under heavy continuous loads, especially at somewhat elevated temperatures.

Alloys with substantially better creep resistance than binary zinc-copper alloys are available. One such alloy is disclosed in U.S. Pat. No. 2,317,179. Alloys disclosed in that patent contain 2 to 3% copper plus high melting metals such as titanium, zirconium, chromium, vanadium and tungsten, singly or in combination in amounts ranging from 0.02 to 0.5%. Another such alloy is disclosed in U.S. Pat. No. 2,472,402. Alloys disclosed in this patent comprise zinc with up to 2% copper plus up to 0.5% titanium. Again substantially improved creep resistances as compared to simple binary alloys are displayed by those compositions.

While these known tertiary alloys do provide superior creep resistance when properly processed, they do require the addition of a refractory metal. Binary zinc-copper alloys of improved creep resistance provide a bridge

or continuum of properties between the known binary and tertiary zinc base alloys.

SUMMARY OF THE INVENTION

It has now been found that major improvements in creep resistance can be imparted to simple binary zinc-copper alloys containing up to about 2 weight-percent copper.

By controlling the degree to which copper is retained by the zinc matrix while simultaneously controlling the form and amount of Zn-Cu epsilon (ϵ) phase precipitated at grain boundaries, creep resistance of these alloys is improved by a factor of 10 or more. Maximum creep resistance is obtained by adjusting the forming or working temperature within a closely controlled range relative to the copper content of the alloy. Specifically, forming or working temperatures must be high enough to dissolve all copper within the zinc during working. Normal air cooling after working then permits precipitation of adequate amounts of finely divided ϵ-phase at available grain boundaries. The retained copper strengthens the matrix and the fine ϵ-phase precipitate retards grain boundary deformation during creep.

Hence, it is an object of this invention to improve the creep resistance of binary zinc-copper alloys.

It is a specific object of this invention to provide a process for substantially increasing the creep resistance of wrought zinc alloys containing up to about 2% copper.

DETAILED DESCRIPTION OF THE INVENTION

The invention will be more clearly understood by reference to the accompanying drawing in which:

The figure is a graphical presentation of experimental data showing the relationship of creep resistance, working temperature and alloy composition for the sheet dimension in the direction of rolling.

In zinc-copper alloys, creep occurs as a result of several different mechanisms. Grain boundary sliding can occur during stressing of zinc and zinc-copper bicrystals, and evidence exists that this is also an important creep mechanism for polycrystalline zinc-copper alloys. Boundary sliding and slip within grains is related to the ability of grains to transmit dislocations, which is inhibited by the copper in matrix solution.

Heavily cold-worked, zinc-copper alloys generally display a much finer grain structure then do hot-worked alloys. Depending upon composition, cold working to 25–50% reduction initiates recrystallization to fine grain sizes. Fine-grained structures contain many more grain boundaries for sliding but this is not the only cause of higher creep rates (lower creep resistance). In cold worked alloys, no significant amount of fine ϵ-phase precipitates at grain boundaries but rather it occurs as globular masses developed with recrystallization during the cold working. Further, the extensive precipitation of globular ϵ-phase does not permit retention of adequate amounts of copper in the matrix phase to effectively retard the passage of dislocations through individual grains. In comparison, the coarser grained hot rolled alloys with many fewer grain boundaries permit adequate distribution of fine ϵ-phase in the available boundaries without excessive depletion of copper from the matrix. In order to simultaneously achieve both desired results; precipitation of fine grained ϵ-phase at crystal boundaries and re-

tention of copper within the zinc matrix, it is necessary to observe the following temperature-composition relationship while working the alloys:

Alloy composition:	Working temperature, °F.
Zn-0.50% Cu	400–560
Zn-.75% Cu	480–560
Zn-1.0% Cu	520–600
Zn-1.5% Cu	600–680
Zn-2.0% Cu	640–720

Temperatures lower than those listed allow precipitation of ϵ-phase to occur at globular masses resulting in depletion of copper from the zinc matrix. Temperatures above those listed for each composition lead to deteriorating creep resistances. At compositions above about 2% Cu, excessive amounts of massive ϵ-phase either do not enter solution or precipitate in a coarse form and no significant improvement in alloy properties is obtained. Working temperature has no significant influence on mechancial properties of alloy compositions containing less than about 0.3–.5% copper.

In the case of rolled sheet, it has been found that creep resistance continues to improve when total rolling reductions are increased to 90% or more from the thickness after initial breakdown hot-rolling, ideally in the range 400° to 560° F. Creep properties of hot-rolled alloys are not enhanced by annealing subsequent to rolling. In fact, annealing after hot working can be detrimental to the creep resistance of these alloys.

Use of this process results in significantly increased creep resistance of zinc alloys containing from about 0.5 to about 2.0% copper. The degree of improvement increases generally as copper content increases and the process is most useful within the general range of about 1.0 to about 2.0 weight percent copper. Lowest creep rates are obtained in alloys containing about 1.5 to 2.0% copper worked in a temperature range of about 600 to 720° F. and allowed to air cool. No significant improvement in properties is obtained at copper contents above about 2.0%. If copper content is increased substantially above 2.0%, excessive amounts of massive ϵ-phase form and properties of the alloys deteriorate.

The following examples are presented to more fully illustrate and point out the novel aspects of this invention.

Example 1

A series of zinc-copper alloys were prepared having copper contents (by weight) ranging from 0.25 to 2.0%. The alloys were cast using a semicontinuous technique described in U.S. Bureau of Mines Report of Investigations 7089 (March 1968). Special high grade zinc (ASTM designation B6–58) and 99.9% electrolytic copper were used. Ingots produced were 8 in. wide by 1 in. thick and were scalped to 0.9 in.

Ingots of each alloy composition were broken down by rolling to 0.3 in. thick at 400° F. followed by an anneal at 400° F. and air cooling. The 0.3 in. sheet was then used as the starting material for rolling to 0.025 in. (92% reduction) at room temperature and at a series of elevated temperatures. Rolling was in one direction only and the sheets were turned over for successive passes. In the hot-rolling runs, the sheets were preheated for 1 hour, reheated for 20 minutes between passes and air cooled after the final pass. Reduction per pass was about 20%. The rolls were lubricated with lard oil at sheet thicknesses below 0.1 in.

Specimens for use in performing creep tests were sectioned from the 0.025 in. sheet in both longitudinal (parallel) and transverse orientations relative to the rolling direction and in the plane of the sheet. Creep tests were performed under a constant load of 12,000 p.s.i. at a temperature of 90° F. Duplicate tests were performed in many instances and the majority of tests were continued to failure.

Results of those creep tests on longitudinal specimens are presented graphically in the figure. In all cases, the temperature indicated is the temperature of the preheated or reheated sheet; not the final temperature after rolling passes. As may be seen from the plot, working temperature has little effect on creep rate until copper content of the alloys reaches 0.3 to 0.5%. Above this level of copper content, working temperature becomes increasingly more important. If the working temperature exceeds the maximum of the range previously listed, creep resistance decreases and surface quality of the sheet deteriorates. This result is illustrated in the date presented for the Zn-1.25% Cu alloy. In all cases, creep rates tested in the transverse direction were somewhat lower than those in the longitudinal direction.

Comparative data on the creep rates of commercial zinc-copper alloys are sparse. However, one comparison may be made. Zilloy-40 is a rolled zinc alloy having a composition as follows: Cu, 0.85 to 1.25%; Pb, 0.10 max.; Fe, 0.012 max.; Sn, 0.0001 max.; Al, 0.001 max.; Cd, 0.005 max.; Zn, remainder. Data given in the ASM Metals Handbook (vol. 1, 8th ed., 1961, page 1172) concerning the creep behavior of 0.024 in. thick rolled sheet of Zilloy-40 is as follows: Creep rate of cold-rolled strip at 12,000 p.s.i. 77° F., tested longitudinal to the rolling direction was 3.7% per day. Creep rates for hot-rolled strip at the same conditions was given as 6.7% per day. These values were converted from inverse rates in day/percent in order to express the data in the same form.

Example 2

Microstructures of number of different alloy compositions, worked both at room and at elevated temperatures, were examined. When more than about 0.5% copper was present, microstructures of the cold-worked alloys were significantly finer grained than were those rolled at elevated temperatures. Matrix grain sizes in the cold-rolled alloys became progressively finer as copper content increased. Globular concentrations of ϵ-phase were present in the cold-rolled alloys as well as in alloys containing above about 0.75% Cu and rolled at moderate temperatures.

Microstructure of the alloys rolled to 92% reduction at 320° F. and above appeared quite different from the cold-rolled structures with the most striking feature being the much larger matrix grain sizes. For a given composition, increased rolling temperature resulted in increased grain size and decreased amount of ϵ-phase. For a given working temperature, increased copper content resulted in decreased grain size and increased ϵ-phase. Microscopic examination also showed that grain boundary regions provided the preferred sites for precipitation of fine ϵ-phase in the alloys rolled at the higher temperatures. It is believed that this fine ϵ-phase precipitated mainly during cooling after completion of the hot working.

By working zinc-copper alloys in the manner taught, creep resistance can be substantially improved thus making possible their successful use in applications where they have previously been found unsatisfactory. While the working technique is particularly applicable to rolling, other mechanical working techniques may be used with similar improvement in creep resistance.

What is claimed is:

1. A method for enhancing the creep resistance of binary zinc-copper alloy sheet containing from about 0.5 to about 2 weight percent copper which comprises working the alloy by rolling to a reduction of at least about 90% at a temperature sufficiently high to allow dissolution of all copper within the zinc matrix, followed by air cooling to precipitate finely divided zinc-copper ϵ-phase at grain boundaries and to retain copper within the zinc matrix.

2. The method of claim 1 wherein the alloy contains from about 1.5 to about 2.0% copper and wherein the rolling temperature is in the range of 600 to 720° F.

3. The method of claim 1 wherein the alloy contains about 0.5% copper and wherein the rolling temperature is in the range of 400 to 560° F.

4. The method of claim 1 wherein the alloy contains about 0.75% copper and wherein the rolling temperature is in the range of 480 to 560° F.

5. The method of claim 1 wherein the alloy contains about 1.0% copper and wherein the rolling temperature is in the range of 520 to 600° F.

6. The method of claim 1 wherein the alloy contains about 1.25% copper and wherein the rolling temperature is in the range of 560 to 640° F.

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