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METHOD OF IMPROVING CREEP-RESISTANCE OF ALLOYS

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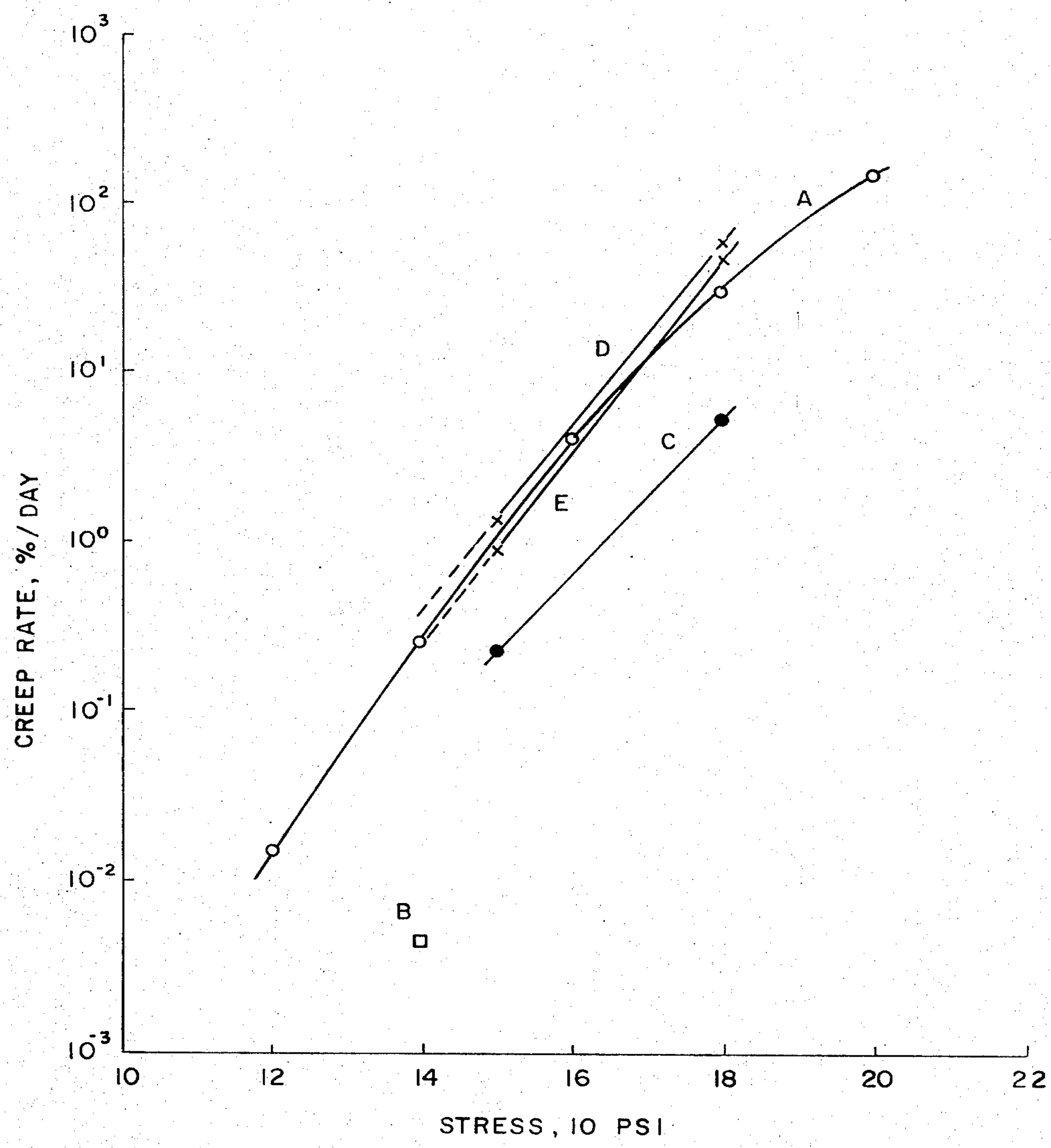

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# METHOD OF IMPROVING CREEP-RESISTANCE OF ALLOYS

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U.S. Cl. 148—11.5 R 7 Claims

## ABSTRACT OF THE DISCLOSURE

Zn-Cu-Ti alloys of improved creep-resistance and low creep anisotropy are prepared by cold-rolling to at least least 67 percent total reduction, followed by annealing preferably at about 300 to 400° F. for a period of about ½ hr. to 8 hrs. Such alloys find utility in a variety of applications such as architectural structures, appliances, automobile parts, etc.

Zinc-copper-titanium alloys having relatively high creep resistance are well known and are useful in a variety of applications, such as architectural structures, hardware, automotive parts, electrical equipment, etc. Such alloys containing less than 2 weight-percent copper, or more precisely 0.5 to 1.5 percent copper and 0.12 to 0.5 percent titanium, are disclosed in U.S. Pat. 2,472,402. The alloy materials of this patent are prepared by rolling the alloy, with or without subsequent annealing.

According to the teachings of said patent, greatest creep resistance in the rolled sheet, or highest inverse creep rate, is obtained by hot-rolling. Cold-rolling, i.e., rolling without application of external heating to either the alloy sheet or the rolls, to a maximum reduction of 50 percent is also disclosed. This treatment is said to result in a decrease in creep resistance, with original creep resistance, that of hot-rolled sheet, being substantially restored by subsequent annealing.

Applicants, however, have found, according to the process of the invention, that cold-rolling the alloy to a reduction of at least about 67 percent, and preferably to reductions of 90 percent or more, followed by annealing preferably at a temperature of about 300 to 400° F., results in alloy sheet having creep resistance substantially greater than that of either hot-rolled alloys, or alloys annealed after cold-rolling up to 50 percent total reduction. In addition, the alloy sheet prepared according to the process of the invention is characterized by low anisotropy in creep rates between the L direction (the direction parallel to the rolling direction and within the sheet plane) and the T direction (the direction perpendicular to the rolling direction and within the sheet plane). In orther words, the difference in creep rate between the L and T directions is much smaller than can be normally obtained. This is obviously a highly desirable characteristic where high creep resistance is required in all directions within the sheet plane when in use, e.g., in architectural, automotive and appliance applications.

The theory underlying the improved creep resistance and anisotropy in L and T directions is believed to be as follows:



When the alloys are finish rolled to more than 67 percent total cold reduction, the matrix continues to move toward completion of a special type of recrystallization to very fine, equi-axed grains with little if any grain growth. This recrystallization starts at less than 33 percent total cold reduction but is not well developed throughout the matrix until cold reduction is 67 percent or more. The recrystallization, which softens the matrix significantly (strain softening), is accompanied by precipitation from solid solution of small globular particles of Zn-Cu epsilon-phase. Tensile and creep strengths become low and ductility high, while anisotropy in tensile and creep strengths between L and T sheet directions becomes low. The small matrix grains remain well within the confines of the fiber layers of rolled-out $TiZn_{15}$ eutectic phase. In contrast to the matrix-soluble Cu addition, the relatively insoluble Ti affects properties mainly by formation of dispersed $TiZn_{15}$ compounds. The matrix basal-plane population aligned toward directions within the sheet plane is substantially greater in cold-rolled Zn-Cu-Ti alloys than in the hot-rolled alloys, and there is less difference between L and T directions. Compared with hot-rolled sheet, the basal-plane population within the plane of the cold-rolled sheet is relatively unaffected by the annealing. Upon annealing the heavily cold-rolled Zn-Cu-Ti alloys, the small matrix grains grow, but tend to remain anchored within the fiber layers of $TiZn_{15}$ when the annealing temperature is not too high. The hot-rolled alloys have basal planes tilted more toward the sheet normal, which provides more opportunity for the matrix grains to grow through the fiber layers upon annealing, because zinc crystallites tend to grow by extension along existing basal planes. Because creep involves grain boundary deformation, creep resistance is improved when grain boundaries are anchored, such as they are by the $TiZn_{15}$ layers when the heavily cold-rolled alloys are annealed properly. The anchoring of grain boundaries by $TiZn_{15}$ is particularly important because fine epsilon-phase does not tend to precipitate at grain boundaries of Zn-Cu-Ti alloys when they are heated and cooled, as it does, e.g., in Zn-Cu alloys. Annealing also tends to re-solubilize the dispersed globules of Zn-Cu epsilon-phase that precipitates during heavy cold-working, helping reharden the matrix. The solubility of Cu in the $TiZn_{15}$ phase, and another Zn-Ti-Cu phase identified in some alloys with more than about 0.3 percent Ti, influences the amount of Cu available for the matrix strengthening. The response to annealing of the unique structure of heavily cold-rolled Zn-Cu-Ti alloys requiring no additions other than Cu and Ti, thereby permits the attaining of the particular desirable combination of properties, which are better than reported previously for either as-rolled Zn-Cu-Ti alloys or for rolled-and-annealed Zn-Cu-Ti alloys.

Alloy sheet prepared according to the process of the invention also exhibits low thermal expansion and low anisotropy of thermal expansion, this being of particular importance in applications such as roofing where uneven expansion in different sheet directions can cause buckling when ambient temperatures change substantially.

The products of the invention are also characterized by low tensile strength anisotropy when in the heavily cold-rolled condition before annealing, and, in addition, the weak and ductile condition of the alloy sheet when heavily cold-rolled facilitates deformation, when desired, between cold-rolling and annealing.

The compositional range of the alloys of the invention is not novel and, although specific amounts or ratios of copper and titanium may provide optimum properties for a particular use, the composition of the alloys does not constitute the essence of the invention. The alloys will contain from about 0.25 to 1.3 percent by weight of copper, about 0.1 to 0.4 percent by weight of titanium, with the remainder consisting essentially of zinc, with no other additions essential, and are prepared by conventional means such as addition of copper and titanium master alloys to a bath of molten zinc, as described in the above-mentioned U.S. patent.

The cold-rolling step of the process of the invention is conventional, except for the degree of reduction, and can be performed with conventional rolling mills. Annealing procedures are also conventional and may consist of heat-



creep rates, as do the units, e.g., whether expressed as percent/day or as inverse rates of days/percent.

Table 1 shows creep data for several Zn-Cu-Ti alloys that were finish rolled hot to 92 percent total reduction at 480° F. (final thickness nominally 0.025-inch) and annealed variously. For comparison with the alloys cold-rolled, these alloys had been rolled at 480° F. (the furnace soaking temperature). Annealing of these alloys containing 0.12 percent Ti improved the T creep rates to a greater extent than the L rates, thereby increasing the anisotropy in creep rates between the L and T sheet directions. When annealing at 480° F., L rates can become more than 10,000 times faster than T rates. Increasing the Ti to as much as 0.36 percent retarded this tendency toward high anisotropy in creep rates, but not nearly to the extent possible when annealing the heavily cold-rolled alloys, as illustrated in the following examples.

TABLE 1

Creep data for alloys finish rolled at 480° F. to 92 percent total reduction (0.025 in.) and annealed

| Examples | Composition, percent | | Orientation | Creep rate, percent/day | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | As-rolled at 480° | Annealing temperature and time | | | | | | |
| | | | | | 320° F. | | 400° F. | | 480° F. | | 560° F. |
| | Cu | Ti | | | ½ hr. | 8 hrs. | 2 hrs. | 8 hrs. | ½ hr. | 8 hrs. | 1/16 hr. |
| 1 | 0.25 | 0.12 | L | 13.0 | 7.7 | 3.6 | 6.0 | 8.4 | 22.0 | 30.0 | 40.0 |
| | 0.25 | 0.12 | T | .061 | .012 | .0034 | .0032 | .0034 | .0046 | .0043 | .0082 |
| 2 | .75 | .12 | L | .25 | .16 | .15 | .081 | .097 | 6.5 | 9.4 | 5.9 |
| | .75 | .12 | T | .016 | .0043 | .0028 | .0018 | .0017 | .00092 | .0016 | .00062 |
| 3 | 1.25 | .12 | L | .090 | .13 | .12 | .058 | .081 | 1.4 | 13.0 | 11.0 |
| | 1.25 | .12 | T | .026 | .015 | .0095 | .0031 | .0031 | .00085 | .00075 | .00032 |
| 4 | 1.00 | .36 | L | .15 | .026 | .011 | | .0084 | | | |
| | 1.00 | .36 | T | .0083 | .0024 | .0012 | | .00089 | | | |

ing in air at the required temperature, or the annealing may be accomplished in a suitable liquid bath such as an oil bath. Temperatures somewhat below 300° F. or above 400° F. may be satisfactory; however, too low a temperature will generally not result in optimum properties of creep resistance, at least in reasonable periods, while temperatures substantially above 400° F. may result in increased creep anisotropy in short periods.

The following examples will serve to more particularly illustrate the invention.

## EXAMPLES

The alloys described in these examples were made from special high grade zinc and relatively pure Zn-Cu and Zn-Ti hardener alloys. They were cast into ingots in a semicontinuous casting machine. Scalped slabs were broken down from 0.9 to 0.3-inch at about 400° F. and were finish rolled on unheated rolls. The finish rolling was started at the 0.3-inch thickness, except for the 0.010-inch final sheet thickness for which finish rolling cold was started at a 0.12-inch thickness. Rolling was in one direction only at a nominal speed of 156 ft./min. Reduction was at about 20 percent per pass during finish rolling. For finish rolling at 480° F., the sheet was reheated between passes.

After rolling, the sheet was annealed in air within 8° F. of the specified temperature for varied periods and was air cooled after removing from the furnace.

The creep rates were determined at a temperature of 90°±3° F., employing a dead-load 14,000 p.s.i. stress, and results are given in percent/day. It should be noted that both stress and test temperature can markedly influence

The contrast in the annealing behavior for the cold-rolled Zn-Cu-Ti alloys is illustrated in Table 2. Before annealing variously, these alloys were finish rolled cold to the same 92 percent total reduction and the same thickness, 0.025 inch. As-rolled cold, the creep resistance is very poor, but there are relatively small differences in creep rates between the L and T directions. This low creep anisotropy is maintained until the annealing temperature is raised above 400° F. Annealing at 320° or 400° F. produced excellent creep resistance for both L and T directions. Best results generally occur for annealing near 400° F. because of the relative insensitivity of the rates to annealing time at 400° F. Increasing annealing times below 400° F. can produce equivalent results. Shorter times above 400° F. can give good results, but annealing much above 400° F. is not recommended because of the danger of over-annealing, with loss in creep strength and increase in anisotropy. This is particularly true for thicker sections such as coils where heat cannot distribute evenly in short periods.

For the cold-rolled alloys with 0.12 percent Ti, the 0.75 percent Cu addition produced upon annealing better results than 0.25 percent Cu, although the Zn-0.25 Cu-0.12 Ti alloy had much better creep resistance after annealing than did the four alloys in Table 1 that were as-rolled at 480° F. The properties of the cold-rolled and annealed Zn-1.25 Cu-0.12 Ti alloy (Table 2) were not nearly as good as for the alloys with 0.25 or 0.75 percent Cu. The better results for alloys with about 0.12 percent Ti occur when the Cu addition is between about 0.6 and 1.0 percent. All the cold-rolled Zn-Cu-Ti alloys with more than 0.12 percent Ti responded very well to annealing.

 

TABLE 2

Creep data for alloys finish rolled cold to 92 percent total reduction (0.025 in.) and annealed

| | Composition, percent | | | | Creep rate, percent/day | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Annealing temperature and time | | | | | | | |
| | | | | As-rolled | 320° F. | | 400° F. | | | 480° F. | | 560° F. |
| Examples | Cu | Ti | Orientation | cold | ½ hr. | 8 hrs. | ½ hr. | 2 hrs. | 8 hrs. | ½ hr. | 8 hrs. | 1/16 hr. |
| 5 | 0.25 | 0.12 | L | 4.9 | 0.052 | 0.0093 | 0.011 | 0.021 | 0.018 | 0.049 | 0.13 | 0.10 |
| | .25 | 0.12 | T | .39 | .0025 | .00084 | .0014 | .00087 | .0012 | .0015 | .0023 | .0015 |
| 6 | .75 | .12 | L | 83 | .17 | .0075 | .0055 | .0048 | .0058 | .0095 | 4.9 | .022 |
| | .75 | .12 | T | 98 | .081 | .0022 | .0020 | .0017 | .0020 | .0016 | .029 | .0016 |
| 7 | 1.25 | .12 | L | 700 | 43 | .084 | .21 | .26 | .46 | 8.2 | 44 | 23 |
| | 1.25 | .12 | T | 310 | 17 | .089 | .14 | .028 | .12 | .18 | 14 | 4.2 |
| 8 | .75 | .24 | L | 220 | | | | | .0033 | | | |
| | .75 | .24 | T | 970 | | | | | .00060 | | | |
| 9 | 1.00 | .24 | L | 290 | | | | | .0022 | | | |
| | 1.00 | .24 | T | 1,200 | | | | | .00055 | | | |
| 10 | 1.25 | .24 | L | 920 | | | | | .0021 | | | |
| | 1.25 | .24 | T | 1,900 | | | | | .00076 | | | |
| 11 | .75 | .30 | L | 560 | | | | | .0018 | | | |
| | .75 | .30 | T | 940 | | | | | .00063 | | | |
| 12 | 1.00 | .30 | L | 96 | | | | | .0020 | | | |
| | 1.00 | .30 | T | 570 | | | | | .00066 | | | |
| 13 | 1.25 | .30 | L | 99 | | | | | .0012 | | | |
| | 1.25 | .30 | T | 770 | | | | | .00058 | | | |
| 14 | 1.00 | .36 | L | 22 | 0.031 | 0.00096 | | | .0030 | | | |
| | 1.00 | .36 | T | 18 | .024 | .0016 | | | .0011 | | | |

In Example 15 in Table 3 are shown data for a Zn-0.75 Cu-0.12 Ti alloy that was also finish rolled to 92 percent total cold reduction, but to a final thickness of 0.010-inch. In Example 17 are data for a T-specimen of the alloy finish rolled to 67 percent total cold reduction (0.10-inch) before annealing. The results reveal the same general behavior as for the final thickness of 0.025-inch representing 92 percent total cold reduction (Example 16); the beneficial creep resistance can be obtained for sheet of different final thicknesses, so long as the total cold reduction during finish rolling is taken to at least about 67 percent before annealing.

In Table 4 are listed ratios of creep rates, longitudinal-to-transverse, for cold-rolled and annealed Zn-Cu-Ti alloys (0.025-inch thick). Each of the alloys listed had L creep rates of 0.008 percent day or less. Most ratios are less than 3, signifying very low anisotropy in creep rates between L and T directions, considering that L and T creep rates for rolled Zn-CuTi alloys can differ by orders of magnitude. For the annealing at 400° F., the alloys with 0.24 or 0.30 percent Ti exhibit lower ratios when Cu is increased to 1.25 percent, but all are low. The Zn-1.00 Cu-0.36 Ti alloy actually had a ratio of less than 1, revealing the quite unusual behavior for a rolled zinc alloy that was not cross-rolled, in that the L direction displayed better creep resistance than the T direction.

This unusual behavior also occurred for a number of other alloys when as-rolled to 92 percent total cold reduction (Table 2). After annealing for 8 hours at 400° F., the strengthened sheet displayed the opposite, usual behavior in which T specimens were more creep resistant than L specimens. In view of this reversal in behavior during annealing, it can be anticipated that, at some lower annealing temperature or shorter time, creep rates could be adjusted to where L and T rates are about equal.

TABLE 3

Creep data for Zn-0.75 Cu-0.12 Ti alloy finish rolled cold to different thicknesses

| | | | | Creep rate, percent/day | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Annealing temperature and time | | | | | |
| | | Thickness | As- | 320) F | | 400) F. | | 480) F. | |
| Examples | Orientation | as-rolled cold, in. | rolled cold | ½ hr. | 8 hrs. | ½ hr. | 8 hrs. | ½ hr. | 8 hrs. |
| 15 | L | 0.010 | 170 | 0.049 | 0.0035 | 0.0054 | 0.0056 | 0.0080 | 18.0 |
| | T | 0.010 | 53 | 0.17 | 0.011 | .0011 | .00097 | .00078 | .15 |
| 16 | L | .025 | 83 | .17 | .0075 | .0055 | .0058 | .0095 | 4.9 |
| | T | .025 | 98 | .081 | .0022 | .0020 | .0020 | .0016 | .029 |
| 17 | T | .10 | 17 | | | | .0023 | | |

TABLE 4

Ratios of creep rates, L/T, for cold-rolled (to 92% total reduction, 0.025 in.) and annealed alloys

| | Composition, percent | | Anneal | | Ratio of creep |
|---|---|---|---|---|---|
| Examples | Cu | Ti | Temp., °F. | Time, hr. | rates, L/T |
| 18 | 0.75 | 0.12 | 320 | 8 | 3.4 |
| | 0.75 | 0.12 | 400 | ½ | 2.8 |
| | 0.75 | 0.12 | 400 | 2 | 2.8 |
| | 0.75 | 0.12 | 400 | 8 | 2.9 |
| 19 | .75 | .24 | 400 | 8 | 5.5 |
| 20 | 1.00 | .24 | 400 | 8 | 4.0 |
| 21 | 1.25 | .24 | 400 | 8 | 2.8 |
| 22 | .75 | .30 | 400 | 8 | 2.9 |
| 23 | 1.00 | .30 | 400 | 8 | 3.0 |
| 24 | 1.25 | .30 | 400 | 8 | 2.1 |
| 25 | 1.00 | .36 | 320 | 8 | .6 |
| 26 | 1.00 | .36 | 400 | 8 | 2.7 |

In Tables 5 and 6 are listed tensile properties and hardness for certain of the alloys annealed after finish rolling hot or cold to 92 percent total reduction. The alloys as-rolled cold had high ductility and low strength, and low anisotropy in tensile strengths between L and T directions. These properties facilitate fabrication of sheet as-rolled cold into final parts. The annealing to produce the high creep strength and low creep anisotropy caused marked increases in hardness, tensile strength, and anisotropy in tensile strength. Tensile ductilities dropped significantly, but remained above 10 percent except in one instance.

TABLE 5

Hardness and tensile properties of alloys finish rolled at 480° F. and annealed

| Examples | Composition percent Cu | Ti | Anneal [1] Temp. ° F. | Time, hr. | Hardness,[2] DPH | Tensile strength,[3] p.s.i. L | T | Tensile elongation, percent L | T |
|---|---|---|---|---|---|---|---|---|---|
| 27 | 0.75 | 0.12 | | | 70 | 27,700 | 38,400 | 33 | 19 |
| | 0.75 | 0.12 | 400 | 2 | 70 | 24,800 | 34,600 | 41 | 15 |
| 28 | 1.00 | .36 | | | 73 | 32,300 | 44,600 | 23 | 13 |
| | 1.00 | .36 | 320 | 8 | 75 | 33,300 | 43,800 | 27 | 24 |

[1] No values signify the condition: as-rolled to 0.025-in. sheet for 92-percent total reduction at 480° F.
[2] Diamond pyramid hardness, 1-kg. load.
[3] At maximum load, strain rate 0.1 in./in./min.

TABLE 6

Hardness and tensile properties of alloys finish rolled cold and annealed

| Examples | Composition, percent Cu | Ti | Anneal [1] Temp.° | Time hr. | Hardness,[2] DPH | Tensile strength,[3] p.s.i. L | T | Tensile elongation, percent L | T |
|---|---|---|---|---|---|---|---|---|---|
| 29 | 0.75 | 0.12 | | | 56 | 22,600 | 25,000 | 91 | 77 |
| | 0.75 | 0.12 | 400 | 2 | 70 | 32,100 | 39,800 | 34 | 12 |
| 30 | .75 | .24 | | | 54 | 21,600 | 22,100 | 100 | 104 |
| | .75 | .24 | 400 | 8 | 67 | 30,400 | 37,000 | 35 | 17 |
| 31 | 1.00 | .24 | | | 52 | 22,200 | 21,800 | 88 | 87 |
| | 1.00 | .24 | 400 | 8 | 72 | 34,200 | 41,100 | 28 | 21 |
| 32 | 1.25 | .24 | | | 50 | 21,000 | 20,800 | 105 | 75 |
| | 1.25 | .24 | 400 | 8 | 75 | 35,700 | 40,700 | 23 | 15 |
| 33 | .75 | .30 | | | 53 | 21,900 | 22,300 | 92 | 78 |
| | .75 | .30 | 400 | 8 | 71 | 33,800 | 37,600 | 21 | 13 |
| 34 | 1.00 | .30 | | | 51 | 22,700 | 22,900 | 82 | 72 |
| | 1.00 | .30 | 400 | 8 | 72 | 34,100 | 41,600 | 21 | 23 |
| 35 | 1.25 | .30 | | | 52 | 22,000 | 22,300 | 78 | 64 |
| | 1.25 | .30 | 400 | 8 | 73 | 34,300 | 40,500 | 17 | 7 |
| 36 | 1.00 | .36 | | | 58 | 24,900 | 26,300 | 62 | 63 |
| | 1.00 | .36 | 320 | 8 | 73 | 34,300 | 40,000 | 29 | 20 |

[1] No values signify the condition: as-rolled to 0.025-in. sheet for 92-percent total cold reduction.
[2] Diamond-pyramid hardness, 1-kg. load.
[3] At maximum load, strain rate 0.1 in./in./min.

Table 7 shows coefficients of linear thermal expansion for selected alloys annealed after finish rolling hot or cold to 92 percent total reduction. The annealing of the hot-rolled alloys increases the average population of basal-planes aligned toward the rolling direction (L), decreases it toward the normal (N) sheet direction (sheet thickness), and leaves that for the transverse (T) direction relatively unchanged. This is deduced because of the much greater expansion of zinc crystallites in the *c*-axis direction than in the *a*-axes (basal-plane) directions. The coefficients for the heavily cold-rolled alloys, which have much higher populations of basal planes aligned toward the L nad T directions than do the hot-rolled alloys, remain relatively unchanged by the annealing; when heated moderately, the cold-rolled and annealed alloys thus exhibit substantially lower thermal expansion within the sheet plane than do the alloys when rolled hot. The N coefficients were calculated from the measured L and T coefficients, using volume coefficiants measured on the thicker sheet before finish rolling was started.

TABLE

Thermal expansion coefficients

| Example | Composition, percent Cu | Ti | Anneal [1] Temp., ° F. | Time, hr. | Coefficient [2] of linear thermal expansion, $10^{-6}$° C. L | T | N [3] |
|---|---|---|---|---|---|---|---|
| | | | Finish rolled at 480° F. | | | | |
| 37 | 0.75 | 0.12 | | | 32.5 | 20.7 | 30.9 |
| | 0.75 | 0.12 | 400 | 8 | 30.5 | 21.6 | 32.0 |
| | 0.75 | 0.12 | 480 | 8 | 27.1 | 20.0 | 37.0 |
| 38 | 1.00 | .36 | | | 28.7 | 19.5 | 35.9 |
| | 1.00 | .36 | 320 | 8 | 26.4 | 19.6 | 38.1 |
| | | | Finish rolled cold | | | | |
| 39 | .75 | .12 | | | 24.8 | 18.2 | 41.1 |
| | .75 | .12 | 400 | 2 | 23.5 | 18.2 | 42.4 |
| | .75 | .12 | 480 | ½ | 23.6 | 18.8 | 41.7 |
| 40 | .75 | .24 | | | 24.7 | 18.1 | 41.3 |
| | .75 | .24 | 400 | 8 | 23.8 | 18.4 | 41.9 |
| 41 | 1.25 | .24 | | | 24.9 | 18.6 | 40.6 |
| | 1.25 | .24 | 400 | 8 | 23.7 | 18.5 | 41.9 |
| 42 | 1.00 | .30 | | | 25.1 | 18.5 | 40.5 |
| | 1.00 | .30 | 400 | 8 | 23.8 | 18.7 | 41.6 |
| 43 | 1.00 | .36 | | | 25.2 | 18.8 | 40.1 |
| | 1.00 | .36 | 320 | 8 | 24.8 | 18.9 | 40.4 |

[1] No values signify the condition: as-rolled to 0.025 -in. sheet for 92-percent total reduction during finish rolling.
[2] For range 20° to 100° C. (68° to 212° F.).
[3] Coefficient for normal (N) sheet direction is calculated.

The figure compares results of the present invention (curve A, point B) with the prior art (curves C, D, and E)), i.e., the above-discussed U.S. Pat. 2,472,402. All data are for the L sheet orientation only. Curve A is for a Zn-0.75 Cu-0.12 Ti alloy that was finish rolled to 92 percent total reduction at 480° F. (to 0.025-inch), and creep tested at stresses between 12,000 and 20,000 p.s.i. at 90° F., to show the effect of stress on creep rate. Point B shows the creep rate (14,000 p.s.i., 90° F.) for the same alloy that was finish rolled to the same reduction, but cold, and then annealed at 400° F. for 2 hours, according to the process of the present invention. Curve C shows creep rates for a Zn-1.0 Cu-0.12 Ti alloy that was finish rolled at 410° F. to 0.021-inch sheet. Curves D and E represent two sheets of the same alloy composition that were finish rolled to 50 percent total cold reduction (to 0.018 inch) and annealed for 5 minutes at 527° F. The cold rolling and annealing (curves D and E) did not produce creep resistance as good as that for the alloy as-rolled hot (curve C). The cold-rolled and annealed alloy with 92 percent total reduction (point B) was more than 50 times as creep resistant as the cold-rolled and annealed alloy with only 50 percent total cold reduction (curves D and E). For ready comparison, the creep rates from U.S. Pat. 2,472,402 were converted from inverse rates given in days/percent (for tests at 77° F.).

We claim:

**1.** A method of treating an alloy consisting essentially of zinc, about 0.25 to 1.3 percent copper and about 0.1 to 0.4 percent titanium, to provide both improved creep-resistance and low creep anisotropy, comprising cold rolling the alloy to at least 67 percent total reduction and subsequently annealing the rolled alloy at about 300 to 400° F. for a period of about ½ to 8 hours.

2. The method of claim 1 in which the alloy is cold rolled to at least 90 percent total reduction.

3. The method of claim 2 in which the alloy is cold rolled to at least 90 percent total reduction.

4. The method of claim 1 in which the annealing is conducted at about 400° F.

5. The method of claim 4 in which the alloy contains about 1.25 percent copper and about 0.24 to 0.30 percent titanium.

6. The method of claim 1 in which the alloy contains about 0.6 to 1.0 percent copper and about 0.12 percent titanium.



7. The method of claim 1 in which the alloy contains about 1.0 percent copper and about 0.36 percent titanium.

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U.S. Cl. X.R.

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