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## MAGNESIUM-BASE ALLOY

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The invention relates to an improved magnesium-base alloy and more particularly relates to improved magnesium-calcium-zinc alloy and the method of rolling.

For the purposes of the specification and claims, the term magnesium-base alloy is intended to mean a magnesium alloy containing at least 80 percent by weight of magnesium.

Heretofore, it has been known that a number of magnesium-calcium-zinc alloys have shown good cold workability when first properly hot worked, as by extrusion, so as to avoid cracking and when worked without cracking have exhibited desirable mechanical strength properties. These alloys have usually contained from 1 to 6 percent by weight of zinc and have hot cracked or hot shorted badly when hot rolled directly from castings.

It is a principal object of the invention to provide an improved rollable magnesium-base alloy containing calcium and zinc and a method of rolling the novel alloy.

It has now been found that magnesium-base alloys containing calcium and zinc can be readily rolled without cracking if the zinc level is kept below 1 percent and if certain critical relations are maintained between the zinc and the calcium contents. These alloys may be improved by the addition of manganese or zirconium. The specific proportions of alloying elements and the desirable methods of rolling the alloys are hereafter more fully described.

The alloys of the invention contains from about 0.01 to 0.8 percent by weight of calcium, from 0.05 to 0.95 percent of zinc and the balance substantially magnesium. In addition, both the quantity of calcium and the quantity of zinc are limited within the recited range to contents whereby the product of the percent of calcium multiplied by the percent of zinc minus 0.2 yields a numerical value not more than 0.1 and, more preferably, a value of about 0.05 to 0.07, the most preferred value being about 0.07. The equation defining this relationship is set forth as follows:

$$\text{Percent Ca}(\text{percent Zn}-0.2)=0.1 \text{ max.}$$

This alloy way be improved by the addition of up to 1.5 percent of manganese and up to about 0.8 percent of zirconium. Additions of manganese and zirconium improve the static strength of the alloy. The addition of zirconium also improves the workability of the alloy and it is thus found that in the presence of zirconium, higher levels of zinc may be employed without adverse effect on rollability. In the presence of zirconium, therefore, the relationship between the calcium and zinc content in alloys according to the invention is defined as:

$$\text{Percent Ca}(\text{percent Zn}-0.35)=0.1 \text{ max.}$$

More preferably, the alloy contains from 0.05 to about 0.5 percent of calcium and from 0.1 to 0.5 percent of zinc, and the balance substantially magnesium, the product of the percent of calcium times the percent of zinc minus 0.2 being a numerical value less than about 0.1 unless zirconium is present when the zinc and/or calcium contents may be higher according to the formula set forth above in which 0.35 is subtracted from the percent of zinc. In an even more preferred range of compositions, the alloy contains from 0.15 to 0.25 percent of calcium and from 0.2 to 0.5 percent of zinc. Generally, in the more

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preferred ranges of composition, higher zinc levels tend to impart higher strength to the alloy.

At very low calcium levels, however, higher strength properties are obtained by limiting the amount of zinc. Thus, very good properties are exhibited by an alloy which contains from 0.01 to 0.08 percent of calcium, from 0.1 to 0.2 percent of zinc and the balance substantially magnesium.

All of the foregoing alloys have excellent properties both at ambient room temperature and at elevated temperatures. In the work hardened condition, these alloys exhibit especially desirable mechanical strength properties. In the softer tempers, these alloys exhibit somewhat lower mechanical strength properties but exhibit high ductility.

The alloy may be made in the desired proportions according to the invention by melting together the alloying ingredients in proper proportions or by using hardeners of magnesium alloys containing the alloying constituents. Protection from oxidation during alloying is effected by the use of a saline flux, as in conventional alloying of magnesium. The molten alloy may be flux refined, if desired, by stirring the alloy with additional flux. The so-refined metal is allowed to settle and then is separated from the flux as by decanting into a suitable casting mold, e.g., a rectangular mold for a rolling slab.

In rolling the cast metal, it is desirable first to scalp the rolling slab to remove surface impurities. The slab is then heated to 700 to 900° F. as often as necessary to avoid cold cracking during rundown, that is, by hot rolling, from a thickness as cast to about 0.1 inch. It is then annealed one hour at about 700° F. and cold rolled 1 to 2 percent per pass through steam heated rolls for a total reduction of approximately 40 percent, and is given a final heat treatment as desired tailored to yield the desired combination of strength and ductility. Solution heat treatment, as by heating one hour at 900 to 950° F. and then water quenching the metal, may be employed prior to cold rolling to enhance certain properties, particularly the mechanical strength properties.

The sheet may also be finished by warm rolling instead of cold rolling. After the hot rundown, the sheet is heated to 700 to 950° F. and taken directly to the rolls of the mill where a reduction of approximately 15 to 50 percent is accomplished with lubricated rolls under conditions of roll pressure and speed that the metal exits at a temperature in the range of 300 to 600° F. If the exit temperature employed is above about 475° F., the metal may be quenched on the exit side of the mill, if desired.

The following examples illustrate the invention and are not to be considered as limiting the scope thereof.

Various alloy compositions according to the invention were prepared in a conventional manner by melting together the requisite amounts of magnesium, calcium and zinc with or without zirconium or manganese. The compositions were flux refined, settled, then cast into rolling slabs. The rolling slabs were scalped, heated to about 750 to 850° F. and subjected to hot rolling to reduce the thickness of the slabs from 2 inches to about 0.1 inch. The metal was then rolled as follows. The metal was warm rolled to effect a 40 percent reduction in thickness in one pass. The metal entered the rolls of the mill at a temperature of 700° F. and exited from the rolls at a temperature of 400° F. Part of the so-rolled metal was heated to 300° F. for one hour to bring the rolled metal to the H26 condition. Part of the so-rolled metal was heated at 500° F. for one hour to bring the metal to the H24 condition. Samples of the metal in each condition were subjected to mechanical testing. The composition employed, the final heat treatment and the results of the mechanical tests are

listed in Table I. The mechanical properties shown are the lower of either longitudinal or transverse properties.

TABLE I

| Test No. | Composition,* Percent by Weight |      |       |       | Final Heat Treatment, ° F. | Mechanical Properties |     |     |    |
|----------|---------------------------------|------|-------|-------|----------------------------|-----------------------|-----|-----|----|
|          | Ca                              | Zn   | Mn    | Zr    |                            | Percent E             | TYS | CYS | TS |
| 1.....   | 0.06                            | 0.20 | ----- | ----- | 300                        | 5                     | 24  | 24  | 36 |
| 2.....   | 0.06                            | 0.20 | ----- | ----- | 500                        | 14                    | 18  | 17  | 32 |
| 3.....   | .05                             | .4   | ----- | ----- | 300                        | 9                     | 21  | 23  | 34 |
| 4.....   | .05                             | .4   | ----- | ----- | 500                        | 17                    | 15  | 15  | 31 |
| 5.....   | .06                             | .5   | ----- | ----- | 300                        | 8                     | 21  | 23  | 35 |
| 6.....   | .06                             | .5   | ----- | ----- | 500                        | 18                    | 15  | 14  | 30 |
| 7.....   | 0.09                            | .2   | ----- | ----- | 500                        | 14                    | 22  | 19  | 32 |
| 8.....   | 0.16                            | .4   | ----- | ----- | 300                        | 5                     | 29  | 29  | 39 |
| 9.....   | 0.16                            | .4   | ----- | ----- | 500                        | 11                    | 23  | 22  | 35 |
| 10.....  | 0.16                            | .4   | ----- | 0.10  | 300                        | 6                     | 30  | 30  | 41 |
| 11.....  | 0.16                            | .4   | ----- | 0.10  | 500                        | 12                    | 25  | 24  | 36 |
| 12.....  | .13                             | .6   | ----- | ----- | 300                        | 4                     | 29  | 30  | 41 |
| 13.....  | .13                             | .6   | ----- | ----- | 500                        | 14                    | 23  | 22  | 37 |
| 14.....  | .13                             | .6   | ----- | .20   | 300                        | 5                     | 30  | 32  | 43 |
| 15.....  | .13                             | .6   | ----- | .20   | 500                        | 11                    | 25  | 25  | 38 |
| 16.....  | .25                             | .2   | ----- | ----- | 300                        | 4                     | 31  | 32  | 42 |
| 17.....  | .25                             | .2   | ----- | ----- | 500                        | 14                    | 24  | 24  | 37 |
| 18.....  | .25                             | .2   | 0.5   | ----- | 300                        | 5                     | 28  | 29  | 39 |
| 19.....  | .25                             | .2   | 0.5   | ----- | 500                        | 11                    | 23  | 23  | 35 |
| 20.....  | .25                             | .2   | ----- | 0.4   | 300                        | 5                     | 30  | 29  | 40 |
| 21.....  | .25                             | .2   | ----- | 0.4   | 500                        | 9                     | 25  | 25  | 36 |
| 22.....  | .25                             | .35  | ----- | ----- | 300                        | 4                     | 29  | 31  | 42 |
| 23.....  | .25                             | .35  | ----- | ----- | 500                        | 12                    | 23  | 23  | 37 |
| 24.....  | .25                             | .63  | ----- | .7    | 500                        | 7                     | 25  | 27  | 38 |
| 25.....  | .5                              | .2   | ----- | ----- | 500                        | 10                    | 24  | 24  | 37 |

\*Balance magnesium.

Percent E=Percent elongation.

TYS=Tensile yield strength in 1,000's of pounds per square inch.

CYS=Compression yield strength in 1,000's of pounds per square inch.

TS=Ultimate tensile yield strength in 1,000's of pounds per square inch.

Other portions of the rolled sheet metal prepared as described above were heated to 700° F. for one hour to bring the metal to the 0 temper condition. Additional sheet metal according to the invention which had been subjected to hot rundown was warm rolled according to a schedule in which the metal was brought to the T8 temper condition. The metal was reduced 20 percent in thickness in one pass on being brought into the mill at a temperature of 950° F. and exiting from the mill at a temperature of 400° F. The so-finish rolled metal was heated to a temperature of 500° F. for one hour. Samples of the metal in the 0 and T8 temper conditions were subjected to mechanical testing

including testing the creep resistance of the metal. The compositions employed, the conditions of rolling and the

final heat treat temperature and the mechanical properties of the alloy are indicated in Table II.

By way of comparison, an alloy containing proportions of calcium and zinc within the range of the compositions of the invention but having a product of the percent of calcium, times the percent of zinc minus 0.2, above a numerical value of 0.1, was similarly prepared, cast and rolled in an attempt to bring the metal to one of the H26, H24, 0 or T8 temper conditions. The metal was extremely difficult to roll and cracked badly.

The mechanical properties shown in the table are the lower of either longitudinal or transverse properties. In each case the percent of creep was determined in the longitudinal direction of rolling.

TABLE II

| Test No.     | Composition, <sup>1</sup> Percent by Weight |     |       |       | Percent of Warm Rolling | Entry Temp., ° F. | Final Heat Treatment, ° F. | Mechanical Properties |       |       |           |
|--------------|---------------------------------------------|-----|-------|-------|-------------------------|-------------------|----------------------------|-----------------------|-------|-------|-----------|
|              | Ca                                          | Zn  | Mn    | Zr    |                         |                   |                            | Percent E             | TYS   | TS    | Percent C |
| 26.....      | .06                                         | .20 | ----- | ----- | 20                      | 950               | 500                        | 13                    | 13    | 29    | .16       |
| 27.....      | .06                                         | .20 | ----- | ----- | 40                      | 700               | 700                        | 16                    | 9     | 27    | .96       |
| 28.....      | .05                                         | .40 | ----- | ----- | 20                      | 950               | 500                        | 14                    | 12    | 29    | .55       |
| 29.....      | .05                                         | .40 | ----- | ----- | 40                      | 700               | 700                        | 18                    | 8     | 37    | RA        |
| 30.....      | .06                                         | .5  | ----- | ----- | 20                      | 950               | 500                        | 15                    | 12    | 29    | .64       |
| 31.....      | .06                                         | .5  | ----- | ----- | 40                      | 700               | 700                        | 9                     | 8     | 27    | RA        |
| 32.....      | .09                                         | .2  | ----- | ----- | 20                      | 950               | 500                        | 10                    | 16    | 32    | .12       |
| 33.....      | .09                                         | .2  | ----- | ----- | 40                      | 700               | 700                        | 23                    | 10    | 37    | .02       |
| 34.....      | .16                                         | .40 | ----- | ----- | 20                      | 950               | 500                        | 11                    | 16    | 30    | .09       |
| 35.....      | .16                                         | .40 | ----- | ----- | 40                      | 700               | 700                        | 20                    | 12    | 29    | .03       |
| 36.....      | .16                                         | .40 | .5    | ----- | 20                      | 950               | 500                        | 12                    | 18    | 32    | .10       |
| 37.....      | .16                                         | .40 | .5    | ----- | 40                      | 700               | 700                        | 20                    | 17    | 31    | .02       |
| 38.....      | .16                                         | .40 | ----- | .15   | 20                      | 950               | 500                        | 10                    | 19    | 32    | .10       |
| 39.....      | .16                                         | .40 | ----- | .15   | 40                      | 700               | 700                        | 20                    | 17    | 30    | .02       |
| 40.....      | .13                                         | .6  | ----- | ----- | 20                      | 950               | 500                        | 10                    | 16    | 29    | .09       |
| 41.....      | .13                                         | .6  | ----- | ----- | 40                      | 700               | 700                        | 20                    | 10    | 28    | .06       |
| 42.....      | .13                                         | .6  | ----- | .20   | 20                      | 950               | 500                        | 10                    | 21    | 35    | .17       |
| 43.....      | .13                                         | .6  | ----- | .20   | 40                      | 700               | 700                        | 20                    | 18    | 32    | .04       |
| 44.....      | .25                                         | .2  | ----- | ----- | 20                      | 950               | 500                        | 10                    | 18    | 29    | .19       |
| 45.....      | .25                                         | .2  | ----- | ----- | 40                      | 700               | 700                        | 19                    | 16    | 30    | .04       |
| 46.....      | .25                                         | .2  | .5    | ----- | 20                      | 950               | 500                        | 11                    | 16    | 28    | .15       |
| 47.....      | .25                                         | .2  | .5    | ----- | 40                      | 700               | 700                        | 20                    | 16    | 31    | .02       |
| 48.....      | .25                                         | .2  | ----- | .4    | 20                      | 950               | 500                        | 10                    | 21    | 34    | .19       |
| 49.....      | .25                                         | .2  | ----- | .4    | 49                      | 700               | 700                        | 19                    | 16    | 32    | .05       |
| 50.....      | .25                                         | .35 | ----- | ----- | 20                      | 950               | 500                        | 10                    | 16    | 32    | .10       |
| 51.....      | .25                                         | .35 | ----- | ----- | 40                      | 700               | 700                        | 18                    | 13    | 30    | .03       |
| Comp. 1..... | .25                                         | .63 | ----- | ----- | ( <sup>2</sup> )        | -----             | -----                      | -----                 | ----- | ----- | -----     |
| Comp. 2..... | .25                                         | .63 | ----- | ----- | ( <sup>2</sup> )        | -----             | -----                      | -----                 | ----- | ----- | -----     |
| 52.....      | .25                                         | .63 | ----- | .7    | 20                      | 950               | 500                        | 8                     | 22    | 36    | .08       |
| 53.....      | .25                                         | .63 | ----- | .7    | 40                      | 700               | 700                        | 18                    | 19    | 32    | .04       |
| 54.....      | .5                                          | .2  | ----- | ----- | 20                      | 950               | 500                        | -----                 | 18    | 33    | .13       |
| 55.....      | .5                                          | .2  | ----- | ----- | 40                      | 700               | 700                        | 18                    | 21    | 31    | .03       |

<sup>1</sup> Balance magnesium.

<sup>2</sup> Difficult to roll.

RA= Ran away under load.

Percent C=Percent creep in 100 hours under 8,000 pounds per square inch and 300° F.

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The alloy and method of the invention having been thus fully described, various modifications thereof will at once be apparent to those skilled in the art, and the scope of the invention is to be considered limited only by the claims appended hereafter.

I claim:

1. A magnesium-base alloy which consists essentially of by weight from 0.01 to 0.8 percent of calcium, from 0.05 to 0.95 percent of zinc, the product of the percent of calcium, times the percent of zinc minus 0.2, being a numerical value not greater than 0.1, and the balance substantially magnesium.

2. The alloy as in claim 1 which contains up to 1.5 percent of manganese.

3. The alloy as in claim 1 which contains up to 0.8 percent of zirconium.

4. A magnesium-base alloy which consists essentially of by weight from 0.05 to 0.5 percent of calcium, from 0.1 to 0.5 percent of zinc, the product of the percent of calcium times the percent of zinc minus 0.2 being a numerical value not greater than 0.1, and the balance substantially magnesium.

5. A magnesium-base alloy which consists essentially of by weight from 0.15 to 0.25 percent of calcium, from 0.3 to 0.5 percent of zinc, and the balance substantially magnesium.

6. A magnesium-base alloy which consists essentially of by weight from 0.01 to 0.08 percent of calcium, from 0.1 to 0.2 percent of zinc, and the balance substantially magnesium.

7. The method of preparing improved roller sheet product of magnesium-base alloy directly from cast ingot which comprises providing a cast ingot of a magnesium-

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base alloy which comprises by weight from 0.01 to 0.8 percent of calcium, from 0.05 to 0.95 percent of zinc, the product of the percent of calcium, times the percent of zinc minus 0.2, being a numerical value not greater than 0.1 and the balance substantially magnesium; hot rolling the cast alloy at a temperature in the range of 700 to 900° F.; annealing the so-rolled metal for about 1 hour at a temperature in the range of 700 to 950° F.; warm rolling the metal to effect a reduction in thickness of 15 to 50 percent with an exit temperature of 300 to 600° F. and thereafter heating the metal to a temperature in the range of 300 to 700° F. for about 1 hour.

8. The method as in claim 7 in which the final heating step is carried out at a temperature of about 300° F.

9. The method as in claim 7 in which the final heating step is carried out at a temperature of about 700° F.

10. A magnesium-base alloy which consists essentially of by weight from 0.01 to 0.8 percent of calcium, from 0.05 to 0.95 percent of zinc, and from 0.1 to 0.8 percent of zirconium, the product of the percent of calcium times the percent of zinc minus 0.35 being a numerical value less than about 0.1, and the balance substantially magnesium.

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