

1

3,416,978

## MAGNESIUM BASE ALLOYS

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No Drawing. Continuation of application Ser. No. 613,967, Feb. 3, 1967, which is a continuation of application Ser. No. 352,322, Mar. 16, 1964. This application Mar. 19, 1968, Ser. No. 714,359

Claims priority, application Great Britain, Apr. 3, 1963, 13,197/63

1 Claim. (Cl. 148—32.5)

This application is a continuation of U.S. application Ser. No. 613,967 filed Feb. 3, 1967, now abandoned, which is in turn a continuation of U.S. application Ser. No. 352,322 filed Mar. 16, 1964 and now abandoned.

This invention relates to magnesium base alloys and its main object is to produce an alloy which in the fully heat treated cast state has a combination of mechanical strength properties hitherto unobtained and in particular a 0.1% proof stress of over 12.5 tons per square inch on test bars made according to British standard specification No. L.101 combined with adequate maximum tensile stress (e.g. at least 17 tons per square inch) and adequate elongation (e.g. at least 3 percent elongation).

In the specification of British Patent 511,137 it was proposed to incorporate zirconium in order to achieve fine grain size and high strength and commercial alloys were developed on this basis including in particular an alloy containing 0.4 to 1.0 percent zirconium and 4 to 6 percent zinc. Fully heat treated cast test bars of such alloys have given about 9–11 tons 0.1% proof stress, 16–17 tons tensile and 2–8% elongation. The specification mentions a list of metals (including silver) which would not precipitate the zirconium from the molten alloy but no suggestion was made that these other than zinc and cadmium would offer any improvement in mechanical properties.

In the further development of these alloys we developed the alloy (known as TZ6) of British Patent 734,011 containing zirconium with 4 to 8 percent zinc and at least 0.5 percent thorium. This alloy in the as cast state gives a 0.1% proof stress of 8.5 tons with 16–17 tons tensile stress. The properties of this alloy can be improved by precipitation heat treatment whereupon the 0.1% proof stress is increased to 9.5 to 11.0 and the tensile stress is increased to 17.0 to 19.5 with elongation 5 to 15 percent. However, this alloy cannot be improved by solution heat treatment.

Another high strength magnesium alloy (known as MSR) described in the specification of British Patent No. 875,929 consists of zirconium up to 1.0%, 0.5 to 3.5 rare earth metals and from 1.5 to 3.5 percent silver, with less than 0.5 percent zinc if any. More than 0.5% zinc in this MSR alloy spoils the properties of the alloy. This alloy can achieve a 0.1% proof stress of 12.0 tons with an ultimate tensile stress of 16.0 tons and 3% elongation.

According to the present invention we provide an alloy consisting apart from impurities of:

|                                              | Percent            |
|----------------------------------------------|--------------------|
| Zinc (preferably 3–7) .....                  | 3 to 8             |
| Silver (preferably 1.5–4.0%) .....           | 1 to 4.0           |
| Zirconium .....                              | 0.4 to 1.0         |
| Thorium .....                                | 0 to less than 0.5 |
| Rare earth metals .....                      | 0 to less than 0.5 |
| Thorium and rare earth metals together ..... | less than 0.5      |
| Manganese .....                              | 0 to 0.15          |
| Cadmium .....                                | 0 to 1.0           |
| Calcium .....                                | 0 to 0.8           |
| Indium .....                                 | 0 to 2.0           |
| Thallium .....                               | 0 to 5.0           |

2

|                 | Percent   |
|-----------------|-----------|
| Lead .....      | 0 to 1.0  |
| Beryllium ..... | 0 to 0.01 |
| Magnesium ..... | Balance   |

For highest strength with full zirconium content we may use a zinc content of 5 to 8 percent whereas for alloys having greater ductility we may use 3.5 to 5.0 percent zinc.

For alloys containing 5 to 7% zinc, heat treatment may be carried out by first effecting solution heat treatment at 450 to 490° C. for at least two hours, followed by precipitation heat treatment at a temperature of 120 to 180° C. for a period of at least 5 hours (preferably 10 to 30 hours). For alloys containing 3 to 5% zinc the solution heat treatment temperature can be as high as 520° C.

It is surprising that whereas an alloy consisting of 4 to 5 percent zinc, zirconium, balance magnesium, cannot be materially improved by full heat treatment, the addition of 1.5 to 4.0 percent silver results in the alloy being somewhat improved by full heat treatment.

After effecting solution heat treatment the alloy should be rapidly cooled. It is found that the aforesaid MSR alloy if cooled with an air blast at this stage suffers loss of mechanical properties and must therefore be quenched in liquid which is less convenient. However, the alloy of the present invention can be cooled by an air blast at this stage and still develops good mechanical properties.

As examples of the mechanical properties achieved by the present invention, the following test results may be cited:

### Alloy A1

|            | Percent |
|------------|---------|
| Zinc ..... | 6       |
| Ag .....   | 3       |
| Zr .....   | 0.75    |

Sand cast test bars to B.S.L.101 type B.

(a) Solution heat treated for 16 hours at 460° C., air blast cooled and aged at 150° C. for 24 hours.

(b) Solution heat treated for 16 hours at 460° C., air blast cooled and aged at 125° C. for 96 hours.

|           | 0.1% proof stress<br>tons per sq. inch | Ultimate<br>tensile stress | Elongation<br>on 2 inches<br>(percent) |
|-----------|----------------------------------------|----------------------------|----------------------------------------|
| (a) ..... | 13.1                                   | 21.4                       | 6                                      |
| (b) ..... | 14.4                                   | 21.6                       | 6                                      |

### Alloy A2

|          | Percent |
|----------|---------|
| Zn ..... | 6       |
| Ag ..... | 2       |
| Zr ..... | 0.75    |

Sand cast test bars to B.S.L.101.

(a) Solution heat treated for 7 hours at 480° C., air blast cooled and aged for 96 hours at 125° C.

(b) Solution heat treated for 2 hours at 490° C., air blast cooled and aged for 16 hours at 150° C.

|           | 0.1% proof stress,<br>tons/sq. inch | Ultimate tensile<br>stress, tons/sq. inch. | Elongation,<br>percent on 2 inches. |
|-----------|-------------------------------------|--------------------------------------------|-------------------------------------|
| (a) ..... | 13.3                                | 19.1                                       | 2                                   |
| (b) ..... | 12.7                                | 18.8                                       | 4                                   |

### Alloy A3

|          | Percent |
|----------|---------|
| Zn ..... | 7       |
| Ag ..... | 2       |
| Zr ..... | 0.75    |

ASTM type test bars solution heat treated 16 hrs. at 460° C., air blast cooled, and aged for 72 hrs. at 125° C.

|                                        |      |
|----------------------------------------|------|
| 0.1% proof stress, tons/sq. inch       | 14.9 |
| 0.2% proof stress, tons/sq. inch       | 16.3 |
| Ultimate tensile stress, tons/sq. inch | 21.4 |
| Elongation, percent on 2 in.           | 5½   |

We have further found that the Mg-Zn-Ag-Zr alloys differ from the other zirconium bearing casting alloys in that whereas, as is well known, full saturation of the metal with zirconium is desirable to suppress micro-porosity, the preferred alloys of the present invention give maximum soundness with a dissolved zirconium content significantly below the saturation level. Such alloys with reduced dissolved zirconium content show greater response to the use of chills and show higher tensile properties in castings owing to the greater soundness, despite slightly coarser grain size arising from the lower dissolved zirconium content.

The increased soundness obtainable with the reduced zirconium content enables higher zinc contents to be effectively utilised than are preferable when the alloys are saturated with zirconium. The useful range of zinc content is then extended, e.g. to about 8%. To provide good ductility at the higher zinc levels, the preferred silver content may then be reduced, e.g. to about 1%. Solution heat treatment temperatures will generally be slightly lower for alloys with reduced zirconium content.

To produce Mg-Zn-Ag-Zr alloys with a controlled lower zirconium content, one convenient procedure is to melt down metal charges consisting of pre-alloyed ingot (containing e.g. 0.1-0.3% Zr) and Mg-Zn-Ag-Zr alloy scrap, and to revivify each melt with a 3% addition of Mg-30% Zr hardener alloy. For full saturation with zirconium, a 5% addition of such hardener would normally be used.

The following data illustrate the increased tensile properties obtained in 1 in. thick sand cast slabs in alloy A1 above when using a reduced zirconium content. Slabs solution heat treated for 16 hours at 460° C., air blast cooled, and aged for 96 hrs. at 125° C.

| Soluble zirconium analysis, percent | Distance from chill (in.) | Tensile properties (full size test bars) |                   |                 |                         |
|-------------------------------------|---------------------------|------------------------------------------|-------------------|-----------------|-------------------------|
|                                     |                           | 0.1% proof stress                        | 0.2% proof stress | Ultimate stress | Elong. percent on 2 in. |
| 0.65-----                           | 1                         | 14.0                                     | 15.2              | 21.4            | 5½                      |
|                                     | 2                         | 13.1                                     | 14.2              | 21.1            | 5½                      |
|                                     | 3                         | 11.4                                     | 13.2              | 21.0            | 6                       |
|                                     | 4                         | 12.4                                     | 13.3              | 20.0            | 3½                      |
|                                     | 5                         | 11.9                                     | 12.9              | 19.2            | 4                       |
| 0.83-----                           | 1                         | 13.8                                     | 15.1              | 21.3            | 5                       |
|                                     | 2                         | 12.5                                     | 13.3              | 21.0            | 9½                      |
|                                     | 3                         | 12.2                                     | 13.1              | 21.0            | 10                      |
|                                     | 4                         | 11.8                                     | 13.0              | 19.04           | 4                       |
|                                     | 5                         | 10.6                                     | 11.8              | 17.7            | 4                       |

The alloys of the present invention may be used for cast parts requiring high strength such as aircraft frame parts but may also be used in wrought forms.

The magnesium content of the alloy should be at least 85 percent preferably at least 90 percent.

The alloy of the kind containing this reduced quantity of soluble zirconium will usually contain up to 8 percent zinc (e.g. 5 to 8 percent) together with 0.4 to 0.7 (preferably 0.5 to 0.7) percent zirconium. The soluble zirconium is soluble in dilute hydrochloric acid as distinct from any additional small amount of zirconium which may be present but which is not soluble in dilute hydrochloric acid. The normal soluble zirconium content of alloys at the 5-8% zinc level is over 0.7, e.g. 0.75 to 0.9 percent.

We claim:  
1. A solution heat treated and precipitation heat treated cast article consisting essentially of 5 to 7% zinc, 1.5 to 4% silver, 0.4 to 1% zirconium, balance magnesium.

References Cited

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| CHARLES N. LOVELL, Primary Examiner. |        |                |
| U.S. Cl. X.R.                        |        |                |
| 75-168; 148-161                      |        |                |