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(54) Titre : ALLIAGE DUCTILE DE MAGNESIUM
(54) Title: DUCTILE MAGNESIUM ALLOY

(57) Abrégé/Abstract:
The present invention relates to a corrosion-resistant magnesium alloy which can be prepared with a justifiable expenditure of energy from scrap or impure copper-containing precursors and displays a ductility such that it can be used as a casting or kneading material. The magnesium alloy contains, relative to the total weight of the magnesium alloy, 1 to 9 wt.-% aluminium, 0.6 to 6 wt.-% zinc, 0.1 to 2 wt.-% manganese, 0 to 2 wt.-% rare earth elements, 0.5 to 2 wt.-% copper, wherein the weight ratio of aluminium to zinc lies in the range from 1:1 to 2:1.

## Abstract

The present invention relates to a corrosion-resistant magnesium alloy which can be prepared with a justifiable expenditure of energy from scrap or impure copper-containing precursors and displays a ductility such that it can be used as a casting or kneading material. The magnesium alloy contains, relative to the total weight of the magnesium alloy, 1 to 9 wt.-% aluminium, 0.6 to 6 wt.-% zinc, 0.1 to 2 wt.-% manganese, 0 to 2 wt.-% rare earth elements, 0.5 to 2 wt.-% copper, wherein the weight ratio of aluminium to zinc lies in the range from 1:1 to 2:1.

# DUCTILE MAGNESIUM ALLOY

The present invention relates to a corrosion-resistant magnesium alloy.

It is known that magnesium alloys are corrosion-resistant if the copper, iron and nickel contents are very small. In the alloys of the AZ (magnesium with aluminium and zinc), AM (magnesium with aluminium and manganese), AS (magnesium with aluminium and silicon) and AJ (magnesium with aluminium and strontium) groups, the maximum permitted levels are mostly set at 250 ppm copper, 10 ppm nickel and 50 ppm iron. According to Bakke et al., Soc. Automotive Engineers, paper 1999-01-0926, 1999, pages 1-10 and Kammer (Ed.): Magnesiumtaschenbuch, Aluminiumverlag Düsseldorf, 2000, 1st edition, marked corrosion occurs above all due to pitting if the maximum permitted levels of copper, nickel and/or iron are exceeded.

Secondary magnesium alloys can be prepared with much less expenditure of energy than primary alloys, but inevitably contain copper, nickel and iron in quantities above the maximum permitted levels. Magnesium alloys with copper, nickel and/or iron contents below the maximum permitted levels can be produced only at very high cost, or not at all, by recycling bought scrap. A corrosion-resistant secondary magnesium alloy is however known from WO 2007/009435 A1. Despite higher copper and nickel contents, the magnesium alloys disclosed in WO 2007/009435 A1 display corrosion properties comparable with or better than a high-purity primary magnesium alloy, and contain 10-20 wt.-% aluminium, 2.5 to 10 wt.-% zinc, 0.1 to 2 wt.-% manganese, 0.3 to 2 wt.-% copper and/or up to 1.5 wt.-% total nickel, cobalt, iron, silicon, zirkon, beryllium. However, these alloys have the drawback that they are comparatively brittle, which makes them unusable for some processing methods

such as extrusion, forging, rolling but also for applications which require energy absorption via plastic deformation.

The object of the present invention is thus to provide a corrosion-resistant magnesium alloy which can be prepared without a very high expenditure of energy by recycling bought scrap and is ductile.

This object is achieved by a magnesium alloy containing, relative to the total weight of the magnesium alloy, 1 to 9 wt.-% aluminium, 0.6 to 6 wt.-% zinc, 0.1 to 2 wt.-% manganese, 0 to 2 wt.-% rare earth elements, 0.5 to 2 wt.-% copper, wherein the weight ratio of aluminium to zinc lies in the range from 1:1 to 2:1. Preferred embodiments result from the dependent claims.

Surprisingly it was found that, despite higher copper contents in the magnesium alloy according to the invention, the corrosion behaviour is similarly good compared with high-purity primary magnesium alloys. Furthermore, the magnesium alloy according to the invention remains ductile.

The aluminium content of the magnesium alloy according to the is preferably, relative to the total weight of the magnesium alloy, 2 to 7.5 wt.-%, more preferably 3 to 6 wt.-%. The zinc content of the magnesium alloy according to the invention is preferably, relative to the total weight of the magnesium alloy, 1 to 5 wt.-%, more preferably 2 to 4 wt.-%. The manganese content of the magnesium alloy according to the invention is preferably 0.1 to 1 wt.-%, more preferably 0.2 to 0.75 wt.-%. The copper content of the magnesium alloy according to the invention is preferably 0.5 to 1 wt.-%, more preferably 0.5 to 0.7 wt.-%.

Furthermore, it was surprisingly found that, by adding rare earths such as cerium, neodymium, yttrium, scandium, gadolinium or mixtures of same, the corrosion behaviour is further improved. In particular the negative influence of nickel can - if present - thus be reduced. The total rare earth elements content preferably lies in the range of up to 2 wt.-%, relative to the total weight of the magnesium alloy.

The magnesium alloy according to the invention can further contain nickel, iron and/or silicon. It is preferred that the nickel content is less than 0.005 wt.-%, relative to the total weight of the magnesium alloy, more preferably less than 0.001 wt.-%, even more preferably less than 0.0005. The iron content should be less than 0.05 wt.-%, relative to the total weight of the magnesium alloy, preferably less than 0.01 wt.-%, more preferably less than 0.005 wt.-% and the silicon content should be less than 0.1 wt.-%, relative to the total weight of the magnesium alloy, preferably less than 0.05 wt.-%.

The magnesium alloy according to the invention can be prepared as a secondary alloy by melting scrap or impure magnesium precursors which contain copper, nickel and/or iron, after which the level of constituents in the alloy is set to correspond to that of a magnesium alloy according to the invention. Such a magnesium alloy can be prepared at favourable cost with a comparatively small expenditure of energy.

The magnesium alloy according to the invention can be used both as a casting material (sand, ingot, die- and semi-solid casting) and as a kneading material for extrusion, forging, rolling, etc.

Example:

The invention will now be explained in more detail with the help of the following examples. The comparative corrosion examinations took place by immersion in 3.5% sodium chloride solution and using the salt-spray test according to DIN 50021. In the immersion measurements, the rate of corrosion was determined by measuring the developed quantity of hydrogen. In the salt-spray test, the mass loss is determined.

In Table 1 the rates of corrosion of a magnesium alloy according to the invention (AMZC), a pure, zinc-containing magnesium alloy (AMZ 503), a pure AM50 alloy and a copper-modified AM50 alloy (AMC) are compared. The aluminium, zinc, manganese, copper, nickel, iron and silicon contents of the magnesium alloys listed in Table 1 (in wt.-%) are given in Table 2. Table 3 shows the mechanical properties of the alloy according to the invention and the comparison alloys AMZ501, AMZ502, AMZ505 and AM50 and also AZC1231 according to WO 2007/009435 A1, wherein the remainder is always magnesium.

Table 1:

| **Alloy** | **Corrosion rate Salt-spray test (mm/year)** | **Corrosion rate Immersion (mm/year)** |
|---|---|---|
| AMZC | 0.6 | 1.7 |
| AMZ503 | 0.17 | 1.1 |
| AM50 | 0.63 | 4.5 |
| AMC | 8.99 | 32.9 |
| AZC1231 | 1.00 | 6.57 |

Table 2:

| **Alloy** | **Al** | **Zn** | **Mn** | **Cu** | **Ni** | **Fe** | **Si** |
|---|---|---|---|---|---|---|---|
| AMZC | 5.59 | 3.18 | 0.25 | 0.54 | 0.00014 | 0.0013 | 0.026 |
| AMZ503 | 5.3 | 3.19 | 0.25 | 0.0077 | 0.00021 | 0.0015 | 0.028 |
| AM50 | 4.9 | 0.02 | 0.26 | 0.0077 | 0.00017 | 0.00068 | 0.026 |
| AMC | 4.84 | 0.023 | 0.26 | 0.52 | 0.000082 | 0.00092 | 0.028 |
| AZC1231 | 11.7 | 3.04 | 0.48 | 0.47 | 0.0032 | 0.0087 | 0.39 |

Table 3:

| Alloy | Yield point (MPa) | Tensile strength (MPa) | Elongation at break (%) |
|---|---|---|---|
| AMZC | 73 | 226 | 10.9 |
| | | | |
| AMZ501 | 67 | 214 | 13.2 |
| AMZ502 | 65 | 207 | 10.2 |
| AMZ505 | 67 | 193 | 11.2 |
| | | | |
| AM50 | 54 | 199 | 13.2 |
| | | | |
| AZC1231 | 152 | 189 | 0.5 |

The data show that the rate of corrosion of the magnesium alloys according to the invention (AMZC) is comparable with the rate of corrosion of the pure alloys AMZ503 and AM50 or is even improved. On the other hand, the copper-modified AM50 alloy displays an unacceptable rate of corrosion.

Without wishing to be bound to a theory, it is presumed that the microstructure of the magnesium alloy according to the invention is characterized by a low level of secondary phases and a change in the beta phase $Mg_{17}Al_{12}$. Unlike the alloys known from WO 2007/009435 A1, the secondary phases do not form a network structure. This has a positive effect on the ductility

of the alloys according to the invention, as is shown in Table 3. The beta phase is presumably modified by alloying with zinc and partially suppressed and replaced by quaternary MgAlZnCu phases. The local element formers copper, nickel, cobalt and iron and their intermetallic phases are bound in this phase and nickel, cobalt and iron additionally via $Al_8Mn_5$ phases and their negative influence on corrosion resistance clearly reduced. The microstructure of the pure AM50 alloy, on the other hand, contains predominantly the beta phase as secondary phase, which accelerates the corrosion via local element formation without formation as a network. The alloy according to the invention can therefore tolerate higher copper, nickel, cobalt and iron contents. The zinc and copper contents increase the strength of the alloy without greatly influencing ductility (see Table 3) and in addition make the alloy more creep-resistant. Also, the magnesium alloys according to the invention, unlike the pure alloys AMZ503 or AM50, can be prepared with a justifiable expenditure of energy as secondary alloys by melting scrap or impure precursors which contain copper, nickel and/or iron, after which the level of the constituents of the alloy can be set.

**THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:**

1. A magnesium alloy, containing, relative to the total weight of the magnesium alloy, 1 to 9 wt.-% aluminium, 0.6 to 6 wt.-% zinc, 0.1 to 2 wt.-% manganese, 0 to 2 wt.-% rare earth elements, and 0.5 to 2 wt.-% copper, wherein the weight ratio of aluminium to zinc lies in the range from 1:1 to 2:1.

2. The magnesium alloy according to claim 1, characterized in that the aluminium content, relative to the total weight of the magnesium alloy, is 2 to 7.5 wt.-%.

3. The magnesium alloy according to claim 1 or 2, characterized in that the zinc content, relative to the total weight of the magnesium alloy, is 1 to 5 wt.-%.

4. The magnesium alloy according to any one of claims 1 to 3, characterized in that the manganese content, relative to the total weight of the magnesium alloy, is 0.1 to 1 wt.-%.

5. The magnesium alloy according to any one of claims 1 to 4, characterized in that the copper content, relative to the total weight of the magnesium alloy, is 0.5 to 1 wt.-%.

6. The magnesium alloy according to any one of claims 1 to 5, characterized in that it further contains nickel, iron and/or silicon.

7. The magnesium alloy according to claim 6, characterized in that the nickel content, relative to the total weight of the magnesium alloy, is less than 0.005 wt.-%.

8. The magnesium alloy according to claim 6 or 7, characterized in that the iron content, relative to the total weight of the magnesium alloy, is less than 0.01 Wt.-%.

9. The magnesium alloy according to any one of claims 6 to 8, characterized in that the silicon content, relative to the total weight of the magnesium alloy, is less than 0.1 wt.-%.

10. A method for the preparation of a magnesium alloy according to any one of claims 1 to 9, characterized in that magnesium scrap or impure, copper-containing precursors are melted and the level of constituents of the alloy is then set according to any one of claims 1 to 9.

11. Use of a magnesium alloy according to any one of claims 1 to 9 as a casting and/or kneading material.