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(54) **DEGRADABLE MG ALLOY**

ABBAUBARE MG-LEGIERUNG

ALLIAGE DE MG DÉGRADABLE

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(56) References cited:  
**EP-A1- 2 116 622** **EP-A2- 1 847 626**  
**CN-A- 103 397 235** **CN-A- 103 397 235**  
**JP-A- 2011 021 274** **US-A1- 2012 156 087**  
**US-A1- 2016 024 619** **US-A1- 2016 024 619**

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**Description**

## TECHNICAL FIELD

**[0001]** The present invention relates to a degradable Mg alloy whose corrosion rate can be arbitrarily adjusted.

## BACKGROUND ART

**[0002]** AM type Mg alloys in which Al and Mn are added and AZ type Mg alloys in which Al, Mn, and Zn are added are known as general purpose magnesium alloys (Mg alloys). A variety of Mg alloys having improved corrosion resistance by adding elements other than these elements or by adjusting the manufacturing method have been proposed.

**[0003]** Patent Document 1 below describes an Mg alloy in which Mg is from 67 to 85% (atomic ratio), Si is from 5 to 20% (atomic ratio), and the balance is Ni. Patent Document 1 describes that an amorphous powder or a nanocrystal powder is produced by a mechanical alloying method (mechanical alloying) using a raw material powder having such a composition. Such an Mg alloy shows excellent corrosion resistance, and is an alloy which is resistant to degradation and corrosion.

**[0004]** Meanwhile, Patent Document 2 below describes an Mg alloy containing Al: from 0.1% to 15.0%; Li: from 0.01% to 10.0%; Ca: from 0.1% to 10.0%; Zn: from 0.1% to 6.5%; In: from 0.01% to 3.0%; Ga: from 0.0% to 2.0%; Si: from 0.1% to 1.5%; Mn: from 0.0% to 0.8%; Zr: from 0.0% to 1.0%; Fe: from 0.016% to 1.0%; Ni: from 0.016% to 5.0%; and Cu: from 0.15% to 5.0%, by mass ratio. This is a degradable Mg alloy used as a member which is introduced into oil wells and natural gas wells to temporarily support the structure and is degraded when it becomes unnecessary. This contains a variety of elements as essential elements in order to have degradability as well as strength characteristics needed for supporting the structure under high pressure environment.

**[0005]** Patent Document 3 below also describes as a degradable Mg alloy an alloy containing Al: from 3.0% to 7.0%; Li: from 0.01% to 1.0%; Ca: from 0.5% to 1.0%; Y: from 0.3% to 2.3%; Si: from 0.3% to 2.0%; Ni: from 0.016% to 0.8%; Cu: from 0.05% to 1.0%; and Fe: from 0.016% to 1.0%, by mass ratio.

**[0006]** Meanwhile, Patent Document 4 below describes an Mg alloy for casting containing Cu: from 0.5% to 10%, Ca: from 0.01 to 3%, and Al: from 0 to 3%, by mass ratio. Patent Document 4 describes an Mg alloy that has excellent creep resistance by containing Cu and Ca and is suitable for use under high temperature environment.

## RELATED ART DOCUMENTS

## Patent Documents

**[0007]**

Patent Document 1: JP2002-249801A

Patent Document 2: CN104004950A

Patent Document 3: CN104651691A

Patent Document 4: WO2008/072435

## SUMMARY OF THE INVENTION

## PROBLEMS TO BE SOLVED BY THE INVENTION

**[0008]** However, degradable Mg alloys used for structural materials to be introduced in oil fields or natural gas fields need to have sufficient mechanical properties for withstanding underground high pressure environment. Meanwhile, since such degradable Mg alloys are introduced into unrecoverable environments, such alloys are desirably degraded without being left in the ground for a long time after the introduction. On the other hand, the degradable Mg alloy described in Patent Document 2 contains Si which has an adverse effect on elongation or toughness as an essential element. An extremely expensive In is contained as an essential element for use in a disposable member.

**[0009]** Likewise, the degradable Mg alloy described in Patent Document 3 uses Si which has an adverse effect on elongation or toughness as an essential element, and the minimum content of Si is higher than that of the degradable Mg alloy of Patent Document 2.

**[0010]** Furthermore, since these degradable Mg alloys described in Patent Documents 2 and 3 contain many kinds of essential elements, mechanical properties other than degradability are not easily secured, and the material itself tends to be expensive, which is problematic. It is inevitably difficult to arbitrarily control the corrosion rate because there are too many influencing elements.

**[0011]** On the other hand, the alloy of Patent Document 1 is an Mg alloy which has enhanced corrosion resistance by generating an amorphous phase or nanocrystals by using a mechanical alloying method, not by improving the degradability by the composition, and the use of the alloy is different.

**[0012]** With respect to the alloy of Patent Document 4, degradation and corrosion characteristics are not taken into consideration at all and Ca, which is strongly influential to corrosion characteristics, is also added, and therefore, it is also difficult to control the corrosion rate.

**[0013]** Accordingly, an object of the present invention is to provide a degradable Mg alloy having a composition having a little kinds of essential elements and having strength required for a structural member that can withstand high pressure and capable of arbitrarily controlling the corrosion rate.

**[0014]** In the present invention, the above problem is solved by a degradable Mg alloy containing:

3.9% by mass or more and 14.0% by mass or less of Al and 0.1% by mass or more and 0.6% by mass or less of Mn; 0.01% by mass or more and 10.0% by mass or less of Ni, Cu, or both of Ni and Cu; and the balance composed of Mg and inevitable impurities. The Mg alloy satisfying these range conditions has sufficient tensile strength properties. Furthermore, the Mg alloy has the property that the corrosion rate can be adjusted by the blending amount of Ni and Cu. The alloy may contain 0.0% by mass or more and 1.0% by mass or less of Zn.

**[0015]** The content of Ni is 0.01% by mass or more and 0.3% by mass or less. When the content of Ni is in the range of 0.01 % by mass or more and 0.3% by mass or less, a correlation is established to such an extent that the relationship between the content of Ni and the corrosion rate can be approximated to a linear function.

**[0016]** The content of Cu is 1.5% by mass or more and 7% mass or less. When the content of Ni is in the range of 1.5% by mass or more and 7.0% by mass or less, a correlation is established to such an extent that the relationship between the content of Cu and the corrosion rate can be approximated to a linear function.

## EFFECTS OF THE INVENTION

**[0017]** The degradable Mg alloy has sufficient mechanical strength while requiring a few kinds of essential elements, the corrosion rate can be adjusted according to the content of Ni and Cu, and the life of a degradable structural material using the degradable Mg alloy can be arbitrarily adjusted.

## BRIEF DESCRIPTION OF THE DRAWINGS

### [0018]

Fig. 1 is a graph of the corrosion rate with respect to the content of Ni in Examples.

Fig. 2 is a schematic diagram of the shape of a test material used in Examples.

Fig. 3 is a graph of the corrosion rate with respect to the content of Cu in Examples.

## MODE FOR CARRYING OUT THE INVENTION

**[0019]** Hereinafter, the present invention will be described in detail.

**[0020]** The present invention relates to a degradable Mg alloy capable of accelerating corrosion at high speed mainly in an aqueous environment in which water is interposed, a degradable structural member using the same, and a method of adjusting the corrosion rate of the degradable structural member.

**[0021]** The content of Al in the degradable Mg alloy according to the present invention is needed to be 3.9% by mass or more, and is preferably 7.0% by mass or more. The degradable Mg alloy has an effect of improving the strength by addition of Al, but when the content of Al is less than 3.9% by mass, such an effect is insufficient. When the strength is insufficient, the durability in a high-pressure environment is insufficient, and there is a high possibility that a member is destroyed before being degraded according to the adjusted degradation rate described below. On the other hand, the Al content is required to be 14.0% by mass or less, and is preferably 13.0% by mass or less. This is because when too much Al is used, not only the toughness (elongation) decreases but also there is a fear that the strength tends to decrease due to easy creep deformation in a medium to high temperature environment, and when the content of Al exceeds 14.0% by mass, there is a possibility that the shape of a member is difficult to be maintained.

**[0022]** The content of Mn in the degradable Mg alloy according to the present invention needs to be 0.1% by mass or more. Mn has an effect of removing some elements contained as impurities, and when the Mn is too small, the corrosion rate of the degradable Mg alloy greatly deviates from the value adjusted by Ni and Cu, which will be described later, and the controllability may be insufficient. On the other hand, the content of Mn needs to be 0.6% by mass or less, and is preferably 0.5% by mass or less. This is because when the content of Mn is too large, precipitation of a large amount

of an intermetallic compound of Mn and Al and an Mn simple substance will make a member brittle and the strength will be lowered.

**[0023]** The degradable Mg alloy according to the present invention may contain Zn in an amount of 1.0% by mass or less. Zn has an effect of improving a strength (particularly proof stress). When the content of Zn exceeds 1.0% by mass, ductility is insufficient, not only a process of forming a structural member such as extrusion processing and forging processing becomes difficult but also an effect of suppressing the corrosion rate appears, which is not preferable for a degradable structural member. On the other hand, Zn may not be contained, or Zn may be contained within the range of inevitable impurities contained in the alloy, which will be described below.

**[0024]** The degradable Mg alloy according to the present invention needs to contain both Ni and Cu. By including predetermined amounts of Ni and Cu, it is possible to arbitrarily adjust the corrosion rate in the aqueous environment of an alloy. In other words, it is possible to degrade a degradable structural member made of the degradable Mg alloy at a timing when the member becomes unnecessary. Although both Ni and Cu contribute to degradability, their influences are different from each other, and therefore the range of desirable content that can be adjusted to the optimum corrosion rate varies.

**[0025]** The degradable Mg alloy according to the present invention contains Ni, wherein the content is required to be 0.01% by mass or more. Ni has a greater effect on corrosion rate than Cu, but when the content is less than 0.01% by mass, it is still difficult to obtain sufficient effect as a degradable Mg alloy. On the other hand, the content of Ni is 0.3% by mass or less. Even when Ni is excessively contained, the corrosion rate is not extremely improved, and the physical properties are difficult to control. When too much Ni is used, the cost burden becomes too large.

**[0026]** When the amount of Ni contained in the degradable Mg alloy is in the range of 0.01% by mass or more and 0.3% by mass or less, the corrosion rate (mg/cm<sup>2</sup>/day) can be linearly approximated to the logarithm of the content of Ni. In other words, it is possible to adjust the corrosion rate of a degradable structural member produced using the degradable Mg alloy according to the content of Ni. By utilizing this property, the time until a degradable structural member produced using the degradable Mg alloy to collapse can be set with high accuracy. Herein, the "corroded state" which is a criterion of the above-described corrosion rate means a state of being decomposed from a mass of the original alloy, being dissolved or dispersed in an aqueous solvent, and being not integral with the mass.

**[0027]** When the degradable Mg alloy according to the present invention contains Cu, the content is required to be 1.5% by mass or more. Cu has less influence on the corrosion rate than Ni, and when the content is less than 1.5% by mass, it is difficult to obtain a sufficient effect as a degradable Mg alloy. On the other hand, the Cu content is 7% by mass or less. Even when Cu is excessively contained, the corrosion rate is not extremely improved, and the physical properties are difficult to control.

**[0028]** When the amount of Cu contained in the degradable Mg alloy is in the range of 1.5% by mass or more to 7.0% by mass or less, the corrosion rate (mg/cm<sup>2</sup>/day) can be linearly approximated to the logarithm of the content of Cu. In other words, it is possible to adjust the corrosion rate of a degradable structural member produced using the degradable Mg alloy according to the content of Cu. By utilizing this property, the time until a degradable structural member produced using the degradable Mg alloy to collapse can be set with high accuracy. Particularly, since Cu has less influence than Ni, adjustment with high precision becomes easy.

**[0029]** The degradable Mg alloy according to the present invention contains both Ni and Cu, and each content may be appropriately adjusted to set an optimum corrosion rate. Since the degree of influence depends on the content, it is preferable to use this difference in adjustment. For example, fine adjustment can be made finely with Cu having a relatively small influence by the content while securing a sufficient corrosion rate with Ni having a relatively strong influence.

**[0030]** The degradable Mg alloy according to the present invention may contain other elements than the above elements as inevitable impurities. These inevitable impurities are inevitably contained contrary to intention due to manufacturing problems or problems on raw materials. Examples thereof include an element such as Ag, Fe, Pb, Cd, Se, Y, Si, Li, In, Ca, Ti, Zr, Ga, or Mm (misch metal). The contents of inevitable impurities need to be in a range not inhibiting characteristics of the degradable Mg alloy according to the present invention, and the content per element is preferably less than 0.2% by mass, and more preferably less than 0.1% by mass. Among them, the contents of Si, Li, In, and Ca are preferably less than 0.1% by mass, and more preferably less than 0.05% by mass. The smaller the content of any element which is an inevitable impurity, the more preferable, because this reduces uncertain factors to be considered in adjusting the corrosion rate by Ni and Cu. It is particularly preferable that the content is less than the detection limit.

**[0031]** The degradable Mg alloy can be prepared by a general method using raw materials containing the above elements in such a manner that the respective contents fall within the above range in terms of % by mass and the alloy has a desired corrosion rate. The above value of the mass% unit is not based on the raw material, but is based on a prepared alloy or a degradable structural member produced by casting, sintering or the like. It is noted that when a degradable structural member which is particularly required to have strength is produced, it is preferable to perform processing such as extruding or forging to reduce the crystal size of the alloy texture to increase the strength. When the degradable Mg alloy is cast, the crystal size is about from 100 to 200 μm, and when the crystal size is reduced to about

10  $\mu\text{m}$  or more and 20  $\mu\text{m}$  or less by the above extrusion, forging, wroughting, or the like, the strength is improved, which is preferable. Even when the crystal size is miniaturized in this manner, the corrosion rate does not change significantly and the corrosion rate can be arbitrarily adjusted depending on the contents of Ni and Cu.

[0032] In particular, when Ni is limited to a range of 0.01% by mass or more and 0.3% by mass or less and Cu is limited to a range of 1.5% by mass or more and 7.0% by mass or less, an increase in the corrosion rate can be suitably approximated to a linear function with respect to an increase in the logarithms of the contents of Ni and Cu. By utilizing this property, the fluctuation of the content of Al, Mn, and inevitable impurities is made as small as possible, the corrosion rate of the decomposable Mg alloy corresponding to the limited range of the content of Ni or Cu is measured for a plurality of points, the inclination and intercept of the corrosion rate with respect to the logarithm of the content of Ni or Cu is calculated, the content of Ni or Cu corresponding to the required corrosion rate is determined, and the composition of the degradable Mg alloy suitable for a degradable structural member to be produced may be determined. For calculation of slope and intercept, a general method such as a least-squares method may be used. Although it is possible to make a linear approximation to some extent even when the contents are less than the above-mentioned limited range, and when the amount of Ni or Cu is too small, it becomes difficult to adjust the actual content with high precision. On the other hand, when the amount of Ni or Cu is too large, the deviation from the linear function is unignorable.

[0033] The degradable structural member according to the present invention has a smaller coefficient of grain size (the above-mentioned slope) than one produced by casting when the grain size is reduced by applying pressure by a technique such as extrusion, and adjustment of the corrosion rate is easier to be performed.

[0034] Examples of a product to which a degradable structural member made of the degradable Mg alloy according to the present invention is applied include tools for drilling oil wells, natural gas wells, and the like. Since such a product is introduced deep under the ground, a strength that can withstand a high pressure environment is required. On the other hand, when such a product becomes unnecessary, the product can be removed by being corroded and degraded at an appropriate timing by being exposed to an aqueous solution introduced for excavation work without taking time to take out from deep underground.

#### Examples

##### < Ni-containing Alloy Test >

[0035] An example in which the degradable Mg alloy was actually prepared and the corrosion rate was measured is shown. First, for an Ni-containing alloy, raw materials were prepared so as to have the composition shown in Table 1, heated to 700°C, and a test specimen was produced by casting. For some examples (Examples 1 to 3, 6, 7, 11, and 12), test specimens subjected to extrusion processing under the conditions of a die temperature of 400°C and a billet temperature of 350°C were prepared. Elements other than those described are Mg and inevitable impurities each less than 0.1% by mass. Each test specimen was immersed in a 2% KCl aqueous solution (93°C), and the corrosion weight loss (mg) of the specimen and the area before and after the test were measured to calculate the corrosion rate per day (mg/cm<sup>2</sup>/day: mcd). The values are shown in Table 1. In the table, "as-cast" is the measurement result of the test specimen by casting and "as-extruded" is the measurement result of the test specimen by extrusion processing.

[Table 1] (None of the example alloys fall within the scope of the present invention)

|           | Composition           |                       |                       | Corrosion rate<br>[mg/cm <sup>2</sup> /day] |             |
|-----------|-----------------------|-----------------------|-----------------------|---------------------------------------------|-------------|
|           | Ni content<br>[mass%] | Al content<br>[mass%] | Mn content<br>[mass%] | as-cast                                     | as-extruded |
| Example 1 | 0.011                 | 8.09                  | 0.20                  | 374.8                                       | 513.7       |
| Example 2 | 0.024                 | 8.32                  | 0.18                  | 915.2                                       | 581.4       |
| Example 3 | 0.031                 | 8.00                  | 0.18                  | 892.9                                       | 741         |
| Example 4 | 0.064                 | 8.09                  | 0.15                  | 2115.9                                      | 1112.9      |
| Example 5 | 0.025                 | 8.37                  | 0.17                  | 1098.1                                      | 762         |
| Example 6 | 0.201                 | 11.14                 | 0.18                  | 2196.6                                      | 1470.8      |
| Example 7 | 0.261                 | 13.27                 | 0.17                  | 2465.9                                      | 1546.2      |
| Example 8 | 0.030                 | 7.99                  | 0.18                  | 1030.5                                      | -           |
| Example 9 | 0.047                 | 8.03                  | 0.17                  | 1403.9                                      | -           |

(continued)

|                       | Composition           |                       |                       | Corrosion rate<br>[mg/cm <sup>2</sup> /day] |             |
|-----------------------|-----------------------|-----------------------|-----------------------|---------------------------------------------|-------------|
|                       | Ni content<br>[mass%] | Al content<br>[mass%] | Mn content<br>[mass%] | as-cast                                     | as-extruded |
| Example 10            | 0.068                 | 8.39                  | 0.15                  | 1773.9                                      | -           |
| Example 11            | 0.110                 | 3.92                  | 0.18                  | 1989.1                                      | 735.2       |
| Example 12            | 0.153                 | 6.63                  | 0.17                  | 1402.9                                      | 838.6       |
| Comparative Example 1 | 0.002                 | 8.16                  | 0.20                  | 4.7                                         | -           |
| Comparative Example 2 | 0.009                 | 8.14                  | 0.18                  | 63.5                                        | -           |
| Comparative Example 3 | < 0.0001              | 5.99                  | 0.24                  | 7.0                                         | -           |

**[0036]** Fig. 1 shows a graph in which Ni contents are plotted on a common logarithm scale on the horizontal axis and the corrosion rate on the vertical axis for Examples 1 to 10. However, with respect to Examples 8 to 10, only data of casting is shown.

**[0037]** Linear approximation by the least-squares method was performed on the logarithm of Ni content and the corrosion rate value. In the casting "as-cast", the section was  $3.4 \times 10^3$ , and the slope was  $1.5 \times 10^3$ . This showed that, when casting a degradable structural material containing about from 8 to 13% by mass of Al and about 0.18% by mass of Mn, the corrosion rate can be adjusted by the content of Ni according to the following Formula (1). In the extrusion processing "as-extruded", the section was  $2.0 \times 10^3$ , and the slope was  $8.1 \times 10^2$ . This showed that, when a degradable structural material containing about from 8 to 13% by mass of Al and about 0.18% by mass of Mn was produced by extrusion processing, the corrosion rate can be adjusted by the content of Ni according to the following Formula (2). These approximate straight lines are also shown in Fig. 1. It was shown that, since, particularly by performing extrusion processing, the coefficient related to an increase in the corrosion rate was suppressed as compared with the case of casting, control of the corrosion rate became easier.

$$\text{corrosion rate (mcd: as-cast)} = 1.5 \times 10^3 \times \log_{10}(\text{Ni}) + 3.4 \times 10^3 \cdots (1)$$

$$\text{corrosion rate (mcd: as-extruded)} = 8.1 \times 10^2 \times \log_{10}(\text{Ni}) + 2.0 \times 10^3 \cdots (2)$$

**[0038]** Further, the corrosion rates of Examples 11 and 12 in which the amount of Al was reduced were measured, and the corrosion rate was measured in the same manner as in Example 1. As a result, values of the corrosion rate as a degradable Mg alloy were practical. However, according to the above-described Formula (1) obtained from Examples 1 to 10 in which the above-mentioned Al was measured in the range of about from 8 to 13% by mass, when Ni = 0.110% by mass and 0.153% by mass, the calculated value of the corrosion rate of as-cast should be  $2.0 \times 10^3$  mcd and  $2.2 \times 10^3$  mcd, respectively, and the calculated corrosion rate of as-extruded should be  $1.2 \times 10^3$  mcd and  $1.3 \times 10^3$  mcd, respectively. The actual values of Examples 11 and 12 were values which were particularly largely deviated from those of the extruded materials as compared with these calculated values. Thus, it is shown that, since the corrosion rate is not approximated linearly depending on the variation of the value of Al, it is desirable to unify the Al content to some extent in order to adjust the corrosion rate value with high accuracy.

**[0039]** On the other hand, in Comparative Examples 1 to 3 in which the content of Ni was less than 0.01% by mass, the corrosion rate was remarkably low, and a corrosion rate improving effect by addition of Ni was not sufficiently obtained.

**[0040]** In addition, for some Examples, the tensile strength, 0.2% proof stress, elongation after extrusion were measured. The measurement method is shown below and the results are shown in Table 2. In all cases, the tensile strength exceeded 275 MPa, and sufficient tensile properties and corrosion rate were exhibited as degradable structural materials to be introduced into oil fields, and the like.

## &lt; Tensile Test Method &gt;

**[0041]** A sample extruded as a round bar of  $\phi 16$  was processed to be a 14A test piece prescribed in JIS Z2241 (ISO6892-1). The specific shape is as shown in Fig. 2. This test piece is a proportional test piece in which the original cross section  $S_0$  and the original gauge length  $L_0$  of a parallel portion have a relation of  $L_0 = 5.65 \times S_0^{0.5}$ . The diameter  $d_0$  of a rod-shaped portion was 10 mm, the original gauge length  $L_0$  was 50 mm, the length  $L_c$  of a cylindrical parallel portion was 70 mm, and the radius  $R$  of a shoulder portion was 15 mm ( $L_0 = 5.65 \times (5 \times 5 \times \pi)^{0.5} = 50.07$ ).

**[0042]** For this test piece, a tensile test was carried out in accordance with JIS Z2241 (ISO6892-1), and the tensile strength:  $R_m$  (MPa), 0.2% proof stress:  $R_{p0.2}$  (MPa), and elongation:  $A$  (%) were evaluated as follows. The tensile strength was defined as the maximum test force  $F_m$  that was tolerated during the test until the test piece showed discontinuous yield in the test. The 0.2% proof stress is a stress when the plastic elongation is equal to 0.2% of the gauge distance  $L_e$  of an extensometer. The elongation is a value obtained by expressing the permanent elongation of a test piece after being tested until the test piece breaks as a percentage with respect to the original gauge length  $L_0$ . All of Examples showed favorable values.

[Table 2] (None of the example alloys fall within the scope of the invention)

|            | Composition        |                    |                    | Tensile properties (as-extruded) |                         |                |
|------------|--------------------|--------------------|--------------------|----------------------------------|-------------------------|----------------|
|            | Ni content [mass%] | Al content [mass%] | Mn content [mass%] | Tensile strength [MPa]           | 0.2% proof stress [MPa] | Elongation [%] |
| Example 1  | 0.011              | 8.09               | 0.20               | 306.8                            | 209.0                   | 17.8           |
| Example 2  | 0.024              | 8.32               | 0.18               | 311.7                            | 218.5                   | 16.0           |
| Example 3  | 0.031              | 8.00               | 0.18               | 310.8                            | 216.9                   | 17.3           |
| Example 6  | 0.201              | 11.14              | 0.18               | 325.7                            | 243.6                   | 13.3           |
| Example 7  | 0.261              | 13.27              | 0.17               | 333.2                            | 256.9                   | 9.6            |
| Example 11 | 0.110              | 3.92               | 0.18               | 280.3                            | 204.0                   | 22.9           |
| Example 12 | 0.153              | 6.63               | 0.17               | 300.3                            | 206.3                   | 19.5           |

## &lt; Cu-containing Alloy Test &gt;

**[0043]** A test specimen was prepared by casting so as to have the composition shown in Table 3 by the same procedure as the Ni-containing alloy test described above, and the corrosion rate was measured by the same procedure. The results are shown in Table 3. For Examples 13 to 16, the corrosion rate after forging (as-forged) at a sample temperature of 430°C was measured. Further, in Examples 17 to 23, test specimens were prepared by extrusion processing in the same manner as in the above Examples 1 to 7, and the corrosion rate was measured by the same procedure. The results are also shown in Table 3. In this Cu-containing alloy test, the value of Cu is not a measured value after the alloy was prepared but a target value at the time of addition of a material.

[Table 3] (All of the alloys fall outside of the scope of the invention)

|            | Composition        |                    |                    | Corrosion rate [mg/cm <sup>2</sup> /day] as-cast | Corrosion rate [mg/cm <sup>2</sup> /day] |           |
|------------|--------------------|--------------------|--------------------|--------------------------------------------------|------------------------------------------|-----------|
|            | Cu content [mass%] | Al content [mass%] | Mn content [mass%] |                                                  | as-extruded                              | as-forged |
| Example 13 | 1.0                | 5.9                | 0.19               | 359.8                                            | -                                        | 470.4     |

(continued)

|                          | Composition           |                          |                       | Corrosion rate<br>[mg/cm <sup>2</sup> /day] as-cast | Corrosion rate<br>[mg/cm <sup>2</sup> /day] |               |
|--------------------------|-----------------------|--------------------------|-----------------------|-----------------------------------------------------|---------------------------------------------|---------------|
|                          | Cu content<br>[mass%] | Al<br>content<br>[mass%] | Mn content<br>[mass%] |                                                     | as-<br>extruded                             | as-<br>forged |
| Example 14               | 3.0                   | 6.1                      | 0.17                  | 1896.2                                              | -                                           | 1538.7        |
| Example 15               | 5.0                   | 6.4                      | 0.18                  | 3551.5                                              | -                                           | 2557.4        |
| Example 16               | 7.0                   | 6.5                      | 0.18                  | 3176.5                                              | -                                           | 3078.1        |
| Example 17               | 1.5                   | 8.1                      | 0.20                  | 269.6                                               | 213.4                                       | -             |
| Example 18               | 2.0                   | 8.1                      | 0.16                  | 506.7                                               | 374.1                                       | -             |
| Example 19               | 2.5                   | 8.1                      | 0.18                  | 791.5                                               | 496.7                                       | -             |
| Example 20               | 3.0                   | 8.3                      | 0.21                  | 954.6                                               | 555.8                                       | -             |
| Example 21               | 4.0                   | 8.5                      | 0.17                  | 1561.9                                              | 749.4                                       | -             |
| Example 22               | 5.0                   | 8.1                      | 0.15                  | 1941.1                                              | 1032.3                                      | -             |
| Example 23               | 7.0                   | 8.3                      | 0.26                  | 2214.9                                              | 1274.5                                      | -             |
| Comparative<br>Example 4 | < 0.001               | 6.0                      | 0.24                  | 7.0                                                 | -                                           | -             |

**[0044]** Furthermore, Fig. 3 shows a graph in which Cu contents are plotted on a logarithm scale on the horizontal axis and the corrosion rate on the vertical axis for Examples 17 to 23. Linear approximation by the least-squares method was performed on the logarithm of Cu content and the corrosion rate value. In the casting "as-cast", the section was  $-4.0 \times 10^2$ , and the slope was  $3.1 \times 10^3$ . This showed that, when casting a degradable structural material containing about 8.0 by mass of Al and about 0.18% by mass of Mn, the corrosion rate can be adjusted by the content of Cu according to the following Formula (3). In the extrusion processing "as-extruded", the section was  $-1.2 \times 10^2$ , and the slope was  $1.6 \times 10^3$ . This showed that, when a degradable structural material containing about 8.0% by mass of Al and about 0.18% by mass of Mn was produced by extrusion processing, the corrosion rate can be adjusted by the content of Cu according to the following Formula (4). These approximate straight lines are also shown in Fig. 3. As in the case of Ni, also in the Cu-containing alloy, it was shown that, since, by performing extrusion processing, the coefficient related to an increase in the corrosion rate was suppressed as compared with the case of casting, control of the corrosion rate became easier.

$$\text{corrosion rate (mcd: as-cast)} = 3.1 \times 10^3 \times \log_{10}(\text{Cu}) - 4.0 \times 10^2 \cdots (3)$$

$$\text{corrosion rate (mcd: as-extruded)} = 1.6 \times 10^3 \times \log_{10}(\text{Cu}) - 1.2 \times 10^2 \cdots (4)$$

**[0045]** For Examples 17 to 23, the same tensile test as above was carried out. As a result, all Examples showed favorable values.

[Table 4] (Noe of the example alloys fall within the scope of the present invention)

|               | Composition           |                       |                       | Tensile properties (as-extruded) |                           |                   |
|---------------|-----------------------|-----------------------|-----------------------|----------------------------------|---------------------------|-------------------|
|               | Cu content<br>[mass%] | Al content<br>[mass%] | Mn content<br>[mass%] | Tensile<br>strength<br>[MPa]     | 0.2%proof stress<br>[MPa] | Elongation<br>[%] |
| Example<br>17 | 1.5                   | 8.1                   | 0.20                  | 309.5                            | 216.7                     | 16.9              |

(continued)

|               | Composition           |                       |                       | Tensile properties (as-extruded) |                           |                   |
|---------------|-----------------------|-----------------------|-----------------------|----------------------------------|---------------------------|-------------------|
|               | Cu content<br>[mass%] | Al content<br>[mass%] | Mn content<br>[mass%] | Tensile<br>strength<br>[MPa]     | 0.2%proof stress<br>[MPa] | Elongation<br>[%] |
| Example<br>18 | 2.0                   | 8.1                   | 0.16                  | 302.6                            | 204.6                     | 16.8              |
| Example<br>19 | 2.5                   | 8.1                   | 0.18                  | 301.8                            | 206.0                     | 15.9              |
| Example<br>20 | 3.0                   | 8.3                   | 0.21                  | 298.9                            | 201.2                     | 16.6              |
| Example<br>21 | 4.0                   | 8.5                   | 0.17                  | 289.6                            | 193.7                     | 16.4              |
| Example<br>22 | 5.0                   | 8.1                   | 0.15                  | 283.3                            | 190.0                     | 15.9              |
| Example<br>23 | 7.0                   | 8.3                   | 0.26                  | 279.2                            | 185.9                     | 14.7              |

**Claims****1.** A degradable Mg alloy consisting of:

3.9% by mass or more and 14.0% by mass or less of Al and 0.1% by mass or more and 0.6% by mass or less of Mn;  
0.01% by mass or more and 10.0% by mass or less of both of Ni and Cu, wherein the content of Ni is 0.01%  
by mass or more and 0.3% by mass or less, wherein the content of Cu is 1.5% by mass or more and 7.0% by  
mass or less;

wherein the balance is composed of Mg and inevitable impurities, and  
wherein the degradable Mg alloy optionally further comprises 1.0% by mass or less of Zn.

**2.** A degradable structural member consisting of the degradable Mg alloy according to claim 1.**3.** A method of adjusting the corrosion rate of a degradable structural member, wherein the corrosion rate is adjusted by the content of Ni and Cu in the degradable structural member using the degradable Mg alloy according to claim 1.**4.** Use of a degradable Mg alloy according to claim 1 for adjusting the corrosion rate of the degradable structural member, wherein the corrosion rate is adjusted by the content of Ni and Cu.**Patentansprüche****1.** Abbaubare Mg-Legierung, bestehend aus:

3,9 Massen-% oder mehr und 14,0 Massen-% oder weniger von Al und 0,1 Massen-% oder mehr und 0,6  
Massen-% oder weniger von Mn;  
0,01 Massen-% oder mehr und 10,0 Massen-% oder weniger von sowohl Ni als auch Cu, wobei der Gehalt an  
Ni 0,01 Massen-% oder mehr und 0,3 Massen-% oder weniger beträgt, wobei der Gehalt an Cu 1,5 Massen-  
% oder mehr und 7,0 Massen-% oder weniger beträgt;

wobei der Rest aus Mg und unvermeidbaren Verunreinigungen zusammengesetzt ist, und  
wobei die abbaubare Mg-Legierung optional weiter 1,0 Massen-% oder weniger von Zn umfasst.

**2.** Abbaubares Strukturbauteil, bestehend aus der abbaubaren Mg-Legierung nach Anspruch 1.

3. Verfahren zum Einstellen der Korrosionsrate eines abbaubaren Strukturbauteils, wobei die Korrosionsrate durch den Gehalt an Ni und Cu im abbaubaren Strukturbauteil unter Verwenden der abbaubaren Mg-Legierung nach Anspruch 1 eingestellt wird.

4. Verwendung einer abbaubaren Mg-Legierung nach Anspruch 1 zum Einstellen der Korrosionsrate des abbaubaren Strukturbauteils, wobei die Korrosionsrate durch den Gehalt an Ni und Cu eingestellt wird.

## Revendications

1. Alliage de Mg dégradable constitué de :

3,9 % en masse ou plus et 14,0 % en masse ou moins d'Al et 0,1 % en masse ou plus et 0,6 % en masse ou moins de Mn ;

0,01 % en masse ou plus et 10,0 % en masse ou moins des deux éléments Ni et Cu, la teneur en Ni étant de 0,01 % en masse ou plus et 0,3 % en masse ou moins, la teneur en Cu étant de 1,5 % en masse ou plus et 7,0 % en masse ou moins ;

le reste étant composé de Mg et d'impuretés inévitables, et

l'alliage de Mg dégradable comprenant éventuellement, en outre, 1,0 % en masse ou moins de Zn.

2. Élément structural dégradable constitué de l'alliage de Mg dégradable selon la revendication 1.

3. Procédé de réglage de la vitesse de corrosion d'un élément structural dégradable, la vitesse de corrosion étant réglée par la teneur en Ni et Cu dans l'élément structural dégradable utilisant l'alliage de Mg dégradable selon la revendication 1.

4. Utilisation d'un alliage de Mg dégradable selon la revendication 1 pour régler la vitesse de corrosion de l'élément structural dégradable, la vitesse de corrosion étant réglée par la teneur en Ni et Cu.

FIG. 1

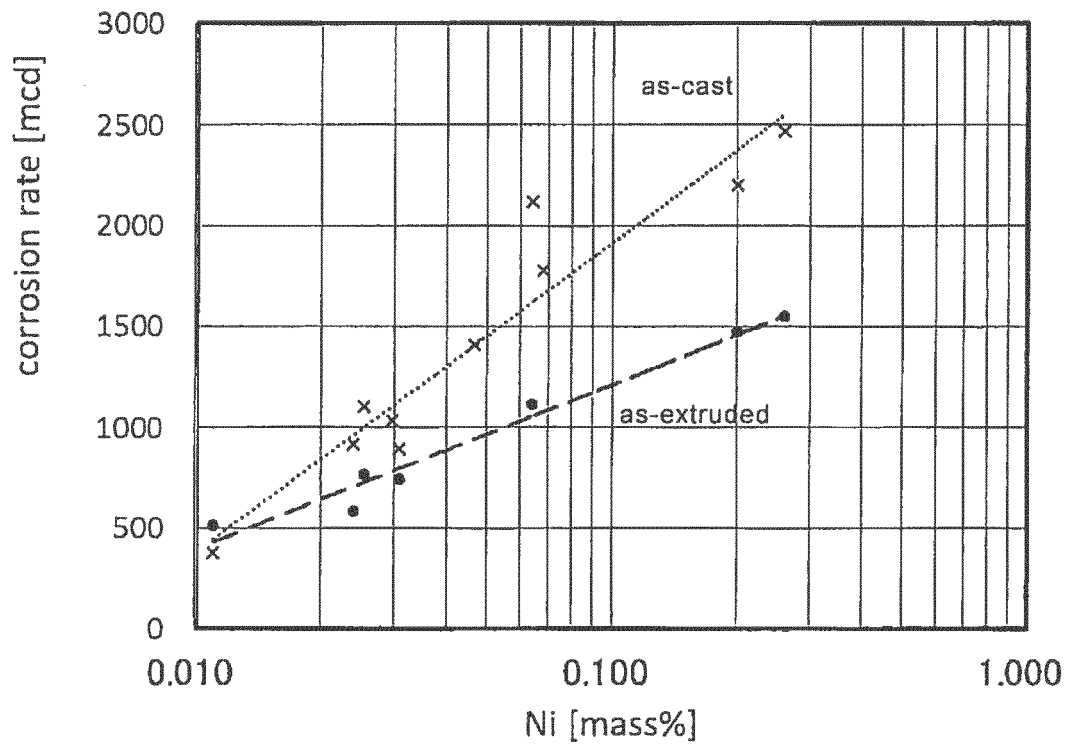


FIG. 2

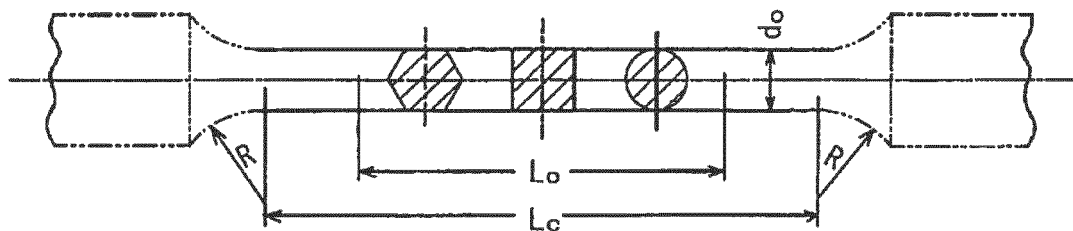
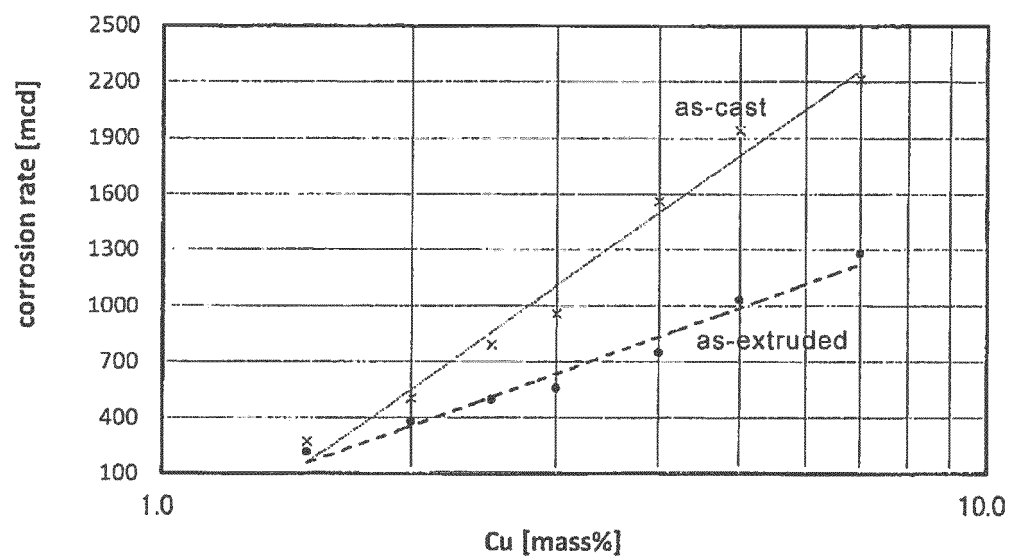


FIG. 3



**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 2002249801 A [0007]
- CN 104004950 A [0007]
- CN 104651691 A [0007]
- WO 2008072435 A [0007]