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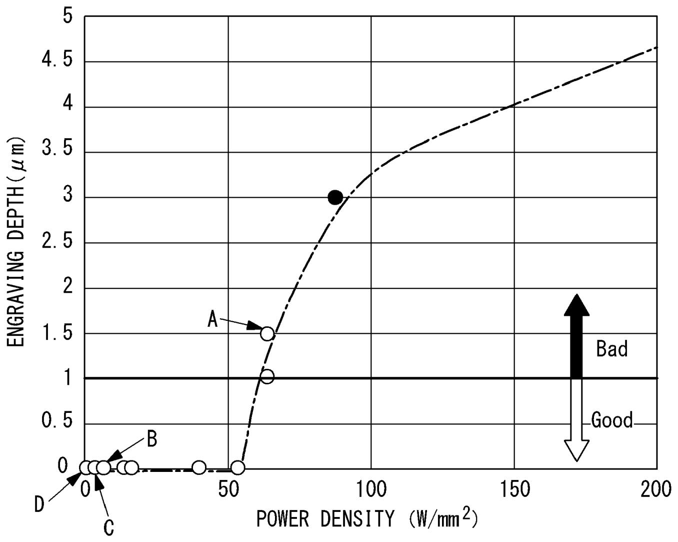
(54) **SURFACE MODIFICATION METHOD OF MG-AL-CA BASED ALLOY**

(57) The object is to provide a surface modification method of an Mg-Al-Ca based alloy that enables formation of an oxide film without damaging a base material. The surface modification method of an Mg-Al-Ca based alloy according to the present disclosure includes: immerging an Mg-Al-Ca based alloy in an alkali solution, and irradiating a surface of the Mg-Al-Ca based alloy immersed in the alkali solution with laser light at a power density that is less than or equal to 60 W/mm^2 and a heat input amount that is less than or equal to 5 mJ. It is preferable that the heat input amount be greater than or equal to 0.3 mJ and less than or equal to 4 mJ.

FIG. 3



EP 4 071 272 A1

Description

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

[0001] The present disclosure relates to a surface modification method of an Mg-Al-Ca based alloy.

2. DESCRIPTION OF RELATED ART

[0002] A magnesium (Mg) alloy is lightweight and has high strength but has lower corrosion resistance than an aluminum (Al) alloy or the like. Thus, the magnesium alloy needs to be used after surface treatment and coating are applied thereto.

[0003] A typical surface treatment method uses chemical conversion treatment and anodization treatment. The chemical conversion treatment causes a chemical treatment agent to act on the surface of a metal material to be treated, so as to chemically form an oxide film. The anodization treatment uses a metal material to be treated as an anode to carry current in a special electrolysis solution, so as to electrochemically produce an oxide film.

[0004] Japanese Patent Application Laid-Open No. 2008-291310 is an example of the related art.

[0005] In the chemical conversion treatment, a chemical liquid of hexavalent chromium or the like is used as a chemical treatment agent. Since hexavalent chromium has a high environmental load, there is a social demand for refraining from the use thereof. Furthermore, since a chemical liquid is used, there are problems of maintenance cost and disposal cost of the chemical liquid.

[0006] Japanese Patent Application Laid-Open No. 2008-291310 discloses a technique to form an oxide film without using hexavalent chromium. In Japanese Patent Application Laid-Open No. 2008-291310, magnesium alone (having 99.9% purity) is subjected to alkali treatment and then irradiated with laser to form a dense oxide film.

[0007] However, according to studies by the present inventors, it has been found that, when a metal material to be treated is replaced with an Mg-Al-Ca based alloy and an oxide film is formed by the method disclosed in Japanese Patent Application Laid-Open No. 2008-291310, a base material of the Mg-Al-Ca based alloy is damaged and the corrosion resistance is reduced.

BRIEF SUMMARY OF THE INVENTION

[0008] The present disclosure has been made in view of the above problems and intends to provide a surface modification method of an Mg-Al-Ca based alloy that enables formation of an oxide film without damaging a base material.

[0009] To solve the above problems, the surface modification method of an Mg-Al-Ca based alloy of the present disclosure employs the following measures.

[0010] The present disclosure provides a surface modification method of an Mg-Al-Ca based alloy. The surface modification method includes: immersing an Mg-Al-Ca based alloy in an alkali solution; and irradiating a surface of the Mg-Al-Ca based alloy immersed in the alkali solution with a laser light at a power density that is less than or equal to 60 W/mm^2 and a heat input amount that is less than or equal to 5 mJ.

[0011] The immersion in the alkali solution causes an $Mg(OH)_2$ film to be formed on the surface of the Mg-Al-Ca based alloy. When the $Mg(OH)_2$ film is irradiated with laser, a dehydration reaction occurs. This modifies the $Mg(OH)_2$ film to be a homogeneous and dense MgO film.

[0012] As long as laser light irradiation is performed under conditions where the power density and the heat input amount are within the range described above, the engraving depth does not exceed the thickness of the $Mg(OH)_2$ film. It is therefore possible to form an oxide film (MgO film) without damaging a base material. This can improve the corrosion resistance.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0013]

Fig. 1 illustrates a laser scanning method as an example.
Fig. 2 is a diagram illustrating a relationship between a power density and an engraving depth.
Fig. 3 is an enlarged view of Fig. 2.
Fig. 4 is a diagram illustrating a relationship between a heat input amount and a corrosion rate.
Fig. 5 is a diagram illustrating corrosion resistance evaluation results.

DETAILED DESCRIPTION OF THE INVENTION

[0014] One embodiment of a surface modification method of an Mg-Al-Ca based alloy according to the present invention will be described below with reference to the drawings.

[First Embodiment]

[0015] A surface modification method of an Mg-Al-Ca based alloy according to the present embodiment includes an alkali treatment step and a laser light irradiation step.

[Alkali Treatment Step]

[0016] An Mg-Al-Ca based alloy is immersed in an alkali solution for a predetermined time. This causes an $Mg(OH)_2$ film to be formed on the surface of the Mg-Al-Ca based alloy.

[0017] After the predetermined time of immersion, the Mg-Al-Ca based alloy on which the $Mg(OH)_2$ film is formed is taken out from the alkali solution.

[0018] The alkali solution contains at least one of magnesium hydroxide ($Mg(OH)_2$), sodium chloride (NaCl), magnesium chloride ($MgCl_2$), and sodium hydroxide (NaOH).

[0019] In the alkali solution, 0.001 g or greater and 0.012 g or less of $Mg(OH)_2$ may be contained as a chemical component in terms of mass in 1 litter of water. In the alkali solution, 0.001 g or greater and 300 g or less of NaCl may be contained as a chemical component in terms of mass in 1 litter of water. In the alkali solution, 0 g or greater and 400 g or less of $MgCl_2$ may be contained as a chemical component in terms of mass in 1 litter of water. In the alkali solution, 0 g greater and 500 g or less of NaOH may be contained as a chemical component in terms of mass in 1 litter of water.

[0020] The immersion time is longer than or equal to 10 minutes and shorter than or equal to 120 minutes, preferably, longer than or equal to 30 minutes and shorter than or equal to 60 minutes. When the immersion time is longer than or equal to 10 minutes, an $Mg(OH)_2$ film having a thickness of more than 1 μm may be formed. Even when immersion is performed for more than 120 minutes, it is not possible to expect a significant increase in the thickness of $Mg(OH)_2$ film.

[0021] The Mg-Al-Ca based alloy has a composition that contains Ca of a atom% and Al of b atom%, with the remaining part made of Mg. The symbols "a" and "b" meet Equations (1) to (3) below.

$$(1)\ 3 \leq a \leq 7$$

$$(2)\ 4.5 \leq b \leq 12\ (\text{preferably, } 8 \leq b \leq 12)$$

$$(3)\ 1.2 \leq b/a \leq 3.0$$

[0022] The Mg-Al-Ca based alloy may contain Mn of k atom%. The symbol "k" meets Equation (4) below. Mn is an element that improves at least one of corrosion resistance and incombustibility.

$$(4)\ 0 < k \leq 0.3\ (\text{preferably, } 0.01 \leq k \leq 0.05)$$

[0023] Even a small addition amount of Mn may improve corrosion resistance, while an increased addition amount of Mn causes a reduction in the ductility. To achieve both good corrosion resistance and ductility, it is desirable to suppress addition amount of Mn.

[0024] It is preferable that $(Mg, Al)_2Ca$ of c volume% be contained in the Mg-Al-Ca based alloy. The symbol "c" meets Equation (5) below. $(Mg, Al)_2Ca$ is dispersed in the alloy.

$$(5)\ 10 \leq c \leq 35\ (\text{preferably, } 10 \leq c \leq 30)$$

[0025] The Mg-Al-Ca based alloy may contain Si of x atom%. The symbol "x" meets Equation (6) below.

$$(6)\ 0.05 \leq x \leq 0.3\ (\text{preferably, } 0.05 \leq x \leq 0.1)$$

[0026] Inclusion of Si in the range described above can improve the ductility. If the ductility is reduced due to addition of Mn, the ductility can be improved by addition of Si.

[0027] The Mg-Al-Ca based alloy may contain Zn, a rare earth element (Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb), and an inevitable impurity. It is preferable that Zn content be greater than or equal to 0.001 atom% and less than or equal to 3 atom%. It is preferable that rare earth element content be greater than or equal to 0.1 atom% and less than or equal to 5 atom%.

[Laser Light Irradiation Step]

[0028] The Mg-Al-Ca based alloy on which the alkali treatment has been performed is irradiated with laser light by using a laser processing apparatus. The laser light is emitted under conditions where the power density is less than or equal to 60 W/mm^2 and the heat input amount is less than or equal to 5 mJ. The heat input amount is preferably greater than or equal to 0.3 mJ and less than or equal to 4 mJ, more preferably greater than or equal to 1 mJ and less than or equal to 4 mJ.

[0029] The laser processing apparatus may be, for example, MD-X1500 by KEYENCE CORPORATION having the maximum output of 25 W(ϕ60 μm), the wavelength of 1064 nm (in YG laser light), the pulse width of about 500 ns to 1000 ns, the frequency of 1 kHz to 400 kHz, the maximum scanning rate of 12 m/s, and the processing area of 125 mm $\times$ 125 mm $\times$ 42 mm.

[0030] The power density may be adjusted to be a desired value by controlling the laser average output and/or the laser beam diameter.

[0031] The heat input amount may be adjusted to be a desired value by controlling the laser average output, the laser scanning rate, the frequency, and the laser beam diameter.

[0032] It is preferable that the laser light be emitted under conditions where the laser average output is greater than or equal to 0.01 W/mm^2 and less than or equal to 2 W/mm^2, the frequency is higher than or equal to 1 kHz and lower than or equal to 500 kHz, the laser scanning rate is greater than or equal to 100 mm/s and less than or equal to 850 mm/s, and the laser beam diameter is greater than or equal to 0.1 mm and less than or equal to 0.5 mm.

[0033] It is preferable that the entire surface of the $Mg(OH)_2$ film formed on the surface of the Mg-Al-Ca based alloy be irradiated with the laser light exhaustively. For example, as illustrated in Fig. 1, the surface is scanned with the laser light (L) in the X direction from one end (lower left corner on the sheet) to the opposite end (lower right corner on the sheet) of the Mg-Al-Ca based alloy 1. After reaching the opposite end, the laser light is shifted in the Y direction (to upper side on the sheet), and the surface is scanned in the X direction from the opposite end to the one end. This is repeated to irradiate the entire surface of the $Mg(OH)_2$ film with the laser light.

[0034] It is preferable that a laser beam overlapping rate (X) be greater than or equal to 0.9% and less than or equal to 0.99%. It is preferable that a laser beam overlapping rate (Y) be greater than or equal to 0.87% and less than or equal to 0.97%.

[0035] When irradiated with the laser light, the $Mg(OH)_2$ film is modified to an MgO film due to a dehydration reaction. The thickness of the formed MgO film is 0.1 μm to 1 μm.

[0036] The MgO film contains 90% or greater of Mg as a cation or is an oxide containing Al, An, Mn, and/or a rare earth element in some cases.

[Example]

[0037] According to the embodiment described above, surface modification was performed on a test plate of the Mg-Al-Ca based alloy.

Test plate: Mg-10Al-5Ca-0.05Mn
Alkali solution: an aqueous solution containing $Mg(OH)_2$: 0.012 g as a chemical component in terms of mass in 1 litter of water

[0038] The thickness of the $Mg(OH)_2$ film formed on the surface of the test plate immersed in the alkali solution for a predetermined time was about 0.1 μm to 1 μm.

[0039] Table 1 illustrates test conditions and results (engraving depths) obtained by observing the surface of the test plate by using a confocal optical microscope.

[Table 1]

Test No.	Immersion time	Laser irrad ia tion								Engravin g depth
		Output (average)	Beam diam eter (average)	Frequency	Scanning rate	Beamoverlapping rate X	Beamoverlapping rate Y	Power density	Heat input amount	
	min	W	mm	kHz	mm/s			W/mm^2	mJ	μm
1	10	11	0.05	200	25	0.995	0.8	1401	22	30
2	10	11	0.05	200	50	0.995	0.8	1401	11	20
3	10	11	0.1	50	500	0.9	0.87	350	2	8
4	10	11	0.2	50	850	0.915	0.925	87.5	3	3
5	60	2	0.1	50	500	0.9	0.87	63.7	0.4	1.5
6	60	2	0.1	50	500	0.9	0.87	63.7	0.4	1
7	60	2	0.2	50	850	0.915	0.925	15.9	0.5	0
8	60	1.7	0.1	50	500	0.9	0.87	53.2	0.3	0
9	60	1.7	0.2	50	850	0.915	0.925	13.3	0.4	0
10	60	1.7	0.3	50	850	0.94	0.96	5.9	0.6	0
11	60	1.7	0.5	50	850	0.97	0.97	2.1	1	0
12	60	1.7	0.5	50	850	0.97	0.97	2.1	0.1	0

[Power Density]

[0040] Fig. 2 and Fig. 3 illustrate the relationship between the power density and the engraving depth. Fig. 3 is an enlarged view of Fig. 2. In Fig. 2 and Fig. 3, the horizontal axis represents the power density (W/mm^2), the vertical axis represents the engraving depth (μm), each white circle plot represents a test plate for alkali immersion time of 60 minutes, and each black circle plot represents a test plate for alkali immersion time of 10 minutes.

[0041] Fig. 2 indicates a trend that, as the power density becomes larger, the engraving depth also becomes larger. Moreover, Fig. 2 suggests that there is a conversion point at which the engraving depth increases sharply in a region of a low power density.

[0042] Fig. 3 shows an enlarged view of the region of a low power density. With reference to Fig. 3, it is found that, while the engraving depth is 0 μm when the power density is below 53.2 W/mm^2 (test No. 8), some of the engraving depths exceed 1 μm when the power density is 63.7 W/mm^2 (test Nos. 5, 6). According to Fig. 3, as long as the power density is less than or equal to 60 W/mm^2, the engraving depth can be less than or equal to 1 μm.

[0043] According to the result obtained by intensive studies by the present inventors, when magnesium alone is immersed in the alkali solution, the $Mg(OH)_2$ film having a thickness of about 30 μm is formed. On the other hand, when an Mg-Al-Ca based alloy is immersed in the alkali solution, it has been confirmed that the thickness of the $Mg(OH)_2$ film formed on the surface is about 1 μm.

[0044] As long as the engraving depth due to the laser light does not exceed the thickness of the $Mg(OH)_2$ film, the base material is not damaged. Thus, when the power density is less than or equal to 60 W/mm^2, it is possible to form an oxide film (MgO film) without damaging the base material and improve corrosion resistance.

[Corrosion Resistance]

[0045] Test plates of test No. 16 to No. 19 described above were immersed in 1 mass% of NaCl aqueous solution for 168 hours, and then the corrosion rates were calculated.

[0046] Calculation of the corrosion rate was performed by using Equation (1) below.

$$Cr = 87600 \times \Delta W \text{ (weight change)}/(A \times t \times r) \ldots (1)$$

Cr: corrosion rate (mm/year)
ΔW: weight difference before and after the test (g)
r: density of the test plate (g/cm^{-3})
A: initial surface area of the test plate (cm^2)
t: immersion time (hr)

[0047] Fig. 4 illustrates the relationship between the heat input amount and the corrosion rate, where the corrosion rate of the test plate (Mg-Al-Ca based alloy) on which no surface modification is performed is one. In Fig. 4, the horizontal axis represents the corrosion rate ratio (a.u.), and the vertical axis represents the heat input amount (mJ).

[0048] According to Fig. 4, it is confirmed that, in irradiation of laser light, when the heat input amount exceeds 5 mJ, the test plate is more likely to be corroded than before the surface modification is performed. When the heat input amount is greater than or equal to 0.3 mJ and less than or equal to 4 mJ, preferably, greater than or equal to 1 mJ and less than or equal to 4 mJ, the corrosion resistance of the test plate is improved due to surface modification.

[0049] Fig. 5 illustrates corrosion resistance evaluation results of test No. 16 to No. 19 (conditions A to D). In Fig. 5, the vertical axis represents the corrosion rate ratio (a.u.). For the corrosion rate ratio, a test plate on which no surface modification is performed (no alkali treatment and no irradiation) is used as a reference.

[0050] According to Fig. 5, in the condition A, the corrosion rate was increased by about 500% compared to a test plate whose surface was not modified. On the other hand, in the conditions B, C, and D, the corrosion rates were reduced compared to a test plate whose surface was not modified. The reduction rates in conditions B, C, and D were 18%, 32%, and 2%, respectively.

[0051] According to Table 1, in condition A, while the heat input amount is less than or equal to 5 mJ, the power density exceeds 60 W/mm^2. On the other hand, in conditions B, C, and D, each of the heat input amount is less than or equal to 5 mJ, and each of the power density is less than or equal to 60 W/mm^2. From these results, it was suggested that it is important not only to set the heat input amount to be less than or equal to 5 mJ but also to set the power density to be less than or equal to 60 W/mm^2 for improvement of corrosion resistance of an Mg-Al-Ca based alloy.

[Supplementary Notes]

[0052] The surface modification method of an Mg-Al-Ca based alloy described in the above embodiment is understood as described below, for example.

[0053] In the surface modification method of an Mg-Al-Ca based alloy according to the present disclosure, an Mg-Al-Ca based alloy is immersed in an alkali solution, and the surface of the Mg-Al-Ca based alloy immersed in the alkali solution is irradiated with laser light at a power density that is less than or equal to 60 W/mm^2 and a heat input amount that is less than or equal to 5 mJ.

[0054] The immersion in the alkali solution causes an $Mg(OH)_2$ film to be formed on the surface of the Mg-Al-Ca based alloy. When the $Mg(OH)_2$ film is irradiated with laser, a dehydration reaction occurs. This modifies the $Mg(OH)_2$ film to be a homogeneous and dense MgO film.

[0055] Since the power density and the heat input amount are defined in the range described above, an oxide film (MgO film) can be formed with the engraving depth not exceeding the thickness of the $Mg(OH)_2$ film. Accordingly, it is possible to improve corrosion resistance without damaging a base material.

[0056] In the disclosure described above, the heat input amount is preferably greater than or equal to 0.3 mJ and less than or equal to 4 mJ, more preferably greater than or equal to 1 mJ and less than or equal to 4 mJ.

[0057] Corrosion resistance can be more reliably improved when the heat input amount is within the range described above.

[0058] In the disclosure described above, it is preferable that the power density be less than or equal to 53.2 W/mm^2.

[0059] This enables the engraving depth of 0 μm.

[0060] In the disclosure described above, it is preferable that the power density be less than or equal to 15.9 W/mm^2.

[0061] This can reduce the corrosion rate compared to a case where no surface modification is performed.

[0062] In the disclosure described above, it is more preferable that the power density be greater than or equal to 3.3 W/mm^2.

[0063] This can further increase the reduction amount of the corrosion rate compared to a case where no surface modification is performed.

[0064] In the disclosure described above, the immersion time may be longer than or equal to 10 minutes and shorter than or equal to 120 minutes.

[0065] When the immersion is performed for 10 minutes or longer, an $Mg(OH)_2$ film having a thickness of more than 1 μm can be formed. Even when the immersion is performed for more than 120 minutes, the effect of a significant increase in the thickness of the $Mg(OH)_2$ film is not expected.

[List of Reference Symbols]

[0066]

1 Mg-Al-Ca based alloy

Claims

1. A surface modification method of an Mg-Al-Ca based alloy, the surface modification method comprising:

    immersing an Mg-Al-Ca based alloy in an alkali solution; and
    irradiating a surface of the Mg-Al-Ca based alloy immersed in the alkali solution with laser light at a power density that is less than or equal to 60 W/mm^2 and a heat input amount that is less than or equal to 5 mJ.

2. The surface modification method of an Mg-Al-Ca based alloy according to claim 1, wherein the heat input amount is greater than or equal to 0.3 mJ and less than or equal to 4 mJ.

3. The surface modification method of an Mg-Al-Ca based alloy according to claim 2, wherein the power density is less than or equal to 53.2 W/mm^2.

4. The surface modification method of an Mg-Al-Ca based alloy according to claim 2, wherein the power density is less than or equal to 15.9 W/mm^2.

5. The surface modification method of an Mg-Al-Ca based alloy according to claim 2, wherein the power density is greater than or equal to 3.3 W/mm^2.

6. The surface modification method of an Mg-Al-Ca based alloy according to any one of claims 1 to 5, wherein time of the immersing is longer than or equal to 10 minutes and shorter than or equal to 120 minutes.

FIG. 1

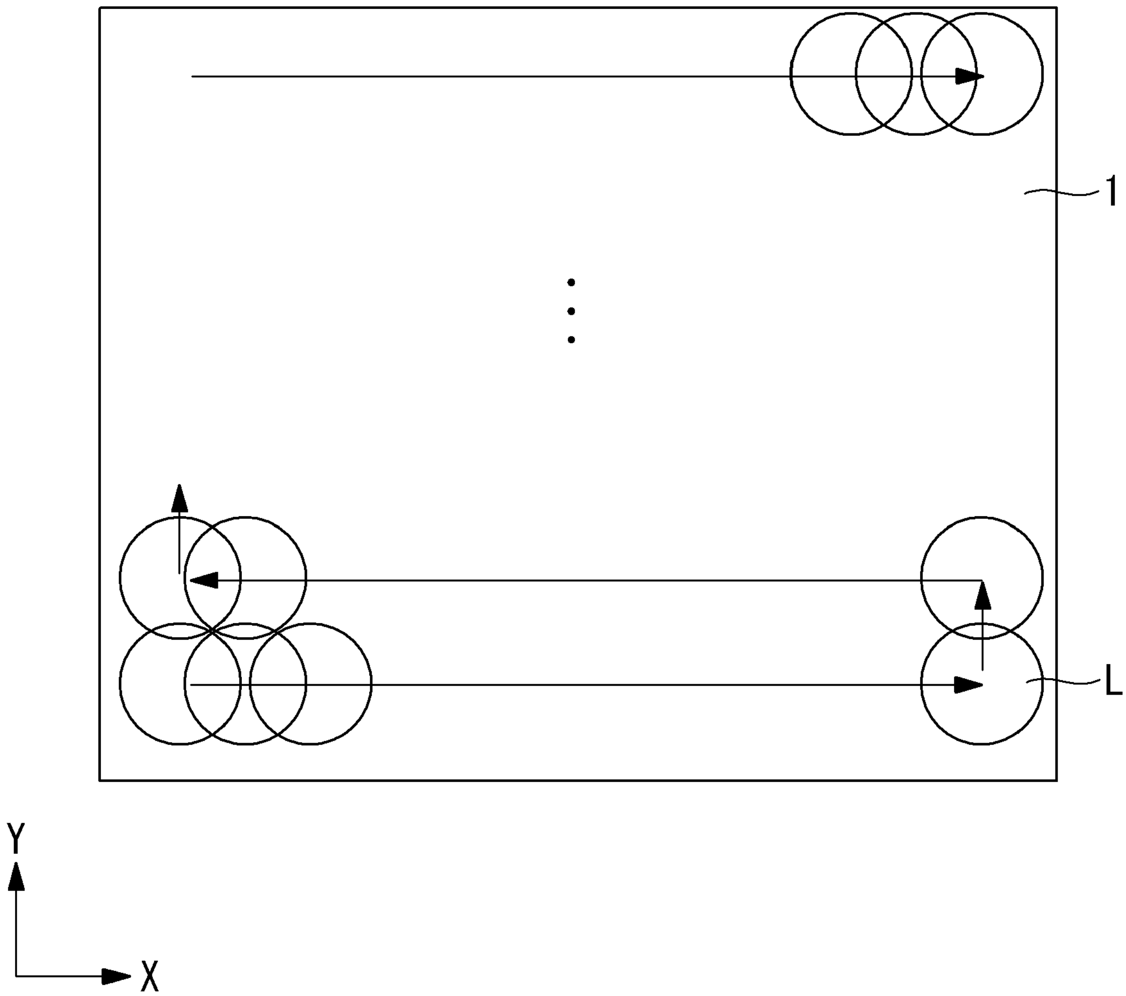


FIG. 2

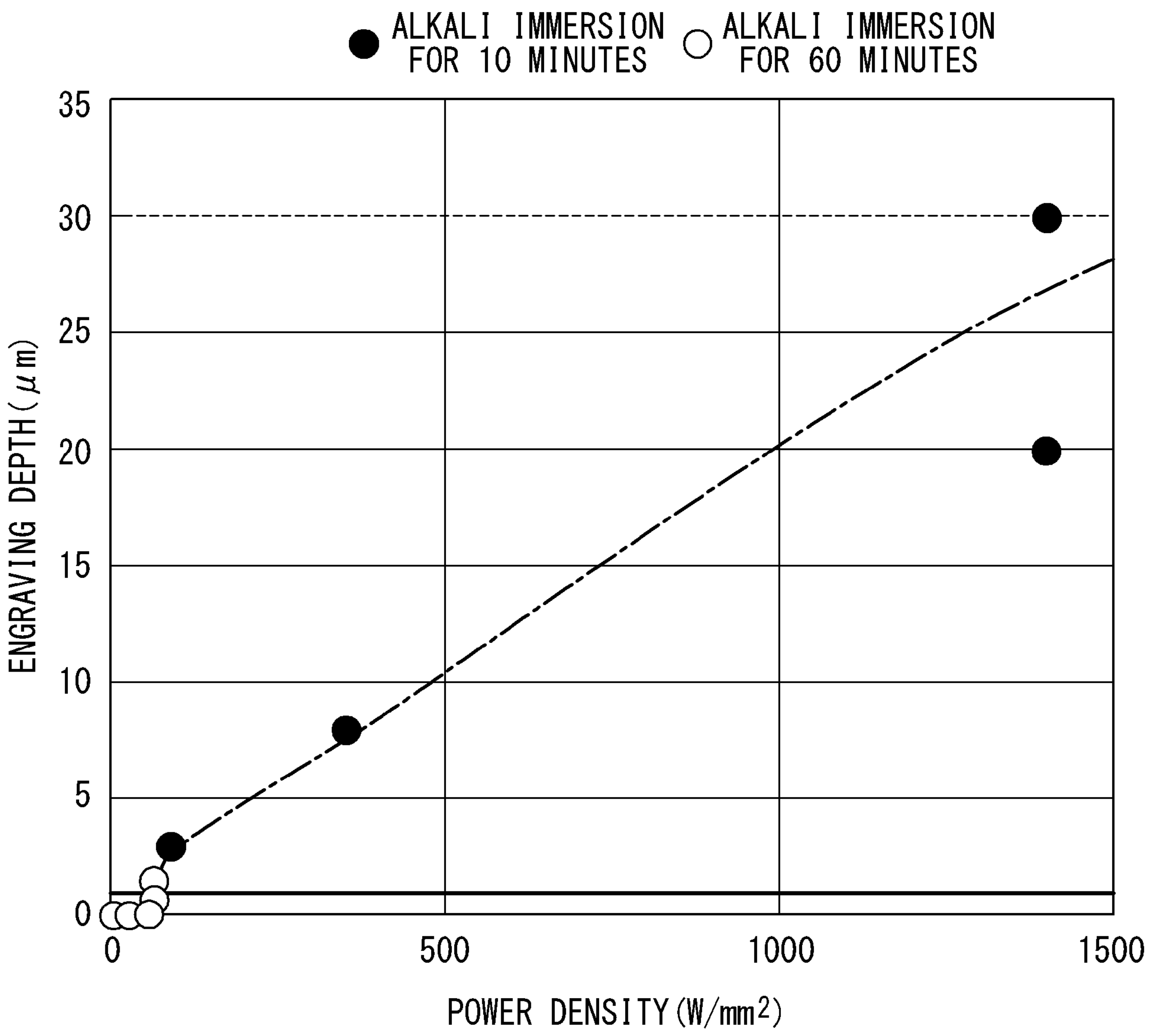

ALKALI IMMERSION FOR 10 MINUTES
ALKALI IMMERSION FOR 60 MINUTES
ENGRAVING DEPTH (μm)
35
30
25
20
15
10
5
0
0
500
1000
1500
POWER DENSITY (W/mm2)

FIG. 3

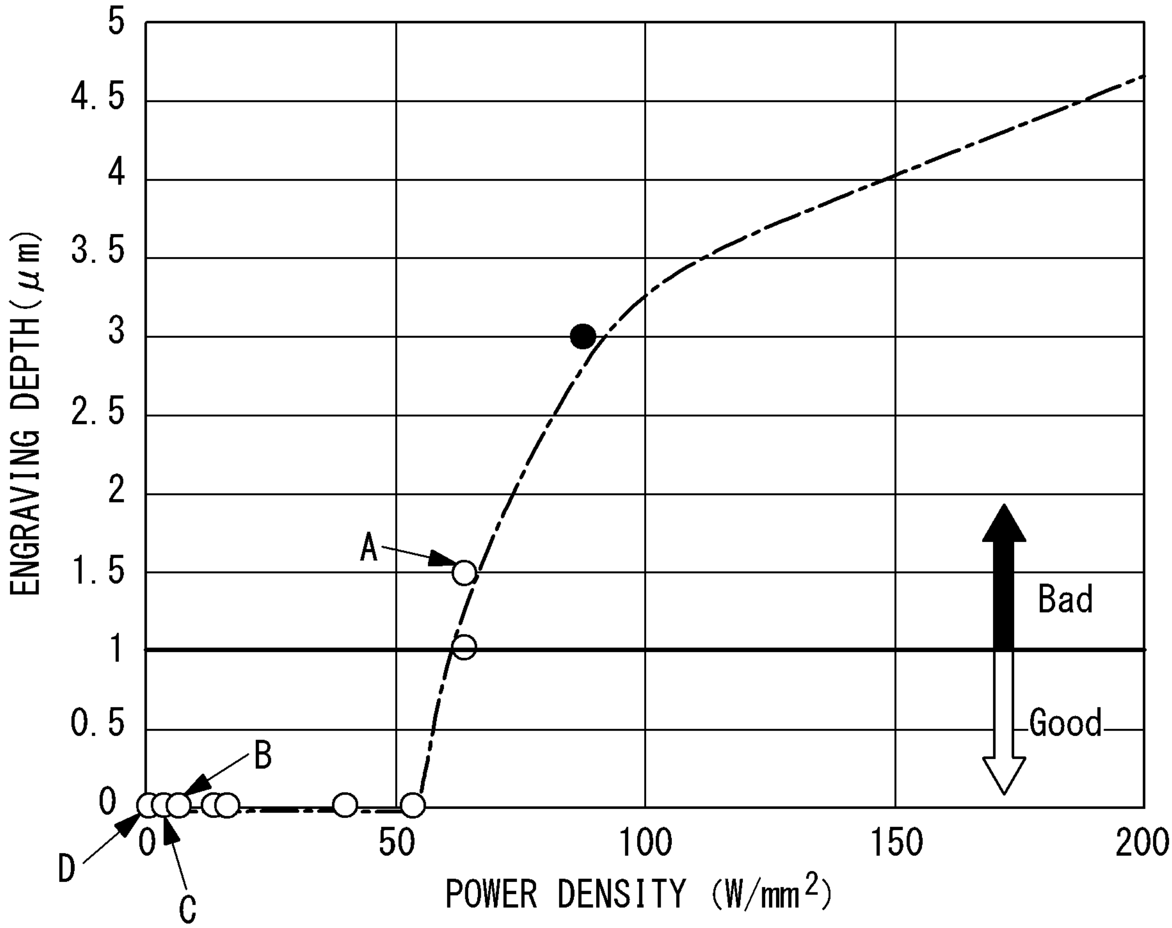

ENGRAVING DEPTH (μm)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
50
100
150
200
POWER DENSITY (W/mm2)
A
B
C
D
Bad
Good

FIG. 4

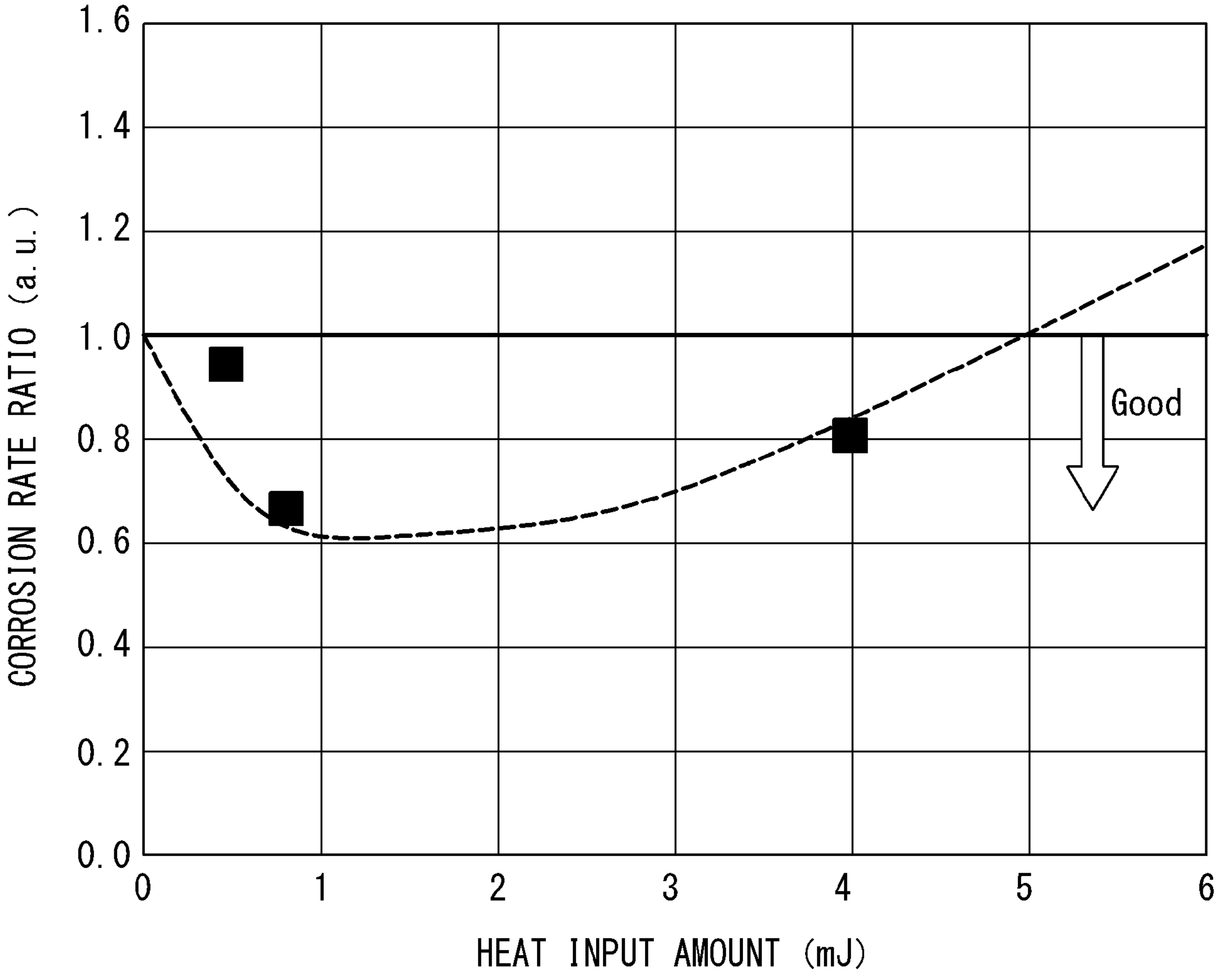
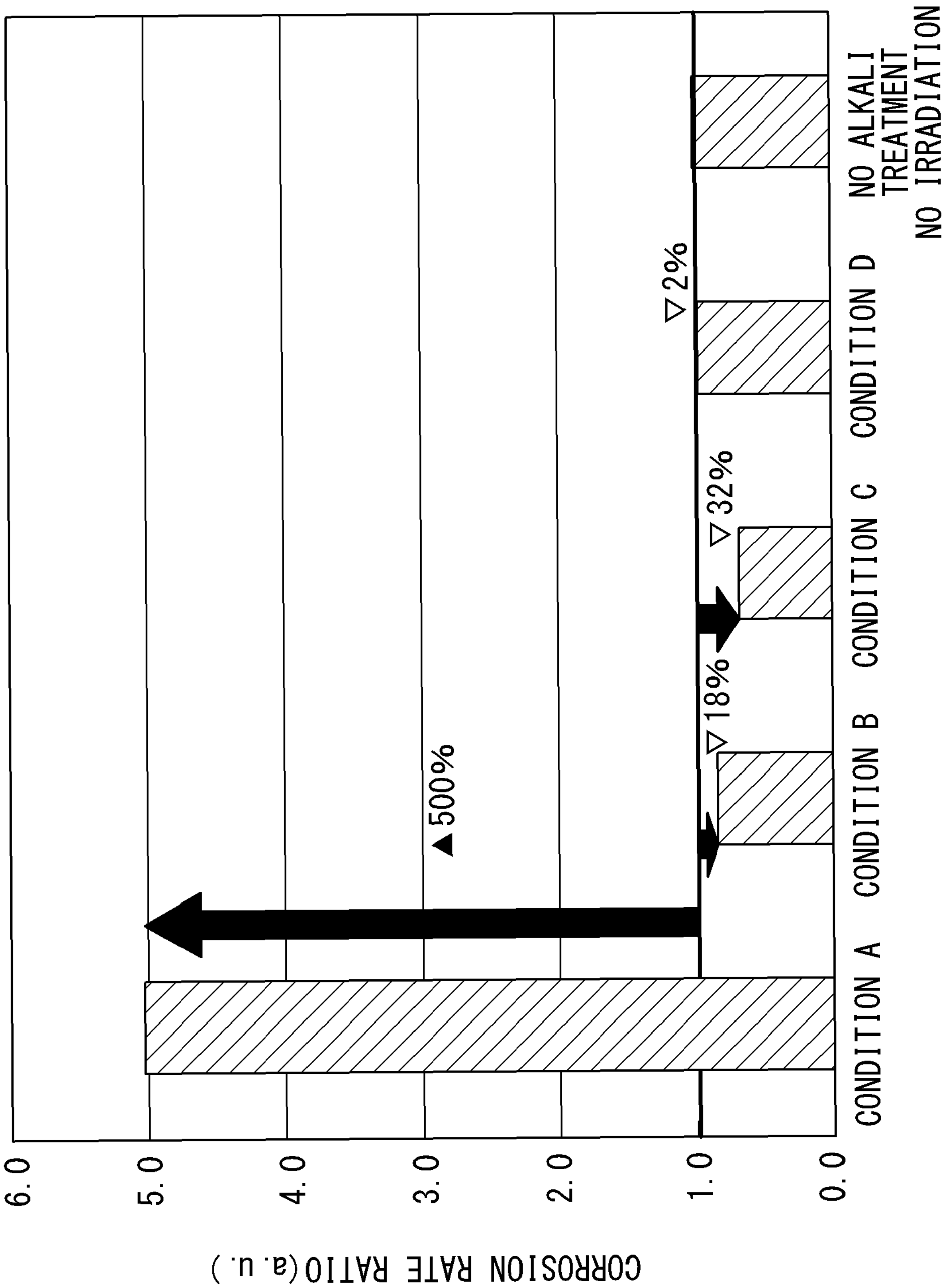

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
CORROSION RATE RATIO (a.u.)
Good
0
1
2
3
4
5
6
HEAT INPUT AMOUNT (mJ)

FIG. 5


CORROSION RATE RATIO (a. u.)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
CONDITION A
CONDITION B
CONDITION C
CONDITION D
NO ALKALI TREATMENT NO IRRADIATION
▲500%
▽18%
▽32%
▽2%

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EUROPEAN SEARCH REPORT

Application Number
EP 21 20 4425

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A,D	JP 2008 291310 A (UNIV KUMAMOTO) 4 December 2008 (2008-12-04) * paragraph [0011] * * paragraph [0021] - paragraph [0022] * * claims 1-6 *	1-6	INV. C23C22/60 C23C22/66 C23C22/82 C22C23/02
A	SHUNSUKE YAGI ET AL: "Surface modification of ACM522 magnesium alloy by plasma electrolytic oxidation in phosphate electrolyte", CORROSION SCIENCE, OXFORD, GB, vol. 57, 27 December 2011 (2011-12-27), pages 74-80, XP028458283, ISSN: 0010-938X, DOI: 10.1016/J.CORSCI.2011.12.032 [retrieved on 2012-01-04] * abstract * * table 1 * * Section 2 *	1-6	
A	US 2016/369378 A1 (KAWAMURA YOSHIHITO [JP] ET AL) 22 December 2016 (2016-12-22) * claims 1-33 *	1-6	TECHNICAL FIELDS SEARCHED (IPC) C23C C22C
T	SPIEKERMANN P: "Alloys - a special problem of patent law", NONPUBLISHED ENGLISH TRANSLATION OF DOCUMENT, 31 December 1993 (1993-12-31), pages 1-20, XP002184689, * page 3 - page 6 *		

The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
The Hague	30 March 2022	Neibecker, Pascal

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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30-03-2022

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