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(54) Creep-resistant magnesium alloy

(57) A creep-resistant magnesium alloy having creep resistance superior to AE42 alloy and having relatively high corrosion resistance. The magnesium alloy has superior castability without any generation of open cracks and is less expensive than AE42 alloy for production. The creep-resistant magnesium alloy is made from 1.5 to 4.0 mass % of AI, 0.5 to 1.8 mass % of Si,

0.05 to 0.6 mass % of RE, 0.005 to 1.5 mass % of Sr or Sb, and the reminder made from Mg and unavoidable impurities. Creep resistance is enhanced when 0.3 to 1.5 mass % of Ca is included. Further, corrosion resistance is enhanced when 0.1 to 0.4 mass % of Mn is included.

Description

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[0001] The present invention relates to light-weight magnesium alloy members used as mechanical parts, such as automobile parts and two-wheeled vehicle parts, and more particularly, to a magnesium alloy, for example, a magnesium alloy for high pressure die-casting, with excellent castability and that does not generate casting defects such as casting cracking, and that has creep resistance, heat resistant strength, and corrosion resistance those required for use in high-temperature environments.

[0002] Magnesium alloys in high pressure die-casting defined by ASTM Standard Specification B93 are examples of conventional magnesium alloys used as materials in automobile parts. Of conventional magnesium alloys, AS-type alloys have excellent heat resistance. Of the AS-type alloys, AS21 alloy has relatively high creep resistance and is used in heat-resistance parts, such as in the transmission case of manual transmission automobiles.

[0003] However, AS21 alloy cannot overcome problems such as corrosion resistance. Also, even higher creep resistance properties are required in the high-temperature environment, such as the transmission case of automatic transmission automobiles.

[0004] When calcium is added to AS21 alloy and AS41 alloy, an alloy can be obtained with even better creep resistance. Also, alloys added with calcium and rare earth elements have creep resistance that is even higher than the creep resistance of AS-type alloys. However, the creep resistance properties are still not satisfactory.

[0005] AE42 alloy is a representative high pressure die-casting alloy that includes rare earth elements. The creep resistance property of AE42 alloy is superior to AS21 alloy and AS41 alloy. However, there are problems with castability, such as mold residue, of AE42 alloy, so high pressure die-casting using AE42 alloy is problematic. Also, AE42 alloy is more expensive and is more difficult to produce in quantity than other alloys, such as AZ91D alloy.

[0006] It is an object of the present invention to provide creep-resistant magnesium alloy that has creep resistance that is superior to AE42 alloy and has relatively high corrosion resistance, that has superior castability without any generation of open cracks, and that is less expensive than AE42 alloy.

[0007] These and other objects of the present invention will be attained by providing a creep-resistant magnesium alloy that contains 1.5 to 4.0 percent by mass of Al, 0.5 to 1.8 percent by mass of Si, 0.05 to 0.6 percent by mass of RE, 0.005 to 1.5 percent by mass of Sr, and the balance Mg and unavoidable impurities.

[0008] The present invention also provides a creep-resistant magnesium alloy that contains 1.5 to 4.0 percent by mass of Al, 0.5 to 1.8 percent by mass of Si, 0.05 to 0.6 percent by mass of RE, 0.005 to 1.5 percent by mass of Sb, and the balance Mg and unavoidable impurities.

[0009] According to these creep-resistant alloys, creep resistance can be greatly enhanced by adding RE and Sr to AS-type alloys, or by adding RE and Sb to AS-type alloys. Corrosion resistance is also improved. Also, the cost can be made less than for AE42 alloy. Further, castability can be improved because Si is included in hypo-eutectic, hypereutectic and eutectic phases.

[0010] In order to enhance creep resistance, it is desirable that 0.3 to 1.5 percent by mass of Ca is included. Creep resistance about twice that of AE42 alloy can be obtained with the addition of Ca. Also, the alloy is easy to handle because of enhancement of flame resistance for magnesium alloy. Also, in order to enhance corrosion resistance, it is desirable that 0.1 to 0.4 percent by mass of Mn is included.

[0011] In the drawings;

Fig. 1 is a graphical representation showing effects on amount of added Si with respect to solubility of RE into Mg;

Fig. 2 shows a shape of samples used in a creep resistance test in an experiment 1;

Fig. 3(a) is a plan view showing the set up of the creep resistance test in the experiment 1;

Fig. 3(b) is a side view showing the set up of Fig. 3(a);

Fig. 4 is a graph showing the results measured for creep resistance in experiment 1 for creep-resistant magnesium alloys according to an embodiment of the present invention and comparative materials;

Fig. 5(a) is a front view showing a cast sample to evaluate cracking in creep-resistant magnesium alloys according to an embodiment of the present invention and comparative materials;

Fig. 5(b) is a side view of the cast sample of Fig. 5(a); and,

Fig. 6 is the graph showing corrosion resistance in an experiment 3 for creep-resistant magnesium alloys according to an embodiment of the present invention and comparative materials.

[0012] A creep-resistant magnesium alloy according to a first embodiment of the present invention will be described. The creep-resistant magnesium alloy contains 1.5 to 4.0 percent by mass of Al (aluminum), 0.5 to 1.8 percent by mass of Si (silicon), 0.05 to 0.6 percent by mass of rare earth elements (referred to as RE hereinafter), 0.005 to 1.5 percent by mass of Sr (strontium), and the remainder being Mg (magnesium) and unavoidable impurities. Also, in accordance with necessity, creep resistance can be enhanced when 0.3 to 1.5 percent by mass of Ca (calcium) is contained. Also, in accordance with necessity, corrosion resistance can be enhanced when 0.1 to 0.4 percent by mass of Mn (manga-

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nese) is contained.

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[0013] If the amount of Al exceeds 4.0 percent by mass, then creep resistance and corrosion resistance decrease so that creep resistance of the level of AE42 alloy cannot be obtained. Accordingly, the amount of Al added was set to 4.0 percent or less by mass. On the other hand, if the amount of Al is less than 1.5 percent by mass, then the castability (with respect to open cracks) does not improve so open crack and fluidity problems occur and proper casting cannot be performed. Accordingly the amount of Al added was set to 2.0 percent or more by mass.

[0014] Creep resistance and castability of a magnesium alloy improve in association with increase in the amount of Si added. However, if too much Si is added, then the liquidus temperature increases so that the casting temperature must be increased. If the amount of Si added exceeds 1.8 percent by mass, then the liquidus temperature will exceed 700 degrees centigrade, so that casting becomes difficult. Also, the corrosion resistance decreases. Accordingly, the amount of Si added was set to 1.8 percent or less by mass. On the other hand, if the amount of Si added is less than 0.5 percent by mass, then creep resistance decreases. Castability, such as tendency for open cracks, is adversely effected, so that casting is difficult. Accordingly, the amount of Si added was set to 0.5 percent or more by weight.

[0015] RE is added to enhance creep resistance. However, as shown in Fig. 1, the solubility of RE tends to decrease with increase in the solubility of Si. Accordingly, considering the lower limit value (0.5%) for the additive amount of Si, the upper limit value of the amount of RE to be added was set to 0.6 percent by mass. On the other hand, when RE is added in amounts of less than 0.05 percent, then sufficient creep resistance strength cannot be obtained. Therefore, the lower limit value for RE to be added was set a 0.05 percent by mass.

[0016] Addition of Sr, even by a small amount of 0.005 percent by mass, results in fine structure so is effective for preventing open cracks during casting and enhances creep resistance. Because this effect does not occur when Sr is added in amounts of less than 0.005 percent by mass, the amount of added Sr was set to 0.005 percent or more by mass. The creep resistance of the magnesium alloy is enhanced with further increase in the amount of Sr added, until the amount of Sr added reaches 1.5 percent by mass. However, if the amount exceeds 1.5 percent by mass, then creep resistance and corrosion resistance decrease. As a result, the amount of Sr added was set to 1.5 percent or less by mass.

[0017] Mn is added to improve corrosion resistance. No further improvement in corrosion resistance can be expected by added Mn in amounts greater than 0.4 percent by mass, and on the contrary compounds are produced so that creep resistance may be affected. Accordingly, the amount of Mn added was set to 0.4 percent or less by mass. On the other hand, if the amount of Mn added is less than 0.1 percent by mass, then no improvement in corrosion resistance is observed. Accordingly, the amount of Mn added was set to 0.1 percent or more by mass.

[0018] When Ca is added, then the creep resistance of the magnesium alloy is enhanced. However, if too much Ca is added, then open cracks easily occur during casting so that a sound cast product cannot be obtained. Accordingly, the amount of Ca added was set to 1.5 percent or less by mass. On the other hand, if Ca is added in an amount of less than 0.3 percent by mass, then sufficient creep resistance strength cannot be obtained. Accordingly, the amount of Ca added was set to 0.3 percent or more by mass.

[0019] It should be noted that unavoidable impurities normally exist in minimal amounts of less than 0.004 percent by mass of Fe (iron), less than 0.001 percent by mass of Ni (nickel), less than 0.08 percent by mass of Cu (copper), less than 0.01 percent by mass of Zn (zinc), and the like.

[0020] Next, a creep-resistant magnesium alloy according to a second embodiment of the present invention will be described. The creep-resistant magnesium alloy is made from 1.5 to 4.0 percent by mass of Al, 0.5 to 1.8 percent by mass of Si, 0.05 to 0.6 percent by mass of RE, and 0.005 to 1.5 percent by mass of Sb (antimony), and a remainder portion made from Mg and unavoidable impurities. Also, in accordance with necessity, 0.3 to 1.5 percent by mass of Ca can be included for enhancing creep resistance. Also, in accordance with necessity, 0.1 to 0.4 percent by mass of Mn can be included for enhancing corrosion resistance.

[0021] When Sb is added in amounts of 0.005 to 1.5 percent by mass, then creep resistance increases. Creep resistance increases even if such a small amount as 0.005 percent by mass is added. No effects occur if less than 0.005 percent by weight of Sb is added, so the amount of Sb added was set to 0.005 percent or more by mass. On the other hand, if the amount of Sb exceeds 1.5 percent by mass, then no improvement in the creep resistance is observed, so the amount of Sb added was set to 1.5 percent or less by mass. The reasons for the limitations set for elements other than Sb are the same as for the creep-resistant magnesium alloy of the first embodiment.

Experiment 1

[0022] Creep resistance experiments were performed for the alloys of the present invention and comparative materials. The change in displacement was measured that occurred over time when samples were subjected to a bending load in an ambient temperature of 200 degrees centigrade. An ASTM standard tensile strength test sample, with diameter of 6.35 mm at the parallel portion, gage length of 50 mm, and length of 210 mm as shown in Fig. 2 was used for sample 1. As shown in Figs. 3(a) and 3(b), three samples 1a, 1b, and 1c were aligned in parallel and supported at

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their ends by supports 2a, 2b. The distance between the support 2a and support 2b was set at 150 mm. The samples 1a, 1b, and 1c were then applied with a load of 2 kg per sample.

[0023] The compositions of the samples used in these tests are as shown in Table 1. Sample 1 is AZ91D alloy, sample 2 is AS41 alloy, sample 3 is AE42 alloy, samples 4 and 5 are alloys of the first embodiment of the present invention, and samples 6 and 7 are alloys of the second embodiment of the present invention.

Table 1

Alloy	Al	Zn	Si	Ca	Sr	Sb	Mn	Fe	Ni	RE	Mg
Sample 1	9.21	0.86	0.02	-	-	-	0.26	<0.0005	<0.0004	-	Bal.
Sample 2	3.90	0.01	1.1	-	-	-	0.25	<0.0005	<0.0004	-	Bal.
Sample 3	4.23	0.01	0.01	-	-	-	0.11	<0.0005	<0.0004	2.0	Bal.
Sample 4	3.52	0.01	0.92	0.61	0.41	-	0.15	<0.0005	<0.0004	0.5	Bal.
Sample 5	3.23	0.01	1.11	-	0.3	-	0.25	<0.0005	<0.0004	0.5	Bal.
Sample 6	3.21	0.01	1.06	0.71	-	0.2	0.27	<0.0005	<0.0004	0.5	Bal.
Sample 7	3.34	0.01	0.98	-	-	0.3	0.27	<0.0005	<0.0004	0.5	Bal.

[0024] Fig. 4 shows the test results. Sample 1 (AZ91D alloy) and sample 2 (AS41 alloy) have poor creep resistance. Samples 4 to 7 (alloys according to the present invention) have creep resistance superior to sample 1 (AZ91D alloy) and sample 2 (AS41 alloy). The experimental results for samples 5 and 7, which are alloys according to the present invention that do not have Ca added, substantially overlap with the experimental result for sample 3 (AE42 alloy) in Fig. 4 and so show substantially the same creep resistance. Although the experimental results for samples 4 and 6, which are alloys according to the present invention that have Ca added, substantially overlap in Fig. 4, both of these samples show better creep resistance than sample 3 (AE42 alloy). From this, it can be understood that by adding RE, and either Sr or Sb, to a Mg-Al-Si alloy, creep resistance can be enhanced, creep resistance is superior to that of AZ91D alloy and AS41 alloy, and an alloy with creep resistance equal to that of AE42 alloy can be obtained. Further, it can be understood that by adding Ca, an alloy with superior creep resistance of twice that of AE42 alloy can obtained. It should be noted that all of the alloys according to the present invention (samples 4 to 7) are less costly than AE42 alloy.

Experiment 2

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[0025] Samples with shape shown in Fig. 5 were made under the two sets of casting conditions shown in Table 2 using alloys with a variety of compositions. The presence of open cracks, closed cracks, and minute cracks was investigated. The alloy composition of each sample used in the experiment is shown in Table 3. Sample 1 is AZ91D alloy, sample 2 is AE42 alloy, samples 3 and 4 are alloys of the first embodiment of the present invention, and samples 5 and 6 are alloys of the second embodiment of the present invention. Conditions 1 of Table 2 are normally-used conditions and conditions 2 are normally not used. The shape of the sample of Fig. 5 has a length of 105 mm at the parallel portion and has holding end portions. The holding end portions have angle portions R with a radius of curvature of 0mm or 2mm.

Table 2

Casting Conditions	Conditions 1	Conditions 2
Temperature of metal mold [° C]	Movable mold:130°C Fixed mold: 140°C	Movable mold:130°C Fixed mold: 140°C
Die Casting Pressure [Mpa]	780	780
Injection Speed [m/s]	2.1	0.96
Temperature of Molten Metal [° C]	690	690
Curing Time [s]	2	2
Shot Time Lag [s]	0	0
Slow Fill Speed [m/s]	0.5	0.5

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Table 3

Alloy	Al	Zn	Si	Fe	Ni	Ca	Cu	Sr	RE	Sb	Mn	Mg
Sample 1	9.18	0.91	0.01	0.0005	0.0005	-	0.0005	-	-	-	0.25	Bal.
Sample 2	4.15	0.01	0.02	0.0005	0.0005	-	0.0005	-	0.5	-	0.25	Bal.
Sample 3	3.45	0.01	1.15	0.0005	0.0005	0.58	0.0005	0.5	0.5	-	0.10	Bal.
Sample 4	3.32	0.01	0.95	0.0005	0.0005	-	0.0005	0.4	0.5	-	0.20	Bal.
Sample 5	3.23	0.01	1.05	0.0005	0.0005	0.6	0.0005	-	0.5	0.3	0.25	Bal.
Sample 6	3.28	0.01	0.98	0.0005	0.0005	-	0.0005		0.5	0.3	0.25	Bal.

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[0026] Open and closed cracks were checked visually, and minute cracks were checked for using color check. An evaluation of susceptibility to cracks was performed by preparing ten of each sample type under to same conditions, adding up the number of samples that had open cracks, closed cracks, and minute cracks after casting, and using the values in an index. The observation results are shown in Table 4.

			٦	Table 4		
Alloy	Condition	R [mm]	Open Cracks	Closed Cracks	Minute Cracks	Non-defective Units
Sample 1	1	0	0	0	0	10
		2	0	0	1	9
	2	0	0	5	5	0
Sample 2	1	0	1	3	4	2
		2	7	1	1	1
	2	0	0	10	0	0
Sample 3	1	0	0	0	5	5
		2	0	0	0	10
	2	0	0	4	6	0
Sample 4	1	0	0	0	5	5
		2	0	0	0	10
	2	0	0	4	6	0
Sample 5	1	0	0	0	6	4
		2	0	0	0	10
	2	0	0	4	6	0
Sample 6	1	0	0	0	4	6
		2	0	0	0	10
	2	0	0	5	5	0

[0027] All of the samples showed some closed cracks or minute cracks under the casting conditions 2, so no nondefective items could be obtained. No open cracks or closed cracks could be found in sample 1 (AZ91D alloy), but open cracks and closed cracks could be found in sample 2 (AE42 alloy) even under the casting conditions 1. No open cracks or closed cracks were found but only minute cracks were generated in samples 3 to 6 (alloys according to the first and second embodiments of the present invention) under the casting conditions 1. From these results, the alloys according to the present invention have slightly inferior resistance to cracking compared to AZ91D alloy, but have good resistance to cracking compared to AE42 alloy.

[0028] The situation of open and closed crack generation is different with differing R, even under the same casting conditions 1. Regarding sample 1 (AZ91D alloy), no cracks were observed when R was 0 mm, but some minute cracks could be found when R was 2 mm. Regarding sample 2 (AE42 alloy), open cracks, closed cracks, and minute cracks

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could be observed when R was 0 mm and when R was 2 mm. Regarding samples 3 to 6 (alloys according to the first and second embodiments of the present invention), minute cracks were observed when R was 0 mm, but none were observed when R was 2 mm. From this, it can be understood that by providing a rounded corner R, the alloys according to the present invention indicate substantially the same resistance to cracking as AZ91D alloy.

Experiment 3

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[0029] Alloys with the composition shown in Table 5 were cast under the conditions 1 shown in Table 2 and prepared samples (10mm x 20mm x 145mm) were used to evaluate corrosion resistance. The surface of the samples were wet polished with emery papers (#150, #400, # 800 and #2000). Corrosion resistance was performed for 65 hours using a salt containing water spray test (JIS Z2371) and corrosion rate (mg/day/dm²(MMD)) was measured. Alloy 1 is AZ91D alloy, alloy 2 is AE42 alloy, alloy 3 is AS41 alloy, alloy 4 and alloy 5 are alloys according to the first embodiment of the present invention, and alloy 6 and alloy 7 are alloys according to the second embodiment of the present invention.

Table 5

Alloy	Al	Zn	Si	Fe	Ni	Ca	Cu	Sr	RE	Sb	Mn	Mg
Sample 1	9.03	0.89	0.01	0.0005	0.0005	-	0.0005	-	-	-	0.25	Bal.
Sample 2	4.12	0.01	0.01	0.0005	0.0005	-	0.0005	-	0.5	-	0.25	Bal.
Sample 3	4.21	0.01	1.12	0.0005	0.0005	-	0.0005	-	-	-	0.10	Bal.
Sample 4	3.35	0.01	1.13	0.0005	0.0005	0.58	0.0005	0.5	0.5	-	0.21	Bal.
Sample 5	3.36	0.01	0.98	0.0005	0.0005	-	0.0005	0.4	0.5	-	0.25	Bal.
Sample 6	3.29	0.01	1.11	0.0005	0.0005	0.6	0.0005	-	0.5	0.3	0.25	Bal.
Sample 7	3.31	0.01	0.99	0.0005	0.0005	-	0.0005	-	0.5	0.3	0.26	Bal.

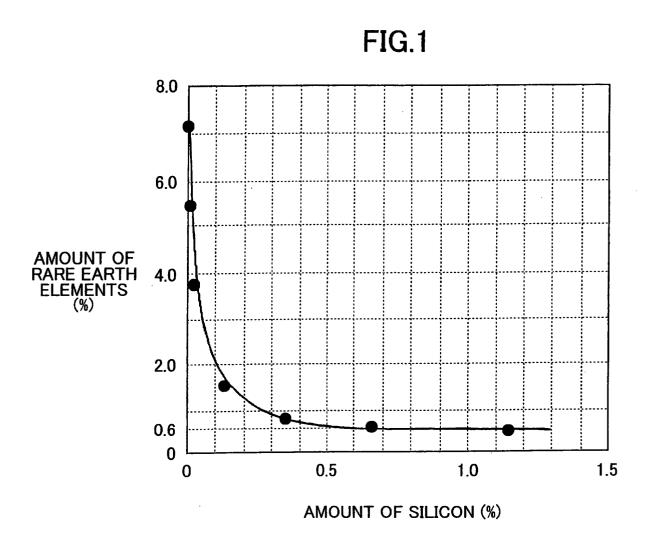
[0030] Fig. 6 shows the results of the experiment. The alloys 4 to 7 (alloys according to the first and second embodiments) indicate better corrosion resistance than alloy 3 (AS41 alloy). Alloy 5 (alloy according to the first embodiment of the present invention, one without Ca added) and alloy 7 (alloy according to the second embodiment of the present invention, one without Ca added) have corrosion resistance inferior to that of alloy 2 (AE42 alloy), but better than alloy 1 (AZ91D alloy). Thus, it can be understood that by adding RE and Sr or Sb to AS-type alloys, corrosion resistance of alloys is improved. Also, alloy 4 (alloy according to the first embodiment of the present invention, one with Ca added) and alloy 6 (alloy according to the second embodiment of the present invention, one with Ca added) indicate substantially the same corrosion resistance as alloy 1 (AZ91D alloy).

Claims

- 1. A creep-resistant magnesium alloy **characterized by** containing 1.5 to 4.0 percent by mass of A1; 0.5 to 1.8 percent by mass of Si; 0.05 to 0.6 percent by mass of at least one rare earth element; 0.005 to 1.5 percent by mass of Sr or Sb; with the balance being Mg and unavoidable impurities.
- 2. The creep-resistant magnesium alloy as claimed in claim 1, **characterized by** further containing 0.3 to 1.5 percent by mass of Ca.
 - 3. The creep-resistant magnesium alloy as claimed in claim 1 or 2, **characterized by** further containing 0.1 to 0.4 percent by mass of Mn.

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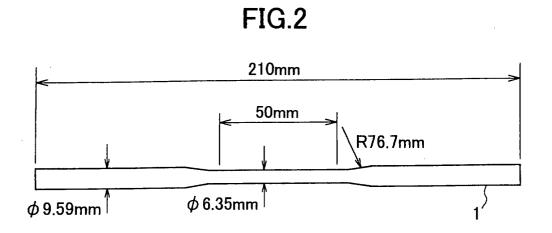


FIG.3(a)

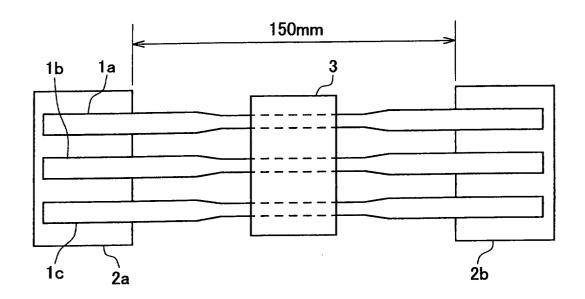
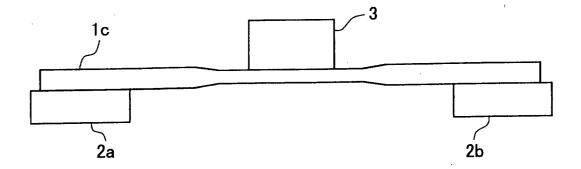
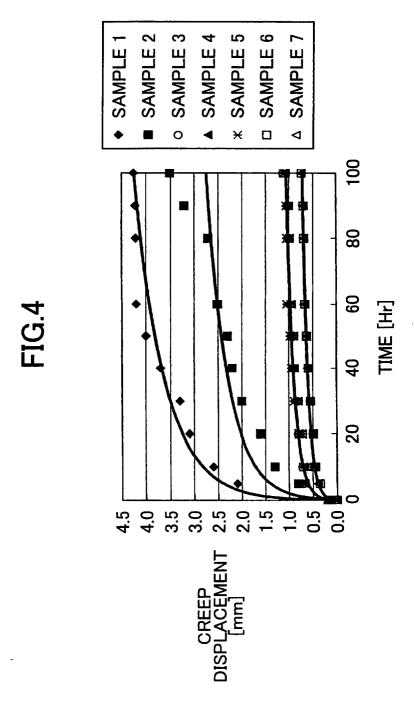
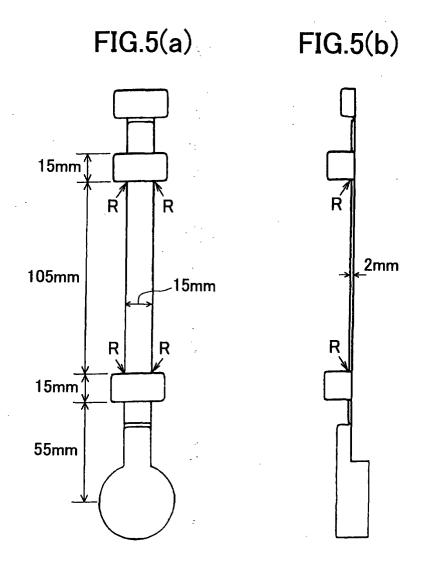


FIG.3(b)







CORROSION RATE [MMD]

ALLOY ALLOY ALLOY ALLOY ALLOY ALLOY ALLOY 1 2 3 4 5 6 7

ALLOY



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2 A	27-08-1997	JP JP DE DE EP US	9291332 69704801 69704801 0791662	A D1 T2 A1	19-11-200 11-11-199 21-06-200 30-08-200 27-08-199 22-09-1998
			JP JP 3 A 15-09-1992 FR CA DE DE EP JP 2 A 27-08-1997 JP JP DE DE DE	JP 2730847 JP 7011374 3 A 15-09-1992 FR 2662707 CA 2043723 DE 69104784 DE 69104784 EP 0465376 JP 4231435 2 A 27-08-1997 JP 3229954 JP 9291332 DE 69704801 DE 69704801 EP 0791662	JP 2730847 B2 JP 7011374 A 3 A 15-09-1992 FR 2662707 A1 CA 2043723 A1 DE 69104784 D1 DE 69104784 T2 EP 0465376 A1 JP 4231435 A 2 A 27-08-1997 JP 3229954 B2 JP 9291332 A DE 69704801 D1 DE 69704801 T2 EP 0791662 A1