Journal of University of Science and Technology Beijing
Volume 11, Number 2, April 2004, Page 127

Galvanic corrosion behavior of die cast AZ91D magnesium alloy in chloride solution

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(Received 2003-03-26)

Abstract: The galvanic corrosion behavior of die cast AZ91D magnesium alloy coupled with H62 brass, 316L stainless steel, A3 steel and LY12 aluminum alloy of different areas in 3.5% NaCl solution was studied. The free corrosion potentials, galvanic potentials and currents of these galvanic couples were measured. The galvanic effects were determined by the mass loss and regression method using three points. The results show that: (1) In these four kinds of couples AZ91D acts as the anode, whose galvanic corrosion behavior is mainly controlled by the cathodic polarization; (2) The free corrosion potentials of these four kinds of couples change a little with time and cathodic/anodic area ratio (CAAR); (3) The galvanic potential of AZ91D/LY12 moves positively with the increase of time and CAAR; (4) The galvanic currents increase with CAAR, but there is difference in the current change between different couples; (5) The anodic dissolution rate of the magnesium alloy increases by 2-3 orders after being coupled with these four kinds of metals and the galvanic effects of these couples have such a relation as $\gamma_{H62} > \gamma_{316L\ S.S} > \gamma_{LY12} > \gamma_{A3}$.

Key words: magnesium alloy; galvanic corrosion; galvanic effect

[*The research work was supported by the Ford-NSFC research and development fund.*]

1 Introduction

Magnesium alloys are the lightest structural material in practical use with high specific strength and stiffness, good electromagnetic shield and damping features as well as excellent machining and polishing performance [1-2]. Thus it is widely used in industries of aviation, automobile and electronic communication. However, magnesium alloys suffer from severe corrosion in moist, sulfide containing and sea atmosphere due to its high chemical activity [3]. Therefore, poor corrosion resistance of magnesium alloys becomes one dominant drawback for their popularization [4-9]. Magnesium alloys may be attacked by such kinds of corrosions as uniform corrosion, galvanic corrosion, high temperature oxidation, pitting, crevice corrosion, intergranular corrosion, stress corrosion and corrosion fatigue, *etc.* [7]. During their service, magnesium alloys are unavoidably in contact with other metal parts, which will cause galvanic corrosion problems to some extent [10, 11]. But reports or papers on the galvanic corrosion laws of magnesium alloys were hardly seen. To carry out deep and thorough research work on galvanic corrosion of magnesium alloys really means a lot not only in extending their applications but also enriching theories of corrosion science.

2 Experiments

2.1 Tested materials

Die cast AZ91D magnesium alloy, H62 brass, 316L stainless steel, A3 steel and LY12 aluminum alloy were adopted to form four kinds of galvanic couples. The compositions of these materials are shown in **table 1**.

AZ91D specimens were fixed with the epoxy resin with an area of 1 cm × 1 cm exposed. Specimens of H62 brass, 316L stainless steel, A3 steel and LY12 aluminum alloy were fixed with the epoxy resin with an exposed area of 1 cm×1 cm, 2 cm×2 cm, 3 cm×3 cm, respectively. All the specimens were abraded to an 800 grit finish on silicon carbide papers.

2.2 Measuring electrochemical parameters of galvanic corrosion

The free corrosion potentials, galvanic potentials and currents of die cast AZ91D magnesium were measured in 3.5% NaCl solution with a ZRA-1 galvanic corrosion meter after it was coupled with H62 brass, 316L stainless steel, A3 steel and LY12 alumi-

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num alloy.

Table 1 Compositions of tested materials

Material	Compositions (mass fraction in %)
AZ91D	Al: 8.5-9.5; Mn: 0.17-0.4; Zn: 0.45-0.9; Si: 0.05(max); Cu: 0.25(max); Ni: 0.001(max); Fe: 0.004(max); Mg: balance.
H62	Cu: 60.5; Pb: 0.08; Fe: 0.15; Sb: 0.005; Bi: 0.002; P: 0.01; Zn: balance.
316L.S.S	Ni: 12.45; Cr: 17.61; Mo: 2.29; C: 0.021; Mn: 1.05; Si: 0.69; P: 0.031; S: 0.002; Fe: balance.
A3	C: 0.1; Si: 0.2; Mn: 0.37; P: 0.019; S: 0.012; Fe: balance.
LY12	Cu: 3.8-4.9; Mg: 1.2-1.8; Mn: 0.3-0.9; Fe: 0.5; Si: 0.5; impurities: <1.5%; Al: balance.

2.3 Measuring the galvanic corrosion rate

Those couples mentioned above were immersed in 3.5% NaCl solution. Then the weight loss of AZ91D was calculated by comparing its mass before and after immersion. Thus the corrosion rate of different couples can be calculated.

2.4 Galvanic effects

After two kinds of metals are coupled, the galvanic effect γ is defined as the ratio of the dissolution current (i_B') of the anodic metal to the corrosion current (i_B) of the metal before being coupled. In this paper the corrosion current of the anode was obtained by weight loss calculation and the corrosion rate of the metal uncoupled was calculated in two ways: (1) according to the weight loss caused by the immersion of the metals in 3.5% NaCl solution for 210 h; (2) by regression method using three points on the polarization curve. The polarization curve was measured in 3.5% NaCl solution and plotted with PS-168 electrochemical measuring system. The scanning rate was 10 mV/s.

3 Results and discussion

Figure 1 shows how the potentials of different materials change with time after they were coupled as mentioned above in 3.5% NaCl solution. In the figures, E_{k2} is the free corrosion potential of AZ91D, E_{k1} the free corrosion potentials of other four kinds of metals, and E_g the galvanic potentials of the couples.

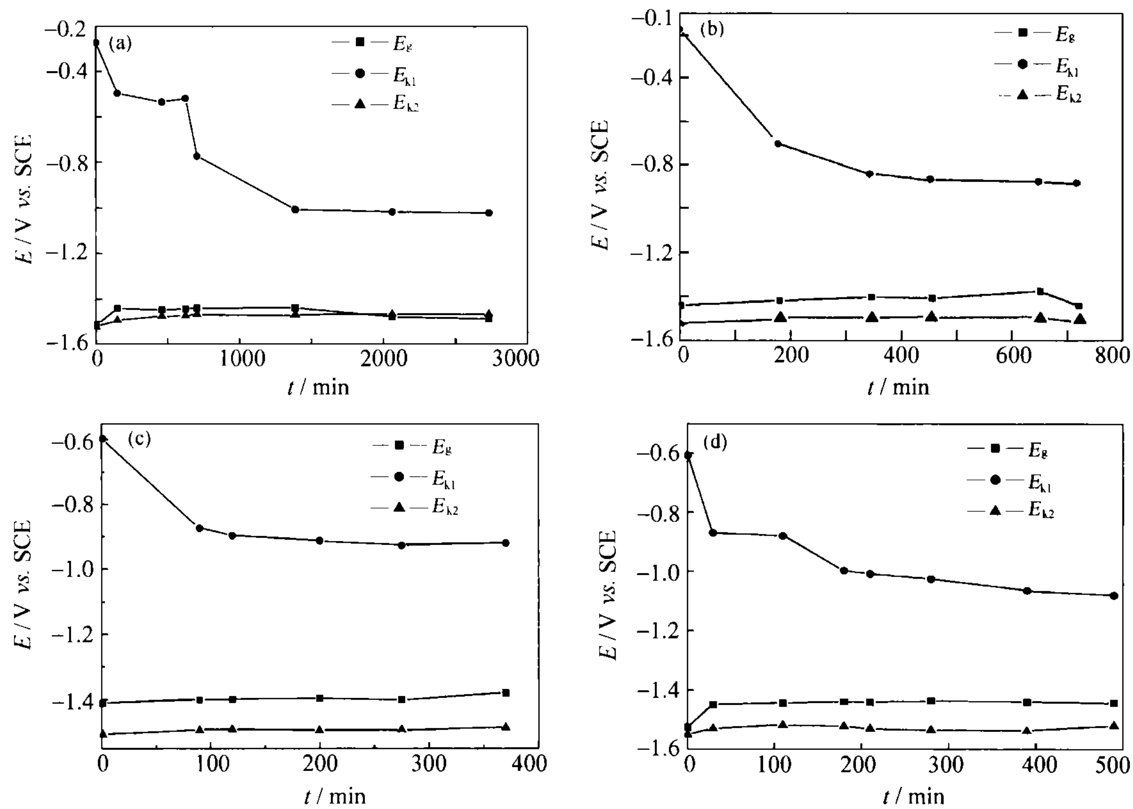
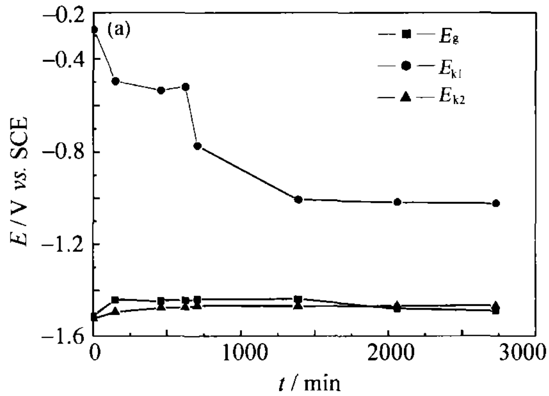
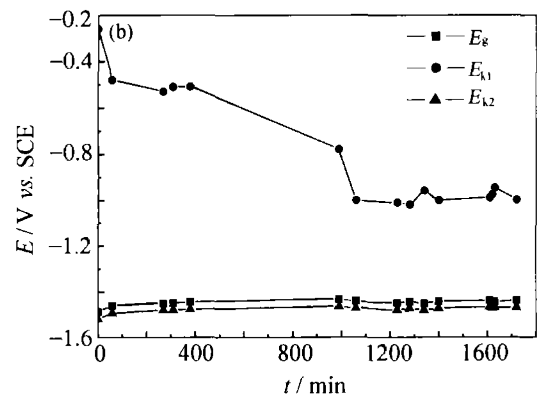


Figure 1 Potential changes of different couples with time: (a) AZ91D/H62; (b) AZ91D/316L; (c) AZ91D/A3; (d) AZ91D/LY12 (1 cm × 1 cm).

Figures 2 and **3** show how the potentials of different couples change with time and CAAR (the cathodic/anodic area ratio) after AZ91D was coupled with H62 brass and LY12 aluminum alloy in 3.5% NaCl solution.

It can be seen from figure 1 that AZ91D always acts as the anode in four kinds of couples. The free corrosion potential of the anode hardly changes with time, while the free corrosion potentials of cathodes reach a stable state after a period of time. In addition, between different couples there is no significant difference in galvanic potentials, which are almost close to the free corrosion potential of the anode. Therefore, it can be considered that the galvanic corrosion of AZ91D is mainly controlled by cathodic polarization.





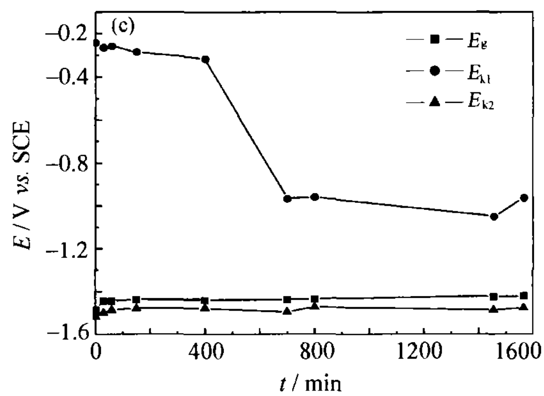
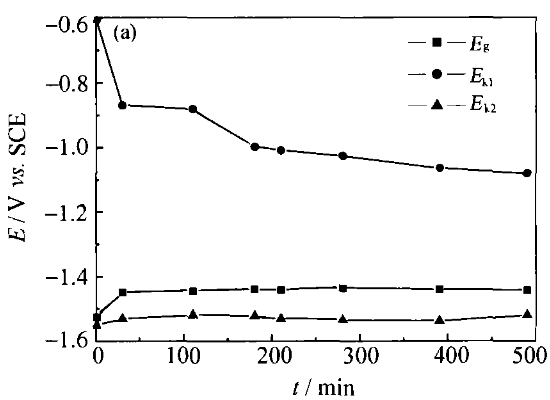
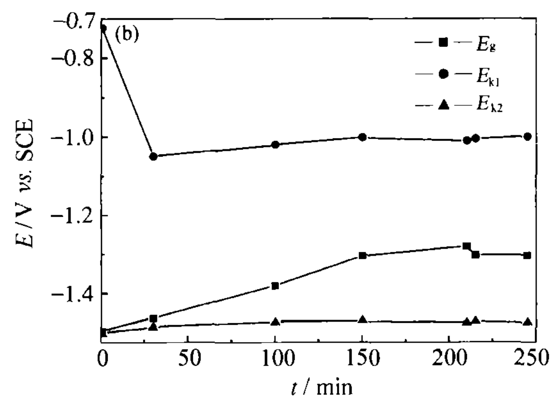


Figure 2 Potential changes of AZ91D/H62 brass couple with time and CAAR: (a) 1 cm × 1 cm; (b) 2 cm × 2 cm; (c) 3 cm × 3 cm.





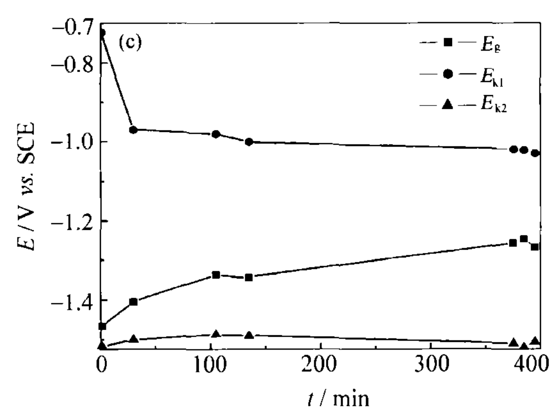


Figure 3 Potential changes of AZ91D/LY12 aluminum alloy couple with time and CAAR: (a) 1 cm × 1 cm; (b) 2 cm × 2 cm; (c) 3 cm × 3 cm.

It can be seen from figures 2 and 3 that the galvanic potential of AZ91D/H62 brass couple hardly change with time and CAAR. After AZ91D was coupled with LY12 aluminum alloy, the galvanic potential at first was near the free corrosion potential of AZ91D, but gradually it began to move positively with the increase of time and CAAR, which may be caused by the change in pH value of the solution with time and the ongoing reactions. The activity of LY12 increased and the effects of the corrosion of LY12 on galvanic corrosion could not be ignored.

Figures 4-7 demonstrate how the galvanic currents (I_g) of different couples composed of AZ91D and different materials of different area ratios change with time.

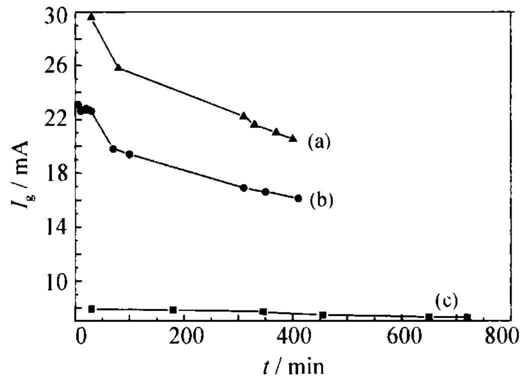


Figure 4 Galvanic current changes of AZ91D/316L stainless steel, the area ratio was 1:9 (a), 1:4 (b), and 1:1 (c).

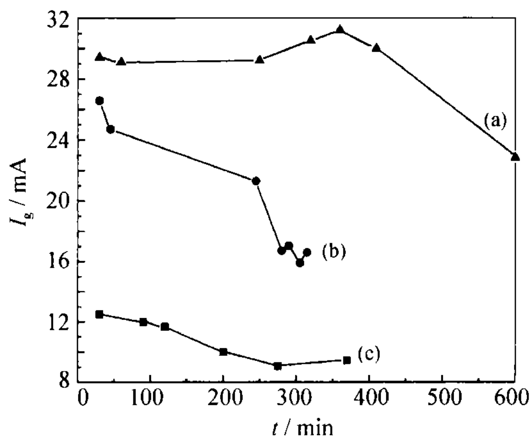


Figure 5 Galvanic current changes of AZ91D/A3 steel, the area ratio was 1:9 (a), 1:4 (b), and 1:1 (c).

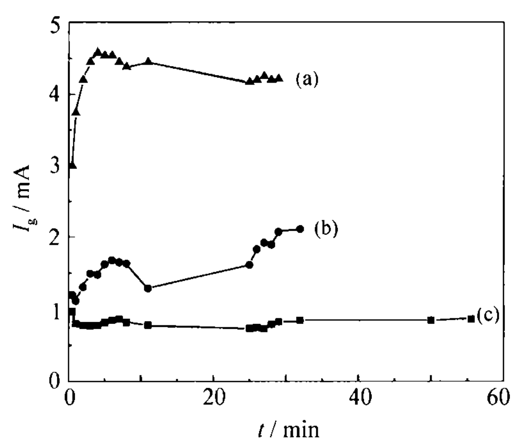


Figure 6 Galvanic current changes of AZ91D/H62 brass, the area ratio was 1:9 (a), 1:4 (b), and 1:1 (c).

Figures 4-7 show that though there is difference in galvanic current between different couples, the galvanic currents increase with CAAR, which indicates that area effect plays an important role in the galvanic corrosion of die cast AZ91D. From the figures it is also observed that the galvanic current density of the anode also increases with CAAR as the galvanic currents increase with CAAR. So the corrosion of the anode was accelerated with the increase of the CAAR.

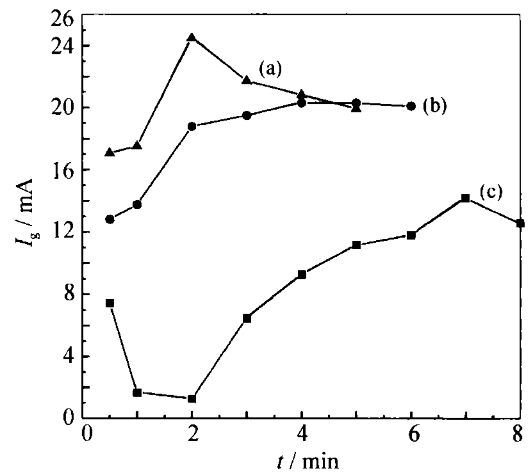


Figure 7 Galvanic current changes of AZ91D/ LY 12 aluminum alloy, the area ratio was 1:9 (a), 1:4 (b), and 1:1 (c).

Table 2 shows the relative data obtained from the immersion test lasting for 320 min in 3.5% NaCl solution after AZ91D was coupled with the four cathodic metals.

It indicates that the galvanic corrosion rates of different couples differ a lot. The corrosion rate of the couple composed of AZ91D and H62 brass is the lowest, that of the couple composed of AZ91D and 316L stainless steel is the second lowest, and those of the couples AZ91D/A3 steel and AZ91D/ LY12 are the highest and there is no great difference between these two rates. Motrover, it also shows that the galvanic corrosion rates of different couples increase with the CAAR.

After immersion in 3.5% NaCl solution for 210 h, the magnesium alloy's relative results are shown in **table 3**.

According to the data in tables 2 and 3, the galvanic effects can be calculated with the formula: $\gamma = i_B' / i_B$, which is shown in **table 4**.

According to the calculation, it is found that there is great difference in galvanic effect between different couples and there is a relation as $\gamma_{H62} > \gamma_{316L\ S.S} > \gamma_{LY12} > \gamma_{A3}$.

Figure 8 demonstrates the polarization curve of AZ91D. It was calculated out by the regression method using three points on the polarization curve that the free corrosion current density i_B of AZ91D uncoupled in 3.5% NaCl solution was 8.65×10^{-3} mA/cm^2. Again the galvanic effects were calculated with the formula: $\gamma = i_B'/ i_B$, the results are shown in **table 5**. It is seen that there is great difference in galvanic effect between different couples and there is a relation as $\gamma_{H62} > \gamma_{316L\ S.S} > \gamma_{LY12} > \gamma_{A3}$, which is in accordance with the results from the immersion test.

Table 2 Results obtained from the immersion test (320 min) of couples composed of AZ91D and cathodic metals*

Cathode	Area of cathode / (cm×cm)	W_1 /g	W_2 /g	ΔW / g	V / (g·h^{-1}·m^{-2})	i / (mA·cm^{-2})
316L stainless steel	1×1	8.56943	8.53281	0.03662	68.664	13.634
	2×2	9.31187	9.25182	0.06005	112.596	22.357
	3×3	9.07780	8.99693	0.08186	153.486	30.476
H62 brass	1×1	9.20640	9.18997	0.01143	21.432	4.255
	2×2	9.40103	9.37816	0.02287	42.882	8.514
	3×3	9.77215	9.73287	0.03928	73.650	14.624
A3 steel	1×1	9.99673	9.95076	0.04597	86.196	17.115
	2×2	9.05051	8.96541	0.08510	159.564	31.683
	3×3	9.37426	9.27101	0.10325	193.596	38.440
LY12	1×1	8.52915	8.48510	0.04405	82.596	16.400
	2×2	8.16037	8.07213	0.08754	164.136	32.591
	3×3	7.58180	7.48773	0.09407	176.382	35.022

Note: *—The mass after removing the corrosion products was obtained by extracting the mass change of the blank specimen in the solution for removing the corrosion products; W_1— the average mass before immersion test; W_2— the average mass after removing the corrosion products; ΔW— the even mass loss; V— the corrosion rate of anode after being coupled; i— the anodic dissolution current density.

Table 3 Results of AZ91D immersed in 3.5% NaCl solution for 210 h*

No.	W_0 / g	W_1 / g	ΔW / g	$\Delta W'$ / (g·m^{-2})	V / (g·h^{-1}·m^{-2})	$\overline{V}$ / (g·h^{-1}·m^{-2})	i / (mA·cm^{-2})
1	1.87316	1.84984	0.02332	11.24688	0.05356	0.0528	0.011794
2	1.81114	1.78572	0.02542	12.90624	0.06146	0.0528	0.011794
3	1.83202	1.81382	0.01820	9.10985	0.04338	0.0528	0.011794

Note: *—The area of these specimens was all 1 cm × 1 cm. The mass after removing the corrosion products was obtained by extracting the mass change of the blank specimen in the solution for removing the corrosion products. W_0— the original mass; W_1— the mass after removing the corrosion product; ΔW— the mass loss; $\Delta W'$— the mass loss of unit area; V— the corrosion rate; $\overline{V}$ —the average corrosion rate; i— the free corrosion current density.

Table 4 Galvanic effect calculated using results of the immersion test

Cathode	i_B' / (mA·cm^{-2})	i_B / (mA·cm^{-2})	γ
H62	4.255	0.011794	360.78
316L.S.S	13.634	0.011794	1156.01
A3	17.115	0.011794	1451.16
LY12	16.400	0.011794	1390.54

Note: i_B'— the anodic dissolution current density; i_B— the free corrosion current density; γ— the galvanic effect.

Table 5 Galvanic effects calculated by the regression method by using three points on the polarization curve of AZ91D

Cathode	i_B' / (mA·cm^{-2})	i_B / (mA·cm^{-2})	γ
H62	4.255	0.008645	492.19202
316L.S.S	13.634	0.008645	1577.09659
A3	17.115	0.008645	1979.75709
LY12	16.400	0.008645	1897.05032

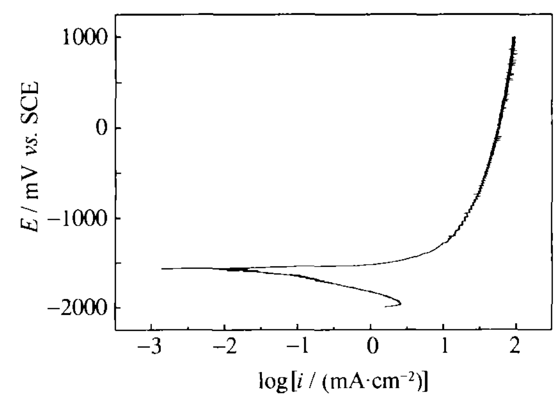


Figure 8 Polarization curve of AZ91D in 3.5% NaCl solution.

4 Conclusions

(1) In the four kinds of couples AZ91D acts as the anode, whose galvanic corrosion behavior is mainly controlled by cathodic polarization.

(2) The free corrosion potentials of these four kinds

of couples change a little with time and CAAR.

(3) The galvanic potential of AZ91D/LY12 moves positively with the increase of time and CAAR, while those of the other three kinds of couples do not change with time and the CAAR.

(4) The galvanic currents increase with CAAR, but there is difference in the current change between different couples.

(5) The anodic dissolution rate of the magnesium alloy increases by 2-3 orders after being coupled with these four kinds of metals and the galvanic effects of these couples have such a relation as $\gamma_{H62} > \gamma_{316L\ S.S} > \gamma_{LY12} > \gamma_{A3}$.

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