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Supplementary Information

Approaching "Stainless Magnesium" by Ca Micro-Alloying

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Supplementary Figures

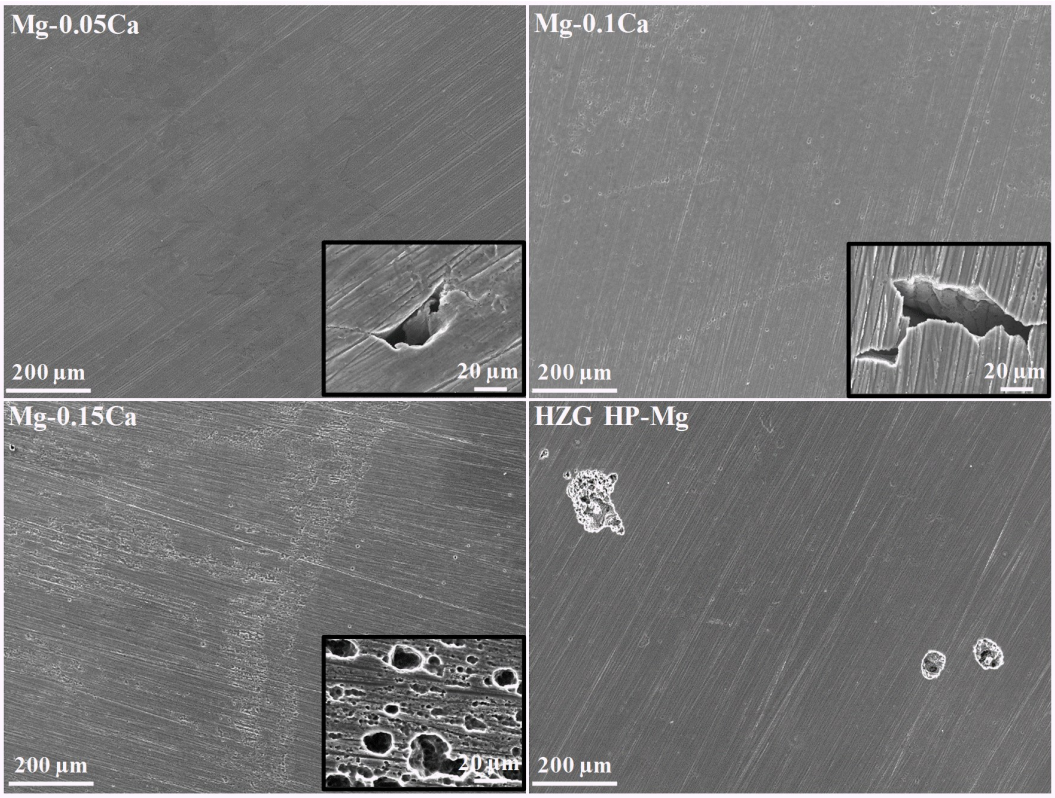

Fig. S1 Surface morphologies of micro-alloyed Mg-Ca and HZG HP-Mg after immersion in 3.5 wt% NaCl solution for 7 days and removing corrosion products with diluted chromic acid.

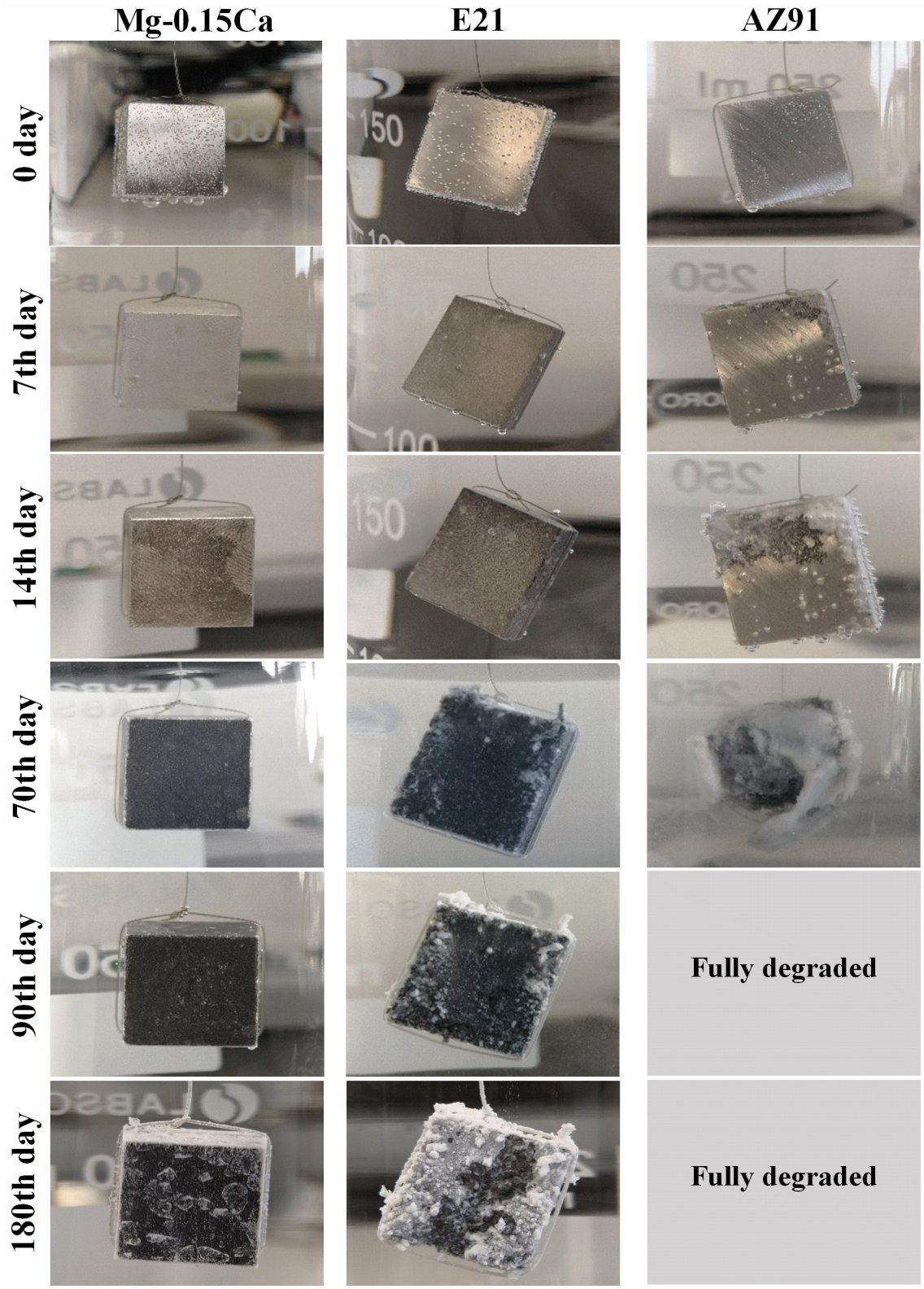

Fig. S2 Surface appearance alteration with time with regard to Mg-0.15Ca, E21 and AZ91 alloys amid immersion in 3.5 wt% NaCl solution for 6 months. The solution was refreshed after 6 months since it became turbid due to precipitation of corrosion products.

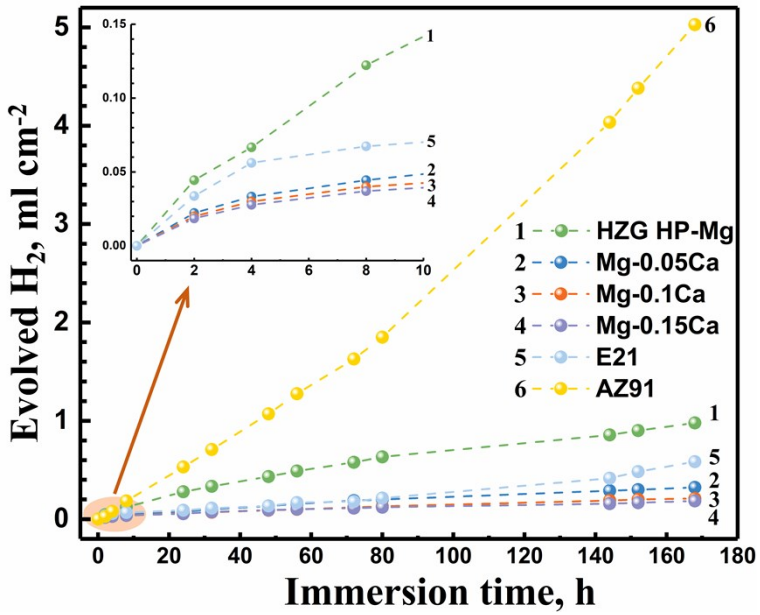

Fig. S3 Hydrogen evolution of micro-alloyed Mg-Ca during immersion in 3.5 wt% NaCl solution for 7 days in comparison to HZG HP-Mg, E21 and AZ91 alloys.

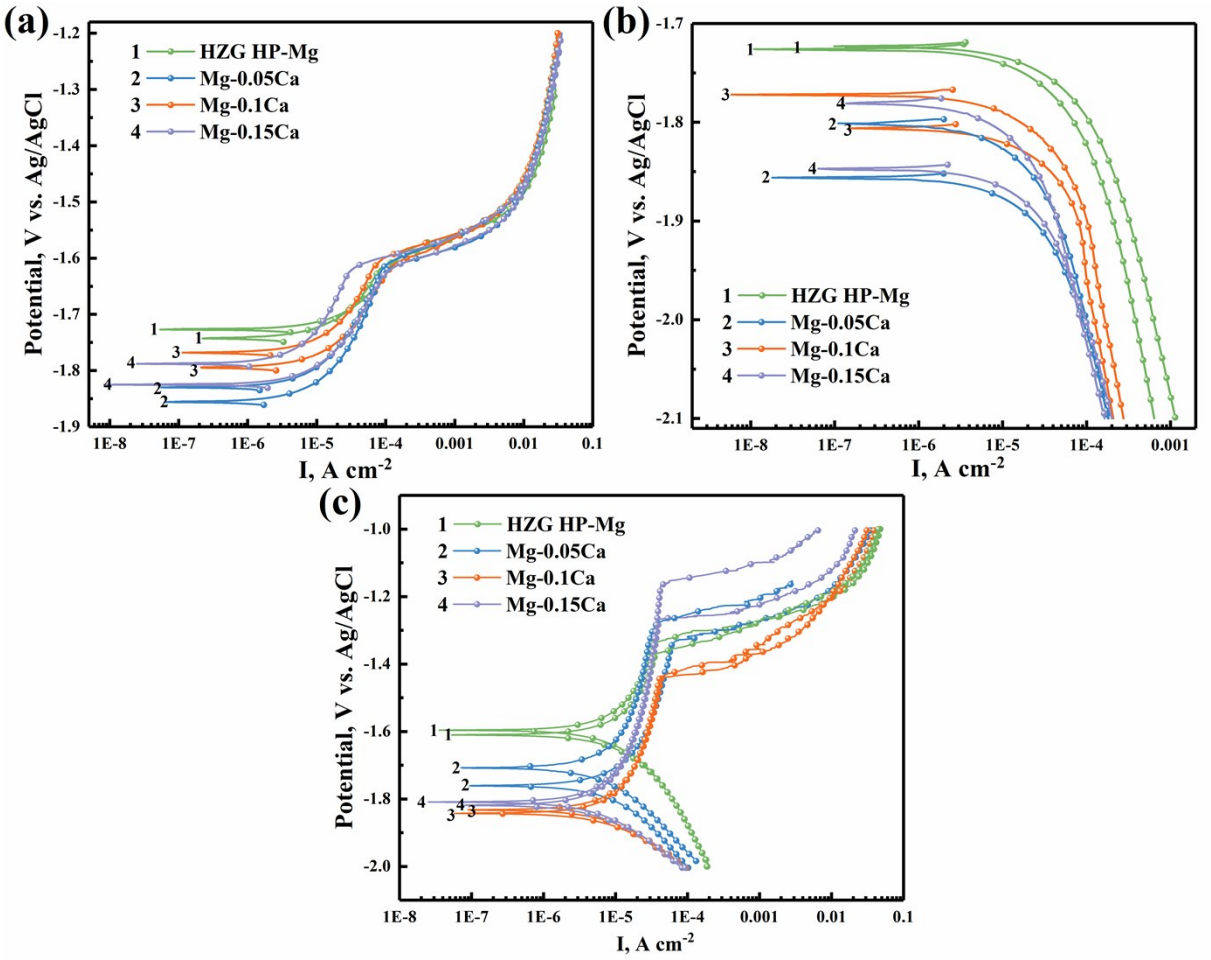

Fig. S4 Data of replicated polarization measurements in 3.5 wt% NaCl solution. (a) Anodic polarization curves after 1 h immersion. (b) Cathodic polarization curves after 1 h immersion. (c) Polarization curves after immersion for 7 days obtained by direct scanning.

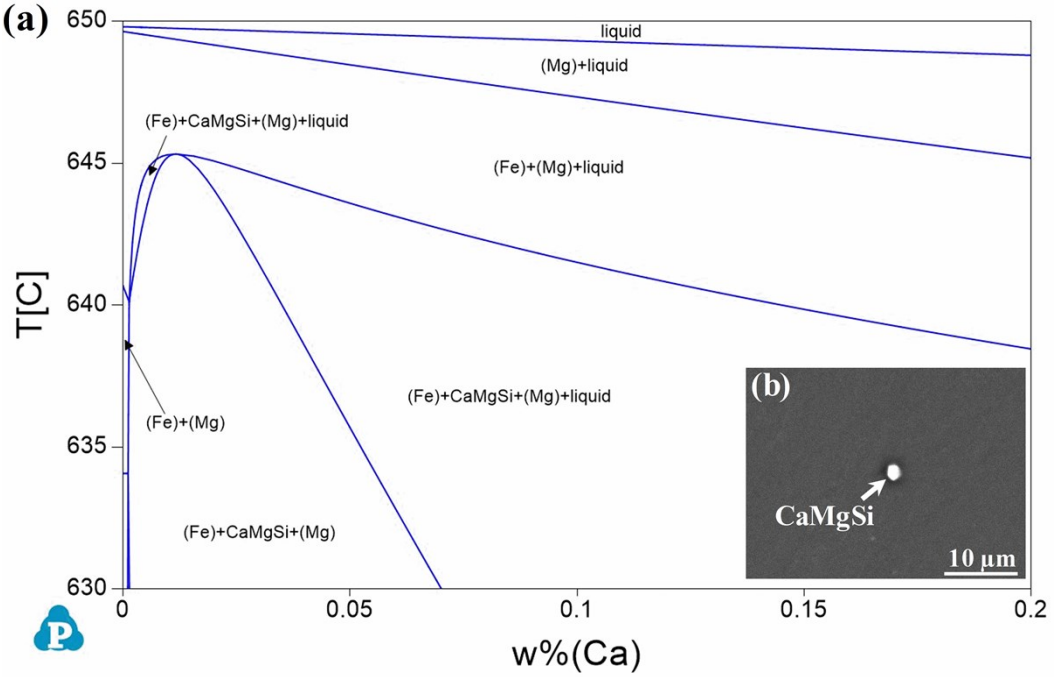

Fig. S5 (a) Calculated Mg-Ca-Fe-Si phase diagram at constant 20 ppm Fe and 50 ppm Si via Pandat program with the PanMg2017 database. (b) SEM (BSE) image of Mg-0.1wt%Ca alloy.

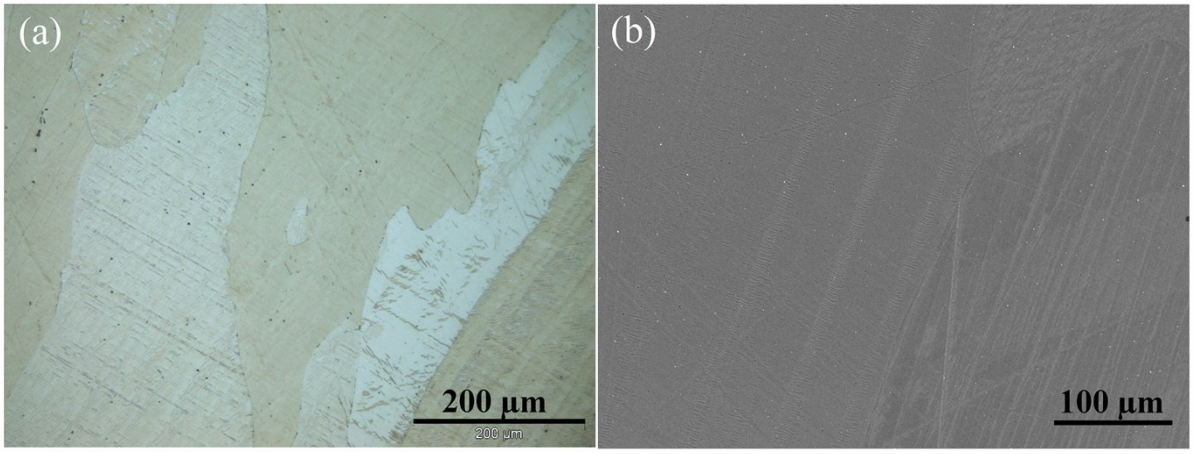

Fig. S6 Microstructure of Mg-0.1wt%Ca lean alloy: (a) OM image; (b) SEM image.

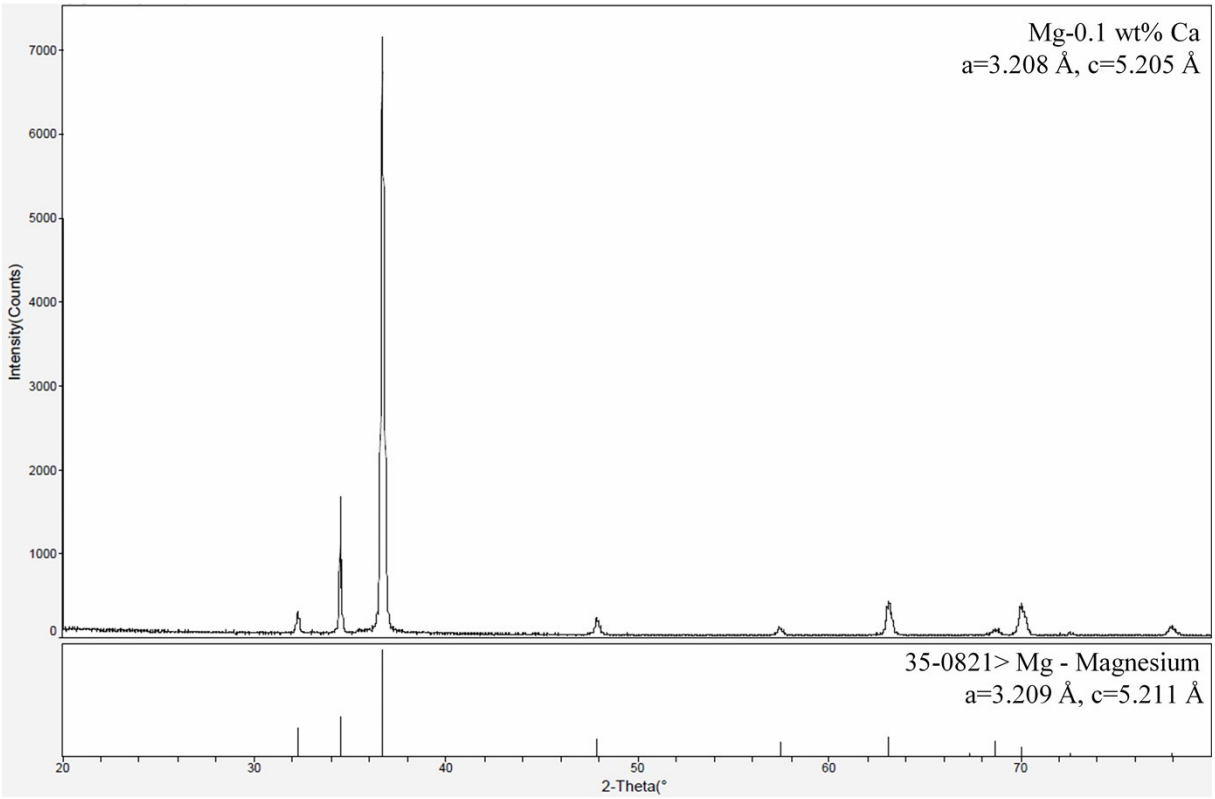

Fig. S7 XRD pattern of Mg-0.1wt% Ca lean alloy. Calculated lattice parameters from the XRD pattern are also displayed.

Supplementary Tables

Table S1 Experimental details of immersion tests for the determination of corrosion rates of diverse Mg materials in the present work. All the samples were hung with fishing line in pH-unbuffered 3.5 wt% NaCl solution. Initial mass indicates the mass of ground samples before immersion. Final mass is the mass of samples after immersion and removal of corrosion products with chromic acid. The corrosion rates were calculated based on the mass loss.

Specimen	Duration (d)	Surface area (cm^2)	Initial mass (g)	Final mass (g)	Mass loss (mg)	Corrosion rate (mm y^{-1})
Mg-0.05Ca-1	7	10.0	3.9919	3.9875	4.4	0.13
Mg-0.05Ca-2	7	9.0	3.4115	3.4077	3.8	0.13
Mg-0.05Ca-3	7	8.9	3.3327	3.3314	1.3	0.04
Mg-0.1Ca-1	7	10.2	4.0835	4.0810	2.5	0.07
Mg-0.1Ca-2	7	10.0	4.0362	4.0343	1.9	0.06
Mg-0.1Ca-3	7	8.6	3.0998	3.0975	2.3	0.08
Mg-0.15Ca-1	7	10.8	4.0320	4.0287	3.3	0.09
Mg-0.15Ca-2	7	10.8	4.0009	3.9983	2.6	0.07
Mg-0.15Ca-3	7	10.4	3.8599	3.8575	2.4	0.07
HZG HP-Mg-1	7	11.6	3.4161	3.4059	10.2	0.26
HZG HP-Mg-2	7	9.0	2.9360	2.9263	9.7	0.32
HZG HP-Mg-3	7	9.2	3.0261	3.0177	8.4	0.27
Elektron 21-1	7	8.9	2.2104	2.2040	6.4	0.22
Elektron 21-2	7	9.3	2.3063	2.3000	6.3	0.20
Elektron 21-3	7	9.2	2.2657	2.2567	9.0	0.29
AZ91-1	7	11.1	4.3827	4.3006	82.1	2.22
AZ91-2	7	11.3	4.5037	4.4406	63.1	1.68
AZ91-3	7	11.8	4.7876	4.7342	53.4	1.36
Mg-0.05Ca-4	15	8.5	2.8342	2.8307	3.5	0.06
Mg-0.1Ca-4	15	8.5	3.0027	2.9983	4.4	0.07
Mg-0.15Ca-4	15	10.7	3.9801	3.9735	6.6	0.09
HZG HP-Mg-4	15	10.9	3.9338	3.9194	14.4	0.19

Table S2 Corrosion rates of various Mg-Al-Zn (AZ), RE-containing (Mg-RE), Mg-Li based and newly proposed low-alloyed Mg-X (X = As, Ge, Sn, Bi, Pb and Sb) alloys collected from literatures. Corrosion rates were determined by mass loss (ML) or hydrogen evolution (HE) in different solutions (1, 3.5 wt% NaCl; 2, 3.5 wt% NaCl saturated with $Mg(OH)_2$; 3, 4 wt% NaCl; 4, 5 wt% NaCl; 5, 5 wt% NaCl saturated with $Mg(OH)_2$; 6, 0.1M NaCl; 7, 0.5 M NaCl; 8, 0.6 M NaCl). All Mg alloys were either cast or treated by specified processing.

Mg alloy	Alloying load (wt%)	Condition	Solution	Method	Corrosion rate (mm y^{-1})	Reference
AZ61-Ca	7.0	extruded	8	ML	0.71	[1]
	7.1				1.69	
	7.5				1.86	
AZ31B	4.5	extruded with varied extrusion ratios	3	ML	3.51	[2]
					1.56	
					2.36	
					2.20	
AZ31B	4.0	rolled	1	ML	210	[3]
		rolled and heat treated			178	
AZ31-Ca	4.0	extruded	2	ML	10	[4]
	4.05				11	
	4.1				8	
	4.2				7.4	
AZ91-Ti	10.2	as-cast	1	ML	74.13	[5]
	10.5				10.92	
AZ31	4.0	extruded	1	ML	2.35	[6]
		rolled			1.51	
		rolled and heat treated			1.23	
					1.05	
AZ31	4.7	extruded	1	ML	29	[7]
		rolled			18	
					8	
AZ80	9.1	rolled	1	ML	4	[8]
		friction stir processed			2	
AZ91	10.2	as-cast	1	HE	9.45	[9]
AZ91	10.0	as-cast	4	ML	0.96	[10]
AZ91	9.8	as-cast	1	ML	0.2	[11]
AZ80	8.8	chill as-cast			0.15	
AZ31	4.1	wrought			12.6	
AZ91-Nd	9.6	extruded	1	ML	2.94	[12]

	9.5				0.38	
	10.2				1.05	
AZ91D	9.3	die-cast	2	HE	0.12	[13]
AZ80	8.9	as-cast	2	HE	0.25	[14]
AZ91D	10.0	thixomolded	4	HE	0.17	[15]
MRI153M	11.1				0.68	
AZ91	10.7	as-cast	1	HE	4.8	[16]
AZ91-Ce	10.3				0.21	
	11.2				0.29	
	11.7				0.09	
AZ91-La	10.5				0.23	
	10.6				0.23	
	12.2				0.08	
AZ91	10.3	as-cast	1	ML	5.7	[17]
AZ91-Sb	10.6				5.2	
AZ91-Si	10.1				6.7	
AZ91-Sb/Si	10.7				3.9	
AZ63	8.4	-	8	ML	20	[18]
AZ91D	10.1	die-as-cast	4	ML	3	[19]
					4	
					6	
Mg-Li	4.0	extruded	6	ML	1.85	[20]
	7.5				3.38	
	14.0				0.86	
Mg-Li-Al	6.1	extruded and	1	ML	40.95	[21]
	6.0	then rolled			35.7	
	5.9				27.3	
	6.0				16.8	
	5.7				10.5	
Mg-Li-Al-Y	12.6	as-cast	1	ML	3.04	[22]
	14.0				7.43	
	17.0				3.27	
	6.0				74.21	
	9.0				2.34	
	10.6				17.6	
	12.0				3.08	
	13.6				2.04	
	15.0				2.76	
Mg-Li-Y-Zn	16.4	extruded	1	ML	20.54	[23]

	9.9				7.56	
	13.2				4.62	
Mg-Li-Al-Zr-Y	15.1	rolled	6	ML	0.8	[24]
		quenched			4.2	
		aged			1.68	
Mg-Li-Al-RE	14.5	as-cast	7	ML	6.47	[25]
Mg-Li-Al-Zn-Zr	16.2	heat treated	1	ML	17.85	[26]
	13.2				6.3	
	10.2				12.6	
Mg-Li-Al-Zn-Zr	16.2	extruded	1	ML	21	[27]
	13.2				4.2	
	10.2				7.56	
Mg-Li-Al-Zn-Nd-Zr	17.5	heat treated extruded	1	ML	210 94.5	[28]
Mg-Li	8.9	heat trated	6	ML	1.47	[29]
		as-cast			1.68	
EV31	4.9	heat treated	2	ML	0.88	[30]
WE43	6.2				0.23	
ZE41	6.2				8.5	
Mg-Al-Nd	5.2	die-as-cast	4	ML	0.32	[31]
EW75	13.5	heat treated	1	ML	2.03	[32]
		compressed			1.32	
Mg-Y-Nd	7.0	friction stir	1	ML	0.10	[33]
		processed			0.13	
		as-rolled			0.23	
		heat treated after rolling			0.38	
Mg-Gd-Y-Zr	9.4	heat treated	4	ML	1.05	[34]
	11.4				1.68	
	13.4				3.57	
	15.4				2.63	
WE43	6.8	heat treated	2	HE	0.7	[35]
					0.36	
Mg-Nd-Zn-Zr	3.6	as-cast	4	ML	0.41	[10]
					2.75	
		heat treated			0.24	
					0.54	
					0.30	
					0.65	

Mg-Y	2.0	as-cast	6	HE	4	[36]
	3.0				20	
	4.0				30	
	7.0				40	
Mg-Gd-Y-Nd-Zr	8.2	extruded	5	ML	0.95	[37]
	8.9				0.85	
	9.0				1.05	
	9.6				1.3	
Mg-Y	5.0	sputter	2	ML	0.35	[38]
	10.0	deposited			0.69	
	20.0				0.85	
	40.0				0.53	
Mg-Gd	5.0				0.79	
	10.0				0.78	
	20.0				0.4	
Elektron 21	4.8	as-cast	2	ML	0.19	[39]
		heat treated			0.15	
					0.11	
					0.12	
					0.14	
ZE41	5.0	as-cast	6	HE	2.3	[40]
Mg-Gd	5.0	rolled	2	ML	1	[41]
Mg-Nd	0.6				3.75	
Mg-La	0.7				4.39	
Mg-Ce	0.9				6.38	
Mg-Gd	5.0	as-cast	2	ML	58.5	[42]
		heat treated			31.75	
Mg-Nd	0.6	as-cast			5.12	
		heat treated			23.9	
Mg-La	0.7	as-cast			17.05	
		heat treated			3.42	
Mg-Ce	0.9	as-cast			10.6	
		heat treated			7.55	
Mg-Y	5.0	as-cast			7.22	
		heat treated			8.95	
MEZ	4.3	sand-cast	4	ML	42	[43]
	4.3				6.2	
NZ30K	3.6	as-cast	4	ML	0.44	[44]
Mg-Ge	0.1	as-cast	6	ML	1.68	[45]
	0.3				0.84	

Mg-Sn	0.5				4.2	
Mg-Pb	0.5				0.7	
Mg-Sb	0.2				1.05	
	0.3				1.26	
Mg-Bi	0.1				1.47	
	0.5				3.15	
AZ31	4.1	wrought	8	ML	0.42	[46]
AZ61	7.2				1.05	
Mg-Y-Nd	7.7	as-cast	1	ML	36.75	[47]
	8.1				25.51	
	8.6				16.69	
Mg-Li-Zn-Al	12.0	as-cast	1	ML	25.2	[48]
Mg-Ca	0.3	as-cast	2	ML	0.99	[49]
		heat treated			1.25	
				HE	0.81	
					0.51	
Mg-Ca	0.5	as-cast	1	ML	0.2	[50]
					0.31	
				HE	0.15	
					0.26	
AZ61	6.78	as-cast	4	ML	7.16	[51]
		heat treated			0.5	
AZ61-Ca	8.67	as-cast			2.6	
		heat treated			0.86	
AZ61	6.78	extruded	4	ML	0.68	[52]
		heat treated			0.42	
AZ61-Ca	8.67	extruded			1.21	
		heat treated			0.44	
AZ61-Ti	7.8	as-cast	1	ML	1.51	[53]
	7.5				30	
	7.6				12.6	
AZ91-Gd	10.55	as-cast with	1	ML	1.41	[54]
	10.47	ultrasonic			0.85	
	11.14	vibration			0.6	
	11.35				0.76	
Mg-Gd-Y-Zn-Zr	17.9	heat treated	1	HE	0.4	[55]
					0.5	
					2.7	
					2.3	

Mg-Gd-Zn-Zr	17.6	as-cast	2	HE	49.16	[56]
		heat treated			6	
Mg-Gd-Zn-Zr	17.6	peak-aged	2	HE	7.02	[57]
		over-aged			4	
Mg-Zn-Gd-Zr	14.6	as-cast	1	ML	6	[58]
	13.9				19.5	
	12.2				15	
	14.6	extruded			4	
	13.9				8	
	12.2				5	
AZ91-Ca/Y	10.3	die-cast	1	ML	0.12	[59]

Table S3 Chemical compositions of all prepared Mg-Ca alloys. The values are in ppm or in wt% when indicated. * Data from reference.[60] **Data from reference.[61]

	Mg-0.05Ca	**Mg-0.1Ca**	**Mg-0.15Ca**	**HZG HP-Mg**	**Elektron 21**	**AZ91**	**UHP-Mg***	**UQ HP-Mg****
Ca	0.04%	0.09%	0.15%	<1	5	<1	<1	30
Fe	16	13	14	51	7	13	2	20
Cu	7	11	7	<1	10	19	<1	<20
Ni	7	5	8	<2	6	5	<1	<10
Si	53	97	34	<1	<5	331	1	100
Mn	80	210	90	8	50	0.43%	2	170
Al	64	68	21	50	14	10.68%	28	0.1%
Zn	18	16	20	10	0.25%	0.72%	48	30
Zr	<3	<3	<3	23	0.48%	26	<1	-
Nd	-	-	-	-	2.69%	-	-	-
Gd	-	-	-	-	1.04%	-	-	-
Mg	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

Reference

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