Corrosion Stress Relaxation in Pure Magnesium and Die-Cast Mg Alloys

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Abstract

The effect of corrosive solutions on stress relaxation behavior of pure Mg and its alloys is studied. Pure magnesium shows a crucial corrosion stress relaxation in 3.5wt.% NaCl even at room temperature in comparison with tests in air. Die-cast Mg alloys AZ91D, AM50 and AS21 at room temperature show a relatively small stress decrease both in air and in different corrosive media. At elevated temperature, all studied die-cast Mg alloys show a strong stress relaxation in a 3.5 % NaCl corrosive solution. In a corrosive environment, the highest sensitivity to stress relaxation was observed both in the alloy with the highest Al content (AZ91D), and in AS21 alloy that contains two intermetallics ($Mg_{17}Al_{12}$ and Mg_2Si). It is shown that the stress relaxation method manifests a high sensitivity to structural homogeneity of alloys, especially in corrosive solutions.

According to TEM investigations of pure Mg, an unloaded specimen comprises a few dislocations in the vicinity of such an obstacle as grain boundary. At a constant strain of about 4×10^{-4}, dislocation networks were found with a sharply increasing quantity of dislocations.

Introduction

The principal drawback of magnesium as a structural material, besides its relatively low corrosion resistance, is poor stress relaxation behavior[6] which limits Mg alloys application in automotive and aerospace industry.

It is well-known[1-7] that the relaxation behavior of a material is characterized by a spectrum of relaxation times or a relaxation spectrum H(τ). To the first approximation,

$$H(\tau) = - [dE(t)/d\ln t]_{t=\tau}$$

where τ is the relaxation time, $E(t) = \sigma(t)/\varepsilon_o$ is the relaxation modulus ; t is time, $\sigma(t)$ is the current relaxation stress changing from the initial value of stress σ_o ($t = 0$) to its final value (the remaining stress) σ_{rem}; ε_a is the initial strain corresponding to the stress σ_o, τ is the relaxation time.

The relaxation time τ corresponding to the maximum of the function H(τ), as well as the remaining stress, are accepted as characteristics of stress relaxation. [1, 7] Earlier we have found that τ strongly depends on casting parameters and porosity. It varies in AZ91D alloy at 150°C from 10 to 20 hours.[4]

The present paper deals with the corrosion stress relaxation behavior of pure Mg and die-cast Mg alloys in 3.5% NaCl (pH ≈ 5), 0.1N $Na_2B_4O_7$ buffer solution (pH 9.3) and the latter solution saturated with $Mg(OH)_2$ having also stable pH ~9.4.

Experimental Methods

Flat specimens (total length 115 mm, gauge sizes 10 x 4 x 42 mm^3) of polycrystalline magnesium (99.9653% Mg) produced by Dead Sea Magnesium Works (DSM, Israel) were cut out from a commercial ingot in the transverse direction. Round specimens (5.9 mm in diameter, gauge length 75 mm) of Mg alloys AZ91D (Mg - 8.4% Al, 0.85% Zn, 0.17% Mn), AM50 (Mg - 5.1% Al, 0.15% Zn, 0.57% Mn) and AS21 (Mg - 2.3% Al, 0.23% Mn,

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1.10% Si were produced on a die-cast machine with the locking force of 3450 kN (Magnesium Research Institute, DSM). Standard mechanical properties of pure Mg and its alloys at room temperature were as follows: ultimate tensile strength *(UTS)* equal to 60, 225, 229 and 221 MPa, tensile yield strength *(TYS)* equal to 24, 170, 136 and 134 MPa, elongation-to-fracture equal to 5.6, 2.8, 11.7 and 9.7% for pure Mg, AZ91D, AM50 and AS21 alloys, respectively. A decrease in tensile yield strength defined in air at 70°C as compared to room temperature was equal to about 12±1 % for each alloy.

Stress relaxation tension tests with the duration of 50 and 100 hours were performed on the universal testing machine Zwick-1445 (Zwick GmbH & Co, Germany) at the temperatures of 25 ± 2°C and 70± 1°C and a constant strain during the entire test. The initial stress in stress relaxation tests varied from 0.67 to 1.15 of tensile yield strength of the alloys. This machine was equipped with a split furnace Carbolite VST 12/75/300 and an electrochemical cell (Figure 1). The same cell had been used earlier in corrosion creep tests.[5]
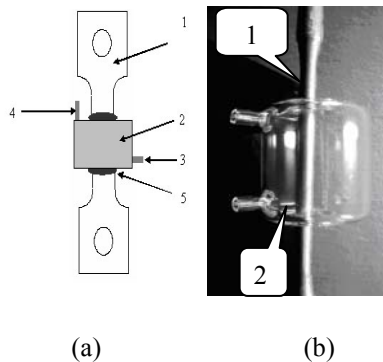

(a)   (b)

Figure 1. Pure Mg specimen (a) and a round sample of Mg alloy (b) fitted to a glass or rubber cell. 1-a specimen ; 2-cell ; 3,4-inlet and outlet for solutions ; 5-sealing.

Specimens were studied after rinsing with distilled water and wiping with acetone. The compositions of electrolytes for corrosion stress relaxation (CSR) tests were as follows: $0.1N$ $Na_2B_4O_7$ buffer solution (pH 9.3), $0.1N$ $Na_2B_4O_7$ solution saturated with $Mg(OH)_2$ (pH~9.4) and 3.5 % NaCl (pH ~ 5). Usually, CSR tests of pure Mg were carried out at a continuous solution feed at the rate of 3-5 cm^3/min. Several sets of CSR tests of Mg alloys in the buffer solution were studied in the cell without a solution flow. During these long-term tests, a certain increase in the pH

value was observed, but it was less than 3%. All solutions were prepared from analytical grade chemicals and distilled water. All tests were carried out using at least 3 specimens for each set of experiments.

Microstructure studies were carried out using an optical microscope "Nicon", a scanning electron microscope (JEOL JSM-5600) and a transmission electron microscope (JEM 2010). Magnesium crystallites are very large, about 2 mm in diameter and more than 8 mm long (Figure 2). The grain size of Mg-Al solid solution in the studied Mg alloys amounts to 1-10 microns and 10-15 microns in the surface layer and in the bulk of die castings, respectively. Some grains of AS21 alloy comprise also needles of magnesium silicide Mg_2Si (Figure 2). Cleaning after tests implied the removal of corrosion products from the surface of specimens by their dissolution in 15% CrO_3 solution at 80°C during 0.5-1 min (the ASTM standard G1-88).

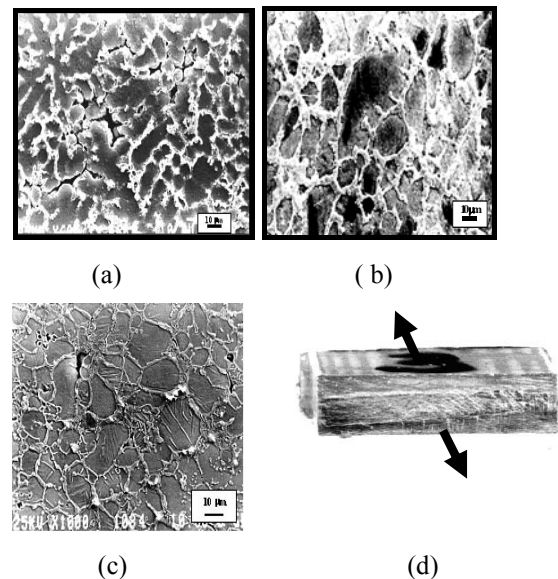(a)   (b)

(c)   (d)

Figure 2. Microstructure of die-cast AZ91D (a), AM50 (b) and AS21 (c) alloys ; (d) a crystallite (dendrite) in the cross-section (10 mm x 4 mm) of a pure Mg sample ; arrows show tensile stress directions.

Results and Discussion

Relaxation tests were carried out for 50 and 100 hours. Since the remaining stress corresponding to the end of tests remained almost unchanged after the exposure exceeding 50 hrs, the majority of tests were performed for 50 hrs (Table 1).

Corrosion Stress Relaxation in Pure Magnesium and Die-Cast Mg Alloys

Table 1. Effect of environment, stress and test temperature on stress relaxation in pure Mg and die-cast Mg alloys

Alloy	Medium	t, ˚C	Initial stress, σ_0, MPa	σ_0/TYS	Remaining stress		100 hr %
					50 hrs		
					%	σ_s/σ_a	
Pure Mg	Air	25	16	0.67	92.5	-	-
	3.5% NaCl	25	16	0.67	21.2	0.23	-
	Air	25	50	2.1	49.7	-	46.7
	3.5% NaCl	25	50	2.1	5.9	0.12	fracture
AZ91D	Air	25	150	0.88	93.3	-	-
		25	195	1.15	84.4	-	82.0
		70	115	0.79	74.1	-	-
		70	150	1.03	66.1	-	-
	0.1N Na$_2$B$_4$O$_7$	25	150	0.88	92.9	1.00	-
	0.1N Na$_2$B$_4$O$_7$ +Mg(OH)$_2$	25	195	1.15	85.3	1.01	82.3
	3.5% NaCl	25	150*⁾	0.88	90.0	0.96	-
		70	115	0.79	64.4	0.87	-
		70	150*⁾	1.03	52.0	0.79	-
AM50	Air	25	115	0.85	91.0	-	-
		25	140	1.03	81.0	-	-
		70	90	0.77	78.4	-	-
		70	115	0.98	60.1	-	-
	0.1N Na$_2$B$_4$O$_7$	25	115	0.85	90.1	0.99	88.4
	0.1N Na$_2$B$_4$O$_7$ +Mg(OH)$_2$	25	140	1.03	81.2	1.00	
	3.5% NaCl	25	115	0.85	88.0	0.97	-
		25	140	1.03	80.1	0.99	-
		70	90	0.77	73.5	0.94	-
		70	115	0.98	58.1	0.97	-
AS21	Air	25	115	0.86	92.0	-	-
		25	140	1.04	79.9	-	-
		70	90	0.78	86.4	-	-
	0.1N Na$_2$B$_4$O$_7$	25	115	0.86	90.2	0.98	88.7
	0.1NNa$_2$B$_4$O$_7$ + Mg(OH)$_2$	25	140	1.04	76.2	0.95	
	3.5% NaCl	25	115	0.86	93.3	1.01	-
		25	140	1.04	79.6	0.99	-
		70	90	0.78	66.4	0.77	-

*⁾ A part of specimens was broken under this stress.

Under the initial stress σ_0 of 16 MPa or ~ 0.7 of tensile yield strength, pure magnesium shows a crucial decrease in stress in 3.5 % NaCl solution. For example, time-dependent stress after 50 hrs decreases from 92.5 % in air to 21.2 % in a corrosive medium Table 1 and Figure 3.
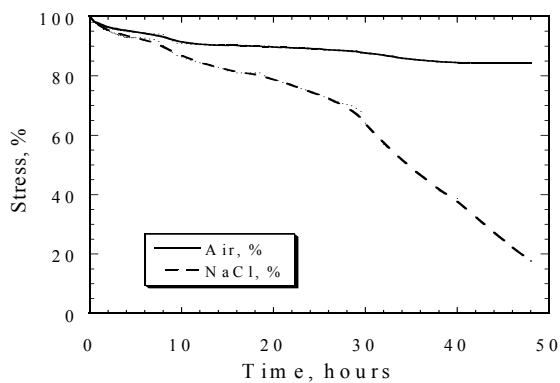

Figure 3. Stress relaxation in pure Mg in air and in 3.5% NaCl solution, 25ºC, σ_o = 16 MPa (0.7 of TYS).

At room temperature under the initial stresses σ_0 varying in the range from ~0.8 to ~1.2 of tensile yield strength, all the alloys under study (AZ91D, AM50 and AS21) show a relatively small decrease in stress both in air and in different corrosive media (Table 1). For example, in AM50 alloy at σ_0 = 115 MPa, the remaining stress σ_{rem} after 50 hrs amounts to 91.0%, 90.1% and 88.0% in air, 0.1N Na$_2$B$_4$O$_7$ and 3.5% NaCl solutions, respectively (Table 1). Growth of the initial stress from 115 MPa to 140 MPa leads to a decrease in σ_{rem} in AM50 from 91.0% to 81.0% in air, and from 88.0% to 80.1% in 3.5% NaCl solution (Table 1).

An increase in the test temperature from 25°C to 70°C leads to a significantly stronger stress relaxation of all alloys in comparison with room temperature, especially in corrosive solutions (Table 1 and Figure 4). For instance, in air under the initial relative stresses close to the yield

strength ($\sigma_0/TYS \sim 1$) corresponding to a given alloy and temperature, the remaining stress decreases from 86.7% to 66.1% in AZ91D and from 81.0% to 60.1% in AM50. In 3.5% NaCl solution under the same relative stress, σ_{rem} for AM50 decreases from 80.1 % to 58.1 % with test temperature growth from 25°C to 70°C (Table 1). It is noteworthy that in 3.5% NaCl at the same initial stress $\sigma_0 = 115$ MPa, AM50 and AZ91D alloys show almost the same relaxation resistance: σ_{rem} equal to 58.1% and 64.4%, respectively.

The sensitivity of magnesium and alloys to a corrosive solution may be defined by σ_s/σ_a ratios, where σ_s and σ_a are the remaining stresses in a solution and in air under the same initial stress. At room temperature, this ratio is significantly less than 1 only for pure Mg, for instance $\sigma_s/\sigma_a = 0.23$ at $\sigma_0 = 16$ MPa, and shows a very high sensitivity to a salt environment (Table 1). Stress relaxation behavior of alloys at room temperature both in the air and in solutions is almost the same (Table 1).

At elevated temperatures, the alloys, especially AS21 and AZ91D, show a higher sensitivity to a corrosive environment in stress relaxation tests in comparison with room temperature. AM50 showed the lowest sensitivity. For instance, in air and in 3.5% NaCl ($70°C$, $\tilde{\sigma}/TYS \cong 0.8$), σ_s/σ_a ratios were equal to 0.77, 0.87 and 0.94 for AS21, AZ91D and AM50, respectively (Table 1). However, in air at the same stress of 90 MPa, AS21 shows a higher relaxation resistance in comparison with AM50 alloy, the remaining stress equals 86.4% and 78.4%, respectively. On the contrary, in 3.5% NaCl, AM50 manifests a higher relaxation resistance (remaining stress in AM50 and AS21 amounts to 73.5% and 66.4%, respectively). Thus, the highest sensitivity to a corrosive environment during stress relaxation testing was observed both in the alloy with the highest Al content (AZ91D), as shown in creep tests,[5] and in AS21 alloy that comprises two intermetallics ($Mg_{17}Al_{12}$ and Mg_2Si).

Relaxation spectra calculated from experimental data can be used for estimating the homogeneity of materials, namely, to the first approximation; the most homogeneous alloy usually gives the narrowest peak. Pure polycrystalline Mg shows a relatively narrow peak of the relaxation spectrum in air and a broad peak in NaCl solution (Figure 5). In comparison with tests in air, corrosive solution displaces the H(t) peak of Mg to the right: the relaxation time is equal to 30 hrs and 45 hrs, respectively (Figure 5).
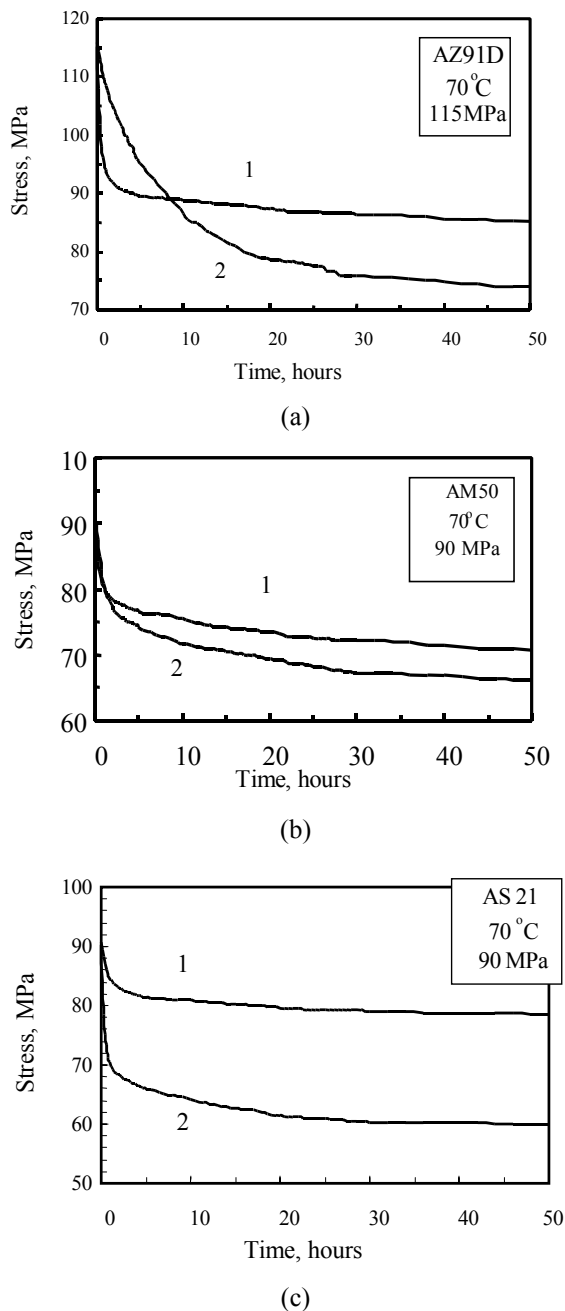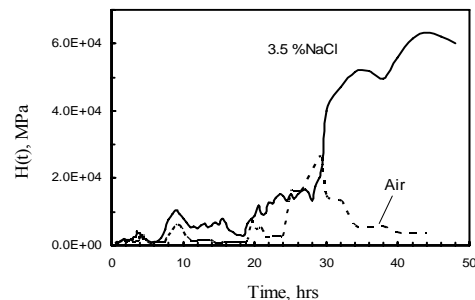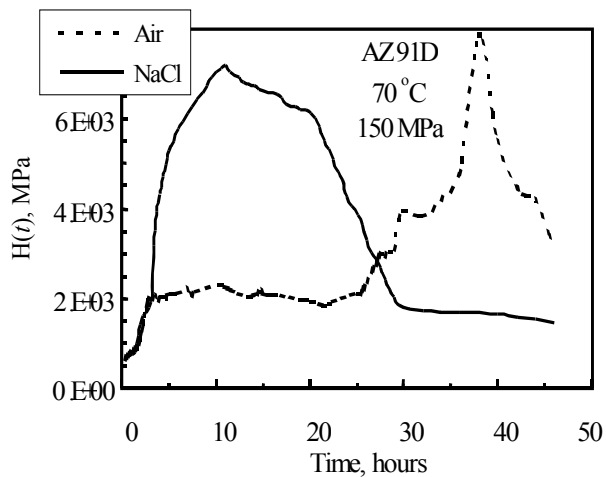

Figure 4. Stress relaxation in die-cast Mg alloys AZ91D (a), AM50 (b) and AS21 (c) in air (1) and in 3.5% NaCl solution (2) at 70°C under the initial stress $\tilde{\sigma} \cong 0.8$ of tensile yield strength.

Figure 5. Relaxation spectra of pure Mg in air and in 3.5% NaCl solution at 25°C under the initial stress of 16 MPa.

AM50 alloy shows very narrow peaks both in air and in corrosive environments. For instance, in Figure. 6 one can see these peaks for all alloys in air and in NaCl at 70°C. Apparently, AM50 alloy having a very narrow peak shows the highest stress relaxation homogeneity.

In contrast to AM50, AS21 and especially AZ91D having in a solution, as a rule, a relatively broad peak of relaxation times, manifests the lowest stress relaxation homogeneity (Figure 6).

A similar behavior of AZ91D alloy was observed earlier in air at 150°C, under the initial stress of 0.8 of *TYS*, spectra of relaxation times represent broad bell-shaped spectra with maximums corresponding to relaxation times τ varying from 8 to 16 hours. [4] Thus, the spectrum of relaxation times obtained from a stress relaxation test is a very sensitive "instrument" showing the degree of structural homogeneity of an alloy.
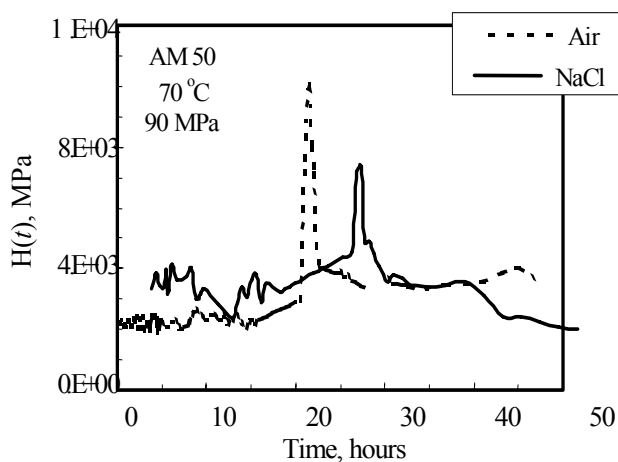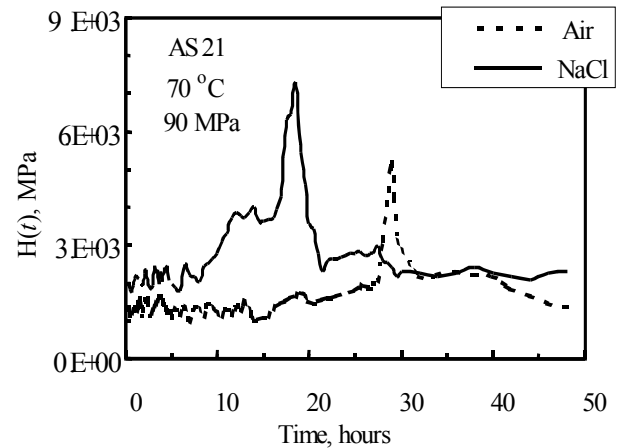
(c)

Figure 6. Relaxation spectra of die-cast Mg alloys AZ91D (a), AM50 (b) and AS21(c) in air and in 3.5% NaCl solution at 70°C under the initial stress of 150 MPa(a) and 90 MPa(b, c).

At room temperature, the environment almost does not affect the relaxation time in AZ91D and AM50 alloys belonging to Mg-Al-(Zn)-Mn system, but for AS21 alloy (Mg-Al-Si-Mn system) we have observed a significant difference between τ values in air and in a corrosive medium (Table 2). At an elevated temperature under the initial stress of 0.8 of *TYS,* the relaxation time corresponding to the maximum of the function $H(\tau)$ decreases in 3.5 % NaCl solution in comparison with that in air from 38 hours to 10 hours in AZ91D and from 29 hours to 18 hours in AS21. These values for a more homogeneous AM50 alloy are equal to 22 and 25 hours, respectively (Figure 6).

In air at an elevated temperature, a higher relaxation resistance of AS21 alloy (a higher remaining stress) in comparison with AM50 alloy is connected with the presence of needle-shaped intermetallics Mg_2Si improving viscoelastic properties. On the contrary, in an aggressive environment (3.5% NaCl) under stress, needle-shaped silicides significantly decrease relaxation resistance of this alloy as compared with AM50 (Table 2). Such intermetallics promote strain hardening and, thus, increase the chemical potential of metal atoms and their mechanochemical dissolution.[2,3]

(a)

(b)

Table 2. Relaxation times in die-cast Mg alloys depending on the environment, stress and temperature, hours

AZ91									
25°C						70°C			
150MPa			195MPa			115MPa		150MPa	
Air	NaCl	$Na_2B_4O_7$	Air	NaCl	$Na_2B_4O_7 + Mg(OH)_2$	Air	NaCl	Air	NaCl
25	26	30	21	22	25	38	10	38	11

AM50									
25°C						70°C			
115MPa			140MPa			90MPa		115MPa	
Air	NaCl	$Na_2B_4O_7$	Air	NaCl	$Na_2B_4O_7 + Mg(OH)_2$	Air	NaCl	Air	NaCl
24	27	26	22	24	25	22	25	24	30

AS21							
25°C						70°C	
115MPa			140MPa			90MPa	
Air	$Na_2B_4O_7$	NaCl	Air	NaCl	$Na_2B_4O_7 + Mg(OH)_2$	Air	NaCl
20	30	28	20	28	28	29	18

SEM and optical micrographs presented in Figures 7-9 show microstructure, pitting and cracking of die-cast magnesium alloys after corrosion relaxation tests in $0.1N$ $Na_2B_4O_7$ solution saturated with $Mg(OH)_2$ and 3.5%NaCl. Here, pitting is present both in micrographs of polished cross-sections representing microstructure in the vicinity of the cast surface of AZ91D and AM50 alloys, with corrosion products filling some pits (Figures 7 and 8) and in micrographs of the cast surface, for example, of AZ91D (Figure 9). One can observe the β-phase (white) on the grain boundaries of α-Mg in AZ91D and AM50, and, in addition, a certain fragmentation of grains in both alloys after stress relaxation tests (Figure 8). The deepest pits were observed at the elevated temperature of 70°C, which strongly accelerates the stress corrosion rate (see, for instance, a pit in AM50); (Figure 7d). In spite of the presence of relatively long cracks both on the cast surface (Figure 7a) and in the center (Figure 7b) of AZ91D specimen, the latter was not broken after 50 hours of testing in the buffer solution. However, in 3.5% NaCl, cracks arise and develop at the same stress, for example, in AZ91D alloy, resulting sometimes in its fracture (Table 1). The crack presented in Fig. 7b shows that cracking of AZ91D alloy originates in a transgranular manner.

TEM investigation of pure magnesium shows that an unloaded specimen comprises only a few dislocations in the vicinity of the grain boundary (Figure 10a). However, there is a sharp contrast between this micrograph and micrographs corresponding to specimens after stress-relaxation test (air, 25°C, initial stress of 20 MPa) during 0.5 hour (Figure 10b). At a constant strain of about 4 x 10^{-4}, dislocation networks with a sharp increase in the quantity of dislocations were found even after a 0.5-hour exposure to stress in the elastic region.

That points to the connection of stress relaxation mechanism with the evolution of dislocation substructure at the expense of relieving

inner stresses by plastic microdeformations. It is known that the change in physico-mechanical properties and fine microstructure (plasticization) of a solid under the influence of chemical (electrochemical) reactions which proceed on its surface causing additional dislocation flux, is called chemomechanical effect.[2,3] Therefore, the influence of active environment on the stress relaxation manifests itself through the influence on the dislocation evolution observed in the form of chemomechanical effect.

Conclusions

1. At room temperature, pure magnesium shows a crucial corrosion stress relaxation in 3.5 % NaCl solution in comparison with tests in air. On the contrary, stress relaxation in die-cast Mg alloys shows a relatively small decrease in the stress both in air and in different corrosive media.

2. An increase in the test temperature up to 70°C leads to a significantly stronger stress relaxation of all alloys in comparison with room temperature, especially in a corrosive solution. The highest sensitivity to a corrosive environment under a constant strain was observed in AS21 and AZ91D alloys, and the lowest in AM50 alloy.

3. It is shown that the stress relaxation method manifests a high sensitivity to structural homogeneity of alloys. Relaxation spectra in various environments show a very narrow peak for AM50 alloy. It points to a single marked relaxation time value both in air and in corrosive environments. On the contrary, AZ91D shows a broad spectrum of relaxation times and a lower homogeneity as compared with AM50.

Acknowledgment

References

1. Bland, D. R. 1980. *The theory of Linear Viscoelasticity*. New York: Pergamon Press.

2. Gutman, E. M. 1967. *Sov. Mater. Sci.* **3(190, 293)** : 401.

3. Gutman, E. M. 1994. *Mechanochemistry of solid surfaces.* Singapore : World Scientific: 322.

4. Gutman, E. M., Unigovski, Ya., Aghion, E., Koren Z. and Eliezer, A. 2000. Effect of die-casting conditions on viscoelastic behavior of Mg-alloy. *J. Mater. Perform. Eng.* **9(3)** : 297-301.

5. Gutman, E. M., Eliezer, A., Unigovski, Ya., and Abramov, E. 2001. Mechanoelectro-chemical behavior and creep corrosion of magnesium alloys. *Mater. Sci. Eng.* **A302** : 63-67.

6. Pettersen, K. and Fairchild, S. 1997. Stress relaxation in bolted joints of die-cast magnesium components. *SAE tech. paper series, Paper No. 970326 : Warrendale, Pa.* : 23-31.

7. Tobolsky, A.V. 1960. *Properties and structure of polymers.* New York : John Wiley & Sons : 331.