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EFFECT OF ANODIC POLARIZATION ON STRESS CORROSION CRACKING OF SOME ALUMINUM ALLOYS

ABSTRACT

The results of some corrosion and stress corrosion tests under constant sustained load, made on Al-Mg and Al-Zn-Mg alloys at corrosion and anodic potentials, are presented. The long term exposure of the alloys at anodic potentials is shown to be accompanied by fast failure, remarkable decrease in the tensile strength, very deep loss of plasticity and substantial uniform or intergranular layer corrosion of surface layer. The artificial aging improves the resistance of the Al-Zn-Mg alloys to failure and corrosion. Stress corrosion cracking is concluded to be mainly caused by dissolution mechanism rather than by entry of hydrogen.

Key words: aluminum alloys, potential, stress corrosion cracking

INTRODUCTION

Some Al-Mg and Al-Zn-Mg alloys are at certain conditions prone to stress corrosion cracking (SCC) in seawater. The mechanism of failure is still far from established and convincing evidence to make a choice among different proposed theories is lacking. In the past, SCC was explained by an intensive electrochemical attack localized along the grain boundaries as a result of difference in electrochemical potential of solid solution, precipitated phases and precipitate - free zone. The dissolution was said - to cause the crack incubation and an appearance of high stress gradients able to propagate the crack between deep pits, to make a rupture of an oxide layer and to result in formation of microcells in which the crack tip had more anodic potential [1-4]. More recently, SCC was attributed to an appearance of atomic hydrogen as a result of chemical reaction between Al and water, or of cathodic charging, followed by hydrogen diffusion into the crack tip. Hydrogen present in the lattice is known to cause failure by decohesion of the lattice, decrease of flow stress in near - boundary area or by formation of brittle unstable hydrides [1,5].

The investigations of an influence of electrochemical polarization on stress corrosion cracking were usually aimed at determining the mechanism of SCC and hydrogen embrittlement (HE) in HCl or NaCl solution. Only few papers reported on the effect of anodic polarization on environmental - related failure of aluminum alloys [6-9]. The crack velocity was observed to always increase at anodic polarization in range of potentials up to 200 [6], 300 [7,8] or 600 mV vs. corrosion potential [9]. The strong

dissolution behavior and mud-crack pattern was reported in [8,10]. In a single paper the anodic potential was shown to cause a remarkable loss in ductility [10].

So far papers have not given a substantial evidence for to explain the contribution of both anodic dissolution and hydrogen entry into cracking and degradation of mechanical properties at anodic potentials. This work is aimed at studying the effect of anodic polarization of the Al-Mg and Al-Zn-Mg alloys undergoing different thermal treatment in order to further clarify the problem of mechanism of stress corrosion cracking at electrochemical polarization.

EXPERIMENTAL PROCEDURE

Three different aluminum alloys were investigated: AlZn5Mg1 conventional alloy, AlZn5Mg2CrZr alloy with increased content of magnesium and an addition of chromium and zirconium, and AlMg4.5Mn alloy, generally known as resistant to stress corrosion cracking. The chemical composition of the alloys is illustrated in Table 1.

Table 1. Chemical composition [wt. %]

Alloy	Zn	Mg	Mn	Cr	Zr	Fe	Si
AlMg4.5Mn	0.03	4.3	0.61	0.13	—	0.31	0.19
AlZn5Mg1	4.35	1.25	0.18	0.14	0.04	0.32	0.16
AlZn5Mg2CrZr	5.3	2.1	0.01	0.17	0.19	0.03	0.15

Ti, Cu - no more than 0.05%; (Al the remainder)

The AlMg4.5Mn alloy was investigated as hot rolled and recrystallized (H321). The other alloys were solution heat treated and then aged at ambient or elevated temperature (natural or artificial aging). The applied thermal treatment, including designations of used tempers, is shown in Table 2.

The 10 mm thickness sheets were cut in long transverse direction and then the smooth round specimens, 60 mm in length and 5 mm in diameter of working part, were prepared. After thermal treatment the mechanical properties of specimens - ultimate tensile strength, yield stress and fracture strain - were determined by tensile machine at a strain rate 10^{-3} s^{-1} .

Two types of experiments were made, both during exposure of specimens for time up to 1000 h in 3.5% NaCl solution. The first stress corrosion tests were carried out for specimens stressed with a constant sustained load equal 0.9 nominal yield stress. In these tests either times to failure were determined or, for specimens - which did not fail during 1000 h, their tensile properties were measured after the exposure. The second corrosion tests were made on specimens exposed without any load for time equal the time to failure of any appropriate alloy (or 1000 h for these alloys which have not failed during stress corrosion tests), and then their tensile strength, yield stress and fracture strain were measured. The results were calculated as the mean values for series of three specimens for every alloy, temper and electrochemical potential.

Table 2. Parameters of thermal treatment

Alloy	Annealing parameters	Cooling medium	Aging parameters
AlZn5MgI- T4	703K/45 min	air	Natural aging 100 days
AlZn5MgI T6 ₁	as above	water 288K	6 days 293K 8h/363K 16h/418K
AlZn5MgI T6 ₂	as above	water 353K	as above
AlZn5MgI T6 ₃	as above	air	as above
AlZn5Mg2CrZr T4	723K/90 min	air	natural aging 100 days
AlZn5Mg2CrZr T6 ₂	as above	water 353K	6 days 293K 15h/368K 10h/423K
AlZn5Mg2CrZr T6 ₃	as above	air	as above

All tests were carried out at corrosion potential and two different anodic potentials: 50 mV and 100 mV more positive than corrosion potential. For exposed specimens the examinations of surface and fracture area were made by optical and scanning electron microscopy. Electrochemical polarization curves in 3.5% NaCl were recorded for all alloys and tempers by potentiostatic technique.

RESULTS

The times to failure for specimens tested under external stress are shown in Table 3. Generally all specimens exposed at corrosion potential did not fail except two single specimens of both Al-Zn-Mg alloys undergoing the natural aging, which cracked after above 900 h exposure. The anodic polarization of 50 mV caused the rapid failure of the AlZn5MgI alloy of the T4 temper and slower cracking of the other alloys except the AlZn5Mg2CrZr alloy aged at elevated temperature. More positive potential of +100 mV vs. E_{cor} resulted always in failure during 1000 h exposure, as a rule very fast except again the AlZn5Mg2CrZr alloy of the T6 tempers.

Table 4 demonstrates the loss of ultimate tensile strength (TS) as measured in corrosion tests (without load). The losses were calculated with regard to the nominal values of tensile strength for no exposed specimens, as $-(TS_{cor}-TS_0)/TS_0$, where indexes "cor", "o", relate to the strength of specimen after and before test. The absolute values of tensile strength are also reported. As a rule, the natural aging increases the relative loss in strength.

Table 5 shows the relative loss of another mechanical property measured in corrosion tests (without load), fracture strain (FS), expressed here, in similar way as above, as $-(FS_{cor}-FS_0)/FS_0$ where indexes "cor", "o", again mean the values measured for specimens after and before testing, relatively. It is worthy to note that, in opposition to the loss in strength, the most remarkable loss of ductility (expressed by tensile elongation) is noted for the alloys undergoing the artificial aging.

Table 3. Time to failure (t_f) in stress corrosion tests

Alloy	t_f E_{cor} [h]	t_f + 50mV [h]	t_f +100mV [h]
AlMg4.5Mn	n. f.	204	109
AlZn5Mgl T4	n. f.*	42	14
AlZn5Mgl T6 ₁	n. f.	530	48
AlZn5Mgl T6 ₂	n. f.	940	58
AlZn5Mgl T6 ₃	n. f.	940	59
AlZn5Mg2CrZr T4	n. f.*	730	61
AlZn5Mg2CrZr T6 ₂	n. f.	n. f.	927
AlZn5Mg2CrZr T6 ₃	n. f.	n. f.	927

n.f. - no failure during 1000 h

* - 1 specimen of three failed in less than 1000 h

Table 4. Relative loss of tensile strength in corrosion tests

Alloy	$\Delta T. S.$ E_{Co} [%]	$\Delta T. S.$ + 50mV [%]	$\Delta T. S.$ +100mV [%] %	T. S. [Mpa]
AlMg4.5Mn	0.0	58.1	57.0	292
AlZn5Mgl T4	10.9	40.1	41.4	384
AlZn5Mgl T6 ₁	8.5	16.3	15.1	398
AlZn5Mgl T6 ₂	2.4	17.4	20.1	373
AlZn5Mgl T6 ₃	0.6	20.9	32.2	354
AlZn5Mg2CrZr T4	8.6	40.1	41.6	397
AlZn5Mg2CrZr T6 ₂	1.1	18.4	20.2	445
AlZn5Mg2CrZr T6 ₃	1.9	24.8	26.4	366

Table 5. Relative loss of fracture strain in corrosion tests

Alloy	$\Delta F. S.$ E_{cor} [%]	$\Delta F. S.$ + 50mV [%]	$\Delta F. S.$ +100mV [%]	F. S. [%]
AlMg4.5Mn H321	2.8	66.7	73.3	18.0
AlZn5Mgl T4	7.5	70.0	82.1	17.3
AlZn5Mgl T6 ₁	7.6	72.4	86.9	14.5
AlZn5Mgl T6 ₂	7.0	70.4	88.7	14.2
AlZn5Mgl T6 ₃	10.7	66.9	85.1	12.1
AlZn5Mg2CrZr T4	3.3	67.5	68.3	12.3
AlZn5Mg2CrZr T6 ₂	4.2	86.1	97.2	7.2
AlZn5Mg2CrZr T6 ₃	6.2	89.6	97.9	9.6

Table 6 illustrates the appearance of surfaces at corrosion and anodic potentials. Sometimes very strong corrosion attack has been noticed which can be identified with a localized layer corrosion along the grain boundaries lying parallel to the rolling direction. Some examples of such behavior are shown in Figures 1-3.

The potentiostatic polarization curves had generally well-known for aluminum alloys picture. The difference in open circuit potentials was observed among the different

alloys rather than among their tempers. The potential values are collected in Table 7 which shows as well the values of current density for the anodic polarization applied.

Table 6. Appearance of specimen's surfaces after stress corrosion tests

Alloy	E [mV]	Appearance
AlMg4.5Mn H321	0	No corrosion.
	+50	Moderate uniform corrosion.
	+100	Intense uniform corrosion.
AlZnSMg1 T4	0	Weak layer corrosion.
	+50	Intense layer corrosion. Separation of surface layer.
	+100	As above, more intensive.
AlZn5Mg1 T6 ₁	0	Weak layer corrosion.
	+50	As of the ta temper.
	+100	As above.
AlZn5Mg1 T6 ₂	0	No corrosion.
	+50	Layer corrosion, less intense than of the T4 temper.
	+100	As above.
AlZn5Mg1 T6 ₃	0	No corrosion.
	+50	As of the above temper.
	+100	As above.
AlZn5Mg2CrZr T4	0	Weak layer corrosion.
	+50	Intense layer corrosion.
	+100	Heavy layer damage. Fragmentation of surface layer.
AlZn5Mg2CrZr T6 ₂	0	No corrosion.
	+50	Weak layer corrosion.
	+100	Intense layer corrosion.
AlZn5Mg2CrZr T6 ₃	0	No corrosion.
	+50	As of the above temper.
	+100	As above.



Fig. 1. Surface and fracture area for AlMg4.5Mn alloy after stress corrosion test for 100 h at +100 mV vs. E_{cor}

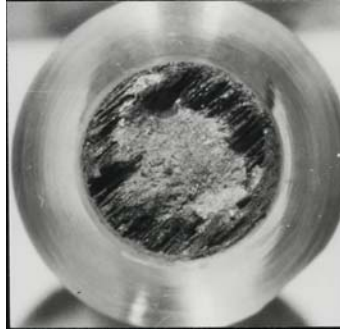


Fig. 2. Fracture area for AlZn5Mg1 alloy of the T4 temper after stress corrosion test for 48 h at + 50 mV vs. E_{cor} .



Fig. 3. Surface and fracture area for AlZn5Mg1 alloy of the T6₁ temper after stress corrosion test for 50 h at +100 mV vs. E_{cor}

Table 7. Anodic current density at different electrochemical potential

Alloy	Potential mV vs. SCE	Current density at + 50 mV [A/m ²]	Current density at +100 mV [A/ m ²]
AlMg4.5Mn H321	-790	120	1000
AlZn5Mgl T4	-900	170	1700
AlZn5Mgl T6 ₁	-890	150	1300
AlZn5Mgl T6 ₂	-890	70	900
AlZn5Mgl T6 ₃	-890	40	720
AlZn5Mg2CrZr T4	-940	60	700
AlZn5Mg2CrZr T6 ₂	-930	10	380
AlZn5Mg2CrZr T6 ₃	-930	16	300

DISCUSSION

The obtained results disclose that chemical composition, thermal treatment and anodic polarization influence on susceptibility to failure, degradation of strength and plasticity, and corrosion resistance.

Observed here good resistance of the Al-Mg alloy has been already known and may be attributed to negligible amounts of grain boundary anodic precipitates [11].

An addition of Zr and Cr to the Al-Zn-Mg alloy improved the SCC behaviour, likely because of change in composition and distribution of precipitating phases rather than inhibition of highly directional grain structure.

The values of time to failure, strength loss and corrosion damage as observed on the surfaces suggest that the T4 temper leads to the structures of the Al-Zn-Mg alloys less resistant to corrosion and stress corrosion cracking. These results correlate with reports on decreased susceptibility of Al-Zn-Mg alloys undergoing natural aging which has been attributed to the formation of continuous precipitates in zone adjacent to grain boundaries [1].

However, the loss of plasticity expressed in terms of change in tensile elongation was the most pronounced for the T6 tempers rather than for the T4 one. The same effect has been reported in study on effect of cathodic polarization on ductility [12]. Previously, the tempers most prone to failure under stress were reported to have originated in the deepest RA losses, at least for studies on hydrogen embrittlement of these alloys. Only in one single paper [13] both discussed effects were observed simultaneously, the positive effect of natural aging on loss of plasticity expressed by tensile elongation and negative influence on the RA change. These two different measures of plasticity loss seem to bring out no corresponding results. Therefore it is very probable that hydrogen entering the sample brings out the drastic loss of plasticity (as e. g. for the T6 tempers of the AlZn5Mg1CrZr alloy) but it does not contribute to an important extent into cracking, and that stress corrosion cracking at anodic polarization is totally or mainly dependent on anodic dissolution.

Anodic polarization promotes more rapid dissolution. The composition of the alloy and its thermal treatment are of importance for susceptibility of alloys to corrosion.

The AlMg4.5Mn alloy is undergoing intensive corrosion at anodic polarization. On the contrary, the other alloys suffer very localized layer (lamellar or exfoliation) corrosion. This is a typical attack associated with preferential dissolution along the grain boundaries parallel to the rolling direction which occurs even for the most resistant alloy.

Anodic polarization may be characterized by the anodic current density, which determines to some extent the susceptibility of the alloys to electrochemical dissolution. As seen here the values of current at different anodic polarization correspond to the corrosion behavior of the tested alloys as observed on the surfaces. The highest currents are characteristic of the T4 tempers, which make the alloys the most susceptible to both electrochemical corrosion and stress corrosion cracking. The difference in current for different tempers is generally not associated with shift in potential so that corrosion of the alloys occurs under anodic control and the difference in current is caused by change in slope of anodic polarization curves, certainly because of change in distribution of intermetallic phases.

It is interesting to compare the strength losses measured for specimens in corrosion tests. Except one alloy (AlZn5Mg1 of the T6₃ temper) these losses are very close to each other for both applied anodic potentials. That may mean that their cracking is due to the dissolution of surface layer and decrease in specimen area so that the effective stress approaches the value of yield stress and then the specimen fails in a short time. This may be an evidence that at least at anodic polarization hydrogen plays less important role in failure of these alloys. In other words, the time to failure may be determined mainly by time necessary to dissolve the surface layer rather than by amount of hydrogen entering the sample and its further effect on ductility.

CONCLUSIONS

1. Even anodic polarization of 50 and 100 mV causes the accelerated failure of the alloys, drastic loss of strength and ductility, and remarkable corrosion dissolution, uniform for the Al-Mg alloy and localized (layer corrosion) for the Al-Zn-Mg alloys.
2. Natural aging of the Al-Zn-Mg alloys promotes stress corrosion cracking and corrosion of the Al-Zn-Mg alloys, and improves the plasticity behavior, at least in terms of loss of fracture strain.
3. Failure and loss of strength at anodic polarization are mainly associated with anodic dissolution of the alloys which results in the increase in stress up to the yield stress at a constant load test.
4. The loss of ductility is likely originated from both hydrogen entry and intergranular corrosion.

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