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MECHANISM OF METAL CORROSION IN NARROW SLITS AND CREVICES

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MECHANISM OF METAL CORROSION IN NARROW  
SLITS AND CREVICESVI. MAGNESIUM AND SOME OF ITS  
ALLOYS

I. L. ROSENFELD, I. K. MARSHAKOV (Moscow)

By its electrochemical properties magnesium sharply differs from other metals (1 - 3) and this determines its behaviour in narrow slits. The laws established for other metals do not describe the behaviour of magnesium and the study of corrosive and electrochemical properties of magnesium and its alloys has, therefore, a certain scientific interest. In view of the broad application of magnesium alloys in industry and especially in aviation this study acquires a practical importance.

Highly purified magnesium, commercial magnesium, and alloys MI - 5 and MA - 8, whose contents are given in Table 1, were investigated.

The method of investigation of metal corrosion in slits was developed previously (4). The products of corrosion has been taken off by 20% solution of chrome anhydrite (with small admixture of  $\text{AgNO}_3$ ) at  $90^\circ \text{C}$  in 5 - 8 minutes.

Corrosive conduct of the magnesium of high purity in slits is represented graphically in Fig. 1. 0,01 N NaCl. was a corrosive medium. The velocity of magnesium corrosion in narrow slits (less than 0,50 mm) is considerably higher than in the electrolyte (curves 1, 2, 3) as it is seen in the diagram. The character of corrosion deductions in slits is also changing. In electrolytic volume highly pure magnesium corrodes uniformly but in narrow slits it is

subjected to strong pitted corrosion (Fig.2) The curves of relation of corrosion velocity and the average depth of the pit with dimension of slit have the same shape and are characterized by the presence of maximums.

Corrosion conduct of commercial magnesium has been studied in distilled water and in solutions of sodium chloride 0,001; 0,01 and 0,5 N. In all cases the velocity ~~velocity~~ of magnesium corrosion in narrow slits is higher than velocity of corrosion in electrolyte. The curve corrosion velocity vs slit dimensions also have a maximum at certain average value but not at minimal slit. With chlorine-ion concentration increasing the maximum shifts to more wide slits.

TABLE 1

CHEMICAL CONTENT OF INVESTIGATED MATERIALS

MATERIAL	content %					
	Fe	Mn	Al	Si	Zn	Mg
high purity magnesium	0,0017	0,0001	0,0011	0,0006	0,0019	balance
commercial (technical)	0,041	—	0,048	0,041	—	same
alloy ML - 5	0,014	0,05	4,80	—	0,68	..
alloy MA - 8	—	1,9	—	—	—	..

The relation between the velocity of corrosion for alloy ML - 5 and the dimension of slit and chlorine-ion concentration is very complex (Fig. 3) In distilled water and in 0,01 N NaCl the velocity of alloy ML - 5 corrosion in slits narrower than 0,25 mm is longer than velocity of corrosion of the same alloy in electrolyte.

In 0.1 N NaCl the velocity of corrosion in narrow slits is lower than in electrolyte. The peculiarity of alloy MA-8 corrosion behaviour consists in the fact that the velocity of corrosion in slits almost did not change with time but the velocity of corrosion in electrolyte diminished greatly. Therefore, the ratio of velocity in slits and electrolytes depends considerably on the duration of our experiment. During shortlasting experiments with alloy MA-8 (up to 3 days) in 0.1 N NaCl the velocity of corrosion in slits is smaller than in electrolytes. At longer experiments the velocity of corrosion in slits becomes greater than in electrolytes. In the meantime, the relationship between the velocity of MA-8 alloy corrosion in slits and chlorine-ion concentration was about the same as for alloy MI-5 (Fig. 3)

The comparative investigation of corrosion and electro-chemical behaviour of those metals and alloys in aerated electrolyte and in oxygen-free electrolyte (rotating electrode) has been carried in order to determine the mechanism of magnesium and its alloys corrosion. The results are given in Table 2.

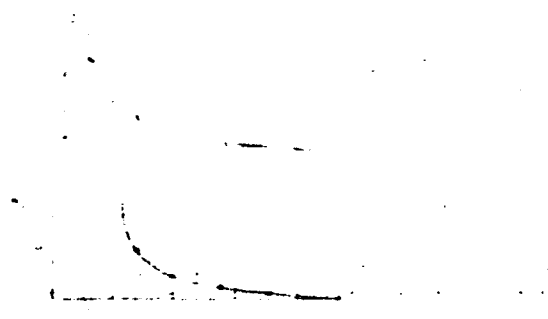


Figure 1 high purity magnesium corrosion in 0.01 N NaCl: 1. corrosion velocity; 2. an average depth of pits (from three maximums) in condition where all surface of metal is in a slit; 3. corrosion velocity in electrolyte; 4. corrosion

velocity in slits at the presence of contact with metal by electrolyte. The ratio of surfaces is 1 : 1; duration of experiments — 7 days.

The study of the results permits us to conclude that the destruction of oxygen diffusion into slits cannot contribute to the increase on velocity of corrosion as a result of disturbed passive state because in deaerated electrolytes velocity of corrosion is lower then in aerated electrolytes. Diminishing in velocity of processes is due to exclusion of corrosion on account of oxygen depolarization which to magnesium and its alloys, according to Paleolog's investigations /3/, has a considerable magnitude in neutral electrolytes. Of certain interest are also the results obtained with rotating electrodes (Fig.4) During rotation of electrode, the velocity of corrosion increases 30 times and potentially shift to the negative 400 mV. The character of corrosion also changes greatly. Fig. 2 (not available in paper for reproduction) represents the picture of magnesium surfaces after corrosion in stationary electrolyte (a) and with rotating electrode (b). In the last the corrosion has distinctly local character.

Table 2

CORROSION VELOCITY AND MAGNITUDE OF MAGNESIUM POTENTIALS IN 0.01 N NaCl. DURATION OF EXPERIMENTS: 24 HOURS WITH ROTATING ELECTRODE, 8 DAYS FOR OTHER CASES

MATERIAL	AERATED ELECTROLYTE		HYDROGEN ATMOSPHERE		ROTATING ELECTRODE 2000RPM	
	$k \cdot 10^{-5}$ gr/cm <sup>2</sup> days	E, V	$k \cdot 10^{-5}$ gr/cm <sup>2</sup>	E, V	$k \cdot 10^{-5}$ gr/cm <sup>2</sup>	E, V
high purity magnesium	13.0	-1.38	6.3	-1.39	380.0	-1.82
alloy MA - 8	6.9	-1.31	6.7	-1.33	—	—
Alloy ML - 5	3.9	-1.23	3.6	-1.24	—	—

By comparison and analysis of the data observed, the following mechanism of slit magnesium corrosion can be offered. Magnesium, as it is known, corrodes considerably even in neutral electrolytes with considerable degree of hydrogen depolarization. Emitting hydrogen, trying to escape from slits, mixes thoroughly in the electrolyte and the mixing in slits is longer than at metal surfaces in electrolyte; the space for bubbles to move in the slits is limited and this movement is complex. The intense movement of electrolyte and bubbles of  $H^2$  in the slits prevents formation of protective film and destroys the existing film which stipulates intense pit corrosion.

Fig. 3 Dimension of Slit

Fig. 3 Alloy ML - 5 corrosion

- a) in distilled water;
- b) in 0.01 N NaCl;
- c) in 0.1 N NaCl;
- d) in slits;
- e) in electrolyte. Duration of our experiments: — 8 days.

In electrolytes with small content of chlorine-ion the velocity of magnesium corrosion and, thus, the amount of eloped hydrogen, are small and therefore, the effect of electrolyte mixing can be detected only in small slits. (Fig. 3) In media containing higher concentration of chlorine-ions the velocity of corrosion and the amount of liberated hydrogen are increasing. This results, on one side, in hydrogen and products of corrosion are filling almost fully small slits and

prevents corrosive media from coming in; on the other hand, more intense evolution of hydrogen brings intense mixing of electrolyte in more wider slits. All this brings the origin to maximums on the curves of metal corrosion velocity vs slit dimension (Fig. 3b) with ~~the~~ (6) increased chlorine-ion concentration the maximum on these curves shifts to the region of wider slits. At higher ion concentration the large importance acquires the condition of withdrawal of the products of corrosion and liberated hydrogen and supply of corrosive media. These conditions are less favorable in slits than in electrolytes, therefore, the effect of intensified mixing of corrosive media in slits already does not play a deciding role and the velocity of corrosion in slits at such concentration of chlorine-ions is smaller than in electrolytes (Fig. 3a). The effect of chlorine-ion concentration during which time the smaller velocity of corrosion in slits, than in electrolytes, is observed, depends on many factors; the metal properties, the velocity of electrolyte movement, temperature, etc.,

Therefore, the strong corrosive destruction of magnesium in slits, is due to the work of microelements and changes in velocity of electrodes reacting on ~~microelement~~ microelectrodes. Microelements, which can originate from the contact of the metal in slits with the metal of electrolytes, are not responsible for such destructions. On the contrary, the presence of such contact in the case of magnesium, results in definite electrochemical protection of metal in narrow slits as the metal in slits is a cathode of ~~micro~~ macroelement. (Fig. 1, curve 4) The alloys ML-5 and MA-8 in 0.1 N NaCl at the presence of metal surface outside of the slits are subjected ~~in~~ in slits to more intense corrosion due to the work of microelements, whose anode is a metal in the slit.

The origin of microelements is explained not only by sharp velocity of mixing of electrolytes in slits and around the surface of metal in electrolyte, but also

in changes in character of corrosive media. The corrosive media in narrow slits is quickly saturated with products of corrosion  $Mg(OH)_2$  and they establish pH determined by product of solubility of these products of corrosion. Our measurement ~~showed~~ showed pH equal to 10.0 — 10.2.

Magnesium potential refines with increased alkalinity and, therefore, part of the material in the slit becomes cathode. The opposite tendency is observed simultaneously. Due to intense mixing of electrolytes by the bubbles of hydrogen the interruption in the continuity of protective films occurs, the ~~maximum~~ magnesium potential becomes less refined, which brings to origin the macroelements, whose anode is a metal in the slits. However, differences of potentials, created in both cases, is very insignificant and the current of elements is small and unstable with the time. Therefore, the influence of macroelements in the slits magnesium corrosion is not too evident.

#### CONCLUSIONS

1. The corrosion ~~conduct~~ <sup>Mg</sup> of magnesium and its alloys in narrow slits were studied. It was shown that in the majority of cases these metals are subjected to ~~greater~~ <sup>greater</sup> corrosion in slits than in electrolytes. Corrosion in slits acquires more prominent local character. The dependence <sup>of the</sup> velocity of corrosion on the dimension of slits is described by complicated curves characterized by the presence of maxima at certain values of the width of the slit.
2. Intensified <sup>Mg</sup> magnesium and its alloys is ~~due not to the obstruction of processes~~ <sup>caused by</sup> of oxygen diffusion but chiefly mixing of electrolyte by the bubbles of H<sub>2</sub> ~~hydrogen~~ and the movements of bubbles preventing <sup>the</sup> formation of protective films and destruction of existing one. Hence, the strong corrosive destruction of magnesium in slits is due to the work of microelements and the changes in character of their work. The part played by macroelements in

development of slit magnesium and its alloys corrosion, contrary to previously investigated cases of slit corrosion, is negligible due to their small effectiveness.

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