Corrosion creep of metals

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Abstract. Creep behavior of some metals (pure polycrystalline magnesium, die-cast Mg and Al alloys and stainless steel 304) assisted by anodic dissolution in aqueous solutions, which we have called “corrosion creep” (CC), was investigated. The effect of environment on the creep behavior of magnesium and steel is mainly connected with plasticization of metal assisted by chemical reactions and mechanically enhanced anodic dissolution of metal. Anodized Mg-alloys reveal a significantly longer creep life in comparison with uncoated die-cast alloys.

1. Introduction

The investigation of environmentally assisted creep is very important as a tool to discover a mechanism of stress corrosion processes in the tip of a crack and as a phenomenon influencing greatly mechanical stability of alloys in real service conditions. This phenomenon for the first time was discovered by Andrade on zinc and cadmium single crystals under the action of metal sulfate solutions [1], then in pure copper [2-4]; Cu-based alloys [5] and in detail studied in magnesium and Mg alloys as "corrosion creep" [6] as well as "corrosion stress relaxation" [7]. For example, creep rate of pure Mg in borate solution increased 10 times with respect to that in air! [8]. The central point of all stress corrosion processes is nucleation and propagation of corrosion-mechanical cracks, the main among them leads to the final fracture. The physico-chemical and mechanical phenomena that develop in the crack tip are key processes, which determine crack propagation rates and finally - life time of constructions.

Different mechanisms of the creep in corrosive solutions were proposed. For example, Revie and Uhlig [2] support the idea of the generation of divacancies by the dissolution process during anodic polarization of pure Cu, and of a corresponding reduction in the surface energy by cathodic polarization. However, Van Der Wekken [3] concludes that the accelerated creep rates of copper single crystal specimens during anodic dissolution in acetate buffer solutions under a constant load are essentially due to an increasing stress. Under the conditions of constant stress achieved by compensating for the reduction in the specimen cross-section during dissolution by proportionally reducing the load on the specimen, the effect largely disappeared in single crystals as well as in polycrystalline wire specimens. The creep rate of brass, e.g., in 3.5% NaCl increased linearly with the increase in the anodic current density as a result of dislocation climb induced by vacancy supersaturation during the anodic polarization or by a mechanism related to hydrogen-facilitated local plastic deformation during cathodic polarization [5]. The cracking and final creep-rupture of pure

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copper [4] and magnesium [8] originated, as a rule, from the pits propagated into the specimen in a transgranular manner due to very thin and strong grain boundaries (figure 1). However, for polycrystalline alloys, it is possible both intergranular and transgranular fracture modes [8].

Figure 1. Pits and cracks in 99.96% pure Mg (a) and in 99.999% pure Cu (b) after creep in corrosive solutions.
(a) - buffer solution (75% of TYS, 25°C, 300 hrs) [8]; (b) - 0.05 M NH₄OH solution (66% of UTS, 150 hrs, 70°C) [4].

Thus, the literature data on environment-assisted creep or corrosion creep are very contradictory. In the present work the effect of corrosive medium on the creep behavior, pitting and cracking of pure magnesium, die-cast magnesium and aluminium alloys and austenitic stainless steel 304, has been investigated.

2. Experimental
Flat specimens of polycrystalline 99.9653% Mg with cross-section of 10 x 4 mm² were produced from commercial ingots produced by Dead Sea Magnesium Works (DSM, Israel). Round specimens 5.9 mm in diameter of Mg alloys Mg-9Al-1Zn (AZ91D) and Mg-5%Al (AM50) were produced on die-cast machines of DSM and Israel Institute of Metals (Technion). A part of AZ91D and AM50 samples were coated by an anodic non-chromate basic coating ALGAN-2 (Algat Co., Israel). Die-cast Al alloy Al-9Si-3Cu-1Zn (A380) and Al-3Si-6Mg alloy (Maxxalloy) were produced by Omen High Pressure Die Castings (Israel). The 1-mm-thick cold drawn stainless steel 304 specimen had the width of 8 mm and the length of 42 mm. Ultimate tensile strength (UTS), tensile yield stress (TYS) and elongation-to-fracture (e) of metals are presented in table 1.

| Table 1. Mechanical properties of materials. |
|---------------------------------------------|
| Pure Mg | Mg-9Al-1Zn (AZ91D) | Mg-5%Al (AM50) | A380 | Al-3Si-6Mg | 304 type steel |
| UTS, MPa | 62 | 225 | 229 | 270 | 308 | 731 |
| TYS, MPa | 37 | 170 | 136 | 165 | 180 | 306 |
| e, % | 5.7 | 2.8 | 11.7 | 1.7 | 6.8 | 72 |

Specimens were studied after rinsing in distilled water and alcohol and wiping with acetone. As active environments, sulphuric acid solution (0.8 g/l) was used for the steel; for pure Mg and Mg alloys - 0.1N Na₂B₄O₇ buffer solution saturated with magnesium hydroxide Mg(OH)₂ (pH = 9.3); 3%Na₂SO₄ and 3.5%NaCl. Aluminium alloys were studied in 3.5% NaCl. All solutions were prepared from analytical grade chemicals and distilled water.
Creep tests were carried out on Model 3 SATEC creep tester in the temperature range from 25±2°C to 175±1°C in air and from 25±2°C to 70±1°C in solutions. The small cell for CC-tests of Mg, Mg alloys and stainless steel was made from the transparent plastic (PMMA) or lightly powdered natural rubber latex [8]. Corrosion creep of die-cast aluminium alloys were performed in air and in solutions at stress of 150 MPa using a 0.5 dm³ volume transparent plastic cell 1 with a sample 2 equipped by extensometer 3, thermocouple 4 and heater 5 (figure 2). The 6-mm diameter specimen with denuded area of about 30 mm in the length was placed into solution (figure 2). The rest side surface was protected from corrosion attack by the Teflon film. The tests were conducted in a non-aerated and in an aerated solution using porous element with flow rate of approximately 0.5 dm³/min. Before loading, the sample was immersed in a solution at the test temperature for 60-90 minutes.

There were two kinds of creep tests performed in solutions: a creep-rupture test and an interrupted test. During the last, the specimen was unloaded after some time, the immersed area of a specimen was examined by an optical microscope and then the specimen with a new rubber cell was placed into an average extensometer of a creep machine under the same load, and the creep strain was measured again. After some time the procedure was repeated. Some speculation was made to fit several curves of such creep cycles to one “master” curve. The point of the beginning of the steady-state stage for each of such cycles coincided with the end of the curve obtained in the previous test.

Cleaning of Al specimens after CC-tests was performed by dipping in concentrated 70% nitric acid for several minutes (ASTM G34-90). Oxide layer was scrubbed lightly in a stream of water with a rubber stopper or a bristly brush so as not to not mechanically abrade this soft material. Cleaning of Mg-based alloys was performed by dissolution in 15% CrO₃ solution at 80 °C for 0.5–1 min (ASTM G1-88).

Microstructure and pitting studies were carried out using an optical microscope ‘Nicon’ and a scanning electron microscope JEOL JSM-5600 with ‘NORON’ energy-dispersive analysis system.

3. Results and discussion

3.1. Creep behavior.

In air at stresses below TTS all metals, e.g., die-cast AZ91D alloy, show only the primary stage typical of low-temperature creep, which occurs at temperatures below about a half of the melting point (in Kelvin), while high-temperature creep is predominantly a steady-state creep (Fig. 3). However, in corrosive solutions, especially containing Na₂B₄O₇, fracture occurred even under stresses less than 70% of TTS (Table 2).

In sodium sulfate solution, stressed Mg-9Al-1Zn alloy experienced fast stress corrosion cracking with very small strain values. Therefore in this solution, time–to-rupture of this alloy is less significant than in buffer solution (Table 2). Effect of kind of solution for pure magnesium is presented in the Table 2 from our earlier work [8]. Its lifetime varied from 12 hours in 3.5% NaCl to ~250 hours in the buffer solution.

In the air, die-cast Al-alloys had practically only elastic deformation under stress of 150 MPa. The fracture wasn't observed in air, but in 3.5% NaCl solution the fracture occurred in all the CC-tests (Fig. 4). Lifetime (time-to-fracture) of conventional 380-type alloy was significantly longer than that of

![Figure 2. The 0.5 dm³ cell designed for CC-tests at elevated temperatures 1 - plastic cup, 2 - a sample, 3 - extensometer, 4 - thermocouple and 5 - heater.](image-url)
Maxxalloy and was equal to 80 and 48 hrs, respectively, (Table 2). In unstressed state, corrosion resistance of Maxxalloy in chloride environment was better than 380-type alloy. The samples of the latter after CC-tests have showed dark and very loose oxide products with respect to more stable oxide layer in Maxxalloy. Besides, Maxxalloy has the strength much higher than A380 (Table 2). However, this alloy shows significantly deeper pits and cracks on the side cast surface in stress-corrosion conditions, than this kind of degradation in A380 alloy. It is of interest that more brittle in common tensile tests A380 alloy showed a higher strain-to-rupture in corrosion creep with respect to Al-3Si-6Mg alloy (Tables 1, 2; Fig. 4).

Figure 3. Examples of common creep in air (a) and corrosion creep in borate buffer solution (b) for die-cast AZ91D Mg alloy.  
(a) – 50 MPa (30% of TYS); 1, 2 – 150°C; 3 – 175°C; Porosity, %: ~1.2 (1, 3) and 4.8 (2).  
(b) – 121 MPa (70% of TYS); 25°C

Table 2. The environment effect on time-to-rupture of metals in the corrosion creep tests.

| Alloy            | Stress, MPa/% of TYS | Solution         | Surface conditions | Time-to-rupture, h |
|------------------|----------------------|------------------|--------------------|--------------------|
| Pure Mg [8]      | 28/75                | 3.5% NaCl        | Machined           | 12                 |
| Pure Mg [8]      | 28/75                | 0.1N Na₂B₄O₇    | Machined           | 250                |
| Mg-9Al-1Zn       | 121/71               | 3% Na₂SO₄       | As-cast            | 60                 |
| Mg-9Al-1Zn       | 121/71               | 0.1N Na₂B₄O₇    | As-cast            | 240                |
| 304 steel        | 398/130              | 0.08%H₂SO₄      | As-rolled          | 27                 |
| A380             | 150/91               | 3.5% NaCl        | As-cast            | 80*                |
| Al-3Si-6Mg       | 150/83               | 3.5% NaCl        | As-cast            | 48*                |
| Mg-5Al           | 121/89               | 0.1N Na₂B₄O₇    | As-cast            | 342                |
| Mg-5Al           | 121/89               | 0.1N Na₂B₄O₇    | Anodized           | 637                |
| Mg-9Al-1Zn       | 159/94               | 0.1N Na₂B₄O₇    | As-cast            | 58                 |
| Mg-9Al-1Zn       | 159/94               | 0.1N Na₂B₄O₇    | Anodized           | 160                |

* Average from five tests

In the air, 304 steel showed the creep strain at 60°C under the stress of 398 MPa (1.3 of TYS) significantly below 0.5% after ~100 hours. However, in 0.8 g/l sulphuric acid solution, plasticization of steel was observed, and after only one hour the creep strain reached ~15% (Fig. 4). The creep of stainless steel in a corrosive solution demonstrates all stages of creep at a relatively low (for steels) temperature with the final fracture of the sample.
Corrosion creep of die-cast Mg-5Al and Mg-9Al-1Zn alloys anodized by a ~8 micron-thick coating showed that anodic coating delays metal dissolution facilitating plastic deformation of the stressed metal, and for this reason alone increases the corrosion creep life of metals (Table 2, Fig. 6). For instance, time-to-fracture of anodized Mg-5Al alloy increases from 340 to 637 hours in comparison with uncoated specimens in the borate buffer solution under stress of 121 MPa. Anodizing leads to a certain increase in the creep strain of Mg-5Al in air during long-term tests without rupture (Fig. 6). An increase in the plasticity of coated alloys in air is connected, probably, with a decrease in the alloy surface energy during the anodizing process in basic electrolytes.

![Figure 5](image-url)

**Figure 5.** Typical creep behavior of 304 type steel in 0.8 g/l sulphuric acid solution. Large round points correspond to the test interruption after 1, 2, 5, 11, 18 and 24 hours for the microscopic evaluation of pitting.

![Figure 6](image-url)

**Figure 6.** Effect of coating on the creep behavior of die-cast Mg-5%Mg alloy in air (a - no rupture) and in buffer solution (b - rupture occurs).

3.2. Microscopic examination.

Pits on the sample surface in stainless steel were observed during the first stage of creep like that for pure Mg [8]. Even after one-hour test duration, there were small pits on the lateral sides of the steel specimen (Fig. 7a). After 2 hours, all pits were somewhat deeper, and during the third stage of creep after 11 hours the same pits appeared on the frontal side of the specimen (Fig. 7). Creep tests on 304 type steel showed that the pits were deeper near the rubber sealing than in the center (neck) of the sample. The neck was subjected to the most severe deformation, but no deep pits or pronounced corrosion products were found in this area. Probably, atmospheric oxygen on the 'air-solution-metal' boundary plays a very significant role in the pit growth, crack initiation and final failure of the steel sample in a corrosive medium. The same behavior was observed earlier in pure Mg [8].

A catastrophic destruction of stressed metals in corrosive solutions in comparison to their stable behavior in air can be explained by the synergetic interaction between mechanical and chemical processes described as mechanochemical phenomena [9]. Mechanically enhanced anodic dissolution of metal causes crack initiation and propagation. Chemical (electrochemical) reactions, which proceed on the metal surface causing additional dislocation flux and localized enhanced plasticity, influence fine microstructure and creep properties of a solid.
Figure 7. Optical micrographs of pits initiated on the lateral (a, b) and frontal (c) surfaces of the 1-mm-thick 304 steel specimen during a CC-test in the sulphuric acid solution correspond to the holding time of 1(a) and 11 (b, c) hours.

Conclusions
Synergistic effect of corrosion and stress on the creep behavior of magnesium, die-cast Mg and Al alloys and stainless steel named corrosion creep is investigated. In air, only the primary stage typical of low-temperature creep of the studied metals was observed. However, in corrosive solutions, marked elongation, especially for stainless steel, and fracture occurred even under stresses less than 70% of TYS. It was found that very small pits were nucleated during CC-tests at the primary stage of creep.

Anodized Mg-alloys coated with non-chromate base coating reveal a significantly longer creep life in comparison with uncoated die-cast alloys.

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