The effect of hydrogen embrittlement on the mechanical properties of aluminum alloy

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Abstract. The effect of hydrogen embrittlement on the mechanical properties of aluminum alloy D1 was investigated. The studies were performed for the test samples of aluminum alloy subjected to electrolytic hydrogenation. It is found that the mechanical properties of aluminum alloy are affected adversely by hydrogen embrittlement. The hydrogenated counterpart of alloy has a lower degree of ductility relative to the original alloy; however, the plastic flow behavior of material remains virtually unaffected. The deformation diagrams were examined for the deformed samples of aluminum alloy. These are found to show all the plastic flow stages: the linear, parabolic and pre-failure stages would occur for the respective values of the exponent n from the Ludwik-Holomon equation. Microhardness tests were performed for as-treated aluminum alloy D1; the measurement results are presented.

1. Introduction

It is the concern of the analyst to confirm to what extent corrosion processes affect the mechanical characteristics and, consequently, the performance of construction metals and alloys [1, 2]. Among thermally hardened aluminum alloys, duralumins hold a firm place due to ready availability, satisfactory strength characteristics and high corrosion resistance owing to the protective surface inert oxide film [3]. In view of the above, these materials find wide applications in various branches of industry; to mention just a few, structural components for aircraft, aerospace, ship building and other structural applications. Due to the exposure of constructions or components to environmental factors, the protective surface oxide film would be thinned down, thus entailing corrosion process development, which would affect adversely construction reliability. By and large, aluminum alloys are thought to offer resistance to aggressive media. However, this is only true for alloys having low extent of solid solution supersaturation, whereas alloys having high concentration of alloying additions, duralumin systems included, will undergo corrosion embrittlement under exposure to corrosive media. Hydrogen is also liable to cause metal embrittlement [4-8].

To explain the effects of hydrogen, many microscopic models have been developed [9, 10] based on the dislocation theory. However, such approaches seem to be insufficient, since they do not take into consideration the fact that plastic deformation has a local character during the entire process of flow [11, 12].

In this regards, the effect of electrolytic hydrogenation on the mechanical characteristics of aluminum alloys subjected to thermal strengthening has to be elucidated.
2. Experimental procedure
The investigation was performed for the test samples of duralumin D1, which had been subjected to thermal strengthening. The original duralumin D1 had the following chemical composition: 95% Al; 3.5% Cu; 0.2% Mg; 0.5% Mn; the remainder Si, Fe, S, P and Zn. The test samples having dog-bone shape were stamped out from hot-rolled 2-mm sheet. These were annealed for 1 h at temperatures 300; 320; 340; 350 and 360°C with subsequent cooling down in the furnace to remove internal stresses.

The mechanical tests were carried on at the rate $6.67\times10^{-5}$ s$^{-1}$ at room temperature in a universal testing machine Walter+Bai (Switzerland). Then the plastic flow curves plotted for the samples tested in tension were analyzed to single out individual flow stages.

The electrolytic hydrogenation of alloy samples was carried on for 24 h and 96 h under a controlled cathode potential. The sample was placed in an electrochemical cell containing 1N sulfur acid solution to which 20 mg/l thiocarbonic acid diamide had been added to enhance the process at 323 K [13]. The electrochemical cell was equipped with a graphite anode; a chlorine silver reference electrode was connected in the circuit to maintain a constant potential $U= -430$ mV. To control the three-electrode cell and run the electrochemical reaction, a Potentiostat/Galvanostat IPC-Compact unit was employed.

Using a standard technique, microhardness measurements were made for the original alloy D1 and for the counterpart subjected to hydrogenation. The indentation testing was performed with the aid of microhardness tester PMT-3 equipped with the Wickers tip; the load on the indenter $P=0.15$ N. Prior to testing, the sample work part was polished. Mathematical data treatment was carried on using routine procedures; the data obtained are reported in [14, 15].

3. Experimental results
The loading curves illustrated in Figure 1 were obtained for the test samples of alloy D1, which had been annealed at different temperatures. The curves obtained for the samples tested by uniaxial tension have a characteristic serrated shape, which is indicative of plastic flow instability. The plastic flow would exhibit an unsteady-state behavior from the yield limit up to material failure.

![Figure 1. Loading curves of alloy D1 subjected to annealing at 300°C(1); 320°C(2); 340°C(3); 350°C(4) and 360°C(5) with subsequent cooling in furnace for t=1 h.](image)

Provided their serrated shape is ignored, these curves might be grouped with diagrams of general type [16], which are described by the parabolic function

$$\sigma = \sigma_0 + K\varepsilon^n,$$

where $K$ is the coefficient of deformation hardening and $n$ is the exponent of deformation hardening.

Using the method reported in [17], the loading curve can be represented in the system of functional logarithmic coordinates as $\ln(s - s_0) - f(ln\varepsilon)$ (here $s$ is the true stress which takes no account of...
reduction in the work cross-section and $e$ is the true deformation). This enables individual segments to be singled out on the curve for a constant value of the exponent $n$, which varies discretely on going from one segment to the next. All the loading diagrams obtained in this study were analyzed by the above method. A lot of diagrams had serrated shape, which made it impossible to single out an individual stage. We succeeded in singling out the linear, parabolic and prefracture stages in the diagrams of the samples annealed at $\leq340^\circ$C.

![Graph](image)

**Figure 2.** The values $\sigma_{0.2}$, $\sigma_B$ and $\delta$ as a function of annealing temperature obtained for alloy D1 (curves 1, 2 and 3, respectively)

Evidently, an increase in the temperature of annealing up to 350$^\circ$C and 360$^\circ$C causes a drastic rise in the tensile stress, which will plot as a saw-tooth curve that alludes analyzing. Thus annealing schedules have been determined that are optimal in terms of expected mechanical characteristics of as-treated alloy, i.e. the thermal treatment of material is to be performed for 1 h at 340$^\circ$C with subsequent cooling in furnace. Figure 2 illustrates the variation in the yield stress and ultimate strength of alloy D1 as a function of annealing temperature. It can be seen from figure 2 that the annealing carried on at $T<330^\circ$C would cause a decrease in the yield stress and ultimate strength of alloy D1 and an enhancement in its plasticity.

![Graph](image)

**Figure 3.** Loading curves obtained for the original alloy D1 and the counterpart of the same subjected to hydrogenation for $t=96$ h (curves 1 and 2, respectively).
The effect of hydrogenation on the mechanical characteristics of aluminum alloy D1 was studied. The test sample was subjected to tensile loading as soon as it was taken out of the electrochemical cell. The results of mechanical tests are presented in Figure 3.

Evidently, the loading curves, which have been plotted for the original alloy D1 and the counterpart subjected to electrolytic hydrogenation for 24 h, are practically identical.

Two sets of loading diagrams were matched (see Figure 3). It is found that a 15% decrease in the elongation to rupture is observed for the counterpart subjected to hydrogenation for 96 h relative to the original alloy; hence, the plasticity of alloy D1 has been impaired significantly by the hydrogenation treatment, although its strength characteristics remain unaffected.

The quantitative data on mechanical characteristics of alloys are listed in the Table 1. In the deforming sample of the original alloy, the onset of necking takes place, which is a forerunner of viscous fracture. The deformation curves plotted for the original alloy were represented in functional logarithmic coordinates. Three distinct rectilinear segments are distinguished on the flow curve for strains $\varepsilon$ in the range 1.3-2.3%; 3.6-6.1% and 6.9-13.8% for a constant value $n$. These segments correspond to the linear and parabolic work hardening stages and to the prefracture stage, which occur for $n=1; n \approx 0.5$ and $n \approx 0.3$, respectively. The data agree with the results of previous studies [18].

| Table 1. Mechanical characteristics of the original duralimin D1 (1) and the counterpart of the same alloy subjected to electrolytic hydrogenation for 96 h (2). |
|---|---|---|---|---|---|---|---|
| | $\sigma_{0.2}$, MPa | $\sigma_B$, MPa | $\delta$, % | Linear stage, $n=1$ | Parabolic stage, $n=0.5$ | Prefracture stage, $n=0.3$ |
| | $\varepsilon_i$, % | $\varepsilon_f$, % | $\varepsilon_i$, % | $\varepsilon_f$, % | $\varepsilon_i$, % | $\varepsilon_f$, % |
| 1 | 76.3 | 0 | 180. | 0 | 1 | 1.3 | 2.3 | 3.6 | 6.1 | 6.9 | 13.8 |
| 2 | 77.6 | 6 | 175. | 2.6 | 1 | 1.1 | 2.4 | 3.4 | 5.5 | 5.9 | 11.1 |

Note: $\sigma_{0.2}$ – proof stress; $\sigma_B$ – ultimate stress; $\delta$ – relative elongation to rupture; $\varepsilon_i$ – initial strain range; $\varepsilon_f$ – final strain range.

4. Discussion

An analysis was made of the loading curve obtained for the test samples subjected to electrolytic hydrogenation. We distinguished three work hardening stages on the flow curve, i.e. linear, parabolic and prefracture ones. The latter two flow stages occurring in the original alloy and the hydrogenated counterpart practically coincide (see Table 1). In the case of counterpart hydrogenated for 96 h fracture occurs in the absence of necking.

Microhardness tests were performed by a standard procedure using 20 measurements. Analysis of data was made by the statistic method for physical experimental data treatment using a double $t$-criterion [14]. The microhardness tests were performed for the original alloy D1 and the counterpart, which had been hydrogenated for 96 h; the values obtained are $H_{\mu} = 251.0 \pm 5.5$ MPa and $H_{\mu} = 271.9 \pm 4.9$ MPa, respectively. Thus, using Student’s $t$-criterion, we obtain

$$t = \frac{271.9 - 251}{\sqrt{\frac{136 + 108}{2}} = 5.99}.$$ 

For the confidence level $\alpha = 0.95$ and the number of degrees of freedom $f = 38$, Student’s coefficient $t_{\alpha,f} = 2.02$ [15].

The resultant quantity $|H| \geq t_{\alpha,f}$ suggests that the average microhardness values obtained for the original alloy and the hydrogenated counterpart differ significantly, although on a percentage basis, the physical values differ by about 8%. It can be thus concluded that the hydrogenation treatment would cause an enhancement in the microhardness of aluminum alloy.
Thus, the effect of electrolytic hydrogenation on the mechanical properties of duralumin D1 has been studied. It is found that material strength and plasticity are virtually unaffected by the preliminary hydrogenation for 24 h, while the same properties would be affected adversely by the hydrogenation performed for 96 h. In the latter case, the linear and parabolic work hardening stages as well as the prefracture stage are found to occur on the flow diagram plotted for the deforming sample. However, no necking would take place at the prefracture stage; hence, the test samples undergo brittle fracture. It can thus be concluded that the plasticity of duralumin D1 is affected adversely by the electrolytic hydrogenation carried on for 96 h. Hence, the probability of hydrides forming in as-treated material is high [4-8].

For the case of cracking of aluminum alloys according to the hydrogen embrittlement mechanism there are not theoretically based values of the depth of penetration of hydrogen and its concentration in the area in front of the crack tip necessary for its further advance. The diffusion rate of the hydrogen must agree in order of magnitude with the rate of crack advance \( v_\text{cr} \) if the latter develops in two stages, embrittlement in the first and in the second a jump in the crack by the distance of embrittlement at the speed of sound.

In principle, acceleration of transport of hydrogen is possible at a crack tip if the gradient in the hydrostatic component of stresses is sufficiently high [19]. However, according to improved calculations [20] the distribution of stresses is somewhat different so that the only method of acceleration of transport is transfer of hydrogen by dislocations. The rate of transfer of hydrogen by dislocations is determined by the critical rate \( v_\text{c} \) of breaking away of them from segregations (Cottrell atmospheres) [9]:

\[
v_\text{c} = \frac{4kTD_H}{\beta}
\]  

(2)

Keeping in mind that dislocations effectively capture hydrogen only in the presence in the metal of excess vacancies [21] and also the formation of vacancy-hydrogen complexes it must be taken into consideration that in essence the dislocations transport these complexes. Their specific atomic volume is approximately the same as for a vacancy. In the given situation the parameter of elastic interaction \( \beta \) is equal to 1.6\times10^{-10} J/m. In addition, in place of the coefficient \( D_H \) in equation (2) we may substitute the diffusion coefficient of vacancies, the best known determination of which at room temperature is 10^{-12} m^2/s [10]. As a result, we obtain \( v_\text{c} \approx 10^{-3} m/s \). If the average value for all alloys of \( D_p = 10^{-13} m^2/s \) calculated on the basis of data on its values in pure aluminum and in 7075-T6 alloy [8] is used as the diffusion coefficient of hydrogen, then \( v_\text{c} \approx 10^{-4} m/s \).

5. Conclusion
The corrosion properties of semi-products manufactured from the Al-Cu-Mg alloy system are determined by the composition and distribution of precipitates at the grain boundaries and within the grain bulk and by the extent of copper depletion from the near-boundary regions, which in turn depends on thermal treatment conditions.

The analysis of experimental data [3-7] suggests that the duralumin systems Al-Zn-Mg and Al-Cu-Mg would undergo corrosion cracking, which is largely due to hydrogen evolving during electrochemical reactions; however, the mechanism involved in embrittlement has not been defined unambiguously as yet. There is good reason to believe that the failure in hydrogenated material occurs via a mechanism, which is essentially different from that involved in corrosion cracking. In the former case, material plasticity is affected adversely, which is liable to cause intergranular fracture due to hydride formation. At first hydrogen would diffuse at a low rate towards the grain boundaries; therefore, it takes time for hydrides to form in the material. Corrosion cracking will occur simultaneously with hydrogen embrittlement via electrochemical mechanism, which involves periodic disintegration of passive film due to the local plastic strains at the grain boundaries and to the dissolution occurring locally in the same regions.
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References
[1] Holroyd N J H, Vasudevan A K and Christodolou L 1989 Treatise on Materials Science and Technology Ch. 16: Stress Corrosion of High-Strength Aluminum Alloys (San Diego: Academic Press) p 463-483
[2] Polyanskii V M 1985 Role of hydrogen embrittlement in the corrosion cracking of aluminum alloys Sov Mater Sci 21 301-309
[3] Larignon C, Alexis J, Andrieu E et al. 2013 The contribution of hydrogen to the corrosion of 2024 aluminium alloy exposed to thermal and environmental cycling in chloride media Corros Sci 69 211-220
[4] Lunarska E and Chernyaeva O 2004 Effect of precipitates on hydrogen transport and hydrogen embrittlement of aluminum alloys Mater Sci 40 399–407
[5] Kannan M and Raja V 2006 Hydrogen embrittlement susceptibility of over aged 7010 Al-alloy J Mat Sci 41 5495–5499
[6] Kim S, Han M and Jang S 2004 Electrochemical characteristics of Al-Mg alloy in seawater for leisure ship: Stress corrosion cracking and hydrogen embrittlement Korean J Chem Eng 26 250–257
[7] Kumar S and Namboodhiri T 2011 Precipitation hardening and hydrogen embrittlement of aluminum alloy AA7020 B Mater Sci 34 311–321
[8] Nykyforchyn H, Ostash O, Tsyrul’nyk O, Andreiko I and Holovatyuk Yu 2008 Electrochemical evaluation of the in-service degradation of an aircraft aluminum alloy Mater Sci 44 254–259
[9] Hirth P and Lothe J 1968 Theory of Dislocations (New York: McGraw-Hill) 363
[10] Friedel J 1964 Dislocations (Oxford: Pergamon press) p 371
[11] Barannikova S A, Nadezhkin M V, Mel' nichuk V A et al. 2011 Tensile plastic strain localization in single crystal of austenite steel electrolytically saturated with hydrogen Tech Phys Lett 37 793-796
[12] Barannikova S A, Nadezhkin M V, Lunev A G et al. 2014 Regularities in localization of plastic flow upon electrolytic hydrogenation of an iron bcc-alloy Tech Phys Lett 40 2113-2114
[13] Yagodzinskyy Y, Todoshchenko O, Papula S and Hänninen H 2011 Hydrogen Solubility and Diffusion in Austenitic Stainless Steels Studied with Thermal Desorption Spectroscopy Steel Res Int 82 20–25
[14] Zazhigayev L, Kishyan A and Romanikov Yu 1987 Methods for planning a physical experiment and data processing (Moscow: Atomizdat) 232
[15] Kondrashov A and Shetstopalov E 1977 The Basis of the Physical Experiment and Mathematical Treatment of Measurement Results (Moscow: Atomizdat) 200
[16] Pelleg J 2013 Mechanical Properties of Materials (Springer: Dordrecht) 634
[17] Trefilov V, Moiseyev V, Pechkovsky E et al. 1989 Deformation Strengthening and Fracture in polycrystalline materials (Kiev: Naukova Dumka) 256
[18] Danilov V, Bochkaryova A and Zuev L 2009 Macrolocalization of deformation in material having unstable plastic flow behavior Metal Physics and Metal Science 107 660–667
[19] McMeeking R 1977 Finite deformation analysis of crack-tip opening in elastic-plastic materials and implications for fracture J Mech Phys Solids 25 357-381
[20] Gortemaker P C M, de Pater C and Spierling R M E 1981 Near-crack tip finite strain analysis in: Advanced Fracture Research. Preprint of the 5th International Conference on Fracture (ICF5), Cannes, Franc, Vol. I, Pergamon, Oxford--New York (1981) 151-160
[21] Foster L M, Jack T H, Hill W W and Jeitschko W 1970 Structure revealed in zone refined aluminum by tritium decoration Metallurgical Transactions 1 3117-3124