



PECULIARITIES OF THE INFLUENCE OF HOT DEFORMATION AND HEAT TREATMENT ON THE CORROSION RESISTANCE OF ALUMINUM ALLOYS

M.Kh. Rabinovich and V.G. Trifonov

Institute for Metals Superplasticity Problems, Russian Academy of Sciences, Ufa, 450001, Russia

(Received March 26, 1996)

(Accepted April 13, 1998)

Introduction

The question about the influence of superplastic deformation (SPD) on mechanical properties of materials [1–4] and the reliability of articles made out of these materials [5, 6] was studied sufficiently thoroughly. However, the information about the influence of microcrystalline (MC) structure processed by SPD on corrosion properties is rather limited. In respect to aluminum alloys this question was considered in some works [1, 7]. As known, the corrosion resistance plays a significant role in determining such an important aspect of reliability as endurance. The present paper is devoted to this problem.

Experimental Materials and Procedure

Aluminum alloys 1960 (8.2%Zn, 2.6%Cu, 3.1%Mg, 0.15%Zr and the balance Al) and 1360 (2.4%Cu, 0.68%Mg, 0.71%Mn and the balance Al) were used in the investigations. Hot pressed rods with a non-recrystallized structure and elongated grains were taken as a starting material.

Studies of fine structure were made on a transmission electron microscope. Intercrystalline corrosion was determined on a basis of the optical microstructural analysis.

To evaluate a resistance to intercrystalline corrosion (ICC) samples of the given alloys were immersed into water solution of 30 gr/l NaCl and 10 ml/l HCl at 273 K for 24 hours. Intercrystalline corrosion was estimated on a basis of the following criteria: a corrosion intensity, i.e. a ratio of the total length of affected areas to the overall length of the specimen edge (I), %; an average depth of corrosion penetration into the sample (h), mm; amount of hydrogen released for a period of testing due to hydrogen depolarization.

Testing on stress-corrosion cracking (SCC) consisted in measuring the endurance of samples at the given tensile load in corrosive medium (the solution of 3% NaCl prepared with distilled water).

The corrosion resistance of alloys was studied in the following states: a state with microcrystalline (MC) structure not subjected to superplastic (SP) deformation (MC state), a state with MC structure after SP deformation (MC-SP state), a state with MC structure after hot deformation (MC-HD state), a state with coarse-crystalline structure after hot deformation (CC state). In order to obtain MC structure providing the possibility of SPD realization [1–4] the initial hot-pressed rods were subjected to cold

TABLE 1
The Dependence of Tendency to ICC on the 1960 and 1360 Alloys State

Alloy	Alloy state	I, %	h, mm	The amount of the given off hydrogen, sm^3 per 1 mm^2 of surface
1960	MC	39	0.53	
	MC-SP	49	0.56	0.069
	CC	61	0.63	0.160
1360	MC	26	0.25	
	MC-SP	29	0.28	
	CC	—	0.43	

deformation by 50–70% and to subsequent recrystallization annealing at 743 K (1960 alloy) and at 793 K (1360 alloy). The structure with a recrystallized grain size of 8–10 μm was obtained.

Superplastic deformation was realized by upsetting at the strain degree 50% and hardening temperatures 743 K (1960 alloy) and 783 K (1360 alloy) and the strain rate (ϵ) $7 \cdot 10^{-4} \text{ s}^{-1}$. Hot deformation of alloys with MC structure was conducted at strain rate $7 \cdot 10^{-2} \text{ s}^{-1}$, i.e. at the rate more than an optimum one for SPD. After deformation the billets were subjected to water cooling at 293 K.

The CC state was processed by upsetting of initial hot pressed rods by 50% at the initial strain rate 10^{-2} s^{-1} and at the temperatures of the highest technological plasticity 693 K (1960 alloy) and 733 K (1360 alloy). Then forgings were heated for hardening and subjected to water cooling at 293 K. Hot deformation of alloys with MC structure was conducted at a rate of $7 \cdot 10^{-2} \text{ s}^{-1}$.

After hardening the billets in all the investigated states were aged at 443 K for 14 hours (1960 alloy) and 453 K for 16 hours (1360 alloy).

Experimental Results

The comparison of the results of investigations of alloys in MC and MC-SP states indicate to a direct effect of SPD on the corrosion behavior of the alloy. Of course, it is necessary to keep in mind the conventionality of such evaluation since the effect of the simultaneous action of high temperature and deformation is only approximately equal to the sum of the effects of the former and the latter on the alloy properties.

After SP deformation the alloy has a homogeneous recrystallized MC structure similar to the starting one characteristic of the alloy before SPD. This is due to specific features of the mechanism of SP deformation [1] and relatively low deformation degrees. This fact should be taken into account since at large superplastic deformations the alloy structure undergoes significant changes caused by a dynamic grain growth [8].

In the CC state the alloys retain specific features of the hot pressed rod, namely, non-homogeneous, non-recrystallized structure with distinct metallographic and crystallographic textures. Due to the presence of antirecrystallizers in the composition of alloys (Zr in the alloy 1960 and Mn in the alloy 1360), recrystallization does not occur in them at hot deformation. Besides, their structure has a developed substructure.

It was established that the investigated alloys in the MC-SP state are characterized by a reduced resistance to intercrystalline corrosion as compared to alloys in MC state. SP deformation influences the corrosion resistance, namely, it increases both the corrosion intensity and the depth of corrosion (Table 1).

An increase in the strain rate of the 1960 alloy in MC-SP state results in the enhancement of ICC (Fig. 1). SCC tests demonstrated that at insignificant loading of specimens ($\sigma = 196 \text{ MPa}$ and 216 MPa)

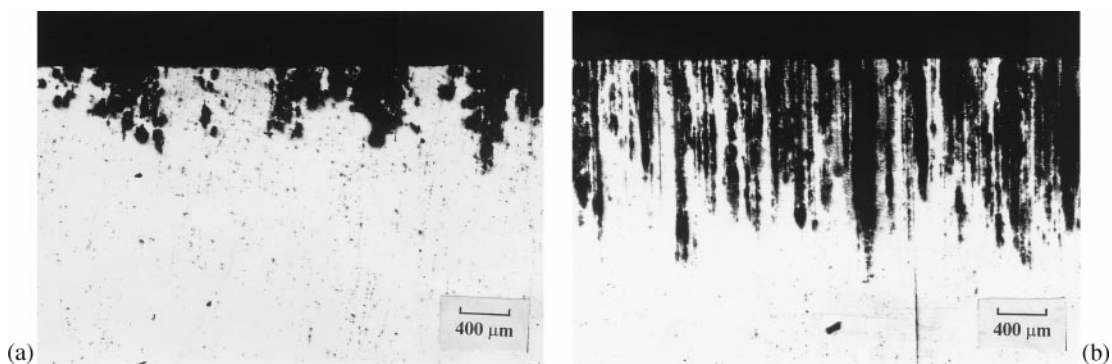


Figure 1. A character of the intercrystalline corrosion of 1360 alloy with microcrystalline structure after SPD (MC-SP state) (a) and with coarse-grained structure after hot deformation (CC) (b).

the resistance to SCC for 1960 alloy in both states differs insignificantly. But at higher loading ($\sigma = 245$ MPa) the time to failure of specimens after SPD is twice as much as the endurance in CC state (Table 2).

Discussion

Structural factors on the level of micro- and fine structure affect the development of corrosion having electrochemical origin. According to [9] the 1960 type alloys can be considered as a four-electrode galvanic system formed to increase the electrode potential: by magnesium-zinc phases of η and T type on the basis of intermetallics $MgZn_2$ and $Al_2Mg_3Zn_3$, respectively; by precipitate free boundary zones (PFZs); by solid solution of alloying elements in aluminum (by matrix) and by aluminides of transition metals. In 1960 alloy this phase is on the basis of Al_3Zr . As shown in Fig. 3 the most electrically negative excess magnesium-zinc phases do not form continuous precipitates on grain boundaries. Therefore, the corrosion affection develops in PFZs [10]. An increase or decrease in PFZ width means a change in an anode area which results in a change of the density of anode current and, correspondingly, in retardation or acceleration of corrosion destruction [11].

Condition of treatment can influence the width of PFZs and the amount of alloying elements (Cu, Mg, Zn) and vacancies in them [12].

In MC and MC-SP states alloys 1960 and 1360 have almost similar microstructure. However, their fine structure is different. After SP deformation PFZs are wider (Table 3). Thus, the decrease in resistance to ICC under the influence of SP deformation cannot be attributed to the change in the anode current density. In this case ICC increase can be caused by a reduction of electrically negative potential

TABLE 2
The Influence of Treatment Type of the Tendency to Corrosion Cracking of 1960 Alloy

State	Time to failure, days		
	Applied stress, MPa		
	196	216	245
CC	60	34	20
MC-SP	60	35	41

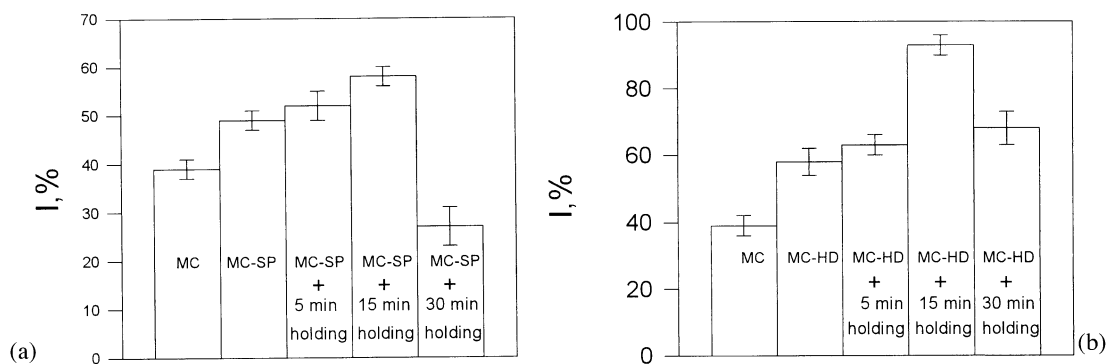


Figure 2. Influence holding before cooling after SPD (a) and hot deformation with rate $7 \cdot 10^{-2} \text{ s}^{-1}$ (b) on ICC 1960 alloy.

of PFZs and grain boundaries due to accumulation of defects, namely, extrinsic grain boundary dislocations and vacancies [1]. This supposition is confirmed by the fact that in MC-SP state the ICC intensity increases with increasing the SP strain rate (Fig 2). The latter correlates well with the increase in the extrinsic grain boundary dislocations density and the concentration of vacancies with increasing SP strain rate [1]. The widening of PFZs during SP deformation can be explained by the fact that this type of deformation is mainly realized by grain boundary sliding. According to [13] this results in an excess of vacancies as compared to their equilibrium concentration. Because of this excess after hardening at vacancies migration to the boundary there occurs dealloying of the near boundary zone for a greater depth (Table 3). Dealloying results from the fact that vacancies migrate to the boundary together with atoms of alloying elements, thus forming complexes with them [14].

As it was mentioned above, in the MC-SP state the 1960 alloy has a higher resistance to all types of corrosion (ICC, cracking corrosion) as compared to the CC state. The 1360 alloy also has an elevated resistance to ICC (h) in the MC-SP state (Table 1). There are some prerequisites for such favourable SPD effect. In this state PFZs are significantly wider (Table 3) that means the decrease in the anode current density. As it has been noted, the widening of PFZs during SP deformation is caused by the excess concentration of vacancies which are responsible for dealloying of the near boundary area. The difference in the concentration of vacancies is connected with the difference in deformation mechanisms: grain boundary sliding at SP deformation and intragranular dislocation slip at hot deformation.

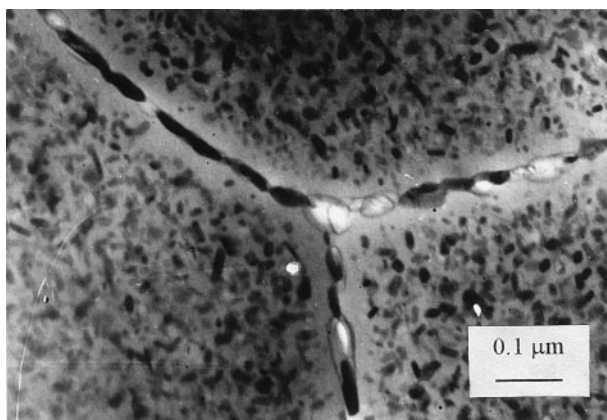


Figure 3. Precipitate-free zones of 1960 alloy with microcrystalline structure after SPD (MC-SP state).

TABLE 3
The Dependence of Near-boundary Precipitate-free Zone on the
State of 1960 Alloy

State	PFZ width, nm
MC	107 ± 4
MC-SP	128 ± 4
CC	94 ± 3
MC-SP + 15 min endurance at 743 K	95 ± 3
MC-SP + 30 min endurance at 743 K	94 ± 3

During SP deformation the electrode potential of PFZs increases that also retards its anodic dissolution. This promotion is mainly a consequence of magnesium and zinc reduction in PFZs. Partial rates of going out of alloying element atoms into the boundary are not the same. Copper is removed at higher rates. This is determined by the energy of atomic links with vacancies. They are equal to 0.25, 0.18 and 0.15 eV for copper, magnesium and zinc, respectively [14]. As the energy of interatomic bond increases, the rate of going out, i.e. the rate of diffusion of “alloying element atom - vacancy” complex, grows. However, at ageing after hardening the difference in partial rates must not influence a degree of dealloying of PFZs by each element.

The possible influence of holding after SP deformation on the ICC resistance of alloys 1960 and 1360 was evaluated. The holding was conducted at a temperature of SP deformation. According to data given in Table 3 holding for 15 min and 30 min can cause a significant reduction in the PFZ width from 128 nm to 93–94 nm. Such an effect of holding can be attributed to migration of excess vacancies into boundaries. This excess vacancies are of a deformation origin. As a result, at ageing after hardening only excess heat vacancies of hardening origin take part in PFZ dealloying and the PFZ width should approximate its width in the MC state. The influence of holding on corrosion was determined by intensity and average depth of ICC. It was established that at first the holding increases the corrosion and then as the time of holding increases to 30 min the resistance to corrosion grows (Fig.2). The increase in corrosion can be explained by PFZ narrowing that results in higher current density in the anode region (in PFZs). The development of the process of dissociation of extrinsic grain boundary dislocations also promotes this. According to [15] this process is accompanied by an increase in grain boundary energy that means a reduction of their electrode potential. Some restoration of corrosion resistance at long holding can be attributed to annihilation of dissociated grain boundary dislocation and to boundaries approaching the equilibrium state [15]. As a result, the excess grain boundary energy and concentration of excess vacancies in PFZs reduces that retards the development of electrochemical corrosion due to the increase in the electrode potential of PFZs and boundaries.

Conclusions

Superplastic deformation of microcrystalline alloys 1960 and 1360 reduces their resistance to inter-crystalline corrosion due to the decrease in electrode potential of near boundary PFZs. Taking into account the considerable difference in the origin of the given alloy one can suggest that such SPD effect might be observed during SPD of all known commercial alloys. The analysis of the electrochemical origin of the SPD influence on corrosion resistance of the alloys testifies this as well. At the same time SP deformation which can be used only in the case of MC materials provides a significant increase in resistance to ICC and SCC as compared to hot deformed coarse-crystalline alloys. This testifies that the

commercial use of SP deformation instead of the conventional method allows to increase the corrosion endurance of articles out of aluminum alloys.

References

1. O. A. Kaibyshev, Superplasticity of Alloys, Intermetallides, and Ceramics, p. 317, Berlin (1992).
2. R. Sawle, Sheet Metal Ind. 55, 696 (1978).
3. J. R. Cahoon, Metal Sci. 9, 346 (1975).
4. M. Kh. Rabinovich, O. A. Kaibyshev, and V. G. Trifonov, Metalloved. Termich. Obrabotka Metal. 9, 58 (1981).
5. M. Kh. Rabinovich and M. V. Markushev, Tenth International Conference on the Strength of Materials, p. 661, The Japan Institute of Materials (1994).
6. M. Kh. Rabinovich and M. V. Markushev, Material Science Forum in Moscow, p. 219, Trans Tech Publications, Switzerland (1994).
7. V. I. Dobatkin, Properties of Construction Aluminum Alloys with Ultrafine Grain, p. 72, Metallovedenie Legkikh Splavov, VILS, Moscow (1985).
8. M. Kh. Rabinovich and V. G. Trifonov, Acta Mater. 44, 2073 (1996).
9. V. S. Sinyavskiy, V. D. Valkov, and G. M. Budov, Corrosion and Resistance of Aluminum Alloys, p. 224, Metallurgia, Moscow (1970).
10. Commercial Aluminum Alloys, Reference Book, p. 526, Metallurgia, Moscow (1984).
11. J. Thomas and I. Nutting, J. Inst. Metall. 88, 2 (1959).
12. The Reference Book of Typical Corrosion Properties of Semifinished Products Made of Aluminum Alloys, p. 148, VILS, Moscow (1978).
13. O. A. Kaibyshev, R. Z. Valiev, and V. V. Astanin, Phys. Stat. Sol. (a). 35, 403 (1976).
14. B. S. Bokshstein, S. Z. Bokshstein, and A. A. Zhuhovitskiy, Thermodynamic and Kinetic of Diffusion in Solid States, p. 279, Metallurgia, Moscow (1974).
15. R. Z. Valiev, V. Yu. Gertsman, O. A. Kaibyshev, Phys. Stat. Sol. (a), 61, K95 (1980).