JOURNAL OF MATERIALS SCIENCE 27 (1992) 1107–1112

Effect of boron on corrosion resistance of Al–2.5 wt% Cu alloy

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The effect of boron on the corrosion resistance of Al–2.5 wt% Cu alloy has been investigated with transmission electron microscopy and particle tracking autoradiography. It is shown that when Al–2.5 wt% Cu alloys are doped with 0.002, 0.004, and 0.006 wt% B, the corrosion resistance of the alloys can be greatly increased. The mechanism for boron to increase the corrosion resistance is that boron addition eliminates the preferential precipitation of a second phase at grain boundaries of the alloys. Moreover, it is shown that the segregation of boron to grain boundaries is importantly responsible for the increase of the corrosion resistance of the alloys.

1. Introduction

Copper is the main alloying element in many precipitation-hardened Al-base alloys. The appearance of copper in the alloys results in a large decrease of partial resistance to corrosion (mainly intergranular corrosion). The mechanism for copper to decrease the partial corrosion resistance of Al-base alloys is that when aged after the alloys have been solution-treated, the precipitation-hardening phase Al_2Cu precipitates preferentially at grain boundaries, which leads to the depletion of copper near the grain boundaries. The electrode potential of the Cu-depletion region is lower than that of the hardening phase or the matrix, which can cause intergranular corrosion of the alloys under certain circumstances [1]. The intergranular corrosion greatly decreases the cohesion between grains and the mechanical properties of the alloys, especially plasticity. This corrosion is therefore very dangerous.

A small quantity of alloying elements (e.g. Cd, Ag) when added to Al-base alloys can reduce the surface energy of precipitation, which changes the morphology and the distribution of precipitation so that the tendency of grain boundary embrittlement is decreased [2–4]. Grove and Judd [5] found that addition of 0.04% Ti to Al–5.32% Zn–1.66% Mg alloy retarded the kinetics of precipitation and prevented segregation of solute to grain boundaries during slow quenching. They suggested that Ti atoms tie up vacancies so that fewer vacancies are available to aid the diffusion of Mg and Zn atoms. Mg and Zn atoms then diffuse more slowly so that fewer reach grain boundaries. This could eliminate the preferential precipitation at grain boundaries. Owing to the above reasons, those alloying elements can also improve the partial corrosion resistance of the alloys.

Consequently, the effects of minor alloying additions appear to be worthy of considerable further study to change the precipitate morphology through changing the surface energy, so that there is less tendency for grain boundary embrittlement and more partial corrosion resistance. It is also possible to control the enhancement of diffusion by excess vacancies by adding a solute which forms solute atom–vacancy complexes with vacancies.

Up to now, investigations of the effects of boron on the various properties of Al-base alloys are rare. It is little known how much boron atoms segregate at grain boundaries of Al-base alloys. It is estimated, from the solid solubility of the equilibrium diagram of Al–B binary alloy [6], that boron atoms will segregate largely at grain boundaries; it is well known that the tendency for grain boundary segregation of the solutes in a binary alloy is inversely proportional to the solid solubility [7]. The nucleation and growth of grain boundary cells in Al-base alloys will therefore be affected by the addition of boron, and further the corrosion resistance of the alloys will also be affected.

This work therefore aimed at investigation of the effects of boron addition on the intergranular precipitation and partial corrosion resistance in an Al–2.5 wt % Cu alloy.

2. Experimental procedure

Al–2.5 wt % Cu alloys were doped with 0.002, 0.004, and 0.006 wt % B. The B-doped Al–Cu alloys were prepared by melting high-purity aluminium, electrolytic copper and Al–1 wt % B mother alloy in high-purity alumina crucibles in argon. The ingots were homogenized at 530 °C for 25 h and then were hot-forged into samples 13 mm × 13 mm × 200 mm in size. The alloy compositions are given in Table I.

All the samples were solution-treated at 535 °C for 70 min, quenched in room-temperature water and then aged at 190 °C for 1, 3, 5, 8, and 12 h. The grain size of the samples heat-treated as above was about 30 μm dia.

TABLE I Alloy compositions

Alloy No.	Composition			
	Cu	B	Zn	Al
0	2.32	–	0.022	Bal.
1	2.83	0.002	0.021	Bal.
2	2.78	0.004	0.023	Bal.
3	2.55	0.006	0.020	Bal.

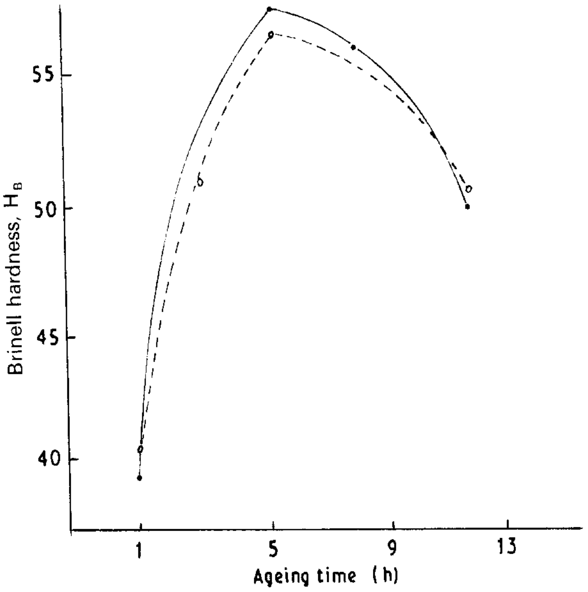

Figure 1 Ageing curves of (——) alloy 0 and (– – –) alloy 3 at 190 °C. Steel ball diameter 5 mm, load 250 kg, loading time 30 s.

The Brinell hardness test was used for measuring the ageing curves of the samples. The results are shown in Fig. 1.

Some of the heat-treated samples were machined again into corrosion samples of size 10 mm × 10 mm × 20 mm. The samples were polished and then corroded by an aqueous solution of 4% NaCl at 80 °C for 50 h. In the corrosion test, the corroding solution was prepared in a solution of 50 ml for each sample. Corroded samples were then washed and dried. Finally, the corroded samples were observed by optical microscopy and measured by an image analyser.

Microstructural features in the samples were examined in transmission using an H-800 analytical transmission electron microscope. Thin foils for electron microscopy investigation were prepared using a standard dual-jet electropolishing technique. The experimental alloys were thinned using an electropolishing solution of 20% perchloric acid and 80% methyl alcohol at 0 °C with 80 V.

In the present work, the distributions of boron in the samples containing boron were detected by particle tracking autoradiography (PTA) [8]. Tri-acetic acid fibre foils were used as detecting foils, whose detecting sensitivity and spatial resolution for boron were respectively 1 p.p.m. and 2 μm. The detecting foils were etched for 20 min at 50 °C with an aqueous solution of 7.5 N NaOH. The surface of each etched foil was then coated with chromium and observed by optical microscopy.

3. Results

The ageing curves of alloys 0 and 3 at 190 °C are shown in Fig. 1, which shows that when the ageing time is shorter than 5 h, the hardness of the two alloys increases with increasing ageing time. Consequently, the peak ageing time is 5 h for the two alloys. The ageing curves of alloys 1 and 2 are similar to those of alloys 0 and 3. Owing to the fact that precipitation-hardened Al-base alloys are used in a state of peak ageing, and peak-aged alloys possess the least corrosion resistance, we only investigate here the partial corrosion resistance of peak-aged alloys.

The corroded surface morphologies of the different alloys aged at 190 °C for 5 h are given in Fig. 2, which shows that partial corrosion decreases with increasing boron content of the alloy in the region of boron content considered in the work.

In order to determine further the relationship between the degree of partial corrosion of the samples and their boron content, the degrees of partial corrosion of the samples aged for 5 h were semi-quantitatively analysed by a Model M-2 image analyser. The degree of partial corrosion was expressed as the area fraction occupied by the parts partially corroded, A. This measuring method is reasonable because all the samples were solution-treated at the same temperature (530 °C) and have close compositions, so that they possess close grain sizes (dia. 30 μm). The measured results are shown in Fig. 3. This shows that the law of variation of the degree of partial corrosion with boron content is very consistent with that in Fig. 2.

Transmission electron micrographs of solution-treated alloys 0 and 3 are shown in Figs 4 and 5, respectively, which show that no apparent second phase precipitates at the grain boundaries and in the grain centres for the two alloys. Figs 6 and 7 show the transmission electron micrographs of alloys 0 and 3, respectively, solution-treated and aged. From Fig. 6, it is seen that the apparent second phase precipitates both at grain boundaries and in the grain centres (see Fig. 6a), and even in some regions only at grain boundaries (Fig. 6b), for alloy 0 solution-treated and peak-aged. Fig. 7 shows that no apparent second phase appears at grain boundaries for alloy 3 solution-treated and peak-aged.

Fig. 8 shows the precipitates in grain centres and their selected-area diffraction (SAD) pattern for alloy 3 solution-treated and peak-aged. Phase analysis showed that the second phase is θ′-Al_2Cu with body-centred tetragonal structure. Moreover, from Figs 6–8 it is seen that all the particles precipitate in a certain crystallographic plane in the matrix.

Owing to the spatial resolution of PTA (2 μm) and the size of etching pits on the detecting foils (dia. 1 μm), a rectangular band of area 3 μm × 10 μm was chosen to determine the apparent area fraction occupied by etching pits inside the rectangular band. When the band was placed on the grain boundary, the apparent area fraction measured was denoted by A', and when placed on the grain centres it was denoted by A'_0. According to $A = -\ln(1 - A')$ [9] which can correct the effect of overlapping between etching pits, then the apparent area fractions A' and A'_0 were

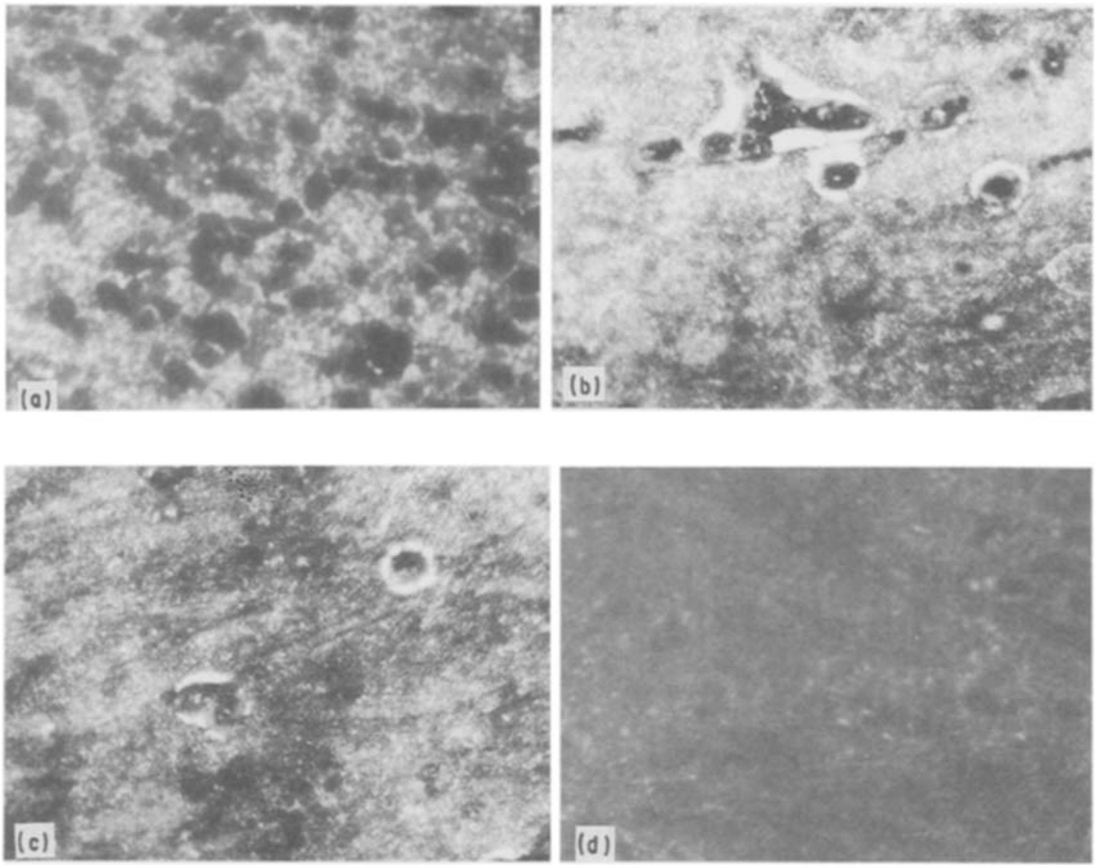

Figure 2 Corroded surface morphologies (×450) of different alloys aged at 190 °C for 5 h: (a) alloy 0, (b) alloy 1, (c) alloy 2, (d) alloy 3.

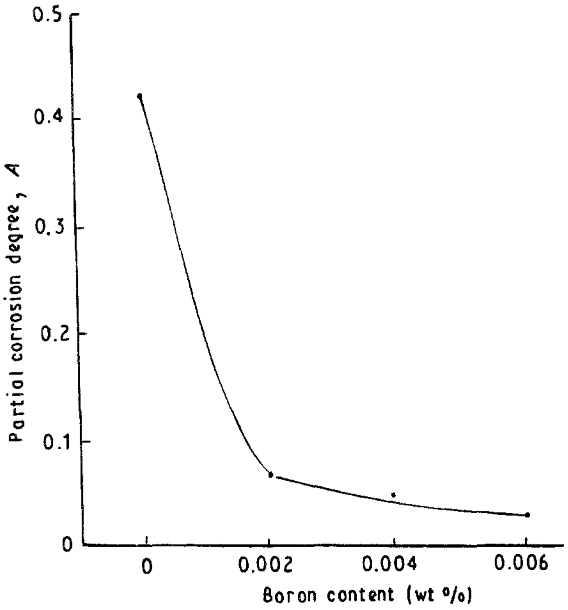

Figure 3 Degree of partial corrosion as a function of boron content for samples peak-aged at 190 °C.

Figure 4 Transmission electron micrograph of alloy 0, solution-treated. × 15 000.

corrected to give the true area fractions A and A_0, respectively. The level of boron segregation at the grain boundary is expressed by the product of the ratio A/A_0 and the concentration C_g of boron in the grain centres, $C_g(A/A_0)$, where C_g is taken from Table I. $C_g(A/A_0)$ as a function of C_g for the samples aged at 190 °C for 5 h is given in Fig. 9, which shows that when the boron content of samples is between 0 and 60 p.p.m., the level of boron grain-boundary segregation increases with increasing bulk concentration of boron.

4. Discussion

Fig. 1 shows that the peak ageing time of all the samples is 5 h. Owing to the fact that precipitation-hardened Al-base alloys are used in a state of peak ageing and peak-aged alloys possess the least corrosion resistance, the effect of boron addition on the corrosion resistance of only peak-aged alloys was investigated in the present work.

Figure 5 Transmission electron micrograph of alloy 3, solution-treated. × 15 000.

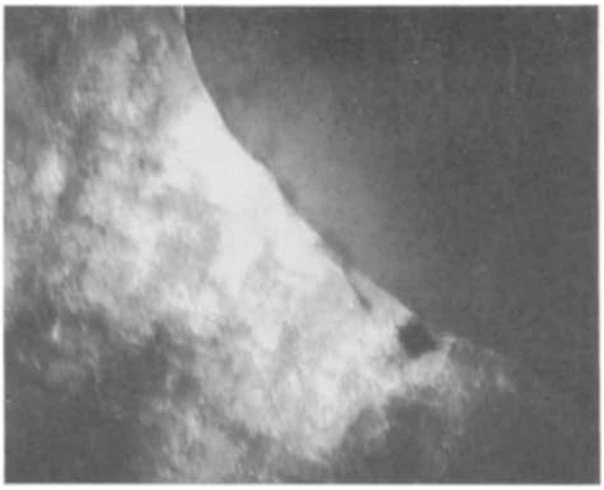

Figure 7 Transmission electron micrograph of alloy 3 solution-treated and peak-aged. × 15 000.

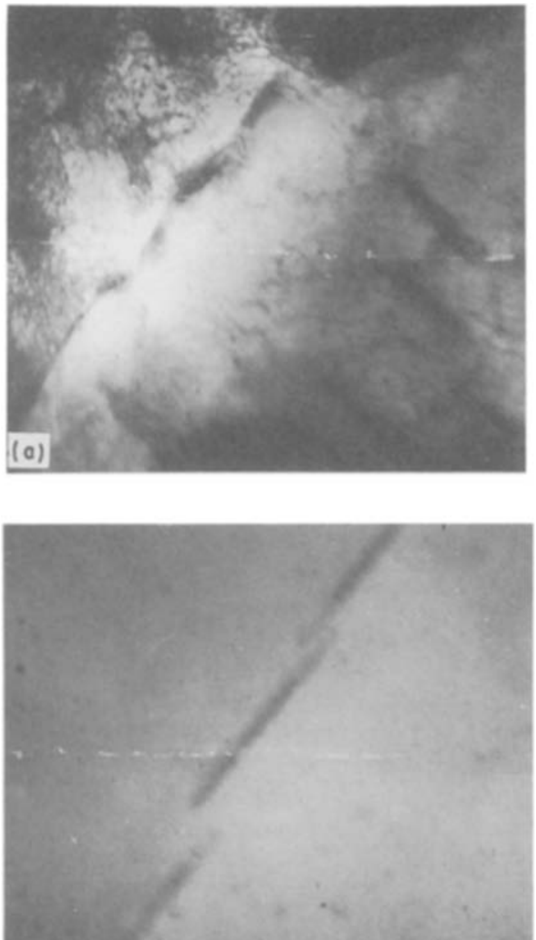

Figure 6 Transmission electron micrographs of alloy 0 solution-treated and peak-aged: (a) × 20 000, (b) × 50 000.

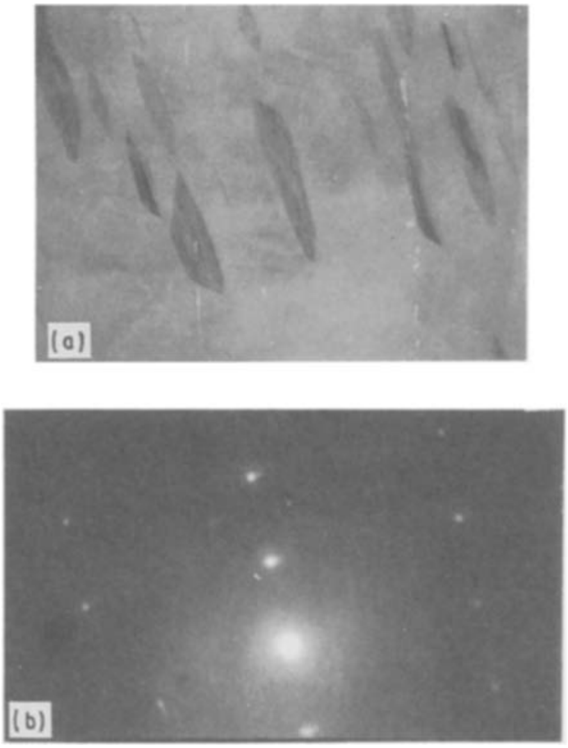

Figure 8 Transmission electron micrographs of alloy 3: (a) morphology of second-phase precipitates in the grain centres (× 50 000) and (b) their selected-area diffraction pattern.

Figs 2 and 3 show that partial corrosion (mainly intergranular corrosion) decreases with increasing boron content of alloys peak-aged in the region of boron content investigated in the work. Figs 4 and 5 show that no apparent second phase precipitates at the grain boundaries and in the grain centres for alloys 0 and 3 when only solution-treated, which indicates that the second-phase particles in the aged structures appear during ageing. Fig. 6 shows that an apparent second phase precipitates both at grain boundaries and in the grain centres (Fig. 6a) or only at grain boundaries (Fig. 6b), for alloy 0 solution-treated and peak-aged. Fig. 7 shows that no apparent second phase appears at grain boundaries, whereas apparent second-phase particles appear only in the grain centres and are determined to be θ'–Al_2Cu by the phase analysis of Fig. 8, for alloy 3 solution-treated and peak-aged. Consequently, it can be believed that the mechanism for the corrosion resistance of the Al–Cu alloys to be increased by boron addition is that boron addition eliminates the preferential precipitation of a second phase (θ'–Al_2Cu) at grain boundaries in the alloys.

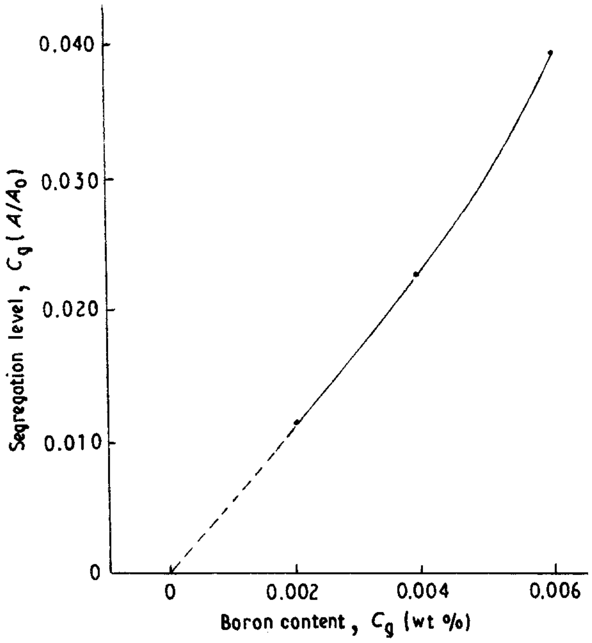

Figure 9 Level of boron grain-boundary segregation, $C_g(A/A_0)$, as a function of C_g for samples solution-treated and peak-aged.

On the intergranular corrosion of Al–Cu alloys, it is well known that when a second phase (Al_2Cu) precipitates preferentially at grain boundaries during ageing, a copper depletion region appears adjacent to the second phase; since the electrode potential of the copper depletion region is lower than that of the second phase or the matrix, intergranular corrosion of the alloys takes place under certain circumstances.

The mechanism by which boron eliminates the preferential precipitation of second-phase θ'–Al_2Cu at grain boundaries in Al–Cu alloys may be that (i) the formation of sufficient boron–vacancy complexes causes the number of copper–vacancy complexes to decrease, so that the kinetics of copper diffusion is retarded and fewer vacancies are available to aid the diffusion of Cu atoms; these atoms then diffuse more slowly and fewer reach grain boundaries, and this could eliminate the preferential precipitation of the second phase at grain boundaries [10]; or (ii) the segregation of boron at grain boundaries decreases the grain boundary energy so that the preferential precipitation of the second phase is eliminated at grain boundaries [11].

In Al–Cu alloys there is a certain binding energy between copper and vacancy. At a given temperature, a certain number of copper–vacancy complexes appear which can promote the kinetics of ageing. This is because the excess saturation degree of vacancies in solution-treated Al–Cu alloys is very large and the movement energy of vacancies is lower ($\sim$ 0.5 eV) so that the copper–vacancy complexes diffuse very easily, which will promote the ageing kinetics of the alloys.

At a given temperature, the concentration of solute atom–vacancy complexes in a B-doped Al–Cu alloy, C_c, is given by [12]

$$C_c = K_c C_l \exp\left(\frac{E_b - E_f}{kT}\right) \qquad (1)$$

where C_l is the concentration of solutes in the matrix, E_b is the solute atom–vacancy binding energy, E_f is the formation energy of vacancy, K_c is a constant, k is Boltzmann's constant and T is absolute temperature. Equation 1 shows that the larger E_b is, the larger the concentration of the complexes. E_b is approximately given by [13]

$$E_b = 8\pi\mu r_0^3\varepsilon^2 \qquad (2)$$

where μ is the shear modulus of the matrix, r_0 is the matrix atom radius and

$$\varepsilon = \pm\frac{r_0 - r}{r_0}$$

where r is the solute atom radius. Data used in calculating E_b and the results are shown in Table II.

Table II shows that the boron–vacancy binding energy is much larger than the copper–vacancy value. Consequently, the addition of a small amount of boron to the alloys can lead to the formation of a large quantity of boron–vacancy complexes, so that the number of copper–vacancy complexes is largely decreased to eliminate the preferential precipitation of a second phase at grain boundaries.

From Figs 3 and 9, the relationship between the degree of partial corrosion and the level of boron grain-boundary segregation for the samples solution-treated and peak-aged can be obtained and is shown in Fig. 10, which shows that the partial corrosion resistance increases with increasing level of boron segregation, i.e. the segregation of boron to grain boundaries is importantly responsible for the increase

TABLE II Data used in calculating E_b and results

	B–V	Cu–V
r (m)	0.97×10^{-10}	1.27×10^{-10}
r_0 (m)	1.43×10^{-10}	1.43×10^{-10}
ε	0.32	0.11
μ ($N m^{-2}$)	1.6×10^{10}	1.6×10^{10}
E_b (eV)	0.75	0.09

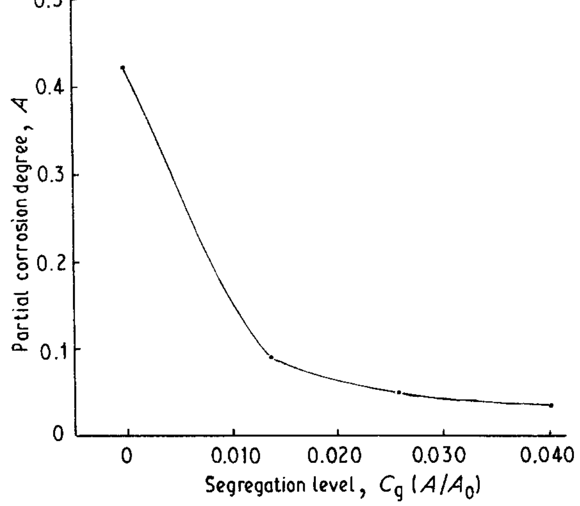

Figure 10 Degree of partial corrosion as a function of the level of boron grain-boundary segregation for samples peak-aged at 190 °C.

of partial corrosion resistance in the alloys. Therefore, it is also believed that the mechanism for boron addition to increase the corrosion resistance of the Al–Cu alloys is that the segregation of boron to grain boundaries decreases the grain boundary energy, so that the preferential precipitation of a second phase at grain boundaries is eliminated.

5. Conclusions

1. When Al–2.5 wt % Cu alloys are doped with 0.002, 0.004, and 0.006 wt % B, the corrosion resistance of the alloys can be greatly increased. The mechanism for boron addition to increase the corrosion resistance is that the boron addition eliminates the preferential precipitation of a second phase at grain boundaries so as to increase the corrosion resistance of the alloy.

2. The segregation of boron to grain boundaries is importantly responsible for the increase of the corrosion resistance of the alloys.

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Received 25 October 1990
and accepted 25 March 1991