JOURNAL OF MATERIALS SCIENCE 33 (1998) 1043–1047

Study of the diffusion of Al–Li alloys subjected to an electric field

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An experimental investigation of the homogenization treatment of 2091 Al–Li alloy in the presence of an electric field, has revealed the phenomena of reduced volume fraction, small size, spherical shape and random distribution of second-phase particles, which bring about an increase in ductility. The results show that the dissolution of second-phase particles is promoted by means of the vacancy mechanism, because of the larger diffusion coefficient of solute atoms than the vacancy–solute complexes at the beginning of the homogenization treatment. By increasing the homogenization time and applying an electric field, the diffusion coefficient of vacancy-solute complexes is raised, whereas that of solute atoms is reduced, because of the decreased potential energy of the second phase at grain boundaries. Therefore, the non-equilibrium segregation of magnesium and copper elements is generated near the surface of the ingot by a complex mechanism. An experimental study of the solution treatment under an electric field, revealed that the lithium non-equilibrium segregation is induced at grain boundaries responsible for the δ precipitates.

1. Introduction

For as-cast Al–Li alloys, owing to a significant amount of dendritic segregation, there is a great risk of collapse during hot rolling. Antes *et al.* [1] have shown that a dramatic improvement in ductility can be achieved by eliminating dendritic segregation. The effect of undissolved second phase on ductility has been investigated by Singh and Flemings [2]. Their results show that the ductility during hot rolling depends not only on the volume fraction but also on the shape and distribution of second-phase particles. For a given amount of second phase, the spherical shape and random distribution of second-phase particles are beneficial for the improvement of ductility.

In order to improve the workability of Al–Li alloys after casting, the homogenization treatment prior to hot rolling is necessary. However, many homogenization methods [3–5] are unsuitable for the homogenization treatment of Al–Li alloys. Therefore, we proposed the method of the homogenization treatment of 1420 Al–Li alloy [6]. In this paper, the homogenization treatment of 2091 Al–Li alloy in the presence of an electric field is investigated.

There are mainly two kinds of diffusion mechanisms in a solid; they are the vacancy mechanism and the interstitial mechanism. As a result of experimental observations [7–9], a vacancy-solute complex mechanism is proposed, in view of the non-equilibrium segregation of solute atoms at grain boundaries [10, 11]. Although the heat treatment of Al–Li alloys with an electric field has been investigated, the diffusion mechanism is not clear. This paper also reports some experimental observations made to reveal the diffusion mechanism in the 2091 Al–Li alloy subjected to an electric field.

2. Experimental procedure

The 2091 Al–Li alloy was melted under an argon atmosphere. Table I gives the chemical composition of the alloy.

TABLE I Chemical composition of the alloy (wt %)

Li	Cu	Mg	Zr	Fe	Si	Na	Al
2.2	2.6	1.2	0.15	0.01	0.01	10 p.p.m.	bal.

The ingots were homogenized at the same temperature (530 °C) and time (16 h), but the homogenization time in an electric field differed. This was 8 h (530 °C × 8 h × 2 kV cm^{-1} + 530 °C × 8 h) (combined homogenization treatment) and 16 h (530°C × 16 h × 2 kV cm^{-1}) in contrast to the homogenization treatment without an electric field (530 °C × 16 h).

In order to investigate the lithium non-equilibrium segregation, the specimens of 2091 Al–Li alloy were solution treated at 530 °C for 20 min, and immediately quenched into cold water. Then, the specimens were immediately aged at 180 °C for 32 h.

The distribution of alloying elements was observed using electron probe microanalysis (EPMA), and the precipitate phases were analysed by transmission electron microscopy (TEM).

3. Experimental results

EPMA observations show the amount (volume fraction), size, shape and distribution of second-phase particles containing magnesium and copper elements. Compared with the homogenization treatment in the absence of an electric field (530 °C × 16 h) (Fig. 1), the combined homogenization treatment accelerates the dissolution of second-phase particles containing magnesium and copper elements (Fig. 2), which brings about the reduced volume fraction of second phase. However, when the homogenization time for applying an electric field is 16 h (Fig. 3), the non-equilibrium segregation of magnesium and copper elements is induced in the vicinity of the surface of the ingot.

Fig. 4 represents the stages of hot rolling simulated by Gleeble-1500. During the first stage of hot rolling, no macrocracks were produced in any of the three cases. However, during the second stage, some macrocracks were formed in the homogenization treatment without an electric field. In the third stage, some macrocracks were found in the homogenization treatment when applying an electric field (16 h), and a significant amount of macrocracking was produced during the homogenization treatment without an electric field. In all the stages, there were no macrocracks produced in the combined homogenization treatment.

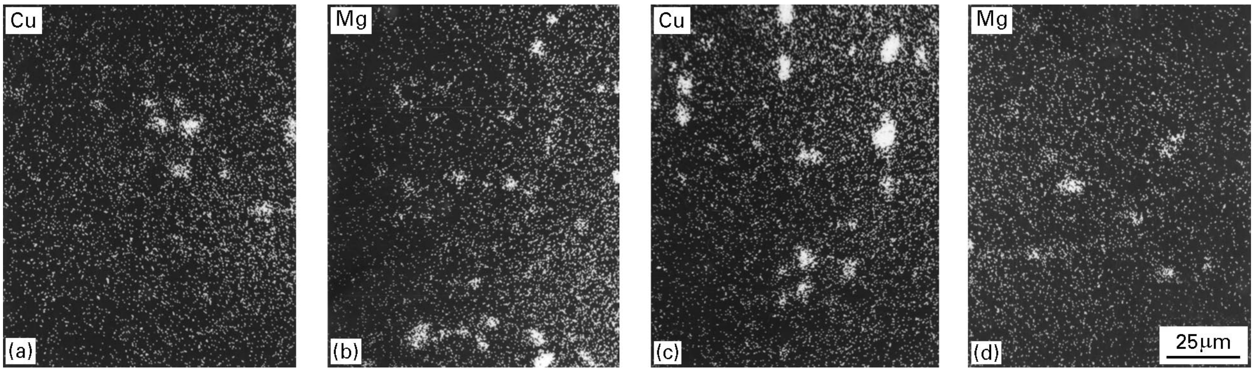

Figure 1 Distribution of alloying elements without an electric field: (a, b) inner part of the ingot, (c, d) in the vicinity of the surface.

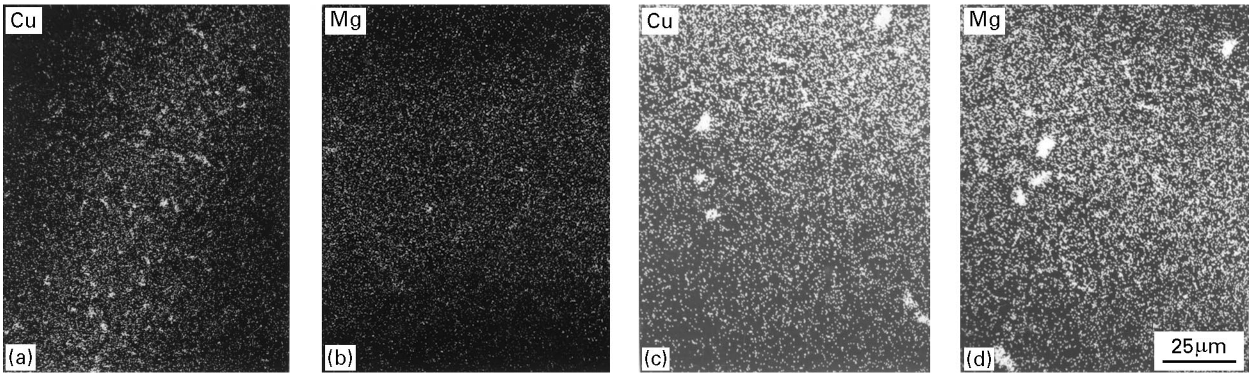

Figure 2 Distribution of alloying elements of the combined homogenization treatment, (a, b) inner part of the ingot, (c, d) in the vicinity of the surface.

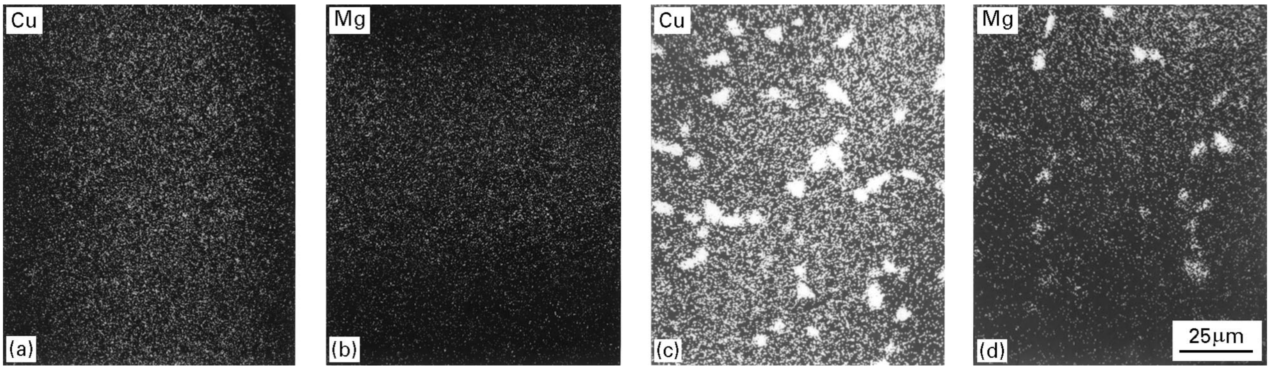

Figure 3 Distribution of alloying elements with an electric field: (a, b) inner part of the ingot, (c, d) in the vicinity of the surface.

Fig. 5 shows the δ′ and δ precipitates. In comparison with the solution treatment in the absence of an electric field, discontinuous δ precipitates were seen at grain boundaries for the solution treatment when applying an electric field.

4. Discussion

4.1. Ductility of 2091 Al–Li alloy

It has been shown by Edelson and Baldwin [12] that ductility depends mainly on the volume fraction of second-phase particles. However, the shape and distribution of the second-phase particles also have an important effect on ductility [13].

The combined homogenization treatment reduces the volume fraction of second-phase particles (Fig. 2), thus increasing the ductility of the alloy. This indicates that the combined homogenization treatment promotes the diffusion of magnesium and copper elements, which results in the accelerating dissolution of second-phase particles. Therefore, the ductility of the alloy increases due to the decrease in the volume fraction of second-phase particles.

It is also observed that the distribution of second-phase particles has an important effect on ductility. A proper homogenization time with an electric field results in a more homogenenous distribution and significantly improved ductility. Excessive application of the electric field, however, brings about uphill diffusion and slightly increased volume fraction of second-phase particles in places adjacent to the surface, while in the interior of the specimen it reduces the particular volume fraction by accelerating the dissolution of the particles. Therefore, inhomogeneous distribution of second phase particles and reduced ductility result if the application time of the electric field is too long (16 h) (Fig. 3).

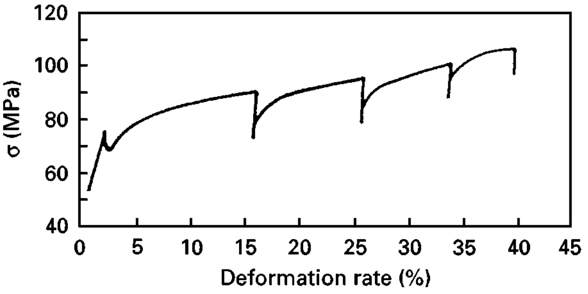

Figure 4 Hot rolling simulated by Gleeble-1500.

Therefore, the combined homogenization treatment is an effective means of the homogenization treatment.

4.2. Diffusion mechanism of 2091 Al–Li alloy

According to the complex mechanism, one criterion is that solutes leading to the non-equilibrium segregation at grain boundaries preferentially interact with vacancies (i.e. a positive binding energy, E_b, exists) [10]. The second condition of the present mechanism is that complexes tend to be thermodynamically stable or metastable. In other words, this would require that the binding energy, E_b, is greater than kT.

Yu and Chen [14] proposed a model for complex diffusion, i.e. a complex is composed of a substitutional solute atom, and a vacancy which keeps jumping around the solute atom which is at the "centre" of the jumping vacancy. Meanwhile, the vacancy also instantly exchanges with the solute atom and changes the position of the "centre" of the jumping vacancy. Based on the above diffusion mechanism of a complex, the condition of non-equilibrium segregation is given, $E_b > H_1 - H_0 + kT\ln 10$, where H_1 and H_0 are the activation energies for vacancy jumping around a solute atom and diffusion into the bulk, respectively, k is Boltzmann's constant, and T is the temperature. Therefore, non-equilibrium segregation of the solute atoms produced is due to vacancy-coupled uphill diffusion of solute atoms towards the vacancy sources and sinks such as dislocations, grain boundaries and the external surface.

Table II gives the binding energy of complexes at 530 °C. On the basis of the thermodynamic condition, in the grain interior, vacancies, solute atoms and vacancy–solute complexes are satisfied by the following equilibrium condition

$$\text{solute atom(A)} + \text{vacancy(V)} \rightleftharpoons \text{complex(VA)} \quad (1)$$

TABLE II Binding energy of vacancy-solute complexes

System	E_0(eV)	$H_1 - \mathrm{H}_0 + kT\ln 10$(eV)
Al–Li	0.25 [10]	0.14
Al–Mg	0.21 [10]	0.20
Al–Cu	0.2 [10]	0.19

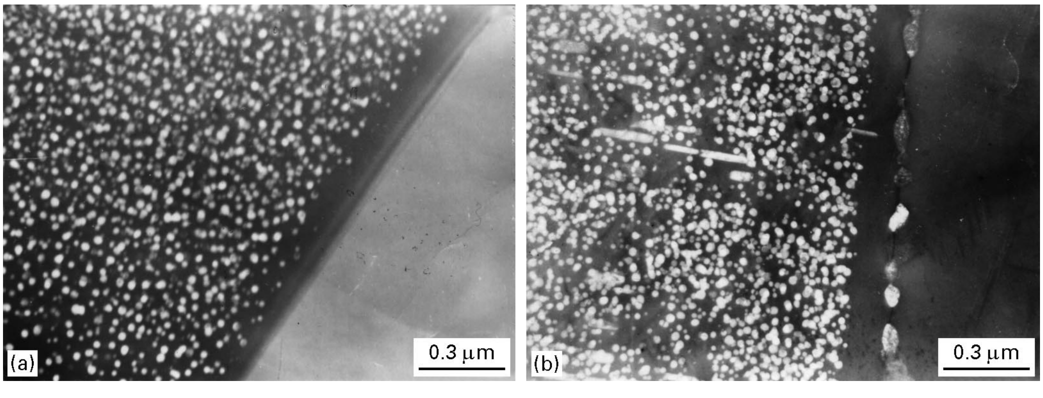

Figure 5 δ′ and δ phases observed by TEM: (a) without an electric field, (b) with an electric field.

In the 2091 Al–Li alloy after casting, a significant amount of second-phase particles at grain boundaries is present. During homogenizing treatment, an equilibrium concentration of vacancies is generated and distributed throughout the lattice. Some complexes are also found at that temperature. The rate of formation of vacancy–solute complexes is equal to the separation rate. Owing to the movement of vacancies at random at high temperature, solute atoms diffuse towards the grain interior, but vacancies migrate to grain boundaries. The solute atoms diffuse towards the grain interior because of a high concentration gradient of solute atoms. Diffusion occurs in the direction opposite to that of vacancy flows according to the vacancy mechanism, which leads to the dissolution of second-phase particles.

Under the conditions of homogenization treatment with an applied electric field (ingot as anode), owing to the perturbation of the electronic state at lattice defects (vacancies or dislocations), the presence of a charge on the defects may occur. The applied field creates a charged surface layer in metallic materials and the interaction of the surface charge with the charged defects, particularly vacancies, when they approach the specimen surface will create an additional vacancy flux (Fig. 6). Simultaneous with the dissolution of second-phase particles towards the grain interior, the complexes migrate to grain boundaries. In the beginning of the homogenization process, due to a high concentration gradient of second phase at grain boundaries, the diffusion rate of solute atoms towards the grain interior is accelerated by the excess vacancy flows, according to the vacancy mechanism compared with that of vacancy–solute complexes towards grain boundaries, according to the complex mechanism. While increasing the homogenization time wtih an electric field, the reduced second phase causes the concentration gradient of solute to decrease, thus leading to the decreasing diffusion speed of solute atoms towards the grain interior, but an increasing diffusion speed of complexes towards grain boundaries. In the interior of the ingot, the solute atoms diffuse by the main vacancy mechanism because of the greater diffusion rate of solute atoms than complexes. In the vicinity of the surface of the ingot, by means of the movement of the excess vacancy flows towards grain boundaries, the non-equilibrium of magnesium and copper elements is induced at grain boundaries by the main complex mechanism, because of the accelerating diffusion of complexes compared with solute atoms.

Owing to the difficulties involved in measuring the lithium concentration, even when using the PEELS technique [8] and the Fresnel contrast method [15, 16], data on the solute distribution of lithium at grain boundaries are difficult to obtain. The case for non-equilibrium lithium segregation is not proved, but it is both theoretically predicted and supported by the only existing experimental data. As shown in Table II, given the high vacancy binding energy of lithium in aluminium, significant levels of non-equilibrium segregation might be expected. Surprisingly, wide solute-enrichment layers have been reported as a result of this process in other more easily analysable systems [14], with similar values for the vacancy–solute binding energy. If non-equilibrium segregation is strong in the 2091 Al–Li alloy rapidly quenched specimens investigated, we could thus envisage δ′ to nucleate first in the solute-enriched regions which would be expected to develop at grain boundaries during quenching, and thus grow to δ phase.

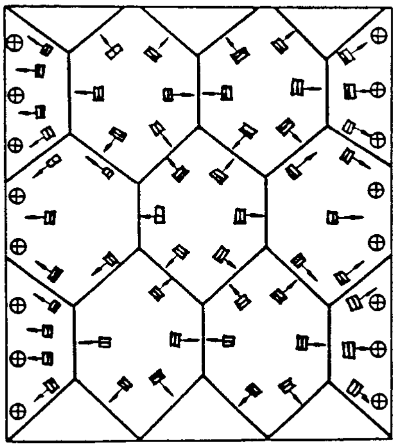

Figure 6 Model of the possible mechanism for the effect of an electric field on vacancy flow: (⊟) vacancy, (⊕) surface charge.

Non-equilibrium segregation of lithium can be proved by the discontinuous δ′ and δ phases at grain boundaries [8]. As shown in Fig. 5, the solution treatment without (530 °C × 20 min) and with (530 °C × 20 min × 2 kV/cm^{-1}) an electric field were investigated by TEM for the same ageing conditions (180 °C × 32 h). The non-equilibrium lithium segregation took place at grain boundaries for the solution treatment in the absence of an electric field. However, there were no δ′ or δ phase at grain boundaries observed, which indicates that little lithium content is not satisfied with the δ′ and δ precipitates at grain boundaries. During the solution treatment with an electric field, there were discontinuous δ phases precipitated at grain boundaries because of the non-equilibrium lithium segregation at grain boundaries. In the grain interior, the non-uniform distribution of δ′ phase is due to the non-equilibrium lithium segregation at subgrain boundaries and dislocations. Because of the same quenching conditions, the non-equilibrium lithium segregation is induced by the excess vacancy flows, according to the complex mechanism during the solution treatment with an electric field at high temperature, although the solution time with an electric field is short.

5. Conclusions

1. The reduced volume fraction of second-phase particles, small size, spherical shape and random distribution of particles for the homogenization treatment in the presence of an electric field, are beneficial for the improvement of the ductility of 2091 Al–Li alloy.

2. The solute atoms diffuse according to the vacancy mechanism which promotes the dissolution of second-phase particles and the complex mechanism

which leads to the non-equilibrium segregation of solute atoms. The non-equilibrium segregation of lithium, magnesium and copper elements in the 2091 Al–Li alloy can be induced by the movement of excess vacancy flows towards the interface.

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Received 1 September 1996
and accepted 24 September 1997