Proceedings of the 9th International Conference on Aluminium Alloys (2004)
Edited by J.F. Nie, A.J. Morton and B.C. Muddle

Formation Mechanisms of Precipitate Free Zones in Age-Hardenable Al Alloys

S. Hirosawa, Y. Oguri, T. Ogura, T. Sato

Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

Keywords: Precipitate free zone, Al-Cu(-Sn) alloy, Al-Zn-Mg(-Ag) alloy, Microalloying elements, Microstructure, Computer simulation

Abstract

The formation mechanism of precipitate free zones (PFZ) has been clarified for Al-Cu(-Sn) and Al-Zn-Mg(-Ag) alloys using transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX) and a Monte Carlo computer simulation. The vacancy depletion mechanism was found to work predominantly in the early stage of aging if the alloys are quickly quenched and aged at moderate temperatures. The simulation model taking into account the effects of vacancy sink well reproduced the experimental results, suggesting that the initial microstructures before aging are quite important to control the microstructure of the vicinity of grain boundaries.

1. Introduction

Precipitate free zones (PFZ) are often observed adjacent to grain boundaries of age-hardenable Al alloys. Two theories are widely accepted to explain the formation mechanism of PFZ by taking into account either solute depletion [1] or vacancy depletion [2, 3] in the vicinity of grain boundaries. However, it is still unclear which mechanism of them works predominantly in an alloy subjected to a particular heat treatment. Experimental approaches to verify the solute depletion mechanism seem to be easier because microchemical analysis such as energy dispersive X-ray (EDX) analysis can be available nowadays. On the other hand, the vacancy depletion is hardly detected through any experimental techniques because PFZ is a quite narrow microstructure of nanometer scale compared with abundant transgranular regions. Note that information from positron annihilation measurement is averaged over the specimen, resulting in the undistinguishable estimation of vacancy concentration within PFZ from that inside grains. Therefore, our developed Monte Carlo computer simulation [4-6] becomes extremely effective in predicting the atomistic behavior of vacancies during the formation of PFZ.

In this work, the formation mechanism of PFZ has been clarified for age-hardenable Al alloys such as Al-Cu and Al-Zn-Mg alloys using transmission electron microscopy (TEM) and EDX. A Monte Carlo simulation model was established to mimic the vacancy depletion mechanism by following the actual procedure of heat treatments. The reason why some additional elements could decrease the width of PFZ was also considered based on the interatomic interactions utilized in the simulation model.

The characteristic features of individual elements well explained not only which formation mechanism of PFZ predominantly works in an Al alloy but also why the modification of PFZ could be achieved by the addition of some microalloying elements.

2. Experimental and Simulation Model

The chemical compositions of the investigated alloys are Al-4.0Cu (-0.05Sn) and Al-4.9Zn-1.8Mg (-0.3Ag) (in mass%). The cold-rolled sheets were solution-treated at 793 and 743K for 3.6ks, followed by iced-water quenching, respectively. The aging treatment was carried out at 433K for various aging times. TEM observation and EDX analysis was performed using a JEOL 3010 transmission electron microscope at an accelerating voltage of 300kV.

A simulation model for the vacancy depletion mechanism was set up on a rigid three-dimensional fcc lattice with 50×50×100 unit cells (total lattice sites: one million) under the periodic boundary condition. As initial simulation microstructures in three regions sitting in sequence from a grain boundary, all the lattice sites were occupied at random by Al and constituent atoms and vacancies with the same composition as that of the experimentally investigated alloy. These microstructures correspond to those under the solution-treatment condition and subsequently experienced the actual procedure of heat treatments; i.e. quenching to 273K and aging at 433K, resulting in the different distributions of solute-rich clusters in the three regions. Note that in this simulation model vacancy concentrations were changed depending on the distance from the grain boundary in order to take into account the effects of vacancy sink during quenching. The actual procedure of diffusion of atoms and the derivation method of simulation parameters are described in [4-6].

3. Results and Discussion

3.1 Formation Mechanisms of PFZ

Figure 1(a) and 2(a) illustrate TEM micrographs showing the existence of PFZ along grain boundaries of the Al-Cu and Al-Zn-Mg alloys aged at 433K for about 10ks. The transgranular precipitates have been identified to be GP(1) zones for the Al-Cu alloy and η' for the Al-Zn-Mg alloy, respectively. The corresponding EDX profiles across the grain boundaries revealed that solute concentrations are highly maintained even within PFZ in the under-aged condition. Similar supersaturation of solute atoms has been reported for Al-Zn-Mg [7, 8] and Al-Mg [9] alloys, suggesting that the vacancy depletion mechanism mainly works for the formation of PFZ in the earlier stage of aging. It should be also noted from Figure 1(a) and Figure 2(a) that the number density of precipitates gradually decreases towards grain boundaries with a slightly larger size than that within grains.

On the other hand, totally different trends were observed in the over-aged condition although the precipitates inside grains changed to GP(2) zones (and scarcely θ'-Al_2Cu) and η-$MgZn_2$ (Figure 1(b) and Figure 2(b)). The continuous decrease in solute concentrations was observed not only within PFZ but also even outside PFZ, leading to a proposal that there is a newly defined region of 'transition area' between PFZ and grain [10, 11]. Such depletion of solute atoms is obviously attributed to the growth of grain boundary precipitates, indicating that the solute depletion mechanism controls the PFZ formation in the later stage of aging.

This change of formation mechanisms well corresponds to the variation in width of PFZ during aging. It is obvious from Figure 3 that the average width of PFZ in the Al-Cu and Al-Zn-Mg alloys monotonously decreases in the earlier stage of aging and then gradually increases with aging time. Similar results have been observed for Al-6Zn-1.2Mg (in mass%) alloys aged at 413-433K [12]. From the experimental results, therefore, PFZ was found to be formed by the combination of the two mechanisms, regardless of alloy system, if the alloys are quickly quenched and aged at moderate temperatures. Note that high aging temperatures and prolonged aging times only increase the width of PFZ due to the formation of a larger amount of grain boundary precipitates [13, 14].

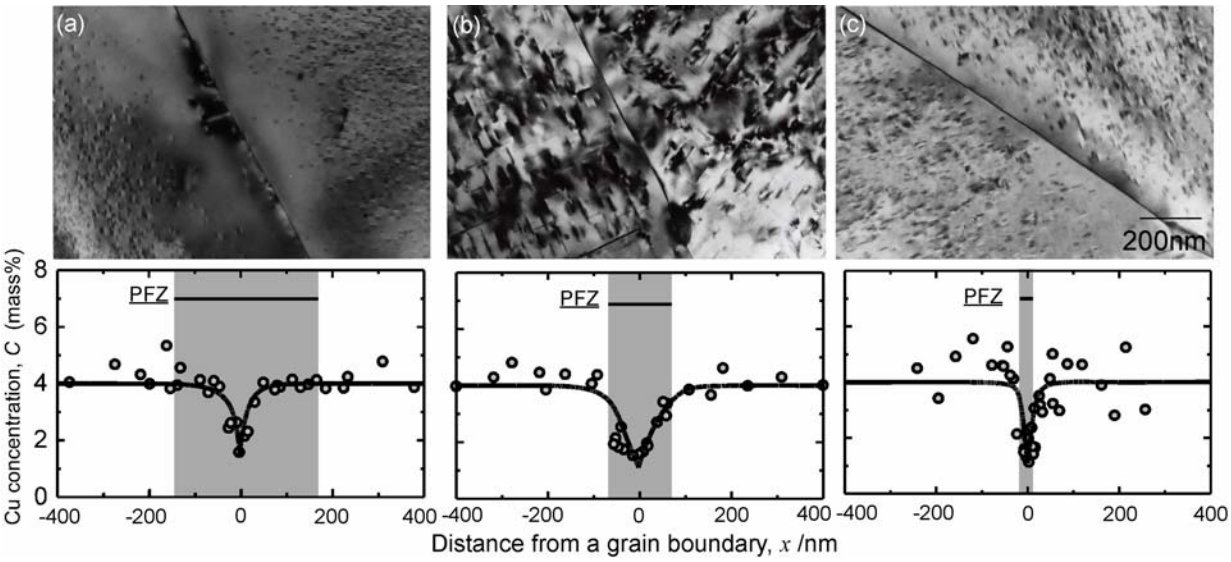

Figure 1: TEM micrographs and EDX analysis results around grain boundaries of the Al-Cu alloys aged at 433K for 7.2ks (a) and 90ks (b). The same set is illustrated in (c) for the Sn-added Al-Cu alloy aged at 433K for 7.2ks.

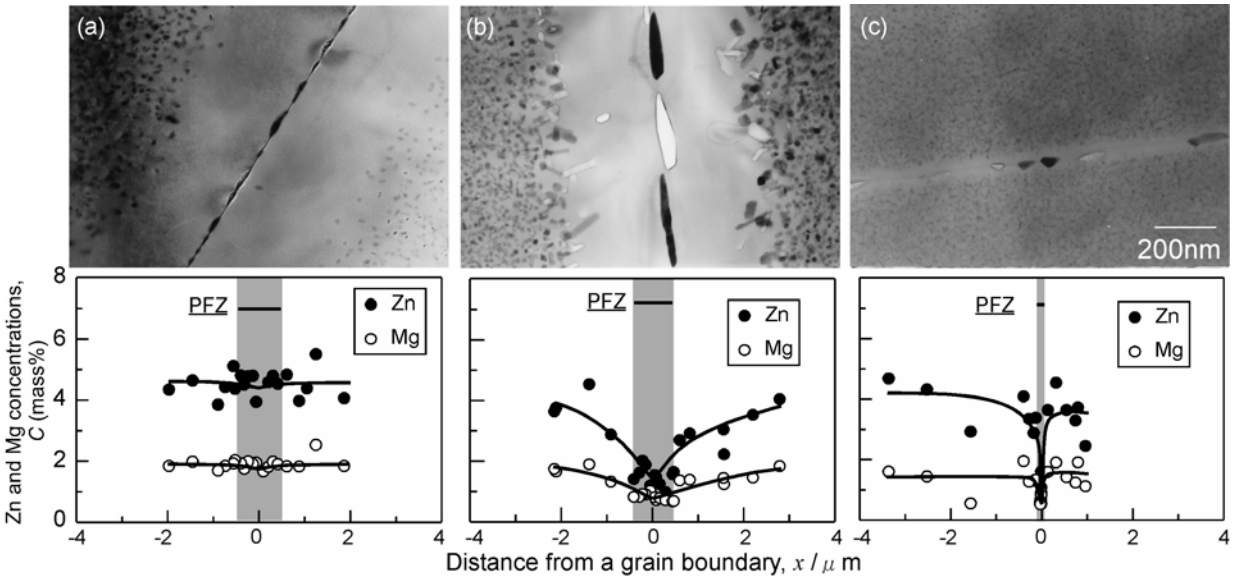

Figure 2: TEM micrographs and EDX analysis results around grain boundaries of the Al-Zn-Mg alloys aged at 433K for 10.8ks (a) and 259.2ks (b). The same set is illustrated in (c) for the Ag-added Al-Zn-Mg alloy aged at 433K for 10.8ks.

3.2 Simulation results

Figure 4 illustrates the simulated evolution of Cu clusters in the three regions sitting in sequence from a grain boundary of the Al-1.74mol%Cu (i.e. 4.0mass%Cu) alloy aged at

473K. Remember that the experimentally investigated Al-Cu alloy exhibited more remarkable decrease in width of PFZ than the Al-Zn-Mg alloy (Figure 3), resulting in a selection as a better example of the vacancy depletion mechanism. As a result of quenching procedure, the different configurations of Cu atoms were found to be obtained in the as-quenched (A.Q.) condition depending on the distance from the grain boundary; i.e. nearly supersaturated solid solution of Cu in region A as opposed to the accelerated formation of fine Cu clusters in region C. This difference of microstructures before aging was produced by a lower vacancy concentration in region A, where the effects of vacancy sink were taken into account, and by a larger number of 'excess vacancies' in region C with the same concentration as the equilibrium one at 793K.

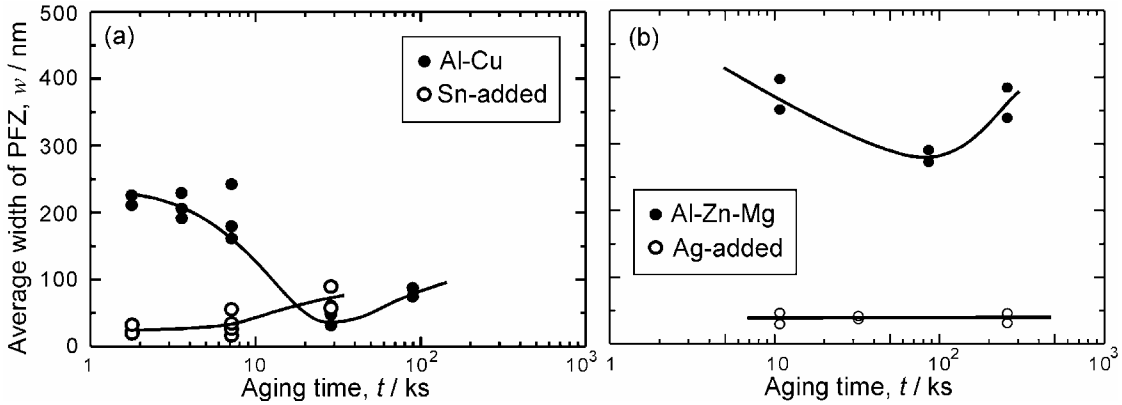

Figure 3: Changes in average width of PFZ in the Al-Cu(-Sn) and Al-Zn-Mg(-Ag) alloys aged at 433K.

On the subsequent aging procedure, furthermore, quite interesting microstructural change was observed in our simulation model in good agreement with the experimental results; i.e. the continuous decrease in width of PFZ and the sparse formation of larger precipitates at the PFZ boundaries (Figs.1-3). It is clearly seen in Figure 4 that regions A and B were initially within PFZ at 1×10^8MCS, but after prolonged simulation steps slightly larger Cu clusters formed in the two regions with a lower number density than that in region C. This simulation result strongly indicates that Cu clusters with larger sizes than a critical one could not dissolve easily during aging treatment, resulting in the denser formation of smaller clusters in region C. This is quantitatively estimated in Figure 5, where the aggregate consisting of more than 40 Cu atoms was counted as a Cu cluster because disk-like GP zones in Al-Cu alloys could be visible by TEM when over about 2nm in diameter. Note that the following equation was utilized to correlate the number of Cu atoms within a spherical cluster formed in our simulation model, n, to the diameter of plate-like GP zones in Al-Cu alloys, D;

$$D = (2n / \pi)^{1/2} a_{Al} , \qquad (1)$$

where a_{Al} is the lattice constant of pure Al (i.e. 0.404nm). It is obvious from Figure 5 that the suppressed formation of Cu clusters in the A.Q. condition is significantly attributed to the sparse distribution of precipitates in region A after prolonged aging times. Therefore, the utilized simulation model seems to reproduce well the formation of PFZ based on the vacancy depletion mechanism. Note that only modelling based on the solute depletion mechanism has been developed with a suggestion that the vacancy also plays an important role in giving rise to PFZ [15, 16].

3.3 Effects of microalloying elements

The effects of microalloying elements on the formation of PFZ are remarkably observed in Figure 1(c) and Figure 2(c). It is evident that the addition of Sn to Al-Cu alloys and the

addition of Ag to Al-Zn-Mg alloys reduced the width of PFZ with highly maintained solute concentrations up to closer regions to grain boundaries. The average widths of PFZ in the investigated alloys are quantitatively compared in Figure 3, where the microalloying additions were confirmed to modify significantly the microstructure of the vicinity of grain boundaries, suggesting that the elongation could be improved without decreasing strengths [11]. Note that similar modification of PFZ has been observed in Sc-added Al-Li [13] and (Ag or Cu)-added Al-Mg-Si [17] alloys.

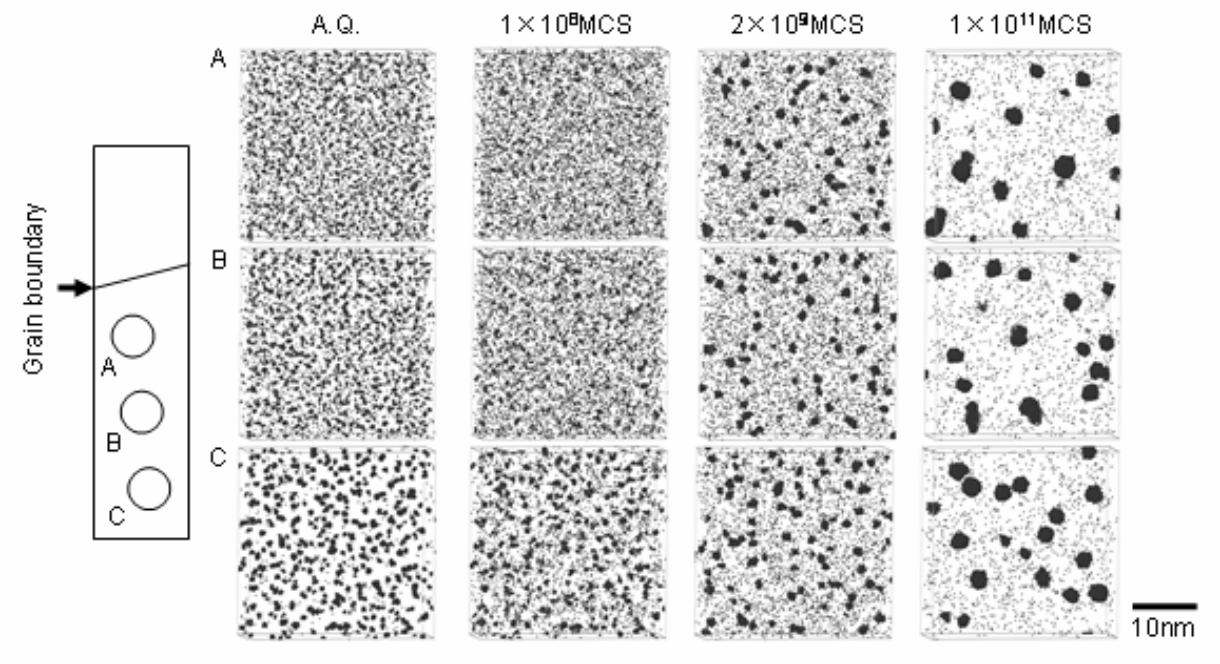

Figure 4: Simulated evolution of Cu clusters in the three regions sitting in sequence from a grain boundary of the Al-1.74mol%Cu (i.e. 4.0mass%Cu) alloy aged at 473K. Only Cu atoms are depicted by black dots for better visibility.

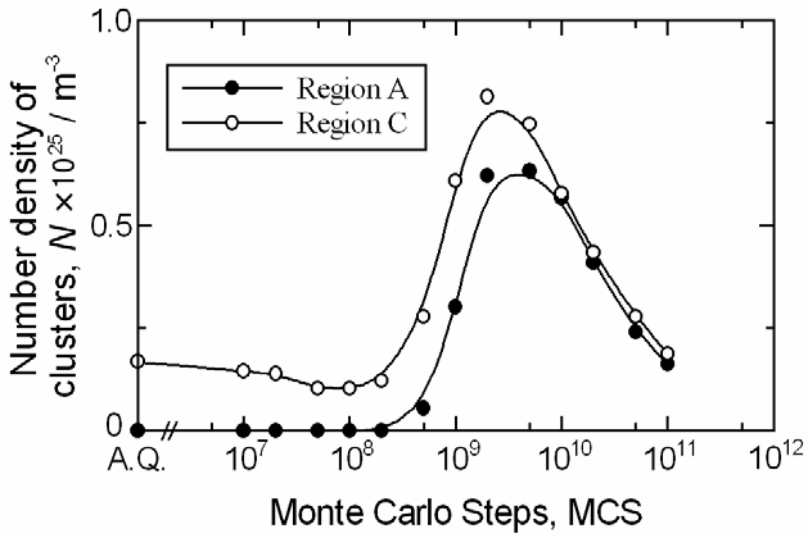

Figure 5: Temporal changes of the number density of Cu clusters in the two regions A and C of Figure 4 for the Al-1.74mol%Cu alloy simulated at 473K.

To understand the reason why the width of PFZ decreases in the Sn-added Al-Cu and Ag-added Al-Zn-Mg alloys, our proposed ordering parameters between elements, $V_{i\text{-}j}$ [4-6] , were utilized as a measure of how much an *i-j* pair interacts in Al. Note that, as a rule of thumb, a smaller value of $V_{i\text{-}j}$ corresponds to the stronger interaction of *i-j*, resulting in the

formation of co-clusters consisting of those elements. In the Sn-added Al-Cu alloy, for example, a smaller value of $V_{Sn\text{-}vacancy}$ (-9.5kJ/mol) than $V_{Cu\text{-}vacancy}$ (0.86kJ/mol) suggests that Sn atoms preferentially trap vacancies, resulting in not only the prevention of vacancy sink during quenching but also the less different distribution of Cu atoms regardless of the distance from grain boundaries. Remember that the similar microstructures in the A.Q. condition will produce the similar distributions of Cu clusters at prolonged simulation steps. In the Ag-added Al-Zn-Mg alloy, in contrast, smaller values of $V_{Ag\text{-}Zn}$ (1.6kJ/mol) and $V_{Ag\text{-}Mg}$ (1.8kJ/mol) will result in the prevention of solute depletion of Zn and Mg due to the formation of Zn-Mg-Ag clusters. In fact, Meloney *et al.* [18] reported by using three-dimensional atom probe (3DAP) that Ag promotes co-clustering of Ag and Zn atoms, followed by Zn-Mg-Ag rich clusters which accelerate the nucleation of the intermediate η' precipitates. Therefore, the systematic prediction of the atomistic behavior of microalloying elements based on our uniquely estimated $V_{i\text{-}j}$ seems to be sufficiently useful to control the microstructure of the vicinity of grain boundaries. Note that our previous papers [5, 6, 19] summarize the actually estimated $V_{i\text{-}j}$ for a variety of *i-j* pairs in the form of 'ordering parameter map', allowing effectively behaving microalloying elements in Al alloys to be proposed.

4. Conclusions

In this work, a computer simulation model was established to mimic the vacancy depletion mechanism, which was experimentally clarified as the predominant mechanism for the PFZ formation of Al-Cu(-Sn) and Al-Zn-Mg(-Ag) alloys aged at moderate temperatures for shorter times. This simulation model well reproduced the experimental results; i.e. the continuous decrease in width of PFZ and the sparse formation of larger precipitates at the PFZ boundaries. It was firstly revealed in this work that the different microstructures produced by quenching procedure are significantly attributed to the resultant distribution of precipitates after prolonged aging times. Such atomistic behaviors of vacancy, constituent and microalloying atoms were well explained in terms of our estimated ordering parameters.

Reference

[1] P.C. Varley, M.K.B. Day and A. Sendork, J.Inst.Metals, 86, 337-351, 1957-58.
[2] J.D. Embury and R.B. Nicholson, Acta Met., 13, 403-417, 1965.
[3] G.W. Lorimer and R.B. Nicholson, Acta Met., 14, 1009-1013, 1966.
[4] S. Hirosawa, T. Sato, J. Yokota and A. Kamio, Mater.Trans.JIM, 39, 139-146, 1998.
[5] S. Hirosawa, T. Sato, A. Kamio and H.M. Flower, Acta mater., 48, 1797-1806, 2000.
[6] S. Hirosawa and T.Sato, Modelling Simul.Mater.Sci.Eng., 9, 129-141, 2001.
[7] P. Doig, J.W. Edington and G. Hibbert, Phil. Mag., 28, 971-981, 1973.
[8] M. Raghavan, Metall.Trans., 11A, 993-999, 1980.
[9] H. Yukawa, Y. Murata, M. Morinaga, Y.Takahashi and H. Yoshida, Acta meter., 43, 681-688, 1995.
[10] T. Ogura, S. Hirosawa and T. Sato, Sci. Tech. Adv. Mater., 5, in print, 2004.
[11] T. Ogura, S. Hirosawa and T. Sato, Proc. 9th Int. Conf. on Aluminum Alloys, 2004.
[12] M. Abe, K. Asano and A. Fujiwara, J.Japan Inst.Metals, 36, 597-604, 1972.
[13] C.H. Jon, K. Yamada and Y. Miura, Materials Science Forum, 331-337, 1037-1042, 2000.
[14] A.J. Cornish and M.K.B. Day, J.Inst.Metals, 97, 44-52, 1969.
[15] H. Jiang and R.G. Faulkner, Acta mater., 44, 1857-1864, 1996.
[16] H. Jiang and R.G. Faulkner, Acta mater., 44, 1865-1871, 1996.
[17] K. Matsuda, K. Kido, T. Kawabata, Y. Uetani and S. Ikeno, J.Japan Inst. Light Metals, 53, 528-533, 2003.
[18] S.K. Maloney, K. Hono, I.J. Polmear and S.P. Ringer, Micron, 32, 741-747, 2001.
[19] T. Sato, S. Hirosawa, K. Hirose and T. Maeguchi, Metall.Mater.Trans. 34A, 2745-2755, 2003.