High Resolution Lattice Images of Ordered Structures in Al–Li Alloys

By Tatsuo Sato*, Nobuo Tanaka** and Tsuneo Takahashi***

Ordered structures formed in Al–Li alloys during the decomposition were investigated by means of high resolution electron microscopy. Image calculations were also performed to interpret the obtained images.

In the initial stage of decomposition (323 K, 86.4 ks), extremely fine domains which had already an ordered structure of the L12-type were formed densely. The domains were separated by the vague and complicated boundary areas with incompletely ordered structure. In the proceeded stage of decomposition (473 K, 86.4 ks), spherical δ' particles were formed and the atomic arrangement of a L12-type ordered structure was clearly observed within δ' particles. The δ'/matrix interfaces were very clear and have a step-like morphology. It appeared that small segments with locally ordered structure were formed in the matrix during the electron microscope observation. Image calculations for the Al-Li alloys proved that atom sites were revealed as bright contrast dots under the proper defocus conditions, and that the image contrast was not changed drastically with the total specimen thickness at least up to 40 nm and depth of the ordered region. This is useful in discussing the formation mechanism and spatial distribution of ordered domains in this alloy by using high resolution electron micrographs.

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I. Introduction

Aluminum-lithium alloys have been extensively investigated in recent years especially for the aerospace applications, because they offer interesting combination of high specific mechanical strength and modulus(1)–(3).

The metastable δ' phase is known to be formed homogeneously before the formation of the stable δ phase with a B32-type (NaTl) structure. Silcock(4) studied the crystal structure by the X-ray diffraction technique and reported that the δ' phase had a L12-type (Cu3Au) ordered structure having cube/cube orientation relationship between the matrix. In Al-Li alloys, extremely high mechanical strength can be achieved by the formation of the δ' phase. It has been also reported that the δ' phase shows a positive temperature dependence in the mechanical strength as is well known in the γ' phase of a Ni3Al compound due to the L12-type ordered structure(5)–(6). This can be explained as a result of the strong interaction between the δ' phase and superlattice dislocations(5)–(7).

The decomposition process in Al–Li alloys has already been studied by many workers and it is believed that the decomposition occurs in a two-stage process; i.e. α→δ' (Al3Li)→δ(Al Li). On the contrary, however, Ceresara et al.(8), Nozato and Nakai(9), and Takahashi and Sato(10) suggested the existence of the structural changes in the initial stage such as the clustering and ordering. Especially, Takahashi and Sato found the precursory structures of the δ' phase by the detailed calorimetric study and reported that the decomposition in Al–Li alloys occurs in a five-stage process. Spooner et al.(11) also suggested through the small-angle scattering studies the existence of the spinodal decomposition in the initial stage.

The structural changes during the phase decomposition have not been fully clarified as was mentioned above. In the present work, a
high resolution electron microscopy technique has been applied to the direct observation of the atomic arrangements to elucidate the alloy structures and ordering process. Furthermore, image calculations were performed to know the features of the high resolution images for the ordered structures in Al-Li alloys.

II. Experimental

Aluminum alloys containing 7.9 and 9.7 at%Li were prepared from 99.99%Al and 99.9%Li under argon gas. The alloys were homogenized at 773 K for 172.8 ks and were hot- and cold-rolled to 0.23 mm thick sheets, which were used for the transmission electron microscopy. All of the specimens were solution treated at 793 K for 1.8 ks in the salt bath, and followed by ice water quenching. The aging treatments were carried out in the oil bath. The loss of Li in the specimen surface during the heat treatments was examined beforehand, and we confirmed that in the present condition the center regions of the specimens were not affected by the Li loss and were suitable for our experiment.

The foils for the electron microscopy were prepared by the ordinary electrolytic jet polishing technique (in methanol : nitric acid = 4:1, at 253 K, 18 V), and were observed by using a JEM 200CX transmission electron microscope with a pole piece and a top entry goniometer for the ultra high resolution operated at 200 kV. The spherical aberration coefficient of the objective lens Cs is equal to 1.2 mm. High resolution images of the alloy structures were taken by the many-beam technique of the axial illumination. Furthermore, calculations of the images were performed by using the multi-slice method to know the imaging conditions and to analyze the obtained images.

III. Results and Discussion

1. Structures formed in the initial stage

In the specific heat vs temperature curves for Al-Li binary alloys aged at low temperatures, two distinct peaks of heat absorption were observed, which appeared at a temperature range between 310 and 400 K and were different from a peak due to the dissolution of δ' precipitates. These peaks are considered to suggest the existence of the precursory structure of the δ' phase in the initial stage of decomposition. Taking into consideration the calorimetric results, we tried to observe directly the initial structures in the Al-Li alloy at a low temperature aging. Figure 1 shows a dark field image of an Al-9.7 at%Li alloy aged at 323 K for 86.4 ks taken with a 100 superlattice reflection and the corresponding diffraction pattern. In the dark field image extremely fine regions with bright contrast were observed distributing homogeneously over the matrix. The diffraction pattern having superlattice reflections is typical of the L12-type ordered structure, and consequently the bright regions in the dark field image are found to be ordered
regions with a L12-type structure. Furthermore, a high resolution image of the structure was taken by using superlattice reflections to know the detail configuration of atoms in the ordered regions as shown in Fig. 2. The image in Fig. 2 was taken using many beams of 000 and eight superlattice reflections around the 000 beam. Bright dots with ~0.4 nm spacing are observed aligned periodically to [100] and [010] directions. This arrangement of bright dots corresponds to the periodicity of an atomic arrangement of the {100} plane in a L12-type ordered structure, and in the present imaging condition bright dots are found to represent the Li atom sites by the image calculations. Each of the ordered regions is separated by the boundary areas in which an ordered structure is formed incompletely, and constructs a domain structure. These domains are extremely small and are distributed homogeneously in the disordered fcc matrix with high number density throughout the alloy. Each domain is about 2-4 nm in size, and the interface or boundary of domains has a characteristic of being so vague and complicated in morphology. These interfaces are quite different from the typical δ'/matrix interfaces, which are very sharp and clear as is described later in Section III.2. In the Al-Li alloy, a rapid breakdown of the supersaturated solid solution is known to occur during the quench and δ' is present even in the as-quenched specimen. Consequently, in the present specimen it is difficult to distinguish the precur- sory structure from an ordered structure of a L12-type. Therefore the actual structures in the initial stage which are suggested by the endotherm peaks in the specific heat vs temperature curves are not clarified here. However, it is possible to presume that the endotherm peaks originate from the dissolution of such domain structures shown in Fig. 2, since the domain structures are considered to have less thermal stability than the δ' phase due to their vague and complicated interfaces. And the degree of order might be also lower in the domains than in the δ' phase if the fluctuation of composition could exist locally in the domains.

![Fig. 2 High resolution image of the structure shown in Fig. 1. Bright dots are aligned periodically to [100] and [010] directions. The image was taken with direct beam and superlattice reflections.](image-url)
These points are required to be investigated further to clarify the precursory structures in an Al–Li alloy.

2. δ' precipitates

In an Al–Li alloy, the δ' phase is known to be the most important precipitate to increase the mechanical strength of the alloy. The δ' precipitate has an ordered structure of a L12-type possessing a cube/cube orientation relationship with the matrix, the stoichiometric composition being Al3Li. The remarkable increase of the mechanical strength is attributable to the strong interaction between the δ' precipitate and superlattice dislocations in the matrix(6)(7). Figure 3 shows a dark field image taken with a 100 superlattice reflection and corresponding diffraction pattern of an Al–7.9 at%Li alloy aged at 473 K for 86.4 ks. Spherical particles with the average size of ~30 nm are observed distributing homogeneously in the matrix. Some δ' particles are observed as if they are in contact with each other in Fig. 3, however, these particles are probably separated toward the z direction (thickness direction) of the specimen. In the thicker regions of a specimen, much overlap of the images of precipitates will be observed. The δ' precipitate has a spherical morphology and has a very clear interface, which is quite different from that of the domain structures in Fig. 1 and Fig. 2. The diffraction pattern gives a typical one of the L12-type ordered structure. Figure 4 is a typical example of the high resolution many-beam images of the δ' precipitates and the matrix. In this image there are dots of three different brightness. The brightest dots with ~0.4 nm spacing correspond to the atom sites of Al and the bright dots surrounded by 4 brightest dots are Li atom sites in a δ' particle respectively, which will be shown by the image calculation in §3. The periodicity of superlattice planes of a L12-type structure is twice that of the fundamental fcc lattice. The lattice image in Fig. 4 reveals directly the atomic arrangements in a spherical δ' particle and the matrix. Since atomic layers in a δ' particle are observed connecting fully to these in the matrix, the δ' phase is considered to be coherent with the matrix according to this image. However, our calorimetric results(10) showed that the heat absorption due to the dissolution of δ' precipitates appeared in two splitted peaks. The splitted peaks must suggest the existence of the slight difference in the structure of the δ' precipitates. One possible difference is the coherency between δ' and the matrix, that is, a δ' particle must lose the coherency gradually by producing interfacial dislocations and be semi-coherent in the later stage. Unfortunately, the electron microscopic image shows the projected atomic arrangements of a δ' precipitate, so it is rather difficult to recognize the interfacial dislocations. The δ'/matrix interface is occasionally found to have a step-like morphology or a ledge structure locally. Further observations are required to know the morphological characteristic of the interface.

It is very interesting that small segments with locally ordered structure are recognized to

Fig. 3  Dark field image of δ' precipitates and corresponding diffraction pattern for Al–7.9 at%Li alloy aged at 473 K for 86.4 ks.
coexist with large $\delta'$ precipitates in the matrix as are indicated by arrows in Fig. 4. It seems to be improbable that such small segments and $\delta'$ precipitates are formed at the same temperature and coexist together, because the size of them are quite different, therefore it could be considered that small segments are formed during the observation by the effect of irradiation in the electron microscope. In fact much amount of segments can be observed in the specimen exposed to the electron beam for a long time in the electron microscope. These segments are similar in morphology to the domain structures shown in Fig. 2 in the respect of the vague interfaces, although the number density of these segments is smaller than that of the domain structures. The thermal stability of these small segments is also considered to be lower than that of $\delta'$ precipitates, and consequently these segments with locally ordered structure are presumably related to the precursory structure of the $\delta'$ phase.

3. Calculations of high resolution images

Calculations of high resolution images were carried out to interpret the obtained images and also to compare them with the real structures in the alloy. First, the structure model was assumed as shown in Fig. 5 for the calculation of images. Figure 5(a) shows the projected atomic arrangement in a $L1_2$-type ordered structure toward [001] direction, where black
and white circles indicate Al and Li atom sites respectively and the lattice parameter is assumed to be 0.4 nm. Figure 5(b) shows a structure model of the L12 ordered region which is composed of four stackings of L12 unit cell and two disordered matrices above and below. This model represents a L12-type region floating in the disordered matrix. In the calculation, the size of the L12 ordered region was fixed to be four times of the unit cell for simplification, and the total specimen thickness and the depth of the L12 ordered region were changed. Calculations were done by the multi-slice method, and the thickness of one slice was taken as the size of a unit cell (that is 0.4 nm).

Figure 6 shows the dependence of the image contrast upon the total specimen thickness ($t$) and depth of a L12 ordered region ($z$) which was calculated with no aberrations (aberration-free images). Figure 6(a) and (b) are for the regions of a L12 ordered structure and disordered matrix respectively. In Fig. 6(a), images corresponding directly to the atomic arrangements in the alloy are obtained for all of the total specimen thickness up to 96 slice (38.4 nm) and depth except the case of the total thickness being 76 slice (30.4 nm), which is nearly equal to the extinction distance. Moreover, in the present thickness conditions, the reversed contrast does not appear, and in the case of total specimen thickness $t=92$ (36.8 nm) and 96 slice (38.4 nm), it is possible to differentiate Al and Li atoms due to the difference of the contrast between them. On the other hand, in the disordered matrix, for all of the total specimen thickness at least up to 92 slice (36.8 nm) the atom sites produce bright contrast except the total thickness $t=76$ slice (30.4 nm), as shown in Fig. 6(b). At the total thickness of 76 slice (30.4 nm), a poor image is obtained because of the very small dynamical amplitude. From these results, it is clarified that atomic arrangements corresponding directly to the L12 ordered structure and the disordered matrix can be obtained in the Al-Li alloy. Furthermore, calculations with the spherical and chromatical aberrations were also performed. Examples of the calculated images are shown in Fig. 7, which agree well with the obtained images experimentally, where total specimen thickness $t=96$ slice (38.4 nm) and depth of ordered region $z=28$ slice (11.2 nm) are assumed. For the condition of defocus $\Delta f=50$ and 65 nm, Li atom site is bright, on the contrary for the defocus $\Delta f=110$ and 125 nm Al atom site is bright. In Fig. 4, all of the bright dots in the disordered matrix correspond to the atom sites, and the brightest dots in the $\delta'$ particle correspond to Al atom sites, the bright dots surrounded by four brightest
dots are Li atom sites, respectively. These calculated images coincide well with the experimental ones in Fig. 4 over the through-focus series.

To summarize, it can be said that the atomic arrangements in the $\delta'$ precipitates and matrix can be observed directly by the high resolution images, and that the contrast of images does not change drastically for the total specimen thickness at least up to ~40 nm and depth of the ordered region investigated in the optimum defocus conditions. In the calculation the size of an ordered region was fixed to be four times of the unit cell. This is, however, reasonable because both of the calculated and experimentally obtained images do not change drastically
with the increase in the size of an ordered region.

In the present work, it was confirmed that the contrast of atom sites does not become reversed depending on the total specimen thickness at least up to ~40 nm and the depth of the ordered regions. This is quite favorable to discuss the lattice phase relation between two neighbouring domains or $\delta'$ particles in this alloy. The lattice phase relation here means whether the lattice layers in two neighbouring domains with $L1_2$-type ordered structure are located in the same phase each other (in-phase relation) or are located in slipping off by half of the periodicity (out-of-phase or anti-phase relation). Some domains are distributed being in-phase and others out-of-phase in Fig. 2. Further quantitative investigation of the lattice phase relation will lead to the confirmation of the nucleation and growth mechanism of $L1_2$-type ordered domains or $\delta'$ particles in Al-Li alloys.

IV. Conclusions

Ordered structures formed during the decomposition in Al–Li alloys were investigated by the high resolution electron microscopic technique including the image calculations. The following results were obtained.

1) In the initial stage of decomposition (323 K, 86.4 ks) extremely fine domains with an ordered structure are formed densely. The boundary of domains is not so clear and complicated in the morphology and is different from that of the $\delta'$ particles.

2) Spherical particles of the $\delta'$ phase are formed in the proceeded stage of decomposition (473 K, 86.4 ks), and the atomic arrangement of a $L1_2$-type ordered structure was clearly observed within $\delta'$ particles. The interface of the $\delta'/\text{matrix}$ is very clear and has a step-like morphology. Small segments with locally ordered structure are found to coexist with $\delta'$ precipitates. These segments are probably formed by the effect of irradiation during the electron microscope observation.

3) Image calculations by the multi-slice method proved that atom sites were revealed as bright contrast dots under the proper defocus conditions and the contrast did not change to the reversed one for the specimen thickness at least up to ~40 nm and the depth of the ordered domains investigated in this work. Through the comparison of the obtained images with calculated ones, the atomic arrangements of the ordered structures were confirmed directly in the controlled specimens.
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