Electron Microscope Observation of Friauf-Laves Phase Mg(Cu_{1-x}Al_x)₂ with $x=0.465^*$

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Electron microscope observation was made on a Mg-base Friauf-Laves phase Mg(Cu_{1-x}Al_x)₂ with $x=0.465$. As-cast specimens exhibited mainly a 4-layer type structure, and annealed ones a 9-layer type. In addition, small regions with other layer types such as 2-, 6-, 10- and 16-layer types were also observed. Two new stacking variants having 6- and 16-layer type structures were analysed by comparing diffracted intensities with calculated ones. The 6-layer type structure is expressed as ABC'B'AB' in terms of the six compound layers of the Friauf-Laves phase. The space group is P6m2 with a unit cell of dimensions $a=5.10$ and $c=25.0$ Å. The 16-layer type structure is expressed as ABC'BCA'CA'B'A'CA'CB'CB' having a space group P6₃/mmc with lattice constants $a=5.10$ and $c=66.7$ Å.

The lattice images of the 2-, 4-, 6-, 9-, 10- and 16-layer type structure were obtained by using a direct beam and several reflected beams. A remarkable correspondence was found between the lattice image and the layer sequence.

(Received May 29, 1976)

I. Introduction

Crystal structures of the Mg-base pseudo-binary Friauf-Laves phase have been extensively investigated in our laboratory, and several stacking variants have been found besides fundamental C14(MgZn₂-type), C15 (MgCu₂-type) and C36(MgNi₂-type) structures. The structural changes as a function of the electron concentration have been well established for the systems Mg(Cu_{1-x}Ni_x)₂, Mg(Cu_{1-x}Zn_x)₂, Mg(Ni_{1-x}Zn_x)₂ and Mg(Zn_{1-x}Ag_x)₂^{(1)~(4)}. However, the changes are not well understood for the system Mg(Cu_{1-x}Al_x)₂^{(5)~(7)} because of the complexity of the phase diagram.

The structures of the Friauf-Laves phase and their stacking variants can be described in terms of the stacking sequence of six compound layers A, A', B, B', C and C', each of which is composed of a Kagomé net and three triangular nets. Two compound layers A and A' are shown in Fig. 1 as an illustration. If A and A'

Fig. 1 Two compound layers A and A' of the Friauf-Laves phase. The parameter z is taken as a fraction of the distance between two Kagomé nets.

are shifted by $1/3$ or $2/3$ to the $[\bar{1}10]$ direction of the hexagonal cell, one obtains B and B', or C and C' layers, respectively. The layer stacking conforms to the spatial requirements of large Mg atoms, that is, each layer can only be followed by the two particular layers. The possible ways of stacking the layers are shown in Table 1.

The stacking variants which have been found up to the present in Mg-base pseudo-binary systems are listed as follows:

* This paper was presented at the 1975 Autumn Meeting of the Japan Institute of Metals, Hokkaido, Japan.

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Table 1 Possible ways of layer stacking.

Layer type	Stacking order
2-layer(C14-MgZn ₂)	AB'
3-layer(C15-MgCu ₂)	ABC
4-layer(C36-MgNi ₂)	AB'A'C
6-layer	ABCA'C'B'
8-layer	AB'AB'A'CA'C
9-layer	AB'ABC'BCA'C
10-layer	ABC'BCA'C'BC'B'
14-layer	AB'ABC'BC'B'AB' A'CA'C ⁽⁸⁾

Electron microscope study on the Friauf-Laves phases was carried out by Allen *et al.*⁽⁹⁾ for the first time, and they observed lattice images and the crystal defects in TiCr₂ and TiCo₂. Three stacking variants (the 4-, 6- and 12-layer types) were found in these alloys besides the 2- and 3-layer types.

In the present study electron microscope observation has been performed on a system of Mg(Cu_{1-x}Al_x)₂. The purpose of the study is to obtain lattice images of various stacking variants and to establish the relation between the lattice image and the stacking sequence. In the course of the investigation two new stacking variants were found, whose structures were determined by the electron diffraction method.

II. Experimental Procedure

The alloys were prepared by melting together pieces of pure Mg, Cu-Al mother alloy, and a necessary amount of Cu in an argon-filled induction furnace. All metals used were the grade of 99.9%. The alloy specimens examined in the present experiment have the prepared composition of Mg(Cu_{1-x}Al_x)₂ with $x=0.465$.

The melt was vigorously stirred and then cast into a cylindrical graphite mold. Ingots were sliced to 0.2 mm thickness. Some of these discs were annealed at 650°C for 60 hr. The discs were then electrolytically polished in a mixed solution of HNO₃ and CH₃OH to obtain thin foils suitable for the electron microscope observation. They were examined under a JEM 200A electron microscope operated at 200 kV. A double tilting specimen holder was installed in the microscope. The specimen was oriented so that its *a* axis of the hexagonal cell lay parallel to the incident beam. The electron diffraction pattern thus obtained shows the *0kl* reciprocal net, from which one can easily identify the layer type of the specimen. In this orientation the lattice images were recorded at a magnification of 56000 after inserting an objective aperture which restricted the number of contributing diffracted beams.

Intensities of the reflections were measured by a microphotometer, and they were compared with the calculated intensities for possible structure models.

III. Experimental Results

1. General features

Most of the electron diffraction patterns of as-cast specimens showed the 4-layer type, but the 2-layer and 9-layer types were sometimes found. The lattice images of the specimens exhibited heavily faulted areas, which contained many stacking faults, grain boundaries and

Photo. 1 Lattice image of the heavily faulted area. The incidence of the electron beam is parallel to the *a* axis of the hexagonal lattice. Regions labeled A, B and C are explained in the text.

Photo. 2 Lattice image and diffraction pattern of the 9-layer type structure.

Photo. 3 Lattice image and diffraction pattern of the 10-layer type structure.

small regions with other types of structure. An example of a heavily faulted area is shown in Photo. 1. The lattice image was obtained by using a direct beam and several reflected beams. The region labeled A in Photo. 1 shows the 4-layer type, the region B the 9-layer type, and the region C other more complex types.

In annealed specimens on the other hand, the 9-layer type was mainly observed but the 10-layer type was also found occasionally. The lattice images of the 9-layer and 10-layer types are shown in Photos. 2 and 3 with their diffraction patterns. The amount of faults observed in these photographs is far less than that observed in the Photo. 1 of the as-cast specimens. In the course of this observation two new stacking variants of the 6-layer and 16-layer types were found in the annealed specimen. The analysis of these new stacking variants will be described in the next section.

2. New stacking variants

Diffraction patterns and lattice images of the

6-layer and 16-layer types are shown in Photos. 4(a), (b) and 5(a), (b), respectively. The incident

Photo. 4 (a) Diffraction pattern and (b) lattice image of the 6-layer type structure.

Photo. 5 (a) Diffraction pattern and (b) lattice image of the 16-layer type structure.

beam is parallel to the a axis. Possible sequences of the 6-layer type structure are limited only to the following two cases by referring the possible ways of layer stacking (Table 1); (1) ABCA'C'B' and (2) ABC'B'AB'. The crystal structure of the former sequence has already been found in the systems of Mg(Cu_{1-x}Ni_x)₂⁽¹⁾ and Mg(Ni_{1-x}Zn_x)₂⁽²⁾. Structure factors of hkl reflections for these layer types are calculated by the following formula:

$$F_{\text{cal}}(hkl) = \sum_{m=0}^5 V_m \exp(im\varphi),$$

where V_m represents the layer form factor⁽⁶⁾ of the m -th layer and φ the phase shift due to one layer, which is equal to $2\pi l/6$ in this case. The layer form factors of A, A', B, B', C and C' are given by

$$V_A = 2f_a \cos(3/8)\varphi \\ + f_b [(-1)^h + (-1)^k + (-1)^{h-k}] \\ + f_b \varepsilon \exp(i\varphi/2),$$

$$V_{A'} = 2f_a \cos(3/8)\varphi \\ + f_b [(-1)^h + (-1)^k + (-1)^{h-k}] \\ + f_b \varepsilon^* \exp(i\varphi/2),$$

$$V_B = V_A \varepsilon^*, V_{B'} = V_{A'} \varepsilon^*, V_C = V_A \varepsilon, V_{C'} = V_{A'} \varepsilon,$$

where $\varepsilon = \exp\{2\pi i(h-k)/3\}$, and f_a is the atomic scattering amplitude for electrons for Mg and f_b that for the other atoms. The relative intensities for 02l thus obtained are listed in Table 2. Observed intensities were estimated visually and they are listed in the last column of Table 2. Comparing the observed intensities with the calculated ones, it can be easily concluded that the layer sequence of the present 6-layer type is ABC'B'AB'. The lattice parameters are $a=5.10$, $c=25.0$ Å. The space group is P6̄m2 with 12 formula units of Mg(Cu_{1-x}Al_x)₂ in the unit cell. The positional parameters thus obtained are listed in Table 3.

Characteristic features of the diffraction pattern of the 16-layer type (Photo. 5(a)) are as follows: (1) the intensity distribution of 0kl reflections is symmetrical with respect to $l=0$, and (2) reflections such as 0k5, 0k11, 0k21 and 0k27 for $k=1$ and 2 are scarcely recognized. More than six hundred possible stacking models can be constructed according to the stacking principle given in Table 1.

Table 2 Comparison between the observed and calculated intensities for the two possible models of the 6-layer type structure.

h	k	l	Type 1 (ABCA'C'B')	Type 2 (ABC'B'AB')	$I(\text{obs})$
0	2	0	0.0	6.7	weak
0	2	1	13.3	7.6	weak
0	2	2	54.3	10.3	weak
0	2	3	100.0	100.0	strong
0	2	4	92.9	17.7	weak
0	2	5	32.8	18.7	weak
0	2	6	0.0	16.0	weak
0	2	7	19.4	11.1	weak
0	2	8	31.6	6.0	weak
0	2	9	17.2	17.3	strong
0	2	10	4.3	0.8	weak
0	2	11	0.7	0.4	very weak
0	2	12	0.0	0.6	very weak

Table 3 Atomic parameters of the newly found 6-layer type structure having a space group P6̄m2.

Atom	Position	x	y	z
Mg	2(g)	0	0	13/48
Mg	2(g)	0	0	19/48
Mg	2(h)	1/3	2/3	1/16
Mg	2(i)	2/3	1/3	5/48
Mg	2(i)	2/3	1/3	11/48
Mg	2(i)	2/3	1/3	7/16
(Cu, Al)	2(g)	0	0	1/12
(Cu, Al)	2(h)	1/3	2/3	1/4
(Cu, Al)	2(h)	1/3	2/3	5/12
(Cu, Al)	3(j)	5/6	1/6	0
(Cu, Al)	3(k)	1/6	5/6	1/2
(Cu, Al)	6(n)	1/6	5/6	1/6
(Cu, Al)	6(n)	1/2	1/2	1/3

If one excludes the structures which have no mirror symmetry with respect to the c -plane, then 64 possible models are left. The structure factors of 01l and 02l reflections are calculated for these 64 models by the same procedure as used in the case of the 6-layer type. From the inspection of these calculated intensities, it is found that the only one of the 64 models shows the characteristic features just described. The sequence of the 16-layer type structure, therefore, is described as ABC'BCA'CA'CA'C'BC'B'. In order to confirm the structure, the observed structure factors are compared with the calculated ones in Fig. 2. The agreement is fairly good even though the diffracted intensities of electron are affected by the multiple diffrac-

Fig. 2 Observed and calculated structure factors of $0\ 2\ l$ for the 16-layer type structure.

Table 4 Atomic parameters of the 16-layer type structure having a space group $P6_3/mmc$.

Atom	Position	x	y	z
Mg	4(e)	0	0	3/128
Mg	4(e)	0	0	13/128
Mg	4(e)	0	0	19/128
Mg	4(f)	1/3	2/3	29/128
Mg	4(f)	1/3	2/3	69/128
Mg	4(f)	1/3	2/3	75/128
Mg	4(f)	1/3	2/3	85/128
Mg	4(f)	1/3	2/3	91/128
(Cu, Al)	4(e)	0	0	7/32
(Cu, Al)	4(f)	1/3	2/3	1/32
(Cu, Al)	4(f)	1/3	2/3	3/32
(Cu, Al)	4(f)	1/3	2/3	5/32
(Cu, Al)	6(g)	1/2	0	0
(Cu, Al)	6(h)	5/6	2/3	1/4
(Cu, Al)	12(k)	1/2	0	1/8
(Cu, Al)	12(k)	1/6	1/3	1/16
(Cu, Al)	12(k)	1/6	1/3	3/16

tion. Then, it is concluded that the 16-layer type is hexagonal and the space group is $P6_3/mmc$ with 32 formula units of $\text{Mg}(\text{Cu}_{1-x}\text{Al}_x)_2$ in the unit cell of dimensions, $a=5.10$, $c=66.7\text{ \AA}$. The positional parameters in the unit cell are listed up in Table 4.

3. Lattice images

The lattice images of the 2-, 4-, 6-, 9-, 10- and 16-layer types are shown in Photos. 6, 7, 4(b), 2, 3 and 5(b), respectively. The 2- and 4-layer types exhibit the lattice images corresponding to their respective periods in c -direction, while the 6-, 9-, 10- and 16-layer types show characteristic fine structures in the lattice images besides their own periods. A remarkable cor-

Photo. 6 Lattice image and diffraction pattern of the 2-layer type structure.

Photo. 7 Lattice image and diffraction pattern of the 4-layer type structure.

respondence between the fine structure and the layer stacking sequence can be found as follows. A lattice image consists of 'dark fringes' (wide or narrow) and 'bright fringes' (wide or narrow). Let a narrow 'dark fringe' be attributed to the A, B or C layer, and a narrow 'bright fringe' to the A', B' or C' layer. Then a wide fringe, either dark or bright, can be considered as corresponding to two such successive layers. We can then construct a layer sequence from a lattice image with the aid of Table 1 which shows the possible ways of the layer stacking. Schematic illustrations of the lattice images are shown in Figs. 3(a)~(f) for the 2-, 4-, 6-, 9-, 10- and 16-layer types. From the lattice image the layer sequence can be easily constructed by the method just described, which is inserted in the figures. The layer sequence thus obtained is consistent with the sequence determined from the X-ray or electron diffraction method.

Fig. 3 Schematic illustration of the lattice images. The layer sequence attached to each figure is that constructed from the lattice image. (a) 2-layer type, (b) 4-layer type, (c) 6-layer type, (d) 9-layer type, (e) 10-layer type and (f) 16-layer type.

IV. Conclusions and Discussion

The new stacking variants of the 6-layer and 16-layer types were found and their stacking sequences were analysed by the electron diffraction method. The stacking sequences were determined to be $ABC'B'AB'$ and $ABC'BCA'CA'CA'CB'CB'$, their space groups being $P\bar{6}m2$ and $P6_3/mmc$, respectively.

Intensities of the electron diffraction are often affected by multiple diffraction. However, the intensity distributions of the new stacking variants are so characteristic that their stacking sequences can be determined uniquely without any confusion.

The lattice images of the 2-, 4-, 6-, 9-, 10- and 16-layer type structures were obtained. It is found that every lattice images have the characteristic fine structures. The layer sequence of the specimen can be determined from the lattice image, if the 'dark fringe' and 'bright fringe' are assigned to A, B or C and to A', B' or C' (one layer or two successive layers depending on a narrow or wide fringe), respectively. These assignments come from the facts that the Friauf-Laves phase consists of two different kinds of layer, i.e., A, B, C are of one kind and A', B', C' are of another kind, and that the stacking sequence containing three successive layers of one kind has not been found in our experiments except for C15 ($MgCu_2$ -type, ABC) and the another 6-layer type structure ($ABCA'CB'$).

The resolution of the electron microscope available to us is $4.5 \text{ \AA}$ in the best condition. Since a layer thickness of the Friauf-Laves phase is about $4.2 \text{ \AA}$, detailed structure in a single layer has not been resolved.

The 9-layer type was mainly observed in the annealed specimens although in the as-cast specimens the 4-layer type was dominant. Laves and Witte⁽⁵⁾ pointed out that near the composition of the present alloy two modifications are stable: the 4-layer type at higher temperatures and the 2-layer type at lower temperatures. The present observation indicates the phase transformation due to temperature from the 4- to 9-layer type contrary to the work of Laves and Witte. The phase diagram of $MgCu_2$ - $MgAl_2$, therefore, seems more complicated than previously supposed⁽⁵⁾⁽⁷⁾.

A coalescence of the several stacking variants were observed in the photographs of the lattice images. Small regions of the 2-, 6-, 10- and 16-layer types are also found besides main regions of the 4-layer or 9-layer type structures. Several reasons can be considered for such a coalescence. One of main reasons might be the small concentration difference from one place to another in the alloy specimen. A small fluctuation of Al concentration corresponds to a considerable difference in electron concentration (e/a). In the Mg-base Friauf-Laves phases the relation between e/a and stacking variants is already evident⁽²⁾⁽³⁾. Several kinds of stacking variants are successively stable in the narrow range of the neighbourhood of $e/a=2.0$. The con-

Table 5 The stacking order, *ch* order and fraction of *h* sequence of various stacking variants observed in this experiment.

Stacking order		<i>ch</i> order	Fraction of <i>h</i> sequence
AB'A'C	(4-layer)	<i>ch</i>	0.5
ABC'BCA'C'BC'B'	(10-layer)	<i>chhch</i>	0.6
ABC'BCA'CAB'A' CA'C'BC'B'	(16-layer)	<i>chhchhch</i>	0.625
ABC'B'AB'	(6-layer)	<i>chchhh</i>	0.667
ABC'BCA'CAB'	(9-layer)	<i>chh</i>	0.667
AB'	(2-layer)	<i>h</i>	1.00

centration of the present alloy lies in this narrow range. Several other causes may be considered as follows: Metastable phases grow during solidification from the melt, and the modified stacking sequences occur by chance due to deformation of the crystal.

The stacking order, the *ch* order and fraction of *h* sequence of various stacking variants observed in this experiment are summarized in Table 5. Fraction of *h* sequence of the newly found stacking variants is not so different from that of the 9-layer type structure.

Acknowledgments

The present authors wish to thank Mr. Mitarai and Mr. Tokunaga of Hiroshima University for preparation of the alloy specimens. This work was partly supported by the Grant-in-Aid for Scientific Research from the Ministry of Education.

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