An Attempt to Image Chemical Ordering in Close-Packed Layer of Mg–Zn–Y 18R Long-Period Stacking-Ordered Structure by Scanning Tunneling Microscopy

Shu Kurokawa^{*1}, Akihiro Yamaguchi^{*2} and Akira Sakai

Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

For the first time, nanostructures of 18R (Mg₈₅Zn₆Y₉) LPSO (long-period stacking-ordered) were examined using STM (scanning tunneling microscopy), which unambiguously confirmed the proposed model of the atomic structure of the LPSO phase in which the Zn–Y clusters are arranged in a two-dimensional hexagonal lattice in the (0001)_{hcp} plane. The typical domain size of this hexagonal arrangement was estimated to range from several nanometers to a few tens of nanometers. In addition, the structures at the domain boundaries of the hexagonal arrangement were imaged and clarified by STM. [doi:10.2320/matertrans.M2013123]

(Received March 26, 2013; Accepted April 24, 2013; Published June 7, 2013)

Keywords: long-period stacking-ordered structures, magnesium, scanning tunneling microscopy, in-plane ordering, 18R

1. Introduction

In recent years, Mg alloys have attracted much attention for a number of industrial applications.¹⁾ In particular, Mg alloys containing Mg–TM (transition metal)–RE (rare earth) phases with LPSO (long-period stacking-ordered) structures have been considered promising structural materials owing to their high strength and ductility.^{2–7)}

However, the reasons why Mg alloys containing LPSO phases have these superior properties are still unclear. The mechanical properties of the LPSO phase will likely provide key information and detailed knowledge of the atomic structure of the LPSO phase will be indispensable for understanding the mechanism for deformation of the material. Moreover, this information will allow further improvement of the properties of this material and the development of other LPSO-based materials.

So far, analyses of the atomic structures of materials have been carried out using TEM (transmission electron microscopy) and other diffraction techniques. However, in many cases, these techniques detect the “averaged” atomic positions in the materials. Thus determination of the atomic structures is not straightforward if the materials have local or disordered structures, as do Mg–Zn–Y LPSO phases.

STM (scanning tunneling microscopy) is a well-known surface microscopy technique with very high spatial resolution. Since STM constructs images of surfaces through the overlap of the wave functions of the scanning tip and the sample surface, basically, STM is sensitive only to the top-surface atoms.⁸⁾ Therefore, STM is suitable for the evaluation of the local atomic structures of materials.

In this short article, we show the results of our first attempts at STM imaging of the chemical ordering in a close-packed atomic layer of the LPSO phase in the Mg–Zn–Y alloy.

2. Experimental

For the evaluation of a material by STM, an atomically flat surface is necessary. In this investigation, we prepare such surfaces using cleavage method.^{9,10)} It is reasonably assumed that no diffusion occurs during the cleavage process, and that the surfaces retain the atomic arrangements found inside the material, although a slight relaxation or reconstruction of the atomic positions at the surface is unavoidable.⁹⁾ In this case, the obtained STM images can be treated as cross-sectional images of the materials.

Mg–Zn–RE LPSO structures are fundamentally long-period stacking variants of the hcp (hexagonal close-packed) structure of the Mg crystal.¹¹⁾ There are quadruple RE-enriched close-packed layers in 18R LPSO phase. In the TEM image, the two atomic layers in the center of the quadruple atomic layers show a brighter contrast than the peripheral layers.^{11,13)} In this article, we refer to the center two atomic layers as the “inner Zn–Y” layers and the peripheral two as the “outer Zn–Y” layers (Fig. 1(a)).

It has been found that the deformation of the LPSO phase progresses through (0001)_{hcp}(11 $\bar{2}$ 0) basal slipping and kink deformation. Examination of the deformation process has revealed that kink deformation is difficult at low temperatures,⁶⁾ so it is expected that the LPSO phase fails through cleavage along the (0001)_{hcp} close-packed atomic plane owing to the restricted deformation processes and slip systems available at low temperatures.

A master ingot of Mg₈₅Zn₆Y₉ (at%) was prepared by induction melting. Directional solidification (DS) of the master ingot was conducted using the Bridgman technique at a growth rate of 10 mm/h under an Ar atmosphere in a carbon crucible. It was confirmed that the volume fraction of the 18R-type LPSO was almost 100%.⁶⁾

The sample was made from a slice of the alloy ingot with a thickness of 0.5 mm. A notch was made, and then, the sample was cleaved at liquid-nitrogen temperature. STM observations were also carried out at this temperature (Unisoku 1200). These procedures were performed in a UHV (ultra-high-vacuum) chamber (base pressure $\approx 1.0 \times 10^{-8}$ Pa) to prevent oxidation of the surface.

^{*1}Corresponding author, E-mail: kurokawa.shu.4m@kyoto-u.ac.jp

^{*2}Graduate Students, Kyoto University

Fig. 1 (a) Schematic illustration of the 18R LPSO structure proposed by Matsuda *et al.*¹¹⁾ A, B and C are the conventional notation for the stacking of close-packed atomic layers. The dashed lines indicate the location of the stacking fault in the 18R structure. (b) In-plane ordering of TM_6RE_8 clusters proposed by Yokobayashi *et al.* for the Mg–Al–Gd LPSO phase.¹²⁾ The clusters are located in the block of atomic layers containing the outer and inner Zn–Y layers. In this illustration, clusters are located in the block of atomic layers indicated by gray hatching in Fig. 1(a).

3. Results and Discussion

Our many initial attempts at STM imaging of the cleaved LPSO surfaces revealed that most of the surface is not flat on the nanometer scale, partly because the samples are polycrystalline and control of the crystal orientation is impossible. However, part of the surface had an atomically smooth terraces-and-steps structure, as shown in Fig. 2(a). We found that step heights corresponding to a single atomic layer or four atomic layers were dominant. In the area shown in Fig. 2, we can see 1-1-4-1-1-4 sequences of step heights (Fig. 2(b)). It is noteworthy that a subunit of the 18R structure consists of six atomic layers. The repeated 1-1-4

Fig. 2 (a) Typical STM image of the surface of the cleaved LPSO phase. Both atomically smooth terraces and steps between the terraces are imaged. Scan area is 80 nm $\times$ 80 nm. (b) Line profile of the topography along the line in (a). The heights of the steps are indicated in the figure. (c) Differential image of (a). Small corrugations are clearly observed in the terrace region.

(with a total of six atomic steps) sequence of step heights suggests that a certain atomic layer is preferred for cleavage. As shown in Fig. 1(a), the subunit of the 18R structure consists of two Mg layers, an outer Zn–Y layer, two inner Zn–Y layers, and an outer Zn–Y layer. Therefore, to reproduce the 1-1-4 sequences, we need to assume that there are at least two planes in different environments that are preferred for cleavage. For example, the 1-1-4 step heights sequence can be explained, if the planes between the two inner Zn–Y layers and the plane between the inner and outer

Fig. 3 STM images of the terrace region. (a) and (b) were obtained with negative ($V_s = -0.8$ V) and positive ($V_s = +1.0$ V) bias voltages on the sample, respectively. The contrast in (a) is due to the spatial variation of the density of filled electronic states under the Fermi level of the sample, while the spatial variation of the density of empty states is responsible for the contrast in (b).

Zn–Y layers are preferred for cleavage. However, other possibilities can be considered. Moreover, step-height sequences other than the 1-1-4 pattern were sometimes observed. Therefore, more detailed observations are necessary to determine how cleavage occurs in the 18R structure.

Figure 3 shows an STM observation of a terrace region of the cleaved 18R LPSO surface, which has a 2D (two-dimensional) hexagonal lattice (equilateral triangular lattice) of bright (Fig. 3(a)) and dark (Fig. 3(b)) spots. The reversal of the contrast between the filled-state (Fig. 3(a)) and empty-state (Fig. 3(b)) images suggests that the contrast in the STM images is mainly due to the difference in the local density of electronic states (chemical difference) rather than the surface topography.⁸⁾

As mentioned above, most of the surface of the sample is rough, and even when atomically smooth surface appear, they have steep slopes. The steepness of the slopes in the terrace regions makes control of the STM tip during scanning very difficult. As a result, the spatial resolution of the STM images in Fig. 3 is very poor, and no inner structure can be seen in

Fig. 4 (a) STM image obtained at the domain boundaries. The 2D hexagonal lattice (white lines) is superimposed on the STM image. Distortion of the image due to thermal drift was removed by assuming the ideal model of the LPSO structure. Noise was also removed by low-pass filtering. (b) Schematic diagram of the arrangement of the clusters. The solid line shows the 2D hexagonal lattice of clusters, which corresponds to the white mesh in (a), while the broken line indicates the lattice of the Mg matrix. The intersection point of the mesh of the solid lines was adjusted to the position of the clusters in the center domain (indicated by solid circles). a_{hcp} and b_{hcp} are primitive translation vectors of the Mg matrix (for example, $1/3[1210]$ and $1/3[\bar{1}120]$). From the figure, the displacement vectors relative to the center domain were measured for domains A to D (see text).

the bright (dark) spots. However, we can still obtain useful information about the atomic structure of the LPSO phase. We calibrated the distance between the bright (dark) spots as ≈ 1.1 nm using observations of the well-known Si(111) 7×7 reconstructed surface⁸⁾ under the same conditions. The 2D hexagonal lattice of spots with a lattice constant of about 1.1 nm is explained very well by the proposed model structure of LPSO (Fig. 1(b)), in which the distance between TM_6RE_8 clusters is $2\sqrt{3}a$ (a is the lattice constant of the Mg matrix).^{12,13)} To our knowledge, this is the first time that the proposed model of the LPSO phase has been supported in such an unambiguous way for the 18R Mg–Zn–Y LPSO phase. In this report, we make further arguments on the basis of this model, and in particular, we assume that the bright (dark) spots correspond to the Zn–Y clusters.

In Fig. 3, there are line-shaped regions with the opposite contrast to the spots in both images. These regions correspond to the domain boundaries of the 2D hexagonal arrangements of bright (dark) spots. In Fig. 4, we show the spatial arrangement of the domains observed in Fig. 3. The displacements of the 2D hexagonal lattice of certain domains relative to the domain indicated by the filled circles were measured (Fig. 4(b)), and found to be $\mathbf{b}_{\text{hcp}}$, $-\frac{1}{2}(\mathbf{a}_{\text{hcp}} + \mathbf{b}_{\text{hcp}})$, $-(\mathbf{a}_{\text{hcp}} + \mathbf{b}_{\text{hcp}})$ and $\mathbf{a}_{\text{hcp}}$ for domains A, B, C and D, respectively. We noted that at all boundary regions, the smallest distances between clusters are larger than the “ideal” distance of $2\sqrt{3}a$. If the distances between clusters were to become smaller than the ideal value, the outermost Y atoms of each cluster would be adjacent in the matrix of the close-packed layer. Our result shows that such configurations are considerably energetically unfavorable.

From Fig. 3 and other measurements, the size of domains of 2D hexagonal arrangements can be estimated as being from several to a few tens of nanometers. Such small domain sizes should be one reason why analysis using conventional techniques has failed to obtain clear results for the atomic structure of the Mg–Zn–Y LPSO phase so far. However, we should point out that we can access only a very small fraction of the surface using STM, as mentioned above, owing to the roughness of the surface. Further investigations are needed to provide the whole picture of the arrangement of the clusters in this material. Also, the detailed atomic structure of Zn–Y clusters will be a target of next investigations.

4. Conclusion

Our first attempt at STM observation of the 18R (Mg₈₅Zn₆Y₉) LPSO phase unambiguously supports the proposed model of the LPSO phase, in which the TM–RE clusters are arranged in a 2D hexagonal lattice in the (0001)_{hcp} plane. We have successfully determined the local arrangement of the clusters in the LPSO phase for the first time.

As demonstrated in this article, STM can be used to observe local atomic arrangements that are very difficult to

access using other analysis techniques. Although, information from other techniques or theoretical calculations is required to determine the atomic structures of materials, STM can be used in conjunction with these methods to provide unique information about the local atomic structures of materials.

Acknowledgments

We are grateful to Prof. Y. Kawamura and Prof. K. Hagihara for helpful advice and sample preparation.

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Synchro-LPSO” from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 24109503).

REFERENCES

- 1) M. Bamberger and G. Dehm: *Ann. Rev. Mater. Res.* **38** (2008) 505–533.
- 2) Y. Kawamura, K. Hayashi, A. Inoue and T. Matsumoto: *Mater. Trans.* **42** (2001) 1172–1176.
- 3) A. Inoue, Y. Kawamura, M. Matsushita, K. Hayashi and J. Koike: *J. Mater. Res.* **16** (2001) 1894–1900.
- 4) Y. Kawamura, T. Kasahara, S. Izumi and N. Yamasaki: *Scr. Mater.* **55** (2006) 453–456.
- 5) Y. Kawamura and M. Yamasaki: *Mater. Trans.* **48** (2007) 2986–2992.
- 6) K. Hagihara, N. Yokotani and Y. Umakoshi: *Intermetallics* **18** (2010) 267–276.
- 7) K. Hagihara, A. Kinoshita, Y. Sugino, M. Yamasaki, Y. Kawamura, H. Y. Yasuda and Y. Umakoshi: *Acta Mater.* **58** (2010) 6282–6293.
- 8) R. Weisendanger: *Scanning Probe Microscopy and Spectroscopy*, (Cambridge University Press, 1994) pp. 291–300.
- 9) O. Kolesnychenko, R. Kort and H. Kempen: *Surf. Sci.* **490** (2001) L573–L578.
- 10) N. Guisinger, T. Santos, J. Guest, T. Chien, A. Bhattacharya, J. Freeland and M. Bode: *ACS Nano* **3** (2009) 4132–4136.
- 11) M. Matsuda, S. Ii, Y. Kawamura, Y. Ikuhara and M. Nishida: *Mater. Sci. Eng. A* **393** (2005) 269–274.
- 12) H. Yokobayashi, K. Kishida, H. Inui, M. Yamasaki and Y. Kawamura: *Acta Mater.* **59** (2011) 7287–7299.
- 13) D. Egusa and E. Abe: *Acta Mater.* **60** (2012) 166–178.