Determination of the atomic width of an APB in ordered CoPt using quantified HAADF-STEM

Reference:

Akamine H., Van den Bos Karel, Gauquelin Nicolas, Farjami S., Van Aert Sandra, Schryvers Dominique, Nishida M..-
Determination of the atomic width of an APB in ordered CoPt using quantified HAADF-STEM
Journal of alloys and compounds - ISSN 0925-8388 - 644(2015), p. 570-574
DOI: http://dx.doi.org/doi:10.1016/j.jallcom.2015.04.205
Handle: http://hdl.handle.net/10067/1270080151162165141

Determination of the atomic width of an APB in ordered CoPt using quantified HAADF-STEM

H. Akamine[1,2,*], K.H.W. van den Bos[2], N. Gauquelin[2], S. Farjami[3], S. Van Aert[2], D. Schryvers[2], M. Nishida[3]

1 Department of Applied Science for Electronics and Materials, Interdisciplinary Graduate School of Science and Engineering, Kyushu University, Kasuga 816-8580, Japan
2 Electron Microscopy for Materials Science (EMAT), University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
3 Department of Engineering Science for Electronics and Materials, Faculty of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan

*Corresponding author: Hiroshi AKAMINE
Email: 3ES14001R@s.kyushu-u.ac.jp

Keywords
Transmission electron microscopy (TEM), scanning/transmission electron microscopy (STEM), high-angle annular darkfield (HAADF), Z-contrast microscopy, antiphase domains

Abstract

Anti-phase boundaries (APBs) in an ordered CoPt alloy are planar defects which disturb the ordered structure in their vicinity and decrease the magnetic properties. However, it has not yet been clarified to what extend the APBs disturb the ordering. In this study, high-resolution HAADF-STEM images are statistically analysed based on the image intensities estimated by the statistical parameter estimation theory. In the procedure, averaging intensities, fitting the intensity profiles to specific functions, and assessment based on a statistical test are performed. As a result, the APBs in the stable CoPt are found to be characterized by two atomic planes, and a contrast transition range as well as the centre of an inclined APB is determined. These results show that the APBs are quite sharp and therefore may have no notable effect on the net magnetic properties due to their small volume fraction.

Introduction

Near-equiatomic Co-Pt, Fe-Pd and Fe-Pt alloys undergo an A1-$L1_0$ disorder-order transformation as schematically shown in Fig. 1 in which three orientation variants are formed due to the

cubic-tetragonal lowering of the symmetry. In the past the morphological growth dynamics of these variants have been studied by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) [1-5], in order to understand the high uniaxial magnetocrystalline anisotropy of $L1_0$-ordered crystals as controlled by the variant selection during the transformation. In contrast to the growth dynamics, the characteristics of anti-phase boundaries (APBs) have not been sufficiently clarified in spite of the fact that a high density of APBs are continuously interacting in the dynamical growth process of the variants.

One of the important unknown characteristics of an APB is the variation of degree of order near the interface, where a lower degree of order gives rise to a decrease of magnetic anisotropy. However, it has been difficult to evaluate the degree of order by conventional TEM, since there is no parameter which can be directly related to the number of atoms included in each atomic column. In earlier work conventional two-beam imaging was used to determine the lattice relaxation at non-conservative APBs in Ni_3Mo [6] while conventional high resolution TEM (HRTEM) was used to investigate the wetting of the APB in $Co_{30}Pt_{70}$ [7]. In the present study, statistical approaches will be performed to high-angle annular dark field (HAADF) STEM images to determine the occupation of atomic columns near and at the APB. It is well-known that the Z-contrast of a HAADF-STEM image is strongly related to the number and types of atoms in each atomic column. Statistical parameter estimation theory for HAADF-STEM [8, 9] has been developed accompanied with the improvement of spatial resolution in STEM by aberration correction. It allows the quantitative extraction of local structural and chemical information with good accuracy and precision clarifying the characteristics of the APBs at atomic resolution.

Experimental Procedure

A single crystalline rod of CoPt (Co-50 at.%Pt) was grown by the floating zone method and homogenized at 1273 K for 168 hours in an evacuated quartz tube (2.0×10^{-4} Pa) followed by quenching into ice water. After determining the crystallographic orientation by the Laue method, some cubic specimens with $<100>_{A1}$ surface normals were cut out with edges of approximately 2.0 mm long.

Normally, three tetragonal variants are formed upon $L1_0$ ordering from the A1-disordered matrix. In this study, one of these variants was preferentially grown by the specific heat-treatment in a magnetic field [10]. Therefore, the sample, after heat-treatment, only included single-variant $L1_0$ domains with several APBs and is sufficiently demagnetized by an ensuing magnetic field-free heat-treatment.

(S)TEM samples are prepared by mechanical polishing, dimpling, and precession Ar^+ ion milling.

TEM observations were carried out with a JEOL 2000EX at the Ultramicroscopy research center (Kyushu) and the X-Ant-EM FEI Titan^3 at the EMAT laboratory (Antwerp), the latter equipped with probe aberration corrector. For STEM imaging, the Titan microscope was operated at 200 kV with a convergence angle of 21 mrad and the collection of the HAADF detector ranges from 91-160 mrad. 1st and 2nd order aberrations had to be corrected between each image due to the remaining local magnetic nature of the sample.

Results

Figure 2 shows a typical $[100]_{L10}$ selected area electron diffraction pattern and a corresponding low magnification bright field image. The diffraction pattern only includes (001) superlattice reflections from a single variant while the bright field image shows APB contrast within the corresponding single variant region. In the present case the *c*-direction of the ordered lattice thus lies within the plane of observation. This image results from a larger area of more than 10 micron in size which confirms that the single-variant state is successfully obtained by the specific heat-treatment in the magnetic field as indicated above.

From Fig. 2(b) it can be seen that the APBs are smoothly curved and do not follow a well-defined and fixed indexed plane. With the present sample having a stoichiometric composition of 50/50 a planar APB would be expected to be conservative, i.e. with a displacement vector parallel with the boundary. Since the latter is curved, however, and the relation between the two adjacent ordered regions is fixed, the conservative character will not be complete over the entire APB but on average still no concentration effects are expected. This curved morphology is different from that of similar but planar APBs in CuAu I films which have been reported to be characterized by a $(1/2)a[101]_{L10}$ or $(1/2)a[011]_{L10}$ antiphase vector showing good agreement with the theory on preferential displacement directions in the $L1_0$ ordered structure from the viewpoint of strain and conservation of alloy composition [11,12]. This difference in morphology may be attributed to the lower tetragonality of CoPt, where the lattice parameter ratio (c/a) is equal to 0.974 [4], whereas that of CuAu is reported to be 0.926 [11]. Since this lower tetragonality introduces a smaller strain in CoPt, this may explain why the APBs are not always following the low index planes, as shown in Fig. 2(b). This also suggests that the interfacial energy of APBs in CoPt is rather isotropic, and thus the characteristics of the APBs are homogeneous in the stable ordered state. On the other hand, also for CoPt the reduction of net interfacial energy is still a component to take into account so there will still be a driving force for APBs to grow along some well-defined indexed planes.

Figure 3 shows an HAADF-STEM image including a single APB within an $L1_0$ ordered matrix observed in the same orientation as Fig. 2, i.e. with pure Co and Pt columns parallel with the incident

$[100]_{L10}$ beam (when assuming complete ordering). On the left side of the image, the APB shows a curved habit plane while at the top-right corner it becomes parallel with the (001) planes of the present variant. With the displacement vector in the present example being equal to $1/2[011]_{L10}$ direction, the character of the APB in this zoomed area is non-conservative. More specifically, in the top-right corner the displacement vector is inclined to the boundary and one would expect two adjacent Pt or Co planes for a perfectly sharp APB. Following the Z-contrast concept, it can be concluded that the dark and bright columns in the areas away from the APB correspond to Co and Pt columns, respectively. The images on the right hand side of Fig. 3 are zooming in on the corresponding areas a and b in the two regions marked with the white dotted lines along the APB. In Fig. 3(a), atomic columns in the vicinity of the APB exhibit intermediate brightness between pure Co and Pt columns, indicating that these columns are a mixture of Co and Pt along the projection direction. In Fig. 3(b), the APB lies along the (001) plane and the width of the region having an intermediate contrast seems narrower than in Fig. 3(a). These gradual changes in contrast may be attributed to three reasons: (i) the degree of order near the APB gradually changes from pure Co to pure Pt or vice versa; (ii) the APB is tilted with respect to the incident direction causing overlap of the regions on both sides of the APB; (iii) the APB plane is not flat and has a certain level of roughness, which does not affect the width of the APB at the atomic scale (as is the case in (i)), but widens the range showing intermediate contrast in the resulting image. Murakami et al. [13] reported a gradual change in the degree of order over a few nm of the transition area in the Heusler alloy $Ni_{50}Mn_{25}Al_{12.5}Ga_{12.5}$ based on STEM observations and magnetization measurements by electron holography. However, it should be noted that the type of APB in this study is different from that observed in Heusler Ni-Mn-Al-Ga. In the latter, both side regions of the APB have the same major Ni sublattice, while the minor Mn and Al/Ga sublattices are switched (see also Fig. 1 of [13]). In the present $L1_0$ alloy, there is a perfect anti-phase relation between the Co and Pt sublattices on either side of the boundary. This difference may affect the characteristics of the APBs. Following the isotropic and homogeneous characteristics of APBs discussed above, it is difficult to obtain the image in an exact edge-on condition, but it is still possible to attribute an upper limit to the width of an APB from a single image close enough to the edge-on condition, since the APB must uniquely exist within the region having an intermediate contrast and all APBs should have a similar width. In addition, as this sample is in the thermodynamically stable state it can be assumed that the atomic scale roughness of the APBs is negligible to a first approximation, since this would result in a strong increase of the total area of the APBs and thus interfacial energy.

Discussion

In HAADF-STEM imaging, sufficient advances have been made using aberration-corrected

imaging in combination with statistical parameter estimation theory to not only measure atomic displacements [14, 15] but also to measure the number of atoms in an atomic column [16-19] and to measure the local chemical composition [8, 9]. This theory provides the means to calculate the total scattered intensities of atomic columns [14, 8, 9]. These intensities scale with the average atomic number Z of the respective column and can therefore be used to quantify the chemical composition of the individual atom columns near the APBs. Total scattered intensities have been estimated for all atomic columns of Fig. 4(a), which is a zoom of the area next to the top-right part of Fig. 3, where the APB is parallel to the cubic plane. Based on these intensities, mean values have been computed for the columns along each horizontal (001) plane. This averaging operation will compensate for the small fluctuations in intensities inherent to the experimental acquisition of the image.

In Fig. 4(b) the average scattered intensities along the vertical, (010) direction are shown. The alternation of relatively low and high scattered intensities evidences the $L1_0$-ordering. In the profile, the centre of the APB contrast area can be identified by the two planes having intermediate values of the total scattered intensity, also indicated in Fig. 4(a) by short black arrows. In order to determine the width of the APB contrast area, it is necessary to determine whether the columns in the neighbouring horizontal planes are pure or mixed. Therefore, it is assumed that the scattered intensities increase linearly when the composition changes from pure Co to pure Pt [9]. Based on this assumption, two ramp functions, one corresponding to the odd and one to the even horizontal planes, were simultaneously fitted to all data both inside and outside the grey region by using the weighted least squares method. In this fit, the two ramp functions were linked together by considering the same parameter values for both slopes, the centre of the APB contrast area and the average scattered intensity of the pure Pt and Co columns on both sides of the APB. From the fitted parameters and their 95% confidence intervals it was found that the APB contrast area is characterised by 3.5 ± 2.4 mixed columns.

Due to the ion milling surface imperfections are present resulting in fluctuations in the total scattered atom column intensities (see, e.g., V-shaped dark contrast above grey region in Fig. 4(a)). As can be seen in Fig. 4(b) the averaging operation does not compensate enough to level out all those fluctuations. Furthermore, since this may limit the precision of the estimated parameters, the APB was also studied by using the so-called two sample t-tests [20, 21]. With these tests, it is possible to decide whether the mean values of the scattered intensities of two different horizontal planes can be assumed identical. Since this method requires a reference set of observations with identical external conditions, a stable region around the centre of the boundary, indicated by the grey region in Fig. 4(b), was selected. The results of the first approach indicated that the atomic columns in this grey region and close to its borders are most definitely pure columns. Using the scattered intensities of these atomic columns as a reference, the two-sample t-test showed that only the two central horizontal planes consist of mixed columns, which could in fact be a way for the system to

solve the local non-conservative character. Therefore, the boundary area is considered to be sharp, indicating a high tendency for a perfect $L1_0$ ordering up to the centre of the APB contrast area.

In Fig. 5(a) an enlarged image of the central part of Fig. 3 is shown, where the APB is inclined. In this region pure Co and Pt columns are gradually transforming along the horizontal (001) planes into each other. A constant distance with respect to the centre of the transition area is indicated by the white contour lines. Therefore, the contour lines have the same inclined orientation as the APB and the columns along these lines are parallel with the APB. In order to find the exact centre of the transition area (corresponding to the reference columns indicated by 0), the total scattered intensities were used in combination with the assumption that the composition of the atomic columns in this centre is 50-50 Co-Pt. An averaged total scattered intensity profile parallel to the white lines was then obtained, which is shown in Fig. 5(b). The obtained averaged profile shows from left to right a linear transformation of pure Co columns into pure Pt columns. The larger error bars away from the transition zone are due to a fewer number of included atomic columns at these distances. For determining the width of the transition zone, a ramp function was fitted, similar to Fig. 4(b). From the fitted parameters and their 95 % confidence intervals the width of the transition zone was found to be 15 ± 2 atomic columns. Since Fig. 4(a) and Fig. 5(a) both zoom in on the same APB it is most likely that the boundary in Fig. 5(a) is also sharp but is tilted with respect to the incident beam direction. In this case, the atomic columns in the transition area must be mixed columns consisting of Co atoms at the bottom and Pt atoms at the top or vice versa.

If we roughly assume that the density of the APBs is 10 $\mu m^2/\mu m^3$ by tracing the APBs in Fig. 2(b) and apply the result that the APBs in stable CoPt are characterized by approximately two atomic planes, then the volume fraction disturbed by the APBs is estimated as 0.38 % using the lattice parameters in Ref. [4]. This is quite small and therefore the effect of the APBs on the magnetic properties may be sufficiently negligible.

Conclusions

In this study, we have presented a statistical way to characterize the width of APBs in ordered $L1_0$ CoPt alloys based on an analysis of atomic column intensities which were estimated by the statistical parameter estimation theory for HAADF-STEM imaging. The result for the APB observed close to edge-on condition showed that this APB is characterized by two atomic planes, indicating that APBs in the CoPt system are quite sharp and therefore will have no remarkable effect on the net magnetic properties of the material due to their small volume fraction. Another calculation for the inclined APB determined the centre of the APB and transition distance from the column intensities. These statistical estimations can be applied to many other alloys and therefore provide an efficient new way to characterize planer defects at the atomic scale.

Acknowledgments

The authors acknowledge financial support from the Research Foundation Flanders (FWO, Belgium) through project fundings (G.0368.15N, G.0369.15N and G.0374.13N), a Ph.D. grant to Karel van den Bos. N.G. acknowledges support from the European Research Council under an ERC starting grant No. 278510 VORTEX and the Japan Society for the Promotion of Science (JSPS, Japan) through the Strategic Young Researcher Overseas Visits Program for Accelerating Brain Circulation (R2408). The X-Ant-EM microscope was partly funded by the Hercules fund from the Flemish Government.

References

[1] B. Zhang, M. Lelovic and W.A. Soffa, Scr. Metall. Mater. 25 (1991) 1557.

[2] B. Zhang and W. A. Soffa, Scr. Metall. Mater. 30 (1994) 683.

[3] P. Ghatwai, E. Vetter, M. Hrdy, W.A. Soffa, J.A. Floro, J. Mag. Mag. Mater. 375 (2015) 87.

[4] H. Akamine, S. Farjami, M. Mitsuhara, M. Nishida, T. Fukuda, T. Kakeshita, Mater. Trans. 54 (2013) 1715.

[5] S. Farjami, T. Fukuda, T. Kakeshita, J. Alloys and Comp. 577 (2013) S327.

[6] G. Van Tendeloo, S. Amelinckx, Phys. Stat. Sol. 22 (1974) 621.

[7] C. Leroux, A. Loiseau, M.C. Cadeville, D. Broddin, G. Van Tendeloo, J. Phys.: Condens. Matter 2 (1990) 3479.

[8] S. Van Aert, J. Verbeeck, R. Erni, S. Bals, M. Luysberg, D. Van Dyck, G. Van Tendeloo, Ultramicroscopy 109 (2009) 1236.

[9] G.T. Martinez, A. Rosenauer, A. De Backer, J. Verbeeck, S. Van Aert, Ultramicroscopy 137 (2014) 12.

[10] S. Farjami, M. Yasui, T. Fukuda and T. Kakeshita, Scr. Mater. 58 (2008) 811.

[11] M.J. Marcinkowski, Theory and Direct Observation of Antiphase Boundaries and Dislocations in Superlattices, in: G. Thomas, J. Washburn (Eds.), Electron Microscopy and Strength of Crystals; Proceedings of the First Berkeley International Materials Conference: the Impact of Transmission Electron Microscopy on Theories of the Strength of Crystal, Interscience Publishers, New York, 1963, pp. 337.

[12] D.W. Pashley, A.E.B. Presland, J. Inst. Metals 87 (1958) 419.

[13] Y. Murakami, K. Yanagisawa, K. Niitsu, H.S. Park, T. Matsuda, R. Kainuma, D. Shindo, A. Tonomura, Acta Mater. 61 (2013) 2095.

[14] A.J. den Dekker, J. Gonnissen, A. De Backer, J. Sijbers, S. Van Aert, Ultramicroscopy 134 (2013) 34.

[15] P. Kundu, S. Turner, S. Van Aert, N. Ravishankar, G. Van Tendeloo, ACS Nano 8 (2014) 599.

[16] S. Van Aert, J. Batenburg, M.D. Rossell, R. Erni, G. Van Tendeloo, Nature 470 (2011) 374.
[17] S. Bals, S. Van Aert, C.P. Romero, K. Lauwaet, M.J. Van Bael, B. Schoeters, B. Partoens, E. Yücelen, P. Lievens, G. Van Tendeloo, Nature communications 3 (2012) 897.
[18] S. Van Aert, A. De Backer, G.T. Martinez, B. Goris, S. Bals, G. Van Tendeloo, A. Rosenauer, Physical review B 87 (2013) 064107.
[19] A. De Backer, G.T. Martinez, A. Rosenauer and S. Van Aert. Ultramicroscopy 134 (2013) 23.
[20] Student, Biometrika 6 (1908) 1.
[21] A.M. Mood, F.A. Graybill, D.C. Boes, Introduction to the theory of statistics, third ed., McGraw-Hill, Singapore, 1974.

Figure Captions

Fig.1 (a) A1 (fcc) disordered lattice and (b) $L1_0$ ordered lattice. In (a) Co and Pt atoms randomly occupy each lattice point, while they are alternatively layered along the *c*-axis in (b) (Co white, Pt black).

Fig.2 (a) Selected area electron diffraction pattern with the incident beam along the $[100]_{L10}$ direction and (b) corresponding low magnification bright field image clearly revealing many curved APBs.

Fig.3 $[100]_{L10}$ HAADF-STEM image of single-variant of CoPt including a single APB. Dark and bright columns correspond to Co and Pt columns, respectively. The APB starts from the lower-left corner (at white arrowhead) and curves towards the top-right corner where it follows the horizontal cubic plane. (a) and (b) are enlargements of the corresponding dotted rectangles.

Fig.4 (a) An HAADF-STEM zoomed in on the top-right part of Fig. 3, where the APB is parallel to the cubic plane. The two horizontal planes containing the centre of the APB are indicated by the black arrows. The vertical axis shows the distance of the other horizontal (001) planes with respect to this centre. (b) Mean values with their corresponding standard deviation of the total scattered intensities of the atomic columns along the horizontal (001) planes shows the alternation between pure Co and Pt columns. A stable region without large fluctuations is indicated in both figures by the grey region.

Fig.5 (a) An enlarged HAADF-STEM image of the central part of Fig. 3, where the APB is inclined. The pure Co and Pt column are transforming along the horizontal (001) plane into each other. The centre of this transition area is indicated by the 0-contour line. The distance of the atomic columns

with respect to this centre is indicated by the white contour lines. (b) Mean values with their corresponding standard deviation of the total scattered intensities of the atomic columns parallel to the contour lines in (a) show the linear transformation of pure Co columns into pure Pt columns.