Electron microscopy study of striation contrast in Al–Cu–Co–Si decagonal quasicrystals

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Abstract. Detailed transmission electron microscopy study was carried out in single crystals of a decagonal phase in the Al–Cu–Co–Si quaternary system. X-ray diffraction and convergent beam electron diffraction patterns of the powder samples confirmed the structures to be decagonal quasicrystals. No microcrystalline nor crystalline phases could be identified. Thin slices normal to the 10-fold directions were prepared for transmission electron microscopy. Diffuse streaks along symmetric directions around the fundamental spots were observed in the diffraction patterns. Bright field images and dark field images showed discontinuous lines or striations lying perpendicular to the direction of diffuse streaking. The striation contrast appears to be originating from anti-phase boundary (APB) in the decagonal superstructures. The diffuse streaks seem to be a characteristic feature of a partially ordered decagonal superlattice structure. The atomic rearrangement or phasonic movement in certain symmetric directions along the pentagrids or Ammann lines in the structure has obviously caused the type of contrast observed in the images. The evolution of rhombic domains consisting of APBs in localized regions can be understood as one of the signature of an intermediate structural state formed prior to a superstructure formation.

Keywords. Decagonal quasicrystals; ordering; electron microscopy; diffuse intensity.

1. Introduction

After the discovery of stable decagonal quasicrystals (DQC) in the Al–Cu–Co system (He *et al* 1988; Tsai *et al* 1989), extensive efforts have been made to study the synthesis, characteristics and stability of DQC and related approximants in Al(Si)–Cu–Co ternary or quaternary systems (Launois *et al* 1990; Dalton and Kelton 1991; He *et al* 1991; Liao *et al* 1992; Grushko and Urban 1994). Gasga *et al* (1992) and Mukhopadhyay *et al* (1995) suggested that more than 1% Si does not remain in DQC phase produced by slow cooling technique. The basic structure of DQC proposed by Steurer and Kuo (1990) for Al–Cu–Co was later refined for Al–Co–Ni by Steurer *et al* (1993). Yamamoto *et al* (1990) and Hiraga (1991) advocated a cluster model (with 2.0 nm clusters) on the basis of HREM images. Later, Burkov (1993) suggested another cluster model which is consistent with above mentioned structural models. However, all these models have considered only 0.4 nm periodicity along c-axis. But it has now been established that the stable quasicrystals in Al–Cu–Co and Al–Ni–Co exist in two different variations with c-axis parameter of ~0.4 and ~0.8 nm, respectively. Ritsch *et al* (1995) have elegantly demonstrated the relations between these variable periodicities via ordering reaction in the decagonal

structure. They have also reported two different types of superstructure having 0.8 nm periodicity. These superstructures transform to disordered structures with 0.4 nm period after electron beam irradiation. It is interesting to mention that earlier Edagawa *et al* (1992, 1994) reported the existence of an ordered superlattice in decagonal Al–Ni–Co and established an order–disorder transformation at 800°C. However, superlattice order has not been observed by them in Al–Cu–Co. Though, Hiraga (1991) observed superlattice ordering in Al–Cu–Co, many other ordering possibilities such as types I and II superstructures (Ritsch *et al* 1997) have also been reported. The replacement of diffuse streaks by sharp superlattice spots as a result of thermal treatment has been observed by Fettweis *et al* (1995). The existence of superlattice reflections at certain positions along the P-directions (Hiraga 1991; Edagawa *et al* 1992, 1994) have been reported.

Song *et al* (1991) studied X-ray and electron diffraction patterns as well as the electron microscopic images in Al–Cu–Co system. They proposed the model of twinning of the microcrystalline (MC) phases in order to interpret the tweed contrast in TEM images. Recently, Zhang *et al* (1995) have reported diffuse intensity and tweed contrast in Al–Cu–Co DQC phase and interpreted this as due to strain arising from the formation of localized crystalline phases in the DQC structure. It is obvious that there is a need to understand the subtle diffraction features and

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image contrast that are often encountered in DQC phases. Here, DQC of $\text{Al}_{62}\text{Cu}_{20}\text{Co}_{15}\text{Si}_3$ was selected for a detailed electron microscopic study. Attempts were made to discuss the results in the framework of the structure of decagonal quasicrystals.

2. Experimental

An Al–Cu–Co–Si alloy was prepared by melting the constituent elements (close to the $\text{Al}_{62}\text{Cu}_{20}\text{Co}_{15}\text{Si}_3$ composition) in a mono-arc melting furnace. The as-cast alloy was remelted and kept at 1360°C and annealed for 8 h and then cooled to 600°C at $0.04^\circ\text{C}/\text{min}$ to synthesize large size single crystals of DQC phase. The individual needles formed during solidification were extracted and ground to powder for X-ray diffraction using $\text{CuK}\alpha$ source and TEM. Thin slices were cut from this needle by spark cutting and then thinned by mechanical polishing, dimple grinding and ion milling in a Gatan ion mill at 3 kV, using a liquid nitrogen cooled stage. The thinned sample was observed in a Philips CM-12, transmission electron microscope operating at 120 kV.

3. Results and discussions

Figure 1 shows a convergent beam electron diffraction (CBED) pattern conforming to 10-fold symmetry. X-ray diffraction pattern of the powder also confirmed the presence of the decagonal phase; no other phase could

be detected. The quasilattice constant (a_r) was found to be 0.397 nm and periodic lattice constant (c) to be 0.8 nm following the indexing procedure proposed by Mukhopadhyay *et al* (1990). It should be noted that the present DQC phase has 0.8 nm period indicating the possibility of superstructure formation. Figure 2 shows a 10-fold diffraction pattern displaying many subtle features. Diffuse streaks are observed around the most intense spots along all the P directions $\langle 100\ 000 \rangle$. The intense spots in the D directions $\langle 110\ 000 \rangle$ (marked by small arrow) are non-circular in shape and show diffuse streaks radiating along the P directions. It is now well understood that this shape distortion is a result of the superposition of reflections from five variants of the B2 phase with the DQC spots. From analysis of diffraction patterns taken near the edge and away from edge of the sample, the existence of disordered B2 crystals was already established in an earlier report (Mukhopadhyay *et al* 1995). Further, one observes that the reflections along the systematic row (along the P-direction) are also identical in both cases. The spots contain diffuse streaks along all the P directions and thus become star shaped in general. Diffuse streaks are also present at positions marked by the arrowhead. These are distinguished from the other streaks by the fact that only three of the five pronged sides of the pentagon of spots are connected by the streaks. The spread of the diffuse streaks corresponds to a length of 2.0–2.4 nm in real space.

Figure 3 shows a bright field image corresponding to the 10-fold diffraction pattern (shown in figure 2). The parallel linear features marked by arrows are dominant

Figure 1. CBED pattern showing 10-fold rotational symmetry.

Figure 2. 10-fold diffraction pattern obtained from an ion milled specimen. Diffuse streaks and distortion of the diffraction spots are observed.

in five directions and are 72° apart. Further, under a slightly magnified view, the picture shows that these lines do not continue all across the field of the micrograph, but are confined to approximate lengths of 100 nm, forming nearly rhombic domains. The interline spacing works out to be of the order of 7–8 nm. After correcting for image rotation, each of these five sets of lines are found to be perpendicular to a $\mathbf{g}_p$ direction. The observation of the sets of parallel lines in a low magnification image, is generally unexpected for a decagonal phase. In order to understand the origin of these features, systematic dark field imaging from various P-spots was carried out. Figure 4 shows a bright field image in a near two-beam condition ($\mathbf{g}_p$) where some weak spots of the systematics row survive, revealing tweed contrast along with one set of lines lying perpendicular to $\mathbf{g}_p$. The other sets of lines seen in figure 3 are not visible in this image. The important features of this image are the prominent rhombic domain structure, the fine parallel lines perpendicular to $\mathbf{g}_p$ as noted already, and dark patches of contrast within the domains. Earlier the tweed

structure has been reported and interpreted by Song *et al* (1991) as being due to twinning of a microcrystalline (MC) phase. However, our analysis (to be discussed later) does not confirm the idea of multiple twinning of MC phases. In dark field imaging using a $\mathbf{g}_p$ reflection (011 0T0) type, we observe bright striations (marked by arrow) of variable spacing as shown in figure 5. The striations are perpendicular to the selected $\mathbf{g}_p$ vectors and they approximately define the rhombic domains described earlier.

Similar DF imaging experiments were performed for other $\mathbf{g}_p$ vectors (rotated by 36°). The striations appear consistently in all orientations normal to the P directions. This image shows the lowest fringe spacing resolved in this study (~ 0.5 – 0.6 nm) along with bright striations as observed in the other micrographs. The various spacings observed for bright striations in all the DF images were found to be in the order of $\sim 1, 2, 3, 5, 8, 13$ and 21 nm with an accuracy of ± 0.1 nm. Some interesting features can be noted from the analysis of the DF images. Firstly, their spacing vary and follow the Fibonacci relation, i.e.

Figure 3. Bright field image of sample looking along the axis of 10-fold symmetry. Five sets of lines along pentagrids making angles of 72° or multiple of it can be noted.

any larger spacing can be dissociated into a combination of smaller spacings. Secondly, the striations are perpendicular to the diffuse streaking observed in figure 2. The spacings and their orientations suggest that the fringes lie along the Ammann lines of the decagonal quasiperiodic structure.

The striation contrast described here has been observed earlier by Zhang *et al* (1995) and Mukhopadhyay *et al* (1995). Zhang *et al* (1995) attributed the contrast to the strain field associated with the small crystalline regions observed by them in their HREM pictures. In their study, the striations were perpendicular to two-fold g vectors and by careful tilting experiments they observed the superposition of defect contrast arising from B2 crystalline phase on the surface due to ion milling of the samples. Striation contrast was present up to a length scale of 100 nm. On the contrary, the fine, so-called crystalline regions in their HREM images extended only to 4–5 nm in length and were one unit cell thick. The edge of the unit cell did not coincide with the pentagrid. Several other workers (Dalton and Kelton 1991; Hiraga 1991;

Edagawa *et al* 1992, 1994) have observed a localized periodicity in the decagonal quasiperiodic tiling from HREM images obtained from Al–Cu–Co and Al–Ni–Co decagonal phases. These periodic rhombic tiles were treated as local phason defects in the Penrose tiling, wherein the bond orientational order of the tiles was preserved giving rise to decagonal patterns. These regions were attributed to partial superlattice order in the deca-structure with attendant diffuse intensity streaks in the 10-fold diffraction pattern. Hiraga (1991) points to the possibility of perfectly ordered Penrose tiling in HREM images of Al–Cu–Co and Al–Ni–Co alloys quenched from 800°C. Perfect ordering of this deca-structure at this temperature can also be inferred from the experimental data of Fettweis *et al* (1995). We disagree from the interpretation of the striation contrast given by Zhang *et al* (1995) on the basis that the information contained at lower magnification in the images does not correlate well with their HREM picture. The contrast features found within the striations are similar to domain boundaries observed in crystalline long

Figure 4. Bright field image taken in nearly two-beam condition showing the linear fringe type contrast perpendicular to g_p vector. Tweed contrast can also be observed.

Figure 5. High magnification dark field image of g_p vector, showing striations displaying various Fibonacci related spacings.

period superlattice (LPS) structures (Hirsch *et al* 1965). A number of ordered alloys in crystalline systems which exhibit a regular arrangement of APBs over a narrow range of temperature give rise to periodic image as first shown by Ogawa *et al* (1958). The most common example is Al-Cu alloy which shows such a periodic antiphase structure in temperature range 380–415°C.

Similar rhombic domains were observed earlier by Song *et al* (1991) and interpreted as due to twinning of microcrystalline phases. However, their interpretation of the domains as microcrystals (20–500 nm in size) was not supported by their HREM images. We failed to find any microcrystalline region of the same dimension in our HREM images and CBED patterns conforming to the symmetry of MC phases. Rather the CBED patterns continued to show decagonal symmetry even at incident beam size of 10 nm. The rhombic domains in our case reveal boundaries with different spacings in different regions. However, these are τ -related as noted earlier and display an angular relation of 72° between adjoining boundaries when all the boundaries are imaged. Thus, they conform to the geometry of the underlying quasiperiodic lattice.

4. Conclusions

The diffuse streaks observed in the SADPs are attributed

to partial ordering in decagonal structures. The structural rearrangement in DQC phase leads to an unusual striation contrast in the images, giving rise to features similar to ordered domains with typical antiphase boundaries (APB). Our samples did not exhibit twinning of MC phases, nor did they show the existence of crystalline phase. The unusual striation and rhombic domain contrast can be satisfactorily explained in terms of a partially ordered superlattice structure of the decagonal phase. The processing condition and the composition are very important parameters to obtain a particular type of decagonal phase. In the present study we have obtained a DQC phase which has an inherent tendency to transform towards a superlattice decagonal phase. However, this is a signature of the fact that the phase tries to attain a superlattice decagonal structure, very similar to Al-Ni-Co, but the ordering reaction is incomplete due to improper alloying or thermal treatment.

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