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A combined single crystal X-ray diffraction and electron diffraction study of the T_2 phase in Al–Li–Cu alloys

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Both single crystal X-ray diffraction techniques and convergent beam electron diffraction have been employed to examine the structure of the T_2 (Al_6CuLi_3) phase in three particular Al–Li–Cu alloys. It is shown that T_2 displays icosahedral symmetry both in a high purity laboratory melt and in two "impure" alloys which had been processed industrially. Possible reasons for the five-fold symmetry of T_2 are discussed.

1. Introduction

Alloys which are based on the Al–Li–Cu system are of considerable scientific and industrial importance due to their potential applications in the aerospace industry [1–3]. However, these alloys exhibit complex microstructural characteristics, and the exact structures of both the equilibrium and metastable phases present are still in doubt.

Hardy and Silcock [4] investigated the Al–Li–Cu system using Debye–Scherrer powder X-ray techniques. They documented the presence of three equilibrium ternary phases in the aluminium-rich corner of the ternary phase diagram: T_B ($Al_{7.5}Cu_4Li$), T_1 (Al_2CuLi) and T_2 (Al_6CuLi_3). Although Hardy and Silcock obtained interplanar spacings for the T_2 phase, the X-ray diffraction patterns were not indexed and no structural information was given.

Recent work by Ball and co-workers [5, 6] has demonstrated the existence of a phase in an Al–Li–Cu–Mg–Zr alloy which displays apparent icosahedral symmetry; however, this phase was not identified. In addition, Sainfort *et al.* [7] investigated a similar alloy and reported that the T_2 phase in their alloy displayed five-fold symmetry. It is also interesting to note that Crooks and Starke [8] presented an electron diffraction pattern of a grain boundary phase in an Al–Li–Cu–Mg–Zr alloy which displayed five-fold symmetry, but did not comment on it.

In the present paper, the icosahedral symmetry of T_2 is examined using standard single crystal X-ray diffraction techniques and convergent beam electron diffraction (CBED). To the authors' knowledge, this is the first report of "single crystal" X-ray diffraction patterns from a phase which displays icosahedral symmetry. In addition, the combined X-ray and electron diffraction data from a high purity alloy which was fabricated in the authors' laboratory, have permitted the unambiguous identification of T_2 in two commercial alloys.

2. Experimental procedures

2.1. The high purity Al–Li–Cu alloy

High purity aluminium (99.999%), copper (99.999%) and lithium (99.95%) metals were mixed in a ratio corresponding to the proposed stoichiometry of the T_2 phase and encapsulated in a tantalum tube. The mixture was heated to 850° C and held at this temperature for a time sufficient to produce a homogeneous liquid solution. Following ice water quenching, the alloy was aged at 450° C for one week and ice water quenched. Specimens for scanning electron microscopy were prepared using standard techniques and etched in 50% HNO_3 in water. The alloy was then examined by standard powder and single crystal X-ray diffraction techniques.

Specimens of the T_2 phase for examination in the transmission electron microscope were prepared by crushing and dispersing, and were examined in a Philips EM420T operating at 120 kV.

2.2. The commercial Al–Li–Cu–Zr alloys

The commercial alloys were supplied by the Alloy Technology Division of Alcoa Laboratories (Alcoa Center, Pennsylvania, USA) and had the following nominal compositions (wt %):

Alloy A, Al–2% Li–3% Cu–0.12% Zr

Alloy B, Al–3% Li–1% Cu–0.12% Zr

Following hot rolling, alloy A was solution treated at 550° C for 30 min and water quenched. Certain specimens were "stretched" by 2% prior to ageing at 190° C (for times in the range of 1.25–520 h) whilst others were aged at 190° C in the "unstretched" condition. Alloy B was processed in a similar fashion and aged at 190° C for 50 h.

Specimens for transmission electron microscopy were prepared in a twin-jet electropolisher using a 25% nital solution at −20° C and at a potential of 12 V. The thin foils were examined in a Philips EM420T operating at 120 kV.

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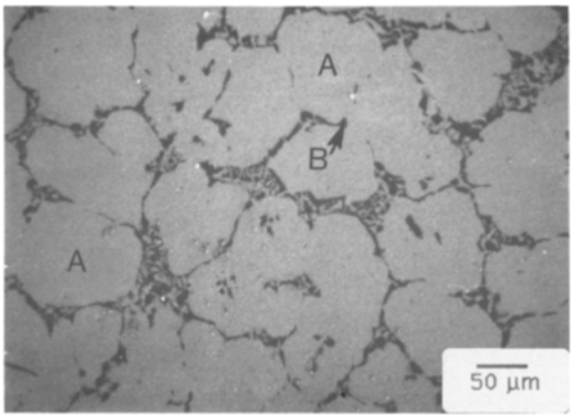

Figure 1 A backscattered electron image of the high purity Al–Li–Cu alloy. The matrix is T_2 and the second phase (arrowed "B") in the interdendritic regions is the α-aluminium solid solution.

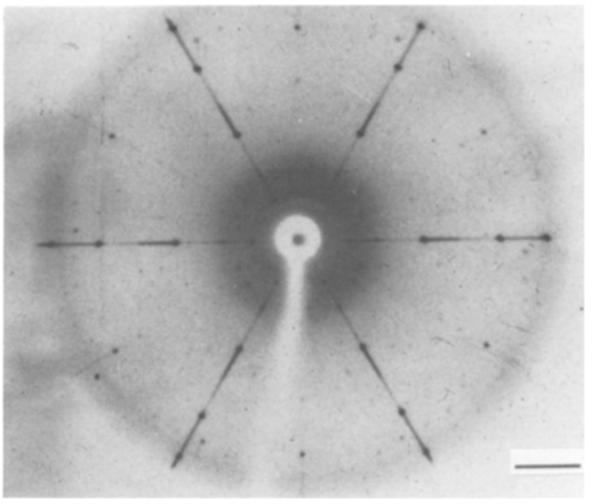

Figure 3 Precession X-ray photograph of the T_2 fragment down the three-fold axis. $\bar{\mu}$ = 18.5° Mo$K\alpha$. Scale bar, 2.5 nm^{-1}.

3. Results

3.1. The high purity Al–Li–Cu alloy

Fig. 1 shows the microstructure of the laboratory alloy after ageing for one week at 450° C. The predominant phase (A in Fig. 1) was identified from Debye–Scherrer X-ray photographs as T_2 by matching the observed interplanar spacings with those given by Hardy and Silcock. The minor phase (B) is the aluminium rich α-solid solution. The size of the T_2 grains was estimated to be of the order of 0.1 to 0.2 mm.

"Single crystal" fragments of the T_2 phase were obtained from the aged material and studied using single crystal X-ray diffraction techniques. The sparseness of reflections in both the rotation and Weissenberg diffraction patterns and the apparent absence of a reasonable lattice for T_2 were taken as indications of the possibility of quasicrystallinity. Hence, one fragment which was roughly 0.01 to 0.02 mm in size, mounted so that its rotation axis was perpendicular to a mirror, was examined using precession techniques, with Zr-filtered Mo$K\alpha$ radiation. The resultant diffraction patterns are shown in Figs 2, 3 and 4. These patterns show the two-, three- and five-fold axes, respectively, which are consistent with the point group symmetry $m\bar{3}\bar{5}$ and are similar to the electron diffraction patterns which were first presented for a quasicrystalline phase by Shechtman *et al.* [9]. The photographs down the three- and five-fold axes were obtained by rotating the crystal about the spindle axis of the camera by 21° and 58°, respectively, from the two-fold axis. These values correspond to those which can be determined from the $m\bar{3}\bar{5}$ stereogram (Fig. 5).

Since X-ray diffraction (and indeed electron diffraction) techniques always "add" a centre of symmetry to the diffraction pattern, the symmetry of the zero level pattern shown in Fig. 4 is 10 mm. However, the 5 mm symmetry observed in an upper level of the reciprocal lattice perpendicular to the same axis (Fig. 6) confirms that the symmetry is indeed five-fold. The reciprocal lattice level in Fig. 6 corresponds to the first non-zero level ring observed on a precession cone axis photograph. However, it is interesting to note that, if this material is quasicrystalline, the reciprocal space is everywhere dense with points, and Fig. 6 could not be formally described as a first level photograph.

All the X-ray diffraction patterns have been indexed according to the method of Bancel *et al.* [10]. The intensities of the reflections have been measured on a

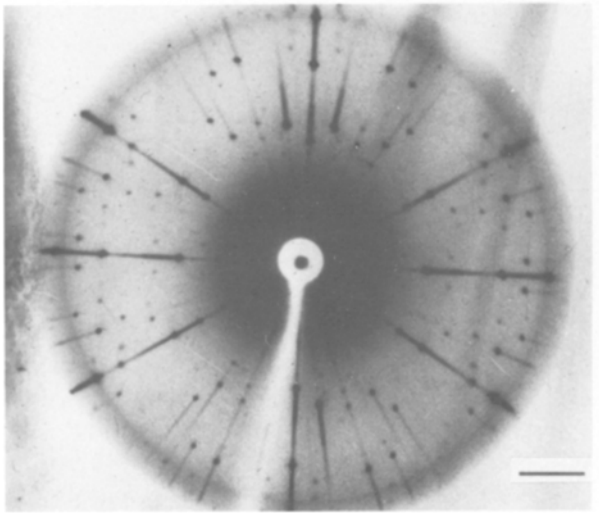

Figure 2 Precession X-ray photograph of the T_2 fragment down the two-fold axis. $\bar{\mu}$ = 18.5° Mo$K\alpha$. Scale bar, 2.5 nm^{-1}.

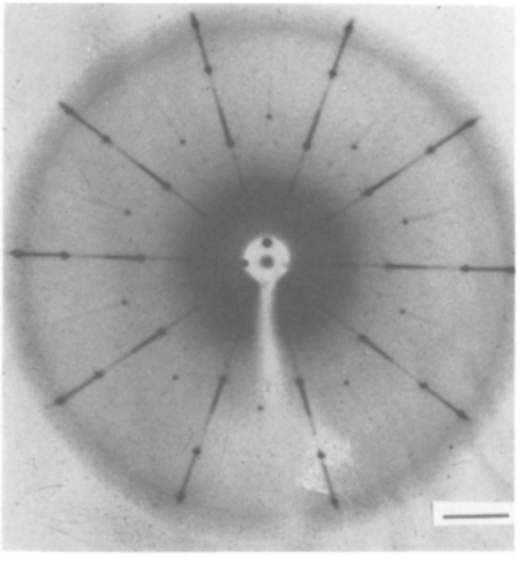

Figure 4 Precession X-ray photograph of the T_2 fragment down the five-fold axis. $\bar{\mu}$ = 18.5° Mo$K\alpha$. Scale bar, 2.5 nm^{-1}.

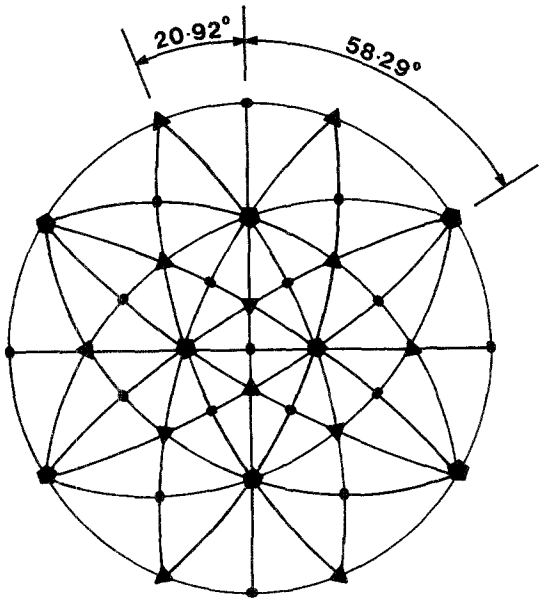

Figure 5 Stereographic projection of the symmetry elements of the icosahedral group (modified from Shechtman *et al.* [9]).

single crystal counter diffractometer, and a structure analysis is under way.

As stated in Section 2.1, fragments of the T_2 phase were examined in the transmission electron microscope. However, convergent beam electron diffraction (CBED) patterns were difficult to obtain since the T_2 particles became unstable when irradiated by the electron beam, regardless of operating voltage, and underwent a transformation. Fig. 7 is a bright field (BF) image of a transformed T_2 fragment. In this instance, the transformation has yielded a microcrystalline aggregate from what was initially a "single crystal" of T_2. Both the cause and nature of this transformation are presently under intensive investigation.

In rare instances, it was possible to obtain CBED patterns from T_2 particles prior to the transformation, and Fig. 8 clearly shows electron diffraction evidence for the icosahedral symmetry of T_2 in the high purity Al–Li–Cu alloy.

3.2. The Al–Li–Cu–Zr alloys

According to the only available isothermal section of

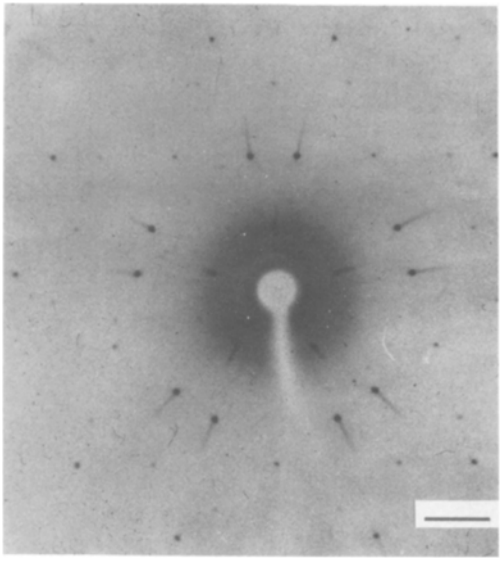

Figure 6 Upper level precession X-ray photograph of the T_2 fragment down the five-fold axis. $\bar{\mu}$ = 18.5° Mo$K\alpha$. Scale bar, 2.5 nm^{-1}.

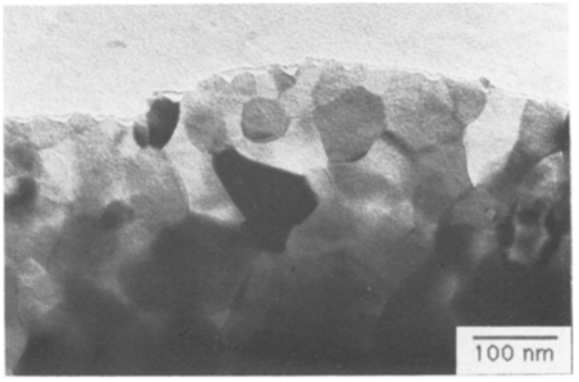

Figure 7 Bright field image of a transformed T_2 fragment which was obtained from the high purity Al–Li–Cu alloy. The transformation leads to a microcrystalline aggregate.

the ternary Al–Li–Cu phase diagram [11], T_2 should be in equilibrium with the α-matrix in alloys A and B at a temperature of 190° C.

Fig. 9a is a BF image of alloy A which had been aged, in the unstretched condition, at 190° C for 1 h. For this ageing time, T_2 is only observed at high angle grain boundaries (i.e., it may be termed a "grain boundary phase"); three such T_2 precipitates are arrowed in Fig. 9a. The other phases present in the alloy are $\delta'(Al_3Li)$, $\theta'(Al_2Cu)$, $T_1(Al_2CuLi)$ and $\beta'(Al_3Zr)$. Further details on the phases present and the microstructures developed are given by Tosten *et al.* [12, 13]. Fig. 9b is a CBED pattern of the T_2 precipitate marked B in Fig. 9a. The striking similarity between this pattern and that shown in Fig. 8 is evidence for the icosahedral symmetry of T_2 in an impure industrial alloy. Figs 9c and d are CBED patterns from the same precipitate particle, and display the two- and three-fold symmetry, respectively. In common with the X-ray photographs (Figs 2–4), the CBED patterns are characteristic of a phase which displays the point group symmetry $m\bar{3}\bar{5}$.

Fig. 10a is a BF image of a specimen (alloy A) which had been stretched by 2% and aged for 520 hours at 190° C. A single T_2 precipitate (at "A") is located on a sub-grain boundary. Fig. 10b is a CBED pattern of the T_2 precipitate shown in Fig. 10a; the five-fold symmetry is readily apparent.

Finally, Figs 11a and b are a BF image and a corresponding CBED pattern from alloy B. The five-fold symmetry displayed by Fig. 11b shows that the

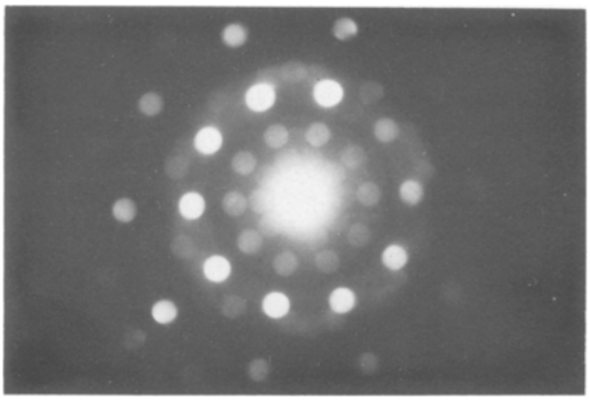

Figure 8 A CBED pattern from a T_2 fragment from the high purity Al–Li–Cu alloy. The five-fold symmetry is evident.

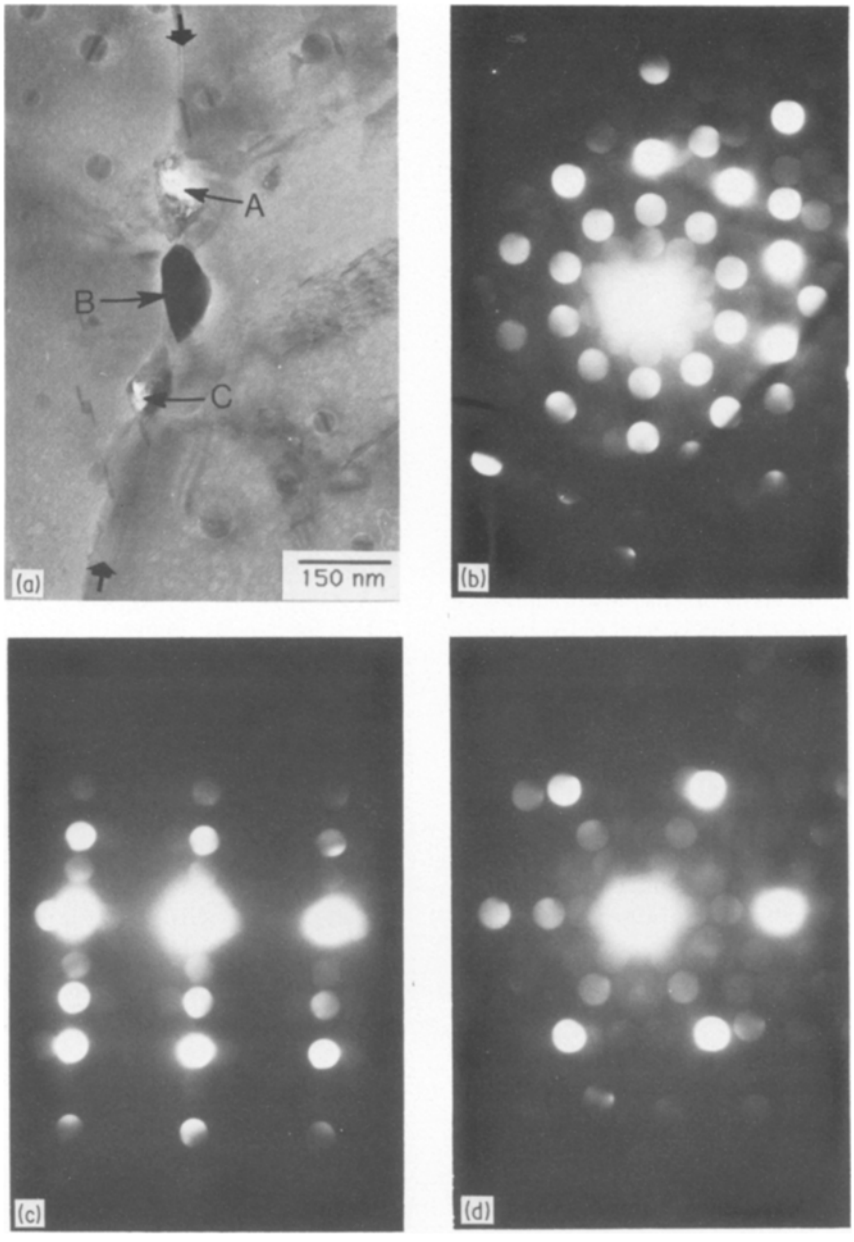

Figure 9 (a) Bright field image (alloy A — one hour ageing) of T_2 precipitates (A, B, C) on a high angle boundary (arrowed). The spherical features in the matrix are β' precipitates. (b–d) CBED patterns of precipitate B (Fig. 9a) which display (b) five-fold, (c) two-fold and (d) three-fold symmetry.

icosahedral nature of T_2 is a constant for all the dissimilar alloy chemistries and thermomechanical treatments employed in this investigation.

Some general comments concerning the transmission electron microscopy investigation are listed below.

1. In alloy B, it is possible that δ (which is also a grain boundary phase [14]) should also be in equilibrium

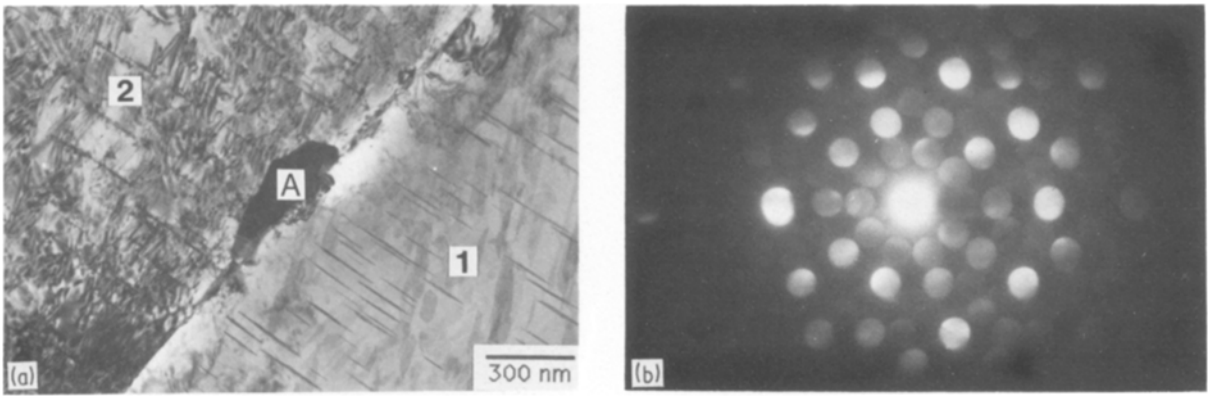

Figure 10 (a) Bright field image (alloy A, 520 h ageing) of a single T_2 precipitate (at "A") on a sub-grain boundary. The "linear features" observed in grain 1 are plate-like T_1 precipitates which are viewed edge-on. (b) A CBED pattern from the T_2 precipitate, again showing five-fold symmetry.

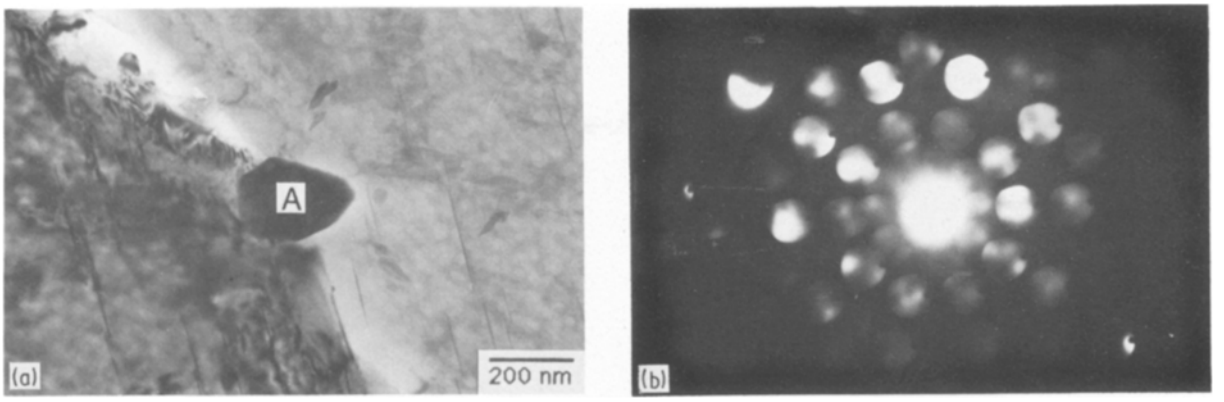

Figure 11 (a) Bright field image of alloy B after 50 h ageing. (b) A CBED pattern from the T_2 precipitate (at "A") shown in Fig. 11a.

with the α-matrix [11]. To date, no precipitates have been identified as δ. However, δ is highly reactive, which might explain its apparent absence. No evidence for the R phase has been obtained, although Cassada *et al.* [15] have suggested that the R phase is present in an alloy which contains approximately 2.5% Li and 2.5% Cu.

2. In many instances, grain boundary precipitates were microcrystalline and exhibited characteristics which were similar to those shown in Fig. 7. Indeed, the precipitates arrowed A and C in Fig. 9a are microcrystalline. It is tempting to suggest that these are T_2 precipitates which have "transformed" in a manner similar to that described in Section 3.1. The nature of these "microcrystalline precipitates" is currently being studied.

3. The CBED patterns show in Figs 8, 9b, 10 and 11b display ten-fold symmetry since only the zero order Laue zone is shown. However, when higher order Laue zone (HOLZ) rings were observed, they confirmed the five-fold symmetry. Fig. 12a is a low camera length CBED pattern of a T_2 precipitate and the five-fold symmetry displayed by the HOLZ ring is evident. Fig. 12b is the same CBED pattern but overexposed to delinate the Kossel–Mollenstedt lines which are associated with this "quasicrystalline" phase.

In view of the fact that there is some uncertainty surrounding the nature of a phase which does not appear to possess translational symmetry (see Section 4) an investigation has been initiated to study the structure of the T_2 phase using lattice imaging. Fig. 13 is such an image; five sets of lattice fringes (at angles of 72° to each other) are observed. This image is very similar to that presented by Ball and co-workers [5, 6].

4. Discussion

The X-ray photographs presented in Section 3.1. provide unequivocal evidence that T_2 displays icosahedral symmetry. These photographs, together with the CBED pattern in Fig. 8, can also be used to show that the grain boundary phase which is observed in alloys A and B (i.e., the alloys supplied by Alcoa) is indeed T_2 and that the icosahedral symmetry is maintained. This is consistent with the results of Sainfort *et al.* [7] for their Al–Li–Cu–Mg–Zr alloy. Owing to the great similarities between the CBED patterns and lattice images of the present investigation (Section 3.2.) and those of Ball and co-workers [5, 6] it seems a reasonable deduction that their icosahedral phase is also T_2.

The X-ray diffraction results are unique in that they demonstrate that icosahedral symmetry can be observed in macroscopic portions of materials. This indicates that the structural scheme responsible for this type of symmetry can extend over a much greater range than has been observed previously.

The observed icosahedral symmetry may be attributed to the existence of quasicrystallinity, a state of solid matter which is neither amorphous nor crystalline in the usual sense. Quasiperiodic structures exhibit long range bond orientation order, but not the translational symmetry ordinarily observed in three-

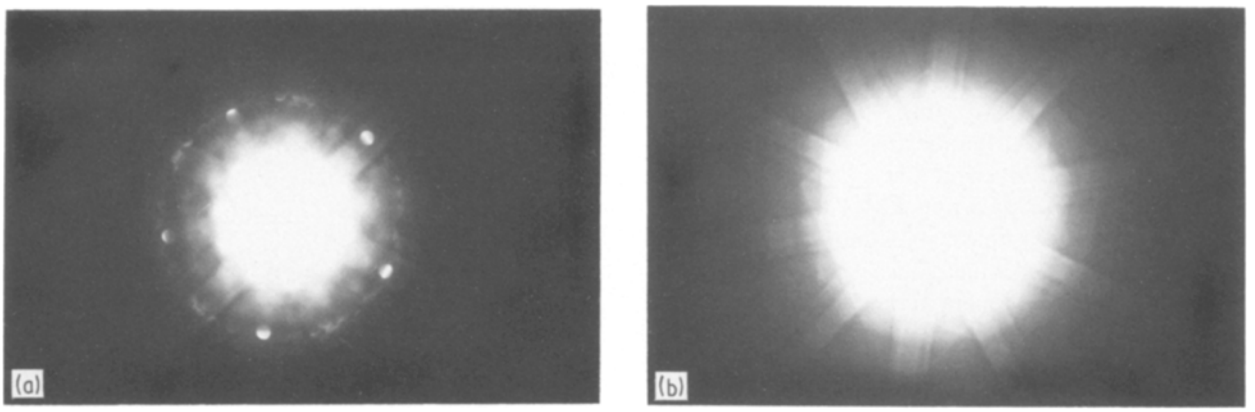

Figure 12 Low camera length CBED patterns from a T_2 precipitate (alloy A, 520 h ageing). (a) A higher order Laue zone which confirms the five-fold symmetry; (b) An overexposed pattern which shows the presence of Kossel–Mollenstedt lines.

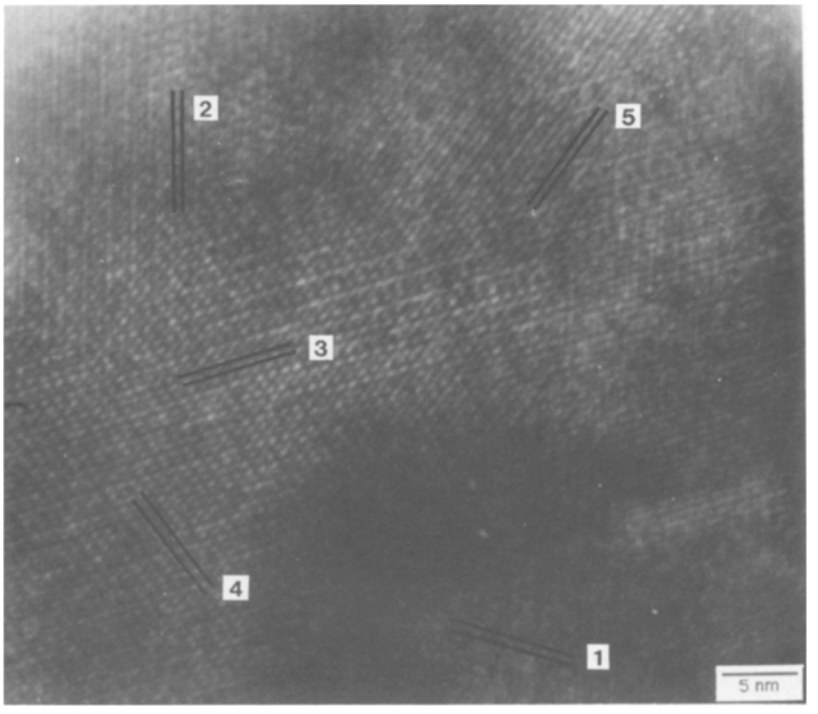

Figure 13 A lattice image of a T_2 precipitate. Five sets of lattice fringes are observed. (For discussion, see text.)

dimensional lattices. The diffraction patterns presented here closely resemble those obtained by computer calculations of patterns for quasicrystalline materials by, for example, Levine and Steinhardt [16]. The problem of their apparently incommensurate nature is resolved by indexing them through the use of a six-dimensional vector set now commonly used to describe quasilattices. A second approach to the description of structures which exhibit icosahedral symmetry is that of Pauling [17] and others, who proposed that that which is being called quasicrystallinity is just an extreme case of twinning (i.e., microtwinning). In reality, the microtwinning model suggested by Pauling might more aptly be described as a lineage structure, with the lineages stemming from a very small seed. Ball and Lloyd [5] interpreted their lattice images in terms of multiple twinning and their five-fold electron diffraction patterns in terms of both multiple twinning and double diffraction. The similarities between the lattice images obtained in the present study and those of Ball and Lloyd [5] might indicate that the multiple twinning model is valid. On the other hand, Lubensky *et al.* [18] have simulated lattice images for an icosahedral phase, and certain features of their simulated images are very similar to the lattice images obtained in this and other investigations. For example, they predict that "jags", which occur when one line of high density points stops and another parallel but displaced line begins, would be present. These jags are observed in the experimental lattice images such as that shown in Fig. 12. Hence, a clear distinction between quasicrystallinity and multiple-twinning for T_2 cannot be made at present.

One desirable component in the complete structural description of T_2 would be a determination of the positions of the atoms, and, as mentioned previously, such a study is in progress. The structural model being used is related to the structure of the R phase (Al_5CuLi_3) in this alloy system. The R phase exhibits the $Mg_{32}(Al, Zn)_{49}$ structure [19], a structure which is based upon the packing of Friauf polyhedra.

5. Conclusions

1. The X-ray diffraction patterns from "single-crystals" of T_2 provide unambiguous evidence that T_2 displays icosahedral symmetry.

2. The T_2 phase which is present in industrial Al–Li–Cu–Zr alloys also displays icosahedral symmetry.

3. Further work is required before it can be concluded that T_2 is either truly quasicrystalline or multiply-twinned (microcrystalline).

Acknowledgements

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