THE 4TH INTERNATIONAL CONFERENCE ON ALUMINUM ALLOYS

Al_5Li_3Cu (R) AND Al_6Li_3Cu (T2) PHASES: FROM PLANAR DEFECTS TO ICOSAHEDRAL ORDER

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Abstract

Transmission electron microscopy investigations of the crystalline R-Al_5Li_3Cu and quasicrystalline T2-Al_6Li_3Cu phases are here reported. The identification of the structural defects in the R-phase allows to interpret the electron diffraction patterns of the intermediate states found at the interface between the R and T2 phases. These results are used to propose an understanding of the deviations of the T2-phase from the icosahedral symmetry.

Introduction

In the field of quasicrystalline materials, the AlLiCu system remains famous as the first system in which it has been possible to prepare icosahedral quasicrystals by conventional casting (1). This quasicrystal has a composition close to Al_6Li_3Cu and is usually called the T2 phase. Because of its conventional elaboration, this phase was claimed to be a stable quasicrystal. Unfortunately, this discovery was not entirely satisfactory since the T2 phase shows small but numerous deviations to the icosahedral symmetry. Later on, perfect quasicrystals obtained in the AlCuFe and AlPdMn systems by conventional casting have clearly shown that quasicrystals are stable phases. It remains then to understand the nature of the T2 phase.

A natural approach of the problem is to compare the T2 phase with close crystalline phases. Such phases are called approximant phases: they are crystals with large parameter cell and a chemical composition very close to the quasicrystal one. As far as their structure is known their motives exhibit mostly icosahedral packing of atoms (for a general approach of approximant phases see references 2 and 3). There is such a phase in the vicinity of the T2 phase: the R-phase of composition Al_5Li_3Cu is a body-centered cubic crystal with a cell parameter 1.39 nm (4).

In order to understand the nature of the deviations of the T2 phase from icosahedral symmetry, we have undertaken a microstructural study of R-phase sample by means of

Organization of the planar defects

Another remarkable feature of the R-phase microstruture concerns the density of defects in the as-cast samples. Repeated observations show that this density is strongly variable. The spacing between π-boundaries might be of several hundred of nanometers (Figure 1) but might also become very small. In particular, some areas such as the ones indicated by arrows in Figure 1 exhibit a very high density of defects.

Diffraction patterns taken on such highly faulted area (Figure 2a) shows extra-spots along with the diffraction spots of the R-phase lattice spots. For clarity, a density map of the Figure 2a diffraction pattern is provided in Figure 2b. These extra-spots are encountered along any zone axis except the <111> zone axis. As exemplified by the extra-spots shown on the density map, all the extra-spots correspond to rational value of the R-phase spot indices. In other words they are related to planes of the R-phase. Since the area is characterized in image mode by a high density of defects, the extra-spots are interpreted as the consequence of the organization of the π-boundaries. This is confirmed by a detailed study of moderately to highly faulted areas encountered in the as-cast R-phase (9.).

The indexation of the extra-spots of Figure 2a provides the direction of the faulted planes. The faulted planes belong to following families: {1, 2, 3}, {2, 3, 5},{0, 2, 3},{2, 3, 3}. It is worth noting that in highly faulted area, owing to the defect organization, it is possible to know with accuracy the faulted planes.

Amazingly, some of these plane directions are related to the icosahedral shape. This fact is obvious on the sequence of plane indices: 1, 2, 3 and 2, 3, 5 belong to the Fibonacci sequence. In other words, such directions are close to the 2-fold axes of an icosahedron. Consequently the faulted planes are almost parallel to the facets of a triacontahedron, a polyhedron characterized by the icosahedral symmetry.

Owing to this information, the R-phase microstructure can be described as a network of π-boundaries separating crystalline polyhedral domains, the shape of the domains being related to the icosahedral symmetry.

The diffraction pattern shown in Figure 2a has been recorded along the <023> zone axis. Though all the spots in this pattern can be indexed with R-phase cubic system, it should be noted that this pattern has a strong resemblance with a 5-fold diffraction pattern. It stems then quite naturally that the highly faulted R-phase areas differ from an icosahedral quasicrystalline structure only by an incommensurate modulation. This point is going to be developed owing to samples exhibiting the coexistence of R and T2 phases.

Mechanism of transformation of R-phase in T2-phase

A R/T2 transformation similar to the one suggested by the previous works has been provided by samples elaborated during a work devoted to growth of the T2 phase. The thermal treatment required to elaborate these samples has been made according to a dedicated procedure realizing Lithium confinement at high temperature (10.).

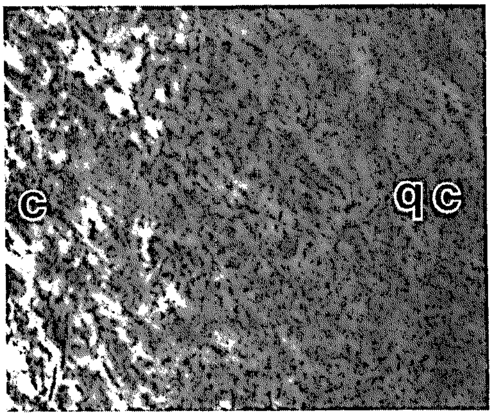
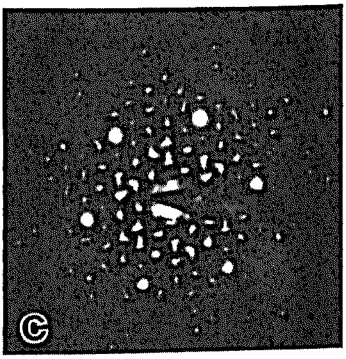


Figure 3: Interfacial area between the R-phase (c) and the T2-phase (qc).



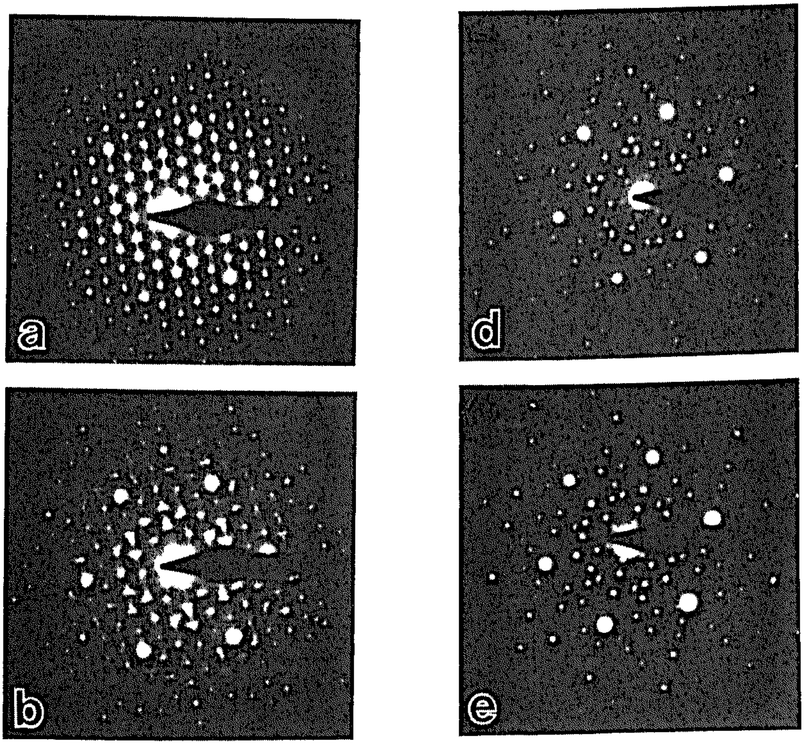


Figure 4a, b, c, d, e : The R-phase <111> zone axis transforms in a icosahedral 3-fold axis

Obtaining interface between R and T2 phases

The starting material was a small cylinder (Ø=1cm, 2 cm long) cut from a 900 cm3 ingot (average composition: Al6.4Cu0.9Li2.7) obtained by conventional casting under an Argon atmosphere of pure Al, Li and AU70 alloy (Al-Cu70wt%) at the Péchiney Research Centre. The initial alloy contains submillimetric T2 dendrites along with the T2+Al and Al2LiCu(T1)+Al eutectics. But, because of the ingot average composition, after remelting, the R-phase solidifies first. Remelting achieved at a 640°C temperature is followed by slow solidification. The sample is lifted through a temperature gradient of 40°C/cm at a rate of 3 cm/24 h (cooling rate 5°C/h) until complete solidification.

Opposite to as-cast R-phase samples, the initial melt composition is here close to the peritectic point: Liq+R -> T2+ δ-AlLi. As-cast samples consist in primary R-phase surrounded by the T1+Al eutectic, without occurrence of the T2 phase. The present sample solidification path is quite different from the conventional one. Optical microscopy reveals millimetric R-phase primary grains surrounded, first, by a T2 layer then by the T2 + Al and T1+Al eutectics. TEM investigations undertaken on these samples allow to examine the interface between the R and T2 phase. The crystalline area (indicated by c on Figure 3) is characterized by a large density of planar defects. These defects are responsible for a contrast very similar to the one of the quasicrystal (area indicated by qc on Figure 3). The interface is not sharp but displays intermediate states of organization as evidenced by series of diffraction patterns.

Figure 4 and 5 gives the sequences of electron diffraction patterns (EDPs) taken in successive zones from the crystalline phase to the quasicrystalline one (diameter of the selected area aperture: Ø = 0.2 micron). These EPDs show that the <111> and the <023> cube directions transform respectively in 3-fold and 5-fold icosahedral axes.

Electron diffraction patterns analysis

Analysis of these EDPs has been made possible owing to the work on the as-cast R-phase reported above. However, EDPs are very complex and a detailed analysis cannot be made here (for a full explanation see 11.). Figure 4a corresponds to the <111> zone axis pattern of the R-phase crystal. The extra-spots on the 3-fold axis EDPs (Fig. 4b) are due to a high density of planar defects whose directions are close to 2-fold icosahedral axes. Further on, the crystalline lattice is upset by the defect ordering as shown by the loss of intensity of the cubic lattice diffraction spots (Fig. 4c). Finally, a quasicrystal diffraction pattern (Fig. 4e) is obtained by selection of some diffraction spots in the previous diffraction pattern (Fig. 4d).

EDPs taken along a <023> zone axis show similar effects. First, an organized defect network is generating extra-spots (Fig.5a). Afterwards aperiodic spots appearing along the [001] reciprocal row (Figure 5b) achieve the transformation into a 5-fold axis (Fig. 5c). This aperiodic effect corresponds to the anomalous spot selection noticed in the 3-fold axis diffraction pattern (Figure 4d).

Both sequences of EDPs indicate that the transformation involves high density of planar defects. The defect organization which is, at once, crystalline upsets the cubic crystal lattice

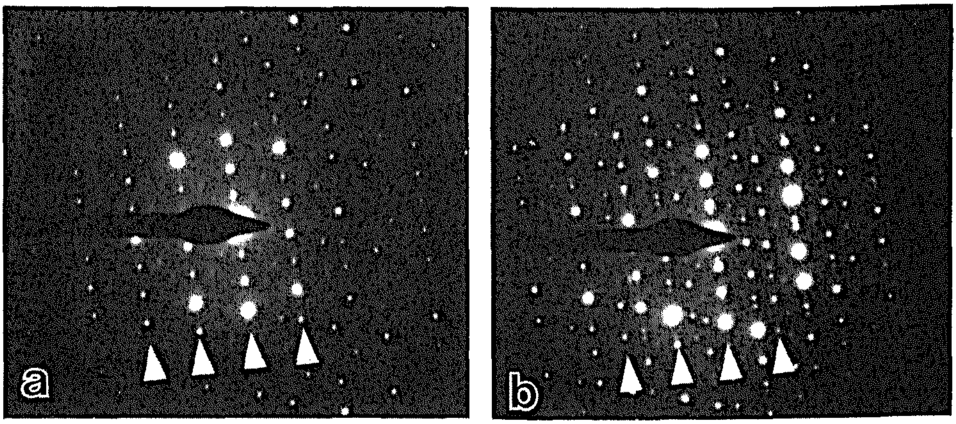
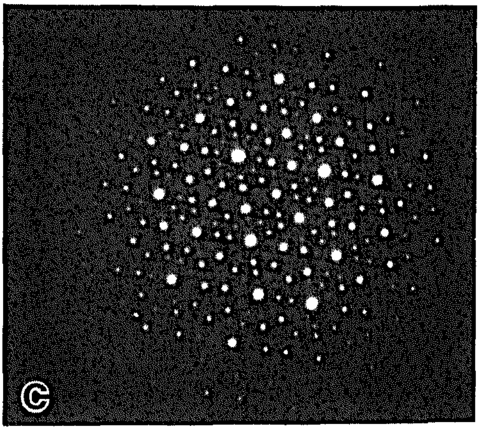


Figure 5a, b, c: Transformation of the R-phase <023> zone axis (Fig.5a) in an icosahedral phase 5-fold axis (Fig.5b). Notice the aperiodical extra-spots that appear in Fig. 3b along the diffraction rows indicated by arrows.



and finally becomes non-crystallographic. A comparison with the observations on as-cast R-phase samples shows that the pseudo-5 fold axis in Figure 2 corresponds to the beginning of the R-T2 phase transformation.

The present mechanism suggests that the transformation in T2-phase is continuous. Consequently it should be expected that sometimes the transformation is not fully achieved. In that case, there will be reminiscence of the cubic phase. This interpretation provides an understanding for the non-equivalence of the five diffraction rows on a 5-fold T2-phase diffraction pattern (12.).

Conclusion

The detailed study of the approximant R-phase provides new information in order to understand the nature of the T2-phase. The planar defects of the R-phase, which are identified as π-boundaries, have a key role in the transformation in T2-phase. They act as mediator of the transformation to a non-crystalline order. Regarding the nature of the T2-phase, the present work indicates that the T2 phase results from a non-crystallographic organization. However, as the transformation involved a sequence of very close states, deviations to icosahedral symmetry are expected. It means that obtaining perfect T2 phase icosahedral is certainly possible but requires a dedicated procedure.

Acknowledgments: The author is grateful to the Péchiney Research Centre for providing the as-cast R-phase sample

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