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Growth morphology of single-crystal grains obtained by directional crystallization of an Al-Cu-Fe alloy

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Abstract

Quasicrystalline as well as crystalline faceted single grains of four phases have been obtained during directional crystallization of an Al-Cu-Fe alloy by the Bridgman technique. The monoclinic λ phase $\text{Al}_{13}(\text{Cu,Fe})_4$ dominating at high temperatures formed single-crystal lamellas 0.5mm to 1mm thick. The second type of attractive morphological forms exhibiting flux dissolution terraces has been observed on spherical single crystals of β phase $\text{Al}(\text{Fe,Cu})$. Rectangular, hexagonal and octagonal shape of dissolution terraces can be seen in the positions of two-, three- and four-fold symmetry axes, respectively. Single quasicrystalline ψ phase $\text{Al}_6\text{Cu}_2\text{Fe}$ exhibited the icosahedral symmetry with growth forms of a dodecahedron with pentagonal facets. The flux dissolution of β phase plays apparently an essential role in a peritectic reaction leading to quasicrystalline ψ phase formation. Polygonal single grains of ω phase $\text{Al}_7\text{Cu}_2\text{Fe}$ exhibiting the tetragonal symmetry formed the fourth type of thermodynamically stable growth forms. Single grains of the ω phase crystallized in a form of pellets with an octagonal cross-section. The growth morphology of stable phases has been investigated by the scanning electron microscopy. The chemical composition of the growth forms described has been confirmed by the X-ray microanalysis using a scanning electron microscope whereas the phase composition has been determined by the electron selected area diffraction and X-ray powder diffraction.

Keywords: phases in Al-Cu-Fe system, quasicrystal growth morphology, flux dissolution.

§ 1. Introduction

Investigations of the phase composition of Al-Cu-Fe system lead to working out reliable and detailed phase diagrams [1-6] defining conditions for crystallization of the quasicrystalline icosahedral stable phase. Rapid solidification as well as normal casting process of the alloy combined with thermal annealing and subsequent quenching were commonly used [7-12]. The icosahedral ψ phase $\text{Al}_6\text{Cu}_2\text{Fe}$ has common equilibrium phase fields with three phases at 800 °C (β , λ and liquid), at 700-720 °C the equilibrium field covers four phases (β , λ , ω and liquid) and at 680 °C the ψ phase is in equilibrium with β , λ and ω phases [2]. At 680 °C the perfectly stable icosahedral quasicrystalline ψ phase occurs in the range of compositional triangle $\text{Al}_{62.4}\text{Cu}_{24.4}\text{Fe}_{13.2}$, $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$ and $\text{Al}_{61}\text{Cu}_{28.4}\text{Fe}_{10.6}$ [5]. The β phase $\text{Al}(\text{Cu,Fe})$ (Pm3m space group) has a CsCl type structure, the monoclinic dominant λ phase $\text{Al}_{13}(\text{Cu,Fe})_4$ is described by C2/m space group and the ω phase $\text{Al}_7\text{Cu}_2\text{Fe}$ (P4/mnc space group) exhibits the tetragonal symmetry. The structural characteristic of the phases has been reported earlier by Liu and Köster [13] and by Gigla et al. [14].

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Millimetre sizes of Al-Cu-Fe alloy icosahedral single grains have been obtained by annealing at 1095 K for a few dozen hours and followed by immediate quenching carried out by Ishimasa and Mori [8]. Large single grains of the quasicrystalline icosahedral Al-Cu-Fe ψ phase have been prepared by multiple cyclic heat treatments by Lograsso and Danley [12].

The most evident form of thermodynamically stable process of quasicrystals crystallization was confirmed by the polyhedral faceted growth morphology. The flux growth technique was successfully applied by Fisher et al. [15] for growth of faceted large single-grain quasicrystals from high-temperature metallic solutions. The authors used decanting technique to grow icosahedral quasicrystals of single grain alloys of Ho-Mg-Zn, Al-Pd-Mn and Al-Ga-Pd-Mn exhibiting the dodecahedral morphology as well as for the growth of decagonal Al-Ni-Co and Al-Pd-Mn approximate single grains distinguished by decaprismatic columns (ten prism faces with the 10-fold axis as the rotation axis).

The paper reports on the growth equilibrium morphology of both quasicrystalline as well as periodic phases obtained during a directional crystallization of an Al-Cu-Fe alloy for a chemical composition close to the above mentioned compositional triangle of the ψ phase occurrence. The phases crystallized as polygonal single crystals. A single-grain morphology of four phases crystallized in the same ingot will be described: a monoclinic dominant λ phase, belonging to the cubic system β phase, quasicrystalline phase ψ and periodic phase ω with tetragonal symmetry. In the case of β phase the flux dissolution morphology is described.

§ 2. Experimental

Polyhedral equilibrium phases were formed in ingots of an Al-Cu-Fe alloy, for which the nominal composition was 65 at. % Al, 20 at.% Cu and 15 at.% Fe. The ingots of total mass of approximately 40 g, 15 mm in diameter and 60 mm high, were sharpened at the bottom. The specimens were synthesized in a helium atmosphere inside alumina crucibles starting from 99.997% pure Al, 99.9% pure Cu and 99.98 % Fe using the Bridgman-Czochralski-Growth (BCG) apparatus equipped with an induction furnace. The initial temperature of the melt was increased up to 1550 °C and the crystallization rate during Bridgman directional crystallization was 6 mm/h resulting in an approximate cooling rate of 1.3 °C/min. Single crystal grains have crystallized in the melt or were subject to the flux dissolution until the melt has been removed by the solidification shrinkage. In our experiment the samples were not quenched in order to prevent a structural transformation from the icosahedral phase to non-icosahedral approximate structure. The ingot was crushed into several pieces and different growth forms previously closed inside cavities and pores were subject to the investigation of growth morphology by the scanning electron microscopy (SEM) using primary and secondary electrons. The selected area diffraction (SAD) as well as X-ray powder diffraction confirmed the phase identification of the predicted phase composition in the Al-Cu-Fe system. Positions of X-ray diffraction lines were recalculated into interplanar distances.

§ 3. Results

Four faceted morphology forms have been found inside cavities: monoclinic λ phase grown in a shape of lamellas with a rhomboidal cross section, terraced forms of icosahedral β phase revealing symmetry elements, dodecahedrons with pentagonal facets of icosahedral ψ phase and octagonal pellets of ω phase.

3.1. Growth morphology of the λ phase

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3 The first type of faceted single crystals was formed inside the ingot by the dominant
4 monoclinic λ phase $\text{Al}_{13}(\text{Cu,Fe})_4$ (C2/m space group). Growth morphology forms observed
5 inside cavities revealed lamellas up to 50 μm thick, terminated by smooth (010) crystal facets
6 in a shape of rhombi (Fig. (1)). A fragment of lamella is also seen in the lower part of Fig. 2.
7 The characteristic angle $\beta = 108^\circ$ for the monoclinic λ phase structure is marked in Fig. 1.
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10 3.2. Flux dissolution morphology of the β phase

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12 The second type of attractive morphological forms observed inside shrinkage cavities were
13 spherical single grains of β phase $\text{Al}(\text{Fe,Cu})$ (Pm3m space group, $a = 0.29076$ nm) [14]. The
14 solidified colonies of droplets of β phase exhibit apparently flux dissolution terraces (Fig. 2).
15 Positions of threefold symmetry axes have the same orientation in all spherical single grains
16 (Fig. 2). Rectangular, hexagonal and octagonal shape of the dissolution terraces can be seen in
17 the positions of two-, three- and four-fold symmetry axes, respectively (Fig 3 (a) and (b)).
18 Therefore flat steps of terraces are parallel to $\{110\}$, $\{111\}$ and $\{100\}$ crystallographic planes,
19 respectively. Spatial positions of symmetry elements observed on droplets of the β phase
20 correspond to the distribution of symmetry elements in the cube (Fig. 3). The flux dissolution
21 of the surface of β phase revealed (111) planes inclined to the surface (Fig. 4) as well as
22 terraced hollows with an amphitheatric architecture (marked as A in Fig. 4). The width of
23 terraces extends up to 12 μm whereas the height of terrace steps is less than 1 μm . Single
24 crystal droplets of the β phase existed at the very initial stage of flux dissolution (Fig. 5).
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29 3.3. Morphology of Al-Cu-Fe single quasicrystals

30 Single quasicrystals of ψ phase $\text{Al}_6\text{Cu}_2\text{Fe}$ exhibited the icosahedral symmetry with
31 dodecahedral growth forms – 12 faces perpendicular to the 5-fold axes (Fig. 6). The
32 symmetry was confirmed by the electron diffraction (see the insert in Fig. 6a). The
33 dodecahedra have irregularities and different dimensions of edges extending up to 160 μm .
34 The faces of dodecahedra are not perfectly smooth and emerge from the residual flux (Fig. 6
35 (b)).
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38 3.4. Growth forms of the ω phase

39 Polygonal single grains of ω phase $\text{Al}_7\text{Cu}_2\text{Fe}$ (P4/mnc, $a = 0.6336$ nm, $c = 1.482$ nm)
40 exhibiting tetragonal symmetry form randomly distributed pellets between terraced growth
41 forms of the β phase (Fig. 7). In general the surfaces of pellets are not smooth, however an
42 octagonal cross section can be observed (the insert in Fig. 7). The pellets exhibit eight lateral
43 facets, four of $\{100\}$ type and four between them of $\{110\}$ type. The tetragonal prisms are
44 about 50 μm in diameter and 60 μm high.
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48 3.5. Phase identification

49 The selected area diffraction (e.g. inserts in Fig. 1 and Fig. 6 (a)) and X-ray powder
50 diffraction confirmed the inherence of all phases described above. Positions of X-ray
51 diffraction lines were recalculated into interplanar distances. The lattice parameter of the β
52 phase was determined as $a = 0.29076$ nm, for the λ phase $a = 1.5849$ nm, $b = 0.8083$ nm and
53 $c = 1.2476$ nm, $\beta = 107.7^\circ$ and for the ω phase $a = 0.6336$ and $c = 1.482$ nm.
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56 § 4. Discussion and conclusion

57 Faceted single crystals of three crystalline phases: monoclinic λ , cubic β and tetragonal ω
58 surround the polygonal single units of quasicrystalline phase ψ . The melting point of the λ
59 and β phase is above 1100 $^\circ\text{C}$. Both ψ and ω phase are formed during peritectic reactions in
60 the temperature range 700 – 872 $^\circ\text{C}$ and 700 – 740 $^\circ\text{C}$, respectively [16]. Therefore four

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3 phases can coexist in the overlapping temperature area of 700 – 740 °C. In our experiment the
4 overheating of the melt directly before the directional crystallization was a favourable factor
5 for pores and cavities formation – the melt temperature was increased up to 1550 °C. Gas
6 bubbles as well the material shrinkage during cooling provided a helpful micro-space for the
7 morphology visualization of single crystal units after the ingot crushing.
8

9 The main result of the paper is related to the flux dissolution of the high temperature β
10 phase which apparently provides necessary material for peritectic formation of
11 quasicrystalline phase ψ . We assume that solid droplets of the β phase, formed primary by the
12 surface tension of liquid in a space of a bubble or shrinkage, may have a significant
13 contribution during the flux dissolution (Fig. 4 and 5) to the peritectic reaction $\beta + \lambda + L \rightarrow \psi$
14 identified e.g. by Lograsso and Delaney [12]. The β phase consumption by dissolution was
15 confirmed during investigations of phase transformations of AlCuFe alloys performed by
16 Zhang et al. [10]. An attractive flux dissolution morphology of cubic β phase confirms a high
17 structural perfection of the primary crystallized droplet-like single crystals. Note that all ten
18 arrowed threefold axes (Fig. 4) have the same spatial orientation, therefore all the colony of
19 droplets forms apparently one single crystal. The flux dissolution morphology of the β phase
20 reveals three kinds of crystallographic planes $\{111\}$, $\{100\}$ and $\{110\}$. The flux dissolution of
21 β phase droplets follows from chemical potential differences between the melt and the solid
22 phase.
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26 The tetragonal ω phase was formed in the smallest amount in the ingot apparently by
27 an analogous peritectic reaction $\lambda + L \rightarrow \omega$ [17].

28 The quasicrystals of face centred icosahedral Al-Cu-Fe grow with dodecahedral
29 morphology exhibiting 12 faces perpendicular to the 5-fold axes. Some of as grown facets
30 were decorated in a similar way as fivefold facets of Al-Pd-Mn quasicrystals found by Beeli
31 and Nissen [18]. The results concerning the decorations will be published elsewhere.
32

33 The shape of different observed single grains confirms our SAD and X-ray powder
34 diffraction phase identification. The four phases detected indicate that sample was not in a
35 thermodynamic equilibrium. However, the observed stable growth forms can be explained in
36 relation to Scheil-Gulliver approach of non-equilibrium process of solidification. This
37 approach approximates a non-equilibrium solidification by assuming a local equilibrium of
38 the advancing solidification front at the solid-liquid interface [19].
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20 Figure captions (Caution: major reduction of pictures size on Fig. 2 – Fig. 5 will make photos
21 useless)
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23 Fig. 1. Morphology of single crystal monoclinic λ phase; visible rhombi are (010) planes.
24 Characteristic angle $\beta = 108^\circ$ is marked. Inserts: the selected area diffraction pattern and a
25 fragment of single lamella of λ phase.
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28 Fig. 2. Single crystal droplets of the β phase Al(Fe,Cu). Arrows show positions of threefold
29 symmetry axes revealed apparently by the flux dissolution.
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32 Fig 3. Spatial positions of 2-, 3- and 4-fold symmetry axes revealed on terraced single crystal
33 droplets of the β phase.
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35 Fig. 4. Flux dissolution morphology of the surface of the β phase; terraces are formed by
36 (111) crystallographic planes which are inclined to the surface. A – a hollow with an
37 amphitheatric architecture.
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40 Fig. 5. Flux dissolution initiation of terraces on spherical droplets of the β phase.
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42 Fig. 6. Pentagonal dodecahedra of quasicrystalline ψ phase Al₆Cu₂Fe. (a) Pentagonal faces of
43 a single grain. (b) Solidified residual flux covering dodecahedra. Insert in (a) shows an
44 electron diffraction pattern of icosahedral ψ phase.
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47 Fig. 7. Randomly distributed pellets of the ω phase Al₇Cu₂Fe between terraced growth forms
48 of the β phase. The insert reveals octagonal cross section of a single pellet.
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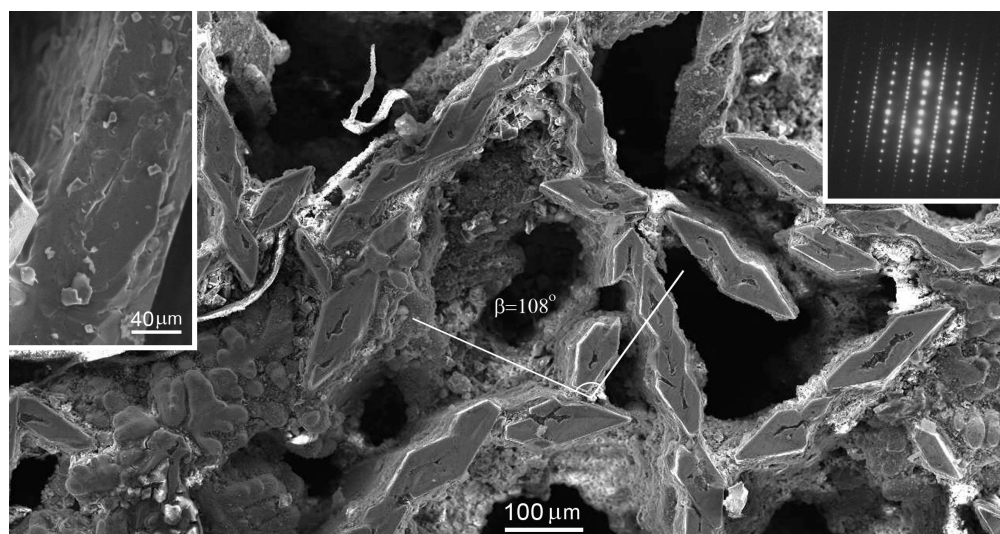


Fig.1. Morphology of single crystal monoclinic λ phase; visible rhombi are (010) planes. Characteristic angle $\beta = 108^\circ$ is marked. Inserts: the selected area diffraction pattern and a fragment of single lamella of λ phase.
199x105mm (300 x 300 DPI)

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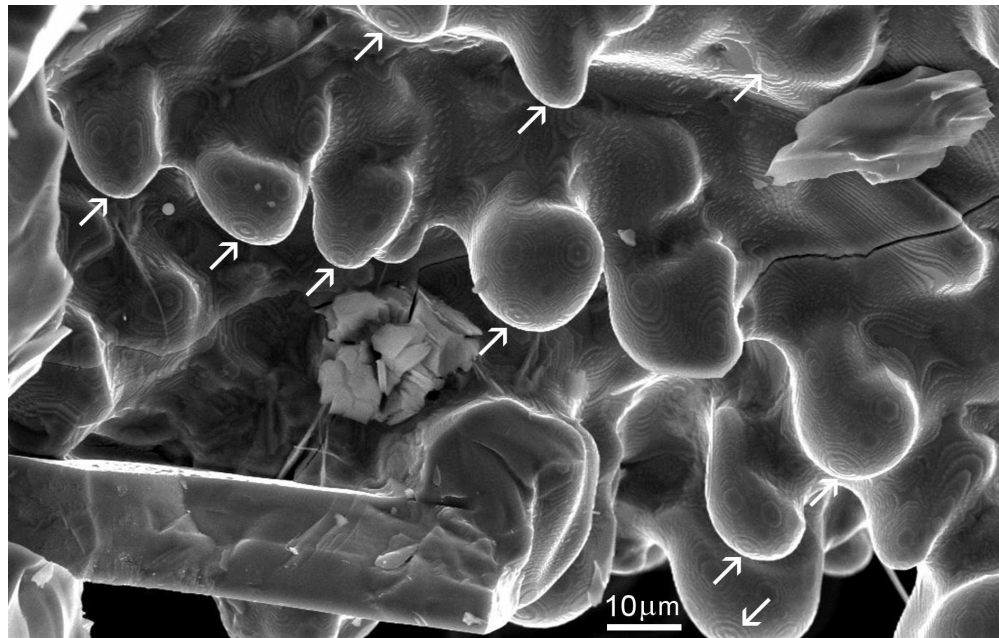


Fig. 2. Single crystal droplets of the β phase Al(Fe,Cu). Arrows show positions of threefold symmetry axes revealed apparently by the flux dissolution.
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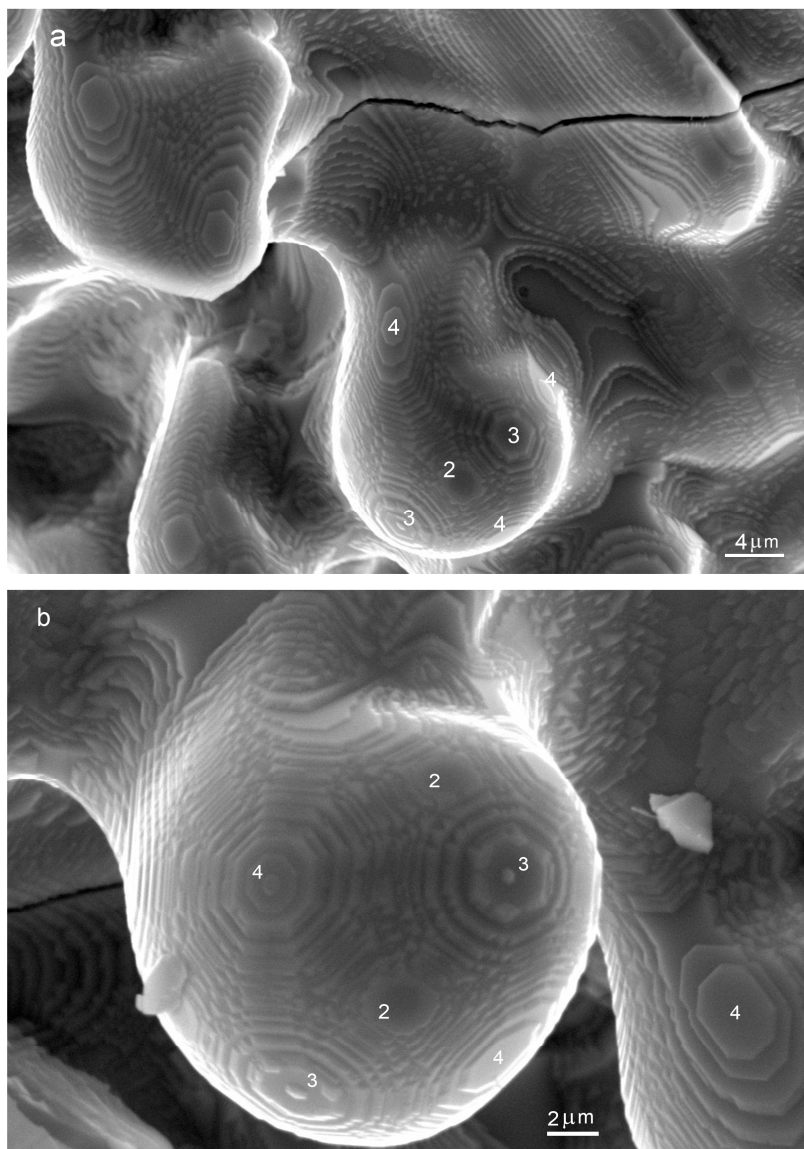


Fig. 3. Spatial positions of 2-, 3- and 4-fold symmetry axes revealed on terraced single crystal droplets of the β phase.
209x297mm (300 x 300 DPI)

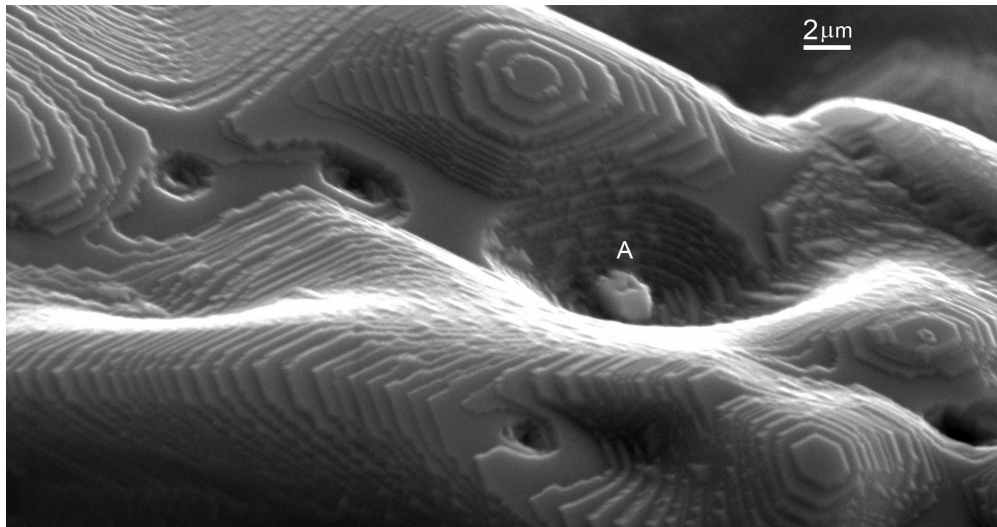


Fig. 4. Flux dissolution morphology of the surface of the β phase; terraces are formed by (111) crystallographic planes which are inclined to the surface. A – a hollow with an amphitheatric architecture.

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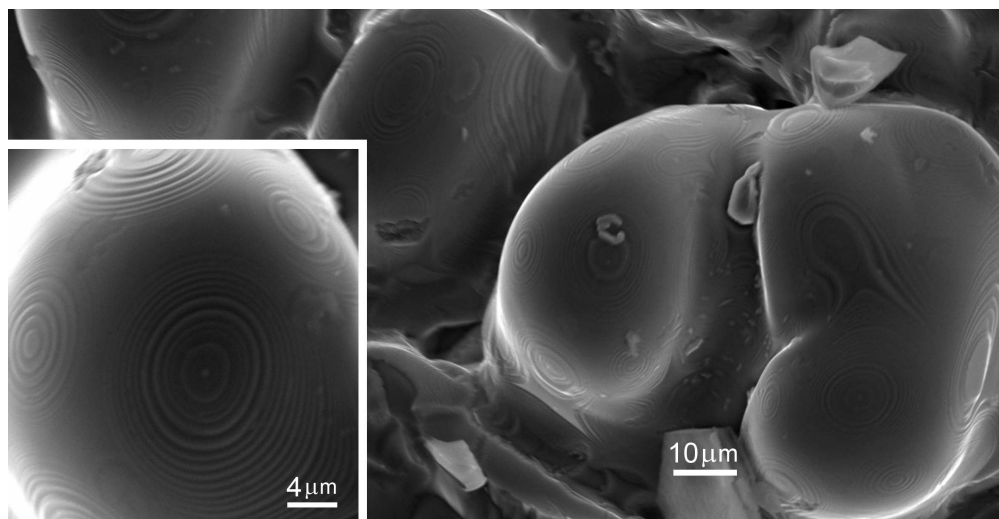


Fig. 5. Flux dissolution initiation of terraces on spherical droplets of the β phase.
199x102mm (300 x 300 DPI)

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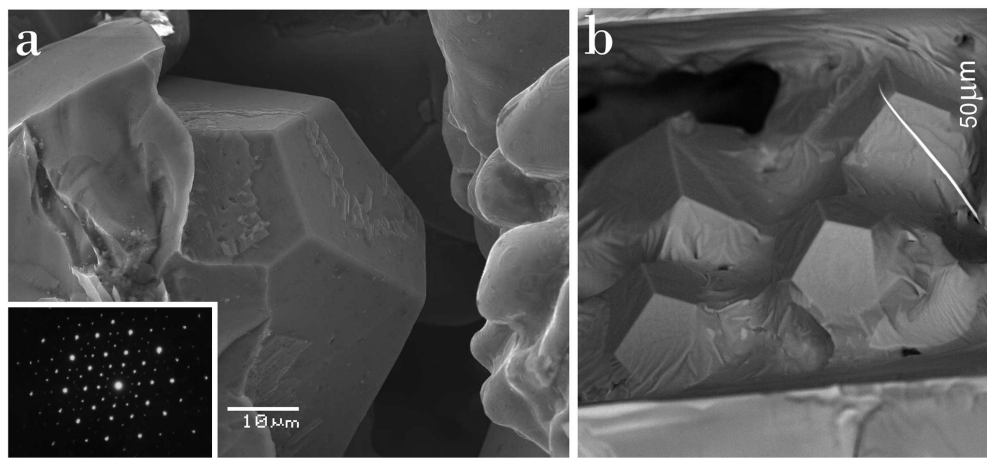


Fig. 6. Pentagonal dodecahedra of quasicrystalline ψ phase $\text{Al}_6\text{Cu}_2\text{Fe}$. (a) Pentagonal faces of a single grain. (b) Solidified residual flux covering dodecahedra. Insert in (a) shows an electron diffraction pattern of icosahedral ψ phase.
199x91mm (300 x 300 DPI)

Review Only

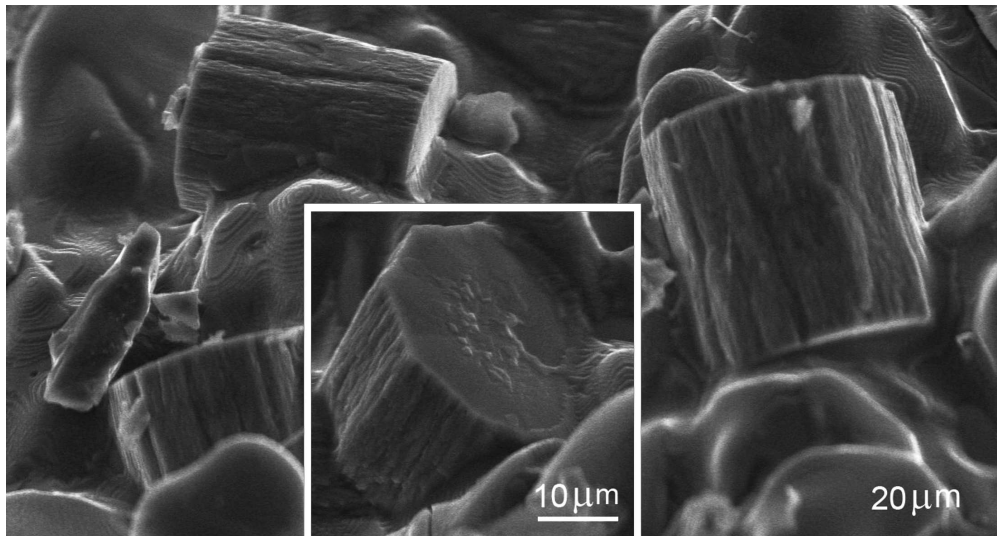


Fig. 7. Randomly distributed pellets of the ω phase $\text{Al}_7\text{Cu}_2\text{Fe}$ between terraced growth forms of the β phase. The insert reveals octagonal cross section of a single pellet.
187x99mm (300 x 300 DPI)