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***In situ* study of the quasicrystal growth by synchrotron X-ray imaging**

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ABSTRACT

One of the main challenges of the quasicrystal science is to elucidate how the quasiperiodic order can extend so far, i.e. up to several centimeters according to the size of the single grains of various alloys routinely grown nowadays [1, 2, 3]. Noticing that most of the present knowledge on the growth of quasicrystal grains has been collected after their cooling at room temperature, we have carried out the first *in situ* and real time observation of this peculiar process which has clearly disclosed both, the shape of the growing interface and its defective state. Therefore we have studied the solidification of an AlPdMn alloy giving quasicrystal grains by synchrotron X-ray imaging, combining thereby the radiography and X-ray topography techniques. Radiography allowed us to clearly evidence a faceted growth proceeding by lateral motion of ledges at the solid-melt interface and controlled by the interface kinetics rather than by the local heat flow as widely thought. Thus a realistic estimate of the kinetic coefficient was deduced from the solid-melt interface undercooling which indicates that the quasicrystal growth is more likely comparable to both semiconductor and oxide growths than to pure metal growth. The X-ray topographs recorded simultaneously with radiographs, revealed that a lot of strains and defects are generated in the quasicrystal grains during their growth, which could be related to the growth process itself and very informative on the origin of the stability of the quasicrystal lattice.

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1. Introduction:

How the quasiperiodic order can extend up to the several centimetre size, reached by the single grains of various alloys routinely grown nowadays [1, 2, 3], remains a mystery. Thus, whether these peculiar solids have to follow local rules during their growth [4], or need long-range atomic correlations to form their stable structures [5] is still undetermined. Because they lack translation symmetry, it seems impossible that quasicrystals can be obtained, like crystals, by an attachment of single atoms, repeating unit cells and generating thereby a network. However, as icosahedral clusters have been identified recently in undercooled intermetallic liquids [6], the old idea of an aggregation of these clusters during the liquid-solid transition [7], which could be the basis of both the nucleation and the growth mechanisms of the quasicrystalline structure, is reviving. Besides, as quasicrystal grains often display, after growth, facets perpendicular to the symmetry axes (5, 3, 2 for icosahedral quasicrystals) it has also been suggested, from room temperature observations, that quasicrystals could grow by a forward movement of facets swept by terraces and steps [8], the latter being predicted as abnormally high by theory [9]. But this is conflicting with Shroers et al. conclusions [10] since they interpreted the results they obtained, from their low resolution observation of the growth of quasicrystalline phases from undercooled melt, within the current theories of dendritic growth. Accordingly, whether the quasicrystal growth has a faceted character or a dendritic one remains controversial. Just as the necessity this growth has to incorporate defects in order to ensure the stability of the quasicrystal lattice, which set supporters of the energy influence [11] against those of the entropy effect [12].

To address this problem, we have performed, by combining synchrotron X-ray radiography and X-ray topography techniques, the first *in situ* and real time observation of the growth of quasicrystals which has both disclosed clearly the shape of the solid-melt interface and given information on strain and defects generated in the growing grains. The results we acquired confirmed the faceted character of the quasicrystal growth and revealed that this growth is accompanied by a lot of strains and defects which could be related to the growth process.

2. Experiments:

Synchrotron X-ray radiography and X-ray topography experiments were carried out at the ID 19 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Both techniques were combined using the polychromatic incident beam delivered by a wiggler source. Synchrotron White Beam X-Ray Topographs (SWBXRT) were recorded discontinuously on High Resolution films after the incident beam has crossed the sample solidifying in a graphite crucible. Synchrotron X-Ray Radiographs (SXRR) were obtained simultaneously, in the live mode, using a CCD camera [13] oriented toward the incident beam, which was monochromatized and thereby deviated parallelly after crossing the solidifying sample. This combination based on a polychromatic incident beam had the advantage to allow recording several X-ray topographs of good quality, at once, but offered only poor resolution radiographs because these were acquired from a beam monochromatized after crossing the solidifying samples. In order to get radiographs of better quality, displaying sharper absorption and phase contrasts, we carried out, in addition, *in situ* synchrotron X-ray radiography experiments only, using an incident beam monochromatized before striking the solidifying samples.

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3 The solidification set-up based on the Bridgman technique and allowing to control
4 both the pulling velocity and the temperature gradient (unidirectional solidification) was
5 previously described in [14].
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7 Five Al-Pd-Mn samples (flat polygrained sheets 700 μm thick) prepared at the
8 composition $\text{Al}_{72.4}\text{Pd}_{20.5}\text{Mn}_{7.1}$ known to grow easily icosahedral quasicrystal grain [1] were
9 firstly melted then solidified at various pulling rates (0.4 – 3.6 $\mu\text{m/s}$) under the same
10 temperature gradient of 35 K/cm.
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12 13 14 **3. Results:**

15 16 **3.1. Facetted grains:**

17 It can be seen in synchrotron X-ray radiographs, recorded *in situ* during the
18 solidification of the five investigated Al-Pd-Mn samples, that all quasicrystal grains remained
19 distinctly facetted all along their growth. Figure 1 shows three stages of the growth of two
20 grains in one of the five samples. Figure 1a corresponds to the end of the growth sequence
21 with a pulling rate of 0.4 $\mu\text{m/s}$. The interface between the liquid and the two grains exhibits a
22 cusp at the level of the grain boundary. Two facets are merely visible on grain 1 and three on
23 grain 2. During the growth of grains, some facets disappeared and new ones appeared. In both
24 cases the inclination of moving facets varied continuously. Therefore it was difficult to
25 measure the velocity of each individual facet (along their normal direction), which often
26 forced us to estimate it from the displacement of edges of projections of the facets on
27 radiographs (radiograph images are orthogonal projections of samples features along the
28 incident beam). On average this velocity was close to the applied pulling rate.
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31 As soon as we increased substantially the pulling rate (about three times) the
32 solidification front moved back to the coolest part of the furnace (Figure 1b) while new
33 facetted grains were nucleated in the liquid just above the solid-melt interface (Figure 1b, c)
34 and transverse striations developed on facets. At the same time, the velocity of the former
35 growing grain increased up to the value of the new pulling rate ((Figure 2) unless they meet
36 newly nucleated grains. In this case the growth velocities of all grains (former and new)
37 started decreasing and fell down to zero when impingement occurred (Figure 2). The new
38 facetted grains were identified as dodecahedrons according to both, their images on
39 radiographs and their Laue diagrams recorded *in situ*.
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43 44 **3.2. Strained growing grains:**

45 Synchrotron X-ray topographs have revealed that quasicrystal grains are strained
46 during their facetted growth. This can be seen in Figure 3 which displays synchrotron X-ray
47 radiographs and synchrotron X-ray topographs recorded simultaneously during their growth.
48 Whatever the growing grains (former or new ones) it is clear that their facets appear not so
49 sharp in topographs (Figures 3b and 3d) as in radiographs (Figures 3a and 3c) which means
50 that they are distorted and they contain numerous defects. As these defects can not be
51 resolved it can be said that their density is higher than the resolution limit of X-ray
52 topography which is of about 10^4 - 10^5 cm/cm³.
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56 57 **4. Discussion:**

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59 This *in situ* observation of the evolution of quasicrystal grains during solidification
60 provides the first unambiguous evidence of their facetted growth and reveals that they are
constrained all along the growth process.

4.1. Facetted growth:

Actually this observation corroborates both the predictions worked out from the faceting usually displayed by grains after growth [8] and the assumption made by Dong et al. of a growth of grains “in the form of regular polyhedrons” [15]. Moreover, in this latter case, it specifies that polyhedrons are dodecahedrons (at least for the icosahedral phase of Al-Pd-Mn) and that the maximums of the plots of volume fraction growth velocities as a function of time, they reported in their figure 7, correspond very probably to the beginning of a slowing down due to the meeting of all facetted growing grains (Figure 1c).

Despite it has been impossible to determine the true velocities of each facet (section 2), the measurements of their average velocities in the growth direction, we performed at each jump in pulling rate, allow us to value the growth kinetic coefficient μ . More precisely, taking into account that at each jump the growth velocities reached progressively the new pulling rate and the solidification front globally receded to a lower temperature (section 2), we had access at two important parameters of the solidification transient which took place in these conditions: the growth velocity jump ΔV and its corresponding undercooling ΔT . In addition, by considering, on the one hand that the transverse striations which develop on facets in the same time, have to be related to ledge growth (lateral motion of macrosteps or bunches of macrosteps) [16] and on the other hand that the ledges are generated at facet edges and vertices where undercooling and solid-liquid interface roughness are locally higher, it was possible to relate ΔV and ΔT linearly: $\Delta V = -\mu \Delta T$ [17]. Using the results of our experiments, a value of $\mu = 0.9 \mu\text{m}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$ was inferred from this formula [18]. Therefore, the resulting quasicrystal growth kinetic coefficient appears two orders of magnitude larger than the value obtained by Dong et al. [15] who used the Avrami equation in the case of an isothermal growth. This disagreement can be explained by considering that Dong et al. measurements [15], were performed during the latest stage of the growth, when facetted grains were meeting as above-mentioned. Nevertheless, a discrepancy with the kinetic coefficients of pure metals, which are much more higher ($\mu = 1.25 \cdot 10^4 \mu\text{m}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$ for pure Sn), remains. The value we obtained is more comparable to that of semiconductors or oxides ($\mu = 0.826 \mu\text{m}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$ for $\text{Bi}_3\text{Ge}_3\text{O}_2$ [19]) which are known to have a facetted growth. Accordingly, it can be stated that the quasicrystal growth is facetted and not dendritic as it was concluded by Shroers et al. [10]. If some doubts were remaining, the radiographs we recorded at the beginning of the growth, when quasicrystals appeared, could allow to get rid of them. This is clearly illustrated in the Figure 4 which shows that quasicrystals grew, immediately facetted, at the expense of the dendritic grains of the primary phase which has a similar chemical composition. Therefore, from an atomistic point of view, it can be concluded that models based on a thick diffuse interface region [4,5,7] are not suited to describe the quasicrystal growth and that the attachment of atomic species is uneasy as indicated both by the slow growth kinetic and the solidification front recoil caused by the sudden increase of the pulling rate.

4.2. Is the quasicrystal growth constrained?:

When synchrotron X-ray topographs of facetted growing grains (both the former ones which are columnar and the latter ones which are dodecahedral) are compared to those of the other grains we recorded previously, after cooling at room temperature [20][21], it is surprising to note that they display much more strain and defects. Lattice planes reflecting X-rays (X-ray topography is a diffraction imaging technique) are so strained that the facetted shape of these growing grains can not be distinguished in topographs (Figure 4) whereas, in the ones of as-grown grains, the curved boundaries can be recognized [21]. That is the opposite of what we observed during the solidification of pure metals and alloys for which

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3 only very few defects were generated by the growing melt-solid interface while most of them
4 appeared during cooling [22][23].

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6 Two origins of this strained state of the growing quasicrystal grains can be put
7 forward:

8 1°) it could be ascribed to the sticking of growing grains on the walls of the
9 graphite crucible and to the related thermal stresses.

10 2°) it could also result from the growth process itself according to Joseph et al.
11 ... who suggested that “tears” (dislocations) could be embedded in the growing
12 interface so as to insured an entropic stabilisation of the quasicrystalline
13 structure [7][24].
14

15 We have to check the sticking possibility and eventually to try to diminish it, before
16 invoking a phenomenon intrinsically related to the growth process. In the case of
17 consideration of this latter event, we would have to conciliate the systematic generation of
18 defects with a faceted growth because Joseph et al. ... supposed a diffuse interface and a
19 dendritic growth, which completely disagrees with our observations.
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22 23 24 **5. Conclusion:**

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26 This first *in situ* and real time observation, by synchrotron X-ray imaging combining
27 radiography and X-ray topography techniques, of the solidification of an AlPdMn alloy giving
28 quasicrystal grains, allowed us to clearly evidence a faceted growth. It has been determined
29 that this growth proceeds by lateral motion of ledges at the solid-melt interface and is
30 controlled by the interface kinetics rather than by the local heat flow as widely thought. Thus
31 a realistic estimate of the kinetic coefficient was deduced from the solid-melt interface
32 undercooling, which indicates that the quasicrystal growth is more likely comparable to both
33 semiconductor and oxide growths than to pure metal growth. The X-ray topographs, we
34 recorded simultaneously with radiographs, revealed that a lot of strains and defects are
35 generated in the quasicrystal grains during their growth, which could be related to the growth
36 process itself and very informative on the origin of the stability of the quasicrystal lattice.
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41 **Acknowledgments:**

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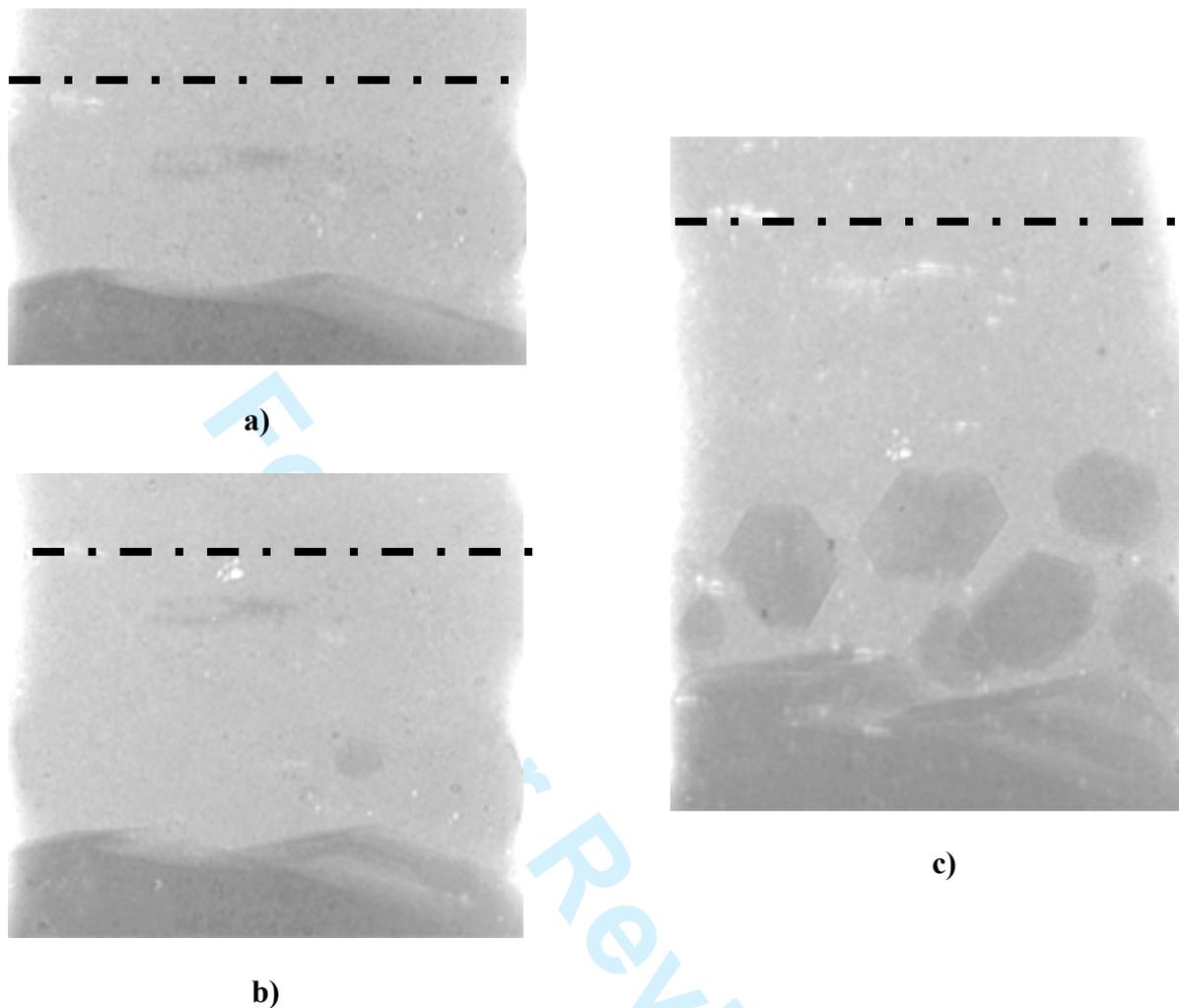


Figure 1

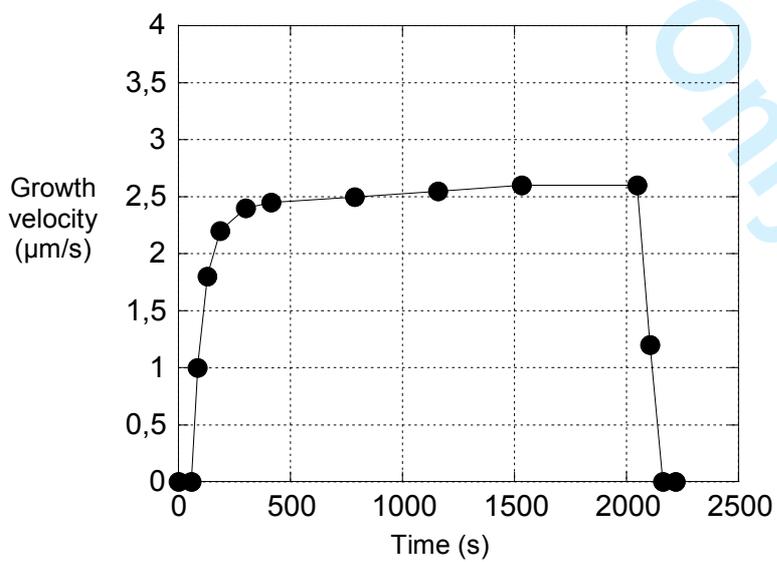
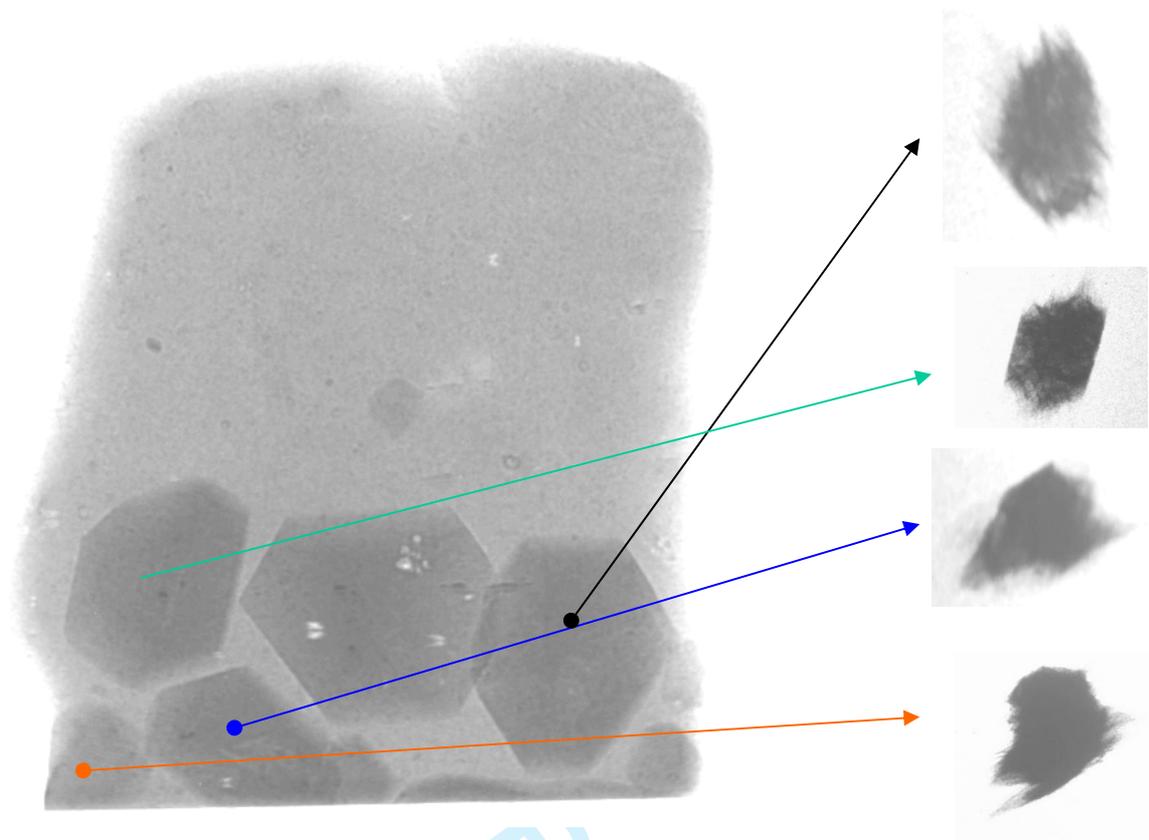


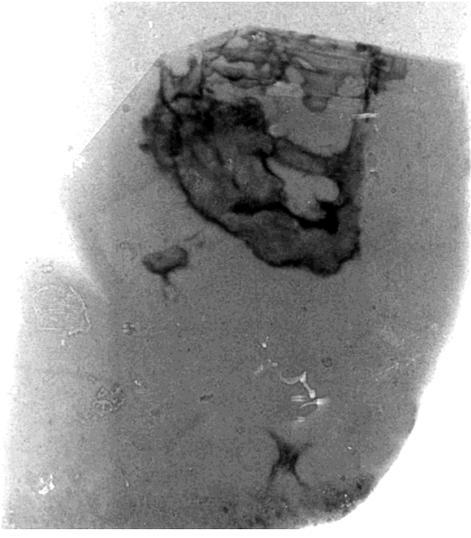
Figure 2

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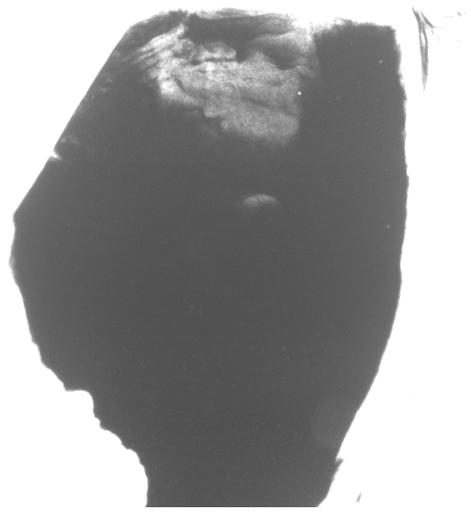


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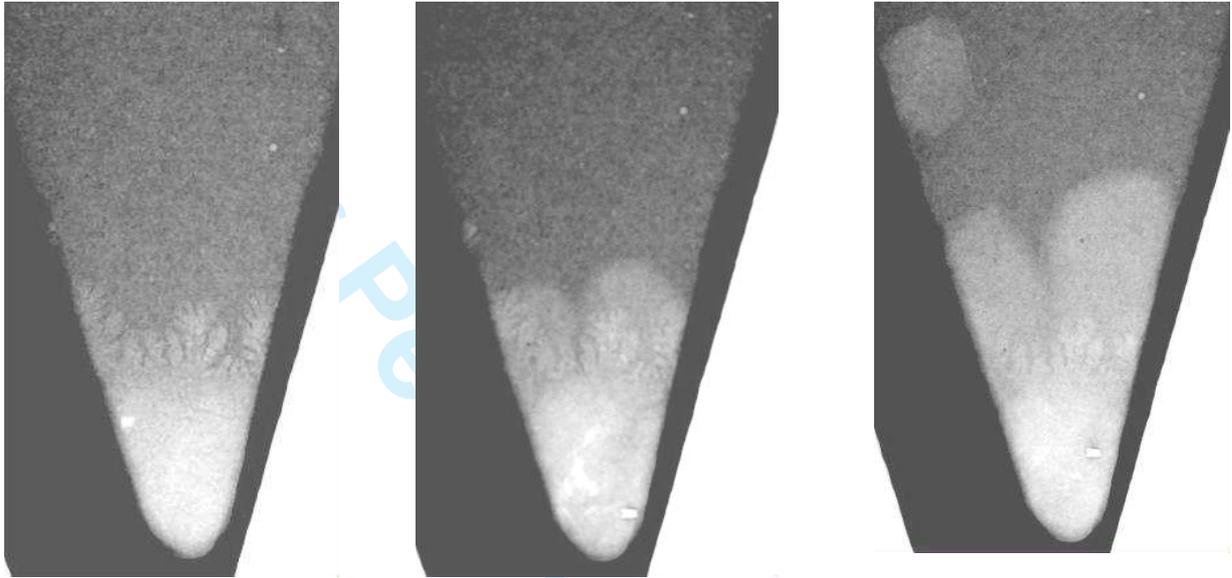


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Figure 3



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Figure 4

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Figure captions:

Figure 1: synchrotron X-ray radiographs showing faceted grains, a) at the end of a growth sequence with a pulling rate of $0.4 \mu\text{m/s}$, b) just after an increase of the pulling rate to $1.2 \mu\text{m/s}$, c) later on at this last pulling rate. Note the recoil of the growth front relatively to the sample datum line (dotted line).

Figure 2: Plot of the time evolution of the growth velocity of a quasicrystalline grain after an increase of the pulling rate from ? to $3,6 \mu\text{m/s}$. The decrease to zero of the growth velocity is due to an induced nucleation and growth of new dodecahedral grains ahead of the growth front.

Figure 3: synchrotron X-ray radiographs and their corresponding synchrotron X-ray topographs, respectively for dodecahedral grains a), b) and for columnar grains c), d). Note that the deformed shapes of the synchrotron X-ray topographs indicate that growing icosahedral grains are distorted.

Figure 4: synchrotron X-ray radiographs showing icosahedral quasicrystal grains growing at the expense of the dendritic grains of the primary phase which has a similar chemical composition.