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# In situ observation of pore evolution during melting and solidification of Al-Pd-Mn quasicrystals by synchrotron X-ray radiography

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## Abstract

It is now generally admitted that pores are intriguing special features of quasicrystals. Therefore, we have performed an “in situ” and real time observation of the pore evolution during directional solidification and melting cycles of an icosahedral Al-Pd-Mn bi-grained sample, by synchrotron X-ray radiography. Rather surprisingly, no pore was observed to grow during the solidification stages. Nucleation and growth of pores were firstly seen during melting. These pores were subsequently shrinking either just being absorbed or during resumption of directional solidification. It is concluded that the vacancy origin of pores is certainly valid whereas the vacancy supersaturation, needed thereby to explain their growth, would be more probably related to the peculiar structure of quasicrystal than to the destruction of the thermal equilibrium.

## I Introduction:

Since they have been successively observed in thin foil of the Al-Cu-Fe icosahedral phase [1], both at the surface and in the volume of bulk icosahedral Al-Pd-Mn grains [2] [3] and in the volume of quasicrystalline grains of some other alloys and structures [4], pores are generally admitted as important special features of quasicrystals. However as all these previous studies were carried out at room temperature, as well after interrupted [5] [6] as complete [7] [8] growth, it is difficult to decide between the two hypotheses which have been put forward to explain their origin, namely the thermal vacancy condensation [7] and the hierarchical structure [8]. Therefore, we have performed an “in situ” and real time observation of the pore evolution during directional solidification-melting cycles of an Al-Pd-Mn bi-grained sample, by synchrotron radiography, in order to grasp, more precisely, the origin of these intriguing species.

## II Experiments:

The synchrotron experiments were carried out at the ID 19 beam line of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). One thin Al-Pd-Mn sample ( $40 \times 6 \times 0.7 \text{ mm}^3$ ) cut in an ingot prepared at the composition which gives quasicrystal grains soon after the beginning of the solidification process ( $\text{Al}_{72.4}\text{Pd}_{20.5}\text{Mn}_{7.1}$ ), was melted and solidified two times inside a graphite crucible held vertically in a two heating-zone furnace. This furnace, described previously in detail [9], is permeable to X-rays and thereby allowed us to follow the course of the solidification/melting of the investigated sample, under a 20K/cm gradient, a pressure of about  $3 \times 10^{-7}$  mbar and pulling velocities ranging from 0 to 3.6  $\mu\text{m/s}$ . Radiographs were recorded all along the processes, at the X-ray energy of 24 keV,

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either by using a CCD camera developed at the ESRF [10] or exposing High Resolution (<1µm) photographic plates (Ilford L4). The camera was fitted with an optics leading to an effective pixel size of 7.46 µm and a large field of view (15x15 mm<sup>2</sup>). According to the high coherence of the beam delivered by the ESRF synchrotron source, phase contrasts were recorded in addition to absorption contrasts on radiographs, which increased the sensitivity to grain inhomogeneities of the technique.

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### III Results:

The sample, as cut in the master ingot (section II), was completely melted before being submitted to two partial solidification/melting cycles. Rather surprisingly, no pore was detected during the solidification stages at the spatial resolution allowed by our technique ( $\cong 1\mu\text{m}$ ). The appearance of micrometric pores was firstly observed during melting, at about 2 mm ahead of the regressive interface, while these pores were growing (Fig.1). Regions close to the melting interface, the external surfaces and the grain boundaries were depleted of pores. Actually, it was impossible to visualize the nucleation stage of these pores because of the poor spatial resolution of the imaging technique used. Nevertheless, it was clearly seen that the pores were shrinking either during a resumption of growth (Fig. 2) or just being absorbed by the regressive interface (Fig. 3). The mean velocity of enlargement of pores  $\Delta D/\Delta t$  (D diameter of pore, t time) was estimated to about five times that of their shrinking ( $\cong 0.5\mu\text{m}/\text{min}$  against  $0.1\mu\text{m}/\text{min}$ ) during re-growth and of the same order just being absorbed by the melting interface.

### IV Discussion:

This "in situ" observation of pore evolution during melting and solidification disclose, for the first time, that the pores encountered in as-grown quasicrystal grains [2][3][4], with sizes ranging from some micrometres to a few ten micrometres, do not appear during the solidification process. The fact that they were only detected when growing in a band at about two millimetres ahead of the melting interface (Fig. 1), could explain the irregular distribution of these pores noticed by A. R. Ross et al. [5]. In the same way, our observation agrees with some other results reported previously like, the absence of pore both close to the external surfaces and to grain boundaries [6], the pore morphology evolution from non-faceted to faceted (dodecahedral) [5] and the pore shrinking during post-growth grain annealing [11]. Accordingly our results confirm that pores have very likely a vacancy origin as stated by Beeli et al., but disagree with the pore formation mechanism they proposed. If the above-mentioned results indicate that a vacancy supersaturation  $S_{(T)}$ :

$$S_{(T)} = C_T / C_{(e)T}$$

$C_T$  = actual concentration of vacancies in the grain at a temperature T,

$C_{(e)T}$  = concentration of vacancies given by the thermal equilibrium at the same temperature T,

is actually needed, the fact that pores were observed growing to such a big size at the melting temperature precludes that the invoked vacancy supersaturation stems from the destruction of the thermal equilibrium. Indeed, if a rapid calculation of the thermal vacancy supersaturation  $S_{(T)}$ , which stands for example at 1 cm ahead of the melting interface, is made,

$$S_{(T)} = \exp [- \Delta H_f (1/T_m - 1/T) / k]$$

$\Delta H_f$  = vacancies formation enthalpy,

k = Boltzman constant

taking into account the temperature gradient (20K/cm) and the value of  $\Delta H_f$  in AlPdMn given by K. Sato et al. [12] which is of 2.3 eV and supposing that all vacancies present at the melting temperature  $T_m$  condense into pores at  $T < T_m$  (not taking into account the grain cooling rate or taking an infinite value), it is found that this supersaturation is very low, of about 1.5, not very different from that calculated for pure Al ( $\Delta H_f = 0.76$  eV). At 2 mm from the melting interface (distance at which pores were observed growing) this supersaturation is only 1.08. It is not sufficient to create a chemical (osmotic) force strong enough to nucleate so large vacancy clusters ( $S_{(T)} > 1000$ ) [13]. Thus the necessary vacancy supersaturation can be supposed as resulting from other processes such as growth or melting. In the past these possibilities were discarded for crystals [13]. In so far as our study points out also, that melting favours the vacancy aggregation far from the solid-liquid interface, it seems that the vacancy supersaturation is higher in the volume than close to this interface, which could exclude the melting and growth processes themselves. But, in this way, the supersaturation of vacancies could result from the very particular structure of quasicrystals which seems not exactly in a stable equilibrium state, immediately after growth [14]. This would agree with the unusual high concentration of structural vacancies inside the volume of quasicrystals reported by numerous authors [12][14] which is of about  $10^{-3}$  at Room Temperature, i.e. higher than that of thermal vacancies in crystals at the melting temperature ( $10^{-4}$ ). It would also correspond to the concentration of vacancies calculated by L. Mancini et al. [3] to account for the pore density encountered in as-grown Al-Pd-Mn grains. The fact that pores became visible at a distance, not very close to the solid-liquid interface, is strongly reminiscent of the nucleation and growth of droplets observed in a constitutionally superheated transparent alloy [15]. Thus the observation of the pores shrinking at the approach of the melting front suggests a concomitant decrease of the vacancy supersaturation in the volume. This phenomenon may be connected to the increasing proximity of the vacancy-attracting solid – liquid interface.

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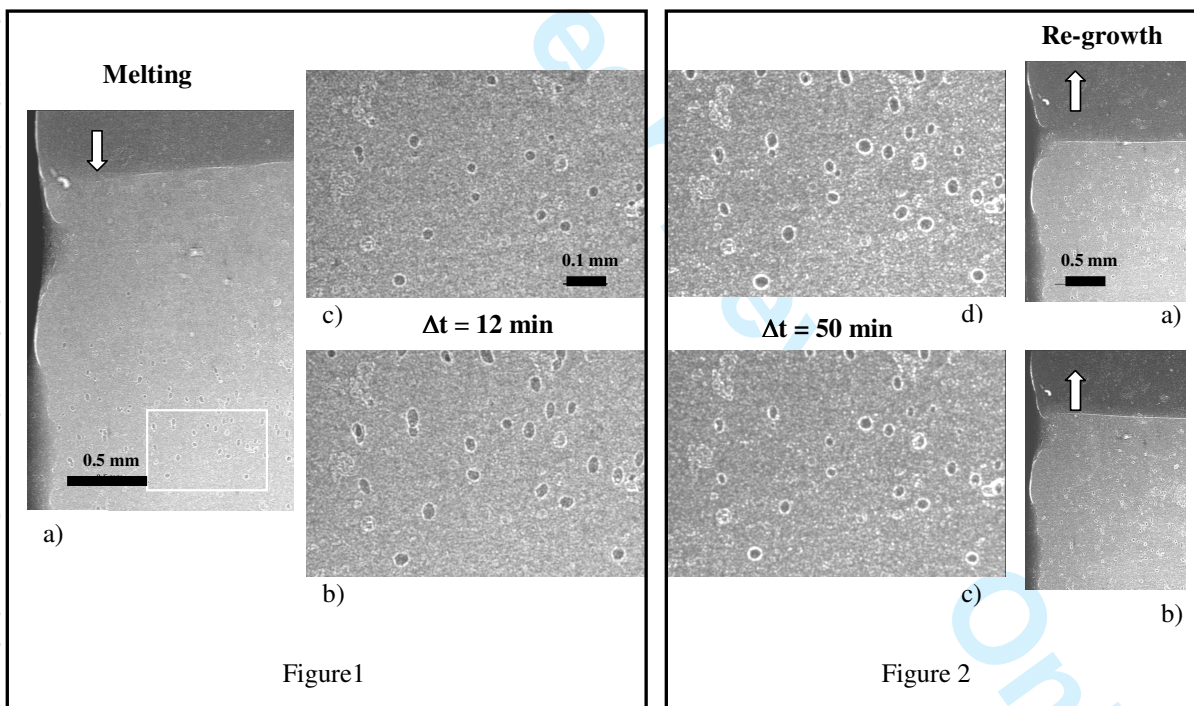
#### Acknowledgments:

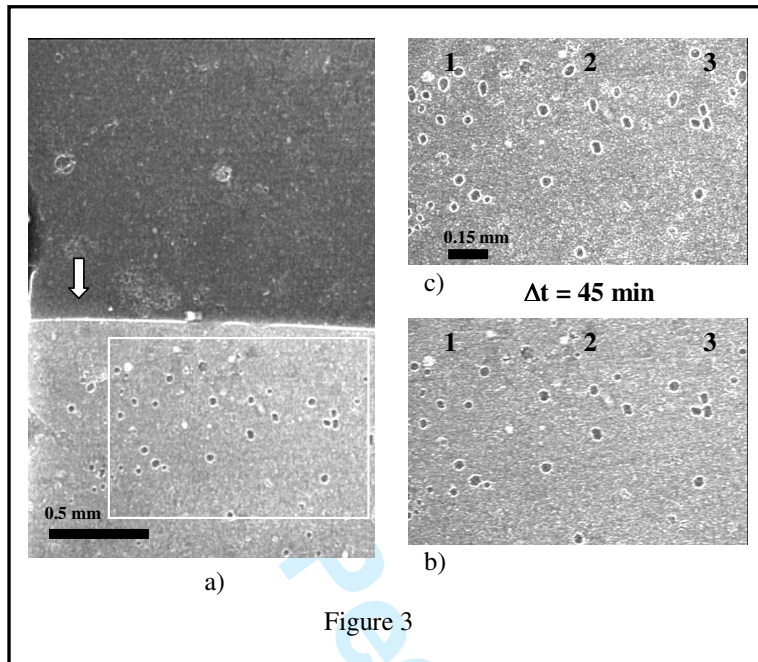
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### Figure Captions

**Figure 1:** Radiographs showing the size increase of pores during melting. a) Pores are growing in a band at about 2 mm from the regressing interface. b) Enlargement of the rectangular region of image a). c) Enlargement of the same region of an image recorded 12 minutes before a).

**Figure 2:** Radiographs showing the shrinking of pores during a resumption of growth following the melting stage displayed in figure 1. a) and b) are low magnification radiographs indicating the grain re-growth. c) Enlargement of a region of image b) which corresponds to the rectangular region in figure 1a). d) Enlargement of the same region of an image recorded 50 minutes before b).

**Figure 3:** Radiographs showing the shrinking of pores just before being absorbed by the regressing interface. a) The interface is arriving at the level of pores. b) Enlargement of the rectangular region of image a). c) Enlargement of the same region of an image recorded 45 minutes before a). 1, 2, 3 focus on pores rapidly shrinking or disappearing very close to the interface.