ESRF	**Experiment title:** **“In situ” and real time study of metallic alloy solidification by synchrotron X-Ray imaging**	**Experiment number**: ME-691
Beamline: ID19	**Date of experiment**: from: 11/16/2004 to: 11/23/2004 from: 03/15/2005 to: 03/22/2005	**Date of report**: 07/06/2005
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Report:

It is well known that the properties of grown materials are strongly determined by the solidification step, so that a precise mastering of growth processing is essential to reproducibly tailor products of specified quality. Accordingly, during the growth segregation of chemical species may be induced by defects (grain boundaries, dislocations, ..), grains structure (columnar or equiaxed growth) [1] or the solidification microstructure itself [2]. A complete understanding of growth processing, from the microscopic to the macroscopic scale is a key point both from technological and fundamental science points of view.

As most of the phenomena involved are dynamical, our objective is to achieve in situ and real time investigations of the solidification of metallic alloys using most advanced X-ray imaging techniques (radiography and diffraction topography) with the increased capabilities of 3rd generation synchrotrons. More precisely, the project addresses three different issues:

- Columnar growth of non refined binary alloys (Al –3.5 wt% Ni)
- Columnar and equiaxed growth of refined and non-refined binary alloys (Al –3.5 wt% Ni)
- Quasicrystal growth mechanism (Al-Pd-Mn system) [3]

[1] Martorano, M.A., Beckermann, C. & Gandin, Ch.-A., Metall. and Mater. Trans. A, 34A (2003) 1657.

[2] Mullins, W.W. & Sekerka R.F., J. Appl. Phys. 35 (1964) 444.

[3] Janot, C. & Dubois, J-M., *Les Quasicristaux : Matière à paradoxes* (EDP Sciences, Les Ulis, France, (1998) Ch. 3.

For all issues, directional solidification is a key technique which allows one to analyze independently the effect of solute concentration, temperature gradient and pulling rate on the solid-liquid interface. For this project, an experimental set-up has been developed in collaboration with ID19 beamline team members. It is composed of an Ultra-High-Vacuum furnace for “in situ” and real time observations of solidification by X-ray imaging. Its specificity lies in that it allows both to control the two main parameters of unidirectional solidification (pulling velocity and temperature gradient) and to record X-ray radiographs and X-ray topographs, either independently or simultaneously. During previous allocated beam time (6 months project), we performed a series of tests and the preliminary results showed that **[4]** it is necessary to use a furnace ensuring a vertical growth direction instead of a horizontal one, in order to avoid disturbances of the solidification process induced by natural convection. During these preliminary investigations, X-ray imaging techniques have also been tested in close relation to the scientific objectives.

Therefore, during the 1st part of the 1st year of the project, in collaboration with the ID19 engineering staff (Pascal Bernard and René Chagnon), we have mainly performed the experimental development of the UHV-furnace and X-Ray imaging techniques (absorption/phase contrast radiography and topography). The vertical axis furnace was successfully tested. Then, in the 2nd part of the 1st year of the project, several outstanding observations were obtained, often for the first time. These results were presented in international conferences and published in international revues. Some of these results were also considered as highlights among the ESRF scientific production, and were published as highlight scientific results in the ESRF web site, and on the “2004 Highlights” volume (published in February 2005). For the different issues, the most striking observations are presented in the following.

- **Quasicrystal growth:**
  - Facetted growth **[5,8,9,10]**
  - Nucleation and free growth of grains above the interface at high growth rate **[5,8,9,10]**
  - Pore evolution during melting and solidification of Al-Pd-Mn quasicrystals **[12]**

In Fig.1 the facetted character of the growth of icosahedral quasicrystals from a $Al_{72.4}Pd_{20.5}Mn_{7.1}$ melt is, for the first time to our best knowledge, directly brought to light. Indeed, quasicrystals still keep stimulating imagination, in particular to elucidate how orientation order builds over long distance during their growth. In Fig.1a, two facet edges are visible on grain 1 and three on grain 2, and there is a narrow cusp at the level of the grain boundary. Following the increase of the applied pulling rate to 3.6 µm/s, the cusp evolves into a deep and wide liquid groove, and the facets exhibits salient evidences of layer-motion controlled growth (Fig.1b). Actually, possibly due to the skeletal instability of layer motion, striations are running parallel to the interface and notches are repeatedly forming on the left side of grain 2. After a while, new grains nucleate and grow facetted in the liquid, just above the two initial grains whose growth gets blocked.

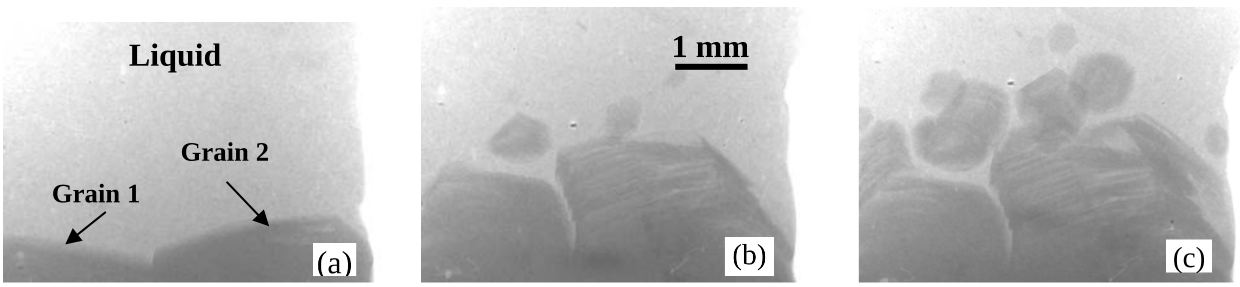

Figure 1: Images recorded by in situ and real-time X-ray radiography of AlPdMn quasicrystals growing from their melt (sample thickness = 500 µm). (a) Steady-state growth of AlPdMn quasicrystal grains at 0.4µm/s. (b) and (c): evolution of the two initial grains at the beginning of their screening by new grains 750 sec after increasing the pulling rate to 3.6 µm/s (b).

- **Columnar dendritic growth:**
    - Initial transient **[5,7,9]**
    - Bending of secondary arms during dendritic growth **[7]**

Fig.2 displays the dynamical interaction between dendrite formation and buoyancy-driven convection, common in casting and welding. After the breakdown of the smooth solid – liquid interface, the corrugations progressively increase in amplitude and sidebranches begin to show up on largest ones (Fig.2a), which indicates the inception of dendrites. Fluid flow in the melt induces significant solute accumulation and transition to eutectic pattern on the right of Fig.2b, and localisation of dendritic growth on the left. Neighbour screening eventually results in the coupled growth of a large single dendrite, protruding into the liquid, far ahead of the eutectic at its base (Fig.2c).

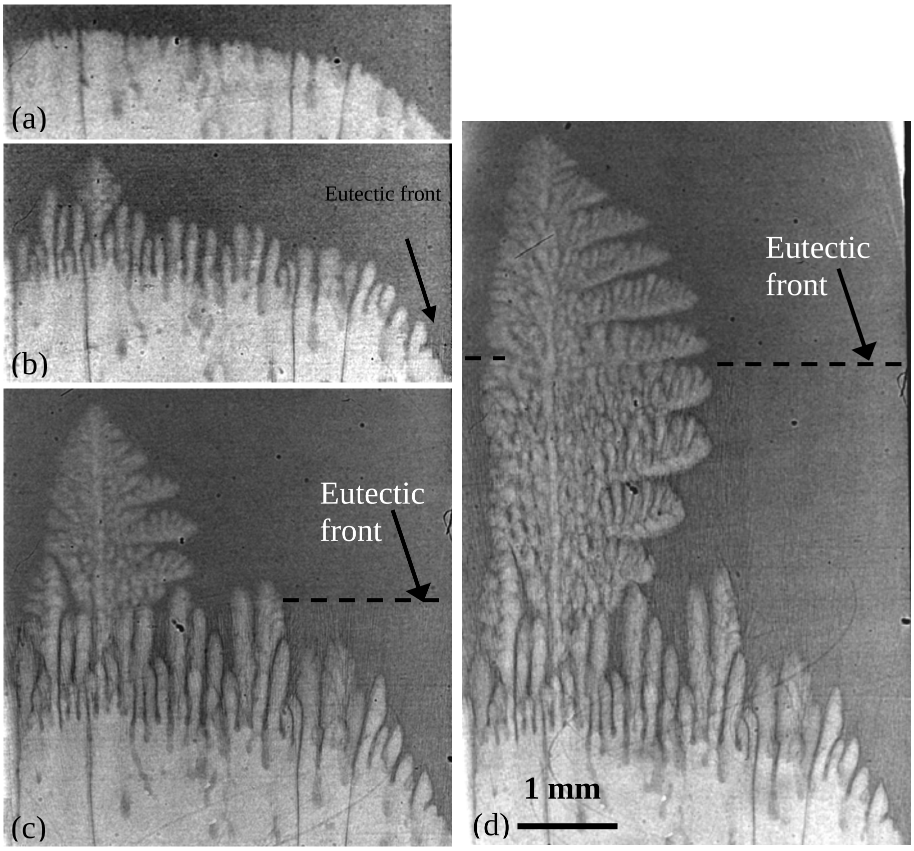

Figure 2: Sequence of 4 images of Al-3.5wt% Ni solidification, recorded during the initial transient by X-ray radiography, G= 20 K/cm, V = 1 µm/s:
a) $t = t_0 + 240$ sec,
b) $t = t_0 + 1344$ sec
c) $t = t_0 + 3206$ sec
d) $t = t_0 + 4254$ sec.

The solid phase mainly constituted of aluminium appears in grey while the Ni enriched liquid is dark.

Conversely to LURE experiments, preliminary ESRF solidification experiments were performed with only X-ray radiography. Thus, mechanical effects were not so easy to reveal as in X-ray topography experiments. Nevertheless, the mechanical bending of secondary arms was also visible when the arm length is long enough. This is shown in Fig.3 for one secondary arm, with an orientation indicated by the dashed line *(1)*, which suddenly switched to a new orientation *(2)* with a rotation angle of 5.5°. By this way, the secondary arm reached a final position parallel to the arms below. This phenomenon was observed between two images, taken with a time interval of 21 seconds, which confirms that this effect is complete in a very short time.

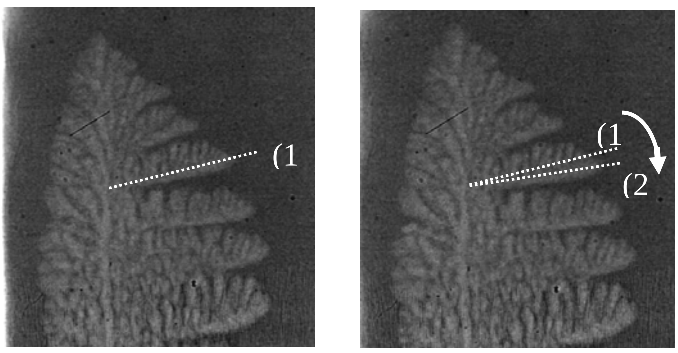

Figure 3: Two successive images recorded by in situ and real-time X-ray radiography of Al – 3.5 wt% Ni alloy solidification at V = 1.0 µm/s, showing the rotation of a secondary arm from orientation (1) to (2) (elapsed time between the two images is 21 seconds)

- **Columnar to equiaxed transition and equiaxed growth:**
    - Dynamical arrangement of equiaxed dendrites in the equiaxed regime **[5, 6, 11]**
    - Grain structure maps and columnar to equiaxed transition **[6, 11]**

In refined alloys (refiners are particles added to act as nucleation sites for equiaxed grains) one way to provoke CET (Columnar Equiaxed Transition) consists of applying successive velocity jumps from low values (about 1 µm/s) to higher ones (about 10 µm/s). Fig.4 displays the columnar to equiaxed transition induced by a velocity jump from 4 to 6 µm/s, for a refined Al – 3.5 wt % Ni alloy, in a thermal gradient of 20 K/cm. At low velocity, a columnar microstructure composed of few dendrites is visible at the bottom of the picture. Due to a horizontal temperature gradient inside the sample, these dendrites are localised on the right of the sample, leaving a liquid channel on the left. After a velocity jump from 4 to 6 µm/s, nucleation of small grains in the undercooled region is observed just ahead of the columnar microstructure. The existence of an effective front (macroscopic envelope at the top of the closely packed equiaxed grains) is clearly visible in the picture and may explain why the equiaxed regime can be self-sustained and extend after the columnar to equiaxed transition has started. Besides, some equiaxed grains fall down in the liquid channel, due to gravity. During their fall, these grains can rotate and their shape evolution can be followed in real time. At higher pulling rate (thus larger undercooling), more refining particles become active which results to finer and finer grain size.

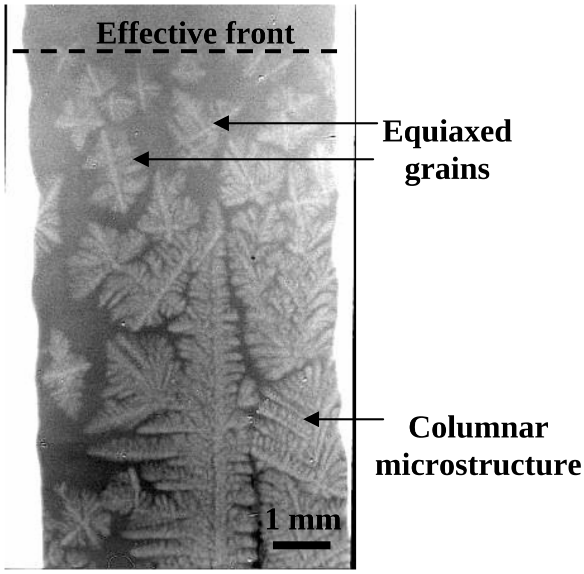

Figure 4: Image of refined Al-3.5wt% Ni solidification, recorded by X-ray radiography and showing the columnar to equiaxed transition following a velocity jump from 4 to 6 µm/s, G = 20 K/cm.

The solid mainly constituted of aluminium appears in grey while the Ni enriched liquid is dark.

Conclusion: For metallic alloys, ESRF X-ray source has timely allowed in situ and real-time X-ray imaging with high spatial and temporal resolution. Using absorption and phase contrast radiography, we present outstanding results on dynamical pattern formation in thin Al-based alloys solidified upwards in the specific Bridgman facility installed at the ID19 beamline of ESRF. These appealing results require more dedicated and systematic experiments to test the influence of control parameters or experimental procedure, aiming to a better understanding of the physical phenomena. This task was partially carried out during the LTP ME-691. Nevertheless, due to the vast field of research and new questions opened by these results, it is necessary to continue this project in the next years.

In addition, during the LTP the observations were performed by mainly X-ray radiography, conversely to previous LURE experiments,. Thus, mechanical effects were not so easy to reveal as in X-ray topography experiments. However, some preliminary tests demontrated that it is possible to obtain very clear topographs with the present experimental apparatus (Fig.5). Some improvements are still required in order to record simultaneously both X-ray radiograph and topograph.

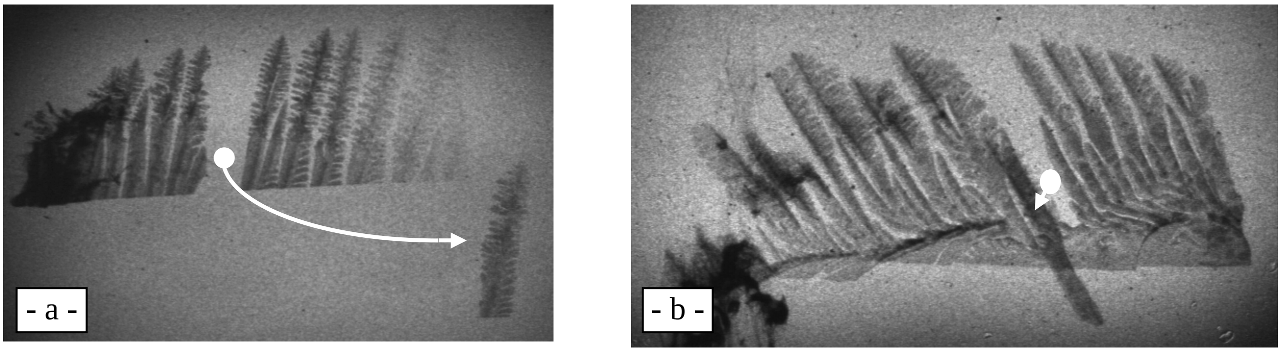

Figure 5: Two X-ray topographs of dendritic array recorded on HR films during directional solidification of non-refined Al-3.5wt% Ni, G = 20 K/cm. These pictures show the effect of disorientation of one single dendrite in the array, leading to a jump of the dendrite image. In Fig.5a the dendrite image is completely shift out the array, whereas in Fig.5b the dendrite image is superimposed on the array.

List of articles (with abstract):

[4] *H. Nguyen Thi.,H. Jamgotchian, J. Gastaldi, J. Härtwig,T. Schenk, H. Klein, B. Billia, J. Baruchel, Y. Dabo*
Preliminary in situ and real time study of directional solidification of metallic alloys by X-ray imaging techniques.
Journal of Physics D: Applied Physics, vol. 36, p.83-86, 2003
Abstract: *During directional solidification of a binary alloy, the solid–liquid interface exhibits a variety of patterns that are due to the Mullins-Sekerka instability and governed by the growth conditions. It is well known that properties of the grown material are largely controlled by the microstructures left in the solid during processing. Thus, a precise mastering of the solidification is essential to tailor products in a reproducible fashion to a specified quality. One major difficulty for this study is the real time and in situ observation of the interface, especially for metallic alloys. A possibility is to use an intense and coherent 3rd generation X-Ray beam. By combining different X-ray imaging techniques (absorption/phase contrast radiography and diffraction topography), we have studied the directional melting and solidification of aluminium-based alloys. The preliminary results show the great potential of these techniques for the study of the coupling between stress effects and microstructure formation in solidification processing.*

[5] *T. Schenk, H. Nguyen Thi, J. Gastaldi, G. Reinhart, V. Cristiglio, N. Mangelinck-Noël, H. Klein, J. Härtwig, B. Grushko, B. Billia, J. Baruchel*
Application of Synchrotron X-ray imaging to the Study of Directional Solidification of Aluminium – based Alloys
Journal of Crystal Growth, 275/1-2 (2005) pp151-158
Abstract: *3rd Generation Synchrotron X-ray sources like ESRF (European Synchrotron Radiation Facility) have enhanced the capabilities of in situ and real-time X-ray imaging so that it is possible to follow the solid – liquid interface dynamics on metallic alloys with improved spatial and time resolution. In this paper, we focus on the solidification patterns of Al-based alloys, visualised by absorption and phase contrast radiography at ESRF. Two metallic systems were selected for this study: - i) Al – 3.5 wt% Ni (with and without refiners) for the analysis of columnar growth and equiaxed growth, and the influence of the refiners on the columnar to equiaxed transition (CET), which is a key point in solidification processing, - ii) $Al_{72.4}Pd_{20.5}Mn_{7.1}$ for the analysis of interface shape of growing*

quasicrystals (QCs). For both alloys, striking features were observed and a preliminary discussion is presented. Those results demonstrate the high potential of ESRF Synchrotron source for the characterisation of the dynamical formation of the solid microstructure in materials processing.*

[6] *N. Mangelinck-Noël, H. Nguyen-Thi, G. Reinhart, T. Schenk, V. Cristiglio, M.-D. Dupouy, J. Gastaldi, B. Billia, J. Härtwig, J. Baruchel*
In situ analysis of equiaxed growth of aluminium-nickel alloys by x-ray radiography at ESRF
Journal of Physics D: Applied Physics, vol.38 (2005) A28-A32
Abstract: *We present results obtained, at the ID19 beamline of the ESRF, by Synchrotron X-Ray Radiography during the solidification of Al-Ni alloys. We focus on the dendrite regime and more particularly on columnar dendritic solidification and equiaxed solidification, and the transition between both regimes. The columnar to equiaxed transition is a critical and still pending issue in metallurgy. Making use of the high potential of synchrotron experimental tools for in situ and real-time characterisation of the solid-liquid interface during directional solidification, we were able to provide insight on key physical phenomena, in particular: sedimentation, interaction and arrangement of equiaxed grains.*

[7] *G. Reinhart, H. Nguyen-Thi, J. Gastaldi, B. Billia, N. Mangelinck-Noël, T. Schenk, J. Härtwig, J. Baruchel.*
In situ and real time investigation of directional solidification of Al - Ni alloys by synchrotron imaging
Material Science Forum, accepted
Abstract. *Solidification is a dynamic phenomena and, as a consequence, it is of major interest to be able to investigate this process by in situ and real time observation. With synchrotron sources, this can be achieved by applying X-ray Imaging techniques (Radiography and Topography). Hence it is possible to follow the dynamical selection of solidification pattern on metallic alloys and to observe strain effects during growth process. In this paper, we present results obtained by using separately the two imaging techniques for the study of the microstructure formation during Al – Ni alloys solidification.*

[8] *T. Schenk, G. Reinhart, V. Cristiglio, G. Gastaldi, H. Klein, B. Grushko, H. Nguyen-Thi, N. Mangelinck-Noël, J. Härtwig, B. Billia and J. Baruchel*
Live Observation of the Growth of Quasicrystal Grains
ESRF Spotlight, 04/10/2004

[9] *T. Schenk, H. Nguyen-Thi, J. Gastaldi, G. Reinhart, V. Cristiglio, N. Mangelinck-Noël, H. Klein, J. Härtwig, B. Grushko, B. Billia, J. Baruchel*
Application of Synchrotron X-ray Imaging to the Study of Directional Solidification of Aluminium-based Alloys
ESRF Highlights, , (2005) pp110-111

[10] *H. Nguyen-Thi, J. Gastaldi, T. Schenk, G. Reinhart, N. Mangelinck-Noel, V. Cristiglio, B. Billia, B. Grushko, J. Härtwig, H. Klein, J. Baruchel*
Probing the dynamics of quasicrystal growth using synchrotron live imaging
Physical Review Letters, submitted
Abstract. *Quasicrystals constitute a distinct class of solids as they differ both from crystals, because they are not periodic, and from glasses, because they have long-range orientation order. The main challenge of quasicrystal physics is certainly to elucidate how the quasiperiodic order extends up to the centimetre size of the single grains routinely grown nowadays[1-3]. In particular, the dynamics of quasicrystal growth remains an unsolved problem in condensed matter. Here, owing to synchrotron live imaging, we show evidences that the solidification front of icosahedral AlPdMn quasicrystal is*

facetted all along the growth which proceeds by the tangential motion of ledges at the solid-melt interface, with a measurable effect of interface kinetics. Increasing the applied solidification rate, the kinetic undercooling becomes large enough for the nucleation and free growth of new facetted grains in the melt. The evolution of these grains is explained in details, which reveals the crucial role of aluminium rejection, both in the poisoning of grain growth and driving fluid flow.

[11] *G.Reinhart, N. Mangelinck-Noël, H. Nguyen-Thi, T. Schenk, J. Gastaldi, B. Billia, P. Pino, J. Härtwig, J. Baruchel*
Investigation of Columnar-Equiaxed Transition and Equiaxed growth of Aluminium Based Alloys by X-Ray Radiography
Materials Science and Engineering A, accepted
Abstract. *Among solidification processes, the columnar to equiaxed transition (CET) and equiaxed growth are still raising issues both from the metallurgical point of view and for the understanding of the fundamental related physical phenomena. The phenomena involved are complex and most of the time intimately related to the dynamical events happening during the solidification. Bridgman solidification of Al – Ni alloys is performed at the ID19 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The use of a 3rd generation synchrotron X-ray source allows in situ and real-time observation of the solid – liquid interface, in particular at the CET. To provoke the CET, refined alloys are used and the pulling rate is increased following several profiles. The experiments give direct access to specific behaviours and enable the measurement of several key parameters during the CET and equiaxed growth, which can be discussed.*

[12] *Gastaldi J., Schenk T., Reinhart G., Klein H., Härtwig J., Mangelinck-Noël N., Grushko B., Nguyen Thi H., Pino P., Billia B., Baruchel J.*
In situ observation of pore evolution during melting and solidification of Al-Pd-Mn quasicrystals By Synchrotron X-ray radiography
Phil. Mag., accepted
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.*