The Influence of Growth Rate on Porosity in Al-Pd-Mn Icosahedral Quasicrystals.

Amy R. Ross†, Ian R. Fisher*, Paul C. Canfield†‡, and Thomas A. Lograsso†§
† Ames Laboratory and, ‡ Department of Physics and Astronomy, and § Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011-3020, USA, * Stanford University, Stanford, Ca 94305, USA

ABSTRACT

Growth experiments have been carried out to characterize the occurrence and development of porosity in Bridgman and flux grown Al-Pd-Mn icosahedral quasicrystals. The porosity level has been observed to fluctuate between values of 0.0 and 3.75 percent along the length of Bridgman single crystals implying that the development of porosity is affected by the local growth conditions. Experiments were conducted to evaluate the influence of the rate of solidification on the occurrence of porosity. Alloys were solidified with different growth rates, 1mm/hr and >10 mm/hr, using the Bridgman configuration and at different cooling rates, ranging from 0.29°C/hr to 10°C/hr, using the flux growth method. Porosity levels were analyzed via optical image analysis. These experiments indicate that porosity percentages are greatly influenced by cooling rates and crystal size.

INTRODUCTION

Many experiments have been conducted to determine the source of porosity in Al-Pd-Mn quasicrystals since first reported by Beeli in 1992 [1]. Beeli, Gödecke and Lück proposed that quasicrystal pores formed via thermal vacancy migration and condensation [3]. Additional work by Beeli et al. confirmed that pore size and spacing corresponded to diffusion models [4]. Two other hypotheses regarding the origin of porosity were based on quasicrystalline structural arguments [5,6]. The self-similar model proposes that porosity develops from specifically located vacancies that are inherent in the quasicrystal structure [5]. A modification of the self-similar model, the random covering theory, maintains the inherent and specifically located vacancies but increases the ability for deviation from the perfect arrangement by reducing the strict scaling laws [6].

Bridgman experiments studying how growth conditions affected porosity characteristics determined that some aspect of solidification influenced porosity content [7]. These experiments which documented the porosity occurrence, distribution, and characteristics, revealed a striking fluctuation in porosity level within any given sample. In contrast, the flux-grown quasicrystals were found to be virtually pore free [10]. The significant difference in the two crystal’s porosity characteristics invite comparison, however, crystals grown with these two processes cannot be directly compared because their thermal histories are not the same. Bridgman crystals are grown with cooling rates greater than those of the flux method and undergo some annealing as the crystal is continuously cooled to room temperature. Alternatively, crystals grown with the flux method are quenched after cooling slowly through a predetermined temperature range. Two sets of experiments were designed to provide samples that would bridge the growth regime between the two processes. The first set explored the affects of cooling rate by slowing the Bridgman cooling and accelerating the flux cooling rates. The second set of experiments investigates post-solidification thermal history, i.e. what happens if a Bridgman growth is interrupted by
quenching before it completely solidifies and what happens if a flux growth is allowed to completely solidify by continuous cooling. These process manipulations provide the unique opportunity to isolate affects of the growth processes.

SAMPLE PREPARATION

Single and polycrystalline samples were grown using the standard Bridgman growth process as described in Ross et al 1999 [7]. Standard flux growth samples were grown following procedures described in Fisher et al. 1999 [8]. One set of samples was grown using flux growth processes that were modified to approach Bridgman cooling rates. Other hybridized growth techniques modified Bridgman growth processes to approximate flux growth processes. Nominal compositions for all processes were either Al72Pd19Mn8 (standard flux composition) or Al72Pd19.5Mn8.5 (standard Bridgman composition).

All samples were prepared for analysis using the same technique. Samples were sectioned through their midpoints using an electro-discharge machining center and then polished using standard metallographic techniques. Inspection was completed using optical microscopes, an image analysis system, and a scanning electron microscope with EDS capability.

RESULTS

The percentage of porosity for growth under various conditions is shown in Table I. Standard Bridgman growths have the highest percentage of porosity whereas the standard flux growth has the least. Both growth methods responded to changes in cooling rate. The Bridgman growths indicate that porosity content is reduced by reducing cooling rate. Alternatively, flux growth samples showed an inverse relationship between cooling rate and porosity content. The accelerated and continuously cooled flux growth crystal is almost pore free.

Table I: Summary of the experiments listed by growth parameters and the resultant porosity percentages

<table>
<thead>
<tr>
<th>Growth Method</th>
<th>Melt Composition</th>
<th>Cooling Rate</th>
<th>Percent Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Bridgman</td>
<td>Al72Pd19.5Mn8.5</td>
<td>Est. &gt;10°C/hr</td>
<td>0.84 ± 0.3</td>
</tr>
<tr>
<td>Bridgman approaching Flux</td>
<td>Al72Pd19.5Mn8.5</td>
<td>1°C/hr</td>
<td>0.45 ± 0.1</td>
</tr>
<tr>
<td>Standard Flux</td>
<td>Al73Pd19Mn8</td>
<td>0.29°C/hr</td>
<td>0.053 ± 0.01</td>
</tr>
<tr>
<td>Accelerated Flux 1</td>
<td>Al73Pd19Mn8</td>
<td>0.83°C/hr</td>
<td>0.095 ± 0.03</td>
</tr>
<tr>
<td>Accelerated Flux 2</td>
<td>Al73Pd19Mn8</td>
<td>3.32°C/hr</td>
<td>0.44 ± 0.2</td>
</tr>
<tr>
<td>Flux approaching Bridgman (continuous cool)</td>
<td>Al73Pd19Mn8</td>
<td>10°C/hr</td>
<td>~0</td>
</tr>
<tr>
<td>Accelerated Flux 1, post HT</td>
<td>Al73Pd19Mn8</td>
<td>0.83°C/hr</td>
<td>0.264 ± 0.05</td>
</tr>
</tbody>
</table>

The porosity distribution in these experiments was also affected by the presence of defect sinks such as grain boundaries and free surfaces. In Bridgman samples where more than one crystal was present, a pore free area adjacent to the grain boundary was found as shown in Figure 1A. Likewise, a similar zone was found along the exterior surface of the ingot in contact with the crucible wall (Figure 1B). These surfaces serve as local sinks for vacancies. Porosity free
zones have also been found around pores after extended heating cycles [11]. The flux-grown samples were not noted to exhibit this affect.

The pores in all samples, regardless of which growth process was used to grow the sample, have morphologies as described in Ross et al. 1999 and shown in Figure 2 [7]. Both standard and hybrid Bridgman samples contain Type II and Type III pores. The standard and accelerated flux growth crystals contain some Type II pores although most pores are Type III. The diameters of the pores found in Bridgman samples vary extensively but the pores in the flux-grown samples are all 5-microns in diameter.

Type I pores (a) exist in the first 9mm behind the S/L interface but not directly at the interface. Type II (b) pores are found >9mm behind the interface and gradually transform to Type III pores (c). Type III pores are found in the oldest regions of the crystal.

Figure 2: Illustration of pore morphologies and their relative positions as determined by quenching experiments.
DISCUSSION

The data conclusively indicates that porosity characteristics are influenced by the rate of solidification and thermal history. Both Bridgman and flux-grown samples exhibit a direct relationship between cooling rate and porosity content as well as increased porosity contents following post-growth annealing. This affect had been seen in the quenched Bridgman sample described in Ross et al. 1999 [7] and in other heat treatment experiments [9] but had not previously been observed in flux grown crystals. Both methods indicate that time at elevated temperatures, whether during growth or post-growth annealing, enables vacancy migration and condensation, but that the time necessary to remove all excess vacancies exceeds the growth time.

Crystal size also influences the amount of porosity in an Al-Pd-Mn quasicrystal by affecting the proximity to defect sinks. Bridgman ingots consisting of two crystals show porosity levels similar to single grain Bridgman ingots. However, a Bridgman ingot containing four unequally sized crystals is almost pore free [9]. Although first noticed in Bridgman ingots, this effect was also seen in the continuously cooled flux growth sample. The continuously cooled flux-growth sample was expected to produce crystals with high porosity contents because the growth process mimicked the Bridgman process. However, due to the small crystals grown in this sample and with the extended time at temperature during cooling, most of the defects were able to migrate to a grain boundary or free surface. This hypothesis is supported by the fact that annealing did not change the porosity level. Clearly, decreasing the distance to defect sinks greatly affects the porosity content of a quasicrystal.

The relationships between crystal size, cooling rate, and porosity content can be combined to explain the difference between the standard Bridgman and standard flux growth porosity characteristics. Flux grown samples are cooled more slowly, produce smaller crystals, and are quenched at the end of primary crystallization. On the other hand, Bridgman growths are cooled more quickly than flux-growths, are allowed to cool completely, and typically produce crystals that are much larger than flux growth crystals. These three factors combine to increase the number of defects trapped in a Bridgman crystal during growth and thereby provide an explanation for the difference in porosity levels seen in Bridgman and flux grown crystals.

Finally, the experimental results may be interpreted with respect to the two proposed models of porosity development and found to support aspect of both models. Both theories are easily applied and discussed with respect to the accelerated flux growth data since these samples have the same thermal history. The thermal vacancy model requires all of the flux samples to have the same porosity content because they have been quenched from the same temperature. Therefore, the variation in porosity content with cooling rate implies that defects in addition to the equilibrium thermal vacancies are being trapped in the solidifying crystal. The increase in porosity indicates that kinetics affect the included vacancy population. These kinetically altered vacancy populations may represent those proposed in the random covering model because it establishes that vacancy content can be increased by imperfect solidification. In conclusion, these results indicate that the two proposed models are complementary and therefore when united, provide a reasonable hypothesis for the variation of porosity content in Al-Pd-Mn quasicrystals.
CONCLUSIONS

The correlation between cooling rate, crystal size, and porosity content indicates that porosity in icosahedral Al-Pd-Mn quasicrystals results from and is greatly influenced by solidification kinetics. While the differences in cooling rates do not appear significant enough to induce the dramatic difference between the flux and Bridgman porosity characteristics, this sample group indicates that there is an “ideal” combination of solidification rate and crystal size. Increasing solidification rate increases the number of included pores but by an unidentified mechanism. Time at temperatures amenable to vacancy migration and grain size determines the final porosity content. Aspects of the random covering and thermal vacancy theories may be correlated with experimental results and when united provide a reasonable hypothesis for the variation in porosity content.

ACKNOWLEDGMENTS

The authors would like to thank Hal Salisbury, Materials Preparation Center of Ames Laboratory, for his meticulous care in completing porosity content analyses. Work supported by the Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. W-7405-ENG-82.

REFERENCES:

1. Beeli, Ph.D Thesis, ETH Zürich (Switzerland), 1992
10. I.R. Fisher, (private communications)