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REVIEW

Review on Fabrication of Gasar Porous Alloys

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Abstract: Gasar, which is based on the gap of gas solubility between liquid and solid metals, is a revolutionary process for fabricating porous metal. Recently, the research on fabricating porous alloys with ordered pore structure, has been one of the most popular topics and technical issues concerning the application of Gasar porous metals. The main reasons for difficulties in controlling the ordered porous structure include the influence of the "mushy zone" at the front of the interface during the solidification of the alloy, and the fact that after alloying elements are added, the solid-liquid interface becomes unstable and the solidification mode changes. Preliminary researches mainly focused on reducing the influence of the above two factors on the directional growth of pores from the following two perspectives: preparation technology improvement and alloy composition design (micro-alloying). This study reviewed the research progress of Gasar porous alloys based on the development of preparation techniques (mould casting technique→continuous zone melting technique→continuous casting technique), summarized the main factors that affect pore structure of porous alloys, and analyzed the shortcomings and development trends of future research.

Key words: Gasar; porous alloys; pore structure; solidification mode; mushy zone

Gasar, a new process for the preparation of regular porous materials, was discovered by Shapovalov[1] in his US patent in the 1990s. The main principle of Gasar is unidirectional solidification of a molten metal saturated with a large amount of gas (hydrogen, nitrogen, oxygen, etc). Since the solubility of the gas in the liquid phase is generally greater than that in the solid phase, the solute gas atoms accumulated at the solid-liquid interface will precipitate to form pores after reaching the critical nucleation concentration. The pores grow along with the directional crystallized solids, and the unique porous structure with pores distributed in the metal matrix along the solidification direction is obtained. This process is equivalent to a solid-gas eutectic transformation, so Gasar is also known as the "directional solidification of metal-gas eutectic". Generally, all of porous materials have basic characteristics of light-weight, good mechanical performance, high thermal resistance, and high specific surface[2,3]. Besides, Gasar porous materials have higher stiffness, and they also have easily adjustable pore structure, low-stress concentration, high wear resistance, etc[4-6]. Therefore, Gasar porous materials have application potential in a wide range of industries such as heat sinks, artificial skeletons, filters, catalysts, carriers, self-lubricating bearings, and wear-resistant brake[1,7].

According to Murakami's carbon dioxide-water solution directional solidification experiment, the compositional super-cooling caused by the gas is ignorable, and the solidification interface remains planar during the solidification of Gasar pure metal[7,8]. In this solidification mode, the resistance of pores with interface co-growth is weak, so it is easier to obtain a regular and uniform one-dimensional porous structure. Therefore, the preliminary research mainly focused on pore structure controlling, mechanical/thermal/acoustic performance testing, and solid-gas eutectic solidification mechanism of pure metal matrix[5-7,9-16]. However, porous pure metals generally have insufficient comprehensive performance and can hardly meet the application requirements for some special fields: rocket combustion chamber condensers, high-temperature heat sink, self-lubricating bearings, wear-resistant brake, artificial skeleton, etc[7,17]. Therefore, the fabrication of porous alloys has been the main research direction in the

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Gasar field recently[17-20]. Different from the solidification mode of pure metal, the compositional supercooling due to the addition of alloying elements can lead to the instability of the solidification interface, so it is difficult to maintain a planar interface, and instead, other solidification modes occur, such as cellular, columnar dendrites or equiaxed dendrites. This transformation in the solidification mode may have an extremely adverse impact on the regularity of the directional growth of pores[17-20]. Therefore, fabricating ordered porous alloys that meet the application requirements for various engineering fields by attenuating the influence of non-planar interface solidification modes on pore directional growth, has been one of the hotspots and difficulties in the research of Gasar porous alloys. In this study, from the perspective of preparation process development, the recent research progress of Gasar porous alloys is reviewed, which can provide some references for relevant researchers.

1 Mould Casting Technology

Mould casting technique is the most common process for fabricating Gasar porous metal, as shown in Fig. 1. In an airtight high-pressure furnace, the alloy is melted in the upper crucible after vacuumed to 10^0 Pa, then high-purity hydrogen (or nitrogen, oxygen, etc.) is introduced into the furnace, and finally keep the alloy in constant temperature for a certain time so that the gas is fully dissolved into the alloy melt. Afterwards, the melt is poured into the lower mould, of which the sidewall is insulated, and the bottom is connected with a circulating water-cooled copper seat (chiller) to ensure unidirectional solidification. This approach has advantages of simple design of the preparation apparatus, and easy control of experimental operations and process parameters.

Nakajima ' s[18,21] group in Osaka University, Japan, fabricated Gasar porous stainless steel and Mg-Al alloys [18] with mould casting technique firstly. These researches indicated that when the alloy is solidified, a solid-liquid coexistence zone, i. e. mushy zone, occurs at the front of interface, which is the most important factor affecting the growth of directional ordered pore structure. As shown in Fig. 2, in the (1/3)AZ91D (obtained by melting AZ91D alloy with mass fraction of 1/3 by adding pure magnesium dilution)

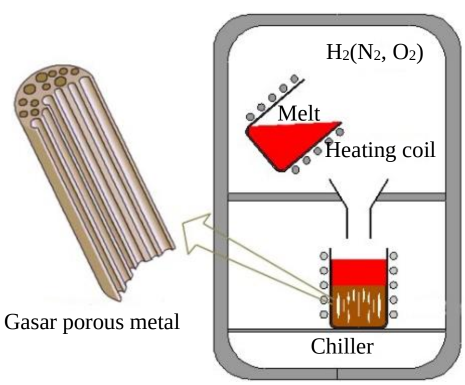

Fig.1 Schematic drawing of the mould casting apparatus

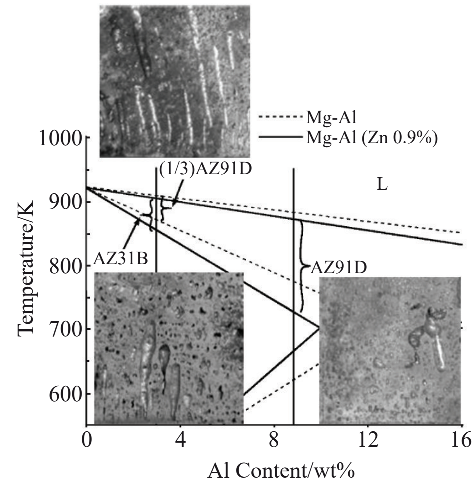

Fig.2 Effect of the width of mushy zone on pore morphology of Gasar porous Mg-Al alloys made by the mold casting technique [18]

specimen, a portion of the cylindrical pores with directional growth and another portion of ellipsoidal pores with no significant growth direction appear, and the pore sizes of the two types of pores are extremely uneven. In the AZ31B alloy specimen, the directional growth of cylindrical pores reduces and the pores are only distributed in the middle and lower part of the specimen, while there are no directional cylindrical pores in the AZ91D alloy specimen. Combining the magnesium-alloy phase diagram and classical solidification theory, the width of the mushy zone l can be described as:

$$l \approx \frac{(T_L - T_S)}{G_L} = \frac{\Delta T}{G_L} \quad (1)$$

where ΔT is the temperature gap between liquidus T_L and solidus T_S, and G_L is the temperature gradient of the liquid phase. Under the same solidification process conditions (G_L is constant), it can be seen that l increases with ΔT due to the addition of Al. The enlargement of the mushy zone will inevitably cause an increase in solid phase above the bubbles, and raise the resistance of pores directional growth, thus resulting in a large number of ellipsoidal pores in the sample (Fig. 3). Ultimately, the regularity of the porous structure of Gasar porous alloys deteriorates.

To attenuate the effect of mushy-zone solidification on the ordered porous structure of Gasar alloys, Li ' s group in Tsinghua University selected a solid solution alloy with

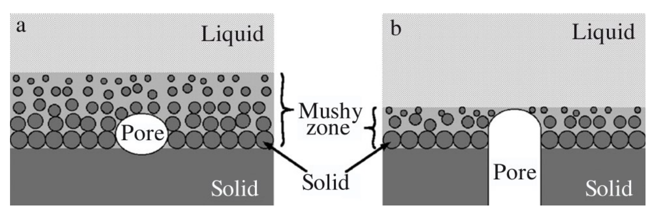

Fig.3 Mechanism of wide (a) and narrow (b) width of mushy zone influencing pore growth of Gasar porous Mg alloys [18]

relatively simple solidification behavior, the Cu-34.6wt% Mn alloy with ΔT approximating to 0, as the research object[17,19]. Gasar porous Cu-Mn alloy was prepared with the mould casting technology, as shown in Fig.4.

In the lower part of a porous Cu-Mn alloy specimen, the pores have a smooth inner wall and a uniform size, and are perpendicular to the bottom surface with a cylinder-like distribution in the alloy matrix. However, as the height of the specimen increases, the amount of directional growth pores decreases. The top of the specimen is full of non-directional pores with uneven size and rough inner wall, as shown in Fig. 4. Further research indicated that the solidification mode is changed by solidification velocity, which decreases with the increase of sample height and is the main factor causing irregular pore structure.

At the lower part of sample, which is close to the chill, the solidification rate is higher, the solid-liquid interface is dominated by the solidification of cell or columnar dendrites. When the distance between the primary arms of the cell or columnar dendrite is less than 1/10 of the pore diameter, the solidification interface can be regarded as planar interface, and thus it is easy to achieve directional growth of pores and ordered porous. On top of the sample, the solidification rate is lower, and the solid-liquid interface is dominated by equiaxed dendrite solidification, which poses a great resistance to the directional growth of pore, and thus it is difficult to obtain an ordered pore structure, as shown in Fig.5.

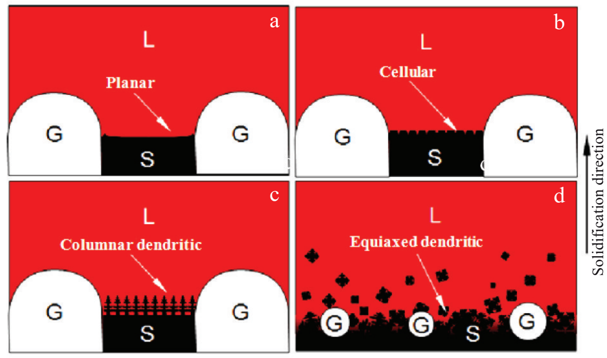

Fig.5 Morphologies of pores with different solidification modes: (a) planar, (b) cellular, (c) columnar dendrite, and (d) equiaxed dendrite[19]

Another approach to reduce the effect of solidification of the mushy zone is micro-alloying for ordered porous alloys. Our research team and professor Li Yanxiang's group used mould casting technology to fabricate eutectic Gasar porous Cu-xCr (x=0.3, 0.5, 0.8, 1.0, 1.3, 1.8, wt%)[22,23] and Mg-xMn (x=1, 2, 3, wt%) alloys[24], respectively. The effects of Cr and Mn contents on the pore directional growth and structural regularity were investigated. Results showed that a small amount addition of Cr (<1.8wt%) and Mn (<3wt%) have less effect on the directional growth of pores in Cu-xCr and Mg-xMn alloys, and the pore structure regularity is uninfluenced too. Besides, the influence of Cr on porosity of porous Cu-xCr alloy is small, and pore size tends to first increase and then decrease, due to the width of mush zone. After Mn is added, precipitation of α-Mn with a high melting point occurs in the crystal or at the grain boundary, promoting the nucleation of bubbles, and increasing the porosity and pore diameter of the Mg-xMn alloy.

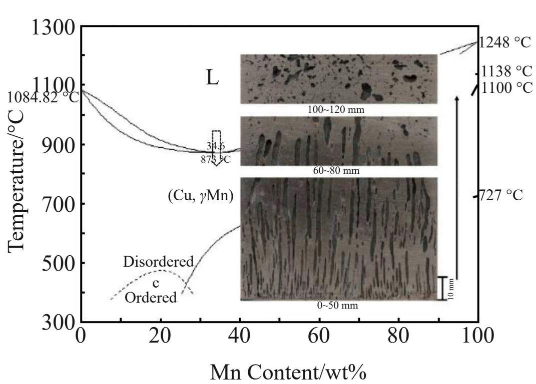

Fig.4 Cu-Mn equilibrium phase diagram and pore morphology of Gasar porous Cu-34.6%Mn alloy[17]

In summary, the ordered pore structure of Gasar porous alloys is mainly determined by the solidification mode of solid-liquid interface and the width of mush zone l. For the mould casting technology, since quantitative control of the solidification velocity cannot be achieved, it is difficult to fine-tuning the solidification mode and width of the mushy zone to suit the directional growth of pores, i. e., it is difficult to prepare ordered porous alloys with complex solidification behavior.

2 Continuous Zone Melting Technology

To achieve the precise control of alloy solidification rate, Nakajima's group[18] first introduced the "continuous zone melting technology" into the fabrication of Gasar porous alloys. In an airtight high-pressure furnace as shown in Fig.6, alloy bars are prepared through a set of high-frequency induction coils, and then moved downwards by servomotors

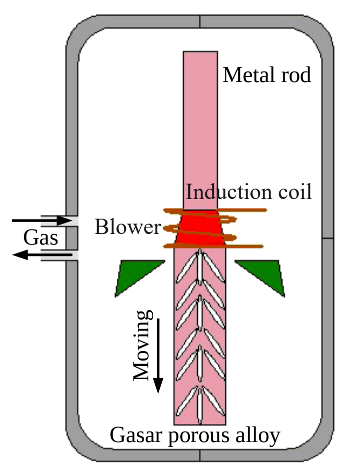

Fig.6 Schematic drawing of continuous zone melting technology

in a vertical direction, with the moving/solidification velocity being quantitatively controlled by the motor speed. The smelting starts after the furnace is filled with working gas (hydrogen, nitrogen, oxygen, etc). Then the alloy rod located in the induction coil is melted and remains intact under the function of surface tension. The working gas is dissolved into the alloy through processes of adsorption, dissociation, diffusion and ionization. After the alloy bar is pulled out of the induction coil, cooling medium is sprayed onto the alloy bar through the blowers distributed under the coil, to achieve directional solidification. Finally, porous alloy is obtained.

Current research on the preparation of Gasar porous alloys by continuous zone melting is only reported by Nakajima's group, such as porous carbon steel[25], stainless steel[26], intermetallic compound Ni_3Al[18] and shape-memory alloy Ti-Ni[18]. Taking stainless steel and carbon steel porous as examples, as shown in Fig. 7, uniform pore size and ordered porous structure are achieved in both specimens. However, due to the solidification of the mushy zone, the pores of porous carbon steel sample exhibit a "pearl chain" growth, making the inner wall extremely rough. Compared with the mould casting technology, the continuous zone melting method achieves quantitative control of the solidification rate, thus making the preparation of multiphase alloy with relatively complicated solidification behavior possible.

However, the porous alloy specimens that can be prepared with this method are general small (<Φ10 mm) in size, due to the skin effect of induced current. In addition, due to the influence of cooling process, the surface pores of sample grow at an angle in the withdrawal direction, wrecking the regularity of the overall pore structure, as shown in Fig.7.

3 Continuous Casting Technology

To meet the requirements of Gasar porous alloys for product size and ordered porous structure in the fields of electronics, chemical engineering, aerospace, and biomedical engineering, Nakajima's group developed a continuous casting apparatus, as shown in Fig. 8. In an airtight high-pressure resistant furnace, a dummy bar for preventing the melt from flowing through the hole is set, a mould is surrounded by copper chiller, pinch rollers to control transference velocity of the dummy bar, which is controlled by a servomotor to obtain a precise transference (solidification) velocity. After the alloy is melted, the working gas is introduced into the chamber. It stands for a while to ensure that the working gas is dissolved sufficiently. Then the continuous casting system is started, and the melt crystallizes to form a porous alloy.

Nakajima[18] has prepared Gasar porous Al-Si[20] and Al-Cu alloys with the continuous casting method. Taking Al-Si alloy as an example, porosity, pore size, and pore morphology are influenced by Si content and transference/solidification velocity. The porosity and pore size increase with the Si content, and decrease with the increase of the transference velocity, as shown in Fig. 9. In addition, the pore roundness decreases with the increase of the primary phase dendrite area fraction (Si content), and the ordered porous structure becomes variable.

Liu[27] and our team conducted the first research on Gasar continuous casting technology in China. Gasar continuous casting apparatus was developed, and porous Cu-xZn (x=2, 6, 10, wt%)[28] and Cu-xNi (x=2, 6, 10, wt%) alloys were prepared[29]. Results showed that the alloy content mainly affects the directional growth of pores and regularity of pore structure, while the transference/solidification rate mainly affects the porosity and pore diameter. Taking Cu-Zn alloy as an example, under a low Zn content (<6%), the directional growth of pores is almost unaffected, and the pore structure is ordered. As the solidification rate increases, the porosity increases and the pore diameter gradually decreases. Under a high Zn content (>6wt%), as the Zn increases, the mushy zone width l increases, and thus the resistance to directional

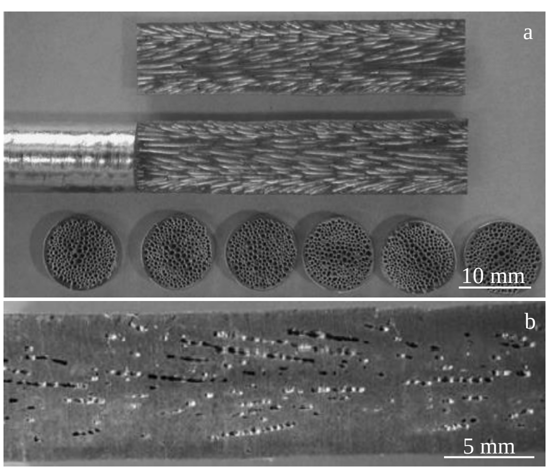

Fig.7 Specimens of Gasar porous stainless steel (a) and carbon steel (b) fabricated by the continuous zone melting technology[25,26]

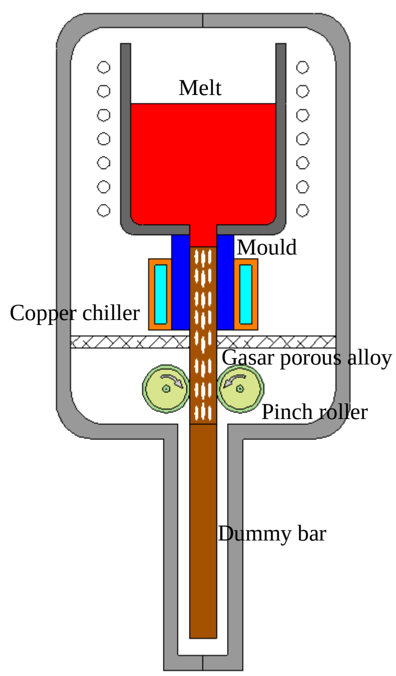

Fig.8 Schematic drawing of continuous casting apparatus

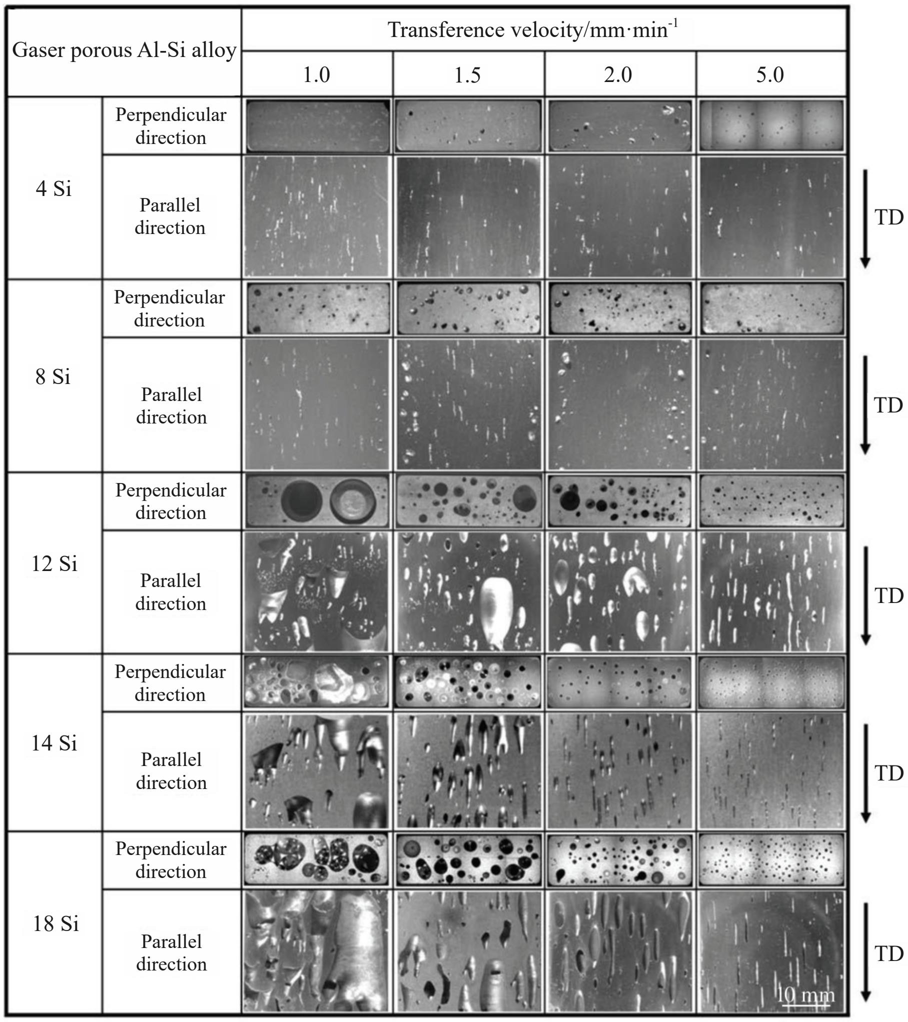

Fig.9 Specimens of Gasar porous Al-Si alloys fabricated by the continuous casting technology[20]

growth of pore increases, resulting in larger pore sizes, rougher inner pore walls, and deterioration of the ordered porous structure, while the porosity first decreases and then increases.

In addition, the continuous casting process can not only change the solidification rate to obtain the porosity, pore size, and pore spacing that meet the requirements for various potential applications, but also prepare large-size and various shape porous alloys by mould design. So far, the largest-size Gasar porous pure copper slab with a cross section of 30 mm× 10 mm was prepared by Nakajima[11]. Based on the continuous casting of porous copper alloy round bars of Φ15 mm[28], our team successfully prepared Gasar porous Cu-6Zn and Cu-6Ni alloy[29] slabs with a cross section of 80 mm×12 mm by solving the moluld design problem, which lays the technology and material basis for low-cost fabrication of large-size porous alloys and related applications, as shown in Fig. 10. The change law of pore structure of the large-size Gasar porous alloy is consistent with the small (Φ15 mm) porous continuous cast specimens. Under the same addition amount, Ni is more resistant than Zn to the directional growth of pores

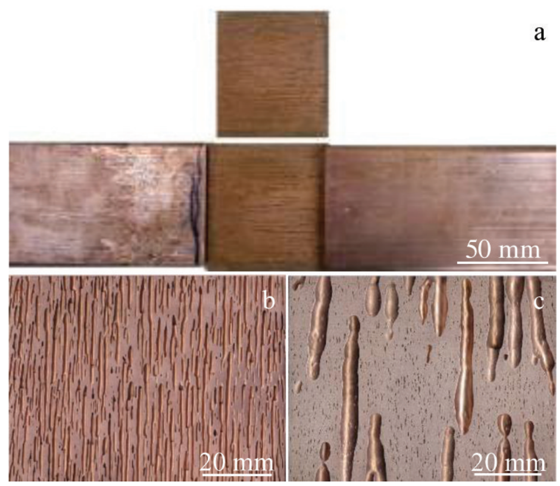

Fig.10 Mass production of Gasar porous Cu-6Zn (a) and Cu-6Ni (b) alloys fabricated by the continuous casting technique[29]

in the mush zone, resulting in extremely poor regularity of porous Cu-6Ni alloy.

4 Conclusion and Outlook

Preparing ordered porous structure by reducing the effect of alloy solidification on the directional growth of pores has been one of the technical bottlenecks in the current widespread applications of Gasar porous materials [30]. From existing research, the main reasons why the ordered porous structure is difficult to control are follows: (1) the influence of the "mushy zone" at the front of the interface during the solidification of the alloy; (2) after alloying elements are added, the solid-liquid interface becomes unstable and the solidification mode changes. Preliminary researches mainly reduce the influence of the above two factors on the directional growth of pores from the following two perspectives: (1) preparation technology improvement; (2) alloy composition design (micro-alloying). Ordered porous alloys with some components in specific alloy systems have been prepared, and some breakthroughs have been made in the corresponding solidification theory. However, the research of Gasar porous alloys needs further refinement and expansion in terms of theoretical systematics and application background. For example, the effect of the temperature gradient G_L, which determines the width of the mush zone l, and the solid-liquid temperature gap ΔT on the directional growth of pore; the influence of the dissolution and precipitation of gas atoms and the formation of pores on the solidification of the matrix alloy; test of mechanical, thermal and physicochemical properties of fabricated ordered porous alloys, and experimental test for the potential application in the fields of microchannel heat sinking, filters, and bio-skeletons, etc. These are of great theoretical and practical importance for broadening the applications of Gasar porous metals.

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Gasar多孔合金研究进展

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摘　要： Gasar是一种基于气体在金属固/液两相中的溶解度差而发展起来的制备多孔金属的新工艺。如何获得气孔结构规则的多孔合金，是当前Gasar多孔材料大规模应用的技术瓶颈和研究热点之一。造成多孔合金气孔结构规则性难以控制的主要原因有：合金凝固时其界面前沿“糊状区”的影响，以及合金元素加入后，固-液界面失稳而导致的凝固模式改变；前期研究主要从制备技术改进和合金成分设计（微合金化）这两个角度，来弱化以上两个因素对气孔定向生长的影响。从制备技术发展（简单模铸法→连续区域熔炼法→连续铸造法）的角度，综述了国内外Gasar多孔合金的研究进展，总结了影响多孔合金气孔结构规则性的主要因素，分析了现有研究的不足，并对今后的发展方向进行了展望。

关键词： Gasar；多孔合金；气孔结构，凝固模式；糊状区

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