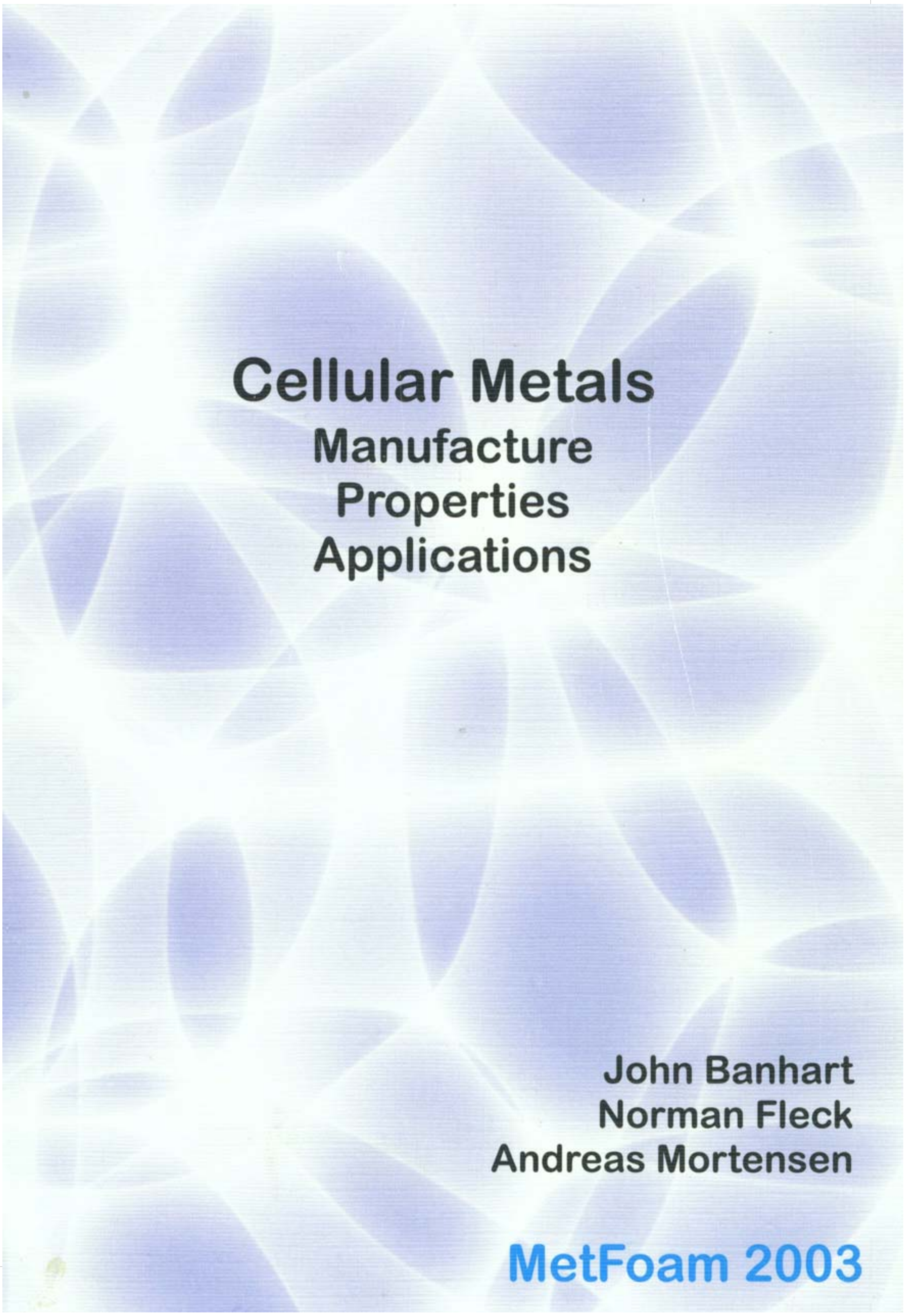

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Gasar - a new class of porous materials: syntheses, structure, properties and prospective application

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The paper summarizes published data and also deals with technology, structure, applications, and properties of gasars – new porous materials based on original findings obtained by authors. The method consists of melting a material in a gas atmosphere to saturate it with hydrogen and directional solidifying under strictly controlled thermodynamic and kinetic conditions. The materials produced by this method, have a monolithic matrix and pores of proper geometric shapes, providing to gasars higher strength, plasticity, thermal and electrical conductivities as compared with those of other porous materials. Gasar is recommended for prospective application as filters, bearings, metal-matrix composites and etc.

1 Introduction

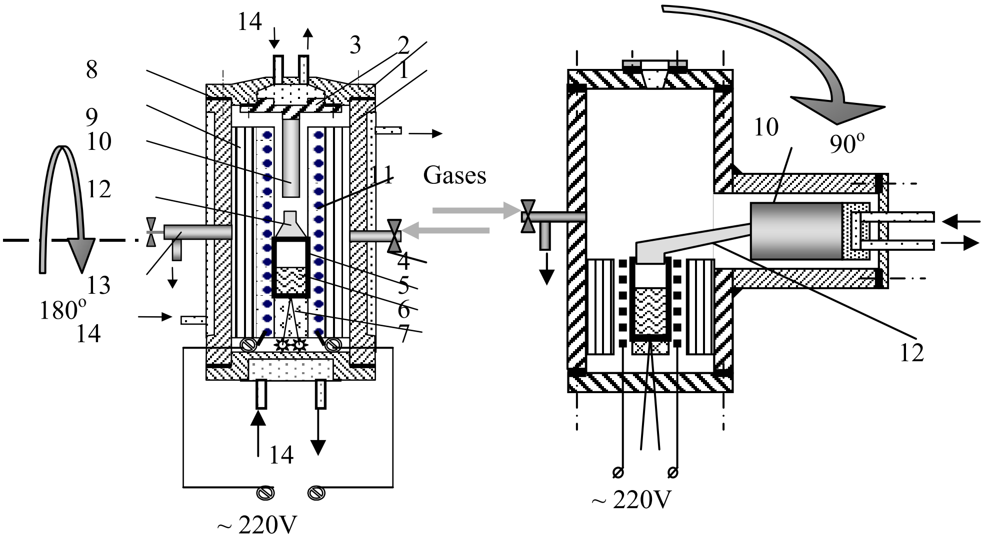
The gasar-process is completely different to well-known techniques, therefore it should be distinguished as new direction in porous material technologies. It is based on gas-eutectic reaction that had been studied for the first time (1974-1979) in detail and got the name in National Metallurgical Academy of Ukraine [1]. The first USSR patents were issued in 1980-1985 as confidential and were not widely highlighted in press. The method got fame just 1993 after USSR collapse [2]. The gasar–process is studding in Ukraine since 1980. It was successfully tested in USA, Japan, Poland, and Russia [1-7].

2 Features of gasar syntheses

2.1 Apparatus

The gasars may be synthesized in a purpose-built unit of hermetic type. There are three kinds of devices: fixed, rotated on 90° and 180° (Fig.1). The apparatuses made it possible to melt metals in a crucible and to solidify them in a casting mould under controllable gas pressure. The built-up moulds have refractory walls and water-cooled copper chill on the bottom. With this mould design, the heat is predominantly transferred from the melt axially via the bottom. Depending on heat removal direction it is possible to form gasars with radial or combined pore orientation too.

The method demands specific equipments for gasar production. Several devices were designed, built and successfully tested in Russia (Moscow, 1987), USA (Washington DC, 1995, NRL; New Mexico, 1996, Sandia NL), and Japan (Osaka University, 1997).



(a) (b)

Fig. 1. Hermetic chambers (schematic) for gasar syntheses: (a) pouring after rotation on 180°, (b) - pouring after rotation on 90°

1 – body; 2– top; 3 – water-cooled bottom, 4 – gas-pressure line, 5 – alumina crucible, 6 – melt, 7 – thermocouple, 8 – gas hermetic seal, 9 – metal sheets, 10 – mold, 11 – molybdenum heating element, 12 – funnels, 13 – vacuum pumping line, 14 – water line

2.2 Gasar technology fundamentals

Key phenomenon underlying gasar technology is gas-eutectic reaction resulting in two-phase structure (Fig.2).

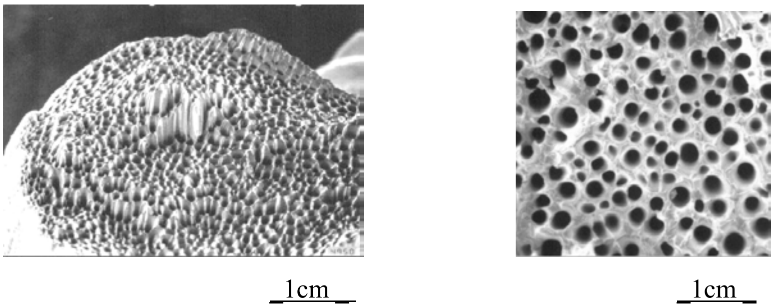


Fig. 2. General view of copper gasar on fracture surface

The features of this process are the simultaneous formation of crystals and gas-bubbles from the liquid solution charged by gas. It resembles traditional eutectic reaction; therefore the solidification in the systems having gas-eutectic phase equilibrium leads to occurrence of the gas-eutectic structure. The materials produced by gas-eutectic solidification are named gasar (acronym of Russian expression meaning "gas-reinforced”).

Basically the gas-eutectic reaction can be observed in Metal-Hydrogen systems such as Cu-H, Fe-H, Ni-H, Co-H, Mg-H, Fe-C-H, Al-H, Be-H, Cr-H, Mn-H, Mo-H, Ti-H, W-H,) displaying gas-eutectic equilibrium in the melting range. Some Metal-Oxygen (Ag-O; Fe-C-O; Cu-O), Metal-Nitrogen systems (Fe-N; Ni-N; Cu-N; Mn-N) and some kind of ceramic saturated with hydrogen, nitrogen or oxygen are perspective for using in the gasar – process also.

2.3 Process parameters selection

Thus during gasar-process it is possible to control hydrogen contents in the melt, the gas pressure during solidification, heat removal from ingots, and regulate the final porous structure in a one-step technical gasar process. Finally, gasars have a monolithic matrix and pores with a smooth surface. Depending on solidification conditions: P_h - partial pressure of hydrogen above the melt surface; P_s - outer pressure during solidification; T_m - melt temperature prior to pouring; V_s - solidification rate, it is possible to control the pore size, quantity, shape and orientation in a matrix

The gas pressure largely determines the gasar structure over the solidifying melt and by the inner hydrogen-liquid interfaces (growing bubble surfaces). Pressure P_h determines the hydrogen content in the liquid metal, which depends on the capability of the melts to interact with this gas. Pressure P_h can be equal to that for melt saturation with hydrogen ($P_h = P_s$), exceed it ($P_h > P_s$), or be lower ($P_h < P_s$). With $P_h = P_s$ melting and pouring of the metal were made under constant partial pressure of hydrogen. With $P_s > P_h$ the metal was molten in hydrogen atmosphere and the total gas pressure in the autoclave was increased to the specified value before pouring by adding inert gas. This suppresses the growth of gas blisters at the crystallization front and produces fine-pore gasars. For higher porosity and larger pore size the partial pressure of hydrogen in the autoclave was lowered at the time of melt solidification – this promoted the growth of the gaseous phase.

The pressure is a very powerful technological parameter and it allows to obtain of different kinds of structure. Different kinds of pore morphology including alternating porous-nonporous layers may be formed due to specific pressured value. Solidification velocity and pouring temperature are less effective parameters in gasar- technology.

3 Structure

The bubble nucleation occurs heterogeneously and always on existing discontinuities in the liquid bulk or at the liquid/solid interface (Fig.3). The discontinuities may vary in nature, like: regions where the liquid does not contact the solidification front; small pits and cracks on the surface of high-melting particles suspended in the melt and on the mould walls, gas bubbles entrained from the atmosphere during melt pouring or stirring, bubbles formed by passing a gas through the melt, bubbles caused by cavitation. For a gasar to form, it is important that the potential nucleation sites are thermodynamically equivalent and uniformly distributed. The nascent solid layer acts as a seed for bubble nucleation, so establishing a qualitative solidification interface that is of paramount importance for producing uniform porosity in gasars.

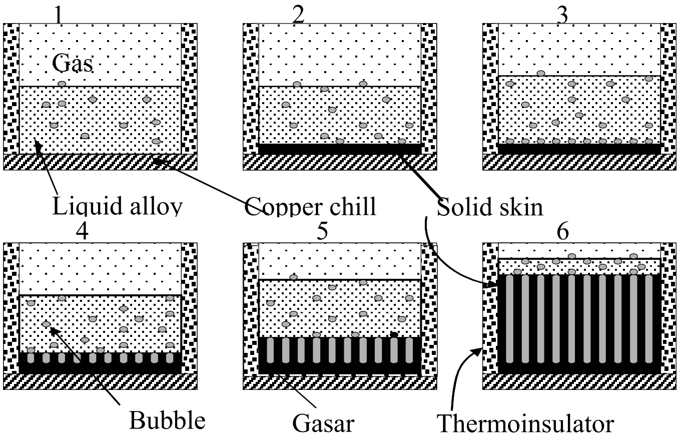


Fig. 3. Pores formation (schematic) on the surface of the native solidification front during unidirectional heat removal: 1-6 - consecutive gasar growth steps

The pressure inside the gas bubbles is not constant due to gas bubble detachment and quasi-boiling occurrence resulting in goffered pore shape formation. Gasars formed during quasi-boiling typically have significant porosity about 55-65%.

The elongated pores always have similar nature of orientation. The general orientation is directed by heat sink conditions during gas-eutectic solidification. The growth velocity vector is always normal to the solidification surface (Fig.4).

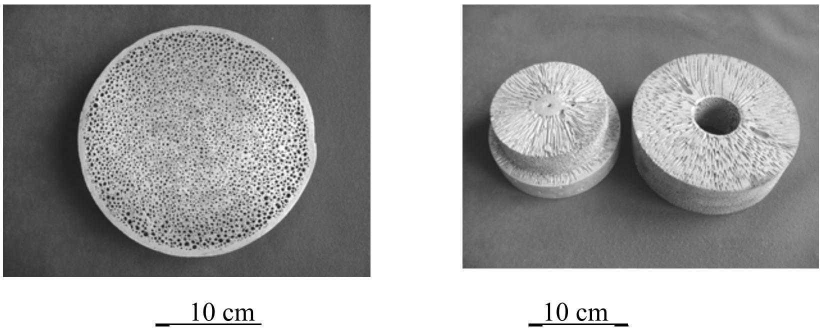


Fig. 4. Magnesium gasar with axial (left) and radial (right) pores

Like other eutectic reactions, the gas-eutectic reaction may result in formation of either ordered or disordered structures depending on the thermodynamic conditions at the solidification front. To distinguish between the two structural types, the term **gasarite** was coined for an ordered pore-solid structure developing due to a coupled growth of the solid and the gaseous phase in gas-eutectic transformation. It is gasarite that imparts some unique mechanical and manufacturing properties to gasars [6,7].

Any of the two phases may be the leader in gas-eutectic solidification. When the solid leads, dendrite centrelines penetrate deep into the melt while bubbles form in interdendritic spaces. These bubbles are mutually isolated and do not contact each other directly, so the final structure is determined by the dendrite skeleton shape. This type of **gasarite** is named **dendritic**. Its pores are isolated and their dimensions compare to the dendrite centreline diameters. When the pore dimensions exceed the dendrite centreline diameter, **bubble gasarite** occurs in which the gas bubbles determine the structure evolution.

The following structural gasar characteristics are now available:

- Porosity 10-65 %,
- Pore diameter 10-1000 μm,
- Pore orientation in casting: radial, axial or their combination
- Pore shape: cylindrical, spherical, and ellipsoidal.

Materials:

- Metals: nickel, copper, iron, magnesium, aluminum, titanium, cobalt etc.
- Alloys: bronze, steel, gray and white iron, Inconel etc.
- Ceramics: Al_2O_3, MgO_2, ZrO_2

The pore size distribution depends on formation conditions and there may be several reasons of nonuniformity: concurrent growth of large and small pores; coalescence as result of pore contacts, local solidification speed changing; local pressure changing on gas-liquid interfaces.

4 Specific properties

Due to original solid-porous structure gasar has following advantages:

- High mechanical properties: strength, plasticity, damping absorption, stiffness;
- Insensitivity and adaptability to temperature extremes; flame resistance;
- Absence of gas evaporation upon low pressure;
- Ability to design special acoustic damping properties in articles due to impregnation of its porous media with polymeric, liquid or powder substances;
- Ability to design articles of different shape: plate, tube, sandwich, porous media with monolithic layer inside;
- Good weldability and fabricability.

5 Prospective application

Gasars are successfully tested for mechanical, physical and filtering properties, filtering elements and filter supports, fuel cells, fluid/particle separators, compact gas diffuser, liquid heat exchanger, mist elimination of water and oils, regenerator for thermal engines (Fig. 5, a) [3,6]. Also the materials can be used like:

- Matrix for metal-matrix composites (bearings, frictional elements, containment matrix and burn rate, catalyst surface enhancer for solid propellants)
- Core structure for high strength panels (Fig. 5, b)
- Energy absorber for auto bumpers
- Flame arresters
- Porous electrodes

2 cm a **1 cm** b

Fig. 5. General view of gasars: (a) – filtering articles, porosity 10-35 % from copper, nickel, bronze; (b) – nickel gasar with porosity 56%

6 Conclusion

Gasars technology is based on a new scientific knowledge about gas-eutectic reaction in gas-metal systems. Thermodynamic and kinetic conditions during solidification allow controlling the terminal solid-porous structure. Specific porous structure provides to gasar high strength, stiffness, thermal and electrical conductivity. Gasars with different porosity and structure may be synthesized for filters, metal-matrix composites, bearings, brakes, damping elements etc.

References

[1] Shapovalov V.I. ”Methods for Manufacturing Porous Articles” U.S. Patent, No. 5,181549, 26 January 1993.

[2] Shapovalov V. I. “Porous Metals”, MRS Bulletin, No. 4, 1994, pp. 24-29.

[3] Shapovalov V.I. Boyko L.V., Baldwin M.D., Maguire M.C., Zanner F.J. Anisotropic porous metals production by melt processing, AVS International Symposium on Liquid Metal Processing and Casting, 1997. – February, - pp.16-19.

[4] Boyko L.V. Formation of porous structures in metal-hydrogen systems. Materials Science. Vol.38, No.4, 2002, pp.544-549.

[5] Boyko L. Structural Features and Properties of Gasar – New Porous Composite Metals for Industry. In: State of Art in Cast Metal Matrix Composites in the Next Millennium. A Publication of TMS. Edited by P.K. Rohatgi. 2000, pp.303-312.

[6] Moore D., Naval aircraft materials and processes. AMP, v.155, No.3, 1999, pp. 23-34.

[7] Foltz J.V., **Metal matrix Composites.** APM, v.154, N6, 1998, pp, 12-33.