Porous Metals

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Introduction

Porous metals are engineered materials; they are designed for special properties. Technological progress necessitates expanding the choices of such materials, making the development of new porous metals a relevant challenge for materials scientists.

Although a wealth of information has already been accumulated on these materials, new results are published every year, extending the engineer's capability to manufacture porous metals and revealing their unknown and often unusual properties. This survey describes the state of the art and some recent accomplishments in the field. This article discusses manufacturing practices, structure, properties, and applications of porous metals. Promising new research issues are also highlighted. Materials whose pores were not formed *in situ*, like honeycomb structures made by high-energy beams etc., are not covered.

Classification of Porous Metals

Porous metals are most often classified by the method of manufacture.[1] Here, a similar classification is given, although it differs from earlier ones because its criterion is the state of matter of the metal or alloy before the gas-crystalline structure of the porous metal is formed. We distinguish methods based on vapor deposition and melt solidification from the formation of pores which involves no change in the state of the base metal or alloy, such as sintering or radiation swelling. Apart from this classification, porous metals may be divided into two large groups, permeable and impermeable.

Classification by pore spatial distribution is also useful. Pore structure can be ordered or disordered, oriented or nonoriented. Porous metals may be distinguished by the geometry of individual voids that may be irregular, spherical, cylindrical, conical, or variable in section; straight or curved; closed, open, or dead-end.

Porous metals also are categorized according to their applications, e.g., friction parts, electrical engineering components, filters, structural components, etc. However, due to the rapidly expanding applications of porous materials this classification has proved inadequate and may mislead the designer.

Powder Metallurgy (P/M)

Porous metals formed by powder processing are rightly ranked as the main class of porous metals. The manufacturing process primarily consists of powder synthesis, compacting, and sintering the structural constituents, namely powder particles, chips, fibers, wire meshes or sheets, or their combinations.

Powder sintering is one of the simplest methods of making porous metals. The base powder is blended with another powder that contains one or more alloys of the base metal and whose composition is such that a liquid phase forms below the melting point of the base powder. The blend is sintered in a non-oxidizing atmosphere at normal pressure. Porosity in such metals may be as high as 60%.

To increase porosity, pore-forming agents like carbonyl are frequently added to the blend. Such agents decompose and are thus removed during sintering. An unsintered "green" part with the desired shape is formed without applying pressure and then heated to the eutectic point. The carbon dioxide which evolves increases the porosity in the part up to 90%.

In making porous tungsten, 2–15% iodine fluoride is added to the blend as the pore-forming agent to assure a more uniform pore distribution and a greater fraction of open pores. In sintering tungsten or molybdenum, copper may serve as a pore-forming agent to be later leached by nitric acid at low pressure. Sometimes a highly soluble mineral like rock salt is added to the blend to be removed by water or acid leaching after sintering.

Slip foaming consists of making a dense suspension of powder in a liquid, foaming it, and baking the foam. A variation of the method includes making air-in-water foam containing surfactants and foaming agents, charging it with the metal to 30–300% of the foam weight, adding a stabilizer capable of polymerization on contact, and finally sintering. Sintering is accompanied by pyrolysis of the stabilizing agent, surfactants, and foaming agents.

Sometimes a liquid organic binder is used for making metal powder suspensions. Furthermore, a particulate organic material with an appropriate particle size is added to act as a foaming agent. The mixture is cured and heated to decompose the binder and organic material without disintegrating the molded part. As heating continues, the carbon is removed as carbon dioxide during powder sintering.

Slip casting involves pouring slip into a porous mold to be dried and baked to produce a green part cast to the desired shape. This method is suited to making cellular metals with up to 90% porosity. Plastic foams, e.g., polyurethane, are commonly used for making molds. The mold is cut to dimension and impregnated with the slip by immersion. The piece is then sintered to provide the desired porosity.

Fiber metallurgy offers several advantages over powder methods. At a given porosity, fiber-derived materials are superior to powder-processed analogs in strength and impact resistance. Fibers are compacted a preset amount, and green compacts are sintered in a non-oxidizing atmosphere.

To improve strength, metallic fibers are sometimes coated with a low-melting-temperature agent before compacting and sintering. Precoating provides better bonding between the constituents. When high strength, plasticity, thermal stability, and permeability are required, wire meshes are used as starting material. The resultant products are called fiber metallurgy materials with controlled structure. They are produced by welding, brazing, sintering, or by resin bonding wire meshes or perforated sheets in a stack. The stack may be sintered before or after forming. Materials produced this way may attain 80% porosity.

Chemical and Electrochemical Deposition

Deposition is often used for making filters, catalysts, and structural parts. Metal is deposited on a porous organic substrate like polyurethane; the substrate is pretreated to make it rigid and conductive. When electroless deposition is used, the substrate surface is pretreated with an oxidizing acid solution to make it hydrophobic and to roughen it through selective etching, thereby improving the mechanical bond for the metal layers to be deposited.

For stronger bonding, deposition is alternated with dissolution. Pore diameter is controlled by the pore size in the organic substrate material, such as polyurethane, polyvinyl acetate, polyvinyl chloride, viscose sponge, etc. To provide pores of uniform diameter, a prefabricated permeable substrate of a sintered alloy is used. A gaseous halide or another metal compound is passed through it. The metal is deposited in the pores, which reduces the pore diameter and brings the pore-size distribution closer to normal.

Physical Vapor Deposition

Physical deposition methods technically resemble chemical and electrochemical deposition from liquids. The difference is that the process is carried out in a vacuum chamber containing a cold porous substrate and a vapor source of the base metal or alloy. Metal atoms condense on the substrate, forming a continuous three-dimensional grid of preset thickness. The substrate is then removed by a thermal, chemical, or other method, leaving porous metal whose macrostructure is a replica of the substrate. The process is suited for making metals with void fractions up to 95%.[1,2] Sometimes physical vapor deposition is used for producing porous metal coatings on parts. In this case, pores form *in situ* due to defects arising in the atom arrangement during the condensation.

Casting

Casting offers no less variety than powder metallurgy. It includes those practices in which the base metal or alloy is molten and then freezes.

Lost-foam casting is a unique process used to make cellular metals in Japan. Connected pores in plastic foam are filled with a castable refractory which is then cured. Upon heating, combustion of the sacrificial foam leads to formation of a spongelike solid. This solid is used as a mold for metal which solidifies in its pores. The process is primarily used for making cellular metals with low melting points.

A porous pattern for making refractory porous metals may be prepared by a different method not involving the use of organic materials. A porous compact is made of a powdered inorganic material that is soluble at least in one solvent. The compact is heated, impregnated with the melt, and cooled to ambient temperature. The inorganic substance of the compact is then removed by a solvent.

Infiltration of a granular bed is in many respects similar to lost-foam casting. It yields a continuous structure by melt infiltration of a bed of granules contained in the casting mold. The granules are made of a soluble but thermally stable material that is removed by chemical treatment. To ensure free flow of the melt, it should be superheated. It is also desirable to preheat the granule bed and pressurize the melt or evacuate the spaces between the granules. An alternative method involves introducing granules into the melt while it is vigorously stirred.

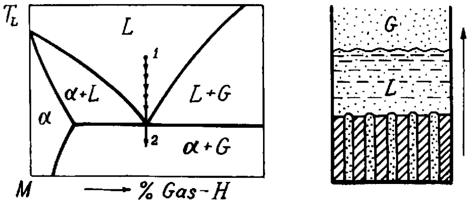

Figure 1. (a) Isobaric section of metal-hydrogen system with gas-eutectic equilibrium. (b) Gas-solid eutectic growth in upward directional solidification.

Foaming consists of adding a foaming agent to the molten metal and solidifying it. The resultant material is a continuous sponge with bubbles encapsulated in solid. Foam is generated through decomposition of a foaming agent injected in the melt. A substance that gives off gas in heating, e.g., a hydride, may be used for a foaming agent.

Melt foam generation is hard to control, and foamed metals contain large bubbles non-uniformly distributed throughout the casting. Numerous attempts have been made to prevent this defect, e.g., by vigorous stirring, application of magnetic field, or thickening (increasing the melt viscosity). Problems, however, persist due to the relatively short time between the introduction of the foaming agent and the generation of foam. Further difficulties arise from premature decomposition of the hydride or another foaming agent. Thickening additives often impair mechanical properties of the foamed metal.

Numerous variations of foaming exist. In some cases foam is generated by introducing gas directly into the melt during solidification, as in a method of continuous casting. Another method involves blowing inert gas through a bubbling unit into the melt contained in the mold, with simultaneous solidification of the melt. To improve strength-to-weight ratio, fiber particles are commonly introduced into the melt foam as a reinforcement.

A method of making foamed aluminum recently developed in Canada deserves special mention.[3] Air or another gas is introduced into a molten aluminum puddle while simultaneously stirring the melt in the bubbling zone. A surfactant (SiC) is injected concurrently with the gas to stabilize the foam. In this continuous process, the foam is fed into a horizontal or vertical mold to freeze, forming sheets, tubes, or other products with cellular structure. The method offers high output, is simple and cost-efficient, and allows pore-size control over a fairly wide range. An important advantage of this technology is the possibility of using aluminum of any degree of purity, and thus recycling aluminum scrap, etc.

Gas-Eutectic Transformation

Gas-eutectic transformation in metal-hydrogen systems is a relatively recent discovery.[4] In this reaction, the liquid decomposes into a solid and a gas phase: $L \rightarrow S + G$. The transformation may take place if the phase diagram for the metal-hydrogen system involves a gas-eutectic equilibrium as in Figure 1a. Making the material consists of two steps:[4]

1. Melt charging with hydrogen to reach the eutectic composition, and
2. Melt solidification in a conventional or continuous casting mold.

No melt foaming occurs because the gas is evolved as the melt freezes (Figure lb). The process is in many ways similar to conventional eutectic solidification, the distinction being that the liquid decomposes into a solid and a gas rather than into two solids. The main process variables that govern the amount of porosity and the size, shape, and orientation of the pores are the hydrogen level in the melt, gas pressure over the melt in solidification, direction and rate of heat removal, and alloy chemical composition. Changing these variables, one can control the pore structure over a wide range.

The Structure of Porous Metals

Porous metal structure may be described by a number of special parameters, the most important being the amount of porosity, average pore size, pore shape, pore orientation, degree of pore interconnection, pore distribution in macro- and microregions, pore-size distribution, connectivity, and specific surface. Pore structure is determined by processing, the emphasis of this survey.

The structure of a ***sintered porous metal*** depends on the shape of particles or other constituents to be sintered, the degree of compacting before sintering, and the sintering conditions.[5]

Powder compacting and sintering results in three-dimensional labyrinth porosity (Figure 2a), whose characteristics depend on the powder particle size and shape. Maximum porosity is usually achieved by sintering hollow spherical particles; somewhat lower amounts of porosity are obtained when particles are of irregular shape. Porous metals made by sintering spherical powders have minimum porosities.

When tubular or solid fibers in parallel alignment or in grids are sintered, the result is an ordered, oriented structure whose parameters are controlled by fiber dimensions. When fibers are not oriented, the pores are arranged more or less at random (Figure 3). In this case, the structure is controlled not only by fiber length and diameter but also by the method of their presintering, bending, crimping, or spiraling. Pore surface topography is determined by that of the particles or other components to be sintered and is always heavily contaminated with oxides and foreign matter.

Cellular metals are different from sintered porous metals in structure. Whatever the manufacturing process, the structure of cellular metal invariably features a continuous three-dimensional grid of the base alloy (Figure 4a).

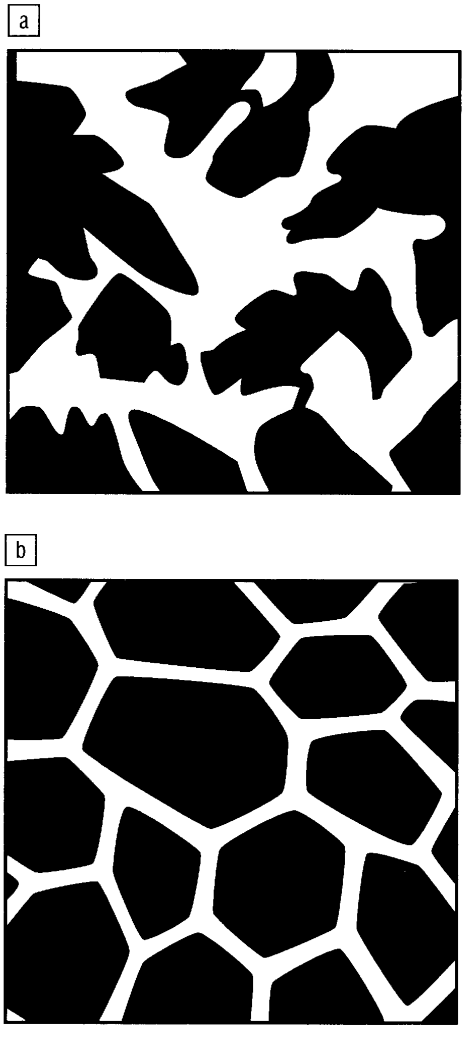

Figure 2. (a) Schematic diagram of the structure of porous metal produced by sintering irregular particles. (b) Schematic diagram of the structure of foamed metal.

When produced by melt foaming, the cellular structure is described by the average values of cell (bubble) diameter and interpore wall thickness. The walls separating cells are poreless and may contain only the base alloy and particles introduced for reducing the surface tension at the gas-melt interface, if any (Figure 2b). If, however, a P/M (powder metallurgy) method or deposition on an organic substance is employed, the walls will have a more complex structure due to their own porosity resulting from the removal of the substrate on which the powder particles or metal atoms were deposited. The deposit itself will contain fine pores, too (Figure 4b).

In cellular metals made by melt foaming, pore walls have a clean, nearly lustrous surface and are not interconnected. Cellular metals made by P/M and deposition methods have interconnected pores and a gridlike structure. The pore wall surface is rough and contaminated with oxides and products of decomposition of the substrate material removed (Figure 4b). Cellular metals may have a non-oriented general structure, which is always the case with foamed metals, or an oriented one depending on the structure of the substrate to be removed.

Materials produced by gas-eutectic solidification are so different structurally from all other porous metals that a new word was coined for them—*gasar*, which is an abbreviation of the Russian term for "gas-reinforced." Gasars may be manufactured in diverse structural variations depending on the process variables previously discussed.[4] Figure 5 illustrates the main structural types embodied in gasars. Gasar pore size may be varied between 10 μm and 10 mm as desired, and the amount of porosity may reach 75%.

The pore wall surface is always entirely clean. In most cases it has a high luster but is sometimes not so smooth due to the exposure of grown-out dendrites. The interpore walls are poreless and free of any secondary porosity or undesirable inclusions.

The relationship between the average pore diameter and the amount of porosity is an important structural characteristic of porous materials. A summary of these data for various porous metals, including gasars, is presented in Figure 6. No method is presently available for making porous metals that combine fine pore size with high void fraction. Clearly, the existing technologies are complementary in that any of them is applicable to a specific area of engineering problems.

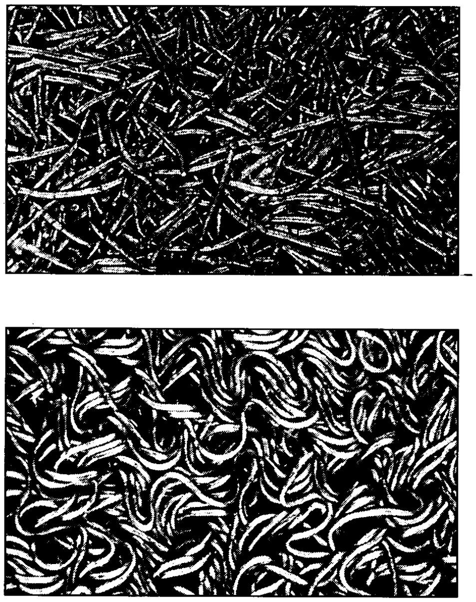

Figure 3. (a) The structure of porous metal produced by sintering short straight fibers. (b) The structure of porous metal produced by sintering long crimped fibers.

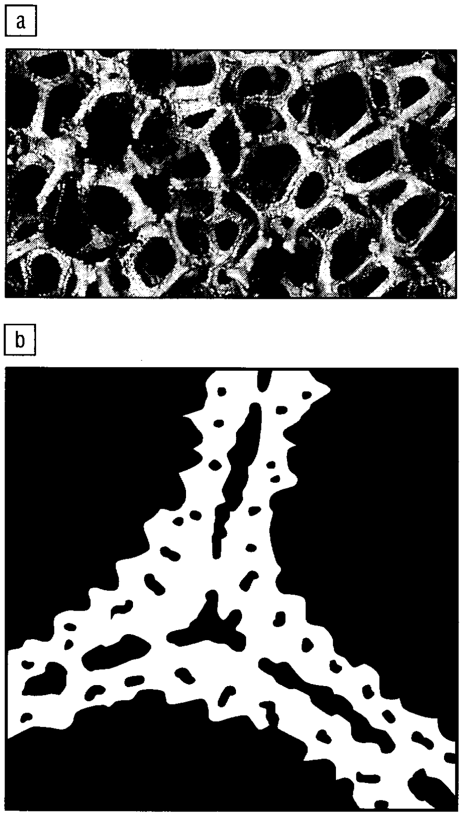

Figure 4. (a) The structure of a high-porosity cellular metal. (b) Schematic diagram of pore space inside the "grid" of a cellular metal.

Properties of Porous Metals

Mechanical Properties

Strength decreases faster than expected based on the volume fraction of the solid phase. The reason is that mechanical properties are highly sensitive to pore shape. Pore edges act as stress concentrators, reducing strength and especially plasticity.[1,2,5,6] The strength of porous metals made by powder sintering depends not only on the amount of porosity and the powder material identity, but equally on the particle size and the sintering temperature and time. The greater the number and area of particle contacts, the better the mechanical properties of a sintered porous metal.

At a given porosity, sintered fibers yield far better strength properties than sintered powders. Sintered knitted meshes exhibit even greater strengths. The general behavior of impact resistance and plastic properties is similar to that of strength. Foamed metals and high-porosity cellular materials with a gridlike structure feature disproportionately low strengths, particularly in tension.

All factors being equal, gasars are the strongest. For instance, at 20% porosity, the strength of copper gasar is 1.9 times that of sintered porous copper, and 4 times stronger at 45%. Moreover, strengthening was observed at porosities below 20% and pore diameters below 50 μm; a full understanding of this effect is yet to be achieved. Gasars far outperform other porous metals in impact resistance and plasticity as well.

Thermal Properties

Heat transmission in porous materials may occur by solid conduction, convection, and radiation. In sintered porous metals, solid contact conduction predominates, although at high temperatures the contribution of radiation becomes substantial. Convection is of secondary importance here, so sintered porous materials always have lower conductivities than similar poreless metals.

In a gasar with closed hydrogen-filled pores, convection plays a far more important part. The reason is that hydrogen has high thermal conductivity and low viscosity. When its pressure in the pores is high enough, the contribution of convection will increase so that the gasar's thermal conductivity will exceed that of the similar poreless metal. The apparent thermal conductivity of gasars may be controlled over a wide range by varying the amount of porosity and the pressure of hydrogen in the pores.

Electrical Conductivity

As the porosity is increased, the electrical conductivity of a porous metal declines in a disproportionate manner similar to that of the thermal conductivity. This decrease is due to the imperfect nature of particle contacts where energy of electrons is dissipated. In a gasar with its monolithic matrix, however, the reduction in the electric conductivity is almost strictly proportional to an increase in the amount of porosity.

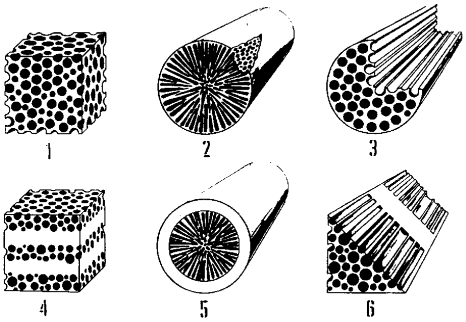

Figure 5. Gas-solid structures formed in gasars under various conditions of gas-eutectic reaction.

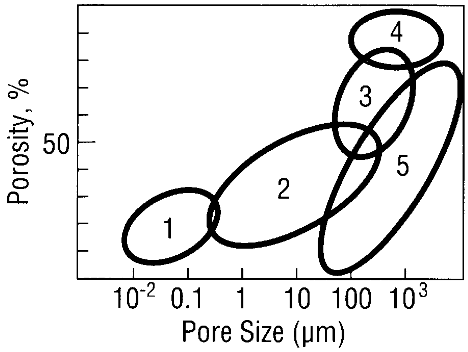

Figure 6. Relationship between the pore size and the amount of porosity in various porous metals: (1) irradiation-induced pores, (2) sintered powders, (3) sintered fibers, (4) foamed metals and cellular metals with a "grid" structure, and (5) gasars.

Acoustic Damping

Acoustic energy attenuation in porous materials is chiefly due to the internal friction of the gas filling the pores. Another energy sink results from the thermal conduction in the gas and the metal. An acoustic wave gives rise to the compression and expansion of gas in the pores. The compression is accompanied by gas heating, and the evolving heat is dissipated in the solid. When the solid is highly plastic, additional attenuation is possible owing to the deformation in the pore walls. Theoretical prediction of acoustic adsorptivity of actual porous metals is hardly feasible because of the complex shape of the pore space. Therefore, acoustic damping is evaluated in tests.

Corrosion Resistance

Porous metals feature poorer corrosion resistance than poreless ones because they have large specific surface and many areas with negative curvature. Another adverse factor is chemical inhomogeneity, which is particularly significant in powder porous metals. Corrosion tests routinely used for solid materials are generally not suited for porous metals; porous metals are commonly evaluated based on changes of resistivity or mechanical strength. Basically, all factors contributing to corrosion resistance of poreless metals have a positive effect on porous metals.

Pressure Drop

Flow resistance is highly important for the permeable porous metals that are frequently used in filters. This characteristic is very sensitive to the pore space topology. Pressure drag generally declines as the amount of porosity is increased. At a given porosity, however, a material with less tortuous pores will be more permeable. Ideal in this respect are those gasars that have parallel cylindrical pores of preset diameter in a monolithic matrix.

Applications of Porous Metals

Permeable porous metals have the widest range of applications, including filters, catalysts, mufflers, flame arresters, heat exchangers, fuel cells, electrolytic cells, fluid substance separators, fluid flow regulators, ionizers of ionic rocket engines, self-lubricating bearings, thermal screens, silencers, and vibration dampers. The development of solar and nuclear power generation technologies has made porous metals candidates for electromagnetic and neutron absorbers. It is highly probable that porous metals will be used for the inner walls of nuclear fusion reactors. Some experience has been gained in using porous metals in structural applications as fillers for laminated panels in shipbuilding and aerospace constructions. Permeable porous metals may be used as matrices of composite materials.

Impermeable porous metals are used less extensively, limited to applications as lightweight structures capable of absorbing noise, vibrations, and shocks. High-porosity foamed metals, particularly aluminum, are well-suited for thermal insulation in construction and engineering.

Impermeable porous metals are used for seals in turbojet engines. The development of hydrogen energy technologies suggests the use of porous metals for hydrogen storage.

Prospects

Several disadvantages prevent the application of porous metals on a wider scale. The majority of porous metals are not strong enough, especially at porosities in excess of 50%. Another drawback is the high cost due to the multiple steps involved in the manufacturing process, and the low production rates. There are also difficulties in engineering a desired pore space structure. Problems are posed by the poor corrosion resistance, machinability and weldability, and by the complexity of mechanical joining with similar materials or poreless parts. Clearly, the prospects of porous metals depend on whether these and other disadvantages will be eliminated, be it through improvements in conventional processes or by the advent of revolutionary technologies.

Porous metals formed by gas-eutectic reaction are particularly promising. Among the advantages of gasars over conventional porous metals, are:

- improved strength and rigidity,
- flexibility in regard to the permeability,
- possibility of making regular structures,
- wide range of the pore diameter (10 μm to 10 mm),
- feasibility of control over pore shape and orientation,
- ease of fabrication and relatively low cost,
- good weldability and fabricability, and
- unprecedented formability.

Also, it is believed that the new method of making foamed aluminum[3] is highly promising because it eliminates some engineering problems which were considered intractable.

Acknowledgments

I wish to thank Dr. Raymond F. Decker, past president of ASM International and president of USP Holdings, Inc., for his support and useful discussions; Drs. V.Y. Karpov, I.P. Serdyuk, L.V. Boiko, and V.V. Trofimenko, researchers at the Splav Laboratory, for valuable information on gasars; Mr. V.A. Polskii, the translator of the text; and Dr. L.M. Snagovski, who helped to prepare the manuscript.

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