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REVIEW PAPER

Cellular Metals and Ceramics for Defence Applications

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ABSTRACT

Among cellular metals, aluminium foams are the most commonly produced, and provide a unique combination of properties such as: very low density, high energy absorption under static and dynamic compressions, blast amelioration, sound absorption, and flame resistance. Applications in automotive and defence sectors have been reported. Foams based on high melting point metals such as nickel and its alloys are also under active development throughout the world for applications requiring corrosion and oxidation resistance coupled with high temperature strength and relatively high thermal conductivity. Ceramic foams were developed elsewhere in the world primarily for biomedical applications, but are also suitable for defence applications for high temperature insulation. These cellular materials will provide new materials options to designers of aerospace, transport, and other defence systems.

Keywords: Cellular materials, *Al* foam, *Al*/*SiC* foam, ceramic foam, foam properties, defence applications

1. INTRODUCTION

A cellular material or foam is a dispersion of a gas in a solid matrix. The presence of a large proportion of gas phase in the foam helps in significant weight reduction, and imparts special mechanical properties vastly different from its bulk material. The use of cellular materials allows the simultaneous optimisation of stiffness, strength, energy absorption, overall weight, thermal conductivity, surface area, and gas permeability (the last two for open-cell foams). As such, these materials are highly desirable for a wide range of engineering applications, and can be found commonly in the natural world (e.g., wood and bone). Until recently, however, only wood was used to a great extent. Only during the twentieth century have man-made polymer foams been available for insulation, cushioning, padding, and packaging, but the high structural efficiency of cellular materials has been little used. Techniques now exist for fabricating foams not only of polymers, but of metals, ceramics, and glasses as well. These newer foams are increasingly being used structurally, for insulation, and in systems for absorbing the kinetic energy of impacts. The purpose of the review is to introduce the cellular materials which are having a unique combination of properties and their possible applications in defence and other sectors. The useful properties are described[1] in Fig. 1. These properties can be exploited to have novel engineering designs pertaining to defence, aerospace, and automobile applications.

Foams are commonly classified into two types: closed-pore foams and open-pore (or reticulated) foams. The closed-pore foams have structures resembling a network of soap bubbles and have higher compressive strength due to their structures. DMRL-developed aluminium foam, e.g., belongs to this category. The open-pore foams are identical to the closed-cell ones except the membranes have been removed which produce large channels of interconnected cells, the main advantage of which is its 'flow-through' capability and access to their internal surface. Liquids and gases can flow through the structure with minimal resistance. If the non-solid phases of the structure are non-random and in the form of closely-spaced channels, it is usually called honeycomb structure. This honeycomb structures have one-directional channel with anisotropic mechanical properties and permeability. The channel diameter can vary from several microns to several milimeters based on a variety of metals and alloys[2].

There is a special class of closed-cell foams called syntactic foams. Syntactic foams are composite materials synthesised by filling a metal, polymer or a ceramic matrix with hollow particles called microballoons. The presence of hollow particles results in lower density, higher strength, a lower thermal expansion coefficient, and, in some cases, radar or sonar transparency. Tailorability is one of the biggest advantages of these materials. The matrix material can be selected from almost any metal, polymer or ceramic. A wide variety of microballoons are available, including cenospheres, glass microspheres, carbon and polymer microballoons. The compressive properties of syntactic foams primarily depend on the properties of microballoons, whereas the tensile properties depend on the matrix material used in their structures. There are two ways of modulating properties of these materials. The first method is to change the volume fraction of microballoons in the syntactic foam structure. The second method is to use microballoons of different wall thicknesses[3].

These materials were developed in early 1960s as buoyancy-aid materials for marine applications; the other characteristics led these materials to aerospace and ground

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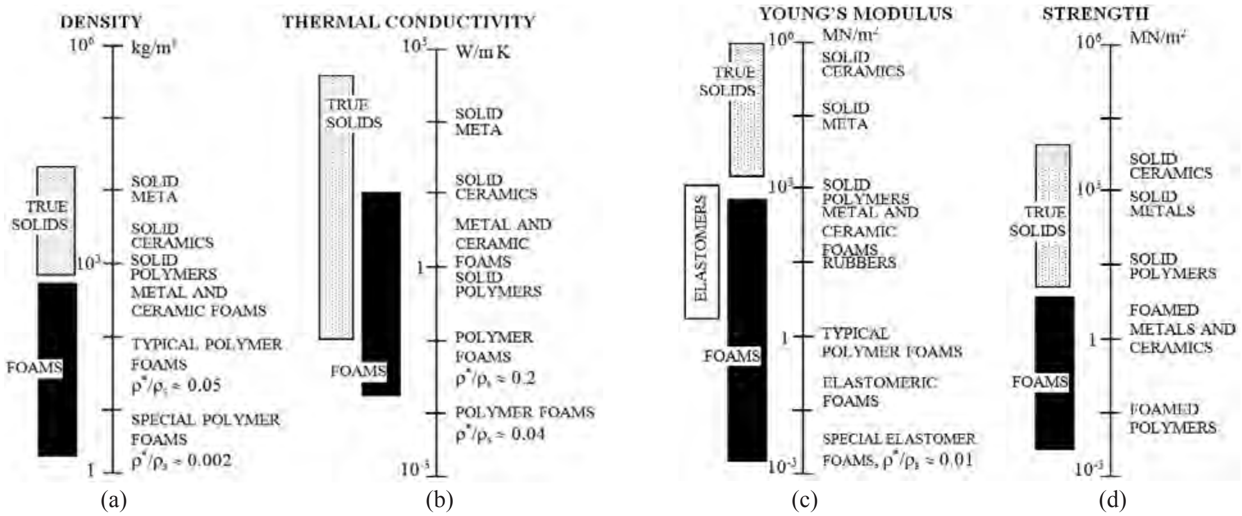


Figure 1. The range of properties of different cellular solids (a) density, (b) thermal conductivity, (c) Young's modulus, and (d) compressive strength.

transportation vehicles applications. Among the present applications, some of the common examples are buoyancy modules for marine-drilling risers, boat hulls, and parts of helicopters and airplanes. New applications are coming up in sports industry, snow skis and Adidas soccer balls, to name a few[3].

Current research focuses on development of foams for different functional requirements. High temperature-resistant foams based on *Ni-Cr-Al* alloys are under development for filtration and for solid-oxide fuel cells operating at elevated temperatures[4]. To obtain higher permeability, lotus materials or gasars being developed by Osaka University, Japan, by advanced solidification techniques using high pressure gas method. Various materials are now produced on a laboratory/pilot plant scale (*Cu*, *Ni*, *Al*, *Mg*, *Si*, *Ti-Al*, alumina). Possibility of using chemical foaming agent is also explored instead of using large volume of pressurised gas so as to avoid potential hazard risks for the large-scale manufacturing with the traditional high gas pressure method.

One of the areas of research is to use metallic foams for various new and improved treatments, i.e., bone augmentation, graft-free vertebra for the treatment of degenerative disk diseases, etc. Materials such as titanium alloys and nitinol have been developed for these applications. Better initial stability of the foam with the surrounding bone, faster bone ingrowth, and development of improved process to reduce production cost are the key areas of focus in their development[4].

Nanoporous metallic structures are of the most recent fields of interest among scientific communities. These materials have high specific surface areas and fine pore sizes. These are been considered for electrodes, catalyst, sensors, actuators, and filtration applications. Research is carried out on de-alloying techniques to produce porosities in gold, silver, and copper alloys. Other processes are under development, e.g., selective dissolution techniques or leaching for *Ni*-based superalloys to produce sub-micron porosities. This technique can be used to produce fine membranes of these materials suitable for applications where fine porosity, high thermal stability, mechanical strength, and ductility are required [4].

2. DISTINGUISHING PROPERTIES

In general, the properties such as plastic strength, elastic modulus, energy absorption, permeability, thermal conductivity and dielectric constant, etc depend on per cent porosity, cell size and microstructure of cell walls. Foams with different pore size distributions, pore orientation, and pore morphology can be produced as per the requirements for different applications[5]. Porosity achievable in metal foams is as high as 97 per cent depending on the method employed during its manufacture.

The reticulated foam process results in ceramic foams with porosity exceeding 90 per cent and pore size ranging from 10's of μm to several mm. Foams prepared by this route have poor mechanical properties due to highly open pore structures and hollow struts left behind after burning of polyurethane. The microstructure of reticulated foams is most suited for applications requiring high permeability[6].

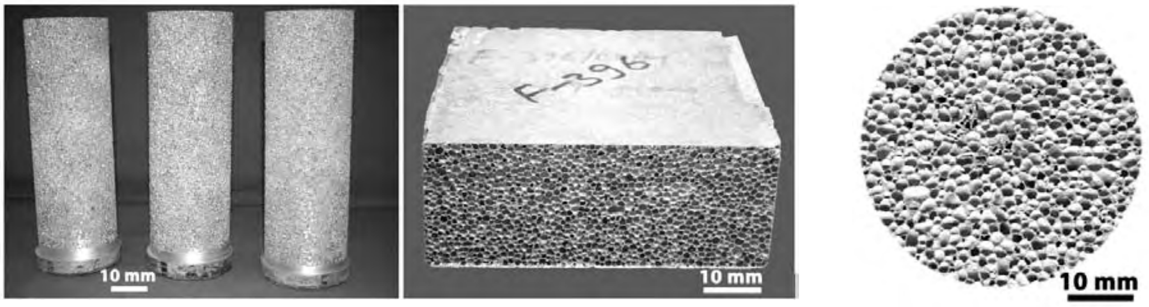
Closed-cell foams have the lowest thermal conductivity as compared to of any conventionally non-vacuum insulation. Several factors limit heat flow such as low volume fraction of solid phase, small cell size which virtually suppresses convection and reduction in radiation through repeated absorption and reflection at the cell walls and poor conductivity of the enclosed gas. Heat transfer has direct relation with cell sizes such that heat transfer increases with cell size due to less reflection of radiation because of less number of barriers. Cell size > 10 mm has direct contribution to convection of heat through the cell. Open cells affect heat transfer, but to a lesser extent. Coefficient of thermal expansion is also another major factor considered during selection of the materials [1, 5].

3. PROCESSING METHODS FOR METAL FOAMS

Cellular metallic materials can be manufactured by many methods on the basis of their physico-chemical properties. Overviews of possible production routes for different metals and alloys[2,7]. Among various metals, production methods for

Table 1. Methods of production and producers of aluminium foams[8]

Method	Proccess	Manufacturer (products)
Direct foaming	Melt alloy Make alloy foamable Create gas bubbles Collect foam, Solidify foam	Cymat, Canada (SAF) Foamtech, Korea (Lasom) Hütte Kleinreichenbach (HKB), Austria (Metcomb) Shinko-Wire, Japan (Alporas) (Distributor: Gleich, Germany)
Indirect foaming	Prepare foamable precursor Remelt precursor Create foam Solidify foam	Alm, Germany (AFS) Alulight, Austria (alulight) Gleich-IWE, Germany Schunk, Germany



(a) (b)

Figure 2. (a) DMRL foam cylindrical and plate products, (b) cross-section of foam revealing cell structure.

nickel and aluminium foams will be described here due to their wide application potential.

3.1 Aluminium-based Foams

Among metals, aluminium is the most predominantly foamed metal commercially. A variety of processing techniques exist for foam production. Table 1 lists some important closed-cell aluminium foam manufacturers and the methods of manufacturing[8]. However, processes based on liquid metal processing gained prominence due to their simplicity and low cost. In this method, pure aluminium melt containing *Ca* is allowed to foam upon the addition of a gas evolving foaming agent (TiH_2). DMRL has established an in-house process to make closed cell aluminium foams[9]. Figure 2 shows typical foams and the cell structure in a cross-section.

Aluminium alloys can also be foamed and their lower liquidus temperatures can be advantageous from the foam preparation view point as has been demonstrated at DMRL (Fig. 3). As shown in Fig. 3(a), with one of the most prominent cast *Al* alloys, LM25 (*Al-Si-Mg*), good quality foams were obtained using Al-foam scrap turnings as thickening agent in place of conventionally used *Ca* metal[10] .

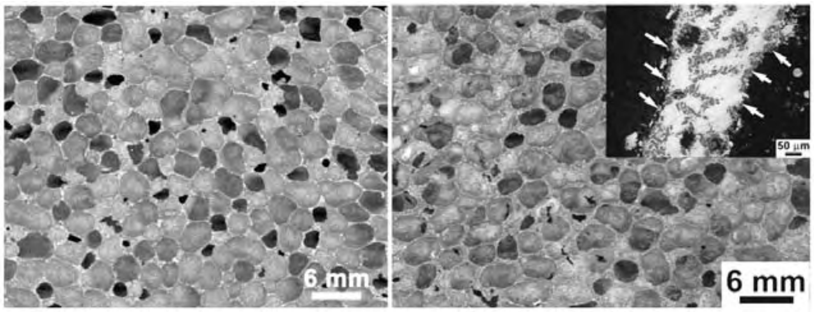
Instead of *Ca* or *Al-Ca* foam turnings, ceramic reinforcements such as *SiC*, Al_2O_3 can be used as foam stabilisers and metal-matrix composite (MMC) foams can be fabricated. In addition to their cost effectiveness, these foams are amenable for continuous foaming process where large foam panels could be manufactured. The effectiveness of ceramic particles in stabilising the foam depends on their size and volume fraction and their wetting tendency with aluminium alloy melt. Work is in progress at DMRL on LM25/SiC_p foams [Fig. 3(b)].

3.2 Nickel-based Foams

In literature, three methods for production of nickel and nickel-based superalloy foams have been reported:

(a) Impregnation of polymer foam by superalloy slurry and then burning off the polymer [5].

(b) Electro-deposition of pure nickel foam on polymer foam and subsequent cell wall thickening by superalloy slurry impregnation method as above. A slight modification of the second process involves chemical vapour deposition of metal instead of electro-deposition, and is called the 'INCO' method[11]. The polymer foam is then burnt out and a sintering process follows to fill up the hollow ligaments



(a) (b)

Figure 3. *Al*-alloy based foams being developed at DMRL (a) LM25 (*Al-Si-Mg*) alloy foam, and (b) LM25/SiC_p composite foam (inset) microstructure exhibiting cell wall decoration with particles (as shown by arrows).

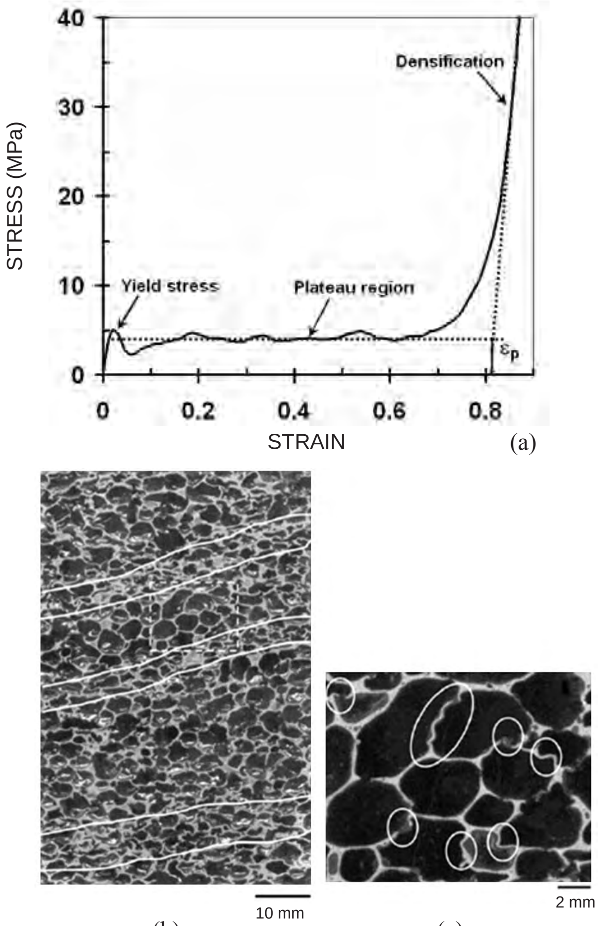
left out by the deposition step. The CVD process has been extended to other refractory metals such as niobium, tantalum, tungsten, and rhenium.

(c) Mixing superalloy powder with sodium chloride, compacting, and then dissolving sodium chloride (the ‘space holder’ method). The space holder method has limitations on porosity, due to the lower limit on the packing density of sodium chloride powder[12].

4. PROPERTIES OF METAL FOAMS

4.1 Mechanical Properties

Closed-cell foams of aluminium can absorb very high amounts of compressive energy at a constant peak stress Fig. 4(a). So, these are suitable for crash (impact)[13] and blast-resistant applications[14]. Good stiffness of these closed-cell foams make them suitable for lightweight structural applications. Cell size variation strongly influences variability of mechanical properties[15]. The deformed cell bands formed during compression of aluminium foam can be seen in Fig. 4(b)[15]. During deformation, the cell walls buckled as shown in Fig. 4(c)[16].



(b) (c)

Figure 4. (a) Typical compression stress-strain curve showing a plateau region followed by densification. ε_p is the plateau or densification strain (b) Aluminium foam section showing deformed cell bands after 30 per cent total strain, and (c) showing buckled cell walls adjacent to a deformed band[16].

Stiffness of metal foam is a function of the modulus of the parent metal and density: foam stiffness = constant (Young’s Modulus of a solid) * $(\rho_{foam}/\rho_{solid})^n$ $2.3 \ge n \ge 1.7$, so different metals and alloys will have different stiffness, and selection of foam may be based on the requirement[1, 5].

4.2 Damping and Acoustic Properties

Metal foams act as excellent dampers for vibration and also for sound absorption. The loss factor η for structure-borne sound indicates what fraction of the vibratory (reversible) mechanical energy is lost (i.e., converted into heat) in one cycle of the vibration. It was observed that the loss factor of aluminium foam was increased with foam density[17]. In comparison to the dense material, aluminium foams show a significantly higher loss factor which indicates their better applicability for structure-borne sound-sensitive structures. It is also shown that foams have exceptionally higher sound-damping capability in the mid-frequency range.

4.3 Electromagnetic Wave Shielding

Electromagnetic wave shielding is used to protect electronic devices and room interiors from the negative influence of electromagnetic waves. The ability to reflect the electromagnetic energy can be defined by the shield effectiveness. Recent experiments carried out on foams have revealed their excellent electromagnetic wave shielding properties (Fig. 5).

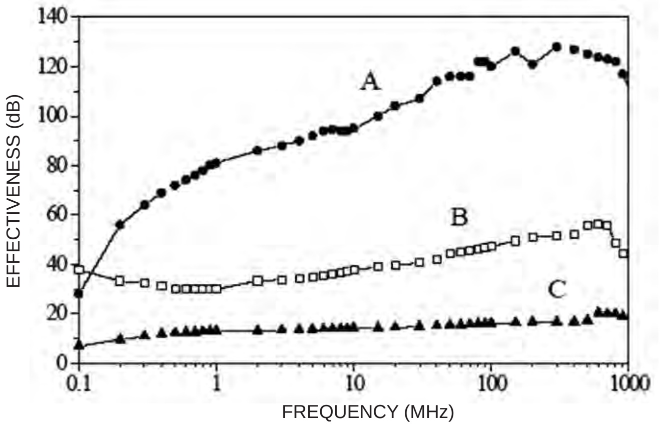


Figure 5. Electron magnetic wave shielding effectiveness as a function of frequency for aluminium foam (A), *Si*-steel (B), bulk aluminium, (C) at the same weight of the samples[1,15].

4.4 Thermal and Electrical Properties

Metal foams exhibit reduced thermal and electrical conductivities in (somewhat nonlinear) proportion to their densities[1,18]. Tables 2 and 3 show the thermal and electrical conductivities respectively.

5. APPLICATIONS OF METAL FOAMS

Aluminium foams for their high stiffness and energy-absorption properties are suitable for automotive industry and for a number of structural applications.

Table 2. Thermal conductivity of aluminium foam [$Wm^{-1} K^{-1}$] at different temperatures

ρ_{rel}	30 °C	100 °C	200 °C	300 °C	400 °C	500 °C
0.066	5.88	5.91	5.76	5.78	5.86	6.13
0.090	9.07	9.16	9.09	9.15	9.69	9.93
0.171	17.77	16.68	16.95	17.21	18.1	18.77

Table 3. Electrical conductivity of aluminium foam

Relative density	0.066	0.09	0.171
Electrical conductivity [M Ohm m]$^{-1}$	1.66	2.03	3.43

5.1 Lightweight Construction

Aluminium foams have been used in utility transport vehicles to optimise the weight-specific bending stiffness of engineering components. Lightweight construction exploits the quasi-elastic and reversible parts of the load-deformation curve (Fig. 6).

Figure 6. Base of a lifting arm made from aluminium foam sandwich panels[19].

5.2 Energy Absorption

Aluminium foams can absorb a large quantity of mechanical energy when they are deformed, while stresses are limited to the compression strength of the material. Foams can therefore act as impact energy absorbers, which limit accelerations in crash situations. This mode exploits the horizontal regime of irreversible deformation in the load-deformation diagram (Fig. 4). Figure 7 shows that incorporation of foam in the tube enhances the number of folds during deformation, and the energy absorption substantially increases. For given impact loading conditions, an optimum density of foam may exist that may absorb energy to its fullest capacity, thus reducing impact force to the greatest extent[20].

5.3 Defence and Space Applications

Alm Germany, in collaboration with German Aerospace Society (DLR) and French Aerospace Agency (CNES) in building the transition cone of the Ariane Rocket V booster (Fig. 8). The cone having a base diameter of 3936 mm has been produced in 12 segments of aluminium foam sandwich (AFS), and welded. The incorporation of AFS has generated higher compressive strength per unit weight, isotropic behaviour and steady crack growth. Another advantage with AFS in this application is its excellent electromagnetic shielding [21].

The radome shield of Airbus with a metal-foam hybrid structure is now being tested[22] for a high speed impact bird hit (Fig. 9).

Figure 7. DMRL aluminium foam-filled pipes (below) develop more folds during impact than empty pipes (above), and absorb more energy and reduce impact force (impact tests carried out at BARC Facilities)[20].

Figure 8. Ariane 65 rocket cone prototype made of aluminium foam sandwich. Arrow shows the location of part in the rocket[21].

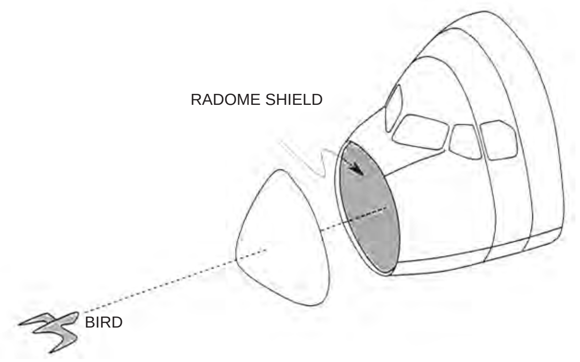


Figure 9. Radome shield of Airbus to be replaced with foam[22].

5.4 Future Applications

In space sector, studies revealed that at the component level, high efficiency heat exchanger system, cryogenic gas storage application, and surface tension/wick application may emerge as potential applications, while at the system level, the applications, as crushable mechanisms with thermal protection system capability and micrometeorite and orbital debris protection system for heat pipes may emerge soon[21]. Several applications in building, transport and acoustic industries have been described. A recent research has shown the use of porous Nickel-manganese-gallium alloy with shape memory properties[23]. It is believed that the porous alloy has great potential for uses that require lightweight and a large strain, such as space and automotive applications, and tiny motion control devices or biomedical pumps with no moving parts.

Metal foams with available high porosity can act as porous electrodes of a battery (*Li*-ion battery, Metal-gas battery etc)[24]. High-capacity and high-output can be achieved because the three-dimensional net-like structure leads to high retention ability of active-material and high specific surface area (Fig. 10).

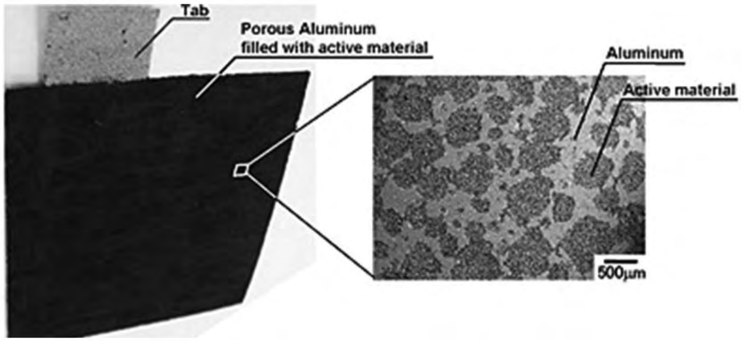


Figure 10. Aluminium foam as an electrode filled with hydrides or other active materials.

5.5 Bonding and Joining

Adhesive bonding, laser welding, friction-stir welding, and ultrasonic welding have been reported, each having its own merits and demerits. Recent work shows that sheet metal and aluminium foam sandwich may be joined by ultrasonic welding technology without melting or causing any other damage to the cell structure[25]. Parameters such as energy input, welding pressure, and welding amplitude need to be optimised to produce sound joints. Adhesive bonding usually produces lower mechanical strength, but may be considered for its simplicity and low capital costs.

6. OPEN-PORE CERAMIC FOAMS

Several techniques are used to produce open-pore ceramic foams, and are similar to those adopted for making open-pore metal foams, as described in Section 3 above.

6.1 Applications

Ceramic foams are known to have applications[6,26,27] in diverse areas such as

- Catalysis for high efficiency combustion burners, heterogeneous catalysis in diesel engines and gas turbines, solar radiation conversion, etc.
- Structural applications as in molten-metal filtration, kiln furniture, preforms for metal–ceramic composites, armour systems, high specific strength materials, impact-absorbing structures in hypervelocity spacecraft and satellites, etc., and
- Functional applications such as thermal insulation of spaceshuttle, biomedical implants, gas filtration, heat exchangers, shock and sound absorbers, media for solid oxide fuel cells.

With respect to defence systems, the following applications may be examined:

- Silica foam for thermal insulation
- *SiOC* foam for high impact-absorbing structures in hypervelocity spacecraft and satellites
- *SiC* foam for lightweight space mirrors
- Porous ZrO_2 to be used as anode for solid oxide fuel cells
- Porous alumina for room temperature structural applications
- Honeycomb structures for load-bearing applications.

Besides above applications, ceramic titania open-pore (reticulated) foams, like open-pore ceramic foams in general, can be used as templates in preparing metal foams. The molten metal is poured into the porous foam and after cooling, the ceramic is removed by a high pressure water jet.

6.2 Manufacture of Open Pores Ceramic Foams

Reticulated open-pore ceramics are produced via the replication of a polymeric porous structure[28-30]. The patent on this technique, called the ‘replication’ or ‘polymersponge’ method, was first filed by Schwartzwalder and Somers in 1963. It is the standard method for producing titania foams, as well as silica, alumina, zirconia, silicon carbide and other ceramic foams.

The foams are obtained by soaking polyurethane foam in ceramic slurry. The polymer, having already the desired macrostructure, simply serves as a sacrificial scaffold for the ceramic body. The slurry infiltrates the structure and adheres to the surface of the polymer. Excess slurry is squeezed out leaving a ceramic coating on the foam struts. After drying, the polymer is slowly burned out to minimise damage to the porous coating. Once the polymer has been removed, the ceramic is sintered to the desired density. The process replicates the macrostructure of the polymer, and results in a rather distinctive microstructure within the struts. The structure of the ceramic foam produced by this process of infiltration is limited by the structure of the polyurethane perform, and the process results in foams with poor mechanical properties due to the hollow struts. Preparation of polyurethane pre-foams and their burnout may result in toxic NO_x emissions.

Another method developed by Ferreira, *et al* to produce porous ceramics uses insoluble organic fugitive materials in ceramic suspensions, which burn out leaving open porosity[31,32]. The most common fugitive materials have been starches, carbon black, and sawdust. In this method, production of highly porous bodies requires use of a relatively large volume of the fugitive phase, which must be burnt-out later. Recently, pre-ceramic polymers[33,34] have been used to produce ceramic bodies with a combination of micro- and macro-porosity. The process is limited to specific polymeric systems that result in ceramic compositions on pyrolysis and are accompanied by rapid gas evolution during transformation of the polymer to the ceramic.

Fukasawa[35], *et al.* have demonstrated a novel method to fabricate porous ceramics with aligned macroscopic pores and associated micropores using phase-separation technique. The method involved freeze-drying of aqueous ceramic suspensions in a controlled manner that allowed directional growth of ice. The sublimation of ice under reduced pressures gives rise to aligned macro-pores and micro-pores. Pore structure can be controlled by composition of the slurries and the samples with up to 50 per cent porosity.

An indirect fused deposition method has been used to produce porous mullite bodies[35]. Initially a polymeric mold with a structure negative of the desired porous ceramic body was produced using fused deposition. The polymeric mold was then infiltrated with an aqueous mullite suspension, slowly dried, and subjected to binder burnout and sintering. This process is useful for producing non-random porosity of controlled size and can also be used to fabricate structures with a gradient in size and volume of porosity.

An innovative technique to produce continuous or stepwise porosity gradients has been proposed by Cichoki[38], *et al.* where wedge-shaped polymeric foams are compression molded into shapes that have graded porosity. Alternatively, individual layers of polymer foams, compression molded into different percent porosity, are laminated together to get polymeric structure with stepwise graded porosity. These polymeric preforms were now infiltrated and subjected to binder burnout and sintering.

Most of the processing methods discussed above involve creation of porosity by removal of a fugitive phase. Recently, the gelcasting[37-39] process has been successfully used for direct fabrication of porous bodies[41-44]. The process involves the use of aqueous ceramic suspensions containing surfactants, which are foamed by mechanical agitation. The setting of the foam requires thorough mixing of a small volume of the initiator (ammonium persulphate (APS)) and catalyst (tetra-methyl-ethylene-diamine (TEMED)) into the large volume of foamed ceramic slurry. This mixing of APS and TEMED in foamed slurries, without affecting the foam, is usually quite difficult, and unless the setting reaction is conducted under inert environment (nitrogen), the presence of oxygen inhibits the free-radical reaction, and results in low green strength. The requirement to carry out the process under nitrogen makes the process difficult.

Recently, another technique has been proposed to form ceramic foams with microstructure comparable to that produced via solgel[45,46]. Foams with porosity as high as 96 per cent and pore size between 50 μm to 2000 μm have been produced by this process. The foam is generated using $AlCl_3$ crystals that contain the metal component and all the foaming ingredients. Upon heating, the crystals form a solution, within which a reaction takes place, forming polymer chains. After the chains grow sufficiently, the solution separates into solvent and polymer phases. At this point, the solvent begins to boil, forming a large number of bubbles that blow the polymer into foam that is stabilised by the polymer chains. Subsequent heating to high temperatures leaves behind the ceramic foam. Although the process has a significant potential in producing large volume of foam with homogeneous microstructure, the precursor used is costly and is restricted to producing alumina foams.

Recently, Dhara, *et al.* fabricated alumina component using an innovative protein coagulation casting technique[47-50]. Using this technique, a wide variety of samples were made from highly dense component (density > 99.9 per cent) to porous ceramics up to as high as 96 per cent porosity. Slurry rheology was found to be the main parameter that influenced foaming of slurries and the resultant microstructure of sintered ceramic foams. The foaming behaviour of the slurries was seen to be a strong function of the viscosity that directly affects the micro structural parameters in sintered alumina foams. Foams made from slurries with higher viscosity always have lower total porosity, cell size and increase in number of cells per unit area, cell separation. Alumina foam prepared using PCC technique has closed-cell like microstructures due to low fraction area of interconnection (7 per cent) even with 87 per cent open porosity (Fig. 11).

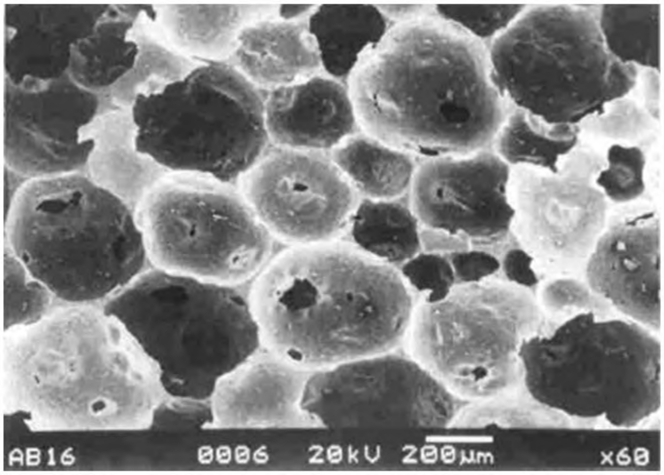


Figure 11. Microstructure of alumina foam using protein coagulation casting of ceramics.

7. CONCLUSIONS

Metal and ceramic foams offer a wide combination of properties, depending upon the foam material, pore volume and nature of cell structure. The range of properties includes high energy absorption, impact force reduction, blast amelioration, thermal insulation, electromagnetic shielding, etc. A variety of processes have emerged to make foams. Metals foams are manufactured on commercial scale in various countries.

DMRL has been actively pursuing development of aluminium and ceramic foams, and has established necessary laboratory-scale facilities. The processes can be scaled up depending upon the requirements. Several possible defence applications have been mentioned in the paper and a concerted effort by component designers and materials developers will result in early value assessment and possible utilisation of foams.

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