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Liquid and solid foams / Mousses liquides et solides

Application and future of solid foams

Applications et avenir des mousses solides

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ABSTRACT

To conclude this series of chapters on solid foam materials, a review of industrial current applications and of mid-term market perspectives centred on manmade foams is given, making reference to natural cellular materials. Although the polymeric foam industrial development overwhelms the rest and finds applications on many market segments, more attention will be paid to the emerging market of inorganic—especially metallic—foams (and cellular materials) and their applications, present or upcoming. It is shown that the final applications of solid foams are primarily linked to transport and the present-day development of the different classes of solid foams is contrasted between functional applications and structural applications.

RÉSUMÉ

Pour conclure cette série d'articles sur les mousses solides, celui-ci propose une revue des applications industrielles actuelles et des perspectives de mise sur le marché à moyen terme, centrée sur les mousses artificielles, ceci faisant référence aux matériaux cellulaires naturels. Bien que le développement industriel des mousses polymères surclasse le reste et trouve des applications sur de nombreux segments de marché, on s'attardera davantage sur les marchés émergents des mousses (et matériaux cellulaires) inorganiques – plus particulièrement métalliques – et sur leurs applications, actuelles ou à venir. On montre que les applications finales des mousses solides sont d'abord liées au transport et que le développement de différentes classes de mousses solides auquel on assiste de nos jours est contrasté, entre des applications fonctionnelles et structurales.

1. A short “historical” introduction

Artificial cellular and foam materials were first developed after World War II. Mass production started in the late 1950s with polymeric (mostly polyurethane) foams; however, long before that, in prehistoric ages, man had mastered the attractive attributes of natural cellular materials, like wood and bone, for hunting and building, but also for manufacturing various tools, exploiting their advantageous specific strength (strength/density) or their thermal insulation properties. Some textiles are likely to be the first (semi-)artificial flexible solid cellular materials (not to be further considered). We will include some rigid cellular materials in this presentation. A cellular material may be described as a 2D lattice of tubes, while foam presents a 3D sponge-like structure. As suggested below, the polymeric (and elastomeric) foam development is mature and

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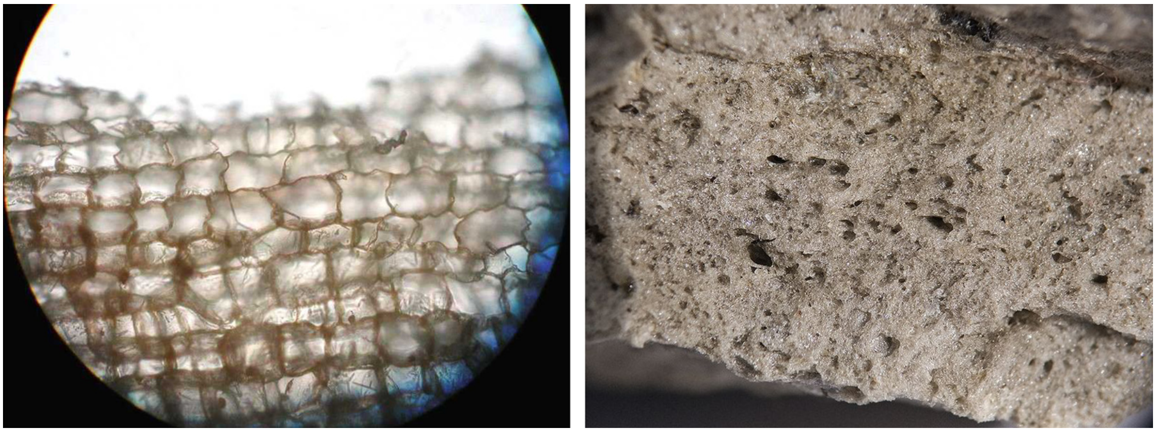

Fig. 1. (Colour online.) Microstructure of natural cellular and foam material. (a) Cork microstructure "à la Hooke". Hooke [2] was the first to identify the cellular structure of cork. From D.B. Fankhauser [4]. (b) Pumice stone with a foam structure. Density may be as low as 0.25 g/cm^3. From Benjamin 444 [5].

will not be developed at great length here, as most of the readers are well informed on if not in daily "contact" with such materials. Metallic foams are still far from maturity and ceramic foams are mature, but have a large potential for further development; we will thus focus on these, referring chiefly to polymeric foams in the context of their use in the fabrication of inorganic foams, some of which are produced starting with polymeric foam prototypes in "replication" processes. We will distinguish solid foams by the material class they belong to, more than by the structure, open or closed cell type. A consideration of the use of natural cellular materials is of interest, since man has a tendency (sound or not?) to mimic nature.

2. Natural cellular materials, applications and market

No natural metallic cellular material is known to the author, although native metals are still to be found on the Earth, of meteoritic origin or of mineral origin, in alluvial deposits for instance (this natural occurrence concerns noble or semi-noble metals plus mercury).

Natural organic cellular materials are extensively used today, and among them wood is prominent, being used extensively for lightweight construction and thermal insulation. Industrial round wood is likely to be, after concrete, the second most widely used material upon the Earth, just ahead of steel [1] with 1.5 billion tons a year, but wood can be both a material and an energy source, which makes statistics difficult to handle. Balsa lumber is a special case since it is light (typically 150–200 kg/m^3) and strong. It is still used in some composite structures and until now in shock-absorbing containers for precious goods.

Cork is a particularly light cellular wood product (which does not require the cutting of the tree to be harvested, since it is positioned in the bark). Natural cork has been studied by materials scientists since Hooke [2]. In spite of its low density, global cork production tops 340,000 tons and 1.5 billion €/year, with wine cork being the most profitable sector, followed by floor and wall covering [3]. It seems that cork oak tree is only grown around the Mediterranean Sea, where it is linked to 30,000 jobs (in the forests and in the transformation of cork). Portugal is by far the biggest producer. Cork, like balsa wood, is a closed-cell cellular material (Fig. 1a). Its useful properties are derived from its closed-cell structure and from a low Poisson ratio, making bottling easier and allowing a good bottle seal. Thermal and sound insulation are appreciated for covering applications in buildings and homes. Synthetic polymeric cellular material substitutes are now available in replacement of wine cork to avoid the rare but unpleasant "corked" taste that can occur in the wine when cork is contaminated. However those materials (solid skin and polymer foam core) ban any exchange between the bottle liquid and the atmosphere, which confers part of its pleasant taste to old wines and the long-term tightness of that recent material is not established yet, which limits their application to cheaper wines today.

Natural cellular ceramic materials are generally of volcanic origin; they include pozzolans, zeolites and tuffs. Pozzolan compositions are based on aluminosilicates, in a vitreous state with bubble gas evolution when the volcanic lava is cooled and solidified. They are advantageously ground and mixed with mortar and lime to produce concrete with lower energy content. Their cellular nature makes them insensitive to freezing/thawing temperature cycles. They tend to be replaced by blast furnace slags, blocky or granulated, i.e. water atomised with a size distribution typical of some natural sands to be incorporated in cement (bringing ~15 wt% alumina and ~40 wt% lime in addition to silica). Some of the volcanic minerals may be lighter than water, like pumice stone (Fig. 1b). The extraction of some of these minerals is now banned in a number of countries, since the volcanic areas in which they are extracted have often become natural parks. Owing to their extremely fine structure, zeolites are used for ultrafiltration and as absorption media or catalytic substrates. Coral is also a natural cellular ceramic (with closed cells), but its extraction is forbidden as it is protected nowadays. Trabecular bone is an open cell natural foam material that is not exploited any more as a material.

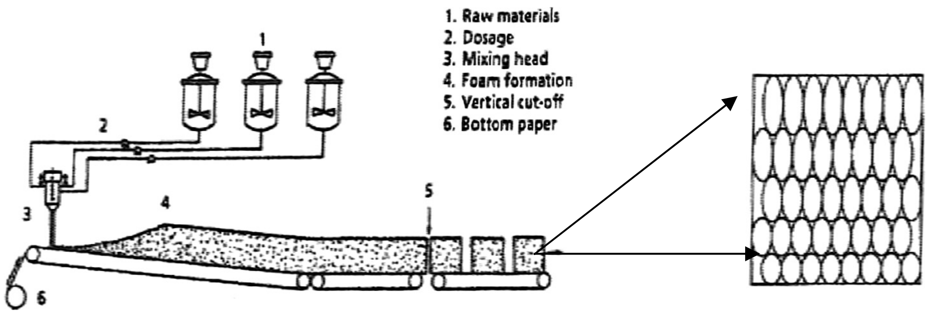

Fig. 2. Schematic representation of a PU continuous foaming industrial equipment (flexible foam) and of the internal arrangement of the cells, showing an elongation of cells increasing from the bottom to the top, after Goussery [7].

3. Polymeric foams

Their production accounts for more than 10% of all polymers, with some 27 Mt/year worldwide. Polyurethane is leading with 15 Mt ahead of polystyrene, PVC and polyolefins. The 2011 market is valued at 40 billion € a year [6], growing to 100 billion in 2020. Applications concern:

- lightweight structures,
- absorption of sound, vibrations, energy,
- thermal insulation,
- some filtering applications,
- precursor scaffolds for the production of metallic or ceramic foams, or as a pattern material in foundries (lost foam process). In this class of applications, the foam "model" is destroyed.

The manufacturing of PU foams (Fig. 2) is based on a polyaddition foaming reaction associated with, for instance, a combination of polyols and toluene-di-isocyanate, with the addition of a catalyser and of a surfactant. The influence of gravity induces an elongated closed-cell shape that varies from the bottom to the top of the bed, this being about half a meter high. An open-cell structure may be obtained by controlled hydrogen–oxygen explosion within the foam in an autoclave that bursts and melts the cell walls to form the strong struts. Various grades of foams, flexible or rigid, can be produced by adjusting the type of starting materials and their proportion.

The established growth rate of the market of the polymeric foams is 1 to 4% a year in volume. A large number of companies are involved in the production of organic foams, but the five major ones may account for 60% of the volume.

4. Ceramic foams

The market for ceramic foams and for ceramic cellular materials is nearly mature, meaning that materials and associated technologies are at hand and that current offer meets demand. Porous ceramics and ceramic membranes are used primarily in filtering applications (gases, liquids), as high-temperature catalytic substrates and also for insulation (noise or heat—for high-temperature applications, the materials may be classified as refractories). A multitude of producers are active, making the evaluation of the market size a difficult task. Ceramic foams and cellular ceramic materials are not in competition with polymeric foams, with the exception of the filtering of cold liquids. They now compete with metallic filters and substrates for the filtration and catalytic applications at elevated temperatures (up to 1000°C).

Most ceramic foams are produced by either of two processes involving polymeric foams as a prototype or scaffold [8]:

- replication of polymer foams (first patented in 1963): prepare a ceramic slurry (ceramic powders, orthophosphate binder, some 20% water), immerse open cell polymer foam in slurry, remove excess air by kneading, excess water by calendaring, oven dry, heat slowly to 500°C, 1 h hold time to decompose polymers, fire...;
- bubble processing (first patented in 1973), ceramic slurry including a foaming agent and the ingredients necessary for the polyaddition reaction to form a polymeric foam in the first part of the cycle, the second part being the same as above, decomposition of polymer and firing. Foams produced this way show some cell walls and some closed porosity. This process is better suited to produce large size filters. An example of this type of filter (dimensions about 50 × 50 cm^2) in Fig. 3 shows hollow struts, typical to the replication process.

Cellular ceramic monoliths as well as ceramic foams address the same application. We shall see later that both are also competing with metallic cellular monoliths.

Liquid metal filtering using ceramic filters was first introduced in the 1970s and is now a standard practice, as most foundry processes (sand, investment, permanent mould casting) benefit from filtering, which produces improved metal

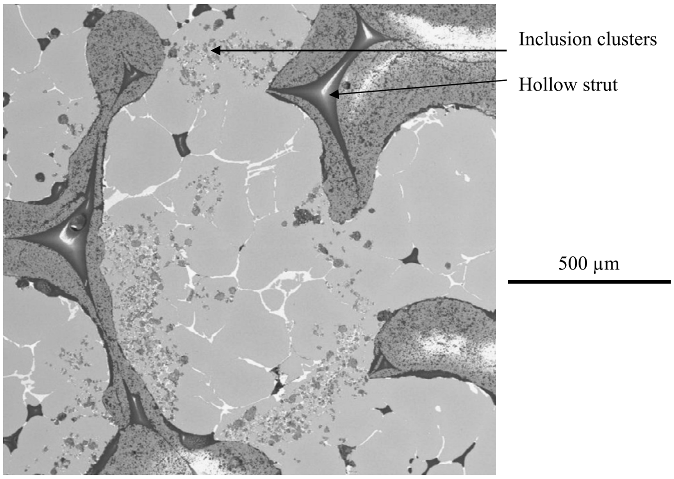

Fig. 3. Ceramic foam filter after casting of a 7XXX aluminium bath for an aerospace application; the filter is nearly clogged by inclusion clusters (from [9]).

Table 1
Comparison between the three most common types of ceramic filtration systems through a selection of commercial products (more information on the websites of the companies).

Structural type	Company and *Trade name*	ppi or mesh/ceramic	Metals/process
Ceramic foam	Foseco-Vesuvius *Sedex, Selex Pro*	10/50 ppi SiC, alumina	Cast iron < 1500°C
	Pyrotek *Sivex*	10/80 ppi Alumina	Aluminium
	Ashland/Porvair *Selee*	10/50 ppi Silicon carbide	Cast irons
	Lanik *Vukopor*	10/60 Alumina, SiC, zirconia	Aluminium or ferrous metals
Extruded ceramic honeycomb	Ashland *Exactflo*	10/20 ppi Silica-alumina	Aluminium/cast irons < 1300°C
	Induceramic	10/20 ppi Mullite/alumina/cordierite/SiC	Cast irons
	Foseco and Corning	10/30 ppi Cordierite	Cast irons
Glass fiber fabric	Comanche Technology *CerraFlex TorrentFlow*	25/400 mesh Zirconia coated glass fibre	Investment casting 1800°C

cleanliness. Pressure die casting does not often use filtering, nor does centrifugal casting, since the flow rates of metal are high and flow occurs over a short period and also since the centrifugal forces “filter” the lighter inclusions by segregating them to the inner diameter. Ceramic filters are used for the semi-continuous casting of aluminium, magnesium and copper. Filtering is also a must for refining recycled metals. It is not usually used in the continuous casting of steel or copper or aluminium, since the filter is expected to last hours without mechanical failure or clogging by inclusions. Filters differ in size (up to 1 m^2, a few centimetres in thickness), in the nature of ceramic used and in their structural type, packed powder bed filter, extruded ceramic (often called cellular), or ceramic foams.

The number of filters of all kinds (most of them are ceramic) used worldwide per year to regulate the flow of liquid metal and retain inclusions may be estimated at some 200 millions units. This corresponds to a (small) part only of the world casting production (roughly 100 Mt/year (mostly ferrous)). Aluminium is the metal that is most extensively filtered and it also benefits from the availability of an in-process liquid metal inclusion count control. The filtering efficiency is usually between 70 and 90%. Filters are specified “one-shot” items, but some founders do not hesitate to recondition used filters. Foam or extruded honeycombs require preheating, while glass fibres sieves do not. Filter cups also serve the purpose of thermal insulation after investment casting. The selection of a filter type is made easier using pieces of software provided by manufacturers of filter systems (see Table 1); the variables considered in the models are available space, metal throughput, mass of casting, temperature, and alloy type. Alumina, mullite-based and silica filters are used for aluminium, Cu-based alloys and Fe-based ones. Bonded SiC filters may last for up to two months in molten Al filtration. The transport industry is the largest end-user of filtered metal and of ceramic filters.

Gas filtration and depollution today rely on electrofilters or on bag filters that are suited for temperatures below 300°C. For higher temperatures, the most popular solution is solid ceramic filters and catalytic converters, cellular or foam types. The larger systems are used for stationary applications in chemical engineering or power plants, but most units are for transport applications with a volume of the order of one litre for light duty vehicles, more for heavy duty and off-the-road

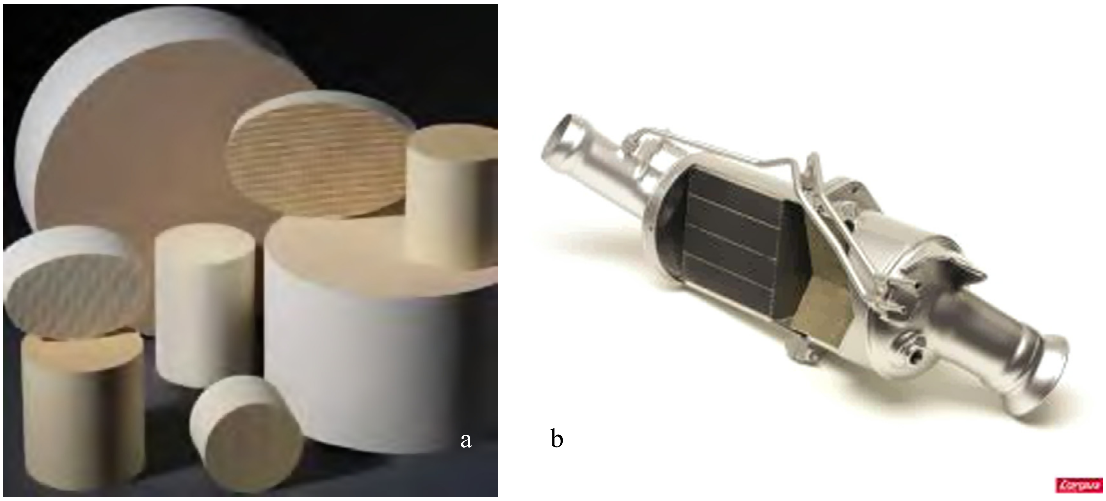

Fig. 4. (Colour online.) (a) Extruded cordierite filters, Corning Cellcor [10]. (b) PSA combined catalyser and particle trap (silicon carbide honeycomb from NGK-Ibiden). From a L'argus/PSA document.

applications, as shown in Fig. 4 for cellular filters. Their porosity ranges from 40 to 75%, depending on cell size and on wall thickness.

The production of ceramic honeycombs for those applications currently reaches several tens of million units a year. Particulate traps, used today for diesel internal combustion engines (in a near future also for gasoline burning engines), and catalytic converter substrates both for diesel and gasoline combustion engines are compulsory on most vehicles in many countries.

Ceramic (diesel) particulate traps, DPT, are usually modified extruded honeycomb filters with microporous cell walls. The trap is of the wall-flow type, i.e. the exhaust gases enter one inlet cell, the end of which is closed, so that they have to permeate through the wall, which contains a network of open (microscopic) porosity before exiting along the neighbouring exit cells (surface filtration). PSA (Peugeot) was the first car manufacturer to install such a system based on extruded silicon carbide cellular elements (Fig. 4). Corning and other manufacturing companies later introduced similar systems based on cellular oxide ceramic filters. Such technologies are credited with >99.5% filtering efficiency, but are associated with an unacceptable (from the standpoint of internal combustion engine performance) back pressure, as "soot" rapidly clogs the cell walls in the absence of a periodic or permanent combustion of soot (mostly carbon and hydrocarbons), called "filter regeneration". Periodic regeneration means, for instance, electrical heating of the filter to trigger the combustion of soot, and continuous regeneration means, for instance, catalytic oxidative combustion of unburnt hydrocarbons and addition of cerium oxide solutions catalyser (no platinum group metal then). Sensors and a microprocessor are associated with the particle trap. A two-chamber filter is used, as shown in Fig. 4b, with a small catalyser and the DPT.

Ceramic catalyser substrates were introduced long before DPT on gasoline combustion engines exhaust lines. A large majority of substrates are of a cellular type, some 80% ceramic, the rest metallic. The ceramic catalyser substrates are similar to the extruded honeycomb ceramic monoliths introduced earlier and shown in Fig. 4a.

Ceramic foams are not yet used to a large extent as DPTs and as catalyser substrates, because they are more fragile than the corresponding extruded honeycomb ceramics. Researchers at EMPA in Switzerland and Umicore in Belgium together with Fiat Powertrain expect to be able to launch a high-strength ceramic-foam catalyser substrate, with the advantage of a better performance of the catalysts compared to the extruded honeycomb substrates [11], which could be a decisive advantage if more severe regulations are imposed on NO_x emissions. One advantage of the deep bed filtration over wall flow technology is reduced backpressure, ΔP. As shown in Fig. 5, the backpressure variation with gas velocity, v, follows a second-order polynomial expression, known as Forcheimer's law, which can be viewed as a modification of Darcy's law:

$$\Delta P = k_1 v + k_2 v^2$$

where the two k constants are associated respectively with viscous drag and kinetic energy of the gas arrested by the strut's surface. They are linked to density, cell size, and morphology.

Thermal insulation may become the next application of ceramic foams if a ban on ceramic fibres fabrics for elevated temperature insulation (furnaces) is imposed. Induceramic proposes three alumina–silica foam products coming in large sizes with high-temperature capability up to 1700°C, low thermal conductivity at 1000°C (<0.3 W/mK) and low density (0.2 to 0.5 g/cm^3) [13]. A spin-off company of the Institute for Non-metallic Inorganic Materials of ETH, Zürich, Switzerland, de Cavis, has been launched to develop closed-cell ceramic foams for thermal insulation [14]. Foam glass is a low-cost ceramic insulating material already used in the construction industry. Foam glass pellets may be produced cheaply, starting from recycled glass. Pellet production by a dozen companies worldwide reaches a cumulative tonnage of several million

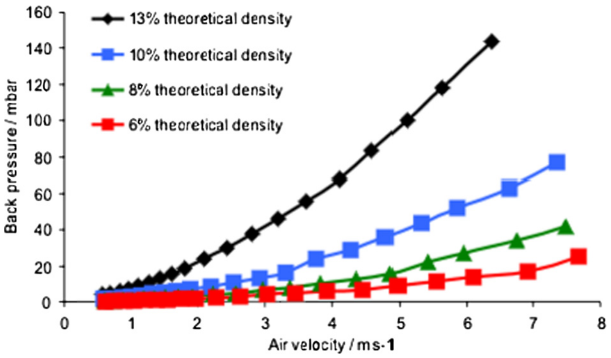

Fig. 5. Pressure drop, ΔP, as a function of the gas (air) velocity, v, from Materials from A to Z [12].

tons a year. These are incorporated in various construction materials for noise and thermal insulation as well as for strength [15], just as the pozzolan natural foam materials presented earlier. Foam-glass pellets are also used as such in farms and gardens to reduce water evaporation from soils.

Blast furnace slag has already been mentioned as a “mineral foam” by-product of steelmaking. Several hundred million tons a year are produced and slag heaps of past centuries may be reclaimed and exploited for their iron content and for the slag itself. It is used in road construction mostly and in the cement industry.

Aerogels are a special class of micro and mesoporous ceramic foam materials based on amorphous silica, carbon, cellulose, and other components. With 95% and more porosity, they are still lighter than ceramic foams and cellular materials presented above. They are formed by special sol–gel and foaming reactions. Originally developed for space applications (space shuttles and astronaut suites thermal insulation) they may also be used to help achieve the thermal performance of low-energy certified buildings whatever the building materials used (concrete, wood, bricks...). The Enersens company, developed over the last 20 years in France by PCAS parent company and in collaboration with Mines—ParisTech/Armines for low cost thermal insulation [16] is marketing a few products, like granules, to be incorporated in construction materials, and is announcing more upcoming applications (insulation panels and blankets). Carbon aerogels may be used for PEMFC fuel cells electrodes (some ceramic and metallic foams may also be used as electrodes for SOFC).

5. Metallic foams

According to a recent review by Quadbeck et al. from FhG IFAM Dresden [17], the polymer foam replication technique for metal foams was first introduced in 1966 in the USA for nickel batteries. In the 1970s, Russian (Soviet Union) researchers developed similar products for catalytic reactions and for filter applications. The polymer foam replication techniques are still (and by far) the most significant industrial open cell metallic foam fabrication routes. The number of research papers on metallic foams reached 200 a year in 2009, which testifies to the interest in those materials and the hopes for growth of the market for metallic foams. We classify the metallic foams according to the manufacturing process before coming to applications and markets.

Four (or rather 3.5 as explained later) variants of the polymer **foam replication techniques** for open-cell metallic foams are distinguished, according to the mode of deposition of the metal, from an ionic solution, from a vapour or from a suspension of solid power particles.

Polymer foam replication–electrodeposition route: it is a nearly continuous process developed to a large extent for pure metals like nickel and to a lesser extent (from the standpoint of industrial development) for copper and silver. The insulating open-cell polymer foam (PU usually), a few millimetres thick, coming in coils, is first made into a sufficient electrical conductor following two sub-variants: carbon slurry impregnation or vacuum magnetron sputtering. The latter is more expensive, but leads to a better quality of foam. It was developed by CNRS and Sorapec, then by Nitech in France, with a collaboration of Mines ParisTech [18]. The electrodeposition stage follows, starting from nickel carbonyl balls in an aqueous electrolyte bath. This stage limits the thickness of the foam, since the deposits on the polymer foam struts in the centre of the foam are less than on both faces. In a second continuous furnace treatment reaching 600°C, the PU skeleton is then destroyed under the air. This slightly oxidizes the nickel foam. A final continuous heat treatment at a temperature of the order of 1000°C under an H_2/N_2-rich atmosphere reduces the Ni oxide and consolidates the dendritic nickel units of the struts produced during electrodeposition, producing a satisfactory compromise between strength and ductility. Due to the initial anisotropy of the foamed and slit or peeled PU blocks and to the processing stresses on the coil, the nickel foam is not isotropic [18]. Hollow struts measure some 50 μm in thickness and their walls are 10 μm or less thick, with only very few grains across a strut (Fig. 6c). The process for copper and silver foams is similar to that described for nickel. The replication technique may also apply to composites using electrophoretic deposition, but the application to alloys is difficult so that a mixed process had to be devised (see later). The market for this family of processes is the largest for metallic foams, as will be discussed later.

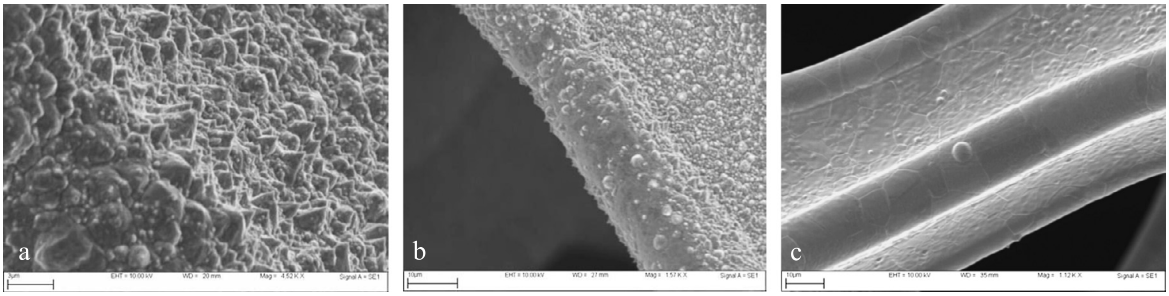

Fig. 6. SEM observations of surface of struts, (a) after electrodeposition, (b) after elimination of the PU scaffold, (c) after final annealing/sintering – note grain boundaries. Length bars are 3 μm, 10 μm, 10 μm for (a), (b), (c) Nitech route from V. Goussery [7].

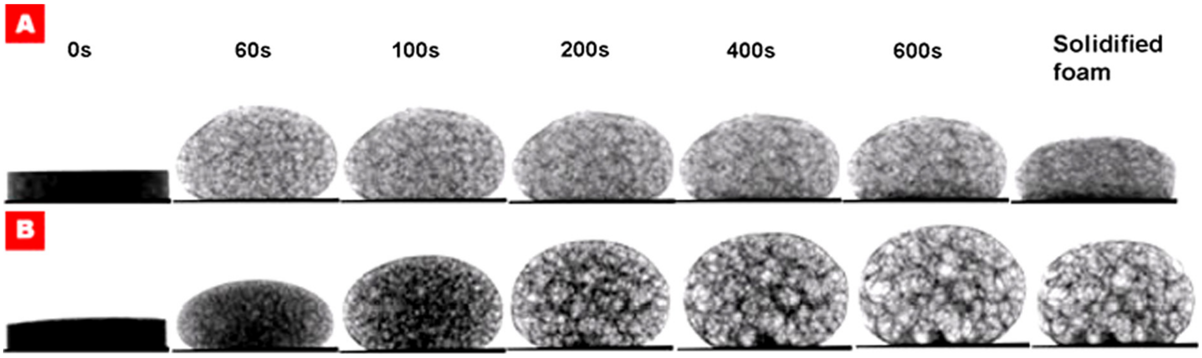

Fig. 7. (Colour online.) X-ray radiography of aluminium foaming experiments comparing the effect of two foam cell stabilizers, same foaming agent content – University of Nottingham/TU Berlin [21].

Polymer foam replication route – CVD Carbonyl process deposition route: the INCO process of Incofoam™ involves running open cell PU foam through a CVD reactor, in which nickel carbonyl gas, $Ni(CO)_4$, is heated up to about 180°C, in the presence of a catalyst for the carbonyl decomposition into solid nickel and gaseous carbon monoxide (CO). At this stage, the foam is brittle and, like the electroplated nickel foam just presented, it has to be subjected to a sintering/annealing treatment under a reducing atmosphere to remove the PU and confer to the foam the desired mechanical and electrical performance. Due to the hazards involved with reactors containing a CO-rich atmosphere and a toxic nickel carbonyl gas, few plants in the world operate using this process. Carbonyl CVD of iron, molybdenum or tungsten is also feasible. The morphology of the nickel foam is similar to that produced in the previous route. The total relative porosity is usually of the order of 95% for this established technology, with a cell size of 400/500 μm, the material being not more than 3 or 4 mm thick.

Polymer foam replication, powder deposition route: the PU foam prototype is first slurry coated with a binder containing fine ($<$20 μm) metal particles in suspension. Upon heating, the PU foam is decomposed, then the metallic powder mass is debinded and finally sintered under vacuum or a reducing atmosphere. The process is then similar to the metal injection process. Application has been demonstrated on carbonyl iron, stainless steels, phosphorous containing steels, copper, and titanium. Applications to catalytic converter substrates or gas surface burners have been investigated with success [17].

Hybrid polymer foam replication–electrodeposition/powder deposition route, by electrodeposition followed by powder deposition: a fourth and mixed process has been developed by Inco special products and FhG–IFAM, Dresden, with a collaboration with Mines—ParisTech/Armines, combining the first process for which huge production capacities for nickel foam are available and the third that brings the capacity to alloy the nickel foam with prealloyed FeCrAl type powders, producing a stainless steel composition reinforced with nickel aluminides [19]. This mixed process was further developed in a joint venture (Inco and SüdChemie) for a metallic foam particle trap, Alantum, still growing (mentioned later).

The **powder route using a metallic precursor and a foaming agent** is well suited to produce closed-cell foams, which makes the process original among the others mentioned in this presentation. Its application is primarily concerned with light metals (initial trials with magnesium in the USA in the late 1950s – "revival" in the 1990s by J. Baumeister at FhG IFAM Bremen with aluminium), but we are aware of attempts to foam cast iron and steel that met with limited success. A recent review by J. Banhart gives more details on a 20-year-long development leading to some industrial achievements [20]. A powder precursor (light metal prealloyed powders and less than 1% in mass of a foaming agent, usually TiH_2, but carbonates can also be used) is hot pressed, hot rolled or hot extruded in a can to a high density. In a second step, at a temperature just above the melting point of the alloy, the foam expands under the pressure of the hydrogen or CO_2 gas pressure associated with the decomposition of the foaming agent (Fig. 7).

The solidification of metallic (aluminium) foams route has been developed with different technologies, but similar ingredients are used: a metal thickener to increase the liquid metal viscosity and the lifetimes of bubbles, a foaming agent of the type

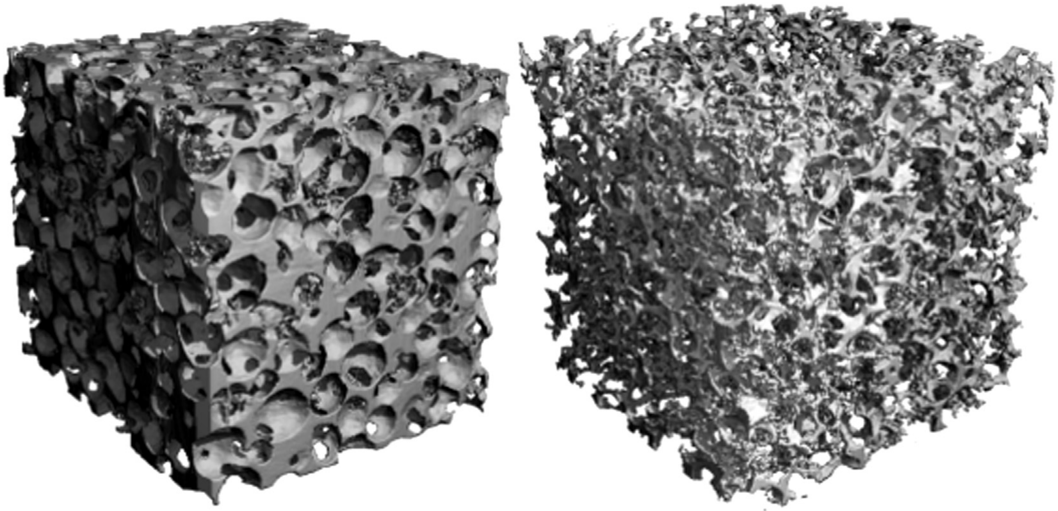

Fig. 8. (Colour online.) Computed tomography, open cell stochastic aluminium foams produced by the soluble salt bead preforms, from [24].

Fig. 9. (Colour online.) Photograph of a section of a periodic foam in 16-5 PH steel, cell size is 10 mm (CTIF–Mines—ParisTech).

already mentioned, TiH_2 or carbonates. Aluminium melt thickeners can be calcium additions, but it can also be the addition of ceramic particulates such as oxides, silicon carbides or aluminium nitrides. These stabilize the cell walls and counteract the decay mechanisms (liquid drainage along cell walls). Discontinuous processes produce large ingots like the "Alporas" products of Shinko Wire in Japan. In some processes, a gas is blown, replacing the addition of a foaming agent. With specially designed injectors, series of bubbles with controlled size are formed, improving the homogeneity of cell size in the solidified foam (LKR process in Austria) [20]. Both Norsk Hydro and Alcan developed continuous foaming using rotating immersed gas injection rotating nozzles [20]. Casting may be continuous using a foam elevator or discontinuous by pressing periodically a block of liquid foam into a mould. Process variants combine foaming and joining to form foam with solid skins, parallel plates or even to foam aluminium inside cavities in an aluminium component.

The investment and sand-casting route, using special cores or soluble preforms is the most recent route for metallic foam processing. Compared to the replication routes presented so far, we may call this route a "negative replication" one since the liquid metal fills the volume available between the cores or in the porous performs. It was initiated in the 1960s in the USA and promoted by the EPFL, Lausanne, Switzerland (Mortensen et al.) for stochastic foams of submillimetric pore size [22] and later by CTIF for periodic foams with pore sizes of several millimetres [23]. Foams with porosity up to 85% may be processed, but pressure casting is necessary to infiltrate such low permeability performs: a few bars of inert gas pressure for the salt performs or a metallostatic head of half a meter for the CTIF gravity casting process. After solidification, the sand core or "salt" preform is eliminated. The optimum compromise between quality of foam and density corresponds to about 80% porosity. The liquid metal must only "see" low-conductivity sand or salt for a full infiltration. For component volumes of several litres, like in the CTIF process (Figs. 8 and 9), a numerical model is necessary to design the cores and gating.

The market for metallic foams, with the exception of that for nickel open foams for applications in electrochemistry or filtration (developed since the seventies) is not at the level of that of the ceramic foams and cellular ceramic monoliths. Also it is not to the level of expectations considering the interesting specific properties presented in the literature and by previous authors in this review. The reason has mostly to do with cost. For instance, the plants producing a majority of the nickel foams in 2000 in Europe (except Recemat) and North America (except Porvair-Selee) closed during the first decade of this century, leaving room to new delocalised plants in China with Inco Vale or Nitech technologies. Dalian today is the

Fig. 10. (Colour online.) Metallic substrates for catalytic converters for motorcycle to Diesel engine locomotive, from RosiArvinMeritor/Metal'Cat-Europe [26]. Compare with ceramic counterparts in Fig. 4a.

world capital of nickel foams. It seems that metallic foams find a market whenever they can fulfil a function that existing materials cannot. This may be a niche market but, as mentioned below, the "niche" may be a very large one. For those reasons, it seems appropriate to distinguish "functional applications" and "structural applications" for which solid metallic foams face a tough competition with full density materials with dedicated architectures.

Functional applications of metallic foams and cellular monoliths. Applications to nickel batteries are justified by the combination of electrical conductivity and strength/corrosion resistance offered by these foams. The nickel foam contains nickel compounds that participate in the electrochemical reactions of the battery and manage the flow of electricity on a local scale. The market of nickel foams is indeed tied to that of Ni–MH and Ni–Cd rechargeable batteries, which is about stable at one third in value of that of the Li-ions batteries that do not incorporate Ni foams today. Hybrid car drivers are the end-users of most of the nickel foam produced by Chinese companies and Sumitomo Electric in Japan. The production of Ni foams for batteries (mostly for hybrid vehicles) is estimated to about 14 Mm^2 or about 7000 t nickel/year and of the order of 200 M€/year, and should keep at the same level. As mentioned earlier, these foams are produced by a PU foam replication route using electrodeposition and for a minor part CVD. A new application emerges, driven again by automotive applications for Ni based foams: part of the Ni foam is converted to alloy foams (Ni–Fe based superalloys) by the combined powder deposition route described previously (Inco, FhG IFAM). Alantum, a venture of Korean nickel in Korea and in China, produces one million litres or some 500 tons a year, to be used in DPF (diesel particulate filters (deep bed technology) for diesel engines exhaust gas cleaning), but also in the chemical industry as a substrate for high-temperature catalytic reactions instead of ceramic blocks [25]. The large permeability of the metallic foam is valued and results in energy savings (the reactors may operate at lower temperatures since they are more uniform in temperature).

At this point, it is worth mentioning also the **metallic cellular monoliths** produced as catalyst substrate for the depollution of internal engines (Fig. 10). They are produced using FeCrAl foils (40 to 100 μm thick), a flat foil and a sinus-shaped foil, wrapped together and inserted in a stainless steel casing and joined by high-temperature vacuum brazing. After wash-coating, they are impregnated with a catalyst. Compared to the extruded honeycomb ceramic substrates, they are more expensive to produce, but, with thin walls, they offer a greater porosity and density of cells, with as a consequence a lower backpressure. Also, they offer a lower thermal inertia leading to a catalytic action less than 30 s after a cold start against a few minutes for ceramic substrates. The higher thermal conductivity also leads to lower levels of thermomechanical stresses. Their high-temperature oxidation behaviour slowly transforms them partly into a ceramic (alumina) and they offer a longer life expectancy than their ceramic counterparts when exposed to temperatures up to 1250°C. They are preferred for sport cars and for powerful gasoline engines. In addition, they resist better shocks and vibrations than ceramic substrates. A few companies offer this product, led by Emitec Gmbh [26] with close to three million parts a year and Metal'cat [27], Blackthorn [28] and Nippon Steel with Sumikin [29] who favour thinner substrate foils (25 μm). One related application is abradable seal materials for the air tightness of aeroengine gas turbines. A metallic honeycomb is assembled from a refractory metallic foil, by laser spot welding followed by brazing (just like the above mentioned long monoliths). The short honeycomb is filled with abradable powders and brazed to the interior of the casings (stators). In service, the rotor blade tips machine their way through the seal.

The next and last but fast growing "functional application" is heat exchangers. Both metallic cellular and open cell foam materials may be used (also silicon carbide). Heat exchangers for solar power (warm water production) and for oil circuit in internal combustion engines are targeted applications for a near future.

Structural applications of metallic foams have always been given top priority, at least for the aluminium foams. Automotive applications have been numerous, but most of them short lived, the time for a car model, i.e., a few hundred thousand parts containing metallic closed cell foams. AFS (Aluminium Foam Sandwich) produced along the FhG–IFAM Bremen powder route presented previously is well positioned. The AFS components (Fig. 11) may be machined and assembled like aluminium. Lightweightness and crashworthiness are the advantages offered.

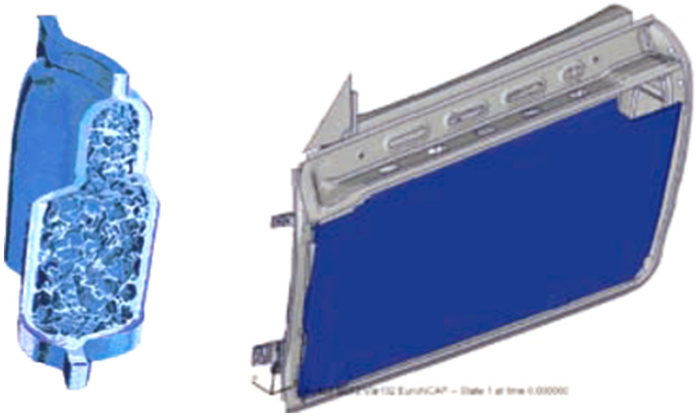

Fig. 11. (Colour online.) AFS Sandwich applications to complex-shape components from the Metalfoam Pohltech brochure. Other applications include decorative and insulating façade plates [30].

Table 2
A selection of companies producing metallic foams (websites accessed April 2014).

Company/country	Metal foam/*Route*	Website
ERG Materials and Aerospace/USA	Duocel® – aluminum, copper, carbon and silicon carbide foam	www.ergaerospace.com
Cymat/Canada	Stabilized aluminum foam *Liquid metal foaming*	www.cymat.com
SELEE Corp. Porvair/USA	Metpore® aluminum, stainless steels, iron–chromium alloys, and copper alloys	www.selee.com
Metalfoam Pohltech Gmbh/Germany	Metalfoam® sandwich, AFS, *Powder route*	www.metalfoam.de
Aluinvent Inc./Hungary	Aluhab® aluminum alloy foam *stabilized liquid foaming route*	www.aluinvent.com
Alveotec and FTB Foundry/France	CTIF open cell Castfoam® aluminum, copper, steel *sand casting route*	www.alveotec.fr
Sumitomo Electric/Japan	Celmet® open cell nickel foam electrodeposition replication route	http://www.sumielectric.com/new-materials.html
Recemat/The Netherlands	Recemat® nickel and Ni alloys foams	http://www.recemat.nl/eng/
AMC ETEC/France	Ecocontact® silver foam	www.amcetec.com
Shanghai Zhonghui/China	Aluminum, copper, nickel foams	www.honghuiaf.com

Since 2012, Aluinvent near Miskolc, Hungary, is offering aluminium alloy foams with maximum block size 50 × 180 × 1200 mm^3 (other geometries on demand) and cell size can be varied between 0.5 and 20 mm using a patented liquid foaming route (inspired by LKR developments in Austria) with ceramic particles to stabilize the liquid foam. Foam density depends on the cell size and varies between 0.2 and 0.5 g/cm^3. Building and construction application are a priority and space application is another one.

Table 2 lists a selection of companies specifying products and manufacturing routes whenever possible. A longer list of some three dozens companies active in metallic foams is produced by Metfoam.net, http://www.metalfoam.net/ (Website administrator, Professor John Bahnart) giving also direct access to the company's website. Those companies are connected to an industrial group and operate as an advanced materials venture, except Cymat, ERG, and Aluinvest, who have at least one established long-term contract with aerospace or defence. Constellium, together with Innovationcells and EPFL, is developing the commercial application of cast aluminium Corevo® foams with soluble salt preforms [31].

Specialized materials retailers like Goodfellow and American Elements have on their shelves several kinds of solid foams to serve for tests and preliminary research, http://www.goodfellow.com/catalogue/GFCatalogue.php?Language=F and http://www.americanelements.com/AEfoams.html.

This review of present and potential markets can be complemented by purchasing a market analysis by market specialists [32–34].

6. Midterm perspectives for solid foams

The market for ceramic foams in hot gas and liquid metal filtering segments should show a steady but limited growth. Particle traps for diesel (and soon gasoline engines) should be an area of growth for both cellular ceramic monoliths and foams with more stringent regulations coming up. Monoliths are less expensive to produce and slightly more efficient in filtering (surface filter) than foam types, but soot retention capacity is larger for foam deep bed filters. Metallic foams will compete with ceramic materials with the advantage of higher strength and shock absorption capacity offset by higher cost.

The heat exchanger market is well suited for metallic foams and cellular monoliths. It is a growing market with green and moderate temperature energy generation development.

Construction applications of metallic foam sandwich panels will develop with architects becoming aware of their thermal and aesthetic benefits. The market for foamed glass and blast furnace slag granules as ingredients in construction materials is already very large. Cellular concrete was not covered in this review, but it is the product of some porous fly ash addition and of a foaming reaction developing more than 50% porosity as in the case of ceramic foams.

In transport applications, metal foams face a cost disadvantage over dense materials for stiffness and shock absorption. Light steel foams made of very high-strength stainless steels could emerge with an energy retention capacity of more than 15 $\mathrm{MJ/m^3}$, while aluminium foams will be limited to 2 or 3 $\mathrm{MJ/m^3}$.

A niche market also develops for metal foams, especially titanium foams, with about 50% relative porosity for orthopaedic or dental implants [35].

New techniques are emerging for the fabrication of metallic foams and of highly porous structures. Additive manufacturing is used to produce small series of lattices of trusses as small as 1 mm in diameter with cell sizes of the same order of magnitude [36]. These materials are, for the moment, limited to niche applications because of their manufacturing cost—one example is heat exchangers for space applications.

Last but not least, **recycling issues** should be tackled. The recycling of ceramic foams and monoliths is not usually considered, only the few grams of platinum group metals catalysts if any are recovered from a catalytic converter and from a DPF. The recycling of metallic foams is done by charging them in melting furnaces (after densification by cold pressing to increase density). Some thick polymer foams (blocks) can be recycled in thinner foam products for less demanding applications. Polymer (PU) foams can be burnt provided that the cyanide compounds that may have formed in their combustion are destroyed by a high-temperature flame treatment of the fumes leaving the furnace.

7. Conclusions and perspectives

Three classes of solid foam (and also cellular) materials have been covered, polymers, ceramics and metals in this review leading to distinguish:

- one generic manufacturing process for solid polymer foam production, close to 30 Mton worldwide, 100 billion € predicted in 2020 [33];
- two or three generic processes for technical ceramic filters and depollution systems totalling an estimate of 30,000 tons (although it is advisable to distinguish the value of liquid metal filters and that of Diesel particulate trap monoliths!). If we include ceramic foams for thermal insulation materials and for the fabrication of porous construction materials, we are again in the tens of Mtons/year;
- a dozen or so processes for metallic foam manufacturing which can be lumped in four groups, namely polymer foam replication processes, liquid metal bubbling with foam stabilizers, casting routes using special cores or preforms and a powder route with foam expansion (only for predominantly closed cells). These processes are used to produce a rough (and personal) estimate of 10,000 tons evaluated at some 250 M€ a year.

Finally, we point out that the reader should avoid drawing rapid conclusions from comparisons of the various (manmade and natural) foam and cellular materials market segments for several reasons. First, the density of ceramic foams is usually larger than that of metallic foams, and of course more than that of polymer foams. Second, the value of the metallic and ceramic foam markets should be similar considering the value of nickel, copper and silver, not to mention that of aluminium metal. Third, the growth of the metallic foam market is the fastest of the three. Heat exchanger markets, DPF, shock absorption and construction applications seem to be the drivers of that growth. One may note that research on metallic foams is very active, with many of the researchers coming from the powder metallurgy research community, which is not surprising considering the similarities between both families of materials. Considering the steady growth of PM, there is one more reason for optimism.

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References

[1] FAO Website information (yearly statistics since 1947), pp. 1–2, http://www.fao.org/fileadmin/user_upload/newsroom/docs/2011%20GFP%20Facts%20and%20Figures.pdf, April 2014.

[2] R. Hooke, in: Micrographia, 1665, pp. 112–116.
[3] Cork Quality Council, http://www.corkqc.com/production/production2.htm.
[4] D.B. Fankhauser, Cells, the functional units of microorganisms, Clermont College, University of Cincinnati, pp. 1–3, http://biology.clc.uc.edu/fankhauser/labs/cell_biology/cells_lab/cells.htm, website accessed 23 April 2014.
[5] Benjamin 444, Wikimedia, http://en.wikipedia.org/wiki/File:Pumice_stone_detail444.jpg, accessed 23 April 2014.
[6] University of Burgos, Cellmat technologies document, http://crono.ubu.es/innovationh2020/pdf/cellmat.pdf, 23 April 2014.
[7] V. Goussery, PhD thesis, Mines—ParisTech, 2004, http://tel.archives-ouvertes.fr/docs/00/04/73/66/PDF/tel-00007551.pdf.
[8] L. Montanaro, Y. Jorand, G. Fantozzi, A. Negro, Ceramic foams by powder processing, J. Eur. Ceram. Soc. 18 (1998) 1339–1350.
[9] S. Ray, B. Milligan, N. Keegan, Measurement of filtration performance, filtration theory and practical applications of ceramic foam filters, in: Aluminium Cast House Technology 2005, 9th Australasian Conference and Exhibition, 2005.
[10] Corning Environmental Technologies, Products & Services, Brochure, http://www.corning.com/environmentaltechnologies/publications/technical_papers/filters_substrates.aspx, accessed 23 April 2014.
[11] EMPA publication, Science Daily, April 23, 2014, http://www.sciencedaily.com/releases/2013/04/130425132526.htm, accessed 25 April 2013.
[12] Ceramic foams – processing and applications as filters, the A to Z of materials, http://www.azom.com/article.aspx?ArticleID=1869, accessed 22 April 2014.
[13] http://www.induceramic.com/industrial-ceramic-product/ceramic-foam-insulation.
[14] S. Schlaefi, in ETH Life, 26.06.201, Ceramic foam for efficient thermal insulation, 2014, http://www.ethlife.ethz.ch/archive_articles/100826_Keramikschaum_sch/index_EN, accessed 26 April 2014.
[15] J. Hurley, A UK market survey for foam glass, WRAP, The Waste and Resources Action Program, Banburry, UK, March 2003, http://geofilbubbles.com/downloads/eng/doc/wrap.pdf, accessed 24 April 2014.
[16] Enersens website http://www.enersens.fr/en/produits/, accessed 26 April 2014.
[17] P. Quadbeck, K. Kümmel, R. Hauser, G. Standke, J. Adler, G. Stephani, Open cell metal foams – application-oriented structure and material selection, in: Proceedings of the International Conference on Cellular Materials, CellMat 2010, Dresden, Germany, 27–29 October 2010, 2010.
[18] A. Burteau, F. Nguyen, J.D. Bartout, S. Forest, Y. Bienvenu, S. Saberi, D. Naumann, Impact of material processing and deformation on cell morphology and mechanical behavior of polyurethane and nickel foams, Int. J. Solids Struct. 49 (2012) 2714–2732.
[19] G. Walther, B. Kloeden, B. Kieback, R. Poss, Y. Bienvenu, J.-D. Bartout, New PM process for manufacturing of alloyed foams for high temperature applications, in: Proc. Powder Metallurgy World Congress & Exhibition, PM2010, Florence, Italy, 10–14 October 2010, vol. 4, 2010, pp. 109–116.
[20] J. Banhart, Light-metal foams – history of innovation and technical challenges, Adv. Eng. Mater. 15 (3) (2013) 82–111.
[21] A. Kennedy, Porous metals and foams, in search for the holey grail, the A to Z of materials, http://www.azom.com/article.aspx?ArticleID=5940, accessed 28 April 2014.
[22] R. Goodall, A. Marmottant, L. Salvo, A. Mortensen, Spherical pore replicated microcellular aluminium: processing and influence on properties, Mater. Sci. Eng. A 465 (2007) 124–135.
[23] J. Dairon, Y. Gaillard, D. Balloy, G. Degallaix, J.C. Tissier, Parts containing open-celled metal foam manufactured by the foundry route: processes, performances, and applications, Adv. Eng. Mater. 13 (11) (2011) 1066–1071.
[24] A. Jinnapat, A. Kennedy, The manufacture and characterisation of aluminium foams made by investment casting using dissolvable spherical sodium chloride bead preforms, Metals 1 (1) (2011) 49–64.
[25] Alantum, Chemical Process Technologies, http://www.alantum.com/fileadmin/user_upload/alantum/chemicals/downloads/en/Alantum_BU_brochure_CPT.pdf accessed 29 April 2014.
[26] Emitec Gmbh, http://www.emitec.com/en/home.html, accessed 27 April 2014.
[27] MetalCat (formerly ArvinMeritorRosi), http://metalcat-europe.com/, accessed 29 April 2014.
[28] Blackthorn, UK, http://www.blackthorn.net/blackthorn-exhaust-technologies–|–exhaust-emission-control-systems, accessed 29 April 2014.
[29] Nippon Steel & Sumikin, http://www.nsmat.nssmc.com/nsmat/english/business_domain/bd08.html/, accessed 27 April 2014.
[30] Pohltech Metalfoam, Gmbh 05-2011 brochure, www.metalfoam.de, accessed 27 April 2014.
[31] Innovation cells and Constellium, Corevo metal foam product, http://www.innovationcells.ch/en/projects/aluminium-foam/just-mix-salt-flour-water-and-aluminium.html#item21, accessed April 30, 2014.
[32] Reuters, Research and Markets: Metal Foams: Theory – Manufacturing – Fundamentals and Applications, 558 pp., DEStech Publications, Lancaster Inc, PA, USA, November 2012.
[33] Freedonia, US market analysis for specialty foam up to 2009, published 2005, 201 pages, may be purchased on a per page basis, http://www.freedoniagroup.com/Specialty-Foams.html, accessed 2 May 2014.
[34] Polymer foam market by types global trends & forecasts to 2018, by marketsandmarkets.com, July 2013, Report Code: CH 1465, http://www.marketsandmarkets.com/Market-Reports/foams-market-1011.html, accessed 2 May 2014.
[35] L.P. Lefevre, E. Baril, Properties of titanium foams for biomedical applications, Adv. Eng. Mater. 15 (2013) 159–165.
[36] H.N.G. Wadley, Cellular metals manufacturing, Adv. Eng. Mater. 4 (2002) 726–733.