

Open Cell Metal Foams – Application-oriented Structure and Material Selection

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High porosity permeable materials have been manufactured on the basis of the highly uniform structure of foamed polyurethane since the early 60th. Open cell ceramic foams on the basis of a replication method for foundry filtration have been used. Such replication methods were transferred to the production of open cell metal foams. Open cell metal foams exhibit key benefits for applications where stringent operating conditions require extraordinary combinations of properties. Since the replication method is basing on powder metallurgical technologies, a broad range of different materials may be fabricated. The present paper reviews the development of open cell PM foams on the basis of unalloyed or low alloyed steels, highly alloyed austenitic and ferritic steels, cellular PM foams on the basis of titanium alloys, and also open cell molybdenum foams. Thus, open cell PM foams show a wide range of the physical and mechanical properties, which may be adapted to a multiplicity of requirements. E.g., automotive industry needs high temperature resistant materials with high permeability and good strength for catalytic converting. Beyond, the network-like metal foams exhibit a natural bone-like structure, which enables ingrowth of bone cells and blood vessels. As permanent or degradable implants, these material developments are focussed on titanium, tantalum, or steel. Furthermore, lightweight molybdenum foam is used for heat insulation applications in industrial furnaces. In summary, the powder metallurgical replication route represents an economic method in order to process open cell metal foams with a unique combination of properties for a wide range of applications.

1 Introduction

Open cell foams, made on the basis of reticulated polyurethane foams are well known and widely used since decades. Polyurethane foams have been commercially produced since the 1950s [1]. They are a practically ideal porous organic structure with porosities between 97 and 98 pct. First attempts to transfer these structures into ceramic foams by a powder slurry replication technique has been described by Schwartzwalder in 1961 [2], and nowadays such foams are produced in the order of 160 mio per year in order to use them as filter in the cast shop. The replication technique has been transferred into the manufacturing of metal foams firstly in 1966 in order to use them as porous battery electrodes [3]. In the 1970s notable work has been done by Russian research groups, where metal foams made by replication method mainly were used in catalysis or filtration applications [4]. Since approx. ten years the method has been reinvented by various groups. Mainly open cell foams on the basis of highly alloyed steels were produced [5-8], but also foams on the basis of copper [9] or titanium alloys for the use as permanent biomedical implant [10] or low alloyed steel for degradable implants [11] were investigated. At Fraunhofer, open cell metal foams made by replication technique have

been investigated since the early 2000s, and various steels like SUS 316L, SUS 314, 4110, SUS 430L, FeCrAl, mild steels and non ferrous metals like foams on the basis of molybdenum, tantalum and the titan alloy Ti6Al4V have been developed. The present paper reviews the main properties and applications of replicated PU based metal foams.

2 Technology

The replication method essentially involves three production steps: First a reticulated polyurethane sponge is coated by slurry infiltration. In the next step, the template is thermally removed and finally the debinded metal structure is sintered. Thus, complete transformation of the open network of the polymer foam to the metal foam is possible. The processing in principle is rather simple, but however, in order to obtain defect-free structures with optimum properties every single processing step needs for proper development. Firstly, in order to obtain complete impregnation of the PU foams fine metal powders are needed. The use of particle size distributions with sizes $>25 \mu\text{m}$ frequently leads to formation of structural defects and voids in the centre of voluminous parts as a consequence of filtration effects on the surface of the PU templates. Since the commercial availability of fine powders is limited, only a small assortment of materials is producible.

Table 1. Metal powders and sintering regime used in the present study

material	DIN	powder size d_{50}	sintering temperature	sintering atmosphere
carbonyl iron		4 μm	1120 °C	H ₂
SUS 316L	1.4404	6 μm	1250 °C	H ₂
SUS 314	1.4841	13.9 μm	1290 °C	H ₂
SUS 430L	1.4016	6 μm	1250 °C	H ₂
FeCrAl	1.4767	15 μm	1300 °C	vacuum, H ₂
4010	1.7225	6 μm	1250 °C	H ₂
Ti6Al4V		17.9 μm	1350 °C	vacuum
Molybdenum		10 μm	1920 °C	H ₂

Furthermore, a well balanced suspension rheology is needed [12,13]. On the one hand the suspensions should show pseudoplastic properties in order to allow for complete and stable impregnation; on the other hand the wettability should be kept low enough to avoid closing of cell windows. The impregnation step then is conducted by roller coating or by centrifugation. Beside structural effects, metallographic inhomogeneities may play an important role. In particular carbon residuals harm the mechanical and corrosion properties. Thus, enhanced control of carbon content is needed. Residual carbon is due to the debinding step, where the polymeric binder and the shape-forming polyurethane are removed thermally. In-situ IR absorption measurements have shown, that the backbone of the template and the binder decomposes at temperatures $<500 \text{ }^\circ\text{C}$, but in particular in hydrogen atmosphere considerable amounts of carbon are removed by the formation of methane at $T > 700 \text{ }^\circ\text{C}$ [14]. After debinding in a MIM debinding furnace the components are transferred to a sintering furnace, and sintering is carried out at typical sintering temperatures as seen in table 1. The heat treatment is carried out in

a batch pilot plant, but also continuous heat treatment in a MIM furnace has been carried out successfully.

3 Properties

3.1 Structure

The porous structure of replicated open cell PM foams is given by the PU foam structure, where the main structural element is a pentagonal rotation ellipsoid with cell windows, typically 1/3 of the size of the large cell (see Fig. 1a). In the ideal case, each large cell is surrounded by twelve neighbours and has twelve edges. The struts show a typical triangular shape with concave areas, which originates from the foaming process of the polyurethane. Traditionally, the cell size of PU foams is given in pores per inch (ppi), but however, this measure is only a rough classification and not very exact. After the heat treatment, the replicated metal foams closely resemble the original PU structure with hollow struts as a typical feature. Figure 1b) shows the structure of a high porosity stainless steel SUS 316L foam (porosity 93 pct). When the suspension coating mass is increased, the shape of the struts becomes more and more rounded. This is demonstrated by Figure 1c) on cellular Ti6Al4V with a porosity of 75 pct. Thus, the physical property of the material is not only affected by the higher density, but also by a changed shape of the struts. Another important aspect is shown in Figure 1d): The impregnation of the PU foams frequently is correlated with the appearance of different structural defects. In the figure, an early stage of development of 4110 steel with a typical strut edge defect is shown, which originate from incomplete covering of the edge tips. Such defects occur preferably when high porosities are aimed at. Further characteristic defects are closed cell windows, whose appearance is correlated to lower porosities. In order to avoid such defects a proper suspension development is essential.

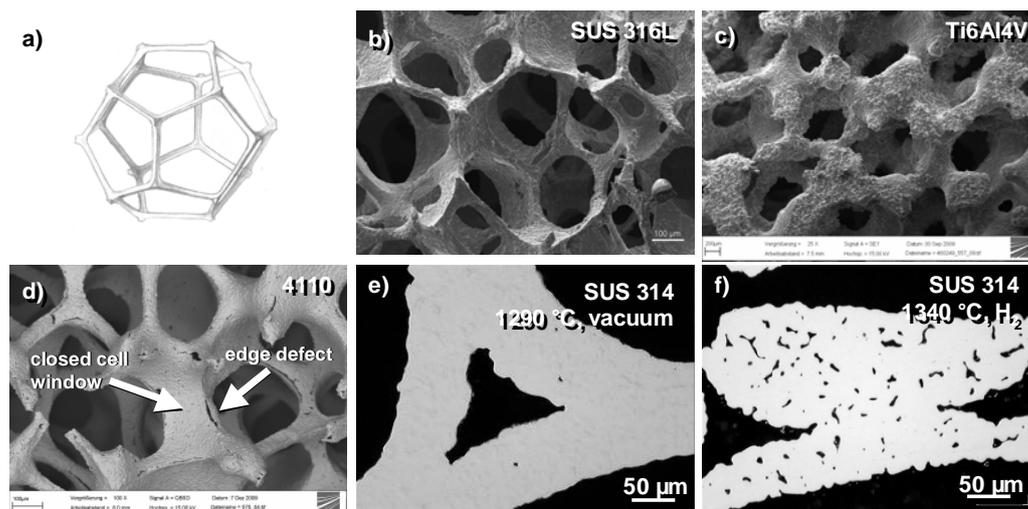


Figure 1: The structure of replication PM foams is basically given by the structure of the PU foams (Fig. a). Low density foams closely resemble the PU foam (Fig. b), whereas high density foams show a rounded strut shape (Fig. c). Furthermore, impregnation defects (Fig. d) and the microporosity of the cell struts (Fig. e+f) is an influencing factor on the foam properties.

Beyond the effects of the macrostructure, the properties (mainly mechanical properties) of metal foams are affected by the microstructure of the cell struts. A considerable role plays the microporosity of the cell struts. E.g., Figure 1e) shows a stainless steel SUS 314, which was sintered at 1290 °C in vacuum. Here, the cell struts exhibit nearly no microporosity. The same material sintered at 1340 °C in hydrogen displays a distinct porosity, originating by incomplete sintering (Fig. 1f). Such pores weaken the mechanical strength and decrease the corrosion resistance due to an additional inner surface.

A further strengthening of the carbon steel foam structures can be achieved by martensitic hardening. Due to the thin strut diameters, full hardening is possible, even when the cooling rates are moderate (Fig. 2). Attention has to be focussed on corrosion effects during the heat treatment, since the specific surface of the foams is rather high.

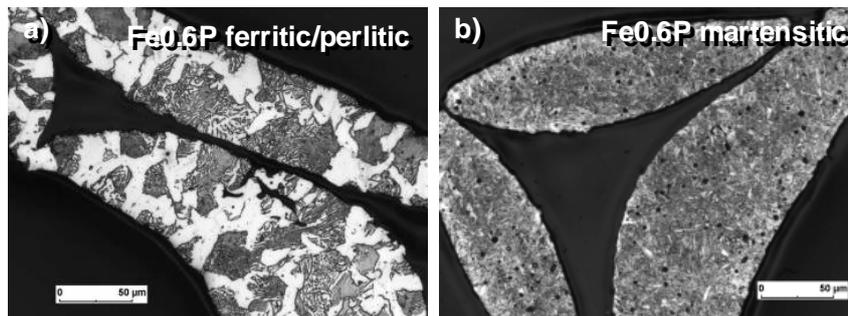


Figure 2: As-sintered low alloyed carbon steels show typical perlitic/ferritic microstructure (Fig. a). They may be strengthened by martensitic hardening of the cell struts (Fig. b).

3.2 Mechanical Properties

In spite of the fact, that in particular applications of cellular metal foams aim at functional properties of such materials, the mechanical properties of metal foams always have been in the focus of the research work. Three main parameters influence the strength of metal foams: The structural density, the strength of the matrix material and to a lesser extent the shape of the cellular structure. This fact is depicted by Figure 3. The figure 3a shows the yield strength of open cell foams on the basis of various matrix materials. The data covers a wide range of strength, where low values are characteristic for matrix materials with low yield strength. E.g., fully dense austenitic steel SUS 316L and pure Tantalum exhibit a yield strength of 195 MPa and 170 MPa, respectively. On the other hand, the ferritic steel 4110 and Ti6Al4V represent high yield strength of 550-750 MPa and 1100 MPa, respectively. Considering the cellular metals, a remarkable strength of 50 MPa is obtained using Ti6Al4V as matrix material. The microstructural influence is demonstrated by the data of low alloyed steels: As sintered Fe0.6P foams (carbon content 0.4 %) show a yield strength of approx. 9 MPa, whereas foams with identical macrostructure but martensitic microstructure exhibit values of 14.5 MPa. The effect of the structural density is shown in Figure 3b. In the diagram, the normalized strength vs. density data points are fitted by

$$\sigma_{cell}/\sigma_{matrix} = C \cdot (\rho_{cell}/\rho_{matrix})^{3/2}, \quad (1)$$

where C is a geometric form-factor, σ_{matrix} the yield strength of the cellular metal, σ_{matrix} the yield strength of the matrix material, ρ_{cell} the density of the cellular metal and ρ_{matrix} the density of the matrix material. Eq. 1 describes an analytical model, which is basing on some simple geometric assumptions [15]. However, this model is a practical tool since it obviously

describes the mechanical properties in a realistic manner. The form factor of the analyzed foams should not vary too much, hence significant deviations from the fit curve give useful information for the structure development. E.g., at low cellular densities distinct deviations occur, which may be attributed to the appearance of defects due to incomplete impregnation. Another example of low relative strength is the Ti6Al4V-foam with a relative density of 0.14, which represents an early stage of development. Enhanced suspension receipts and heat treatment parameters increase the relative strength significantly.

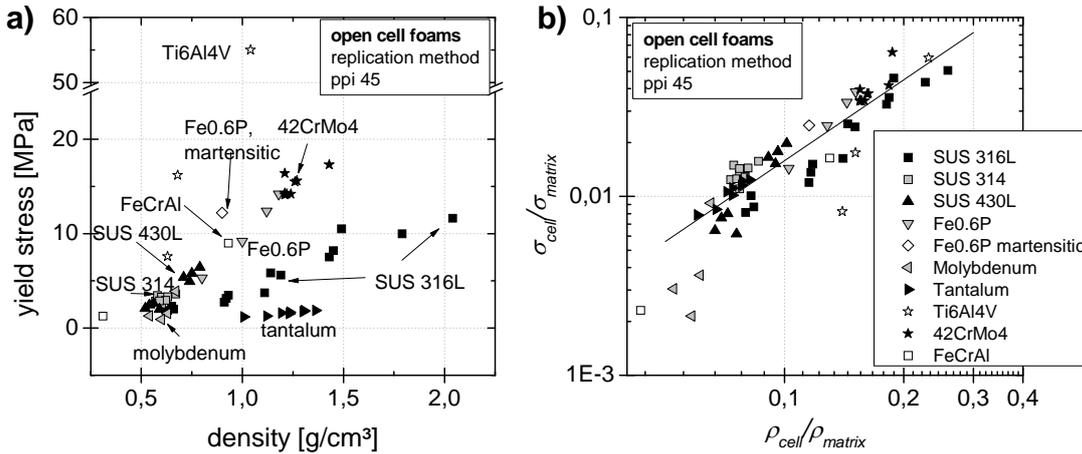


Figure 3: Yield strength of various metal foams made by replication technique (Fig. a). The data may be fitted by Eq. (1), thus exposing materials with structural defects (Fig. b).

3.3 Flow Properties

Fluid flow through porous media is an important subject for foaming technology, in particular where foams aim at catalytic converter applications. The pressure drop of open cell SUS 316L foam with cell from ppi 20-80 sizes and a density of about 0.7 g/cm³ is shown in Figure 5. The graphs reveal the typical shape, which may be fitted by the Darcy/Forchheimer-equation as follows [16]:

$$\Delta p = \frac{\eta}{k} \cdot d \cdot v + \beta \cdot \rho \cdot d \cdot v^2 \quad (2)$$

where η is the dynamic viscosity of the air, k the Darcy-permeability, d the sample thickness, v the gas velocity, β an inertial coefficient and ρ the gas density. The first term on the right hand side of the equation indicates pressure drop due to friction of the gas at the cell walls, whereas the second term denotes energy losses caused by internal friction of the gas. Agreeing different authors give Darcy-permeabilities of 10^{-7} m^2 and inertial coefficients of 10^2 m^{-1} for cell sizes of 10 ppi and $k = 2 \cdot 10^{-9} \text{ m}^2$ and $\beta = 2 \cdot 10^3$ for cell sizes of 80 ppi [17-19]. Smaller cell diameters are related to a higher pressure drop. This is caused by higher degrees of turbulences, which are generated by the smaller cells. However, the Darcian k is extremely sensitive to pore size variation for cell diameters < 2 mm [16]. Relating to the porosity of network-like structures, the pressure drop of network-like structures has a minimum at 90 % at fluid velocities of 3 – 9 m/s [20].

Since low energy losses are required in many applications, and high pressure losses are mainly generated by turbulences, laminar gas flow is desired. The degree of laminar flow is characterized by the Reynolds number. Critical Reynolds numbers indicate formation of tur-

bulent flow. In comparison, 2-dimensional honeycomb structures show larger critical Reynolds numbers than network-like cellular metals out of NiAl, even when the porosity is much lower. Leonov et al. give $Re_{crit} = 1500$ at porosities of 80 pct for honeycombs, compared to $Re_{crit} = 15$ at a porosity of 95 pct for network-like metals [21].

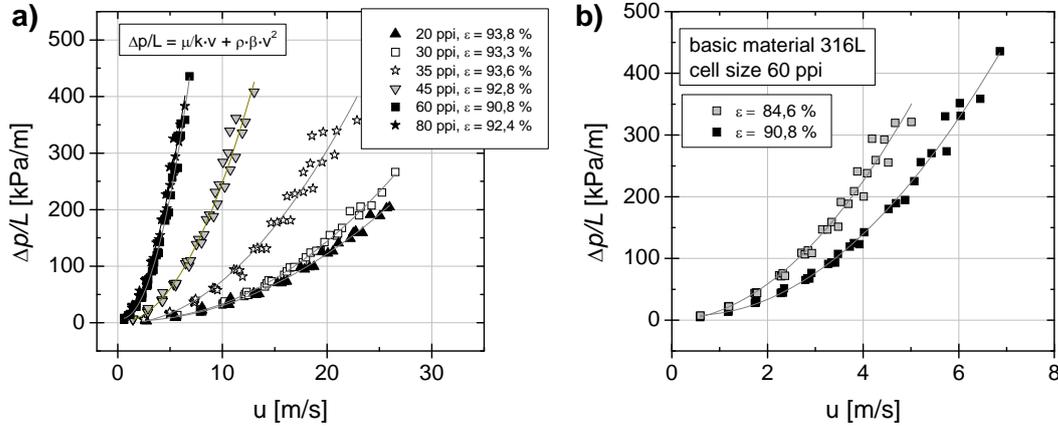


Figure 5: Yield strength of various metal foams made by replication technique (Fig. a). The data may be fitted by Eq. (1), thus exposing materials with structural defects (Fig. b).

3.3 Thermal Properties

The apparent thermal conductivity of porous structure has four contributions: besides the thermal conductivity of the solid cell walls also the conductivity of the enclosed gas, convection and radiation effects have to be taken into account. At higher temperatures, thermal conductivity is decreased due to the disproportionately high portion of the radiation ($\lambda_{radiation} \sim T^4$). Typically, open cell foams show a thermal conduction of 1-5 pct of the matrix material. Experimental measurements have determined a functional relationship between the network thermal conductivity and the density as $\lambda_s \rho_r^{1.8} < \lambda_f < \lambda_s \rho_r^{1.65}$, where ρ_r is the network relative density, λ_f the network conductivity, λ_s the solid conductivity [22]. Higher material conductivity is associated with higher density materials. On the other hand structures with larger cells exhibit a slightly decreased conductivity [23]. Since network-like structures exhibit an almost isotropic distribution of mass [24], the thermal conductivity of such materials accordingly is fairly isotropic. In contrast, directed structures like e.g. honeycomb structures show anisotropic properties [25], e.g. honeycomb structures out of Inconel 617 show relative thermal conductivity of 1.2 % in the lateral direction and 0.7 % in axial direction.

Table 2. Thermal conductivity at RT of open cell metal foams made by replication technique.

material	density [g/cm ³]	porosity [%]	pore size	thermal conductivity [W/m-K]	rel. thermal conductivity [%]	reference
Molybdenum	0.6	94.1	ppi 45	4.62	3.1	Fraunhofer
FeCrAl	0.36	90	ppi 30 - 90	0.35	3.7	[26]
FeCrAl	0.72	95	ppi 30 - 90	0.2 - 0.3	1.2 - 1.8	[26]
SUS 316L	0.7	91	ppi 10- 80	0.75	4.7	[27]
	0.8	89.9	ppi 45	0.82	5.5	Fraunhofer
Copper	0.8	91.9	ppi 60	12.7	5.8	
	0.9	89.9	ppi 60	24.7	2.9	[9]

The heat transfer coefficient of a network-like structure mainly is influenced by the cell diameter and by the porosity. On the one hand, smaller pores give better heat transfer capability, on the other hand, the permeability of structures with smaller pores decreases [26]. Concerning the density, structures with cell size of 10 ppi (cell diameter appr. 5 mm) and a porosity of 85 % exhibit a higher heat transfer capability than structures with cell size of 30 ppi (cell diameter 1.8 – 2 mm) and a porosity of 90 % [5]. Inserting a FeCrAl-network into a flow tube interestingly give heat transfer coefficients which are at high fluid velocities 40 times higher than those of the pure tube. However, at low fluid velocities the additional effect of the network is rather low [28].

3.4 Corrosion Properties

High temperature oxidation resistance typically is characterized by the weight gain per area caused by oxide-scales which are formed during heat treatment. Since regular scale formation follows a logarithmic law $\Delta m/A = k_p \cdot t^{1/2}$, comparable data may be generated by determine the characteristic oxidation constant k_p . Therefore, the ratio of weight gain per surface area $\Delta m/A$ is measured as a function of the time t .

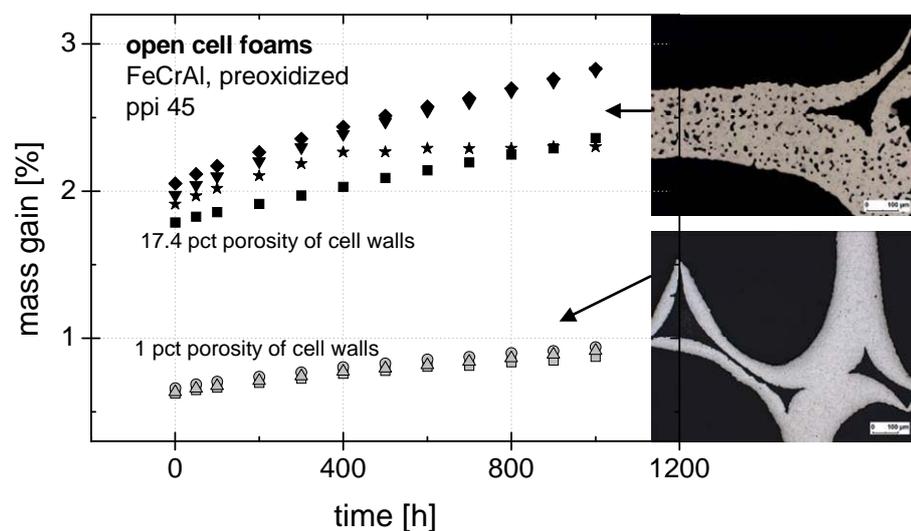


Figure 6: Mass gain of open cell FeCrAl structures during 1000 h heat treatment at 900 °C.

Figure 6 gives the mass gain of preoxidized open cell FeCrAl-foams at 900 °C over a period of 1000 h. The dark data points represent foams with a considerable microporosity of the cell struts, and the brighter dots give the mass gain of foams with allmost dense cell walls. Here, a parabolic mass gain is observed. But, as expected, foams with higher microporosity of the cell walls reveal a higher mass gain, which is correlated with a reduced life time. Thus, high temperature applications like catalytic converter strongly require highly dense cell walls.

4 Applications

The PM replication technique historically has been developed to produce battery electrodes with high specific surface. Since the first attempts, a wide property range has been covered.

Thus, open cell foams have been tested and developed for the use in various applications. Here, it is a considerable pro that the replication technique allows to choose the adequate material for each application.

Catalytic converters on the basis of high temperature steels (e.g. FeCrAl or SUS 314) have been focussed already in early work on open cell metal foams due to their permeability and their high specific surface [4]. As a high strength alternative they have been discussed to replace ceramic monoliths or pellet substrates. Coated with Pt/Pd-catalysts they can be used in Three Way Catalysts (TWC) to convert CO and hydrocarbons and reduce NO_x [29]. They have been used in diesel oxidation catalysts for buses and trucks, where an oxidation catalyst upstream of the filter oxidises HCs and CO to CO₂ and water, and also converts NO to NO₂ [30]. Further types of catalysts to use open cell metal foams are selective catalytic reduction (SCR), where NH₃ is injected to reduce NO_x, or the use in shift gas reactors [31]. However, since typical catalyst converter need for surface areas of ~100 m²/g [29] and open cell metal foams exhibit surface areas in the range of 2 m²/g, a further coating is needed. Therefore, typically γ -Al₂O₃ washcoats are used [32].

For the use as heat exchanger, the thermal conductivity of the matrix material is crucial. Thus, most heat exchanger applications base on aluminium foams, whose manufacturing on the basis of a replication process has not been carried out yet. Nevertheless, in high temperatures and highly demanding environments foams on the basis of FeCrAl have been tested. The conductivity of the bare aluminium is approximately ten times that of FeCrAl, however, the heat transfer performance of aluminium foam is only 2-3 times greater than FeCrAl. This demonstrates that the foam structure, and therefore the turbulences induced in the process fluid substantially improve the heat transfer performance [5].

Due to their high permeability, open cell FeCrAl foams were used as surface burner elements [33]. Compared to ceramic state-of-the-art burner at comparable operating conditions they show 50 °C lower surface temperatures. Regardless the fact that typically higher temperatures correlate to higher NO_x emissions, the steel foam burner exhibit lower NO_x emissions than the ceramic burner.

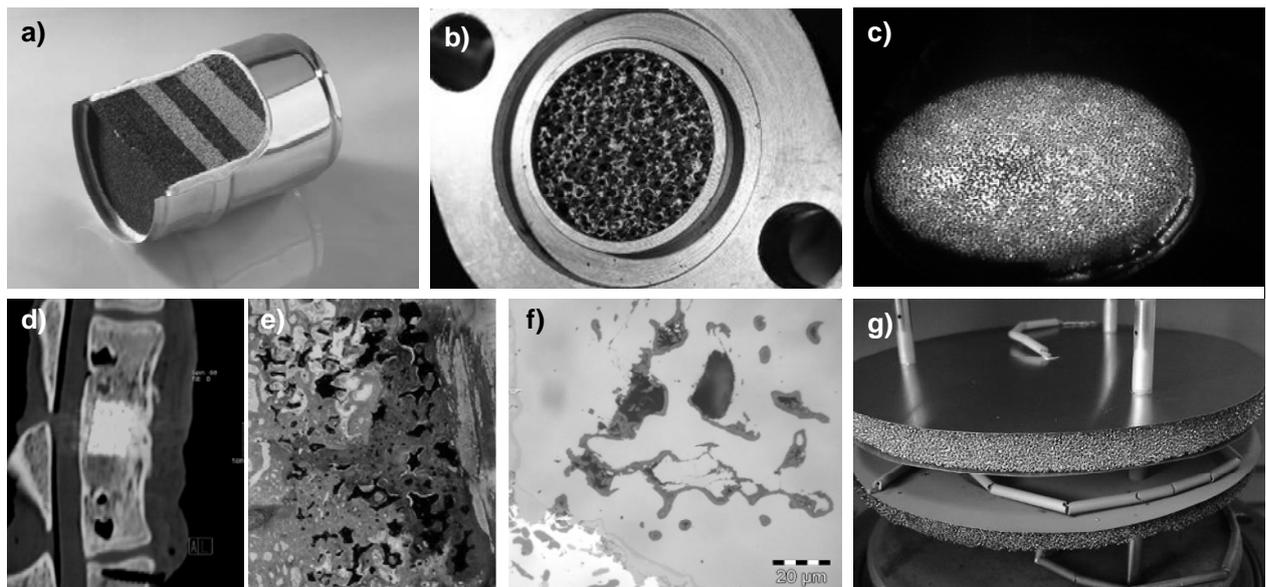


Figure 7: Open cell foams have been tested in various applications, like catalytic converting processes (a), heat exchanger devices (b), surface burners (c), medical bone implant materials (d+e), as local strengthening composite material, and as heat insulation material (g).

The attempt to use open cell foams as bone implant material traces back to the 70th, where it has been realized, that such material allow the bone and blood vessels to be incorporated and to overcome the stiffness mismatch between the bone and the implant material [34]. The latter is crucial since bone formation is induced due to biomechanical load, and stiff implants greatly exceed the stiffness of the surrounding bone and assume the load at this point. For cellular implants, titanium has been established as the material of choice [35]. This is mainly because of its extraordinarily strong biocompatibility, coupled with an excellent corrosion resistance. For bone replacement materials, this means that contact with the bone is free of connective tissue and inflammation. The good osteoconductivity of titanium also argues in favour of its use as an endoprosthesis. For this reason, among metallic replacement materials, titanium and its alloy Ti6Al4V enjoy the highest acceptance on the market. The first tests with permanent vertebral implants (Fig. 7d) demonstrated an outstanding in-growth of bone cells into the material (Fig. 7e).

As a reinforcing element, open cell steel foams may be infiltrated e.g. in cast aluminium components (Fig. 7f). Thus, local strengthening is achievable. This is of particular interest in components, where high local loads occur (e.g. in screw fittings).

Using the relatively low thermal conductivity, lightweight molybdenum foams for heat insulation applications were developed (Fig. 7g). Network-like structures with porosities up to 95 % and cell sizes of 0.8-1.2 mm were synthesized using a powder-metallurgical replication technique. In first tests, the heat insulation capability of the material was tested in an industrial vacuum furnace. In comparison, to the conventional shielding plates, the temperatures at the cold zones only show differences of about 2 %, when the molybdenum foam heat insulation was used. At the same time, the mass of the heat insulation was reduced by factor 4 [36].

5 Market Considerations

It is a common place that the use of metal foams technically spoken only makes sense in cases, where various “good” properties are used in combination. Nevertheless, in the predominant number of applications economic considerations play the main role whether a new material is used or not. Thus, if metal foams should become accepted commercially, the productions costs have to get under control. In the specific case of open cell metal foams made by replication technique, a predominant role plays the cost factor of fine powders. Our first cost calculation for a continuous mass production show, that the portion of the powder costs range between 20 pct and 50 pct. This is of particular importance in automotive applications. Hence, the development of methods for the production of cheap fine powders is essential to commercialize open cell foams. Furthermore considerable costs can be saved when the production of foams is carried over into an automated continuous production. Beyond technological and economical considerations, also psychological constraints have to be conquered as market surveys show [37]. In conclusion, a variety of application of replicated PM foams has been developed and it is likely, that such materials will emancipate from the status of being a “candidate” into a commercial successful material.

7 References

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