LOW DENSITY MATERIALS

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Metallic Microlattices

EPMA Powder
Metallurgy Summer School 2016
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Contents
- Introduction. Scope of the subject
  - What are cellular materials
  - Open – closed cells
  - Classification
- PM manufacturing methods
- Characteristics and applications
- Summary
Low density materials \(\rightarrow\) porous / cellular materials

Different than light metals – ceramics – polymers

Restricted to materials produced by PM techniques

Interesting because lightweight... but not only

From traditional applications to current / innovative products
Introduction. Scope of the subject

The concept of CELLULAR MATERIALS

All possible dispersions of one phase in a second one

The term “foam” in its original sense is reserved for a dispersion of gas bubbles in a liquid. Solidification of liquid → solid foam

Solid foams are a special case of what is more commonly called a “cellular solid”

Cellular solids are not necessarily made from the liquid state → any morphology → open structures: sponges

Source: J. Banhart. Prog.Mat Sci 2001
Introduction. Scope of the subject

POROUS MATERIALS

**Composites** solid – gas
solid phase (metal, ceramic, polymer) + gas phase (pores)

Properties influenced by
- Pore size and morphology
- Total porosity
- Properties of the base material or alloy
- Open / closed cells
Introduction. Scope of the subject

What are cellular metals and metal foams?

**CELLULAR METAL**
The most general term: metallic body in which gaseous voids are dispersed. Close cells contain gaseous phase.

**POROUS METAL**
A special type of cellular metal restricted to a certain type of voids. Pores are usually round and isolated from each other.

**METALLIC FOAM**
A special case of porous metals obtained from liquid metal foams. Cells are closed, round, or polyhedral and are separated from each other by thin films.

**METAL SPONGE**
A continuous network of metal co-exists with a network of empty space or interconnected voids.

aluminium foam  
cellular based material with cells extending in one dimension (MER Corp.)  
oridinary sintered bronze powders form a sponge "sinter metal" or "porous metal"  
aluminium sponge could be called cellular  
nickel sponge (Inco)

Sources: [http://metalfoam.net](http://metalfoam.net)
J. Banhart. JOM. Dec 2000
Introduction. Scope of the subject

Cellular solids: 3D porous structures divided in cells

A cell $\rightarrow$ an empty space delimited by solid boundaries

CLOSED CELL
The material is distributed in the faces and the struts of the cells
Individual cells are all separated from each other by material boundaries

OPEN CELL
The material is distributed only in the struts of the cells
The cells connect through open faces

Determine the applications

Closed cells  Mixed cells  Open cells  Partially open cells

Source: Salvo et al. Comptes Rendus Physique 2014
Cellular solids: 3D porous structures divided in cells

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**Applications**

 Mostly structural
Load-bearing applications
Good mechanical properties
No access to internal surface

 Mostly functional
Functions associated with the interior of the material
Introduction. Scope of the subject

Applications as a function of the type of porosity

Adapted from: J. Banhart. Prog. Mat Sc 2001
Introduction. Scope of the subject

Applications as a function of the type of porosity

.... and the type of material also important

- Structural
  - SS. Ti, NiCrAl
  - Ti, Ta
  - Al, Mg, Ti

- Functional
  - Open
    - Heat exchangers
    - Anodes fuel cells
  - partially open
    - Catalyst supports
    - Filters
    - Silencers
  - closed
    - Bearings
    - Load bearing components
    - Energy absorbers
    - Sound absorbers
    - Bio-medical implants
  - Cu, Stainless steel
  - Composites Ni-YSZ

Adapted from: J. Banhart. Prog. Mat Sci 2001
Introduction. Scope of the subject

Applications as a function of the pore size

IUPAC* classification of porous materials depending on pore diameter:

- **Microporous**, smaller than 2 nm
- **Mesoporous**, between 2 and 50 nm
- **Macroporous**, larger than 50 nm

→ Focus on **macroporous materials**

* International Union of Pure and Applied Chemistry

Ohji, Int. Mat. Reviews 2012
Introduction. Scope of the subject

Applications as a function of the pore size
Introduction. Scope of the subject

POROUS METALS and metal foams have COMBINATION OF PROPERTIES that cannot be obtained by dense materials or polymeric/ceramic foams

- Mechanical strength
- Stiffness
- Energy absorption
- Thermally and electrically conductive
- Maintain mechanical properties at much higher T than polymers
- Generally more stable in harsh environments than polymer foams
- Ability to deform plastically and absorb energy
- If they have open porosity, they are permeable and can have very high specific surface areas, characteristics required for flow-through applications or when surface exchange are involved.
Introduction. Scope of the subject

PROPERTIES of porous metals depend on porosity

Example for porous Ti

Compressive elastic modulus

Compressive strength

Introduction. Scope of the subject

PROPERTIES of porous metals depend on porosity

Energy absorption

Typical compressive stress - strain curve of porous metals

stainless steel hollow sphere foam before and after compression (60% strain)

Source: Neville, Mat & design, 2008
PROPERTIES of porous metals depend on porosity

Energy absorption

Typical compressive stress - strain curve of porous metals

Compressive stress - strain curve of porous Ti as a function of porosity

Processing routes of porous structures

CELLULAR METALS

METAL VAPOUR
- Vapour deposition

LIQUID METAL
- Direct foaming with gas
- Direct foaming with blowing agents
- Gasars
- Powder compact melting
- Casting
- Spray forming

POWDER METAL
- Sintering of powders or fibres
- Sintering of hollow spheres
- Gas release or space holder
- Slurry foaming
- Pressing around fillers - replication
- Extrusion of polymer/metal mixtures
- Additive manufacturing

METAL IONS
- Electrochemical deposition

Tendency to close pores

Mostly for metals with low melting point (Al)

Open morphology

For metals with high melting point or reactive (Ti, Mg)

Adapted from: Banhart. Prog.Mat Sci 2001
Processing routes of porous structures

**CELLULAR METALS**

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- Direct foaming with blowing agents
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**POWDER METAL**
- Sintering of powders or fibres
- Sintering of hollow spheres
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- **Slurry foaming**
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**METAL IONS**
- Electrochemical deposition

**Solid state processes**
→ the powder remain solid during the entire process

Adapted from: Banhart. Prog. Mat Sci 2001
Powder compact melting

**Starting materials:**
- metal powder
- foaming agent

**Preparation:**
- mixing of powders
- compaction of mixture

**Foaming agents:**
- TiH₂, ZrH₂ (<1 %)

**Steels**
- Carbonates (SrCO₃, CaCO₃)

**Method developed at Fraunhofer Institute**

**Heat treatment at temperatures near the melting point of the matrix material**

**Porosity 60 – 90 %**
- Closed cells
- quite irregular

Al, Zn

J. Banhart. Prog.Mat Sci 2001
Sandwich panels

Al foam core (thickness 12 mm) and two steel face sheets

Commercially available
The cellular structure of aluminium foam offers various properties like:

- High Impact **energy absorption**
- Compressive strength
- Vibration reduction
- **Sound absorption**
- Structural **damping**
- Resonance damping
- Electro magnetic - **shielding**
- Low electric conductivity
- Low thermal **conductivity**
- Flame resistance
- **Low weight** (density 0.4 – 1.2 g/cm³)
Applications of Al foams

<table>
<thead>
<tr>
<th>Field of application</th>
<th>Range of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive industry</td>
<td>Car body knots, longitudinal beams, crash absorbers</td>
</tr>
<tr>
<td>Engineering</td>
<td>Fast moving vibrating devices</td>
</tr>
<tr>
<td>Building industry</td>
<td>Light floor-and wall elements with integrated confort function, e.g. heat storage and fire protection</td>
</tr>
<tr>
<td>Shipbuilding industry</td>
<td>Hatches, doors, ribs, superstructures</td>
</tr>
<tr>
<td>Railway vehicles</td>
<td>Paving tiles, crash absorbers, complete front modules</td>
</tr>
<tr>
<td>Design</td>
<td>Partitions, adornments, decoration</td>
</tr>
</tbody>
</table>

Crash energy absorber for a tram built for the COMBINO vehicle system

Schunk – Siemens - Hübner
Applications of Al foams

Demonstrator: cone 3936 as used in Ariane 5
French/German research project

Calibrated cone segment with details of flange and upper edge

Cone after assembly

Applications of Al foams

Karmann car prototype with parts made of aluminium foam (from IFAM, Bremen, Germany) along with collision types and associated in-vehicle injury cost
PM Processing routes of porous structures

Complementary classifications

- Sintering of powders or fibres
- Sintering of hollow spheres
- Removable space holder or gas release
- Replica techniques
- Gas entrapment


Sintering of powders or fibres

Mass production of many applications

- Self lubricated bearings
- Filters
- Batteries

Materials:

- Bronze
- Stainless steel
- Titanium, superalloys

Porosity 20 – 80 %

GKN SINTER METALS

AMES, S.A.
Sintering of powders or fibres

FILTERS:
Different processing routes

co-axial pressing + sintering

CIP + sintering
asymmetrically constructed metallic membranes

Moulding + loose sintering

GKN SINTER METALS
Sintering of powders or fibres

SELF LUBRICATED BEARINGS

Metallic components with porosity (20-25% in volume), impregnated in a lubricant oil

Materials:
- Bronze
- Iron, Fe-C, Fe-Cu, Fe-Cu-C
- Fe-based composite materials

Applications:
- Automotive
- Electric motors and gearboxes
- Actuators
- Household appliances
- Hole appliances
- Industrial
Sintering of hollow spheres

Materials:
- Copper, Nickel
- Steel
- Titanium

- Chemical and electrical deposition of the metal onto polymer spheres
- Atomization

Sphere diameters: 0.8 - 8 mm
Wall thicknesses: 10 to 200 μm
Combination open – close cells
Density: 0.1 – 0.3 g/cm³

Cross-section of a 3.7 mm low carbon steel sphere
(B.P. Neville, Mat&Design, 2008)
Sintering of hollow spheres

Creating sintering necks between spheres during sintering
filling the interstices between the spheres with
• metal powder followed by sintering
• liquid metal (infiltration) → syntactic foams

Typical Ti structure: 36% interstitial porosity, 44% porosity in the sphere cavity; a solid volume in the sphere walls of 20%
→ overall density of 0.9 g/cm³

open structures

closed structures

The pore size distribution is not random but can be tailored by a proper selection of the hollow spheres
mechanical and other physical properties are more predictable
cross-section of composite foams:
1.4 mm low carbon steel spheres with the matrix completely filling the spaces between spheres

(a) 3.7 mm and (b) 1.4 mm low carbon steel spheres with low carbon steel matrix
density 3.06 g/cm³ (38.9 %) - 2.55 g/cm³ (32.4%) (B.P. Neville, Mat&Design, 2008)
Sintering of hollow spheres

Applications

Example

CMPs combining casting and PM
- stop armour-piercing bullets
- shield radiation (X-rays, gamma rays, neutron radiation)
- extremely good thermal insulation
- automotive and train – energy absorption

“Composite Metal Foams” (CMF) Advanced Materials Research Lab (AMRL) at North Carolina State University, USA IPMD News, April 2016

Removable space holder

Space holders (pore forming agents):
- Carbamide (urea), $\text{CO(NH}_2\text{)}_2$
- Salts, $\text{NaCl}$
- Polymer grains
- Hollow spheres
- Crystalline carbohydrate (sugar)
- Mg granules

Materials:
- Titanium
- Stainless steel
- Superalloys
- MAX phases
Bimodal structures

→ for biomedical applications

Multi-scale porous scaffolds perform better than one dimensional porosity

Combination of (pore size $>100$ µm) and (pore size $<20$ µm) and pores must be interconnected

Structure of samples pressed at 350 MPa with 70 vol.-% of ammonium bicarbonate after sintering at (a) 1200°C for 1 h; (b) 1300°C for 3 h

Laptev, Powder Met. 2003
Removable space holder

MAX phase foams using crystalline carbohydrate (sugar) as space holder

Ti2AlC \( (D_{50}=10 \, \mu m) \)

- Mixed: 30 minutes
- Pressing: 1. Uniaxial, 2. Isostatic
- Dissolution: Water \( (60 \, {\degree}C, \, 24h) \)
- Sintering: Vacuum \( (1400 \, {\degree}C, \, 4h) \)

Removable space holder

MAX phase foams using crystalline carbohydrate (sugar) as space holder

Porosity: EXPERIMENTAL vs THEORETICAL

Removable space holder

MAX phase foams using crystalline carbohydrate (sugar) as space holder

Space holder size: 250-400 µm

Increasing porosity

Porosity: 60 %

Opening and closed porosity

Homogeneous distribution of porosity

Easily machinable

B. Velasco. PhD, UC3M, under development
What are MAX phases?

$n:1-3$

Location on the periodic table of the elements of MAX phase [1].

Ti$_2$AlC

- lightest.
- most oxidation resistant.
- good thermal and electrical conductivity.

Crystal structures of all the MAX phases: “M-X” layers (red and black atoms) are interleaved with layers “A” (blue atoms) [1].

New materials with great potential for many applications.

Why MAX phases foams?

Foams

• Low density with unique properties not achieved by dense materials.
• Materials in development.
• Processing methods are yet imperfectly controlled → variability in properties.

MAX phases

• Unique properties:
  • Good electrical & thermal conductivity, machinability, damage tolerance, ...
  • High elastic modulus, oxidation resistance, capabilities at high temperature, ...

Foams for high performance applications
Heat exchangers, solar volumetric collector, diesel particular filters, impact resistant structures, catalyst substructures, material for extreme conditions,...

Control on the porosity (%Porosity & pore size) → Tailor functional and mechanical properties for specific applications.
Foaming from a gas

Gas release in suspensions → Foaming a liquid metal (Al foams)

Gas release in semi-solid → Powder compact melting (see before)
  Cell size: 2 - 10 µm; relative densities 0.3–0.7

Gas release in a liquid → Powder blending - CIP – heating to semisolid → casting and foaming → complex shape
  Cell size: 1 - 5 µm; relative densities 0.1–0.5

Dispersion of metal/ceramic particles in aqueous media

Pores are created by:
- Addition of blowing agent
- Creating air bubbles

Cell size: 10 µ - 1 mm; porosity up to 95%
Colloidal Processing

\[ V_T = V_A + V_R \]

**Attractive Potentials**  
Van der Waals forces

\[ V = -\frac{A}{6D} \frac{r_1 \cdot r_2}{(r_1 + r_2)} \]

Always present  
Strongly depend on distance

**Repulsive Potentials**  
Electrostatic  
Steric  
Electrosteric

STABLE SUSPENSIONS→ dominating REPULSIVE FORCES
Colloidal Processing

Repulsion Mechanism – Interparticle potentials

Electrostatic

Steric

Electrosteric

Potential energy

Distance

Primary minimum

Secondary minimum

Potential energy

Distance

Potential energy

Distance

Steric mechanism provided by polyelectrolytes

→ STABILIZERS
Examples from suspensions
- Ti
- Ni-YSZ composites

Suspension
- Gel forming agent: Metilcellulose (MC)
- Blowing agent: Ammonium carbonate (NH₄)₂CO₃

Foaming from a gas
- Suspension → milling → casting → Drying (gelification) ≈ 50 °C → Sintering → Green part

Porosity up to 70%

E. Molero, PhD, ICV-CSIC, January 2016
Replica techniques

Electro-deposition technique

- polymer foam
- add conductive coating
- electroplate
- remove polymer

J. Banhart. Prog. Mat Sci 2001

Electroless deposition technique

- melamine resin reaction
- Electroless plating (Ni Co Cu)
- burning away the template

Ag foam  |  Ni foam  |  Co foam  |  Cu foam

Fabrication scheme of ultralight metal foams

Replica techniques

Impregnation of template with metal or ceramic suspension

300 °C – 800 °C

total open porosity: 40%–95%
pores sizes: 200 μm - 3 mm

Suspensions must have
Shear thinning behaviour
additives: clays, sillica,
carboxymethyl cellulose...

Studart 2006, J.Am.Cer.Society

Ti foams
(Fraunhofer IFAM Dresden)

http://www.ifam.fraunhofer.de/en.html

Alumina single crystal fibers

MAX phases foams (UC3M)

http://www.ifam.fraunhofer.de/en.html
Replica techniques

Alumina single crystal fibers

MAX phases foams (UC3M)
Replica techniques

Microstructures of porous ceramics produced via the replica technique.

Synthetic and natural templates

Alumina-based open-cell structure obtained using polyurethane sponge templates

detail of a strut of a cellular ceramic produced from polymeric sponges, illustrating the typical flaws formed upon pyrolysis of the organic template

transversal view of a highly-oriented SiC porous ceramic obtained after infiltration of a wood template (the longitudinal view is shown in the inset)

macroporous hydroxyapatite obtained from a coral structure (lost-wax method)

Studart 2006, J.Am.Cer.Society
Replica techniques

Processing routes to transform cellular wood structures into macroporous ceramics

- Porosity mainly open 25%–95%
- Pores sizes 10 - 300 μm (lower than polymer template)

- Highly oriented porous structures
- Application in catalysis and in the filtration of liquids and hot gases

Anisotropic properties

Studart 2006, J.Am.Cer.Society
Replica techniques

Electrodeposition + powder deposition $\rightarrow$ alloy foams

joint venture (Inco and SüdChemie)
### Applications of Alantium foams

<table>
<thead>
<tr>
<th>Applications</th>
<th>Advantages</th>
<th>Foam</th>
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<tbody>
<tr>
<td>Filter</td>
<td>large surface area</td>
<td>NiCrAl NiFeCrAl FeCrAl STS</td>
</tr>
<tr>
<td></td>
<td>high heat resistance</td>
<td></td>
</tr>
<tr>
<td></td>
<td>low pressure drop</td>
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<tr>
<td></td>
<td>high corrosion resistance</td>
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<tr>
<td></td>
<td>strong adhesion</td>
<td></td>
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<tr>
<td>Composite Material</td>
<td>low density</td>
<td>NiCrAl NiFeCrAl FeCrAl STS</td>
</tr>
<tr>
<td></td>
<td>high tensile strength</td>
<td></td>
</tr>
<tr>
<td></td>
<td>high porosity</td>
<td></td>
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<tr>
<td>Battery</td>
<td>large surface area</td>
<td>Ni Cu</td>
</tr>
<tr>
<td></td>
<td>high conductivity</td>
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<td></td>
<td>high purity</td>
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<tr>
<td>Catalyst Substrate</td>
<td>large surface area</td>
<td>NiCrAl NiFeCrAl FeCrAl STS</td>
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<td>strong adhesion</td>
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<td>low precious metal usage</td>
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<td>Heat Transfer Media</td>
<td>high thermal conductivity</td>
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<td></td>
<td>large surface area</td>
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</table>
Additive manufacturing

**Origin:** Rapid Prototyping (RP)

Stereo Lithography (SL),
Fused Deposition Modeling (FDM),
3D printing,
Laminated Object Manufacturing (LOM).

**Developments:**

**Powder bed techniques**
- Electron Beam Melting—EBM,
- Laser Beam Melting—LBM,
- Selective Laser Sintering—SLS

**Direct Deposition technologies**
- Electron Beam Fabrication FreeForm—EBF3
- Direct Laser Fabrication—DLF
- Direct Metal Deposition—DMD or **Laser Metal Deposition (LMD)**
- Wire Arc Additive Manufacturing—WAAM

Grid structure for use in the medical field (material: Cobalt chrome alloy) fabricated using SLM
Additive manufacturing

Electron beam melting system

Engine part with lattice structure fabricated by EBM using Ti6Al4V
Arcam A B.
http://www.arcam.com

Additive manufacturing

Electron beam melting system

(CAD) model for open cellular foams based upon micro-CT-scans for aluminum alloy foams

Additive manufacturing

Biomedical applications – bone replacement

Porous Plasma Spray (PPS) titanium coating in femoral (A) and tibial component (B) for total knee replacement.

(A) Tantalum trabecular metal tibial baseplate for uncemented total knee replacement.
(B) X ray shows implant osteointegration at 1 year of follow-up.

F. Matassi et al. Clinical Cases in Mineral and Bone Metabolism 2013
Additive manufacturing

Custom-fit femoral implants & adapted Young’s modulus

- Patient custom-fit implants
- Better distribution of the stresses
- Reducing stress-shielding
- Reducing micro-motion between bone & sinkage
- Surface roughness for strong fixation
- Hydroxyapatite coating eased up
- Complex biodegradable scaffolds combining HAP & βTCP
Additive manufacturing

Custom Cranio-Maxillofacial implant

Trabecular Structures using the EBM technology.
Arcam A B. http://www.arcam.com
Additive manufacturing

Stereo Lithography (SL)

A controlled laser is used to cure a photopolymer resin to shape the component from a 3D CAD model.

2D and 3D structures made of YSZ for solid oxide fuel cell components.

Hernandez-Rodriguez, Boletin SECV 2014
Robocasting

Ti scaffolds for biomedical applications from aqueous suspensions
Robocasting

Ti scaffolds coated by EPD* with TiN nanoparticles

*Electrophoretical deposition
Summary

- Porous materials can be manufactured from a wide range of metals and alloys as well as ceramics
- Pore size from 0.5μm up to 10mm
- Porosity can be tailored up to 97% and it can be adjusted to specific requirements
- Different geometries, design, net shape products
- Density from 0.2 to 2 g/cm³
- Special properties, combination of properties
  - Excellent sound absorption
  - Good thermal insulation
  - Excellent stuff for filtration purposes
  - High specific energy absorption
  - Good deformability and machinability
- Properties depend on the amount, type and distribution of porosity
- Porous materials can be further coated to modify properties
- Widespread application in many industrial areas
THANK YOU FOR YOUR ATTENTION