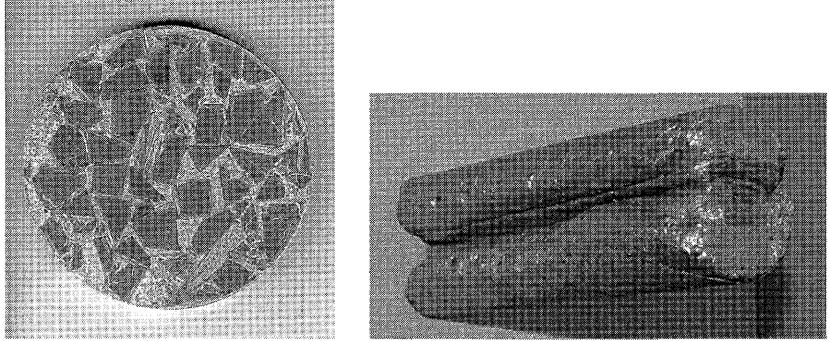


### 2.3

#### **Making Cellular Metals from Metals other than Aluminum**

*G. Rausch and J. Banhart*

The previous section was dedicated exclusively to aluminum foams. For many applications one would like to use cellular materials made from metals or alloys other than aluminum. There have been some attempts to manufacture metal foams by simply adapting the powder-compact process originally developed for aluminum to other metals by adjusting the properties of the foaming agent and the process parameters. This procedure was successful in some cases. However, for high-melting alloys the powder-compact foaming technique is difficult to implement and especially for titanium no promising results could be obtained. Here alternative routes based on advanced powder metallurgy yielded better results. Therefore, in the current section the topic will be slightly extended from “foamed” to “cellular or porous metals” in a more general sense.



**Figure 2.2-4.** Left) top of aluminum foam part made by inserting various pieces of foamable material into the mold (dark figures indicate original size of the precursor pieces). Right) foam part made of two pieces of precursor without achieving bonding between the two pieces.

face, which has to be broken up by expansion of the individual foam pieces. Incomplete foaming may cause the foamed pieces to remain separated even after the foaming process (Fig. 2.2-4b). A relative movement of the foam pieces to each other helps to break up the oxide films. Fig. 2.2-4 shows an example of a successful formation of a foamed body from various pieces of the precursor and an example of failure. In the former case the location of the original individual foam pieces can still be identified from the contrast in gray scales between the various regions: darker gray identifies oxide layers of extruded surfaces, brighter gray is the new (expanded) surface. This effect is currently exploited to create foam panels and other foamed parts for making designer objects.

### 2.2.3

#### State of Commercialization

Currently the foaming technique described is still in the stage of industrial implementation. Nevertheless, a number of companies have already made commitments for a future production and are building up facilities [14]. The joint effort of *Schunk Sintermetalltechnik* (Gießen) and *Honsel GmbH&Co KG* (Meschede) is one example. Owing to their collaboration with Karmann the activities are preferentially directed towards foam and foam sandwich parts with a complex 3D geometry (see Section 3.3). *Alulight International GmbH* is another example. It is a joint venture of *SHW* (Germany) and *Eckart Austria*. The company offers aluminum foam panels in sizes up to 625 mm × 625 mm, with thickness of 8–25 mm. *Neuman Alufoam*, another Austrian company, also offers foamable precursor material (extrusions) and foamed parts.

## 2.3.1

**Zinc**

Zinc can be foamed by a straight-forward modification of the powder-compact technique. The foaming agent used for aluminum ( $\text{TiH}_2$ ) can be used, although  $\text{ZrH}_2$  seems to yield slightly better results. Powder properties and mixing procedures are quite similar to aluminum. Only the pressing and foaming temperature has to be chosen slightly lower than for aluminum due to the melting temperature of zinc at  $419^\circ\text{C}$ . Foamed zinc shows a very uniform pore structure. This can be attributed to the fact that the decomposition temperature of the foaming agents  $\text{TiH}_2$  matches with the melting temperature of the metal. Therefore, melting and pore formation occur simultaneously and round bubbles are created from the very beginning. In contrast to aluminum, there is no solid state expansion range with corresponding crack formation. Fig. 2.3-1a shows an example of a zinc foam.

## 2.3.2

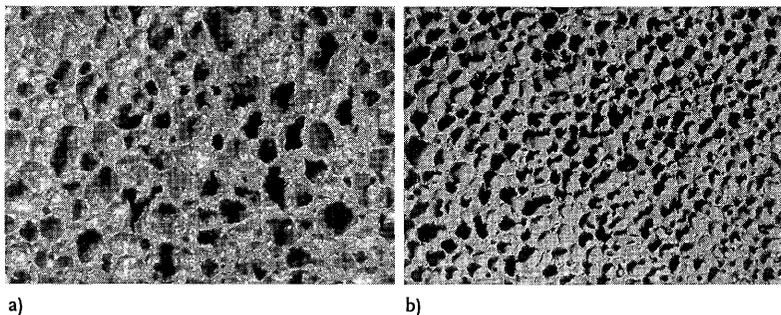
**Lead**

Lead and lead alloys such as  $\text{Pb-Sn}$  and  $\text{Pb-Sb}$  can be foamed by another modification of the process.  $\text{TiH}_2$  and  $\text{ZrH}_2$  cannot be used as foaming agents because of the low melting temperatures of pure lead ( $327^\circ\text{C}$ ) and even lower solidus temperature of the alloys. Quite good foams have been obtained by using lead(II) carbonate as a foaming agent: it decomposes above about  $275^\circ\text{C}$  and releases  $\text{CO}_2$  and water, which act as foaming gas. Fig. 2.3-1b shows an example of a lead foam

## 2.3.3

**Titanium**

Owing to its high melting temperature ( $1670^\circ\text{C}$ ) and relatively low density ( $4.51\text{ g/cm}^3$ ), titanium and its alloys are excellent materials for lightweight applications at elevated temperatures and are widely used in aeronautical applications. Porous ti-



a)

b)

Figure 2.3-1. Zn and Pb foams (width of sample is about 5 cm).

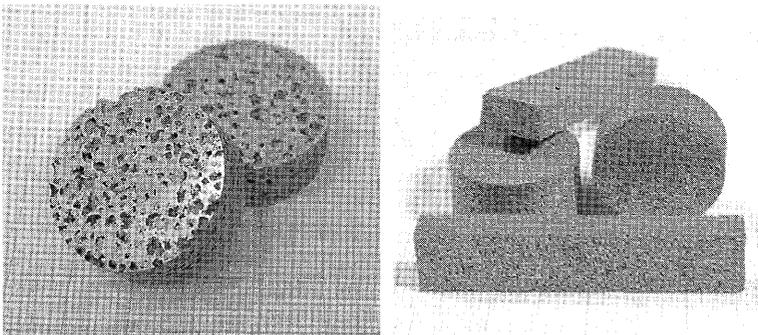
tanium structures have an additional potential for weight reduction and could even be suitable for functional applications if the pore structure were open.

In principle, there are many possible production methods for cellular materials based on titanium (see Section 2.4), most of them starting from metal powders.

1. Consolidation of slurry-saturated plastic foam.
2. Foaming and sintering of powder slurries.
3. Reaction sintering of elemental powder mixtures.
4. Foaming of powder compacts containing foaming agents (powder-compact melting process).
5. Hot isostatic pressing and creep expansion of titanium compacts with entrapped inert gas.
6. Sintering of hollow spheres.
7. Sintering of compacted or loose powder–filler mixtures.

While some of these methods (1–3) have not yet been investigated very intensively, the feasibility of the foaming agent process (4) for titanium has been demonstrated [1]. However, owing to the high temperatures during foaming titanium, the reactivity of this metal with practically any non-inert gas and the lack of appropriate foaming molds, this method is not suitable for producing shaped titanium foam components. Hot isostatic pressing of titanium powder with gas entrapment (5) has been successfully developed for some aircraft applications [2]. Metal hollow spheres (6) can be produced using wet chemical methods for coating Styrofoam spheres [3]. Shaping and sintering of these hollow structures typically result in materials with very low porosity.

One of the most promising methods for manufacturing open porous titanium materials is the sintering of compacted or extruded mixtures of powders and fillers that contain removable space-holder materials. The materials are mixed and shaped by conventional PM techniques. After removal of the space holder the green samples are sintered at temperatures of 1100–1400 °C. Bram and coworkers use urea and ammonium hydrogen carbonate as space holders [4], which can be removed by thermal treatment below 200 °C. Depending on the size and shape



**Figure 23-2.** Open porous titanium made by space-holder technique: (left) pore size 1–4 mm; (right) pore size about 500  $\mu\text{m}$ , porosity 55–80%.

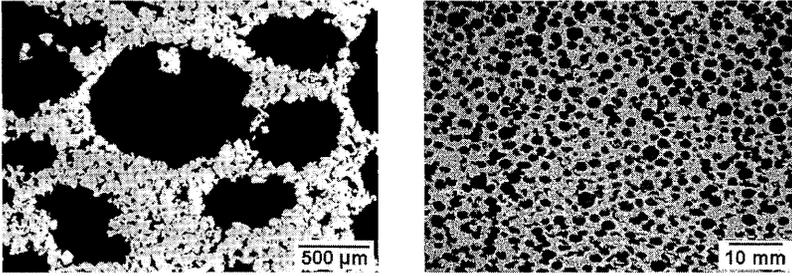


Figure 2.3-3. Pore structure of open porous titanium with 67% porosity.

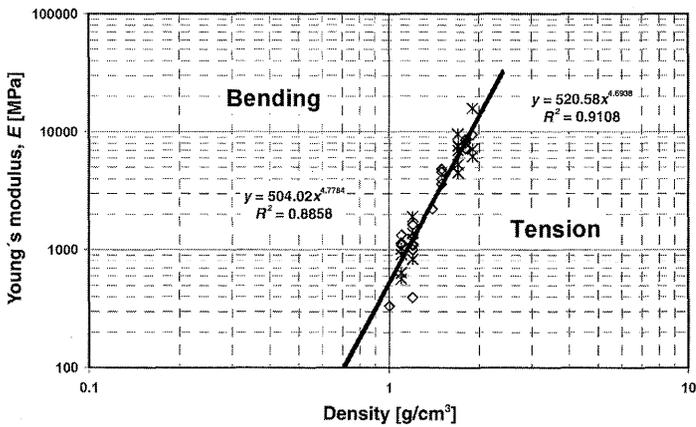
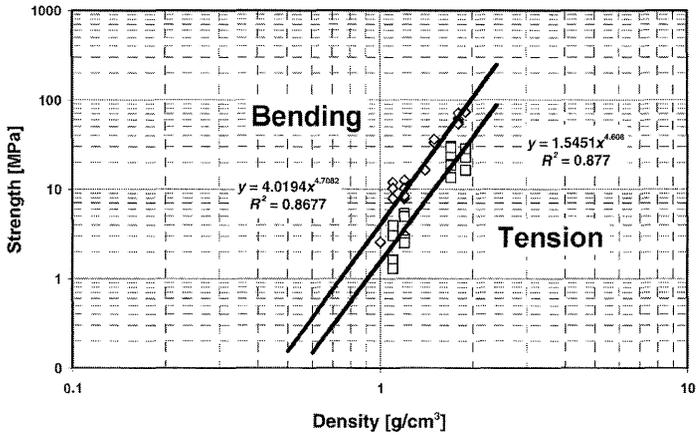


Figure 2.3-4. Strength and Young's modulus as a function of density obtained from bending and tension tests [5].

of the space-holder powder, spherical and angular pores in the range 0.1–2.5 mm can be obtained, resulting in overall porosities of 70–80 %. It was found that the sintering activity can be increased by partially substituting titanium by titanium hydride, thus yielding an increased compression strength.

At Fraunhofer IFAM, polymer granules were used as the space holder. They were removed by a chemical process at temperatures around 130 °C, after pressing. After space-holder removal, samples are sintered in vacuum at temperatures of 1100–1250 °C. Depending on the particle size of the granules, average pore diameters in the range 200–3000 μm can be obtained. Fig. 2.3-2 shows some typical samples. Fig. 2.3-3 shows the typical pore structure of samples based on spherical space-holder granules. Beyond the primary pore structure, some microporosity (secondary pores) inside the sintered network is visible. It was shown that the secondary porosity has a strong influence on the overall strength of the samples and can be reduced by either changing the sintering parameters and/or partially replacing titanium powder by titanium hydride [4]. As for all porous materials, the mechanical properties of cellular titanium are a function of density. Fig. 2.3-4 shows the strength and Young's modulus obtained from bending and tension tests as a function of density.

#### 2.3.4

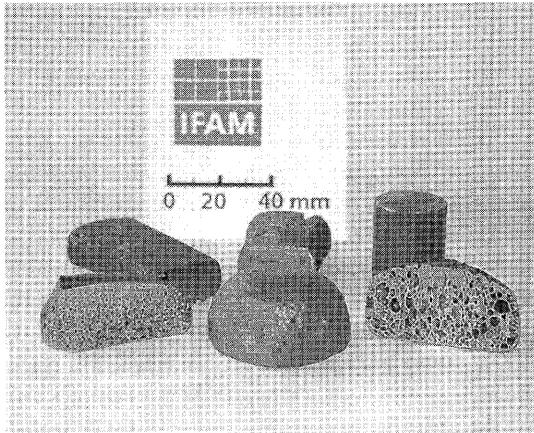
#### Steel

##### 2.3.4.1 Powder-Compact Foaming Technique

The long experience in making aluminum foams from powder metallurgy (PM) precursors encouraged researchers to transfer this process to higher-melting materials such as iron-based alloys and steels. The major requirements for an adaptation of the foaming agent process to this group of materials are the following.

- Selection of suitable foaming agents.
- Development of alloys qualified for good “foamability”.
- Evaluation of compaction methods.
- Adaptation of the foaming process.

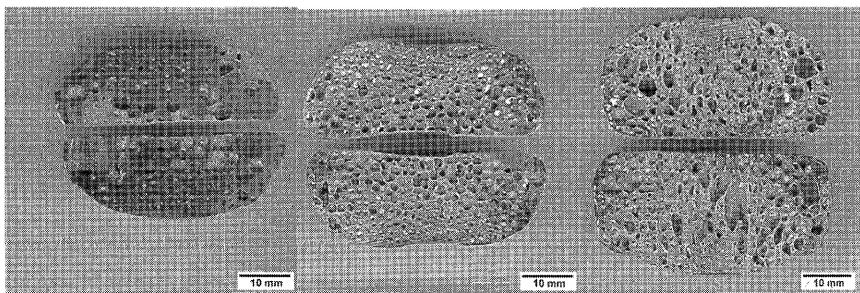
The basic requirements for foaming agents are: point of gas emission above 1000–1200 °C (depending on the alloy composition), broad temperature range of gas emission (up to 1550 °C for nearly pure iron), and sufficient volume of gas release. It was found that especially metal nitrides and certain carbonates show a significant gas emission and qualify for being useful as foaming agents. Examples are manganese nitride, chromium nitride, molybdenum nitride, calcium carbonate, strontium carbonate, and barium carbonate [5,6]. Theoretical investigations [5,7] have shown that both the iron–carbon and the iron–boron system [7] are able to meet the basic requirements for being foamed to iron-based metallic foams, namely: a low melting point matching the decomposition temperature of the foaming agent, and a broad two-phase semisolid region in the phase diagram, thus creating a wide foaming interval. As for the production of Al based foamable pre-



**Figure 2.3-5.** Iron-based foams obtained from the foaming agent process.

cursor material, extrusion has been successfully used for compacting iron powder mixtures. The resulting samples are shown in Fig. 2.3-5.

Experiments with powder mixtures of iron and carbon have shown that free carbon without any additional foaming agent already leads to a certain degree of porosity. Carbon is oxidized during the foaming process and the resulting gaseous CO and CO<sub>2</sub> creates pores. However, pore size distributions are not uniform and pore shape is usually rather irregular. The porosity mainly results from large, isolated pores (Fig. 2.3-6). Adding 0.25% SrCO<sub>3</sub> leads to an increase of porosity to 55.5% (Fig. 2.3-7). The pore structure at this composition appears to be more homogeneous and the average pore size is obviously lower. Increasing the amount of SrCO<sub>3</sub> results in a further increased porosity (64.3%). From that it can be concluded that SrCO<sub>3</sub> has a significant influence on the achievable porosity and the maximum expansion. The foaming agent technique has therefore been shown to be feasible for steel. However, foaming of stainless steel or even superalloys has not yet been successful and the general state-of-the-art of foaming steel with the foaming agent method is still far behind the aluminum foaming technology.



**Figure 2.3-6.** Iron-based metal foams made from extrusion-pressed powder mixtures of Fe + 2.5% C: (left) 0.0% SrCO<sub>3</sub>, (middle) 0.25% SrCO<sub>3</sub>, (right) 0.50% SrCO<sub>3</sub>.

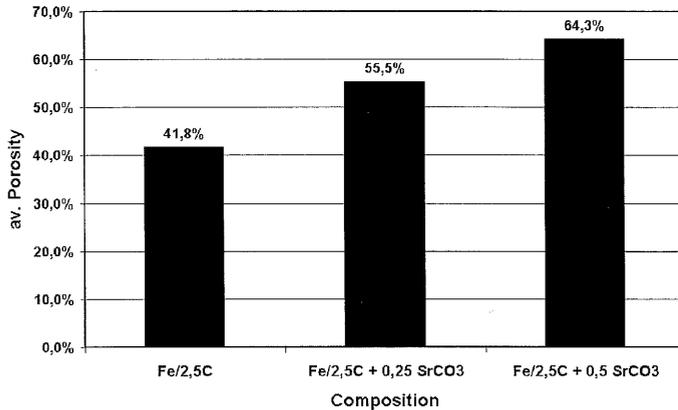


Figure 2.3-7. Average porosity as a function of foaming agent content ( $\text{SrCO}_3$ ).

#### 2.3.4.2 Steel Foams from Powder–Filler Mixtures

All foamed metals have essentially closed cells. For certain applications (filters, membranes, biomedical applications) open porosity is required. For this class of materials the space-holder technique (see also Section 2.3) can be used. The process used for steel is very similar to the one described in the titanium section. The process starts with a mixture of metal powders and the filler powder. The mixture is compacted, usually by axial compression in a conventional powder press. If necessary, an additional bonding agent is used in order to achieve a better strength of the green samples. After pressing an additional drying step is optional. After this the filler/bonding agent phase is removed from the samples, in a chemical (catalytic) or thermal process. After complete filler removal the samples are sintered in a furnace under hydrogen atmosphere. Either urea [4] or plastic granules [8] can be used as space holders. In Fig. 2.3-8 examples of porous 316L and Inconel 600 materials are given, developed by Forschungszentrum Jülich GmbH. The porosity of these materials is about 70% with an average pore size of 1.0–1.4 mm.

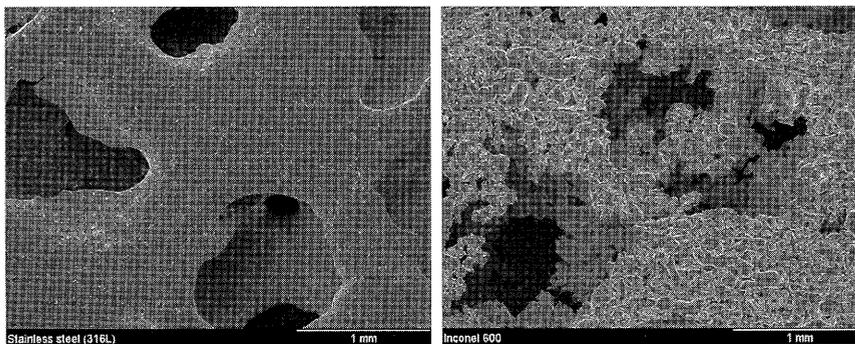


Figure 2.3-8. SEM images of sintered specimen: left) stainless steel 316L, 1100°C, 1 h, particle size  $<16 \mu\text{m}$ ; right) Inconel 600, 1250°C, 1 h, particle size 100–200  $\mu\text{m}$  [4].

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