Metallic hollow sphere structures - status and outlook

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Introduction

During the last two decades several types of cellular metals were developed and investigated. A highly homogeneous type of cellular structures with particularly reproducible pore size distribution is represented by Metal Hollow Spheres (MHS) and Metal Hollow Sphere Structures (MHSS). The manufacturing process bases on a powder metallurgical route. Thus, a variety of metals and alloys as well as ceramic materials can be processed. In the present work it has been focused on metal hollow spheres and structures. Within the last years an industrial manufacturing process has been developed in order to commercialize the material. Therefore standard manufacturing technologies from pharmaceutical industry, packing industry and metal injection moulding processing have been adapted. With this know-how, MHSS were successfully tested in numerous applications like crash damping, high temperature heat insulation, sound absorbing, stiffening of lightweight construction elements and others. Further development has been carried out by modifying and functionalizing the spheres and structures, which led to an expansion of their property and application spectrum. E.g., by filling the metal spheres with free movable ceramic powder excellent vibration damping properties were generated. Furthermore, filling the spheres with phase change materials creates small moveable heat storage units with high thermal capacity and high charging respectively discharging speed. This paper gives an overview on the recent fabrication technologies, extended functionalities, the properties and applications of the materials.

Manufacturing Technologies

To manufacture metal hollow spheres different routes are useable. Within the last 15 years the most research and development was done using a powder metallurgical route [1]. Other ways to manufacture metal hollow spheres are blowing a melt [2] or galvanic methods.

Hollow Sphere Structures by Powder Metallurgical Method

The basic manufacturing technology for MHS and MHSS using a powder metallurgical route was developed at Fraunhofer IFAM in co-operation with Glatt Systemtechnik GmbH Dresden, Germany and later with hollomet GmbH Dresden, Germany and was described in several papers. [1], [3]-[6]. Using this method spheres and structures of a large variety of metals and alloys can be made. So we have experiences in manufacturing of iron and carbon steel spheres as well as in manufacturing of spheres from stainless steels, high temperature resistant steels, nickel alloys, super alloys, titanium, tungsten, molybdenum, rare metals and more. The cell size diameter is adjustable in the range from approx. 1.5 mm to approx 8 mm. A shell thickness from approx. 20 µm up to approx. 2 mm can be made.

The manufacture route consists of 4 main steps:

(1) coating of expanded Styrofoam spheres by a slurry of metal powder and binder using a special fluid bed reactor
(2) molding of parts (bonding of spheres to parts using steam or a mixture of alcohol and water)
(3) debinding (removal of all organic components such as Styrofoam and binder)
(4) sintering

Debinding and sintering temperatures as well as furnace atmospheres are depending on the material of the spheres.

An overview of the hollow sphere manufacture process is shown in Fig. 1

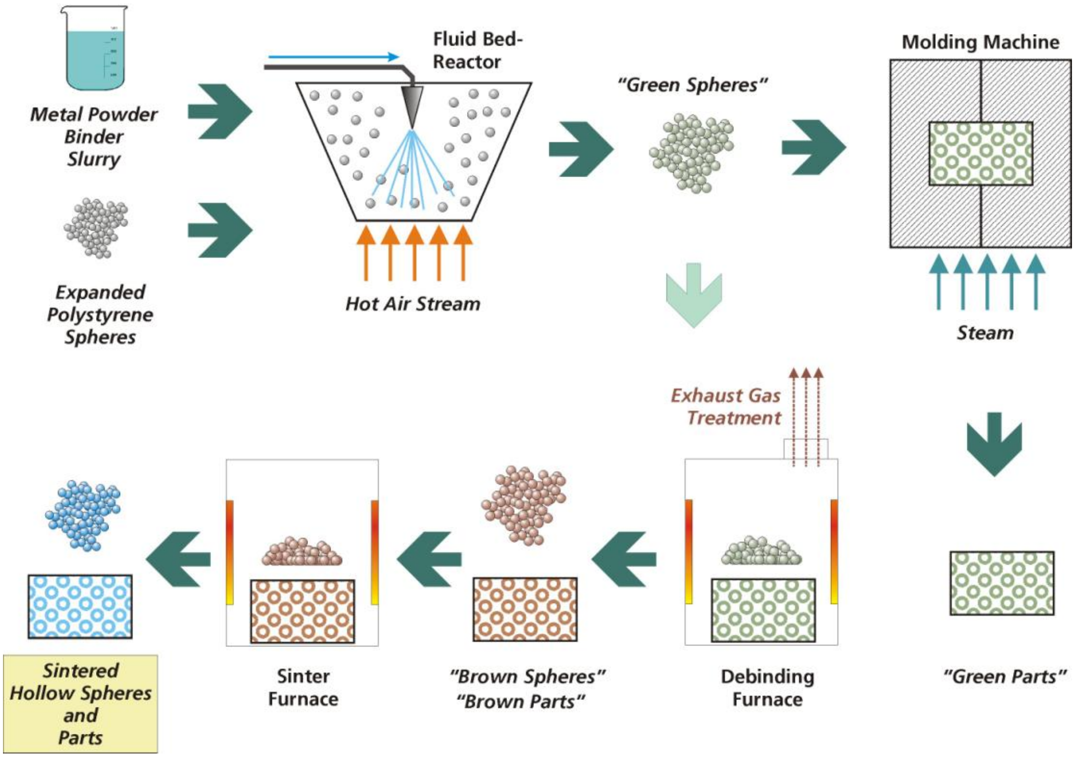

Figure 1: Manufacture Process of Metal Hollow Sphere Structures

One of the major advantages of this process is the excellent adjustability of properties of the structures. Tab. 1 is showing possibilities to influence some mayor properties of hollow sphere structures.

Table 1: Adjustability of Properties

Property	Adjustable by
Cell size and cell size distribution	Selection of diameter of polystyrene spheres
Density	Material, cell size, shell thickness
Mechanical properties	Material, cell size, shell thickness, sinter temperature, heat treatment
Acoustic properties	Material, cell size, shell thickness
Thermal properties	Material, cell size, shell thickness
Infiltratability (shell porosity)	Powder particle size, sinter temperature

The common way to create complex shaped parts is to machine sintered MHSS. Alternative ways of manufacturing of hollow sphere structures are adhesive bonding of sintered spheres using organic or ceramic adhesives as well as brazing or casting. Fig. 2 shows an overview about types of structure types.

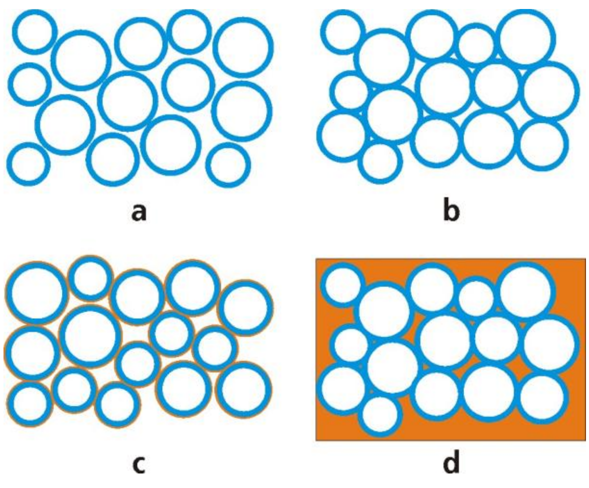

Figure 2: Different types of hollow sphere structures:
(a) lose spheres
(b) sintered structure
(c) adhesive bonded or brazed structure
(d) cast structure (matrix: metal or polymer)

Equipment for spraying of green spheres, a moulding machine and several debinding and sintering furnaces are available at Fraunhofer IFAM Dresden as well as at hollomet GmbH Dresden. Batches from 2 or 3 litres up to a few hundred litres can be manufactured now.
Based on this well equipped basic technology during the last few years several methods were developed to expand the portfolio of outstanding properties.

Special Types of Hollow Spheres

Particle Filled Hollow Spheres

To increase their vibration damping a filling of the MHS by floating powders such as ceramics can be very helpful. For this purpose we use the property of ceramic powders to sinter at much higher temperatures compared to the most metals. The ceramic powder has to be placed inside the metallic shell before spraying the metal layer. This can be done either by using a ceramic particle filled Styrofoam or by spraying an inner layer of ceramic powder on the surface of the template before spraying an interface layer and the metal. In the further course the processing is similar to the processing of non-filled spheres. So the manufacture of sintered structures is possible as well as brazing, adhesive bonding or casting [7]-[9].

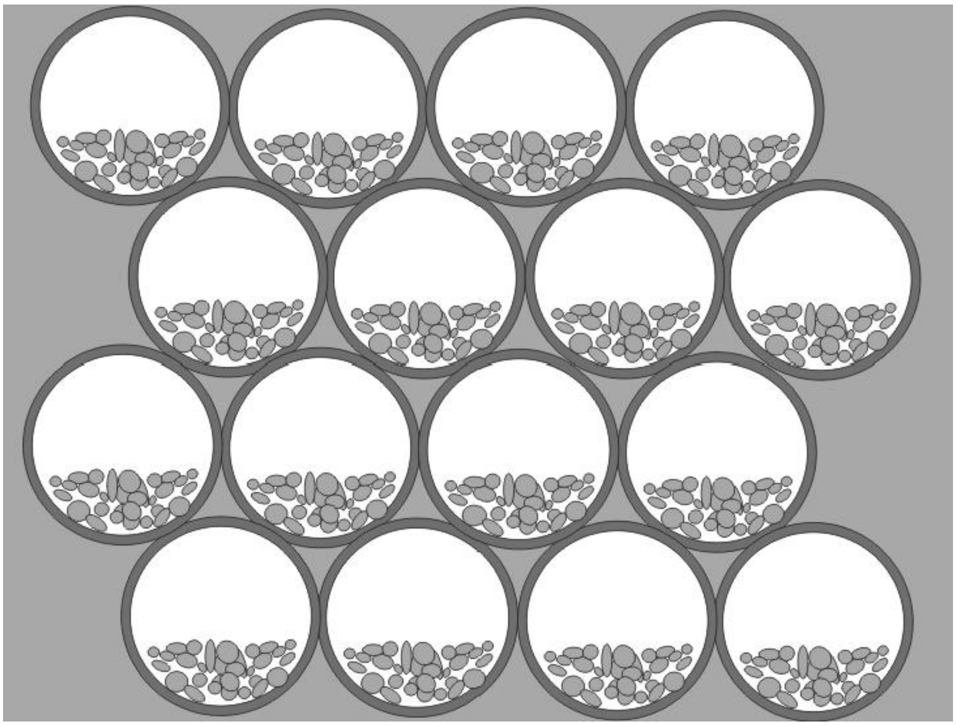

Figure 3: Particle filled hollow sphere structure, scematic view

PCM Filled Hollow Spheres

Phase change materials (PCMs) are commonly used to create heat storage equipment using their latent heat at phase transition from liquid to solid and reverse. The creation of “moving heat capacities” and of fast-acting heat storage systems is possible by use of PCM filled hollow spheres. [10], [11]
Single hollow spheres are manufactured using the method described above. Sintering at relatively low sinter temperature leads to porous shells. After sintering the spheres will be filled with a PCM (such as parrafine, salt hydrates, molten salt mixtures or others) under vacuum and then sealed by galvanic methods e.g.

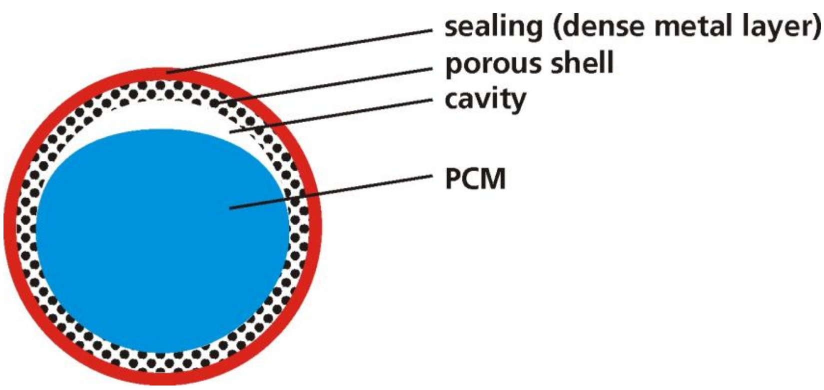

Figure 4: PCM filled hollow sphere, scematic view

Ground Hollow Spheres

Another special type of MHS is represented by the ground hollow sphere. Ground hollow spheres have a low weight and a low inertia but on the other hand a surface and sphericity comparable to common bearing balls. Ground hollow spheres can be made of a variety of metals and alloys and can be uses in fast moving ball bearings and linear guides, in fast moving magnetic ball valves and for some other purposes like jewellery e.g. [12]

To achieve a good roundness and a narrow diameter distribution the template styrofoam spheres are subjected to a thermomechanical treatment using a special machine developed at Fraunhofer IFAM. After spraying and/or after sintering the spheres will be screened. The sintered and screened spheres will be ground and polished using a small ball grinding machine.

For the most applications relatively thick shells of very low porosity is necessary to withstand the grinding process and the stress during use.

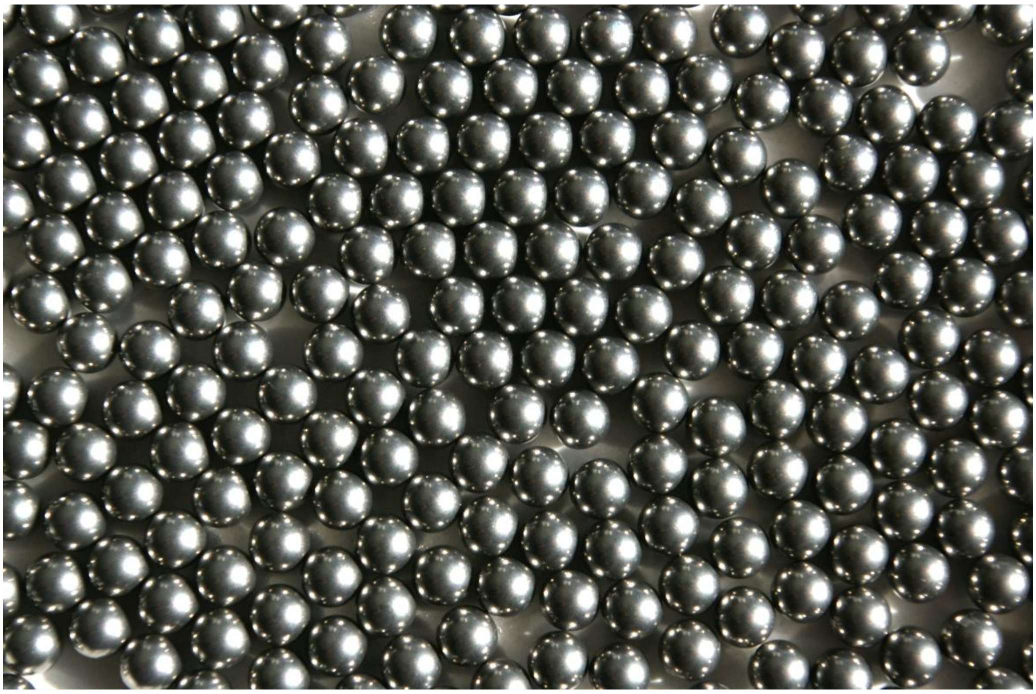

Figure 5: Ground and polished stainless steel hollow spheres

Properties and Applications

Due to their unique morphology MHS and MHSS are showing interesting properties. So they have a low thermal conductivity, high sound absorption coefficient, a relatively high strength allowing the construction of self-supporting elements and a good heat and oxidation resistance. Using these properties elements for multifunctional applications can be designed.

Thermal insulation

For heat insulation applications MHSS should be used in the range of higher temperatures particularly, using their good corrosion resistance and mechanical strength compared to common insulation materials in this range [13], [14]. Fig. 6 is showing the heat conductivity of a 1.4841 steel sandwich structure in the temperature range from 100 to 800°C. Such sandwich elements can be used as combined heat shields and energy absorbing structures (see also 3.4) in space applications for example (Fig. 7).

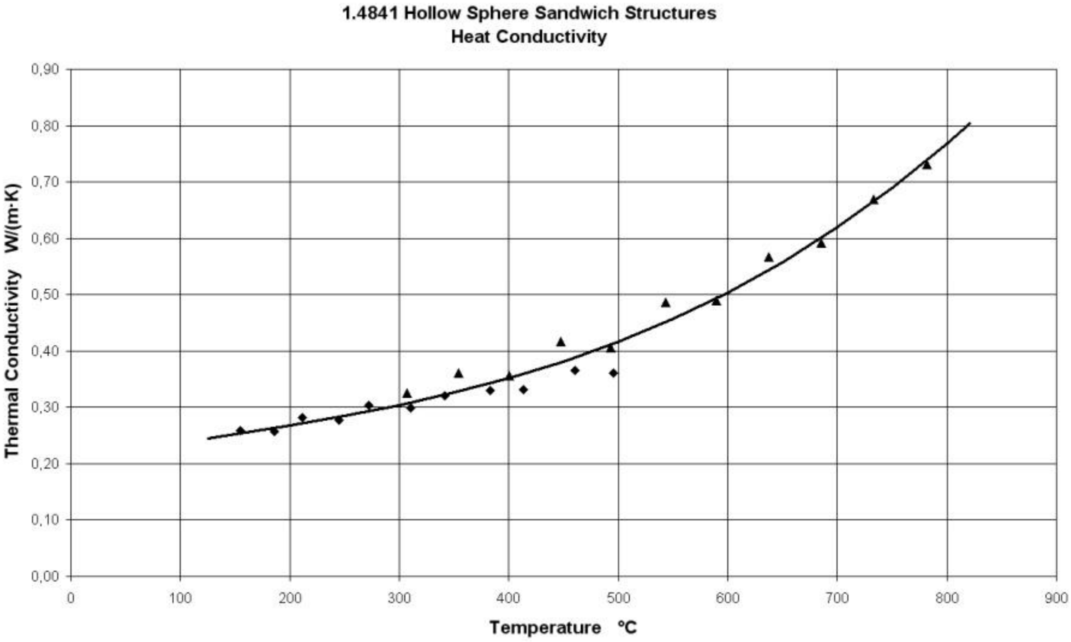

Figure 6: Heat conductivity of 1.4841 heat resistant steel from 100 to 800°C

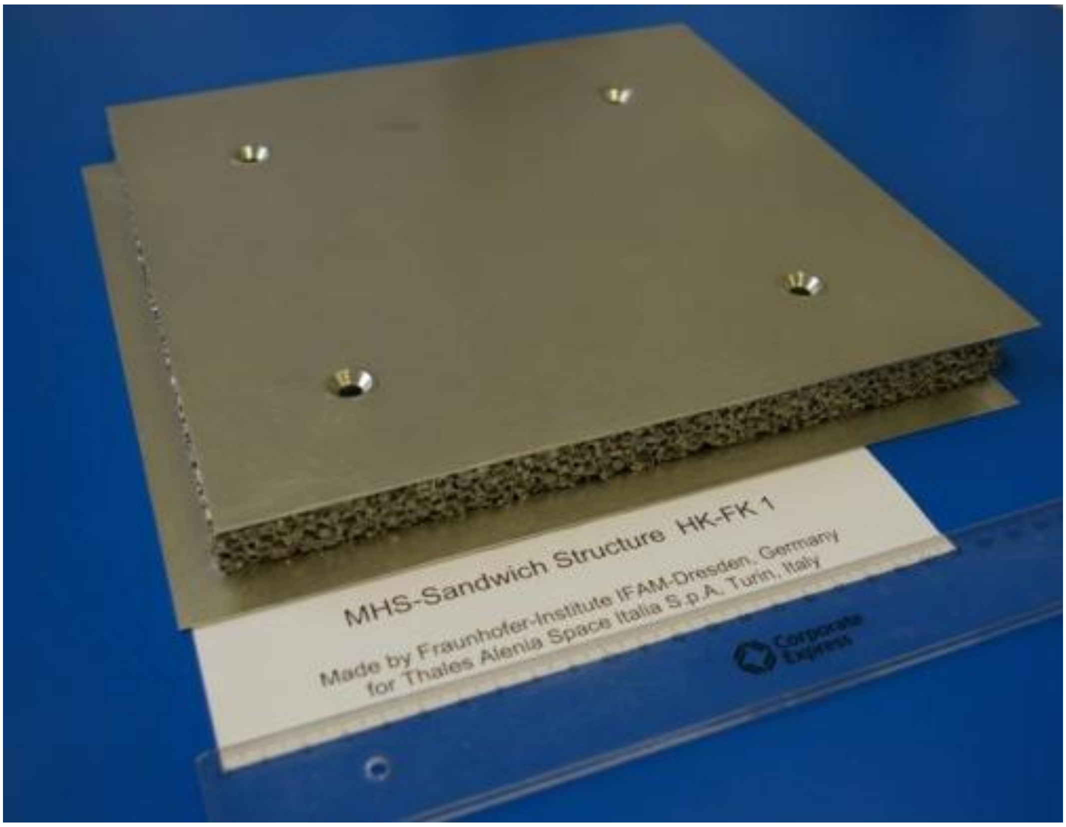

Figure 7: 1.4841 steel hollow sphere sandwich structure (demonstrator for space applications)

Sound absorption

The unique morphology of the structures, especially their open porosity leads to a very good sound absorption. Due to their mechanical strength and their heat resistance self-supporting absorber systems can be designed. In combination with other cellular metals such as open cell foams or fibre structures the creation of multifunctional elements like muffler and catalyst or muffler and particle filter is possible [4], [13], [15]-[17]. Several functional models and prototypes of silencers for exhaust systems and tooling machines have been manufactured within the last years.

Fig. 8 is showing typical values of sound absorbing coefficients of hollow sphere structures and common mineral wool dependent on frequency. In Fig. 9 a part of a sound absorber unit for a small combustion engine is shown.

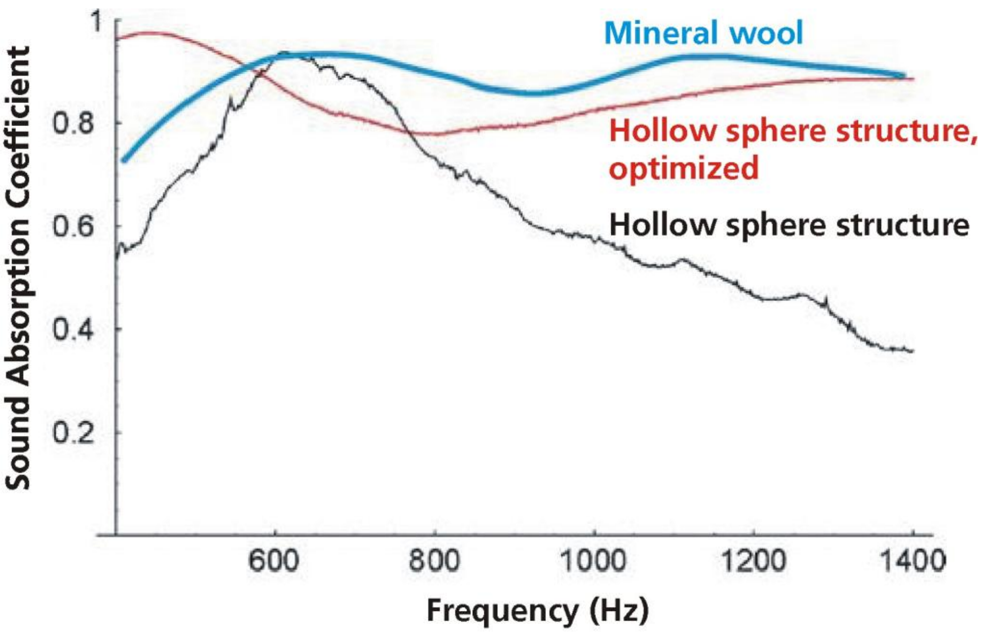

Figure 8: Sound absorption coefficient of hollow sphere structures compares to mineral wool (examples)

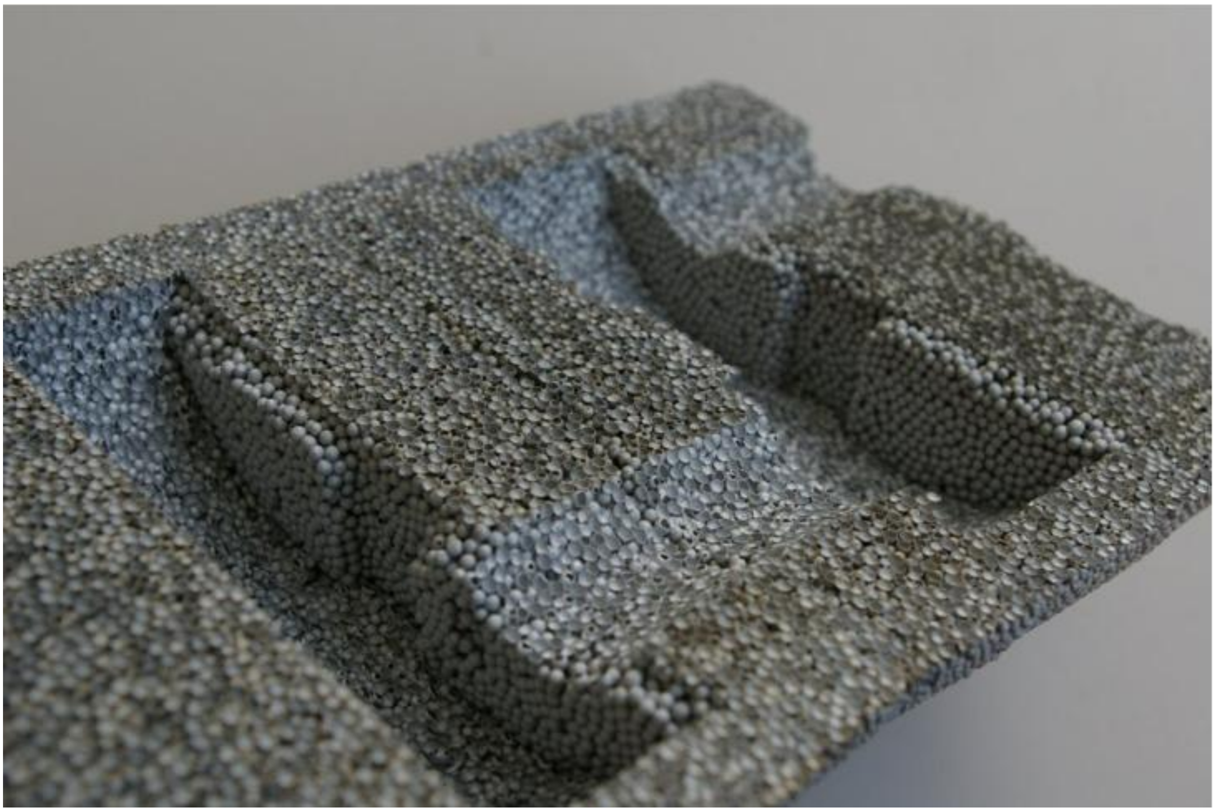

Figure 9: Sound absorber unit for a small combustion engine made of steel hollow spheres

Vibration Damping

Like other cellular structures MHSS are showing good vibration damping properties. The vibration damping can be increased by more then one order if the closed cells are filled by particles (see 2.2.1) [7]-[9]. So particle filled spheres can be used for vibration damping and stiffening of machine parts, in automotive applications and others.

Fig. 10 is showing the damping of unfilled and filled MHSS compared to several well known materials such as metals, polymers and wood. Damping values comparable to wood and polymers can be reached, combined with the high stiffness and heat and oxidation resistance of the metal structure.

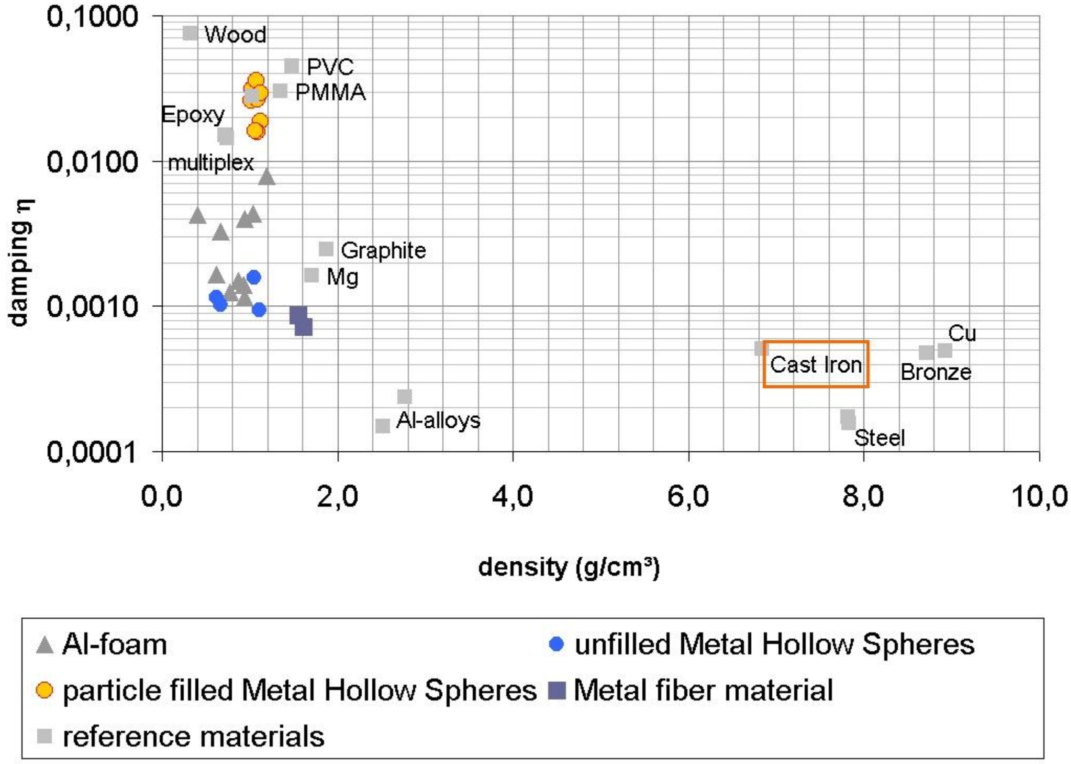

Figure 10: Damping and density of unfilled and particle filled hollow spheres compared to several common materials

Crash Absorption and Stiffening

The typical stress-compression-curves with a distinct plateau make hollow sphere structures to a suitable and interesting material for crash absorber systems. The shape and the middle value of the plateau can be controlled by choosing the suitable material, sphere diameter, shell thickness and shell porosity. Furthermore the compression strength of steel spheres can be controlled by hardening and annealing (Fig. 11) [18]. Fig. 12 is showing a typical stress compression diagram of a 316L stainless steel MHSS and micrographs of the structure in the different states of deformation.

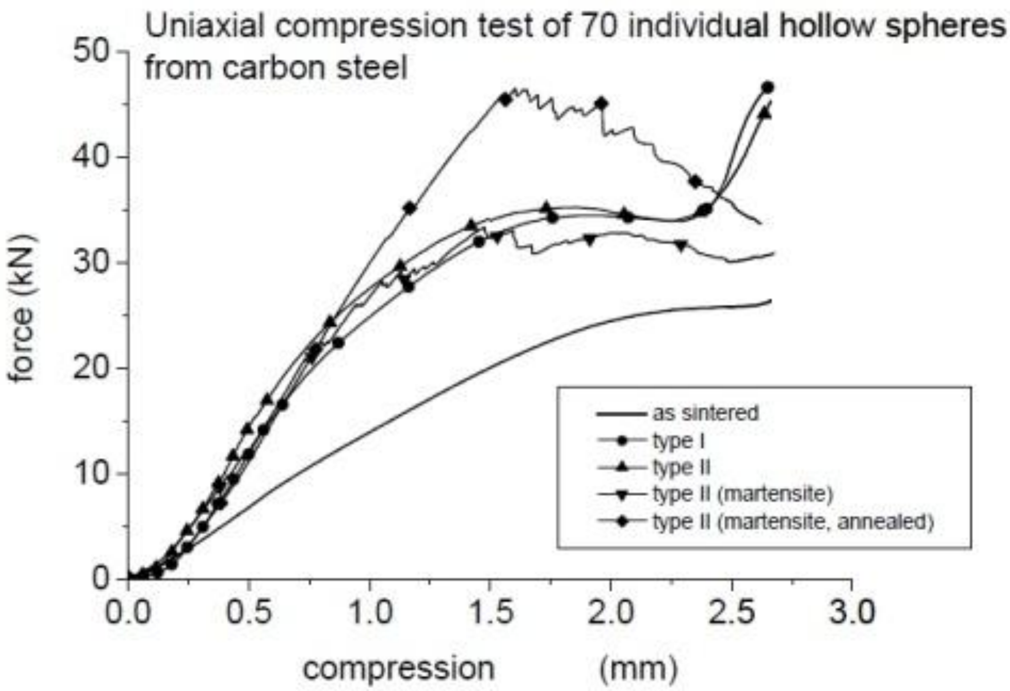

Figure 11: Increase of compression strength of steel spheres after additional heat treatment

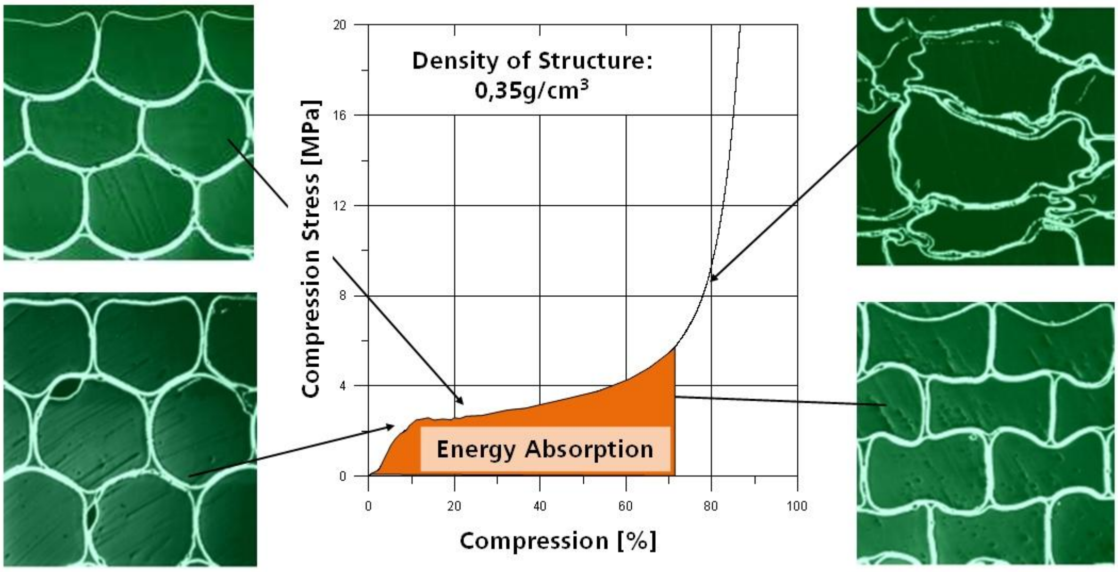

Figure 12: Stress compression diagram of a typical 316L stainless steel hollow sphere structure

Despite the good energy absorption hollow spheres can be used for stiffening of construction elements and for construction of lightweight profiles and sandwich elements with high mass-specific bending stiffness. An example for a steel sandwich using hollow sphere structures is shown in Fig. 8 above.

Storage of Thermal Energy

As described in 2.2.2 hollow spheres can be filled with phase change materials (PCMs) to increase their heat capacity and make them suitable for using as temperature buffer, thermal storage, heat exchanger systems or for increase of thermal capacity of heat transfer fluids. The buffer temperature of the system depends on the PCM used. So, spheres for an operating range from below 0°C up to more than 100°C can be designed. The heat capacity of the spheres is depending on the heat capacity of the used PCM. The increase of the heat capacity of heat transfer oil by PCM filled hollow spheres dependent on their volume fraction is shown in Fig. 13. Fig. 14 is showing a schematic sketch of a heat exchanger using classical PCM units, PCM units with thermal conductive structures and PCM filled hollow spheres. The good permeability of the hollow spheres and their large surface leads to an intensive and fast heat exchange compared to other solutions.

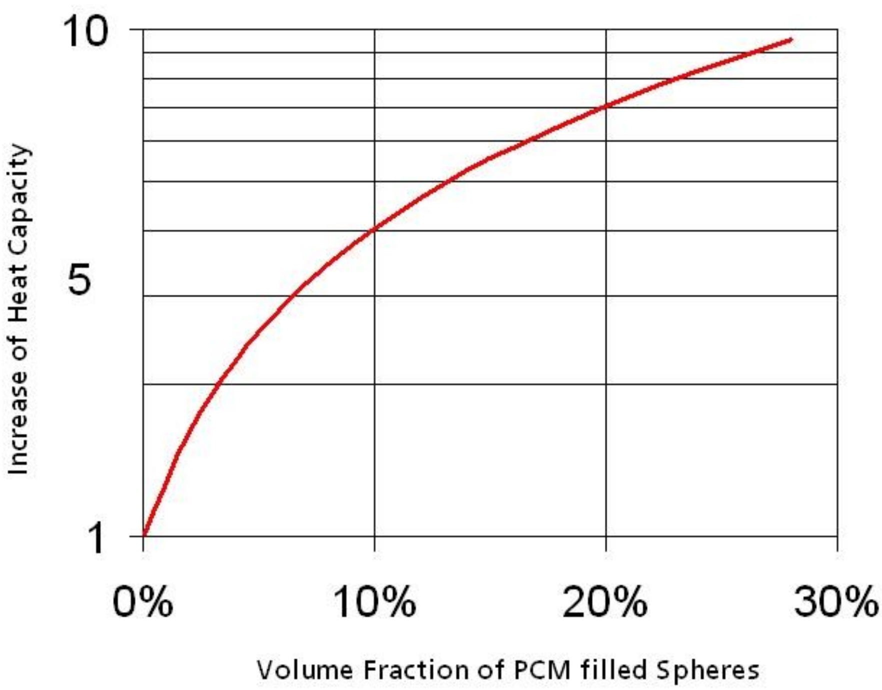

Figure 13: Increase of heat capacity of a heat transfer oil by PCM filled hollow spheres

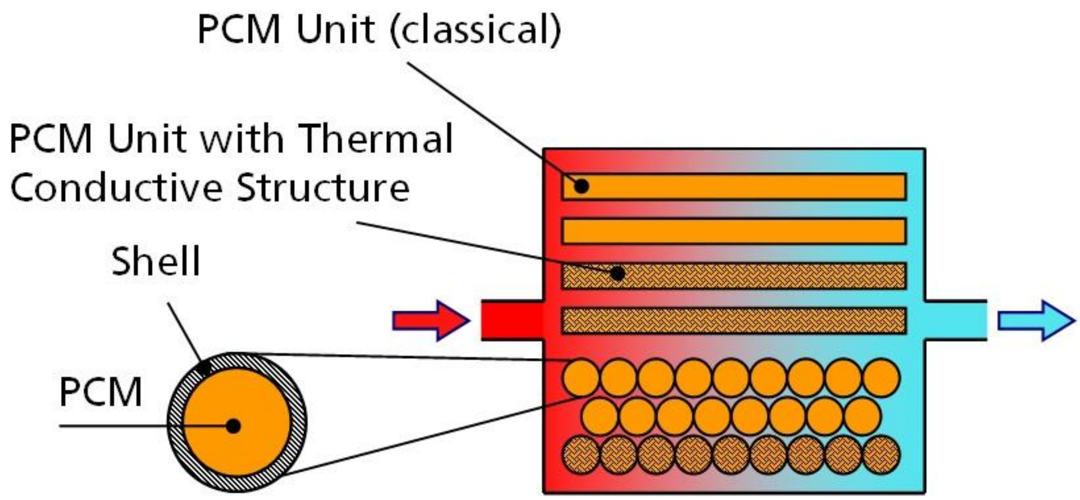

Figure 14: Heat exchanger (schematic sketch: classical PCM unit, thermal conductive structure and hollow spheres)

Conclusion and Outlook

In the early years, the main focus was on the development of the basic manufacturing technology of hollow sphere structures and on the evaluation of their basic properties. Topics of the current research are to extend the range of properties of structures by modification of themselves and opening up of new applications using modified structure types and creating multifunctional structures. So particle filled hollow spheres for vibration damping applications, PCM filled spheres for heat exchange and heat storage and ground spheres for bearing applications were developed. Both IFAM and hollomet GmbH have the necessary equipment for a manufacture of hollow spheres now. While IFAM is focussed to a lab scale manufacture for research purposes hollomet can provide small series. Hollomet GmbH is planning up-scaling of production scale and the entry into the industrial marked within the next years whereas Fraunhofer IFAM will act as partner for research and development in the future.

References

[1] Waag, U. et. al.: Metal Powder Report 55 (2000) 1, 29-33
[2] Petrov, Mihail: Untersuchungen zur Hohlkugel- und Schalenherstellung direkt aus der metallischen Schmelze zu ihrer Anwendung in Leichtbaukomponenten, Dissertation, TU Bergakademie Freiberg, 2012 (in print)
[3] Andersen O et al.: Advanced Engineering Materials
2 (2000) 4, 192-195
[4] Göhler, H. et al: EURO PM 2003. Conference Proceedings. Vol. 2. Valencia, Spain, Oct 20-22, 2003. Shrewsbury: EPMA, 2003
[5] Quadbeck P, Reger N in: Kolaska H (Hrsg): Pulvermetallurgie in Wissenschaft und Praxis Band 24, Hagen 2008, 161-180
[6] Augustin C, Hungerbach W: Materials Letters 63 (2009) 1109-1112
[7] Jehring U. et al: Cellmet Dresden 2008: Cellular Metals for Structural and Functional Applications, 179-184
[8] Jehring,U.; Kieback,B.; Stephani,G.; Quadbeck,P.; Courtois,J.; Hahn,K.; Walther,A.; Blase,B.: Proceedings, Metfoam 2009, Bratislva
[9] Andersen, O. et al: Metall (2011) Nr. 1/2 24-28
[10] Meinert, J. et al: Proceedings of the 1st International Conference on Materials for Energy, July 4-8 2010, Karlsruhe, pp. B779-B781
[11] Meinert, J.; Stephani, G.: Zellulare metallische Werkstoffe für innovative Latentwärme-Speichertechnologien in: Aktuelle Beiträge zur Technischen Thermodynamik, Energietechnik und Fernwärmeversorgung, Sonderheft der AGFW, Frankfurt, Germany, 2011, pp. 13 – 20
[12] Metal Powder Report No. 10 November/December 2009 p. 10
[13] Waag U et al: in: Leichtbau mit metallischen Wekstoffen, VDI-Seminar 342805,
30.-31.03.2004, Bremen
[14] E. Solórzano, M.A. Rodríguez-Perez, J.A. de Saja, Materials Letters
63 (2009) 1128–1130
[15] Gasser, St. et al.: Advanced Engineering Materials 6 (2004) 1-2, pp. 97-102
[16] Hübelt J. et al: InterNoise 2006. 35th International Conference and Exposition on Noise Control Engineering; Honolulu, Dec 3-6, 2006; Proceedings. Honolulu, 2006
[17] Göhler, H. et al: Cellular Metals for strustural and functional applications, CELLMET 2008: Proceedings of the International Symposium on Cellular Metals for Structural and Functional Applications held Oct 8 - 10, 2008 in Dresden, Germany. Dresden: Fraunhofer IFAM, 2009
[18] Jehring U. et al: Metaoam Montreal 2007, 165-168