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Multifunctional Metallic Hollow Sphere Structures

Manufacturing, Properties and Application

Springer

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1 Introduction

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Nature frequently uses cellular and porous materials for creating load-carrying and weight-optimized structures. Thanks to their cellular design, natural materials such as wood, cork, bones, and honeycombs fulfill structural as well as functional demands. For a long time, the development of artificial cellular materials has been aimed at utilizing the outstanding properties of biological materials in technical applications. As an example, the geometry of honeycombs was identically converted into aluminum structures which have been used since the 1960s as cores of lightweight sandwich elements in the aviation and space industries. Nowadays, in particular, foams made of polymeric materials are widely used in all fields of technology. For example, Styrofoam® and hard polyurethane foams are widely used as packaging materials. Other typical application areas are the fields of heat and sound absorption. During the last few years, techniques for foaming metals and metal alloys and for manufacturing novel metallic cellular structures have been developed. Owing to their specific properties, these cellular materials have considerable potential for applications in the future. The combination of specific mechanical and physical properties distinguishes them from traditional dense metals, and applications with multifunctional requirements are of special interest in the context of such cellular metals. Their high stiffness, in conjunction with a very low specific weight, and their high gas permeability combined with a high thermal conductivity can be mentioned as examples. Cellular materials comprise a wide range of different arrangements and forms of cell structures. Metallic foams are being investigated intensively, and they can be produced with an open- or closed-cell structure, cf. Fig. 1.1. Their main characteristic is their very low density. The most common foams are made of aluminum alloys. Essential limiting factors for the utilization are unevenly distributed material parameters and relatively high production costs.

Several textbooks cover the topic of cellular materials in general and give an introduction to the whole range of physical properties and possible applications. The books by L.J. Gibson and M.F. Ashby (Cellular Solids: Structures & Properties) [3], M.F. Ashby et al. (Metal Foams: A Design Guide) [1], and H.-P. Degischer and B. Kriszt (Handbook of Cellular Metals: Production, Processing, Applications) [2] are recognized

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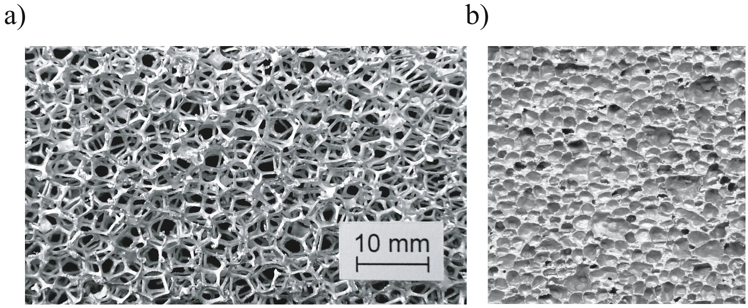

Fig. 1.1. Aluminium foams: a) Open-cell Duocel®; b) closed-cell Alporas®

as standard works on this topic and give the most comprehensive general overview of cellular and porous materials. Cellular materials made of ceramics are treated in the book by M. Scheffler and P. Colombo (Cellular Ceramics. Structure, Manufacturing, Properties and Applications) [5] and the thermal properties of cellular and porous materials are treated in detail in the recent monograph by A. Öchsner, G.E. Murch and M.J.S. de Lemos (Cellular and Porous Materials: Thermal Properties Simulation and Prediction) [4].

Metallic hollow sphere structures (MHSS) are a new group of cellular metals characterized by easily reproducible geometry and therefore consistent physical properties. A new powder metallurgy based manufacturing process enables the production of metallic hollow spheres of defined geometry. This technology brings a significant reduction in costs in comparison to earlier applied galvanic methods and all materials suitable for sintering can be applied. EPS (expanded polystyrol) spheres are coated with a metal powder-binder suspension by fluid bed coating. The green spheres produced can either be sintered separately to manufacture single hollow spheres (cf. Fig. 1.2 a)) or be pre-compacted and sintered in bulk (cf. Fig. 1.2 b)) thus creating sintering necks between adjacent spheres. Various further joining technologies such as soldering and adhering can be used to assemble the single hollow spheres to interdependent structures. For example, adhering is an economic way of joining and therefore can be attractive for a wide

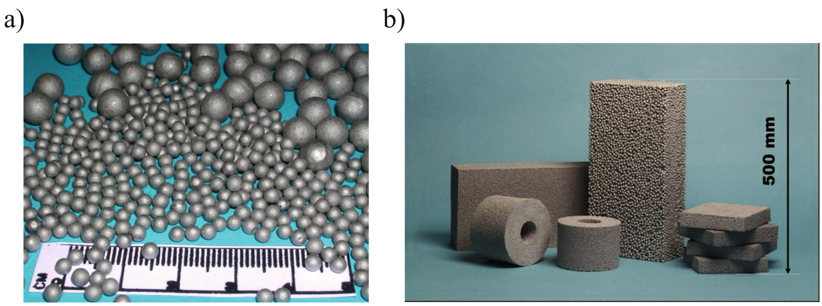

Fig. 1.2. a) Single hollow spheres of different diameter; b) different hollow sphere structures

range of potential applications. Another important advantage is the possible utilization of the physical behaviour and morphology of the joining technique as a further design parameter for the optimization of the structure's macroscopic properties for specific applications.

The idea of this book on *Metallic Hollow Sphere Structures* is to introduce this new composite material and to cover different important physical characteristics, i.e. the mechanical, thermal, acoustic and further properties, in detail from different points of view and for different types of hollow sphere structures and composites. Latest experimental results, numerical prediction methods and analytical modelling are covered by the contributions.

The editors wish to thank all the chapter authors for their participation and cooperation which made this text possible. Special thanks to Ms. Alison Russel for the English corrections of several chapters.

Finally, we would like to thank the team at Springer, especially Ms. Carmen Wolf and Dr. Christoph Baumann, for their excellent cooperation during the whole phase of the project.

References

1. Ashby, M.F., Evans, A., Fleck, N.A., Gibson, L.J., Hutchinson, J.W., Wadley, H.N.G.: Metal Foams: A Design Guide. Butterworth-Heinemann, Boston (2000)
2. Degischer, H.-J., Kriszt, B.: Handbook of Cellular Metals: Production, Processing, Applications. Wiley-VCH, Weinheim (2002)
3. Gibson, L.J., Ashby, M.F.: Cellular Solids: Structures & Properties. Cambridge University Press, Cambridge (1997)
4. Öchsner, A., Murch, G.E., de Lemos, J.S.: Cellular and Porous Materials: Thermal Properties Simulation and Prediction. Wiley-VCH, Weinheim (2008)
5. Scheffler, M., Colombo, P.: Cellular Ceramics. Structure, Manufacturing, Properties and Applications. Wiley-VCH, Weinheim (2005)

2
History and Production of Hollow Spheres

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Abstract. This chapter will deal with historic aspects and offer an insight into the origins of Hollow Sphere manufacturing processes up until the present day, highlighting various interesting Hollow Sphere technologies and ideas from old patents. The second part of the chapter will concentrate on production and process application of the present day Hollow Spheres.

Keywords: History of Hollow Spheres; Production of Hollow Spheres.

2.1 History

2.1.1 The Term "Hollow Sphere"

The term σφαίρα, Hollow Sphere, literally translated to "round shells" dates back to ancient Greece, used in philosophy, mathematics, geography and astronomy. In Plato's astronomic philosophy Timaeus, the shells are depicted with stars hanging from them and rotating around the world. Aristotle in his metaphysics, as well as Plutarch refer to the ancient greek terminology. The Roman scholars adapted the mathematical, astronomical term into Latin, but literally translating it to generally meaning *globe* or in scientific terms *sphere*.

The meaning and understanding was being ever expanded by younger scholars and authors, with the Latin term "sphaerae" mainly used in the new-high-german with regards to philosophy, mathematics and astronomy. Metaphorical connotations of either the Latin "sphaerae" or the German version "Sphäre" cropping up in literary works of Goethe, Lessing, Wienand and Schiller. During this time the German term "Hohlkugel" was introduced, replacing the Greek σφαίρα i.e. the Latin sphaerrae with "Hohlkugel" and becoming a technical term in many areas. The term "Hohlkugel" – for example - is described as a "hollow" filled cannonball in Grimms' dictionary [1].

2.1.2 Patents as a Fundus of Science History

The term "Hollow Sphere" has a long history, having established itself in recent years into a cellular material type with regard to engineering science. In the following we

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will present this approximate 100 year old technology-concept with various specific examples we take out of patents, highlighting the term “Hollow Sphere” has a quite accurate and precisely meaning. Of all the patents from a database searched by the terminus “Hollow Sphere” only a small amount are found that do not represent the “Hollow Sphere” concept in terms of geometrical properties. Of the approximate 150 relevant patents obtained from the Deutsche Patent- and Markenamtes (DPMA) [2] we have handpicked and researched a number of interest.

The patents have varying levels of standard, with some patents coming from hobby thinkerers, who patent their idea without any basic market requirement. Other patents however are quite obviously developed for concrete commercial reasons. Further patents can be found at the rear of this book. Christian Augustin will offer a more precise detailed history of the Hollow Spheres development in his dissertation 2009 [3].

Fundamentally there are three basic technologies regarding the production of Hollow Spheres since 1906:

- Cupping with moulds, mostly for the production of Hollow Spheres with large diameters.
- Spray-drying or a similar technology, for the production of smaller Hollow Spheres.
- Other innovative technologies such as chipping and build-up of separate parts.

We will now underscore these basic technologies by displaying some samples of patents describing the production of Hollow Spheres.

2.1.3 Cupping with Moulds

The first comprehensive Hollow Sphere Patent US 861 403: “Method or Process of making Hollow Metal Balls” [4] was filed on 17.08.1906 by the American Otto Spahr, who later on in the Patent (issued 30.07.1907) claimed to be able “… to make a pressed metal ball the internal and external surfaces which are absolutely concentric at all parts.”, using the well known “cupping” or also known in German as “Zugdruckumformen” moulding technique. According to Spahr’s patent a stamp and punch formed out of a round metal disk or a “mass of metal” the Hollow Spheres within several production stages. In the first step a hemisphere with an elongated edge is punched from metal sheet: “through the agency of punches and dies so constructed and operated that a disk or mass of metal to be operated upon is first caused to assume a hemispherical shape and then successive cylindrical shapes.” This “hemispherical cup” is further treated: “I then cause the outer or open edges of the cylindrical part to be gradually thinned so that any longitudinal section thereof is of a wedge-like nature. I then by successive steps cause the thin edge to be turned inward until the mass of metal assumes a spheroidal shape; finally compressing the metal into a spherical shape with a limited projection of such metal extending beyond the outer surface of the sphere, which projection of metal is ultimately forced inward by pressure until the completed ball assumes the desired symmetry.” Then the Hollow Sphere cup is closed, “…of the ball is now inserted and forced downwards until the upper end is flush with the upper end of the die 6 (cf. Fig. 2.1), thereby causing the material to be firmly set or united together so that the ball is completed and assumes the conformation shown in cross section in Fig 11 (cf. Fig. 2.1), which will be noted is absolutely symmetrical throughout." During the final production stage the "hemispherical cup" is compressed into a Hollow Sphere, with any metal leftovers being bent and moulded inwards until "the mass assumes the confirmation of a perfect sphere".

The following patent specification diagrams present Spahr's method in Fig. 2.1.

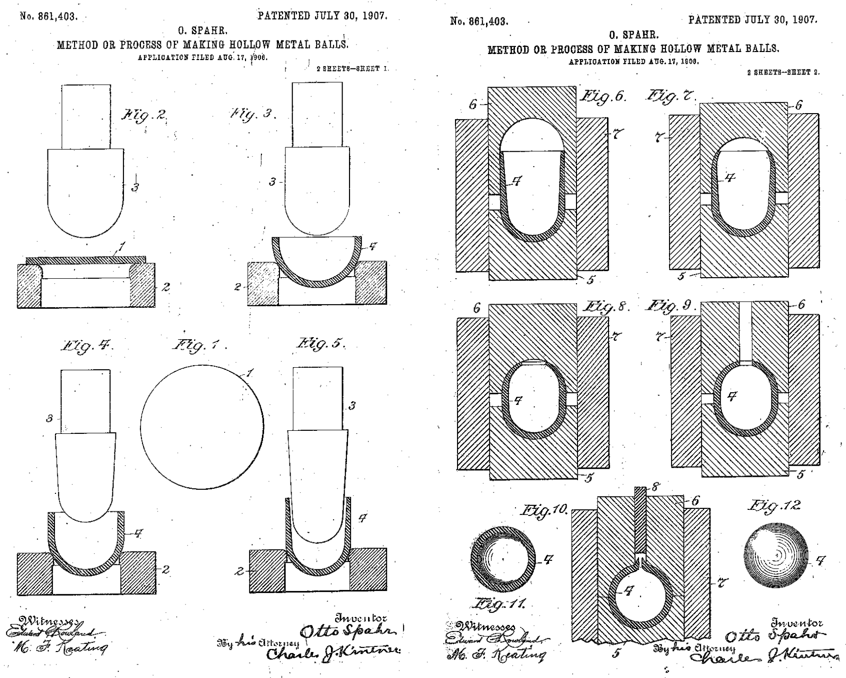

Fig. 2.1. Method or Process of making Hollow Metal Balls [4]

Spahr does not specify how large or dense his Hollow Spheres can be produced to, nor where his technology could be applied to. It was neither possible to ascertain whether his concept was a theory thought up at his desk or whether the process was actually ever put into practice. It is assumed this concept was a pure theoretical one due to the fact that the patent has no mention of size, mass or density, nor any prototypes described.

Spahr's fundamental technology was taken by many other inventors, such as John W. Schatz. In his United States Patent No. 955 698, 25.05.1910 [5] he focuses on a clean connection of the middle part, the closing part, of spheres which are produced according to the engineering process mentioned above. He introduces a "metallic plug" to be inserted into the hemispherical cup to form a Hollow Sphere. Others, in the meantime concentrated on improving the production process, e.g. the "Seamless Hollow Ball Company" (with its Patent US 1278914, priority from 12.04.1917 [6]), founded in Baltimore between 1917 and 1921. Unfortunately there is no mention of any commercial use in the patents, only generally mentioning ball valves and furniture applications.

The "Seamless Hollow Ball Company" however developed the technology and transferred it to Europe within years, demonstrated in their European patents: Austrian Patent No. 103454 of 16.09.1924 "Verfahren und Vorrichtung zur Herstellung von Hohlkugeln aus Metall" [7] and the Swiss Patent No. 112433 of 16.09.1924, 18.30 p.m. "Verfahren und Einrichtung zur Herstellung von metallenen Hohlkugeln" [8]. These patents describe the mechanism which enables to punch out of a pipe a Hollow Sphere in one single process step. The following diagram explains the technology. Figure 1a (all numbers are original numbers in below printed Fig. 2.2) presents a longitudinal section with tapered pipe; Figure 2 is a similar cut, but the picture shows a pipe already formed into a sphere, with both openings (12). Figure 3 is a dissection through a completely closed sphere. Figures 3a and 3b are vertical dissections showing the two phases of the punching process i.e. the before (3a) and after (3b) of the press. Figure 4 is a side-profile of the press, which carries out this technology. Figure 5 is a part diagram of press plate. Figure 6 shows a magnified dissection of two working grooves. Figure 7 is somewhat similar showing the final form of the groove.

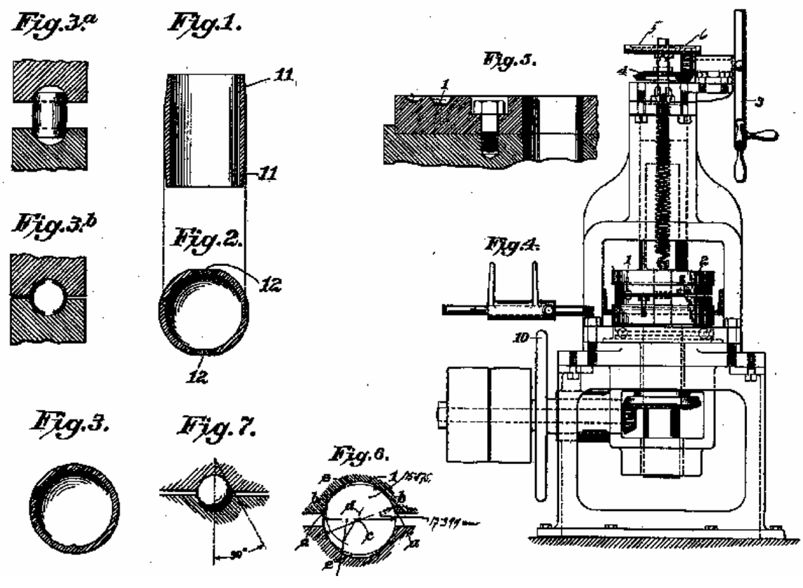

Fig. 2.2. Process and apparatus for the manufacturing of metallic Hollow Spheres [7.8]

Hollow Spheres are still nowadays being produced in this similar technology, with the company Isometall [9] being a perfect example.

2.1.4 Spray Drying

A further technology in the production of Hollow Spheres is spray-drying; the majority of patents only suiting a very few Hollow Sphere fabrication, which are mostly characterized by a large size spectrum of manufactured Hollow Spheres. Due to the hard to control quality of this specific Hollow Sphere technology some patents use the term “spheroid particles” rather than “Hollow Spheres”. Spray drying in conjunction with Hollow Spheres became relevant towards the middle of the last century, where such technology was mostly used to produce ceramic Hollow Spheres. The technology is however not only limited to that of ceramics, as mentioned in some patents, but also works with metals (for example DE 100 39 320 of 07.08.2000, “Verfahren zur Herstellung von Hohlkugeln” [10]). One of the oldest patents is US 2 543 987 of Stark Ceramics “Method of Producing Porous, Lightweight, Burned Argillaceous Material” (registered 23.08.1947) [11] in which “thin free falling stream vertically through a furnace at a temperature sufficient to immediately produce expanded, porous, light weight lumps of burned argillaceous material” are described. Principally dealing with the classic spray-drying technology through which Hollow Spheres are produced by drying. The first part of the patent describes the spray-tower design. The machinery described produces Hollow Spheres as a specific material filler and aggregate for the construction industry: “for the use as and aggregate for concrete, or as a grog for the making of bricks or other burned clay bodies or forms or as filler for rubber of plastic materials, from a raw material such as clay or shale.” The following diagram (cf. Fig. 2.3) from the patent shows a continuous spray process, where “S” is the ceramic binder suspension and 12 the reservoir. The ceramic binder suspension enters the spray-tower 10, where dry hot air is loaded (through the nozzle 11) through gravity and the opening 15. This is how S becomes S’ and finally turns into the Hollow Sphere S’’, exiting the spray tower on a conveyor belt.

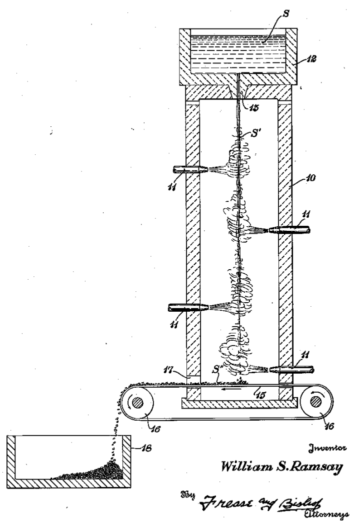

Fig. 2.3. Spray drying Apparatus for a “Method of Producing Porous, Lightweight, Burned Argillaceous Material” [11]

A similar technology and understanding of Hollow Spheres is also mentioned in the German Reichspatent 604 691, dated 27.04.1932 of the Champion Spark Plug Company, Toledo, Ohio, USA [12]. In this patent a technology for the production of small spheres made particularly from ceramic is mentioned; using the underlying technology of spray drying of ceramic materials to produce granulate or Hollow Sphere parts, which are finally put into a "Formteilautomat" (moulding part tool) and moulded into "Förmling" (composite shapes). Fundamentally the patent conveys the fabrication of ceramic parts, but at the same time highlights that "any fluids, solutions, emulsions or suspensions that have the ability to dry can be manufactured into spheres using this technology, with the possibility of either adding a hardener or further heat treatment to a material, which hardens through either heat or compaction." Foundations of this technology are "that with a constant spray and drying process a suspension or solution can be transformed into small spheres, either poured into forms or moulded through bonding pressure and compacted, creating a self-carrying "Förmling".

The patent technology of mechanically producing various different sized "Composite shapes", "Förmlinge", is due to the patent the safest possible routine with a minimal failure rate compared to previous mechanical moulding tools that failed to work, and forced the process to be manually carried out on an old fashioned hand-press, with disadvantages of the pour and mould technologies proving to be more problematic the larger the moulding was intended on. "A perfectly constructed drying process and spray injection can form considerable sized spheres. The sphere size, be it large of small can be manipulated, enabling an array of different sizes." The

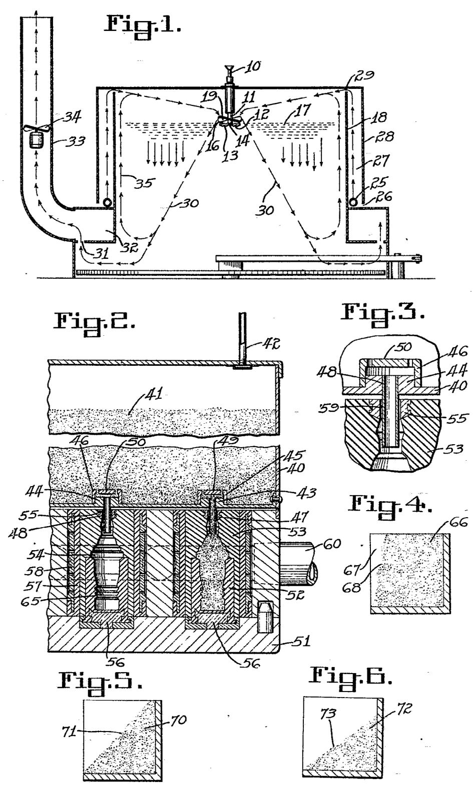

Fig. 2.4. Manufacturing of Hollow Spheres and Production of Sparkplugs out of them [12]

spheres are squashed in the machine, leading to the compacted "moulding" being considerably denser than that of a milled powder product. Advantage of this patent is the ability to manipulate the end products' material characteristics: "Moulding pressure practically does not require much force, which otherwise damages the spheres. Slight pressure will keep the particles intact and leave some equally distributed hollow areas, enabling a passing of gasses both in and out, especially during the first burning phase, which improves the control of the burning process".

Technological advantages of this patent are mentioned, e.g. in the wide variety: "The patent highlighting further technological examples, such as coal or graphite resistances mixed with powdered coal and a binding agent", made possible through the exact controllability of matter density, adjustation and uniform distribution of electric resistance. Proper core-size control and moulding pressure of differing resistances enables moulded parts to be produced in uniform, with the same size and shape. Despite the only technology mentioned being that of spark plug production, the patent does highlight the diverse applications and processes the technology has to offer.

Principally the patent has more to do with the explanation of how the patent wise described machine produces Hollow Spheres rather than the Hollow Sphere itself, which can be clearly seen in the diagram. In this diagram (cf. Fig. 2.4), Figure 1 illustrates the spray-drier production of the Hollow Sphere. Figure 2 illustrates the "moulding part tool" and the production of sparkplugs from Hollow Spheres.

2.1.5 Further Technologies

There are further technologies other than cupping and spray-drying of Hollow Sphere Production. On 30.07.1948 at 06:45 pm a patent (Priority in Austria 31.01.1948) was written up at the Eigenössischen Amt für geistiges Eigentum by Baumat AG, Zürich [13]. This patent (No 266315) dealt with "The production of ceramic Hollow Spheres for use in the construction industry", where for example a ceramic Hollow Sphere is described, as being produced from clay. These Hollow Spheres can be characterized displaying good pressure resistance, low weight, and proving to be of benefit in the construction industry and the production of light-weight cement.

The Hollow Spheres are produced in such a way that the clay, or any other ceramic is moulded into a tube, compressed and separated in a clamp, and forms consistent seamless Hollow Spheres. The following diagram 2.5 shows a clamp.

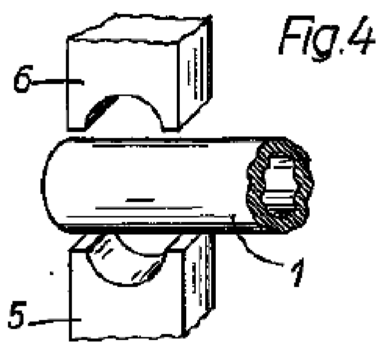

Fig. 2.5. Clamp to produce Hollow Spheres for the construction industry [13]

The patent also mentions that the Hollow Spheres may also be produced using chains or belts, rotated over grinders. The chains or belts have a ring rather than hemispherical notches. Fundamentally this alternative concept is the same, but enables a continuous production on a larger scale. Therefore the author mentions the additional ability to punch tubes parallel or even use wave-like plates, with the dip of the wave glued to the plate. Hollow Spheres manufactured in this procedure were qualitatively not particularly convincing regarding roundness and shell thickness- and consistency, but may suffice for certain applications.

Following compression, during the drying and partially burning process, the patent describes how the Hollow Spheres are subjected to a surface treatment, i.e. rounding the Hollow Spheres. This rounding process is however not described in the patent in detail, but rather highlights the ability to blend burnable aggregates such as coal, charcoal etc. into the Hollow Sphere which combust during the burning process and generates a porous shell. A further factor in the patent is the introduction of material, which in combination with water turns to gas, thus an additional porous surrounding concrete. Principally, the technology deals with a clamp-like concept, which enables a constant mass production of Hollow Spheres, either from just one clay tube or several at a time, or from the wave-like sheets previously mentioned.

Further genius techniques of how to produce the Hollow Sphere can be found in further patents, such as the Deutsche Reichspatent No. 694 903 prepared by Toyo Tokushu Immono Kabushiki Kaisha, dated 17.05.1938 and titled: "Process and

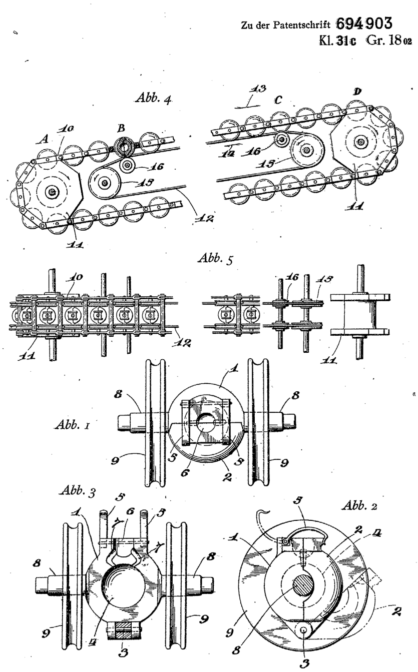

Fig. 2.6. Process and mechanisms to the production of metal Hollow Spheres [14]

mechanisms to the production of metal Hollow Spheres" [14]. The invention concerns a procedure and a manufacturing device for metallic Hollow Spheres in cooled centrifugal casting forms, which swivel around their axle. Liquid metal is poured into a spherical shape. Due to the special reservoir the melted metal stocks in the upper part of the form and closes it (cf. Fig. 2.6, Abb. 3, 7). Centrifugal energy is produced by rotation of the form, with the liquid metal forming the outer wall of the form. While the spherical shape turns around all axles, the liquid metal cools and solidifies into the form of a Hollow Sphere. Ideally (i.e. with even and constant rotation of the forms around their axles) the liquid metal is poured into a spherical shape, and after cooling forms a smooth and immaculate Hollow Sphere. The patent primarily describes a machine for such a continuous procedure, by means in which liquid metal can be brought into a rotating Sphere, and finally hardens in to a Hollow Sphere. This machinery (cf. Fig. 2.6) consists of a belt and arranged ball-like shapes. During the process the belt turns the shapes around their axle.

The patent diagram describes the following: "Procedures for manufacturing metallic hollow balls in cooled, over their axle rotating centrifugal casting forms, thereby characterized that in the gate openings of the forms the remaining liquid metal is brought to the cast in metal quantity to solidifying and then only the forms are set in motion." And: "Device for the execution of the procedure… thereby characterized that forms between two parallel, endlessly rotating belts start rotating only after the remaining metal in the gate has been solidified." The patent does state that the manufacture of Hollow Spheres using cooled forms is well known, but claims to improve the existing technology. "Up to now the forms were locked with a screw bolt, thumbscrews etc. The locking of the forms after filling in the liquid metal, by hand for instance, is not only dangerous, but also requires relatively long; while the metal already partly solidifies; posing questions as to a regular spherical shape. Besides, such a process is obviously not suitable for mass production." A mass production is possible applying this technology: "The process is more continuous when following the steps of the invention. Where filling the forms, and their rotation takes place in one uninterrupted step. Even opening, taking the poured balls out and relocking the forms for the admission of a new batch takes place sequentially according to invention, with mass production made possible in the simplest way." Obviously large commercial usability was assigned during patent application, as it was announced parallel in the USA (2184257 "Process for manufacturing chilled hollow ball", registration 12.05.1938, dispatching 19.12.1939), France (838357 "Procédé appareil destinés à la fabrication the billes creuses", registration 23.05.1938, dispatching 03.03.1939) and in Canada ("Chilled Hollow ball Manufacture/Fabrication de Billes Creuses Trempees", published 26.08.1941). Content wise the patents are equivalent; the inventor being identified as Shinsaku Nakagawa in the US American patent.

A further linear path is described by the US Patent No. 2,553,759 of 20.02.1946, issued to the Carborundum Company, Niagara Falls, NY, claiming a patent on "High temperature insulating refractories and pore-containing bodies or hollow spheroids useful in forming such refactories or for use as porous aggregates" [15]. The claims are formulated as follows: "The process of forming light weight, cellular insulating refractory bodies which comprises producing hollow, substantially spherical sticky globule of combusting material and sintering the finely-divided particles of refractory material in the shell together; forming a shaped body from a plurality of so called hollow pellets with a small amount of vitrifiable ceramic bonding material, and firing the body to mature it." The Hollow Spheres are manufactured in an apparatus, which carries out the spray drying process in an in-vitro process manner, on a conveyor belt system. The following Figure 2.7 at Fig. 1 and Fig. 2 from the patent specification, illustrates the patentwise manufactured Hollow Spheres; Fig. 3 is a sketch of the production process. Fig. 4 and Fig. 5 illustrate possibilities of subsequent Hollow Sphere treatment, with the patent demonstrating the possibility to either calcinate or deep inject the Hollow Spheres.

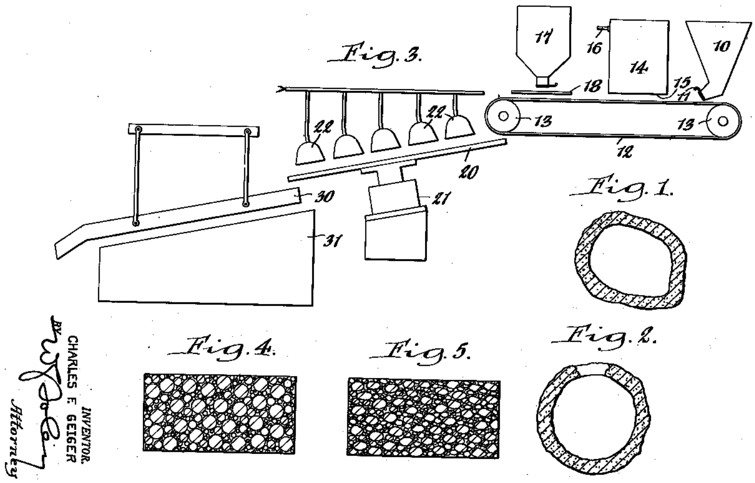

Fig. 2.7. Producing Hollow Spheres attaching powder on a sticky core [15]

In the tool described above the powder, which later on in the process forms the Hollow Spheres is released on to a conveyor belt (number 12 in Fig. 2.7). This belt is in motion and passes a container, from which small droplets are released (number 14 in Fig. 2.7). These droplets hit the powder on the conveyor belt. The viscous drops keep their shape after being released on to the powder, and are further moistened and powdered in transit and under the powder dispenser (illustrated and marked in 17). The conveyor belt finally arrives at a vibrating filter tray (number 30) which compresses the powder-shell and rounds the drops off, where the spheres are subsequently sorted using a sieve. This procedure causes a pulvrige skin to develop around the viscous material drop core, enabling a defined size and shell thickness in the development of the Spheres: "The size of the combustible adhesive cores is so chosen that the coated globules formed by building up a layer around the core, ranging in thickness from about 5 to 30 thousands of an inch, of finely-divided refractory material may be in the size range desired." These "globules" can either be injected and sintered together (the patent speaks of sintering, but in actual fact means calcinating), or individual Spheres sintered and later on injected or glued together (see in Figure 2.7: Fig. 4 and Fig. 5). The inventor however not putting too much emphasis on a precise distribution of shell thickness, porosity nor size distribution as the patent primarily offered a solution for the construction materials industry, which becomes clear by the descriptive materials: "Satisfactory hollow spheroids may be made in according with the present invention from practically any refractory material. Especially good results may be obtained with mullite, kyanite, aluminia, forsterite, clay or kaolin grog or clay itself". Despite the technology having been invented and patented, it is unclear whether theory was ever put into practice, and Hollow Spheres were actually manufactured on an experimental or industrial level using this procedure. The patent nevertheless exhibits interesting process engineering, innovation and finesse with the combustion of the coated inner core a good example. Other similar patents do of course exist, in these however, the material is mostly burned in order to establish porosity, not to lose the core.

2.1.6 Specific Hollow Sphere Production Routines

Another manufacturing process for Hollow Spheres is in the patent specification GB 1083993 (with the German priority DE 1202910 of 07.05.1963) [16]. The Patent entitled "Device for a Production of a Hollow Sphere" describes the production of a Hollow Sphere to bring in radioactive substances and a moderator and/or fertile material. Thereby the patent explains how a solid body can be turned into a Hollow Sphere. The patent refers to the machine, which carries out this process by turning a Hollow Sphere out of a fully solid ball. This procedure is mainly suitable for larger Hollow Spheres and it is however very time and cost intensive. In Figure 2.8, Fig. 1 shows the machine, Fig. 2 the geometrical basic assumptions, which describe the movements of the milling head in the Hollow Sphere.

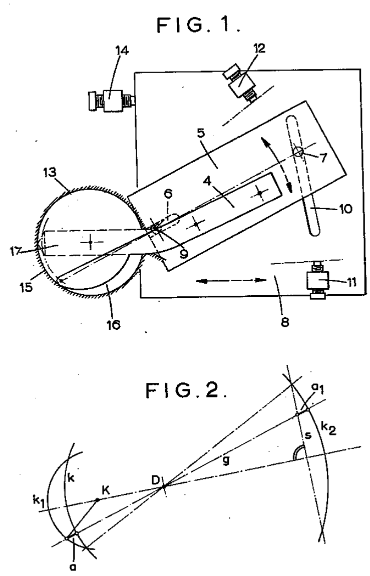

Fig. 2.8. Hollow Sphere being milled out of a solid ball [16]

Not milling but gluing two halves is the core idea of another patent. The main aim of producing seamless Hollow Spheres using pre-fabricated plastic hemispheres was layed out in DE 1 168,058 of 08.07.1960 [17]. The Patent is entitled "Welding body device for connecting two Hollow body halves, e.g. to Christmas tree spheres or such". In the patented tool two plastic hemispherical shells are inserted, which in turn are welded together through pressure and heat. Pressure and heat is generated by turning the sphere halves against one another: "This procedure is thus the basic concept of welding two hemispherical shells together by means of pressure and heat. The thermoplastic raw material softens with the heat, and automatically welds the two halves together". The following diagram (cf. Fig. 2.9) is taken from the patent and illustrates the relatively complex welding-machine.

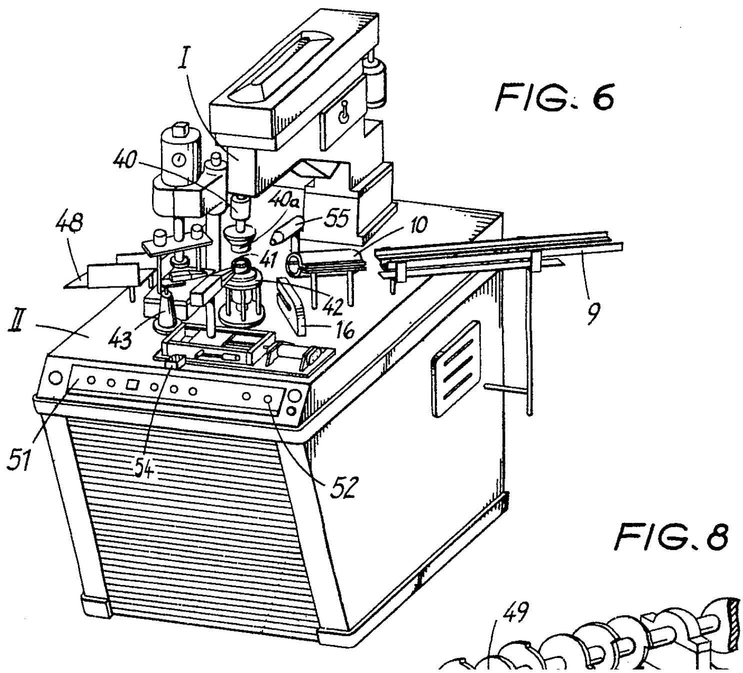

Fig. 2.9. Welding body device for connecting two Hollow body halves, e.g. to Christmas tree spheres or such [17]

The Inventor of the patent "Hollow Sphere and Structural of Element for Constructing same" USA patent No. 3,691,704, submitted to 19.05.1970 [18] also wants to construct Hollow Spheres out of individual parts. This patent has the challenge of producing Hollow Spheres out of separate preformed parts. The following illustration (cf. Fig. 2.10) shows the procedure and the partial elements.

Put into practice the invention is that of "a toy, a container, a gas-filled balloon, or building, for example". The Hollow Sphere consists of a number of relatively small

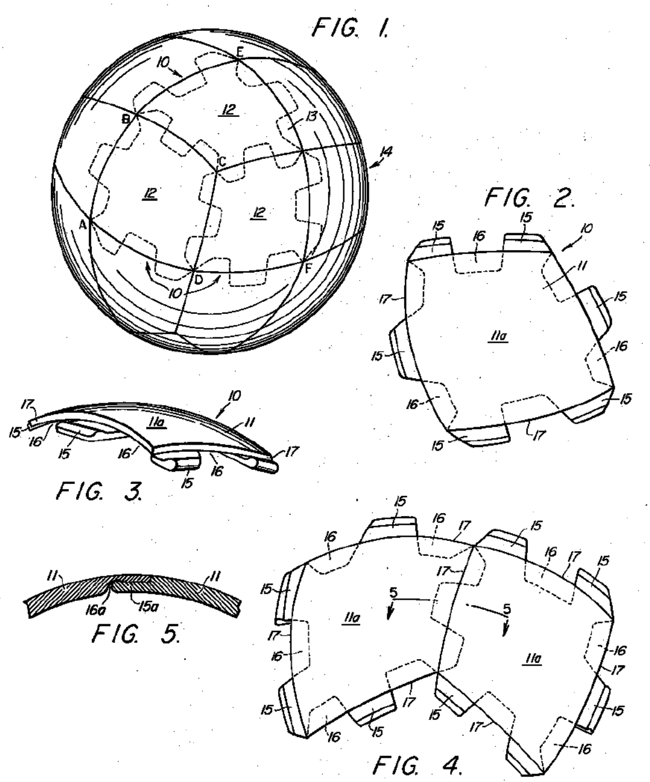

Fig. 2.10. A toy, a container, a gas-filled balloon, or building, for example [18]

sections of almost identical design. These parts can be made of different materials, for instance "inject molding of a plastic material or by molding a foamed plastic material such as "Styrofoam".

A further and somewhat other example is patent No. 231,541 of the Patent Office of the German Democratic Republic (DDR) of 13.12.1984, where a Hollow Sphere for a deodorant stick is described ("Hollow ball for the production of roll-on deodorants") [19]. The purpose of producing this plastic Hollow Sphere with a wall thickness of 1 mm "by means of blowing, rotating, spraying or centrifuge procedure" was primarily to reduce material use. The exact manufacturing technology of this patent however still remains somewhat indefinite. But it is an interesting fact that the patent refers to state-of-the-art technologies to produce such Hollow Spheres for Deodorants.

Patent DE 198 46 784 A1, of 10.10.1998 [20] mentions a porous disintegrating dough Hollow Sphere to attract fish. The Sphere is filled with fish food, thrown into the water and sinks to the bottom of the lake. After a certain period of time the Hollow Sphere begins to dissolve and releases the fish food. According to invention this "controlled, punctual" feeding of the fish enables a more efficient possible catch for hobby and sport anglers. The following picture 2.11 is taken from the patent.

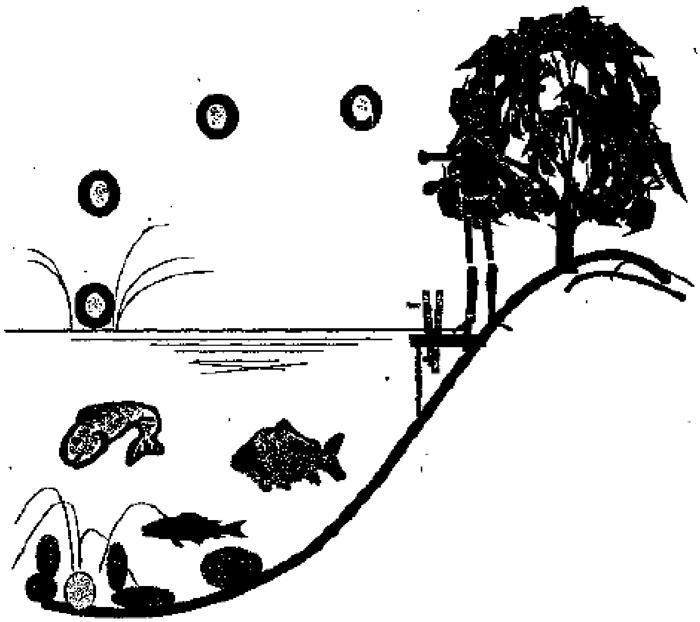

Fig. 2.11. Hollow Spheres attracting fish, too [20]

2.1.7 Conclusion to the Historical Background of the Hollow Sphere Concept

These few patents have highlighted the broad variety of the term Hollow Sphere which connects all these projects not only by name but also by concept, even if the production and application concepts differ. Remarkable however is how the developed procedures are time and time taken up again and continuously improved; partially by means of technology transfers, further development and new and improved concepts of existing inventions. For instance, the concept to produce Hollow Spheres out of a pipe by means of deep-drawing and forming was fundamentally thought of for metals, later on however developed and adapted to produce ceramic Hollow Spheres. All in all it can be said that Hollow Sphere manufacturing techniques mainly orientate themselves around the function they have to carry out. It is also remarkable that only a few patents face the challenging task of describing a universal applicable principle of different sized metallic and ceramic Hollow Spheres on a production scale. This may be a reason why the concept of hollow spheres as a cellular material has not been establish as a broadly used technology compared to metallic foams as an example.

2.1.8 The Path to "Modern" Hollow Spheres

During the 1980s and 1990s, cellular materials within material sciences became a major theme of research. With the main concern of developing new materials for lightweight construction, and to fulfill specific material requisitions, Hollow Spheres became of special interest with regards to cellular materials in the research and development focus of the scientific community. Hollow Spheres are however a special case regarding cellular materials, where commercial use, and an economical large scale manufacturing process of the Spheres or their Structures is of greatest interest. Because only this enables Hollow Spheres to get out of the lab and into applications.

A universal production method was developed in 1982 by Manfred Jaeckel, where he set up a comparatively easier routine, which enabled the production of highly customised Hollow Spheres at a larger scale. For this development, the rapid technical evolution in the 60's, 70's and 80's within polymers, of metal (alloys) and high performance ceramics was an advantage. Thus, he was able to change the initial Hollow Sphere production process to that of today; and enabling the truly multifunctional and customized Hollow Sphere. A first step for this was patent DE 32 10 770 of 24.03.1982 [21] by Manfred Jaeckel, where he describes "metallic, essentially spherical light-weight particles, as well as their use and production process", which can be characterized as being "inside hollow and have closed or porous walls possess." The described process is a wet-chemical production, where a polymer core is wet-chemically metalized. The procedure is accomplished by means of a stirrer. The stirrer "mixes the granulates in the liquid bath, so that the whole surface of the core is exposed to the metallization procedure. This dead metallization can be carried out up to reaching the desired total layer strength of the metal, initially only a thin conducting layer can be applied…" with the metallization finally being continued to the desired layer thickness electrolytically. In such a way coated cores, which consist of a plastic core (e.g. foam material), are decomposed "pyrotolytic at temperatures at for instance 400°C in such a way." The Hollow Spheres are sintered in the subsequent manufacturing. Jaeckel identified several application scopes for his invention, such as:

- "the production of molded articles as fillers of plastic, hardening or sinterable materials ",
- "Production of molded articles cast in a form with liquid metal",
- "metallic light-weight parts (…), as wadding for molded article formations with closed or open-porous cavities, and in particular the creation of light weight molded articles from basic metallic materials are suitable",
- "super-light sintered molded articles…, suitable for applications such as filter technology and sandwich slabs in the aerospace industry".

Jaeckel also sees his invention in the catalysis carriers range. He quotes, that as a result of a controlled manufacturing process and the finished product "a large contact surface for chemical reactions arises."

According to the patent, the spheres' size is influenced by the implemented core and the metal powder used. More generally spoken Jaeckel sees a possible economic production: "… in a size of approximately 0.5 to 3 mm" with a "shell thickness of 5 to 15 μm", resulting in "a middle specific weight of the light body… 0.29-0.35 g/cm³". These statements of size refer to the first wet-chemically metalized core and its shell, which can be built up in a further process. In the patent Jaeckel describes both, the product and the manufacturing apparatus required. Jaeckel's ground breaking invention mainly combines two separate points, which can be found in older patents: a) pyrolysis of the core and b) two stage coating, stage one being through wet chemical methods (electroless and electrolytic) to build up a definite shell size.

Jaeckel was confident about the potential of his invention, and applied to the North German Affinerie AG in order to further develop his technology. Hence, it is no surprise that the disclosure writing of the North German Affinerie AG, Hamburg, No. 36 40 586 of 27.11.1986 [22] describes the next Hollow Sphere development step, being entitled “Procedures for the production of hollow balls or their connection with walls of increased firmness”. In this patent he points out how on one “foamed polymer” layers of metallic powder can be constructed. The patent mentions wet chemically metalized cores which are coated with a second layer using a powder slurry, which can be applied e.g. by a fluid bed apparatus on the polymer carrier. The coating apparatus is not named but only a “Fluid bed apparatus” can be used for such a process. By means of this technology a self-supporting shell is constructed on a foamed core, and not – as pointed out before in DE 32 10 770 [21] - built up using a wet chemical process. To follow, the polymer core is pyrolised at a temperature of 400°C for instance, and afterwards the shell is being sintered to a solid state. The patent also describes that compact or porous shells can be produced, depending upon the particle, binder, type and temperature of the sintering. Jaeckel mentions “closely sintered shells made out of metal or ceramic material, like Al_2O_3”. Furthermore the patent describes different kinds of treatments to manufacture Hollow Sphere Structures, e.g. “by shaking consolidated, if necessary, using minor pressure on the green sphere to interconnect the spheres” as well as the treatment of single spheres in order to glue them together or sinter them into blocks at a later stage”.

Jaeckel recalls the steps of his invention in an private email to the authors: “1. Production of Cu-coated polystyrene balls according to DE 32 10 770 [21] in his cellar laboratory at home, and development of a carbonyl iron suspension. 2. Sending these two components to AEROMATIC, Switzerland and requesting them to coat the Cu-coated polysterene balls. 3. Once he had received the finished coated polystyrene balls, they were sintered in a production furnace with positive results at the Ringsdorff, Bonn, only made possible due to a former research colleague being employed at the company. 4. Based on the results I had the courage to finalize DE 36 40 586 [22] at the North German Affinerie”. Research at the North German Affinerie was continued following this personal commitment. Jaeckel recalls: “That a laboratory size fluid bed coater was purchased at the North German Affinerie to improve the technology of patent DE 36 40 586,8 [22] and widen the range of applications.”

The advancement of this patent is DE 37 24 156 [23], filed 22.07.87 entitled: “Procedure for manufacturing metallic or ceramic hollow spheres”. The patent’s underlying problem definition is to develop: “an economical and easy to handle procedure for the production of metallic or ceramic Hollow Spheres with a dense or micro-porous shell of high stiffness.” In this patent the process described is a clear link to the further developed patents, using the Fluid Bed: “The carriers with a diameter of 1 to 8 mm are placed into a fluid bed and are sprayed with a hydrous suspension consisting of binder and metallic or ceramic particles. In such a way coated and afterwards within the fluid bed dried particles then have a dry powder-coating, a so called “greensphere”, with a sufficient and stable stiffness to handle them. In the next step the core is pyrolized at a temperature in the range of 400 to 500°C; then the oven is heated up between 1000 to 1500°C in order to sinter the Hollow Sphere in motion or stationary”, further on: “The dried powder layers possess sufficient firmness, so the coated, essentially spherical foam particles can be subjected to a pyrolytic decomposition process without the powder-shell losing its spherical shape.”

Generally spoken, the patent is a more specific form of DE 36 40 586 [22], with the key-advantage being reduced manufacturing steps, as the wet-chemical process is no longer required. Jaeckel recalls: “While doing coating experiments with the department head of the pilot plant station at the North German Affinerie, he asks me why we don’t coat the cores with a self supporting powder coat instead of wet-coating a Cu layer first and skip the electrolysis. I responded: “that should be possible, if I have some time to find a suitable polymer binder.” That’s how the idea of DE 37 24 156 [23] was developed at North German Affinerie and submitted to the German patent office in Munich about two years after the initial DE 36 40 586.8 [22].”

The production of metal sponge bodies is also described in a similar procedure. First, a sponge-structure is moistened with a metal-powder suspension, then dried and finally sintered. This section is very briefly mentioned in the patent and does not include any illustrations, which highlights the important developments in the performance of binder-systems. What connects the described manufacturing process of sponges and Hollow Spheres is at the very front the use of a suitable binder to connect the metal or ceramic powder to the (organic) carrier.

The major development of the technology was outlined by Jaeckel, namely the use of the fluid bed coater for coating a foamed core. It is very interesting to see how this technology was developed step by step, which is clearly documented in the patents. Tasks later on arose in manufacturing the Hollow Spheres according to the patent and development at the North German Affinerie was stopped, as during this time the fluid bed apparatus technology was not advanced enough, Glatt GmbH developed a special fluid bed apparatus [24] and improved the process engineering together with the Fraunhofer IFAM of Dresden, enabling a reliable large scale production.

Details regarding the industrial scale production of Hollow Spheres are mentioned the next paragraphs.

2.2 An Advance Technology Platform

Hollomet GmbH, a subsidiary of Glatt GmbH is pleased to introduce a wide spectrum of Hollow Spheres. Hollomet produces metallic and ceramic Hollow Spheres based on the hollomet-manufacturing Process and market them under the brand names “globomet” and “globocer”. In the following paragraphs we will give an insight into the materials required for the production of Hollow Spheres. We also describe the industrial manufacturing process in general, followed by highlighting the possibilities of mechanical treatment.

The development of the Hollow Sphere production process has been made in cooperation with the Fraunhofer IFAM Dresden over several years. Yet hollomet focuses on the industrial production of hollow spheres and the product development. Together with customers we develop solutions along their needs based on metallic or ceramic Hollow Spheres. Several years of research and development were needed to be able to fulfill customer’s needs.

The Fraunhofer IFAM Authors Andersen et al. describes in their paper published 2000 at an early stage [25] a new method to produce metallic Hollow Spheres from arbitrary metals and alloys. They give a general overview about the technology and the properties of metallic Hollow Spheres. Fiedler and Öchsner [26] give in their paper an excellent overview on different kind of Hollow Sphere structures and the impact that manufacturing techniques have on the material parameters. They mainly focus on partially bonded metallic Hollow Sphere structures on the one hand and syntactic metallic Hollow Sphere structures on the other hand. They address the mechanical properties of adhesively bonded metallic Hollow Sphere structures and conduct finite element analyses in order to determine Young's modulus and the initial yield stress dependence on the loading direction. Fiedler and Öchsner describe a numerical analysis of the different kind of Hollow Spheres using a three dimensional unit cell model with a primitive cubic arrangement. The PhD Theses of Thomas Fiedler describes in-depth and in comparison to other cellular metals the properties of metallic Hollow Sphere structures. He puts the main focus on linear elasticity, plasticity and thermal conduction [27]. In comparison to metallic foams metallic Hollow Sphere Structures have the huge advantage that due to the high reproducibility a simulation becomes possible.

2.2.1 Materials Used for Production

Polystyrene Core. A core is used in the production of the hollow sphere. For both metallic and ceramic Hollow Spheres a solid un-foamed polystyrene ball is usually used, which is, prior to the coating process placed into a foamer and expanded (EPS = expanded polystyrene). Grain sizes may vary during the expansion process. Sieving the polystyrene spheres is necessary for a narrow size distribution of the final product.

Coating. Various metal powders can be applied, their ability to be sintered being the only requirement. The grain size of the metal powder determines the minimum coat thickness possible. In order to achieve a solid integral Hollow Sphere after sintering, the coat should approximately be five times larger than the grain size of the metal powder being used. Initial preparation of the metal powder (e.g. water and gas atomization) considerably effects production costs, as well as technical specifications of the end-product. So far various materials such as iron, stainless steel, titanium and molybdenum have been well proven. Hollow Spheres of Alloys can also be produced in situ. Therefore a suspension of different metal powders are simultaneously sprayed on the core, the formation of the alloy takes place during sintering. The approach of combining different metal powders to spheres is not only a more cost effective means of production, but also enables an amalgamation of low and high-cost powders. Using this technique one may improve the technical specification and could reduce the costs of production in comparison to spraying an alloy-powder.

Binder. Prior to coating the metal powders are suspended in a binder-water mixture. Selecting the appropriate binder system depends on certain criteria such its pyrolysis, its gluing ability and its rheological properties. The binding forces glue the metal particles onto the core and interconnect the particles. The binder agent is generally kept at a minimum in the suspension.

2.2.2 Coating

The suspension recipe of metal powder, water and a certain amount of binding agent is weighed and poured into a suspension-container, where the ingredients are stirred,