Consolidation of metallic hollow spheres by electric sintering

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Abstract. This paper considers peculiarities of the technology of production of structures from metallic hollow spheres (MHS) using magnetic fields and electric sintering. In these studies, the raw material was MHS obtained by burning of polystyrene balls coated by carbon steel. MHS had an outer diameter of 3-5 mm and a steel wall thickness of 70-120 microns. Pulsed current generators were used for electric sintering of MHS to obtain different spatial structures. Since MHS have small strength, the compressive pressure during sintering should be minimal. To improve the adhesion strength and reduce the required energy for sintering, hollow spheres were coated with copper by ion-plasma sputtering in vacuum. The coating thickness was 10-15 microns. The ferromagnetic properties of MHS allowed using of magnet fields for orientation of the spheres in the structures, as well as using of perforated tapes acting as orienting magnetic cores. Ultrasonic testing of MHS structures has been tried using through propagation of ultrasound in low kilohertz frequency range. Sensitivity of the propagation parameters to water filling of inter-spheres space and sintering temperature was demonstrated.

1. Introduction
Structures from metal hollow spheres (MHS) are among many new promising cellular structures designed for various applications [1]. Such structures are used as filters, catalysts, and exhaust noise absorbers. Their advantages are low weight, high sorption capacity and other special properties. The raw materials for such structures are MHS typically made of steel. For the production of these structures, different bonding techniques were implemented including brazing, sintering, and infiltration of [2-4]. Technology of consolidation of MHS by electric heating with a welding machine was considered [3]. The technology of consolidation of powder materials introduced in the Riga Technical University applies electrical generators of pulsed discharge currents [5-7]. The complications of using this technology for MHS consolidation were: the need to apply the technological shell (coating) made of a material with a high electrical conductivity, non-uniformity of the material distribution during compaction, limited shapes and sizes of products.

Besides, free unsupported filling of the material doesn’t provide the desired product quality. Thus, the search for new ways to improve quality by perfection of all operations of the electrical sintering process is needful. The need for non-destructive quality control of the sintered bodies is also an urgent task which may have a non-trivial solution because of the specific properties of MHS structures, in particular its extremely high porosity. The ability to use ultrasonic attenuation to characterize structural density in metal foams was showcased by the laser ultrasonic detection method [8]The presence of adhesion and the quality of consolidation was tested by ultrasound in a variety of practical applications [9]. However, these results are not expandable on MHS structures.

2. Experimental procedure
Experimental studies were conducted on MHS made of steel by the technology developed in Fraunhofer IFAM Department of Powder Metallurgy and Composite Materials, Dresden [4]. MHS were obtained by burning of polystyrene balls coated by carbon steel. It had an outer diameter of 3-5
mm and a steel wall thickness of 70-120 microns. The general view of MHS and the structure of its surface are shown in Figure 1 and Figure 2.

Figure 1. Steel MHS diameter of 3-5 mm obtained from Fraunhofer IFAM

Figure 2. 3-D digital optical microscopy of MHS surface.

Electrical sintering was performed by a pulsed current generator with the operating voltage 200-400 V and power consumption of storage capacitor 1-2 kJ. At the discharge moment, a pulsed discharge current of 0.5 - 1, 2 kA with duration of 10-50 ms was passed through a volume filled by layers of MHS. The axial compression of the material was provided by a flat inductor exited by the pulsed generator. The applied force reached 150 N. The electrical sintering process combined with electromagnetic compaction is schematically shown in Figure 3.

Figure 3. Schematic layout of combined method of electromagnetic compaction and electrical sintering:: 1 – pulsed current generator ; 2 – inductor; 3 – punch; 4 – electrical poles; 5 – ceramic mold; 6 – sintered sample of MHS.

3. Results and Discussion
To obtain a material with stable projected properties different approaches were tested. One option was modification of MHS surface by ion-plasma sputtering and providing a 15-30 microns layer of copper coating (Figure 4-Figure 6). Applying of a thin layer of copper on the surface of steel spheres allowed better sintering of MHS due to increased electrical conductivity of the contact layers and reduction of the discharge current. Good sintering was obtained at a current value within 300A [10].
The conducted electric sintering at free filling of MHS allowed consolidation of spheres and formation of a rigid structure (Figure 7). However, a negative aspect is the volatility of properties of the resulting sintered body. This was caused by sintering of MHS to the surface of electrodes and sometimes by the lack of contact between the spheres.

The total porosity of the MHS structure is determined by macroporosity and microporosity. Macroporosity is the space between spheres and a hollow volume inside spheres. Microporosity is tiny pores in the spheres wall and coating. Macroporosity accounts for about 90% of the total volume. It is determined by the spatial arrangement of spheres, where the highest porosity is achieved at geometrically regular square packing of the spheres. The combined regime of pressing and sintering allowed creation of better compaction directly during the sintering process. To create more complicated and purposefully designed spatial structures of MHS for further sintering, additional tools can be used allowing specific orientation or location of spheres in a magnetic field (Figure 8). The method of orientation of MHS in a permanent magnetic field is based on ferromagnetic properties of MHS [11]. A kind of the method realization is usage of a perforated steel tape 1 mm thick with a desired configuration of open space for MHS, where the steel tape takes the function of the form and the magnetic guide.

The purposes of pilot ultrasonic trials on MHS structures were testing of possibilities of registration of ultrasonic waves through the structure and evaluation of the quality of the consolidation between the spheres. MHS can be considered at different structural levels in relation to ultrasonic wavelengths. At high frequencies in the megahertz range, where the wavelength is lesser than the sphere’s size, ultrasonic wave can propagate along a complex trajectory passing along the walls and surfaces of contact between of spheres consolidated by sintering. At low and medium frequencies, from tens of kilohertz to hundreds of kilohertz, where the wavelength is much greater than the spheres’ diameter, the ultrasound carrier is the entire structure, which can be considered as a highly porous but homogeneous material.
MHS structures were tested by through transmission using a pair of broadband ultrasonic piezoelectric transducers with work frequencies of 100, 300, and 1500 kHz. Excitation was produced by sine tone-bursts of 2 periods at the selected frequencies. Spectral characteristics of the received signals were assessed by FFT. Tests showed that due to the high porosity of MHS structures, only waves in a low ultrasonic frequency range can propagate. In particular MHS structures with spheres diameter from 3 to 5 mm, the upper frequency of the detection range was limited by 300 kHz. At frequencies of 1 MHz and higher, no signals were observed. The frequency dependence of ultrasound propagation has changed significantly, when the tests were carried out in the water-filled MHS structures. Because of high open porosity and the presence of large spaces between the spheres, MHS structure was easily filled with water. Three-phase (metal-air-water) medium was formed, where the continuous volumetric liquid component volume appeared conducting sound also at high frequencies. Thus the high frequency components of the spectral characteristics of ultrasound conductivity appeared (Figure 9). The observed effect can be used to evaluate the open porosity by comparing of the spectral characteristics of the structure in dry and liquid-filled conditions.

To test the sensitivity of ultrasound propagation parameters to sintering quality and strength (stiffness) of bonds between spheres, sintering temperature was chosen as a variable. MHS with a copper coating 15-30 micron were used. With the increase of sintering temperature and approaching it to the melting point of copper, the contact surface area between MHS and the diffusion between layers in neighbouring spheres increased, thereby increasing strength of sintering. Ultrasound velocity was measured by through transmission at 100 kHz referring to the arrival time of the ultrasonic signal. By increasing the sintering temperature from 900 to 1000 °C, ultrasound velocity increased significantly - from 1850 to 2620 m/s (Figure 10) demonstrating sensitivity of ultrasound to the quality of sintering.
The absolute values of ultrasound velocity in the sintered MHS structure was much lower than in steel material that is explained by the hollow volume of MHS and total high porosity. Thus, additional accounting for structural parameters are is required to quantify the quality of sintering in absolute terms.

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