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High porosity fly ash/Ni/P composite produced by electroless deposition

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Abstract

The aim of the present study is to create a composite material possessing useful properties enabling the waste fly ash to be utilized. To obtain the final material, fly ash is subjected to separation by size and density. The innovative approach to making the composite material is the use of chemical nickel deposition by which the free particles are bonded as a solid body. Deposition of nickel was carried out by two stages: first Ni-coating of the particles and second – bonding of the particles by nickel deposition. Structure of this material is near to syntactic foam. Some properties of the obtained material as a porosity, density, and permeability with regard to its application have been investigated.

Keywords: fly ash, porosity, permeability, syntactic foam, electroless deposition

1. Introduction

Closed-cell structures are well-known as "syntactic" foams. In the cases well known in the literature, they are obtained by infiltration of metal melts in particle packets [1−8]. The particles used for this purpose are mostly hollow and non-metallic-glass [1,2], ceramic [3−6]. The infiltrated melts are most often Al, Zn, Mg, or alloys on their base [7,8]. Infiltration of metal melts in such systems involves a number of difficulties – high process temperatures; reducing atmosphere; high melt pressures that promote good penetration of the latter. A significant limitation of the known methods is the inability to use melts with melting temperatures above those of the particles. We avoided the noted limitation by bonding of the particles with chemically deposited Ni. After looking at the application areas of fly ash [9], the price and its accessibility, we focused on creating composite material from it.

2. Experimental procedure

2.1. Materials and methods

The main material needed for the study is fly ash. For the next two steps (sensibilisation and activation) are used $SnCl_2$ (Merck N7815), HCl (37%)-p.a. (Merck N317), metallic Sn and $PdCl_2$ (Fluka N76050). In both stages of the metallization of the particles are used $NiSO_4 \cdot 6H_2O$ (Sigma-Aldrich N9758), Trisodium citrate (Reachim USSR), NH_4Cl (Fluka N9700), $NaH_2PO_2 \cdot H_2O$ (DAC Merck N 4646).

Separation by size was carried out by sieving machine type Thyr-2 made by VEB MLW "Labortechnik", Ilmenau, Germany.

Maintaining the temperature in the reactors was by means of the Thermostat U1 made by VEB MLW Prüfgeräte-Werk Medingen / Sitz Freital, Germany.

Permeability of obtained material was investigated at experimental setup assembled by us.

X-ray tomography was carried out by Nikon XT H 225 kV.

2.2. Separation by density and size

Obtaining starting material for our study is done through two separations:

1. Separation by specific densities of the spheres in terms of water density;

2. Separation of size fractions by sieving.

Separation of floating from non-floating spheres is performed by suspending the particles in water. After a while, the lighter particles remain on the surface of water (floating) while the heavier ones sink. This procedure is repeated until sufficient separation of the particles of both species is achieved. To improve the particle wetting and hence the separation quality to the water is added SDS – 120 mg · l^{-1}. The floating particles are separated from the water and dried in a drying furnace at 120 degrees Celsius. The now-dried floating spheres are separated by means of sieve, sizes as follows: 100, 125, 160, 200, and 250 μm. The particles between 200 and 250 μm are separated and used for the following procedures of this study. The further treatment of the particles consists of the following processes: pre-nickel coating, nickel-welding of particles and deposition of nickel mantle on the molded part. The pre-nickeling process is divided into several basic steps – sensitization, activation and metallisation.

2.3. Sensitization and activation

Sensitization and particle surface activation processes are similar to those that are widely used in practice [10]. At sensitization, the particles are mixed in a 1 : 6 volume ratio with a solution having the composition given in Table 1. The process is carried out at room temperature for 8 min. The particles are then washed to the absence of tin ions in the wash water.

Table 1. Sensitization solution

Component	Concentration
$SnCl_2$	20 g/l
HCl (36%)	30 ml/l
Sn	> 2 g/l

Immediately after sensitization with the least possible time of contact with air and light, the particles were treated with activating solution for 3 minutes at room temperature. The composition of the activating solution is shown in Table 2. Then washed with distilled water. The rinsing water is collected and Pd is regenerated.

Table 2. Activation solution

Component	Concentration
$PdCl_2$	0.25 g/l
HCl (36%)	10 ml/l

2.4. Pre-nickeling

The process is carried out with a nickel solution (Table 3) [11,12] in a water jacket reactor (Fig. 1). For more precise temperature control, the water jacket is connected to a thermostat (not shown in the Figure). One of the important factors in pre-nickeling is constant agitation [13]. It ensures the uniform deposition of nickel on the particles of the solution. It is obligatory to stir the solution with a stirrer whose blade is located along the axis of the reactor and does not rub against or touch any of the walls. An important factor is also the material of the propeller lever to be PTFE to soften particle strikes. Otherwise, the generated fragments lead to the intensive deposition of nickel in the solution, and little on the particles.

Table 3. Composition of the nickel solution

Component	Concentration
$NiSO_4$	28 g/l
Trisodium citrate	40 g/l
NH_4Cl	40 g/l
$NaH_2PO_2 \cdot H_2O$	20 g/l

Fig. 1. Water jacket reactor charged with nickel solution. Particles not yet loaded

The metallisation was carried out for 20 minutes at 85−90°C. To obtain the syntactic foam, the nickel particles need to be bonded together. The process is carried out in a specially designed reactor shown in Figure 2.

Fig. 2. Reactor for particle coupling in syntactic foam by deposition of nickel

It is made from PTFE and glass. These materials are selected for their qualities. PTFE is extremely difficult to nickel cover (this eliminates the possibility of undesirable reactions occurring on its surface), and the glass is transparent and allows direct observation of ongoing processes. Particular attention should be paid to the way the solder reactor is charged. The particles should be in the most compact form. It is, as far as possible, to achieve a hexagonal close-packing. Ideally, and in the case of monodimensional spheres, this is achievable through the procedures we propose. In our case, however, particle sphericity is not ideal. Moreover, the distribution by diameters is between 200 and 250 μm. Nevertheless, in order to achieve the maximum tightness of the particles in the reactor, we periodically add water, which favors the closest ordering of the particles. When through this procedure the reactor cannot take over more particles, we close it and place it in an ultrasonic bath. With continuous water flow, we turn on the ultrasonic bath for 240 s. We make a control opening of the reactor and add particles to the released volume. The latter procedures are repeated until more volume is released to add more particles. As a result of the flow and high-frequency vibration, the particles stand as closely as possible to each other. The purpose of this arrangement is to reduce the particle vibrations caused by the flow of the solution for Ni-coating through the reactor. The reactor is vertically located and the solution flow is from the bottom up to completely push the bubbles of hydrogen that are formed during the reaction. Upon completion of the process, the reactor is dismantled and the welded body is pushed out. The resulting body is shown in Figure 3.

Fig. 3. Compact body of ordered hollow ceramic spheres connected with nickel

2.5. Investigating flow through foamy materials

Poiseuille equation for condensed fluid viscosity passed through the cylindrical tube is [14–16]:

$$\eta = \frac{\Delta P t \pi r^4}{8Vl}$$

where:

η is viscosity of fluid,

ΔP is pressure difference before and after the tube,

t is time necessary to leak volume V,

V is fluid volume passed through the cylindrical tube,

r is radius of tube,

l is path longitude of fluid through tube.

Transforming this equation to express geometrical values by residual physical values, we find:

$$\frac{S^2}{l} = \frac{8\pi\eta V}{\Delta P t}$$

The experiment was carried out with fluid distilled water, and ambient temperature 16°C.

Measured data of sample received by us are as follow:

ΔP = 45 800 Pa,

t = 338 s,

$V = 0.3785 \cdot 10^{-3}$ m^3,

$\eta = 1.116 \cdot 10^{-3}$ Pa · s (from handbook).

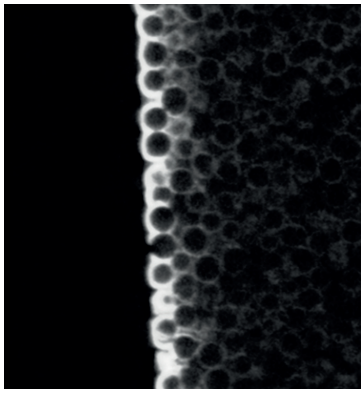
Calculated value for $S^2/l = 6.858 \cdot 10^{-13}$ m^3.

3. Discussion of results

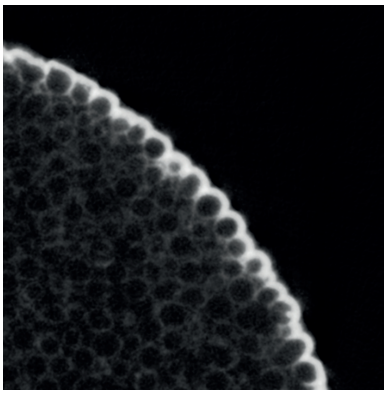
If fluid volume passes through the porous material, geometrical dimensions are not corresponding to real cross section and path longitude of fluid through the porous material. We can make assumption that S is effective area of cross section and l is effective path longitude of fluid through the porous material. S and l are generally functions of material porosity. Their real values cannot be finding easily; moreover, these values cannot be calculated separately by above described method. The ratio of the volume of gas in the enclosed spheres to the volume of the open cavities and the volumes of the ceramic and nickel parts with their respective densities remains sufficient for the body to still float (Fig. 4). The resulting material has a density of 0.5650 g/cm^3 (the density is geometrically determined). Using the non-destructive method, the ratio of open to closed spheres was measured – 61.64% closed, 38.38% open. The removal of particles from the convex position in the body is relatively easy, therefore it has been supplemented with superficial

electrochemical nickel. As a result, this disadvantage has been avoided. Figure 5 shows X-ray tomography of one of the specimens. We see the superficially deposited galvanic nickel as a lighter mantle. This is because the layer is textured, relatively large and thicker (> 120 μm), resulting in strong reflexes. The chemical nickel between the spheres gives very weak reflexes because it is a Ni-P alloy, finely crystalline (close to X-ray amorphous).

Fig. 4. Floating cylinder of arranged hollow ceramic spheres welded in syntactic foam by deposition of nickel



a)



b)

Fig. 5. X-ray tomography of syntactic foam: a) axial cut of sample, b) radial cut of sample

4. Conclusions

A foamy cylinder from fly ash hollow spheres, connected by electroless deposition of Ni is successfully obtained. The following parameters of the obtained cylinders were investigated: density, ratio of open to closed pores, and fluid permeability.

The material we get is promising for the production of new composite materials. One of the many possibilities is the infusion of molten metals into the open cavities of the starting composite material. The advantage is that the wetting between the metallized ceramic and the penetrating metal is incomparably better than that of non-metallized ceramics.

The material can be used as a filter for all gases and liquids to which nickel and ceramics are resistant.

Noting that the structure of the material is characterized by multiple surfaces, both convex and concave, and different phase boundaries – gas / metal / ceramics it can be concluded that this material is very suitable for absorbing shields for sound- and electromagnetic waves.

Also the material is suitable for heat insulating elements.

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