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Application of capillary hysteresis phenomenon for evaluation of recycling possibility of selected MMC

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Abstract

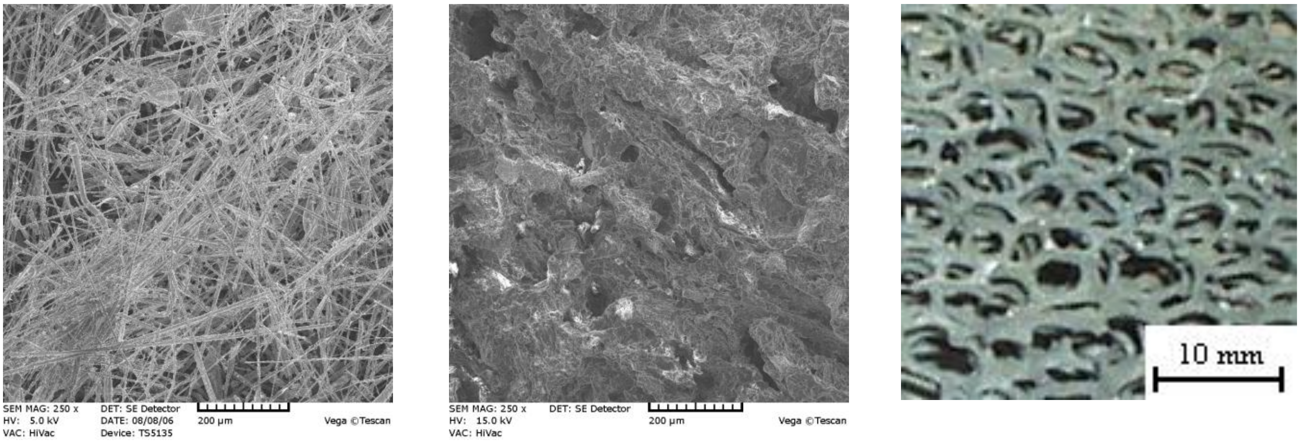
Properties of composites made through saturation of ceramic reinforcement preforms with liquid metal are the cause of growing use of these materials. Taking increasing requirements regarding environment protection into consideration, already during design of such materials one should think of a way of their recycling at the end of life. The recycling of these materials is conducted by separation of components. Determining optimal superficial conditions of a recycling system: liquid metal matrix – reinforcement preform – medium enables automatic course of the recycling process, but does not guarantee high yield of metal. With identical superficial conditions of the recycling system and different structure of reinforcement preforms significant differences in metal yield can be obtained. Identification of a type of a capillary present in reinforcement preforms may allow to determine, already during stage of material design, which types of composites will undergo the recycling process better and for which types one has to accept decreased yield of matrix metal. This identification can be done on the basis of an analysis of results obtained during examination conducted with mercury porosimetry, comparing acquired hysteresis graphs with model graphs proposed by de Boer for adsorbent analysis. Considering the analysis of image of structure of examined reinforcement preforms makes the identification process easier and faster.

Keywords: Metal matrix composites with saturated reinforcement, Structure of reinforcement preforms

1. Introduction

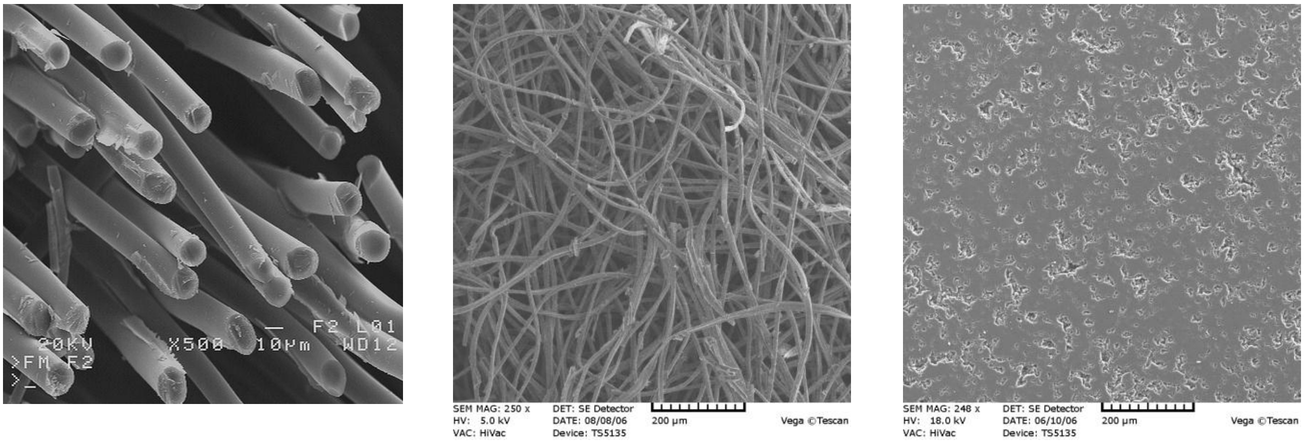
Production of composites consists in linking together materials varying not only in chemical constitution, but also in properties in the first place [1,2]. Thanks to this, properties of obtained composites can be shaped almost freely [2,3]. It increases possibilities of application of such materials, but at the same time causes problems related with their future recycling [4].

One of groups of composite materials more and more often used in production of e.g. cars are metal matrix composite castings [3,5]. These castings are made by saturating porous reinforcement preforms with liquid metal of the matrix, with increased or decreased pressure. As reinforcement preforms for composite castings, mostly ceramic materials are used, with various structure [6,7], which is illustrated with pictures of microstructures (fig. 1 and 2) [8].



a) b) c)

Fig. 1. Structures of aluminosilicate reinforcement preforms: a) short disordered fiber, b) sinter, c) skeleton structure, SEM [8]



a) b) c)

Fig. 2. Structures of graphite reinforcement preforms: a) ordered fibers, b) short disordered fiber, c) sinter, SEM [8]

The single efficient method of recycling of casted metal matrix composites with saturated reinforcement is a separation of its components [4]. It is best to perform by selecting a proper medium for recycling [9,10], to create system with wetting parameters favoring self-contained outflow of liquid metal matrix from porous reinforcement preform. However, analysis conducted in [11] has shown that determination of beneficial wetting parameters does not guarantee high efficiency of recycling process. During the research it has been found that, depending on the character of the reinforcement (shape and number of pores) with identical superficial conditions of recycling system, significant differences in yield of metal can be obtained (table 1).

For example, for system: graphite reinforcement – lead alloy OT7 – dissolved mixture of salts 50%NaCl+50%KCl, depending on the shape of reinforcement preform (short disordered fiber – fig. 2b or sinter – fig. 2c), yield of 87% and 28% has been obtained, which is more than treble difference in quantity of metal originally contained in the composite.

The reason behind this phenomenon is the specific structure of the reinforcement, favoring the so-called "ink bottle" effect, which causes holdup of liquid metal in capillaries of reinforcement preform. In the paper [11] this phenomenon and conditions of its occurrence have been described in greater detail. On the basis of dependencies shown there, it can be determined which structure of capillaries will favor the holdup of liquid metal in porous reinforcement preform and when the structure of the preform will render the process of automatic outflow of liquid metal from porous reinforcement difficult.

Table 1.
Average values of yield of metal (**u_{av}**) obtained during recycling of MMC with saturated reinforcement [10]

REINFORCEMENT PREFORM	MATRIX	MEDIUM	$\theta_{S\text{-}M/O}$ [°]	u_{av} [%]
short aluminosilicate fiber (rys. 1a)	OT7 alloy	Air	153	68
short aluminosilicate fiber (rys. 1a)	OT7 alloy	50%NaCl+50%KCl	149	95
short graphite fiber (fig. 2b)	OT7 alloy	Air	128	19
short graphite fiber (fig. 2b)	OT7 alloy	50%NaCl+50%KCl	149	87
aluminosilicate sinter (rys. 1b)	OT7 alloy	Air	153	19
aluminosilicate sinter (rys. 1b)	OT7 alloy	50%NaCl+50%KCl	149	90
graphite sinter (fig. 2c)	OT7 alloy	Air	128	9
graphite sinter (fig. 2c)	OT7 alloy	50%NaCl+50%KCl	149	28
short aluminosilicate fiber (rys. 1a)	EN AC-AlSi12(b) alloy	Air	162	0
short aluminosilicate fiber (rys. 1a)	EN AC-AlSi12(b) alloy	50%NaCl+50%KCl	162	97
short graphite fiber (fig. 2b)	EN AC-AlSi12(b) alloy	Air	145	1
short graphite fiber (fig. 2b)	EN AC-AlSi12(b) alloy	50%NaCl+50%KCl	163	88
aluminosilicate sinter (rys. 1b)	EN AC-AlSi12(b) alloy	Air	162	4
aluminosilicate sinter (rys. 1b)	EN AC-AlSi12(b) alloy	50%NaCl+50%KCl	162	90
graphite sinter (fig. 2c)	EN AC-AlSi12(b) alloy	Air	145	23
graphite sinter (fig. 2c)	EN AC-AlSi12(b) alloy	50%NaCl+50%KCl	163	63

$\theta_{S\text{-}M/O}$ - extreme wetting angle of reinforcement material (S) by composite metal matrix (M) in the medium (O)

2. Analysis of the problem

Capillaries present in reinforcement preforms may be of different form: cylindrical, conical, bottled or spherical and can have various cross section. They can also arise between planes of different mutual inclination. Capillary shapes occurring in porous reinforcement preforms are presented schematically in the fig. 3 and 4. However, most frequent case is the capillary with various chambers, narrowings of irregular shape and variable inclination angle. Exemplary shape of such capillary is shown in the fig. 3.

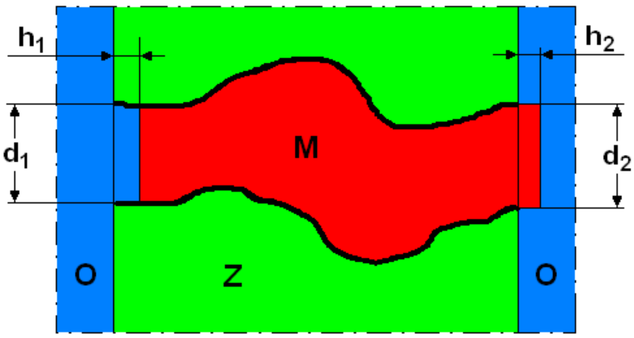


Fig. 3. Diagram of the outflow of liquid composite matrix (M) from the reinforcement capillary (Z) in the presence of an (O)medium [11]

Considerations presented in the article [11] allow to draw conclusions, that for recycling system presented in the mentioned fig. 3 holdup of outflow of liquid metal matrix (M) from capillaries of porous reinforcement (Z) can occur when the ratio of capillary diameters d_1/d_2 is equal to negative value of cosine of extreme wetting angle of reinforcement material by liquid metal matrix in environment of medium (O) $\theta_{Z\text{-}M/O}$:

$$d_1 / d_2 = -\cos\theta_{\frac{Z-M}{O}} \qquad (1)$$

If this ratio will be different from the value of the cosine, then the metal will be able to move within the capillary. The character of the difference (greater or lower) determines the direction of the movement.

Other dependencies shown in the literature [9,10] lead to conclusion, that if the process of liquid metal matrix outflow is to occur at all, value of the extreme wetting angle of reinforcement material (Z) by metal of composite matrix (M) in environment of the medium (O)) $\theta_{Z\text{-}M/O}$ should be as high as possible (always greater than 90°). If it is taken into consideration, then for the correctly selected medium it can be predicted which shapes of capillaries increase the probability of occurrence of the phenomenon of liquid metal matrix holdup in capillaries of reinforcement preform.

Thus, according to presented assumptions, it can be foreseen that probability of holding the metal of the matrix in capillaries shown schematically in the fig. 4A is equal to zero. In case of capillaries shown in the fig. 4B it can occur only if the recycling medium will be selected in a way that $\cos\theta_{Z\text{-}M/O} = d_1/d_2$, but then the simplest solution is to change the medium. Nevertheless, if capillaries of shapes similar to those shown in fig. 4C and D will be present, the probability of holding up the metal will be significantly higher.

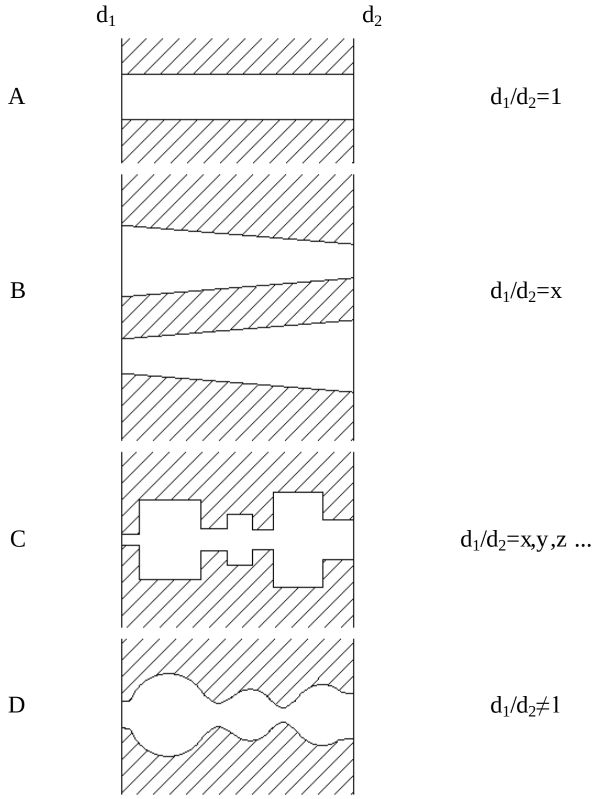


Fig. 4. Schematic illustration of shapes of capillaries of porous reinforcement preforms

In case of real structures of reinforcement preforms, determination of d_1/d_2 ratio is frequently impossible due to variable shape of capillary profile on its length. Despite the availability of various tools allowing visualization of analyzed structures, the problem is also an identification of capillary character. Therefore, the question was asked: is it possible to identify the type of capillaries occurring in the structure of reinforcement preforms with other methods than image analysis? It is important, because the possibility of identification of capillary type occurring in the structure of composite reinforcement preforms allows to determine the susceptibility of manufactured material to the recycling already during the design of the composite.

3. Research assumptions

For examination of variations in porous structure of adsorbents, which similarly to reinforcement preforms are porous materials, the courses of isotherms of adsorption and desorption of nitrogen are used [12].

Depending on the character of the pores, with decreasing the pressure of adsorbate its desorption from the pores may occur with lower pressure than condensation. This phenomenon is named *capillary hysteresis*. It can be observed when during desorption the shape of adsorbate meniscus is different than during adsorption. Shapes of adsorption hysteresis are dependent on character of the pores present in adsorbent. Comparing the shapes of hysteresis loop of examined adsorbents with the model ones proposed by de Boer in 1958, texture of adsorbents can be determined. Shape of hysteresis loop and corresponding pore shapes are shown in the fig. 5 [12,13].

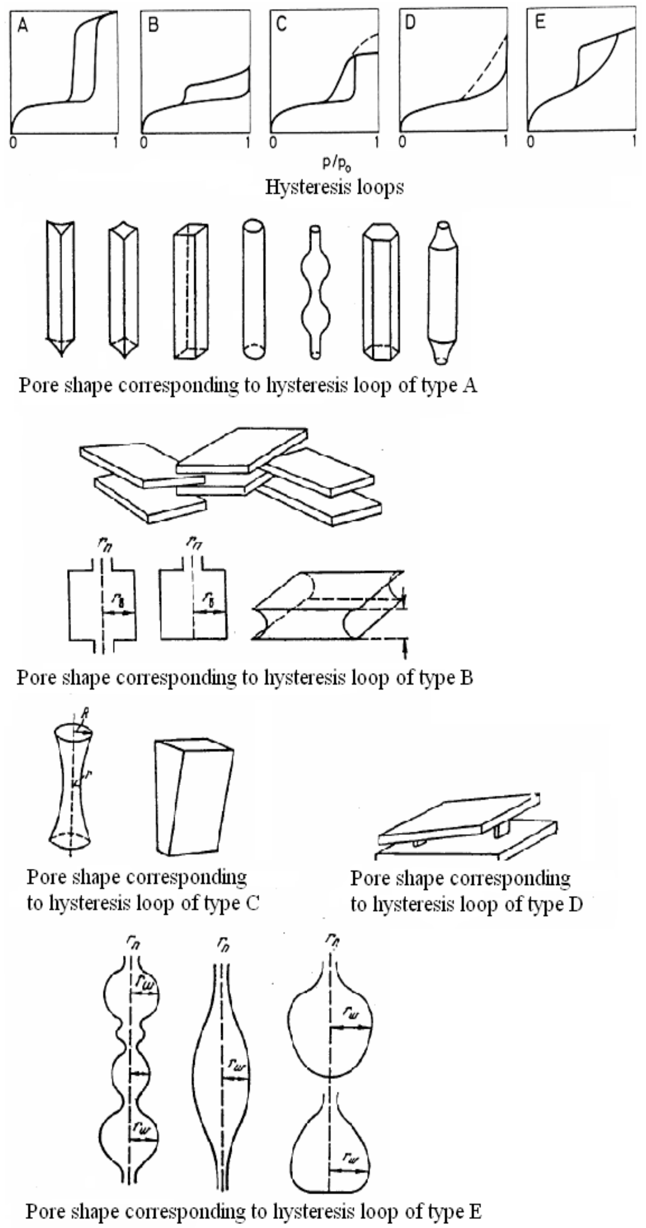


Fig. 5. Hysteresis loops and pore shapes [12, 13]

Type A – it is specific for pores of cylindrical shape of different form of cross section (round, triangular, polygonal), but with similar radius;

Type B – it is specific for pores of bottle shape (narrow entrance to wide interior) and also for pores formed between two planes of different mutual inclination;

Type C, D – they are rarely encountered and can be treated as derivatives of types A and B appropriately:

Type C – conical shape of pores;

Type D – shape of pores formed from two non-parallel planes;

Type E – it has spherical shape of pores, with numerous narrowings and open ends, along with different forms of "ink bottle". Type E is most frequently encountered.

A phenomenon very similar as in the process of nitrogen adsorption and desorption, which has become a basis to identify the pores of adsorbent, can be observed during porosity analysis using mercury porosimetry. Determining the size of the pores using mercury porosimetry method is based upon keeping non-wetting liquids in capillaries (wetting angle > 90°). Such liquid, when making the contact with solid body, is not spontaneously adsorbed through material pores, because of surface tension forces working in direction "outside" the pores. Nevertheless, it is still possible to push it into the pores by applying appropriate pressure. This pressure is dependent on the pore size and this dependency is known and expressed by Washbourne equation [14]. It has been though observed during analysis of results of porosimetric examination that when the mercury pressure in meter circuit was decreasing, outflow from the pores could occur with different pressure than during forcing in. In case of mercury porosimetry this phenomenon (hysteresis) is related to the change of shape of meniscus of used medium and is dependent on the same superficial parameters of the system as in case of hysteresis of nitrogen adsorption. Consequently, evaluation of the shape of capillaries in examined porous reinforcement preforms can be performed using the same models as proposed by de Boer for determining the character of adsorbent pores.

4. Experimental tests

To test assumptions mentioned above, porosimetric examination of earlier studied reinforcement preforms (table 1) was performed. It allowed to check if, according to the assumptions, shape of pores selected basing on hysteresis curve favors the occurrence of liquid metal holdup phenomenon in studied reinforcement preforms. Acquired hysteresis curves are shown in the fig. 6.

Given the capabilities of used measuring apparatus, full hysteresis loop was obtained only for one reinforcement. Despite this, basing on acquired curves, it is possible to identify the character of capillaries occurring in porous reinforcement preforms.

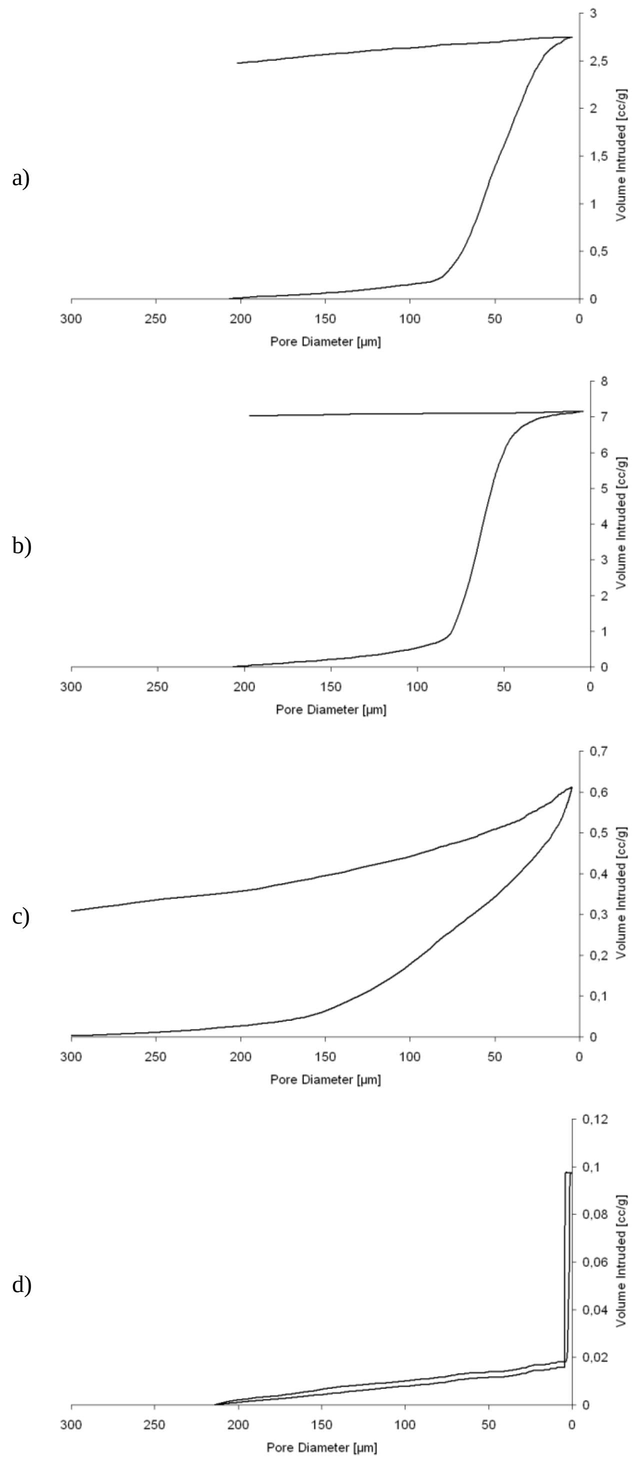


Fig. 6. Hysteresis curves for reinforcement preforms made of:
a) short aluminosilicate fiber, b) short graphite fiber,
c) aluminosilicate sinter, d) graphite sinter

On the basis of acquired curves, capillaries occurring in preforms made of short fibers (fig. 6a and b) can be qualified as B type (fig. 5B), considering the fact that curves were nearly parallel. For this type of capillaries, $d_1/d_2=x$ (fig. 4B). Along with selection of appropriate recycling medium, this allows to obtain substantial yield (table 1). It is a result of small probability of stopping the movement of liquid metal in capillaries of reinforcement preform. Aluminosilicate sinter preforms (fig. 6c) have capillaries of D and E type (fig. 5D and E). It can be inferred from mild rise of the curve resulting from saturation and large drop of the tempering curve. For this type of capillaries, d_1/d_2 ratio can have many different values (fig. 4B, C, D). Still, there is a probability that despite selecting appropriate medium, some amount of matrix metal will remain bound in some capillaries of reinforcement preform (table 1). The last from examined reinforcements (fig. 6d), graphite sinter preforms, should be classified as A type (fig. 5A). They are capillaries definitely most similar to the situation shown in the fig. 4C and D. With such reinforcement preforms, probability of holdup of outflow of liquid metal matrix significantly rises, which may cause considerable drop of yield during recycling of such materials (table 1).

5. Conclusions

1. Selection of proper superficial conditions of recycling system: metal matrix – reinforcement preform – medium allows self-contained course of recycling process, but does not guarantee high yield of matrix metal. With identical superficial conditions of the recycling system and different structure of reinforcement preforms significant differences in metal yield can be obtained.
2. This phenomenon results from variable structure of reinforcement preforms. Capillaries present in porous preforms have various characteristic structure for specific type of material. This structure can favor holdup of outflow of liquid metal in capillaries of porous reinforcement preform.
3. Identification of capillary type occurring in reinforcement preforms may allow to determine already during the design stage, which types of composited will be more susceptible for recycling and which will result in decreased yield of matrix metal.
4. Identification of type of capillary present in reinforcement preforms can be performed on the basis of an analysis of results obtained during examination conducted with mercury porosimetry, comparing acquired hysteresis graphs with model graphs proposed by de Boer for adsorbent analysis.
5. While performing the identification, it is worth to take results of analysis of image of examined preforms structure into consideration. Such analysis makes the identification process faster and easier.

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