MATERIAŁY CERAMICZNE /CERAMIC MATERIALS/, 62, 4, (2010), 521-524

www.ptcer.pl/mccm

Diatoms as a Source of New Materials

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Abstract

Diatoms are unicellular eukaryotic algae which can be found in almost all aqueous and humid environments. Characteristic features of diatoms is that their frustules have a unique morphology (in particular, the pattern of nanostructures, such as pores, ridges, areoles and other forms), and their cell walls are made of silica (hydrated silicon dioxide). Because of this specific morphology, diatoms can be used for manufacturing bio- or chemical sensors, membranes, biotemplates, biocapsules, carriers, or even nanoreactors. For certain applications, diatoms have to be processed and sintered.

The paper presents some initial results obtained in experiments on the consolidation of diatoms. In particular, attention was paid to the preservation of the nanopores that naturally exist in diatoms, since the nanopores present in bulk materials inside the sintered grains can enhance fracture toughness. The diatoms and bulk materials obtained by pressing and sintering were examined by scanning electron microscopy (SEM).

The SEM observations revealed the effects of sintering of diatoms and changes of their morphology. The diatoms were treated as a powder, *i.e.*, they were consolidated by die pressing and then sintered. After the process of consolidation, most of the pores naturally existing in diatoms were closed. The results suggest that because of their highly diversified shapes the diatoms cannot be uniformly consolidated by die pressing. The highest relative density achieved was 83 %.

Keywords: Diatoms, Pressing, Sintering, Microstructure – final

OKRZEMKI JAKO ŹRÓDŁO NOWYCH MATERIAŁÓW

Okrzemki to jednokomórkowe, eukariotyczne algi, które można znaleźć w niemalże wszystkich środowiskach wodnych i wilgotnych. Charakterystyczną cechą okrzemek jest to, że ich skorupki mają unikalną morfologię (w szczególności stanowiącą wzór nanostruktur takich jak pory, grzbiety, otoczki i inne formy), a ich ściany komórkowe złożone są z krzemionki (uwodniony ditlenek krzemu). Z powodu tej specyficznej morfologii, okrzemki mogą być wykorzystane do wytwarzania biosensorów, czujników chemicznych, membran, bioszablonów, biokapsuł, nośników lub nawet nanoreaktorów. W przypadku pewnych zastosowań, okrzemki muszą być przetwarzane i spiekane.

Artykuł przedstawia niektóre wstępne wyniki uzyskane podczas doświadczeń zawiązanych z konsolidacją okrzemek. W szczególności, zwrócono uwagę na zatrzymywanie nanoporów, które w sposób naturalny występują w okrzemkach, ponieważ nanopory obecne w materiałach masywnych wewnątrz spieczonych ziaren mogą podwyższać odporność na pękanie. Okrzemki i masywne materiały, otrzymane drogą prasowania i spiekania, badano za pomocą elektronowej mikroskopii skaningowej (SEM).

Obserwacje SEM ujawniły skutki spiekania okrzemek i zmiany ich morfologii. Okrzemki były przetwarzane jak proszki, tzn. były konsolidowane drogą prasowania w matrycy i następnie spiekane. Po procesie konsolidacji większość porów naturalnie istniejących w okrzemkach uległa zamknięciu. Uzyskane wyniki sugerują, że okrzemki nie mogą być jednorodnie konsolidowane za pomocą prasowania w matrycy z powodu ich skrajnie zróżnicowanych kształtów. Najwyższa wartość gęstości względnej, którą uzyskano, wynosiła 83 %.

Słowa kluczowe: okrzemki, prasowanie, spiekanie, mikrostruktura finalna

1. Introduction

Diatoms are unicellular algae inhabiting fresh and saltwater. Tens of thousands of species form a variety of symmetric amorphous silica skeletons called frustules. The frustules are built of two valves which are fixed together by a connective zone-girdle (Fig. 1) [1]. The skeleton is made of silica (hydrated silicon dioxide) and has a unique morphology (pattern of nanostructures, such as pores, ridges, areoles and others) [1, 2]. The sizes of diatoms range from 2 μm to several millimeters [3].

The above and other features make diatoms a very important source of new materials. Because of its specific morphology, a single diatom can be used as a new type bio- or chemical sensor, biotemplate, biocapsule, carrier, or even nanoreactor [2, 4, 5]. Diatoms are particularly attractive for nanotechnology because they build their highly symmetric skeletons with a nanopattern directly in 3D [1]. Among the potential applications of diatoms, there are also reinforcements for composites and the substrates for the fabrication of bulk materials. Commercial applications of diatoms include building and abrasive materials, fillers and materials used for filtration or insulation [6]. This wide application range results from the fact that diatoms are available in nature in large quantities and at a low cost from sedimentary rock (diatomaceous earth). Moreover, diatoms can be grown in cultures and the number and size of species can be controlled. In all these applications where diatoms are treated as a source to obtain bulk materials it is important to study the consolidation process of diatoms and to characterize the materials produced from them. In particular, it is crucial to examine the possibility of preserving the nanopores that are naturally present in diatoms [1, 2, 7]. This is so since the existence of nanopores in bulk materials, inside the sintered grains, can enhance fracture toughness of the material.

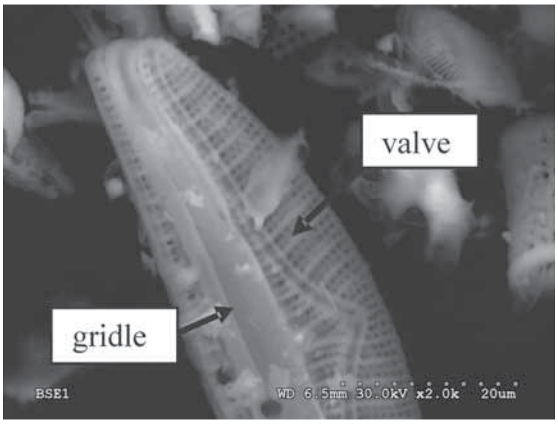


Fig. 1. SEM image of diatoms.

The present paper is concentrated on the consolidation of diatoms by pressing and sintering. The diatom samples in the initial state and bulk materials obtained from them were analyzed by scanning electron microscopy (SEM).

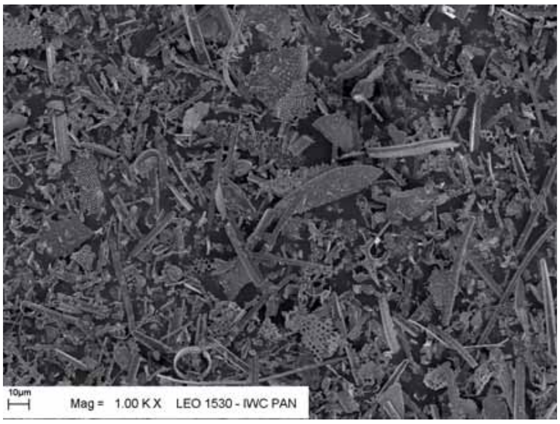
2. Experimental

Two diatom powders were used as the starting materials. One powder (delivered by Sigma-Aldrich), which we called "pink" because of its color, had the density d = 2.324 g/cm^3 (as measured with an Accu Pyc II 1340 helium pycnometer) and the specific surface area d_{BET} = 8.76 m^2/g. The average particle dimension calculated from the specific surface was 0.29 μm. The other powder (Fluka), called "white", had d = 2.341 g/cm^3 (Accu Pyc II 1340 helium pycnometer)), and the specific surface area d_{BET} = 1.52 m^2/g. Its average particle dimension calculated from the specific surface was 1.69 μm. As it can be seen, the "pink" diatoms had the specific surface area several times larger and the average particle dimension several times smaller than the "white" diatoms. The principal component of these diatomaceous materials was SiO_2 (above 99 wt%). However, the color of the "pink" diatoms suggests that they also contain Fe compounds.

In preparing bulk samples of the diatomaceous powders we used the following additives:

– 10 wt% of 10 % poly(vinyl alcohol) (PVA) water solution. Molecular weight of the PVA (Aldrich) was 31000; its degree of hydrolysis was 88 %,
– 20 wt% of water.

The diatoms were first heat treated at 700°C and then mixed together with the additives. The mixture was uniaxially die-pressed under a pressure of 50 MPa. The process



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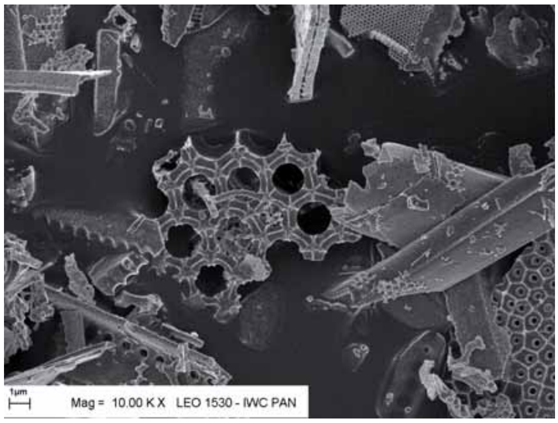

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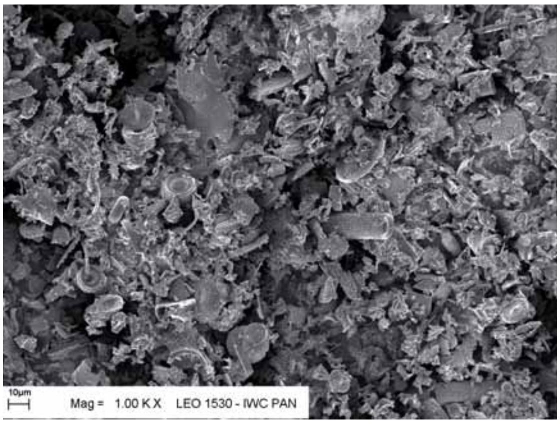

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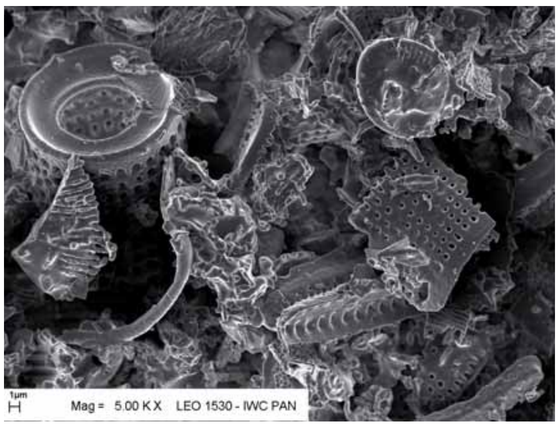


d)

Fig. 2. SEM images of diatoms used as the initial powder: a) and b) "pink" diatoms, c) and d) "white" diatoms.

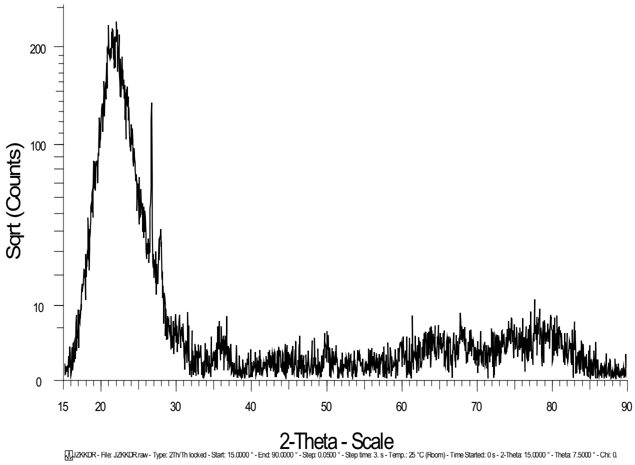
of sintering was carried out in a Carbolite furnace at 1000, 1100, 1300 and 1400°C, with a temperature increase rate of 5°C/min. At the highest temperature, the samples were maintained for 1 h.

After sintering, the properties of the samples, such as apparent density and open porosity (Autopore II 9220, Micrometrics mercury porosimeter), were examined. The microstructure of the sintered diatoms was analyzed using a LEO 1530 SEM. A Philips PW 1830 X-ray diffractometer was used for XRD investigations.

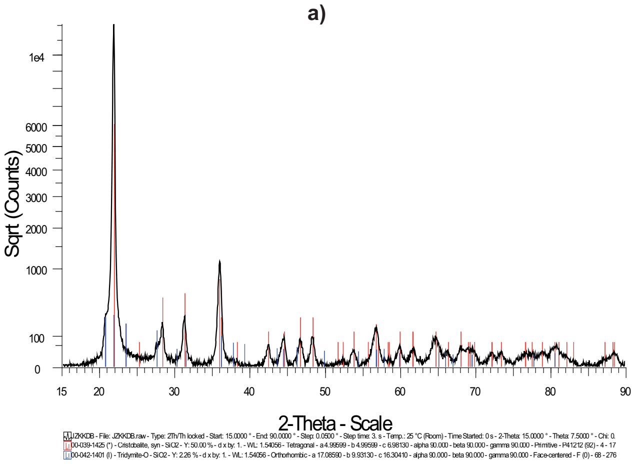
3. Results and discussion

The morphology of the initial "pink" and "white" diatoms is shown in Fig. 2. As it can be seen, the shapes and sizes of the diatoms of both types are varied: the diatoms are oval as well as rectangular in shape. They are crumbled and only some larger fragments differing in morphology and size can be observed. The openings in their frustules are also varied in size. We have pieces that resemble "plasters" with regularly distributed openings, and also remnants of more complicated structures. From the point of view of further consolidation of the diatom powder, this great morphological variety is disadvantageous.

Attempts of consolidation of diatoms without selection of their shapes were, however, undertaken in the present study in order to find whether the available diatomaceous material could be used for synthesizing bulk material of it.



a)

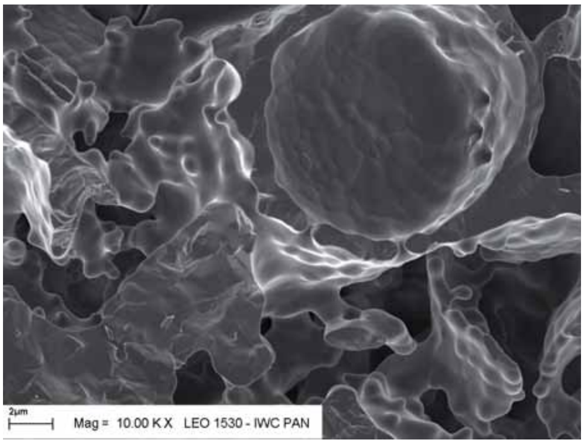


b)

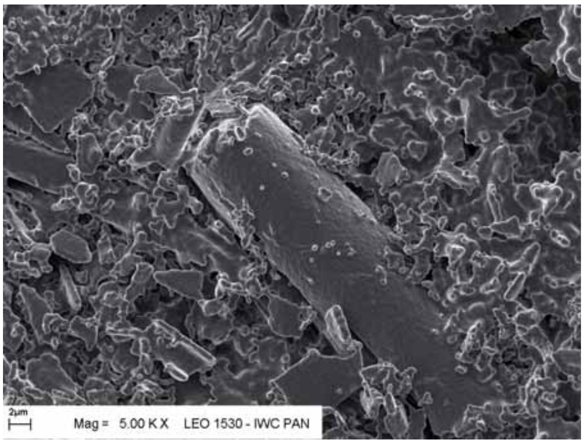
Fig. 3. X-ray diffraction pattern of diatoms: a) "pink", b) "white".

Table 1. Open porosity, soaking and relative density of sintered diatoms as a function of sintering temperature for bulk materials obtained from "pink" diatoms (p) and "white" diatoms (w).

T [°C]	Open porosity [%]		Soaking [%]		Relative density [%]	
	p	*w*	*p*	*w*	*p*	*W*
1000	–	54.1	–	52.4	–	44.6
1100	52.7	59.0	49.6	62.4	45.7	40.6
1300	52.0	46.3	46.9	37.7	47.7	52.5
1400	49.3	7.6	42.1	4.0	50.3	83.0



a)



b)

Fig. 4. *SEM images of fracture surface of heat treated diatoms: a) "pink" diatoms sintered for 1h at 1400°C, b) "white" diatoms sintered for 1 h at 1300°C.*

Fig. 3 shows X-ray diffractograms of the diatoms. We can see that the "pink" diatoms are built of amorphous SiO_2. When subjected to sintering, these diatoms may be expected to crystallize. The "white" diatoms are made of crystobalite, a well-crystallized polymorphic quartz variety.

The results of measurements of the open porosity, relative density and soaking of diatoms as a function of sintering temperature are given in Table 1. We can see that with increasing the sintering temperature the porosity and the soaking of the "pink" diatoms decrease. The sintering at the highest temperature gave the highest density value, but not above 50 %, which is rather a small value for a sintered material. In the "white" diatoms, the porosity and soaking also tend to decrease, except in those sintered at a temperature of

1100°C. The relative densities of the “white” diatoms sintered at 1300 and 1400°C are higher than the values obtained for the “pink” diatoms and, what is more, in the “white” sample sintered at 1400°C, it reaches 83 %. These results suggest that the process of consolidation proceeds differently in different diatoms. A higher relative density is possible to achieve in the diatoms with a greater powder grain size. We can, however conclude, that the varied shapes of diatoms of both types make the process of their compaction difficult. In using diatoms as the source of new bulk materials we must take care to preserve the nanopores present in their frustules. To achieve this, we should produce a sintered diatomaceous material that contains pores between the individual particles of the diatoms as well as the “free” pores in their frustules. This is a difficult technological task. It is commonly known that pores disappear during sintering, with the small pores disappearing already during the first process step. Our SEM observations confirm this effect: Fig. 4 shows examples of the microstructure of diatoms sintered at various temperatures. The pores, naturally existing in their frustules, are mostly closed.

4. Conclusions

Our experiments with the forming and sintering of diatoms have demonstrated that the highly diversified shapes of diatoms are a serious obstacle in their densification by die pressing. By conducting the sintering process at 1400°C for 1 h and using diatoms with larger particle sizes and a crystalline structure, we can produce a porous ceramic material with open porosity below 8 %, but with the pores within the diatoms closed. To obtain a high density bulk material, the diatoms should be selected according to size and shape. It is possible to achieve this when we use diatoms from a culture, where we can select one species with a desired morphology and multiply it. Preparing bulk materials from diatoms in the powder form, so as to preserve the pores naturally existing in the frustules, requires new methods of consolidations to be developed. The experiments in this area are in progress.

Acknowledgements

This research has been financially supported by the Polish Ministry of Science and Higher Education in 2008-2010, project no NN 507 438834.

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Received 1 March 2010; accepted 8 May 2010