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COMPOSITES THEORY AND PRACTICE

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THERMOELECTRIC PROPERTIES OF EXPANDED GRAPHITE AS FILLER OF MULTIFUNCTIONAL CEMENT COMPOSITES

This paper presents the results of investigations on the thermoelectric properties of expanded graphite obtained by different methods. The expanded graphite was subjected to thermal treatment by two different ways: by rapid heating in a furnace and by irradiated microwave. For each of the methods, graphite was expanded in different conditions for the purpose of investigating the influence of thermal treatment on their thermoelectric properties. The bulk density and thermoelectric properties (Seebeck coefficient) of expanded graphite were measured. The results of the investigations show that the method and time of thermal treatment have a major influence on the thermoelectric properties of expanded graphite.

Keywords: **cement composites, expanded graphite, Seebeck effect, smart materials**

WŁAŚCIWOŚCI TERMOELEKTRYCZNE GRAFITU EKSPANDOWANEGO JAKO WYPEŁNIACZA CEMENTOWYCH KOMPOZYTÓW WIELOFUNKCYJNYCH

W pracy przedstawiono wyniki badań właściwości termoelektrycznych grafitu ekspandowanego otrzymanego różnymi metodami. Wykorzystano dwie metody ekspandacji: przez gwałtowne podgrzanie w piecu laboratoryjnym oraz przez poddanie działaniu promieniowania mikrofalowego. W przypadku metody bezpośredniego ogrzewania proces prowadzono w różnej temperaturze w zakresie 500÷1000°C i przy różnym czasie ogrzewania, natomiast w metodzie mikrofalowej zmienną poza czasem procesu była moc dostarczona do próbki. Wyniki pomiaru współczynnika Seebecka pokazały, że metoda ekspandacji oraz czas procesu mają duży wpływ na otrzymane właściwości termoelektryczne grafitu ekspandowanego.

Słowa kluczowe: **kompozyty cementowe, grafit ekspandowany, efekt Seebecka, materiały wielofunkcyjne**

INTRODUCTION

Multifunctional composites exhibit, besides the basic standard features, additional properties which can be applied in some other way. Cement mortars and concretes with electric current conducting additives are a good example. The electric properties of these composites are variable, depending on some external stimulating factors, for example temperature changes, mechanical stress or humidity. The amount of additive should exceed the percolation threshold and form a continuous network with electrical contacts between particular conductive grains. Among the conducting additives which can be taken into account, short fibres are also used because their percolation threshold is attained at a few percent content. In this case, carbon fibres [1-3] and steel fibers [4, 5] were introduced to a cement matrix. However, it is possible to consider the use of some conductive powders, for example nanometric Fe_2O_3 [6], lightweight metal coated microfilers [7, 8] or graphite powder [9-11]. Fine graphite powder, particularly released during the polishing of graphite electrodes in plants and collected in dust filters is a hazardous waste. The implementation of this material as a filler in cement mortars or concretes could be a rational means of its disposal. However, in this case the percolation threshold is attained at a relatively high percentage of additive in the cement matrix (about 30%) [9]. Therefore, a high amount of hydrophobic additive has a significant effect on the rheological properties of the fresh mixture and moreover, the basic properties of the composites, e.g. the mechanical strength decreases. The simultaneous addition of lightweight fillers partially compensates the growth of the thermal conductivity coefficient [11].

Very promising results can be obtained when expanded graphite is introduced to cement composites. Expanded graphite is an extremely lightweight material produced by the rapid heating of graphite intercalated with oxidizing agents. The most conventional heating source is flame through. Alternative methods of intercalated graphite expansion are coupled plasma, laser irradiation or microwave irradiation. Among them, MW irradiation is very promising because it can be conducted at room temperature in a short time with less energy. The porous grains thus formed have a "bellows" - like shape and because of their low strength they can be disintegrated on mixing to form thin packs or even single nanometric flakes, uniformly distributed in the mixture. In the case of a cement matrix with expanded graphite, the percolation threshold can be significantly reduced (by at least 5 times) compared to a mixture with a fine graphite powder [12]. Its negative influence on the strength of cement based composites is small and in some cases a slight increase in bending strength of cement mortars due to the addition of expanded graphite were observed [13].

MATERIALS AND METHOD

Expandable graphite EG290 (Sinograf S.A., Poland) was used. This intercalated graphite was subjected to thermal treatment in two different ways. One was rapid heating in a laboratory furnace up to temperatures of 500, 600, 700, 800, 900 and 1000°C during different periods of up to 900 s for each temperature. Another method of thermal treatment was done by using microwave irradiation in a domestic microwave oven. The samples of expandable graphite were irradiated at 280, 560, 670, 920, 1200 and 1400 W/g, for 15, 30 and 60 s, for each power respectively.

TABLE 1. **Characteristics of used expandable graphite (EG290)**
TABELA 1. **Charakterystyka grafitu expandowalnego EG290**

Carbon content	90%
Granulation	0.2÷0.6 mm
Expansion	200÷300 ml/g
Volatiles max.	<15%
Bulk density	~0.5 g/cm^3

After expansion the fixed quantity of graphite was investigated. In this case, the expanding conditions were 500°C, 15 seconds and 120 W/g. The shortest period of expansion (15 seconds) was probably insufficient to obtain well expanded graphite.

The Seebeck coefficient is measured when both ends of the sample are at different temperatures. Here it was measured in such a way that the temperature set as a benchmark - is at 10°C, and the other was fixed in the sequence of 20, 40 and 60ºC. The temperature of each plate was stabilized by an independent ultrathermostat. The expanded graphite was placed in a polymer tube. On the ends of the polymer tube there were electric contacts from thin sheet copper. The differences in temperature during the measurements were 20, 40 and 60°C respectively, in relation to the 10°C set as the reference temperature.

RESULTS

Figure 1 shows the results of the the bulk density of the expanded graphite for thermal treatment by rapid heating. With increasing expanding temperature, the bulk density value decreases. The lowest bulk density obtained by the temperature of 1000°C was a value of about 0.004 g/cm^3.

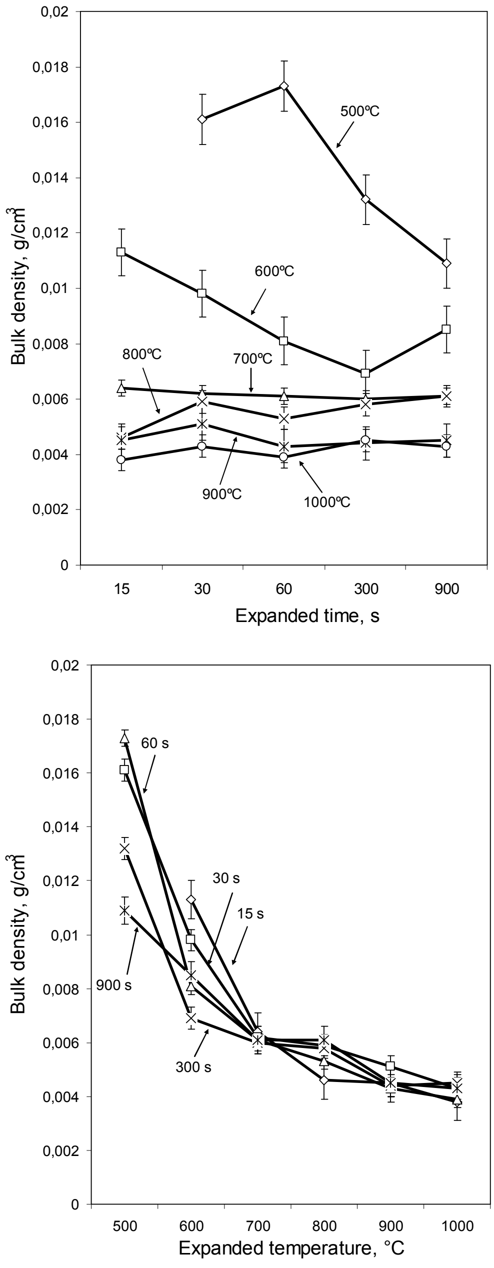

Fig. 1. Bulk density of expanded graphite as function of expanded time at different temperatures using direct rapid heating method

Rys. 1. Gęstość objętościowa grafitu ekspandowanego w funkcji czasu ekspandacji dla różnych temperatur procesu prowadzonego metodą klasyczną bezpośredniego ogrzewania w piecu

For temperatures from 700 to 1000°C, the bulk density decreases slightly, whereas for the expanding temperatures of 500 and 600°C, the graphite bulk density decreases considerably. Moreover the of bulk density value decreases with increasing time of expansion for the temperatures of 500 and 600°C, in contrast for temperatures from 700 to 1000°C, the graphite bulk density value remains constant despite the fact that the process time increases.

It can be seen in Figure 2, that the bulk density value slightly depends on the microwave power and the time of this thermal treatment. Hence it is difficult to determine which expanding conditions are the best to obtain the lowest of bulk density value. Moreover the bulk density values for the microwave irradiation method are higher than for the rapid heating method.

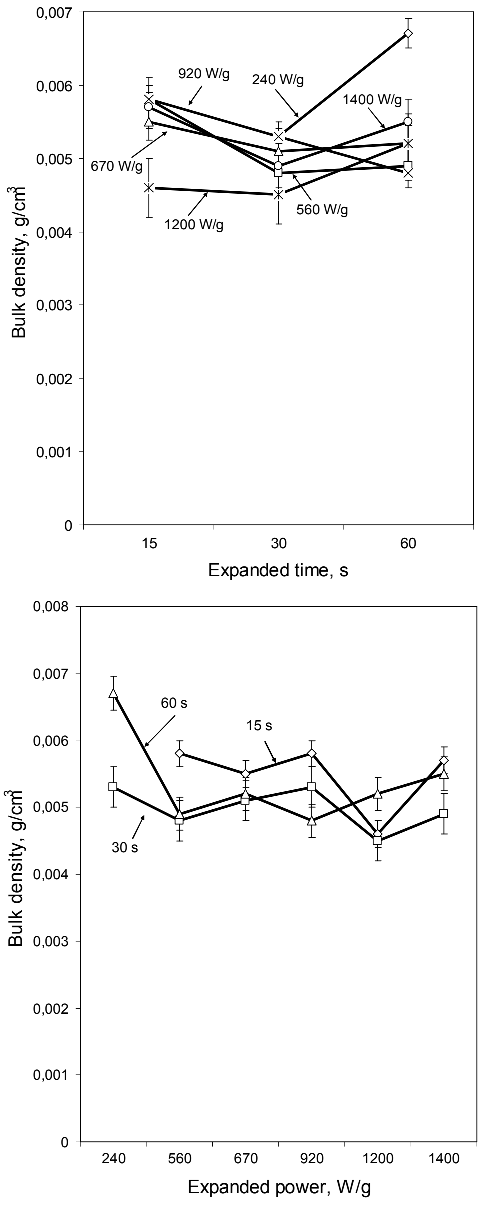

Fig. 2. Bulk density of expanded graphite as function of time for each microwave power

Rys. 2. Gęstość objętościowa grafitu ekspandowanego w funkcji czasu procesu dla różnej mocy dostarczonej do próbki metodą mikrofalową

The results of the Seebeck coefficient show that the thermal treatment method and expansion conditions have a major impact on the thermoelectric properties of expanded graphite. Figure 3 shows the results of the Seebeck coefficient for the thermal treatment of graphite by rapid heating. The highest Seebeck coefficient value was achieved by the temperature equaling 500 (27 μV/K) and slightly less for 600°C (24 μV/K). The Seebeck coefficient value obtained at 700°C is significantly lower than for the temperatures of 500°C and 600°C and reached the highest values at 15 s (12.5 μV/K). The temperatures of 800, 900 and 1000°C, achieved the lowest Seebeck coefficient values. The value obtained for these temperatures varies between 5 to 7 μV/K for each expansion time and it is quite constant. In contrast, for lower temperatures (below 800°C) with increasing time, the Seebeck coefficient value significantly decreases. The values were 12, 9 and 7 μV/K for each temperature and process time equal to 15 min.

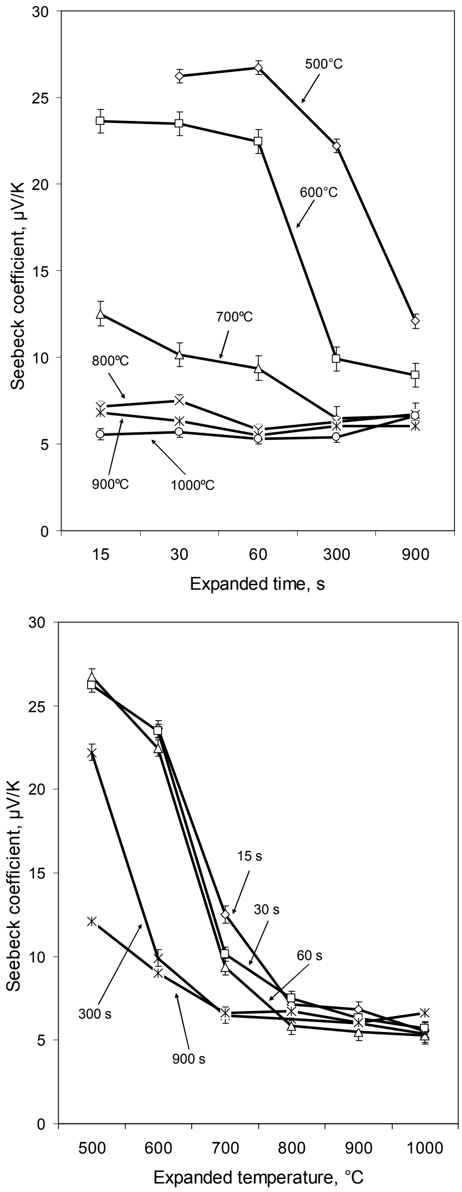

Fig. 3. Seebeck coefficient as function of time of expansion for each temperature using rapid heating method

Rys. 3. Współczynnik Seebecka w funkcji czasu ekspandacji dla różnych temperatur przy ogrzewaniu w piecu

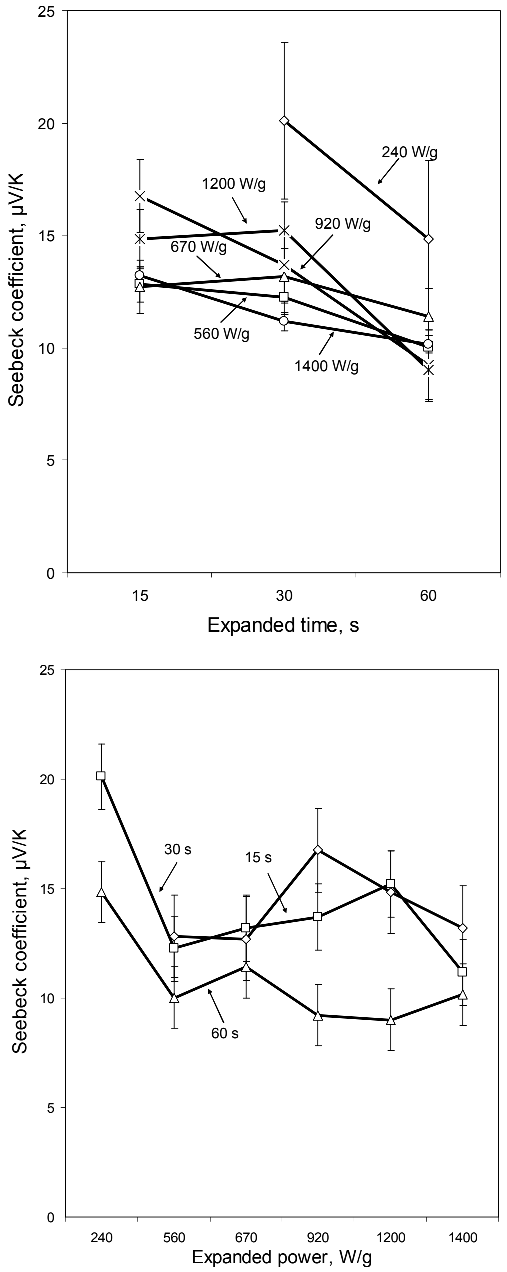

Fig. 4. Seebeck coefficient as function of expanded time for each power using microwave method

Rys. 4. Współczynnik Seebecka grafitu ekspandowanego w funkcji czasu ekspandacji dla różnych mocy dostarczonych do próbki metodą mikrofalową

In contrast to the results obtained by direct rapid heating in a furnace, increasing the power and expansion time does not have a strong influence on the Seebeck coefficient value. The Seebeck coefficient value for the microwave method slightly depends on the expansion process parametric. In this means of thermal treatment, the Seebeck coefficient value does not decrease with increasing power. The thermoelectric properties of expanded graphite for such thermal treatment are less predictable than in the classic rapid heating method. When comparing these two methods of expanded graphite, it can be seen that the Seebeck coefficient values for the microwave method are about three times higher than for the rapid heating method for the same bulk density of expanded graphite.

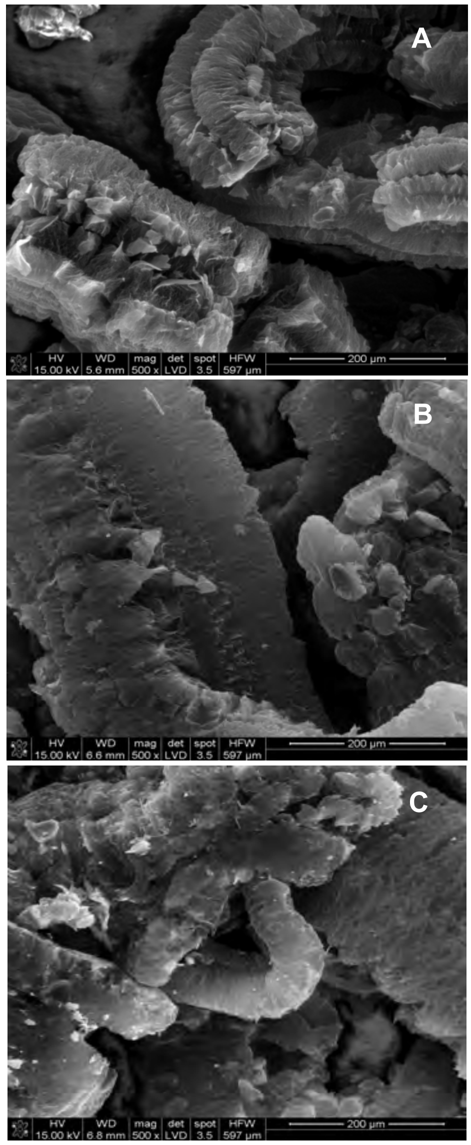

Fig. 5. SEM microphotograph of expanded graphite grains after rapid heating in conditions: A) 500°C/30 s, B) 600°C/30 s, C) 1000°C/15 s.

Rys. 5. Obserwacje SEM ziaren grafitu ekspandowanego metodą szybkiego podgrzewania w warunkach: A) 500°C/30 s, B) 600°C/30 s, C) 1000°C/15 s

The SEM observation of expanded graphite by rapid heating revealed that at the lower expanding temperature (especially at 500°C and to a lesser degree at 600°C) unexpanded or partially expanded grains of graphite remained. For the higher expansion temperature, the graphite grains are well expanded. In the case of thermal treatment by microwave irradiation, the SEM observations show that the microstructures of the expanded graphite grains are quite similar or the differences are insignificant, even between the two extreme expansion conditions. The microstructure of the expanded graphite using the microwave method is also similar to that obtained by the rapid heating method at 1000°C.

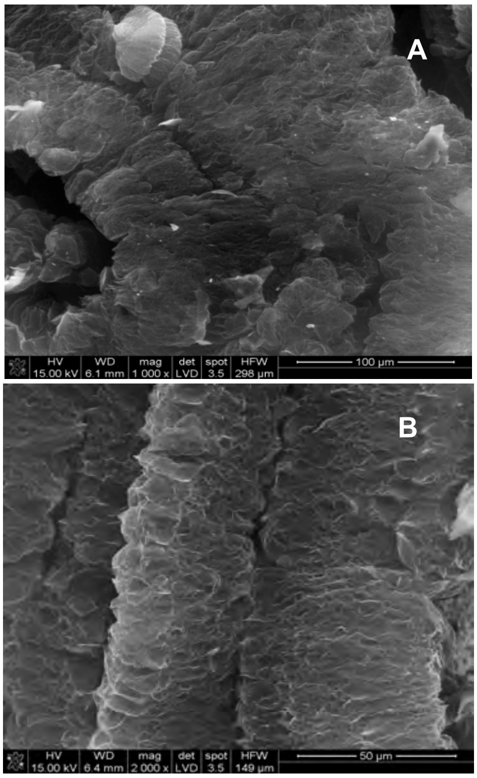

Fig. 6. SEM microphotograph of expanded graphite grains after microwave irradiation in conditions: A) 120 W/g, 30 s, B) 700 W/g, 60 s

Rys. 6. Obserwacje SEM ziaren grafitu ekspandowanego metodą mikrofalową w warunkach: A) 120 W/g przez 30 s, B) 700 W/g przez 60 s

CONCLUSIONS

Based on the results of the experiments, it can be observed that the means and conditions of thermal treatment have a major influence on the thermoelectric properties of expanded graphite. In the rapid heating method of graphite expansion with increasing temperature, the of Seebeck coefficient value decreases significantly. Moreover the Seebeck coefficient value decreases with increasing process time for the lower temperatures. The thermoelectric properties of expanded graphite obtained by microwave irradiation are less predictable, but the Seebeck coefficient value in this method of treatment is about three times higher than for the rapid heating method.

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