# Thermal conductivity of 2D C–C composites with pyrolytic and glass-like carbon matrices

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## ARTICLE INFO

## ABSTRACT

This study examines the relationship of thermal properties of C–C composites with structural and micro-structural features resulting from specific processing steps. Samples were made with the same type of fibres, but using two distinct different methods of matrix formation: liquid impregnation with phenolic resin and the P-CVI technique. In both cases, thermal treatment after densification had decisive effect on increase of composite coefficient of thermal conductivity, due to crystallization of carbon matrix material and thus increase of its own thermal conductivity. Higher values of thermal conductivity were obtained using the pyrolytic carbon matrix processing.

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## 1. Introduction

Current and prospective thermal properties of C–C composites witness growing interest, particularly their thermal conductivity and thermal resistance. However, unlike for more popular mechanical properties, there is no abundance of published literature on problems related to thermal properties of carbon composites [1]. These properties result from contribution of different crystalline phases constituting both fibre and matrix materials. The variety of crystalline structures of carbon fibres as well as the multitude of available carbon matrices, additionally complicated by various possible spatial lay-outs of fibres, may significantly affect the final measured values and thus possible applications.

Thermal properties of carbon matrix in C–C composites depend very strongly on the microstructure of carbon material constituting the matrix [2–5]. In the case of carbon composites made of polymer precursors of matrix material, thermal conductivity is also affected by the type of fibres used in the processing [6,7]. The qualitative relations of thermal conductivity of these strongly anisotropic materials may be generally appropriate, however, the measured values do not correspond to the values expected on the basis of simple rule of mixtures for this type of composite material.

Thermal conductivity of different C–C composites was extensively studied by Kulkarni and Brady [8]. These authors have shown that thermal conductivity of carbon composites cannot be related in a simple way to technological parameters, due to com-

plexity of processes occurring during their fabrication. Composite materials with different spatial arrangement of fibres that they examined were characterized by the isotropy of thermal conductivity, which was quite opposite to the results presented by Fitzer and Heym [6]. Also Laramee et al. [9] have published the results incompatible with Fitzer and Heym, while the high values of thermal conductivity in the direction vertical to fibres could appear somewhat astonishing. However, the authors did not elaborate on these discrepancies, neither did they explain the high value of conductivity obtained.

Physical properties of C–C composites after neutron irradiation were analyzed by Buzhinskij et al. [10]. It was shown that composite deformation takes place dependent on type of fibres, their direction in the carbon matrix and interaction between the carbon fibres and the matrix. Carbon fibres made of polyacrylonitrile (PAN) showed anisotropic size deformation upon neutron irradiation in a carbon matrix; a shrinkage along the fibre axis and swelling in the perpendicular direction [11].

Curry et al. [12] examined thermal conductivity of composites made of graphitized carbon fabric and phenolic resin as a matrix precursor. After first carbonization, the composite has been impregnated threefold with use of furfuran resin and further carbonized. Very low values of thermal conductivity at room temperatures have been found, of the order of 5 W/(mK) along fibres and 3 W/(mK) in perpendicular direction. The values of thermal conductivity increased with increasing temperature, however, these results are substantially different from the majority of results found in other existing publications.

Carbon–carbon composites obtained from pitch precursors are most often processed by pressure impregnation of carbon fibres and consecutive carbonization. As a rule, these processes are

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being repeated several times, until sufficiently high density of the material is obtained. The coefficients of thermal expansion measured in C–C composites processed by thermal decomposition of coal tar mesophase pitches are usually higher that those measured in composites obtained from polymer precursors with identical architecture of fibre packing [13].

Thermal conductivity of C–C composites at high temperatures was examined by Luo et al. [14] and Manocha et al. [15]. Both these works confirmed strong effect of temperature on thermal conductivity, which could have been expected, since the amplitude of atomic vibrations in crystalline lattice increases with increasing temperature, therefore increases the phonon–phonon interaction which is responsible for thermal conductivity [16].

The analysis of published works on thermal conductivity of carbon composites indicates that many issues are not fully recognized yet and the relationships of measured thermal properties with technological parameters of fabrication processes are not quite well defined. The majority of works on carbon composites concentrates on examination of the relationship of processing parameters with mechanical properties.

The present study is devoted to examination of the effects of processing parameters on thermal properties of carbon–carbon composites. Particular attention is paid to understanding the relationship between the different technological stages of carbon composite manufacture and resulting coefficient of thermal conductivity.

## 2. Materials

Two different methods of C–C composite processing were used for sample preparation in this study. First consisted of building the carbon matrix from phenol–formaldehyde resin by thermal treatment in solid phase, while in the second method, the process of matrix carbon crystallization occurred from gas phase precursor (propane). Considering different types of matrix materials being formed during thermal treatment of so different precursors, it was expected that the assumption regarding the effect of the type of the matrix material on thermal properties of carbon composites may be better verified this way.

### 2.1. Sample processing by liquid impregnation with phenolic resin

Following components have been used for processing of C–C composite samples:

- phenol–formaldehyde (F–F) resin,
- carbon fabric (designated 886), made of carbon fibre M40-3K (HM, Torayca Manuf.). Fibres had the coefficient of thermal expansion 80 W/(mK).

In the first stage, the prepregs were prepared in form of sheets containing carbon fibre fabrics saturated with F–F resin in the 1:1 ratio. Prepregs were dried for 20 h at the temperature of 40 °C and then flat sheets with dimensions $250 \times 50$ mm were stock-piled to make a layer of five prepregs. The sample was placed in metal mould for isostatic pressing, then transferred to an autoclave and subjected to pressing under 20 bars. The mould containing prepregs was heated to the temperature of 160 °C at the rate of 30 °C/h and then cooled to room temperature. After curing, 1 mm thick laminate was obtained, from which samples were cut with dimensions $10 \times 77 \times 1$ mm. Carbonization of laminate samples was carried out in vacuum, up to the temperature of 1000 °C. After first carbonization the samples had relatively high porosity, reaching 25%. Four consecutive cycles of impregnation with F–F resin have been applied, each followed by re-carbonization processes.

In the last processing step samples were submitted to high temperature treatment at 2200 °C.

### 2.2. Sample processing with pulse P-CVI technique

Before actual sample fabrication, several preliminary experiments were carried out in order to define the optimum processing parameters. The applied variations of pressure and time of filling and emptying the P-CVI reactor are shown in Fig. 1.

Following were the conditions of impregnation of composite samples with use of P-CVI method:

- propane pressure in reactor $P_{max}$ = 500 mbar,
- time of filling the reactor $t_n$ = 5 s,
- evacuation time $t_0$ = 10 s,
- temperature of pyrolysis process −930 °C.

In fabrication of C–C composite samples with use of this method technical propane was applied and the same type fibres as used before for preparation of samples from F–F resin.

## 3. Methods

Thermal properties of C–C composite materials were determined at each stage of technological process and the components of both matrix precursors and carbon fibres were subjected to examination separately. The changes of geometric dimensions, mass, structural and microstructural parameters of fibres and matrix material were carefully examined at each stage of composite processing. The examination of crystalline structure of composite samples was carried out using RXD method and from Scherrer's equation the crystallite size $L_c$ was determined based on the measurement of half-intensity width of (0 0 2) and/or (0 0 4) X-ray band. The fibre volume fraction of the composite samples was estimated by weighing the fibres and the composite samples and knowing the density of both components. The estimated volume fraction of both types of C–C composite sample was about 50% with the accuracy of 10%.

The coefficient of thermal conductivity was determined using the cut–bar (comparative) method in Steady-State Thermal conditions. The composite samples for this technique were prepared in the form of plates with dimensions $20 \times 30 \times 1$, (cut from the composites after carbonization). In this technique, a test system was composed from two plates of a standard material and the unknown sample (carbon composite). The unknown material was placed between two standards. One end of the standard plates has an electrical heater, while the other end has an electrical heater connecting with heat sink. Two thermocouples were mounted in each segment of the system. Measurements were made by establishing the desired mean temperature and a temperature differential of 10–25 °C across the system with two heaters. When equilibrium was reached, the temperature differences across the composite sample and the standard references were determined.
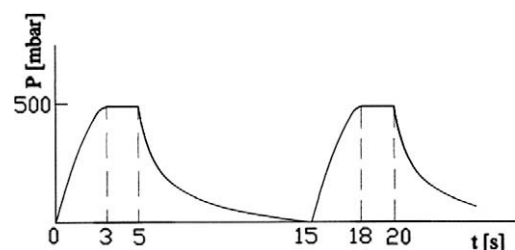


Fig. 1. Propane pressure variations during filling and evacuation of reactor.

Thermal conductivity was calculated using the formulae: $\lambda_c = \lambda_s \Delta T_s / \Delta T_c$, where

$\lambda_c$ – thermal conductivity of composite sample,
$\lambda_s$ – thermal conductivity of standards,
$\Delta T_s$ – temperature difference across standards,
$\Delta T_c$ – temperature difference across composite sample.

This relationship is valid if cross-sectional area of standard and composites and distances between thermocouples are the same. The measurements were made in the temperature range below 100 °C.

Due to applying plain weave carbon fabric (two directional layup), 2D composite materials were obtained. In such samples, there are two main directions of carbon fibre alignment. Due to anisotropic character of the carbon composites thermal conductivity measurements were realized in one of two main directions of the carbon fibre alignment. In both directions (0°, 90° fibre direction) the fibre volume fractions were the same (about 25%). In order to determine and to distinguish the effect of components in the composite (carbon fibres, pyrolytic phase, phenolic-derived matrix), the samples of pure pyrolytic carbon (without carbon fibres) were also obtained separately by CVD method with the use of propane as a source of carbon and by curing and carbonization of pure phenol–formaldehyde resin.

## 4. Results and discussion

### 4.1. Composites obtained from prepregs

Composites with polymer F–F matrix (phenol–formaldehyde resin), being a substrate for carbon composite and designated as No. 0, were subjected to thermal treatment to temperature of 1000 °C without impregnation. Porous C–C composite samples were subjected to consecutive cycles of impregnation with alcohol solution of F–F resin and re-carbonization in order to increase their density. The efficiency of this process was controlled by apparent density measurements. The effects of impregnation of porous carbon matrix and following thermal treatment on sample density after each cycle of their fabrication are presented in Fig. 2. The plots show the variation of apparent density and porosity of composite samples resulting from consecutive cycles of impregnation and re-carbonization, also after additional thermal treatment in different temperatures. The density of initial composite made of
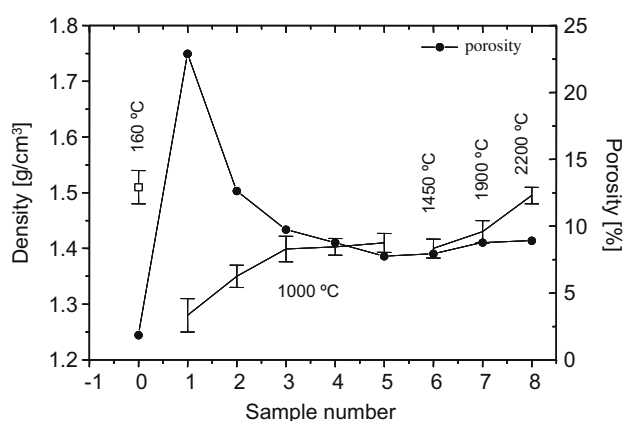
carbon fibres and polymer matrix is also shown in this diagram. This apparent density of the initial composite is about 1.51 g/cm$^3$, and its porosity does not exceed 1%.

Changes of open porosity shown in this diagram correspond to real processes accompanying consecutive stages of impregnation, carbonization and graphitization. The apparent density of composite (No. 1) strongly decreases due to thermal decomposition of polymer matrix and due to formation of the system of open and closed porosity. This stage is accompanied by particularly strong increase of open porosity and the final porosity equals 23%. Total porosity decreases after following processes of impregnation/re-carbonization, however, the rate of decrease is much slower than in the case of first two cycles. The curve of increase of density at this stage of composite fabrication shows that further impregnations and carbonizations at 1000 °C are not effective. This confirms the process of filling the open pores with carbon, particularly those of large dimensions, while closed porosity remains unchanged at this stage.

Composite samples were subjected to thermal treatment at three distinct temperatures in these experiments: 1450, 1000 and 2200 °C. Results are indicated by points 6–8 on X-axis (Fig. 2). Initially, no density increase of carbon matrix can be seen after thermal treatment at 1450 °C. At higher temperatures porosity changes are more pronounced, particularly after treatment at 2200 °C. Finally, the value of apparent density of C–C composite was obtained almost equal to that of initial composite. These results prove that the effect of multiple impregnation of carbon matrix and consecutive carbonization of the composite may be beneficial only until the fourth cycle, after which the impregnation process becomes inefficient. This was confirmed by the examination of geometric dimensions of composite samples, performed with use of standard metallographic microscope. Dimensional changes of composite samples were examined corresponding to their length, width and height. These results proved that densification and carbonization cycles affect only the thickness of the samples, while changes in length and width were not noticeable. Changes occurred mostly during the thermal treatment process and not in densification stage. This was related to both structural (reduction of $d_{002}$ parameter) and microstructural changes of the matrix material, which is shown clearly in Table 1.

Results shown in this table indicate that more pronounced changes of X-ray measured parameters occur above 1900 °C and they relate to matrix material, while the fibres do not undergo any serious structural changes. These results from their manufacturing technology, where they are already subjected to high temperature treatment, therefore, their structural parameters are well formed. The carbon matrix significantly changes its values of $d_{002}$ corresponding to the basic structural parameter of carbonic substance. This value is still quite remote from the value typical for well crystallized graphite structure ($d_{002} = 3.35$ Å), however, the changes of interplanar distance from initial 3.67 Å to the value of 3.51 Å entail the observed changes of sample geometry relative



**Fig. 2.** The variation of apparent density and porosity of C–C composite samples as a function of number of impregnations and the temperature of thermal treatment. Note: sample denoted 0 is the fibre/polymer composite, samples 1–5 are C–C composites after consecutive impregnations and carbonizations, samples 6–8 are materials after additional thermal treatment.

**Table 1**
Crystallographic parameters of carbon fibres and carbon matrix after different stages of thermal treatment.

| Crystallographic parameter | Thermally treated in temperatures from 1000 to 2200 °C | | | |
|---|---|---|---|---|
| | 1000 | 1450 | 1900 | 2200 |
| *Carbon fibres M40* | | | | |
| $L_c$ [Å] | 87 | 88 | 88 | 91 |
| $d_{002}$ [Å] | 3.41 | 3.41 | 3.41 | 3.40 |
| *Carbon matrix* | | | | |
| $L_c$ [Å] | 11 | 10 | 17 | 21 |
| $d_{002}$ [Å] | 3.67 | 3.68 | 3.63 | 3.51 |

to its thickness. The increase of density of the composite results from both the decrease of porosity, particularly during the first cycles of densification, as well as the decrease in $d_{002}$ parameter of the matrix. These changes also entail the changes in thermal conductivity of the composite, which will be discussed in more detail further.

### 4.2. Thermal conductivity of C–C composites from prepregs

Variations of the coefficient of thermal expansion $\lambda$ of C–C composite resulting from consecutive steps of densification and thermal treatment are shown in Fig. 3.

The diagram unequivocally points at strong influence of thermal treatment on thermal conductivity of carbon composite samples. The effects of initial stages of densification and carbonization are weak and composite conductivity may be approximately described by the rule of mixtures, which allows to estimate the contribution of each component phase (fibres and matrix) to thermal conductivity of composite material. Considering that the parameters $d_{002}$ and $L_c$ of the matrix are subjected to additional and noticeable changes after thermal treatment to 2200 °C, it may be assumed that significant improvement of thermal conductivity occurs due to thermal treatment, leading to structural changes of C–C composite matrix itself. This statement may be additionally confirmed by the cumulative diagram, showing the effects of thermal treatment on thermal conductivity of, respectively: pure carbon from decomposition of polymer matrix material, fibres taken alone and C–C composite made of these components (Fig. 4).

This diagram shows the changes of carbon matrix crystallite size, resulting from thermal treatment of analyzed composites. The values of $L_c$, corresponding to ordered lattice areas in [0 0 2] direction in the matrix were determined analytically from decomposition of complex X-ray band corresponding to (0 0 2) plane. In the case of carbon composite, this band is made of sub-bands related to sets of planes within fibre crystallites and to sets of matrix crystallite planes.

As it can be seen from Fig. 4, thermal conductivity of both pure carbon fibres and that of pure matrix material (glass-like carbon) are not subjected to changes. Within the scale range taken for Y-axis the variations of thermal conductivity of pure matrix material are formally negligible, changing from 0.24 W/(mK) to 0.42 W/(mK). These values are typical for glass-like carbons obtained from polymeric precursors. Such small changes cannot be held responsible for significant increase of thermal conductivity of carbon com-
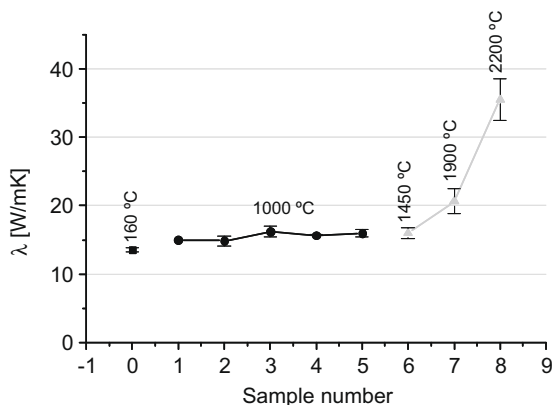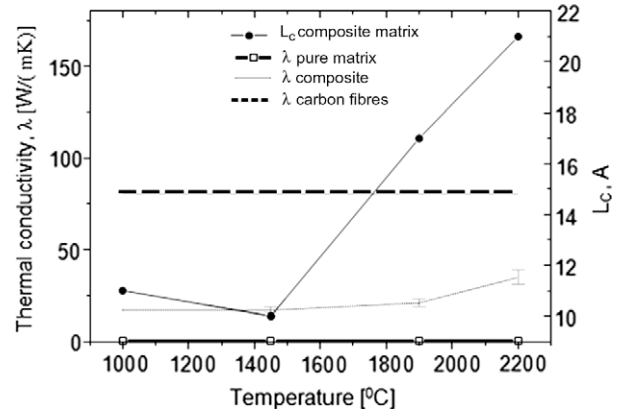


**Fig. 4.** Effects of temperature of additional thermal treatment on thermal conductivity of carbon fibres, pure matrix materials, as well as on the size of carbon crystallites in composite matrix in the presence of fibres.

posite from the value of 17 W/(mK) to 37 W/(mK) within the examined range. It seems to be appropriate, therefore, to interpret the changes of thermal conductivity of composites in relation to curve $L_c$ of the matrix in function of temperature. Since thermal conductivity of fibres does not change during the processing of composites, it appears that the most important role in increase of thermal conductivity of C–C composite may be attributed to changes of structural and microstructural parameters of the matrix after additional thermal treatment of these composites in temperatures of the order of 2200 °C.

Table 2 compares the values of coefficient of thermal conductivity $\lambda$ of the examined composite, as determined experimentally and also as estimated from the rule of mixtures, considering the values for pure components. Calculations were done for composite samples obtained after thermal treatment in 1000 and 2200 °C, for parallel model of the composite made of fibres with volume content 25%, oriented in the direction of conductivity. Total volume content of fibres in the examined 2D carbon composite was set at 50%. Two directional carbon composites have good conductivity along the fibre direction. For two phase system composite system, the simple formulae can be written as follows: $\lambda_c = \lambda_f V_f + \lambda_m V_m$, where $\lambda_c$ is a thermal conductivity of composite, $\lambda_f V_f$ and $\lambda_m V_m$ denote contributions to thermal conductivity of carbon fibres and porous carbon matrix, respectively. Since $\lambda_m V_m \ll \lambda_f V_f$, it can be further written that, $\lambda_c \sim \lambda_f V_f$. In other words, the heat is conducted largely by better conductor (Table 2) and the contribution of matrix material in total thermal conductivity of the composite can be neglected in calculations. Thus, the resulting calculated values of composite thermal conductivity are practically the same [20 W/(mK), $V_f = 25\%$,], irrespective of the temperature of final thermal treatment. The comparison shows clearly that for carbon composite after thermal treatment in 1000 °C, the value of the coefficient determined experimentally is slightly lower than the value calculated from a simpler rule of mixtures. However, for carbon composite subjected to thermal treatment at higher temperature (2200 °C) the relationship is reversed and the experimentally



**Fig. 3.** Variations of coefficient of thermal conductivity $\lambda$ resulting from cyclic stages of densification and re-carbonization (samples 1–5), also after additional thermal treatment (6–8). Point 160 °C represents polymer matrix composite. Other symbols are the same as in previous Fig. 2.

**Table 2**
Comparison of coefficients $\lambda$ for carbon composites and their components, determined experimentally and estimated from rule of mixtures.

| Parameter $\lambda$ W/(mK) [°C] | Components | | Composite | |
|---|---|---|---|---|
| | Fibres | Matrix | Experiment | Rule of mixtures |
| 1000 | 80 | 0.24 | 17 | 20 |
| 2200 | 80 | 0.42 | 37 | 20 |

determined coefficient of thermal conductivity of the composite almost doubles that calculated from the rule of mixtures.

The effect of matrix material on thermal properties of the composite seems to be quite obvious from the presented data. All the data confirm significant influence of the presence of carbon fibres on forced re-crystallization of composite matrix during high temperature treatment. Carbon phase of almost amorphous structure (glass-like carbon) is being formed during carbonization only in the conditions of absence of other phases. When carbon matrix crystallizes in solid state in presence of anisotropic fibres, it is probable, that the ordering of the structure of glass-like carbon takes place and as a consequence, the contribution of carbon matrix in heat transport processes becomes more pronounced. Structural and microstructural parameters of pure carbon, originating in pyrolysis of phenolic resin, do not vary significantly due to additional thermal treatment up to 2200 °C in the absence of carbon fibres. However, they do change seriously in the presence of carbon fibres, i.e. within the composite microstructure.

Thermal properties of carbon composite processed from polymer resin are being formed in the process of densification and high temperature treatment, the latter causing a twofold increase of coefficient $\lambda$, as compared to the value after carbonization.

### 4.3. Composite obtained by the P-CVI method

Fig. 5 presents the variations of apparent density and porosity of carbon composite as a function of number of pulses during the densification phase of manufacturing. The process of vapour infiltration was carried out at the temperature of 930 °C.

Since the time of single pulse and the total number of P-CVI pulses are known, the horizontal axis of the plot indicates also the duration time of densification process. Initially the preform, constituting the scaffold made of piled up sheets of carbon fabric, has the density of 0.83 g/cm$^3$, and the porosity ~55%. After the first stage of densification (10 000 pulses), the perform is still strongly porous as its open porosity is still high. The apparent density after initial infiltration is of the order of 47%. Following further saturation steps, composite density visibly increases and then levels at ~1.42 g/cm$^3$. Further saturation cycles do not bring about the decrease of composite samples' density. The open porosity in this type of composite samples is of the order of 23%, and it is much higher after densification process than in the samples obtained via the prepreg technique. Similarly to composites processes by the prepreg method (with use of F–F resin), the C–C composites processes by P-CVI technique were subjected to next step of ther-
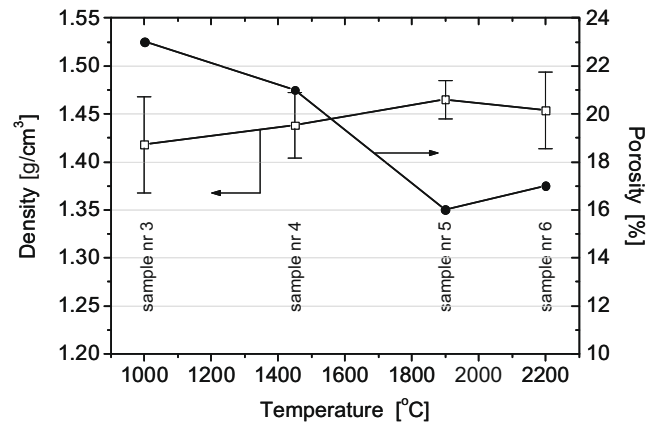


**Fig. 6.** Variations of apparent density and open porosity of C–C composite processed by the P-CVI method, accompanying the additional thermal treatment and final densification (5000 pulses).

mal treatment at the temperature of 2200 °C. The variations of apparent density and porosity accompanying this thermal treatment process are presented in Fig. 6.

Sample 3 in this diagram corresponds to carbon composite after pulse infiltration terminated at the stage of the process carried out to the temperature of 1000 °C (density 1.42 g/cm$^3$). In the following stages, the samples were subjected to additional treatment in temperatures of 1450, 1900 and 2200 °C. After each treatment final saturation of 5000 pulses was added. As the diagram shows density changes accompanying thermal treatment and pulse impregnation are small, in fact much smaller than in the case of density variations observed in the previous method. At the same time, the decrease of porosity of the samples can be observed to the level of 17%. Since the pyrocarbon matrix belongs to the group of materials prone to graphitization, it may be assumed that the variations of composite apparent density are related to increase of ordering of crystalline structure of pyrocarbon matrix itself.

### 4.4. Thermal conductivity of composites processed by the P-CVI method

The effects of saturation and thermal treatment on coefficient of thermal conductivity of C–C composites processed with use of P-CVI method may be followed from the plot in Fig. 7. General trend in changes of coefficient of thermal conductivity is similar to behaviour of carbon composite obtained by prepreg method, with use of F–F resin as the matrix precursor. This relationship indicates strong effect of temperature on the value of thermal conductivity. It is worthwhile to note that the coefficient $\lambda$ is much higher in the case of C–C composite obtained with use of P-CVI method.

In order to better understand thermal behaviour of this composite the X-ray analyses of components were performed after each phase of thermal treatment. Diffractograms were analyzed separately for powdered composites, fibres and matrix material in form of pyrolytic carbon grown on quartz substrate. The pyrolytic carbon samples were subjected to thermal treatment at the same temperatures as the composite. Composite diffractograms were analyzed within the angular range $2\theta$ corresponding to (0 0 2) plane reflections. The values of $L_c$ and $d_{002}$ for different carbon components were determined and the results are given in Table 3.

Values of $L_c$ and $d_{002}$ displayed in this table indicate that thermal treatment leads to significant changes of structural and microstructural parameters of carbon matrix material. Compared to previously analyzed parameters of F–F resin based matrix, the changes in pyrolytic carbon matrix are much more pronounced.
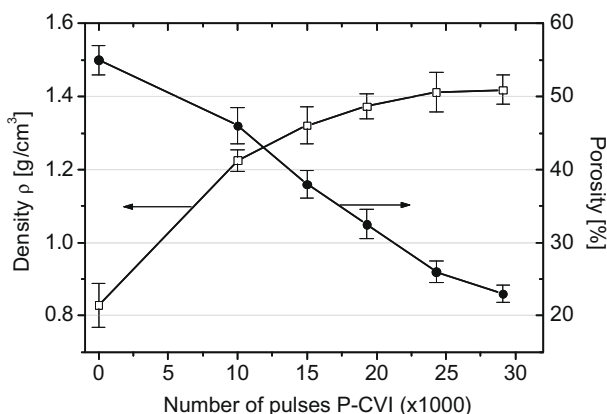


**Fig. 5.** Variations of apparent density and porosity of carbon composites as a function of number of densification pulses applied to carbon preform. Point (0) on X-axis corresponds to initial sample made uniquely of carbon fabric preform before densification.
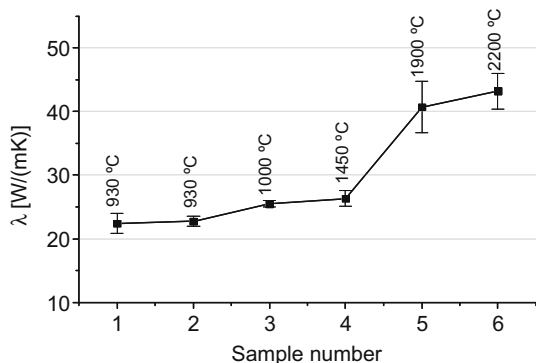
**Fig. 7.** Changes of thermal conductivity caused by P-CVI at 930 °C (points 1 and 2) and subsequent thermal treatment at higher temperatures (points 3–6).

**Table 3**
Structural and microstructural parameters of individual components of C–C composite obtained with use of the P-CVI method.

| Crystallographic parameter | Temperature of treatment from 1000 to 2200 °C | | | |
|---|---|---|---|---|
|  | 1000 | 1450 | 1900 | 2200 |
| *Carbon fibres M40* | | | | |
| $L_c$ [Å] | 87 | 88 | 88 | 91 |
| $d_{002}$ [Å] | 3.41 | 3.41 | 3.41 | 3.40 |
| *Pyrocarbon matrix* | | | | |
| $L_c$ [Å] | 21 | 29 | 109 | 148 |
| $d_{002}$ [Å] | 3.45 | 3.42 | 3.41 | 3.38 |

The data obtained may serve as rational basis for explanation of different values of coefficients of thermal conductivity of two types of composites analyzed.

The results of examination of fibres alone after different stages of thermal treatment indicate clearly that their thermal properties are stable. The coefficient of thermal treatment of these fibres is reported by manufacturer to be 80 W/(mK).

In the first stages of saturation the carbon composite as a preform had the coefficient $\lambda$ within the range from 22 do 26 W/(mK). Seen the fact that fibre volume content along the direction of conductivity did not exceed 25% (2D composite), the determined value of this coefficient conforms well with the value calculated from the rule of mixtures. This proves that carbon fibres are mainly responsible for thermal conductivity of this composite. However, situation changes when samples are subjected to additional thermal treatment in high temperatures, from 1450 to 2200 °C. To clarify this, thermal conductivity of pyrolytic carbon has been determined independently, using samples obtained in form of flat plates. After being subjected to thermal treatment at 2200 °C, these samples showed the values of coefficient $\lambda$ of the order of 183 ± 25 W/(mK). Obviously, these values exceed thermal conductivity of carbon fibres alone. Since the microstructure of C–C composite after multiple saturation with use of P-CVI technique has a form of fibre skeleton tightly surrounded by highly crystalline pyrocarbon phase, it may be accepted that matrix material also contributes to thermal properties of C–C composite subjected to thermal treatment. Considering the volume content of the matrix and the determined value of its coefficient $\lambda$, it appears obvious that its contribution to thermal properties of the composite is even more pronounced than that of the fibrous phase and these results in significant increase of the total thermal conductivity of this composite. The effect of temperature of thermal treatment on thermal conductivity of C–C composite and its components separately is shown in Fig. 8.
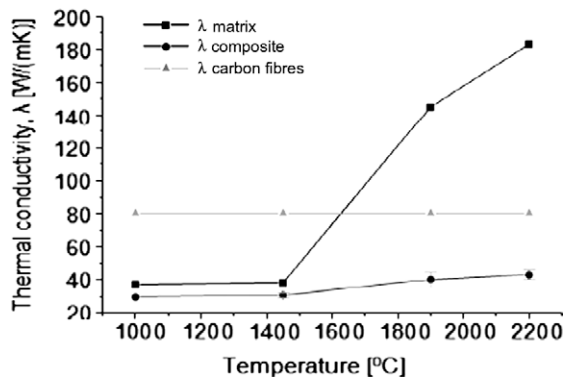


**Fig. 8.** The effects of temperature of thermal treatment on thermal conductivity of carbon composite made by P-CVI method, and its constituents.

The curve relative to carbon matrix is somewhat different from that obtained for polymer precursor in the same system of coordinates. The pyrocarbon phase readily undergoes graphitization in the presence of carbon fibres, which entails significant increase of its thermal conductivity. For temperatures of thermal treatment above 1900 °C, the value of thermal conductivity of pyrocarbon exceeds the conductivity of fibres, therefore, the resultant increase in conductivity of C–C composite is related to larger contribution of the matrix itself.

Thermal conductivity of C–C composite processed with use of P-CVI method is higher than that obtained from polymer precursor, as in this case the matrix contribution to thermal energy transport is much more pronounced than in polymer precursor case. Significant contribution of pyrocarbon matrix to thermal conductivity results from better structural ordering. Since the pyrocarbon matrix is a better thermal conductor than the fibre phase, its contribution to thermal conductivity is much more significant than that of fibres. The qualitative effects of two basic technological parameters of composite manufacturing process (impregnation, thermal treatment) using the P-CVI method are generally similar to these effects observed during processing from polymer precursor.

## 5. Conclusions

- The character of matrix precursor used in processing has the decisive effect on thermal properties of C–C composite.
- Comparing the results of two basic methods of processing the C–C composites, higher values of thermal conductivity may be achieved when applying the pyrolytic carbon matrix processing method as compared to liquid phase.
- Carbon matrix made of polymer undergoes the recrystallization process, particularly in higher temperatures, which leads to increase of density as well as better thermal conductivity of C–C composite processed by this method.
- Both the structure and the microstructure of carbon matrix formed from gaseous phase are not affected by the type of fibres used, but they depend strongly on the conditions of final thermal treatment of the composite.
- The coefficient of thermal conductivity of C–C composite processed with use of the P-CVI method depends on temperature of the final thermal treatment.

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