Preparation and thermophysical properties of Cu alloy/high thermal conductivity carbon fibre composites

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Abstract

Novel heat sink materials based on copper matrix composites containing highly conductive carbon fibres have been made by gas pressure infiltration and subjected to structural studies and thermal conductivity measurements. Light and scanning electron microscopy observations have revealed homogeneous distribution of fibres in matrix and formation of interfacial reaction zone when the copper was alloyed with carbide forming elements. The thermal conductivity of prepared unidirectional composites was calculated from thermal diffusivity measured by means of flash method in both longitudinal and transverse directions with respect to fibre alignment. The conductivity values obtained in the range of 580 W/m·K to 695 W/m·K for longitudinal direction and 57 W/m·K to 88 W/m·K for transverse direction are in a good agreement with values predicted by analytical models.

K e y w o r d s: metal matrix composites, heat sinks, carbon fibres, interface, thermal conductivity

1. Introduction

The growing tendency towards the miniaturisation of microelectronic devices accompanied by the requirement for further improvement of their power output leads to increasing circuit densities and thus to substantially higher amount of locally generated heat, which must be continuously removed to ensure proper performance of the device. Further miniaturisation is however seriously hindered by the ability of current structural materials to spread, transfer and dissipate heat from semiconductors to the surroundings. To avoid overheating and thus failure of electronic parts, novel heat sink materials with radically improved properties are inevitable. The requirements on such materials are very complex, they must possess extremely high thermal conductivity (TC $\gg$ 400 W/m·K), withstand cyclic thermal loading, be easy machinable to provide low surface roughness, be joinable (brazable) to neighbouring structures and moreover, their coefficient of linear thermal expansion (CTE) should match the CTE of adjacent isolation layer ($\sim$ 5–7 $\times$ 10^{-6}/K) to avoid large internal stresses [1–4].

As the thermal conductivity (TC) of pure metals is still insufficient (400 W/m·K for Cu, 430 W/m·K for Ag, 235 W/m·K for Al) and their CTE is significantly higher than required, the current development is oriented toward manufacturing of metal matrix composites containing novel highly conductive carbon structures (thermal conductivity of synthetic diamond, carbon nanotubes, highly graphitised carbon foams or fibres can achieve λ values of $\sim$ 600–3300 W/m·K; $\sim$ 1650 W/m·K, whereas CTE lies in the range of ~ -0.2–2 $\times$ 10^{-6} K^{-1} [1]).

Metal matrix composites reinforced with continuous high modulus (HM) carbon fibres are very promising for application where beside excellent thermal conductivity also machinability, perfect surface finish and well predictable properties that usually obey the rule of mixture, are of prime interest. On the other hand fibre alignment inevitably leads to the aniso-

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Table 1. Properties of K1100 carbon fibres

Tensile strength (GPa)	3.10
Tensile modulus (GPa)	965
Density (g/cm^3)	2.2
Filament diameter (μm)	10
Carbon assay (%)	99+
Specific surface area (m^2/g)	0.40
Thermal conductivity in longitudinal direction (W/m·K)	900–1000
Thermal conductivity in transverse direction (W/m·K)	2.4
Longitudinal CTE at 21 °C (K^{-1})	-1.45×10^{-6}
Transverse CTE at 21 °C (K^{-1})	12.0×10^{-6}

tropy of material properties, whereas the properties along the fibres are mostly determined by the longitudinal properties of fibres and properties perpendicular to fibre alignment by matrix. However, this apparent drawback can be sometimes advantageous, especially in applications where the maximisation of e.g. heat conductivity in one direction is desirable (for instance for quick heat transfer from source to heat sink).

Although copper composites reinforced with carbon fibres can be efficiently manufactured by vacuum diffusion bonding of coated fibres [5–9], this method is not suitable for high modulus carbon fibres, because of their extreme brittleness, which results in intensive fibre fragmentation during coating process. In this case gas pressure infiltration, at which molten matrix metal is forced by the pressurised gas to penetrate fibrous perform, seems to be more appropriate [10]. Gas pressure has to be applied to overcome negative capillary forces in the case of high wetting angle between matrix and fibres, which is typical for most metal-carbon fibre combinations. However, because of the lack of wetting, even relatively high pressures ($\sim$ 10 MPa) are not sufficient for thorough infiltration of continuous carbon fibre tows with pure copper. This problem can be overcome by alloying of copper with some of the carbide-forming elements (e.g. Cr or Zr), whereas the amount of such elements must be optimised in order to keep high conductivity of the matrix and to avoid deterioration of fibre properties [11–15]. This was also the main aim of present investigation.

The main aim of this work was to investigate possibility of production and properties of Cu alloy/pitch based carbon fibres system. Since gas pressure infiltration had been chosen as the preferred preparation method, the low wettability in the Cu/C$_f$ system represented the main problem. The solution was attempted by the proper choice of the matrix alloy.

2. Experimental procedure

Cu/HM C-fibre composite materials were prepared by gas pressure infiltration technique. High modulus pitch based Thornel K1100 carbon fibres with 2000 filaments in one tow have been used as uniaxially aligned reinforcement. Properties of K1100 carbon fibres are given in Table 1. Because of poor wettability of carbon by pure copper and the lack of interfacial bonding, ternary CuCrZr and binary CuCr alloys were experienced as matrix alloys. The nominal composition of CuCrZr alloy was 0.7 wt.% of Cr and 0.3 % of Zr. Binary CuCr alloys contained 0.25 wt.% of Cr (CuCr0.25), 0.50 wt.% of Cr (CuCr0.5) and 1 wt.% of Cr (CuCr1).

The cut continuous fibres (50 mm long) were filled and unidirectionally aligned in appropriate mould, whereas the typical fibre volume fraction was $\sim$ 50–60 vol.%. The inner diameter of the mould was 12 mm and the length 50 mm. During infiltration evacuated mould with fibres was immersed in the molten matrix metal and held there until full solidification. Infiltration parameters were as follows: temperature $\sim$ 1200 °C, nitrogen gas pressure $\sim$ 5.5–6.5 MPa and immersion time in liquid metal $\sim$ 2–11 min.

Thermal diffusivity was measured in the longitudinal and transverse direction by means of the flash method. All measurements were performed at room temperature. The measured composite samples were discs with diameter of 10 mm and thickness of 3–5 mm. The thermal conductivity was calculated from the diffusivity measurements using calculated values of density and specific heat [16, 17].

3. Results and discussion

3.1. Microstructural characterisation

Preliminary experiments performed with CuCrZr did not lead to acceptable infiltration of molten metal into the fibrous preform. The tows of carbon fibres were therefore pretreated in the water dispersion of TiN particles with size in the range of 1–2 μm in order to separate single filaments in fibre tow and allow easier penetration of the molten alloy.

Even though wettabillity in CuCrZr/C$_f$ system is

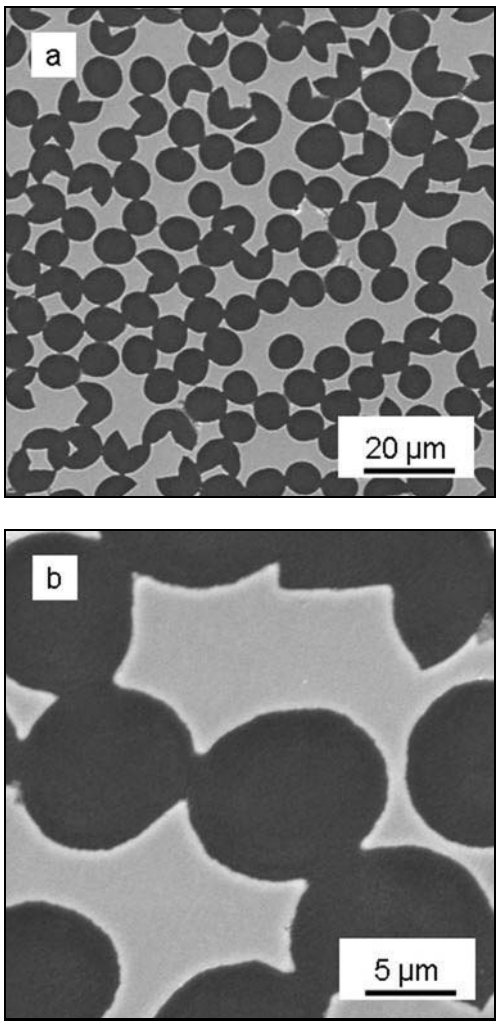

Fig. 1. Structure of the CuCrZr/K1100 composite (V_f = 60 %) showing homogeneous distribution of carbon fibres (secondary electron micrograph) (a) and fine pores between carbon fibres (secondary electron micrograph) (b).

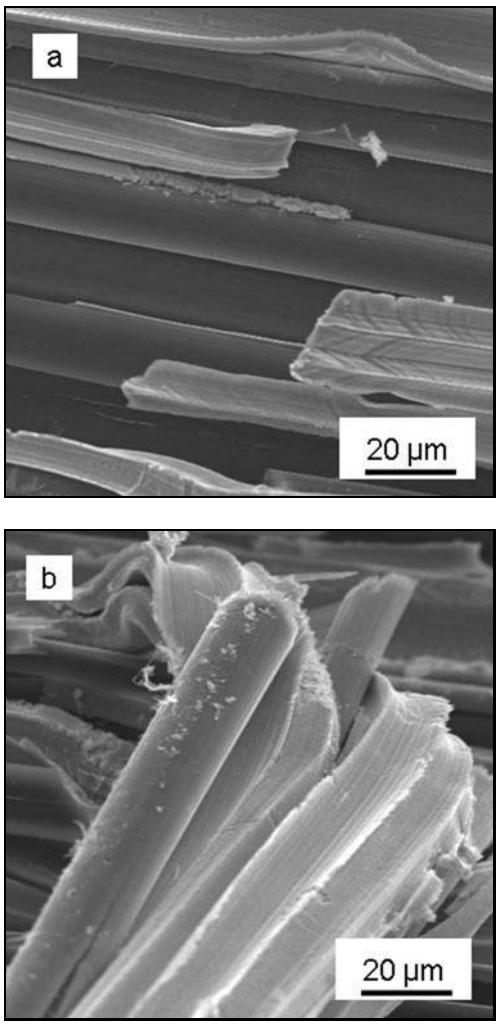

Fig. 2. Fracture surfaces of the CuCrZr/K1100 (V_f = 60 %) composite showing lack of the interfacial bonding (secondary electron micrograph) (a) and (b).

rather poor, light and scanning electron microscopy observations revealed composite structures with homogeneous distribution of TiN treated carbon fibres. Cross-sectional structure of the CuCr0.7Zr0.3/TiN/K1100 sample is presented in Fig. 1. Some uninfiltrated areas are noticeable on few fibre-fibre contacts. Fracture surface observations did not confirm any formation of interfacial carbide layers as shown in Fig. 2. Carbon fibres exhibit smooth surfaces without any carbides and plastically deformed matrix is separated from the fibres, confirming thus insufficient interfacial bonding.

Some composite samples were therefore subsequently annealed at 900 °C for 30 minutes in order to promote carbide forming reaction and improve interfacial bonding. However, as shown in Fig. 3, SEM observations did not reveal any carbide at the fibre-matrix interface on such as-annealed samples. Moreover, the mismatch of CTE between matrix and fibres accompanied with lack of bonding strength led to extensive separation of the matrix from the fibres during this annealing and deterioration of composite properties especially in direction perpendicular to fibre alignment.

It appeared that the performance of the ternary CuCrZr alloy did not meet all the necessary demands as requested for the proper matrix in the Cu/C_f composite material. The crucial drawbacks include the lack of the interfacial bonding and the necessity to use some separator particles to promote the metal penetration.

The performance of binary CuCr alloys was undoubtedly superior to CuCrZr alloy. Introduction of chromium into copper brought significant improvement of the infiltration process without the necessity to use any separator particles. Already small amounts

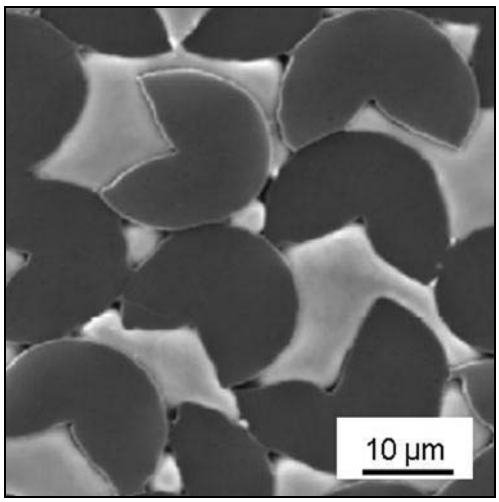

Fig. 3. Structure of the CuCrZr/K1100 composite (V_f = 60 %) showing a sample after annealing at 900 °C for 30 minutes (secondary electron micrograph).

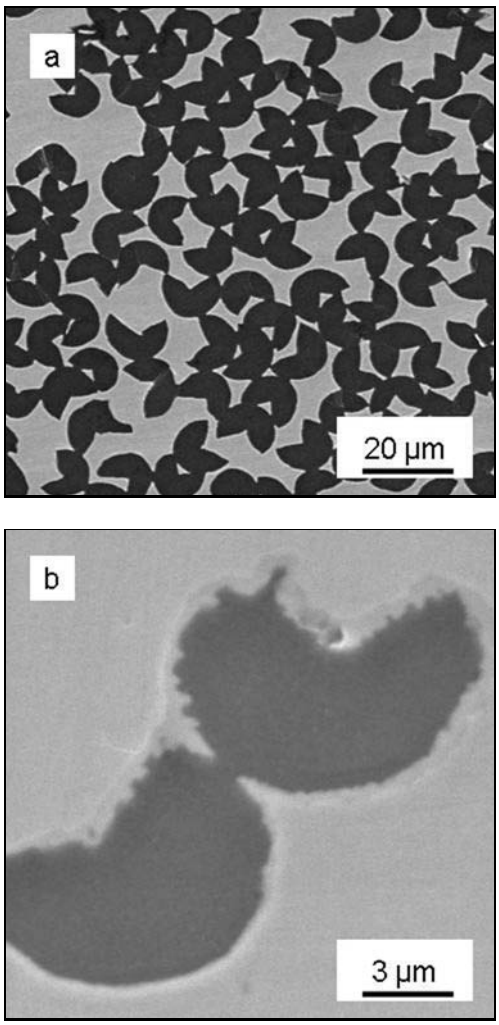

Fig. 4. Secondary electron micrographs of the CuCr0.25/K1100 (V_f = 55 %) sample showing homogeneous distribution of carbon fibres (a) and formation of the chromium carbide layer at the fibre-matrix interface (b).

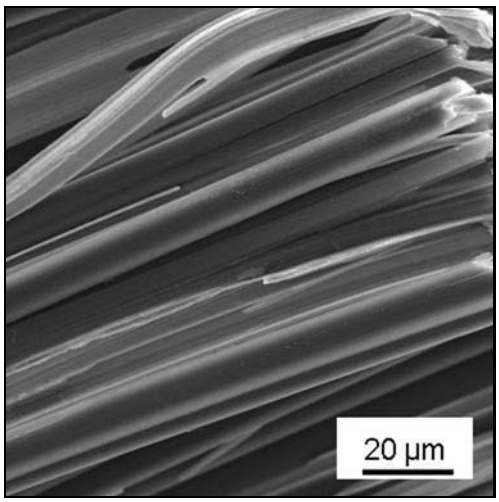

Fig. 5. Secondary electron micrograph of the CuCr0.25/K1100 (V_f = 55 %) sample – debonding of the matrix from the fibres because of insufficient interfacial bonding.

of chromium (CuCr0.25 alloy) provided sound samples with homogeneous distribution of the carbon fibres as shown in Fig. 4.

Continuous carbide layer was detected on the fibre-matrix interface of C-fibres in regions located close to the surface of the fibre perform, which were subjected to initial contact with the fresh molten metal during infiltration. However, Fig. 5 shows that chromium carbides had not been formed on fibres extracted from the middle of the samples. This means that alloying element was depleted during carbide forming reaction in first few millimetres from the sample face end. Nevertheless this fact obviously did not significantly affect the wettability and the infiltration quality was satisfactory also deeper below the surface of the fibrous perform.

Microstructural characterisation of samples with CuCr0.5 and CuCr1 matrix revealed lower amount of small pores at fibre-fibre contacts than in the case of CuCrZr alloy, as shown in Fig. 6 and Fig. 7.

In a case of lower chromium content the fracture analysis showed interfacial debonding as a prevailing deformation mode, which confirmed the lack of sufficient interfacial bonding. Higher Cr amounts ensured more extensive carbide forming reactions resulting in the improved interface even in the most inner parts of the obtained samples, as shown in Fig. 8. The fracture surface of samples with CuCr1 matrix clearly reveals the matrix metal bonded to the surface of carbon fibres. No serious pull out of fibres or other interfacial debonding was observed. However, it remains an open question to which extent can the carbide forming reaction at the interface influence the composite performance.

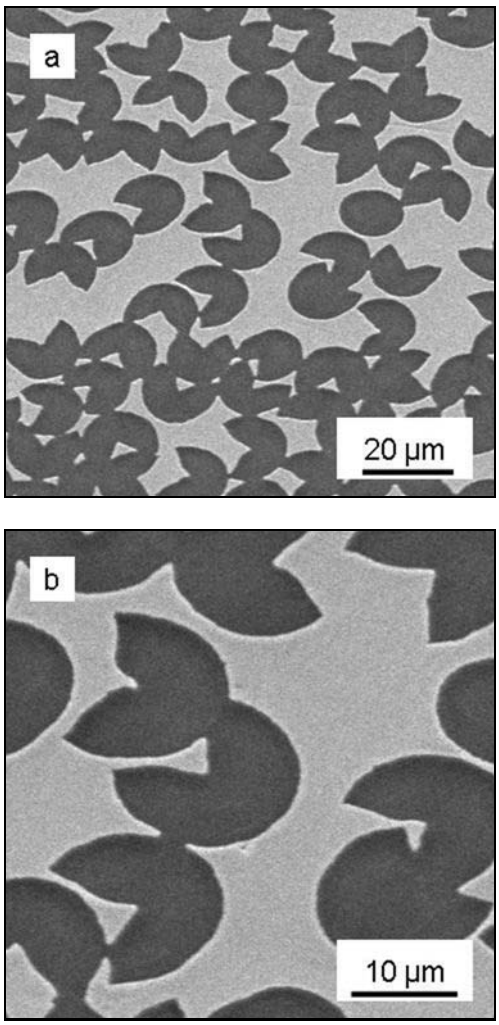

Fig. 6. Secondary electron micrographs of the CuCr0.5/K1100 (V_f = 53 %) sample showing homogeneous distribution of carbon fibres (a) Non infiltrated areas are noticeable on few fibre-fibre contacts (b).

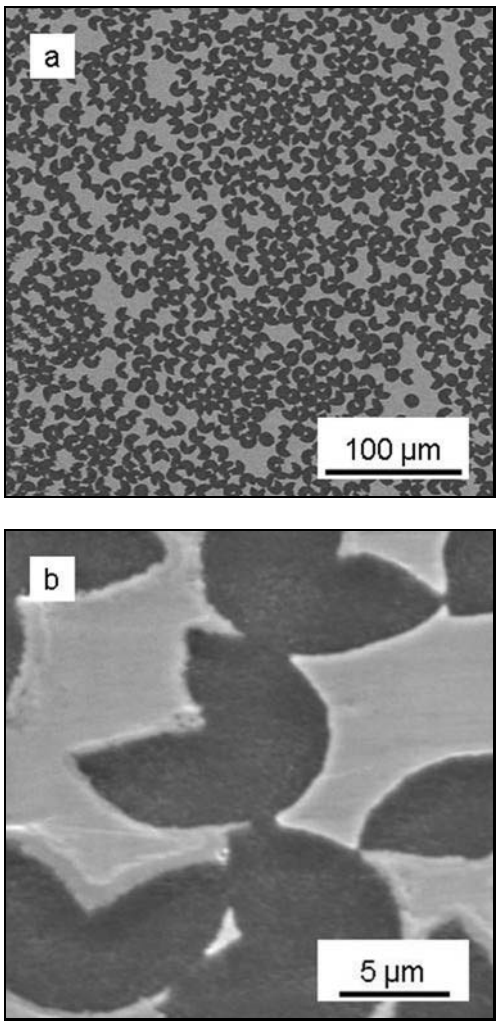

Fig. 7. Secondary electron micrographs of the CuCr1/K1100 (V_f = 52 %) showing homogeneous distribution of carbon fibres (a) and SEM of the CuCr1/K1100 (V_f = 55 %) showing chromium carbide layer at the fibre-matrix interface (b).

3.2. Thermal diffusivity measurements

Thermal diffusivity measurements were performed under the assumption that the measured composite behaves as a homogeneous medium. In the case of studied composites this prerequisite is found to be fulfilled because the sample thickness is much larger than the fibre diameter and the fibre volume is large (> 50 vol.%) [18]. However, it is known that the constituents of the composite have different thermal properties. That is why the heat flow is probably not completely uniaxial, but involves transverse components [19, 20]. Nevertheless, the thermal diffusivity techniques have been successfully applied for different composite systems and provide acceptable tool for characterisation of their thermal behaviour.

The measurement results obtained on prepared samples are presented in Table 2. Extremely high thermal conductivities with values in the range from 580 W/m·K to 695 W/m·K were achieved in longitudinal direction. The lowest thermal conductivity was determined for sample with CuCr0.25 matrix, which exhibited also the smallest interfacial bonding strength. Increased content of chromium resulted in improved interfacial conductance, which was confirmed by highest TC value for CuCr0.5 matrix. However too high Cr content can lead to extensive carbide formation and thus to the reduction of matrix TC (see TC value of 616 W/m·K obtained for CuCr1 matrix). It appears that as far as the thermal conductivity is concerned, there is no need to use alloys containing more than 1 wt.% of Cr.

For prediction of the longitudinal TC a simple rule of mixture (Voight model – Eq. (1)) was used [21]:

Table 2. Thermal conductivity of CuCrZr/K1100 and CuCr/K1100 samples

Sample	Direction	Diffusivity (m^2/s)	Fibre volume fraction	Thermal conductivity (W/m·K)
CuCr0.7Zr0.3+TiN+K1100	Longitudinal 5 mm	2.807E-4	0.60	643
CuCr0.7Zr0.3+TiN+K1100	Transverse 5 mm	2.503E-5	0.60	57
CuCr0.25+K1100	Longitudinal 4 mm	2.352E-4	0.55	580
CuCr0.25+K1100	Transverse 4 mm	2.640E-5	0.55	65
CuCr1+K1100	Longitudinal 5 mm	2.530E-4	0.52	616
CuCr1+K1100	Transverse 3 mm	3.600E-5	0.52	88
CuCr0.5+K1100	Longitudinal 5 mm	2.875E-4	0.53	695

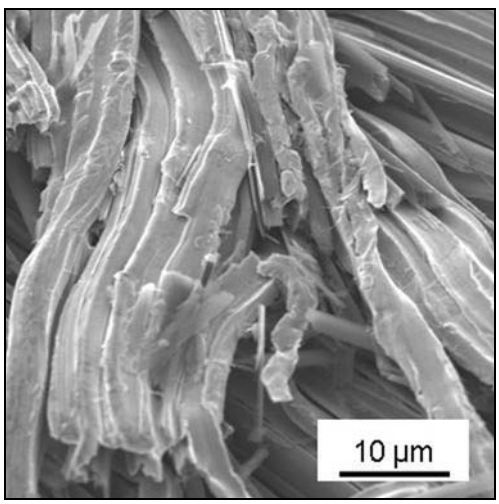

Fig. 8. SEM of the CuCr1/K1100 (V_f = 55 %) sample showing matrix bonded to carbon fibres.

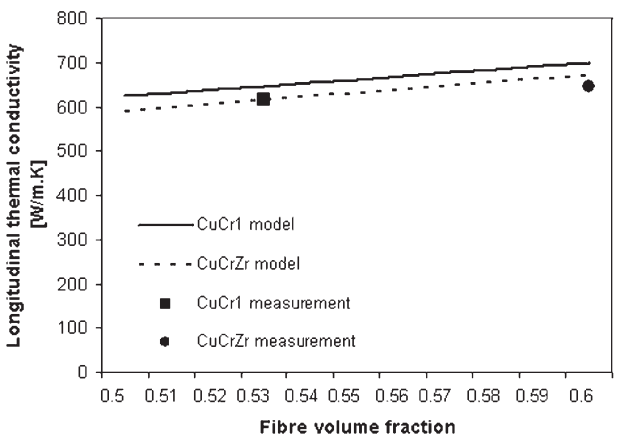

Fig. 9. Comparison of longitudinal thermal conductivity of CuCrZr/C_f and CuCr1/C_f samples with values obtained from the rule of mixture.

$$k_{\mathrm{L}}^{\mathrm{c}} = k_{\mathrm{L}}^{\mathrm{f}} \cdot V^{\mathrm{f}} + k^{\mathrm{m}} \cdot V^{\mathrm{m}}, \tag{1}$$

where k and V represent thermal conductivity and volume fraction, superscripts C, f and m composite, fibre and matrix and subscript L longitudinal direction. The Voight model for both matrix materials is given in Fig. 9, whereas 182 W/m·K was applied for TC of CuCrZr alloy and 249 W/m·K for CuCr1 alloy (these values were also obtained experimentally using the same method as for composites).

It can be seen that thermal conductivities experimentally obtained in longitudinal direction on prepared composite samples are in good agreement with the model for both examined alloys.

The thermal conductivities determined in transverse direction were significantly lower than in the fibre direction (in the range from 57 W/m·K to 88 W/m·K). Strong anisotropy of properties of unidirectional carbon fibre composite confirmed expectations coming from the properties of pitch based Thornel K1100 carbon fibres: longitudinal TC of about 1000 W/m·K and transverse TC of about 2.4 W/m·K [22].

Transversal properties of composites can be predicted using models of Hatta-Taya and Gurtman in [23, 24]. These models assume perfect contact between fibres and the matrix, however without any interlayer. The formula of Hatta and Taya (Eq. (2)) is based on the Eshelby method where the elasticity problem with stress (σ_{ij}), strain (ε_{ij}) and stiffness tensor (C_{ijkl}) corresponds to the thermal problem with heat flux (q_i), temperature gradient ($T,_i$) and the thermal conductivity (k_{ij}):

$$k_{\mathrm{T}}^{\mathrm{c}} = k^{\mathrm{m}} \frac{k^{\mathrm{m}} \cdot \left(k_{\mathrm{T}}^{\mathrm{f}} - k^{\mathrm{m}}\right) \cdot V^{\mathrm{f}}}{k^{\mathrm{m}} + V^{\mathrm{m}} \cdot \dfrac{\left(k_{\mathrm{T}}^{\mathrm{f}} - k^{\mathrm{m}}\right)}{2}}. \tag{2}$$

The model developed by Gurtman et al. (Eq. (3)) is based on a unit cell theory, which presents a unidirectional composite reinforced with anisotropic fibres arranged in a periodic array:

$$k_{\mathrm{T}}^{\mathrm{c}} = V^{\mathrm{f}} \cdot k_{\mathrm{T}}^{\mathrm{f}} \cdot (1 + V^{\mathrm{m}} \cdot A) + V^{\mathrm{m}} \cdot k^{\mathrm{m}} \cdot \left(1 - V^{\mathrm{f}} A\right), \tag{3}$$

$$A = \frac{k^{\mathrm{m}} - k_{\mathrm{T}}^{\mathrm{f}}}{k^{\mathrm{m}} + k_{\mathrm{T}}^{\mathrm{f}} + V^{\mathrm{f}} \cdot \left(k^{\mathrm{m}} + k_{\mathrm{T}}^{\mathrm{f}}\right)}, \tag{4}$$

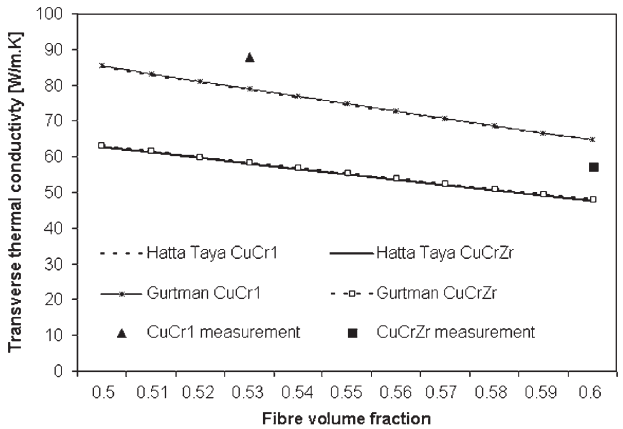

Fig. 10. Comparison of transverse thermal conductivity of $CuCrZr/C_f$ and $CuCr1/C_f$ samples with models suggested by Gurtman and Hatta-Taya.

where the subscript T stands for direction normal to the fibre axis. The thermal conductivity of the fibre in transverse direction was at the level $k_T^f = 2.4$ W/m·K [22].

Figure 10 shows that both models give almost the same predictions. Coinciding lines are probably due to very low transverse thermal conductivity of carbon fibres. Similarly as in the case of longitudinal TC, experimentally obtained values are in good agreement with given models (see also Fig. 10). This may indicate good thermal conductance of fibre-matrix interface.

It should be noted, that matrix properties significantly differ according to its microstructure. As-received CuCrZr and CuCr1 alloys were thermally treated and possessed optimum microstructure with highest electrical/thermal conductivity. On the other hand, re-melted and after infiltration quickly solidified matrices exhibited significantly lower thermal conductivities due to dissolved alloying elements. The thermal diffusivity measurement performed on matrix materials before and after infiltration experiments revealed the reduction of TC from 355 W/m·K to 182 W/m·K for CuCr0.7Cr0.3 alloy and from 335 W/m·K to 249 W/m·K for CuCr1 alloy, respectively. This points out that additional thermal treatment after infiltration is necessary to restore originally high TC of matrix material. On the other hand it indicates some potential for further improvement of thermal properties of investigated composites.

5. Conclusions

The presented work has confirmed that production of copper based composites reinforced with unidirectional pitch based carbon fibres is possible using the gas pressure infiltration technique if the metal matrix is alloyed with carbide forming elements.

Infiltration with ternary CuCrZr alloy was successful when carbon fibres had been pretreated by the water dispersion of TiN particles acting as effective inter-fibre separators. This operation improved the penetration of molten metal into the fibrous preform, however it apparently reduced the interfacial bonding strength, which was confirmed by strong delamination during subsequent thermal treatment.

Alloying with chromium resulted in significant improvement of infiltration quality without needs of additional filament separation with particles. Microscopic observations have confirmed existence of good interfacial bonding and forming of chromium carbides, especially for higher chromium contents.

Measurements of thermal diffusivity and calculation of thermal conductivity have shown extremely high values in longitudinal (580 W/m·K up to 695 W/m·K) and lower values in transverse (57 W/m·K up to 88 W/m·K) directions. These values were in good agreement with analytical predictions.

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