Kovove Mater. 53 2015 451–458
DOI: 10.4149/km_2015_6_451

The microstructure and thermal expansion of Mg/C composite prepared by gas pressure infiltration

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Received 7 May 2015, received in revised form 2 October 2015, accepted 8 October 2015

Abstract

The interface and thermal expansion behaviour of magnesium matrix composite (Mg-2Al) unidirectionally reinforced with continuous high modulus and high thermal conductivity carbon fibres Thornel K1100 prepared by gas pressure infiltration technique was studied. The structure of the fibre-matrix interface was analysed using light microscopy, SEM, EDS, and TEM. Composite samples were subsequently thermally cycled at the heating/cooling rate of 3 °C min^{-1} in the temperature range of 30 to 350 °C in an argon atmosphere to reveal their thermal expansion behaviour.

Key words: metal matrix composites (MMCs), Mg/C interface, thermal expansion, CTE

1. Introduction

It is known that magnesium is the lightest structural metal. Magnesium alloys are 33 % lighter than aluminium, 61 % lighter than titanium and 77 % lighter than stainless steel making them promising candidates as a replacement material for these metals [1]. Magnesium has a high potential to serve in a variety of structural, hydrogen storage, and bio-related applications due to its low density (1.74 g cm^{-3}), low Young's modulus (40 GPa), high specific stiffness, high thermal conductivity (156 W m^{-1} K^{-1}) and possible biocompatibility and biodegradability. Mg belongs to the group of industrially used lightweight metallic materials [2–4]. Magnesium possesses several other benefits including excellent castability, high damping capacity, good electromagnetic shielding and excellent machinability and in production requires less energy than aluminium. The limitations of magnesium include its low elastic modulus and ductility, poor creep and abrasion resistance and high corrosion rate. These can be partially restrained by the addition of reinforcements to create magnesium composites [1].

In conjunction with high modulus (HM) carbon fibres, magnesium matrix composites (MMCs) with specific thermal properties related to high thermal conductivity and low thermal expansion can be produced. Generally, MMCs introduce a new era of engineering materials particularly in application requirements where conventionally available materials of nowadays are not sufficient. Important MMC applications in the ground transportation (auto and rail), thermal management, aerospace, industrial, recreational and infrastructure industries have been enabled by improved functional properties that include high structural efficiency, excellent wear resistance, and attractive thermal and electrical characteristics [5]. MMCs have also been identified as potential candidate materials for primary structural element applications in high-precision space-based system [6]. New magnesium composites are being developed for applications in various branches of industry, mainly for the automotive industry as lightweight structural materials. The aim of developing of magnesium-based metal matrix composites is not only to improve creep resistance but also to reduce the thermal expansion of the material [7].

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Gas pressure infiltration (GPI) is a promising route to produce MMCs. This is due to its potential to produce structural parts of complex shapes, using a high ceramic volume fraction and the possibility of tailoring the properties accordingly to structural demands. The aim of this work is to report on microstructure and thermal expansion of Mg/C composites prepared by this technique.

2. Experimental material and procedure

Prior to infiltration, rod-like carbon fibre preforms were prepared by unidirectional alignment of HM carbon fibres Thornell K1100 using water soluble synthetic polymer – PVA. These preforms with the dimensions of approximately 13 × 13 × 50 mm^3 were inserted in a Mo mould and preheated in a vacuum ~ 47 Pa. As the infiltration temperature of 730 ℃ had been reached, the system was allowed to equilibrate thermally for roughly 5 min. Subsequently the preform was immersed into the molten Mg-2Al magnesium alloy and the infiltration started under the protective nitrogen atmosphere. Nitrogen gas pressure of 8 MPa was applied within 5 minutes. Infiltrated fibre preforms were subsequently removed from the melt in order to limit the potential fibre-matrix reaction.

Structural observations on as-received samples were performed with light microscopy (LM – OLYMPUS GX51) and field emission scanning electron microscopy (SEM – JEOL 7600 FEG)). Structural studies were further performed with conventional transmission electron microscopy (TEM – JEOL 1200 EX); chemical compositions were analysed using energy dispersive (EDS) X-ray spectroscopy (Oxford Instruments INCA EDS6251 microanalysis system). Ion milling at 5 kV accelerating voltage was applied for preparation of thin foils for TEM observations.

Composite samples with the dimensions of 4 × 4 × 10 mm^3 were used for linear thermal expansion measurements in both longitudinal (L) and transversal (T) directions. Designation L and T corresponds to fibre alignment direction with respect to longitudinal sample axes. Samples were subjected to five consecutive heating and cooling cycles at the heating/cooling rate of 3 K min^{-1} in an argon atmosphere using LINSEIS L75VS 1600C dilatometer equipped with a silica holder. Samples were cycled in the temperature range 30 to 350 ℃. Each thermal cycle started with the sample preheating at 30 ℃ for 30 min, followed by heating and subsequent cooling back to the room temperature. One-hour rest time had been included before the next cycle started. Instantaneous CTE values were calculated from the strain-temperature curves as a function of temperature using LINSEIS TAWIN software. All CTEs were calculated in the temperature range 100 to 300 ℃ to eliminate the effect of non-steady state transient stages occurring at the beginning and the end of heating and cooling periods.

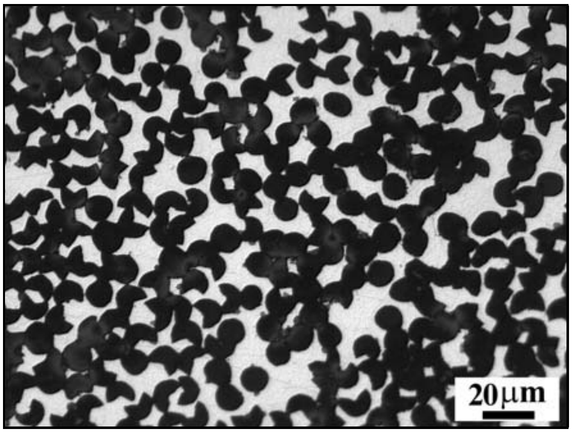

Fig. 1. Light micrograph of the structure of Mg-2Al/K1100 composite.

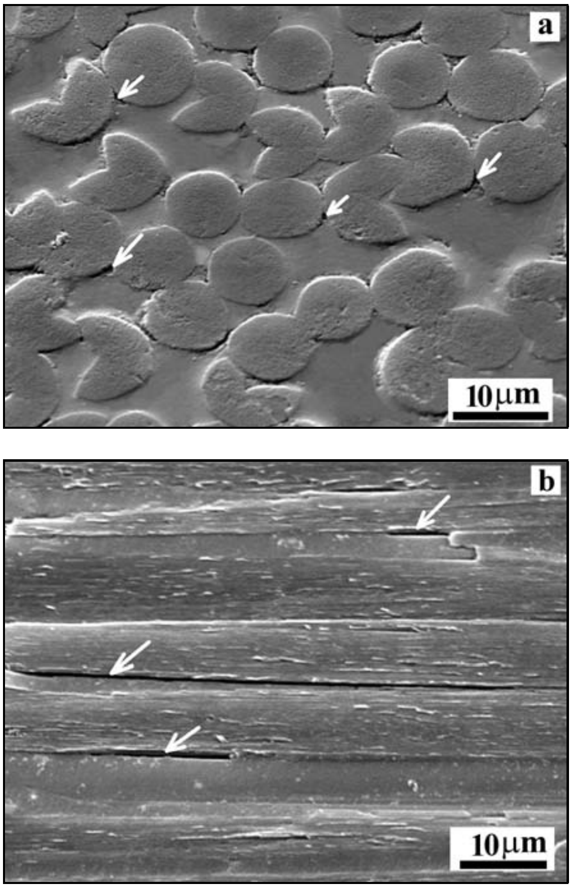

Fig. 2. The structure of Mg-2Al/K1100 composite as revealed by SEM in the transversal direction (a), in the longitudinal direction (b).

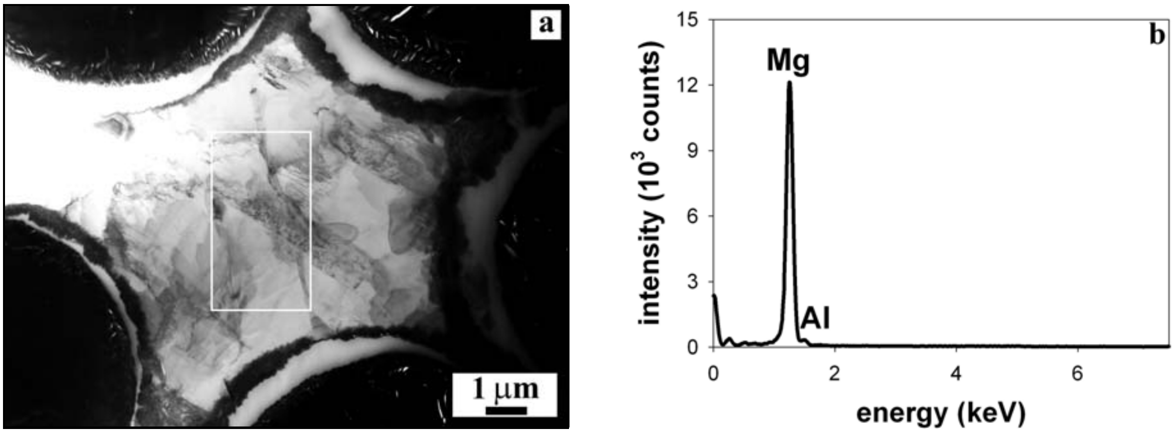

Fig. 3. Bright field TEM micrograph revealing the microstructure of Mg-2Al/K1100 composite (a), corresponding EDS spectrum acquired from the highlighted area (b).

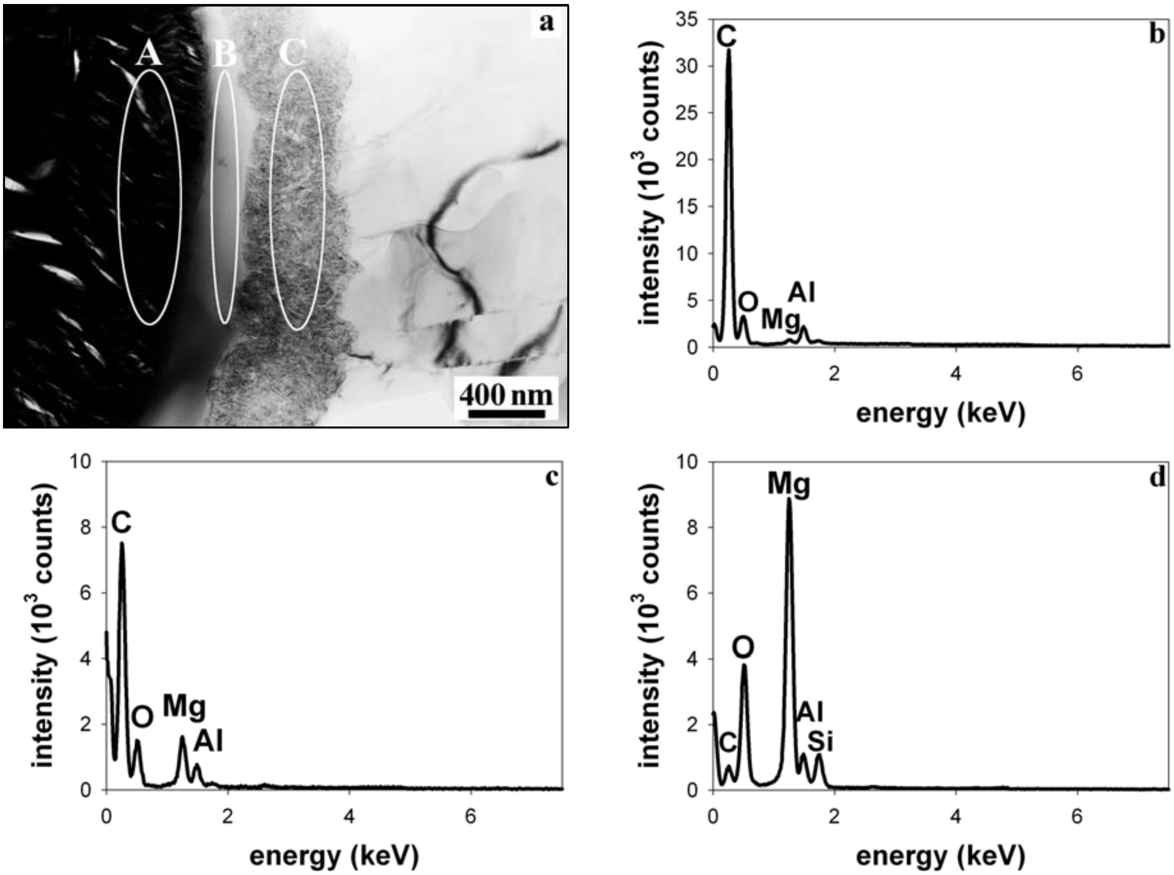

Fig. 4. Bright field TEM micrograph revealing the fibre – matrix interface in Mg-2Al/K1100 composite (a), corresponding EDS spectra acquired from the highlighted area A (b), B (c), and C (d).

3. Results

3.1. Structural studies

Typical microstructure of gas pressure infiltrated microstructure of Mg-2Al/K1100 composite as revealed by LM in a cross-sectional view is presented in Fig. 1. The average fibre volume content as determined via 5 image analysis in different locations was ~ 63.0 %. As can be seen, a relatively homogeneous distribution of carbon fibres was observed.

However, in the inter-fibre locations some clustering of carbon fibres is visible and resulted in several pores (marked with white arrows) in SEM micrographs presented in Fig. 2.

The microstructure of the composite was further

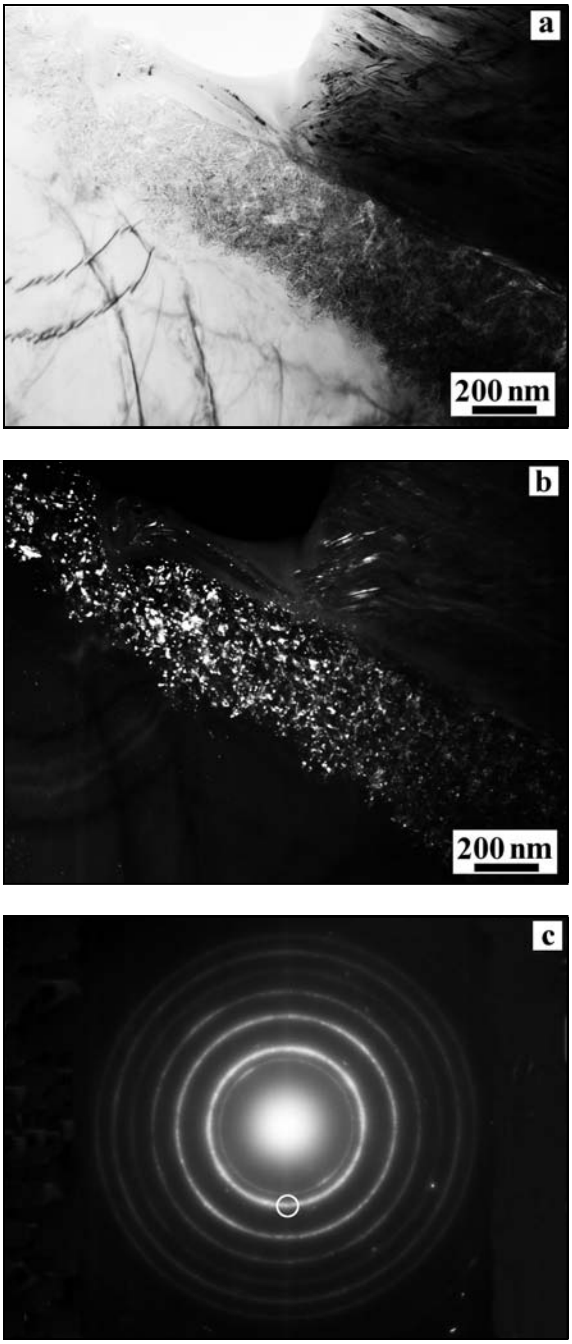

Fig. 5. Bright field TEM micrograph revealing the polycrystalline zone at fibre-matrix interface in Mg-2Al/K1100 composite (a), dark field image formed using ring reflections highlighted in SAED pattern (b), SAED pattern obtained from the polycrystalline zone (c).

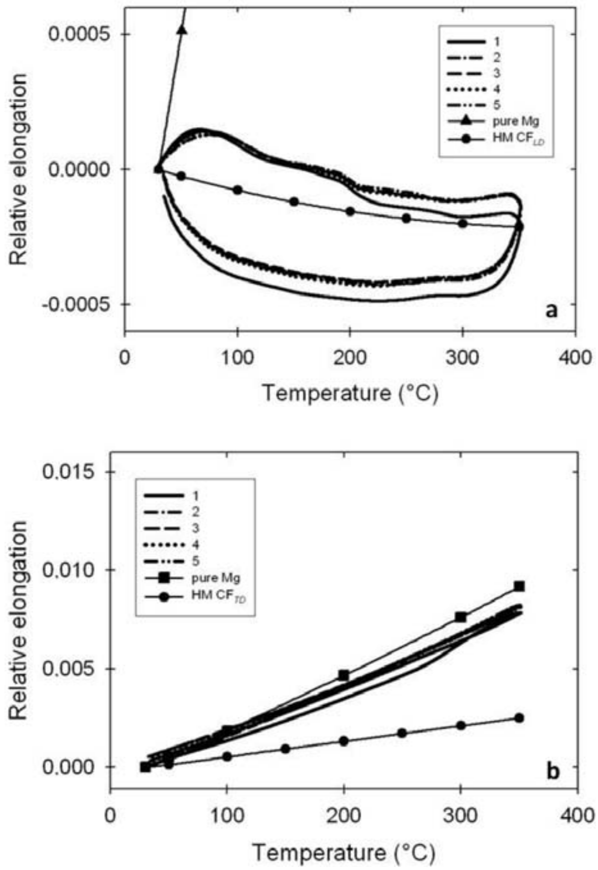

Fig. 6. Temperature dependences of the relative elongation of pure Mg, HM carbon fibres and 5 cycles of Mg-2Al/K1100 composite in L direction (a) and T direction (b).

analysed by TEM and EDS. As can be seen in Fig. 3, two zones can be distinguished between C fibres and the matrix. The bright structure-less zone is adjacent to the fibres; dark appearing zone is adjacent to the matrix. EDS spectrum in Fig. 3b confirms the matrix composition with Mg alloyed with a small addition of Al. The closer analysis of interfacial zone is presented in Fig. 4.

As can be seen in Fig. 4b, a distinct presence of Al in the subsurface regions of C fibre is evident. The composition of approximately 300 nm thick bright structure-less zone B is formed mostly by C with some O, Mg and minor Al. This zone is amorphous. Selected area electron diffraction yielded only diffuse spectra from this layer.

The neighbouring darker zone C is composed of Mg and O with minor amounts of Al and Si. This zone is polycrystalline as confirmed in Fig. 5. The size of crystals is in nanometric scale.

3.2. Thermal expansion

The temperature dependences of the relative elongation of pure Mg, HM carbon fibres (P100) and Mg-2Al/K1100 composite in L and T directions are presented in Fig. 6. The relative elongation of pure Mg was measured at Linseis dilatometer. The precise expansion data of K1100 carbon fibres are not known. However, high modulus P100 fibres reported

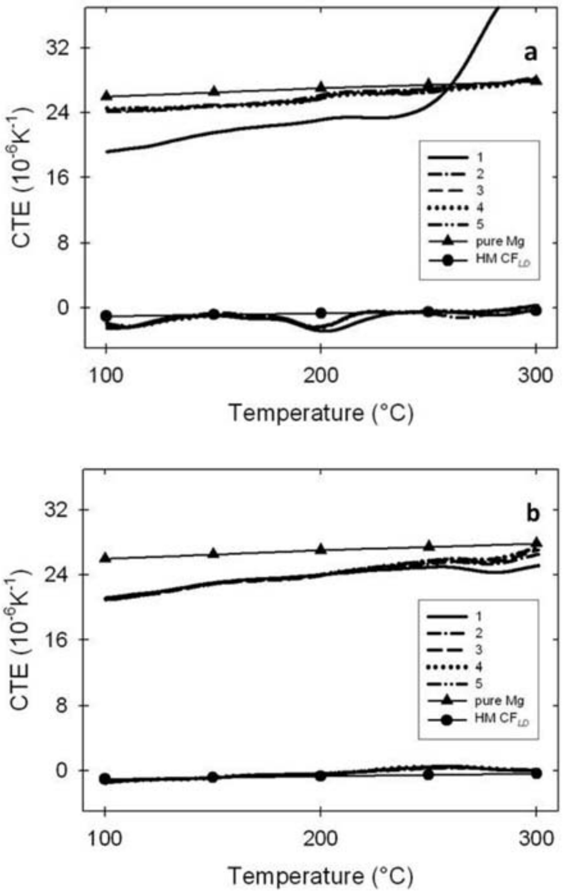

Fig. 7. Temperature dependences of CTE of Mg-2Al/K1100 composite in L and T direction subjected to five consecutive thermal cycles during heating, compared with CTE of pure Mg and HM carbon fibres in L direction during heating (a) and cooling periods (b).

in [8] are recognised as the predecessor and close relative to K1100 and therefore, these were chosen for comparison.

Large differences in relative elongations were recorded in L and T directions. At the end of the first thermal cycle, a permanent relative contraction was recorded in L direction. The rest cycles were nearly identical however with small permanent contractions. All five cycles exhibit hysteresis – i.e. the heating and cooling values do not coincide. However, the relative elongation of the composite is closely related to the relative elongation of high modulus carbon fibres (continuous line with black circles). This confirms that the thermal expansion behaviour of Mg-2Al/K1100 composite is governed by the expansion of K1100 fibres.

In T direction, small residual expansions were recorded in all five thermal cycles. Generally, the relative elongation of Mg-2Al/K1100 composite in T direction followed the expansion of Mg.

The experimental CTE values of Mg-2Al/K1100 composite measured during heating and cooling periods in the temperature range 100–300 ℃ are presented in Fig. 7. The obtained CTE values reflect and further confirm the anisotropy of the composite in L and T directions. They point out the different character of the first thermal cycle. However, the subsequent four cycles are nearly identical for both heating and cooling periods. It is obvious that the CTEs of composite follow the CTE of HM carbon fibres in L direction; in T direction CTEs of the composite are abreast with CTE of Mg.

Table 1. The average CTEs of the composite in L and T directions

CTE (10^{-6} K^{-1})	Heating	Cooling
in L direction	–1.1	–0.4
in T direction	25.7	24.0

The average values obtained from all 5 thermal cycles of the composite are reported in Table 1. In L direction CTE values are negative for both heating and cooling periods. In T direction the average CTE values for Mg-2Al/K1100 composite are below those of Mg.

4. Discussion

4.1. Structural studies

The primary precondition for successful application of GPI is the wetting of the ceramic reinforcement by the metal matrix. This is expressed by a contact angle (θ) of the liquid metal on the ceramic reinforcement ($\theta \leq 90°$ is wetting and $\theta \geq 90°$ is non-wetting condition). Usually, the wetting of ceramics by metals is poor and the contact angle nearly always exceeds 90 [9]. Magnesium does not react with carbon (known magnesium carbides MgC_2 and Mg_2C_2 are regarded as endothermic compounds that are not synthesizable from the elements and are subjected to thermal decay at temperatures above 500 and 650 ℃, respectively). Thus, the infiltration of carbon fibres with magnesium matrix does not form carbides and results in low adhesion between fibre and magnesium matrix [3]. The wettability in this system needs to be improved.

The simplest method how to improve the wettability and interfacial bonding in Mg-C system is to add some carbide forming element to pure magnesium matrix. In this way, Mg matrix has been alloyed with 2 wt.% of aluminium (Mg-2Al). The desired fibre-matrix reaction was facilitated in this way and the interfacial bonding was expected to be improved through the aluminium carbide (Al_4C_3).

It must be pointed out that behaviour of liquefaction magnesium is mainly dependent on the outside

Table 2. Properties of HM carbon fibre Thornel K1100

Property of HM carbon fibre Thornel K1100	Unit	Value
Tensile strength	(GPa)	3.1
Tensile modulus	(GPa)	965
Density	(kg cm^{-3})	2200
Filament diameter	(μm)	10
Electrical resistivity	(μΩ m)	1.1–1.3
Thermal conductivity in longitudinal direction	(Wm^{-1} K^{-1})	900–1000
Thermal conductivity in transversal direction	(Wm^{-1} K^{-1})	2.4
Coefficient of thermal expansion in longitudinal direction	(10^{-6} K^{-1})	–1.5
Coefficient of thermal expansion in transversal direction	(10^{-6} K^{-1})	12

pressure. Beside this, there is an intense exothermic reaction between liquid magnesium and oxygen. Therefore, the whole infiltration needs to be performed under inert protective gas.

The composite sample was pulled out from the molten matrix metal immediately after infiltration to limit the quantity of Al_4C_3 carbide possibly formed due to the high affinity between Al and C. Actually, the Al_4C_3 carbide is strong hygroscopic what, if formed in large amounts, inevitably leads to the composite disintegration. The Al_4C_3 carbide formed at the interface in Al-3Mg/C composites was reported in a previous paper [10].

Structural studies revealed that the fibre distribution in infiltrated samples is quite homogeneous. This is mostly due to the high fibre volume content that does not allow any large redistribution of fibres.

However, closer inspection revealed that fibres anyway tend to group into clusters. The unidirectional alignment of long continuous fibres forms free channels in the inter-fibrous locations that enhance the molten metal penetration. However, the metal needs to enter the preform predominantly from the front (face) side. When it comes from the flank side, it presses on fibres arranging them into clusters in different mould locations. In this case, the fibre distribution is not completely homogeneous and the frequency of appearance of non-infiltrated locations increases [10]. Pores observed in the present composites had been formed during infiltration as they were observed already on as-infiltrated, *i.e.* not thermally cycled samples.

The EDS analysis performed on thin foils revealed the increased amount of Al in K1100 fibre. That is in accordance with the affinity of Al towards C. On the other hand, the absence of Mg reflects the non-reactivity in the Mg-C binary system.

An amorphous layer containing C, O, Mg, and Al has been revealed adjacent to K1100 fibres. The origin of this layer is not quite clear. The fibre preform was prepared using water-soluble synthetic polymer – PVA. It had been applied on the carbon fibres as the most convenient binder to improve the manipulation of the preform. Full decomposition of PVA is supposed at the infiltration temperature (730 ℃) as the decomposition of approximately 90.30 % of the whole weight of PVA was recorded by TG/DTA measurements already at 600 ℃ [11]. However, any reaction of PVA with carbon fibres during the heating through the infiltration cannot be fully excluded. The similar amorphous layer was previously observed also in [10] where K1100 fibre preforms had been infiltrated with Al-3Mg alloy. This layer was composed of C, O and Al.

The polycrystalline zone between the amorphous layer and the matrix is formed mostly by Mg, some Al (Si) and O. This has not been observed in a previous study [10]. Although the precise identification of both, *i.e.* amorphous as well as polycrystalline zones needs further examination, they might be recognised as the reaction product [12] between any absorbed oxygen at the fibre surface and the magnesium (aluminium) matrix at the interface during infiltration.

Contrary to expectations, Al_4C_3 carbide has been neither observed nor analysed. The available amount of Al was probably not sufficient or the time for diffusion of Al to the interface was not enough to complete this reaction. However, the interface is coherent indicating a good interfacial bonding. If this bonding later appears as not sufficient, it can be further improved by increasing the Al content in the matrix or the infiltration time.

4.2. Thermal expansion

HM carbon fibres Thornel K1100 used in this study represent a specific variant of advanced continuous C phases with properties introduced in Table 2. It is important to point out that K1100 fibres have large anisotropy of thermal conductivity and thermal expansion in longitudinal (L) and transverse (T) directions. Recently, there has been considerable interest to investigate the thermal cycling behaviour of magnesium metal matrix composites reinforced with HM carbon fibres particularly in the changing temperature environments, *e.g.* in the course of real working conditions simulated by thermal cycling [7].

Thermal cycling is known to cause significant degradation to most MMC systems. Types of internal damage observed in MMCs include progressive interfacial reaction, microvoid, and microcrack formation at the interface, interfacial bonding and sliding, fibre fracture and plastic deformation of the matrix leading to dimensional instability. Some types of internal damages are known to cause considerable degradation in composite thermo-physical properties [6].

Mg matrix and HM carbon fibres have a different coefficient of thermal expansions and thermal conductivity. The CTE of magnesium matrix is large positive 25×10^{-6} K^{-1} [13] and that of fibres is even negative -1.5×10^{-6} K^{-1}[6, 8]. As Rudajevova described in [14] a mismatch in the coefficients of thermal expansion (CTEs) between the metal matrix and the ceramic reinforcements causes large residual thermal stresses that may be influenced by a large difference between the thermal conductivity of the matrix and the reinforcement during the preparation of Mg/C composite.

Thermal expansion properties of Mg-2Al/K1100 composite samples were compared with experimental values measured for pure Mg. This is not quite precise as the nominal composition of the matrix metal was Mg-2Al. However, it is assumed that a part of Al was consumed in the interfacial reactions and the content of the rest Al is very close to the solubility limit of Al in Mg. No phase transformations are probable in the temperature range up to 350 ℃ what suggests that the thermal expansion behaviour of the matrix can be very close to Mg.

With increasing temperature, the thermal stress in the metal matrix at the interface may exceed the yield stress of the matrix at a certain temperature, and plastic flow can occur to relieve the stress. As Dutta analysed [15] the continuous fibre reinforced composites are not deformed with the matrix and fibre in isostrain condition. So, the plastic flow is complex and strongly temperature dependent. In addition, creep and relaxation phenomena are important at elevated temperatures; they are both time and temperature dependent and may lead to instability in composite dimensions.

During thermal cycling of Mg-2Al/C composite, the slow heating/cooling rates allow the matrix to elongate relative to the fibre via creep. No interfacial debonding occurs and the differential strain between the matrix and the fibres is accommodated by time-dependent diffusional sliding at the interface close to the fibre ends, where large interfacial shear stresses exist [14, 15]. No debonding or degradation was observed at the interface of Mg matrix and HM carbon fibres after thermal cycling.

Thermal expansion basically concerns the volume of the sample. Therefore, the contraction in L direction is compensated by increased expansion in rest directions (T).

The thermal cycling response of the composite is strongly rate dependent. Due to differences in CTE of magnesium matrix and fibres, the matrix is in residual tension and fibres in residual compression after manufacturing cooling (as-received condition) in L direction. The matrix residual tension is during heating relatively quickly relieved. Compressive stress in the matrix builds up with progressive heating. As soon as the compression yield stress is reached the operation of creep mechanism begins stress relief. The knee appearing around 75 ℃ is coincidental with the start of this stress relief leading to the decrease of relative elongation as analysed by Dutta. This tendency proceeds up to the temperature close to 350 ℃ where the non-steady state transient stage occurs. After thermal cycling, the K1100 fibres were protruded from the matrix that is in accordance with calculations of Dutta based on diffusional accommodated interfacial creep mechanism.

The ability of composite to follow the thermal expansion (contraction) of carbon fibres increases with increasing interfacial bonding strength. Current results indicate that the interface of composite seems to be strong enough even without any excessive fibre-matrix reaction.

5. Conclusions

Structural studies and thermal expansion measurements of Mg-2Mg/K1100 unidirectionally reinforced composite were performed in this work.

It appears that the GPI is a convenient technology to supply the molten metal in the fibre perform, moreover it provides means how to modify the interfacial reaction via proper alloying or modifying the time of contact with the molten metal.

Coherent interface with two reaction zones, *i.e.* amorphous and polycrystalline was observed in the fibre-matrix interfacial zone by TEM.

They are believed to be the result of interfacial reaction taking place between oxygen absorbed at the fibre surface and magnesium (aluminium) matrix during infiltration.

The expected Al_4C_3 carbide was not observed most probably due to the lack of available Al in the alloy or short time of fibre contact with the molten matrix.

The thermal expansion measurements confirmed the large anisotropy of properties in L and T directions.

The thermal expansion in L direction is distinguished by a maximum at about 65 ℃. This is related to the start of the stress relief after the compression yield stress of the matrix had been reached.

The thermal expansion in T direction exhibited some permanent elongation resulting from the plastic deformation of the matrix within the thermal cycle.

The thermal expansion of the composite is closely related to the expansion of fibres exhibiting negative CTE throughout the whole temperature range in T direction and positive CTE in L direction following the behaviour of the matrix.

No signs of any disintegration were observed after 5 thermal cycles indicating that the interfacial bonding is strong enough even without any excessive fibre-matrix reaction.

Acknowledgements

The contribution of the project "Establishment of the Centre of Excellence for research and development of structural composite materials for machine, construction and medical applications" (ITMS: 26240120006); "Building of the Centre of Excellence for research and development of structural composite materials – 2nd stage" (ITMS: 26240120020); "Centre of Excellence for glycomics" (ITMS 262401231) supported by the Operational Programme Research and Development using the financial assistance from the European Regional Development Fund (ERDF) is acknowledged. The financial support from the SRDA APVV-0556-12 project is highly appreciated.

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