Evaluation of thermal properties of MMCp composites with silver alloy matrix

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Abstract

Silver, silver alloys, and composites with silver matrix are used mainly as electric contacts, circuit-breakers, and slide bearings. Contacts working conditions require as high as possible thermal and electrical conductivity, wear resistance during electric arc work, low susceptibility to tacking, and chemical stability. Unreinforced silver alloys do not meet those expectations, hence increasing interest in metal matrix composites. Reinforcing with ceramic particles improves tribological wear resistance and minimizes formability of silver alloys. At the same time, introduction of ceramic particles decreases thermal and electrical conductivity. In this paper, manufacturing method of silver-based composites reinforced with particles Al_2O_3, SiC, and glassy carbon was described. Composites were subjected to differential thermal analysis. Furthermore, thermal diffusivity measurements using laser flash method, as well as measurements of linear thermal expansion coefficient using dilatometric method were performed in order to determine heat conductivity of the prepared composites.

Keywords Thermal analysis · MMCP · Composites · Silver matrix · Suspension method

Introduction

The application of metal matrix composites (MMCs) is common in industry [1–4]. Composites based on light metal alloys (aluminum, magnesium) are used in automotive and aerospace industries owing to their low density and simple manufacturing methods [5–7]. Composites based on nickel characterized by high-temperature creep and corrosion resistance are broadly used in space technology and aviation [8, 9]. Zinc- and lead-based composites have good sliding properties and abrasion resistance [4, 10]. Additionally, composites based on silver and copper are used as a contacts in electronics and electrotechnics due to high thermal and electrical conductivity. Furthermore, the Ag- and Cu-based composites are utilized as conductive elements, junctions or terminals [3, 11, 12].

A material dedicated for electric contacts should not change properties after numerous connections, after longer shut-down breaks, and during ongoing current passing. At the same time, it should by characterized by high thermal and electric conductivity preventing from excessive temperature rise in contacts, as well as by high melting temperature ensuring material resistance to welding and tacking [13]. Pure silver has the highest thermal and electrical conductivity and the lowest contact resistance among all metals. Due to significant workability and susceptibility to corrosion caused by sulfur oxides from the atmosphere, silver alloys are applied in industry. Alloying additions such as copper, zinc, manganese, cadmium, nickel, and aluminum increase endurance, wear resistance, sparking resistance, and corrosion resistance of silver alloys [13]. Nevertheless, those materials are susceptible to electric arc, erosion, and have poor weighting strain resistance. In order to improve those properties, reinforcing particles may be introduced into the alloy in a shape of pure elements, carbides or oxides, obtaining in this way MMCp composites with silver alloy matrix [14]. Reinforcing with particles has advantageous impact on hardness, resistance to adhesive and tribological wear, however, it decreases

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thermal and electrical conductivity, which results from higher electrical resistance of reinforcement material.

Manufacturing technologies of metal composite materials are mostly based on casting methods and powder metallurgy [3, 4, 15–17]. Among casting methods, there is gravity, pressure or centrifugal casting. Production of composites using liquid-phase methods has some disadvantages, including the presence of undesirable physicochemical phenomena between reinforcement and matrix, poor wettability, and reinforcing phase segregation. A boundary layer of different composition and properties compared to that of individual composite components is formed in the area of contact between reinforcement and metal matrix. Such phenomenon occurs due to the fact that the layer next to matrix and reinforcement is the main structural element of composites. Thickness of this layer and physicochemical nature may have influence on properties of matrix—reinforcement joint, whereas quality and properties of this joint determines properties of obtained composite. Boundary layer affects composite destruction mechanism [18, 19]. A wettability effect of reinforcing phase through liquid metal, apart from distinct impact on quality of components connection of the composite, influences on possibility of composites manufacturing using low-pressure and gravity methods. A requisite condition of creation of suspended solids in liquid matrix is a particle submersion. A homogenous distribution of particles in a liquid phase is vital for creation of a stable system. As a result of insufficient wettability, a separation of reinforcing phase from liquid metal may occur, leading to floating of particles to the surface. This adverse effect enhances with a decrease in size of particles [19]. Additionally, a reinforcing phase is segregated, and creates clusters, which are a result of various processes affecting reinforcing particles before their introduction, as well as forces from the inside of the system: solid phase–liquid metal. The area consisting of single particles contacting each other with surfaces or peaks is called agglomerate [18].

Based on the research on technologies of metal composites manufacturing, authors, in this work, applied suspension method that is combination of casting and mixing method [14, 17, 20, 21]. For the research, MMCp composites with silver alloy matrix reinforced with Al_2O_3, SiC, and glassy carbon particles were prepared. Composites were extruded on KOBO press. As a result of extrusion, final forming of composite structure with expected endurance and applicable properties occurs. Differential thermal analysis (DTA) was performed in order to determine the influence of reinforcement on temperature of transformations occurring in the composite. Values of

thermal expansion coefficient were determined as well, using measurements of thermal diffusivity and thermal expansion.

Experimental

Initial research and the literature studies proved that it is impossible to create stable suspended ceramic particles such as Al_2O_3 and SiC in pure silver due to insufficient wettability of ceramic particles by liquid silver matrix [22, 23]. In order to resolve this obstacle, techniques of a reinforcement preparation based on change of chemical composition of matrix alloy in order to lower its contact tension in liquid phase were applied. The analysis of equilibrium system of silver alloys enabled to select silver alloy with magnesium as a modification [24]. In order to secure effective wetting by liquid matrix of reinforcing particles before introducing to silver alloy, reinforcement was subjected to surface preparation by creating a composite master alloy. The process was conducted under protective atmosphere of argon, in resistance furnace, by using mixing method with graphite stirrer. Aluminum alloys with 20% magnesium may easily wet ceramic particles Al_2O_3 and SiC, therefore, such alloy was used in this experiment. Substantial fraction of magnesium in alloy matrix enabled introduction of reinforcing particles of around 60% vol. The obtained alloy was casted on cast iron board and after cooling, it was crushed to pieces of 5 mm diameter. Subsequently, master alloy containing reinforcing particles was introduced to silver alloy in induction furnace. The silver alloy with 2% silicon was melted in graphite crucible at 1100 °C, furnace was shut-down, and composite master alloy was introduced and mixed using graphite stirrer. Few cycles were performed to reduce the influence of eddy current on suspension motion in a liquid metal, whereas, also enabled introduction of desired quantity of suspension. The obtained composite was casted to graphite mold.

The composite materials after casting were subjected to direct extrusion with KOBO method. From 60 mm diameter ingots, 12 mm diameter rods were extruded. During conducted experiment, process parameters allowing obtainment of materials in shape of rods without any surface defects were determined: input temperature of 500 °C, extrusion velocity (piston rod velocity): 2 mm min^{-1}, rotation velocity 80 cycles min^{-1}.

Microscopic measurements of microstructure with HITACHI S-3400N scanning electron microscope were performed in high vacuum, using secondary electron (SE) and backscattered electron (BSE). The applied

accelerating voltage was 15 kV. Metallographic specimens were obtained from properly prepared samples cut in lateral direction with respect to material axis.

The differential thermal analysis of the MMCp composites with silver alloy matrix was conducted on thermal analyzer NETZSCH STA 449 Jupiter F3. Measurements were taken in protective atmosphere of argon in alumina crucibles on samples cylinder shaped of 5 mm diameter and 12 mm length. The temperature program was based on heating the sample with 10 °C min^{-1} velocity up to temperature 900 °C, and cooling velocity of 10 °C min^{-1}.

The thermal diffusivity was measured using laser flash method, whereas linear coefficient of thermal expansion was determined via dilatometric method in order to further determination of heat conductivity λ of the studied composites, based on dependence:

$$\lambda(T) = \rho(T) \cdot \alpha(T) \cdot C_{\mathrm{p}}(T) \tag{1}$$

where ρ—material density, α—thermal diffusivity, C_{p}—specific heat.

Thermal diffusivity was determined using NETZSCH LFA 427 device with following process parameters: sample shaped as ring of 12 mm diameter and 3 mm height, initial temperature 20 °C, voltage 450 V, pulse time 0.6 ms, argon flow 50 mL min^{-1}. The measurements of linear coefficient of thermal expansion were made on NETZSCH DIL 402C device. Process parameters were as follows: sample shaped as cylinder of 6 mm diameter and 20 mm length, initial temperature 40 °C, maximum temperature 650 °C heating velocity 5 °C min^{-1}, argon flow 50 mL min^{-1}.

Results

The phase composition of obtained composites is shown in Table 1. Sample micrographs of microstructures may be seen in Fig. 1. Matrix alloy was homogenous. Only the presence of minor contamination was identified. In the case of composite Ag/Al$_2$O$_3$, a homogenous reinforcing phase was obtained in whole volume of the material. In composite Ag/SiC, a homogenous reinforcing phase was distinguished, however, also a higher concentration of particles was identified in the center part of the samples compared to that of close to the edges. A porosity occurred as well. The composite Ag/Gc was characterized with the least homogenous distribution of a reinforcing phase.

A range of thermal stability of composites impacts on a practical aspect of application as electric contacts. With current flow in contacts, a substantial and instantaneous temperature rise occurs on surface that is related to the presence of an electric arc. It might lead to a partial melting of contact surface and as consequence, melting of its junction. Based on DTA thermal analysis, a safe temperature range for thermal work of MMCp composites may be determined.

The results of DTA analysis of MMCp composites with silver alloy matrix are shown in Fig. 2. The melting point of the matrix alloy was 812 °C, and is about 150 °C lower than melting temperature of pure silver. In the case of Ag/SiC composite, on heating curve, two distinct endothermic peaks were identified. The first one, starting at temperature about 400 °C, has no corresponding exothermic peak on cooling curve. This might be related to dissolution of a phase present in the original alloy structure after casting or during plastic work. The second endothermic peak starts at temperature 583 °C, and the corresponding exothermic effect during cooling may be identified at temperature 620 °C. In this case, an apparent phase transition occurs, which requires an additional interpretation. In the composite Ag/Al$_2$O$_3$, the distinct exothermic thermal effect accompanying cooling is present. Presumably, it is related to chemical reactions in a phase boundary between reinforcing particles and alloy matrix. The heating and cooling curves of Ag/Gc composite do not indicate thermal effects apart from the ones related to melting and solidification. Therefore, it can be stated that the

Table 1 Phase composition of studied composites

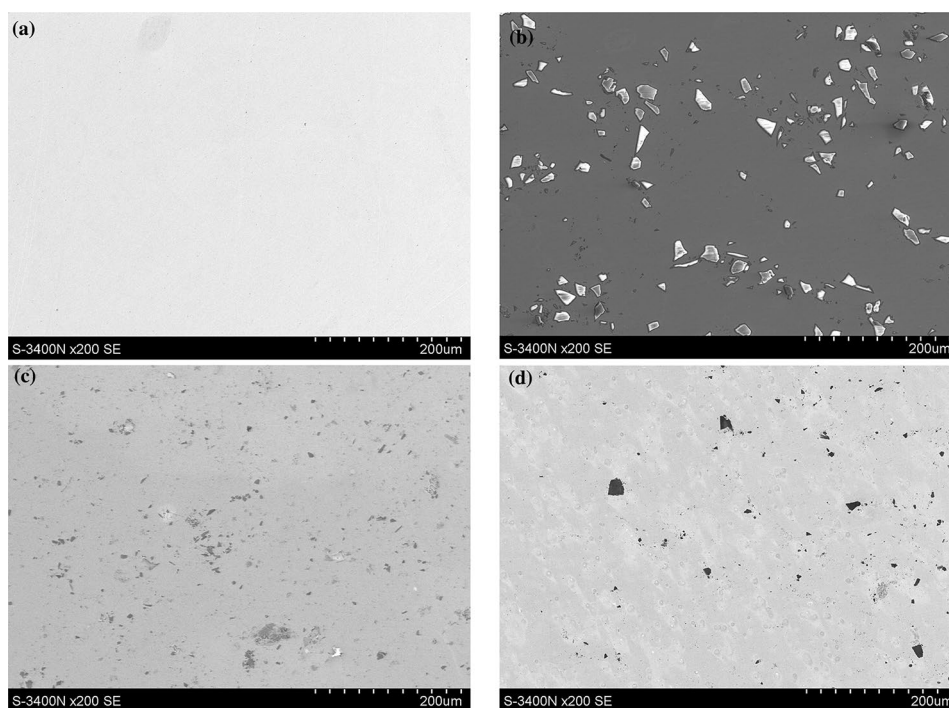| Denotation	Matrix chemical composition, at./%	Particles type	Average particle diameter/μm	Volume fraction of the reinforcing phase/%
Ag/Al$_2$O$_3$	Ag—95, Al—2.5	Al$_2$O$_3$	25–50	10
Ag/SiC	Si—1, Mg—1	SiC	20–40	10
Ag/Gc	Cu + Ni + Ti—0.5	Gc[a]	25–50	10

[a]Glassy carbon

Fig. 1 Microstructure of studied materials: **a** matrix alloy, **b** Ag/Al$_2$O$_3$ composite, **c** Ag/SiC composite, **d** Ag/Gc composite

Ag/Gc composite is stable with temperature increase until melting temperature.

Significant influence of reinforcing phase on melting temperature was stated. Table 2 presents summary of melting temperature results considering melting of pure silver. The lowest melting temperature was registered for Ag/Gc composite, and it was 647 °C. In order to explain this phenomenon, it was decided to perform an additional energy dispersive X-ray spectroscopy (EDS) analysis. The results are presented in Fig. 3. The EDS analysis shows that chemical composition of the matrix of individual composites differs near the reinforcement. Introduction of reinforcing particles into the alloy affects the kinetics of crystallization processes. Surface energy changes, and reinforcing particles also become crystal nucleus [25]. The technology of manufacturing MMCp composites described in this work requires introduction of reinforcing particles into an alloy that provides wettability. The obtained suspension is introduced into a modified silver alloy. In addition, composites were subjected to extrusion with KOBO method. For this reason, chemical composition of the matrix is developed, which makes it difficult to clearly determine the reactions taking place in tested composites.

Figure 4 shows the results of dilatometric measurements. Linear coefficient of thermal expansion of the particular reinforcing particles is several times smaller than in the case of pure silver (18 K$^{-1} \times 10^{-6}$), and is, respectively, about 4.5 K$^{-1} \times 10^{-6}$ for Al$_2$O$_3$, 3.8 K$^{-1} \times 10^{-6}$ for SiC, and 3.7 K$^{-1} \times 10^{-6}$ for glassy carbon (all values for temperature 20 °C). For this reason, the effect of thermal expansion of particles in the tested composites can be considered negligible. On the other hand, the lowest values were obtained for composite reinforced with Al$_2$O$_3$ particles. A similar phenomenon was observed in aluminum-based alloys reinforced with Al$_2$O$_3$. In the paper [25], it was showed that dimensional changes of samples and the shape of dilatometric curves are significantly influenced by the size and content of reinforcing particles. It was noted that at temperature 430 °C, deviation from tangent according to a heating direction can be correlated with polymorphic transition occurring in Al$_2$O$_3$. In the case of composite reinforced with SiC and glassy carbon, linear coefficient of thermal expansion was close to the values obtained for pure silver. It implies that in all examined composites, the presence of reinforcing particles did not influence negatively on the value of linear thermal expansion coefficient, and clearly lowered it in the case
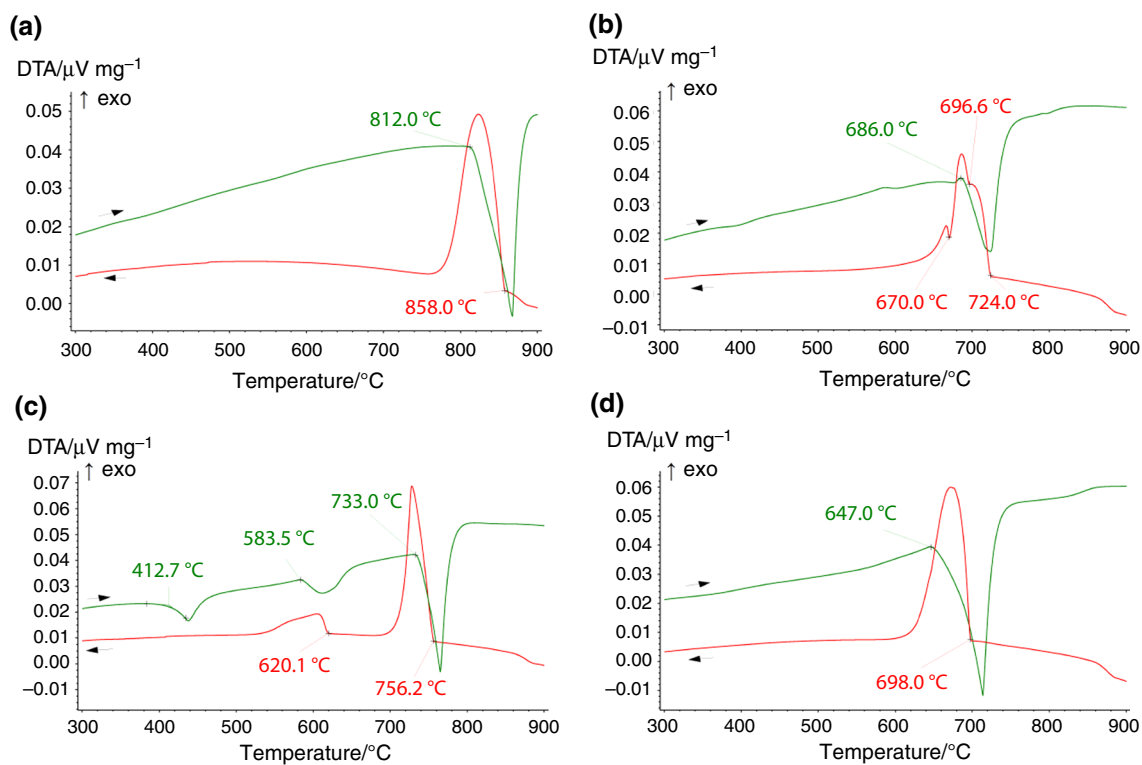
Fig. 2 DTA curves registered during melting and cooling of: **a** matrix alloy, **b** Ag/Al$_2$O$_3$ composite, **c** Ag/SiC composite, **d** Ag/Gc composite

Table 2 Melting temperature of pure silver, matrix alloy, and composites determined during DTA thermal analysis

Material	Melting temperature/°C
Ag	961.8
Matrix alloy	812.0
Ag/Al$_2$O$_3$	686.0
Ag/SiC	733.0
Ag/Gc	647.0

of composite reinforced with particles Al$_2$O$_3$. It is worth to notice that melting effects in the composite sample Ag/Gc at maximum temperature of dilatometric measurement 650 °C were not found. The onset temperature of endothermic peak is very close and equals 647 °C in this case. The explanation should be sought again in complexity of matrix alloy. In comparison with pure metals, melting of alloys is accompanied by a gentler slope of the DTA plot, which implies prior melting of minor quantities of low melting phases.

The results of thermal expansion measurements were used to calculate material density as function of temperature based on formula:

$$\rho(T) = \frac{\rho_o}{\left(1 + \frac{\Delta L}{L_o}(T)\right)^3} \tag{2}$$

where ρ_o—apparent density of material (determined using Archimedes law), L_o—initial sample length, ΔL—an increase in sample length with temperature range $\Delta T = T_k - T_o$, T_k—initial temperature of measurement, T_o—final temperature of measurement. The results are compiled in Table 3.

Figure 5 shows measurement results of thermal diffusivity α. The highest values were obtained for composite Ag/Al$_2$O$_3$, and the lowest for Ag/Gc. In both cases, the decrease in thermal diffusion value is distinct for temperature 650 °C. It may be related to proximity to melting point. However, for Ag/SiC composite, the increase in thermal diffusion at
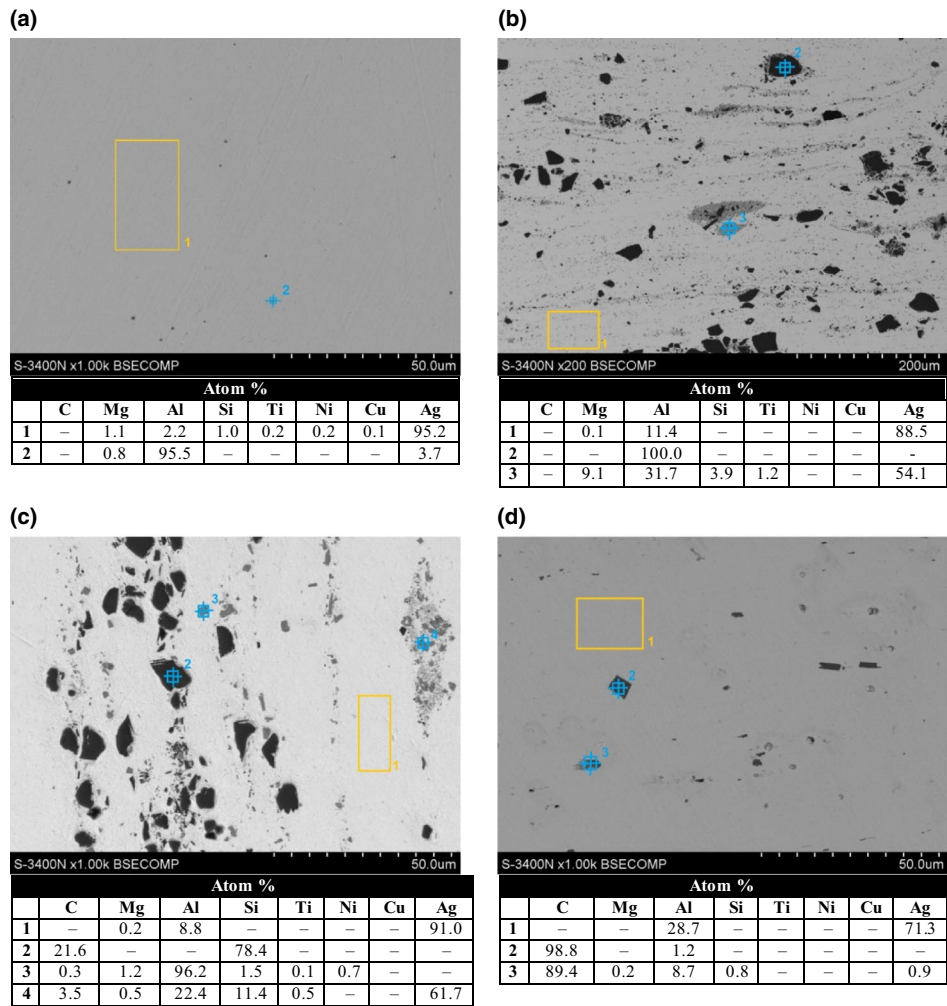
(a)

	C	Mg	Al	Si	Ti	Ni	Cu	Ag
1	–	1.1	2.2	1.0	0.2	0.2	0.1	95.2
2	–	0.8	95.5	–	–	–	–	3.7

Atom %

(b)

	C	Mg	Al	Si	Ti	Ni	Cu	Ag
1	–	0.1	11.4	–	–	–	–	88.5
2	–	–	100.0	–	–	–	–	-
3	–	9.1	31.7	3.9	1.2	–	–	54.1

Atom %

(c)

	C	Mg	Al	Si	Ti	Ni	Cu	Ag
1	–	0.2	8.8	–	–	–	–	91.0
2	21.6	–	–	78.4	–	–	–	–
3	0.3	1.2	96.2	1.5	0.1	0.7	–	–
4	3.5	0.5	22.4	11.4	0.5	–	–	61.7

Atom %

(d)

	C	Mg	Al	Si	Ti	Ni	Cu	Ag
1	–	–	28.7	–	–	–	–	71.3
2	98.8	–	1.2	–	–	–	–	–
3	89.4	0.2	8.7	0.8	–	–	–	0.9

Atom %

Fig. 3 Results of EDS analysis: **a** matrix alloy, **b** Ag/Al$_2$O$_3$ composite, **c** Ag/SiC composite, **d** Ag/Gc composite
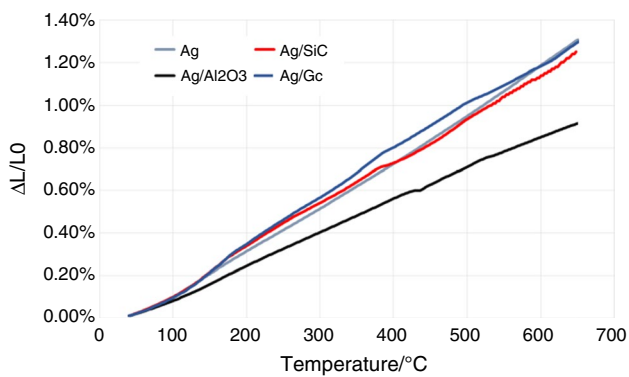

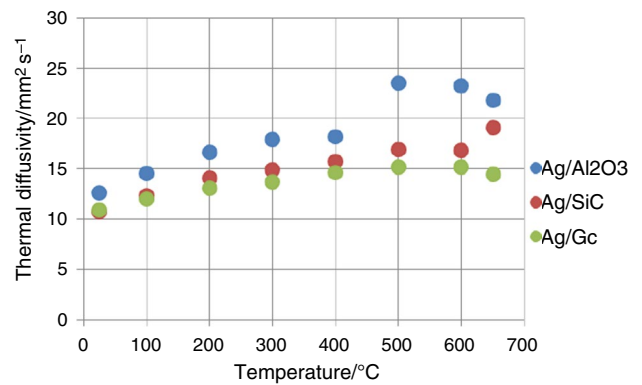**Fig. 4** Dependence of relative elongation from temperature of composites in relation to silver

Fig. 5 Thermal diffusivity of studied composites

Table 3 Calculated values of composites density in relation to temperature

	Ag/Al$_2$O$_3$	Ag/SiC	Ag/Gc
ρ_o/kg m^{-3}	7525	8156	7164
Temperature/°C	ρ (T)/kg m^{-3}	ρ (T)/kg m^{-3}	ρ (T)/kg m^{-3}
100	7503	8132	7143
200	7454	8074	7090
300	7412	8025	7044
400	7376	7981	6995
500	7335	7932	6951
600	7294	7884	6916

Table 4 Thermal conductivity of studied composites

Temperature/°C	Thermal conductivity/W m^{-1} K^{-1}		
	Ag/Al$_2$O$_3$	Ag/SiC	Ag/Gc
25	27.414	27.414	21.930
100	33.373	33.373	26.272
200	40.765	40.765	31.698
300	43.918	43.918	35.208
400	46.267	46.267	39.253
500	61.631	61.631	42.481
600	61.282	61.282	42.246
650	57.550	57.550	40.506
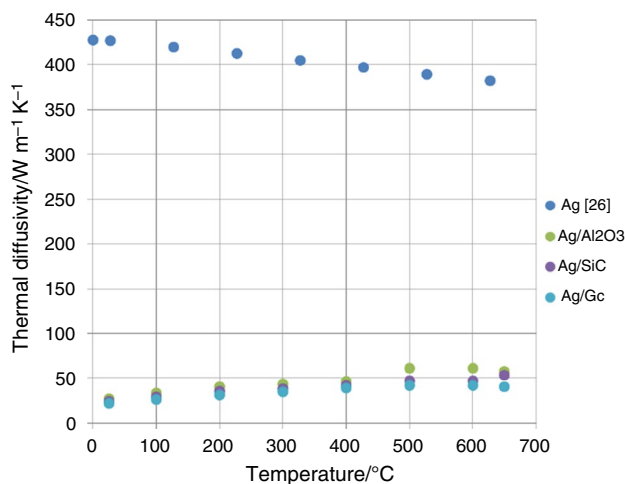
Fig. 6 Thermal conductivity coefficient of studied composites and pure silver

temperature 650 °C is present, which may result from phase transition noted during thermal analysis. The distinct increase in thermal diffusion for temperature between 400 and 500 °C for Ag/Al$_2$O$_3$ might prove the presence of polymorphic phase Al$_2$O$_3$, which was not registered on DTA curves due to low sensitivity, whereas, occurs on dilatometric curve.

Thermal conductivity coefficient λ of examined composites was determined by substituting to formula (1) all obtained results with values of specific heat C_P, determined based on thermodynamic data of pure components based on mixing principle:

$$Cp = \sum_{i=1}^{n} Cp_i \cdot V_i \qquad (3)$$

where Cp_i—specific heat of the component, V_i—volume fraction of the component. The results are combined in Table 4; Fig. 6 compares it with value of coefficient λ for pure silver [26]. The value of thermal conductivity coefficient λ in the tested composites increases with temperature, however, it is few times lower than that of pure silver. It is related to not only the presence of reinforcing phases of Al$_2$O$_3$, SiC and glassy carbon, however, is also connected with chemical composition of matrix alloy, which apart from silver contains 5% of other alloying components.

Conclusions

1. The suspension method was used for preparation of MMCp composites with silver alloy matrix, presented in this paper, enables wetting of Al$_2$O$_3$ and SiC particles by liquid silver.

2. Differential thermal analysis indicated that the presence of reinforcing particles leads to lowering of melting temperature of studied composites due to affect of kinetics and crystallization processes by particles. In the case of composite reinforced with glassy carbon, it is up to 150 °C with regards to alloy matrix.

3. The studied composites indicate thermal stability in the range up to 650 °C. The only exception is composite reinforced with SiC particles, for which, the distinct thermal effects related to phase transition below this temperature were present.

4. The presence of a reinforcing phase in form of particles has an influence on thermal expansion of composites with silver alloy matrix. Aluminum oxide particles clearly reduce thermal expansion as opposed to silicon carbide and glassy carbon particles, which slightly changes it in relation to pure silver.

5. Matrix alloy composition and the presence of a reinforcing phase in form of Al_2O_3, SiC and Gc particles affects thermal conductivity of the composites. With addition of reinforcing particles, there is approximately eight times decrease in thermal conductivity in relation to pure silver.

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