

Lightweight metal matrix composites with
graphitic fillers showing high thermal
conductivity and low thermal expansion.

A Dissertation

submitted in Partial Fulfilment of the
Requirements for the Degree of Dr. rer. nat.

to the Department of Physics of
Freie Universität Berlin

by

Valerio Oddone

Berlin, Dezember 2018

Tag der Einreichung / submission date: Berlin, 12. Dezember 2018

Tag der Verteidigung / defense date: Berlin, 06. Juni 2019

1. Gutachter / supervisor: Prof. Dr. Stephanie Reich

2. Gutachter / second reviewing professor: Prof. Dr. Michael Giersig

Table of Contents

| | |
|---|----|
| Preamble | 4 |
| List of publications..... | 4 |
| Introduction..... | 6 |
| State of the art and motivation..... | 6 |
| Scientific methods | 7 |
| Sample production by Spark Plasma Sintering..... | 7 |
| Thermal diffusivity measurements by flash method | 8 |
| Thermal expansion measurements by dilatometry | 9 |
| Residual strain determination by neutron scattering | 9 |
| Guide through the published papers | 10 |
| Outlook..... | 13 |
| Acknowledgements | 13 |
| Bibliography..... | 14 |
| German abstract..... | 16 |
| Kurzfassung | 16 |
| Eidesstattliche Erklärung | 17 |

Appendix: included first autor publications

Preamble

This doctoral thesis is organized as *cumulative paper* according to §11 of the *Promotionsordnung des Fachbereichs Physik der Freien Universität Berlin* (Doctorate Rules and Regulations of the Physics Department of Freie Universität Berlin). The performed research work and main results are reported in four scientific publications listed below. In line with requirements from the *Promotionsordnung*, the included publications are first author papers and were accepted in internationally recognized scientific journals with a peer-review process. This document presents the motivation of the performed research as well as the state of the art; it describes the used scientific methods in details and the physical background; finally, it guides the reader through the four scientific publications.

List of publications

1. Oddone V, Boerner B, Reich S (2017). *Composites of aluminum alloy and magnesium alloy with graphite showing low thermal expansion and high specific thermal conductivity*. Science and Technology of Advanced Materials, 18 (1), 180-186.^[1]
<https://doi.org/10.1080/14686996.2017.1286222>

I conceived the project and wrote the manuscript. The samples were fabricated and characterized by B. Börner and me. S. Reich commented the data and revised the manuscript.

2. Oddone V, Reich S (2017). *Thermal properties of metal matrix composites with planar distribution of carbon fibres*. Rapid Research Letters, 11 (6).^[2]
<https://doi.org/10.1002/pssr.201700090>

I conceived the project, performed the experimental work and interpreted the data with theoretical models. S. Reich commented the data and theoretical models. The manuscript was written by me and revised by S. Reich..

3. Oddone V, Segl J, Prakasam M, Hartmann M T, Silvain J-F, Edtmaier C, Reich S (2018). *Isotropic thermal expansion in anisotropic thermal management composites filled with carbon fibres and graphite*. Journal of Materials Science, 53 (15).^[3]
<https://doi.org/10.1007/s10853-018-2373-6>

I conceived the project, fabricated the sintered samples, performed the thermal measurements and wrote the manuscript. J. Segl and C. Edtmaier measured the carbide content of the composites. M. Prakasam and J.-F. Silvain produced samples by hot-pressing. M. Hartmann and S. Reich commented the data. All authors revised the manuscript.

4. Oddone V, Wimpory R C, Reich S (2019). *Understanding the negative thermal expansion in planar graphite-metal composites*. Journal of Materials Science, 54 (2).^[4]
<https://www.doi.org/10.1007/s10853-018-2879-y>

I produced the samples, performed the dilatometry measurements, interpreted the data and wrote the manuscript. The neutron scattering measurements were performed by R. C. Wimpory. The project was conceived by S. Reich and me. All authors commented and revised the manuscript.

Three further research works were submitted during the doctorate, but are not part of this thesis:

5. Morfa A J, Oddone V, Giersig M (2016). *Large-area, polarisation-sensitive plasmonic materials from colloidal lithography*. Rapid Research Letters, 10 (5).

A. J. Morfa conceived the project, performed the simulations and wrote the manuscript. I fabricated the nanostructures, measured the optical properties and revised the manuscript. M. Giersig commented the data and the manuscript

6. Oddone V, Giersig M. (2017). *Nanosphere lithography with variable deposition angle for the production of one-directional transparent conductors*. Rapid Research Letters, 11 (3).

I conceived the project, performed the experimental work, interpreted the data and wrote the manuscript. M. Giersig commented the data and revised the manuscript.

7. Mueller N S, Vieira B G M, Schulz F, Kusch P, Oddone V, Barros E B, Lange H, Reich S (2018). *Dark Interlayer Plasmons in Colloidal Gold Nanoparticle Bi-and Few-Layers*. ACS Photonics, 5 (10).

N. Müller performed all optical measurements and the, interpreted the data and wrote the manuscript. B. G. M. Vieira performed the simulations. F. Schulz and H. Lange prepared the nanostructures. F. Schulz performed the TEM measurements. P. Kusch and I helped to set up the optical spectrometer for micro-absorbance measurements. The project was conceived by S. Reich and N. Müller. All coauthors discussed the data and commented on the manuscript.

Introduction

The development of high-performance electronic components shows a trend towards miniaturization and higher electrical power. Apart from recent high energy efficiency applications for battery driven devices, an exponential growth in power density of microchips was recorded^[5,6], which makes thermal dissipation challenging. Heat sinks with excellent thermal conductivity (TC) cannot be exploited to their maximum if the interface to the cooled electronic component is poor due to a thermal paste layer. Direct, solid-solid interfaces achieve a lower interfacial thermal resistance (or Kapitza resistance), but require matching coefficients of thermal expansion (CTE) to avoid mechanical failure^[7,8].

While the semiconductors typically used in microprocessors have a CTE between 4.2 ppm K⁻¹ for silicon and 5.9 ppm K⁻¹ for gallium arsenide, the CTE of thermally conducting metals ranges from 17 ppm K⁻¹ in copper to 24 ppm K⁻¹ in aluminum^[9]. A reduction of this thermal mismatch is the main motivation for investigating materials combining a high TC and a low CTE.

Besides the cooling of high performance electronics, which is the focus of this research work, materials with high TC and tunable CTE are of interest in several areas of engineering experiencing high thermal excursions, for instance in aerospace^[10]. Both for mobile electronic devices and for aerospace application, a third fundamental property is required: a possibly low density.

State of the art and motivation

Metal matrix composites were extensively investigated to combine the above mentioned three properties: high TC, low CTE and low density. Apart from niche applications exploiting the excellent properties of diamond^[11-13], graphite based fillers were used. These have a density of approximately 2200 kg m⁻³ (or lower for nanomaterials), low CTE, high TC and high tensile modulus in one or two dimensions, as reported in Table 1. If the CTE of the composite has to be constrained by the filler, a high modulus is necessary.

Table 1: Thermal properties and elasticity Modulus for selected graphitic fillers.

| | TC / W m ⁻¹ K ⁻¹ | CTE / ppm K ⁻¹ | Modulus / GPa |
|----------------------------------|---|-------------------------------------|-----------------------------------|
| Crystalline graphite | 2000-3000 (x,y), 6-10 (z) ^[14,15] | -1 (x,y), 28 (z) ^[16,17] | 1050 (x,y) ^[18] |
| Graphene | 1500-5000 (x,y) ^[19,20] | -8 (x,y) ^[21] | Up to 1000 (x,y) ^[20] |
| Pitch-based carbon fibers | 1-5 (x,y), 120-1100 (z) ^[9,18] | -1.5 (z) ^[9,22] | 640-960 (z) ^[9,18] |
| PAN-based carbon fibers | 0.8-5 (x,y), 8-70 (z) ^[9,18,23] | -1.5 (z) ^[9] | 220-600 (z) ^[9,18] |
| Carbon nanotubes | 1100-7000 (z) ^[14,24] | 0 (z) ^[24] | 150-1000 (x,y) ^[24,25] |

While nanomaterials such as graphene and carbon nanotubes are used as mechanical reinforcement of composites, they are in spite of their extremely high TC not suited as fillers for thermal management applications. Thermal conduction is mediated by electrons in metals and by phonons in carbon based materials, which causes a high Kapitza resistance at interfaces. Due to the high surface-to-volume ratio of nanofillers the interface losses are particularly relevant.

Instead, two macroscopic graphite based fillers were shown to have promising properties: crystalline graphite flakes^[1,17,26-32] and pitch based carbon fibers^[2,10,23,33,34].

As matrices, well conducting metals are best suited. Excluding the use of silver and gold for bulk applications, copper is the best choice if TC and CTE are the only parameters to optimize. If the weight plays a role, low density metals as aluminum, magnesium and their alloys are a better compromise. Alloys have in general lower TC than pure metals, but significantly higher mechanical strength. For instance, pure aluminum has a TC above $200 \text{ W m}^{-1} \text{ K}^{-1}$ and a tensile strength of 50 MPa, while the high-performance aluminum alloy AL7075 has a TC of $130 \text{ W m}^{-1} \text{ K}^{-1}$ but a tensile strength exceeding 500 MPa. A stronger matrix allows a higher maximal filler concentration in the composite before mechanical failure.

A more extensive literature review for thermal management composites can be found in the published works about graphite-metal composites^[1] and fibers-metal composites^[2].

Scientific methods

Metal matrix composites were produced by powder metallurgy. As matrix powders we used pure metals (aluminum, magnesium, copper), prealloyed powders (aluminum alloys and magnesium alloys) and elemental mixtures forming alloys during sintering. As fillers with high TC we used crystalline graphite flakes and pitch-based carbon fibers. Matrix and filler were mixed by hand. Details on used materials and powder preparation can be found in the published works.

Sample production by Spark Plasma Sintering

The composites of metal matrix and graphitic filler must be solidified without reaching the melting point of the metal (or liquidus temperature in alloys) in order to avoid a separation of phases with different density and to restrain chemical reactions between graphite and metal. A suited technique, the sintering, is known since the invention of ceramic. In the traditional sintering, powders which were pressed and formed in a first step are heated to a temperature below the melting point in a second step. A development of the traditional sintering is the *hot-pressing*, in which compression and heating takes place contemporaneously, achieving better densification of the powder. In this work, *Spark Plasma Sintering* (SPS) was used: a hot-pressing technique using a current flow through sample and crucible to increase the temperature by Joule heating. Very high heating rates exceeding 100 K min^{-1} are achieved and consequently short sinter times, which is helpful to limit the crystal growth in metal powders and chemical reactions between components of a composite material^[35-37]. It is highly controversial whether electric field and current flow through the sample have a direct influence on densification and properties of the material^[38]. Despite its misleading name, in general there are no plasma or sparks between the powder grains in a SPS process^[39,40], unless materials with high hardness and low electrical conductivity are used^[41].

For our research application, the main advantage of SPS in comparison to traditional sintering or hot-pressing is its high sample production rate. In a working day, a single person can produce and characterize five to ten samples with different composition, production parameters or shape. In little time a wide range of production parameters can be tested in order to optimize the sintered material. In this research work, the effect of the following parameters was intensively investigated in theory and experiments:

- Composition and grain size of matrix and filler

- Techniques to produce a powder mixture
- Heating rate and holding times
- Maximum sintering temperature
- Sintering pressure

As SPS system, a *Dr. Sinter Lab SPS-2111x* from *Fuji Electronic Industrial co. Ltd.* (Japan) was used. Figure 1 shows the setup and typical SPS parameters. Metal powders and graphitic fillers were mixed by hand and filled in graphite crucibles with a diameter from 6 to 25 mm. To avoid adhesion between punch and sample, boron nitride or graphite spray was used. Sintering took place in a rough vacuum and a uniaxial pressure of up to 60 MPa was applied to the sample. Heating was provided by a current flow up to 1000 A. Sinter temperatures of 500-600°C were reached in 10-20 minutes. Details on sinter parameters are found in the published papers.

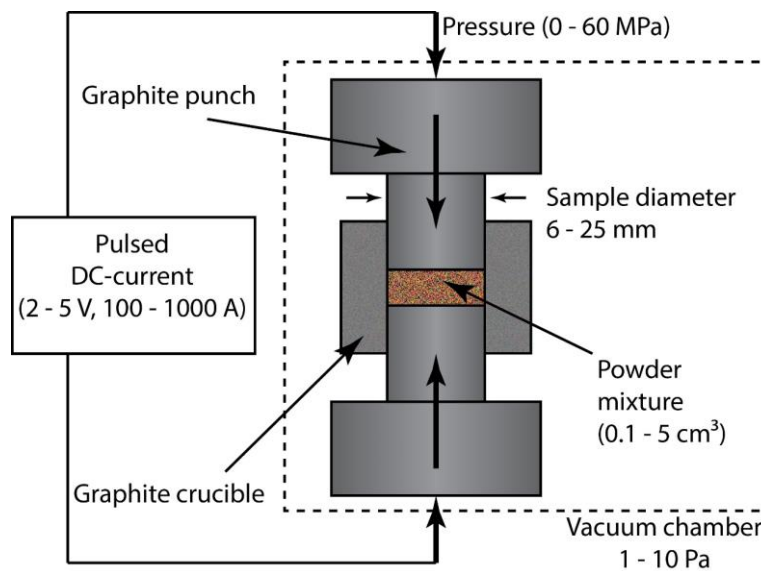


Figure 1. Scheme of the SPS system and typical sintering parameters.

Thermal diffusivity measurements by flash method

Several methods are known for TC measurement of solid materials. We used the flash method, which is suited for fast measurements on small samples.

In the flash method, samples are heated with a short light flash on one side and the temperature growth profile is measured with an infrared thermometer from the other side. The evaluation of the time from the flash to the maximal temperature gives the thermal diffusivity of the sample, whereby the achieved temperature is not relevant. In this way, the method is neither influenced by uncertainty in energy of the flash nor on the capability of the sample to absorb or emit heat radiation (apart from the signal to noise ratio, which is higher for dark samples).

The thermal diffusivity is a measure for the heat transfer rate from the hot to the cold side of a material. By multiplication of thermal diffusivity, specific heat capacity and density of the sample, the TC is obtained.

In-plane thermal diffusivity measurements, i.e. perpendicularly to the heat flow, were performed by radial heat flow method as described by Donaldson et al^[42,43].: a special sample holder was used in which the sample is heated in the central part of the front side and the temperature rise is measured close to the edges on the rear side (Figure 2).

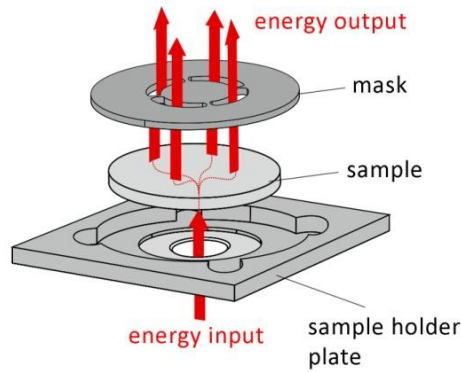


Figure 2. Thermal diffusivity measurement by radial heat flow method.

Thermal expansion measurements by dilatometry

The CTE of the samples was measured by dilatometry, i.e. by heating of the samples in an oven and direct measurement of the thermal expansion. The used samples are cylinders or cubes with 4-6 mm length. Due to the interest in thermal management applications, for most measurements temperatures up to 150°C were investigated. To avoid temperature gradients in oven and sample, slow heating curves with not more than 1 K min⁻¹ were used. Most samples showed an anomalous expansion and contraction during the first heating cycles until internal thermal strains balanced (Figure 3). In this case, several heating-cooling cycles or a thermal treatment of the matrix were performed and the data were evaluated only after the stabilization. Further details on the used parameters can be found in the publications.

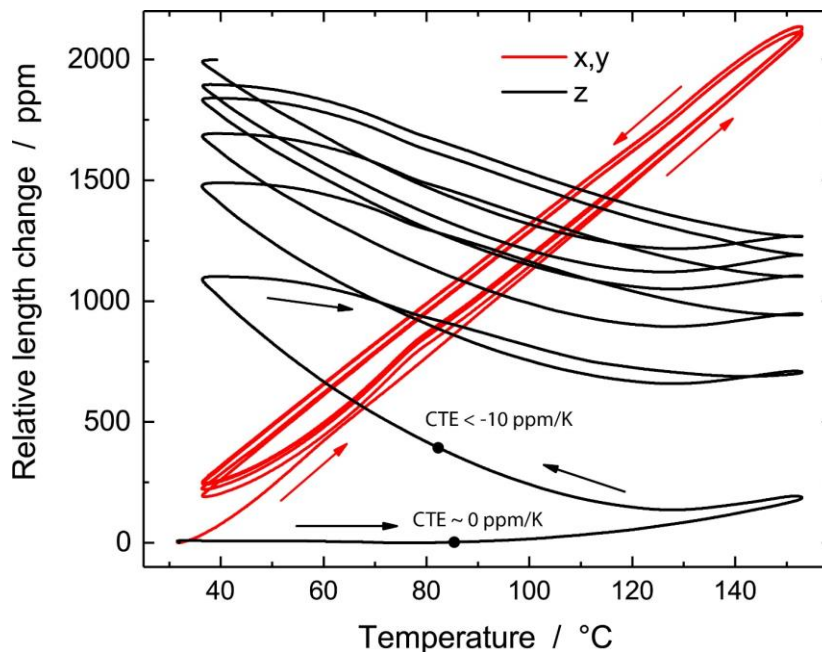


Figure 3. Dilatometry curves for an aluminum-graphite composite needing several heating-cooling cycles before reaching a stable thermal expansion behavior in z-direction, i.e. perpendicular to the graphite flakes.

Residual strain determination by neutron scattering

To develop physical models of the CTE of our sintered composites, the strain induced by the matrix to the filler had to be determined. Since the strain on the sample surface is different than in the bulk, a measurement method with high penetration depth was necessary. Synchrotron

radiation and neutrons have weak interaction with matter, so they may be used for investigating several millimeters or even centimeters below the surface of a bulk sample.

We performed neutron scattering to measure the temperature dependent strain of free and embedded graphite flakes. The measurements were performed at the *Helmholtz-Zentrum Berlin for Materials and Energy*, using the neutron source *BER II* and the experimental setup *E3, Residual Stress Analysis and Texture Diffractometer*.

Fast neutrons are produced in a small pool-type nuclear reactor (10 MW thermal power) and moderated by the cooling water. A monochromator selects neutrons with a wavelength of 0.147 nm (38 meV). The focused, monochromatic neutron beam is scattered on a sample located in an oven. The temperature dependent lattice parameters and related thermal strain are determined according to Bragg's Law.

Guide through the published papers

This research work was inspired the studies of A. Boden and I. Firkowska on copper graphite composites^[31,32]. They investigated the thermal properties of a copper-graphite composite with enhanced TC in a plane and reduced CTE across the plane. The first step of this work was an extension on further metal matrices with a focus on light metals, i.e. aluminum alloys and magnesium alloys. This change in matrix presents two difficulties. First, light metals have strong oxide layers on the surface which obstacles the sintering process. Second, the CTE is on the order of 23-25 ppm K⁻¹, higher than the 16 ppm K⁻¹ of copper. This induces stronger thermal strains in the composites. In the first publication, titled *Composites of aluminum alloy and magnesium alloy with graphite showing low thermal expansion and high specific thermal conductivity*^[1], we showed that despite of these two properties of light metals, high performance composites can be achieved. Using light metals as matrix, we produced composites with lower density than aluminum. To overcome the oxide layer, sinter temperatures near to the melting point had to be chosen. A thermal treatment after sintering was performed to balance the internal strains and increase the strength. The specific TC of the composite, i.e. TC divided by density, was in the x,y-plane over four time higher than in copper and two times higher than in copper-graphite composites for a filler concentration of 50vol% (Figure 4). The CTE along the z-axis was reduced down to -10 ppm K⁻¹, significantly lower than in copper-graphite composites, which always had positive CTE.

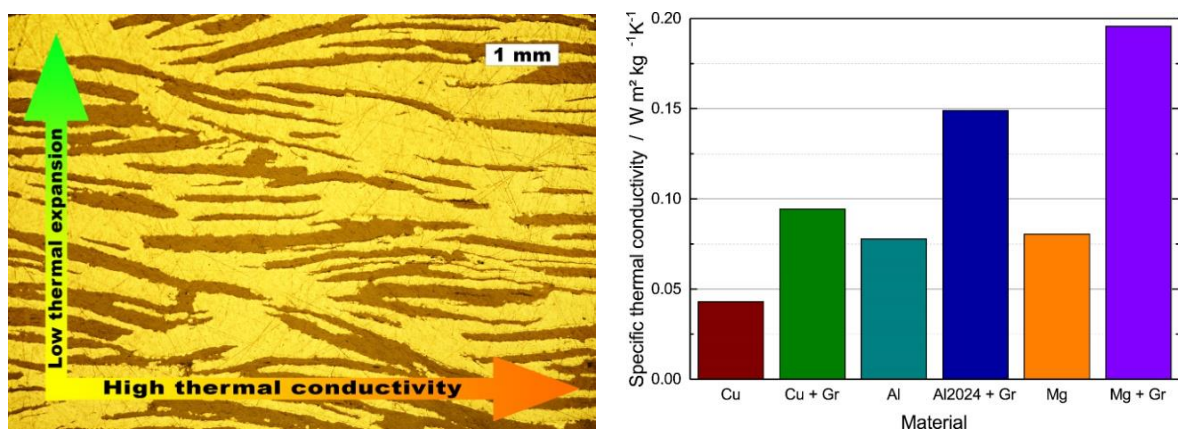


Figure 4: Structure of a sintered aluminum-graphite composite showing the orientation of the flakes (dark) in the x,y-plane, perpendicular to the compression direction (left). Specific thermal conductivity of pure metals and metal-graphite composites (right).

After substitution of the matrix, the research proceeded with new fillers. In the second publication, titled *Thermal properties of metal matrix composites with planar distribution of carbon fibres* [2], the graphite flakes were substituted with pitch-based carbon fibers (CF). For structural purposes, CF derived from polyacrylonitrile (PAN) are typically used. In comparison, pitch-based CF have higher elasticity modulus and approximately two orders of magnitude higher TC (Table 1), both desirable properties for a composite with reduced CTE and high TC. The TC of fibers is lower than in graphite flakes, and, most importantly, is unidirectional and not bidirectional. On the other hand, the fibers are mechanically better suited as filler, allowing higher concentrations up to 65vol% and very stable samples, which could be machined in complex shapes (Figure 5, left). The TC was lower than in composites with graphite but still in the x,y-plane slightly higher than in the pure metal matrix. We achieved here an opposite geometry of the CTE: a two-dimensional reduction on the x,y-plane and an increase along the z-axis. Further we produced samples with a gradient in the fibers concentration (Figure 5, right). If a heat sink is connected at the two sides with devices with different CTE, e.g. copper heat pipes and a semiconductor, its CTE can be tuned with the fibers concentration gradient to match both sides, distributing the strain in the whole volume instead of at a thin interface.

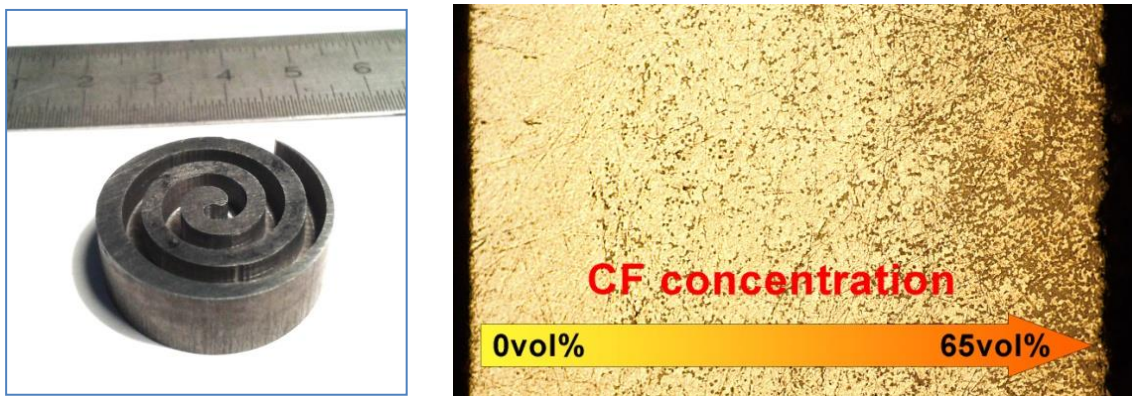


Figure 5. Aluminum-CF composites can be milled into complex shapes with thin walls (left). Sample with a gradient in the CF concentration to achieve two different CTE values at the two sides (right).

The third step was to combine the first two approaches yielding a novel material: if graphite flakes reduce the z-CTE and carbon fibers the x,y-CTE, any geometry in the thermal expansion in between is achieved with a mixture of flakes and fibers (Figure 6). Three-phases composites of metal, graphite flakes and carbon fibers were presented in the third publication, titled *Isotropic thermal expansion in anisotropic thermal management composites filled with carbon fibres and graphite*[3]. With a mixture of 1:3 of fibers to flakes in the filler, the CTE in the composite was isotropic (intersection of the blue lines in Figure 6, right) and reduced to 12 ppm K⁻¹, 50% of the metal matrix. The TC remained similar to pure graphite-metal composites. By further substituting a third of the filler with silicon we obtained a composite with similar CTE, higher isotropy in TC and better mechanical properties.

With the goal of technical applications, we finally showed that the described properties are intrinsic to the material compositions. Sintering parameters such as temperature, heating rate, holding time and pressure only have minor effects on the thermal properties of the material. In particular, materials with similar TC and CTE can be sintered by hot-pressing, which requires simpler and cheaper equipment compared to SPS, but is limited in its heating rates.

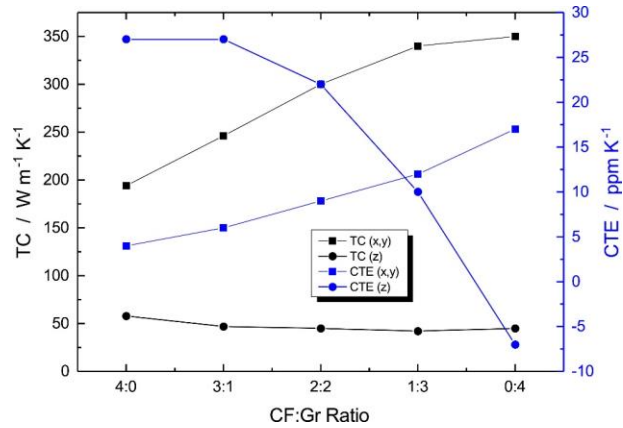
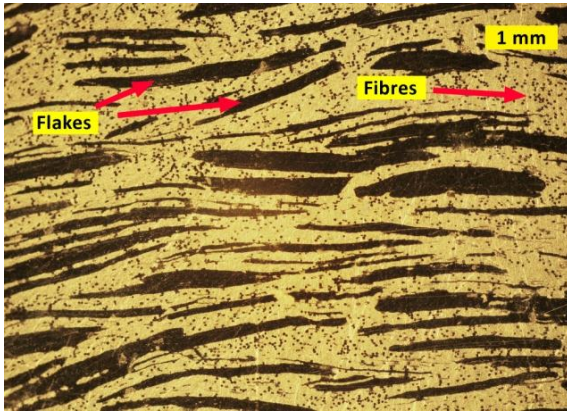


Figure 6. Structure of a composite with Al2024-alloy matrix and a filler mixture of 1:3 of carbon fibers and graphite flakes (left). TC and CTE of the composite parallel (z) and perpendicular (x,y) to the pressing direction (right): for a 1:3 carbon fibers to graphite ratio in the filler the CTE is isotropic (intersection of the blue lines at ≈ 12 ppm K⁻¹).

Finally, an explanation of the low thermal expansion along the z-axis of graphite-metal composites was attempted. Since metals have an isotropic CTE and graphite a positive z-CTE, the negative z-CTE of the composites cannot be explained by the simple stapling of the components. A significant mechanical interaction between matrix and filler must play a role. A previous theory^[32] correctly predicted the z-CTE of copper-graphite composites assuming that the cooling after the sintering process produces a compressive x,y strain in the graphite flakes at room temperature. For increasing temperatures, both matrix and filler would expand equally on the x,y-plane, i.e. the graphite flakes would be stretched by the expanding matrix and consequently contract in z-direction. With knowledge of the measured x,y-CTE and of the temperature dependent elasticity constants of graphite, the z-CTE of the flakes could be determined. Combining this value with the isotropic CTE of the copper matrix, the z-CTE of the samples was calculated.

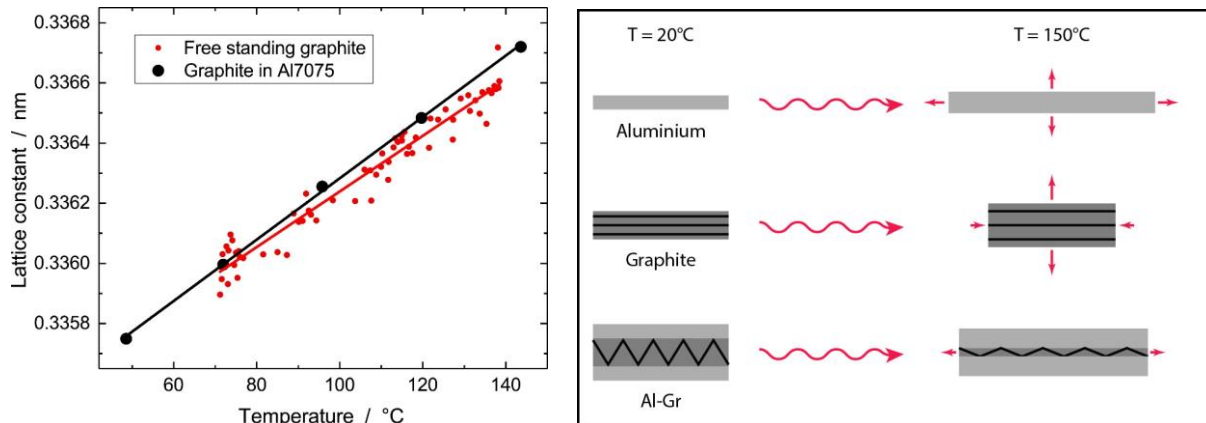


Figure 7. Temperature dependent measurements of the lattice constant in free graphite and embedded graphite in aluminum alloy Al7075: no significant thermal strain can be detected in the composite (left). Proposed model for the description of the low z-CTE assuming a macroscopic folding and unfolding of the graphite flakes in the expanding metal matrix (right).

As presented in the fourth publication, titled *Understanding the negative thermal expansion in planar graphite-metal composites*^[4], neutron scattering measurements did not show any microscopic strain in the graphite flakes. We measured identical lattice constants in free graphite and embedded graphite from 50°C to 150°C (Figure 7, left). This can be easily explained by comparing the elasticity modulus of graphite in the x,y-plane (above 1 TPa) and of the used metal matrices (from 40 GPa for magnesium to 117 GPa for copper): in a 1:1 mixture in volume the metal

can hardly stretch the graphite flakes. We suggest that the low z-CTE is a consequence of a macroscopic folding and unfolding of the flakes in the contracting and expanding matrix (Figure 7, right). This is supported by the observation that the z-CTE is always positive for temperatures above 200-300°C, at which the flakes are probably completely unfolded. This theory might be proved by a temperature dependent measurement of the graphite lattice orientation in the matrix.

Outlook

The presented composites achieved properties that greatly exceeded the expectations at the beginning of the work. For instance, we demonstrated magnesium-graphite composites with a specific thermal conductivity four times higher than in copper. While copper-graphite composites had a z-CTE approaching zero, similar materials with aluminum alloy matrix had a z-CTE below -10 ppm K⁻¹, although the CTE of the matrix is approximately 50% higher. A physical model qualitatively explaining this phenomenon was proposed, whereby an experimental proof is still needed. Finally, the three phase composites with metal matrix and a mixture of carbon fibers and graphite as filler had in spite of the highly anisotropic fillers an isotropic CTE.

The presented materials have surely potential for further improvement. As we showed, the production parameters play a secondary role for the resulting thermal properties^[3]. Therefore further research works should rather concentrate on the composition of matrix and fillers. For carbon fibers as filler we achieved a TC which is lower than predicted^[2]: further studies may focus on the interface between metal and carbon. As next step in view of the first technical applications, larger samples must be sintered. Scale factors could influence the physical properties positively or negatively.

Acknowledgements

I am thankful to Prof. Stephanie Reich and to the colleagues of the group for these three years, Benji Börner, Niclas Müller and Martin Hartmann in particular. Unfortunately, I remained a bit alone in the materials science topic, so I had only rare occasions to work with them. On the other hand I had many occasions to participate to their projects, in particular where technical help was needed. I really appreciated the relaxed atmosphere in the group, the frequent cakes and pies, as well as the freedom in starting projects even if they have nothing to do with the focus of our group – to mention one, a study on the sweet taste of heavy water. Also, I had the incredible luck that almost every idea and experiment was successful and often brought better results than expected.

The whole doctoral thesis was financially supported by the *Evonic Foundation*, to which I am not only grateful for its generosity, but also for its trust: the paperwork was reduced to a minimum and every issue, such as a conference visit, could be solved with a few e-mails instead of filling dozens of forms and gathering bills.

I moved to Berlin in September 2009 and began two weeks later my physics studies at the FU Berlin. I had a great time there, did my Bachelor Thesis at AG Reich, my Master Thesis at AG Giersig and went back to AG Reich for the PhD. I enjoyed the lectures, met interesting people and liked the experimental work in the labs. I cannot avoid mentioning the student workshop, where I spent probably more time than anyone else at the department. I built there devices for my master and PhD thesis as well as for colleagues and for other projects. A particular thank to Michael Prüfer and to the team of the helium liquefaction plant for supervising this workshop and for teaching us how to use the machines.

Bibliography

- 1 V. Oddone, B. Boerner, and S. Reich: *Sci. Technol. Adv. Mater.*, 2017, vol. 18, pp. 180–6.
- 2 V. Oddone and S. Reich: *Phys. status solidi - Rapid Res. Lett.*, 2017, vol. 1700090, p. 1700090.
- 3 V. Oddone, J. Segl, M. Prakasam, M.T. Hartmann, C. Edtmaier, and S. Reich: *J. Mater. Sci.*, 2018, vol. 53, pp. 10910–9.
- 4 V. Oddone, R.C. Wimpory, and S. Reich: *J. Mater. Sci.*, 2019, vol. 54, pp. 1267–1274.
- 5 G. Taylor: *Proc. EPEPS*.
- 6 A. Danowitz, K. Kelley, J. Mao, J.P. Stevenson, and M. Horowitz: *Commun. ACM*, 2012, vol. 55, pp. 55–63.
- 7 R.O. Carlson, H.H. Glascock, H.F. Webster, and C.A. Neugebauer: in *MRS Proceedings*, vol. 40, Cambridge Univ Press, 1984, p. 177.
- 8 D.D.L. Chung: *Materials for Electronic Packaging*, Butterworth-Heinemann, Woburn (MA), 1995.
- 9 P.-M. Geffroy, J.-F. Silvain, and J.-M. Heintz: in *Advances in Composite Materials - Ecodesign and Analysis*, B. Attaf, ed., InTech, 2011, pp. 271–2.
- 10 S. Rawal: *JOM J. Miner. Met. Mater. Soc.*, 2001, vol. 53, pp. 14–7.
- 11 J. Segl, C. Edtmaier, and E. Rosenberg: in *World PM2016*, 2016, pp. 1–7.
- 12 I.E. Monje, E. Louis, and J.M. Molina: *Compos. Part A Appl. Sci. Manuf.*, 2013, vol. 48, pp. 9–14.
- 13 K. Yoshida and H. Morigami: *Microelectron. Reliab.*, 2004, vol. 44, pp. 303–8.
- 14 A.A. Balandin: *Nat Mater*, 2011, vol. 10, pp. 569–81.
- 15 R. Prieto, J.M. Molina, J. Narciso, and E. Louis: *Scr. Mater.*, 2008, vol. 59, pp. 11–4.
- 16 J.B. Nelson and D.P. Riley: *Proc. Phys. Soc.*, 1945, vol. 57, p. 477.
- 17 H. Bai, C. Xue, J. Lyu, J. Li, G. Chen, J. Yu, C. Lin, D. Lv, and L. Xiong: *Compos. Part A*, 2018, vol. 106, pp. 42–51.
- 18 M.L. Minus and S. Kumar: *J. Miner. Met. Mater. Soc.*, 2005, vol. 57, pp. 52–8.
- 19 A. a Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C.N. Lau: *Nano Lett.*, 2008, vol. 8, pp. 902–7.
- 20 X. Huang, X. Qi, F. Boey, and H. Zhang: *Chem. Soc. Rev.*, 2012, vol. 41, pp. 666–86.
- 21 D. Yoon, Y.-W. Son, and H. Cheong: *Nano Lett.*, 2011, vol. 11, pp. 3227–31.
- 22 M. Russell-Stevens, R.I. Todd, and M. Papakyriacou: *J. Mater. Sci.*, 2006, vol. 41, pp. 6228–36.
- 23 J. Koráb, P. Štefánik, S. Kavecký, P. Šebo, and G. Korb: *Compos. - Part A*, 2002, vol. 33, pp. 577–81.

- 24 K. Chu, Q. Wu, C. Jia, X. Liang, J. Nie, W. Tian, G. Gai, and H. Guo: *Compos. Sci. Technol.*, 2010, vol. 70, pp. 298–304.
- 25 R. George, K.T. Kashyap, R. Rahul, and S. Yamdagni: *Scr. Mater.*, 2005, vol. 53, pp. 1159–63.
- 26 J.A. Cornie, S. Zhang, R. Desberg, and M. Ryals: *Met. Matrix Compos. LLC*, 2003, p. 7.
- 27 J.K. Chen and I.S. Huang: *Compos. Part B Eng.*, 2013, vol. 44, pp. 698–703.
- 28 T. Etter, M. Papakyriacou, P. Schulz, and P.J. Uggowitzer: *Carbon N. Y.*, 2003, vol. 41, pp. 1017–24.
- 29 T. Hutsch, T. Schubert, J. Schmidt, T. Weißgärber, and B. Kieback: in *Proceedings of the Powder Metallurgy World Congress & Exhibition PM2010*, 2010, pp. 361–8.
- 30 US 7,851,055 B2: 2010.
- 31 A. Boden, B. Boerner, P. Kusch, I. Firkowska, and S. Reich: *Nano Lett.*, 2014, vol. 14, pp. 3640–4.
- 32 I. Firkowska, A. Boden, B. Boerner, and S. Reich: *Nano Lett.*, 2015, vol. 15, pp. 4745–51.
- 33 G. Korb, J. Koráb, and G. Groboth: *Compos. Part A*, 1998, vol. 29, pp. 1563–7.
- 34 J.-F. Silvain, A. Veillère, and Y. Lu: *J. Phys. Conf. Ser.*, 2014, vol. 525, p. 012015.
- 35 M. Omori: *Mater. Sci. Eng.*, 2000, vol. 287, pp. 183–8.
- 36 T. Ueno, T. Yoshioka, J. Ogawa, N. Ozoe, K. Sato, and K. Yoshino: *Synth. Met.*, 2009, vol. 159, pp. 2170–2.
- 37 A. Daoud: *Mater. Lett.*, 2004, vol. 58, pp. 3206–13.
- 38 Z. a. Munir, U. Anselmi-Tamburini, and M. Ohyanagi: *J. Mater. Sci.*, 2006, vol. 41, pp. 763–77.
- 39 D.M. Hulbert, A. Anders, J. Andersson, E.J. Lavernia, and A.K. Mukherjee: *Scr. Mater.*, 2009, vol. 60, pp. 835–8.
- 40 D.M. Hulbert, A. Anders, D. V Dudina, J. Andersson, D. Jiang, C. Unuvar, U. Anselmi-Tamburini, E.J. Lavernia, and A.K. Mukherjee: *J. Appl. Phys.*, 2008, vol. 104, p. 33305.
- 41 R. Chaim: *Mater. Sci. Eng. A*, 2007, vol. 443, pp. 25–32.
- 42 A.B. Donaldson and R.E. Taylor: *J. Appl. Phys.*, 1975, vol. 46, pp. 4584–9.
- 43 F.I. Chu, R.E. Taylor, and A.B. Donaldson: *J. Appl. Phys.*, 1980, vol. 51, pp. 336–41.

German abstract

Kurzfassung

Die Entwicklung von Hochleistungselektronik zeigt eine Miniaturisierung der Komponenten und gleichzeitig einen Anstieg im Energieverbrauch. Abgesehen von aktuellen hocheffizienten Anwendungen in batteriegetriebenen Geräten, ein exponentielles Wachstum der Leistungsdichte von Mikroprozessoren verzeichnet sich, welches deren Kühlung zu einer Herausforderung macht. Kühlkörper mit guter Wärmeleitfähigkeit können nicht optimal ausgenutzt werden, wenn die Kontaktoberfläche zum gekühlten Bauteil mit einer Schicht Wärmeleitpaste versehen ist. Mit einem direkten Kontakt wäre eine höhere Wärmeleitfähigkeit (*thermal conductivity* oder TC) möglich, aber die Wärmeausdehnungskoeffizienten (*coefficient of thermal expansion* oder CTE) von Bauteil und Kühlkörper müssen übereinstimmen, um mechanische Belastungen und Schäden zu vermeiden.

Übliche Halbleitermaterialien, die in Mikroprozessoren verwendet werden, haben deutlich niedrigere CTE als die in Kühlkörpern verwendeten Metalle. Das Hauptziel dieser Arbeit ist die Entwicklung eines Materials, welches eine niedrigere CTE als Kupfer und Aluminium hat, ohne Einbuße in der TC aufzuweisen. Gleichzeitig wurde eine möglichst niedrige Dichte für die Anwendung in mobilen Geräten sowie in der Luft- und Raumfahrt angestrebt. Verbundwerkstoffe mit Aluminium- und Magnesiumlegierung als Matrix wurden mittels Spark Plasma Sintern hergestellt. Als Füllstoffe wurden Graphitflocken und Kohlenstofffaser mit hoher TC verwendet. Verfahrensbedingt orientieren sich die Füllstoffe in einer Ebene (x,y-Ebene) senkrecht zum angewandten Pressdruck (z-Richtung), sodass das hergestellte Material eine hohe TC entlang der x,y-Ebene erhält.

In der ersten Veröffentlichung^[1] (*Composites of aluminum alloy and magnesium alloy with graphite showing low thermal expansion and high specific thermal conductivity*) wurden Graphitflocken in bis zu 50vol% als Füllstoff eingesetzt und untersucht. Dabei wurde die TC in der x,y-Ebene erheblich erhöht und die CTE in z-Richtung bis auf negative Werte reduziert. In der zweiten Veröffentlichung (*Thermal properties of metal matrix composites with planar distribution of carbon fibres*) wurden Kohlenstofffaser bis zu 65vol% als Füllstoff eingesetzt. Dabei wurde die CTE in der x,y-Ebene reduziert. Die dritte Veröffentlichung (*Isotropic thermal expansion in anisotropic thermal management composites filled with carbon fibres and graphite*) ist eine Kombination aus den ersten zwei: Hier wurden Kohlenstofffaser und Graphit in unterschiedliche Verhältnisse als Füllstoff verwendet, um die Geometrie der CTE zu steuern. Unter anderem wurden Materialien mit einer isotropen CTE erreicht, die halb so hoch ist wie die der Metallmatrix. Weiterhin wurde gezeigt, dass die Eigenschaften des Materials nicht vom speziellen Herstellungsverfahren, sondern von der Zusammensetzung abhängig sind. In der vierten Veröffentlichung (*Understanding the negative thermal expansion in planar graphite-metal composites*) wurde der physikalische Hintergrund der CTE-Geometrie von Graphit-Metall-Verbundwerkstoffen untersucht. Obwohl das Graphit sich in z-Richtung und nicht in der x,y-Ebene ausdehnt, ist die CTE des Verbundwerkstoffes am kleinsten oder sogar negativ in z-Richtung: Zum ersten Blick ein Widerspruch. Ein früheres Modell für dieses Phänomen, welches eine Streckung der Graphitflocken durch die Metallmatrix voraussetzt, wurde mithilfe von Neutronenstreuungsversuchen widerlegt. Ein alternatives Modell wurde vorgeschlagen, welches von einer makroskopischen Krümmung der Graphitflocken ausgeht.

Eidesstattliche Erklärung

Hiermit versichere ich, dass ich alle verwendeten Hilfsmittel und Hilfen angegeben und die vorliegende Arbeit auf dieser Grundlage selbstständig verfasst habe. Diese Arbeit ist nicht schon einmal in einem früheren Promotionsverfahren eingereicht worden.

Valerio Oddone

