

MASTER THESIS

Research and development of advanced aluminium/graphite composites for thermal management applications

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Major: Metallurgy

Specialty: Foundry Engineering

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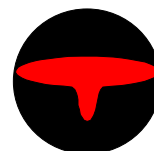
Thesis assessment:

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**Badania i rozwój zaawansowanych kompozytów
aluminium/grafit w zastosowaniach zarządzania
ciepłem**

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Abstract

Thermal management materials are continuously gaining importance as a consequence of everlasting evolution in performance of electronic and electric devices. In particular, by improving the heat exchanger's materials' properties (i.e. thermal conductivity) it is possible to boost further performance and miniaturization of such devices. Due to their high thermal conductivity, Copper and Aluminium are currently the most commonly used materials for thermal management applications. However, the mismatch in thermal expansion between Copper/Aluminium and Silicon is limiting the heat transfer at the interface between the electronic chip and the heat exchanger. Furthermore, Copper is indeed characterized by a high thermal conductivity but at the same time its high density (8.9 g/cm^3) increases weight of the final product, which in most of the cases does not meet specific application requirements. High cost of these materials is another constraint which limits their application.

Due to aforementioned facts, monolithic metals used as thermal management materials cannot simultaneously satisfy characteristics of high thermal conductivity, low thermal expansion and low density. As an answer to this demand, an ongoing research is observed to investigate advanced composites as an alternative to conventional monolithic structures. Among variety of compositions, the Aluminium-Graphite reinforced metal matrix composite seems to be a promising solution due to its superior thermal properties and low cost. Several variants of composites are presented in this thesis, starting with a study and simulation of their properties, production process and refinement, finalized with experimental measurements of thermal and mechanical properties of the final compositions. Conducted research and development works led to interesting results – created composites outrun pure Aluminium's thermal conductivity while keeping adequate mechanical properties: very low coefficient of thermal expansion and density.

Key words: *Al/C composite, thermal conductivity, coefficient of thermal expansion, thermal management applications, powder metallurgy, non-destructive testing*

Streszczenie

Wraz ze wzrostem wydajności urządzeń elektronicznych i elektrycznych coraz większe znaczenie zyskują materiały przeznaczone do efektywnego zarządzania ciepłem. Korzystne właściwości cieplne wspomnianych materiałów umożliwiają dalszy postęp w miniaturyzacji i zwiększaniu wydajności wspomnianych urządzeń. Z racji na wysoką przewodność cieplną, *miedź* i *aluminium* są obecnie najpowszechniej wykorzystywanymi materiałami w produkcji elementów chłodzących. Jednakże brak dopasowania rozszerzalności cieplnej pomiędzy miedzią/aluminium, a krzemem ogranicza przenoszenie ciepła na powierzchni międzyfazowej pomiędzy płytką krzemową a wymiennikiem ciepła. Ponadto, miedź mimo bardzo wysokiej przewodności cieplnej charakteryzuje również wysoka gęstość (8.9 g/cm^3), która bezpośrednio wpływa na zwiększenie wagi finalnego produktu, co często ogranicza możliwości jego użycia w konkretnych zastosowaniach. Wysoki koszt materiału jest kolejnym czynnikiem ograniczającym wiele zastosowań.

Ze względu na wyżej wymienione charakterystyki, monolityczne metale przeznaczone do zarządzania ciepłem nie mogą jednocześnie spełnić wymagań wysokiej przewodności cieplnej, niskiego współczynnika rozszerzalności cieplnej i niskiej gęstości. Aby rozwiązać powyższe kwestie, obserwuje się wzrost zainteresowania badaniami nad zaawansowanymi kompozytami, jako alternatywa dla konwencjonalnych monolitycznych metali. Pośród wspomnianych materiałów zbrojony kompozyt Al/C (aluminium-grafit) z osnową metalową wydaje się być obiecującym rozwiązaniem ze względu na znakomite właściwości cieplne i niską cenę. W niniejszej pracy przedstawionych zostało kilka kombinacji kompozytu Al/C, proces ich wytwarzania i ulepszania, oraz eksperymentalne pomiary ich właściwości mechanicznych i termicznych. Przeprowadzone działania badawczo rozwojowe ujawniły ciekawe kompozycje materiałów, które swoim przewodnictwem cieplnym wyprzedzają przewodność czystego aluminium zachowując jednocześnie zadawalające właściwości mechaniczne: niski współczynnik rozszerzalności termicznej i gęstość.

Słowa kluczowe: kompozyt Al/C, przewodność cieplna, współczynnik rozszerzalności cieplnej, zastosowania w zarządzaniu ciepłem, metalurgia proszków, badania nieniszczące

Kraków, dnia 2014 r.

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Imię i Nazwisko

O Ś W I A D C Z E N I E

Oświadczam, świadomy(-a) odpowiedzialności karnej za poświadczenie nieprawdy, że niniejszą pracę dyplomową wykonałem(-am) osobiście i samodzielnie i że nie korzystałem(-am) ze źródeł innych niż wymienione w pracy.

Tytuł pracy:

***Research and development of advanced aluminium /graphite composites
for thermal management applications.***

Oświadczam również, że przedstawiona praca jest identyczna z załączoną wersją elektroniczną.

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czytelny podpis studenta

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1. INTRODUCTION

The goal of this chapter is to introduce the reader to the context information explaining the motivation and origin of this thesis. It presents the CERN laboratory together with its material engineering research activities. Scope, structure and goals of the thesis are defined and the content outline of this thesis is defined.

1.1 CERN and material sciences

CERN, the *European Organization for Nuclear Research* is a High Energy Physics (HEP) laboratory located on the Franco-Swiss border near Geneva. It is a joint international effort of 21 member states to pursue the research in particle physics as well as other areas like chemistry, computing or material sciences. This laboratory complex is home to the greatest tool ever built by the human beings – the *Large Hadron Collider (LHC)* which is currently the most powerful particle accelerator in the world. It is installed in a circular tunnel of 26.7 km circumference at the depth of 50 to 175 m between Geneva and the Jura mountains.

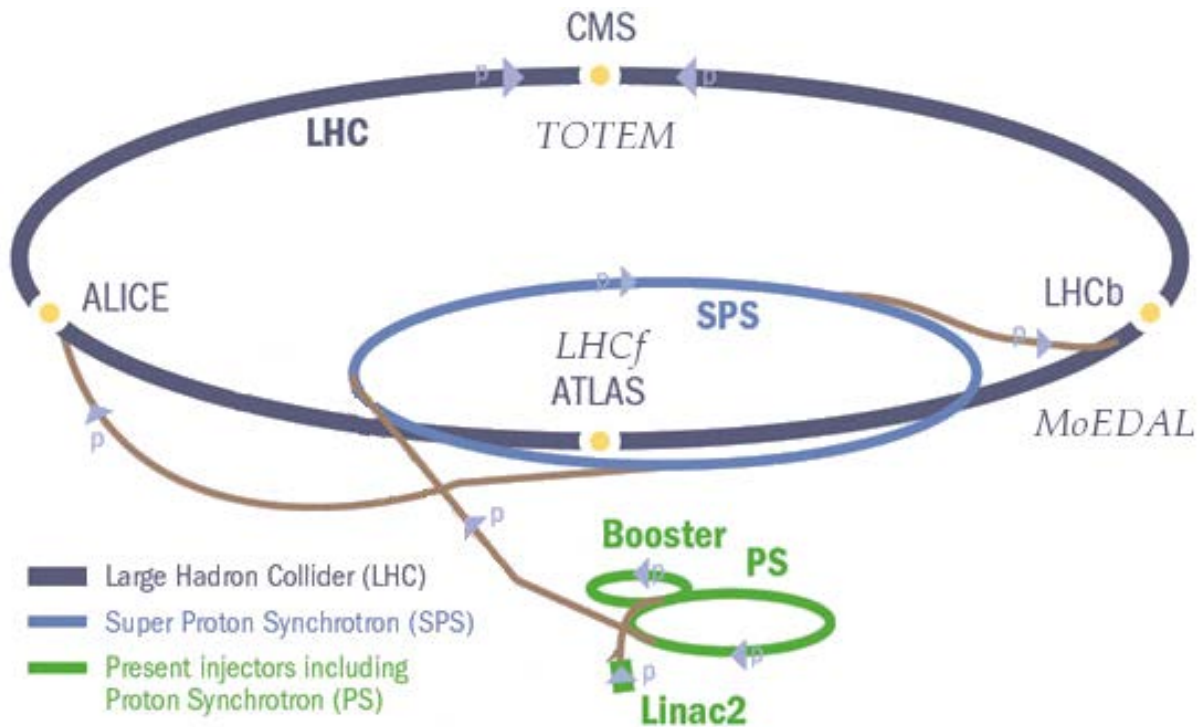


Figure 1 The LHC and its injectors

The schematic view of the LHC and its injectors is presented in Figure 1. Elementary particles, prior to being injected to the main LHC pipes, are first prepared in a chain of smaller accelerators which increase their energy level. Protons, or heavy ions start their run in a linear accelerator Linac3 which accelerates them to the energy of 50 MeV. Resulting beam feeds the Proton Synchrotron Booster (PSB) and with the energy level of 1.4 GeV enters the Proton Synchrotron (PS), where it is accelerated to 26 GeV. At this stage particles are already moving with at 99,9% of the velocity of light. It is here, where the point of transition is reached, when the energy added to the protons by the pulsating electric field cannot be translated to the increase of the speed. Instead, the added energy manifests itself as increasing mass of the protons and at current stage they are 25 times heavier than at rest. Super Proton Synchrotron (SPS) is used to boost the energy of the particles from 26 GeV up to 450 GeV. Finally, particles are distributed into LHC pipes both in a clockwise and anticlockwise direction, where the energy of 3.5 TeV is reached by each beam resulting in 7 TeV when colliding. The nominal energy of the single beam, still to be achieved will be 7 TeV per beam resulting in 14 TeV collisions energy. The machine technical upgrade program, carried out during the stop period called Long Shutdown 1 in order to meet these requirements, have just finished at the moment of this thesis creation and the LHC is actually performing the last warm up procedure to start the the second run in years 2015-2018.

Scientific instruments like LHC allow the physicists to study the basic constituents of matter – the fundamental particles described theoretically by the Standard Model. Collisions recorded by massive detectors installed around the LHC (e.g CMS, ATLAS, ALICE or LHCb) give the physicists clues on how the particles interact, providing insights into the fundamental laws of nature. However, besides pure theoretical research performed at CERN there is a large demand on research in engineering areas in order to design, build and maintain such complex devices like the LHC.

At CERN, the *importance of material engineering cannot be dismissed*. For many devices the working environment is unique – they need to sustain extreme conditions like very high temperature excursions, high pressure or ionizing radiation produced by the particle beam, just to name a few. Among many interesting challenges faced by the engineers at CERN, there is the problem of **collimation**. Particles which are accelerated in the LHC are being kept on the circular orbit and focused to the center of the vacuum chamber by means of superconducting magnets. In order to maintain the superconductive regime, these devices must operate at cryogenic temperature, near the value of 1.9 K, and even relatively small increases in temperature will lead to the local loss of the superconducting properties, resulting

in a cascade heating of the magnet with catastrophic consequences. This is particularly important inside the accelerator because the particles traveling in the accelerator tend to deviate from their central path and escape the vacuum chamber due to their charge repulsion. In such undesirable cases, the particles hit the magnets and depositing their energy, and increasing the temperature of the magnet itself. These phenomena may put the magnets out of the superconducting state and provoke the heating cascade effect that can cause the beam to be dumped or, even worst, introduce some serious damage to the entire machine.

To cope with these potentially catastrophic scenarios, special devices called ***collimators*** are used to “clean” the beam of particles in the areas close to the walls of the vacuum chamber. Collimators are installed in two main locations around the LHC ring, called regions of Momentum cleaning and Betatron cleaning, separated from the sections of cryogenic magnets in order for them to conveniently clean the beam and protect the superconducting magnets. This also implies that *collimators need to meet very strict requirements regarding resistance to the influence of the beam*. In order to tackle this problem, very special materials characterized by high thermal conductivity to evacuate the heat, low expansion to keep precise dimensions, tuned density to have the chosen beam cleaning have been developed. The metallurgic analysis as well as destructive and non-destructive material testing, mechanical dynamic and static measurements are of great importance to study and enhance the quality of materials used to build such equipment, which defines a clear need for dedicated unit to handle such activities.

Development and tests of the mentioned devices as well as research in other areas of material sciences is among the objectives of the Mechanical & Material Engineering group of the Engineering Department at CERN (EN-MME). Very promising results obtained during the ongoing R&D on collimators materials led to the creation of a parallel activity with the aim to develop materials for thermal management applications. As a Technical Student in the Engineering Design & Simulations (EDS) section of the EN-MME group I had the chance to participate in the early stage of the research – this thesis is completely based on the works I performed during my stay at CERN. It is worth to mention that the investigations would not start without the support of the Knowledge Transfer group at CERN which financed the presented project. The main aim of the Knowledge transfer group is to facilitate technology transfer from the laboratory to industrial applications.

1.2 Motivation

Understanding and controlling **heat transfer**, thermal stress, and warping is a problem of significant interest in practical applications concerned with heat management. Heat dissipation is a problem in current technologies, e.g., microelectronics. Microprocessors need to dissipate increasingly more thermal energy which is split through a combination of heat sinks, fans, and heat pipes. Problem concerning heat dissipation is presented schematically in Figure 2.

Heat is generated in electronic components whenever electric current flows through them. Generated heat causes the temperature of the material to increase and the resulting temperature difference drives the heat away from the components through a path of the smallest thermal resistance. The temperature of the components stabilizes when the heat dissipated equals the heat generated. In order to minimize the temperature rise of the components, effective heat transfer paths must be established between the components and the final heat sink, which is usually the atmospheric air. The selection of a cooling mechanism for electronic equipment depends on the magnitude of the heat generated, reliability requirements, environmental conditions, and cost. For low-cost electronic equipment, inexpensive cooling mechanisms such as natural or forced convection with air as the cooling medium are commonly used. For high-cost, high-performance electronic equipment it is often necessary to recourse to expensive and complicated cooling techniques.

In order to meet thermal dissipation requirements for electronic packaging applications, materials with high thermal conductivity and low thermal expansion must be developed (1).

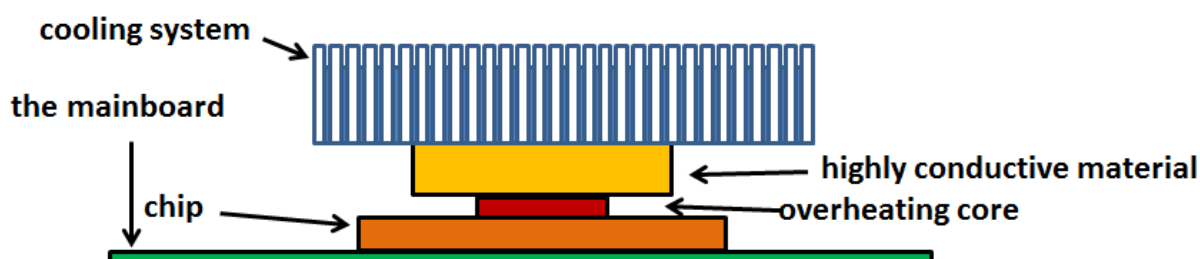


Figure 2 Scheme of a heat dissipation system of a CPU

Until now the traditional electronic packaging materials were mostly pure metals e.g. Au, Al, Cu, and Ag due to their high thermal conductivity. At the same time, these metals are characterized by high coefficient of thermal expansion (which may cause thermal stress and

warping), high density and high costs. Aforementioned factors may limit many potential applications of mentioned metals.

The increasing requirement imposed on **thermal management materials** in microelectronics and semiconductors brings an idea to develop advanced composites with high thermal conductivity to effectively dissipate heat as well as tailor the coefficient of thermal expansion to minimize thermal stress. That's why it is now of paramount importance to enhance the performance while reducing weight and dimensions of the cooling systems (importance of ratio: thermal conductivity/density) for the growing market of electronic mobile devices. Life expectation and reliability of electronic devices must increase too (2).

The research performed within the scope of this thesis aimed at finding a suitable composite which could be a substitute for the commonly used materials by providing better properties at lower density and cost of the product. As it was proven during the research, the Al/C composite can become a promising candidate to meet such requirements. Results of the study could be of potential interest to the electronic industry or any other field where heat management is of great importance.

1.3 Objectives of the thesis

Author defines the following four main objectives of this thesis:

1. Give adequate theoretical background information about all the materials, tools, methods and models used in the research and development activities;
2. Different variants of the Al/C composite design and manufacturing;
3. Deep study of created composites and application of appropriate refinements;
4. Evaluation of the obtained results and assessment of possible composite usage in the heat management applications.

Creation of a material with better characteristics than the traditionally used constitutes a big challenge. To obtain satisfactory results of the study, produced composite should fit into the characteristic presented below. The research and development works aim at obtaining:

- thermal conductivity in the range between **500 – 700 W/mK**,
- electrical conductivity between **5 – 25 MS/m**,
- coefficient of thermal expansion between **2÷6 $10^{-1}K^{-1}$** ,
- density between **2÷5 g/cm³**,
- good mechanical strength **~ 100 MPa**,
- low production costs.

The aforementioned requirements will serve as evaluation criteria of the constructed materials.

1.4 Thesis outline

The master thesis contains four chapters divided into several sections and subsections. The chapter 1 provided basic information about this thesis origin and its goals.

Chapter 2 contains six sections and gives a detailed description of the main materials, investigation tools and methods as well as characteristics of the chosen production process used in the Al/C composites manufacturing. Sections 2.1 and 2.2 provide the most important information and characteristics of graphite and aluminium, their structure and properties. Section 2.3 contains the overview of powder metallurgy production method and describes in detail the processing phases like powder manufacture, solid state sintering and liquid phase sintering. In Section 2.4 general information about metal matrix composite, its advantages and applications as well as information about aluminium matrix composite is provided. Al/C diagram phase is also described in this section. Section 2.5 provides introduced analytical models used to predict physical properties of the Al/C composites. Section 2.6 gives an overview of Scanning Electron Microscopy (SEM) investigation principles, Back-Scattered Electron Detector (BSE) and Energy Dispersive Spectrometry (EDS) methods. It also describes the operation principles of the device used to measure the coefficient of thermal expansion and briefly demonstrates the device for thermal conductivity measurements. This section provides information about electrical and mechanical properties measurements.

The experimental part of the thesis is presented in Chapter 3. It is composed of eight sections describing in detail the conducted research and development process, presenting preliminary results and their analysis. Section 3.1 schematically explains the research and development process on a workflow chart. In Section 3.2 the choice of proper powder for production is emphasized. Section 3.3 discusses the manufacturing process of the composites. Sections from 3.4 to 3.8 focus on the experimental properties measurements of created composites together with presenting the results obtained at each step of the investigations.

Chapter 4 is dedicated to summarize and conclude the research results. Summary of thesis goals and their accomplishment is given in Section 4.1. Obtained results are discussed and compared to other solutions available on the market. Thesis is finalized by proposal of future works in Section 4.2.

2.BACKGROUND INFORMATION

This chapter contains five sections and gives a detailed description of the main materials, investigation tools and methods as well as characteristics of the chosen production process used in the Al/C composites manufacturing.

2.1 Graphite characterization

As it was introduced in the previous chapter, *graphite* due to its high potential and numerous advantages plays a crucial role in the investigated composite. This chapter provides the most important information and characterization of graphite, its structure and properties. Choice of this element is given a thorough justification by explaining its role in the investigated composite.

2.1.1 Introduction

The origin name of **carbon** comes from the Latin “carbo”, which to the Romans meant charcoal. In the contemporary world, carbon is the most desirable element for variety of applications and markets. Its processing techniques are well-established allowing its production by different segments of industry. Carbon is well known as an allotropic material, it means that it possesses different properties depending on its structure. The most pure and expensive form of carbon is diamond which is the hardest material known until now. It is transparent and has excellent thermal conductivity. Another form of carbon is graphite. It is characterized as a good conductor (along in plane direction), it is very soft and has a grey color. Other variants of carbon include carbon fibers and glassy carbon. These materials are made of the same carbon atoms - the only difference is the result of varying arrangements of their atomic structure (3).

Carbon in the form of (highly oriented) graphite is a good candidate for use in thermal management materials due to its high thermal conductivity, low coefficient of thermal expansion, low density and in addition – its low cost. The properties of graphite are discussed more in details in the following subsections.

2.1.2 Graphite structure

Graphite is rarely found in the form of monocrystals. It mostly occurs in the form of flakes or lumps. Graphite is an allotropic form of the carbon element, which is formed by layers of hexagonally arranged carbon atoms in a planar condensed ring system shown schematically in Figure 3. The circles on the structure indicate the location of the carbon atoms.

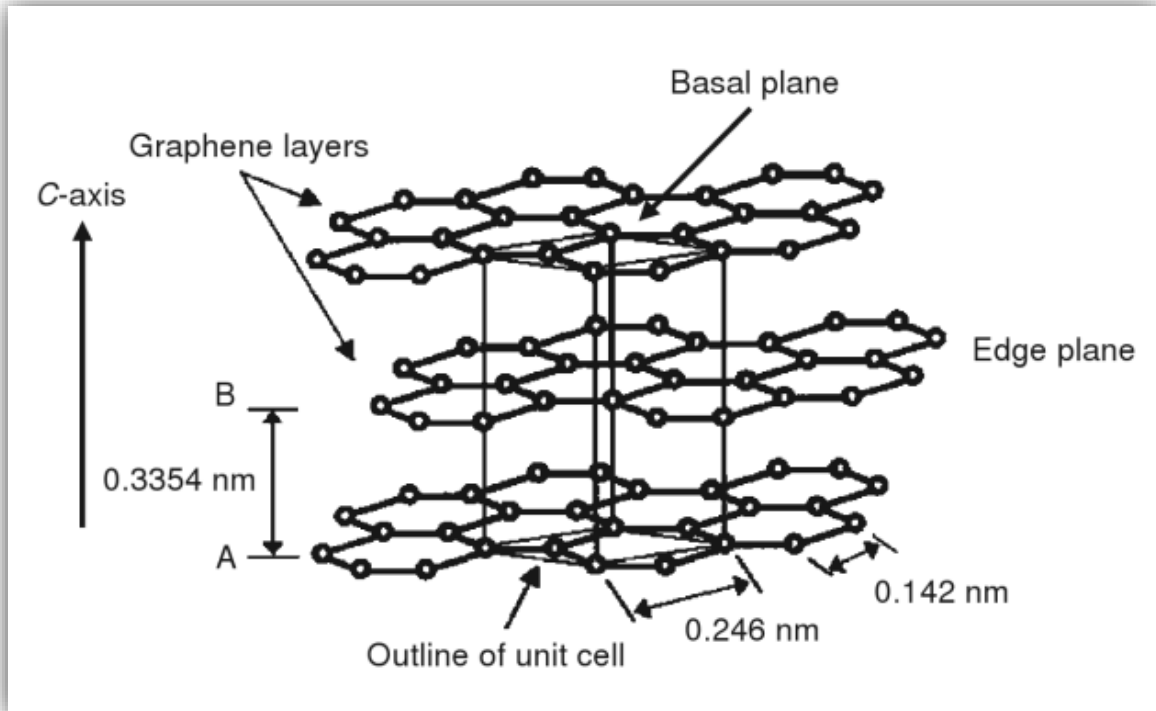


Figure 3 Crystal structure of graphite (4)

Graphite consists of many flat layers of hexagons which are called **graphene sheets**. The graphenes are bonded to each other by weak Van der Waals forces which allow for low friction sliding of the planes between each other. This effect determines the high softness and self-lubricating property of graphite.

In each graphene carbon layer, atoms are covalently bonded to three other atoms in the plane (the angle between two bonds is 120°). The outermost electron shell of a carbon atom has four valence electrons, three of which are used by the covalent bonds. The fourth valence electron does not take part in covalent bonds and may be easily displaced from the electron shell by an electric field. These electrons provide electrical conductivity of graphite.

Hexagonal (alpha) graphite is the most common stacking sequence of the graphite crystal (3). Figure 4 presents crystal structure of graphite showing ABAB stacking sequence.

In temperature above 2200 °C the graphitization process of carbon is started and the well aligned structure is created.

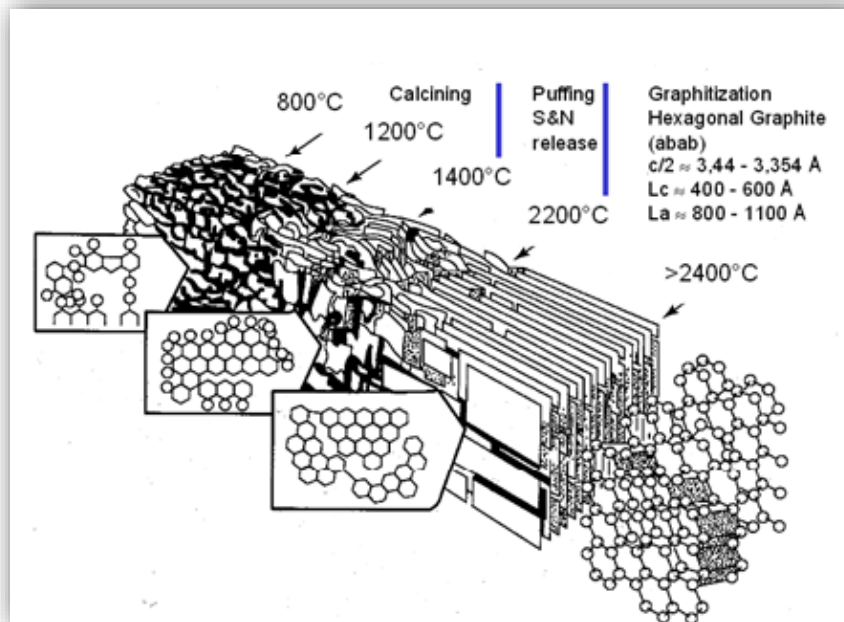


Figure 4 Crystal structure of graphite showing ABAB stacking sequence and unit cell (4)

Figure 5 presents the difference between graphitized and non-graphitized carbon. Graphitized carbon (a) is characterized by well aligned sheets which ensure excellent electrical and thermal conductivity while non-graphitized carbon (b) is irregularly spread which decreases its usability in the thermal applications.

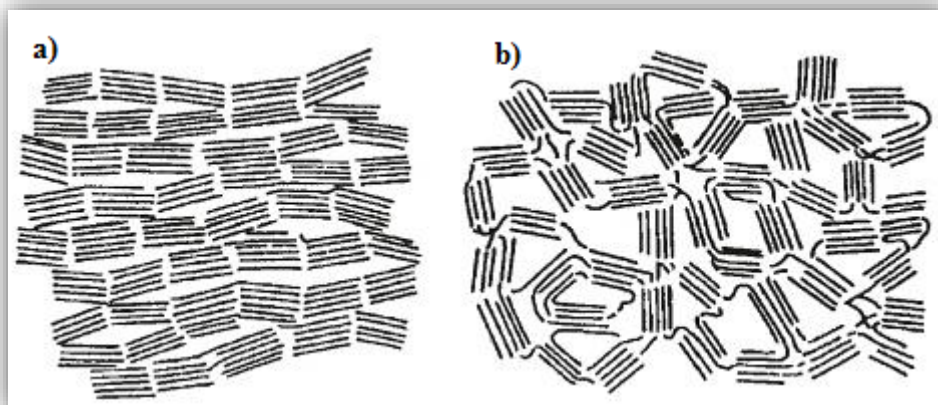


Figure 5 Differences between a) graphitize, b) and non-graphitize carbon (4)

2.1.3 Physical properties of graphite

The special crystal structure of graphite leads to the considerable anisotropy of the material. This means that the material has different properties when measured along ab directions

(within the plane) or the c direction (perpendicular to the planes). The most characteristic physical properties possessed by graphite are as follows:

- high thermal stability (no degradation or phase changes up to 4000K)
- softness and slipperiness – this features are used e.g. in pencils and as a dry lubricant (used in pencils, graphite sheets are rubbed off and stick to the paper),
- density lower than diamond - this is because of the relatively large amount of space that is "wasted" between the sheets,
- insolubility in water and organic solvents. Reactions between solvent molecules and carbon atoms will never be strong enough to overcome the strong covalent bonds in graphite,
- electrical conductivity. The delocalized electrons are free to move throughout the sheets.

Table 1 summarizes the most notable physical properties of graphite.

Table 1 Physical properties of Graphite (3)

Crystalline form	hexagonal
Lattice parameters	$a_0=0,246$ nm, $c_0 = 0.671$ nm
Color	black
Theoretical Density	2.25 g/cm ³
Atomic volume	5.315 cm ³ /mol
Sublimation point at 1 atm (estimated)	4000 K
Triple point (estimated)	4200 K
Boiling point (estimated)	4560 K
Heat of fusion	46.84 kJ/mol
Pauling electronegativity	2,5

2.1.4 Thermal properties of graphite

Thermal conductivity

Graphite, thanks to its superior structure (discussed in Section 2.1.2) is recognized as an excellent heat conductor along in-plane direction. In general, in nonmetals (like graphite) heat conductivity is primarily possible due to lattice vibrations. Thermal conductivity of a graphite crystal can be as high as 4180 W/(mK) in the ab directions for highly crystalline, stress annealed pyrolytic graphite. However, the average value for commercial pyrolytic graphite is much lower, around 390 W/(mK) in ab directions and 2 W/(mK) in c direction. The thermal conductivity of graphite decreases with temperature (3).

Specific heat

Specific heat is defined as the amount of heat per mass unit required to raise the temperature by one degree Celsius. The specific heat of graphite is known as 8.033 – 8.635 J/mol*K at 25°C and increases with the following relationship (T in degree K) (3):

$$C_p = 4.03 + (1.14 * 10^{-3})T - \frac{(2.04 * 10^5)}{T^2}$$

Coefficient of thermal expansion

Another important graphite property is the coefficient of thermal expansion (CTE) which is defined as the extent to which a material expands upon heating. The interatomic spacing between the carbon atoms of graphite is a function of temperature. At 0 K these atoms have their lowest energy position. When the energy increases, the temperature rises. In consequence, the atoms start to vibrate and move further apart. In the strongly bonded graphite in the ab directions the amplitude of vibration is small and during the outward motion of the atoms the atomic bonds are not overstretched. As a consequence, the dimensional changes remain small. When the atomic bond is weak (like in the c direction), the vibration amplitude and the dimensional changes are large. This is why the thermal expansion factor of a graphite crystal is different in two considered directions.

The CTE increase with temperature is not linear - in c direction it increases slowly and gradually. At 0°C the coefficient of thermal expansion is around $25 \times 10^{-6} \text{K}^{-1}$ and at 400°C can reach $28 \times 10^{-6} \text{K}^{-1}$. In the ab direction the thermal expansion is actually negative ($-0.5 \times 10^{-6} \text{K}^{-1}$) up to approximately 400°C with a minimum at 0°C. It is possible that this observed negative expansion is due to the internal stress (Poisson effect) associated with the large expansion in the c direction. The large thermal expansion anisotropy often results in large internal stresses and structural problems such as delamination between planes (3).

2.1.5 Electrical properties of graphite

Electrical conductivity is another characteristic graphite property, even though graphite is a nonmetal. In electrical insulators, electrons are strongly bonded to the nucleus and are not free to move. Graphite is considered as a semi-metal, it means that is a conductor in the basal plane and insulator normal to the basal plane. Electrical conductivity is possible due to the fact that the outermost electron shell of carbon has four valence electrons where three of them are used for the covalent bonds and the forth can be easily displaced from the electron shell by an electric field. These electrons provide electrical conductivity of graphite. In the c

direction, the spacing between planes is large and it is difficult for the electrons to move from one plane to another. This is why in that direction electrical conductivity is low (3).

2.1.6 Mechanical properties of graphite

Graphite, in spite of its high mineral softness, is used to produce high-strength, low weight composite materials which can be found in automobiles, aircrafts or even golf club shafts. It is possible due the sapient usage of the highly-oriented graphite hexagonal planes: when the graphite sheets are rolled up into fibers, and then twisted into threads, it is possible to take advantage of graphite strengths along the fiber axis. The threads are then molded into a rolled shape and embedded inside a binder, such as an epoxy resin, which provides a stable connection between the threads. The resulting composites have some of the highest strength-to-weight ratios of any materials (excluding diamond crystals and carbon nanotubes). In graphite, the bond between the atoms in the basal plane of a graphite crystal is significantly stronger than the bond between the planes.

The aforementioned superior properties of graphite e.g. low density, high thermal conductivity (in plane direction), low coefficient of thermal expansion, fair electrical conductivity and mechanical strength, contribute to the choice of graphite element as the reinforcement in the discussed Al/C composite.

2.2 Aluminium characterization

Aluminium as the second constituent of the investigated composite requires detailed description of its features and applications. These topics are presented in the subsequent paragraphs.

2.2.1 Aluminium acquiring

Aluminium is the third most commonly occurring chemical element on earth. In nature, aluminium never appears as a sole entity - it is only found in chemical compounds with other elements such as sulphur, silicon, and oxygen. For the sake of material engineering it is essential to obtain the form of metal. Several techniques of aluminium production are well-established in the industry. For example as a result of electrolytic refining (5) of aluminium, the purity of aluminium may reach 99.95 - 99.955%. Aluminium compounds occur in all types of clay, but the one which is the most useful for pure aluminium production is bauxite. Bauxite consists of 45-60% aluminium oxide, along with various impurities such as sand, iron, and other metals. In general, aluminium is manufactured in two phases: the

Bayer process (5) of refining bauxite ore to obtain aluminium oxide, and the Hall-Heroult (5) process of smelting the aluminium oxide to release pure aluminium.

2.2.2 Atomic structure of aluminium

The way in which the atoms of all materials are bonded together *is determined by their atomic structure*. The atomic number of aluminium is 13, which stands for 13 protons in its nucleus, together with 14 neutrons. Aluminium atomic structure is presented in Figure 6. As shown in the figure, the outer electron shell contains three electrons which contribute to the free electron gas of aluminium crystal. The free electron gas is a collection of randomly moving free electrons (detached from their parent atoms) in a metal or semiconductor. Thanks to the positive ions repulsion, the transfer of the electric charge is possible. This enables the electrical conductivity of metals - aluminium possesses electrical conductivity equal to 37 (MS/m).

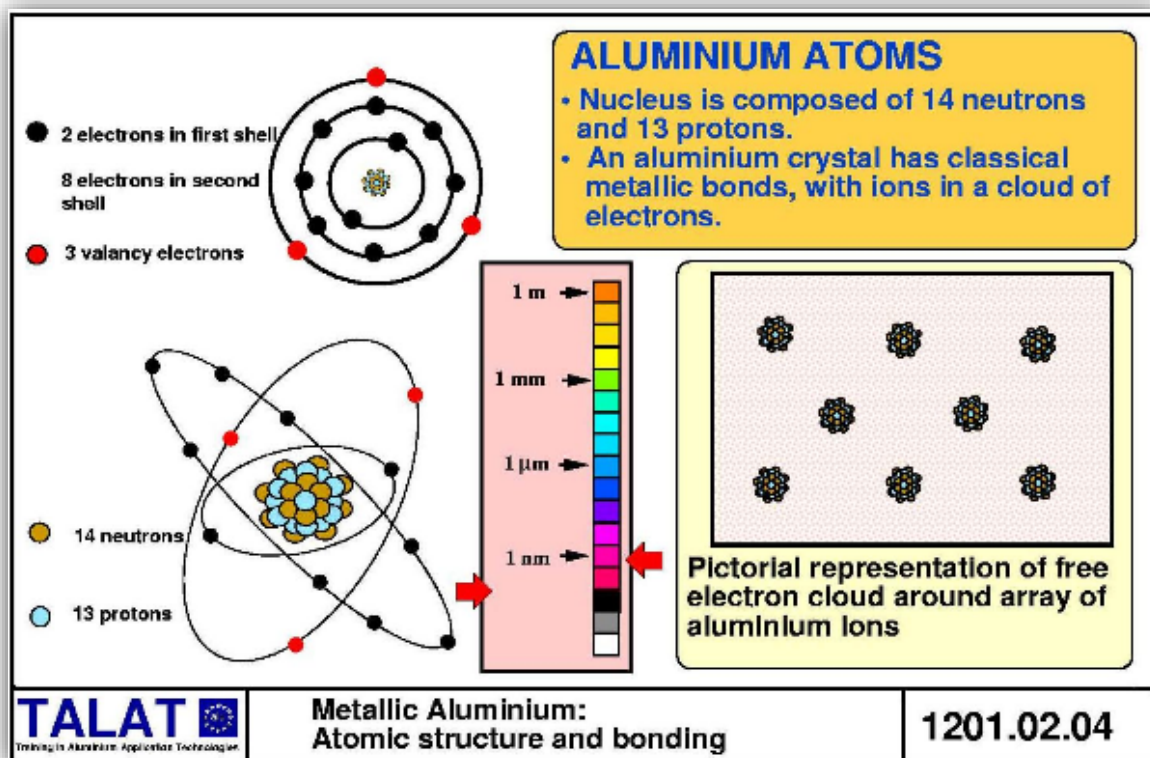


Figure 6 Atomic structure of aluminium (6)

2.2.3 Aluminium properties

Aluminium is known as a lightweight and metallic element. It is malleable and ductile due to its polycrystalline structure. It is a good conductor of heat and electricity and is easily shaped by moulding and extruding. Aluminium is created of grains (or crystals) aggregating

together when the metal is cooled. Each grain consists of rows of atoms in an ordered lattice arrangement, giving an isotropic structure.

From the point of the conducted research, aluminium has *two main advantages over other metals*. Firstly, it has low density (2.69 g/cm^3) which is about one third that of iron and copper. Secondly, although the surface of aluminium quickly oxidizes in air, it forms a thin tough oxide layer which resists further oxidation. This removes the need for surface protection coatings such as those required with other metals, in particular with iron. Furthermore, aluminium can easily and economically be recycled into new products. Aluminium, due to its superior properties, has found application in variety of domains, e.g. home, transport on land, sea and in the air as well as in the industry and commerce. The most important aluminium properties are presented in Table 2.

Table 2 Specification of aluminium properties (7)

Property	Value	Unit
Atomic number [Z]	13	
Density [ρ]	2.6989	[g/cm ³]
Melting point	660.32	[°C]
Boiling point	2519	[°C]
Recrystallization temperature	200	[°C]
Thermal conductivity [λ]	210	[W/(mK)]
Specific heat [C_p]	900	[J/(kgK)]
Coefficient of thermal expansion [α] at 20-100°C	24	[10 ⁻⁶ K ⁻¹]
Coefficient of thermal expansion [α] at 20-300°C	25.5	[10 ⁻⁶ K ⁻¹]
Electrical conductivity [ρ]	37	[MS/m]
Young modulus [E]	68	[GPa]
Ultimate tensile strength [UTS]	110	[MPa]
Poisson's ratio	0,36	
Shear modulus	25	[GPa]

2.3 Powder metallurgy

This section gives an overview of powder metallurgy production method and describes in detail the processing phases like powder manufacture, solid state sintering and liquid phase

sintering. This processing technique requires detailed description since it was chosen as the manufacturing process of the investigated composite.

2.3.1 Introduction

Powder Metallurgy (PM) is recognized today as one of the most important manufacturing processes for producing industrial elements. In particular, the growth of PM was phenomenal during the last quarter of the 20th century with the development of novel material processing techniques such as Atomization (8), Mechanical Alloying (MA) (9), Rapid Solidification Process (RSP) (10) for powder production, Cold Isostatic Pressing (CIP) (11) and Hot Isostatic Pressing (HIP) (11) for component fabrication.

Nowadays, Powder Metallurgy ranks very high among the major methods of manufacturing since *it can produce near net shape components* with properties that are comparable with those of conventionally formed parts. All classes of materials can be processed by powder metallurgy, including ceramics and polymers (e.g. PTFE or Teflon), even though PM indicates only metal powder processing. In addition, processing temperatures can be much lower than melting point of the constituent metals.

The growing importance of PM in the present day manufacturing can be seen from the fact that increasing number of PM parts are being used in automobiles, household appliances such as television, washing machines, air conditioners, office equipment (copiers and computer parts) apart from industrial and aerospace sectors (12).

Powder Metallurgy also plays an important role in manufacturing of the composites, which are characterized by a number of advantageous properties enumerated below:

- Composites can be produced with high content of reinforcing phase resulting in particularly high stiffness and extremely low thermal expansion;
- Powder metallurgical processes are carried out in the solid state – this minimizes reactions between the ceramic reinforcement and metal matrix which reduces the risk of brittle interphase boundaries creation
- Powder preparation from a liquid phase (e.g. by spraying) can be used. Performing such process under high cooling rate results in a fine crystalline structure which determines better mechanical characteristics of the composites obtained at ambient and elevated temperatures (13).

Thanks to the aforementioned advantages, powder metallurgy process has been chosen to manufacture the Al/C composite.

2.3.2 Powder metallurgy process

Powder metallurgy process is divided into several steps including: powder preparation and moulding compositions as well as the main operations of mixing, forming, consolidation and sintering. Figure 7 presents a general flow chart for powder metallurgy process. Initially, raw materials obtained from various processes (atomization, splat cooling etc.) or alloy powders are mixed together with different additives (e.g. graphite). Obtained powders mixture may be formed using one of the following techniques:

- Hot compaction: by applying directly pressure and high temperature - in this method further sintering is not necessary;
- Cold compaction: where only pressure in ambient temperature is given - further sintering process is required.

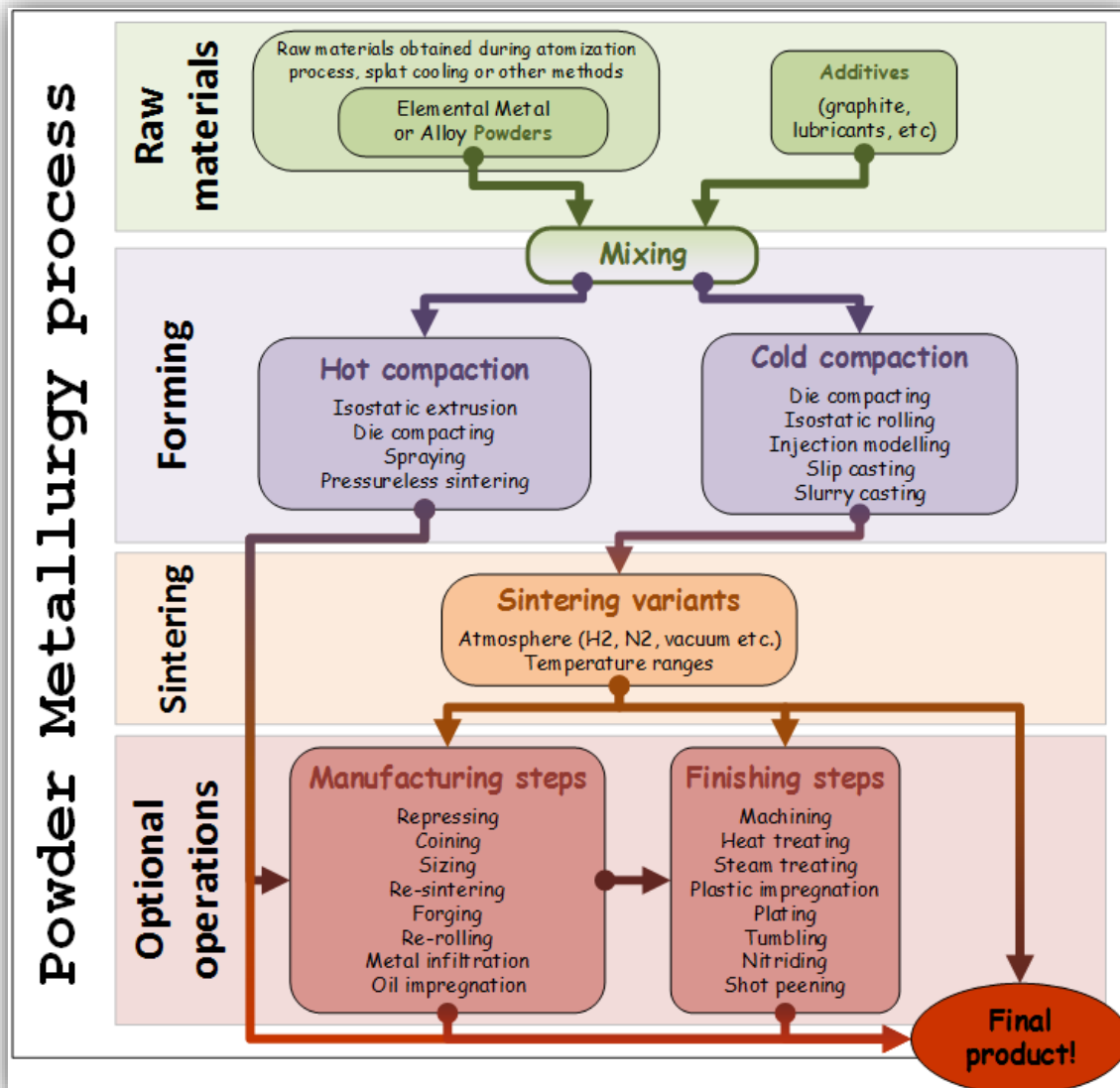


Figure 7 Flow chart of Powder Metallurgy component production

Prepared “green compact” is sintered in a defined combination of environmental conditions: temperature, time and pressure. Sintering usually takes place in a protection atmosphere like vacuum, nitrogen or under reductive atmosphere (hydrogen). In order to improve the properties of the material, optional operations (enumerated in Figure 7) can be applied after sintering. Phases indicated in the diagram are described in more detail in the subsequent subsections.

2.3.3 Powder manufacturing

Powder manufacturing is the entry point of the powder metallurgy part processing. Quality of the powder has significant influence on the material properties obtained in the next phases of the process. Desired powder characteristics include high purity and fine particles’ shape – these features decrease the risk of macro agglomeration creation which could result in closed porosity. There are several well-known methods of powder production used in the industry, including: atomization, splat cooling or centrifugal disintegration. These methods are given a short overview in the following paragraphs.

Atomization – is the most widely used process of aluminium powder production. In this technique aluminium is melted, alloyed and sprayed through a nozzle to form a stream of very fine particles that are rapidly cooled, most often by an expanding gas. **Splat cooling** – is a process which enables higher cooling rates than those obtained in the atomization method. Aluminium is melted and liquid droplets are sprayed or dropped against a chilled surface of high thermal conductivity, for example a cooper wheel that is water-cooled internally. The resultant splat particulate is removed from the rotating wheel to allow subsequent droplets to contact the bare, chilled surface (14) . In the **centrifugal disintegration** method, metal to be powdered is formed into a rod which is introduced into a chamber through a rapidly rotating spindle. Opposite the spindle tip there is an electrode from which an arc is established which heats the metal rod. As the tip material fuses, the rapid rod rotation throws off tiny melt droplets which solidify before hitting the chamber walls. A circulating gas sweeps particles from the chamber (15). There are many other methods of powder production where it can be made from machining chips or via chemical reactions. Such powder should be carefully cleaned before degassing and consolidation (14).

Aluminium powder used in the Al/C composite manufacturing has been obtained using atomization techniques. Ready to be used powder has been delivered to the partner company, BrevettiBizz where it entered the powder metallurgy process.

2.3.4 Powder compaction

Powder compaction is the next step in the Powder Metallurgy production process. Just like powder preparation, compaction degree of the sample is of great importance since it significantly affects the subsequent properties of the material. Compaction of powder mixtures is generally carried out using dies machine. Dies are made mostly from steel or cemented carbides - they have to be resistant while the high pressure is applied. Design of the dies plays an important role as well since it must ensure easy ejection of the compact - this is why the cylindrical shape is generally used.

The powder type and its characteristics influence the compaction pressure. The basic purpose of the compaction is to produce a pressed part with sufficient strength to withstand further operations. The pressed part, usually called "green compact" is then taken for sintering. Consolidation of powders may also be carried out at high temperatures. This allows to melt one of the ingredients and improve the interface boundary which in consequence affects the general improvement of the material properties (12).

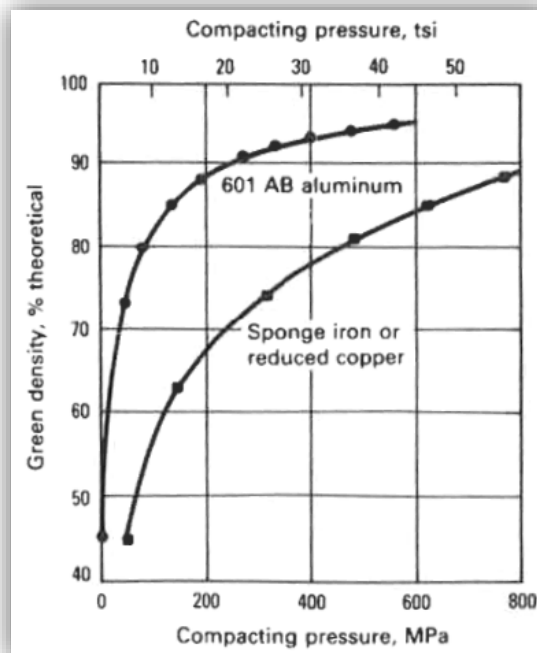


Figure 8 Relationship of green density and compaction pressure (12)

Figure 8 presents the relation of green compact density from the compaction pressure. This plot indicates that the compaction rate increases while higher pressure is applied. However, some of the materials which are soft and fragile (e.g. material composed of graphite majority and some aluminium addition) may cause degradation of the material or its

properties. In such cases the applying pressure should be first investigated in order to find the best value.

2.3.5 Sintering

Sintering is the main phase of P/M processing – the final material properties depend highly on the chosen environmental conditions while sintering. It is the consolidation process of a loose aggregate of powders or of the “green compact”. It is performed under controlled conditions of temperature and time.

During sintering, the green compact is usually heated in a protection atmosphere such as argon, hydrogen or nitrogen. The individual powder's particles (which were either loose or physically bonded together) are bonded to produce a solid structural part with the desired properties. Several changes take place during sintering process like shrinkage, formation of solid solution and development of the final microstructure. In many cases, sintering results in reduction/elimination of porosity and leads to densification. *Sintering is the culmination of powder processing operations which determines the final product.* During this process, the green compact is consolidated forming its final shape and microstructure.

Sintering process is influenced by several factors:

- Temperature
- Time
- Atmosphere
- Pressure (during green compact production)
- Pressure during sintering
- Particles dimensions and shapes
- Phase changes
- Formation of liquid phase

One of them is the process duration. The processing time typically ranges from 10 min to several hours depending on the type of powder, its characteristics, and size of the component etc. In case of powder mixtures, sintering may take place in the presence of a liquid phase where the sintering temperature is above the melting point of the low melting constituent. Examples are tungsten carbide and cobalt-based tool materials. Sintering also requires effective control over heating rate, process duration, temperature as well as atmosphere for reproducible results.

Sintering can be considering as a two-sphere model, where two spherical metal particles are in contact. During compaction, the individual powder's particles being in contact

are brought together. When the compact is heated to a high temperature, diffusion occurs. The atoms can move readily along the particle surfaces at the contact points - these contact areas formed during the compaction grow with time. Recrystallization and grain growth occurs between particles in contact, causing the grains in a solid metal to join together. However, voids between the particles will still be present. Unfortunately not all porosity is removed during the process. For good densification, sufficient time and temperature must be allowed during sintering. The increase in the density results in improved properties such as strength, ductility, toughness as well as electrical/thermal conductivity (12).

Solid state sintering

In solid state sintering, *the densification is a result of atomic diffusion in solid state*. Solid state sintering is a complex process, which may be divided into three stages presented in Figure 9.

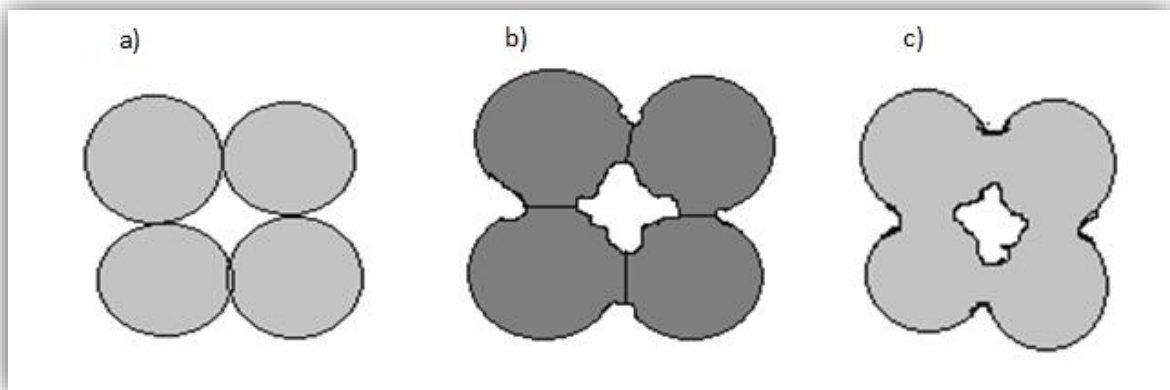


Figure 9 Schematic two-dimensional diagram of sintering progress: a) particles in contact, b) formation of necks, grain boundaries and pore, c) final sintered geometry

In the first step, necks are formed at the contact points between the particles which continue to grow. During this step the pores are interconnected and their shapes are irregular. In the second step the pore channels become more cylindrical. The interfacial energy is the driving force during this stage and the curvature gradients near the necks are responsible for the mass flow during this step. The curvature gradient is high for small neck size leading to faster sintering. With sufficient time at the sintering temperature, the pore becomes rounded. As the neck grows, the curvature gradient decreases and the sintering rate also decreases. During this stage, pore rounding may also occur, without any shrinkage. This means change in pore shape, but no change in pore volume, i.e. pores may become spherical and isolated, but there will not be any shrinkage sintering. With continued sintering, these cylindrical pore

channels become unstable, progressively squeeze and close. In the final step the pores become isolated and are no longer interconnected. The residual individual pores are located either at the grain boundaries or within the grains. In this stage, the porosity does not change and small pores remain even after long sintering times. The densification proceeds at a very slow rate (12) .

Liquid phase sintering

A common method of achieving rapid densification of the powders is *by forming a liquid phase during sintering*. In this type of sintering, the densification is increased thanks to the high mobility of the liquid phase. The composition of the powder compact and the sintering temperature are chosen so that sufficient amount of liquid is formed between the solid particles of the compact to infiltrate the voids and but without leaving contraction cavities. During cooling, the liquid crystallizes or forms a solid phase at grain boundaries and binding the grains. The application of temperature initially results in some degree of densification due to solid state sintering. When the material starts to melt, the liquid phase wets the solid particles. During this stage, there is the filling of the interstitials between solid particles leading to increase in density, with also a small effect of particles rearrangement. The densification can also be enhanced by the simultaneous application of pressure during sintering (12).

2.4 Metal-Matrix Composites

This section contains general information related to metal-matrix composites, their advantages and applications as well as information about aluminium-matrix composite. Al/C composite as the major interest of this thesis is introduced in this section, based on the Al/C phase diagram.

2.4.1 Introduction

A metal-matrix composite (MMC) is a material composition of at least two constituent parts, one being a metal. The second ingredient may be another kind of metal or material such as ceramics or an organic compound. Metal-matrix composites are generally distinguished by characteristics of the utilized reinforcement: particles, whiskers or short/continuous fibers. The main role of the reinforcement is to increase the strength, stiffness and thermal capabilities while reducing the thermal expansion coefficient of the resulting MMC. Metallic matrix of high density combined with reinforcement reduces density of the whole composite, thus enhancing its properties such as specific strength. However, the choice of an appropriate

matrix needs careful consideration due to possible chemical reactions between the matrix and the reinforcement. Furthermore, thermal stresses due to thermal expansion mismatch between the reinforcements and the matrix should be taken into account.

Nowadays, metal-matrix materials have found applications in many areas of the industry. These materials' design can be adjusted according to the needs of the application field, which makes them very attractive. Metal-matrix composites is a class of materials with a potential of wide structural and thermal management applications. They are capable of providing higher-temperature operating limits than their base metal counterparts and they can be tailored to give improved strength, stiffness, thermal conductivity and other properties (14).

Metal-matrix composites have several advantages over monolithic materials when it comes to their better fatigue resistance, lower coefficients of thermal expansion and better wear resistance just to name a few. This is why they are receiving growing attention on a variety of markets. MMCs with high thermal conductivity and tailorable coefficient of thermal expansion have already found widespread applications in electronics and thermal management.

2.4.2 Aluminium-Matrix Composite

Among various matrix materials available on the market, aluminium is widely used in the fabrication of the MMCs. Low weight, ease and prevalence of processing techniques, low cost, high thermal and electrical conductivity – all these characteristics make it a good candidate for versatile applications. The most commonly used materials as a reinforcement in the aluminium-matrix composite are usually graphite (C), carbon fibers (CF), silicon carbide (SiC) and alumina (Al_2O_3) while main manufacturing methods used to produce aluminium MMCs are squeeze casting, infiltration and powder metallurgy.

The main problem encountered when manufacturing the aluminium-matrix composites are the interfacial chemical reactions possible to occur in high temperatures as well as lack of wettability between the reinforcement and the matrix. Several solutions can be considered to mitigate the risk of aforementioned reactions, e.g. modification of the matrix composition, coating of the reinforcement, specific treatments to the reinforcement and control of process parameters. Among the aforementioned techniques, coating of the reinforcement is considered as the most efficient. The nature of the interface has significant influence on the metal matrix composite properties which depend on the strength of the interfacial bond between the matrix and the reinforcement. Strong interfacial bonds permit transfer and

distribution of the load from the matrix to the reinforcement. In general, chemical bonding occurs when the atoms of the matrix and the reinforcement are in a direct contact - it is then realized by an exchange of electrons. The properties like coefficient of thermal expansion, thermal conductivity, fatigue, stiffness are also affected by the nature of the interface (16).

2.4.3 Al/C composite

Aluminium/graphite composite is the main subject of this thesis. Chapter 3 is dedicated entirely to the experimental research performed on several variants of this composite. In this section, general theoretical information is given.

Deriving from the characteristics of aluminium and graphite, a composite of these two materials seems to be of high potential in thermal management applications due to characteristics which should be possible to obtain: high thermal conductivity, tailorable coefficient of thermal expansion and low density. Forecast of obtaining such characteristics already caught attention of the researchers around the world and triggered intensive research in this area which manifests itself in a number of publications, i.a. (1) (17) (18). The investigations performed in the EN-MME section at CERN were based on the newest results in this field and attempted to enhance the Al/C composite characteristics to suit the thermal management industry requirements.

The main problem regarding Al/C composites' manufacturing is the chemical reaction occurring between graphite and aluminium in temperatures above 660.32°C (which is the melting point of aluminium). As a result of aforementioned reactions Al_4C_3 phase is created. This phase is usually formed on the interphase border and deteriorates properties like thermal conductivity and strength. In order to avoid such reactions the manufacture process of Al/C should be carefully performed in "safety" temperatures. The most popular methods to produce Al/C composite are liquid infiltration and powder metallurgy. During liquid infiltration process Al_4C_3 phase may be easily created when melted aluminium infiltrates the graphite preform for some time. The amount of time when graphite stays in contact with melted aluminium decides if the reaction occurs. The risk of aluminium carbide creation increases with time and temperature. In order to mitigate this risk, coating of the reinforcement is usually used. The manufacturing method of such composites which allows controlling parameters like temperature and time is the powder metallurgy. Therefore, for the purpose of performed research, powder metallurgy has been chosen to manufacture Al/C composites.

An entry point to investigations of a new material should be the phase diagram analysis of the considered composite elements. Such study provides precautions about phases creation in a specific temperature with a given percentage of the ingredients. The calculated Al/C phase diagram is presented in Figure 10.

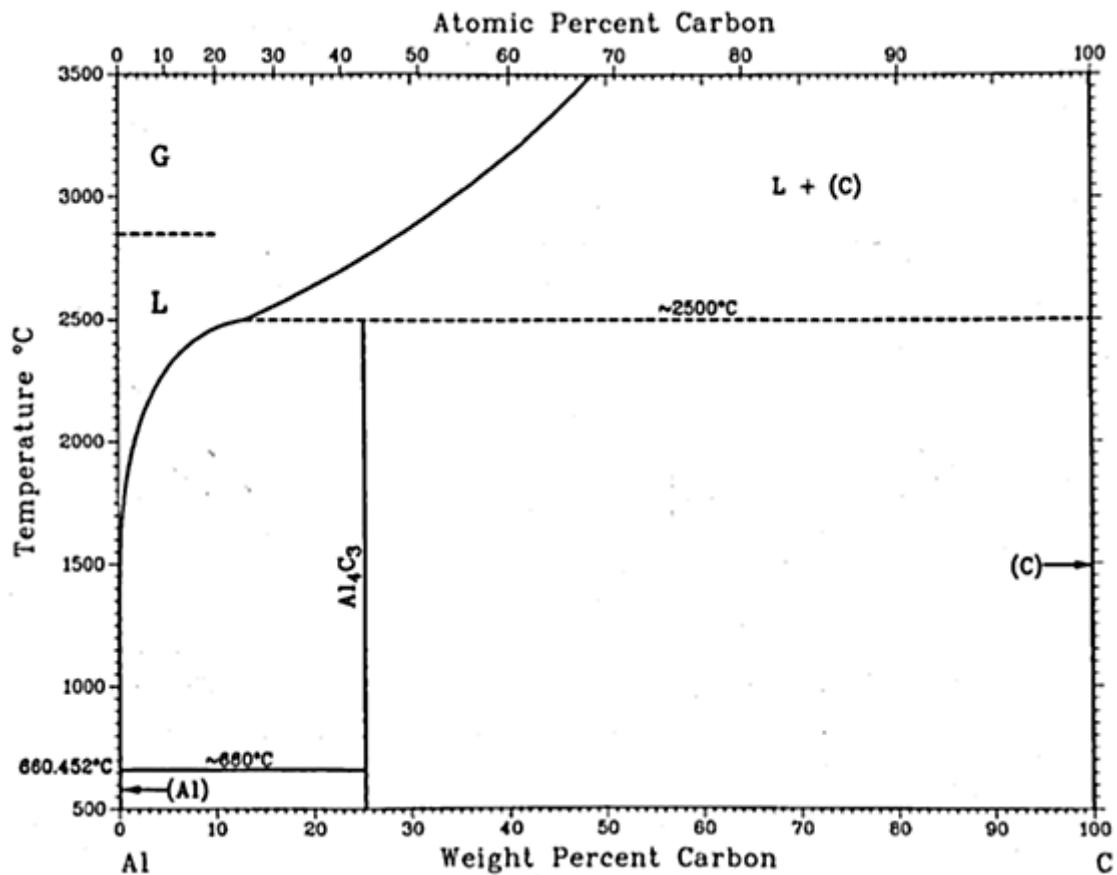


Figure 10 Calculated phase diagram of the Aluminium – Carbon system

According to the calculated phase diagram it has been reported that above the melting point of aluminium (660.32°C) reactions between aluminium and graphite may occur. It is also reported that the “safe region” - free of any reactions takes place in temperatures below 660°C with the weight percentage of aluminium up to 25 and more than 75 of carbon. Above this temperature with mentioned percentage of carbon and aluminium (but not only in such configuration of ingredients) chemical reaction may occur. This happens due to the fact that aluminium is easily reactive and when it melts it starts to react with the graphite. The calculated phase diagram serves as a guideline of ingredients' proportions and potential reactions between them. However, it should not be considered as the final criteria in all cases since the presence of the phases largely depends on the utilized manufacturing process and thus the characteristics may not necessarily match with the diagram information. Creation of Al_4C_3 - indeed takes place in a certain temperature but it is also dependent on other factors.

For instance, in case of powder metallurgy, sintering process conducted in temperature 700°C does not necessarily mean that Al_4C_3 phase will appear. When time of the sintering is chosen properly (it should be relatively short), then even in such temperature creation of the aluminium carbide can be avoided. Thus, temperature and time should be optimized during the investigation process.

2.5 Analytical methods of composite properties prediction

Very often, manufacturing of the material is an expensive procedure. It gets even more expensive when a wrong composition has been chosen and the production process needs to be repeated. In order to decrease the risk of producing a wrong composition and as a result lower the production cost it is common to predict the potential properties of created materials using analytical models. It turns out it is possible to predict some of the composite properties by application of well-established methods described in the following subsections.

Rule of Mixture

Rule of Mixture (ROM) (19) is method to estimate the composite material properties. It is based on an assumption that a composite property is the average weighted volume of the phases' properties (i.e. matrix and reinforcement phase). The following properties can be calculated using the ROM method:

- **Density [g/cm³]** is defined as a mass of the material per volume unit $\rho = \frac{m}{V}$. Density is predicted according to the following equation:

$$d_c = (d_m V_m) + (d_r V_r)$$

Where:

d_c, d_m, d_r – density of the composite, matrix and reinforcement phase respectively,

V_m, V_r – volume fraction of the matrix and reinforcement phase respectively.

- **Coefficient of thermal expansion (CTE) [10⁻⁶K⁻¹]** in longitudinal direction (e.g. along the fibers) it is calculated according to the following equation:

$$\alpha_{cl} = \frac{(\alpha_m E_m V_m) + (\alpha_r E_r V_r)}{(E_m V_m) + (E_r V_r)}$$

Where:

$\alpha_{cl}, \alpha_m, \alpha_r$ – CTE of composite in longitudinal direction, matrix and reinforcement respectively,

E_m, E_r – modulus of elasticity of matrix and reinforcement phase respectively.

Coefficient of thermal expansion in transverse direction (perpendicular to the fiber):

$$\alpha_{ct} = (1 + \mu_m)\alpha_m V_m + (\alpha_r V_r)$$

Where:

μ_m – Poisson's ratio of matrix

Poisson's ratio is the ratio of transverse contraction strain to longitudinal extension strain in the direction of applied force.

- **Modulus of Elasticity [GPa]** in the longitudinal direction is calculated as follows:

$$E_{cl} = (E_m V_m) + (E_r V_r)$$

Where:

E_r – modulus of elasticity of reinforced material,

E_m – modulus of elasticity of matrix material,

V_m – volume fraction of the matrix,

V_r – volume fraction of the reinforcement

Modulus of Elasticity in transverse direction is calculated as follows:

$$\frac{1}{E_{ct}} = \frac{V_m}{E_m} + \frac{V_r}{E_r}$$

- **Shear modulus [GPa]** - is the ratio of shear stress to the shear strain. In order to predict shear modulus the following formula should be used:

$$G_{ct} = \frac{G_r G_m}{V_r G_m} + V_m G_r$$

Where:

G_r – shear modulus of elasticity of reinforced material,

G_m – shear modulus of elasticity of matrix material.

- **Poisson's ratio** is predicted according to following equation:

$$\mu = (V_r \mu_r) + (V_m \mu_m)$$

Where:

μ_r – Poisson's ratio of reinforced material,

μ_m – Poisson's ratio of matrix material.

- **Tensile strength [MPa]** of reinforcement in longitudinal direction is calculated as follows:

$$\sigma_c = (\sigma_m V_m) + (\sigma_r V_r)$$

σ_c , σ_m , σ_r – tensile strength of the composite, matrix and reinforced phase respectively.

ROM is a basic properties prediction method – it does not take into account factors like size and shape of the particles or interphase bonding etc. Maxwell model (20) is one of the

most popular among theoretical models of thermal conductivity calculation. This model is based on an assumption that the filler particles have a spherical shape and it is applied for the composite with a large content of filler. Due to the fact that the constructed composite is foreseen to have a big content of reinforced phase in the matrix it is a suitable method of thermal conductivity calculation. The Maxwell model neglects the thermal resistance generated of filler-binder boundary and non-spheroidicity of the filler particles. Thermal conductivity according to Maxwell is calculated as follows:

$$\lambda_c = \lambda_m \left[\frac{2V_p \left(\frac{\lambda_p}{\lambda_m} - 1 \right) + \left(\frac{\lambda_p}{\lambda_m} + 2 \right)}{V_p \left(1 - \frac{\lambda_p}{\lambda_m} \right) + \left(\frac{\lambda_p}{\lambda_m} + 2 \right)} \right]$$

Where:

λ_m – is the thermal conductivity of the continuous matrix,

λ_p – is the thermal conductivity of a uniformly distributed filler (particles),

V_p – is the volume fraction of the particles

Another method used for thermal conductivity prediction is Hasselman and Jonson model (20). This model based is on Maxwell equation, however it takes into account the thermal resistance at filler-binder boundary. The Hasselman and Jonson model is presented as follows:

$$\lambda_c = \lambda_m \frac{2 \left(\frac{\lambda_p}{\lambda_m} - 1 - \frac{\lambda_p}{rG} \right) V_p + \frac{\lambda_p}{\lambda_m} + 2 + 2 \frac{\lambda_p}{rG}}{\left(1 - \frac{\lambda_p}{\lambda_m} + \frac{\lambda_p}{rG} \right) V_p + \frac{\lambda_p}{\lambda_m} + 2 + 2 \frac{\lambda_p}{rG}}$$

Where:

G – is the boundary thermal conductance,

r – is the radius of spherical filler particles.

Kerner's and Turner's models

To predict the coefficient of thermal expansion, several theoretical models have been used, namely: ROM (introduced at the beginning), Turner and Kerner models. These methods are based on different assumptions. For instance ROM considers the matrix as a liquid, Kerner's model assumes spherical filler and perfect adhesion at the interface of the two phases whereas Turner's model assumes there is no restriction on the shape of the filler and includes the bulk modulus of the two components. The various expressions of CTE by mentioned models are as follows:

Kerner's model:

$$\alpha_c = \alpha_m + V_r(\alpha_r - \alpha_m) \frac{K_m(3K_r + 4G_m)^2 + (K_r - K_m)(16G_m^2 + 12G_mK_r)}{(4G_m + 3K_r)[4V_rG_m(K_r - K_m) + 3K_mK_r + 4G_mK_m]}$$

Where:

α_m, α_r – is the coefficient of volume thermal expansion of matrix, reinforcement respectively

V_r - is the volume fraction of reinforcement,

K_m, K_r – is the bulk modulus of the matrix, reinforcement respectively,

G_m, G_r – is the shear moduli of the matrix, reinforcement respectively.

Turner's model:

$$\alpha_c = \frac{\alpha_m K_m \frac{F_m}{\rho_m} + \alpha_r K_r \frac{F_r}{\rho_r}}{K_m \frac{F_m}{\rho_m} + K_r \frac{F_r}{\rho_r}}$$

Where:

F_m, F_r – the weight fraction of the matrix, reinforcement respectively,

ρ_m, ρ_r – density of the matrix, reinforcement respectively.

2.6 Measurement tools and methods used in the Al/C composite investigations

In this section, a variety of measurement tools and methods used during the investigation of the Al/C composite are presented.

2.6.1 Microscopy observations

The first compulsory step of any material investigation is a microscopy observation. Several methods have been chosen from a wide range of available microscopy techniques which enable deep characterization of the material and its structure. These have been enumerated and described in the following sub-sections.

Scanning electron microscope (SEM)

SEM permits the observation and characterization of heterogeneous organic and inorganic materials on a nanometer (nm) to micrometer (μm) scale. The popularity of SEM stems from its capability of obtaining three-dimensional-like images of the surfaces of a very wide range of materials. In the SEM, the area to be examined or micro volume to be analyzed is irradiated with a finely focused electron beam, which may be swept in a raster across the surface of the specimen to form images or may be static to obtain analysis at one position.

The types of signals produced from the interaction of the electron beam with the sample include secondary electrons, backscattered electrons, characteristic x-rays, and photons of various energies.

The imaging signals of greatest interest are the secondary and backscattered electrons because these vary primarily as a result of differences in surface topography. The secondary electron emission, confined to a very small volume near beam impact area for certain choices of the beam energy, permits images obtained at a resolution approximating the size of focused electron beam.

In the SEM, characteristic x-rays are also emitted as a result of electron bombardment. The analysis of the characteristic x-radiation emitted from samples can yield both qualitative identification and quantitative elemental information from regions of a specimen nominally $1\mu\text{m}$ in diameter and $1\mu\text{m}$ in depth under normal operating conditions. The scanning electron microscope is one of the most comprehensive instruments available for the examination and analysis of the microstructural characteristics of solid objects. A major reason for the SEM's usefulness is the high resolution which can be obtained when bulk objects are examined. Another important feature of the SEM is the large depth of field, which is responsible in part for three dimensional appearance of the specimen image (21).

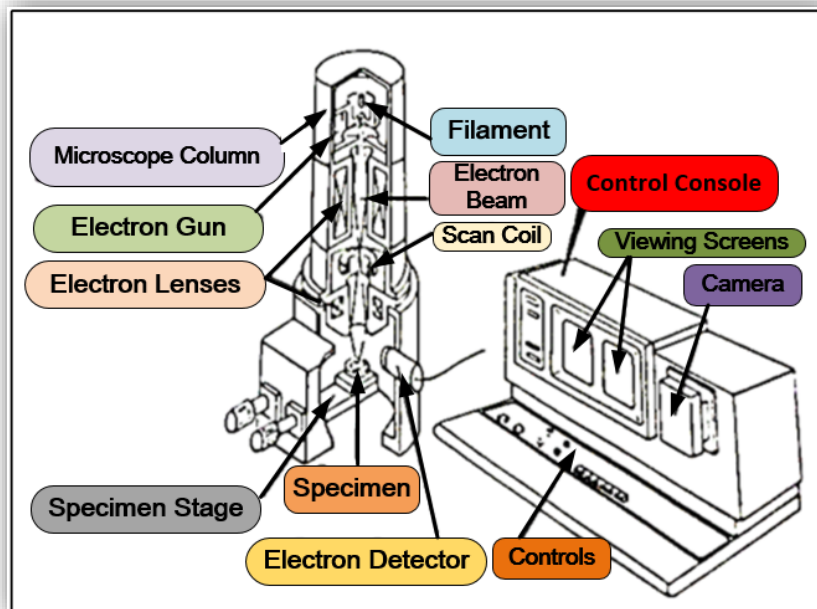


Figure 11 Two major parts of SEM

The basic components of the SEM are the lens system, the electron gun, the electron collector, the visual and photo recording cathode ray tubes and the associated electronics. Full SEM characteristic is being show in the Figure 11.

Back-scattered Electron Detector (BSED)

Another important technique used for material microstructure characterization is backscattered electrons used in the beam of SEM. This method is based on interactions of an accelerated electron beam with the target which produces variety of elastic and inelastic collisions between electrons and atoms within the sample. This is schematically presented in Figure 12.

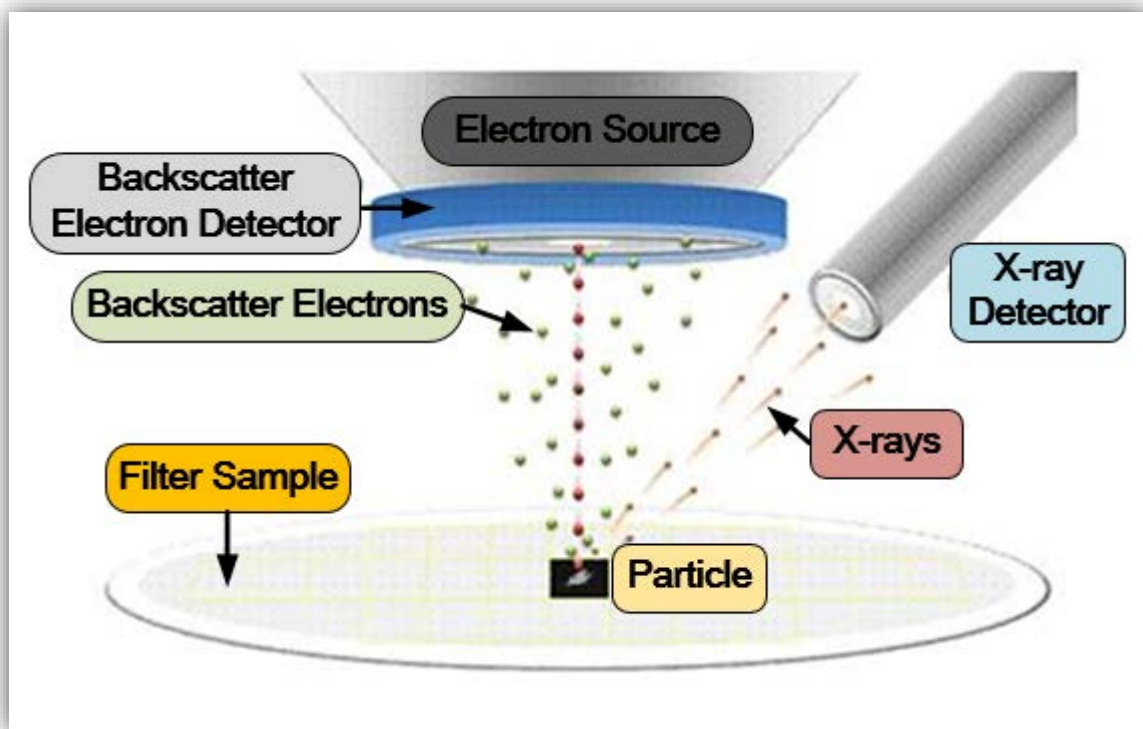


Figure 12 BSE detected by the backscatter electron detector (BSED) (22)

Elastic scattering changes the movement path of the incoming electrons beam interacting with the target sample without significant change in their kinetic energy. Essentially, elastic scattering consists in small particles (electrons) colliding with large particles (atoms). Larger atoms (with a greater atomic number Z) have higher probability of producing an elastic collision because of their greater cross-sectional area. Consequently, the number of backscattered electrons (BSE) reaching a BSE detector is proportional to the mean atomic number of the sample. Thus, the brighter BSE intensity correlates with greater average Z in the sample whereas dark areas have lower average Z value. An example of the

BSE investigation result is presented in Figure 13. BSE images are used for obtaining high-resolution compositional maps of samples and for quick distinction of different phases. These are often used in conjunction with spot probe analyses by either EDS or WDS methods (23).

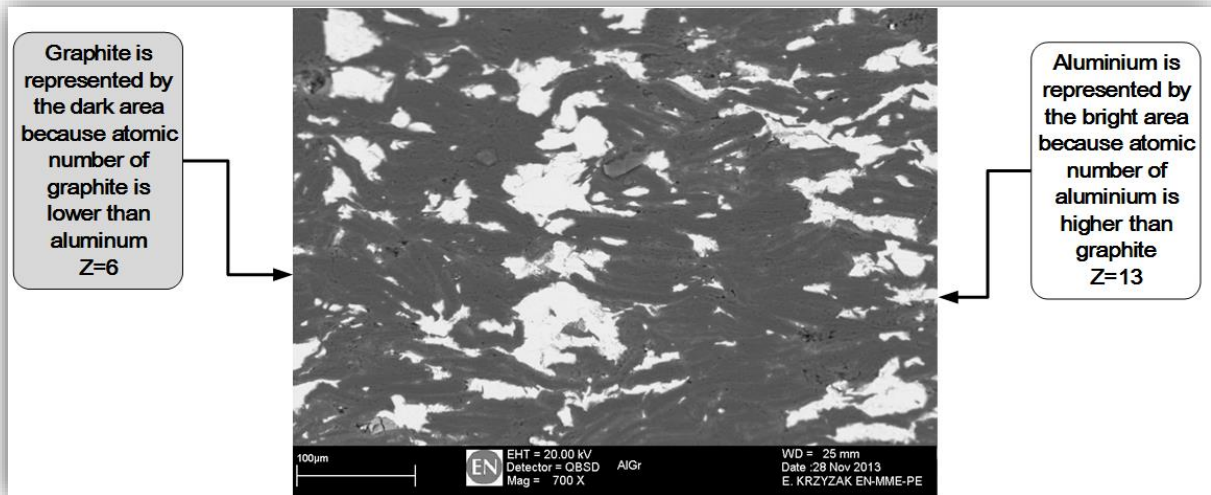


Figure 13 Al/C structure obtained by BSE detector

BSE images can be obtained nearly instantly and at any magnification within the instrument range. Thus, they are a quick mean of determining the number of phases in the investigated material and their mutual textural relationships. In most cases the polished samples are scanned in back-scatter mode to produce a BSE image of the surface. The gain of the detector can be tuned to maximize contrast between phases with similar Z.

EDS method

One of the techniques which help to deeply characterize the chemical structure of a material is the **energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS)**. It relies on an interaction of some source of X-ray excitation and a sample. EDS is based on the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum (24). Dispersive Spectrometer (EDS) micro-analysis is performed by measuring the energy and intensity distribution of X-ray signals generated by a focused electron beam on the specimen. With the attachment of the energy dispersive spectrometer, the elemental composition of the materials can be obtained (25). The principle of the EDS method is presented schematically in Figure 14.

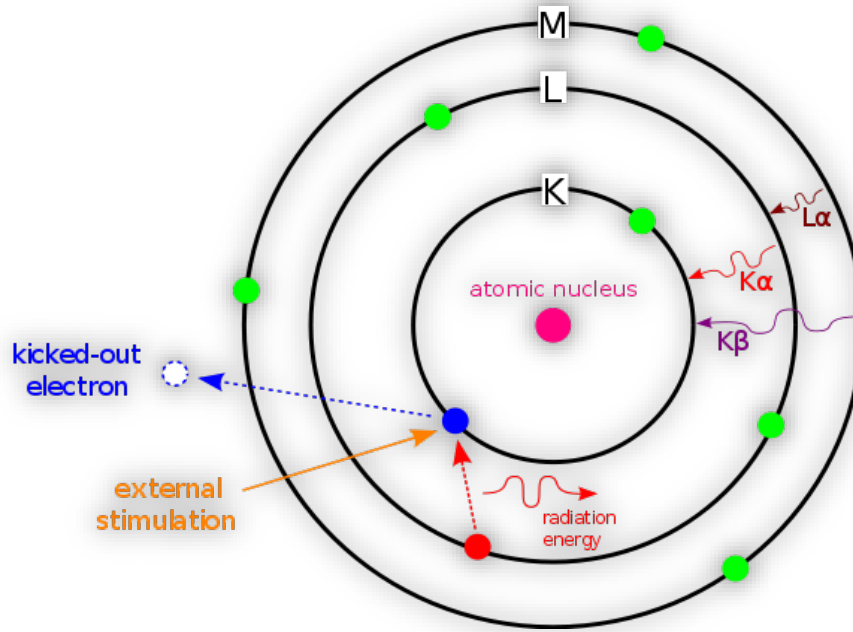


Figure 14 Principles of EDS (24)

When the incident beam reflects through the sample it leaves thousands of sample's atoms with holes in the electron shells (they are placed in the previous position of the secondary electrons). If these holes are in the inner shells, the atoms are not in a stable state. To stabilize the atoms, electrons from outer shells will drop into the inner shells. However, because the outer shells are at higher energy states, the atom must lose some energy. The energy ballast is emitted in a form of X-rays. The X-rays emitted from the sample's atoms have a characteristic energy and wavelength (26). Figure 15 shows the example of Al/C composite EDS spectrum obtained during investigation.

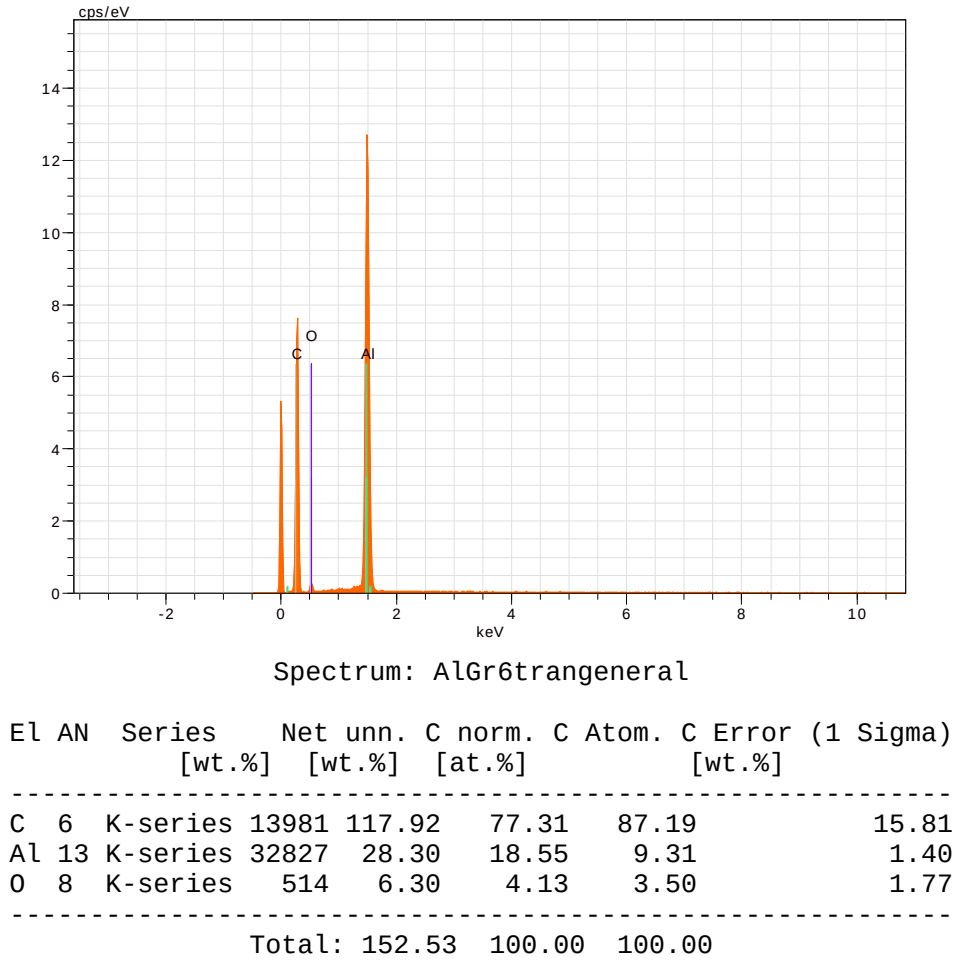


Figure 15 EDS spectrum of one of the Al/C samples obtained at CERN

2.6.2 Coefficient of thermal expansion measurement

The coefficient of thermal expansion plays a key role during the heat dissipation in many electronic devices and its measurement is of great importance while performing material characterization. **The coefficient of linear thermal expansion (CTE, α_1)** with a unit of 10^{-6}K^{-1} is a material property that is indicative of the extent to which a material expands upon heating. The change in length with temperature for a solid material can be expressed as:

$$\frac{l_f - l_o}{l_o} = \alpha_1 (T_f - T_o)$$

$$\frac{\Delta l}{l_o} = \alpha_1 * \Delta T$$

$$\alpha_1 = \frac{1}{l_o} \left(\frac{\Delta l}{\Delta T} \right)$$

Where:

l_o , l_f – are respectively the original and final lengths,

ΔT – is a change of temperature from T_o to T_f ,

α_1 – coefficient of thermal expansion with unit $10^{-6}/K^{-1}$

To determine the thermal expansion coefficient, two physical quantities (displacement and temperature) have been measured on the Al/C sample that is undergoing a thermal cycle. Three of the main techniques used for CTE measurement are dilatometry, interferometry, and thermo-mechanical analysis (27). During the investigation of Al/C samples the dilatometry technique has been chosen. Dilatometry is a thermo-analytical technique used to measure the expansion or shrinkage of solids, powders, pastes and liquids under negligible load when subjected to a controlled temperature/time program. A precise understanding of this behavior can provide the influence of additives and raw materials, densification and sintering properties, reaction kinetics, phase transitions, and thermal shock (28).

For measurement of coefficient of thermal expansion, the NETZSCH Dilatometer DIL 402 E has been used. The technical specification of mentioned dilatometer is presented in Table 3. This type of device is based on a push rod system in which the alumina or graphite bar is kept in contact with the sample, which expands during controlled heating. The measurements are performed with high precision to obtain the relative expansion for the given temperature variation. Samples used for this experiment are presented in Figure 16. They have a various size: length of the tested sample should be in the range of 6 – 25 mm.



Figure 16 Al/C samples prepared for the CTE measurements

Table 3 Technical specification of the NETZSCH DIL 402 E (28)

Temperature range	: -180°C to 500°C, RT to 1600°C, RT to 550°C to 2400°C, RT to 650°C to 2800°C (exchangeable furnace types)
Heating and cooling rates	0.01 K/min to 50 K/min (dependent on furnace and temperature range)
Sample holder	fused silica <1100°C Al ₂ O ₃ <1700°C graphite 2800°C
Measuring ranges	500/5000 µm
Sample length	25/50 mm
Sample diameter	max. 12 mm
Δl resolution	0.125 nm / 1.25 nm
Atmospheres	inert, oxidizing, reducing, static and dynamic
Highly vacuum-tight	up to 10 ⁻⁴ mbar (10 ⁻² Pa)

Figure 17 presents the construction of NETZSCH DIL 402 E.

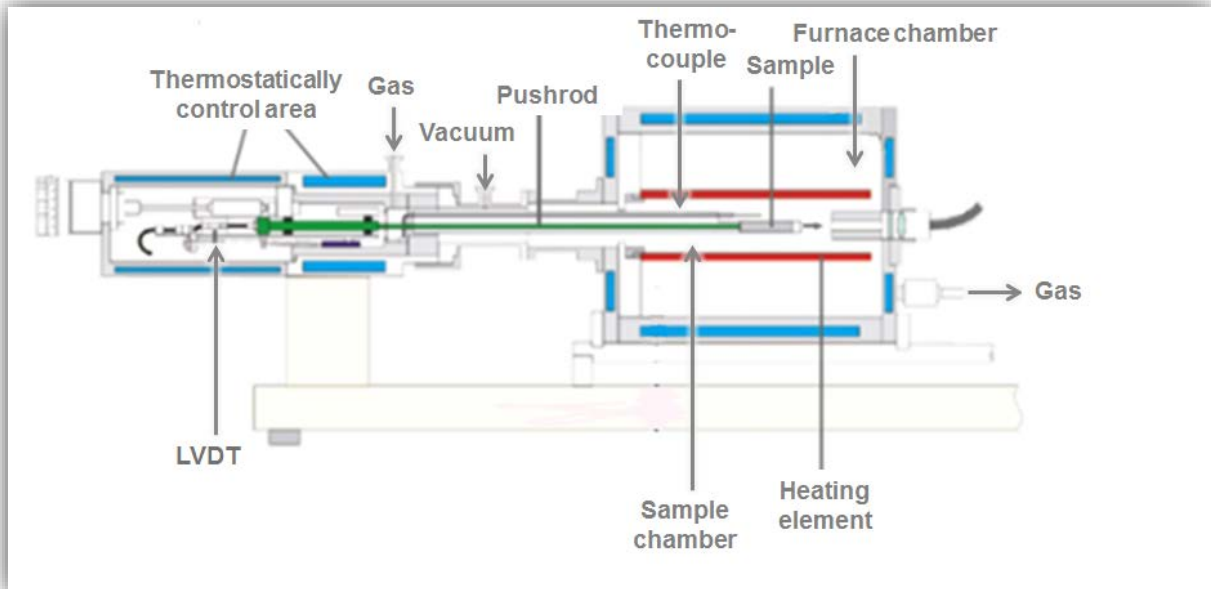


Figure 17 The construction of NETZSCH DIL 402 E (28)

Figure 18 presents the NETZSCH DIL 402 E assembly at CERN in the Mechanical Laboratory where the measurements of CTE took place.

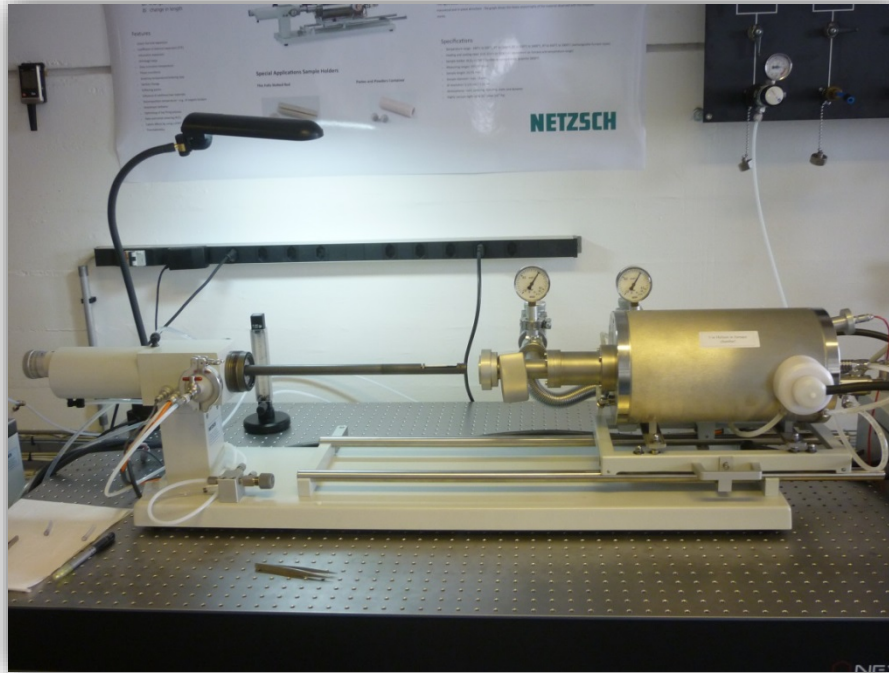


Figure 18 Position to study the thermal expansion coefficient

2.6.3 Thermal conductivity measurement

Due to the ever-increasing number of materials being used in high-temperature applications, knowledge of their thermo-physical properties, especially thermal conductivity, is of paramount importance. One of the most widely used methods for determining the thermal conductivity is to measure the thermal diffusivity (α), specific heat (C_p) and density (ρ) as a function of temperature, and then to compute the thermal conductivity (λ) from these data.

Thermal conductivity (TC) λ with unit [**W/(mK)**] is a material-specific property used for characterizing steady heat transport and the transient heat exchange. It can be calculated using the following equation:

$$\lambda(T) = \rho(T) * C_p(T) * \alpha(T)$$

Where:

α - is thermal diffusivity (mm^2/s)

C_p – is specific heat capacity ($\text{J}/(\text{kg}\cdot\text{K})$)

ρ - is density (kg/m^3)

Thermal conductivity describes the transport of energy – in the form of heat – through a body of mass as the result of a temperature gradient. According to the second law of thermodynamics, heat always flows in the direction of the lower temperature.

Specific heat (C_p) [J/(kg·K)] is the amount of heat per unit mass required to increase the temperature by one degree Celsius. The relationship between heat and temperature change is usually expressed in the form shown below where C_p is the specific heat.

$$Q = C_p * m * \Delta T$$

Where:

Q – is heat added (J)

C_p - is specific heat (J/(kg·K))

m – is mass of the body (kg)

ΔT - is change in temperature (K)

The specific heat capacity of a material on a per mass basis is:

$$C = \frac{\partial C}{\partial m}$$

Which in the absence of phase transitions is equivalent to:

$$C = E_m = \frac{C}{m} = \frac{C}{\rho V}$$

Where:

C - is the heat capacity of a body made of the material in question,

m - is the mass of the body,

V - is the volume of the body, and

$\rho = \frac{m}{V}$ - is the density of the material.

Thermal diffusivity (α) is a material-specific property for characterizing unsteady heat conduction. This value describes how quickly a material reacts to a change in temperature. The formula for thermal diffusivity is given by:

$$\alpha = \frac{k}{\rho * C_p}$$

Where:

k - is thermal conductivity (W/(m·K))

ρ – is density (kg/m³)

C_p - is specific heat capacity (J/(kg·K))

For this purpose the NETZSCH laser flash apparatus LFA 427 which is presented in the Figure 19 has been used.

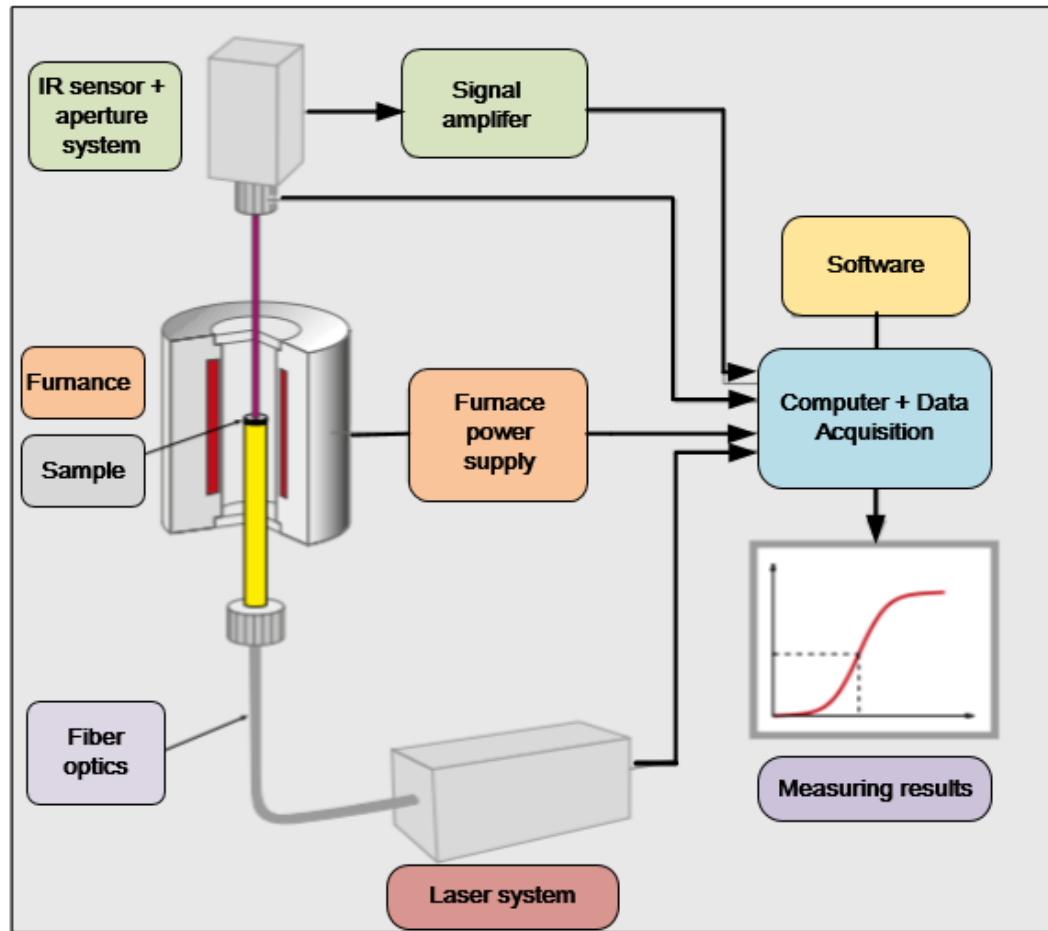


Figure 19 Principle of operation of the LFA 427 (28)

. Compared with the direct measurement of thermal conductivity, the advantages of this non-contact, non-destructive method are: sample geometry, easy sample preparation and small sample size, as well as applicability for a wide range of diffusivity values and excellent accuracy and reproducibility. The technical specifications of the LFA 427 are presented in Table 4.

Table 4 LFA 427 - Technical Specifications (28)

Temperature range	-120°C to 400°C, RT to 1300°C, RT to 1575°C, RT to 2000°C, RT to 2800°C (5 furnace types)
Heating- and cooling rates	0.01 K/min to 50 K/min (dependent on furnace)
Laser power	25 J/pulse
Contactless measurement of temperature rise	with IR detector
Measuring range	0.01 mm ² /s to 1000 mm ² /s (thermal diffusivity)
Measuring range	0.1 W/mK to 2000 W/mK (thermal conductivity)

Sample dimensions	6 mm to 12.7 mm diameter (20 mm special version), 10x10 mm square
Sample holder	Al ₂ O ₃ , graphite
Atmospheres	inert, oxidizing, reducing, static, dynamic
High vacuum-tight assembly	up to 10 ⁻⁵ mbar

In order to start the investigations of an Al/C composite by the LFA 427 device, the sample has been mounted on a carrier system which is located in a furnace. After the sample reaches a predetermined temperature, a burst of energy emanating from the pulsed laser is absorbed on the front face of the sample, resulting in homogeneous heating. The relative temperature increase on the rear face of the sample is then measured as a function of time by an IR detector.

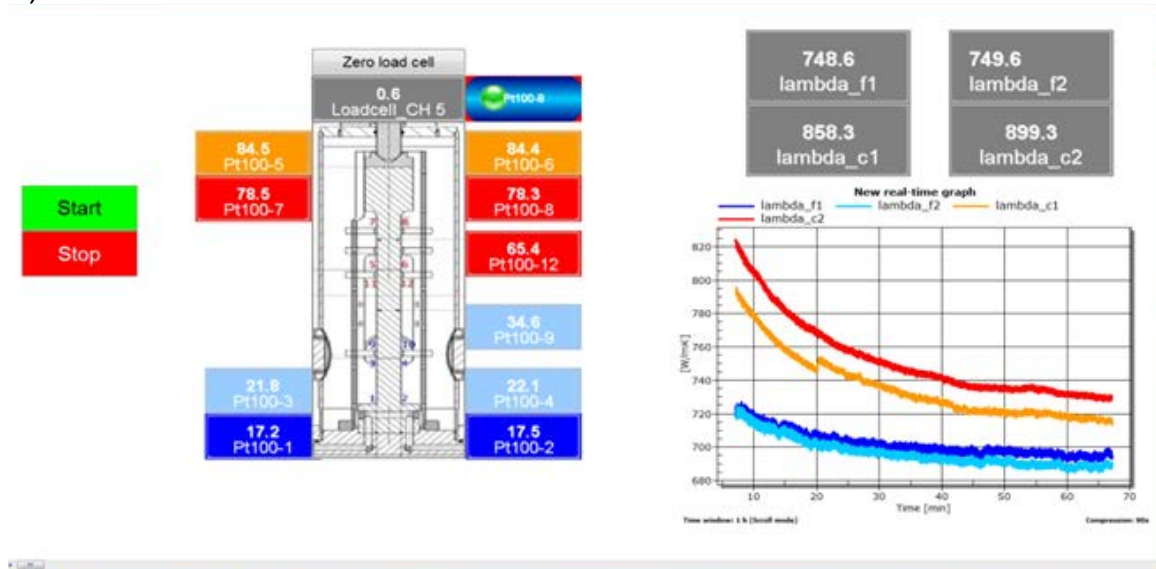
Figure 20 shows the samples prepared for measurements of thermal conductivity in both directions: longitudinal and transversal. For this apparatus the sample must be a disk-shaped with diameter 12,7mm and thickness 2 mm or the smallest size with diameter of 6 mm and thickness 2 mm.



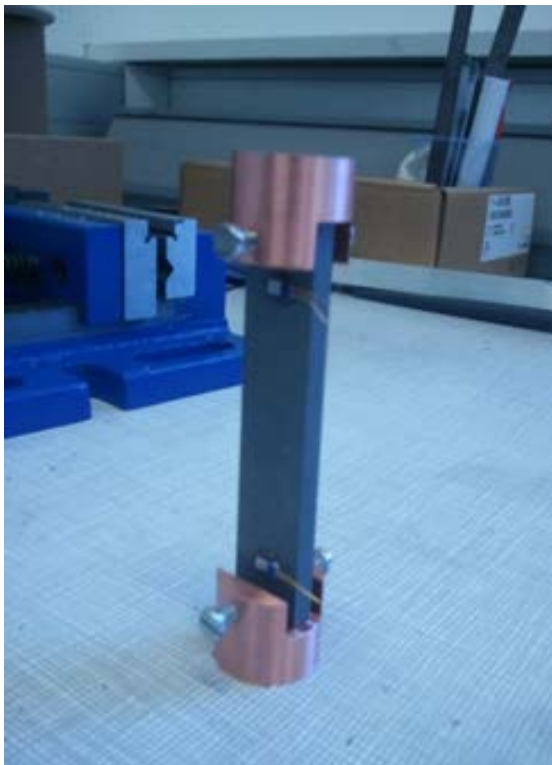
Figure 20 Samples prepared for the thermal conductivity measurement by the LFA 427 in both directions; longitudinal and transversal

Thermal conductivity of aluminium/graphite composites has not been only measured by LFA 427. Since the LFA 427 device has been delivered at the end of presented research, the thermal characterization has been conducted thanks to a tool designed and assembled at CERN (see Figure 21). The tool can measure thermal conductivity of metals, ceramics and composites ranging between 15 – 700 W/(mK) with an accuracy of 10%. The measurements have been performed along the in-plane direction.

a)



b)



c)

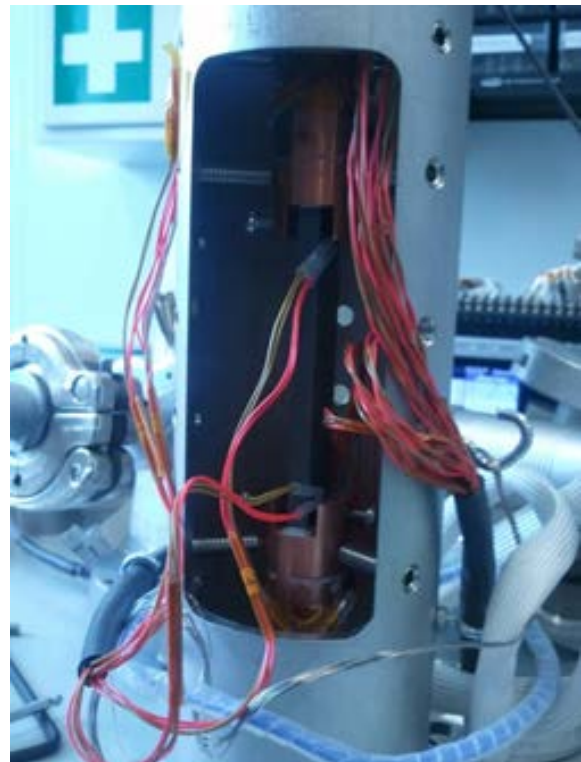


Figure 21 Measurement procedure of the thermal conductivity on the in-house built device: a) measurements result presented in the Catman application b) assembly sample between two copper pieces c) device prepared to test

The method presented in Figure 21 relies on the generation of a stationary heat flux passing in series through reference pieces and the sample itself, the temperature distribution

along the reference pieces and the sample being measured by thermal probes. The heat flux is then evaluated by measuring the δT_{ref} along a known section (A_{ref}) of the reference piece (having a known k_{ref}) by:

$$Q = k_{ref} * A_{ref} * \frac{\delta T_{ref}}{\delta x_{ref}}$$

and then the thermal conductivity of the sample k is easily determined knowing the heat flux and the geometry of the sample by inverting the equation. This method is based on the ASTM E1225 - 09 Standard (Test Method for Thermal Conductivity of Solids by Means of the Guarded-Comparative-Longitudinal Heat Flow Technique) and gives a direct, density and specific heat independent, measurement of the final thermal conductivity of the material along the heat flux direction (29).

For thermal conductivity tests, samples have been prepared at different sizes according to the specification of the device. Figure 22 shows the sample ready for thermal conductivity tests with dimensions 70 mm of length, 4 mm thickness and 25mm width for measurement in longitudinal (in plane) direction on the in-house built device.



Figure 22 Sample prepared for the thermal conductivity measurement (on the in-house built device)

2.6.4 Electrical properties

Electrical conductivity is another property of great interest in the performed research. **Electrical Conductance [S]** is an expression of the ease with which electric current flows through a substance. When a current of one ampere [A] passes through a component across which a voltage of one volt [V] exists, then the conductance of that component is 1 siemens [S]. Thus **electrical conductivity [MS/m]** is a measure of the material capability to conduct an electric current, whereas electrical resistivity is an intrinsic property that quantifies how strongly a given material opposes to the flow of electric current (21). Many resistors and conductors have a uniform cross section with a uniform flow of electric current, and are made of one material.

In this case, the electrical resistivity ρ is defined as:

$$\rho = R \frac{A}{l}$$

Where:

R - is the electrical resistance of a uniform specimen of the material (measured in ohms, Ω),

l - is the length of the piece of material (measured in meters, m)

A - is the cross-sectional area of the specimen (measured in square meters, m^2).

Conductivity is the inverse:

$$\sigma = \frac{1}{\rho}$$

The electrical conductivity test has been performed using the SIGMATEST 2.069 device, presented in Figure 23, which is an eddy current instrument that measures the electrical conductivity of non-ferromagnetic metals in units of %IACS or MS/m.



Figure 23 SIGMATEST 2.069 for electrical conductivity measurements

Electrical conductivity measurements can be used to determine material composition, structure, and heat-treat condition. The capabilities of presented device are as follows:

- Fast and reliable determination of electrical conductivity with high accuracy
- Large measuring range from 0.5 to 65 MS/m (1% to 112% IACS)
- Distance correction up to 500 μm (0.02 inch) for maintaining high accuracy when measuring on painted, coated, or dusty surfaces
- Five selectable operating frequencies (60 / 120 / 240 / 480 / 960 kHz)

- Consistently high accuracy on test pieces of various thickness
- Correction of electrical conductivity values as a function of variations in the test piece temperature is possible using either an internal or external temperature sensor and a user defined temperature coefficient
- Multi-lingual operating system
- Data transfer to PC-based applications via compact flash card
- Remote control via RS-232 interface (30)

2.6.5 Flexural strength

Mechanical properties of the Al/C composite play a significant role in the potential industrial applications. From its nature graphite is the material of great fragility and brittleness, which is preventing from obtaining successful results of mechanical strength. Therefore the mechanical characterization should not be neglected.

The mechanical characterization of the Al/C composite is based on the **flexural strength** measurements. The flexural strength is the stress at failure of the material under a flexural load. To define flexural strength of Al/C composite, samples have been subjected to a four-point bending setup which is presented schematically in Figure 24. Having dimensions of the sample variable with the defined load is possible to calculate the flexural strength according to the following equation:

$$\sigma = \frac{3FL}{4bd^2}$$

- F is the load (force) at the fracture point (N)
- L is the length of the support span (mm)
- b is width (mm)
- d is thickness (mm)

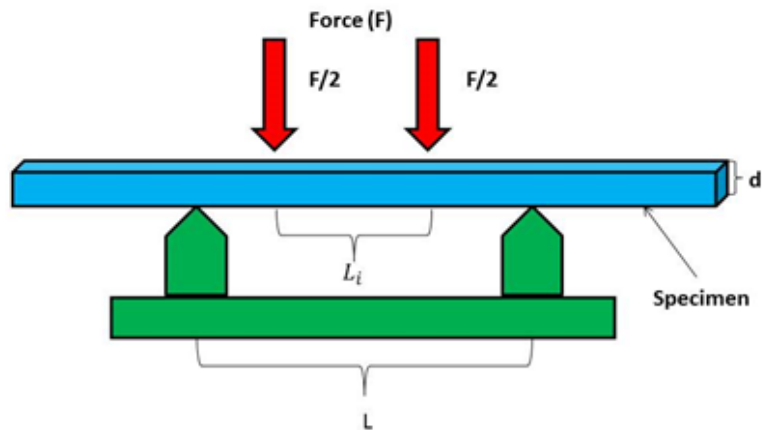


Figure 24 Beam under 4 point bending

The strength measurement has been performed in the EN-MME Mechanical Laboratory at CERN. Figure 25 presents the part of the device where a sample is put inside the fixtures which are made of stainless steel with bearings of hardened steel. The fixtures have been produced in three dimensions: for large samples 60x5.5x4 mm (Fixture with $L=50$ mm), medium samples 40.9x4x4 mm (Fixture with $L=35$ mm) and small samples 25x2x1.5 mm (Fixture with $L=20$ mm). Al/C samples have been tested using large fixture with $L=50$ mm and have been subjected to four point bending test. Measurements have been carried out according to the ASTM Standard C 1161 - 2c (31).

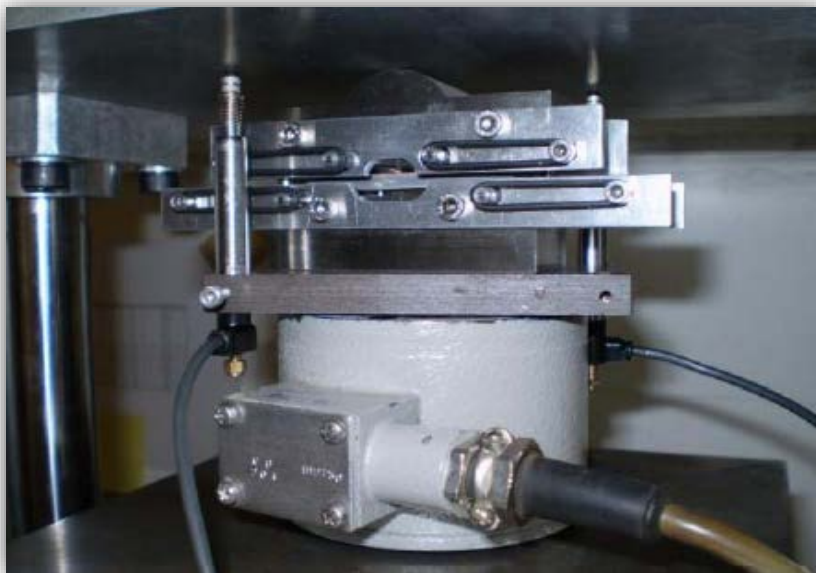


Figure 25 Assembly sample for the flexural test (Photo: A. Slaathaug, E. Gallay, M. Guinchard EN/MME)

3. EXPERIMENTS

This chapter describes the conducted research and development process in detail, presenting preliminary results and their analysis.

3.1 Work organization

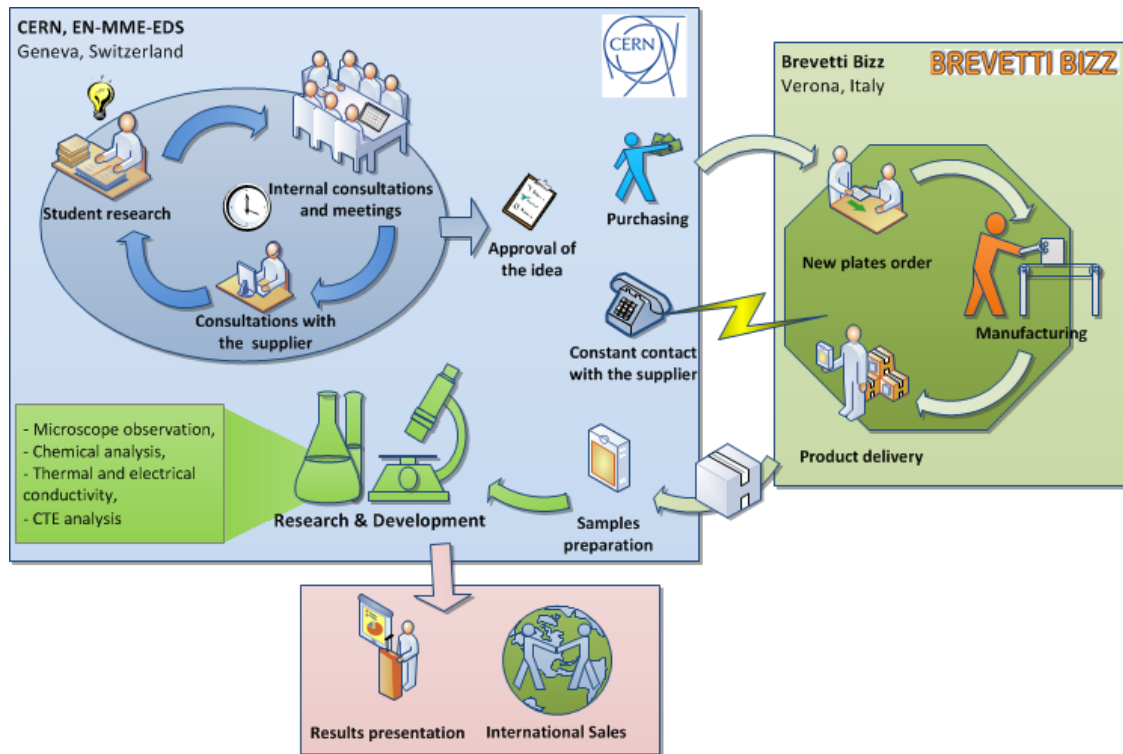


Figure 26 Workflow diagram

The following list resumes the main tasks to be performed while conducting research on the studied materials:

- Identification of suitable aluminium/graphite compositions, prediction of their physical and mechanical properties by analytical means
- Theoretical study of the prototyped composites and their feasibility study
- Commission and supervision of the production process
- Analysis and interpretation of the material's microstructure and deep characterization of the composite properties by: Scanning Electron Microscopy (SEM), Back-Scattered Electron Microscopy (BSE), Energy Dispersive Spectrometry (EDS), X-

Ray Diffraction Microscopy, Flexural Tests, Thermal Conductivity and Coefficient of thermal expansion measurements.

- Interpretation and assessment of obtained results: comparison against already obtained results and state of the art materials used in the industry. Feedback to the first phase
- Final definition of the composition, the processing and characteristics of new, appealing thermal management materials for general applications.

In order to follow the aforementioned guidelines, an appropriate work methodology was established and is schematically presented in Figure 26. At first, it is essential to get familiar with materials concerned. Detailed study of their features and analytical calculations to predict the composite properties were performed. Every proposal was discussed during the internal meetings at CERN as well as with an external partner company. This was an iterative process until a promising composition was agreed on. Due to its significant experience and professionalism in the powder metallurgy domain, the BrevettiBizz Company (located in Verona, Italy) was chosen as a manufacturer of the plate samples used in the investigations. After agreement on the composite structure, the production process began. During the plate manufacturing process, constant contact with the supplier was kept to discuss emerging issues and refinements which could be applied. After plate delivery, the investigation process could start. Plates were cut for the desired shapes for variety of tests and measurements. Every created sample was comprehensively characterized and described which is shown in the subsequent sections.

3.2 Powder analysis

Raw materials play an important role in the production process of the Al/C composite. Since these are the main ingredients of the created material, their role is discussed in detail in the following paragraphs.

During the test of powders it is important to determine their properties: their shape, size, internal structure, surface area, chemical composition (oxidation degree) and the physical properties. The sample powder designated for the investigation must be representative - this means that the properties of the sample have to be similar to the entire batch of powder.

Most of the aluminium powders are porous in their nature. Therefore, for this purpose, microscopic observations were carried out. Figure 27 shows aluminium powder 45 μm

observed by Scanning Electron Microscopy (SEM). During the analysis, a few big macro-agglomerations which may have porosity inside have been found. Presence of macro-agglomerations may have an impact on the final density of the material and consequently on the final properties. Since the density is an important factor, powder as the main building material has to be properly checked.

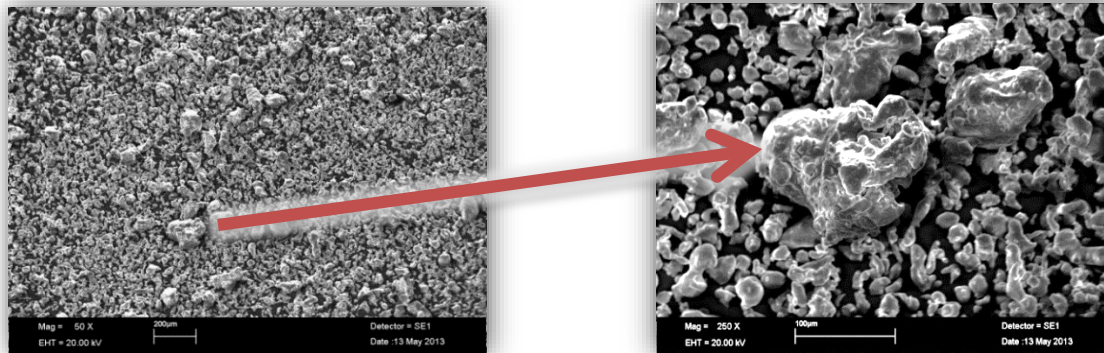


Figure 27 Observation of macro agglomerations of aluminium powder, magnification: 50x and 250x, SEM

In order to improve the final density and decrease the amount of porosity, selection process had to be applied. Figure 28 shows the aluminium powder after selection. This selected powder has been used for the production of Al/C composite.

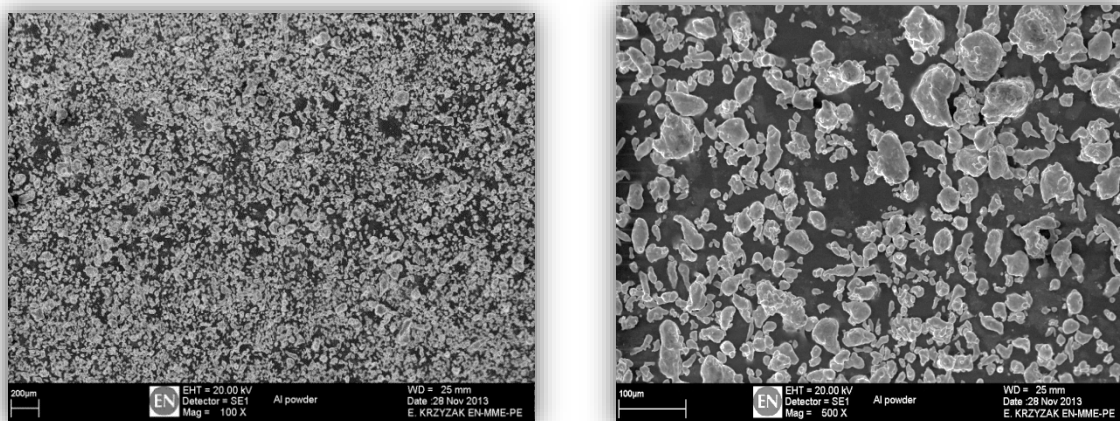


Figure 28 Observation of aluminium powder after selection, magnification: 100x and 500x, SEM

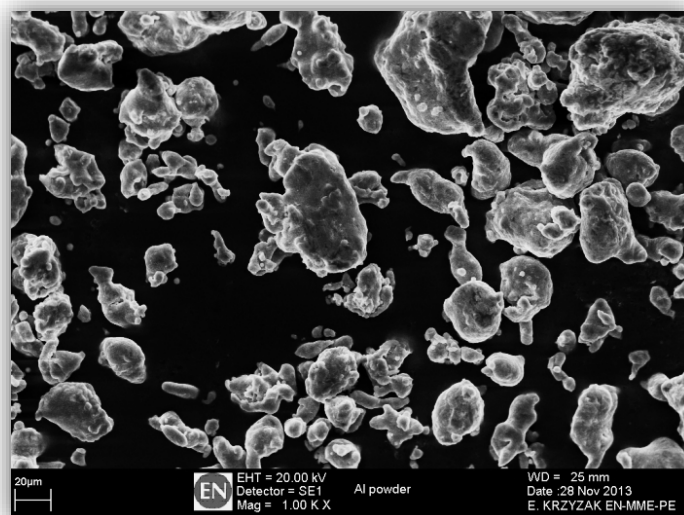


Figure 29 Observation of aluminium powder after selection, magnification at 1000x, SEM

Another important component which forms the investigated composite is graphite. Due to its excellent thermo-physical properties (see Section 2.1) it is expected to ameliorate the final properties of the constructed composite. Its properties mainly depend on the graphitization degree, its structure and morphology.

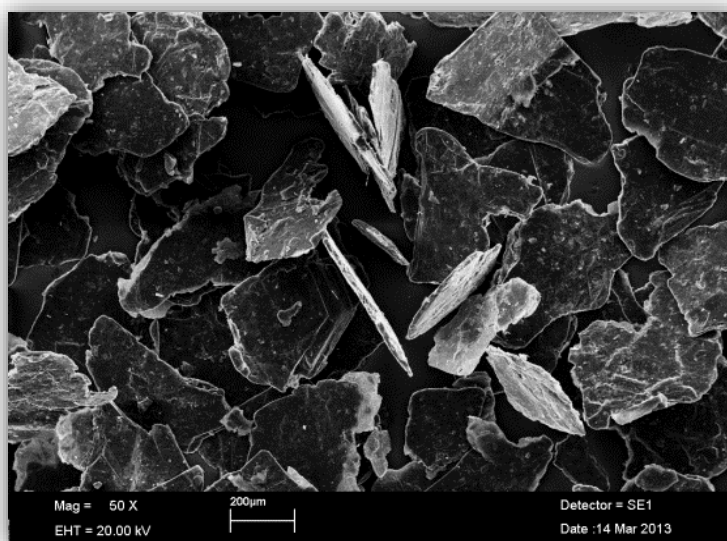


Figure 30 Natural graphite flakes with average diameter 300-500 µm, magnification 50x, SEM

In the following project, several different kinds of natural graphite flakes with a wide variety of shapes have been tested. Each of them offers different structures and, at the same time, ensures different properties. Figure 30 presents the big graphite flakes with diameter of 300-500µm with irregular round shape and rough surface. This type of graphite provides

good thermal properties due to the large surface of flakes but at the same time it can impact the mechanical characteristics. Figure 31 demonstrates more regular circular shape and smoother surface. This kind of graphite ensures good thermal and fair mechanical properties. Figure 32 shows irregular sizes and shapes of flakes which is very attractive from the point of view both the conductivity (even out of plane direction) and the flexural strength.

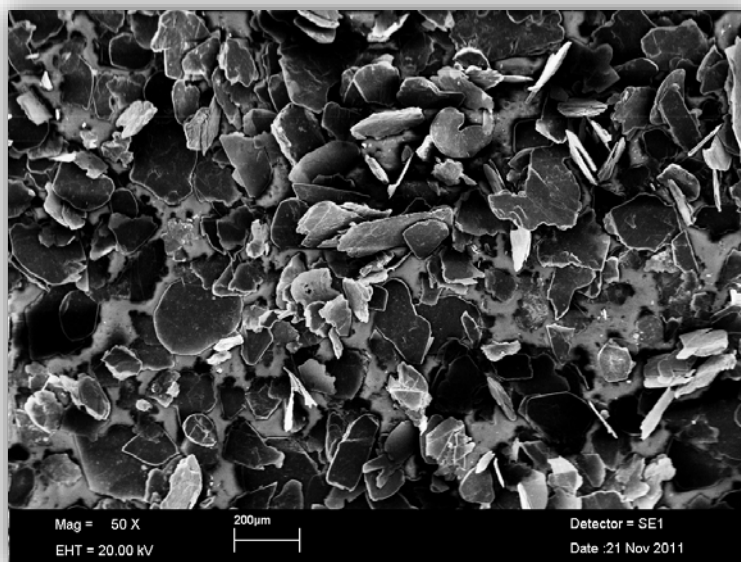


Figure 31 Natural graphite flakes with average diameter 100-200 μm , magnification 50x, SEM

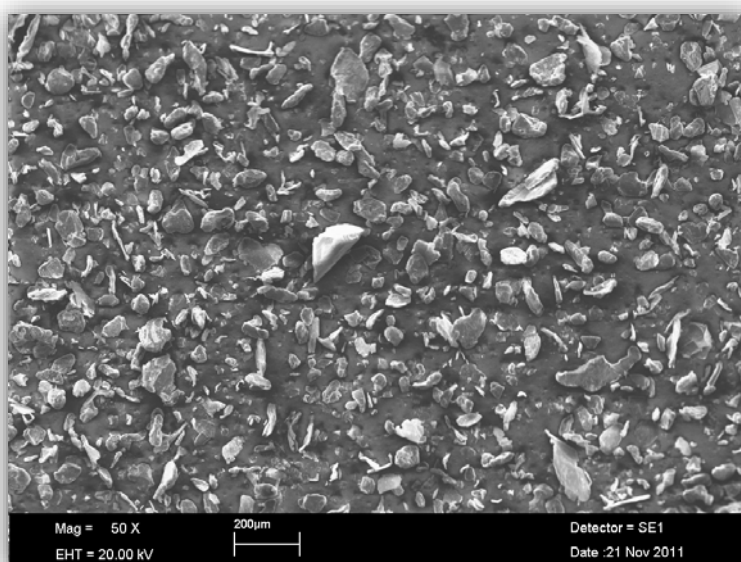


Figure 32 Unselected graphite ashes, average size around 80 μm , magnification 50x, SEM

3.3 Al/C composite manufacturing using Rapid Hot Pressing Technique

To manufacture the chosen variants of the aluminium/graphite composite, the Rapid Hot Pressing (RHP) Technique has been used. This method is well-known in the powder metallurgy field and permits to achieve very good compaction rates. It is one of the sintering methods used to consolidate cold-pressed or loose powders.

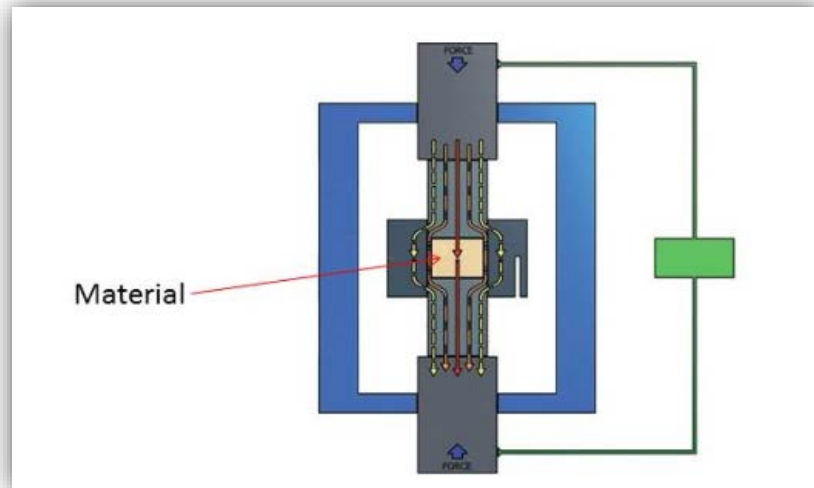


Figure 33 Scheme of the Rapid Hot Pressing Device

All Aluminium-Graphite plates have been produced using already mentioned RHP technique which is illustrated schematically in Figure 33. The RHP method permits to sinter the mixture of powder in the conditions of controlled atmosphere, pressure and temperature. The RHP device is constructed with a vacuum chamber heated by a current flow passing between the upper and lower electrodes. The powders are placed in a graphite mould and pressure is applied by the two graphite punches (32).

Table 5 Comparison of important aspects of consolidation techniques

System	HP	SPS	RHP
Cost	Med	High	Low
System size	Med	Large	Small
Heating rate	Slow	Fast	Fast
Chemistry effect	None	Problem	None
Design flexibility	Med	Small	Large
Scale up	Easy	Hard	Easy

The first step in fabrication of Al/C composite is to mix 25% of aluminium powder with 75% of graphite flakes. All powders were carefully mixed in rotatory barrels and were cleaned by a preliminary wash using a reducing gas to reduce the oxygen content absorbed at the surfaces. The prepared powders are then inserted in a graphite mould for the rapid hot pressing cycle: hot press process was performed always under vacuum in different temperatures, pressures and sintering time. These parameters have been controlled and changed according to our demand and observations. After hot pressing, plates with diameter of ϕ 90 mm and 4 mm thickness have been obtained (see Figure 34). The plates were cut for the finer samples and prepared for the SEM, EDS, X-ray observation as well as for flexural strength and thermal characterization.



Figure 34 Compressed Al / Gr plate after Rapid Hot Pressing

3.4 Microstructures

Observation of the microstructure is the basic investigation during material characterization process. From observed patterns of the microstructures it is possible to reason on the actual properties of analyzed samples. The properties concerned depend on the structure arrangement, presence of porosity or undesired carbides which are usually created on the interface as a result of chemical reaction in high temperatures. These carbides have negative influence on the final material's properties: they are brittle which degrades

mechanical strength of the material and, since they constitute an isolating barrier, they block the natural heat transfer between aluminium and carbon elements. The microscopy techniques which were used for Al/C observation have been described in section 2.6.1.

Among many investigated Al/C plates, five most representative samples have been chosen and described in more detail in this thesis. For the microscopic observation, the Scanning Electron Microscopy (SEM) has been used. Before starting the microscopy observations all samples have been polished and cleaned by ultrasound in alcohol, carefully dried and stocked. Afterwards samples have been put into degassing chamber to reduce the degassing time inside the SEM vacuum chamber. Figure 35 - Figure 40 show the Al/C composite structure consisting of different types of graphite flakes. These composites have been produced in different manufacture cycles in order to find the most optimal process parameters which could ensure the best properties of the final composite. All samples have been observed in transversal direction. Bright fields on the microstructure indicate aluminium phase whereas the dark fields represent the graphite phase.

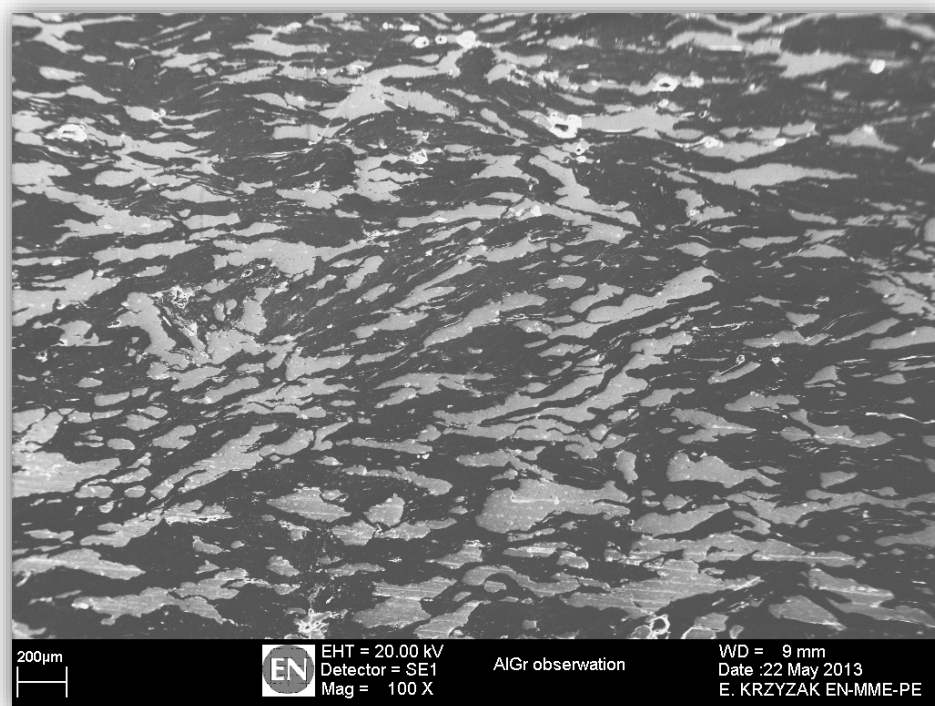


Figure 35 AG-22-B (2/1) sample in transversal direction, microstructure at 100x magnification, SEM

Microstructures in Figure 35 and Figure 36 represent samples which have been produced in the same process using the same graphite type with dimensions: 300-500μm. Sample AG-22-B (2/1) (Figure 35) represents denser material with the compaction rate of

96% and more homogenous structure comparing to the AG-22-B (2/4) (Figure 36) with compaction rate of 93% (which has more porosity inside the material). White particles visible on the microstructure are basically dirt which fell down on the sample. Black hole visible on the AG-22-B (2/4) is the graphite detached during polishing.

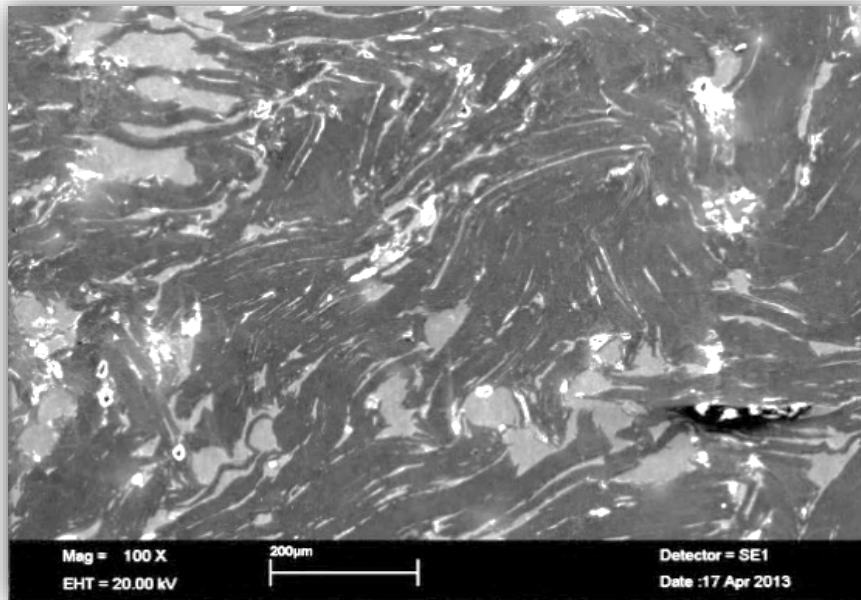


Figure 36 AG-22-B (2/4) sample in transversal direction, microstructure at 100x magnification, SEM

Large graphite flakes (300-500 μm) used in the Al/C composites ensures a well-aligned structure as seen in sample AG-22-B (2/1) (Figure 35). This contributes to high thermal and electrical conductivity and low CTE in plane direction. However, application of graphite flakes with a large diameter adversely affects the mechanical properties of the material. The presence of Al_4C_3 in both cases has not been identified.

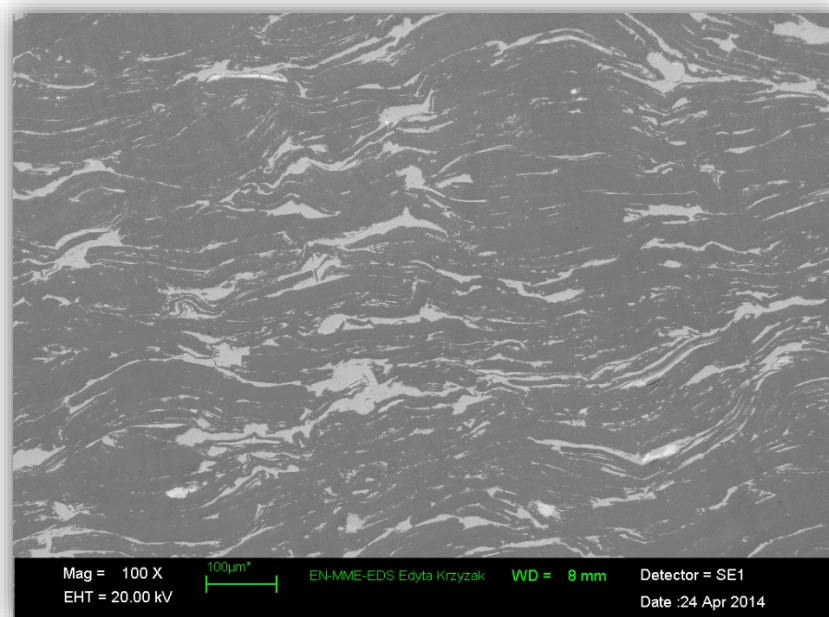


Figure 37 AG-22-K sample in transversal direction, microstructure at 100x magnification, SEM

Sample AG-22-K (13C) (visible in Figure 37) presents a microstructure consisting of the large graphite flakes as well (300-500 μm), however in this case some process parameters have been altered. Temperature and pressure have been slightly increased, resulting in a uniform structure and denser material. It has been observed that the increase of temperature and pressure generally improves the desired properties, in particular the material strength.

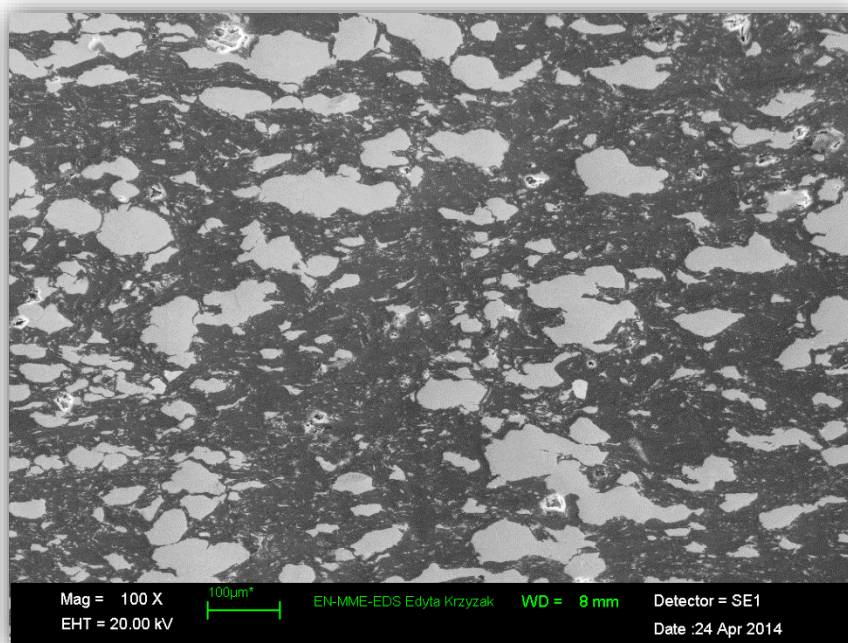


Figure 38 AG-66-K (13B) sample in transversal direction, microstructure at 100x magnification, SEM

Sample AG-66-K (13B) (depicted in Figure 38) presents a structure with not selected graphite particles (mixed 80 μ m particles and small ashes). This sample has been produced in the same process parameters as the sample presented in Figure 37. As it was mentioned before, growth of temperature and pressure during the composite plate sintering has a positive impact on the material properties of the material. It has been noticed that small graphite particles contributed to increased strength of the material. AG-66-K (13B) microstructure shows small and big aluminium phases mixed together which have been created and arranged due to the type of graphite (mixed 80 μ m particles and small ashes). Like in the previous structures, the Al_4C_3 has not been observed.

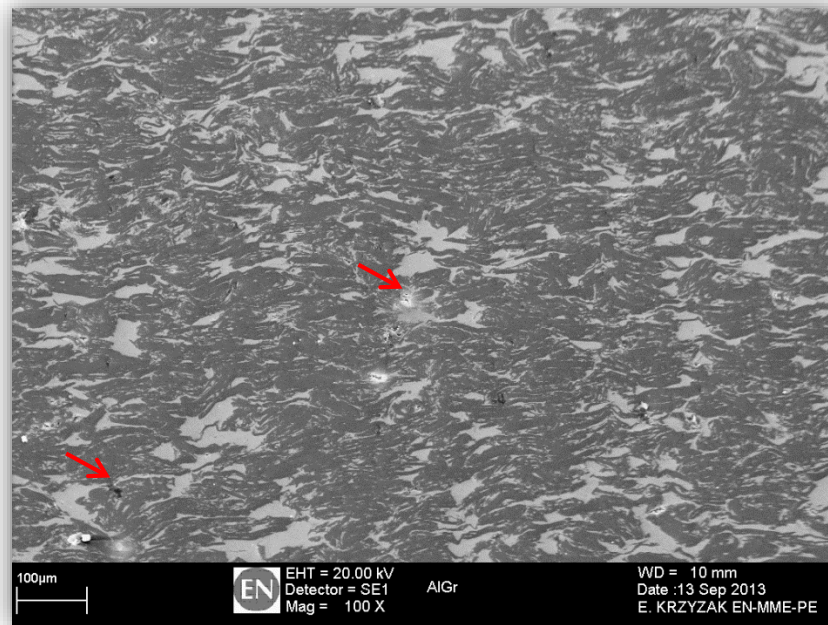


Figure 39 AG-46-D sample in transversal direction, microstructure at 100x magnification, SEM

Sample AG-46-D (Figure 39) presents a microstructure consisting of small graphite particles like in the AG-66-K (13B) sample, however it has been manufactured in lower temperature. As a result, higher presence of porosity has been observed. Lower temperature contributed to general decrease of desired properties since aluminium and graphite have not been well bonded together. As a consequence, some porosity in the material has been found. It is pointed by the red arrows in Figure 39.

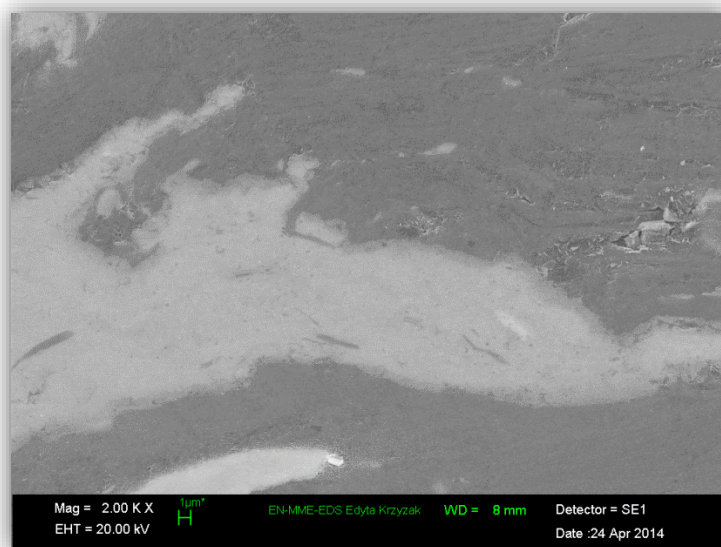


Figure 40 Observation of the interface at high magnification on the example of AG-22-K (13C)

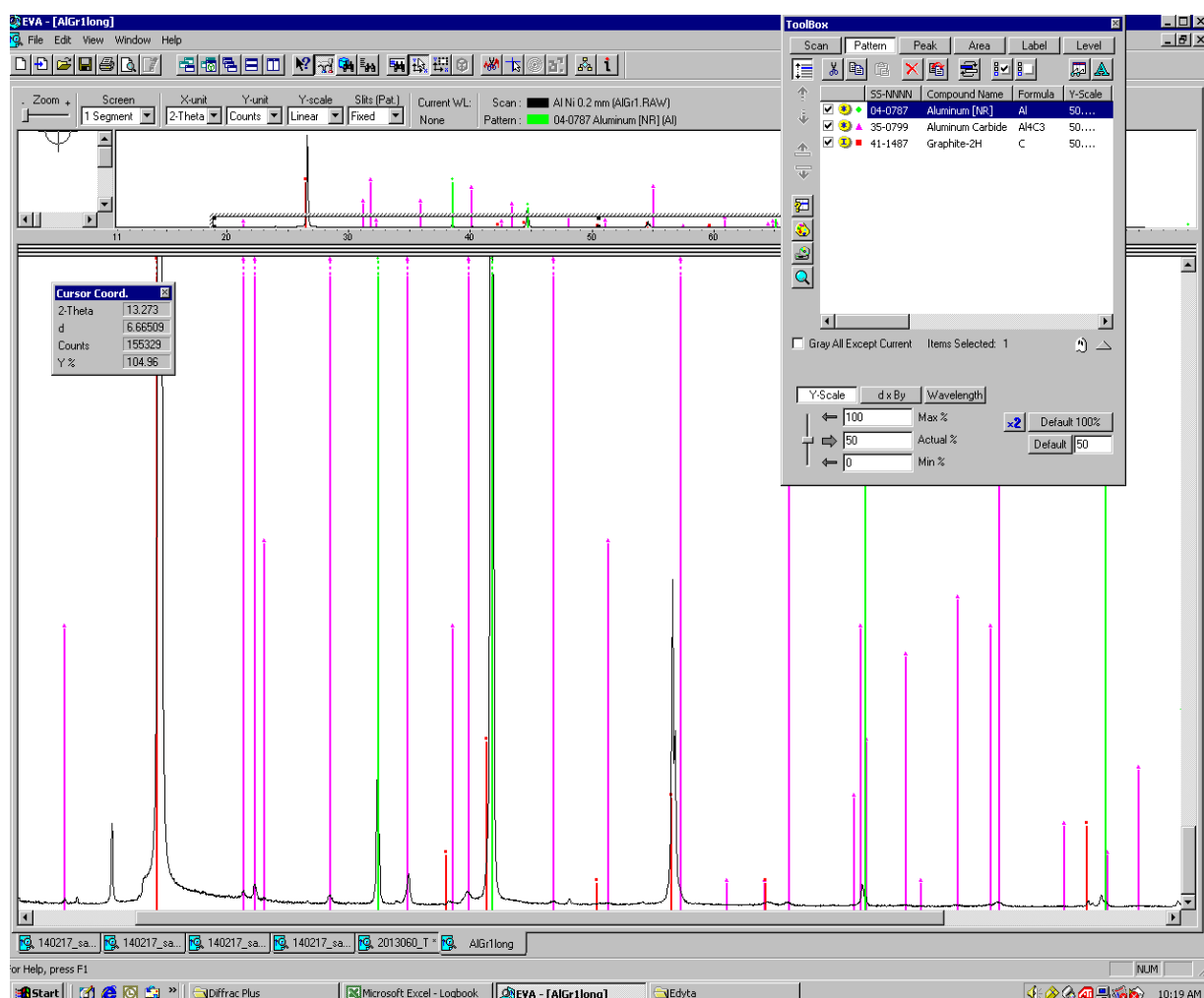


Figure 41 X-ray analysis indicate presence of Al_4C_3

Among all tested materials, the presence of undesired aluminium carbide (Al_4C_3) has not been observed on the interface. Figure 40 presents the interface on the example of AG-22-K (13C) at high magnification – it indicates there aren't porosity and carbides. Creation of Al_4C_3 phase usually takes place when the sintering temperatures exceed 700°C (it depends on the time of sintering as well). One experiment which demonstrates the creation of the Al_4C_3 phase has been conducted. The composite has been manufactured in temperature 815°C and investigations indicated presence of Al_4C_3 which was confirmed by the X-ray analysis. The result is shown in the Figure 41.

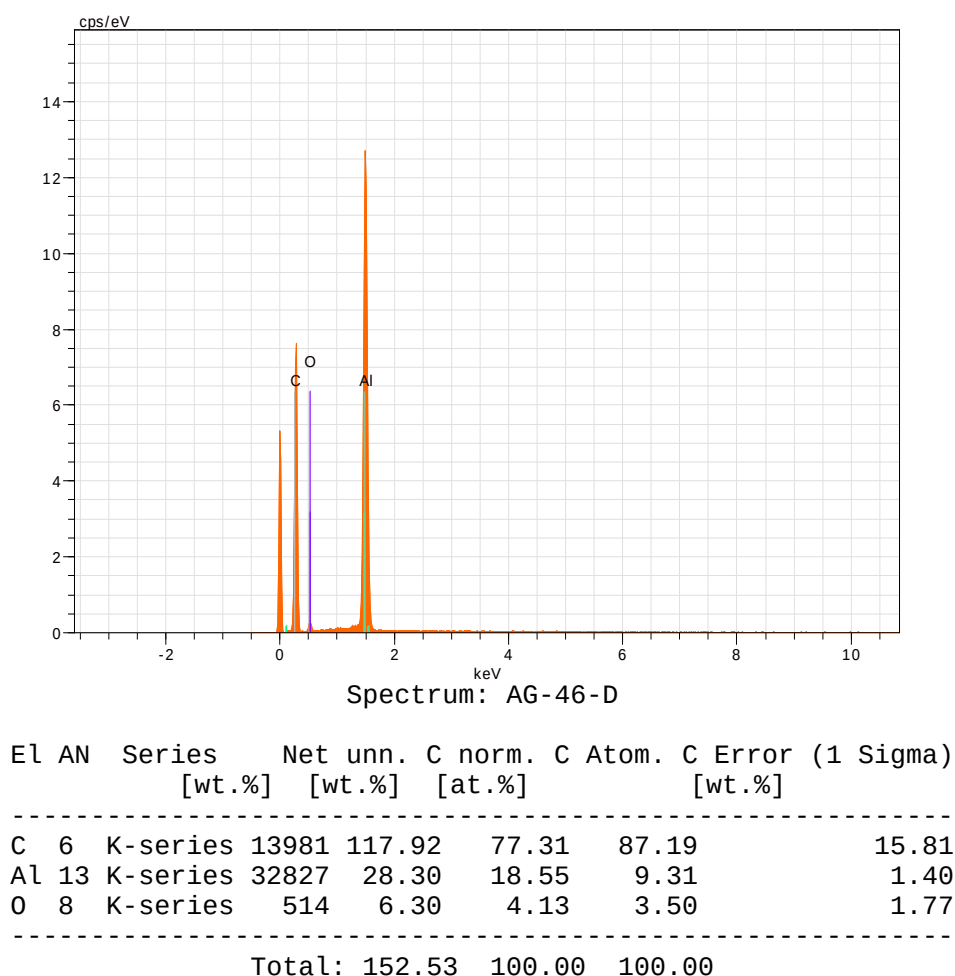


Figure 42 EDS chemical analysis of a chosen Al/C composite (AG-46-D)

Figure 42 shows the results of chemical analysis (EDS) of the chosen AG-46-D composite (chemical structure of all mentioned samples is similar). Chemical analysis indicated that inside of the material there are always trace contents of other elements (e.g. O, Si and Fe) which may naturally come from aluminium element.

3.5 Thermal conductivity, specific heat and thermal diffusivity

Thermal characterization of the investigated Al/C composite is the most important indicator of its potential thermal management applications and thus is described in great detail in the following paragraphs.

Thermal conductivity of investigated composites has been measured thanks to the tool designed and assembly at CERN (its description is given in section 2.6.3). The measurements have been performed along the in-plane direction. More precise thermal characterization with high precision measurement and entire application range from -120°C to 2800°C was enabled by another device – the NETZSCH Laser Flash Apparatus LFA 427 (described in Section 2.6.3). Among many tested samples, five most representatives have been chosen and described in the following paragraphs. Table 6 presents the final values of obtained thermal conductivity, diffusivity and specific heat in both directions: longitudinal and transversal. Not all samples have been fully characterized due to the late receiving of the Laser Flash Apparatus. Moreover, some of the produced plates did not have the proper thickness which, as well, prevented to measure their properties.

Table 6 Results of thermal conductivity, diffusivity and specific heat for Al/Gr composite in temperature range between 25 – 250 °C

No.	Name of the samples	Thermal conductivity in plane (W/(m*K))	Thermal conductivity out of plane (W/(m*K))	Thermal diffusivity in plane (mm ² /s)	Thermal diffusivity out of plane (mm ² /s)	Specific Heat in plane (J/g/K)	Specific Heat out of plane (J/g/K)	Comp. rate (%)
1	AG-46-D*	256*	-	-	-	-	-	92
2	AG-22-B (2/1)	385*	44 - 31	-	22 - 9	-	0,9 – 1,4	96
3	AG-22-B (2/4)	245	45 - 32	-	24 - 12	-	0,75 – 1,35	93
4	AG-66-K	252	49 - 35	119	24,5 – 11,5	0,84	0,9 – 1,4	95
5	AG-22-K	556*, 473	24 - 19	248	15 - 6	0,854	0,7 – 1,3	94

*measured by in-house built device

For thermal conductivity tests, samples have been prepared with different sizes, according to the specification of the device. Samples AG-46-D, AG-22-B (2/1), AG-22-B (2/4) and AG-22-K have been measured by means of in-house built device for thermal conductivity measurement. Samples with the following dimensions: 70 mm of length, 4 mm thickness and 25mm width have been measured in plane direction. Only AG-66-K, AG-22-K samples have been measured in both directions by means of the Laser Flash Apparatus. For this apparatus, disk-shaped samples have been prepared with 12,7mm in diameter and 2mm

of thickness or as the smallest size with diameter of 6mm and 2mm thickness. The results presented on the plots have been analyzed in the range of temperature $> 250^{\circ}\text{C}$.

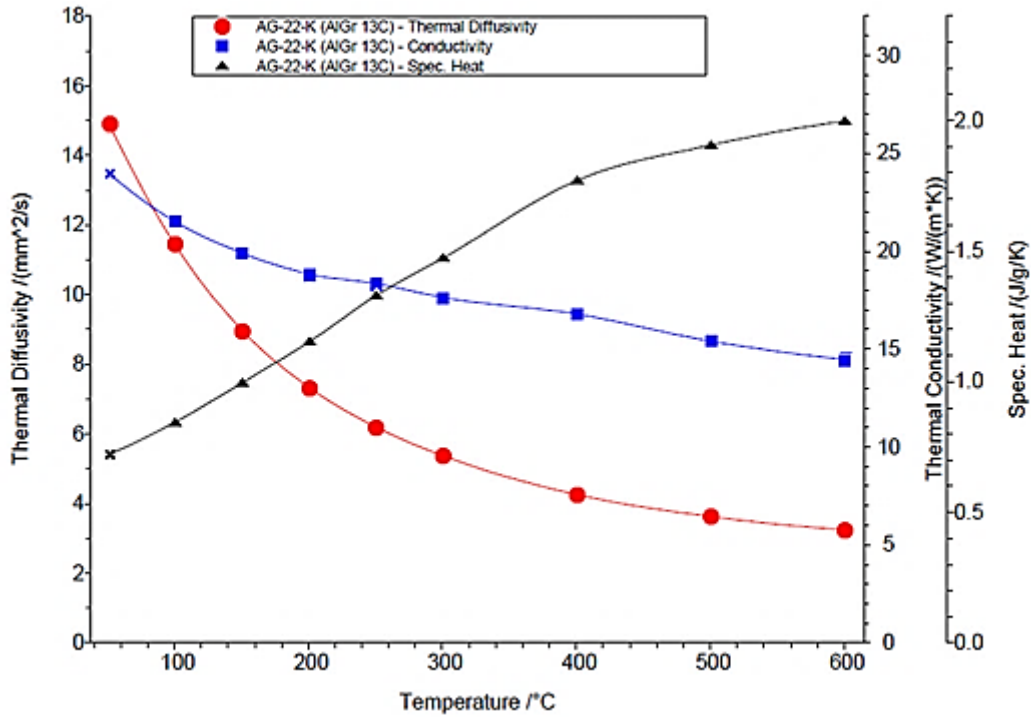


Figure 43 Results of thermal conductivity, diffusivity and specific heat for the AG-22-K composite in transverse direction

Figure 43 presents a plot with thermal characterization of the AG-22-K sample with the compaction rate of 94% in transverse (out of plane) direction. The plot indicates that thermal conductivity and diffusivity decrease while specific heat increases with the raise of the temperature. Mentioned sample is characterized by:

- a very low thermal conductivity (at temperature 25°C its value is 24 W/(mK)),
- very low thermal diffusivity – $15 \text{ mm}^2/\text{s}$,
- specific heat of $0,7 \text{ J/g/K}$.

It is the result of graphite anisotropy and large graphite flakes which in plane direction ensure high thermal conductivity (473 W/(mK)) due to their large surface - which provides continuous passages for heat transfer. However, they have disproportionally low properties in the "bad" direction (24 W/(mK)) which is clearly visible in Figure 43.

Figure 44 presents the plot with thermal characterization of the AG-22-K sample in longitudinal (in plane) direction. The values of thermal conductivity and diffusivity measured in the "good direction" at a temperature of 25°C are significantly higher. Thermal conductivity is 473 W/(mK) , diffusivity $248 \text{ mm}^2/\text{s}$ and specific heat $0,854 \text{ J/g/K}$. This high

disparity of results between two directions is a result of graphite anisotropy, where well-aligned structure in plane direction ensures high conductivity. However this effect of high anisotropy is somewhat an advantage for the components for thermal management applications. In order to enhance thermal conductivity in one direction means losing in the second.

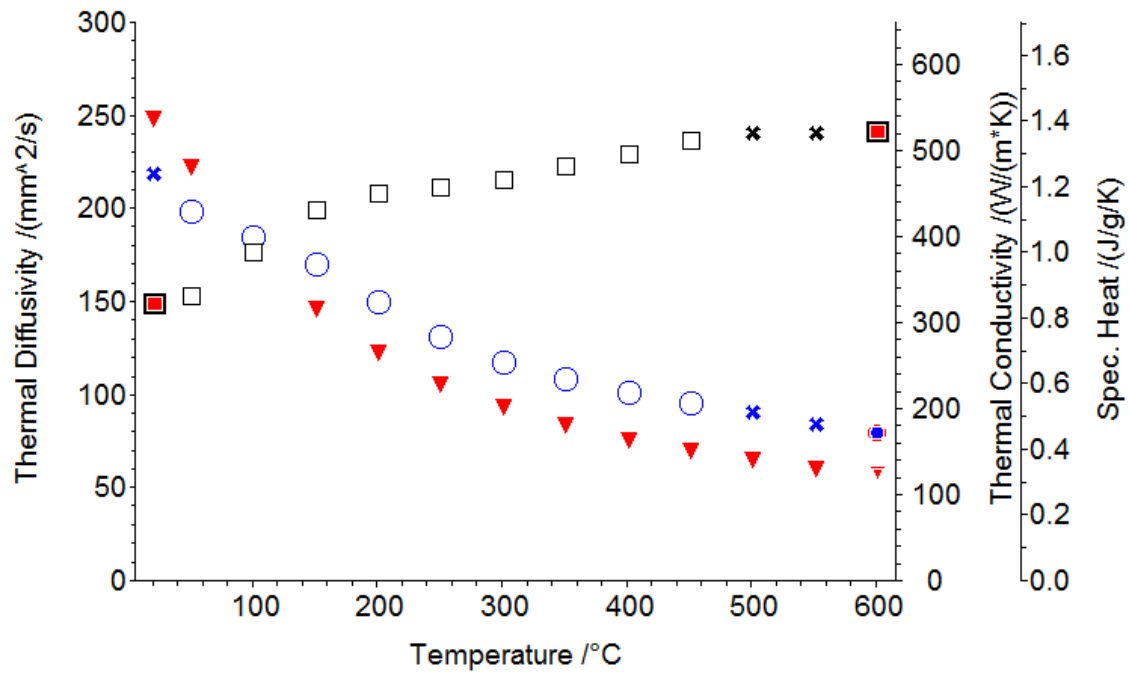


Figure 44 Results of thermal conductivity, diffusivity and specific heat for the AG-22-K composite in longitudinal direction

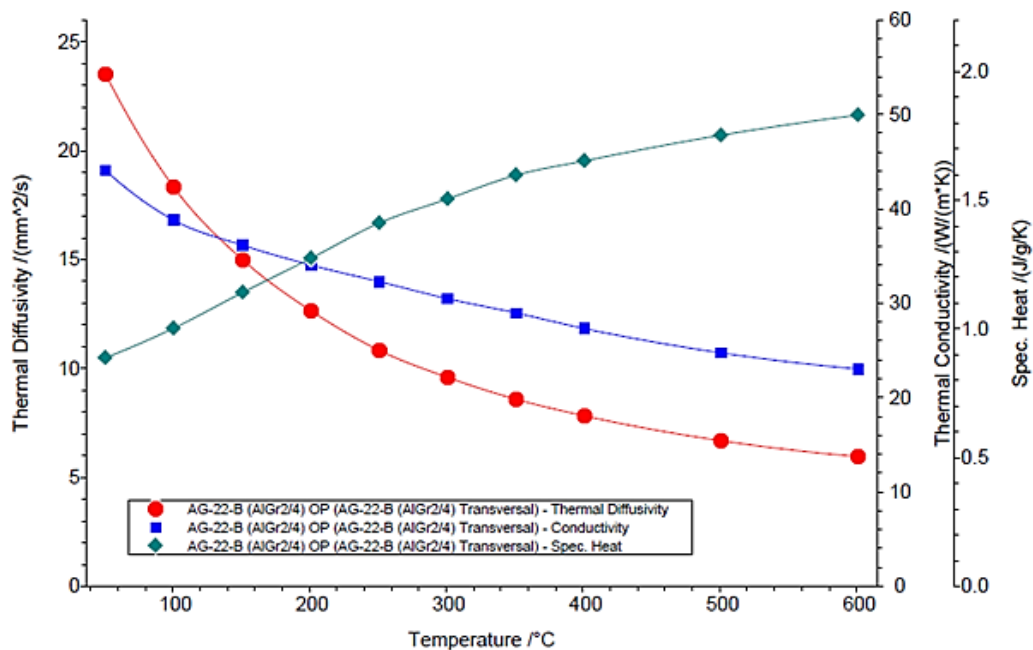


Figure 45 The results of thermal conductivity, diffusivity and specific heat for the AG-22-B (2/4) composite in transverse direction

Figure 45 presents the results of AG-22-B (2/4) sample with compaction rate of 93% in transverse (out of plane) direction. The sample was made of large graphite flakes but has been produced in lower temperature and pressure comparing to the previous sample AG-22-K. The plot shows the following values: at temperature 25°C conductivity is 45 W/(mK), diffusivity is 24 mm²/s and specific heat is 0.75 J/g/K. These results are slightly better in this direction compared to the AG-22-K measured in the same direction.

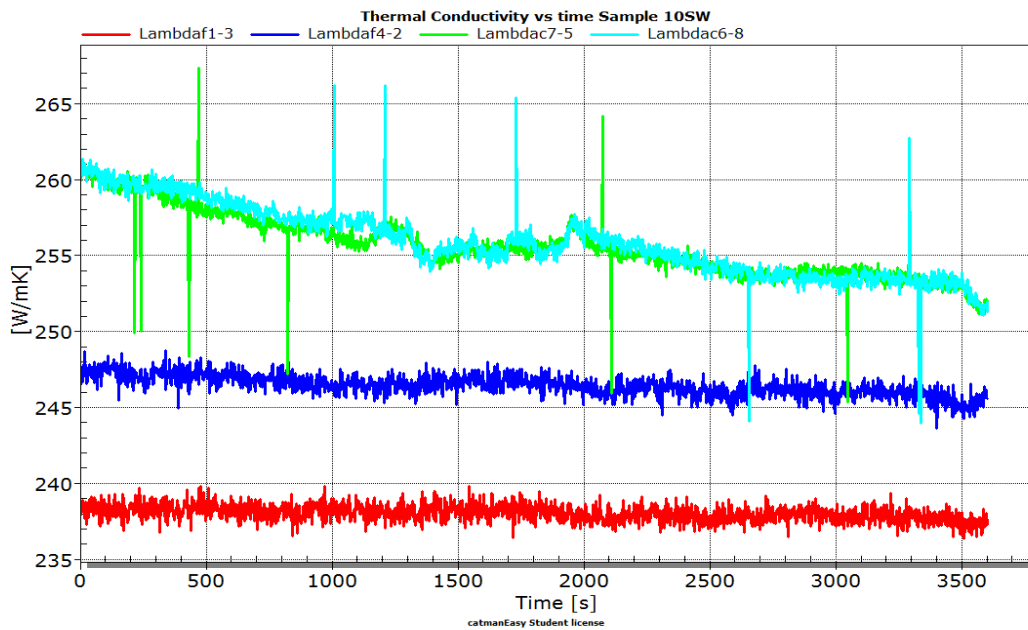


Figure 46 Results of thermal conductivity AG-22-B (2/4), measured in longitudinal (in plane) direction using in-house built device

Figure 46 presents thermal conductivity results of the AG-22-B (2/4) sample measured in plane direction using in-house built device. The plot shows the four signals (curves) which come from four temperature probes during thermal analysis. The value of thermal conductivity is an average value of those 4 curves and in this case has been calculated as 245 W/mK.

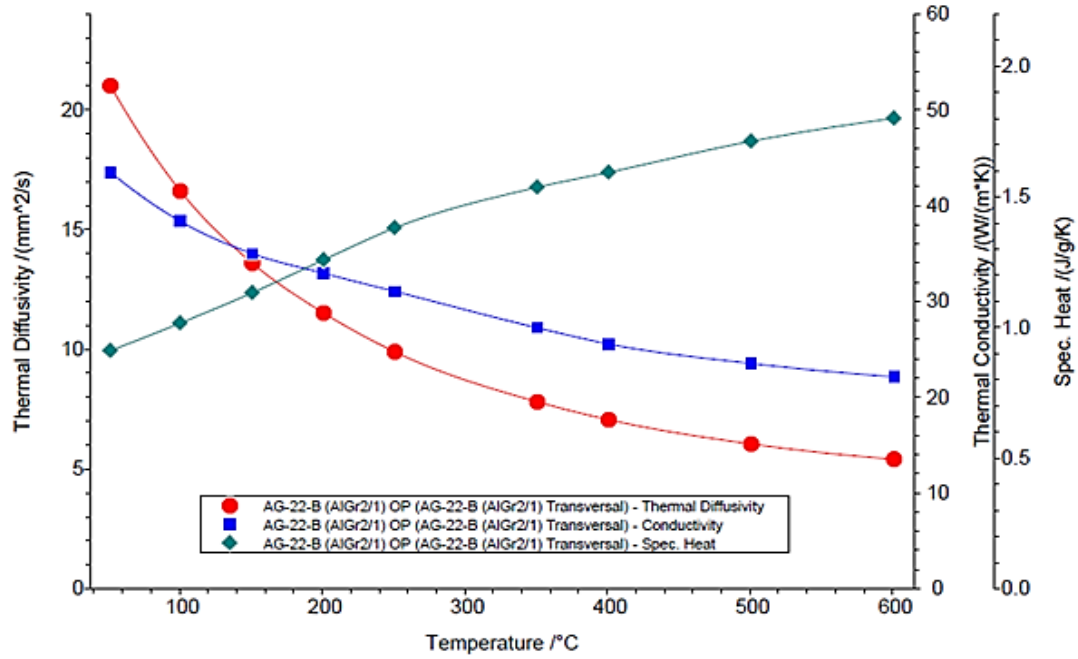


Figure 47 The results of thermal conductivity, diffusivity and specific heat for the AG-22-B (2/1) composite in transversal direction

Figure 47 shows the results of AG-22-B (2/1) with compaction rate of 96% measured in transversal (out of plane) direction. This sample has been produced in the same process as AG-22-B (2/4) and is made of the same graphite flakes. However, these two plates have different compaction rates which slightly affect their properties. The values at temperature 25°C are the following: thermal conductivity is 44 W/(mK), diffusivity is 22 mm²/s and specific heat is 0.9 J/g/K.

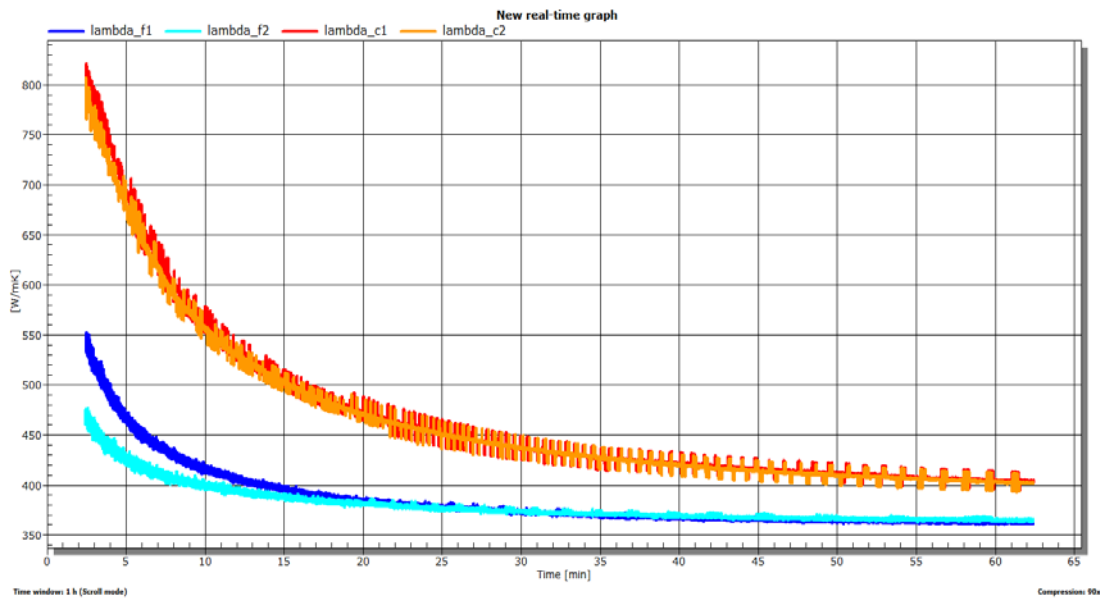


Figure 48 Results of thermal conductivity of AG-22-B (2/1), measured in longitudinal (in plane) direction using in-house built device

The results of AG-22-B (2/1) measured in longitudinal (in plane) direction using in-house built device is present in Figure 48. Thermal conductivity has been reported as 385 W/(mK) which means it is much higher than the conductivity represent by AG-22-B (2/4) in the in plane direction. The densification of the sample plays a key role affecting the final thermal characteristic.

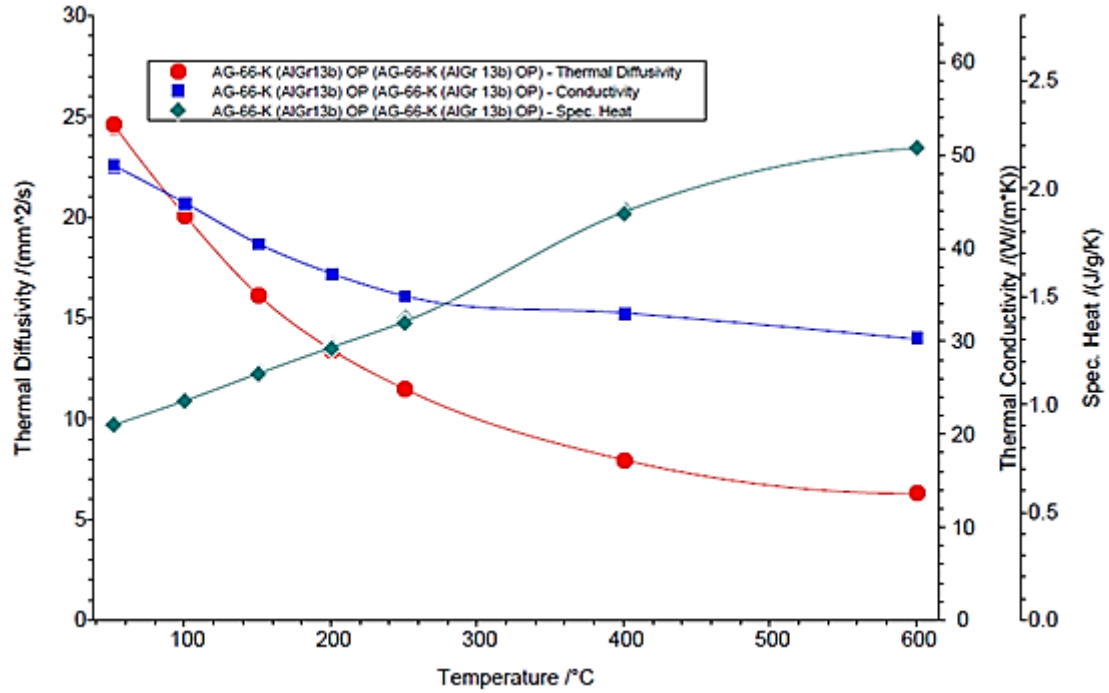


Figure 49 The results of thermal conductivity, diffusivity and specific heat for the AG-66-K composite in transverse direction

Figure 49 shows the results of thermal conductivity, diffusivity and specific heat of the AG-66-K (13B) composite with compaction rate of 95% in transverse direction. This sample has been produced in the same cycle as AG-22-K but using smaller particles with average size of 80µm. In consequence, obtained properties at temperature 25°C are as follows: thermal conductivity – 49 W/(mK), diffusivity – 24.5 mm²/s and specific heat - 0.9 J/g.K. This sample represents the highest value of thermal conductivity among tested sample in transversal direction. Small particles do not exhibit such big anisotropy of the material as large well aligned flakes.

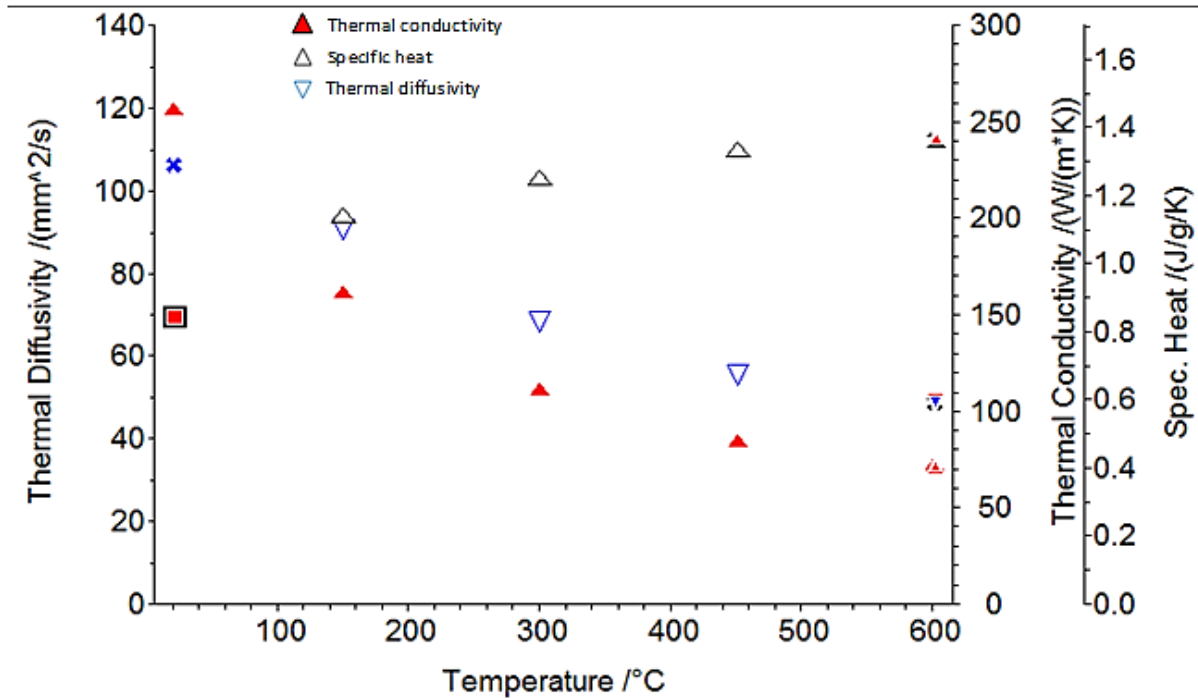


Figure 50 The results of thermal conductivity, diffusivity and specific heat for the AG-66-K composite in longitudinal direction

The results of thermal conductivity, diffusivity and specific heat for the AG-66-K composite in longitudinal direction are shown in Figure 50. Reported results at temperature 25°C are as follows: thermal conductivity – 252 W/(mK), diffusivity – 119 mm²/s and specific heat - 0.9 J/g/K.

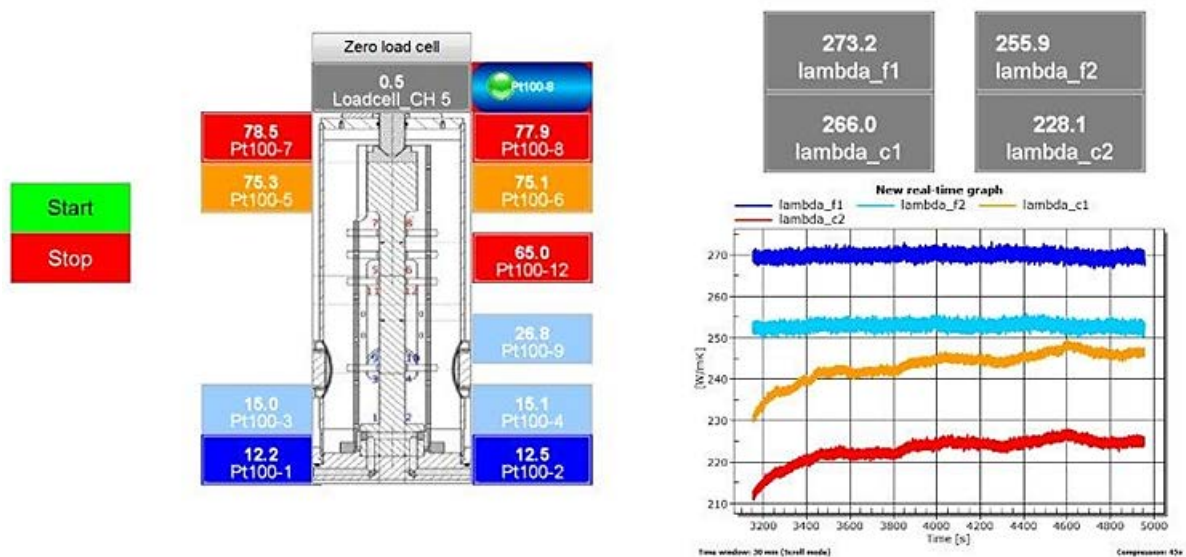


Figure 51 Results of thermal conductivity of AG-46-D, measured in longitudinal (in plane) direction using in-house built device

Figure 51 presents the thermal conductivity results of AG-46-D sample with 92% compaction rate measured in the longitudinal direction using in-house built device. This material has been produced in a different cycle than other samples and consists of small graphite particles of 80 μm in diameter. Thermal conductivity is reported as 256 W/(mK) which is similar to the results obtained by the sample AG-66-K.

3.6 Coefficient of thermal expansion

Another property of interest is the coefficient of thermal expansion (CTE). The CTE measurements were carried out using an advanced apparatus - NETZSCH Dilatometer DIL 402 E (described in section 2.6.2). Samples were measured in two directions: longitudinal and transversal. Measurements have been performed and analyzed in temperature ranges between 25 and 400°C. Table 7 presents the analyzed results of CTE performed in two directions in temperature range between 25 and 200°C.

Table 7 Results of CTE in longitudinal and transversal direction measured by NETZSCH Dilatometer 402 E in temperature 25 – 200°C

Nb	Name of the sample	Coefficient of thermal expansion in plane ($10^{-6}/\text{K}^{-1}$) in 25°C	Coefficient of thermal expansion in plane ($10^{-6}/\text{K}^{-1}$) in 200°C	Coefficient of thermal expansion out of plane ($10^{-6}/\text{K}^{-1}$) in 25°C	Coefficient of thermal expansion out of plane ($10^{-6}/\text{K}^{-1}$) in 200°C
1	AG-46-D	5,44	7,4	-	-
2	AG-22-B (2/1)	5,73	10,33	-	-
3	AG-22-B (2/4)	4,5	6,00	-	-
4	AG-66-K (13B)	~6	6,8	7,14	13,2
5	AG-22-K(13C)	3,8	8,88	12	14

Table 8 presents the values obtained in high temperature (400°C) in two directions.

Table 8 Results of CTE in longitudinal and transversal direction measured by NETZSCH Dilatometer 402 E in high temperature 400°C

Nb	Name of the sample	Coefficient of thermal expansion in plane ($10^{-6}/\text{K}^{-1}$) in 400°C	Coefficient of thermal expansion out of plane ($10^{-6}/\text{K}^{-1}$) in 400°C
1	AG-46-D	7,43	-
2	AG-22-B (2/1)	10	-
3	AG-22-B (2/4)	6,9	-
4	AG-66-K (13B)	7,9	15,8
5	AG-22-K	10	17

As it has already been mentioned in the previous sections, CTE increases with the temperature. The value of CTE depends on the material structure and parameters which have

been chosen during the production process. Aluminium is characterized by a very high CTE: $25 \times 10^{-6} \text{K}^{-1}$ while in contrast for graphite its value may be $-0.5 \times 10^{-6} \text{K}^{-1}$ in plane direction. These two materials combined together may offer desired CTE properties.

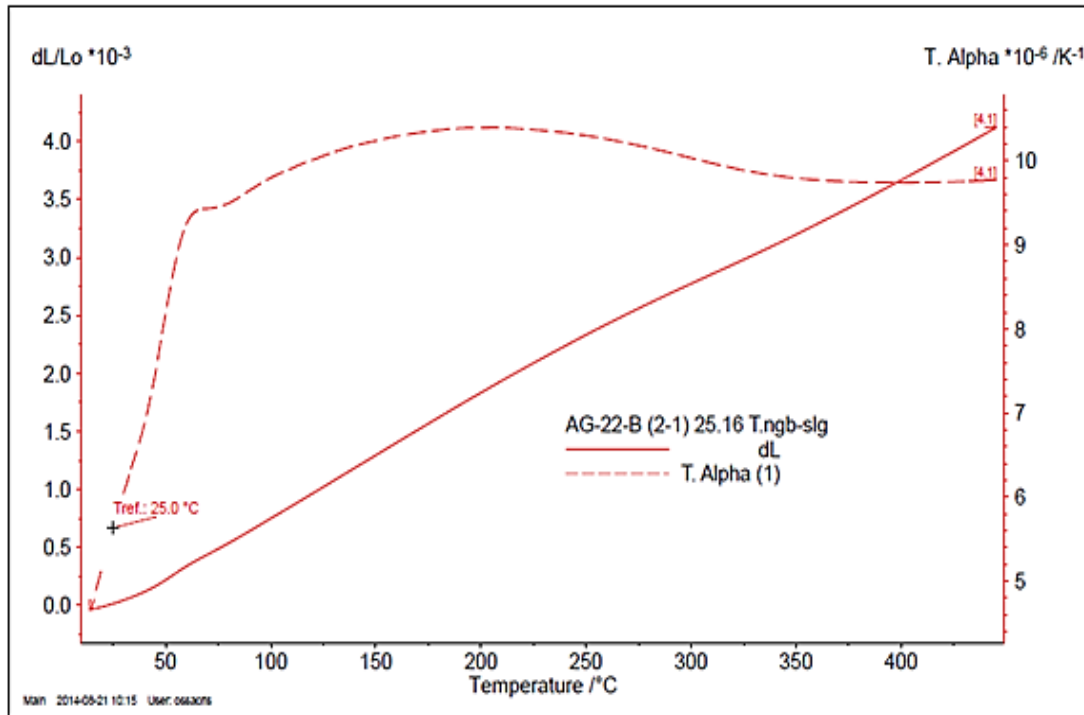


Figure 52 CTE measurements of the AG-22-B (2/1) in plane (longitudinal) direction

A result of the AG-22-B (2/1) sample made of large graphite flakes is shown in Figure 52. CTE in plane direction in temperature 25°C has been reported as $5.7 \times 10^{-6} \text{K}^{-1}$, in 200°C – $10.3 \times 10^{-6} \text{K}^{-1}$, in 400 °C it stabilized at $10 \times 10^{-6} \text{K}^{-1}$. Up to 50°C the rapid growth of CTE has been observed while in the higher temperatures the value stabilized. Unfortunately, the CTE measurement out of plane direction has not been conducted due to the fact that the produced plate is too thin and did not meet the dimensional requirements to perform the measurements.

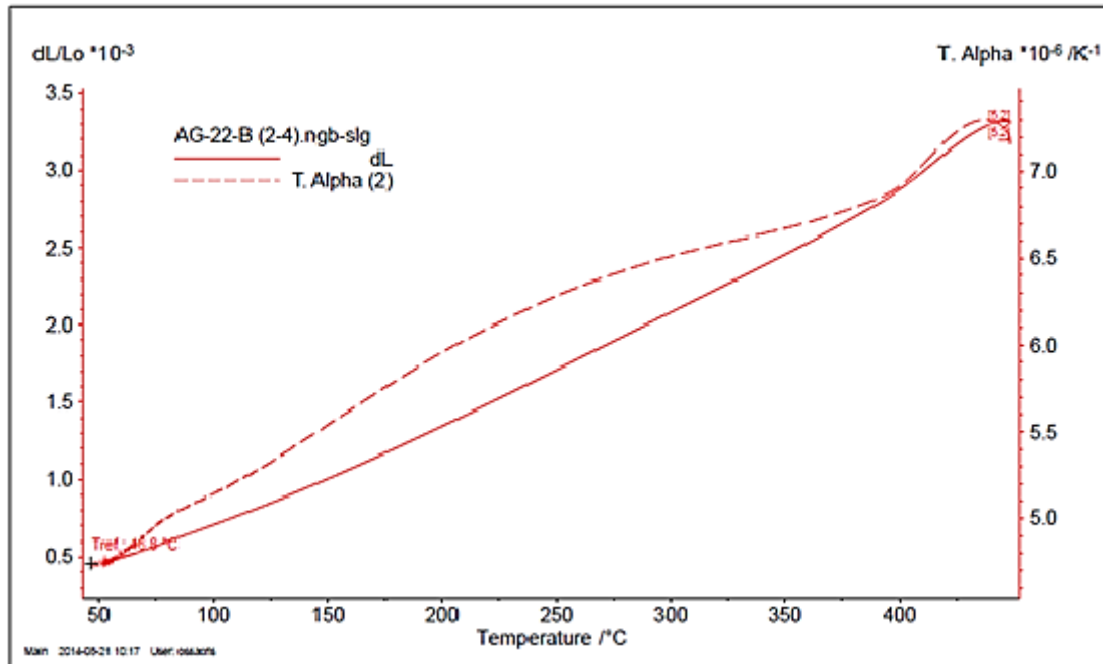


Figure 53 CTE measurements for the AG-22-B (2/4) in plane (longitudinal) direction

Figure 53 presents the result for the AG-22-B (2/4) sample which has been produced in the same cycle as AG-22-B (2/1) and measured in plane direction. Analysis of the CTE in plane direction revealed the value of $4.5 \times 10^{-6} K^{-1}$ in the temperature of 25°C , $6 \times 10^{-6} K^{-1}$ in 200°C , and $6.9 \times 10^{-6} K^{-1}$ in 400°C . In this case CTE increases almost linearly and no significant difference between the value in temperature 25°C and 400°C has been observed.

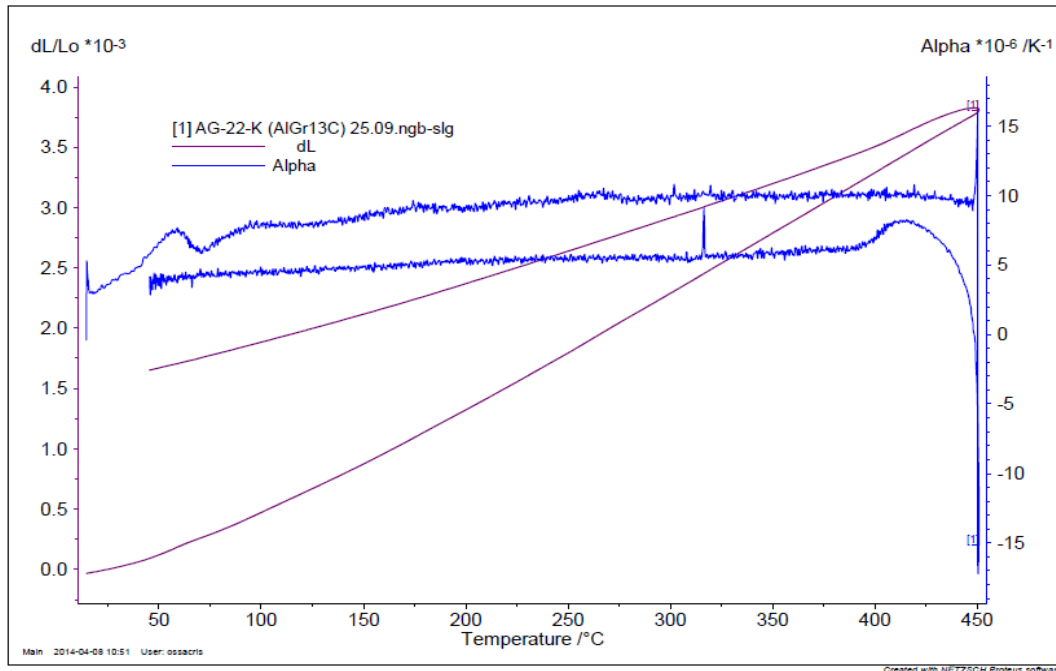


Figure 54 CTE measurements for the AG-22-K (13C) in plane (longitudinal) direction

Figure 57 shows the results of the AG-22-K (13C) sample made of large graphite flakes, however produced in higher temperature and pressure comparing to the AG-22-B (2/4) and AG-22-B (2/1) samples. CTE result has been obtained in the in plane direction and the values are as follows: in the temperature of 25°C it is $3.8 \times 10^{-6} \text{K}^{-1}$, $8.8 \times 10^{-6} \text{K}^{-1}$ in 200°C and $10 \times 10^{-6} \text{K}^{-1}$ in 400°C.

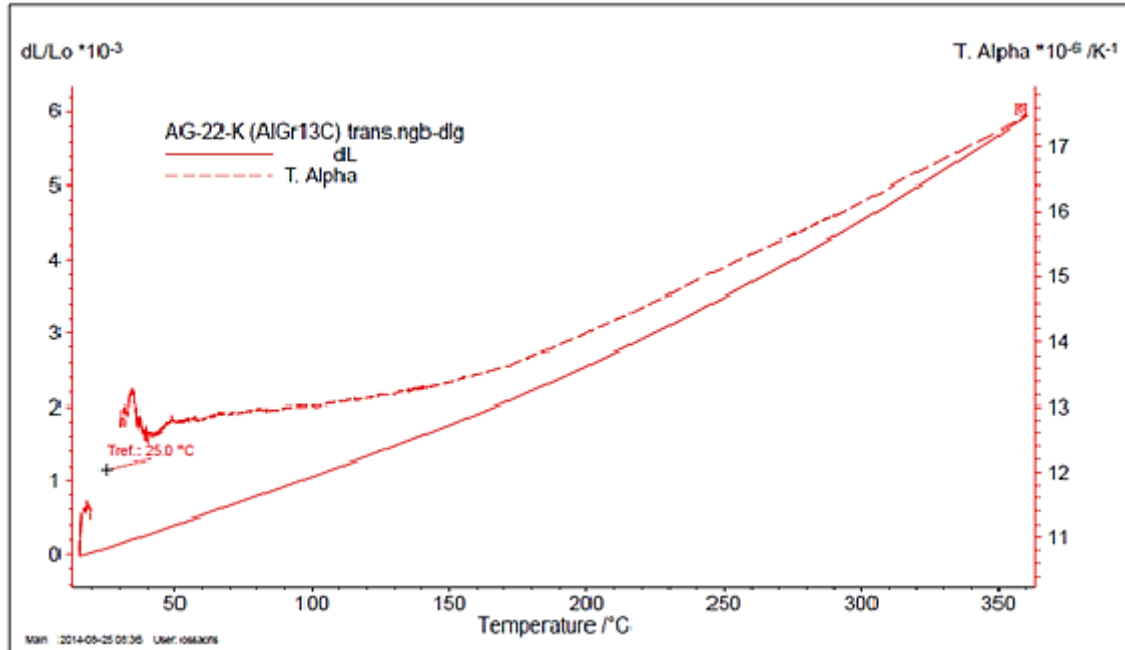


Figure 55 CTE measurements for the AG-22-K (13C) out of plane (transversal) direction

CTE result of the AG-22-K (13C) measured in the out of plane direction is presented in Figure 55. Results are as follows: $12 \times 10^{-6} \text{K}^{-1}$ in 25°C, $14 \times 10^{-6} \text{K}^{-1}$ in 200°C, and $17 \times 10^{-6} \text{K}^{-1}$ in 400°C. It has been noticed that sample made of large graphite flakes exhibits big anisotropy of the material. In “good direction” it is characterized by low CTE value while in “bad direction” the value is very high. CTE in this case increases linearly with the temperature.

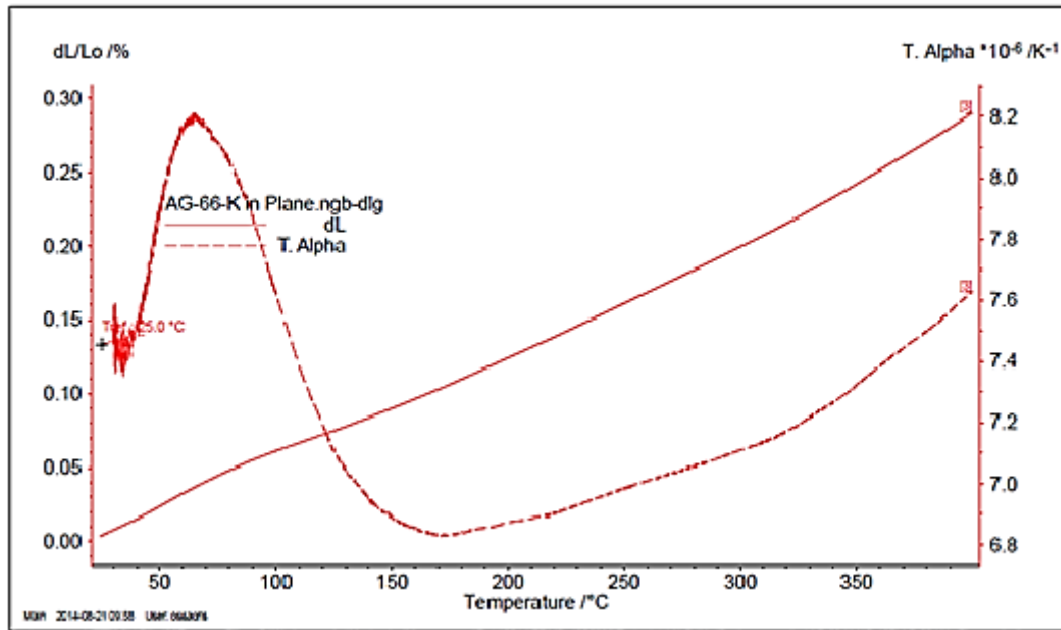


Figure 56 CTE measurements for the AG-66-K (13B) in plane (longitudinal) direction

Figure 56 presents the CTE results for the AG-66-K (13B) sample made of small graphite particles and produced in the same cycle as AG-22-K (13C). CTE in 25°C has been reported as $7.45 \times 10^{-6} \text{K}^{-1}$. Unexpected pick visible in range of temperatures between 50 and 80°C could be a result of the vibrations which may have occurred in the laboratory where the measurements of the CTE have been performed (at the time of the investigations there were ongoing renovation works in a building close to the laboratory). Usually in such cases, where some unexpected picks occur, it may be the reason of phase transition. At a temperature of 200°C, a drop of the CTE is observed and its value is $6.8 \times 10^{-6} \text{K}^{-1}$. At higher temperatures, the coefficient slightly increases: at 400°C it is at the level of $7.6 \times 10^{-6} \text{K}^{-1}$.

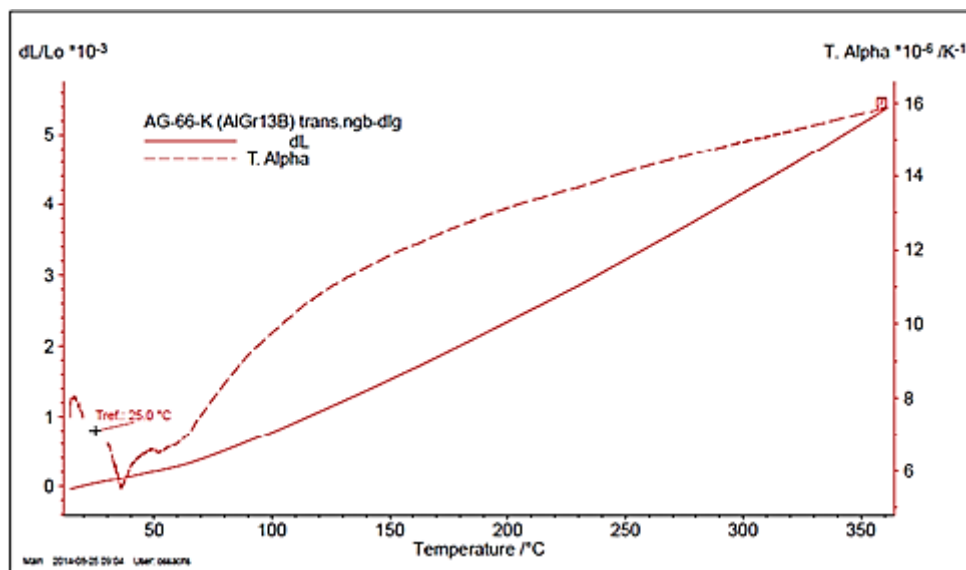


Figure 57 CTE measurements of the AG-66-K (13B) out of plane (in transversal) direction

CTE results of the AG-66-K sample, measured in the “bad direction”, is shown in Figure 57. The values are as follows: $7.14 \times 10^{-6} \text{K}^{-1}$ in 25°C , $13.2 \times 10^{-6} \text{K}^{-1}$ in 200°C and $15.8 \times 10^{-6} \text{K}^{-1}$ in 400°C . CTE measured in this direction increases with temperature and shows anisotropy of the material. Small particles used for the production of the Al/C composite make the coefficient increase slightly with temperature and exhibits lower anisotropy comparing to the large flakes.

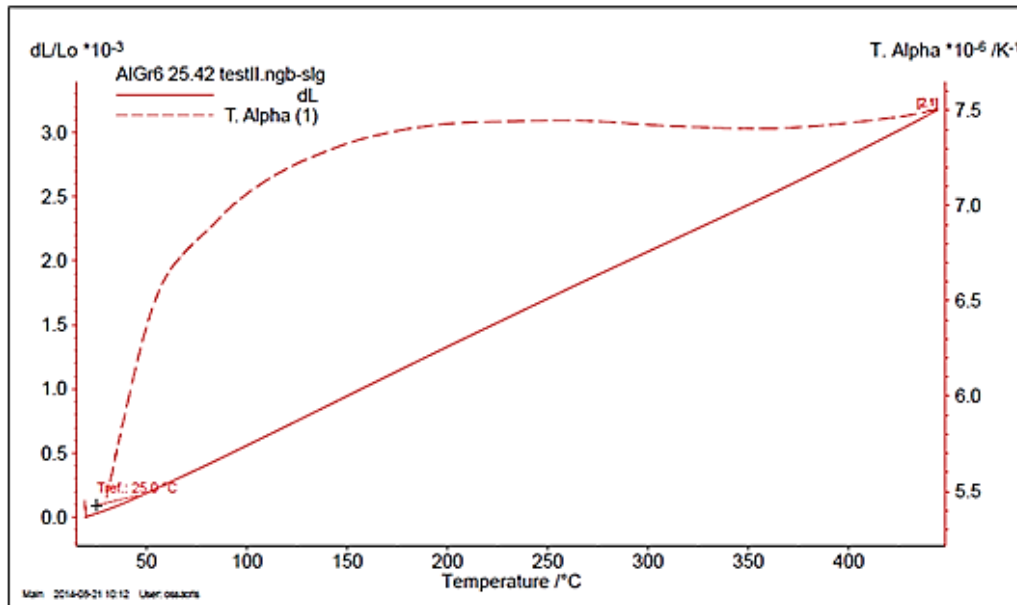


Figure 58 CTE measurements for the AG-46-D in plane direction

Figure 58 shows the CTE result of the AG-46-D sample made of small graphite particles and produced in lower temperature than the AG-66-K sample. The measurement has been performed in the in-plane direction. The plot indicates rapid growth of CTE up to 150°C and finally stabilizing at higher temperatures. CTE values are as follows: $5.4 \times 10^{-6} \text{K}^{-1}$ in 25°C , $7.4 \times 10^{-6} \text{K}^{-1}$ in 200°C and $7.46 \times 10^{-6} \text{K}^{-1}$ in 400°C .

3.7 Electrical properties

The electrical conductivity test has been conducted with the SIGMATEST 2.069 device (its characteristics have been described in Section 2.6.4). Table 9 presents the electrical conductivity results together with the given graphite flake size and densification rate in order to show the dependence between these two factors on the measured property.

Table 9 Electrical conductivity results

Nb	Name of the samples	Graphite flake size [μm]	Electrical conductivity [MS/m]	Compaction rate [%]
1	AG-46-D	Unselected ashes	1,12	92

		average size around 80		
2	AG-22-B (2/1)	300-500	3,28	96
3	AG-22-B (2/4)	300-500	2,18	93
4	AG-66-K (13B)	Unelected ashes average size around 80	1,66	95
5	AG-22-K(13C)	300-500	1,7 – 5.7	94

It has been noticed that the most significant impact on the electrical properties depends mainly on the nature of the graphite (size, shape) and lack of porosity. High electrical conductivity has been observed when the composite is made of large graphite flakes 300-500 μm . This dependence is presented in Figure 59. The degree of densification and average graphite size has been set at the same time in order to show the influence of these two factors on the final electrical properties. The factor which limits the good electrical conductivity results is the presence of porosity. Obtained results show that the sample which was highly compressed (96%) exhibits the better electrical conductivity. The sample with compaction rate of 94% has worse properties than the sample with compaction rate of 93%. In this case, an irregular distribution of the aluminium phase on the Al/C plate has been observed. In the middle of the plate, the big macro-agglomerations of aluminium have been created during the sintering phase. This part indicated electrical conductivity equal to 5.7 MS/m while, on the border, average value has been reported at the level of 1.7 MS/m.

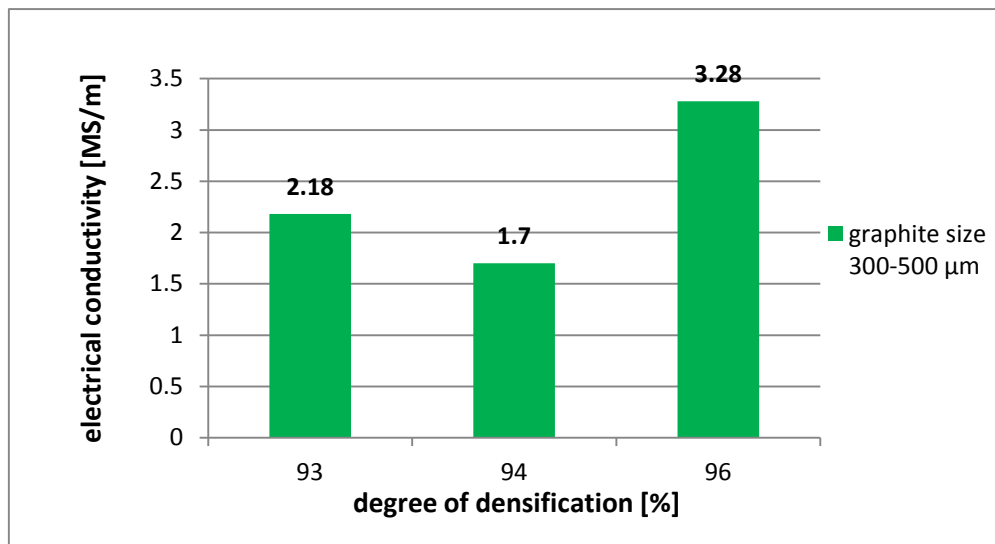


Figure 59 Influence of large graphite flakes and densification degree on the electrical properties

Figure 60 presents a similar plot as it has been already discussed, however this figure shows the influence of small graphite particles on the electrical conductivity. Comparing to

the bigger flakes, small graphite particles lead to a worsening of the electrical properties. Electrical properties increase with the densification degree.

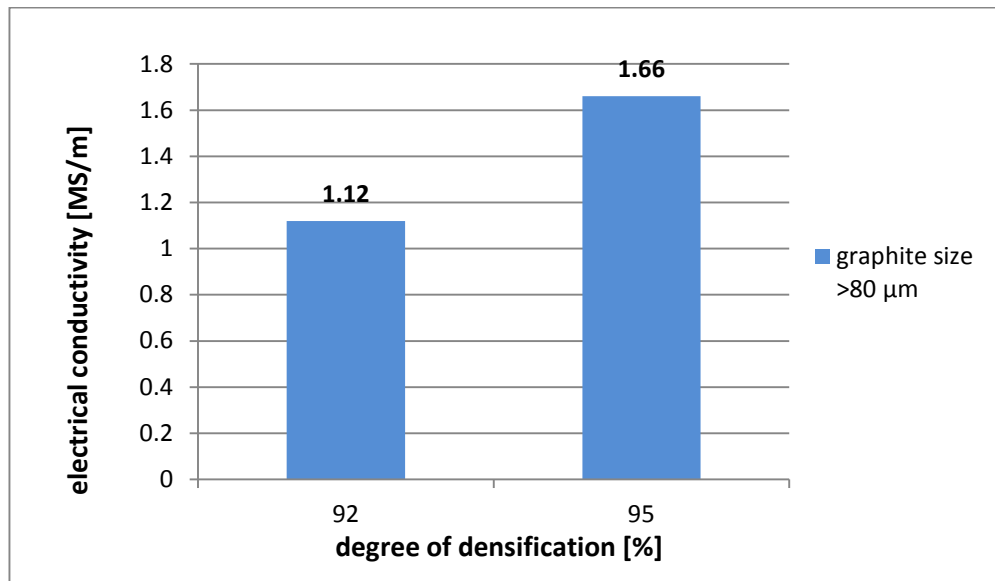


Figure 60 Influence of small graphite flakes and densification degree on the electrical properties

3.8 Flexural strength

According to the requirements specified in Section 1.3, the mechanical properties are an important measure of the aluminium/graphite composite taking into account the desired application in the thermal management applications. Both aluminium and graphite are soft materials; together, they form a composite which is easy to break under a considerably low load. As a consequence, it is necessary to conduct a mechanical characterization in order to check and try to improve the flexural strength of the investigated material.

Table 10 Flexural strength results

Nb	Name of the samples	Graphite flake size [μm]	Flexural strength [MPa]	Compaction rate [%]
1	AG-46-D	Unselected ashes average size around 80 μm	43,5	92
2	AG-22-B (2/1)	300-500	15	96
3	AG-22-B (2/4)	300-500	Not measured	93
4	AG-66-K (13B)	Unselected ashes average size around 80 μm	48	95
5	AG-22-K(13C)	300-500	35	94

Table 10 presents the flexural strength results, conducted on the chosen five samples. Results have been presented along with the size of graphite flakes and compaction rate in order to show their influence on the final mechanical properties.

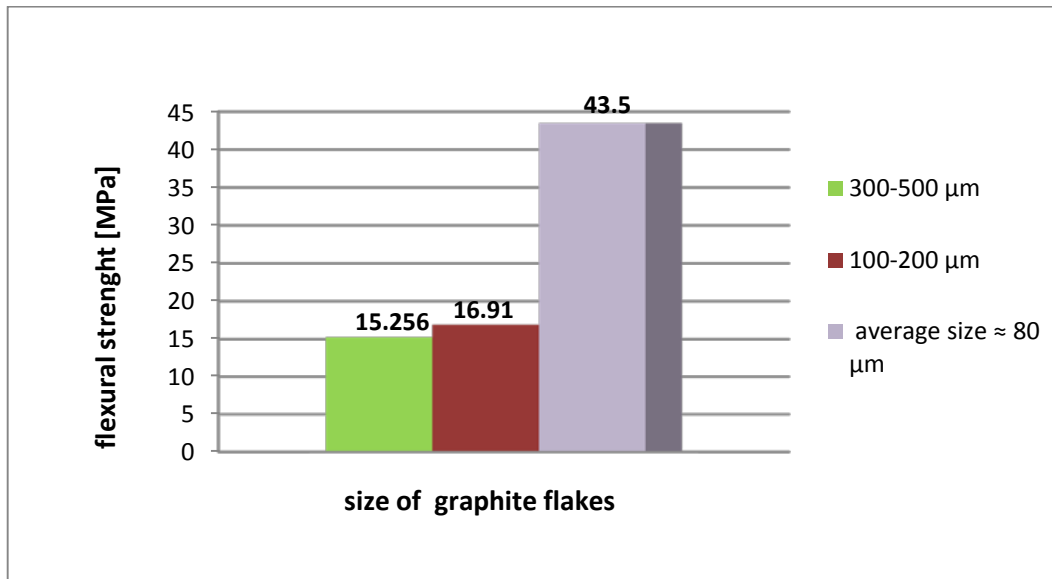


Figure 61 Dependence of flexural strength on the kind of graphite flakes, preliminary results

Figure 61 presents the influence of graphite size on the final material properties. It has been observed that the mechanical properties enhance with the decreasing size of graphite flakes. The best strength value has been obtained in the AG-66-K sample where not selected graphite particles with average size of $80\mu\text{m}$ have been used.

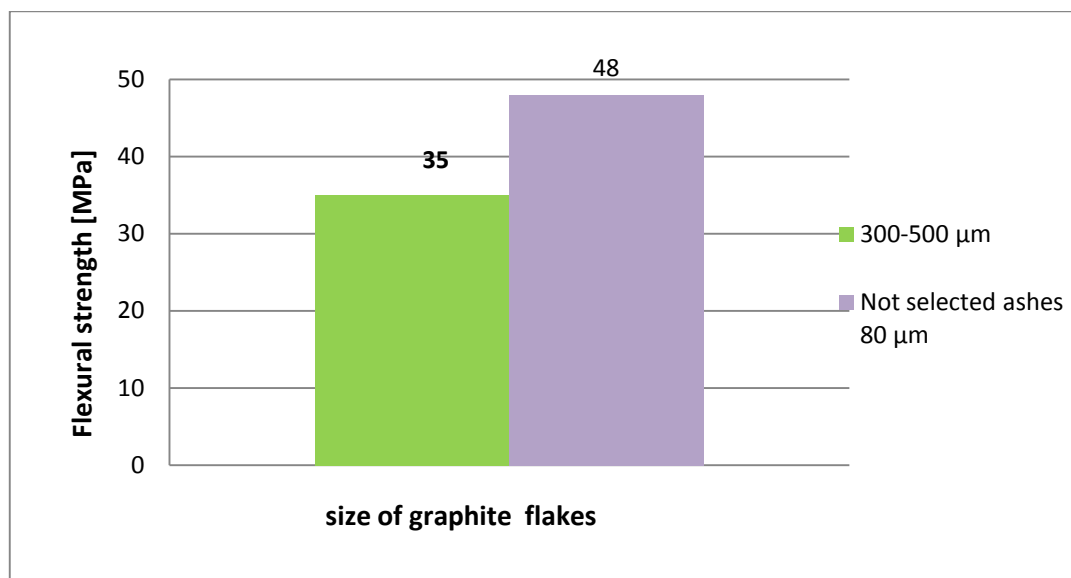


Figure 62 Dependence of flexural strength on the size of graphite flakes, results obtained by given higher pressure

Figure 62 depicts the values of flexural strength in relation to the size of the graphite after application of higher pressure and temperature during production process. Such conditions contributed to the increase of the compaction rate and in turns to improved mechanical properties.

To determine the flexural strength of the considered composite, three samples of each investigated composite have been tested. The measurement results were recorded and calculated by the machine control program.

The factor which notably affects the mechanical properties of the examined composites is the size of the particles, their shape and distribution. Since graphite represents a significant part of the composite, it is a challenge to obtain high value of flexural strength.

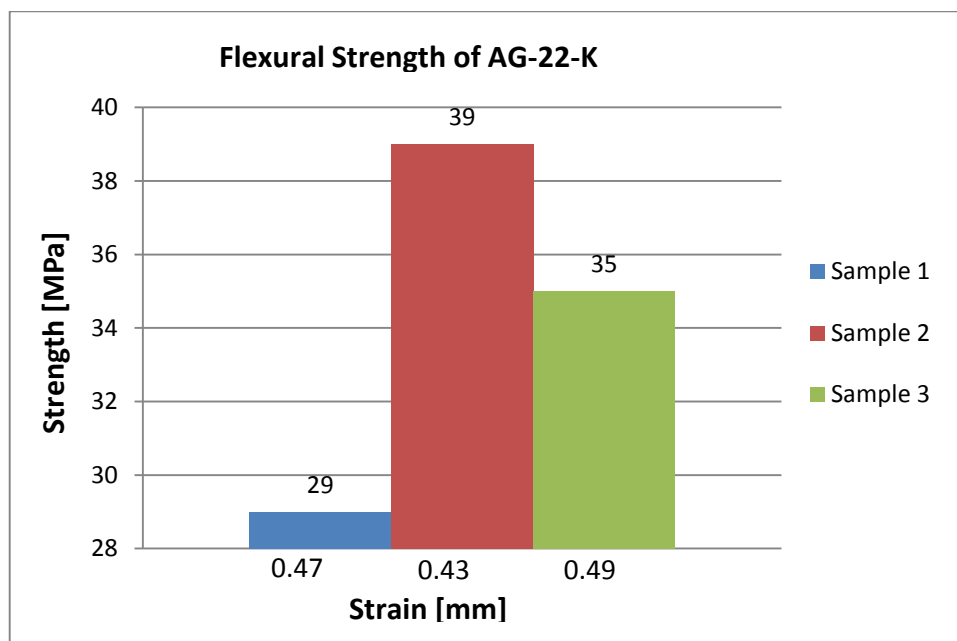


Figure 63 Flexural strength results of AG-22-K

Figure 63 shows the results for the AG-22-K sample. Dimensions of the samples, together with applied force and bending stress, are indicated in the diagram. The considered sample has been made of large graphite flakes (300-400 μ m) which in general do not bring successful results. An average value of obtained strength is 35 MPa. It is worth to mention that this sample has been produced in higher temperature and pressure comparing to the AG-22-B (2/1) and AG-22-B (2/4) samples which were produced using large graphite flakes. These samples are described in the upcoming paragraphs.

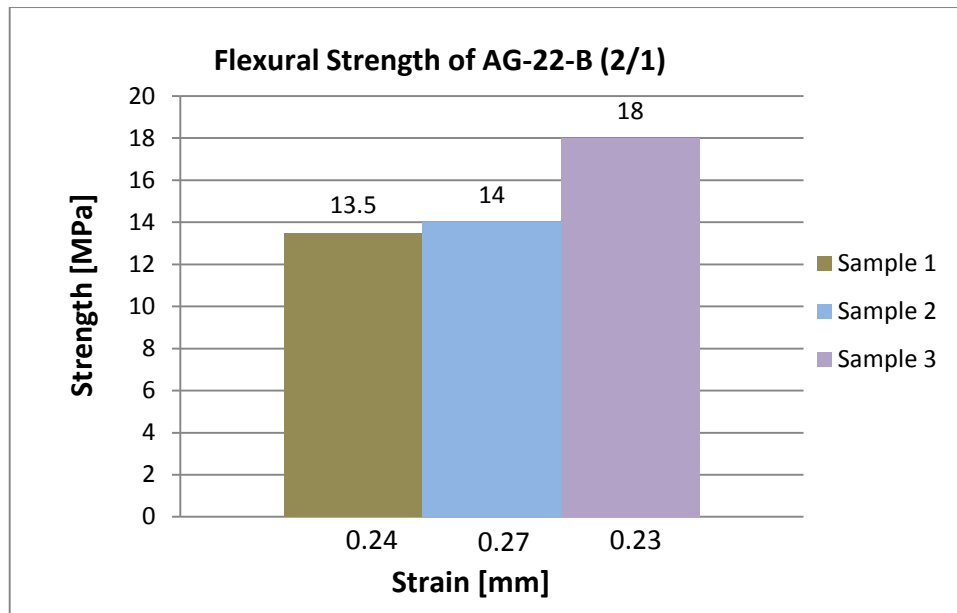


Figure 64 Flexural strength results of AG-22-B (2/1)

The flexural strength result of the AG-22-B (2/1) sample (96% of compaction rate) is presented in Figure 64. This material was made of large graphite flakes and has been produced in lower temperature and pressure comparing to the AG-22-K sample. These two factors manifested in low strength of the sample which is only 15 MPa. Another sample AG-22-B (2/4) (93% of compaction rate), which has been produced during the same cycle as AG-22-B (2/1), was too soft. As a result, the measurement could not be conducted.

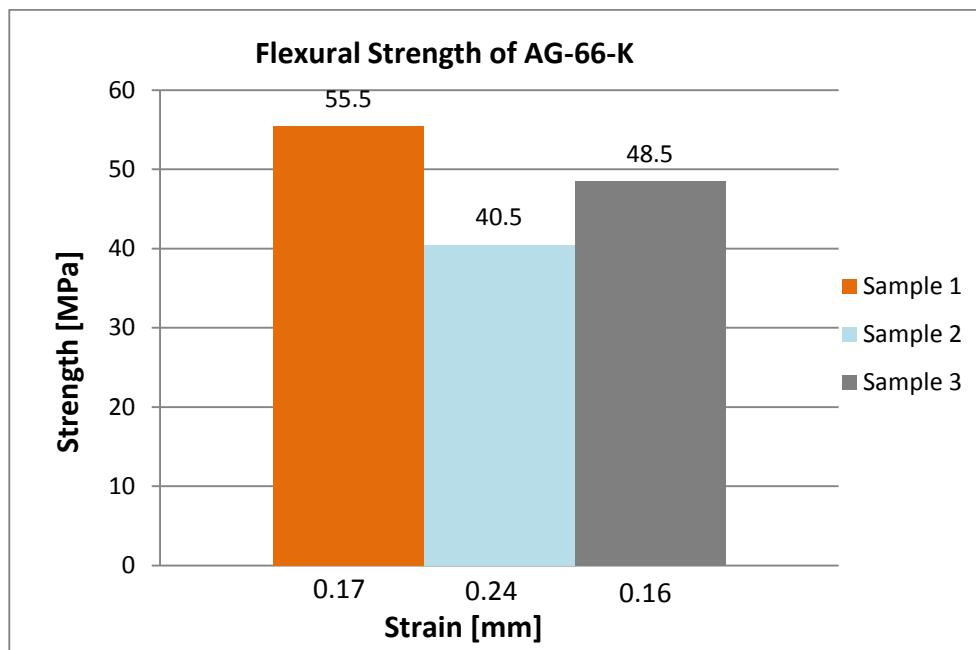


Figure 65 Flexural strength results of AG-66-K (13B)

Figure 65 shows the results of the AG-66-K sample (95% of compaction rate) made of small graphite particles (not selected particles, average size 80 μ m) and produced in the same cycle as AG-22-K. Small regularly distributed particles contributed to high strength of the composite, which was measured to be at the level of 48 MPa.

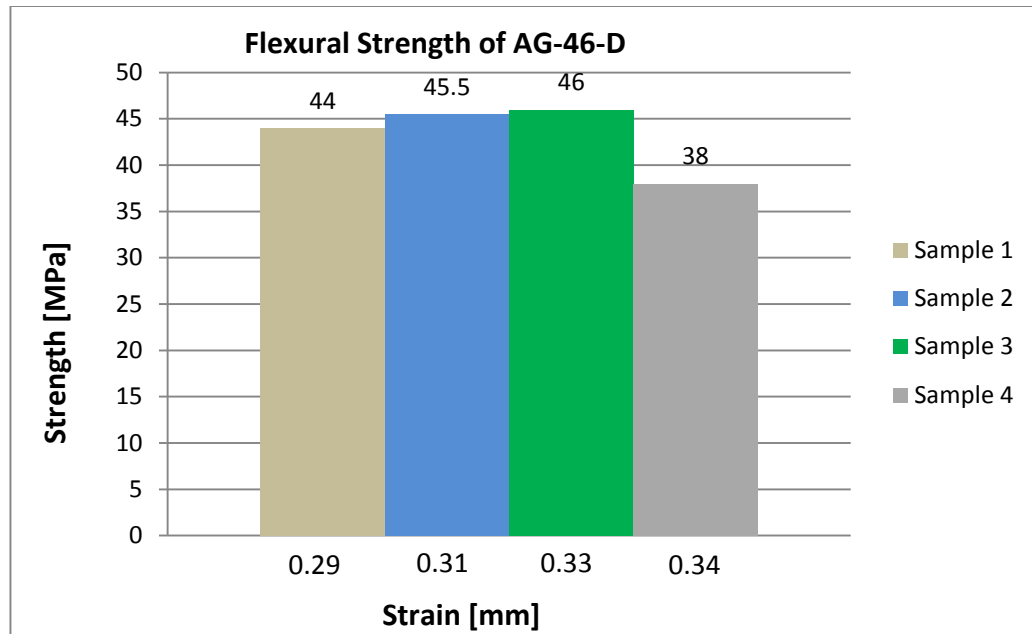


Figure 66 Flexural strength results of AG-46-D

The result of the AG-46-D sample which is made of small graphite particles (average size 80 μ m) is presents in Figure 66. This sample has been produced at lower temperature than AG-66-K (13B) and possesses slightly lower strength, which is 43 MPa. Lower value of strength may be a result of higher porosity of the material.

In order to improve the strength of aluminium/graphite composite, small graphite particles have to be used. Another approach is to remove the porosity from the material by applying higher pressure and slightly reducing its graphite content.

4. CONCLUSIONS

This section is dedicated to summarize and conclude the results of the research performed. Thesis goals accomplishment is discussed in Section 4.1. Obtained results are assessed and compared to other solutions available on the market in Subsection 4.1.3. Thesis is finalized with a proposal of future works enumerated in Section 4.2.

4.1 Summary of the results obtained

During the investigation process of the Al/C composite a number of interesting facts and dependencies have been observed. The following list enumerates the most important conclusions drawn from the research together with an attempt to generalize them:

- Al/C composite can be successfully fabricated using the powder metallurgy techniques, which allow easy control of the process parameters i.e.: temperature, pressure and time. These adjustable factors have a big influence on the final properties of the investigated composite.
- The strong effect of the shape of graphite flakes has been assessed during the work by verifying its influence on the final thermal properties of the composite. This is due to the higher conductivity provided by the large graphite flakes, at least in the planar direction. The flakes formed a continuous network of graphitic planes which allowed for optimal heat transfer along the planar direction. Other factors which have significant effect on the thermal conductivity are: conditions in which composite has been produced (sintering temperature, time, pressure and atmosphere) and compaction rate. The thesis allowed to develop very performing materials, upon them the AG-22-K showed the best values of thermal properties with a conductivity of 473 W/(mK).
- The electrical properties strongly depend on the graphite morphology (as for thermal conductivity) and the final densification. By increasing the compaction rate up to 96% (sample AG-22-B) it was possible to obtain electrical conductivity equal to 3.275 MS/m. However, this property should be further studied in order to obtain a better value.

- Obtaining high value of flexural strength is possible whenever small graphite particles are used. Uniformly-distributed small particles ultimately lead to high mechanical strength: 48 MPa in case of AG-66-K sample. In order to improve the strength of aluminium/graphite composite the small round shaped particles have to be used.
- Microstructures analyses indicated that there is no interaction between the matrix and the reinforcement. It has been proved that the sample produced at a temperature of 815°C showed presence of the Al_4C_3 phase. In order to avoid this undesired phase, the sintering temperature should not exceed 700°C. Some small porosity on the interface has been observed in case of a sample with a low compaction rate. Moreover, it has been observed that even small porosity at the interfaces may reduce properties like thermal conductivity, electrical properties, CTE etc. therefore it is necessary to work on densification improvement.
- Low values of the coefficient of thermal expansion (CTE), which is $3.8 \times 10^{-6} \text{K}^{-1}$ [at 25°C] in the in-plane direction, is exhibited by the AG-22-K sample. This value has been obtained thanks to large graphite flakes and the parameters combination selected during manufacturing of the composite. On the other hand, CTE of the same sample measured in out of plane direction indicated value of $12 \times 10^{-6} \text{K}^{-1}$ at the temperature of 25°C. It is an example of high anisotropy of tested material. It has been noticed that the CTE increases with the temperature. Using small graphite particles (like in case of the AG-66-K sample) the anisotropy is less visible than in case of large flakes. Furthermore, CTE of the sample with small particles increases slowly with temperature. For instance, the CTE of AG-66-K in 25°C has $6 \times 10^{-6} \text{K}^{-1}$, in 200°C $6.8 \times 10^{-6} \text{K}^{-1}$ and in 400°C has $7.9 \times 10^{-6} \text{K}^{-1}$ but the CTE of the sample with large flakes (AG-22-K) in 25°C has $3.8 \times 10^{-6} \text{K}^{-1}$, in 200°C $8.58 \times 10^{-6} \text{K}^{-1}$ and in 400°C has $10 \times 10^{-6} \text{K}^{-1}$.

4.1.1 Goals achieved

In the introduction of this thesis a set of goals have been defined, answering to which would make the envisioned study complete. The main aim of the thesis was to produce a material characterized by high thermal conductivity, low coefficient of thermal expansion, fair mechanical properties, low density and good electrical conductivity. Low cost of the material was the paramount constraint which would indicate its application potential. The new advanced Al/C composite was successfully produced and fully characterized. Interesting

properties have been obtained during the research. Requirements specification correlated with the results obtained are presented in Table 11.

Table 11 Comparison obtained results with specify requirements

Property	Requirement values	Obtained results
thermal conductivity [W/mK]	500 - 700	473 - 556
CTE $10^{-6}K^{-1}$ [25°C] in plane	2 - 6	3.8
Density [g/cm ³]	2 - 5	2.18 – 2.36
electrical conductivity [MS/m]	5 - 25	3.27 – 5.7
Flexural strength [MPa]	~ 100	48

The list of requirements for the desired properties values starts with the thermal conductivity in a range between **500** and **700 W/mK**. Over the investigation process, conductivity of **473 W/(mK)** measured by LFA 427 and **556 W/(mK)** measured by in-house made device has been obtained. The value of thermal conductivity is close to the expected results. Better value could be obtained by applying higher pressure in the compaction process, nonetheless the time constraints of the research did not allow to work on this factor enhancement and some promising improvement propositions have not been fully verified.

The successive requirement is the electrical conductivity in the range between **5** and **25 MS/m**. This requirement has been satisfied with a value ranging from **3.27 MS/m** to **5.7 MS/m**. The higher value was obtained due to non-uniform distribution of aluminium (big macro agglomeration in the center of the plate). Since aluminium is highly conductive, it resulted in higher electrical conductivity in this place. The overall value of electrical conductivity could be increased by elimination of porosity and improvement of the manufacturing process (e.g. by applying higher pressure).

Obtaining good mechanical strength of a material produced with high percentage of graphite phase poses a big challenge. It was possible to reach the strength of **48 MPa** while the desired properties should be around **100 MPa**. In order to obtain higher value of flexural strength the small graphite particles have to be used. Furthermore, applying higher pressure during manufacturing process could also contribute to better results.

A great success of the research is the investigation of the coefficient of thermal expansion. The optimization pursued leads to a value of **$3.8 \times 10^{-6} K^{-1}$** at the temperature of **25°C** measured in plane direction, while the desired result should be located in the range

between $2 \times 10^{-6} K^{-1}$ and $6 \times 10^{-6} K^{-1}$ [at 25°C] in plane direction. The excellent result has been obtained thanks to the application of large graphite flakes and properly carried out production process of the composite. Final density of the investigated composites has been obtained in the range of $2.18 - 2.36 \text{ g/cm}^3$ while according to our specification, the value should lie between $2 \div 5 \text{ g/cm}^3$.

4.1.2 Results discussion

During the investigation process many samples have been characterized in search of the optimal composition, used type of graphite and suitable parameters of the production process. After long studies, the most representative five samples have been chosen among many produced Al/C composites. Results have been gathered and compared clearly showing evolution of the research and applied improvements. Table 12 shows the results which have been obtained at the beginning of the study. Sample AG-22-B exhibits high thermal properties and low CTE due to the large graphite flakes in its structure, while AG-46-D shows better mechanical properties due to its small graphite particles and fair thermal properties.

Table 12 First results

Results	AG-22-B	AG-46-D
thermal conductivity [W/mK]	385	256
thermal conductivity [W/mK] (out of plane)	44	-
CTE $10^{-6} K^{-1}$ [25°C]	6.5	~8
CTE $10^{-6} K^{-1}$ [25°C] (out of plane)	-	7,14
Density [g/cm ³]	2.27	2.18
electrical conductivity [MS/m]	3.27	1.1
density [g/cm ³]	2.27	2.18
compaction rate [%]	96	92
Flexural strength [MPa]	15	44
Specific heat [J/(kg*K)]	-	-
Thermal diffusivity [mm ² /s]	-	-

Gained knowledge about material structure, its behavior under influence of various factors like temperature, pressure or sintering time gave us hints on how to improve the properties obtained so far. Table 13 presents results of two materials which have been produced in higher temperature, under higher pressure. Sample AG-22-K was produced using large graphite flakes while AG-66-K was made of small graphite particles. Results presented in the table below clearly indicate a general improvement of the properties. In the case of

sample with larger graphite flakes, the composite exhibits higher thermal conductivity, lower CTE and higher strength. The sample made of small graphite particles shows lower CTE, lower density and higher strength. The red color of font indicates improved results in comparison to the ones presented in Table 12. It has been noticed that adopting higher temperature and pressure during the production process resulted in a general improvement of the properties.

Table 13 Final results after process modifications

Results	AG-22-K	AG-66-K
thermal conductivity [W/mK]	473 - 556	252
thermal conductivity [W/mK] (out of plane)	24	49
CTE $10^{-6}K^{-1}$ [25°C]	3.8	~7
CTE $10^{-6}K^{-1}$ [25°C] (out of plane)	12	-
Density [g/cm ³]	2.23	2.25
electrical conductivity [Ms/m]	1.7-5.7*	1.66
density [g/cm ³]	2.36	2.25
compaction rate [%]	94	95
Flexural strength [MPa]	35	48
Specific heat [J/(kg*K)]	854	840
Thermal diffusivity [mm ² /s]	248	119

*result obtained on the middle of the sample with big concentration of aluminium

4.1.3 Comparison with state-of-the-art results

Due to the high potential of the Al/C composite many companies and researchers already tried to develop similar material compositions. In this subsection results of the research on advanced Al/C composite performed at CERN have been compared with other aluminium/graphite composites available on the market or presented in scientific articles and reports. Values obtained at CERN have been compared with the results achieved by industrial companies e.g. RHP Technology, Austria (33), Hoffmann & Co Elektrokohle AG, Austria (34) and by researches from the Institute and University in Taipei (1). The comparative list is shown in Table 14.

Table 14 Comparative list of obtained results at CERN with other companies

Results	CERN EN-MME-EDS	RHP TECHNOLOGY	Institute of Materials Science and Engineering, National Taipei University of Technology	Hoffmann & Co Elektrokohle AG
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thermal conductivity [W/mK]	473	200 - 350	324- 783	220
thermal conductivity [W/mK] (out of plane)	24 – 49	50 - 80	-	-
CTE * 10⁻⁶K⁻¹ [25°C]	3.8	6 – 10	16.9 – 2.5	8
CTE * 10⁻⁶K⁻¹ [25°C] (out of plane)	7 – 12	-	-	-
electrical conductivity [Ms/m]	1.7-5.7	-	-	2.77
density [g/cm3]	2.18-2.36	-	-	2.28
compaction rate [%]	94	-	98	-
Specific heat [J/(kg*K)]	854	-	-	810
Thermal diffusivity [mm²/s]	248	-	-	-
Flexural strength [MPa]	48	-	-	90

Not all the data have been made available by these companies; however, revealed values can serve as determinants of relevance for our research. The RHP Technology Company used the rapid hot pressing technique for the production process, as in our case. The highest thermal conductivity which has been obtained by this company is reported as 350 W/mK while the lowest coefficient of thermal expansion is $6 \times 10^{-6} \text{K}^{-1}$ in plane direction. The Hoffmann & Co Elektrokohle AG for the production process of Al/C applied liquid infiltration technique. This technique allowed achieving high outcome of flexural strength of 90 MPa but at the same time contributed to obtain average thermal conductivity and CTE. Researchers from Institute and University in Taipei, performed research on Al/C composite using Hot Pressing Technique. Their studies were mostly focused on investigation of thermal conductivity and coefficient of thermal expansion by increasing successively amount of graphite to the aluminium form 10% in weight up to 90%. The maximum value of thermal conductivity is reported as 783 W/(mK) and the lowest CTE is equal $2.5 \times 10^{-6} \text{K}^{-1}$. Conducted investigations at CERN with cooperation of Manufacture Company BrevettiBizz, exhibit interesting properties among other researches which conducted study on the same material.

4.2 Future works

The results presented in the previous sections satisfied a majority of the requirements specified in the introduction to this thesis. However, there is still a large area for improvements which could be topics for further research and development activities on graphite-based composites. The following approaches could be considered to improve the results exhibited by the existing materials:

- Mechanical properties need the highest attention since the values obtained are only 50% of the desired value, which is mainly due to the high content of graphite phase. Based on the current observations it is possible to improve this value by the following treatments:
 - Keep on using small graphite particles but applying higher pressure, in the range of 50 MPa. Higher pressure may ensure better compaction rate, with an expected improvement of the thermo-physical properties (flexural strength, thermal and electrical conductivity, CTE);
 - Slightly decrease the amount of graphite content. This can help to enhance the strength of the material, however, because of the smaller amount of graphite responsible for providing good thermal characteristic, it may decrease other properties like thermal conductivity or coefficient of thermal expansion.
 - An interesting solution may be the application of carbon fibers which should significantly improve strength of the material. The percentage of carbon fibers in a volume should be around 50% in order to avoid macro agglomeration of the fibers. Carbon fibers are much more expensive than graphite flakes, therefore the aforementioned suggestions should be investigated at first.
- Another property which could be improved is the thermal conductivity. This may be possible in the following way:
 - Use of large graphite flakes with diameter of 300-500 μ m or even higher should certainly enhance the thermal conductivity. Large flakes ensure high anisotropy of the material. This option might be interesting in order to find the maximum value of thermal conductivity which can be achieved (unavoidably decreasing other properties like mechanical strength)
 - Applying higher pressure up to 50 MPa may contribute to reduced porosity – in consequence it could ensure better transfer of heat in the composite. In order to obtain good properties and avoid carbides creation at the interphase

the sintering should be performed in temperature ranges between 640 and 700°C.

4.3 Final words

I hope that the effort put in the presented project will bring benefits to the research performed in EN-MME-EDS section at CERN. The thesis contains enough details to be used by other material engineers to get introduced into the aluminium/graphite composite characterization.

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