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THESIS

STUDIES AND RESEARCH ON OBTAINING AND CHARACTERIZING FUNCTIONALLY GRADED MATERIALS OF TYPE AA6060/TiB₂ AND AA6063/ZrB₂

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Introduction

For the development of metal matrix composites, different metals such as titanium, magnesium, copper and aluminium are used. Of these, the most widely used base metal is aluminium due to its low density, high mechanical strength, excellent thermal and electrical properties.

Aluminium alloys are widely used for commercial applications in the transportation, construction and other similar industries. Currently, the focus is on aluminium as the base material for the matrix, due to its unique combination of good corrosion resistance, low electrical resistance and excellent mechanical properties.

Aluminium-based composites, reinforced with hard ceramic particles, have become increasingly attractive for study in the field of structural composites. The addition of ceramic particles, such as TiB₂, SiC, Al₂O₃, B₄C, to an aluminium-based matrix does not significantly change the density of the material but instead leads to a significant increase in the strength and specific modulus of the composite.

There are different methods of obtaining metal matrix composites. Due to the addition of reinforcement material to the matrix, there are two different processing techniques for the manufacture of CMMs, these being ex-situ and in-situ. The manufacture of in-situ composite materials involves the synthesis of the reinforcement phases directly in the matrix. This approach is different from ex-situ composites, where the reinforcing elements are obtained separately and introduced into the matrix during a secondary process such as melting, infiltration or powder processing [1].

Studies in the literature show that in-situ aluminium CMMs reinforced with TiB₂, ZrB₂ and TiC have good mechanical properties and have a uniform distribution of reinforcement phases.

The major development objectives for light composites are:

- Increased flow resistance and tensile strength at room temperature or high temperatures, while maintaining minimum ductility;
- Increased creep resistance at higher temperatures compared to conventional alloys;
- Increased resistance to fatigue, especially at higher temperatures;
- Improving thermal shock resistance;
- Improving corrosion resistance;
- Increasing Young's modulus.

Chapter 1. Metal matrix composites

The choice of reinforcement phases becomes more complicated with the increase of the melting temperature of the matrix materials.

High melting points, good corrosion resistance, high-temperature stability and compressive strength make ceramic-based matrices preferred for applications that require a material that does not yield at temperatures above 1500°C.

1.1. Classification of composite materials according to matrices

Composite materials are classified according to the basis of the matrix used, they are classified into the following categories: polymer matrix composites, ceramic matrix composites and metal matrix composites.

Polymer matrix composites

Polymer matrix composites are used more often than other composites because they have low density and their processing is easy. Most thermoplastics and rubbers are used as a material - matrix in composites with a polymer matrix. Polymer matrix composites have problems with high-temperature resistance and have an increased sensitivity to radiation and moisture.

Ceramic matrix composites

Ceramic matrix composites use materials such as glass, carbon, SiC (silicon carbide), alumina and zirconia as reinforcement phases. Ceramic matrix composites have improved characteristics of hardness, high-temperature resistance, chemical inertia, wear resistance and low density. Ceramic matrix composites have disadvantages such as poor ductility and low plasticity, they cannot withstand tensile and impact loading.

Metal matrix composites

In metal matrix composites, alloys based on aluminium, magnesium, titanium and nickel are generally used as matrix materials. Metal matrix composites have the properties of high strength, durability at high temperatures, high ductility and improved electrical conductivity. Metal matrix composites have disadvantages such as high density, lower mechanical properties compared to polymer matrix composite. Metal matrix composites are mostly used due to their properties, such as improved strength, use at high temperatures and wear resistance. In MMCs, most aluminium alloys have been used in the continuous phase and reinforced with ceramic particles, because the processing of these composites is done at low cost.

1.2. Classification of composite materials according to the reinforcement phase

A simple scheme for the classification of composite materials is shown in Figure 1.1, which consists of two main divisions: particle-reinforced and fibre-reinforced composites.

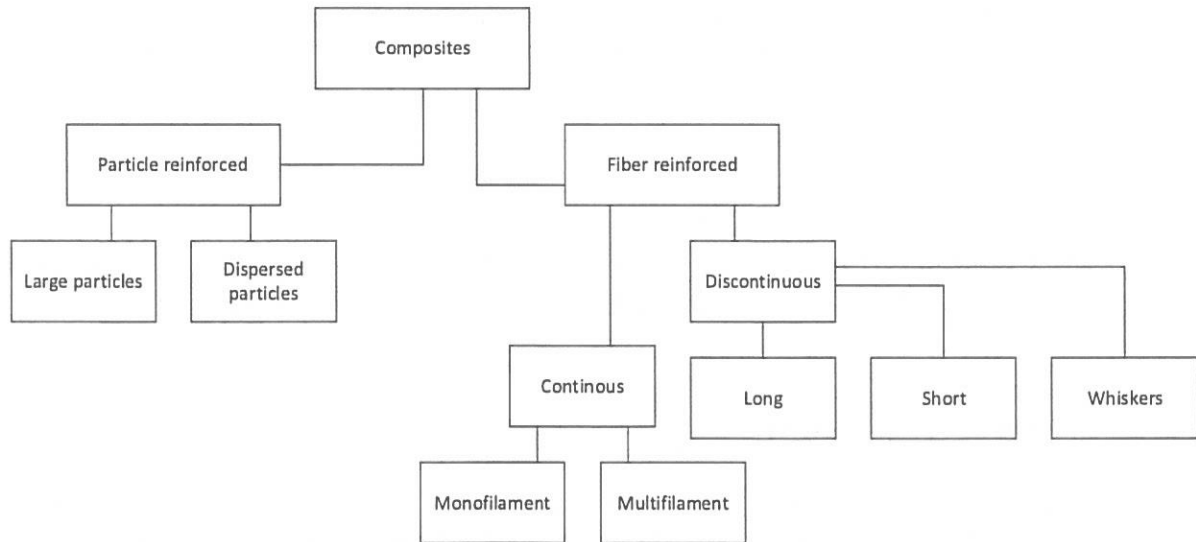


Figure 1.1. The classification scheme for different types of composite materials [2]

As seen in Figure 1.1, composites with large particles and dispersed particles are the two subclassifications of composites reinforced with particles. The distinction between them is based on the reinforcement or reinforcement mechanism.

Composites reinforced with fibres and particles usually consist of a phase that is continuous. This continuous phase is also known as the matrix, and the material distributed through the matrix is known as the dispersed phase. The dispersed phase is sometimes called the reinforcement phase if it is an added phase to increase the resistance.

The matrix (continuous phase) performs several critical functions, including keeping the fibres in the correct orientation, proper spacing, protecting them from abrasion and the environment.

The reinforcement phase ensures the strength and rigidity of the composites through the addition of high-performance metallic or ceramic materials. In most cases, reinforcement is more difficult to obtain, stronger and more rigid than the matrix. Reinforcement is usually done with *fibres* or *particles*.

The types of reinforcement are presented in the following subsections:

Particle reinforcement

For **large particles** (Figure 1.2), the term "large" is used to indicate that the interactions between the particle and the matrix cannot be treated at the atomic or molecular level. For most of these composites, the particle phase is harder and stiffer than the matrix. These reinforcing particles tend to restrict the motion of the matrix phase in the vicinity of each particle. For composites reinforced with dispersed particles, the particles are normally small, with diameters between 0.01 and 0.1 μm (10 and 100 nm). The particle-matrix interactions that occur in the reinforcement phase take place at the atomic or molecular level.

Metals and metal alloys can be reinforced by uniform dispersion of several voluminous percentages of fine particles of very hard and inert material. The dispersed phase can be metallic or non-metallic; metal oxides are often used. The reinforcement phase is maintained at high temperatures and for long periods because the dispersed particles are chosen not to react with the matrix phase.



Figure 1.2. Schematic presentation of the large particles [3]

Fibre reinforcement

The mechanical properties of a fibre-reinforced composite depend not only on the properties of the fibre but also on the degree to which an applied load is transmitted to the fibres through the matrix phase.

Fibre is much longer than its diameter. The length-to-diameter ratio (l / d) is known as the size ratio and can vary greatly [4].

Continuous fibres have long size ratios, while discontinuous fibres have short size ratios.

Discontinuous reinforcement

The most used reinforcement materials for discontinuously reinforced MMCs are SiC and Al₂O₃, although, in some specialized applications silicon nitride (Si₃N₄), TiB₂, graphite and others have also been used.

There are three types of MMCs with the reinforcement phase consisting of discontinuous fibres, these are classified as short, long fibres and whiskers.

The most used fibres in the reinforcement phase are alumina, boron carbide, silicon carbide, titanium carbide and tungsten carbide [5].

Whiskers (Figure 1.3) must offer superior properties due to their larger size ratio (length divided by diameter). However, whiskers are fragile and tend to fall apart, in shorter lengths, during processing. This reduces their reinforcement efficiency and does not justify its high cost [5].

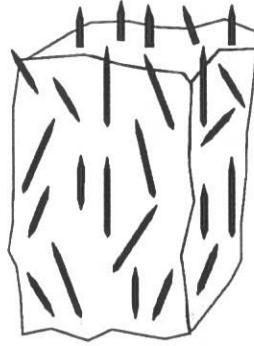


Figure 1.3. Schematic presentation of whiskers [3]

Continuous reinforcement

In fibre reinforcement, the most used method is the continuous reinforcement, in which many types of fibres are used; most of these are carbon or ceramic fibres.

Monofilaments (Figure 1.4) are large-diameter fibres (100 to 150 μm), usually produced by chemical vapour deposition (CVD) made of either SiC or B in carbon fibre or from W wires. The bending flexibility of monofilaments is low compared to multifilaments.

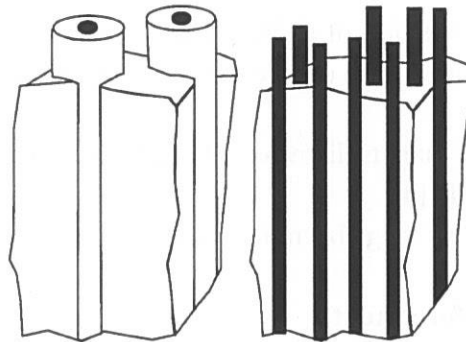


Figure 1.4. Schematic presentation of monofilaments and multifilaments [3]

Multifilament fibres, such as carbon and ceramic fibres Nextel (alumina-based) and Nicalon (silicon carbide), have been used in aluminium and magnesium matrices; however, smaller and more numerous multifilament fibres are difficult to impregnate using solid-state processing techniques, such as diffusion bonding, due to their small size [4].

1.3. Properties of metal matrix composites compared to the structure of other materials

Strength and deformability

The deformability and strength properties of particle-reinforced aluminium metal matrix composites are significantly better than those of the aluminium matrix. For example, at a volume fraction of 40% reinforcement with silicon carbide particles, the strength is about 65% higher than that of the aluminium matrix, and the modulus of elasticity is doubled [6].

Wear resistance

The wear resistance of metal matrix composites is excellent compared to that of unreinforced metals and PMC, due to the presence of hard ceramic particles. For example, in one test, the abrasive wear of 2024 aluminium under a load of 1 kilogram was shown to be 6 times greater than the wear of the same alloy containing the volume fraction of 20 per cent of silicon carbide whiskers [7].

Breaking strength and hardness

There is a wide variation in the breaking strength of CMMs, although it is generally lower than that of unreinforced metal. The breaking strength can vary between 65 and 100% of the breaking strength of the unreinforced metal alloy [8].

The formation of the interface has a crucial influence on the behaviour of metallic composites. The influence of elastic constants and mechanical properties on the structural defect is substantial. For example, changing the growth behaviour of cracks in fibre-reinforced composites.

In the case of poor adhesion, a crack can move along the fibre, the interface is delaminated and the stress successively leads to the rupture of the fibres. With poor adhesion, the fibres or particles function like pores thus leading to weaker structural properties than those of unreinforced matrices. [9].

In the case of very good adhesion of the matrix on the fibre, delamination does not take place.

Thermal properties

The introduction of silicon carbide particles into aluminium forms materials with lower coefficients of thermal expansion, the desired property for certain types of applications. By choosing a suitable composition, the coefficient of thermal expansion can be close to zero in some MMCs. MMCs also tend to be good heat conductors. Using graphite fibres with high thermal conductivity, MMCs with aluminium matrix or copper matrix can have a very high thermal conductivity, compared to other types of composites [10].

Property flexibility

In some applications, metal matrix composites offer unique combinations of properties that cannot be found in other materials. For example, aircraft encapsulation requires a combination of several difficult-to-achieve properties, requiring a low coefficient of thermal expansion, high thermal conductivity and low density. Certain MMCs can meet these requirements by replacing beryllium, which is rare and has toxicity problems. For example, a high heat transfer coefficient is desirable for radiators, this property is provided by copper, aluminium and titanium-reinforced with graphite fibre (although the latter fibre/matrix combination has, unfortunately, some interface reaction problems) [11].

Chapter 2. Functionally graded materials

The progress of materials synthesis technologies has stimulated the development of a new class of materials, called functionally graded materials (FGM), with promising applications in aerospace, transportation, energy, electronics and biomedical engineering.

There is a substantial difference between FGMs and traditional composite materials (MMCs). MMCs are a class of advanced materials, consisting of one or more materials combined in solid states with distinct physical and chemical properties [12].

Grading properties in an FGM reduces thermal stresses, residual stresses and stress concentrations found in traditional composites.

Unlike traditional composites which are homogeneous mixtures and involve a compromise between the desired properties of the component materials; significant proportions of FGMs contain the pure form of each component, therefore the need for compromise is eliminated [13].

Functional gradient materials can be characterized by gradually varying their composition and structure, leading to corresponding changes in their properties. Materials can be designed for specific functions and applications.

FGM is a multiphase material with volume fractions of component elements that gradually vary in a predetermined and designed profile, thus obtaining a non-uniform microstructure in a material with continuous gradient properties. They eliminate the discontinuous interfaces existing in the composite material, where structural defects are triggered [14]. It replaces the discontinuous interface with a gradient interface that produces a smooth transition from one material to another [15].

2.1. Types of functionally graded materials

The different types of functional gradient materials that are now produced are those formed by chemical composition gradient, porosity gradient and microstructural gradient. Each of these types of FGM is discussed in detail in the following sections.

The manufacturing process of an FGM can usually be divided into the construction of the inhomogeneous spatial structure ("gradation") and the transformation of this structure into a raw material ("reinforcement"). Radial particle arrangement processes can be classified into constitutive, homogenization and segregation processes [16]. The constitutive processes are based on a gradual construction of the powdered graded structure [17].

Vapour deposition technique

There are different types of vapour deposition techniques, which include: sputter deposition, chemical vapour deposition (CVD) and physical vapour deposition (PVD). These vapour deposition methods are used to deposit functional gradient surface layers and provide an excellent microstructure but can only be used for deposition of the thin coating [18]. They are energy-intensive and produce poisonous gases as their by-products [19].

Powder metallurgy

Powder metallurgy is used to produce material with a functional gradient [20] [21], through three basic steps, namely: weighing and mixing the powder according to the pre-designed spatial distribution, dictated by the functional requirement and stacking the pre-mixed powders and finally sintering [22]. The powder metallurgy technique gives rise to a discontinuous structure (Figure 2.1 b). If the continuous structure is desired (Figure 2.1 a), the centrifuged method is used [23].

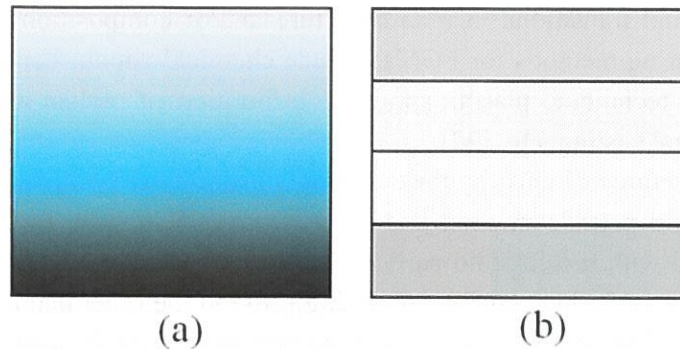


Figure 2.1. Types of FGM structure: (a) continuous and (b) discontinuous [24]

Centrifugal method

The centrifugal method is similar to centrifugal casting, where centrifugal force is used by rotating the mould to form the raw functional gradient material [25]. Functionally graded material is produced in this way due to the difference between material densities and mould rotation [26].

In a centrifugal cast material, the hardness will not be uniform due to phase segregation.

The presence of reinforcing particles in materials with functional gradient leads to variations in physical, mechanical and tribological properties. The mechanical properties vary depending on the degree of propagation of the reinforcement phase in the microstructure. In the case of FGMs, the difference of properties in the matrix will be much larger due to the transient distribution of phases and particles.

2.2. Fields of application of functionally graded materials

Functionally graded materials are currently applied in several industries, with enormous potential for use in other applications in the future. Current application areas include the following industries: aerospace, automotive, biomedical, defence, electrical/electronic, energy, maritime, optoelectronics and thermoelectric.

Future areas of application of functional gradient materials will also expand when the production costs of these important advanced materials are reduced.

Chapter 3. Studies and research on obtaining functional gradient metal matrix composites

Functionally graded materials (FGM) are mostly composites that have a continuous variation in composition in a certain direction. Functionally graded metal matrix composites (FGMMCs) are materials comprising two or more component phases, one of the phases being the base metal matrix and the other being the radially arranged reinforcement phase in the gradient. They present gradual transitions in microstructure and/or composition in a specific direction. Various manufacturing methods for FGMs include chemical vapour deposition, physical vapour deposition, sol-gel technique, plasma spraying, infiltration of molten metals, high-temperature synthesis, centrifugal casting, etc. [27]

The manufacture of FGMs by the centrifugal method can be classified into two categories: the centrifuged solid particle method and then centrifuged in situ method. In the case of the centrifuged method with mixed solid particles (Figure Figure 3. 1), the dispersed phase remains solid in a liquid matrix during centrifugal casting.[28] On the other hand, if the centrifugal force is applied during solidification in both the dispersed phase and the matrix, we have the in-situ centrifuged method [28].

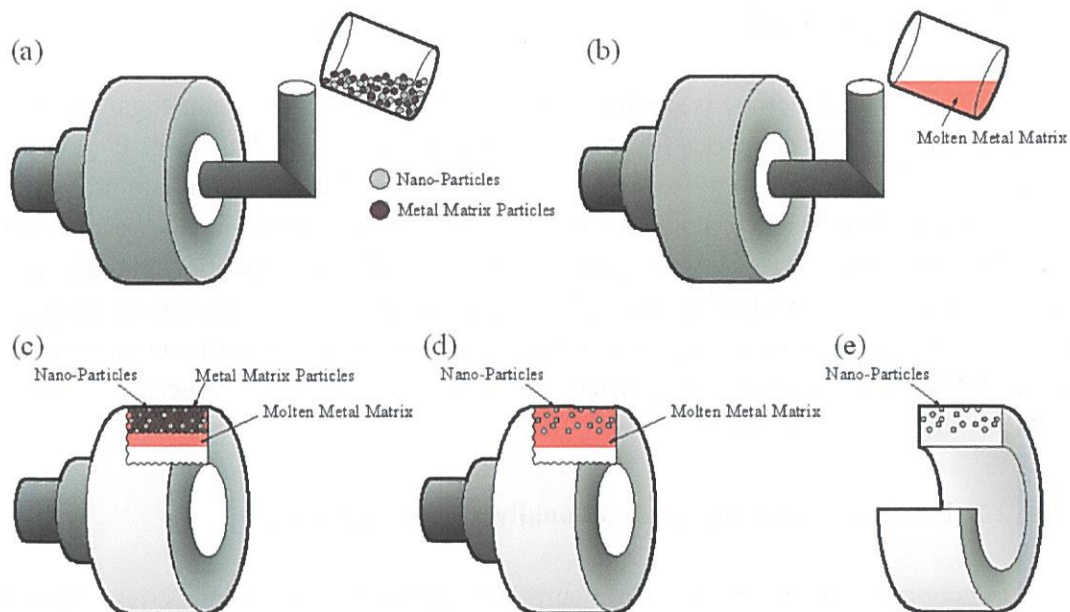


Figure 3. 1. Schematic illustration showing the process of the mixed powder centrifuged method[28]

The presence of reinforcement particles in functional gradient materials leads to variations in physical, mechanical and tribological properties. Mechanical properties vary depending on the degree of propagation of the reinforcement phase in the microstructure. In the case of FGMs, the difference in properties in the matrix will be much greater due to the transient distribution of phases and particles.

3.2. Study of ternary and quaternary alloy systems

3.2.1. Al-Mg-Si System

Al-Mg-Si alloys have started to be used more and more in the automotive and aerospace industries, especially for critical structures, because they can be easily cast, are resistant to corrosion. In these alloys, Mg is intentionally introduced to be able to induce artificial ageing by precipitating the metastable phase Mg₂Si or the formation of Guinier-Preston zones.[29]

Guinier-Preston areas are small-scale metallurgical phenomena that involve early-stage precipitation of the metastable phase Mg₂Si. GP areas are associated with the phenomenon of ageing, where reactions to room temperature continue to occur in material over time, leading to changes in physical properties. This happens in the 6xxx and 7xxx series of aluminium alloys. Physically, GP areas are extremely fine (dimensions 3-10 nm), areas with high concentrations of Mg₂Si, which provide physical obstacles in the movement of dislocations.

The Al-Mg-Si ternary phase diagram is very important for understanding the structure and properties of some alloys, it is also necessary for the analysis. of more complex diagrams containing Mg and Si (e.g. Al-Fe-Mg-Si).

In the Al-Mg-Si phase diagram, shown in Figure Figure 3.2, in the corner with a high concentration of aluminium it is observed that Al may be in equilibrium with Mg₂Si, Al₈Mg₅ or (Si). Quasi-binary cross-section between (Al) and Mg₂Si corresponds to the concentration ratio Mg:Si = 1.73. This cross-section divides the phase diagram into two simple eutectic diagrams: Al-Mg-Mg₂Si and Al-Si-Mg₂Si.

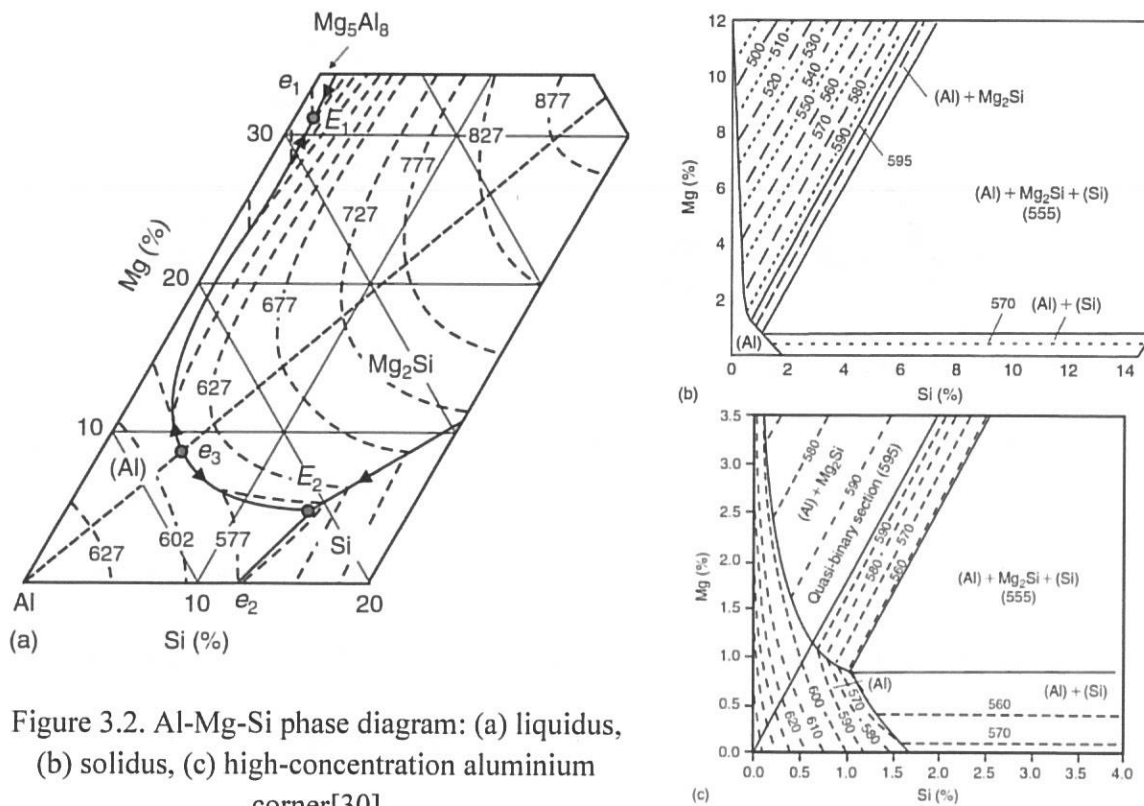


Figure 3.2. Al-Mg-Si phase diagram: (a) liquidus, (b) solidus, (c) high-concentration aluminium corner[30]

3.2.2. Al-Fe-Si System

The Al-Fe-Si system is used for the analysis of lxxx alloys, pure commercial aluminium with minor impurities of Fe and Si and Al-Si foundry binary alloys (which, as a rule, contain certain amounts of Fe impurities). The solubility of iron in silicon is very small, even negligible.

The Al-Fe-Si phase diagram is very complex. There is still debate about the existence of ternary phases, temperatures, or compositions to the invariable phase transformations.

3.2.3. Al-Fe-Mg System

The analysis of this phase diagram provides the possibility to track the role and influence of iron additions and impurities on the phase composition of Al-Mg foundry alloys containing small amounts of silicon, manganese, and other possible elements.

3.2.4. Al-Fe-Mg-Si System

This system is important for many industrial foundry alloys, especially Al-Si and Al-Mg. This is primarily related to the existence of the quaternary compound, which makes it impossible to analyse ternary phase diagrams to determine the composition of the alloy phase. The quaternary compound, often designated as phase π , has a narrow field of homogeneity around the composition corresponding to the chemical formula $\text{Al}_8\text{FeMg}_3\text{Si}_6$. Figure 3.3 shows the projection of the liquidus surface (a) and the distribution of solid-phase areas (b) for Al-Fe-Mg-Si alloys.

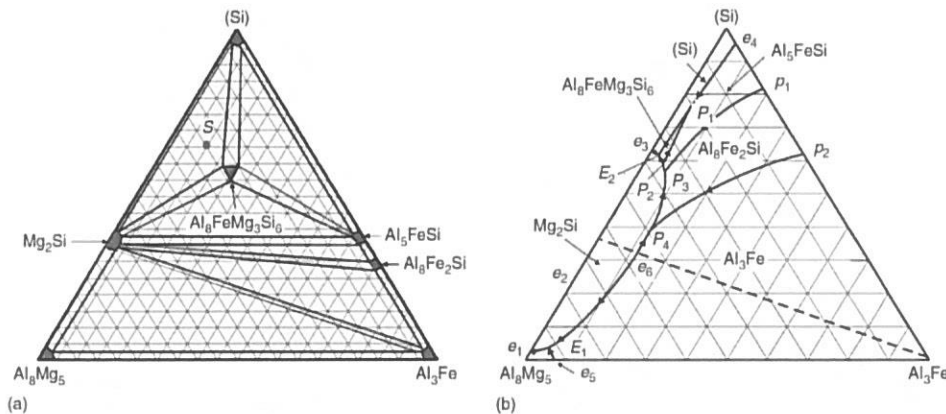


Figure 3.3. Quaternary phase diagram Al-Fe-Mg-Si: (a) polythermal diagram and (b) distribution of solid-phase fields in high aluminium concentration corner[30]

3.3. Influence of alloying elements on technological characteristics and parameters

To obtain functionally graded materials, having TiB₂ and ZrB₂ as reinforcement elements, we must consider the influence of the following parameters: viscosity, temperature, melting temperature at the time of pouring in centrifugal form, matrix temperature, casting shape speed, solidification speed, particle size and concentration.

The study by A.T. Dinsdale et al. [31] shows that an increase in the concentration of Ti, Ni, Cr, Mn, Mg tends to increase viscosity, while viscosity decreases with the increase in the concentrations of Zn and Si. Also, reducing non-metallic alloy inclusions decreases viscosity.

3.4. Studies for the viscosity relationship – composition in the systems of alloys researched

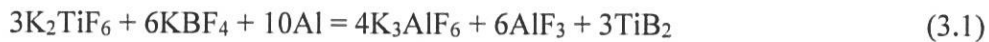
Cooksey et al. [32] observed that the fluidity/composition ratio is roughly the inverse of the viscosity/composition relationship in the Al-Si system.

However, in the case of composite suspensions, strict reciprocity is rarely observed between the decrease in measured fluidity and the increase in viscosity measured or calculated as a result of particle addition. When the liquid metal contains a dispersion of particles, the actual or apparent viscosity rises significantly above the viscosity of pure melts.

In concentrated suspensions, it is necessary to consider hydrodynamic interactions, particle rotation, particle collision and particle formation. In large volume fractions, the relationship between viscosity and concentrations becomes nonlinear. As a result, the prediction of rheological behaviour becomes more difficult

3.5. Thermodynamic studies on composite 6060/TiB₂

The study was done using the HSC Chemistry program, thus we calculated the thermodynamic data in the 973.15 – 1173.15 K temperature range, indicating the possibility of the formation of Al₃Ti, TiB₂, AlB₂ compounds for reactions 3.1 to 3.6.



3.6. Thermodynamic studies on composite production 6063/ZrB₂

In the study conducted by Degang Zhao et.al. [33] the authors used Gibbs free energy values given in Table **Error! Reference source not found.** and calculated according to [34].

Table 3.1. Reactions and standard values of Gibbs free energy at 1000K

Nr. crt.	Reactions	ΔG° , kJ/mol, 1000K
(3.9)	$2KBF_4 + 3Al = AlB_2 + 2AlF_3 + 2KF$	-404.31
(3.10)	$K_2ZrF_6 + 13/3Al = ZrAl_3 + 4/3AlF_3 + 2KF$	-276.24
(3.11)	$ZrAl_3 + AlB_2 = ZrB_2 + 4Al$	-77.98

The authors point out that AlF₃ and K₃AlF₆ are gases and are released from the melt, which is then degassed with hexachloroethane.

Chapter 4. Experimental research on the development of AA6060/TiB₂ and AA6063/ZrB₂ composites for the production of functionally graded materials

4.1. Elaboration of AA6060/TiB₂ composites

4.1.1. Raw materials and materials

In the first experimental part, the TiB₂ particles were obtained in an electric furnace with KANTHAL resistance and a graphite crucible, through the aluminothermic process between the aluminium melt and the KBF₄ + K₂TiF₆ + Na₃AlF₆ salt mixture, at 750 – 950°C [35]. Potassium hexafluorotitanate (K₂TiF₆ with melting temperature 780°C and molecular mass 240.09 g/mol) and potassium tetrafluoroborate (KBF₄ with melting temperature 530°C and molecular mass 125,91g/mol), and for the protection of the metal bath and the dissolution of oxides cryolite (Na₃AlF₆). **Figure 4.1** shows the general design of the installation used to obtain TiB₂ reinforced composites obtained by centrifugal solidification, as well as the mould.

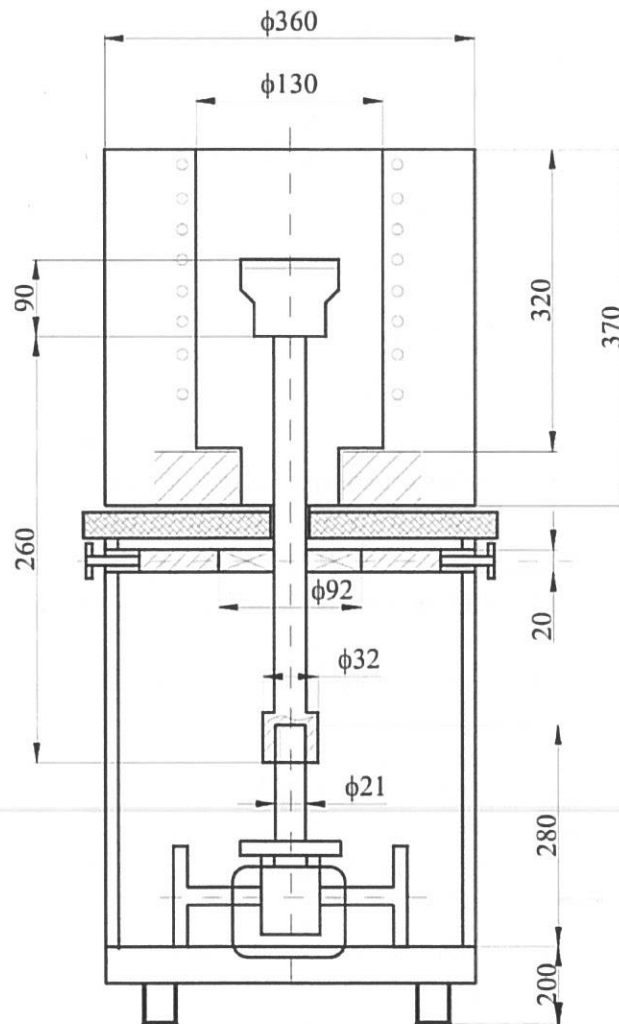


Figure 4.1. The overall design of the experimental installation [35]

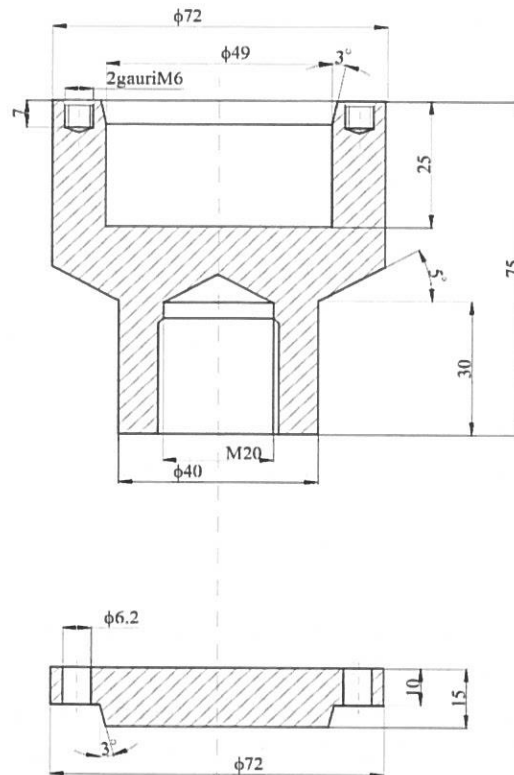


Figure 4.2. The mould of the realized experimental installation [35]

4.1.2. Method of preliminary research and experimentation

To highlight the mechanism and kinetics of the formation of boron particles in aluminium alloys, 3 batches with AA6060 were used to obtain different concentrations of titanium diboride - 5%, 10% and 20% TiB₂, respectively.

Starting from the optimized parameters of obtaining materials with aluminium matrix and TiB₂ nanometric reinforcement particles we achieved, by centrifuged solidification, composite materials with layers of different particle concentrations.

Table 4.1. Physical properties of titanium diborides [36]

Name IUPAC	Theoretical chemical formula, [CASRN]	Crystallographic system/ Pearson symbol/ Space group/ Prototype / Structure parameters	Density (ρ , kgm ⁻³)	Electrical resistance (ρ , $\mu\Omega$ cm)	Melting point(° C)	Thermal conductivity (k.Wm ⁻¹ K ⁻¹)	Specific heat capacity (c_p , J kg ⁻¹ K ⁻¹)	Linear thermal expansion coefficient (α , 10 ⁻⁶ K ⁻¹)
Diborură de titan	TiB ₂ [12045-63- 5] 69.489	Hexagonal $a = 302.8$ pm $c = 322.8$ pm C32, $hP3$, $P6/mmm$, AlB2 type ($Z = 1$)	4520	16-28,4	2980- 3225	64,4	637,33	7,6-8,6

Young's Module (E,GPa)	Resistance to bending (Kt, MPa)	Vickers hardness HV	Other physicochemical properties, corrosion resistance and uses	Name IUPAC
372-551	240	3370	Gray crystals, superconducting at 1.26 K. High-temperature electrical conductor, used in the form of a cermet as a crucible material for handling molten metals such as Al, Zn, Cd, Bi, Sn, and Rb. It is strongly corroded by liquid metals such as Tl, Zr, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, and Cu. Begins to be oxidized in the air above 1100–1400 °C. Corrosion-resistant in hot concentrated brines. Maximum operating temperature 1000 °C (reducing environment) and 800 °C (oxidizing environment).	Titanium diboride

Load calculation

The quantity of K₂TiF₆ and the quantity of KBF₄ were calculated according to the reaction:



Starting from the capacity of the crucible it was established that for good preparation of in-situ composites to use a quantity of 200g 6xxx aluminium alloy.

Samples were collected from the materials obtained for analysis by optical microscopy, electron microscopy, DSC, EDS, XRD. Samples were also carried out to determine the hardness of composite materials with uniform particle distribution and radial distribution of wear resistance and crystal size.

To highlight these ceramic particles, an AA6060/TiB₂ composite sample was solubilized in concentrated hydrochloric acid, washed several times with distilled water, and the resulting powder was dried in a drying stove and then dimensional analysis of TiB₂ particles was performed using Malvern's Zetasizer Nano ZS analyser.

From the materials obtained, samples were developed for layer analysis (Figure 4.4), macro and optical microstructures (Figure 4.4), electron microscopy and EDS (Figure 4.5), XRD (Figure 4.6), TEM (Figure 4.7 DSC analysis (Figure 4.8,), distribution of sizes by volume (Figure 4.9), Vickers microhardness (Figure 4.10).

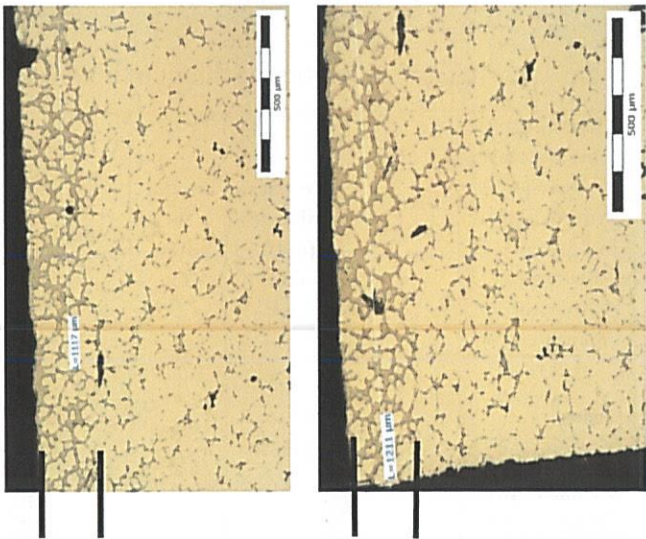


Figure 4.3. Layer analysis of composite A concentration is kept constant over 2977 μm (3 mm)

[35]

Characterization of materials obtained (Composite A)

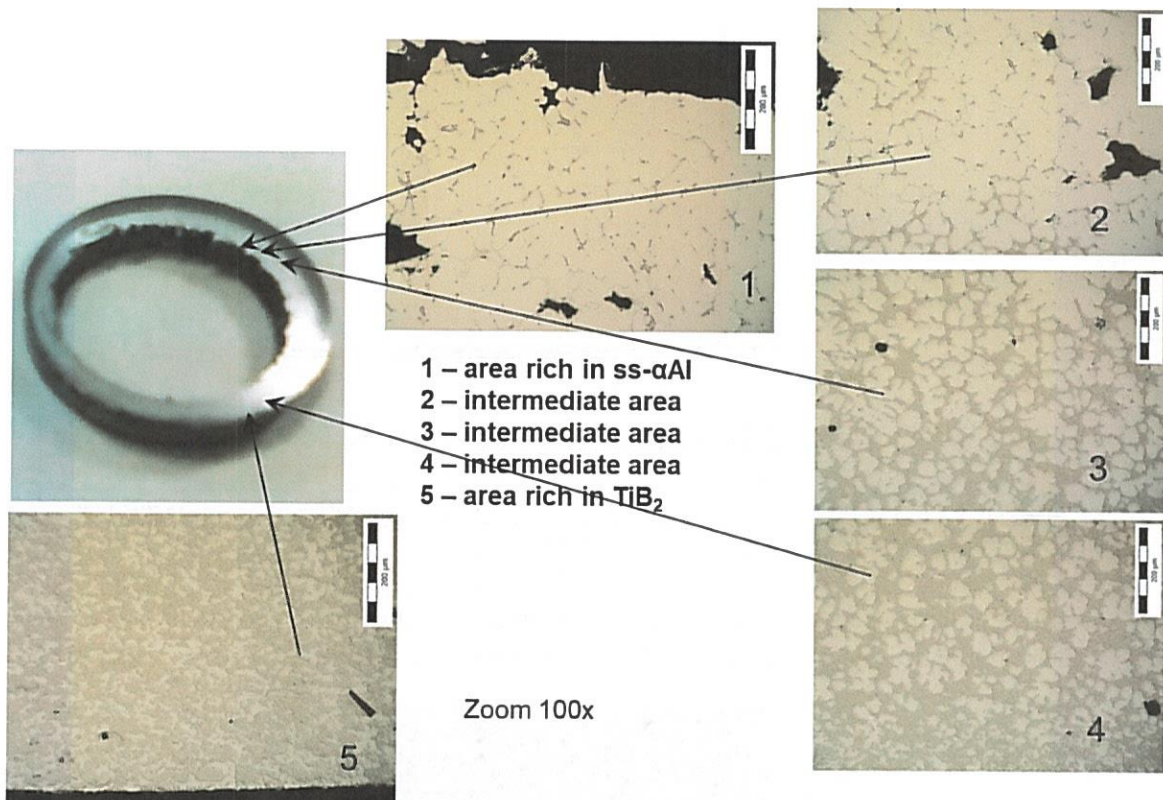


Figure 4.4. Microstructure and macrostructure of composite A [35]

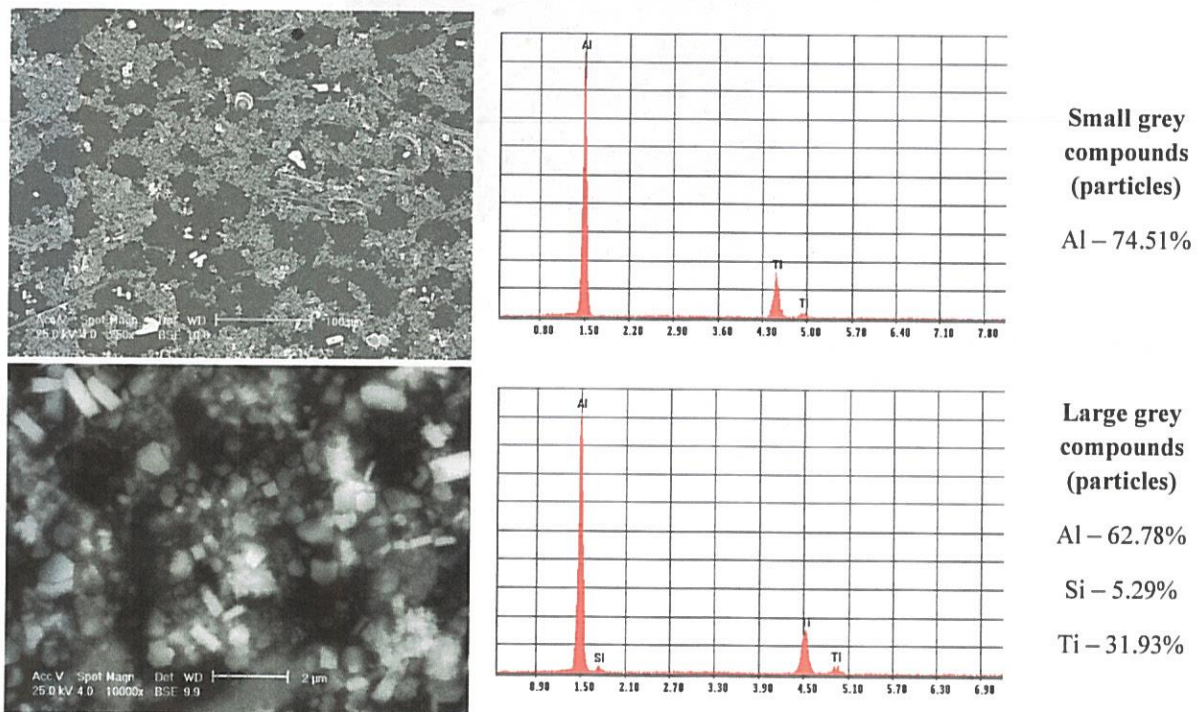


Figure 4.5. Analysis by electron microscopy and analysis of EDS with the chemical composition [35]

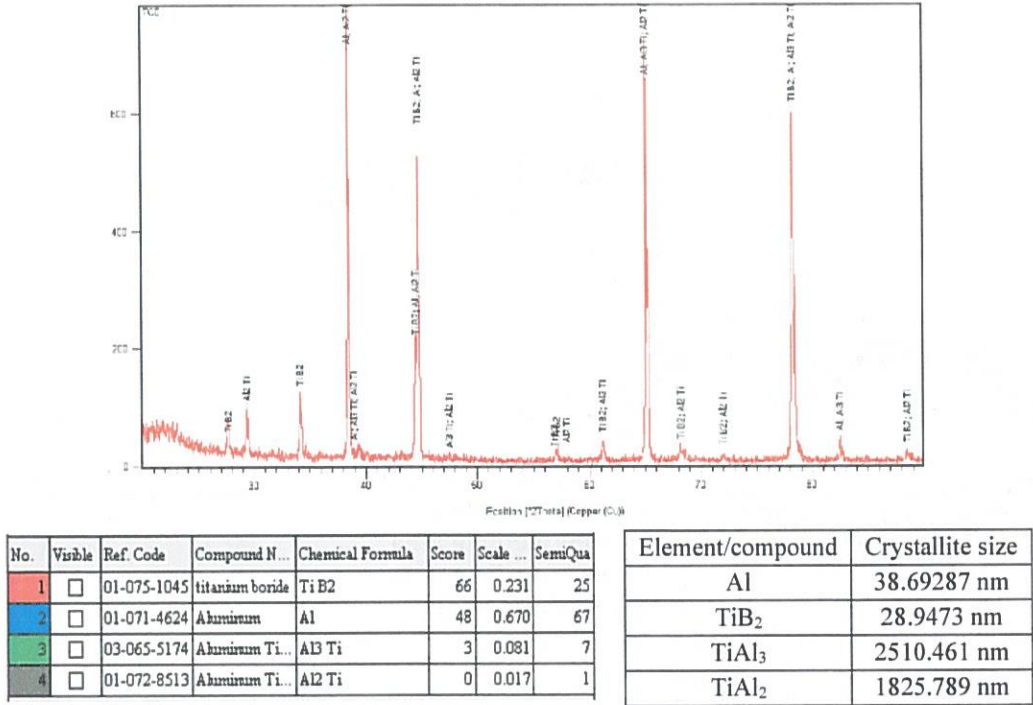


Figure 4.6. Diffractogram of the layer with high TiB₂ content and compositional analysis. Crystallite dimensions determined by calculation with Debye-Scherrer formula [35]

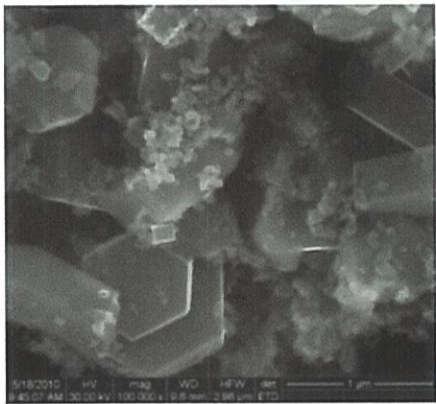


Figure 4.7. TEM Composite A[38]

The DSC analysis provides information on the peritectic transformation temperature of 665°C from the Al-Ti binary diagram.

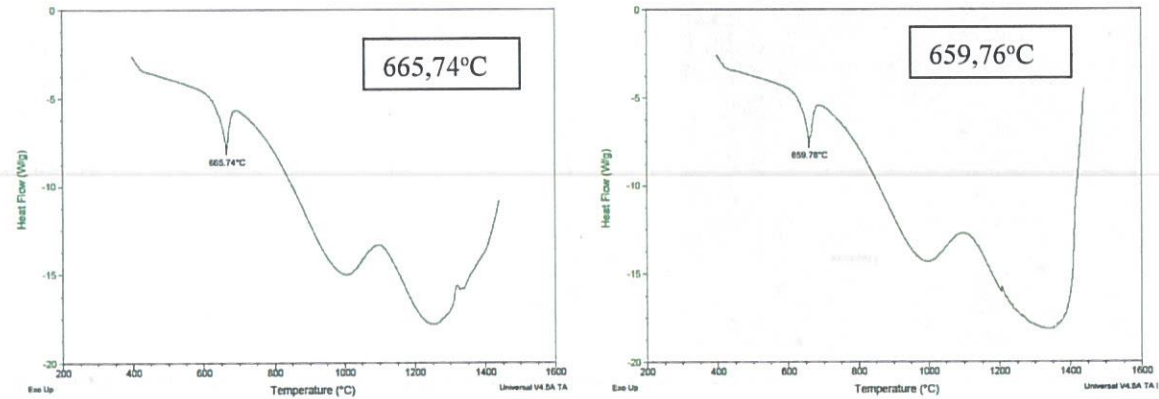


Figure 4.8. DSC analysis of the layer with high TiB₂ concentration (left) and lower TiB₂ concentration (right)

Results Table

Size d.nm	Intensity %	Size d.nm	Intensity %
0.4000	0.0	68.06	0.0
0.4632	0.0	78.82	0.0
0.5365	0.0	91.28	0.0
0.6213	0.0	105.7	0.0
0.7195	0.0	122.4	0.0
0.8332	0.0	141.8	0.0
0.9649	0.0	164.2	0.0
1.117	0.0	190.1	0.0
1.294	0.0	220.2	0.0
1.499	0.0	255.0	0.0
1.736	0.0	295.3	0.0
2.010	0.0	342.0	7.5
2.328	0.0	396.1	19.8
2.696	0.0	458.7	27.7
3.122	0.0	531.2	25.1
3.615	0.0	615.1	13.8
4.187	0.0	712.4	2.7
4.849	0.0	825.0	0.0
5.615	0.0	955.4	0.0
6.503	0.0	1106	0.0
7.531	0.0	1281	0.0
8.721	0.0	1484	0.0
10.10	0.0	1718	0.0
11.70	0.0	1990	0.0
13.54	0.0	2305	0.0
15.69	0.0	2669	0.0
18.17	0.0	3091	0.0
21.04	0.0	3580	0.0
24.36	0.0	4145	0.0
28.21	0.0	4801	0.0
32.67	0.0	5560	3.5
37.84	0.0	6439	0.0
43.82	0.0	7456	0.0
50.75	0.0	8635	0.0
58.77	0.0	1.000e4	0.0

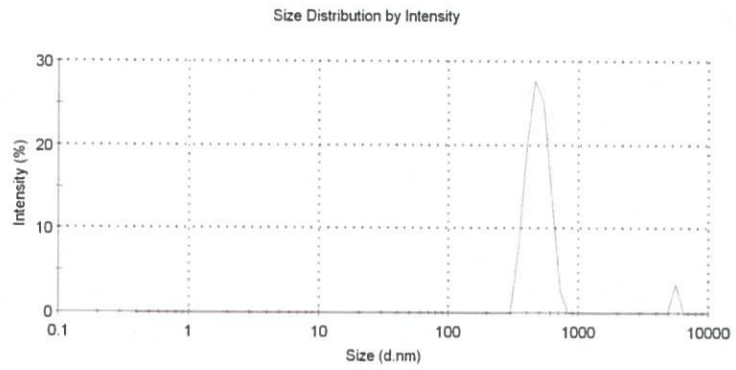
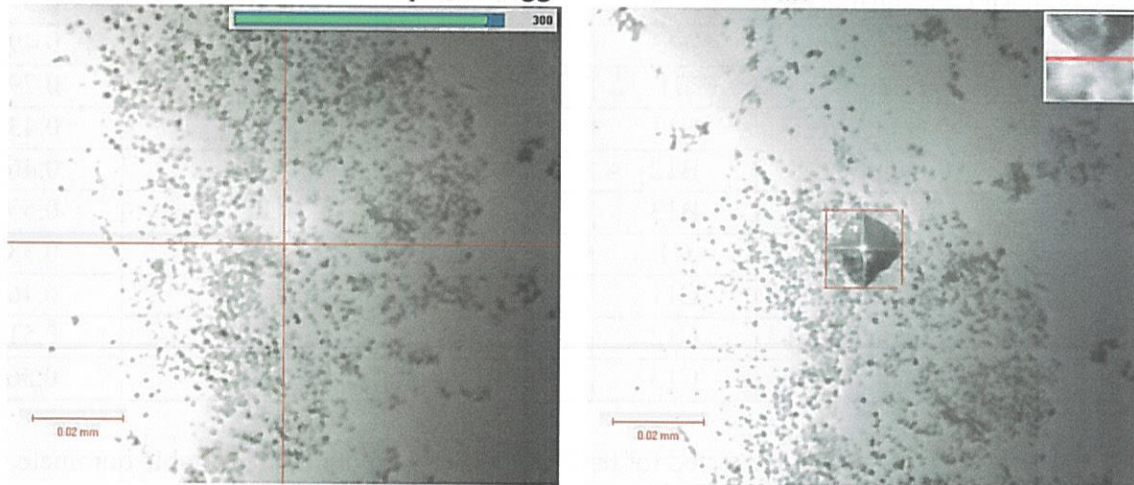


Figure 4.9. Distribution of volume sizes for composite A

A2-2 particle agglomeration 67 HV_{0.01}



A3-4 particle agglomeration 130/128 HV_{0.01}

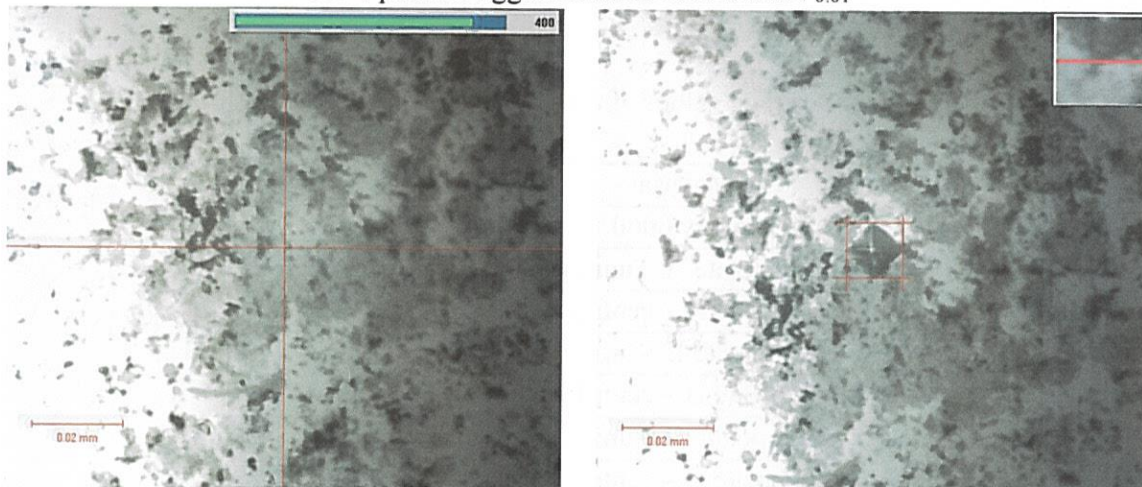


Figure 4.10. Microhardness HV_{0.01} for sample A

Microstructural analysis by electron microscopy was performed on an SEM FEI Quanta Inspect F microscope, with field emission and equipped with an energy dispersion spectrometer (EDS). Microstructures were measured directly using the Olympus UC30 camera and processed using Olympus Stream image processing software.

Compositional influence of the layer on wear resistance

Samples for the determination of wear resistance were taken from the materials obtained. Composite materials with uniform distribution of reinforcement elements as well as those obtained by centrifugal solidification were tested. Also, to make a more accurate assessment of the characteristics of the layers obtained, samples were prepared at different depths, i.e. at 200µm, 500µm and 800µm, as can be seen in Table Table 4.2.

Table 4.2. Materials used to determine the wear resistance

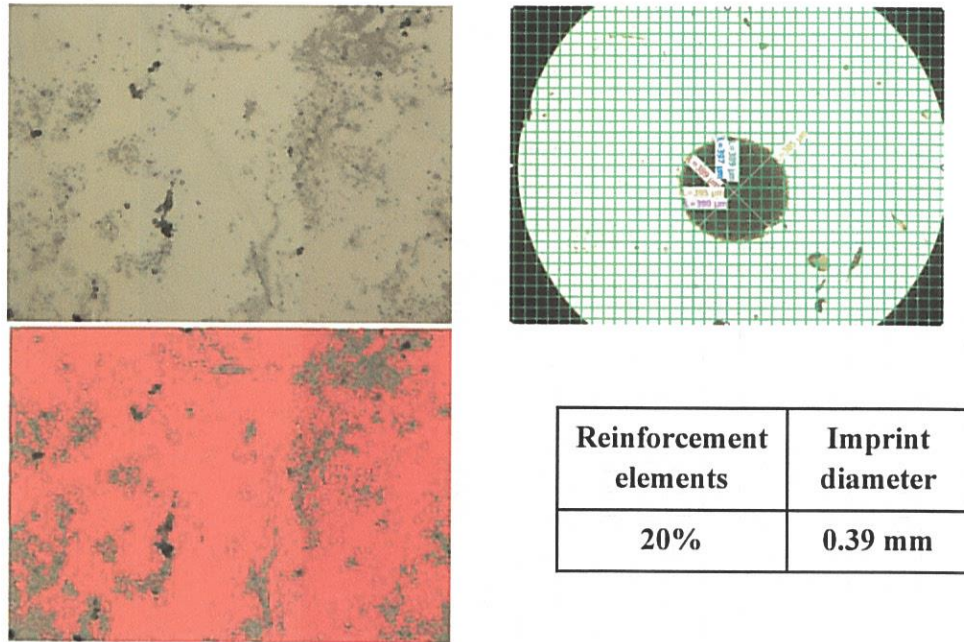
Material	Notation	Layer Depth	Reinforcement elements	Imprint Diameter
Composite A – uniform	A1		20%	0.39
Composite A-centrifuged	A11	200µm	66%	0.31
Composite A-centrifuged	A12	500 µm	55%	0.37
Composite A-centrifuged	A13	800 µm	50%	0.49
Composite B – uniform	B1		13%	0.79
Composite B -centrifuged	B11	200 µm	43%	0.43
Composite B -centrifuged	B12	500 µm	34%	0.46
Composite B -centrifuged	B13	800 µm	30%	0.53
Composite C – uniform	C1		3%	0.33
Composite C -centrifuged	C11	200 µm	7%	0.46
Composite C -centrifuged	C12	500 µm	4%	0.51
Composite C -centrifuged	C13	800 µm	2%	0.56

The samples taken were tested for hardness by the Leeb method (portable durometer). The resulting average values are shown in Table 4.3. Table 4.3. Average values of the hardness of the materials studied

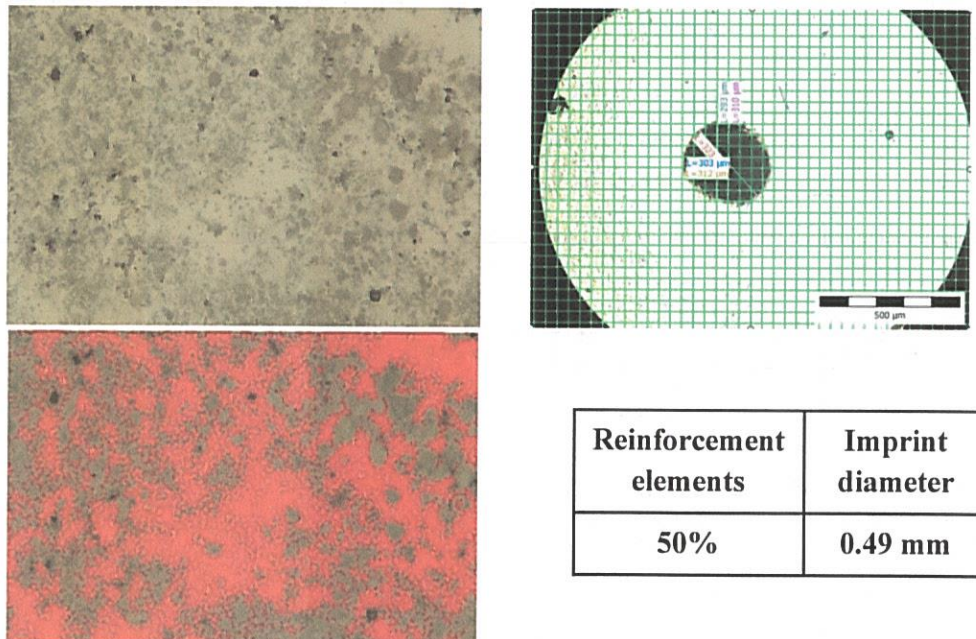
Table 4.3. Average values of the hardness of the materials studied

Material	Hardness value, HL
Alloy 6060	238
Composite A – uniform	413
Composite A – centrifuged	423
Composite B – uniform	263
Composite B – centrifuged	432
Composite C – uniform	250
Composite C – centrifuged	453

Samples were taken to highlight the concentration of reinforcement elements, images were taken with the Olympus UC30 camera and processed with Olympus Stream software (phase analysis).



A1



A13

Figure 4.11. Microstructure, phase analysis and diameter after testing A1 low concentration of reinforcement elements and A13 increased concentration of reinforcement elements

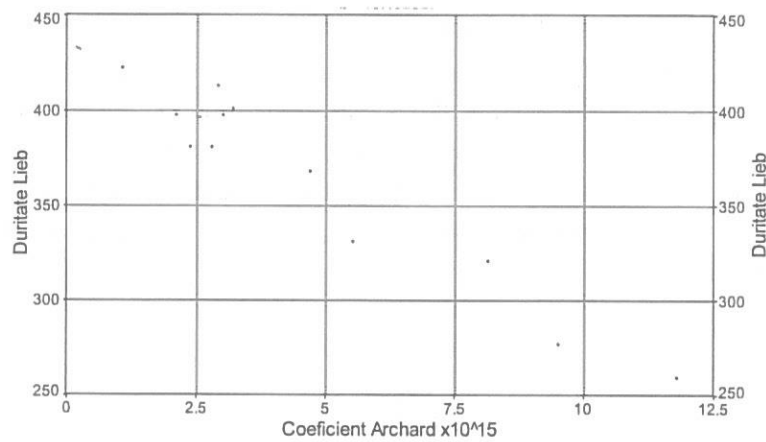
The resulting samples were subjected to an abrasive wear test using the CSEM CALOWEAR installation. The diameters of the traces left over from the wear test were determined by optical microscopy using the same Olympus UC30.

Table 4.4. The values measured and calculated for the determination of the Archard coefficient for reinforced composite with TiB₂

Notation	Time [s]	F Press [N]	Nr. cycles shaft	Nr. ball cycles	L slide (m)	Imprint Diameter (mm)	Crater (m)	Removed volume (m ³)	k – Archard wear coefficient
A0	240	0.371	1641	1181.52	85.33	0.33	0.0003253	4.33E-14	1.37E-15
A1	240	0.357	1644	1183.68	85.49	0.39	0.00039	8.94E-14	2.93E-15
A11	240	0.39	1641	1181.52	85.33	0.31	0.00031	3.57E-14	1.07E-15
A12	240	0.354	1646	1185.12	85.59	0.37	0.00037	7.24E-14	2.39E-15
A13	240	0.364	1644	1183.68	85.49	0.49	0.00049	2.23E-13	7.16E-15
B1	240	0.375	1640	1180.8	85.28	0.79	0.00079	1.51E-12	4.71E-14
B11	240	0.366	1641	1181.52	85.33	0.43	0.00043	1.32E-13	4.23E-15
B12	240	0.354	1642	1182.24	85.38	0.46	0.00046	1.73E-13	5.73E-15
B13	240	0.364	1644	1183.68	85.49	0.53	0.00053	3.05E-13	9.80E-15
C1	240	0.358	1644	1183.68	85.49	0.33	0.00033	4.58E-14	1.50E-15
C11	240	0.368	1640	1180.8	85.28	0.46	0.00046	1.73E-13	5.51E-15
C12	240	0.376	1643	1182.96	85.43	0.51	0.00051	2.61E-13	8.14E-15
C13	240	0.376	1643	1182.96	85.43	0.56	0.00056	3.80E-13	1.18E-14

Notation	k – Archard wear coefficient x10 ⁻¹⁵
A0	1.37
A1	2.93
A11	1.07
A12	2.39
A13	7.16
B1	47.1
B11	4.23
B12	5.73
B13	9.80
C1	1.50
C11	5.51
C12	8.14
C13	11.8

The purpose of these hardness tests was to establish connections between the mechanical properties of this material and wear resistance. Leeb hardness data (a quick test with a handheld device, directly per piece) and wear resistance data were statistically processed using the Jandel Scientific program, to establish a mathematical model describing the link between the Archard coefficient and the Leeb hardness.



Rank 5 Eqn 1 $y=a+bx$

r^2 Coef Det	DF Adj r^2	Fit Std Err	F-value
0.9356925097	0.9214019563	14.223318536	145.50288080

Parm	Value	Std Error	t-value	95% Confidence Limits	P > t
a	436.4925172	7.369981667	59.22572632	420.0711747	452.9138597
b	-15.4825272	1.283530094	-12.0624575	-18.3424105	-12.6226439

Area Xmin-Xmax	Area Precision
3614.5341385	6.143104e-20

Function min	X-Value	Function max	X-Value
253.79869620	11.800000000	419.92618251	1.0700019765
1st Deriv min	X-Value	1st Deriv max	X-Value
-15.48252721	3.0014033945	-15.48252721	1.0700019765
2nd Deriv min	X-Value	2nd Deriv max	X-Value
0.0000000000	3.0014033945	0.0000000000	1.0700019765

Soln Vector	Covar Matrix				
Direct	LUDecomp				
r^2 Coef Det	DF Adj r^2	Fit Std Err	Max Abs Err		
0.9356925097	0.9214019563	14.223318536	21.871287488		
Source	Sum of Squares	DF	Mean Square	F Statistic	P>F
Regr	29435.639	1	29435.639	145.503	0.0000
Error	2023.0279	10	202.30279		
Total	31458.667	11			

Figure 4.12. The graph of the mathematical model between the Archard coefficient and the Leeb hardness.

4.2. Elaboration of AA6063/ZrB₂composites

4.2.1. Raw materials and materials

The proposed procedure for the second experiment is the in-situ aluminothermic reaction between the 6063 aluminium alloy melt, which has matrix function, potassium hexafluorozirconate (K₂ZrF₆) and potassium tetrafluoroborate (KBF₄) for the formation of ZrB₂, in the presence of cryolite (Na₃AlF₆) to avoid the formation of aluminium oxide barriers (Al₂O₃).

The materials were obtained using a new experimental installation (Figure 4.13) for centrifugal casting of metal matrix composites and are based on the same operating principle as the installation used in the first experimental part, the exception being that interchangeable graphite crucibles with different shapes and walls of different thicknesses can be used in the new installation. Figure 4.13

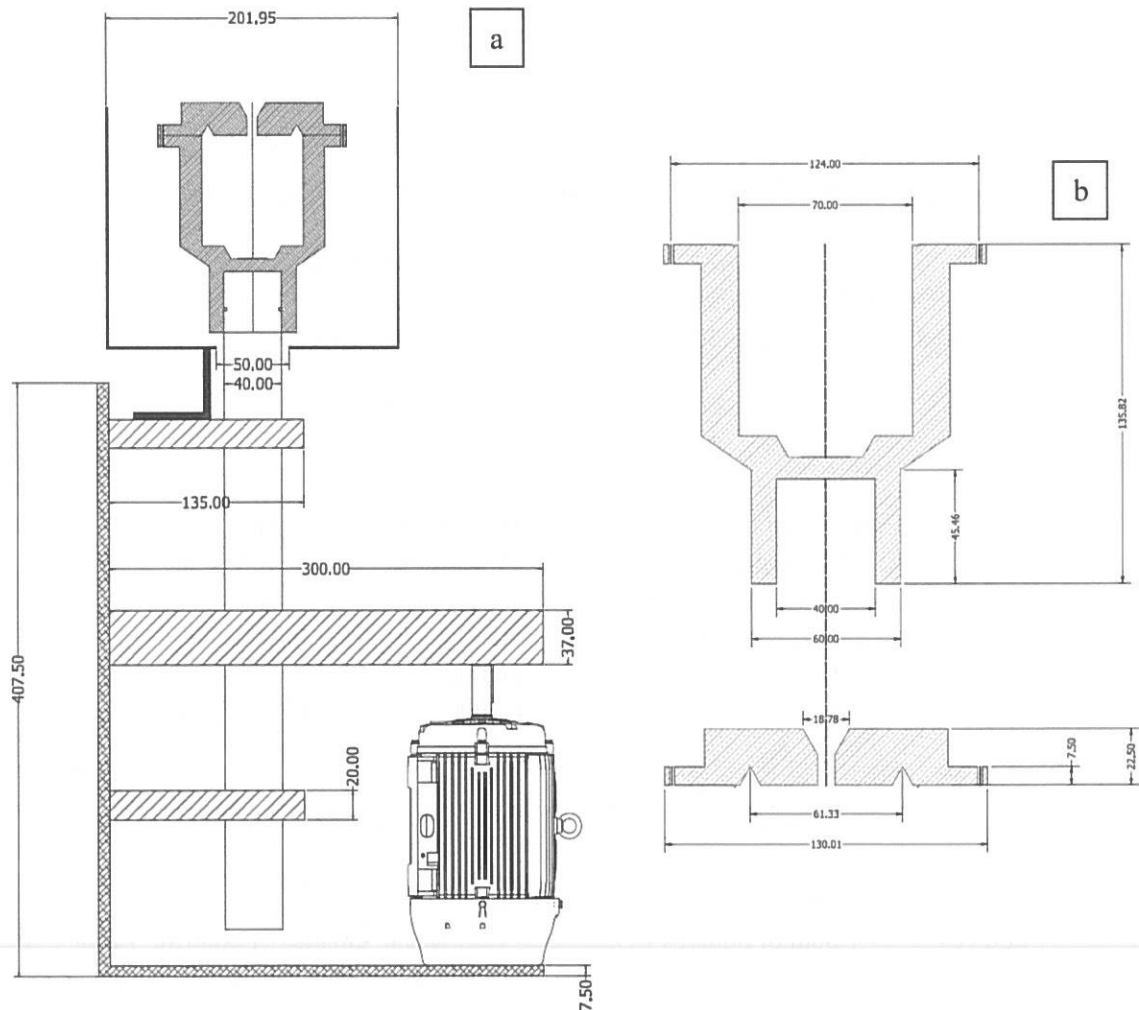


Figure 4.13. The overall scheme of the new experimental installation (a) and the mould with cap (b)

4.2.2. Method of preliminary research and experimentation

Starting from the optimized parameters of obtaining materials with aluminium matrix and ZrB₂ reinforcement particles we achieved, by centrifuged solidification, composite materials with layers with different particle concentrations (Table Table 4.5).

Table 4.5. Composites studied

Composition of the material	Notation	Stirring time, min	The solidification starting temperature of composite, °C
200 g alloy 6063 + 12.5g K ₂ ZrF ₆ + 12.5g KBF ₄	A	2	660
200 g alloy 6063 + 25g K ₂ ZrF ₆ + 25g KBF ₄	B	2	
200 g alloy 6063 + 35g K ₂ ZrF ₆ + 35g KBF ₄	C	2	
200 g alloy 6063 + 50g K ₂ ZrF ₆ + 50g KBF ₄	D	2	

Table 4.6. Physical properties of zirconium diboride [36]

IUPAC name	Theoretical chemical formula, [CASRN]	Crystallographic system / Pearson symbol/ Space group/ Prototype / Structure parameters	Density (ρ, kgm ⁻³)	Electrical resistance (ρ, μΩ cm)	Melting point (°C)	Thermal conductivity (k.Wm ⁻¹ K ⁻¹)	Specific heat capacity (c _p , J kg ⁻¹ K ⁻¹)	Linear thermal expansion coefficient (α, 10 ⁻⁶ K ⁻¹)
Zirconium diboride	ZrB ₂ [12045-64-6]	Hexagonal a = 316.9 pm c = 353.0 pm C32, hP3, P6/mmm, AlB ₂ tip (Z = 1)	6085	9.2	3060-3245	57.9	392.54	5.5-8.3
Young's modulus (E, Gpa)	Flexural strength Kt, Mpa)	Vickers Hardness HV	Other physicochemical properties, corrosion resistance and uses					IUPAC name
343-506	305	1900-3400	Gray metallic crystals, excellent thermal-shock resistance, greatest oxidation inertness of all refractory hard metals. Hot-pressed material is used in crucibles for handling molten metals such as Zn, Mg, Fe, Cu, Zn, Cd, Sn, Pb, Rb, Bi, Cr, brass, carbon steel, and cast iron, and also molten cryolite, yttria, zirconia, and alumina. It is readily corroded by liquid metals such as Si, Cr, Mn, Co, Ni, Nb, Mo, and Ta, and attacked by molten salts such as Na ₂ O, alkali carbonates, and NaOH. Severe oxidation in air occurs above 1100–1400 °C. Stable above 2000 °C under inert or reducing atmosphere.					Zirconium diboride

Load calculation

The quantities of K₂ZrF₆ and KBF₄ were calculated according to the reaction below, for the determination of the salt requirements for the production of boron-containing composites in quantities of 5, 10, 15, 20 g of ZrB₂, per 200 g alloy used:



Starting from the capacity of the crucible it was established that for good preparation of in-situ composites to use a quantity of 200 g aluminium alloy.

4.2.3. Experimental results and discussions

Following the experiments, cylindrical samples were obtained with $\phi_M = 60$ mm $\phi_m = 30$ mm, $h = 65$ mm, middle thickness 30mm, top thickness 5 mm as seen in Figure 4.14, where ϕ_M represents the large diameter, ϕ_m the small diameter and h height.

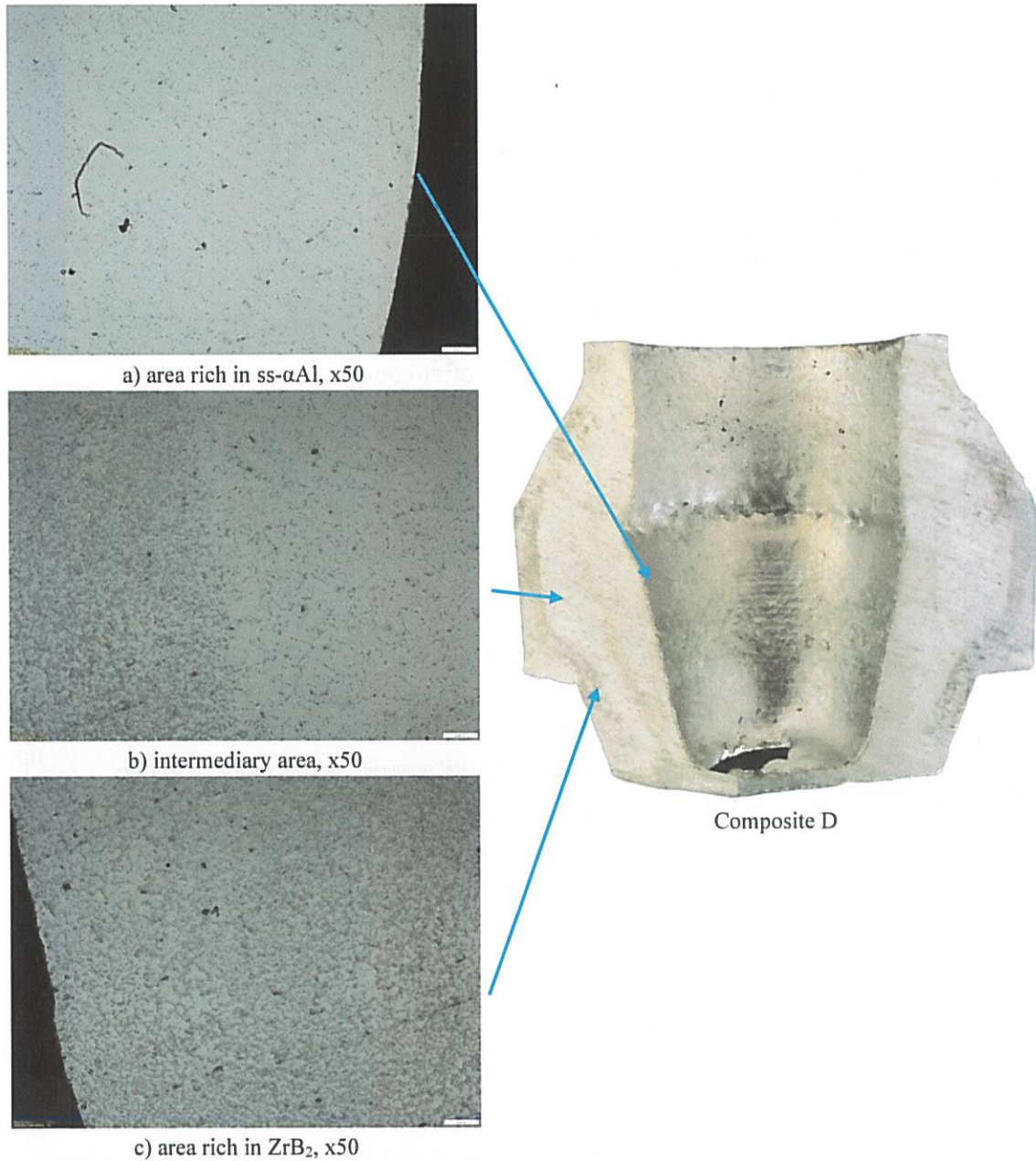


Figure 4.14. Layer analysis of composite D

Analyses similar to those in the first experiment were carried out from samples developed for the determination of optical macrostructures and microstructures (Figure 4.15), electron microscopy and EDS (Figure 4.16), XRD (Figure 4.17), DSC (Figure 4.18), distribution of sizes by volume (Figure 4.19), Vickers microhardness (Figure 4.20)Figure 4.15Figure 4.16Figure 4.17Figure 4.18Figure 4.19Figure 4.20.

Composite A

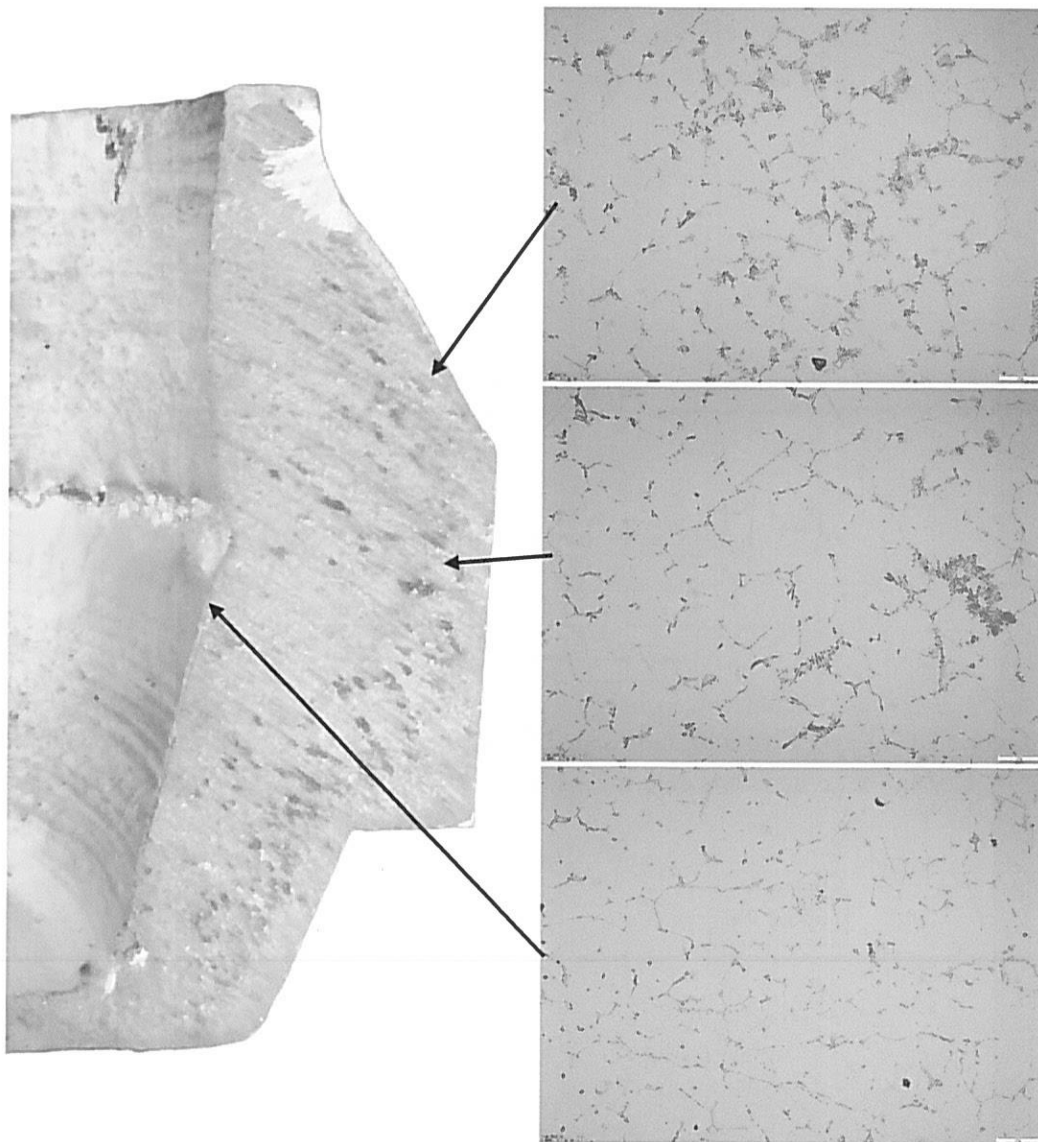
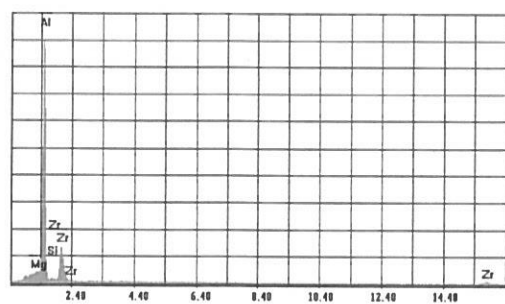
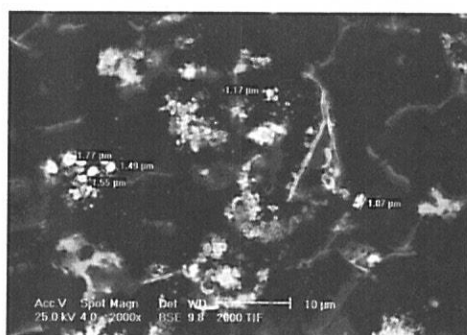


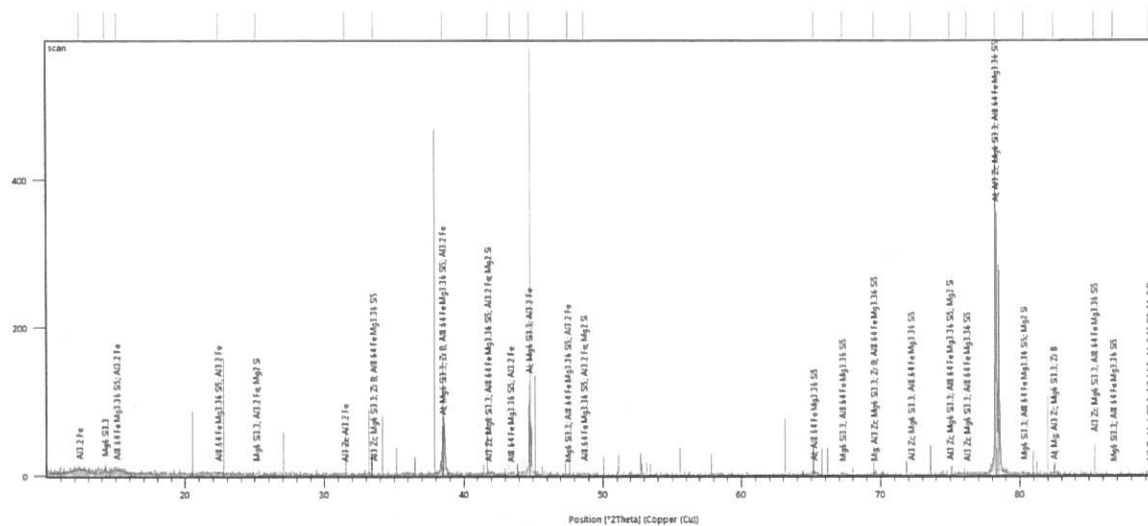
Figure 4.15. Microstructure and macrostructure of composite A



Agglomerated particles

Al – 65.86%
Zr – 31.87%
Mg – 2.27%

Figure 4.16. Analysis by electron microscopy and analysis of EDS with the chemical composition



Element/compound	Crystallite Size
Al	54.76 nm
ZrB ₂	39.39 nm
ZrAl ₃	2315.43 nm

Figure 4.17. Layer diffractogram with 2.5% of ZrB_2 content and compositional analysis. Crystallite dimensions determined by calculation with Debye-Scherrer formula

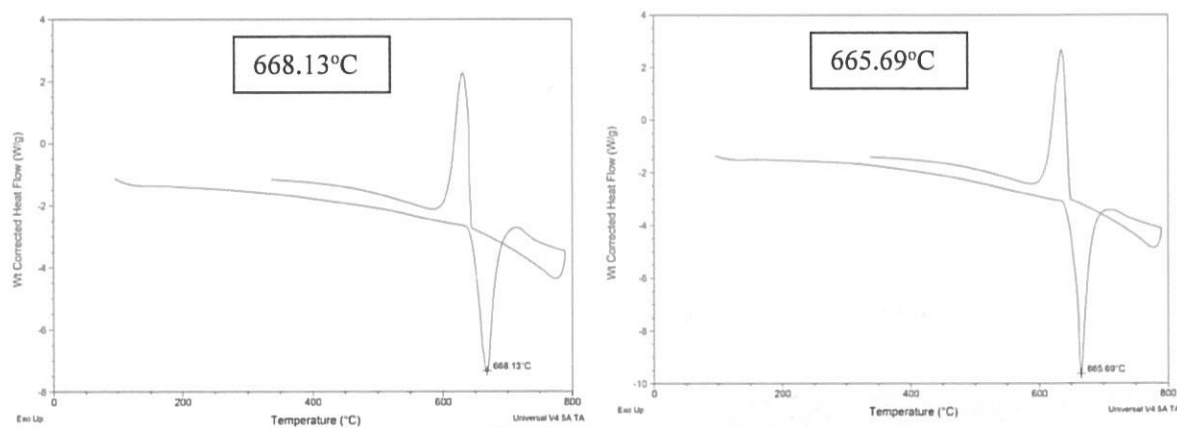


Figure 4.18. DSC analysis of the layer with high ZrB₂ content (left) and lower ZrB₂ content (right)

Results Table

Size d.nm	Intensity %	Size d.nm	Intensity %
0.4000	0.0	68.06	0.0
0.4632	0.0	78.82	0.0
0.5365	0.0	91.28	0.0
0.6213	0.0	105.7	0.0
0.7195	0.0	122.4	0.0
0.8332	0.0	141.8	0.0
0.9649	0.0	164.2	0.0
1.117	0.0	190.1	0.0
1.294	0.0	220.2	0.0
1.499	0.0	255.0	0.0
1.736	0.0	295.3	0.0
2.010	0.0	342.0	0.0
2.328	0.0	396.1	11.7
2.696	0.0	458.7	31.8
3.122	0.0	531.2	36.8
3.615	0.0	615.1	19.7
4.187	0.0	712.4	0.0
4.849	0.0	825.0	0.0
5.615	0.0	955.4	0.0
6.503	0.0	1106	0.0
7.531	0.0	1281	0.0
8.721	0.0	1484	0.0
10.10	0.0	1718	0.0
11.70	0.0	1990	0.0
13.54	0.0	2305	0.0
15.69	0.0	2669	0.0
18.17	0.0	3091	0.0
21.04	0.0	3580	0.0
24.36	0.0	4145	0.0
28.21	0.0	4801	0.0
32.67	0.0	5560	0.0
37.84	0.0	6439	0.0
43.82	0.0	7456	0.0
50.75	0.0	8635	0.0
58.77	0.0	1.000e4	0.0

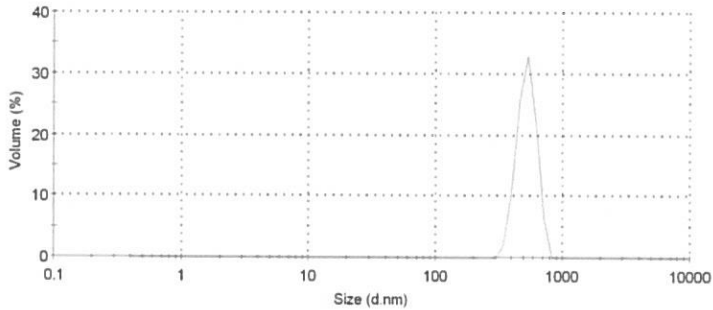
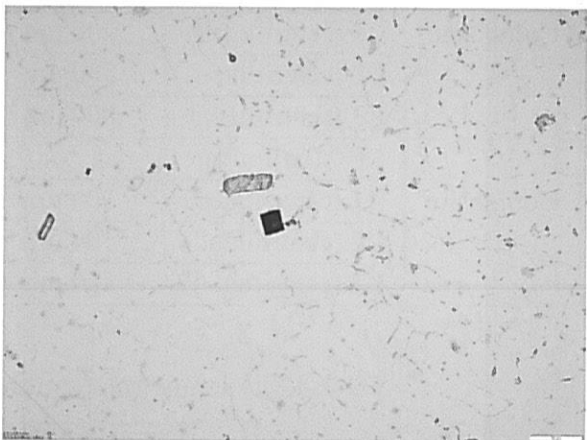
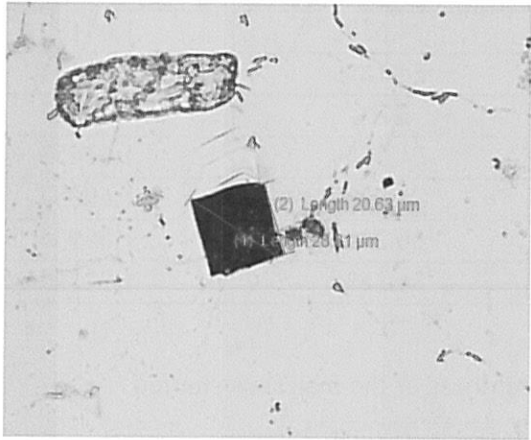


Figure 4.19. Distribution of sizes by volume for sample A

AS 214 HV_{0.01}



AS 214 HV_{0.01}

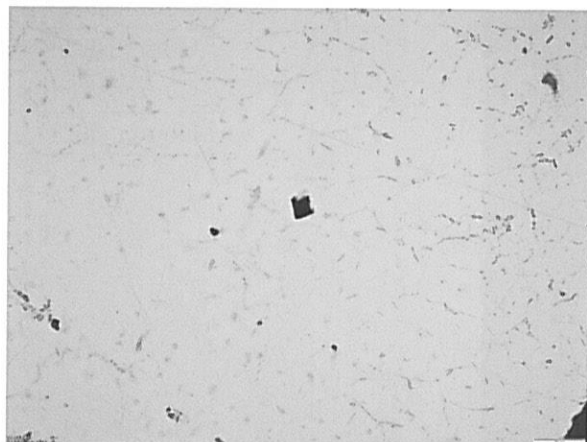
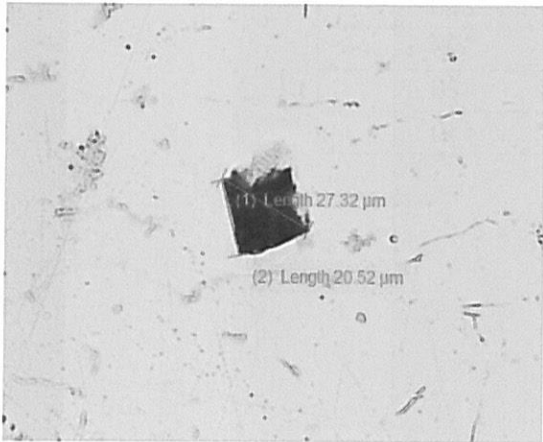


Figure 4.20. Microhardness HV_{0.01} for sample A

Compositional influence of the layer on wear resistance

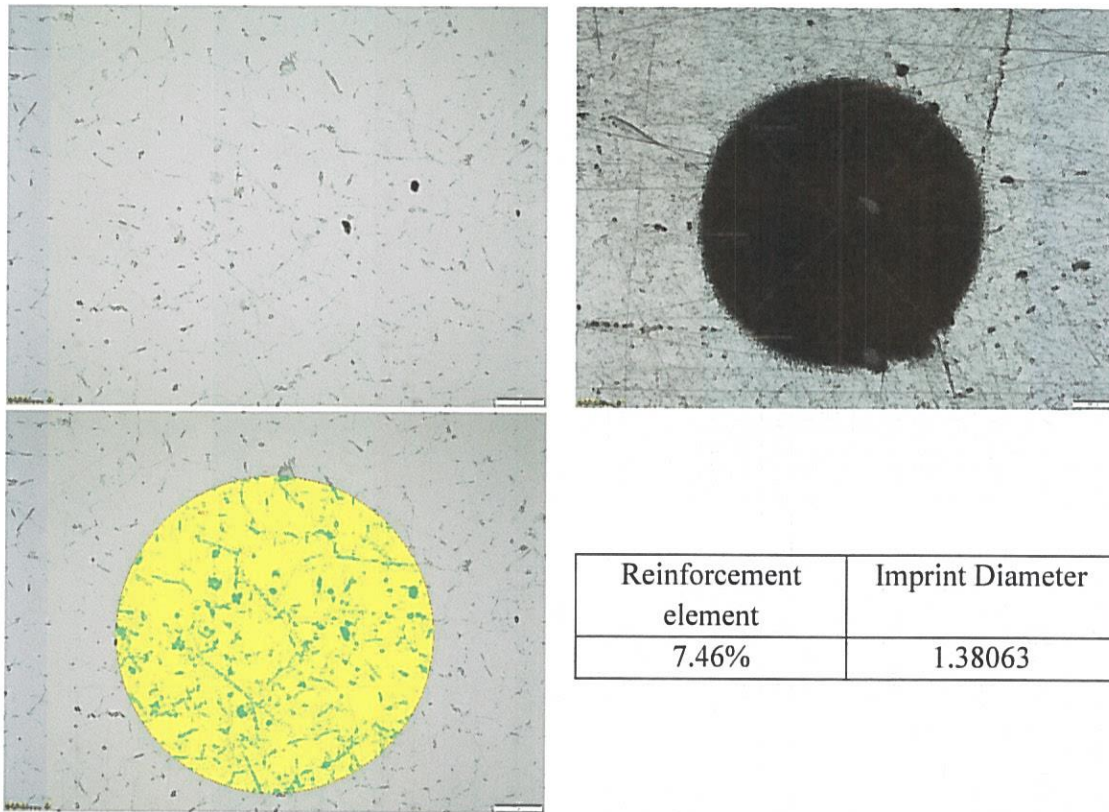
Samples for the determination of wear resistance were taken from the materials obtained. Composite materials with uniform distribution of reinforcement elements as well as those obtained by centrifugal solidification were tested. Also, to make a more accurate assessment of the characteristics of the layers obtained, samples were prepared at different depths, i.e. at 200µm, 500µm and 800µm, as can be seen in Table Table 4.7.

Table 4.7. Materials used to determine the wear resistance

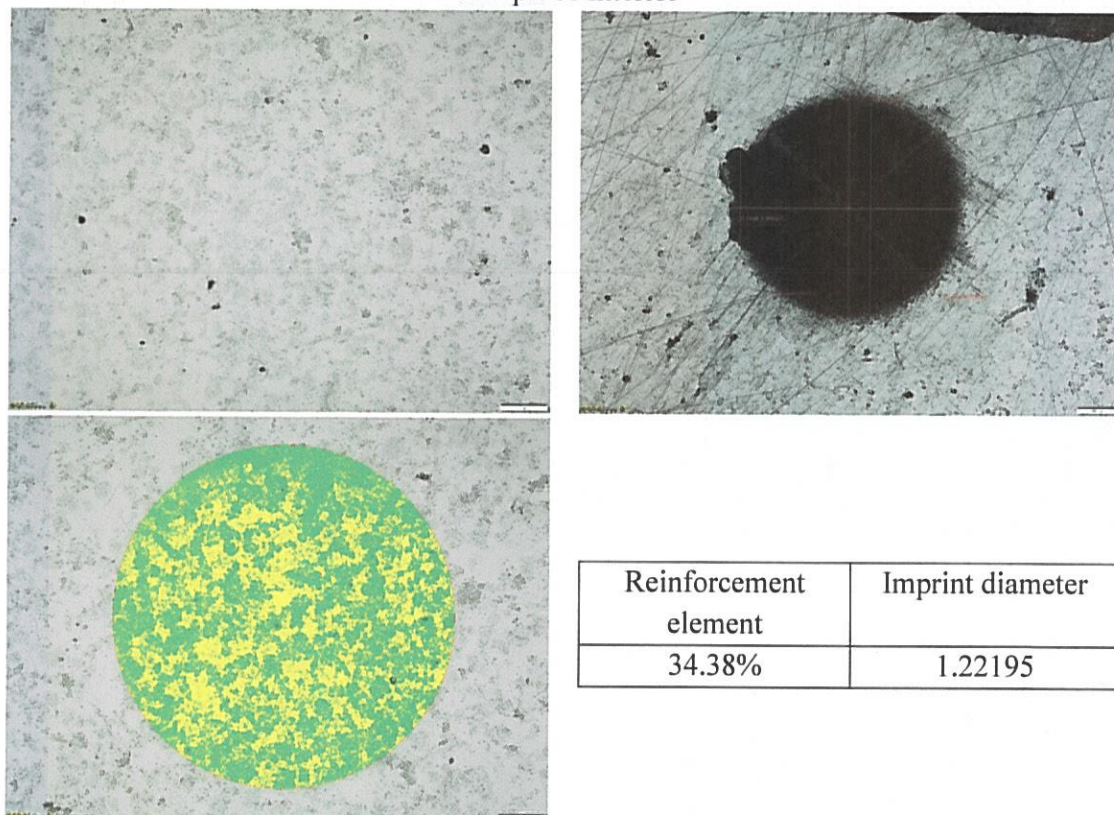
Material	Notation	Layer Depth	Reinforcement elements	Imprint Diameter (mm)
Composite A	A0 (uniform)		5.53%	1.41531
	A1 (centrifuged)	200µm	7.46%	1.38063
	A2 (centrifuged)	500 µm	6.89%	1.35136
	A3(centrifuged)	800 µm	7.23%	1.53827
Composite B	B0 (uniform)		7%	1.45785
	B1 (centrifuged)	200 µm	14.32%	1.41434
	B2 (centrifuged)	500 µm	25.23%	1.19667
	B3 (centrifuged)	800 µm	25%	1.19183
Composite C	C0 (uniform)		15%	1.27717
	C1 (centrifuged)	200 µm	24.62%	1.09180
	C2 (centrifuged)	500 µm	26.18%	1.26454
	C3 (centrifuged)	800 µm	27%	1.47322
Composite D	D0 (uniform)		21.56%	1.61453
	D1 (centrifuged)	200 µm	24.23%	1.69087
	D2 (centrifuged)	500 µm	36.23%	1.55933
	D3 (centrifuged)	800 µm	34.38%	1.22195

Table 4.8. Average values of the hardness of the materials studied

Material	Hardness value, HL
Alloy 6063	235
Composite A	280
Composite B	390
Composite C	420
Composite D	430



Sample A Interior



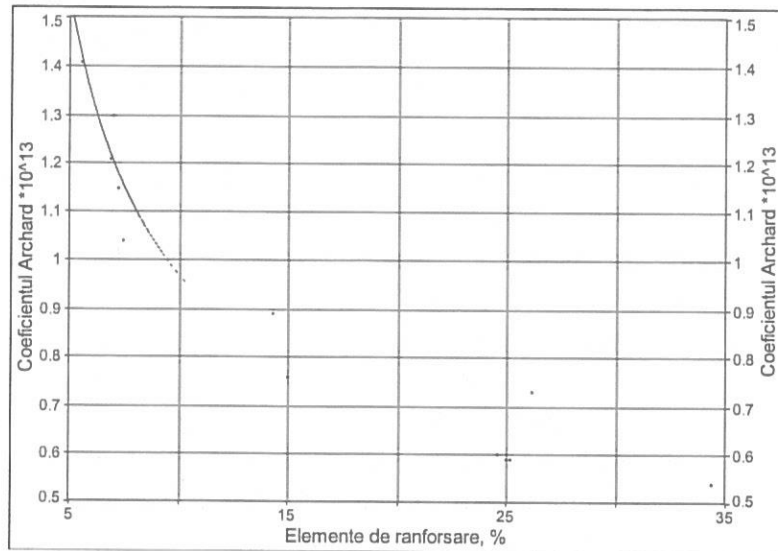
Sample D Medium

Figure 4.21. Microstructure, phase analysis and diameter of the test results at wear – Low concentration of reinforcement elements (A Interior), increased concentration of reinforcement elements (D Exterior)

Table 4.9. The values measured and calculated for the determination of the Archard coefficient for reinforced composite with ZrB₂

Notation	F Press [N]	F Ball Press [N]	Time [s]	Nr. ball cycles	L sliding (m)	Imprint Diameter (mm)	Crater (m)	Removed volume (m ³)	k - Archard wear coefficient
A0	0.39	0.70	900	4842	349.7	1.415313	0.001415313	1.57569E-11	1.15534E-13
A1	0.39	0.73	900	4842	349.7	1.38063	0.00138063	1.42682E-11	1.04619E-13
A2	0.39	0.84	900	4842	349.7	1.351363	0.001351363	1.30963E-11	9.60258E-14
A3	0.39	0.71	900	4842	349.7	1.53827	0.00153827	2.19882E-11	1.61224E-13
B0	0.38	0.67	900	4842	349.7	1.4578	0.0014578	1.77358E-11	1.30044E-13
B1	0.39	0.86	900	4842	349.7	1.414348	0.001414348	1.57139E-11	1.15219E-13
B2	0.39	0.76	900	4842	349.7	1.1966	0.0011966	8.05111E-12	5.90331E-14
B3	0.39	0.67	900	4842	349.7	1.191837	0.001191837	7.92369E-12	5.80988E-14
C0	0.38	0.92	900	4842	349.7	1.27717	0.00127717	1.04485E-11	7.66116E-14
C1	0.39	0.71	900	4842	349.7	1.091808	0.001091808	5.58014E-12	4.09152E-14
C2	0.39	0.74	900	4842	349.7	1.264548	0.001264548	1.00416E-11	7.36276E-14
C3	0.39	0.72	900	4842	349.7	1.473223	0.001473223	1.84984E-11	1.35636E-13
D0	0.39	0.64	900	4842	349.7	1.61453	0.00161453	2.66836E-11	1.95652E-13
D1	0.39	0.64	900	4842	349.7	1.690873	0.001690873	3.20999E-11	2.35366E-13
D2	0.39	0.76	900	4842	349.7	1.55933	0.00155933	2.32173E-11	1.70236E-13
D3	0.39	0.68	900	4842	349.7	1.221953	0.001221953	8.75544E-12	6.41974E-14

Notation	k - Archard wear coefficient, x10 ¹³
A0	1.15
A1	1.04
A2	0.96
A3	1.61
B0	1.30
B1	1.15
B2	0.59
B3	0.58
C0	0.76
C1	0.40
C2	0.73
C3	1.35
D0	1.95
D1	2.35
D2	1.70
D3	0.64



Rank 6 Eqn 36 $\ln y = a + b/x^{0.5}$

r^2 Coef Det DF Adj r^2 Fit Std Err F-value
0.9530885175 0.9426637436 0.0704732542 203.16742655

Parm	Value	StdError	t-value	95% Confidence Limits	P > t
a	-1.14520274	0.092684880	-12.3558745	-1.35171753	-0.93868796
b	3.516455268	0.266456197	13.19712321	2.922753862	4.110156674

Area Xmin-Xmax Area Precision
22.197924793 3.602511e-12

Function min	X-Value	Function max	X-Value
0.5795648400	34.380000000	1.4192733410	5.5300083826
1st Deriv min	X-Value	1st Deriv max	X-Value
-0.191890053	5.5300083826	-0.005054967	34.380000000
2nd Deriv min	X-Value	2nd Deriv max	X-Value
0.0002646377	34.380000000	0.0779937803	5.5300083826

Soln Vector	Covar Matrix				
Direct	LUDecomp				
r^2 Coef Det	DF Adj r^2	Fit Std Err	Max Abs Err		
0.9530885175	0.9426637436	0.0704732542	0.1128798197		
Source	Sum of Squares	DF	Mean Square	F Statistic	P > F
Regr	1.0090269	1	1.0090269	203.167	0.00000
Error	0.049664796	10	0.0049664796		
Total	1.0586917	11			

Figure 4.22. The graph of the mathematical model between the Archard coefficient and the percentage of reinforcement elements.

Chapter 5. Summary of the author's main scientific and technical contributions

The new generation of internal combustion engines and other similar low-noxious equipment has required the development and construction of materials with special, wear-resistant properties. This category also includes metal matrix composites reinforced with radially arranged ceramic particles made within the thesis. To this end, the author started from the current centrifuged moulded materials and designed an original casting process.

The author designed a casting installation with a vertical rotating mould. This resulted in an original material with a controlled radial distribution of ceramic particles that reinforce the structure of the aluminium metal matrix. By controlling the distribution of ceramic particles in the aluminium melt, materials useful to various applications in aerospace, biomedical, automotive, defence, energy, navy, optoelectronics, etc. can be obtained.

The original manufacturing process developed in the work can be summarised as follows: the installation can accept an interchangeable negative graphite mould with variable geometry to obtain parts of different shapes and walls of different thicknesses. This solution was achieved through modelling, simulation, multiparametric and multi-physical optimization, resulting in a detailed comparison between different composite materials with the metal matrix.

Metallic matrix composites consist of a ceramic reinforcement phase embedded in a metal matrix that can offer advantageous properties compared to base metal alloys. These include improvement of physical, elastic, mechanical and thermal characteristics (mass, volumetric, density, thermal conductivity, thermal deformation factor, specific heat, longitudinal and transverse elasticity modules/shear, volumetric elasticity modules, transverse contraction coefficients, mechanical tensile or compression resistance).

The application areas of the study are very varied, but they require various types of distributions of alloy components. Of these, the author has thoroughly studied the mechanism of obtaining materials with a functional gradient using composites with metal matrix aluminium 6xxx series. Thus, composite materials with a functional gradient containing reinforcing particles have been obtained, the volume fraction of which varies continuously, thus creating an uneven microstructure with variable properties favourable to different applications.

Functionally graded materials (FGM) are often developed with a specific spatial distribution of constituent phases, such as metals, ceramics and polymers with a continuous and subtle variation in composition. Fundamental research and recent applications have demonstrated that the incorporation of compositional gradients into multi-layered structures can be beneficial.

FGMs made in this centrifuged casting sentence allow variable properties to be obtained in concentric layers with variable concentration of ceramic particles, which cannot be made inhomogeneous materials. The composition gradient is obtained by the difference in density between the molten metal and the solid particles. The movement of particles from a viscous liquid under a centrifugal force is subject to Stokes' law.

Aluminium metal matrix composites (AA6060 and AA6063) reinforced with ceramic particles (TiB₂ and ZrB₂) were developed using the in-situ technique. The paper presents the different methods of drawing up metal matrix composites (CMM) with functional gradient such as the technique of chemical deposition from the vapour state, powder metallurgy and the centrifuged method, etc.

The in-situ method studied by the author is based on the aluminothermic reaction of salts (KBF₄, K₂TiF₆, K₂ZrF₆) with the metal aluminium melt in the presence of cryolite (Na₃AlF₆), thus forming the ceramic reinforcement particles. The interaction reactions between the metal melt and the salts were studied in detail.

The author also investigated the influence of different process parameters on the viscosity of the melt, the ratio of particle segregation (k), particle distributions involving particle size and the volume fraction of the particles of TiB₂, ZrB₂, TiAl₃, Mg₂Si, ZrAl₃.

The major advantage of FGMs, unlike other composites, is the production of adapted morphologies and structural properties, such as the physical and mechanical gradient in a specific direction.

The cross-sections of the centrifuged cast samples were metallographically processed (cut, polished and polished) to observe particle segregation. From the macroscopic analysis, the particles have a different distribution in two areas: in the inner layer there is a low concentration of reinforcing particles, and in the outer layer there is a crowding of the reinforcing particles. Subsequently, by analysing the layers by optical microscopy, a gradual distribution of the reinforcement elements in the radial direction was found.

The microstructures of the samples in the two experiments were determined by optical and electronic microscopy. The particle volume fractions in functional gradient materials were measured directly from microstructures using image processing software called Olympus Stream.

The use of different concentrations of salts in the presence of cryolite led to an optimal structure of the castings. This was confirmed using the XRD and EDS analysis of composites AA6060/TiB₂ and AA6063/ZrB₂. Thus, the formation of the ceramic particles TiB₂ and ZrB₂ which occur as a result of the aluminothermic reduction reaction of the salts K₂TiF₆, K₂ZrF₆, and KBF₄ in the presence of cryolite (Na₃AlF₆).

Chapter 6. Conclusions and subsequent research directions

This work led to the creation of new materials with controllable properties in the radial direction. The following results of the thesis may be considered as original:

- Extensive documentary study on composite materials - their classification according to the basic matrix, the reinforcement elements.
- Documentary study on the structure and properties of composite materials compared to the structure and properties of classical metal materials.
- Extensive documentary study on functionally graded materials: types of such materials, areas of use.
- Experimental studies and research on methods of obtaining materials with functional gradient: analysis of ternary and quaternary systems for the prediction of intermetallic compounds possible to obtain; the influence of certain alloying elements on certain characteristics/properties of the composites obtained; the influence of intermetallic compounds and volume fractions of ceramic particles and alloying elements on the relative viscosity of the melt during centrifugal casting.
- Study of the thermodynamics of phenomena that occur in the AA6060 - K₂TiF₆ - KBF₄ system during the aluminothermic reaction.
- Study of the thermodynamics of phenomena that occur in the AA6063 - K₂ZrF₆ - KBF₄ system during the aluminothermic reaction.
- Establishing the conditions for obtaining parts by centrifugal casting according to temperature, speed, viscosity and solidification speed for composites in the AA6060 - K₂TiF₆ - KBF₄ system.
- Microstructural characterization of AA6060/TiB₂ composite materials by optical and electronic microscopy.
- Characterization of the composites that were obtained in-situ by X-ray diffraction (XRD) and energy dispersion spectroscopy (EDS) for different phases formed.
- Calculation of the crystallite dimensions of compounds formed by aluminothermic reaction in the system AA6060 - K₂TiF₆ - KBF₄, using the Debye-Scherrer formula.
- TEM analysis of the TiB₂ compound for examination of structure, composition and properties in detail.
- Determination by differential scanning calorimetry of fusion and crystallization temperatures, as well as transition temperatures for layers with different concentration of reinforcing particles, for the AA6060 - K₂TiF₆ - KBF₄ system.
- Analysis of granulometric distribution by volume for different concentrations of reinforcing particles, AA6060 - K₂TiF₆ - KBF₄. To highlight these particles, a AA6060/TiB₂ composite sample was solubilized in concentrated hydrochloric acid, washed several times with distilled water, and the resulting powder was dried in a drying stove and then the dimensional analysis of the TiB₂ particles was carried out using Malvern's Zetasizer Nano ZS analyzer.
- Vickers microhardness in different areas of the functionally graded materials reinforced with TiB₂ ceramic particles.

- Influence of particle distribution on wear resistance for TiB₂ depending on layer depth. Composite materials with uniform distribution of reinforcing elements as well as those obtained by centrifugal solidification were tested.
- Leeb hardness in different areas of the functionally graded materials reinforced with TiB₂ ceramic particles.
- Making a mathematical model that establishes the link between abrasive wear resistance and mechanical properties of AA6060/TiB₂ composite materials, using the ratio of the Archard coefficient to Leeb hardness.
- Construction of an original installation for centrifugal casting of composites to produce functionally graded materials.
- Microstructural characterization of AA6063/ZrB₂ composite materials by optical and electronic microscopy.
- Establishing the conditions for obtaining parts by centrifugal casting according to temperature, speed, viscosity and solidification speed for composites in the system AA6063 - K₂ZrF₆ - KBF₄.
- Characterization of in-situ obtained composites by X-ray diffraction (XRD) and energy dispersion spectroscopy (EDS) for different phases formed.
- Calculation of the crystallite dimensions of compounds formed by aluminothermic reaction in the system AA6063 - K₂ZrF₆ - KBF₄, using the Debye-Scherrer formula.
- Determination by differential scanning calorimetry of fusion and crystallization temperatures, as well as transition temperatures for layers with different concentration of reinforcing particles, for the system AA6063 - K₂ZrF₆ - KBF₄.
- Analysis of granulometric distribution by volume for different concentrations of reinforcing particles, AA6063 - K₂ZrF₆ - KBF₄.
- Vickers microhardness in different areas of the functionally graded materials reinforced with ZrB₂ ceramic particles.
- Influence of particle distribution on wear resistance for ZrB₂ depending on layer depth. Composite materials with uniform distribution of reinforcing elements as well as those obtained by centrifugal solidification were tested.
- Leeb hardness in different areas of the functionally graded materials reinforced with ZrB₂ ceramic particles.
- Making a mathematical model that establishes the link between abrasive wear resistance and mechanical properties of AA6063/ZrB₂ composite materials, using the ratio of the Archard coefficient to Leeb hardness.

Future Research Directions

1. Analysis of physical-mechanical behaviour, completion of mechanical testing.
2. Mathematical determination and modelling of other correlations such as tensile strength or elasticity module and some material constants.

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