SYNTHESIS OF NOVEL AA7075 COMPOSITE MATERIALS, REINFORCED IN-SITU WITH TiB_2, FOR SPECIAL APPLICATIONS

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Metal matrix composites were synthesized by integrating an aluminium matrix with a high concentration of TiB_2 particulates via the in-situ casting method. The objective was to produce composites with significant proportions of TiB_2. To obtain these composites, the molten mixture underwent treatment while in a liquid state to eliminate undesired reaction compounds, thereby refining the final structure. The synthesized samples were characterized using optical and electron microscopy techniques, such as SEM and EDS analysis with Mapping, enabling observation and identification of different phases. Additionally, the mechanical properties were evaluated through rigorous testing, providing valuable insights into their performance.

Keywords: titanium diboride, metal matrix composites, SEM, EDS, Mapping, compressive test, tensile test

1. Introduction

The development of metal matrix composites (MMC) with reinforcing elements such as titanium diboride (TiB_2) has received increasing attention in recent years due to their superior mechanical and physical properties. The addition of TiB_2 to the metal matrix can significantly enhance the mechanical properties of the composite material, including its strength, stiffness, and hardness. TiB_2 can also improve the thermal and electrical conductivity of the composite material, making it suitable for a range of high-performance applications. Several techniques can be used to manufacture TiB_2-reinforced metal matrix composites such as powder metallurgy, in-situ formation, mechanical alloying, additive manufacturing, casting. [1-4]

In-situ formation is a technique used to form reinforcing elements during the synthesis or processing of an alloy. This technique involves adding appropriate precursors to the molten alloy during the casting process, resulting in the formation of the reinforcing elements in-situ. For instance, TiB_2 or SiC can be formed in-situ during casting. The in-situ formation of reinforcing elements leads to a uniform

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distribution of the particles, which can enhance the mechanical properties of the material. This technique is advantageous as it eliminates the need for additional processing steps and can lead to cost savings.[5]

The process parameters, such as pouring temperature, stirring speed, and stirring time, can be optimized to achieve the desired microstructure and mechanical properties of the composite material. Metal matrices can be selected based on mechanical, tribological, oxidation, and corrosion resistance properties. In general, Al, Ti, Mg, Ni, Cu, Pb, Fe, Ag, Zn, and Sn are used as matrix metals in MMC, with Al, Ti, and Mg being the most common. [6,7].

A wide range of deformable or castable aluminium alloys, or even metallic aluminium in powder or compact form, can be used to produce aluminium matrix composites in situ by aluminothermic reactions. Aluminium and aluminium alloys have a low density (approx. 2.7g/cm^3), low melting temperatures, facilitating liquid phase processing. These matrices are cheap compared to other light alloys, such as Ti-based or Mg-based ones.

Aluminium matrices can be plastically machined and cast by any conventional process, thus aluminium matrix composites can be obtained by casting or deformation methods (forging, rolling, extrusion) similar to those used for alloys. The matrix must be chosen with both the desired properties of the composite material and the processing method in mind. As a result, while matrix alloys of the 7xxx series have better mechanical properties (strength and stiffness) for aerospace applications than alloys of the 2xxx series, the latter are more commonly used. This is due to the fact that 7xxx series alloys degrade easily at the interface with reinforcing elements (ceramics), leading to a decrease in the mechanical characteristics of these composites. Alloys of the 2xxx, 6xxx and 7xxx series are the most commonly used as matrices for MMC, being precipitation hardenable [6]. The 7xxx series alloys (Al-Zn-Mg-Cu) offer high mechanical properties and the 6xxx series alloys (Al-Mg-Si-Cu) have high corrosion resistance in different environments and good processing properties [7]. The main reinforcing elements used in the production of metal matrix composites, their size and the concentration of reinforcing elements are presented by P. Rohatgi, A. Kumar and D. Weiss [7]. To obtain metal matrix composites by the aluminothermic method, different matrix materials can be used: primary aluminium (99.73% Al) [6,7], aluminium powder and aluminium alloys (4xxx, 5xxx, 6xxx, 7xxx series) [6 – 15].

2. Thermodynamics of composite reactions

In the in-situ process, TiB_2 particles are formed in situ by the aluminothermic reduction of potassium hexafluorotitanate (K_2TiF_6) and potassium tetrafluoroborate (KBF_4) with liquid aluminium, according to the reactions below:

$$3K_2TiF_6 + 6KBF_4 + 10Al = 3TiB_2 + 12KF + 10AlF_3 \quad (1)$$

$$3K_2TiF_6 + 6KBF_4 + 10Al = 3TiB_2 + 6AlF_3 + 4K_3AlF_6 \quad (2)$$

Table 1 presents the thermodynamic data of the reactions calculated using the HSC Chemistry 6 program. The data reveals that within the operational temperature range of 650 to 950oC, ΔG exhibits a significantly negative value, suggesting a strong likelihood of reaction occurrence and progression.

For reaction (2) the thermodynamic data are shown in Table 1.

The aluminothermic reduction of salts can take place according to reactions (3) and (4):

$$3K_2TiF_6 + 13Al = 3Al_3Ti + K_3AlF_6 + 3KAlF_4 \quad (3)$$

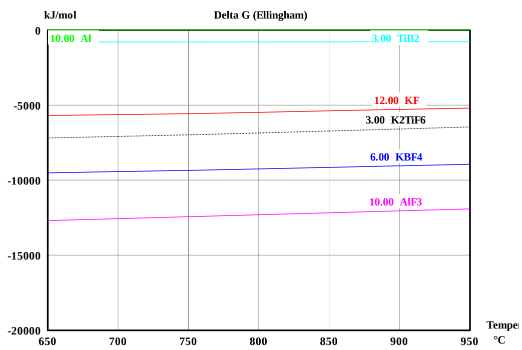
$$2KBF_4 + 3Al = AlB_2 + 2KF + 2AlF_3 \quad (4)$$

The calculated thermodynamic data indicate, in the temperature range 650 - 950°C, the clear possibility of the two reactions taking place, with negative $\Delta G^o{}_T$.

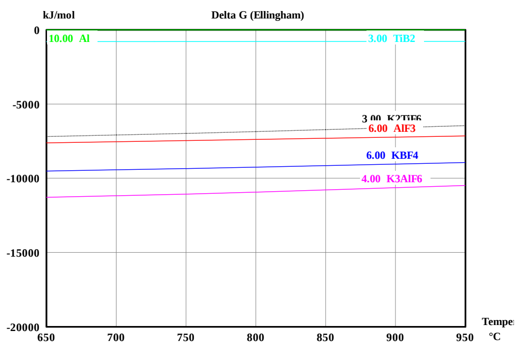
Table 1.

The result of the thermodynamic calculation of the reactions

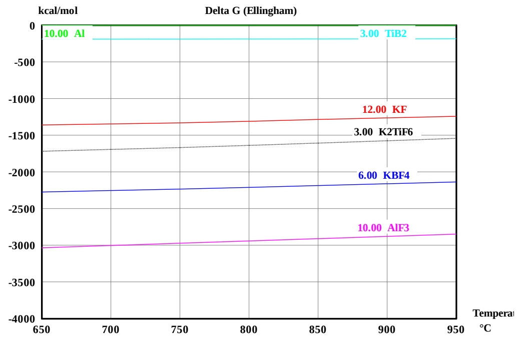
$3K_2TiF_6 + 6KBF_4 + 10Al = 3TiB_2 + 12KF + 10AlF_3$ (1) $3K_2TiF_6 + 6KBF_4 + 10Al = 3TiB_2 + 6AlF_3 + 4K_3AlF_6$ (2) $3K_2TiF_6 + 13Al = 3Al_3Ti + K_3AlF_6 + 3KAlF_4$ (3) $2KBF_4 + 3Al = AlB_2 + 2KF + 2AlF_3$ (4) $3AlB_2 + 3Al_3Ti = 3TiB_2 + 12Al$ (5)					
T, °C	deltaG1, kJ	deltaG2, kJ	deltaG3, kJ	deltaG4, kJ	deltaG5, kJ
650	-2478.794	-2993.017	-1109.300	-1382.049	12.554
700	-2473.964	-2993.492	-1124.036	-1354.303	4.375
750	-2469.632	-2994.665	-1139.094	-1325.286	-5.252
800	-2466.932	-2997.658	-1155.924	-1296.091	-14.917
850	-2465.835	-3002.427	-1174.467	-1266.758	-24.610
900	-2478.787	-3008.936	-1200.909	-1243.559	-34.319
950	-2495.331	-3017.150	-1229.983	-1221.312	-44.035



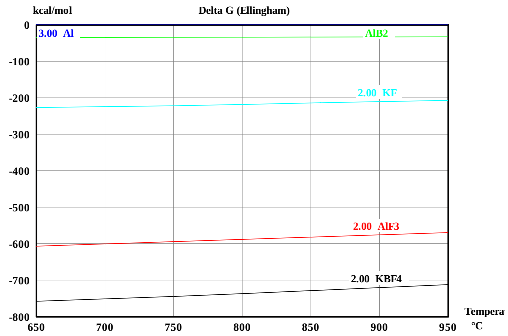
(a)



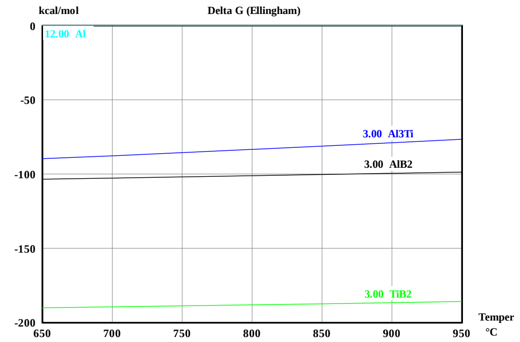
(b)



(c)



(d)



(e)

Fig. 1. Ellingham diagrams ΔG^{o}_{T} = f(T), at TiB_2 formation (a) (reaction 1), TiB_2(b) (reaction 2), $TiAl_3$ (c) (reaction 3), AlB_2 (d) (reaction 4) and the formation of TiB_2 from the reaction of $TiAl_3$ and AlB_2 compounds (e) (reaction 5)

At working temperature, under exothermic reaction heat release conditions, the Al_3Ti and AlB_2 particles resulting from reactions (3) and (4) can react rapidly, resulting in the in-situ formation of the reinforcing compound TiB_2:

$$3AlB_2 + 3Al_3Ti = 3TiB_2 + 12Al \qquad (5)$$

3. Experimental technique

An aluminium alloy from the 7xxx series, namely the AA7075 alloy, was used in the experiments. The standardized chemical composition of this alloy is shown in Table 2.

Table 2

Alloy	Chemical composition, %				
	Cu	Mg	Zn	Al	Others
7075	1.2 - 2,0	2.1 – 2.9	5.1 – 6.1	rest	total < 0.15%
	Si < 0.4%; Fe < 0.5%; Mn < 0.3%; Cr < 0.18 ÷ 0.28%; Zr + Ti < 0.25%				

K_2TiF_6 and KBF_4 salts were used for titanium and boron input. Calculations were made for the amount of TiB_2 reinforcing element in percentage of 20%.

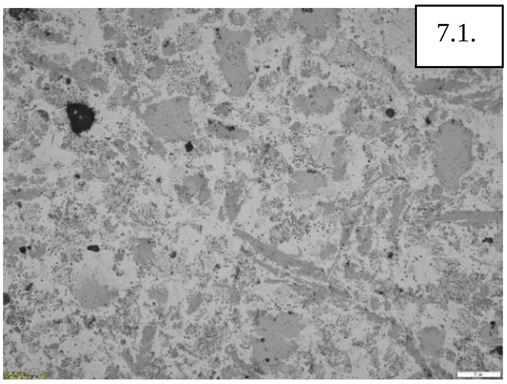
Cryolite (Na_3AlF_6) was used to avoid the formation of an Al_2O_3 film at the separation surface between the molten salts and the 7075 alloy. Samples were taken from the obtained specimens for the compression/tensile test. Samples were also taken for metallographic preparation and optical microscopy analysis.

The samples were microscopically examined using optical (Fig. 2) and electron microscopy (SEM) (Fig. 3), as well as an X-ray spectrum with energy dispersion (EDS) and EDSMapping of the AA7075 / 20% TiB_2 composite for phase observation and identification (Fig. 4 &5).

The samples were imaged using the Olympus BX51M optical microscope with Olympus UC 30 sensor at x200 magnification.

By using optical microscopy, porosities in aluminium metal matrix composites can be observed and analysed. Pores appear as darker or more transparent areas in the image and can be identified by adjusting the focus and illumination. The optical microscope allows the size measurement and evaluation of pore distribution in the composite. Causes of porosities can include gases dissolved in the melt that appear with melt recrystallisation, chemical reactions, inadequate heating and cooling, and impurities in the material. Porosity can adversely affect the properties of the composite, weakening the structure and reducing strength and toughness. Control of porosity is essential and can be achieved through the appropriate choice of manufacturing processes, optimisation of processing parameters and the use of appropriate degassing techniques.

There are two different specimens used in testing labelled 7.1 and 7.2. The specimens labelled 7.1 are samples that were obtained via the usual in-situ casting route. The samples labelled 7.2 are specimens that were further refined.



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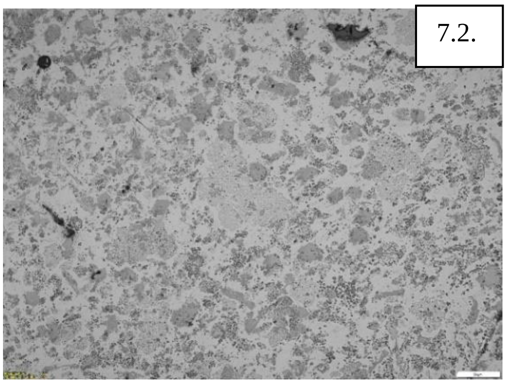

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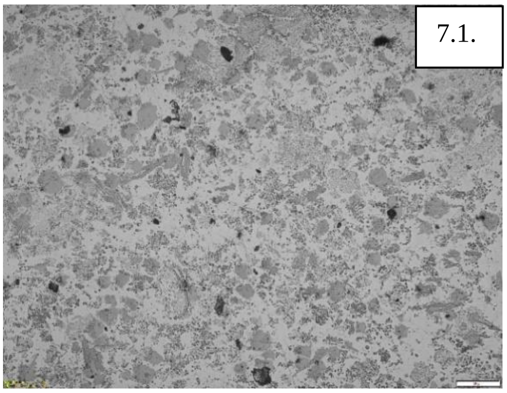

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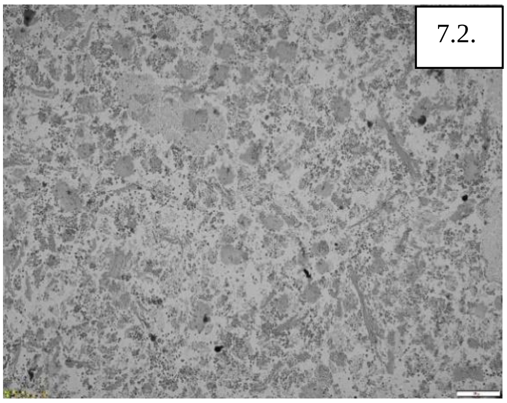


X200

Fig. 2. Optical microscopy analysis of the obtained samples

In order to obtain more detailed images and investigate the surface of samples on a smaller scale, the scanning electron microscope (SEM) was used. SEM uses an electron beam and a detection system to generate high-resolution images of the sample surface.

SEM analysis was performed using the SEM(VEGA II LMU) installation. A fully PC controlled SEM with conventional tungsten heated cathode with maximum resolution 5nm @ 30kV, SE and BSE detectors, low vacuum mode down to 250Pa, motion: X = 80mm-motorized Y = 60mm-motorized Z = 47mm-motorized PG - 6 MHz high-speed pattern generation hardware, 16-bit DAC vector scanning beam deflection, 2 ns scan rate resolution, TTL and 100V lock signal drivers is used for general purpose SEM imaging using secondary electrons (topography) and backscattered electrons (composition) and sub-50nm resolution electron beam lithography.

It provided information on the morphology and surface texture of the composites, as well as the distribution of reinforcing elements. SEM also allowed detailed examination of the interaction between the aluminium matrix and the reinforcing elements at the interface. Thus, it was possible to identify tight bonds and adequate adhesion between the matrix and the reinforcing elements.

The combination of using optical microscopy and scanning electron microscopy (SEM) provided insight into the characteristics and properties of aluminium metal matrix composites. These imaging techniques have facilitated the analysis and evaluation of structure, composition.

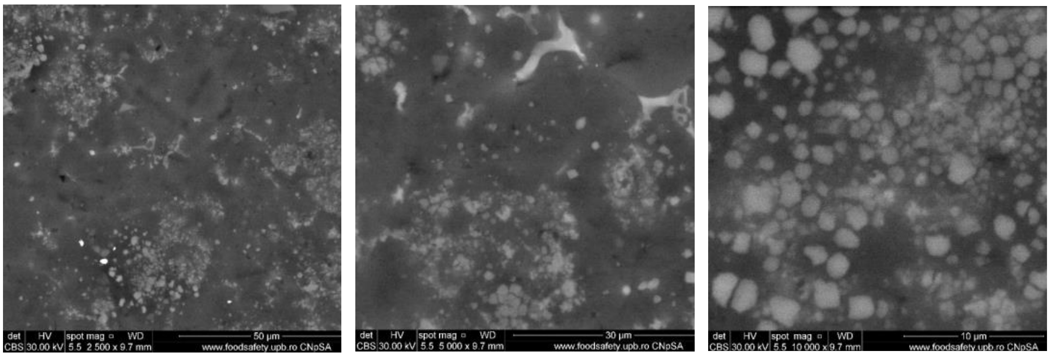
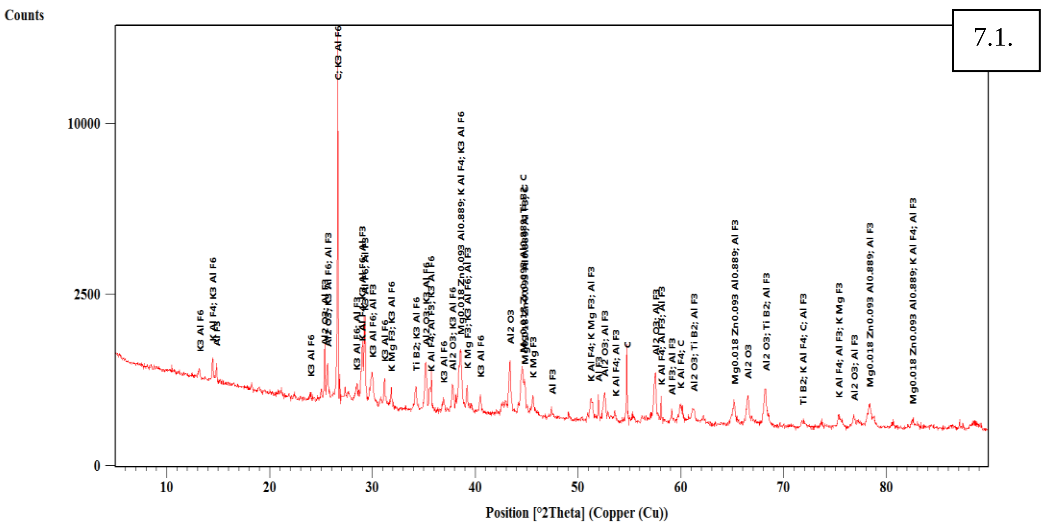
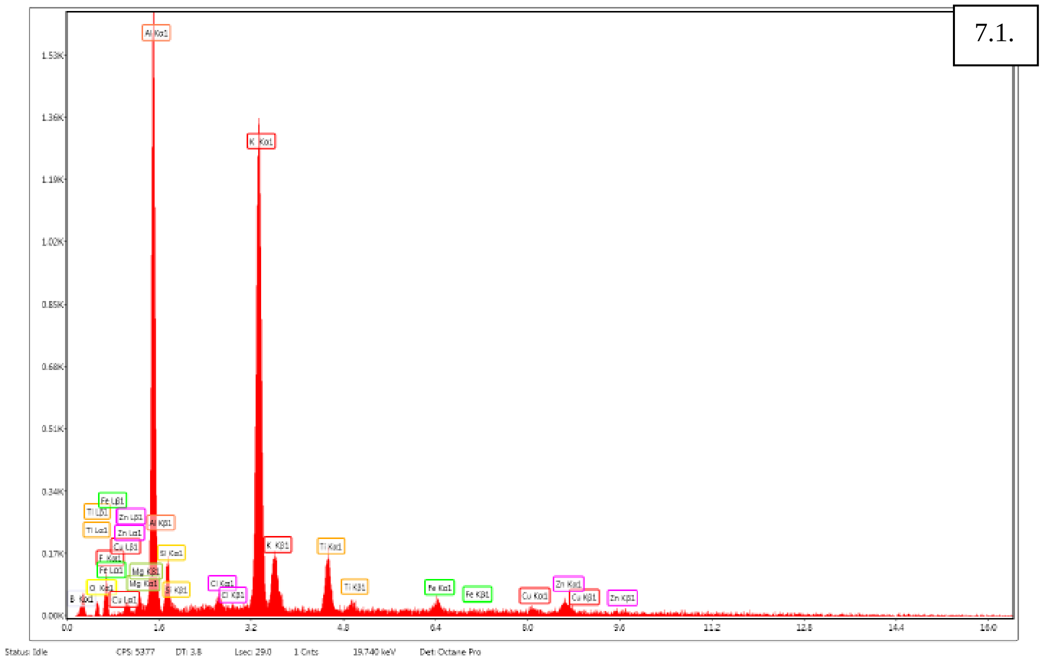
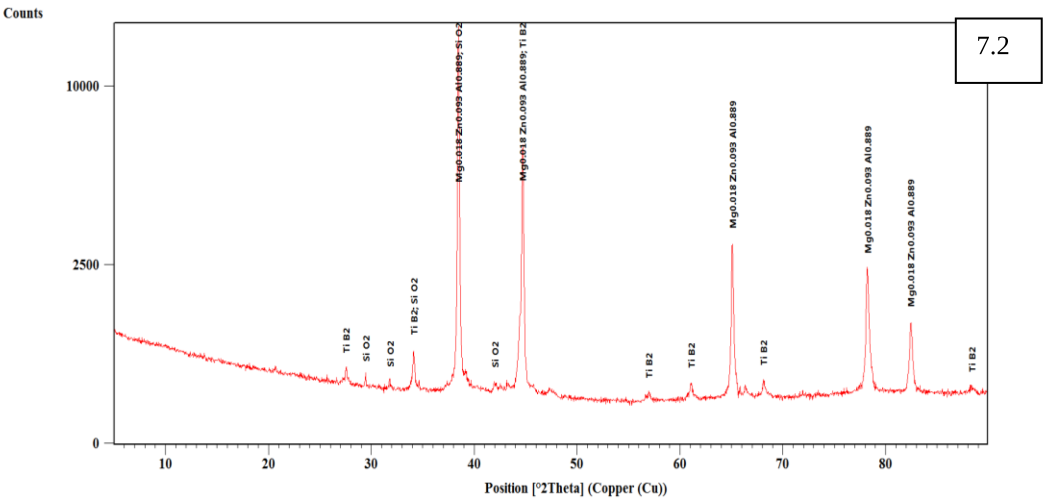


Fig. 3. SEM analysis

It was observed in the EDS analysis that many of the reaction products (mainly salts) used in the experiment, in order to obtain the reinforcing elements, were still present in the cast sample. We further refined the metallic bath using refining and degassing fluxes mixed with inert gas bubbling (N_2), thus resulting the sample marked 7.2.




7.1.
Al Kα1
K Kα1
Ti Kα1
Status: Idle
CPS: 5377
DT: 3.8
Lsec: 29.0
1 Cnts
19.740 keV
Det: Octane Pro


7.2
Counts
10000
2500
0
10
20
30
40
50
60
70
80
Position [°2Theta] (Copper (Cu))
Mg0.018 Zn0.093 Al0.889; Si O2
Mg0.018 Zn0.093 Al0.889; Ti B2
Mg0.018 Zn0.093 Al0.889
Ti B2; Si O2
Ti B2
Si O2

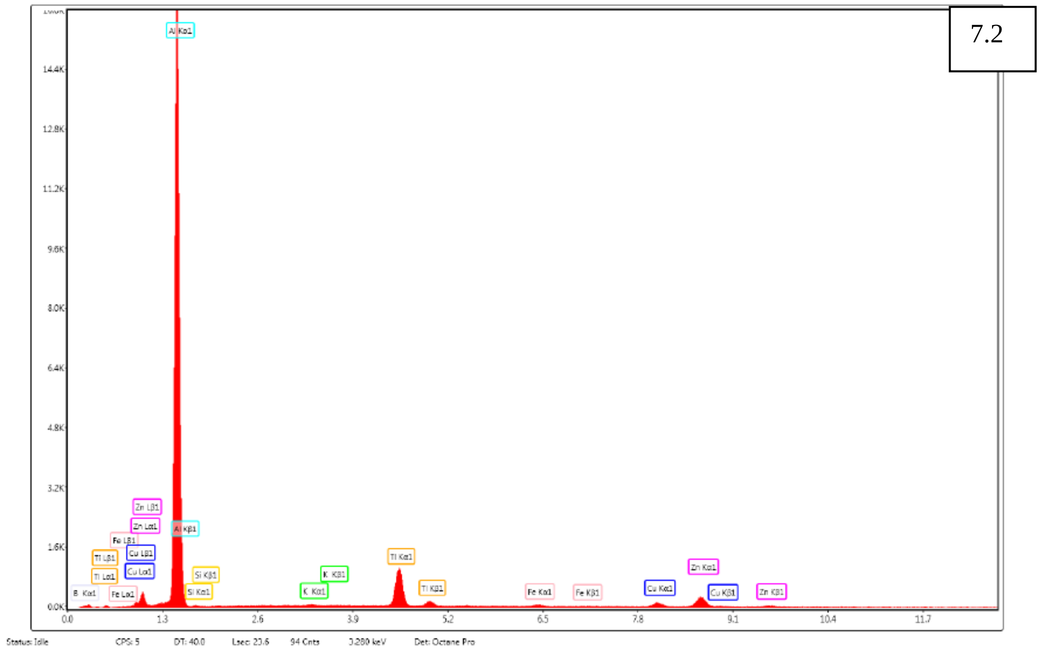
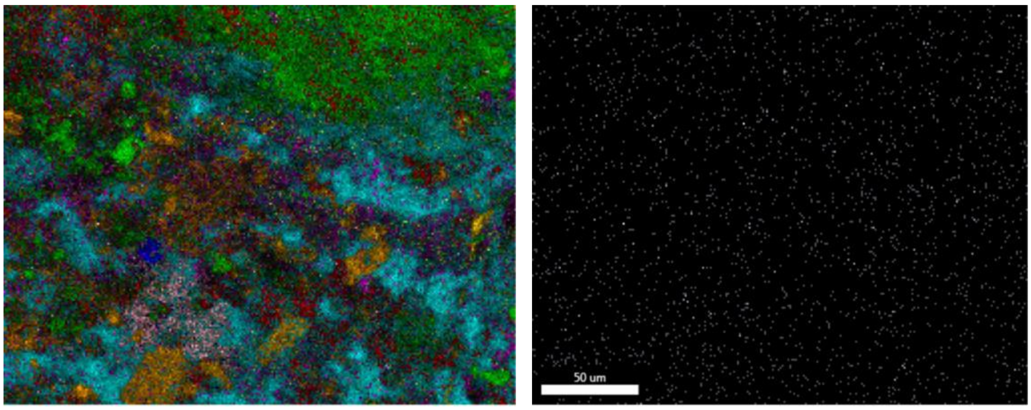
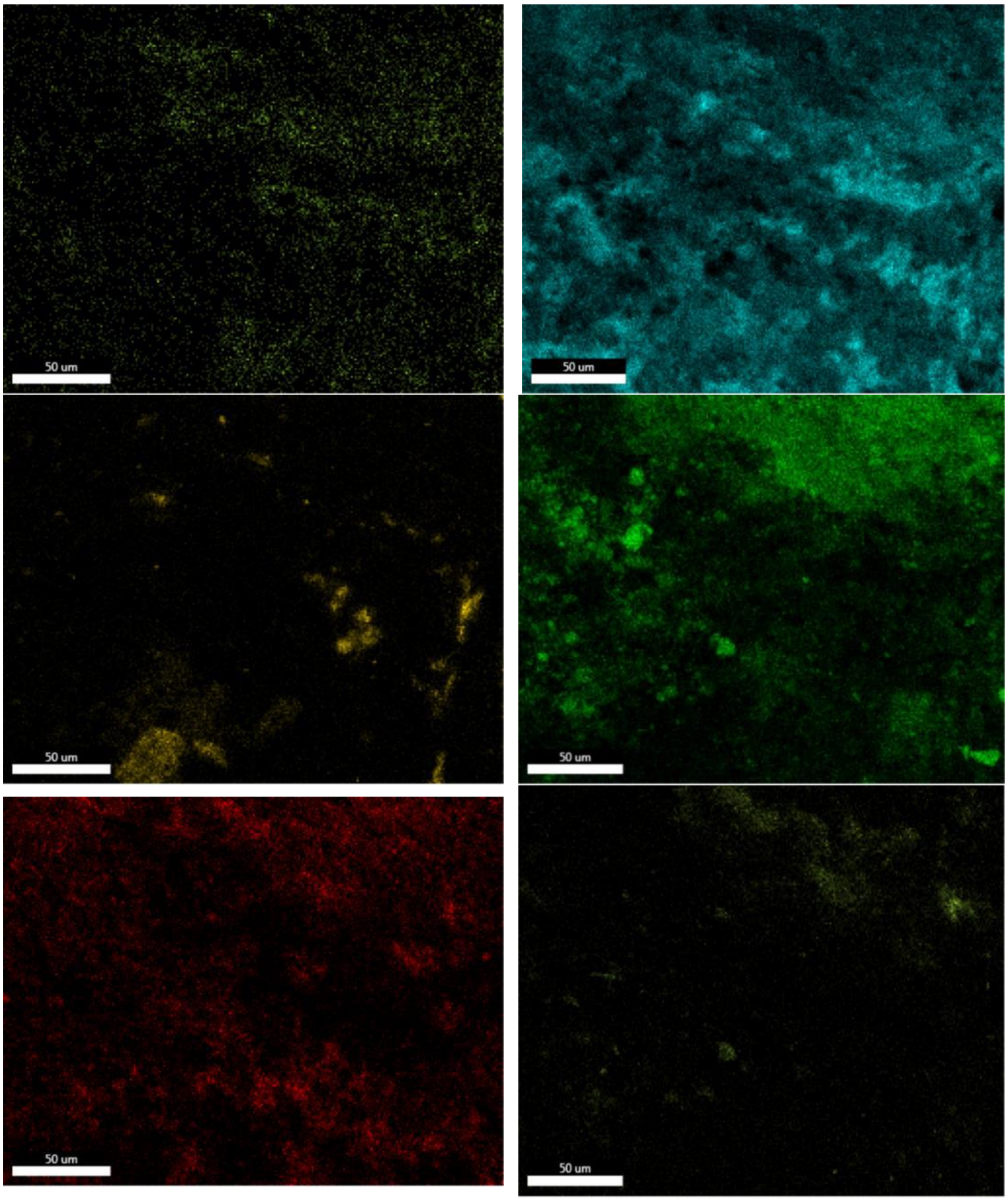


Fig. 4. EDS analysis of the Al/TiB_2 composite before (7.1) and after further refining (7.2)

Through the combined use of scanning electron microscopy (SEM) and EDS Mapping technique, detailed information on the structure, composition, and distribution of elements in aluminium metal matrix composites is obtained.

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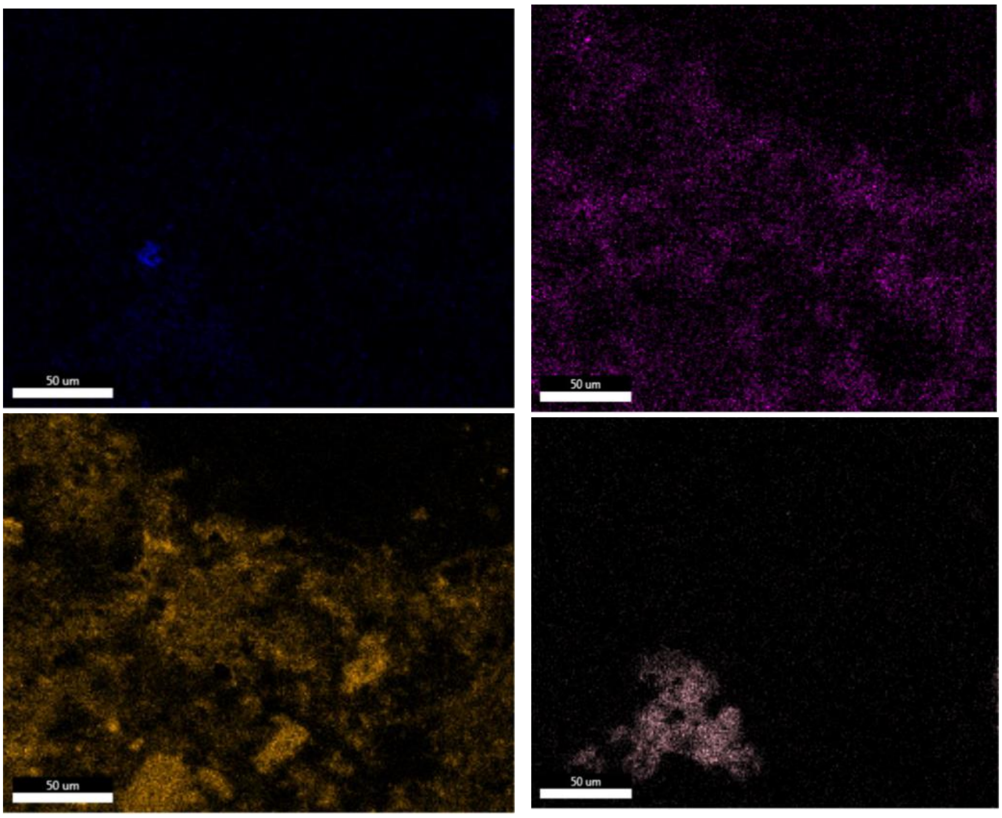
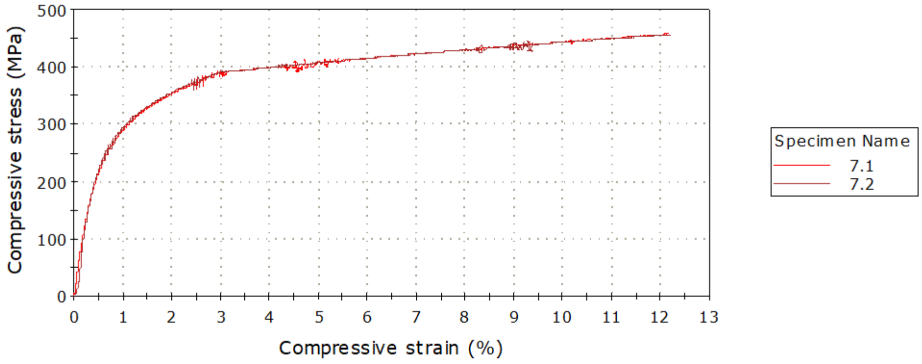


Fig. 5. SEM mapping of elemental distribution and EDX spectrum of Al/TiB_2 composite

Compressive and tensile tests and results

The mechanical properties of the samples were tested using the Instron 8872 universal testing machine that is widely used in material science and engineering research for conducting mechanical tests on various materials, including composites, metals, and plastics. The machine is particularly useful for conducting compressive tests, which are used to determine the mechanical properties of materials under compressive loads. The machine is equipped with a load cell that measures the force applied to the sample and a displacement sensor that measures the deformation of the sample. For static axial testing, the machine can apply compressive or tensile loads to a sample at a constant rate of deformation or a constant load. The machine is capable of measuring the strength, stiffness, and other mechanical properties of the sample.

Compressive test results

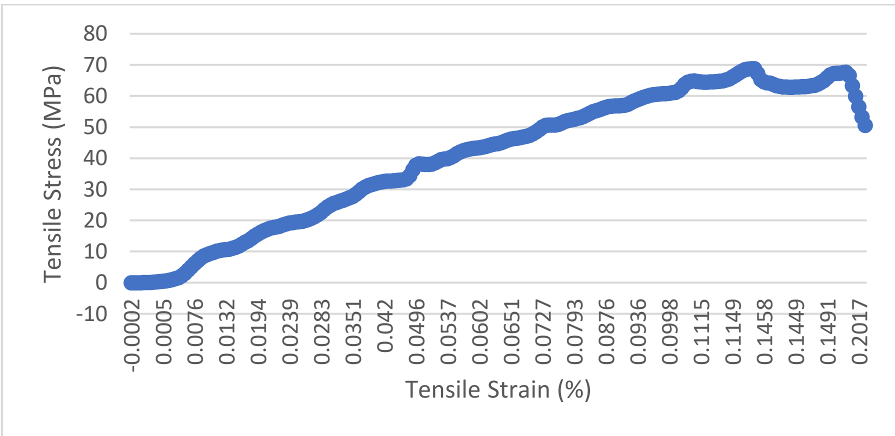


Specimen label	Diameter (mm)	Anvil height (mm)	Modulus (Segment 0.1 % - 0.15 %) (MPa)
7.1	10.01	14.90	53292.16628
7.2	10.14	15.17	85591.78304

Specimen label	Modulus (Segment 0.05 % - 0.15 %) (MPa)	Modulus (Segment 0.17 % - 0.27 %) (MPa)
7.1	59093.19946	45348.64477
7.2	57608.13377	54728.30928

Fig. 6. Compressive strength test of the Al/TiB_2 composite before (7.1) and after further refining (7.2)

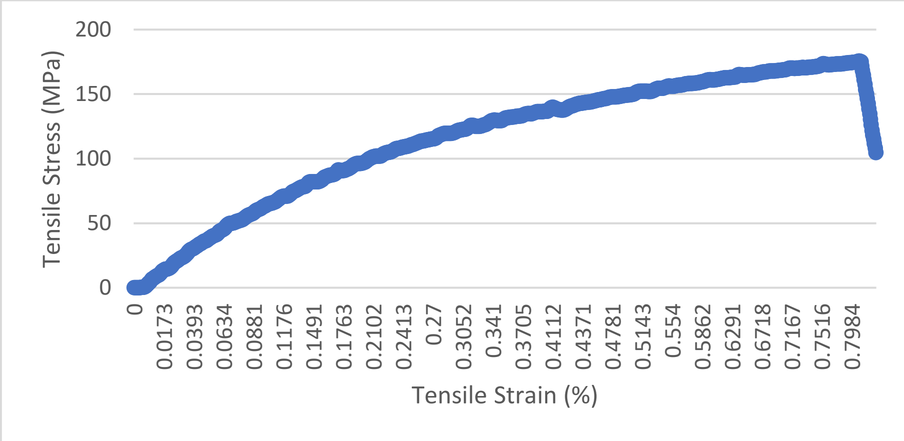
Tensile test results



Specimen label	Diameter [mm]	Length [mm]
7.1	4.94	25.00

Maximum Tensile stress [MPa]	Tensile strain (Strain 1) at Maximum Tensile stress [%]	Modulus (Segment 0.01 % - 0.02 %)
68.81	0.12	79484.16

Fig. 8. Tensile strength test of the Al/TiB_2 composite before refinement (Sample 7.1)



Specimen label	Diameter [mm]	Length [mm]
7.2	4.90	25.00

Maximum Tensile stress [MPa]	Tensile strain (Strain 1) at Maximum Tensile stress [%]	Modulus (Segment 0.01 % - 0.02 %) [MPa]
175.56	0.81	79176.06

Fig. 7. Tensile strength test of the Al/TiB_2 composite after further refinement (Sample 7.2)

4. Conclusions

There are some challenges to consider when obtaining 7xxx/TiB_2 composite materials with a high concentration of reinforcing elements using the in-situ method.

- an increase in the viscosity of the composite material, making separation of the reaction products (slag) from the metal melt difficult.
- an increase in the amount of slag
- settling of high specific gravity compounds (borons) due to long reaction time
- decrease in melting temperature as a result of the slag being separated (removed) for a longer period of time.
- increased viscosity causes casting difficulties.

Acknowledgement

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