OBTAINING OF AA6063/VB_2 COMPOSITES PRODUCED BY ALUMINOTHERMIC REACTION

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AA6063/VB_2 metal matrix composites, at different concentrations of reinforcing ceramic elements (1%, 2%, 3%, 4%, 5% and 10% VB_2) were prepared in a silicon carbide resistor furnace at about 850°C using Al-10%V(wt%) master alloy and KBF_4 salt, all in the presence of cryolite (Na_3AlF_6), for the solubilization of possible Al_2O_3 films formed. From the analysis of binary diagrams (Al-V, B-V) and thermodynamic studies, it was predicted that VB_2 particles are stable vanadium borides, highlighted in this paper by MO, SEM (EDS) and EDS Mapping.

Keywords: aluminothermic reaction, vanadium diboride (VB_2), thermodynamic analysis, EDS Mapping

1. Introduction

Transitional metal borides (TiB_2, ZrB_2, VB_2, CrB_2) have special physical and mechanical properties, with possible applications in high-end industrial sectors [1 - 13]. For this reason, physicomechanical properties (high melting temperature, high elastic modulus, low expansion coefficient, low specific gravity, very good wear resistance, good electrical and thermal conductivity, excellent thermal and chemical stability, high strength), have been intensively studied from the point of view of the crystallographic structure [1, 2, 6, 8, 13] (Table 1.1). By means of various methods of preparation - CVD, solid-state reactions, carbothermic reduction, boron carbide process, aluminothermic/silicothermic/magneziothermic reduction, self-propagating high-

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temperature reactions or combined methods, crystals of these borides have been obtained which in combination with other ceramic materials or as reinforcement elements of certain matrices, form the basis of composite materials with exceptional properties.

Table 1.1.

Properties of transition metal borides [2-13]

	Melting temperature ^oC	Density g/cm^3	Grain size (μm)	Young's Modulus GPa	Poisson ratio	Thermal expansivity (10^{-6}, $^oC^{-1}$)	Crystal structure / space group
VB_2	2450	5.1		268	0.12	6.8	Hexagonal / P6/mmm
ZrB_2	3038 - 3250	6.085	20 – 50	489 - 520	0.12	5.9	Hexagonal / P6/mmm
TiB_2	2897 - 3225	4.52	20 - 50	529	0.11	6.4	Hexagonal / P6/mmm
CrB_2	2200	6.17		211	0.12	11.1	Orthorhombic / Cmcm

2. Obtaining AA 6063/VB_2 composites

2.1. Theoretical Aspects

The paper presents the studies performed to obtain aluminium alloy matrix composites from the 6xxx series, reinforced with vanadium diboride produced by in-situ aluminothermic reactions. The binary Al-V and V-B diagrams have been studied in order to know the structures that can be formed, the concentrations of the substances used and the temperature of processing.

Al-V binary diagram

Microscopic analysis has highlighted intermediate phases of the VAl_3, VAl_2, V_2Al_3, VAl and V_2Al can form. [14, 15]. In the area with a high concentration of aluminium, VAl_6 compounds are considered to be formed (with 23.94% V) and VAl_5 (with 27.41% V). VAl_7 (with 21.25% V) and VAl_4 (with 32.07% V) resulted from peritectic reactions at approximately 750°C and 950°C respectively.

The horizontal line at 660^{o}C is considered to be a peritectic reaction at a concentration of 0.1 %V. The solid-state solubility of V in Al was determined to be 0.37% V at 630°C and does not appear to change at a decreasing temperature. Supersaturated solid solutions with up to 1.0% V are formed by extremely fast solidification.

VAl_3 crystallizes in a tetragonal system, with the elementary cell type $TiAl_3$ ($D0_{22}$) with lattice parameters a = 0.5345 nm, c = 0.8322 nm, c/a = 1.557. VAl_5 or VAl_6 compounds are considered to crystallize in the cubic system, with the lattice parameter a = 1.450 nm.

Subsequently [14] the existence of four intermediate phases were reported: VAl_{11} (α) at 8.33% at. V, ~ VAl_6 (β) at 14.29% at. V, VAl_3 (γ) and V_5Al_8 (δ) at 38,46% at. V. However, there is evidence that there is in fact a fifth compound, possibly VAl_7, having a peritectic horizontal very close to that of VAl_{11} at 700°C.

VAl_{11} compound crystallizes in the cubic system, with the lattice parameter a = 1.4586 nm, with 192 atoms per cell unit; ~ VAl_6 (β) crystallizes in a hexagonal system, with lattice parameters a = 0.7718 nm, c = 1.715 nm; V_5Al_8 crystallizes in the cubic system, with the lattice parameter a = 0.9207 nm, with 52 atoms per cell unit; the lattice parameter for (V) increases with increasing Al content.

In references [16] it is considered that in the Al-V system (Fig. 2.1), upon solidification, the following structures are obtained: (Al) – which crystallizes in the cubic system, with the Pearson symbol cF4, space group $Fm\bar{3}m$, at concentrations between 0 ÷ 0.46% V; $Al_{21}V_2$ – which crystallizes in the cubic system, with the Pearson symbol cF176, space group $Fd\bar{3}m$, at concentrations between 15.3 ÷ 15.9% V; $Al_{45}V_7$ – which crystallizes in the monoclinic system, with the Pearson symbol mC104, space group C2/m, at a concentration of ~ 23.1% V; $Al_{23}V_4$ – which crystallizes in the hexagonal system, with the Pearson symbol hP54, space group $P6_3/mmc$, at a concentration of ~ 24.7% V; Al_3V – which crystallizes in the tetragonal system, with the Pearson symbol tI8, space group I4/mmm, at a concentration of ~ 39% V; Al_8V_5 – which crystallizes in the cubic system, with the Pearson symbol cI52, space group $I4\bar{3}m$, at a concentration of 54.2% V; (V) – which crystallizes in the cubic system, with the Pearson symbol cI2, space group $Im\bar{3}m$, at concentrations between ~ 65 ÷ 100% V; AlV_3 – which crystallizes in the cubic system, with the Pearson symbol cP8, space group $Pm\bar{3}m$; β_{AlV3} – which crystallizes in the hexagonal system and α_{AlV3} – which crystallizes in the tetragonal system.

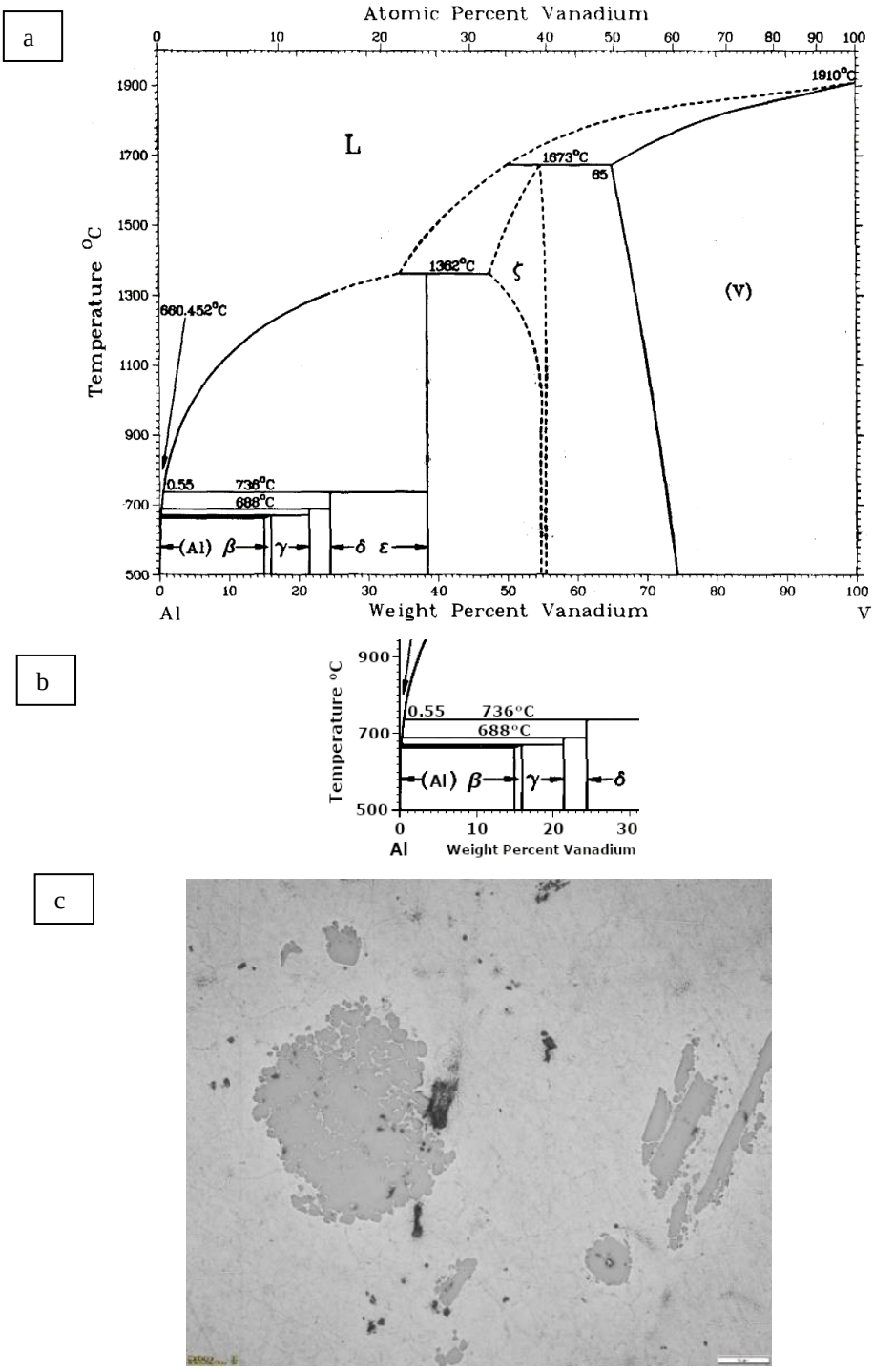


Fig. 2.1. Al-V binary diagram (a) [16], with detail in the corner with a high concentration of aluminium (b) and the characteristic microstructure of the AlV10 alloy (c)

B-V Binary diagram

The existence of VB (17.52% B) and VB_2 (29.81% B) was reported in the references [14, 15]. The crystal structure of VB is rhombic, with the elementary cell type CrB, with lattice parameters a = 0.310 nm, b = 0.817 nm and c = 0.298 nm. VB_2 compound crystallizes in a hexagonal system with the elementary cell type AlB_2 (C32), with lattice parameters a = 0.2998 nm, c = 0.3057 nm, c/a = 1.02.

An alloy with approximately 0.5% B presents a small amount of eutectic, but an alloy with approximately 5% B contains primary crystals surrounded by peritectic and eutectic structures. This would indicate that the eutectic is less than 5% B and that the VB phase is formed following the transformation liq + $VB_2 \rightarrow$ VB at a temperature determined to be approximately 1780°C. The melting point of VB_2 was given as 2100 ± 60°C.

Other authors from references [14, 15] confirmed the rhombic structure of the VB compound, with the following network parameters: a = 0.3058 nm, b = 0.8026 nm and c = 0.2971 nm. Furthermore, two new phases were detected, which were observed in several compositions with excess V_2B, prepared by electric arc melting followed by prolonged annealing, in some cases at temperatures of 1500°C and 1700°C. These specimens were analysed by X-ray diffraction to highlight the two new compounds with an unknown crystalline structure. Only one of these phases was present in the untreated melts; all heat-treated specimens contain both phases in approximately equal quantities. The melting temperature of VB_2 was also considered to be 2400°C. V_3B_4 boride (22.07% B) crystallizes in the rhombic system, with lattice parameters a = 0.3030 nm, b = 1.318 nm and c = 0.2986 nm, with isotypic structure with Cr_3B_4.

Other authors [16] consider that in the B-V system (Fig. 2.2), upon solidification, the following structures are obtained: (V) – which crystallizes in the cubic system, with the Pearson symbol cI2, space group $Im\bar{3}m$, at concentrations of 100% V; V_3B_2 – which crystallizes in the tetragonal system, with the Pearson symbol tP10, space group P4/mbm, at concentrations of 12% V; VB – which crystallizes in the rhombic system, with the Pearson symbol oC8, space group Cmcm, at concentrations of 18% V; V_5B_6 – which crystallizes in the rhombic system, the spatial group Ammm, at concentrations of 20,3% V; V_3B_4 – which crystallizes in the rhombic system, with the Pearson symbol oI14, space group Immm, at concentrations of 22% V; V_2B_3 – which crystallizes in the rhombic system, the spatial group Cmcm, at concentrations of 24% V; VB_2 – which

crystallizes in the hexagonal system, with the Pearson symbol hP3, space group P6/mmm, at concentrations of 30% V; β-B – which crystallizes in the hexagonal system, with the Pearson symbol hR108, space group $R\bar{3}m$, at concentrations of 100% B.

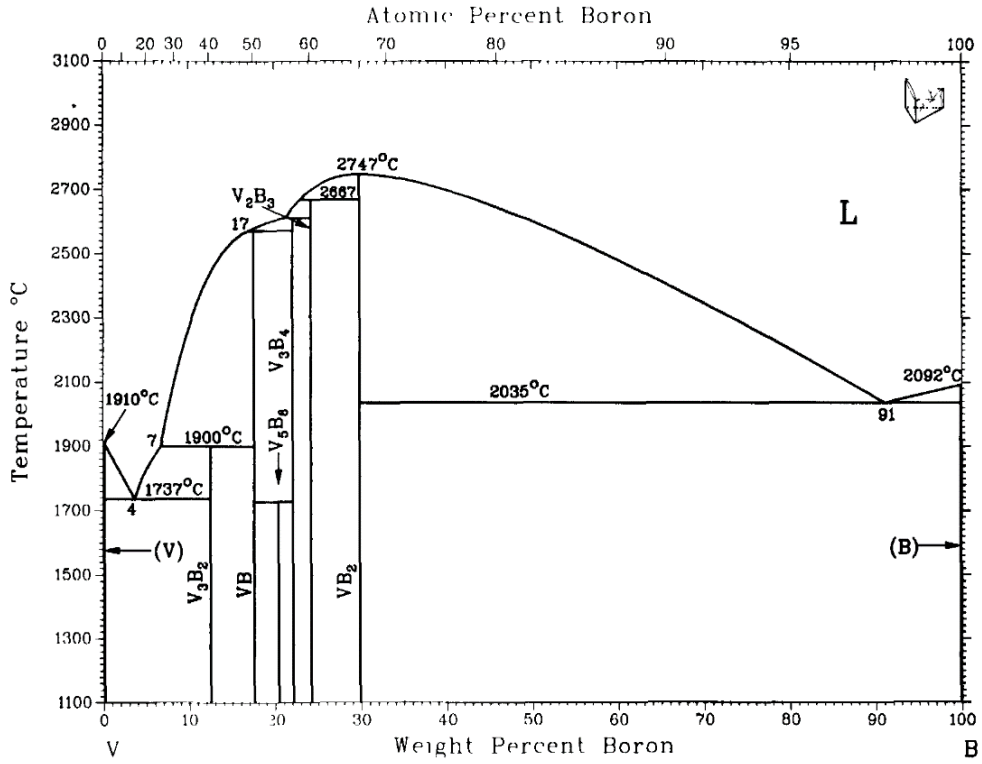


Fig. 2.2. B-V Binary diagram [16]

2.2. Experimental technique

In this study, in order to research the improvement of the microstructures of AA6063/VB_2 metal matrix composites, VB_2 reinforcing particles were obtained using the in-situ synthesis method of molten AA6063 alloy with AlV10 master alloy and KBF_4 salt.

A series of composites were successfully fabricated using the in-situ method through the aluminothermic reaction:

$$6KBF_4 + 3V + 6Al = 3\mathbf{VB_2} + 2K_3AlF_6 + 4AlF_3 \qquad (1)$$

In order to obtain tensile test bars and samples for microstructure analysis, the composite melts were poured into the pre-heated rod-shaped mould with ϕ =

12 mm and h = 90 mm at different VB_2 concentrations (1%, 2%, 3%, 4%, 5% and 10%).

Table 2.1.

Chemical composition profile without impurities, according to standard

	Si	**Fe**	**Cu**	**Mn**	**Mg**	**Cr**	**Zn**	**Ti**	**Other elements**	**Al**
AA6063	0.2 - 0.6	0.35	0.10	0.10	0.45 - 0.9	0.10	0.10	0.10	< 0.05%	Rest
Nominal	0.49	0.33	0.02	0.02	0.72	0.06	0.03	0.04	< 0.05%	Rest

The Gibbs free energy formations for aluminium and vanadium borides were tested using HSC Chemistry at temperatures ranging from 500ºC to 1000ºC (Table 2.2). Fig. 2.1 shows the stability curves of the various possible reactions.

Through thermodynamic analysis of the reactions occurring in the melt, we found that reaction (1) was the most likely reaction to occur during the composite development.

$$6KBF_4 + 3V\ (AlV10) + 6Al\ (AA6063) = 3VB_2 + 2K_3AlF_6 + 4AlF_3 \quad (2)$$

$$2KBF_4 + V + 2Al = VB_2 + 2KF + 2AlF_3 \quad (3)$$

$$3Al + 1.5V + Na_3AlF_6 + 3KBF_4 = 1.5VB_2 + K_3AlF_6 + 3AlF_3 + 3NaF \quad (4)$$

Table 2.2.

The Gibbs free energy formations for the reactions

Temperature, ºC	Delta G (2)	Delta G (3)	Delta G (4)
500	-918.402	-528.998	-196.355
550	-911.001	-523.291	-194.314
600	-901.758	-516.317	-191.728
650	-891.194	-508.426	-188.783
700	-879.188	-499.538	-185.491
750	-866.790	-490.354	-182.103
800	-854.363	-481.121	-178.705
850	-841.922	-471.849	-175.302
900	-829.477	-464.627	-171.892
950	-817.040	-457.723	-168.455
1000	-804.620	-450.811	-165.071

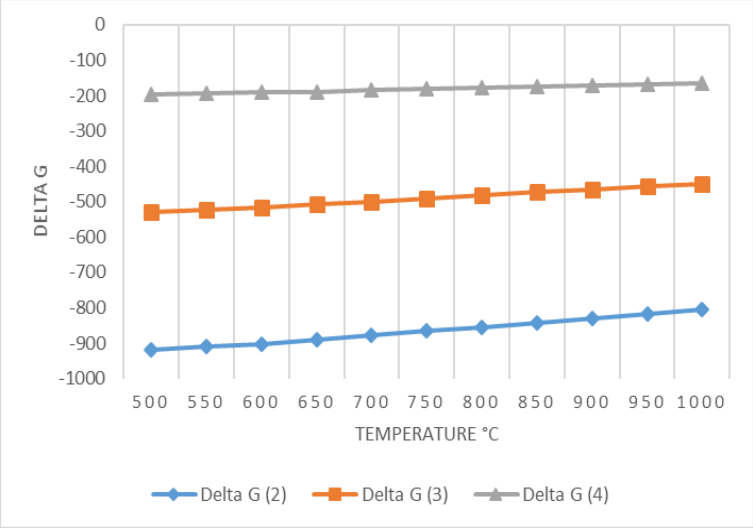
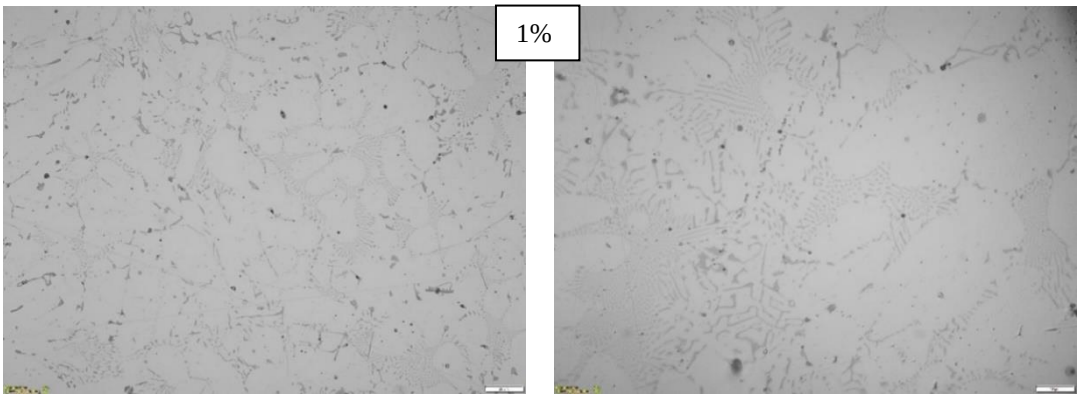


Fig. 2.1. The Ellingham temperature diagram for the reactions

3. Experimental results

Metallographic samples were processed using the DELTA Abrasimet Cutter, SIMPLIMET 1000 embedding machine and the Beta/1 Single sanding/polishing machine. The samples were then analysed using the Olympus UC30 optical microscope at various sizes (Fig. 3.1).

Optical and electron (SEM) microscopic analysis of the samples were carried out along with, X-ray spectrum with energy dispersion (EDS) (Fig. 3.2) and EDS Mapping of the AA6063 10% VB_2 composite for phase observation and identification (Fig. 3.3). SEM analysis (EDS) and Mapping show the formation of the VB_2 particles.



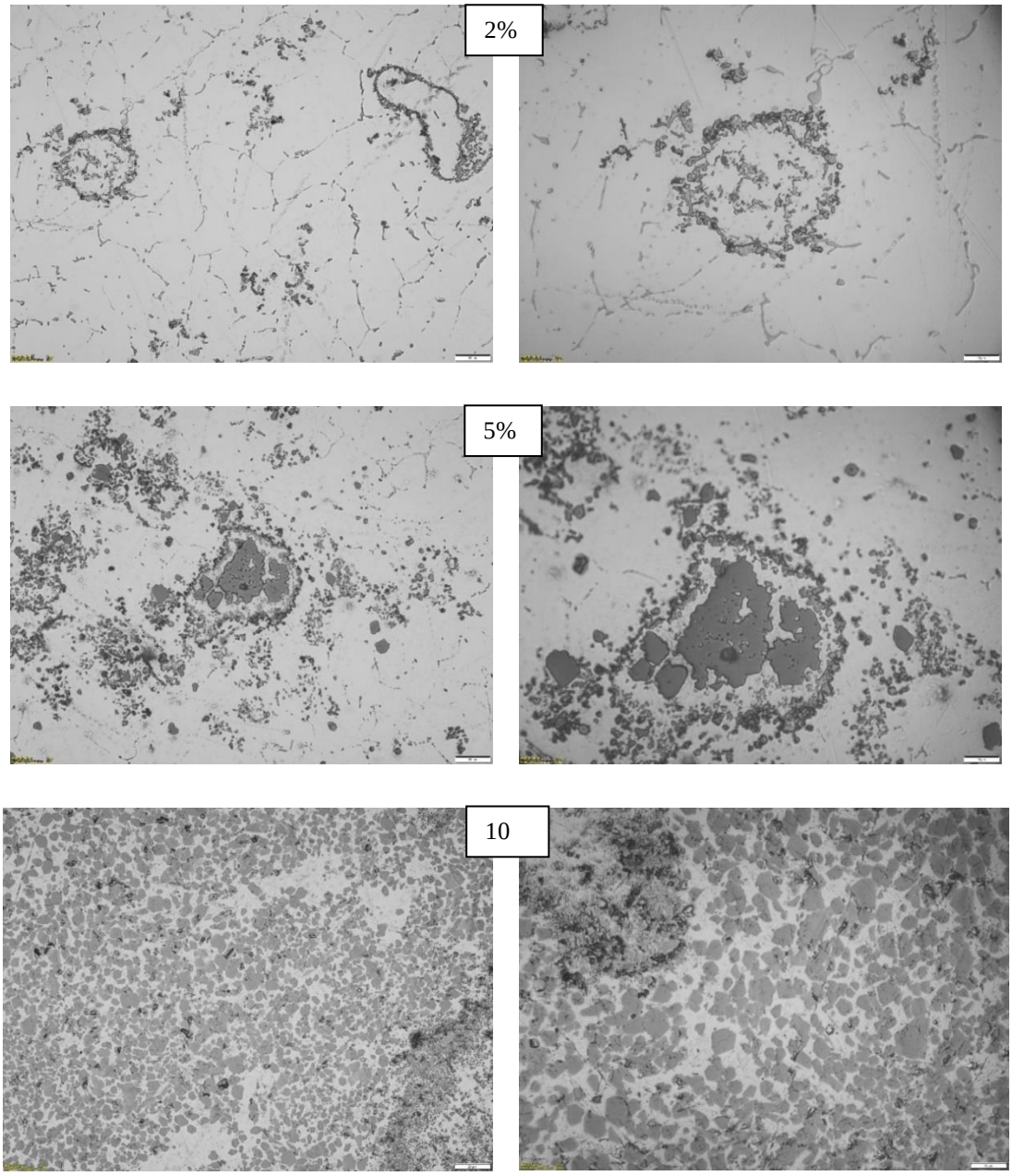
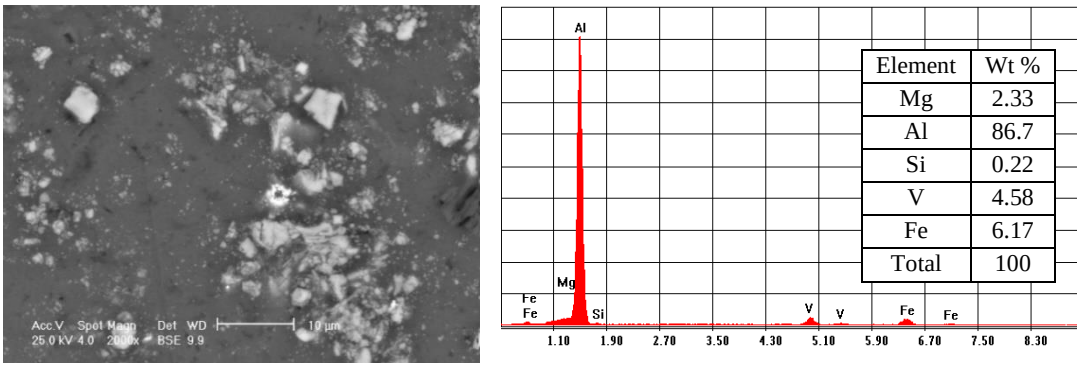


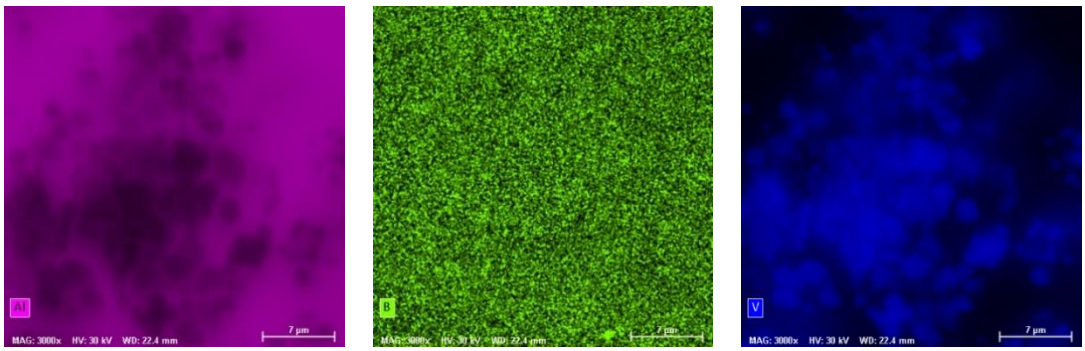
Fig. 3.1. The microstructure of the AA6063/VB_2 composite at different concentrations and magnifications



Element	Wt %
Mg	2.33
Al	86.7
Si	0.22
V	4.58
Fe	6.17
Total	100

Fig. 3.2. Electron microscopy analysis and EDS analysis with the chemical composition

Through EDS Mapping analysis, on the HITACHI SUB230 equipment, the presence of boron was highlighted in the form of VB_2. [17].



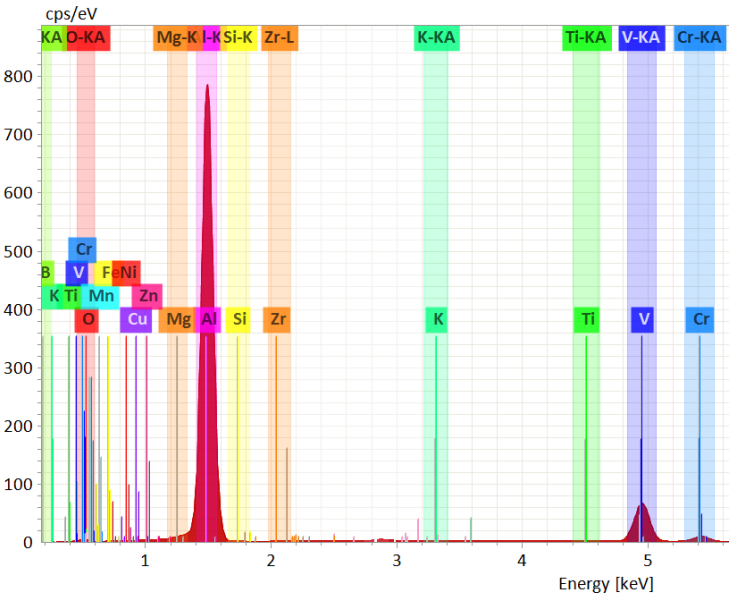


Fig. 3.3. EDS Mapping of the AA6063 / VB_2 composite

4. Conclusions

To improve the mechanical properties of Al-Mg-Si alloys, vanadium boride particulates were used as reinforcement materials. Like other transition metal borides, vanadium borides have a high melting point, good wear and corrosion resistance, high hardness, high electrical and thermal conductivities, and high chemical stability.

Metal matrix composites (MMC's) have been developed in the paper using the in-situ method which is based on the aluminothermic reaction of KBF_4 salt and AlV10 master alloy with aluminium metallic melt in the presence of cryolite (Na_3AlF_6), forming ceramic reinforcement particles. The interactions between the metal melt and the salts have been studied in detail.

In the cast sample, optical and electron microscopy analysis highlighted the presence of small VB_2 particles located in groups/agglomerations inside the grains, the EDS mapping results confirm the presence of V, B and Al elements, which form VB_2.

The average grain sizes of the VB_2 particles are about 2μm and are distributed uniformly in the AA6063 matrix. At lower concentrations of VB_2, the ceramic particles act as grain refiners.

Acknowledgments

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