

Thermal Analysis on the Milled Al+B₂O₃+Si+WO₃ System to Synthesize Al₂O₃-W_xSi_y-W_xBy Powders

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Composites including silicide of tungsten and boride of tungsten intermetallic compound as reinforced agents in alumina matrix have a good mechanical properties in low and high temperature (high friction resistance, strength, resin stance to creep and relatively high thermal shock resistance), moreover, they have chemical neutral with a high corrosion resistance in a high corrosive and high temperature environment. The purpose of this study is to investigate thermal analysis, phase and microstructural evaluation during synthesis of above mentioned composite by combustion aluminothermic processing in three systems 1-Al+Si+WO₃, 2-Al+B₂O₃+WO₃ and 3-Al+B₂O₃+Si+WO₃. A Ball-milled starting material according to stoichiometric ratio was thermal analyzed (DTA-TGA) for each of above mentioned system. The XRD results never show any new phase during ball-milling even up to 10 hours. The forming of tungsten silicide (W_xSi_y) is in lower temperature in comparison with tungsten boride (W_xB_y) during the thermal analysis experiments. The presence of Si in the Al+B₂O₃+WO₃ system facilitates the formation of tungsten borides. The microstructural observations show a uniform and dense distribution of silicide and boride of tungsten in the alumina matrix. Silicide phases are small grain with spherical morphology whereas; the boride phases are coarser and relatively elongated with irregular morphology.

Keywords: Aluminothermic combustion synthesise, Al+B₂O₃+Si+WO₃ system, Phase analysis, Thermal analysis, gravity analysis, Micro structure analysis.

1. Introduction

Ceramic based composite in comparison with metals and alloys have special advantages including high thermo mechanical properties high reaction, high chemical stability, low density, and high resistance to oxidation. In this respect, they are prioritized in high temperature components and structures such as cutting tools and aerospace applications. Due to the low coefficient of expansion and the lack of phase transformations and relatively high thermal conductivity for tungsten based intermetallic compounds (especially borides and silicide); these materials have relatively high thermal shock resistance. As such, nowadays cermet and composite materials containing such compounds are used as parts or as protector coating layer on the surface of metals and alloys¹⁻⁵. One of the most well-known ceramics is alumina, which has special mechanical and physical properties. The results of our studies show that if nitride, boride, carbide and silicide compounds as secondary phase (reinforced phase) are added to Al₂O₃ as the matrix phase, mechanical and physical properties are significantly increased⁶⁻¹³. Various methods have been used for synthesis of composite powders including 1-in situ synthesis (mechanical alloying, reaction sintering, combustion synthesis (CS), self-propagating high temperature synthesis (SHS), carbothermic reduction, sol-gel, vortex casting and...)¹⁴⁻¹⁸ and 2-non in situ synthesis (powder metallurgy)^{19,20}.

Froyen and Feng produced Al-Al₂O₃-ZrB₂ cermet in Al-ZrO₂-B₂O₃ using hot press method, which results in a composite with a tensile strength about 300 MPa²¹. The composites of Al₂O₃-WSi₂, Al₂O₃-WB and WSi₂-Mullite were synthesized by SHS aluminothermic (SHS-AT) processing in Al-Si-WO₃, Al-WO₃-B₂O₃²² and Al-SiO₂-WO₃-B₂O₃²³ systems and composite WB₂-Mullite in Al-SiO₂-WO₃-B₂O₃ system²³.

The advantages of the combustion synthesis (In-situ CS and SHS) in comparison with other methods are having more simplicity, non-complex equipment, short time (high speed of process), energy savings, high homogeneous and stronger bond of reinforcement-matrix. In this study, combustion synthesis method was used in aluminothermic system of Al+Si+WO₃+B₂O₃ for synthesizing powder composite including WSi₂, WB₂ and Al₂O₃. Thermal analysis experiments were carried out to study the physicochemical reactions that take place during combustion synthesis processing. X-rays analysis and electron microscopy observation were applied to identify the phase and microstructure of obtained composites powders.

2. Materials and Methods

Aluminum, silicon, born oxide and tungsten oxide powders were used with chemical formulations of Al, Si, B₂O₃ and WO₃ (Table 1). The mixture of raw materials based on the stoichiometric composition and according to

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Table 1. Important properties of raw materials.

Powder material	Particles size (μm)	Purity (%)	Melting temperature ($^{\circ}\text{C}$)	Boiling Temperature ($^{\circ}\text{C}$)	Standard heat formation ΔH°_{298} (Kj.mol^{-1})	Molar mass (gr.mol^{-1})	Density (gr.cm^{-3})	Company
Al	200-300	99.9	660	2470	-	27	2.7	Aldrich
B_2O_3	300-400	99.9	450	1860	-1253.50	70	2.5	Merck
WO_3	400-500	99.9	1473	1700	-842.70	232	7.2	Merck
Si	200-300	99.9	1414	3265	-	28	2.3	Aldrich

Table 2. The composition of the weight percentages of the primary mixtures and result composite obtained based on stoichiometric calculations in different aluminothermic systems.

weight percentages of the primary mixtures				weight percentages of result composite obtained				
Si	WO_3	B_2O_3	Al	Primary mixtures	Composites obtained	WB_2	WSi_2	Al_2O_3
16.37	67.84	-	15.79	ASW	ASW	-	70.18	29.82
-	56.58	17.08	26.34	ABW	ABW	50.24	-	49.76
7.74	61.71	9.31	21.54	ABSW	ABSW	27.39	31.92	40.69

Table 3. Standard Card Number for XRD Analysis

Phase type	Standard card number
B_2O_3	(00-013-0570)
WO_3	(01-1465-072)
Al	(00-1180-001) (00-1386-043)
WSi_2	(00-0195-011) (00-1085-044)
W_5Si_3	(00-0261-016)
WB	(00-0738-035)
WB_2 or W_2B_5	(00-1386-043)
W_2B	(00-0990-025)
$\text{Al}_6\text{Si}_2\text{O}_{13}$	(00-15-0776)
W	(00-0806-04)
Al_2O_3	(01-1125-071) (00-0712-005) (00-1468-042) (01-1126-017)
B(OH)_3	(00-0199-030)
$\text{Al}_{18}\text{B}_4\text{O}_{33}$	(00-0003-032)
Si	(01-2108-077)

the reactions performed in different systems including ASW, ABW, ABSW (Table 2), were homogenized in satellite mill (PBM 210-Nano shot-Ar-300 rpm) for 10 hours with a ball weight ratio of alumina to a powder of 10 to 1.

In order to investigate the physic-chemical alterations and to determine the temperature range of stability for each of the oxide, boride and silicide phases, the mixture of ball-milled powders were analyzed by differential thermal (DTA) and thermal gravity analysis (TGA) with a heating rate of $20^{\circ}\text{C} \cdot \text{min}^{-1}$, under the atmosphere of argon (STA 504, Bahr Gmb 11-Germany). HSC software was used for calculations and thermodynamic studies²⁴. X-ray Diffraction (XRD) analysis (GNR-Explorer, copper anode, 40 kV, 30 mA, counting time 0.5 seconds, step size 0.02) were used to determine the phase composition and scanning electron microscope (SEM) observation used for microstructure studies (Mira 3- XMU). Phases in the XRD spectra have been identified using standard cards as shown in Table 3.

3. Results and Discussion

3.1 ASW system

According to Figures 1a and 1b, the results of the thermal analysis and its XRD for ASW system respectively formed the tungsten silicide (W_5Si_3 and WSi_2) along with the alumina phase^{25,26}. The DTA diagram (Figure 1a) shows a generally positive slope indicating that the reaction of aluminothermic and the formation of tungsten silicide (Reaction 1 to 4 in Table 4) become more and more exothermic by the increase of the temperature. The exothermic rate is intensified after the melting of aluminum (Endothermic peak at 660°C) in such a manner that it raises up to 1000°C . Tungsten oxide reduction reaction by Al (Reaction 1) while having more negative free energy changes (Figure 2) is dominant. In such condition, reaction 4 (Table 4) is performed simultaneously and tungsten silicides are formed. It should be mentioned that in all temperature ranges, free energy changes of forming W_5Si_3 (Reaction 2) relative to WSi_2 is more negative so that exothermic peak is formed at 1100°C in relation to W_5Si_3 and exothermic peak is formed at 1250°C in relation to WSi_2 (Reaction 3). The XRD results in Figure 1b represent the dominant phase of WSi_2 , which is in accordance with the stoichiometry composition of the ASW system (Table 2).

3.2 ABW system

Figures 3a and 3b show the results of the thermal analysis up to 1300°C and its XRD for the ABW sample. As such, according to Figure 3b, the tungsten phase is the main phase. Indicating the range of temperature up to 1300°C is not sufficient for the formation of tungsten borides (Reactions 6, 7, 8 in Figure 4). The WO_3 and B_2O_3 have been reduced by Al up to 1200°C (Reaction 1, 5 in Figure 4). Therefore, it is necessary to carry out heat treatment at higher temperatures to form tungsten boride. It should be noted that the non-appearance of boron and boron oxide in the range of XRD products can be due to their amorphous forms. The presence of the exothermic peak at 1000°C in DTA curve (Figure 3a) belongs to aluminothermic reaction of WO_3 reduction and the exothermic peak at

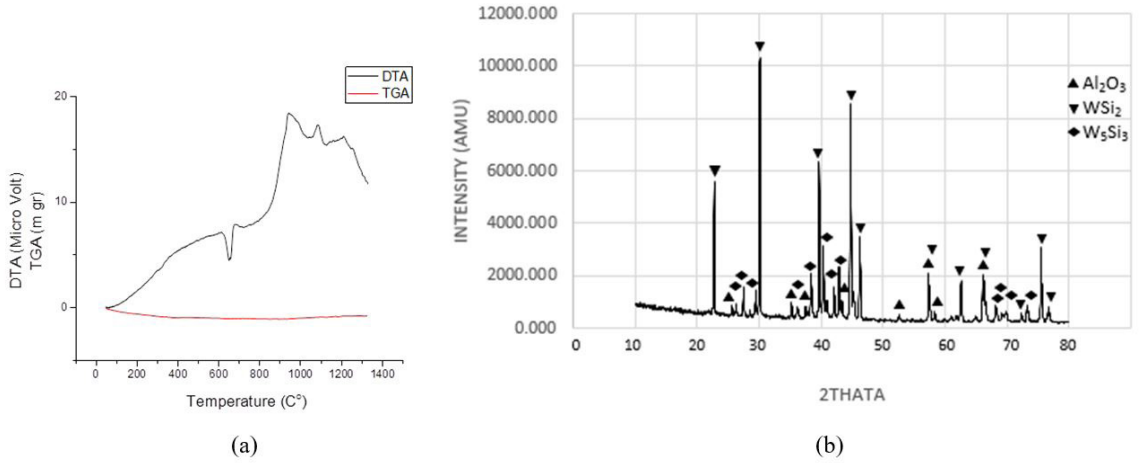


Figure 1. ASW system a) DTA-TGA with heating rate of 20 °C.min⁻¹ and atmosphere of argon, b) XRD analysis of thermal analyzed sample.

Table 4. Thermodynamic information of reactions.

Number	Reaction	ΔG°_{1273K} (kJ.mol ⁻¹)	ΔG°_{1573K} (kJ.mol ⁻¹)	ΔG°_{1773K} (kJ.mol ⁻¹)	ΔG°_{1973K} (kJ.mol ⁻¹)	ΔG°_T (kJ.mol ⁻¹)
1	2Al+WO ₃ =Al ₂ O ₃ +W	-750.668	-723.022	-703.180	-675.641	-850.200+0.089T
2	5W+3Si=W ₅ Si ₃	-169.891	-178.229	-176.042	-164.085	-231.180+0.051T
3	W+2Si=WSi ₂	-83.999	-81.465	-74.447	-60.783	-151.060+0.057T
4	12Al+6WO ₃ +5Si= W ₅ Si ₃ + WSi ₂ + 6Al ₂ O ₃	-4.757.900	-4.597.825	-4.469.572	-4.278.712	-5483.400+0.642T
5	2Al+B ₂ O ₃ =Al ₂ O ₃ +2B	-310.093	-274.171	-250.105	-226.060	-354.370+0.047T
6	2W+B=W ₂ B	-75.651	-77.556	-78.662	-79.631	-75.977-0.001T
7	W+B=WB	-72.307	-74.035	-75.106	-76.105	-75.422+0.002T
8	W+2B=WB ₂	-35.996	-36.596	-36.996	-37.396	-33.450-0.002T
9	10Al+4WO ₃ +B ₂ O ₃ =5Al ₂ O ₃ +2WB+ WB ₂	-2.682.385	-2.579.185	-2.510.385	-2.441.585	-3120.297+0.344T
10	1.5 Si+WO ₃ =1.5 SiO ₂ +W	-504.937	-499.372	-490.243	-468.367	-603.820+0.085T
11	1.5Si+B ₂ O ₃ =1.5SiO ₂ +2B	-64.362	-50.522	-37.168	-18.786	-107.990+0.043T
12	3Al ₂ O ₃ +2SiO ₂ =Al ₆ Si ₂ O ₁₃	-7.170.875	-7.253.357	-7.308.375	-7.363.375	-6820.800-0.275T
13	28Al+12WO ₃ +6B ₂ O ₃ +12Si=5Al ₂ O ₃ +3Al ₆ Si ₂ O ₁₃ +3WSi ₂ +6WB+3WB ₂	-10.288.182	-9.850.182	-9.558.182	-9.266.182	-12146.762+1.460T
14	B(OH) ₃ = HBO ₂ + H ₂ O	-	-	-	-	177.119-0.044T
15	2HBO ₂ = B ₂ O ₃ + H ₂ O	-	-	-	-	61.108-0.035T

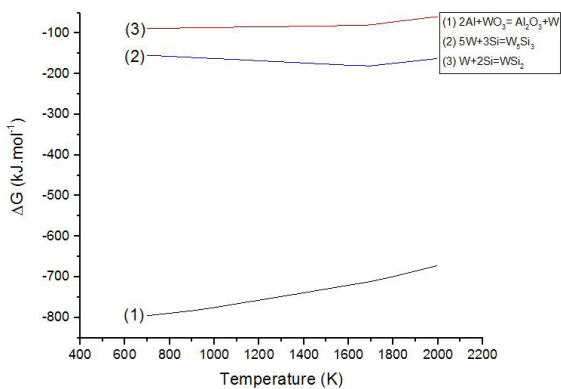


Figure 2. Free energy changes of reactions in ASW triple system as a function of temperature.

1200 °C belongs to simultaneous reduction of WO₃ and B₂O₃ (Reactions 1, 5 and strictly 9). It should be noted that thermodynamics only predicts the probability of reactions, but there is no debate about the kinetics of reactions. Investigations have shown that the kinetics of reactions in binary system of B-W (Rate of reaction – time), is S-shaped, that indicates the dependence of reactions on the atoms diffusion at a specified temperature²⁷. Therefore, the heat treatment up to 1300 °C at a heating rate of 20 °C.min⁻¹ has not been able to process the conditions for the formation of tungsten borides, and only formed a very small part of the W₂B and WB phases indicating the low boron activity and the low diffusible for solid-state reactions, especially when WB₂ is forming (X_B=0.66). The spinel phase of A₁₈B₄O₃₃ (9Al₂O₃.2B₂O₃) in XRD spectra (Figure 3b) was formed by no reduction of B₂O₃ and Al₂O₃ (formed by aluminothermic reaction).

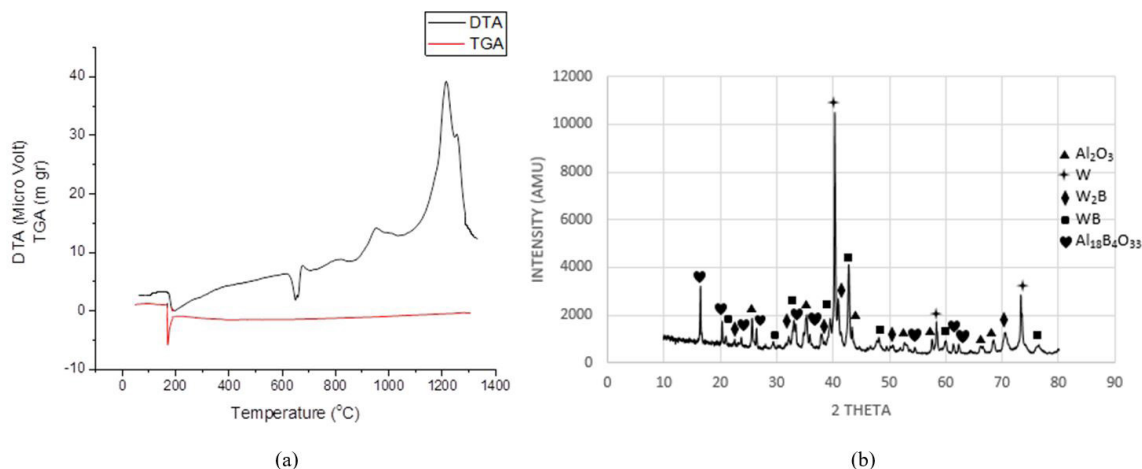


Figure 3. ABW system a) DTA-TGA with heating rate of $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and atmosphere of argon, b) XRD analysis of thermal analyzed sample.

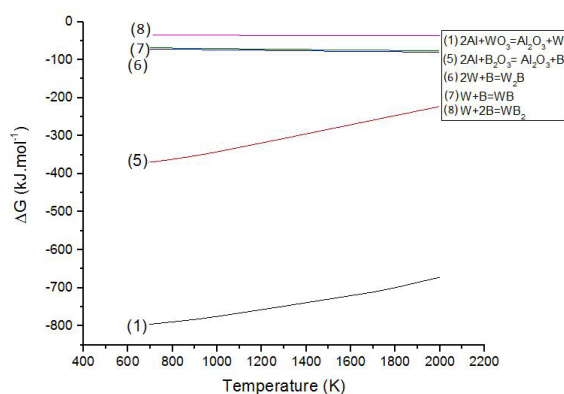


Figure 4. Free energy changes of reactions in ABW triple system as a function of temperature.

Demonstrative decreasing of the intensity of Al_2O_3 peak is according to Figure 3b. By performing re-testing of thermal analysis at temperature up to $1650\text{ }^{\circ}\text{C}$ (Figures 5a and 5b), a peak at about $1650\text{ }^{\circ}\text{C}$ (Figure 5a) is appeared that is related to forming of tungsten from boron and tungsten (Reactions 7, 8) according to Figure 5b. The XRD analysis in Figure 5b show complete removal of tungsten and the formation of tungsten borides. As a result, the role of increasing the temperature is important in improving the reactions between boron and tungsten elements. It must be marked that the middle phase of W_2B , (Appeared in Figure 3b) has completely changed into WB and WB_2 (W_2B_3) by increasing the temperature ($\text{W}_2\text{B}+\text{B}=\text{WB}$, $\text{WB}+\text{B}=\text{WB}_2$).

A small endothermic peak in $200\text{ }^{\circ}\text{C}$ in the DTA curve and corresponded weight loss in TG curve (Figures 3a and 5a) is related to removing of molecular water and the decomposition of $\text{B}(\text{OH})_3$ into B_2O_3 . It should be noted that $\text{B}(\text{OH})_3$ decomposes to B_2O_3 during two stays (Reactions of 14 and 15 in Table 4) at temperatures lower than $400\text{ }^{\circ}\text{C}$ ²⁸. The $\text{B}(\text{OH})_3$ compound is formed during the ball-milling process of starting the mixture of materials for two systems ABW and ABSW (Figure 6).

3.3 ABSW system

The ABSW system was studied (Table 2) to simultaneously benefit the advantages of tungsten silicide and borides. According to the results of XRD, for only ball-milled ABSW sample up to 10 hours no specific peak was observed relating to aluminothermic reaction and only a very small amount of B_2O_3 has transformed into $\text{B}(\text{OH})_3$ due to presence of the moisture. It can be concluded that higher activation energy (Mechanical and thermal) is required for the initiation of aluminothermic reactions.

Figure 7a shows the results of DTA-TGA analyses performed on the ball-milled ABSW sample is in agreement with the results of ASW and ABW systems. Taking into account the thermodynamic data of Table 4, Figure 8 and Figures 7a and b, reactions of 1, 4 and 10 (Simultaneously) and reactions of 3,5,9,11,13 (Simultaneously) and reactions of 7, 8 were take placed at temperature range up to $1000\text{ }^{\circ}\text{C}$, $1100\text{--}1400\text{ }^{\circ}\text{C}$, $1450\text{ }^{\circ}\text{C}$, $1700\text{ }^{\circ}\text{C}$ respectively. Due to the occurrence of several peaks simultaneously at temperature range from 1100 to $1400\text{ }^{\circ}\text{C}$; a spread peak with high intensity is formed. The peak occurred at $1700\text{ }^{\circ}\text{C}$ (Reaction 8) for the ABSW is significantly stronger than the ABW system that can be related to higher temperature in the ABSW system ($1700\text{ }^{\circ}\text{C}$ against $1650\text{ }^{\circ}\text{C}$: It should be noted that the maximum temperature available in the thermal analysis system is $1700\text{ }^{\circ}\text{C}$.) and presence of Si in the ABSW system. On the other hand, thermodynamic and kinetic conditions of boron reduction and the formation of tungsten borides will be easier in presence of Si in such a manner that the phase is not appeared in the ABSW system (Figure 7b). For the ABW system, even up to $1650\text{ }^{\circ}\text{C}$, the spinel phase at $\text{Al}_{18}\text{B}_4\text{O}_{33}$ is still stable (Figure 5b). According to the DTA curve in Figure 7a while increasing the temperature, the DTA curve is steadily increased and this can be related to the intensification of alumino and silicothermic reactions. It should be noted that the formation of mullite in ABSW system can be due to the role of silicon in the reduction of tungsten oxide or boron oxide and the formation of SiO_2 (Reactions of 10 and 11) and its reaction with Al_2O_3 (Reaction 12),

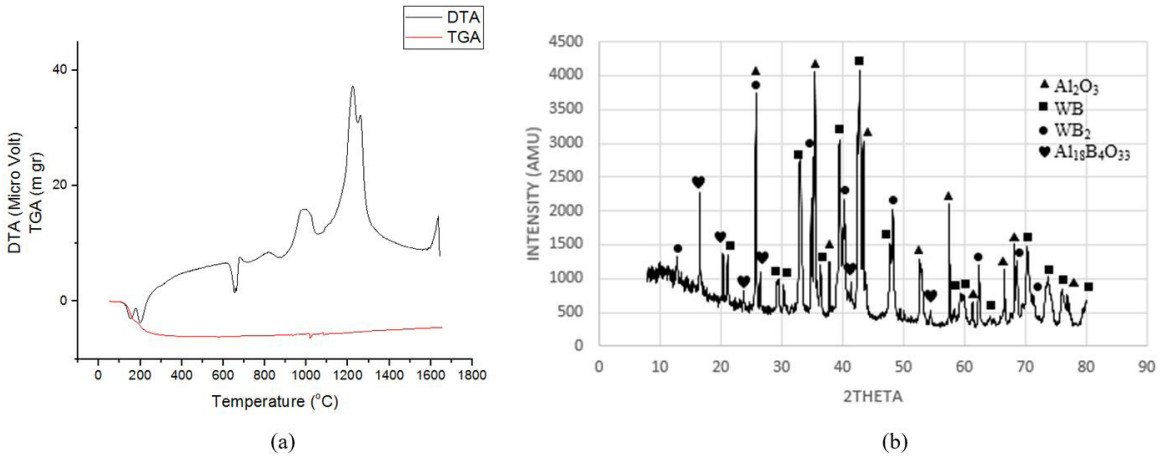


Figure 5. ABW system a) DTA-TGA with rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and atmosphere of argon, b) XRD analysis of thermal analyzed sample.

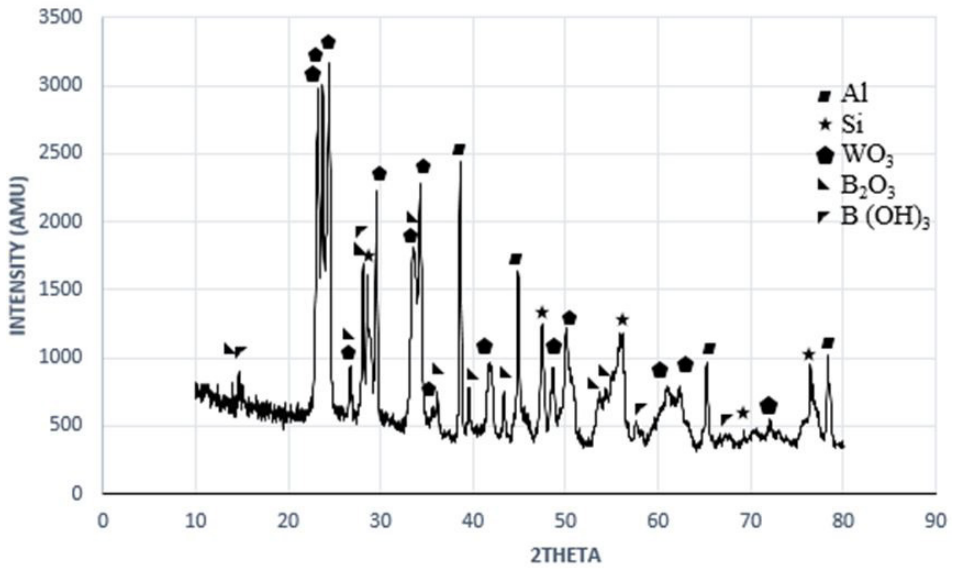


Figure 6. XRD analysis of the milled sample in the ABSW system for 10 hours.

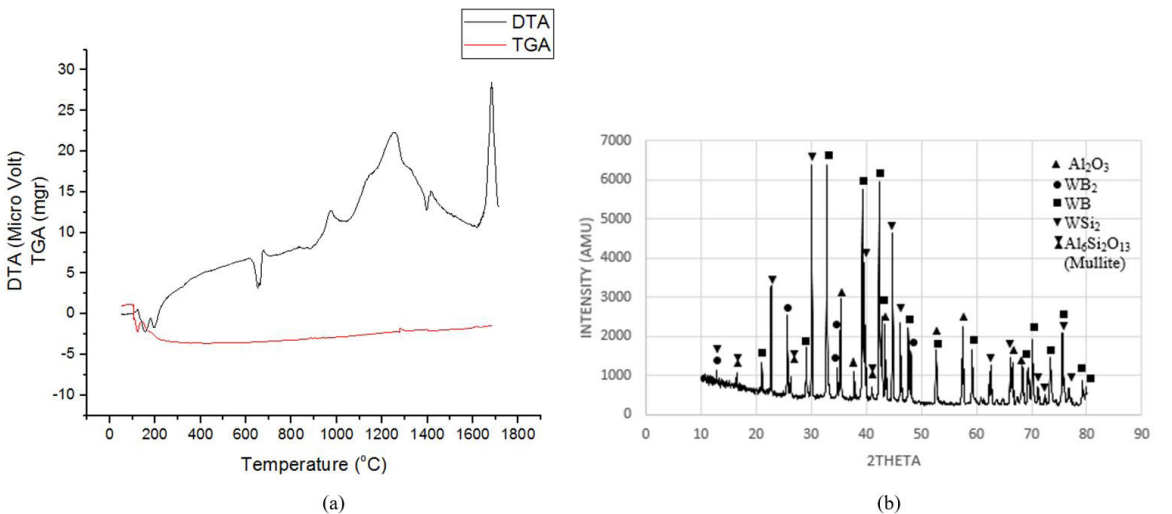


Figure 7. ABSW system a) DTA-TGA with rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and atmosphere of argon, b) XRD analysis of thermal analyzed sample.

The adiabatic temperature of combustion by using the given information in Tables 1 and 5 and the assumptions of non-melting components when considering the Equations 1 to 3 is calculated for three systems of ASW, ABW and ABSW. The result is given in Table 6. For the all three systems, according to merzanov criterion^{29,30}, self-propagating high temperature synthesis is occurred ($T_{ad} > 1800$ k).

$$\Delta H^{\circ}_{298} = (\Delta H^{\circ}_{WB_2} + \Delta H^{\circ}_{WSi_2} + 3\Delta H^{\circ}_{Al_2O_3}) - (2\Delta H^{\circ}_{WO_3} + \Delta H^{\circ}_{B_2O_3}) \quad (1)$$

$$\Delta H^{\circ}_{298} \int_{298}^{T_{ad}} C_P^S = B_2 \int_{298}^{T_{ad}} C_P^S + i_2 + 3 \int_{298}^{T_{ad}} C_{P12O_3}^S \quad (2)$$

$$438.04T + 0.034T^2 + 10730000T^{-1} = 2387963.04 \quad (3)$$

Respectively according to Figures 9 and 10 SEM images and EDS analysis of the ABSW samples (Table 7), there is a uniform and dense distribution of reinforcing phases (Borides and silicide of tungsten) in the alumina matrixes. Silicide phase is the small grain with spherical morphology (Point A) whereas; the borides phase is more coursing and relatively elongated (Point B). The alumina phase is appeared as the coaxial grains with hexagonal morphology. Needle-shaped blades (D-points) are related to the mullite phase. The measurements of fine silicide grains size on FE-SEM images show an average of 200 nm (Figure 11a). Figures 11b and 11c show the hexagonal state of borides crystals obviously.

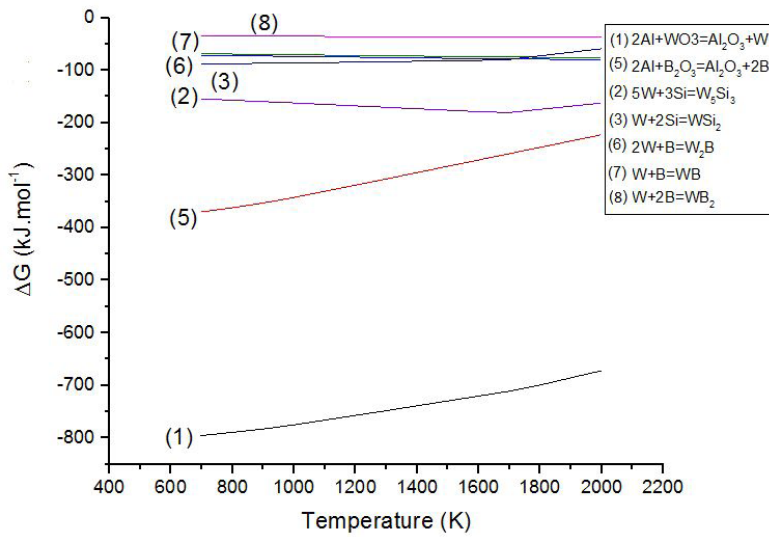


Figure 8. Free energy changes of reactions in ABSW triple system as a function of temperature.

Table 5. Thermodynamic information related to the calculation of the adiabatic temperature of the combustion front.

Composition	Standard formation enthalpy ΔH°_{298} (kJ.mol ⁻¹)	Solid state specific heat C_P^S J. (mol.K) ⁻¹
WB ₂	-33.50	50.42+0.003T-1569000T ²
WSi ₂	-92.90	67.82+0.011T-611000T ²
Al ₂ O ₃	-1676.90	106.6+0.017T-2850000T ²

Table 6. Adiabatic temperature of different systems.

Adiabatic Temperature	Stoichiometric	Mixture
4240	2Al+2Si+WO ₃	ASW
4070	4Al+WO ₃ +B ₂ O ₃	ABW
4125	6Al+2Si+2WO ₃ +B ₂ O ₃	ABSW

Table 7. EDS analysis for points A, B, C and D in Figure 10.

Related phases	Stoichiometry atomic percentage	Atomic percentage	Specified point
silicide tungsten	WSi ₂ : 67 Si, 33 W	49.95 Si, 53.05 W	A
	W ₅ Si ₃ : 37.5 Si, 62.5 W		
tungsten boride	WB: 50 B, 50 W	83.51 B, 16.49 W	B
	WB ₂ : 67 B, 33 W		
Alumina	60 O, 40 Al	58.21 O, 41.79 Al	C
Mullite	62 O, 9.5 Si, 28.5 Al	71.66 O, 21.28 Al and 7.06 Si	D

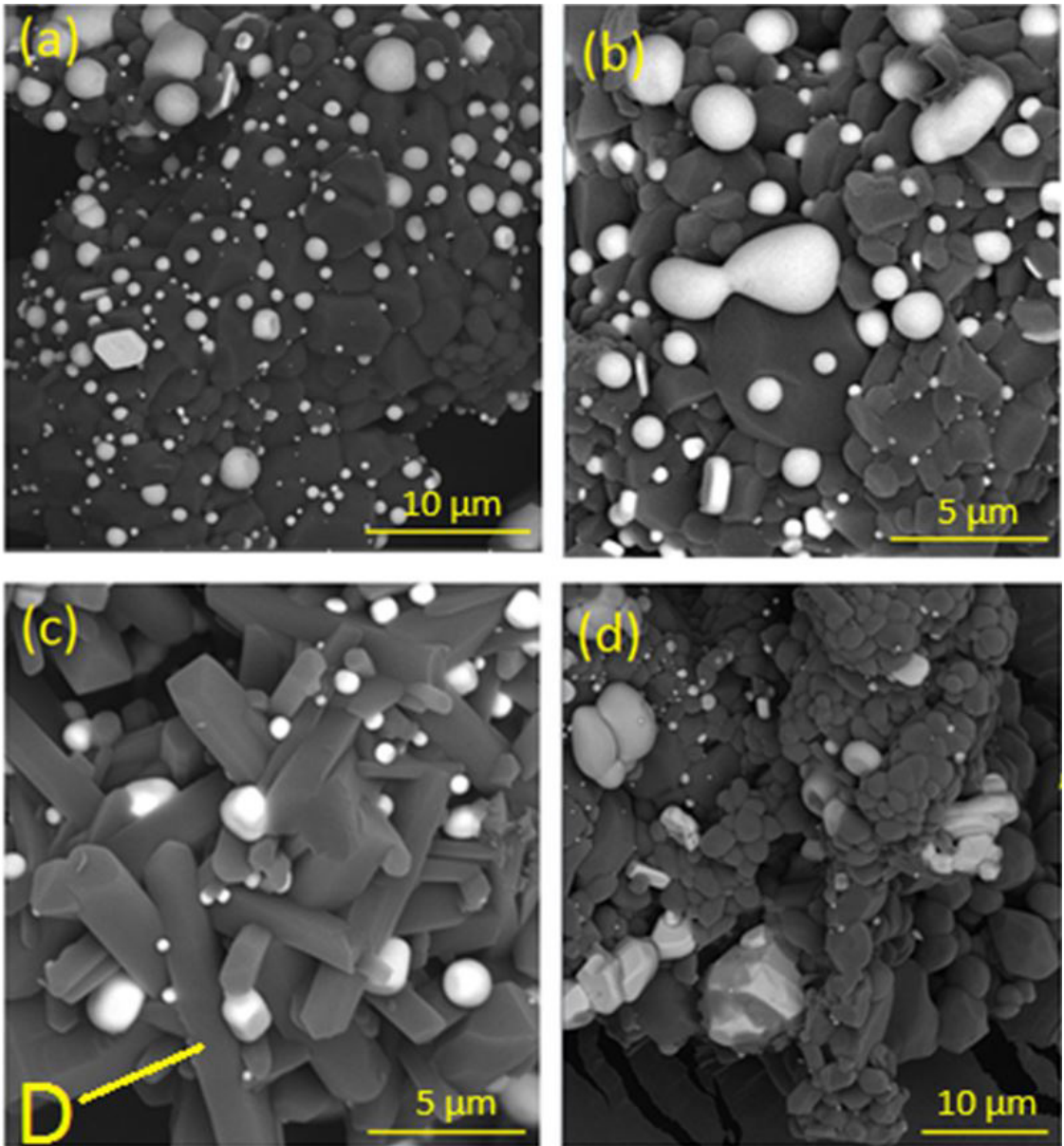


Figure 9. SEM images of the microstructure of different parts of the composite produced during the heat treatment at 1700 °C and the heating rate 20 °C.min⁻¹ under argon atmosphere in ABSW system.

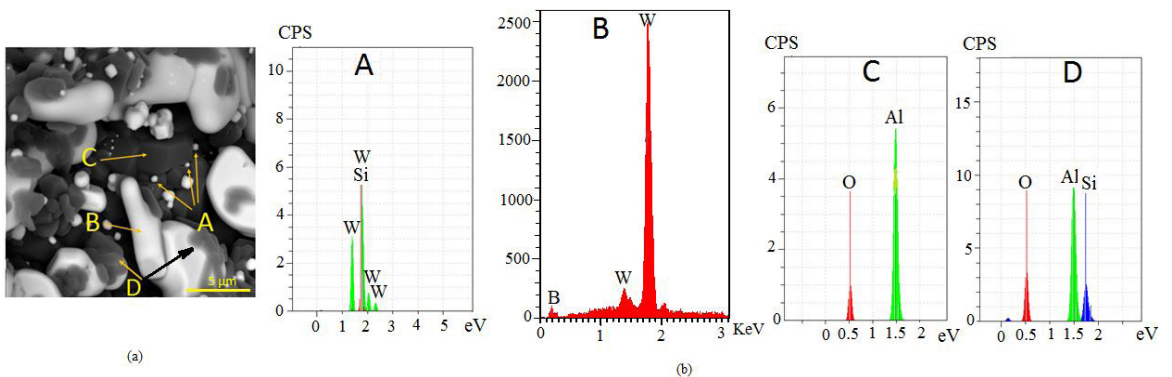


Figure 10. (a) SEM image and (b) EDS images of a heated sample at 1700 °C and a heating rate of 20 °C.min⁻¹ under argon atmosphere in ABSW system, A: tungsten silicide, B: tungsten boride, C: Alumina, D: Mullite.

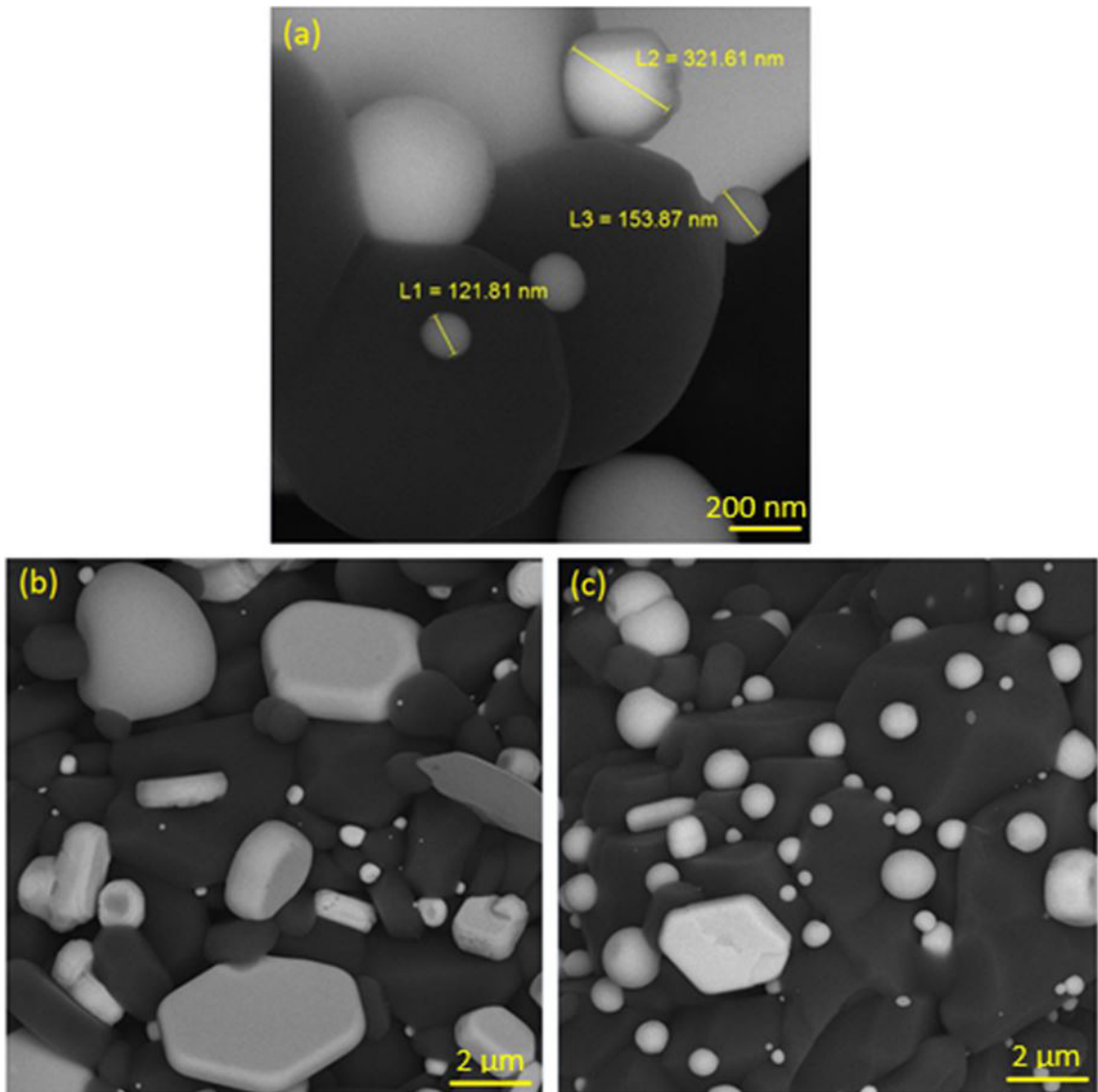


Figure 11. FE-SEM image of composite produced during heat treatment at 1700 °C and heating rate 20 °C.min⁻¹ under argon atmosphere in ABSW system.

4. Conclusions

The obtained composite powder by combustion synthesis process in Al-B₂O₃-Si-WO₃ system shows a uniformly distribution of different phases of WSi₂, WB, WB₂ (Coarse grain with hexagonal morphology), mullite (Acicular grains) and Al₂O₃ (Hexagonal morphology). By the ball-milling process up to 10 hours for mentioned system, no new phase is observed and mechanical activation is only occurred. Results of thermodynamical studies show that, the combustion processing for all three systems of Al-B₂O₃-WO₃, Al-Si-WO₃ and Al-B₂O₃-Si-WO₃ is self-combustion process (Calculated T_{ad} is higher than 4000K). The tungsten silicide is formed at temperature ranges of 1000-1050 °C and 1200-1300 °C in the aluminothermic systems of Al-Si-WO₃ and Al-B₂O₃-Si-WO₃ respectively. While, the Carbide based compounds (WB and WB₂) are formed at temperature ranges

of 1100-1400 °C and 1600-1700 °C in the aluminothermic systems of Al-B₂O₃-WO₃ and Al-B₂O₃-Si-WO₃ respectively. It is necessary to mention by the presence of Si in the Al-B₂O₃-Si-WO₃ system the formation of WB₂ is promoted.

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