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Research Article

The Effect of the Aluminum (Al) Ratio on the Synthesis of the Laminated Mn_2AlB_2 MAB Phase

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Abstract

MAB phases have recently garnered significant interest due to their excellent properties, such as high thermal and electrical conductivity, oxidation resistance, and exceptional corrosion resistance. Although the Mn_2AlB_2 phase has been synthesized using multiple methods recently, it requires long experimental durations (up to 7 days), high costs, and extensive experimental efforts to achieve high purity. In our study, the Mn_2AlB_2 MAB phase was synthesized using Al, B, and Mn as precursor materials. Specifically, we investigated the effect of Al ratios (Al:1.3, Al:3, and Al:10) on the formation of the Mn_2AlB_2 MAB phase. The precursor powders were mixed homogeneously in stoichiometric ratios using ball milling and cold-pressed in a 1-inch die set to form green pellets, which were then sintered in a high-temperature vacuum furnace at 1200°C. The resulting Mn_2AlB_2 MAB phase was characterized in terms of crystal structure, impurity, and microstructure using XRD, FESEM, and EDS.

Keywords: Mn_2AlB_2 MAB phase, crystal structure, XRD and FESEM

Tabakalı Yapıdaki Mn_2AlB_2 MAB Fazının Sentezinde Alüminyum (Al) Oranının Etkisi

MAB fazları iyi termal ve elektriksel iletkenliklerinin yanı sıra oksidasyon direncinin yüksek ve mükemmel korozyon direncine sahip olması gibi mükemmel özelliklerinden dolayı son zamanlarda büyük ilgi görmektedir. Özellikle Mn_2AlB_2 fazı yakın zamanda birden fazla yöntem kullanılarak sentezlenmiş olmasına rağmen, uzun deneysel süre (7 güne kadar), yüksek maliyet ve mükemmel saflıkta sentezlenmesi için deneysel çalışmalara ihtiyaç duyulmaktadır. Yaptığımız çalışmada ise öncü materyaller olarak Al, B ve Mn kullanılarak Mn_2AlB_2 MAB fazı sentezlenmiştir. Çalışmamızda özellikle Al (Al:1.3, Al:3 ve Al:10) oranının Mn_2AlB_2 MAB fazının oluşumuna olan etkisi incelenmiştir. Öncü tozlar stokiyometrik oranlarda bilyalı öğütme ile homojen bir şekilde karıştırılmış ve fiziksel bağların oluşumu için 1 inç'lik die-set ile soğuk preslenerek ham peletler elde dilmiş ve daha sonra 1200 ^{o}C'de yüksek sıcaklık vakum fırınında sinterlenmiştir. Elde edilen Mn_2AlB_2 MAB fazının kristal yapısı, safsızlık ve mikro yapısı XRD, FESEM ve EDS kullanılarak karakterize edilmiştir.

Anahtar kelimeler: Mn_2AlB_2 MAB fazı, kristal yapı, XRD ve FESEM

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1. Introduction

Studies have been carried out in recent years on similar MAB phases due to using MAX phases as a leading material in synthesizing 2D structures. Theoretical and experimental studies have proven MAB phases obtained by replacing the carbon and/or nitrogen corresponding to the element X in the MAX phases with boron (Ade and Hillebrecht, 2015; Chai et al., 2015; Bai et al., 2017). Recent studies on MAB phases have mainly focused on single crystal growth and crystal structure determination (Ade and Hillebrecht, 2015), electronic properties (Lu et al., 2017), mechanical properties (Siriwardane et al., 2020), and oxidation resistance (Kota et al., 2016).

MAB phases are layered orthorhombic transition metal borides similar to MAX phases but with higher structural stability. In the MAB phase, M represents the transition metals such as Cr, Mo, W, Fe, Mn, or solid alloys of these elements (FeB, CrB, and MnB), A represents the III-A or IV-A group element, and B represents the boron element. They have shown a unique diversity in crystal chemistry and bonding patterns, where the binding of boron atoms is often determined by the transition metal (M: B) ratio. These can be considered materials consisting of stacked M-B blocks, which consist of face-sharing triangular BM_6 prisms interwoven with planes of A atoms or more complex A sheets between minerals (Kota et al., 2018a). MAB phases have a significant structural diversity. Among them are well-known phases MoAlB, WAlB, Fe_2AlB_2, Cr_2AlB_2, and Mn_2AlB_2, which have attracted significant attention recently. As a result of the atomic structure of MAB phases, the name MAB is given because the thickness of the metal boride layer (n) resembles the large carbide structure of MAX phases. MAB phases have more than one crystal structure (space group). For example, Mn_2AlB_2 (space group C_{mmm}), MoAlB (space group C_{mcm}), Cr_3AlB_4 (space group I_{mmm}), Cr_4AlB_6 (space group C_{mmm}), Cr_4AlB_4 and Ru_2ZnB_2 (space group $I4_1/amd$). In general, $(MB)_{2z}A_x(MB_2)_y$, wherein ($z = 1–2$, $x = 1–2$, $y = 0–2$); M is a transition metal (M = Mo, Cr, Mn, Fe, W, Hf, Ru, Y), A is typically Al, and B is boron. Having the M_2AB_2-type structure ($x = 1$, $y = 0$, $z = 1$), the Mn_2AlB_2 crystallizes in the C_{mmm} space group.

MAB phases can also be synthesized using methods similar to MAX phases (Kota et al., 2018b). The synthesis of MAB phases involves sintering at high temperatures (1000-1500 °C) under an argon (Ar) atmosphere. Elemental (Al, B, Cr, W, Mo, Mn, Fe) or alloy (FeB, CrB, MnB) can be precursor materials. There are few studies in the literature on the synthesis of Mn_2AlB_2. Kota et al. attempted to prepare Mn_2AlB_2 by using hot press sintering technology at 1050 °C, pressure up to 36 MPa, and mixing Mn, Al, and B powders as starting materials (Kota et al., 2018a). In another study, using Mn, Al, and B powders as precursor materials, Mn_2AlB_2 was synthesized by heat treatment sintering at 1050 °C for 15 hours. Despite attempts to synthesize Mn_2AlB_2, the cost of synthesis is high due to the methods used, such as hot-pressure sintering. As for the heat treatment technique, the fact that the experiment lasts approximately 15 hours may cause problems in terms of equipment, and the impurity of the obtained Mn_2AlB_2 MAB phase is relatively low. Therefore, Mn_2AlB_2 synthesis requires new and efficient techniques. In another study, Mn_2AlB_2 was synthesized by arc melting at 1450 °C with Mn:B:Al atomic ratio of 1:1:30 (Ade and Hillebrecht, 2015). Additionally, Zhai et al. obtained Mn_2AlB_2 using arc melting

under the Ar atmosphere at 900 °C for 7 days (168 hours). Mn_2AlB_2 was also produced using Al Flux techniques, where a mixture of Mn, Al, and B (Al:Mn:B = 10:1:2) was heated to 1150 °C for 15 hours (Roy et al., 2023).

In this study, it was aimed to synthesize the Mn_2AlB_2 MAB phase using Al, B and Mn as precursor materials and to investigate the effect of different Al concentrations (Al:1.3, Al:3 and Al:10) on the formation of the phase and to obtain it by high-temperature sintering with a synthesis time that is lower duration than the studies in the literature.

2. Materials and Methods

Figure 1. Experimental materials and steps used in the synthesis of Mn_2AlB_2 MAB phase.

As shown in Figure 1, Manganese (99.3 %, 325 mesh), aluminium (99.5 %, 325 mesh), and amorphous boron (98 %, 325 mesh) powders weighed in an atomic ratio of 2:x:2 (x=1.3, 3 and 10) respectively. After the precursor materials and yttria-stabilized zirconia (YSZ) balls were placed in the jar, they were sealed in an Argon atmosphere in the glove box. Then, the powders were mixed via rotary ball milling for 18 h. After mixing, the powders were cold-pressed into pellets with loads corresponding to a stress of 15 MPa in a steel die. To react with the pressed pellets at high temperatures, they were placed in an alumina boat, placed in a high-temperature vacuum furnace with a heating rate of 5 °C/min, and sintered for 2 hours at 1200 °C in a pre-vacuumed 200 sccm Argon atmosphere. After cooling at room temperature, the pellets were crushed into fine powders in an agate mortar and pestle and passed through a 325-mesh sieve

for further characterization. The synthesis parameters of the Mn_2AlB_2 MAB phase are given in Table 1.

Tablo 1. Synthesis parameters of Mn_2AlB_2 MAB phase.

Stochiometric ratio	Diameter of balls (mm)	BPR (Ball to powder ratio)	Mixing powders (rpm)	Time (h)	Pressure (MPa)	Sintering temperature (°C)/Time (h)
Mn:Al:B → 2:x:2 x=1.3, x= 3, x=10	5	5:1	200	18	15	1200 °C / 2 h

3. Results and Discussion

When synthesizing MAB phases, Al is added more in molar ratio (Tan et al., 2013; Wang et al., 2021). This is because the melting point of Al is lower than other elements in the MAB phase. However, the effect of Al concentration on the synthesis of the Mn_2AlB_2 phase is not yet fully understood. Therefore, we changed the Al concentration by varying x=1.3, 3, and 10, corresponding to $Mn_2Al_{1.3}B_2$, $Mn_2Al_3B_2$, and $Mn_2Al_{10}B_2$ labelled samples. Crystalline structures of the samples were investigated in the 2θ range (step size: 0.05°) from 10° to 80° using X-ray diffraction (XRD) patterns obtained from PANalytical Empyrean with Cu-K_α radiation of wavelength (λ) of 1.5406 Å. The XRD patterns of $Mn_2Al_{1.3}B_2$, $Mn_2Al_3B_2$, and $Mn_2Al_{10}B_2$, corresponding to Al concentrations of x=1.3, 3, and 10, respectively, are shown in Figure 2. In XRD patterns, it was observed that most of the peak positions correspond to the orthorhombic (C_{mmm} space group) crystal structure of the Mn_2AlB_2 phase, as indicated by the JCPDS card No: 072-0103 (Figure 3).

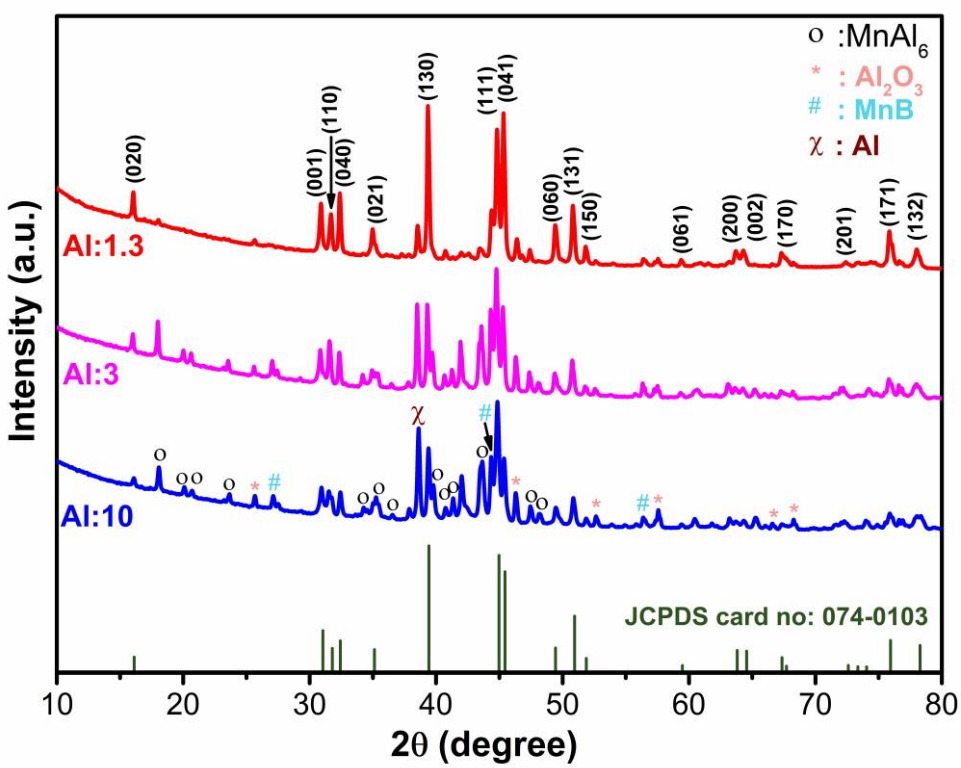

Figure 2. XRD pattern of Mn_2AlB_2 MAB phase according to the amount of Al.

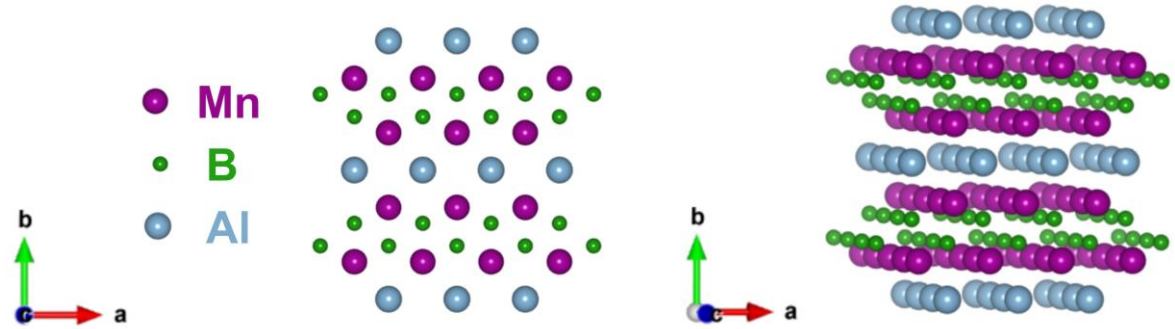

Figure 3. 2D and 3D visualization of the orthorhombic (C_{mmm} space group) crystal structure of 212-type Mn_2AlB_2 MAB phase.

The main phase identified in the sample with an Al content of 1.3 was Mn_2AlB_2 with high purity, alongside minor MnB, $MnAl_6$, Al_2O_3, and Al (Table 2). In contrast, the sample with an Al content of 3 exhibited more MnB, $MnAl_6$, Al_2O_3, and Al impurities compared to the sample with an Al content of 1.3, indicating an increase with higher Al content. However, increasing the initial mixture's Al content to 10 did not effectively enhance the purity of Mn_2AlB_2; instead, the quantity of Mn_2AlB_2 MAB phase decreased. As the Al content increased, some characteristics, for example (002), (001), (004), peaks intensity of Mn_2AlB_2 decreased, leading to a higher formation of MnB, $MnAl_6$, Al_2O_3, and Al impurities alongside Mn_2AlB_2, as observed in Figure 2. In the XRD pattern with an Al content of 1.3, the intensity of reflections from the (002) crystal plane was significantly higher than Al content of 3 and 10, indicating better crystallinity of the Mn_2AlB_2 phase. Additionally, the peak intensity of the (002) crystal plane decreased as the ratio of Al increased. Furthermore, the presence of Al_2O_3 in each sample is likely due to the reaction between Al and O adsorbed on the surfaces of precursor powders.

Tablo 2. Starting mixture with different molar ratios and resulting phases.

Starting mixture	Molar ratio	Resulting phases
Mn/Al/B	2:1.3:2	Mn_2AlB_2 (s), $MnAl_6$ (w), MnB (w), Al_2O_3 (w), Al (m)
	2:3:2	Mn_2AlB_2 (m), $MnAl_6$ (m), MnB (m), Al_2O_3 (w), Al (s)
	2:10:2	Mn_2AlB_2 (w), $MnAl_6$ (m), MnB (m), Al_2O_3 (w), Al (s)

Symbols means: ′s′:strong; ′m′: medium; ′w′ weak.

Field Emission Scanning Electron Microscopy (FESEM) measurement and elemental mapping of the MAB phases were performed using the FEI Quanta 450 FEG device and AMETEK Materials Analysis Division on the FESEM device, respectively. In Figure 4, as seen in the low and high magnification, FESEM images of samples passed through a 325-mesh sieve after crushing and grinding steps following sintering, the particle size is less than 38 µm. Generally, Mn2AlB2 MAB phases where Al is utilized in varying ratios, like commonly synthesized MAX phases, exhibit a well-defined crystalline structure and a morphology resembling a laminated structure.

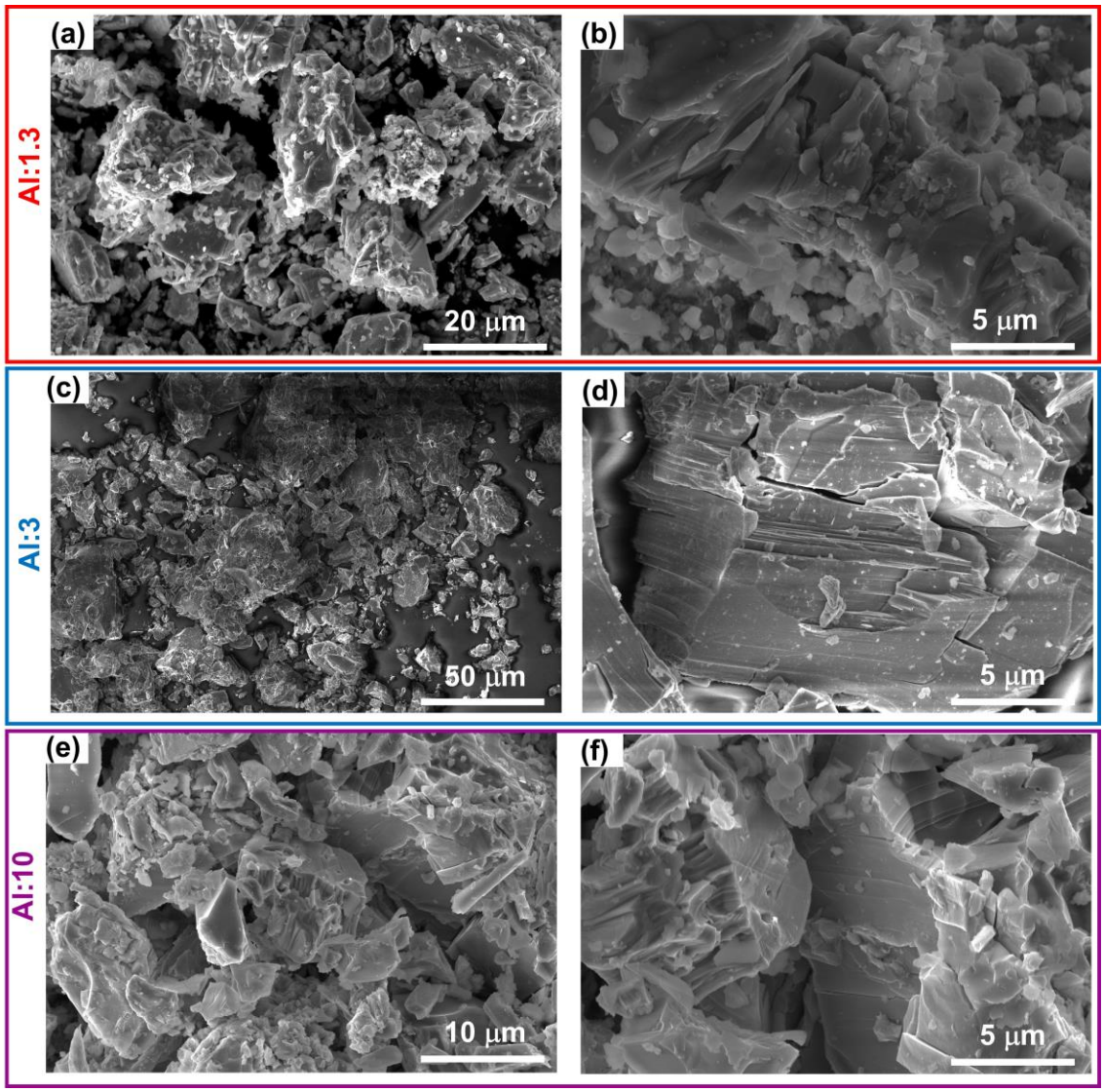

Figure 4. FESEM images of Mn_2AlB_2 MAB phase according to the amount of Al, (a, b) Al:1.3, (c, d) Al:3, and (e, f) Al:10.

EDS analysis was conducted to investigate the effect of varying amounts of Al on forming the Mn_2AlB_2 MAB phase. Figure 5 presents the EDS results regarding the atomic concentration of Mn, Al, and B elements. Generally, no impurities containing different elements were detected in the MAB phases, and full-area measurements indicate a homogeneous distribution of Mn, Al, and B. However, in the MAB phases of samples Al:3 and Al:10, where the Al concentration is increased, a slight increase in the ratio of Al impurity is observed. This phenomenon likely reduces the content of the Mn_2AlB_2 MAB phase in the final compound, as indicated by XRD results within the powder. It is known that adding excessive amounts of Al during the synthesis of MAX phases plays a crucial role in compensating for the loss of Al due to evaporation. However, increasing the amount of Al can reduce the formation rate of MAB phases with low thermal stability or lead to the formation of additional impurities.

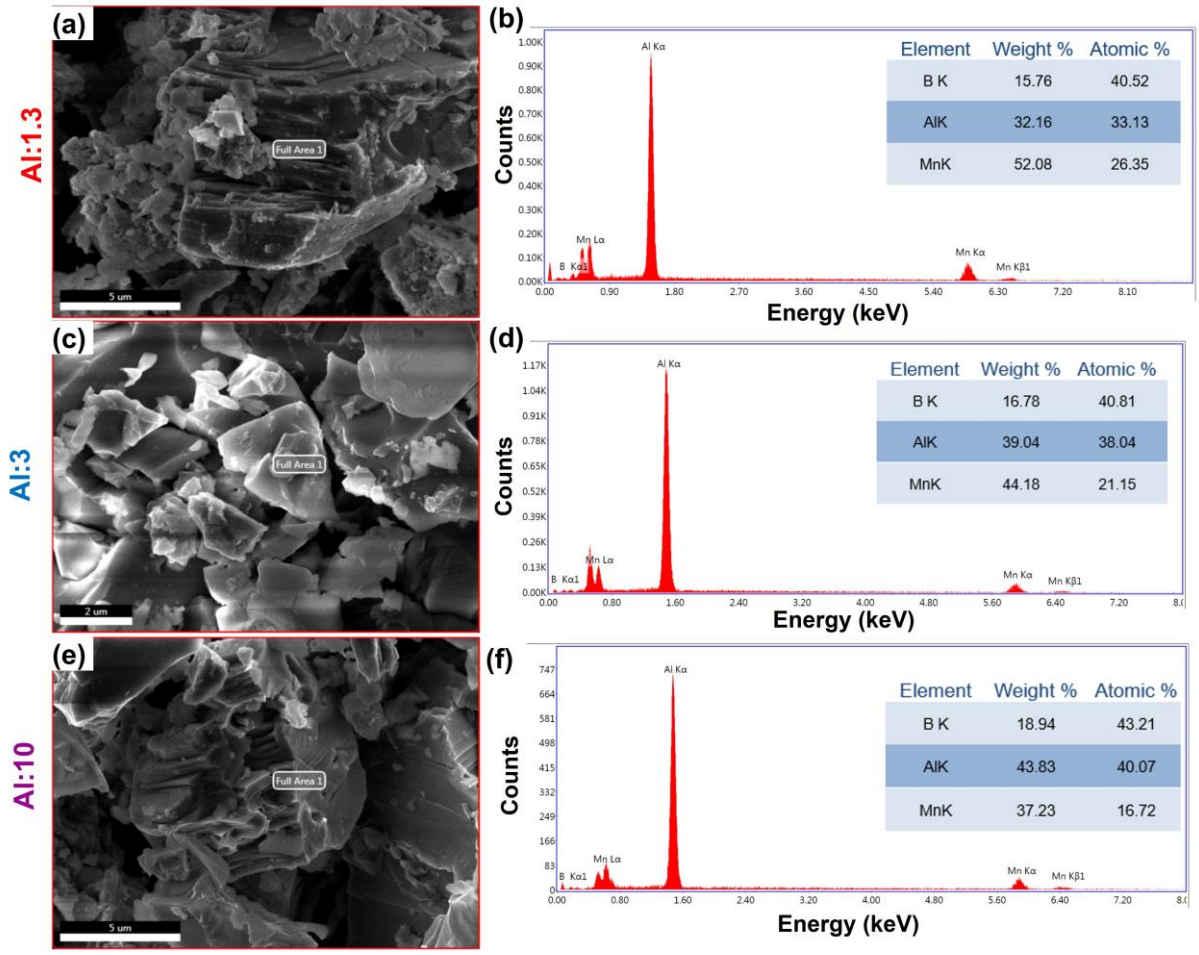

Figure 5. Full area EDS analysis of Mn_2AlB_2 MAB phase with atomic concentrations according to the amount of Al, (a, b) Al:1.3, (c, d) Al:3, and (e, f) Al:10.

4. Conclusion

In this study, the Mn_2AlB_2 MAB phase was obtained by sintering at 1200 °C for 2 hours in a vacuum environment in a high-temperature furnace. The effect of Al content (Al:1.3, Al:3 and Al:10) on the formation of the Mn_2AlB_2 MAB phase was investigated. In the sample with an Al content of 1.3, the main phase Mn_2AlB_2 was obtained in high purity orthorhombic crystal structure and small amounts of MnB, $MnAl_6$, Al_2O_3 and Al impurities were found. As the Al content increases, the proportion of the Mn_2AlB_2 phase decreases, and the proportion of impurities such as $MnAl_6$, MnB and Al_2O_3 increases. XRD and FESEM analyses showed that the Mn_2AlB_2 MAB phase grows perfectly in a layered structure and maintains high crystal quality.

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Ethics in Publishing

There are no ethical issues regarding the publication of this study.

Author Contributions

Fatma Nur Tuzluca Yesilbag: Ideas; formulation or evolution of overarching research goals and aims; Acquisition of the financial support for the project leading to this publication.

Yasar Ozkan Yesilbag: Preparation, creation, and presentation of the published work, specifically visualization/ data presentation.

Ahmad Huseyin: Performing the experiments and data collection.

Ahmed Jalal Salih SALIH: Performing the experiments or data/evidence collection.

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