

Research Letter



Magnetofunctional response of AIFe₂B₂ powders synthesized in open air via molten salt shielded/sintering method

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Abstract

Predominantly single-phase $AIFe_2B_2$ powders were synthesized by a molten salt sintered/sintering (MS³) method wherein a green compact comprising of AI, Fe and B powders encapsulated in a KBr salt was heat treated at 1000°C for 12 h in open air. Results reveal that the magnetofunctional properties of $AIFe_2B_2$ powders synthesized via the novel MS³ method is comparable to that of powders produced via melt-based or powder metallurgy methods that have been previously reported in the literature. Since no inert environment or post-fabrication annealing or acid treatments is required, it is construed that the MS³ processing scheme is the most cost-effective and energy-efficient method to synthesize $AIFe_2B_2$ powders to date.

Introduction

Transition-metal ternary borides (particularly MAB Phase) demonstrate rich crystal chemistry, with covalent boron arrangements ranging from 1-dimensional linear chains and 2-dimensional planar sheets to complex 3-dimensional networks. The diversity of these crystal structures results in a wide range of properties (e.g., mechanical, magnetic, and catalytic behavior) and applications.^[1,2] Modifying the complex bonding configurations between the metal and boron atoms within the structure facilitates greater control and tuning of material properties. These compounds are categorized on the basis of their metal-to-boron atomic ratio (M/B), which generally ranges from >1:4 for metal-rich compounds (also known as low borides) to $\leq 1:4$ for boron-rich compounds (or higher borides).^[3,4]

High temperatures, often exceeding 1200°C, and inert atmospheres are required to produce borides due to the covalent character of their chemical bonds and, consequently, their high melting temperatures and low self-diffusion coefficients.^[5] Solid and melt state processing of borides from the primary reactants typically results in dense samples, which are crushed, milled, and sieved laboriously into fine powder for further processing. Typically, an inert atmosphere is needed to prevent spontaneous oxidation during high-temperature synthesis-a requirement which leads to high-energy consumption and high production costs. Against this backdrop, it was recently demonstrated that the molten salt shielding and sintering (MS^3) method is a sustainable, energy-efficient process that uses no inert gas, relatively low temperatures, and moderately short reaction times to synthesize boride powders with uniform chemical composition and high-phase purity.^[6] Building on

this report, in this work, we focus on elucidating the functional properties of powders of the ferromagnetic boride $AlFe_2B_2$ synthesized using the MS³ processing method.

AlFe₂B₂ is a ferromagnetic compound with a layered orthorhombic crystal structure that demonstrates a tunable magnetic transition temperature T_c (ferromagnetic FM \leftrightarrow paramagnetic PM) near room temperature with reported magnetic moments in the range 0.95 to 1.30 µB/Fe-atom.^[1,6,7] First-principal investigations of the magnetocrystalline and concomitant experimental efforts reveal that the magnetic moments in AlFe₂B₂ are oriented along the crystallographic a-axis. Other technologically important aspects of AlFe₂B₂ include good chemical and mechanical stability complemented with good heat transfer characteristics (high thermal conductivity 6.84 W/mK^[8] and a low heat capacity $C_p = 115$ J-mole⁻¹ K⁻¹).^[9] In the proximity of T_c , magnetic entropy change ΔS_{mag} and adiabatic temperature change ΔT_{ad} values ranging from 2.1 to 4.4 J·kg⁻¹ K⁻¹ and 1–1.6 K, respectively, have been reported at moderate magnetic fields of $\mu_0 H_{app} = 2$ T in polycrystalline specimens-a feature that renders this materials system promising for magnetic cooling applications.^[7,10–18] Beyond, magnetic technologies, AlFe₂B₂ is also a remarkable stable water oxidation electrocatalyst for sustainable production of hydrogen via water splitting.^[19] In particular, the crystal structure can be viewed as composed of Al layers, which represent the conductive layer, and [Fe₂B₂] layers, which represent the active sites for oxygen evolution reaction (OER) catalysis.^[19] Within the [Fe₂B₂] slab, the B atoms form infinite B-B zigzag chains along the a-axis, with Fe-B bonds stitching these chains into the two-dimensional structure.^[1] Thus, the AlFe₂B₂ structure can potentially serve as a pre-catalyst for the in-situ formation of active electrocatalytic sites during hydrogen production.^[19]

In both magnetic and catalytic applications, the AlFe₂B₂ working material needs to be processed into the powder form. To this end, Table I lists the wide variety of melt-solidification and solid-state powder metallurgy processing methods used to produce AlFe₂B₂ to date. Conventional melt processing techniques such as arc-melting and suction-casting as well as direct energy deposition additive manufacturing schemes involve repeated melting of precursor powders of elemental Fe, B and B powders or FeB and Al powder mixtures, resulting in polycrystalline samples consisting of varying amounts of the desired AlFe₂B₂ phase and secondary impurities such as Al₁₃Fe₄, FeB and AIFe₆.^[6-10,12,16-18,20-29] It is essential to anneal the multiphase samples for prolonged time periods ranging 3-14 days at high temperatures in the range 1000-1200°C to achieve single-phase materials.^[6-10,12,17,18,20,23-25,28] Since Al has a low melting point, excess Al (~20-50 mol% above stoichiometry), is often added to compensate for its evaporation and to suppress the formation of Al₁₃Fe₄ impurities.^[21] Removal of $Al_{13}Fe_4$ from the parent compound thereafter requires the use of corrosive acidic solutions. Challenges associated with melt-based processes may be overcome using reactive powder metallurgy techniques (spark plasma sintering, microwaveassisted sintering, reactive hot pressing) of iron monoboride and aluminum powder mixtures can achieve dense samples that are largely single-phase, in comparatively reduced heat treatment times (12 h to 3 days), while utilizing lower amounts of excess Al (10–15%).^[10,20,30]

From the perspective of manufacturing cost and energy efficiency, it is worthwhile to note that except for the MS^3 method, all the powder metallurgy and melt-based synthesis routes listed in Table I, require high heat treatment temperatures in the tune of 900–1200°C and inert atmospheres. The availability of high-quality powders, combined with energy and cost savings, removes one of the bottlenecks for these materials' industrial magnetic cooling and catalytic application. Currently, it is unclear if the magnetofunctional response of AlFe₂B₂ powders produced via MS³ is comparable to that of bulk samples produced by powder metallurgy and melt-based synthesis routes. This study addresses this gap in literature.

Experimental methods

In this study, two samples of nominal stoichiometric composition $AIFe_2B_2$ phase were synthesized using elemental powders of Fe (purity \geq 99%, Sigma Aldrich), Al (purity 99.5%, Alpha Aesar), B (purity \geq 95%, Alpha Aesar). As per guidance obtained from the pseudo-binary FeB-Al phase diagram,^[21] 20% excess Al was added to the base compositions to maximize the $AIFe_2B_2$ phase content and reduce formation of detrimental boride phases after heat treatment. The powders were mixed in a high-energy ball mill (8000 M mixer Mill, SPEX SamplePrep) and then uni-axially cold pressed in a stainless-steel die under 182 MPa stress to form green compacts (12.5 mm diameter and around 5 mm height).

One compact was heat treated at 850°C for 2 h and at 1000°C for 12 h in an Ar atmosphere, and then crushed in a mortar and pestle and sieved into-325 mesh. Henceforth, in this paper, this sample shall be referred to as the "control" or "reactive sintered (RS) sample". The second compact was subjected to the molten salt shielded synthesis/sintering (MS³) process, and to this end, it was covered with KBr salt in a larger steel die and cold-pressed at 46 MPa stress for 30 s twice to make compact salt pellets with the sample encapsulated in it. The salt-coated pellets were then further shielded by loose salt and then heat-treated in the open air in a high-temperature alumina tube furnace. To recover the AlFe₂B₂ powder, the alumina crucible was submerged in a beaker of distilled water at 70°C. Following salt dissolution, the remaining solution was stirred for 1 h. The powder was then filtered, washed 5 times with deionized water, and dried at 100°C for 12 h. The powder was then filtered, washed several times with deionized water, and dried at 80°C for 18 h. The dried samples were then further crushed in a mortar and pestle and sieved into-325 mesh.

The microstructure of the powdered samples was characterized using optical microscopy and field emission scanning electron microscopy (SEM, Hitachi SU-70). Room-temperature X-ray diffraction (XRD) data was measured using a Rigaku diffractometer SmartLab, Rigaku, Japan) with a Cu-Ka radiation source to allow determination of lattice parameters and phase purity employing the Rietveld refinement feature in the Highscore Plus software. Magnetic characterization was carried out using Vibrating Sample Magnetometry (Quantum Design PPMS DynaCool and VersaLab models) in magnetic fields up to $\mu_0 H_{app} = 5$ T in the temperature range 1.8 K \leq T \leq 400 K. The Curie temperature T_c was determined from the inflection point of the M vs. T curve as the maximum of the derivative of M with respect to T (i.e., $\partial M \partial T$). The magnetocaloric behavior of AlFe2B2 in the magnetic field range $0.5\!<\!\mu_0 H_{app}\!<\!2$ T was quantified indirectly from magnetic entropy change curves (ΔS_{mag} vs. T) constructed by applying Maxwell's relation,^[31]

$$\Delta S_{mag}(H,T) = \mu_0 \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH$$

to data obtained from isothermal M(H) curves measured in the vicinity of the Curie temperature. Here, μ_0 is the permeability of free space, $\frac{\partial M}{\partial T}$ is the temperature derivative of the magnetization and H_{max} is the maximum applied field.

Results and discussion

Figure 1(a) shows the SEM micrographs of $AIFe_2B_2$ samples prepared via molten salt shielding/sintering method. The preliminary powders exhibit distinct particles that measure approximately $30\pm10 \ \mu m$ in size. Figure 1(b) shows the room temperature XRD patterns peaks of $AI_{1,2}Fe_2B_2$ samples prepared



Synthesis Method	Post processing methods		Magnetic properties			References		
	Al/Fe/B	Heat treatment Acid et		Acid etching	\overline{g} Tc (K)	Ms (emu/g)	$\Delta S(J/Kg^{-1} \ K^{-1})$	
		Gas	Temp (K)					
Powder metallur	·gy							
Molten salt sintering	1.2/2/2	Air	1273	Ν	300	62 at 1.8 K	3.8 at 2 T	Present Work
Reactive sintering	1.2/2/2	Ar	1273	Ν	288	69 at 1.8 K	4.6 at 2 T	Present Work
Single step reactive hot pressing	1/2/2	Under Vacuum	1473	Ν	280	70 at 50 K	2.4 at 2 T 5.3 at 5 T	30
Spark plasma sintering	1/2/2	Under Vacuum	1183	Ν	274	6.2 at 5 K	3.1 at 2 T 6.4 at 5 T	10
Microwave sintering	3/2.6/2	Under Vacuum	1173	Y	287	1.11 μB/Fe atom	3.31 at 2 T 6.45 at 5 T	20
Melt based proc	esses							
Arc melting	3/2/2	Under Vacuum	1173	Y	282	1.15 μB/Fe atom	4.4 at 2 T 7.3 at 5 T	23
Arc melting	1.5/1/1	Ar	1073	Ν	320	0.95 μB/Fe atom	_	16
Arc melting	3/1/1	Under Vacuum	1173	Y	285	$0.9\ \mu B/Fe$ atom	1.3 at 1 T 4.5 at 5 T	17
Arc melting	3/2/1	Under Vacuum	1173	Y	299	_	_	24
Arc melting	(2-3)/2/2	Under Vacuum	1073	Υ	290	_	_	10
Arc melting	3/2/2	_	_	Y	285	78 at 50 K	2.4–3.6 (hard/ easy axis) at 2 T	7
Arc melting	3/2/2	_	_	Y	286	$0.7 \ \mu B/Fe$ atom	-	18
Arc melting	2/2/2	_	_	Ν	290	55.8 at 100 K	1.85 at 2 T 4 at 5 T	25
Arc melting	2/2/2	_	_	Y	294	72.3 at 100 K	3.07 at 2 T 6.49 at 5 T	25
Arc melting	3/2/2	_	1173	Y	303	91.35 at 5 K	3.4 at 2 T 7.2 at 5 T	12
Arc melting	3/2.6/2	Under Vacuum	1173	Y	286	1.23 μB/Fe atom	3.75 at 2 T 7.21 at 5 T	20
Arc melting	1/2/2	Under Vacuum	1178	Ν	278	_	6.3 at 7 T	26
Arc melting	1.2/2/2	Ar	1323	Ν	-	_	_	27
Arc melting/ suction casting	1.2/2/2	Ar	1313	Ν	272	78 emu/g at 50 K	2.7 at 2 T	22
Suction cast	1/2/2	Ar	1313	Ν	293	76.7 at 50 K	_	21
Suction cast	1.2/2/2	Ar	1313	Ν	282	68.7 at 50 K	_	21
Ga flux stoi- chiometric	1.5/1.8/2	Under Vacuum	1173	Y	307	1.03 μB/Fe atom	4.1 at 2 T 7.7 at 5 T	23
Al flux	5/3/2	Ar	1473	Y	274	$2.40 \ \mu B/f.u$	3.78 at 2 T 4.87 at 3 T	28
Al flux	0/1/2/5(Al):1(AlFe2B2)	Ar	1673	Y	_	_	_	10
R-F melting	7/7/6	Ar	1873	Y	293	1.28 μB/Fe atom	3.1 for 2 T 6.75 for 5 T	20
R-F melting	3/2.6/2	Ar	1873	Y	287 K	1.13 μB/Fe atom	3.38 for 2 T 6.47 for 5 T	20
Induction melting	1.2/2/2	Under Vacuum	1173	Ν	302	79.9	7.2 for 5 T	29

Table 1. Summary of synthesis methods, magnetic and magnetocaloric properties of $AIFe_2B_2$ prepared using molten salt reactive sintering, compared with samples prepared using different synthesis methods.

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Synthesis Method	Post processing methods			Magnetic properties				References
	Al/Fe/B	Heat treatment		Acid etching	Tc (K)	Ms (emu/g)	$\Delta S(J/Kg^{-1} K^{-1})$	
		Gas	Temp (K)					
Induction melting	1.2/2/2	_	_	N	300	_	5.1 for 5 T	29
Induction melting	1.8/2/2	Under Vacuum	1173	Ν	285	69.9	4.8 for 5 T	29
Induction melting	1.8/2/2	_	-	Ν	268	-	1.8 for 5 T	29
Direct energy deposition	4/2/4	Ar	1313	Ν	284	65.2 at 50 K	2.2 for 2 T	9

Table I. (continued)



Figure 1. (a) SEM micrographs of $AIFe_2B_2$ samples prepared via molten salt shielding; (b) Normalized room temperature XRD patterns of $AIFe_2B_2$ samples prepared via molten salt shielding/sintering method (red data points). For reference, data corresponding to $AIFe_2B_2$ powders produced using reactive sintering synthesis methods in Argon atmosphere is also shown (black data points).

using molten salt shielded/sintering synthesis method and reactive sintering method. In the molten salt shielded sample, we observe major peaks corresponding to AlFe₂B₂ phase (~92.5%) and minor peaks of Al₂O₃ (~4.8%) and FeB (~2.7%). In comparison, the AlFe₂B₂(1.2) sample prepared by reactive sintering (RS) method shows major phase peaks of AlFe₂B₂ and small amount of FeAl₆ (~2.9%) and Al₂O₃ (~3.1%) peaks. Insight regarding the presence of the secondary FeAl₆ and FeB phases obtained in the samples may be obtained from^[32] that describes the AlFe₂B₂ formation mechanism from powder precursors, wherein the synthesis reaction begins with Al reacting with Fe to form the FeAl₆ phase: Fe+6Al \rightarrow FeAl₆. Subsequently, Fe reacts with B to form the FeB phase: $Fe+B \rightarrow FeB$. Finally, the AlFe₂B₂ phase is formed by the consumption of FeAl₆ intermetallic and FeB: FeAl₆+11 FeB+B \rightarrow 6 AlFe₂B₂. Given that the AlFe2B2 reaction path consists of the consumption of transient phases (FeB, Fe_xAl_y, and B), it is not expected that FeB and FeAl₆ impurity phases are present in the samples synthesized in this study. The presence of the minor Al2O3 phase is ascribed to slight oxidation during the sintering process. It is also worthwhile to note that slight differences were observed in the crystallographic properties of the primary $AIFe_2B_2$ phase in the two samples. In particular, all three lattice parameters of the orthorhombic unit cell and consequently the unit cell volume of the sample fabricated by the molten salt shielded sintering method was larger than that of the sample synthesized via reaction sintering, Table II.

Temperature-dependent magnetization curves of the AlFe₂B₂ samples, obtained upon heating from 1.8 to 400 K at applied fields $\mu_0 H_{app}$ of 0.1 T, are consistent with the existence of a ferromagnetic-to-paramagnetic phase transition that takes place upon heating, Fig. 2(a). It was found that the Curie temperature (Tc) of the molten salt prepared sample is T_{C,MS3} = 300 K, relatively higher than that of the reactive sintered sample that demonstrates a T_{c,reactive sintered}=288 K. The ferromagnetic background below T_c in the magnetothermal curve of the molten salt shielded sample is attributed to the presence of the ferromagnetic FeB impurity in the sample. Consistent with



Synthesis Method	Phase Analysis (wt%)	Lattice Parameters	Unit Cell Volume
Molten Salt Shielding	AlFe ₂ B ₂ (~92.5%), Al ₂ O ₃ (~4.8%), FeB (~2.7%)	a=2.923 Å b=11.039 Å c=2.873 Å	V=92.67 Å ³
Reaction Sintering	AlFe ₂ B ₂ (~94%), FeAl ₆ (~2.9%) and Al ₂ O ₃ (~3.1%)	a=2.917 Å b=11.033 Å c=2.872 Å	V=92.43 Å ³

Table II. Crystallographic properties of the AlFe₂B₂ samples under investigation in this study.



Figure 2. (a) Magnetothermal characteristics of the samples prepared by the molten salt shielded/sintering synthesis method (red data points) and reactive sintering method (black data points) at an applied magnetic field of μ_0 H = 0.1 T; (b) Field-dependent magnetization curves of the samples in the magnetic field range – 2 T to 2 T at 1.8 K.

the M-T data, Fig. 2(b) shows the field-dependent magnetization curves of the samples at 1.8 K indicate that the overall magnetization of reactive sintered sample is greater than that of the molten salt shield sample (M_{s.reactive sintered}=69 emu/g; $M_{sMS3} = 62 \text{ emu/g at } \mu_0 H = 2 \text{ T}$). The differences in the magnetism of the two samples may be understood by examining the Al-Fe-B ternary phase diagram wherein the width of the AlFe₂B₂ phase field encompasses the stoichiometric composition (40.0 at. % Fe and 20.0 at. % Al).^[33] Within this compositional range, minor changes in the Al and Fe solubility (~1 at. %) can have dramatic effects on the crystallographic and magnetic properties of the system, such that the lattice parameters and magnetic transition temperatures (Tt) increases monotonically with increase with Fe:Al at% ratio.^[22,33] Given that the Tc and Ms of the sample prepared by molten salt sintering is larger than that of the reaction sintered sample, it is deduced that this sample possesses a slightly higher Fe: Al at%, likely due to KBr encapsulation of the compacted precursor powders prior to sintering.

Last, the calculated magnetic entropy change curves $(\Delta S_{mag} \text{ vs. T plots})$ of the AlFe₂B₂ samples, shown in Fig. 3, indicate that the magnitude of the maximum magnetic entropy change of the molten salt prepared sample $(\Delta S_{mag,MS3} = 3.8 \text{ J/})$



Figure 3. Magnetic entropy change of the samples prepared by the molten salt shielded/sintering (red data points) and reactive sintering method (black data points) at an applied magnetic field of $\mu_0H=2$ T.

kg/K) is slightly lower than the sample prepared by reactive sintering ($\Delta S_{mag,reactive sintered} = 4.6 \text{ J/kgK}$) under an applied field of 2 T—an observation that is tentatively attributed to



Figure 4. 3D printed lattice structures of $AIFe_2B_2$ prepared by the molten salt shielded/sintering and printed via extrusion-based 3D printing.^[36] (a) cylindrical sample (5 mm height, 10 mm diameter) with 900 µm hexagonal channels; (b) cylindrical sample (2 mm height, 10 mm diameter) with 200 µm foil-shaped channels (c) cylindrical sample (2 mm height, 10 mm diameter) with 150 µm rectangular channels.

the slightly lower phase purity of $AIFe_2B_2$ in the sample. Given the moderate strength of the applied magnetic field, the ΔS_{mag} values noted in these samples is in the range of 1.3–4.6 J kg⁻¹ K⁻¹ reported for samples synthesized by other conventional and additive manufacturing methods (see complete list in Table I). have explored the ability to 3D print $AIFe_2B_2$ lattice structures using a patented direct ink writing extrusion-based additive manufacturing scheme, Fig. 4.^[36,37] The performance of the 3D-printed $AIFe_2B_2$ magnetocaloric heat exchanger structures and the novel 3D freestanding electrode with $AIFe_2B_2$ lattice as the catalyst support will be presented in future publications.

Conclusion

High-temperature synthesis of refractory ternary borides conventionally is typically an expensive energy-intensive process that requires inert atmospheres. To overcome these processing challenges, the $AlFe_2B_2$ polycrystalline powders in this work were synthesized using a 'molten salt shielded synthesis/sintering' process (MS³), which uses non-reactive molten salts to protect the precursor powders from oxidation during high-temperature processing in open air, The use of molten salt further reduces the synthesis temperature, resulting in additional cost savings. The MS³ process can be scaled up to industrial scale by simply increasing the batch size or making the process continuous, and is recognized as sustainable manufacturing process because the KBr salt used is not volatile or harmful. Moreover, recycling of the salt is also potentially possible.

In this work, the phase purity of the MS³ processed powders produced in the open air was comparable to that of a control sample reaction sintered in Argon atmosphere (>90% phase purity). Magnetic measurements reveal that the magnetofunctional properties of the MS^3 sample (T_c ~ 300 K, $M_s \sim 69 \text{ emu/g and } \Delta S_{max} \sim 3.8 \text{ J/kgK}$ at $\mu_0 H = 2 \text{ T}$) falls within the range reported for Fe₂AlB₂ synthesized by other methods in the literature, Table I. Since no inert environment or postfabrication annealing or acid treatments are required for this processing scheme, it is construed that MS³ is the most costeffective and energy-efficient method for large-scale production of AlFe₂B₂ powders to date. From an applications perspective, for both magnetic cooling devices and catalysis platforms, it will be beneficial to 3D print AlFe₂B₂ powders into topologically ordered, three-dimensional open-celled structures with controlled geometric shape, pore dimension, and spatial arrangement of the cells.^[34,35] In an ongoing research effort, we

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Data availability

Raw data pertaining to graphs and tables presented in this work may be provided upon request.

Declarations

Conflicts of interest

The authors declare that they have no conflict of interest/competing interests related to the article.

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