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ORIGINAL REPORT



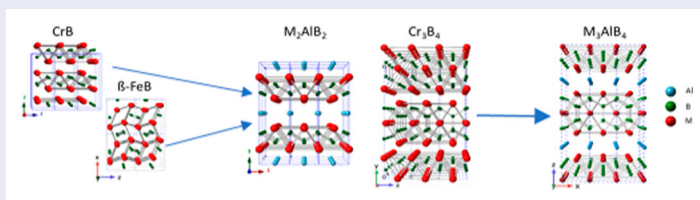
Formation mechanisms of Cr_2AlB_2 , Cr_3AlB_4 , and Fe_2AlB_2 MAB phases

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ABSTRACT

Quenching studies of CrB-Al, CrB-Al-B and β -FeB-Al mixtures revealed that all three undergo a topotactic transformation in the presence of Al to form Cr_2AlB_2 , Cr_3AlB_4 , and Fe_2AlB_2 MAB phases, respectively. The formation mechanism is intercalation for the Cr-based compounds, and reconstructive for the β -FeB based mixture.



IMPACT STATEMENT

In this work, quenching studies were performed to capture the reaction mechanisms leading to the topotactic transformations to form three unique MAB phases: Cr_2AlB_2 , Cr_3AlB_4 , and Fe_2AlB_2 .

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Topotaxy; Fe_2AlB_2 ; Cr_2AlB_2 ; Cr_3AlB_4 ; MAB phases

Introduction

The MAB phases are a group of atomically laminated, transition metal borides (TMB), wherein M is a transition metal, A is typically Al, and B is boron. Their atomically laminated crystal structures are comprised of transition metal boride layers (M-B) interleaved with Al layer(s). Depending on the number of transition metal planes comprising the M-B layers and whether Al mono-layers or bilayers separate them, the MAB phases take on the M_2AlB_2 , M_3AlB_4 , M_4AlB_6 , M_4AlB_4 or $\text{M}_2\text{Al}_2\text{B}_2$ -type structures (Figure 1) [1]. One of the hallmarks of the MAB phases, and the leitmotiv of this work, is their close structural relationship to their binary borides. The germane binaries are the CrB, Cr_3B_4 and β -FeB-type structures, the other boride structures are not relevant to MAB phase formation. The former crystallizes in the *Cmcm* space group wherein the B chains are aligned along the *a*-axis (Figure 1(A)). The latter crystallizes in the *Pnma* space group, where the MB layers are comprised of singly-capped trigonal prisms [2] (Figure 1(B)). Furthermore, the two binaries are structurally related, as the β -FeB-type structure can be obtained from the CrB-type by transposing the MB slabs of the latter by

$1/2 \langle 001 \rangle$ [3]. The Cr_3B_4 binary crystallizes in the *Immm* space group and is shown in Figure 1(C).

Regardless of the structure type, the BM_6 trigonal prisms making up the M-B layers strongly resemble, and in most cases are identical to, those found in their corresponding binary TMBs with the same M:B ratio [4]. This is exemplified by comparing the crystal structures of CrB and Cr_3B_4 with those of M_2AlB_2 (Figure 1(D)) and M_3AlB_4 (Figure 1(E)), respectively.

A notable consequence of having isolated Al layer(s) is that they tend to be relatively more weakly bonded to the M-B layers than the strong covalent M-B bonds. This fact is demonstrated by their mechanical behavior, high-temperature thermal decomposition, and dissolution behavior in acids [4–7]. For example, the MAB phases are softer than their corresponding binaries [1]. At high temperatures, the Al atoms tend to de-intercalate and evaporate/sublimate from the MAB phases, precipitating the corresponding binary borides [6–9]. In the case of MoAlB , the Al atoms react with ambient air at high temperatures to form well-adhered alumina layers that are protective in air up to 1300°C. The same compound can oxidatively self-heal cracks and has excellent ablation

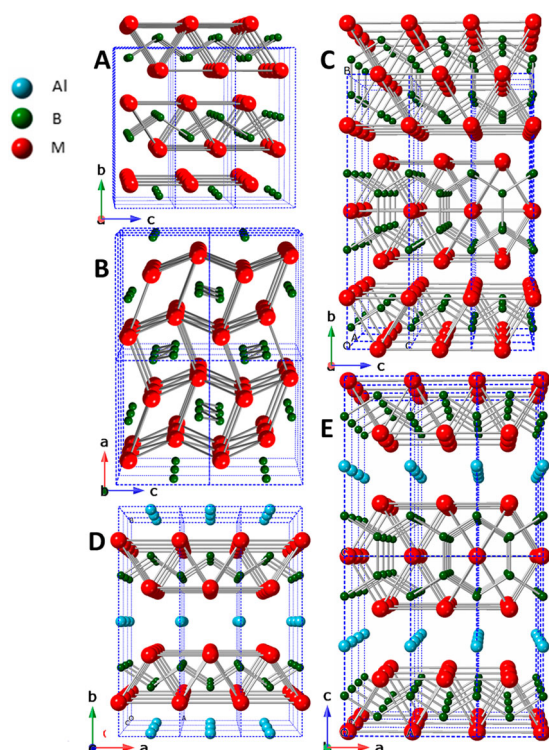


Figure 1. Crystal structures of (A) CrB, (B) β -FeB, (C) Cr_3B_4 , (D) M_2AlB_2 and (E) M_3AlB_4 .

resistance even at oxyacetylene flame temperatures [10,11]. Zhou *et al.* observed that Al selectively dissolved from Cr_2AlB_2 particles at ambient temperatures when exposed to hydrochloric acid which in turn led to the precipitation of CrB particles [12]. Similarly, Alameda *et al.* [5] and Kim *et al.* [13] found that only one of the Al layers in the $\text{Mo}_2\text{Al}_2\text{B}_2$ crystal structure can be topochemically de-intercalated upon exposure to LiF and HCl solutions to form the metastable Mo_2AlB_2 phase, whose structure had previously only been observed as stacking faults in MoAlB grains.

In this work, topotactical reactions are paramount. By definition, topotaxy requires that one crystalline phase transforms into another with a well-defined crystallographic orientational relationship between them [14]. Topotactic transformations can range from simple intercalation reactions to complex reconstructive ones [15]. As indicated above, the M-B bonding in the crystal structures show virtually unchanged bond lengths relative to their binary counterparts. For example, it has been noted that the Cr_2AlB_2 crystal structure can be visualized as an intercalation of Al atoms into the CrB structure while causing each the Cr-B blocks in the latter to shift by $0.5 \langle a+c \rangle$ along [101] [16]. Combined with the absence of binary Cr-Al and Al-B phases after CrB + Al or CrB + Al + B mixtures were heated to synthesize Cr_2AlB_2 and Cr_3AlB_4 , respectively [17],

Table 1. Initial compositions and quenching temperatures.

Initial molar composition	Temperatures
2CrB + 1.5Al	680°C
	820°C
	970°C
	970°C – 15 h
3CrB + 1.5Al + 1B	680°C
	750°C
	820°C
	1020°C
	1020°C – 10 h
2 β -FeB + 1.5Al	680°C
	850°C
	1050°C
	1050°C – 10 h

we hypothesized that these MAB phases can form by a topotactic intercalation of Al atoms into CrB and Cr_3B_4 , respectively [16].

The purpose of this work was to understand how the binary borides transform into their respective MAB phases. Given their close structural resemblances, our working hypothesis was that there is a topotactic relationship exists between them. To test this hypothesis and to shed light on the reaction mechanisms, mixtures of CrB and Al or CrB, Al and B powder mixtures were heated and quenched from various temperatures. Using X-ray diffraction, XRD, we thus followed how the reactions developed at intermediate temperatures. Since Fe_2AlB_2 is isostructural with Cr_2AlB_2 and β -FeB is considered a twinned, distorted form of CrB [3], we carried out analogous experiments with β -FeB and Al mixtures to assess the effect of precursor structure on the reaction paths. Herein we show that for both CrB cases, the Al simply intercalates in between the Cr-B blocks [12] converting them to their MAB counterparts. However, in the FeB case, the Al first reacts with the Fe, forming an intermetallic before completing the reaction to form Fe_2AlB_2 .

Methods

All samples for quenching were prepared via a powder metallurgical route starting with CrB (H.C. Starck, 1–2 μm average particle size), β -FeB (See [18], < 44 μm), amorphous B (Alfa Aesar, 98%, < 44 μm) and Al (Alfa Aesar, 99.5%, < 44 μm) in molar ratios of 2CrB:1.5Al, 3CrB:1B:1.5Al, or 2FeB:1.5Al. The large excess of Al was used to facilitate a more uniform reaction at the lower temperatures. The mixtures were mechanically ball-milled at 60 rpm in 8 g batches for 24 h in a plastic jar using an equal mass of 5 mm diameter yttria-stabilized zirconia media. Green bodies were cold pressed at a load corresponding to a stress of 200 MPa into 2 g pellets, with a diameter of 13 mm and a height of ≈ 10 mm. Pellets

were heated one at a time in a horizontal tube furnace under a flowing Ar atmosphere. The pellets were heated at a heating rate of 5°C/min to the temperatures indicated in Table 1, and allowed to equilibrate for 3–5 min before quenching directly into distilled water at ambient temperature. The quenching temperatures were chosen to evaluate the status of the reaction as it progressed from reactants to the final products. The lowest temperature, 680°C, was chosen to evaluate the beginning of the liquid phase reaction between Al and the transition metal borides. The maximum temperature reflects typical reaction temperatures used for the synthesis of various MAB phase [1,16,17]. Lastly, one sample of each composition was reacted at the highest temperatures used for an extended time (see Table 1) in an attempt to achieve equilibrium and/or a fully reacted state.

The surfaces of all samples were lightly sanded to remove any surface oxides and drilled using a cobalt steel bit to produce a fine powder. This powder was characterized by using a X-ray diffractometer (Rigaku SmartLab) with a Cu K_{α} source ($\lambda = 0.0154$ nm) and a detector-side graphite monochromator. The quantitative analysis was performed using MDI Jade 6.5 with the Easy Quant package using the RIR method [19].

Results & discussion

Cr_2AlB_2

XRD patterns of the quenched samples, starting with CrB and 1.5 Al to produce Cr_2AlB_2 , are shown in Figure 2. Quenching from 680°C, there is no evidence of the formation of the MAB phase. This is not too surprising since this temperature is just over Al's melting point and

had insufficient time to react with the CrB (Figure 2A). Quenching from 850°C, a large quantity of Cr_2AlB_2 forms, though unreacted CrB and Al still remain in the sample (Figure 2B). Quenching from 970 °C shows the continued consumption of the CrB and Al precursors, as shown by the decreased relative intensities of the CrB peaks relative to the 850°C quench (Figure 2C). After reacting at 970°C for 15 h, a further reduction of the CrB peak intensities indicate that the Al was able to further intercalate between the CrB layers (Figure 2D). The ratio of intensities between the (130) peak of Cr_2AlB_2 and the (021) peak of CrB shows the evolution of the MAB phase with increasing temperatures and after reacting for 15 h (Figure 2E). Based on these results, it is reasonable to conclude that the following single-step reaction is operative:



The Al present after 15 h at 970°C is simply due to the large molar excess of Al present in the initial reagent mixture. Note that this result implies that Cr_2AlB_2 is in most probably in equilibrium with molten Al.

Cr_3AlB_4

XRD patterns of the 3 CrB, 1.5 Al and 1.0 B mixture after quenching from different temperatures and after holding at the maximum temperatures for 10 h are shown in Figure 3. XRD of the samples evidences a three-step evolution. First, the elemental B reacts with CrB to form CrB_2 , followed by the formation of Cr_3B_4 at higher temperatures. The last reaction is one with Al to form Cr_3AlB_4 . At 680°C, there is some indication that CrB_2 has started to form, but a majority of the

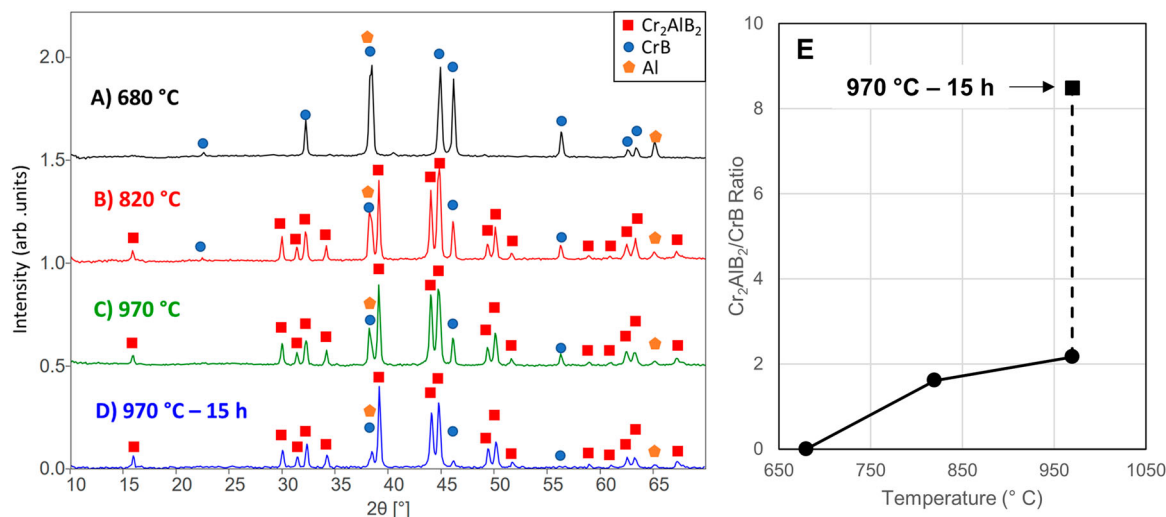


Figure 2. XRD patterns for 2 CrB + 1.5 Al quenched from, (A) 680°C, (B) 820°C, and (C) 970°C. For reference, (D) 970°C for 15 h. (E) The ratio of Cr_2AlB_2 to CrB over the range of quenching temperatures and after a 15 h at 970°C.

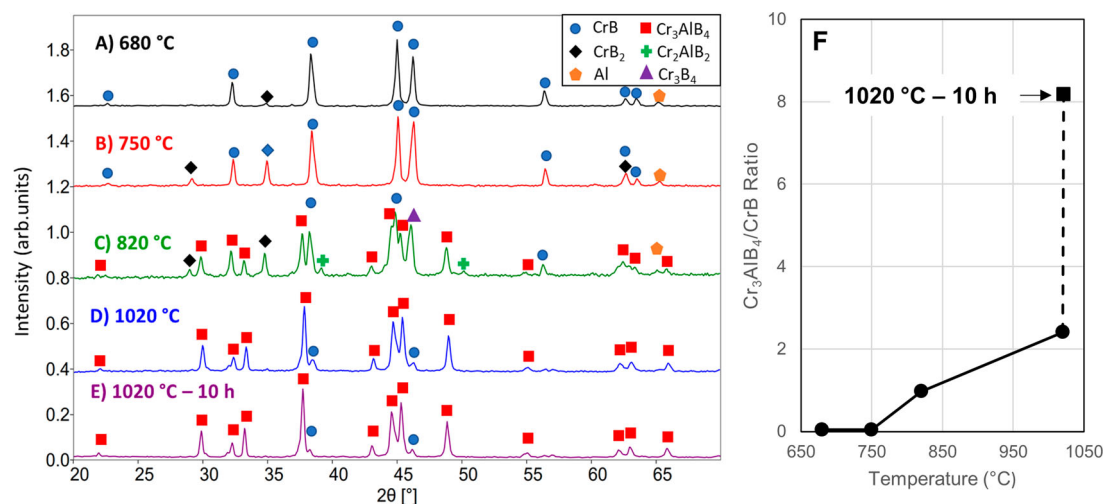


Figure 3. XRD patterns of 3 CrB + 1.5 Al + 1 B after quenching from (A) 680°C, (B) 750°C, (C) 820°C, and (D) 1020°C. For reference, (E) 1020°C for 10 h. (F) The ratio of Cr₃AlB₄ to CrB over the range of quenching temperatures and after 10 h at 1020°C

CrB and all the Al remains unreacted (Figure 3A). It should be noted that B is not detected by XRD because it remains amorphous at temperatures below 1100°C [20]. At 750°C, the CrB reacts further with the B forming more CrB₂ (Figure 3B). However, no peaks corresponding to Cr₃AlB₄ or Cr₂AlB₂ are present in the pattern, despite the fact that Cr₂AlB₂ showed signs of formation between 680–820°C in Figure 1. Once the sample reaches 820°C, the CrB and CrB₂ react and form Cr₃B₄, which in turn reacts with Al and the formation of Cr₃AlB₄ begins (Figure 3C). At this temperature, Cr₃B₄ and Cr₃AlB₄ are the majority phases present, with some CrB and Cr₂AlB₂ impurities present. At 1020°C, only small amounts of CrB and Cr₃B₄ impurities exist with almost all the binary borides reacted to form Cr₃AlB₄ (Figure 3D).

After reacting for 10 h, there is a negligible amount of CrB present, yet Cr₃B₄ remains at the same levels

(Figure 3E). As the reaction temperature increases, the ratio of relative intensities of the (102) peak of Cr₃AlB₄ to the (021) peak of CrB illustrates the progression of the reaction (Figure 3F). Between 820°C and 1020°C, the Cr₃AlB₄:CrB ratio more than doubles, and after reacting for 10 h there is a fourfold increase in Cr₃AlB₄. The near absence of Cr₂AlB₂ at higher temperatures implies that it is most likely an impurity phase, not a step along the reaction pathway. Once the Cr₃B₄ has formed, the Al intercalates between the layers forming the 314 MAB phase structure. This process can be represented by the following reactions:

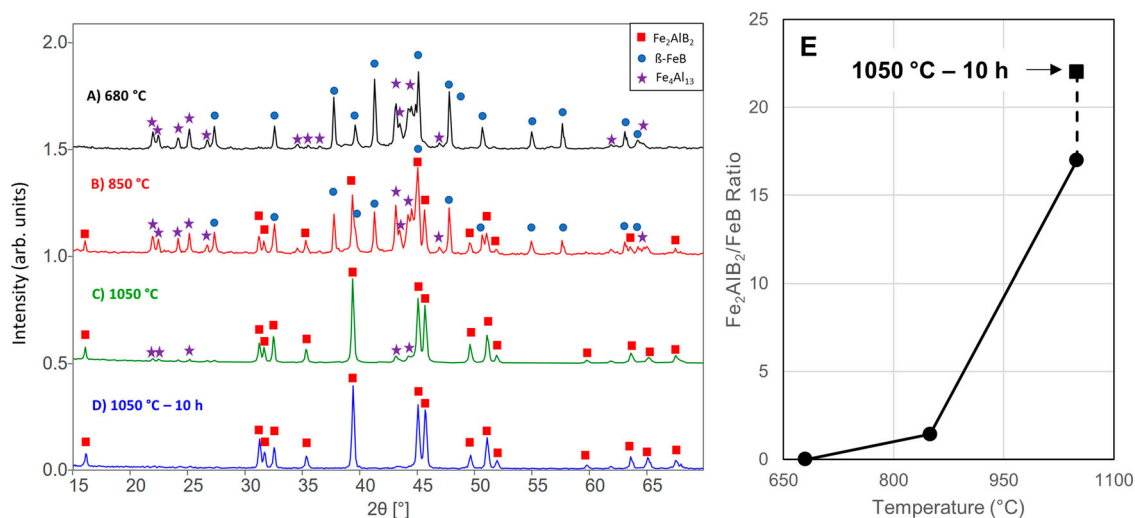
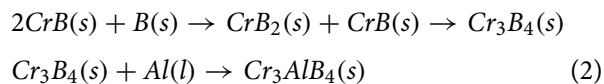
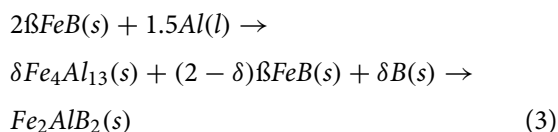


Figure 4. XRD patterns of 2 β-FeB + 1.5 Al after quenching from (A) 680°C, (B) 850°C, and (C) 1050°C. For reference, (D) 1050°C for 10 h. (E) The ratio of Fe₂AlB₂ to FeB over the range of quenching temperatures and after 10 h at 1050°C.

Fe₂AlB₂

Unlike the Cr based MABs, the Fe₂AlB₂ XRD patterns show a different reaction mechanism, as the Al does not directly intercalate into the FeB structure (Figure 4). Even at 680°C, the Al reacts with the β-FeB to form the intermetallic Fe₄Al₁₃ (Figure 4A). This low temperature formation of Fe₄Al₁₃ is described by Li et al. [21] as taking place at temperatures as low as 650°C and would result in the formation of free B. As in the Cr₃AlB₄, this free B required to mass balance the reaction (see Equation 3) is not detected by XRD due to its amorphous nature. At 850°C the reaction shifts to the third step as the β-FeB peak intensities decrease, and Fe₂AlB₂ begins to form (Figure 4B). However, the intensities of the intermetallic peaks remain constant over this temperature range. At 1050°C, all of the β-FeB has reacted, forming a majority phase of Fe₂AlB₂ with some remnant intermetallic impurities (Figure 4C). After reacting for 10 h, there is no discernible presence of the intermetallic phase as the reaction goes to completion (Figure 4D). This reaction sequence can be represented by the equations:



Discussion

Based on these results, the formation of both Cr₂AlB₂ and Cr₃AlB₄ both seem to be a product of a high-temperature intercalation of Al atoms between atomic layers of CrB and Cr₃B₄, respectively. In this reaction, the CrB and Cr₃B₄ structures were retained in each M-B layer during this process, as noted by the lack of additional phases.

As discussed previously, a topotactic transformation is solely concerned with the relationship between the initial and final crystal structure. Though the formation of Fe₂AlB₂ from FeB and Al does not follow the same classic intercalation mechanism as occurs during the formation of Cr₂AlB₂ and Cr₃AlB₄, it still undergoes a topotactic transformation. The β-FeB structure can be considered to be a deformed CrB structure and is therefore related to the final Fe₂AlB₂ structure. The decomposition of the β-FeB and subsequent intermediate formation of the Fe₃Al₁₄ intermetallic are steps along the reaction pathway.

Summary and conclusions

To investigate the formation mechanisms of Cr₂AlB₂, Cr₃AlB₄, and Fe₂AlB₂, high temperature quenching

experiments were carried out. The Cr₂AlB₂ reaction path was single step as the Al began reacting with the CrB to form the Cr₂AlB₂ between 680°C and 820°C. The Cr₃AlB₄ reaction path was three steps: formation of CrB₂ from CrB and B, formation of Cr₃B₄ from CrB and CrB₂, and finally the reaction with Al between 750°C and 820°C. Both systems undergo a similar topotactic transformation, as the Cr-B structure is retained after the Al reaction. The final products of the reactions are dependent on the initial stoichiometry, as no Cr₃AlB₄ formed from 2CrB + 1.5Al case and an insignificant amount of Cr₂AlB₂ formed when the initial mixture was 3CrB + 1B + 1.5Al.

Unlike the Cr based MABs, the Al did not simply intercalate between the binary boride layers; the system underwent a reconstructive reaction instead. The Al first reacted with the Fe to form an intermetallic at low temperatures. As the temperature increased, the β-FeB and intermetallic reacted to form Fe₂AlB₂.

Disclosure statement

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