Electronic Supplementary Information

Topochemical Synthesis of Phase-Pure Mo$_2$AlB$_2$ through Staging Mechanism

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EXPERIMENTAL SECTION

**Synthesis of MoAlB.** The mixture of MoB (High Purity Chemicals, Japan) and Al (High Purity Chemicals, Japan) was pelletized under 40 MPa pressure and heated to 1200 °C for 1 h under Ar atmosphere using a high-frequency induction furnace. The heated pellet was powdered by milling with zirconia balls.

**Synthesis of Mo₂AlB₂.** 500 mg of MoAlB powder was slowly poured into a solution consisting of 2.3 g (3 M) of LiF (Wako Chemicals, Japan) and 30 mL of 10 M HCl (Kanto Chemicals, Japan). The mixture was continuously stirred for 48 h at 40 °C. The resulting precipitate was stirred in a 1 M HCl solution, then filtered, washed with deionized water until the pH reaches to neutral. The separated powder was dried at 60 °C for 12 h under vacuum.

**Material Characterization.** Crystal structures of the obtained materials were analyzed by X-ray diffraction (Rigaku, RINT-TTR III) in the 2θ range of 3‒80° with a step size of 0.02° using Cu Kα radiation. SEM and TEM images of the obtained materials were collected using a scanning electron microscope (Hitachi, S-4800) and transmission electron microscopy (JEOL, JEM-2100 and JEM-2800), respectively. Chemical composition was determined with energy-dispersive X-ray spectroscopy (JEOL, JEM-6510LA and Oxford X-Max).

**Calculation.** First-principle calculations were performed using Vienna Ab-initio Simulation Package (VASP), based on density-functional theory (DFT). The exchange–correlation energy is calculated using general gradient approximation (GGA) with the Perdue–Burke–Ernzerhof (PBE) exchange–correlation functional. The plane wave cutoff energy is 500 eV. The convergence condition for the energy is 10⁻⁴ eV, and the structures were relaxed until the force on each atom was less than 0.01 eV/Å. Spin polarization was considered in all calculations. A 3 × 3 slab was chosen to calculate the formation energies of Al removal from MoAlB phase. The c axis parameter was set as 40 Å to ensure
enough vacuum to avoid interactions between two periods, and the $k$-point meshes of $3 \times 3 \times 1$ and $6 \times 6 \times 1$ in the Monkhorst Pack\textsuperscript{5} sampling scheme were used for geometry optimization and electronic self-consistent computation, respectively. The crystal structures were drawn using VESTA.\textsuperscript{6} For the first three steps in Figure 3, the energy to generate an Al defect from MoAlB phase is defined as, $E = E_f - E_i + E_{Al}$, where $E_f$, $E_i$, and $E_{Al}$ are the formation energies of the phase after Al removal, the phase before Al removal, and an elemental Al atom, respectively. For the Stage I and Stage II in Figure 3, the energy to remove an Al layer from MoAlB is defined as, $E = (E_s - E_i + N \cdot E_{Al})/N$, where $E_s$ and $E_i$ are the formation energies of the phases after and before Al removal, and $N$ is the number of Al atoms in an Al layer.

References

**Table S1.** EDX results for MoAlB and Mo₂AlB₂.

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<thead>
<tr>
<th></th>
<th>Mo</th>
<th>Al</th>
<th>O</th>
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<tbody>
<tr>
<td></td>
<td>atomic%</td>
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</tr>
<tr>
<td>MoAlB</td>
<td>46.0±3</td>
<td>43.7±2</td>
<td>10.3±2</td>
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<tr>
<td>Mo₂AlB₂</td>
<td>58.9±5</td>
<td>27.1±5</td>
<td>14.0±4</td>
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**Figure S1.** TEM images for (a) MoAlB and (b-d) Mo₂AlB₂.
Fig. S2 Powder X-ray diffraction patterns for MoAlB, the sample after 24 h etching, and the sample after 48 h etching. After 24 h etching, a new diffraction peak appears at $2\theta = 13^\circ$, corresponding to the interlayer distance of $d_{\text{inter}} = 6.8$ Å (presumably, $\text{Mo}_4\text{Al}_3\text{B}_4$). Based on the calculation results, staging transformation from MoAlB through $\text{Mo}_4\text{Al}_3\text{B}_4$ to $\text{Mo}_2\text{AlB}_2$ should occur.