

Electronic Supplementary Information

Topochemical Synthesis of Phase-Pure Mo_2AlB_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 $K\alpha$ 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),¹ based on density-functional theory (DFT).^{2,3} The exchange–correlation energy is calculated using general gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional.⁴ 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 Pack⁵ sampling scheme were used for geometry optimization and electronic self-consistent computation, respectively. The crystal structures were drawn using VESTA.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

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Table S1. EDX results for MoAlB and Mo₂AlB₂.

	Mo atomic%	Al atomic%	O atomic%
MoAlB	46.0±3	43.7±2	10.3±2
Mo ₂ AlB ₂ (LiF/HCl)	58.9±5	27.1±5	14.0±4

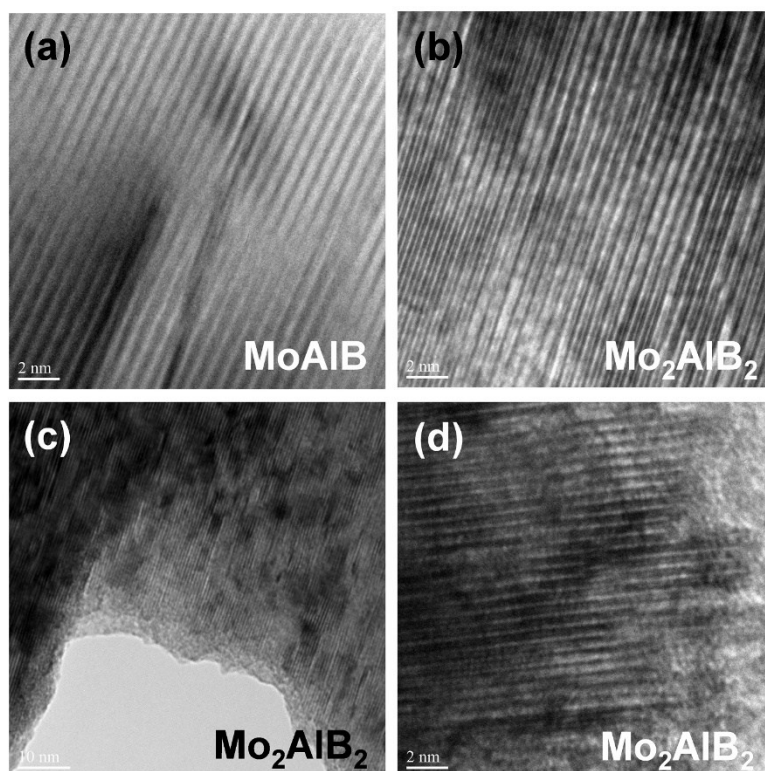


Figure S1. TEM images for (a) MoAlB and (b-d) Mo₂AlB₂.

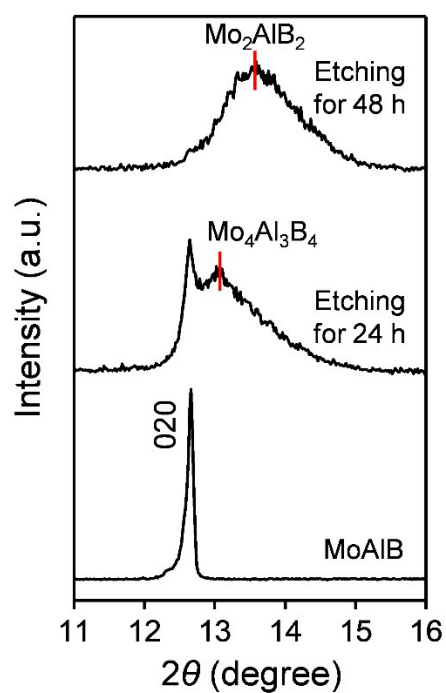


Fig. S2 Powder X-ray diffraction patterns for MoAlB, the sample after 24 h etching, and the sample after 48 h etching. After 24 h etching, a new diffraction peak appears at $2\theta = 13^\circ$, corresponding to the interlayer distance of $d_{\text{inter}} = 6.8 \text{ \AA}$ (presumably, $\text{Mo}_4\text{Al}_3\text{B}_4$). Based on the calculation results, staging transformation from MoAlB through $\text{Mo}_4\text{Al}_3\text{B}_4$ to Mo_2AlB_2 should occur.