

Synthesis, Crystal Structure and Characterizations of the Ternary Borides TMAIB (TM=Mo, W) with UBC Type Structure

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UBC 型構造を有する三成分系ホウ化物 TMAIB (TM=Mo, W) の合成, 結晶構造及び評価

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Abstracts: Single crystals of MoAlB and WAlB with UBC type structure were prepared from high temperature aluminum solutions using molybdenum metal or tungsten metal and crystalline boron powders as starting material under an argon atmosphere. Growth conditions for obtaining crystals of relatively large size were established. The MoAlB and WAlB single crystals were obtained as thick platelets with large *b*-planes and needle-like rectangulars extending in *c*-axis direction. The crystal structure of MoAlB was studied by single-crystal X-ray diffractometry. The chemical analysis and the structural characteristics of MoAlB are discussed. The Vickers microhardness and electrical resistivity of the crystals were measured, and oxidation at high temperature in air was studied. The Vickers microhardness values on *b*-planes of MoAlB and WAlB crystals are in the range of 10.3(±0.2) GPa and 19.3(±0.7) GPa, respectively. The electrical resistivity determined on MoAlB and WAlB crystals are as follows: for MoAlB: 67.1 μΩcm; for WAlB: 243.6 μΩcm. The oxidation reaction of MoAlB and WAlB crystals begin to proceed at about 740°C and 440°C, respectively.

Keywords: MoAlB, WAlB, unit cell parameter, chemical analysis, crystal structure, microhardness, electrical resistivity, oxidation in air

1. Introduction

The ternary MoAlB (UBC type structure¹⁾) (orthorhombic; space group *Cmcm*) phase was first reported by Rieger et al²⁾, and then the crystal structure was determined by Jeitschko³⁾ using single crystal film technique. Prior to these two publications, in the Mo–Al–B system, ternary phase Mo₇Al₆B₇ (MoAl_{0.86}B) had been reported⁴⁾. This phase has a composition very close to that of MoAlB but completely different unit cell parameters. Since MoAlB was studied by single-crystal methods, it was suspected that the diffraction pattern of Mo₇Al₆B₇ might have been indexed incorrectly. Recently, we have found that single crystals of a new compound WAlB (orthorhombic; space group *Cmcm*)⁵⁾ and of the earlier known MoAlB can be grown by using the aluminum solution technique⁶⁾. However, there is a little information about chemical and physical properties of MoAlB and WAlB crystals. The purpose of this paper is to clarify the conditions for growing relatively large single crystals of MoAlB and WAlB in aluminum solutions, and the results of the structure analysis

of this compound by single-crystal X-ray diffractometry. The crystals were examined by X-ray diffraction, crystal size, crystal morphology, and chemical analysis. The Vickers microhardness and the electrical resistivity of the crystals were measured, and oxidation at high temperature in air was studied.

2. Experimental details

Synthesis of the ternary MoAlB and WAlB crystals were performed by the high-temperature metal solution method using aluminum flux. The purities of the starting materials were as follows: molybdenum metal (average particle size, 3.5 μm; purity 99.9%), tungsten metal (average particle size, 3.2 μm; purity 99.9%), crystalline boron (particle size, <130 μm; purity 99.5%) and aluminum metal chips (purity 99.99%). Mixtures of these materials in various atomic ratios (B/Mo=0.3–4.0, Al/Mo=53.3)⁶⁾ and (B/W=0.5–4.0, Al/W=102.2)^{5),7)} were placed in an alumina crucible and heated in an argon atmosphere at 1500°C for 5 to 10 h, and then cooled to room temperature at a rate of 50°C·h⁻¹. The crystals were

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separated from the solidified mixture by dissolving the excess Al with 6 mol dm⁻³ hydrochloric acid for 5 to 7 days.

Typical experimental conditions for the growth of the single crystals are shown in Table 1. Relatively large crystals of MoAlB and WAIB were selected under stereomicroscope for chemical analysis. The crystal morphology was examined by an optical microscope and a scanning electron microscope (SEM) (JEOL, JSM-35C). Some of the crystals were examined with an electron probe microanalyzer (EPMA) (JEOL, JSM-35C) and an energy-dispersive detector (EDX) (Horiba, EMAX-2770). The chemical composition of the crystals grown were determined by means of the inductively coupled plasma (ICP) (Shimadzu, ICP-50)⁸⁾ emission analysis.

Phase analysis and determination of unit cell parameters were performed by using a powder X-ray diffractometer (Rigaku, RINT-2500VHF) with monochromatic CuK α radiation ($\lambda=0.154183$ nm) and a Guinier-Hägg focusing X-ray powder diffraction camera (XDC-1000) with strictly monochromatic CuK α_1 radiation ($\lambda=0.15405982$ nm)⁹⁾ and semiconductor grade silicon as an internal calibration standard¹⁰⁾. The unit cell parameters were determined by least-squares refinement using the program UNITCELL¹¹⁾.

The X-ray intensities were measured with a automatic four-circle single crystal diffractometer (Rigaku AFC-6R) using graphite monochromated MoK α radiation ($\lambda=0.07107$ nm) and ω -2 θ scan technique. Six standard reflections were measured at every 150 reflections to check the stability of the primary X-ray beam and the equipment. A long-term systematic decrease in intensity within the time period of measurement was observed (about 1%). The collected intensity data were first corrected for Lorentz-polarization effects. A linear decay correction was then applied using the Gaussian grid technique. All these pre-refinement corrections on the original reflection data were carried out using the TEXSAN software system¹²⁾.

The Vickers microhardness of the as-grown MoAlB and

WAIB crystals were measured in several directions on *b*-planes, at room temperature in air. A load of 100 g was applied for 15 s at about 5–8 points for each crystal, and the values obtained were averaged. The electrical resistivity of the crystals were measured by a direct-current four-probe technique at room temperature in air.

3. Results and Discussion

3.1 Synthesis of MoAlB and WAIB single crystals

Typical experimental conditions for the growth of MoAlB and WAIB single crystals are listed in Table 1. The variation of the atomic ratios of the starting materials B/Mo and B/W gave different product phases. With increased boron concentration, binary borides MoB⁶⁾ or δ -WB and WB₂ (W₂B_{5-x} type)⁷⁾ phases of more boron-rich phases were formed. While, crystals of Mo₇Al₆B₇, Mo₂B, MoB₂, MoB₂(Mo₂B_{5-x} type), MoB₄, W₂B, and WB₄¹³⁾ were not detected by powder X-ray diffraction. Under these conditions, MoAlB single crystals, having silver color and metallic luster, were generally obtained as thick platelets with large *b*-planes (Fig. 1-a) and needle-like rectangulars extending in *c*-axis direction (Fig. 1-b). WAIB single crystals, having silver color and metallic luster, were generally obtained as needle-like rectangulars extending in *c*-axis direction (Fig. 2). The largest crystals prepared have maximum dimensions of about 0.3 × 7.0 × 9.3 mm³ and 1.0 × 1.0 × 5.1 mm³ for MoAlB and WAIB, respectively.

Table 1 Typical growth conditions of MoAlB and WAIB single crystals.

| Compound | Crystal structure | Composition of the starting mixture in atomic ratio | | | Soaking temperature and time |
|----------|-------------------|---|-----|-------|------------------------------|
| | | Mo or W : B : Al | | | |
| MoAlB | Orthorhombic | 1 | 1.0 | 53.3 | 1500°C, 10 h |
| WAlB | Orthorhombic | 1 | 1.0 | 102.2 | 1500°C, 5 h |

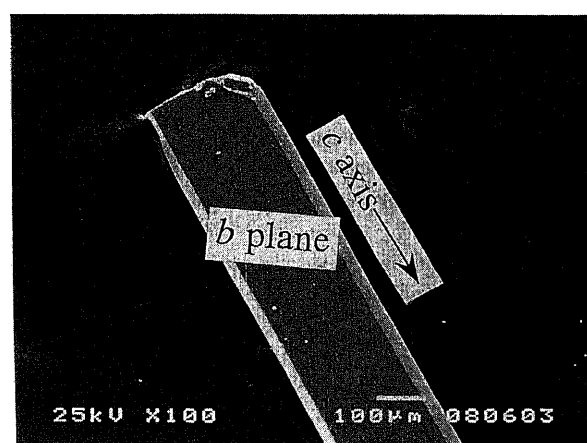
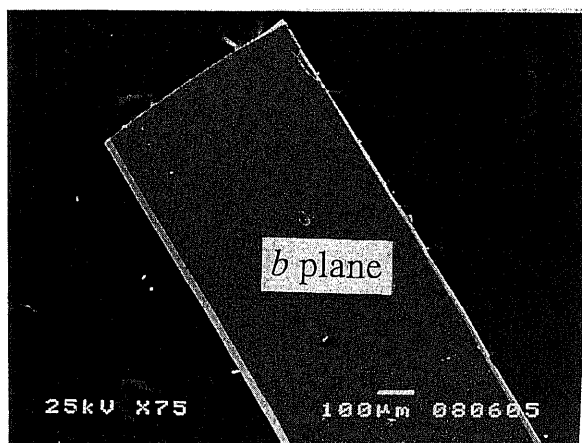


Fig. 1 SEM photographs of MoAlB single crystals.

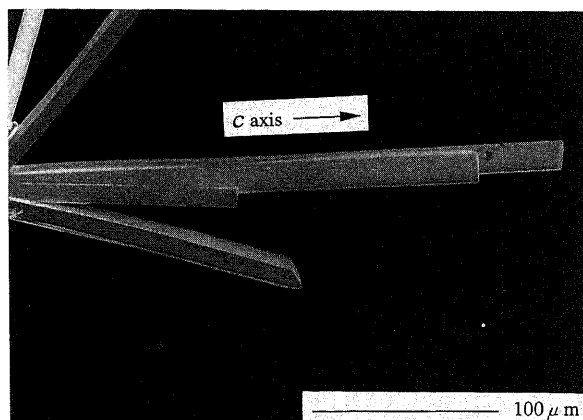


Fig. 2 A SEM photograph of WAlB single crystals.

3.2 Description of the crystal structure of TMAIB (TM=Mo, W)

The fundamental crystallographic data and chemical analysis are listed in Table 2. The unit cell parameters of MoAlB and WAlB crystals obtained are in comparatively good agreement with previously published data ($a=0.3212$ nm, $b=1.3985$ nm, $c=0.3102$ nm, $V=0.1393$ nm³ and $a=0.3209(1)$ nm, $b=1.3980(1)$ nm, $c=0.3100(1)$ nm, $V=0.1391$ nm³ for MoAlB; $a=0.3205(1)$ nm, $b=1.3947(1)$ nm, $c=0.3108(1)$ nm, $V=0.1389$ nm³ for WAlB)^{3),5),14),15)}. The chemical compositions obtained by the chemical analysis are approximately homogeneity ranges. The ICP analysis established the occurrence of traces of iron, calcium and silicon. Incorporation of oxygen might come from the alumina crucible, was found to be negligible; this was confirmed by the occupational refinement of atom sites coupled with a difference preparation and by precise measurements of interatomic distances in the crystals. Guinier-Hägg X-ray diffraction intensities for WAlB are shown in Table 3 together with observed and calculated interplanar spacings (d_{obs} and d_{calc} , respectively). A well characterized WAlB has so far not been reported.

The crystal structure of MoAlB is illustrated in Fig. 3³⁾. The structure is conveniently described in terms of the trigonal prismatic arrangement of six molybdenum atoms surrounding each boron atom. There are two boron and one aluminum atom situated outside the rectangular faces of the trigonal prism. The prisms are packed in such a manner that all prism axes are parallel to the b direction, while the boron atoms form the B-B zigzag chains in the c direction. The aluminum atoms form strongly puckered metal layers interleaved between the molybdenum double layers. A more detailed structure description of MoAlB is given in Ref. 2. In addition, the ternary TM'AlB (TM'=Ti, Zr, Hf, V, Nb, Ta) phases of the UBC type structure were not obtained from the single crystal growth experiment in the TM'-Al-B systems using the same crystal growth method¹⁶⁾⁻²⁰⁾.

It was noted by Jeitschko³⁾ that the Mo₇Al₆B₇ (MoAl_{0.86}

Table 2 Crystal data and chemical analysis of MoAlB and WAlB single crystals.

| Formula | MoAlB | WAlB |
|------------------------|--|---|
| Crystal system | orthorhombic | orthorhombic |
| a (nm) | 0.3213(1) | 0.3205(1) |
| b (nm) | 1.3986(1) | 1.3947(2) |
| c (nm) | 0.3103(1) | 0.3108(1) |
| V (nm ³) | 0.1395(1) | 0.1389(1) |
| Space group | $Cmcm$ | $Cmcm$ |
| Z | 4 | 4 |
| Mo (wt%) | 72.0 | - |
| W (wt%) | - | 79.6 |
| Al (wt%) | 19.6 | 12.0 |
| B (wt%) | 7.5 | 4.7 |
| Total (wt%) | 99.1 | 96.3 |
| Chemical composition | Mo _{1.09} Al _{1.04} B _{1.0} | W _{1.00} Al _{1.02} B _{1.0} |

Table 3 Powder X-ray diffraction data of WAlB.

| $h k l$ | d_{calc} (nm) | d_{obs} (nm) | I_{calc} | I_{obs} |
|----------|------------------------|-----------------------|-------------------|------------------|
| 0 2 0 | 0.6963 | 0.6971 | 80.4 | 79.4 |
| 0 4 0 | 0.3482 | 0.3484 | 35.2 | 35.0 |
| 1 1 0 | 0.3120 | 0.3122 | 100.0 | 100.0 |
| 0 2 1 | 0.2832 | 0.2834 | 85.7 | 83.2 |
| 0 6 0 | 0.2321 | 0.2322 | 33.0 | 31.9 |
| 0 4 1 | 0.2315 | 0.2316 | 65.4 | 67.2 |
| 1 1 1 | 0.2199 | 0.2200 | 64.2 | 61.0 |
| 1 5 0 | 0.2101 | 0.2102 | 75.3 | 71.9 |
| 1 3 1 | 0.2008 | 0.2009 | 96.5 | 92.5 |
| 0 6 1 | 0.1858 | 0.1860 | 6.2 | 2.8 |
| 0 8 0 | 0.1741 | - | 2.6 | - |
| 1 5 1 | 0.1739 | 0.1740 | 9.4 | 4.8 |
| 1 7 0 | 0.1690 | 0.1690 | 13.0 | 21.9 |
| 2 0 0 | 0.1600 | 0.1601 | 20.2 | 16.4 |
| 2 2 0 | 0.1560 | 0.1560 | 3.5 | - |
| 0 0 2 | 0.1550 | 0.1551 | 18.6 | 20.8 |
| 0 8 1 | 0.1518 | 0.1519 | 22.4 | 16.5 |
| 0 2 2 | 0.1513 | 0.1514 | 3.2 | - |
| 1 7 1 | 0.1484 | 0.1485 | 14.7 | 12.9 |
| 2 4 0 | 0.1454 | 0.1454 | 7.0 | 5.5 |
| 0 4 2 | 0.1416 | 0.1416 | 6.6 | 2.9 |
| 2 2 1 | | | | |
| (1 9 0) | 0.1393 | 0.1393 | 25.6 | 31.7 |
| 0 10 0 | | | | |
| 1 1 2 | 0.1388 | 0.1390 | 23.6 | 22.9 |
| 2 6 0 | 0.1318 | 0.1318 | 14.7 | 12.6 |
| 2 4 1 | 0.1316 | 0.1316 | 28.9 | 25.1 |
| 0 6 2 | 0.1289 | 0.1289 | 14.1 | 8.9 |
| (1 9 1) | 0.1271 | | | |
| (0 10 1) | 0.1270 | 0.1271 | 37.3 | 32.5 |
| 1 5 2 | 0.1247 | 0.1247 | 39.1 | 40.5 |
| 2 6 1 | 0.1213 | 0.1213 | 4.3 | - |
| (2 8 0) | | | | |
| (1 11 0) | 0.1177 | 0.1177 | 13.3 | 9.7 |
| 0 12 0 | 0.1161 | 0.1162 | 4.7 | 2.2 |
| 0 8 2 | 0.1158 | 0.1158 | 2.1 | - |

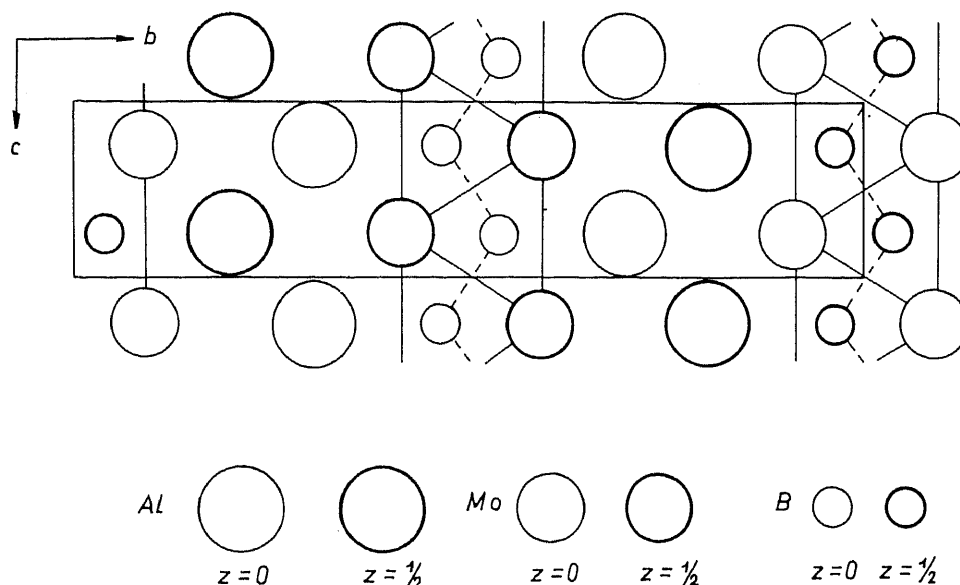


Fig. 3 The crystal structure of MoAlB.

B) phase reported by Halla et al⁴⁾ has a composition very close to MoAlB. The unit cells reported, however, differ completely, which indicates that there are indeed two different phases with nearly the same composition in the system. It has also been reported²⁾ that MoAlB has a range of homogeneity. Since MoAlB was studied by single crystal methods³⁾, it was suspected that the diffraction pattern of Mo₇Al₆B₇ might have been indexed incorrectly. The refined parameters for the originally reported unit cell of Mo₇Al₆B₇ were $a=0.7036(4)$ nm, $b=0.6340(4)$ nm, and $c=0.5757(4)$ nm. The refined parameters for a cell isotypical with MoAlB were $a=0.3237(2)$ nm, $b=1.4007(6)$ nm, and $c=0.3111(2)$ nm. This indicates that the phase Mo₇Al₆B₇ reported by Halla and Thury⁴⁾ is the same phase as MoAlB. This conclusion is also in agreement with the ternary phase diagram of the Mo–Al–B system presented by Rieger et al²⁾.

The presently known phases crystallizing in the UBC type structure are collected in Table 4 together with the unit cell parameters and cell volumes. It is noted that the prototype structure UBC deviates from the other structures in several aspects, to which some extent arises from the large atomic radius of uranium. The degree of space filling is much lower for UBC¹⁾ than for the other compounds, which is a consequence of the fact that the cell volumes are relatively equal while the large aluminum atoms are replaced by small carbon atoms in the uranium compound. The values of the a - and c -axes are determined by the large atomic radius of the uranium atom and therefore considerably large than those of the other representatives. The b -axis of UBC, on the other hand, is considerably shorter than those the other phases. This is a consequence of the fact that the bonding between the uranium double layers is mainly due to the small carbon atoms, which occupy the positions of the relatively large alumi-

Table 4 Representatives of the UBC type structure.

| Phases | Unit cell parameters | | | | Ref. |
|--------|----------------------|-----------|-----------|------------------------|-----------|
| | a (nm) | b (nm) | c (nm) | V (nm ³) | |
| UBC | 0.3591 | 1.1950 | 0.3372 | 0.1447 | (1) |
| MoAlB | 0.3212 | 1.3985 | 0.3102 | 0.1393 | (3) |
| MoAlB | 0.3209(1) | 1.3980(1) | 0.3100(1) | 0.1391 | (14) |
| MoAlB | 0.3213(1) | 1.3986(1) | 0.3103(1) | 0.1395(1) | This work |
| WAlB | 0.3205(1) | 1.3947(1) | 0.3108(1) | 0.1389(1) | (5) |
| WAlB | 0.3205(1) | 1.3947(2) | 0.3108(1) | 0.1389(1) | This work |

num atoms in the other representatives.

3.3 Properties

The Vickers microhardness of as-grown MoAlB and WAlB crystals was measured in several directions on the b -planes. The Vickers microhardness and the electrical resistivity are listed in Table 5. As seen from Table 5, essentially, both ternary compounds reveal relatively high hardness. It is found that the microhardness of MoAlB, $10.3(\pm 0.2)$ GPa, is comparatively lower than that of the WAlB, $19.3(\pm 0.7)$ GPa. The microhardness values of MoAlB and WAlB crystals are not reported in the literature. The electrical resistivity of as-grown crystals was measured at room temperature on the b -planes for MoAlB and WAlB. The electrical resistivity are listed in Table 5. The electrical resistivity values of both compounds were found to be relatively similar for the values.

The oxidation process of the crystals was studied at temperatures below 1200°C by thermal gravimetric (TG) and differential thermal analysis (DTA), as shown in Fig. 4. The oxidation reaction of MoAlB and WAlB crystals began to proceed at about 740°C and 440°C, respectively. In contrast, the exothermic peak of the DTA curve was

Table 5 Vickers microhardness and electrical resistivity of MoAlB and WAIB single crystals.

| Compound | Microhardness | Electrical resistivity |
|----------|-------------------|--|
| | Hv (GPa) | ρ ($\mu\Omega \cdot \text{cm}$) |
| MoAlB | 10.3(± 0.2) | 67.1 |
| WAIB | 19.3(± 0.7) | 243.6 |

found at about 700°C and 820°C for MoAlB, and at about 970°C for WAIB. The crystals were heated for 5 min at temperature intervals of 50°C between 400°C and 1200°C, and the oxidation products were analyzed by a powder X-ray diffractometer at room temperature. The final oxidation products of MoAlB crystal contain MoO₃ (orthorhombic *Pbnm*), Al₅(BO₃)O₆ (orthorhombic *Cmc2₁*), and Al₁₈B₄O₃₃ (orthorhombic *Amam*), respectively. The identified oxidation products of WAIB crystal are WO₃ (orthorhombic -), Al₂(WO₄)₃ (orthorhombic *Pnca*), and Al₁₈B₄O₃₃ (orthorhombic *Amam*), respectively. In all cases, a B₂O₃ phase was not detected by powder X-ray diffraction, and noncrystalline B₂O₃ was probably formed during the oxidation reaction.

4. Conclusions

Single crystals of MoAlB and WAIB with UBC type structure were prepared from high temperature aluminum solutions using molybdenum metal or tungsten metal and crystalline boron powders as starting material under an argon atmosphere. The chemical analysis and the structural characteristics of MoAlB are discussed. The Vickers microhardness and electrical resistivity of MoAlB and WAIB crystals were measured, and oxidation at high temperature in air was studied. The author can draw the following conclusions from this study.

(1) The single crystals of the ternary boride MoAlB and WAIB were successfully grown by the flux method using molten Al as a solvent. The MoAlB and WAIB single crystals were obtained as thick platelets with large *b*-planes and needle-like rectangulars extending in *c*-axis direction. The largest crystals prepared have maximum dimensions of about 0.3 × 7.0 × 9.3 mm³ and 1.0 × 1.0 × 5.1 mm³ for MoAlB and WAIB, respectively.

(2) The chemical compositions for the crystals are approximately homogeneity ranges, and the structural characteristics of MoAlB are discussed.

(3) The Vickers microhardness and the electrical resistivity determined on MoAlB and WAIB crystals are as follows: for MoAlB: Hv=10.3(± 0.2) GPa, ρ =67.1 $\mu\Omega\text{cm}$; for WAIB: Hv=19.3(± 0.7) GPa, ρ =243.6 $\mu\Omega\text{cm}$.

(4) The oxidation reaction of MoAlB and WAIB crystals begin to proceed at about 740°C and 440°C, respectively. The final oxidation products of MoAlB crystal contain MoO₃, Al₅(BO₃)O₆, and Al₁₈B₄O₃₃, respectively. The identified oxidation products of WAIB crystal are WO₃, Al₂(WO₄)₃, and Al₁₈B₄O₃₃, respectively.

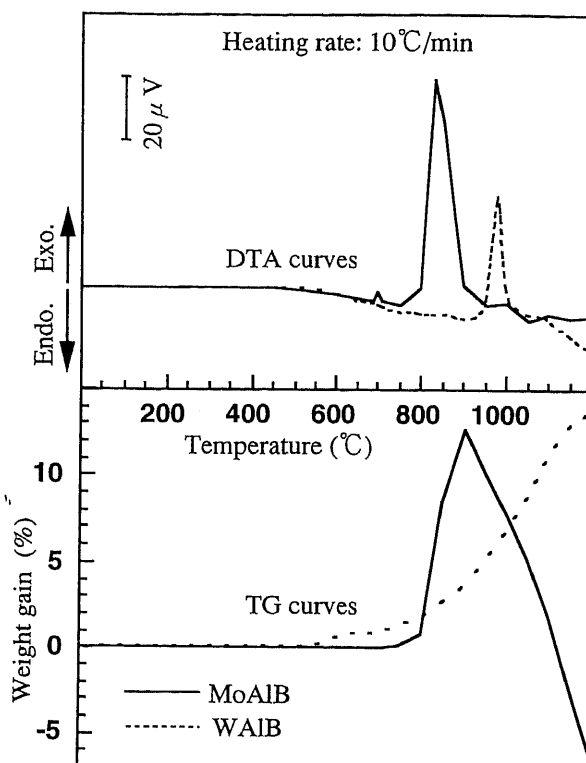


Fig. 4 Differential thermal analysis (DTA) and thermal gravimetric (TG) curves of MoAlB and WAIB crystals heated in air.

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