# Growth Conditions of $Ta_3B_4$ Single Crystals Prepared by the Aluminium-Flux Method

Shigeru OKADA* and Torsten LUNDSTRÖM†
Department of Applied Chemistry, Faculty of Engineering,
Kanagawa University, Kanagawa-ku, Yokohama 221
†Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden
(Received September 30, 1991)

Tantalum boride crystals have been prepared from high temperature aluminium solution using tantalum and boron powders as starting materials in an argon atmosphere. The growth conditions for obtaining relatively large crystals of $Ta_3B_4$ in a pure form containing no extra phases were established. The optimum growth conditions for growing $Ta_3B_4$ single crystals are the following: Atomic ratios of starting materials B/Ta=1.33 and Al/Ta=16.77, soaking temperature 1650 °C, soaking time 5 h and cooling rate 25 °C $h^{-1}$. The single crystals of $Ta_3B_4$ display a grey color, metallic cluster, and a trapezoidal shape. The largest crystals prepared have dimensions of about 0.37 mm×0.37 mm×0.40 mm. The crystals are orthorhombic with space group Immm and unit cell dimensions $a$=3.2914(8), $b$=13.994(3), $c$=3.1327(6) Å, and $V$=144.29(8) Å$^3$. The X-ray density is 13.490(3) g $cm^{-3}$.

Tantalum borides have several unique chemical and physical properties, which are high melting points, chemical stabilitiy, high electrical and thermal conductivity, high hardness and high mechanical stiffness.[1] In the tantalum-boron system, the intermediate phases $Ta_2B$, $Ta_3B_2$, TaB, $Ta_5B_6$, $Ta_3B_4$, and $TaB_2$ have been reported.[2-4] Recently we have prepared single crystals of TaB, $TaB_2$, and $Ta_5B_6$ from high temperature aluminium solutions using tantalum metal and crystalline boron powders as starting materials in an argon atmosphere.[3-5] However, growth of $Ta_3B_4$ single crystals by the high temperature solution method has not been reported. In the present work, which is the first crystal growth study of $Ta_3B_4$, we report the optimum conditions for obtaining relatively large single crystals of $Ta_3B_4$ in a pure form, containing no extra phase.

## Experimental

The starting materials were tantalum metal powders (particle size, −325 mesh; purity, 99.9%, H. C. Starck, Goslar), crystalline boron powders (particle size, −115 mesh; purity, 99.5%, H. C. Starck, Goslar), and freshly prepared aluminium metal chips (purity, 99.995%, Gränges-Essem, Finspong, Sweden). Mixtures of these materials in various atomic ratios (B/Ta=1.20—1.40, Al/Ta=3.35—201.20) were placed in an alumina crucible (purity, 99.8%). The amount of tantalum in the starting material was fixed at 2.0 g throughout all the experiments. The synthesis of crystals was carried out in a tantalum element resistance furnace. The temperature of the furnace was increased at a rate of 300 °C $h^{-1}$ up to a temperature of 1650 °C in an argon atmosphere. Subsequently, the speciment was kept at this temperature for 5 h, cooled to 1000 °C at a rate of 25 °C $h^{-1}$ and then cooled slowly to room temperature. After solidification, the crystals and matrix were separated by dissolving the excess matrix metal in 6 mol $dm^{-3}$ hydrochloric acid. The experimental conditions for each run as well as the crystalline phases obtained are presented in Table 1. Phase analysis and determination of the unit cell dimensions were carried out using an XDC-1000 Guinier-Hägg foucusing X-ray powder diffraction camera with strictly monochromatic Cu $K\alpha_1$ radiation (wavelength $\lambda$=1.5405982 Å) and semiconductor grade silicon powders (purity, 99.9999%) as internal calibration standard.[6] Some crystals were examined to collect data for crystal plane orientations and space group determination using osicillation and Weissenberg cameras, and a four-circle type automatic diffractometer (Rigaku Denki Co., Ltd.) with graphite-monochromatized Mo $K\alpha$ radiation (wavelength $\lambda$=0.710678 Å). The crystal morpholgy was examined by a stereomicroscope and a scanning electron microscope (SEM)(JEOL, JSM-840). The impurities of the crystals were examined using electron probe microanalyzer (EPMA)(JEOL, JSM-35C).

Table 1. Growth Conditions of $Ta_3B_4$ Crystals from Molten Aluminium Solution, Soaked at 1650 °C for 5 h

| Composition of starting material (atomic ratio) | | | Phases identified |
|---|---|---|---|
| Ta | B | Al | |
| 1 | 1.20 | 100.60 | $Ta_3B_4$, $Ta_5B_6$, TaB |
| 1 | 1.25 | 100.60 | $Ta_3B_4$, $Ta_5B_6$, TaB |
| 1 | 1.30 | 100.60 | $Ta_3B_4$, $Ta_5B_6$, TaB, $TaB_2$ |
| 1 | 1.33 | 100.60 | $Ta_3B_4$, $Ta_5B_6$, $TaB_2$ |
| 1 | 1.35 | 100.60 | $Ta_3B_4$, $TaB_2$, $Ta_5B_6$ |
| 1 | 1.40 | 100.60 | $Ta_3B_4$, $TaB_2$, $Ta_5B_6$ |
| 1 | 1.33 | 3.35 | $Ta_3B_4$ |
| 1 | 1.33 | 8.38 | $Ta_3B_4$ |
| 1 | 1.33 | 16.77 | $Ta_3B_4$ |
| 1 | 1.33 | 50.30 | $Ta_3B_4$, $Ta_5B_6$, $TaB_2$ |
| 1 | 1.33 | 100.60 | $Ta_3B_4$, $Ta_5B_6$, $TaB_2$ |
| 1 | 1.33 | 201.20 | $Ta_3B_4$, $Ta_5B_6$, $TaB_2$, TaB |

Tantalum metal powders: 2.00 g, Crystalline boron powders: 0.144—0.168 g, Aluminium chips: 1.0—60.0 g.

## Results and Discussion

The experiments were initially performed under constant conditions of an atomic ratio Al/Ta=100.60, heating rate 300 °C $h^{-1}$, soaking temperature 1650 °C, and soaking time 5 h, the atomic ratio B/Ta in the starting materials being varied from 1.20 to 1.40. The results of

the phase analysis are listed in Table 1. As seen from Table 1, TaB, $Ta_5B_6$, $Ta_3B_4$, and $TaB_2$ crystals were formed. The variation of the atomic ratios of the starting materials B/Ta gave different product phases. With increased boron concentration, tantalum borides of more boron-rich phases were formed. The four tantalum borides TaB, $Ta_5B_6$, $Ta_3B_4$, and $TaB_2$ were obtained in varying proportions depending on the atomic ratios of starting materials, while crystals of $Ta_2B$, $Ta_3B_2$, $AlB_2$, $AlB_{10}$, $\alpha$-$AlB_{12}$, $\beta$-$AlB_{12}$, $\gamma$-$AlB_{12}$, and $Ta_5Al_3B_x$[2] were not detected by X-ray diffraction. The desired $Ta_3B_4$ crystals were generally obtained together with 2—3 other phases for most atomic ratios B/Ta used. However, the relative X-ray intensities of the formed $Ta_3B_4$ became remarkably large for B/Ta=1.33, Al/Ta=3.35—16.77, and no other was then detected. The most favorable B/Ta ratio for obtaining $Ta_3B_4$ is thus 1.33.

Based on the above results, the synthesis conditions of $Ta_3B_4$ crystals were studied by varying the amounts of aluminium flux in the starting material. The B/Ta ratio and soaking temperature were kept constant at 1.33 and 1650 °C, respectively. When using mixtures of the Al/Ta=3.35 to 16.77, the $Ta_3B_4$ phase forms without being accompanied by any other crystalline phases. Furthermore, the $Ta_3B_4$ crystals were obtained as a phase mixture together with crystals of $Ta_5B_6$ and $TaB_2$ or TaB for Al/Ta=50.30 to 201.20. However, from starting materials containing a very small amount of aluminium (Al/Ta $\leqslant$8.38), only small $Ta_3B_4$ crystals were obtained. From the results thus far described, it is concluded that the optimum conditions for growing $Ta_3B_4$ single crystals by using the aluminium solution method are the atomic ratios of the starting materials: B/Ta=1.33 and Al/Ta=16.77, respectively.

The single crystals of $Ta_3B_4$ were enclosed by two large {010} faces, two small {100} and two small {061} faces, so that the {100} planes exhabit a trapezoidal shape. The large crystals prepared in the present work attained maximum dimensions of about 0. 37 mm×0.37 mm×0.40 mm. A SEM photograph of the single crystals having the typical crystal form is shown in Fig. 1. $Ta_3B_4$ crystals had a grey color and metallic luster. Aluminium is occasionally present in the voids as an inclusion. In addition to the aluminium metal, only traces of Ca, Si, and Fe ions were detected. The unit cell dimensions of $Ta_3B_4$ single crystals in Table 2 were obtained from Guinier–Hägg X-ray powder diffraction films.[7] The unit cell dimensions of $Ta_3B_4$ crystals obtained in the present experiment closely agreed with

Table 2. Crystal Data of $Ta_3B_4$ Single Crystal

| | |
|---|---|
| Formula unit | $Ta_3B_4$ |
| Crystal system | Orthorhombic |
| $a$/Å | 3.2914(8) |
| $b$/Å | 13.994(3) |
| $c$/Å | 3.1327(6) |
| $V$/Å$^3$ | 144.29(8) |
| Space group | *Immm* |
| $d_{X\text{-ray}}$/g cm$^{-3}$ | 13.490(3) |
| $Z$ | 2 |

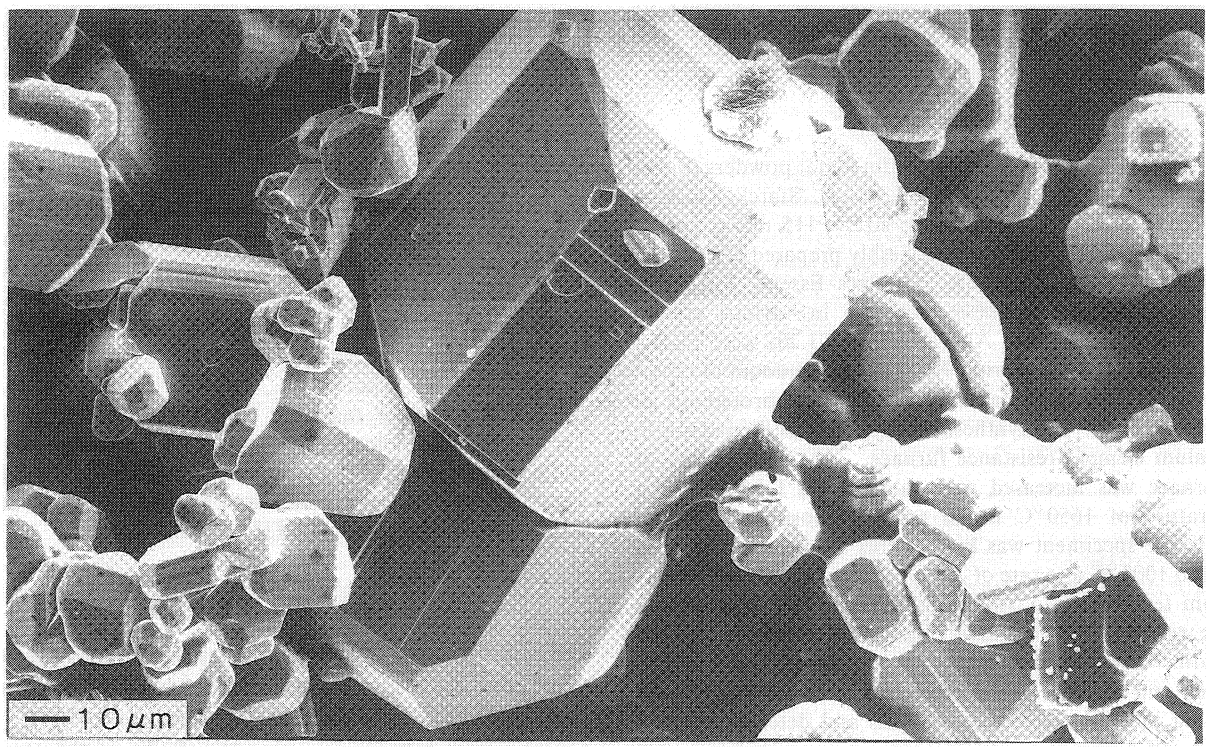


Fig. 1. Scanning electron microphotograph of $Ta_3B_4$ single crystals.

Table 3. Powder X-Ray Diffraction Data of $Ta_3B_4$

| $h$ | $k$ | $l$ | $d_{calcd}$ | $d_{obsd}$ | $(I/I_1)_{calcd}$ | $(I/I_1)_{obsd}$ | $h$ | $k$ | $l$ | $d_{calcd}$ | $d_{absd}$ | $(I/I_1)_{calcd}$ | $(I/I_1)_{obsd}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 2 | 0 | 6.997 | 6.985 | 7.7 | 9.1 | 1 | 1 | 2 | 1.407 | 1.407 | 13.7 | 30.6 |
| 0 | 4 | 0 | 3.499 | 3.498 | 9.6 | 13.9 | 1 | 9 | 0 | 1.406 | — | 0.1 | — |
| 1 | 1 | 0 | 3.204 | 3.203 | 59.2 | 64.9 | 0 | 10 | 0 | 1.399 | 1.399 | 5.9 | 13.2 |
| 0 | 1 | 1 | 3.057 | 3.055 | 0.7 | 0.1 | 0 | 9 | 1 | 1.393 | 1.392 | 9.3 | 11.2 |
| 1 | 3 | 0 | 2.689 | 2.689 | 9.5 | 18.9 | 2 | 3 | 1 | 1.391 | 1.391 | 37.2 | 50.5 |
| 0 | 3 | 1 | 2.601 | 2.600 | 100.0 | 100.0[a] | 1 | 8 | 1 | 1.385 | 1.385 | 39.5 | 65.4 |
| 0 | 6 | 0 | 2.332 | 2.332 | 29.7 | 36.5 | 1 | 3 | 2 | 1.354 | 1.353 | 3.1 | 9.3 |
| 1 | 0 | 1 | 2.269 | 2.269 | 9.2 | 16.9 | 2 | 6 | 0 | 1.345 | 1.345 | 13.5 | 31.1 |
| 1 | 2 | 1 | 2.159 | 2.159 | 97.2 | 84.8 | 0 | 6 | 2 | 1.300 | 1.300 | 12.6 | 32.6 |
| 1 | 5 | 0 | 2.132 | 2.132 | 64.4 | 73.6 | 2 | 5 | 1 | 1.292 | 1.292 | 2.7 | 6.1 |
| 0 | 5 | 1 | 2.087 | 2.086 | 4.7 | 14.8 | 1 | 5 | 2 | 1.262 | 1.262 | 32.9 | 64.2 |
| 1 | 4 | 1 | 1.904 | 1.904 | 14.5 | 31.2 | 2 | 8 | 0 | 1.199 | 1.199 | 1.9 | 4.8 |
| 0 | 8 | 0 | 1.749 | 1.750 | 2.3 | 4.8 | 1 | 10 | 1 | 1.191 | — | 0.3 | — |
| 1 | 7 | 0 | 1.709 | 1.709 | 0.5 | 2.6 | 1 | 11 | 0 | 1.187 | 1.187 | 16.4 | 37.1 |
| 0 | 7 | 1 | 1.685 | 1.685 | 13.3 | 21.7 | 0 | 11 | 1 | 1.179 | — | 1.7 | — |
| 2 | 0 | 0 | 1.646 | 1.646 | 18.7 | 31.3 | 2 | 7 | 1 | 1.177 | 1.178 | 12.0 | 32.6 |
| 1 | 6 | 1 | 1.626 | 1.627 | 2.5 | 7.5 | 0 | 8 | 2 | 1.167 | — | 1.9 | — |
| 2 | 2 | 0 | 1.602 | 1.602 | 0.4 | 3.1 | 0 | 12 | 0 | 1.166 | 1.166 | 1.2 | 11.1 |
| 0 | 0 | 2 | 1.566 | 1.566 | 16.4 | 33.4 | 1 | 7 | 2 | 1.155 | 1.155 | 0.5 | 0.8 |
| 0 | 2 | 2 | 1.529 | 1.528 | 0.4 | 0.1 | 2 | 0 | 2 | 1.135 | 1.135 | 17.8 | 33.4 |
| 2 | 4 | 0 | 1.489 | 1.489 | 2.1 | 5.2 | | | | | | | |
| 2 | 1 | 1 | 1.449 | — | 0.2 | — | | | | | | | |
| 0 | 4 | 2 | 1.430 | 1.429 | 1.9 | 6.0 | | | | | | | |

a) Probably this line is underestimated due to too strong exposure.

those previously published ($a$=3.29, $b$=14.0, $c$=3.13 Å, $V$=144.2 Å$^3$).[2,8] Guinier–Hägg X-ray diffraction intensities for $Ta_3B_4$ are presented in Table 3 together with observed and calculated interplanar spacings ($d_{obsd}$ and $d_{calcd}$, respectively). In the previously published study of $Ta_3B_4$ the sample material was never obtained in pure form.[8] The chemical composition in EPMA as well as the crystal structure is only a proposed one.[2]

Financial support from the Swedish Natural Science Research Council and Swedish National Board for Technical Development is gratefully acknowledged. The authors wish to thank Dr. L.-E. Tergenius for calculating Table 3.

**References**

1) B. Aronsson, T. Lundström, and S. Rundqvist, "Borides, Silicides and Phosphides," Methuen, London (1965).
2) G. V. Samsonov and I. M. Vinitskii, "Handbook of Refractory Compounds," IFI/Plenum, New York (1980), p. 5.
3) S. Okada, T. Atoda, and Y. Takahashi, *Nippon Kagaku Kaishi,* **1985**, 1535.
4) S. Okada, K. Hamano, I. Higashi, T. Lundström, and L.-E. Tergenius, *Bull. Chem. Soc. Jpn.,* **63**, 687 (1990).
5) H. Bolmgren, T. Lundström, L.-E. Tergenius, S. Okada, and I. Higashi, *J. Less-Common Met.,* **161**, 341 (1990).
6) R. D. Deslattes and A. Henins, *Phys. Rev. Lett.,* **31**, 972 (1973).
7) S. Andersson and B. Callmer, *J. Solid State Chem.,* **10**, 219 (1974).
8) R. Kiessling, *Acta Chem. Scand.,* **3**, 608 (1949).