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Synthesis and Investigation of Large Crystals of $(Cr_{1-x}TM_x)_3B_4$ with $TM =$ Ti, V, Nb, Ta, Mo, and W

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Single crystals of the ternary borides $(Cr_{1-x}TM_x)_3B_4$ ($TM =$ Ti, V, Nb, Ta, Mo, W) were grown by the flux method using molten aluminum as a solvent. The substances were subjected to chemical analyses and measurements of the unit cell parameters. Crystals of $(Cr_{1-x}TM_x)_3B_4$ were grown in the form of thick platelets with large {010} planes. The largest crystals obtained show maximum dimensions of about $6\times0.4\times0.4$ mm^3. The solid solubilities of Mo and W in Cr_3B_4 are discussed. In addition, measurements of microhardness and electrical resistivity were carried out, and the oxidation resistance at high temperature in air was studied. © 2000 Academic Press

Key Words: **Cr_3B_4; solid solution; single crystal; chemical analysis; crystal morphology; Vickers microhardness; thermal property.**

INTRODUCTION

Earlier, we performed the synthesis and structure analysis of Cr_3B_4; single crystals were obtained by the molten metal flux method using aluminum as solvent (1, 2). In our previous work, we also attempted to grow single crystals of ternary compounds $(Cr_{1-x}TM_x)_3B_4$ ($TM =$ Ti, V, Nb, Ta, Mo, W) and to determine the ordering of the metal atoms in $(Cr_{1-x}W_x)_3B_4$ using single-crystal X-ray diffractometry (3). However, the question of crystal growth and the properties of ternary compounds in the solid solution $(Cr_{1-x}Mo_x)_3B_4$ and $(Cr_{1-x}W_x)_3B_4$ are still not elucidated completely. In this paper, we report the experimental conditions for growing $(Cr_{1-x}TM_x)_3B_4$ crystals using molten aluminum as solvent. For single crystals of $(Cr_{1-x}TM_x)_3B_4$, unit cell parameters, crystal size, and morphology were investigated. In addition, measurements of the Vickers microhardness, electrical resistivity, and oxidation resistivity at high temperature in air were studied.

EXPERIMENTAL DETAILS

Sample Preparation

Single-crystal growth of ternary borides $(Cr_{1-x}TM_x)_3B_4$ ($TM =$ Ti, V, Nb, Ta, Mo, W) was performed by the high-temperature metal solution method using aluminum flux (1). The purities of the starting materials were as follows: Cr, 99.9%; Ti, 99.5%; V, 99.6%; Nb, 99.9%; Ta, 99.9%; Mo, 99.9%; W, 99.9%; B, 99.6%; Al, 99.99%. They were weighed at atomic ratios $B/(Cr + TM = 1.45$, $Cr/TM = 3.0$ and $Al/(Cr + TM) = 28.0$. The amount of Cr in the starting materials was fixed at 2.0 g throughout all experiments. The mixture of the starting materials was placed in a dense alumina crucible. The mixture was heated at the rate of 300°C h^{-1} and held at 1650°C for 5 h. The solution was cooled to 1000°C at the rate of 50°C h^{-1} and then quenched to room temperature. The crystals were separated from the solidified mixture by dissolving the excess Al with 6 mol dm^{-3} hydrochloric acid.

X-Ray Analysis and Characterizations

The morphological properties and purity of the crystals were investigated by optical microscopy, scanning electron microscopy (SEM) (Hitachi, S-4000), and energy-dispersive X-ray analysis (EDX) (Horiba, EMAX-2770). Chemical compositions were analyzed by electron probe microanalyzer (EPMA) (Jeol, JSM-35C) and inductively coupled plasma (ICP) (Shimadzu, ICP-50) emission spectroscopy. Phase analysis and determination of the unit cell parameters were performed using an X-ray powder diffractometer (Rigaku, RU-200) with monochromatic Cu$K\alpha_1$ radiation and a Guinier–Hägg focusing X-ray powder diffraction camera with strictly monochromatic Cu$K\alpha_1$ radiation and semiconductor-grade silicon as an internal calibration standard (4). Thermogravimetric (TG) and differential thermal (DTA) analyses were performed between room temperature

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TABLE 1
Chemical Compositions and Unit Cell Parameters of $(Cr_{1-x}TM_x)_3B_4$ Crystals

Phase	Chemical composition	Unit cell partameter (nm) *a*	*b*	*c*	$V(\times 10^{-3}\ nm^3)$	Ref.
Cr_3B_4	—	0.30004(8)	1.3018(3)	0.29516(8)	115.3(1)	(8)
$(Cr_{1-x}Ti_x)_3B_4$	$(Cr_{0.97}Ti_{0.03})_3B_4$	0.2956(4)	1.2929(9)	0.2918(4)	111.5(3)	This work
$(Cr_{1-x}V_x)_3B_4$	$(Cr_{0.89}V_{0.11})_3B_4$	0.3002(4)	1.3008(7)	0.2952(1)	115.3(2)	This work
$(Cr_{1-x}Nb_x)_3B_4$	$(Cr_{0.93}Nb_{0.07})_3B_4$	0.3015(1)	1.3025(2)	0.2958(1)	116.1(1)	This work
$(Cr_{1-x}Ta_x)_3B_4$	$(Cr_{0.86}Ta_{0.14})_3B_4$	0.3021(4)	1.3028(6)	0.2964(1)	116.7(1)	This work
$(Cr_{1-x}Mo_x)_3B_4$	$(Cr_{0.85}Mo_{0.15})_3B_4$	0.30628(4)	1.3140(1)	0.29783(3)	119.86	(3)
$(Cr_{1-x}W_x)_3B_4$	$(Cr_{0.80}W_{0.20})_3B_4$	0.30700(7)	1.3193(3)	0.2984(1)	120.86	(3)

and 1200°C to study the oxidation resistivity of the compounds in air (5). A specimen of 20–25 mg was heated at the rate of 10°C min^{-1} to 1200°C. The Vickers microhardness for the crystals was measured at room temperature as described in Ref. (6). A load of 100 g was applied for 15 s, and 5 to 10 indentations were recorded for the crystals. The electrical resistivity of the crystals was measured by means of a direct-current four-probe technique at room temperature in air.

RESULTS AND DISCUSSION

Crystal Morphology and Characteristics of $(Cr_{1-x}TM_x)_3B_4$ *(TM = Ti, V, Nb, Ta, Mo, W)*

Crystals of $(Cr_{1-x}TM_x)_3B_4$ (*TM* = Ti, V, Nb, Ta, Mo, W) were grown from starting mixtures in the atomic ratio Cr:TM:B = 0.9:0.1:1.45. The corresponding $(Cr_{1-x}Zr_x)_3B_4$ phase was not obtained. This indicates that Zr has no solid solubility in Cr_3B_4. The results of chemical analysis, phase analysis, and measurement of the unit cell parameters for as-grown $(Cr_{1-x}TM_x)_3B_4$ crystals are listed in Table 1. In the present investigation of the ternary systems of Cr–*TM*–B, some information on the solid solubilities of the transition metals (*TM* = Ti, V, Nb, Ta, Mo, W) in Cr_3B_4 can be obtained by comparisons of the atomic radii of the metals (7). In our previous work, the ternary phase MoAlB and the quaternary phase $Mo_xCr_{1-x}AlB$ ($x = 0.28$) (5), which crystallize in the UBC-type structure, were not obtained together with $(Cr_{1-x}Mo_x)_3B_4$ in the Cr–Mo–Al–B system. According to Yu and Lundström (3), the Mo atoms in $(Cr_{1-x}Mo_x)_3B_4$ are found to occupy the positions of the Cr atoms, and 16 at% Mo was found to dissolve in Cr_3B_4. On the other hand, considering the similarities of the atomic radii of Mo and W (8), an attempt was made to grow single crystals of $(Cr_{1-x}W_x)_3B_4$ in the Cr–W–Al–B system. The crystals structure of $(Cr_{0.80}W_{0.20})_3B_4$ is illustrated in Fig. 1 (3). It can be described as a kind of slab packing along the *b* axis, similar to descriptions of the Cr_2B_3-type (8) and Ta_5B_6-type (9) structures. Each slab is composed of two layers of close-packed $B(TM'')_6$ trigonal prisms (TM'' = Cr, W). Direct contacts between the TM'' atoms exist between each slab, forming rectangular TM'' pyramids. These boron zig-zag chains extend in the *c* axis direction on the *b*–*c* plane; there are double chains in the structure of $(Cr_{0.80}W_{0.20})_3B_4$.

Crystals of $(Cr_{1-x}W_x)_3B_4$ have a silver color and metallic luster. They were obtained in the form of thick-platelet crystals having well-developed {010} faces (Fig. 2). The largest crystals prepared have maximum dimensions of about $6 \times 0.4 \times 0.4\ mm^3$.

Properties

As listed in Table 2, the Vickers microhardness for crystals of $(Cr_{1-x}TM_x)_3B_4$ was measured on the {010} faces. The microhardness of $(Cr_{0.80}W_{0.20})_3B_4$ was comparatively lower than that of Cr_3B_4 (2) and other $(Cr_{1-x}TM_x)_3B_4$.

As seen in Table 3, the electrical resistivity values of $(Cr_{0.85}Mo_{0.15})_3B_4$ and $(Cr_{0.80}W_{0.20})_3B_4$ crystals were found to be higher than the values of other $(Cr_{1-x}TM_x)_3B_4$ and of CrB, Cr_3B_4, and Cr_2B_3 (2, 10).

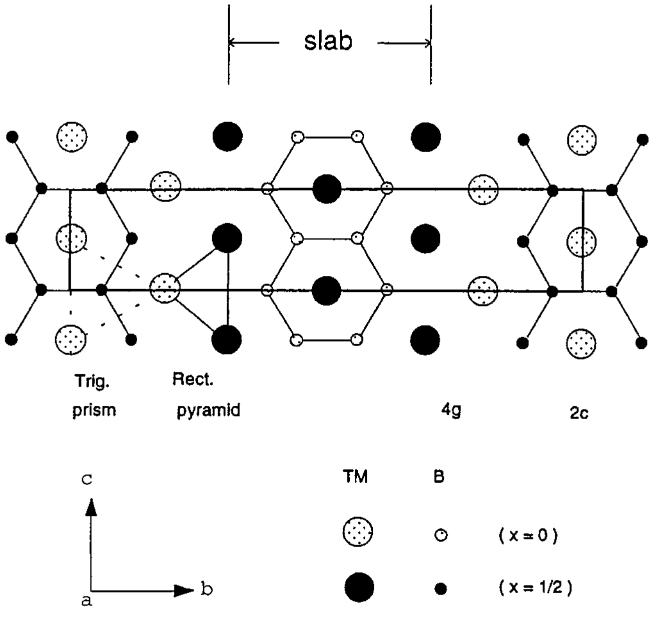

FIG. 1. Crystal structure of $(Cr_{0.80}W_{0.20})_3B_4$ projected along the *a* axis (3).

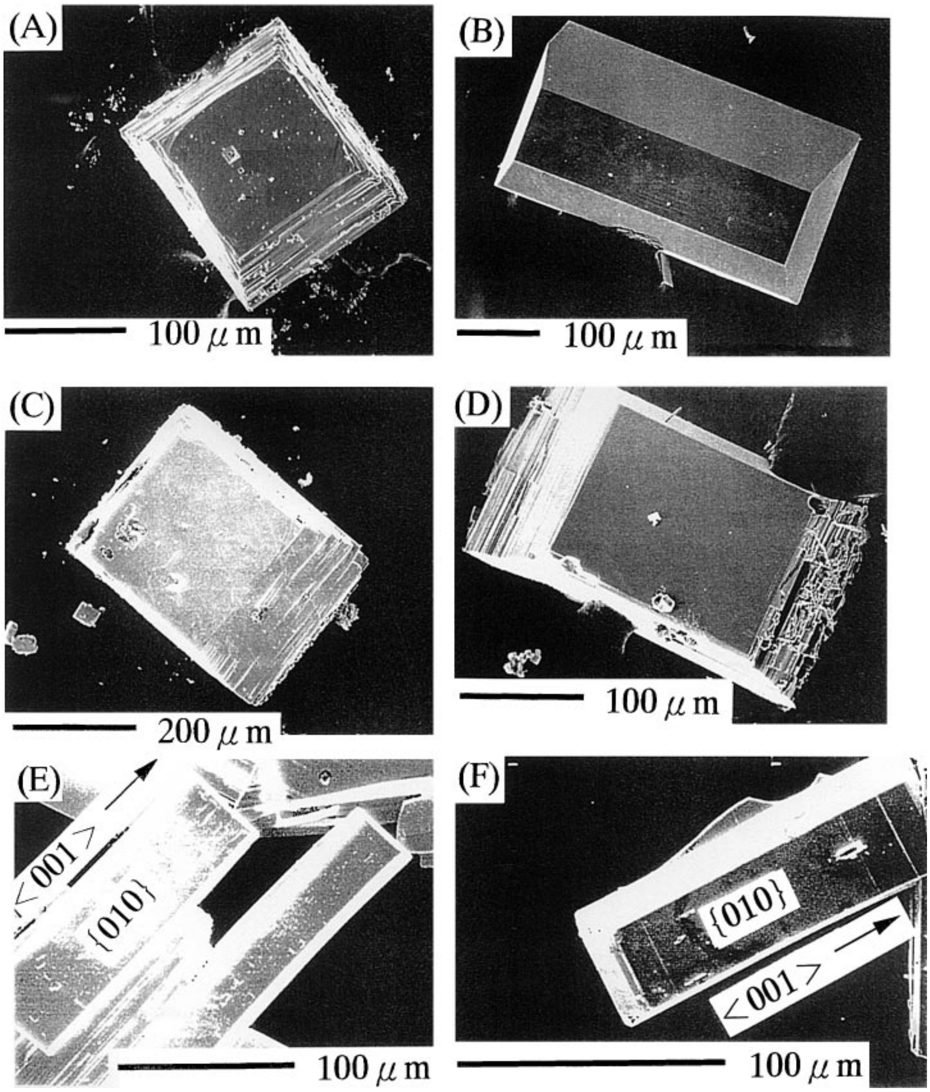

FIG. 2. Scanning electron micrographs of $(Cr_{0.97}Ti_{0.03})_3B_4$ (A), $(Cr_{0.89}V_{0.11})_3B_4$ (B), $(Cr_{0.93}Nb_{0.07})_3B_4$ (C), $(Cr_{0.86}Ta_{0.14})_3B_4$ (D), $(Cr_{0.85}Mo_{0.15})_3B_4$ (E), and $(Cr_{0.80}W_{0.20})_3B_4$ (F) single crystals.

Figure 3 shows TG–DTA curves for Cr_3B_4, $(Cr_{0.85}Mo_{0.15})_3B_4$ and $(Cr_{0.80}W_{0.20})_3B_4$. The DTA–TG determination for $(Cr_{1-x}TM_x)_3B_4$ (TM = Ti, V, Nb, Ta) was not carried out because of the small quantity of the samples. According to the TG curves, oxidation of Cr_3B_4, $(Cr_{0.85}Mo_{0.15})_3B_4$, and $(Cr_{0.80}W_{0.20})_3B_4$ starts at about

TABLE 2
Vickers Microhardness of $(Cr_{1-x}TM_x)_3B_4$ Crystals

Compound	Indentation plane	Load (g)	Microhardness Hv (GPa)	Ref.
Cr_3B_4	{010}	200	21.9 (±1.0)	(2)
$(Cr_{0.97}Ti_{0.03})_3B_4$	{010}	100	22.1 (±0.4)	This work
$(Cr_{0.89}V_{0.11})_3B_4$	{010}	100	21.8 (±0.9)	This work
$(Cr_{0.93}Nb_{0.07})_3B_4$	{010}	100	21.6 (±0.8)	This work
$(Cr_{0.86}Ta_{0.14})_3B_4$	{010}	100	22.2 (±1.2)	This work
$(Cr_{0.85}Mo_{0.15})_3B_4$	{010}	100	21.5 (±0.2)	This work
$(Cr_{0.80}W_{0.20})_3B_4$	{010}	100	16.8 (±0.1)	This work

TABLE 3
Electrical Resistivity of $(Cr_{1-x}TM_x)_3B_4$ Crystals

Compound	Direction	Electrical resistivity ($\times 10^{-6}\,\Omega$cm)	Ref.
Cr_3B_4	⟨001⟩	64.3 (±8.5)	(2)
$(Cr_{0.97}Ti_{0.03})_3B_4$	⟨001⟩	68.1 (±3.4)	This work
$(Cr_{0.89}V_{0.11})_3B_4$	⟨001⟩	60.5 (±6.1)	This work
$(Cr_{0.93}Nb_{0.07})_3B_4$	⟨001⟩	62.5 (±9.2)	This work
$(Cr_{0.86}Ta_{0.14})_3B_4$	⟨001⟩	70.9 (±2.3)	This work
$(Cr_{0.85}Mo_{0.15})_3B_4$	⟨001⟩	175.4 (±12.0)	This work
$(Cr_{0.80}W_{0.20})_3B_4$	⟨001⟩	110.0 (±8.1)	This work

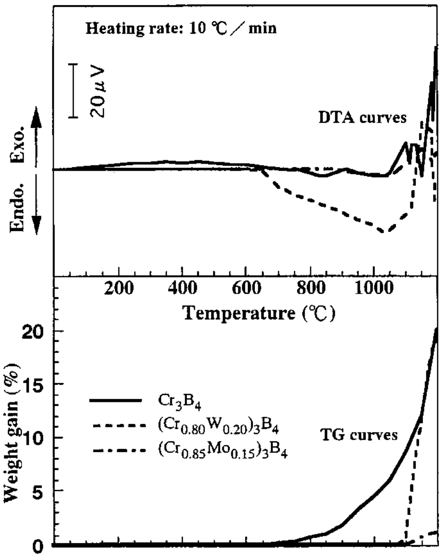

FIG. 3. Traces of the differential thermal analysis and thermal gravimetry of Cr_3B_4, $(Cr_{0.85}W_{0.15})_3B_4$, and $(Cr_{0.80}W_{0.20})_3B_4$.

680, 1095, and 1083°C, respectively. The weight gains of the same compounds after heating in air up to 1200°C are 20.3 wt% (2), 1.8 wt%, and 20.6 wt%, respectively. The exothermic peaks of the DTA curves were found at about 820, 1080, 1115, and 1175°C for Cr_3B_4, at about 1146°C for $(Cr_{0.85}Mo_{0.15})_3B_4$, and at about 1138°C for $(Cr_{0.80}W_{0.20})_3B_4$. The oxidation resistivity of $(Cr_{0.85}Mo_{0.15})_3B_4$ crystals was found to be higher than the resistivity of Cr_3B_4 and $(Cr_{0.80}W_{0.20})_3B_4$. The oxidized products are mixed phase of $CrBO_3$, Cr_2O_3, and MoO_3 or WO_3. In all cases, B_2O_3 was not detected by X-ray diffraction; noncrystalline B_2O_3 was probably formed during the oxidation procedure.

CONCLUSION

The single crystals of ternary boride $(Cr_{1-x}TM_x)_3B_4$ (TM = Ti, V, Nb, Ta, Mo, W) have been grown by the flux method using molten Al. The as-grown $(Cr_{1-x}TM_x)_3B_4$ crystals were subjected to chemical analyses and measurements of unit cell parameters. The solid solubilities of transition metals in Cr_3B_4 are discussed. In addition, measurements of microhardness, electrical resistivity, and oxidation resistivity in air were carried out. The microhardness value of $(Cr_{0.80}W_{0.20})_3B_4$ was comparatively lower than that of Cr_3B_4 and other $(Cr_{1-x}TM_x)_3B_4$. The electrical resistivity values of $(Cr_{0.85}Mo_{0.15})_3B_4$ and $(Cr_{0.80}W_{0.20})_3B_4$ crystals were found to be higher than the values of other $(Cr_{1-x}TM_x)_3B_4$. The oxidation resistivity of $(Cr_{0.85}Mo_{0.15})_3B_4$ crystals was found to be higher than the resistivity of Cr_3B_4 and $(Cr_{0.80}W_{0.20})_3B_4$. A mixed phase of $CrBO_3$, Cr_2O_3, and MoO_3 or WO_3 is identified by X-ray diffraction as oxidized product for $(Cr_{0.85}Mo_{0.15})_3B_4$ and $(Cr_{0.80}W_{0.20})_3B_4$ compounds.

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