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Simultaneous densification and phase decomposition of TiB_2–WB_2 solid solutions activated by cobalt boride addition

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Abstract

In order to apply simultaneous densification and phase decomposition of TiB_2–WB_2 solid solutions occurred by pressureless sintering using induction heating, the effect of CoB as the additive agent have been investigated. The sintered products were evaluated using X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy analyses. Dense product with a relative density of 95%, which was produced with a CoB addition of 0.5 wt.% and an induction heating time for 600 s, was identified as $(Ti,W)B_2$ and $(W,Ti)B_2$ phases. Platelet crystals of the $(W,Ti)B_2$ phase were precipitated in grain boundary of the $(Ti,W)B_2$ phase. The mechanical properties of the product, which improved by the densification and decomposition of $(Ti,W)B_2$, are also presented.

Keywords: Sintering; Composite; Microstructure; Mechanical properties; Borides; TiB_2; WB_2

1. Introduction

Transition metal diborides are the compound materials with high melting point, hardness, electrical conductivity and thermal conductivity.[1] Particularly, TiB_2 has used as a monolithic ceramic or as a second phase in composites. TiB_2 addition to SiC and B_4C ceramics is thought to improve their mechanical properties for such application as wear resistant parts.[2,3] However, densification of transition metal diborides by sintering is difficult because the dominant mechanism in material transport is evaporation–condensation with no net shrinkage.[4] In addition, many diborides such as TiB_2, WB_2 and CrB_2 form extensive solid solutions at high temperatures, and the decomposition of unusual microstructures containing the second phase in the form of highly oriented precipitates occurs by annealing at low temperatures. The TiB_2–WB_2 solid solutions can be decomposed into the two phases of $(Ti,W)B_2$ and $(W,Ti)B_2$ by heat treatment, and the phase decomposition can control the microstructure.[5,6] The microstructural control can improve the mechanical properties such as the fracture toughness.

Solid solutions of TiB_2–WB_2 and TiB_2–WB_2–CrB_2 have been produced by annealing mixtures of two borides, a process that requires high temperatures at ∼2000 °C and long times for ∼8 h.[6,7] In the previous studies, the formation of the TiB_2–WB_2–CrB_2 solid solutions by field activation using the spark plasma sintering (SPS) apparatus has been investigated.[8] SPS was conducted using elemental reactants which reacted under the influence of a high, pulsed dc current and a uniaxial pressure. The $(Ti,W,Cr)B_2$ phase obtained at 1900 °C for 10 min has a relative density of 94%. The decomposition of those solutions to two phases has been found to be kinetically slow. In a recent investigation,[9] the present authors have produced the TiB_2–WB_2 solid solutions by induction field activated combustion synthesis (IFACS)[10,11] for 2 min, using elemental reactants. Moreover, nickel or cobalt, which are known as the additive agent of pressureless sintering of TiB_2,[12–16] was added in $(Ti,W)B_2$ for simultaneous sintering and phase decomposition of the solid solutions produced by the IFACS method.[17] The phase decomposition occurred within 6 min by induction heating, however, the products were not dense bodies. Therefore, other additive agents are needed for the densification with the phase decomposition.

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In the present work, we investigated the effect of the addition of cobalt boride on simultaneous densification and phase decomposition of (Ti,W)B_2. The addition of boride with orthorhombic structure such as cobalt boride and nickel boride leads to the densification by liquid phase sintering because the pseudobinary eutectic reaction occurs at relatively low temperature.[18–22]

2. Experimental procedure

Powders of 99.5% pure titanium, with an average particle size of ∼22 μm (Sumitomo Sitix Inc., Amagasaki, Japan), 99.9% pure tungsten, with an average particle size of ∼8 μm, 99% pure crystalline boron, with a particle size <45 μm, and 99% pure cobalt, with an average particle size of ∼5 μm, were used in this work. The W, B and Co powders were obtained from Kojundo Chemical Laboratory, Inc. (Sakaido, Japan). The Ti, W and B powders were weighed out in mole ratios of Ti/W/B = 1/1/4.6 to give a composition of (Ti,W)B_2 and were dry-mixed in an automatic agate mortar for 1 h. Excess boron was used because of previous experience indicating the loss of this element (due to the evaporation of its oxide) during synthesis.[9]

The reaction in the powder compact was ignited by induction under the conditions of 85 V, 170 A, 70 kHz and 120 s. Detail of the experimental setup was provided in previous publications.[9–11] The image of an apart of the apparatus is shown in the insert picture of Fig. 2. The powders of resulting (Ti,W)B_2 phase were crushed by ball milling using silicon nitride jar and balls until an average particle size of 2 μm was obtained.

Heat treatment by induction heating was conducted for pressureless sintering and decomposition of the solid solutions. To the powder of (Ti,W)B_2 phase, the powder in mole ratios of Co/B = 1/1 (CoB) was added at levels from 0 to 7.5 wt.%, and was dry-mixed in an automatic agate mortar for 30 min. From these mixed powders, cylindrical compacts, about 16 mm in diameter and 10 mm long were formed by cold isostatic pressing at 250 MPa. The powder compact which has a packing density of ∼60% was placed in a cylindrical carbon sheet, about 47 mm in diameter and 17 mm long. The carbon crucible with the compact was placed in commercial casting sand inside the silicon nitride crucible described above. The heat treatment was performed by induction heating (85 V, 170 A, 70 kHz) under atmospheric pressure of air. The sample, being embedded in the carbon sheet, experienced a reducing environment.

The sample temperatures were measured with W–$Re_{5\%}$/W–$Re_{26\%}$ thermocouples using a data acquisition recorder as described in previous publications.[9–11] The products were analyzed by X-ray diffraction (RINT2500: RAD-C system, Rigaku Inc.) using Cu Kα radiation. Microstructural and elemental analyses were conducted on cross-sections of the annealed samples using scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) (JSM-330; JEOL). The density of the products was measured by the Archimedes method. Hardness and fracture toughness of the products were determined by Vickers microhardness (HMV-2000; Shimazu, Inc.; load: 19.6 N, dwell time: 10 s) with indentation crack measurements.[23]

3. Results and discussion

Pressureless sintering was performed by induction heating under atmospheric pressure for simultaneous densification and decomposition of (Ti,W)B_2 phase with a WB_2 composition of 50 mol%. The TiB_2–WB_2 system is a eutectic type as shown in Fig. 1.[5] A solid solution of TiB_2–WB_2, that is (Ti,W)B_2 phase, has a relatively large region of the solid solution, and WB_2 content in (Ti,W)B_2 is approximately 63 mol% at eutectic temperature (2230 °C). On the other hand, (W,Ti)B_2 has a relatively limited solubility of TiB_2, and TiB_2 content in (W,Ti)B_2 is approximately 3 mol% at eutectic temperature. A typical temperature profile of the sample which added 1.0 wt.% CoB to (Ti,W)B_2, is shown in Fig. 2. The sample heated by induction current through carbon sheets, and the temperature was increased at a heating rate of 10 °C/s in the initial stage of the elevating temperature. And then the temperature smoothly reached until the maximum temperature of 1840 °C after 300 s from heating up. CoB in the sample, which has a melting point of 1460 °C, melts during sintering. As shown in the phase diagram of Fig. 1,

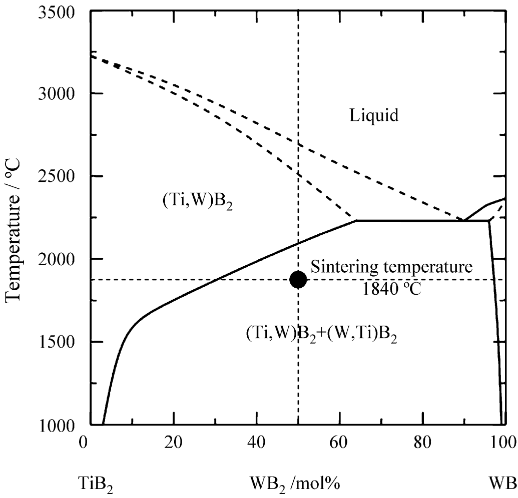

Fig. 1. Quasi-binary phase diagram of TiB_2–WB_2 system: after Ref. 5.

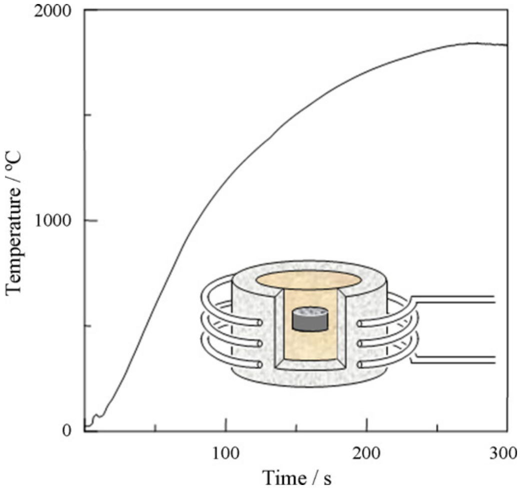

Fig. 2. Temperature profile of (Ti,W)B_2 + 1 wt.% CoB sample by induction heating.

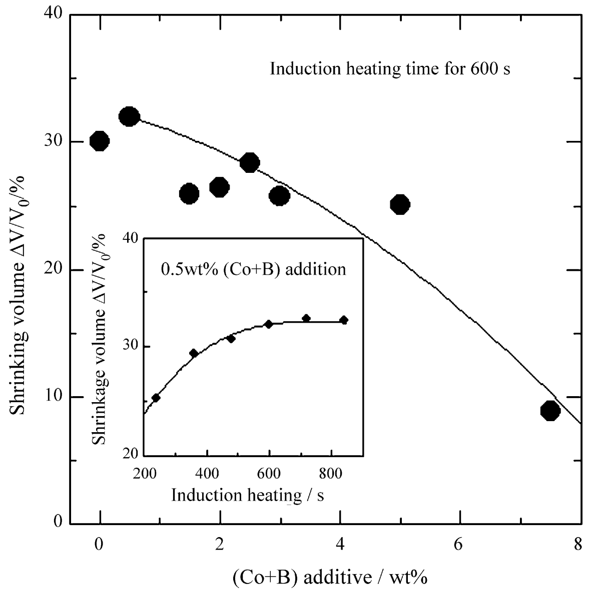

Fig. 3. Effect of CoB additive on volume shrinkage of the samples sintered by induction heating for 600 s (inset figure: effect of heating time on volume shrinkage of the samples in addition of 0.5 wt.%).

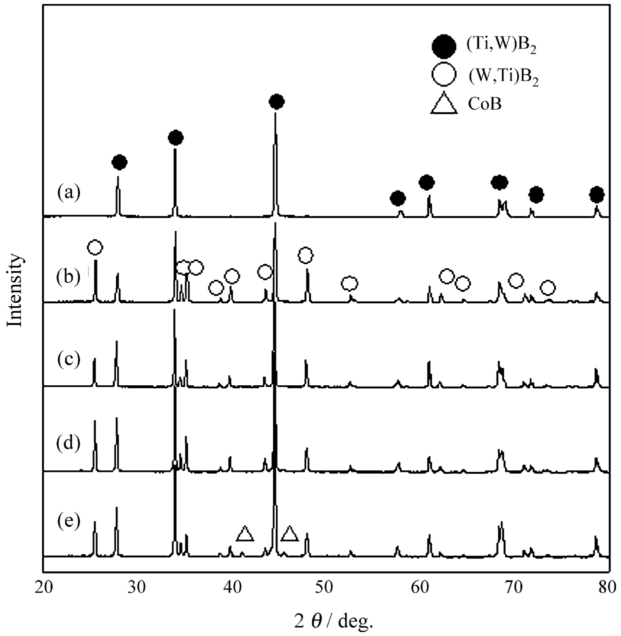

Fig. 4. X-ray diffraction patterns of the products sintered by induction heating for 600 s; $(Ti,W)B_2$: (a) 0, (b) 0.5, (c) 2.5, (d) 5.0, and (e) 7.5 wt.% CoB.

the decomposition of the $(Ti,W)B_2$ phase with a WB_2 composition of 50 mol% easily occurs at 1840 °C.

Fig. 3 shows the effect of CoB addition on volume shrinkage of the samples sintered by induction heating for 600 s. The volume shrinkage ratio of the sample in a CoB addition of 0.5 wt.% is maximum, 32%, and decreases with increasing additive amount. The reason for decreasing volume shrinkage would be thought that the excess additive caused the selective evaporation of liquid phase and the sweating phenomena. The sweating phenomena in this case occurred with an addition higher than 5 wt.%, and Watanabe et al. also reported the generation of the sweating phenomena in TiB_2 with an addition of CoB higher than 3 wt.%.[24] As shown in the insert figure, the volume shrinkage of the samples with an addition of 0.5 wt.% CoB gradually increases with induction heating time until 600 s and almost reaches the equilibrium. It indicates that the sample was sintered under the raising temperature for 300 s and a holding temperature of 1840 °C for 300 s as shown in Fig. 2. Thus, it was found that slight addition of CoB and induction heating for 600 s are effective for the densification of the product.

X-ray diffraction patterns of the products sintered by induction heating for 600 s are shown in Fig. 4 as a function of addition of CoB: (a) 0, (b) 0.5, (c) 2.5 (d) 5.0 and (e) 7.5 wt.%. The peaks of the product without CoB addition are those belonging to the $(Ti,W)B_2$ phase which corresponded closely to the diffraction peaks of TiB_2 (hexagonal AlB_2 structure, *P6/mmm*). On the other hand, the patterns of the products with the CoB addition contain the diffraction peaks belonging to $(Ti,W)B_2$, $(W,Ti)B_2$ which has the hexagonal W_2B_5 structure (*P*6_3*/mmc*). With a CoB addition of 7.5 wt.%, the peaks of CoB appear at last. The decomposition occurs and rapidly saturates by slight CoB addition, as the peak intensity of $(W,Ti)B_2$ does not increase with amount of the addition. The XRD peaks of the products with the addition show a shift to lower 2θ values for the (0 0 1) peak (at $2\theta = 28.0$ for the sample without addition) as well as the case of the Ni or Co.[17] In view of the dependence of the lattice parameters on the composition in the solid solutions,[9,17,25] this observation is consistent with the decrease in W content of the solid solution as a result for the precipitation of the second phase. The decomposition time is very short by the CoB addition, compared with the previous works which required annealing for 2–8 h at 1600 °C after hot press[7] or for 14 h at 1500 °C after spark plasma sintering.[8] The accelerated of the decomposition by the addition of CoB can be explained by the influence of boron transfer enhanced in molten Co or CoB. That is, the decomposition occurs by the transfer of the boron atoms. EXAFS (extended X-ray absorption fine structure) studies on $(Ti,W)B_2$ composites[5] indicated that a high amount of the boron atoms is transferred from near titanium environment to tungsten neighborhood during high temperature treatment.

The microstructure and phases identification of the products were examined by scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS). Fig. 5 shows SEM (backscattered electron images) of cross-section of the products sintered by induction heating for 600 s. In the product without CoB addition, the presence of a single solid solution phase with some large pores is shown in Fig. 5(a). The two phases shown in Fig. 5(b)–(d) were identified, by measurement of EDS area scanning, as the $(Ti,W)B_2$ (gray phase) and $(W,Ti)B_2$ (white phase), respectively. The densification is enhanced by a CoB addition of 0.5 wt.%, and then the porosity of the products increases with increasing CoB addition. With a CoB addition of 7.5 wt.%, CoB with darker gray color is also observed in the grain boundary between the $(Ti,W)B_2$ and $(W,Ti)B_2$ phases, and the pores would be formed by the sweating phenomena of the liquid phase. With a CoB addition of 0.5 wt.%, the platelets of the $(W,Ti)B_2$ phase were precipitated in grain boundary of the $(Ti,W)B_2$ matrix.

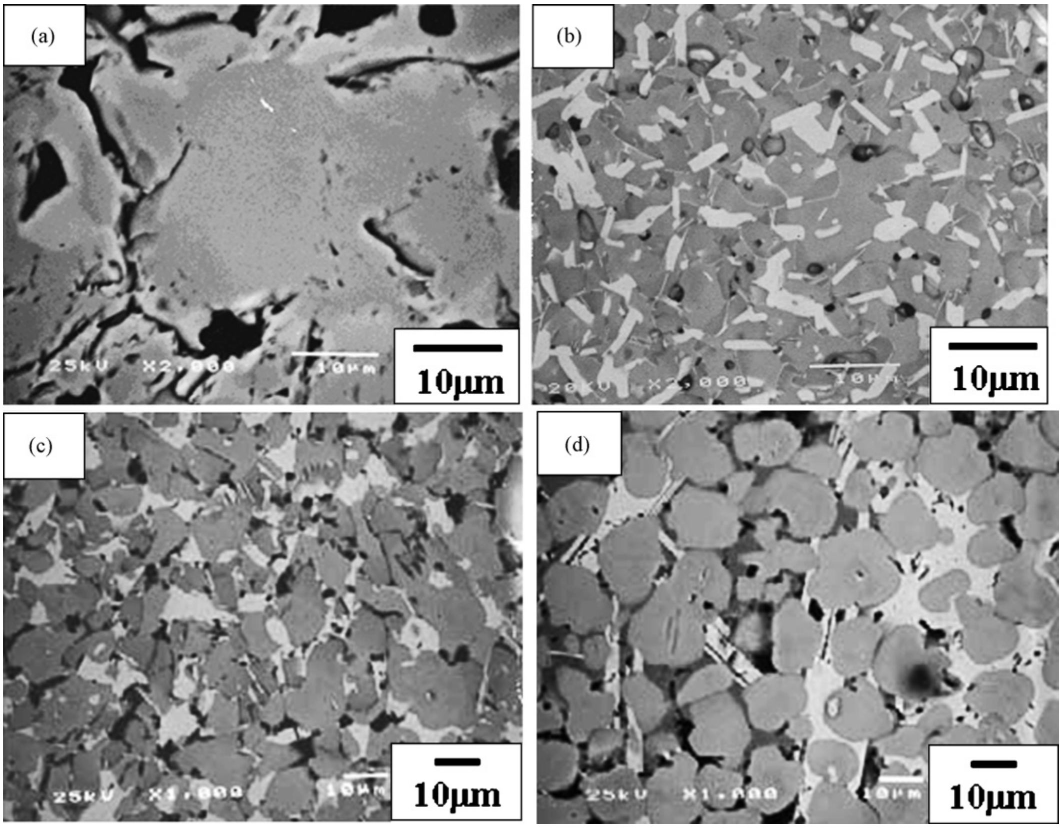

Fig. 5. SEM photographs (BEI) of lapped cross-section of the products sintered by induction heating for 600 s; (Ti,W)B_2: (a) 0, (b) 0.5, (c) 2.5, and (d) 7.5 wt.% CoB.

The size of these platelets is ~1.5 μm in length and ~6.0 μm in long. An epitaxial precipitation of very fine platelets of W_2B_5-type crystals with $(0\,0\,0\,1)_{W_2B_5}$ parallel to $(0\,0\,0\,1)_{TiB_2}$ of the matrix is well known.[5] The (W,Ti)B_2 platelets also are observed in the case of Ni or Co addition.[17] Results for EDS analyses on the (Ti,W)B_2 and (W,Ti)B_2 phases indicated that the former contains less tungsten because of the deposition of (W,Ti)B_2. For (Ti,W)B_2 with a WB_2 composition of 50 mol%, the concentration of WB_2 in (Ti,W)B_2 after decomposition is equivalent to ~40 mol%. The concentration of WB_2 in (Ti,W)B_2 does not change by increasing amount of the CoB addition. Therefore, it is clear that the grain growth of the (W,Ti)B_2 phase, which increased with increasing CoB addition, occurred by condensation of some (W,Ti)B_2 platelets.

The density of the products decreases by a CoB addition higher than 0.5 wt.% as found from the results for the volume shrinkage and the SEM observation. The density with an addition of 0.5 wt.% is 8.40 g cm^{-3}, corresponding to 95% of the theoretical value calculated from the lattice constants determined by the XRD measurement and the results for the EDS analyses. The mechanical properties of the products were improved by the addition of CoB. Table 1 shows the Vickers microhardness and the fracture toughness of the product obtained in this work and the literature values. The Vickers microhardness and the fracture toughness K_{IC} of the product with an addition of 0.5 wt.% CoB exhibit the maximum values, i.e., ~22.0 GPa and 6.0 MPa $\mathrm{m}^{1/2}$, respectively. In spite of pressureless sintering for 10 min, these values almost correspond to the literature values for the dense (Ti,W,Cr)B_2 phase formed by SPS at 64 MPa for 10 min[8] and the TiB_2–TiN nanocomposite produced by SPS at 70 MPa for 12 min.[26]

We found that simultaneous densification and phase decomposition of the TiB_2–WB_2 solid solutions using pressureless induction heating for 600 s can be performed by a CoB addition of 0.5 wt.%. The cause of the densification in this system is not clear but would be the same as for the TiB_2–CoB system. Watanabe et al. reported the mechanism of the densification in the TiB_2–CoB system as follows.[24] Amount of the liquid phase in TiB_2–0.5 wt.% CoB at 1900 °C can be assumed lower than about 0.5 vol.%. This amount of the liquid phase is insuffi-

Table 1
Vickers microhardness and fracture toughness of the product in this work and TiB_2 based composite

	Relative density (%)	Hardness (GPa)	Fracture toughness (MPa $\mathrm{m}^{1/2}$)	Reference
(Ti,W)B_2–0.5 wt.% CoB	95	22.0	6.0	
(Ti,W,Cr)B_2 (SPS; 64 MPa)	94	22.7	–	8
TiB_2–TiN (SPS; 70 MPa)	97	21.8	5.1	26

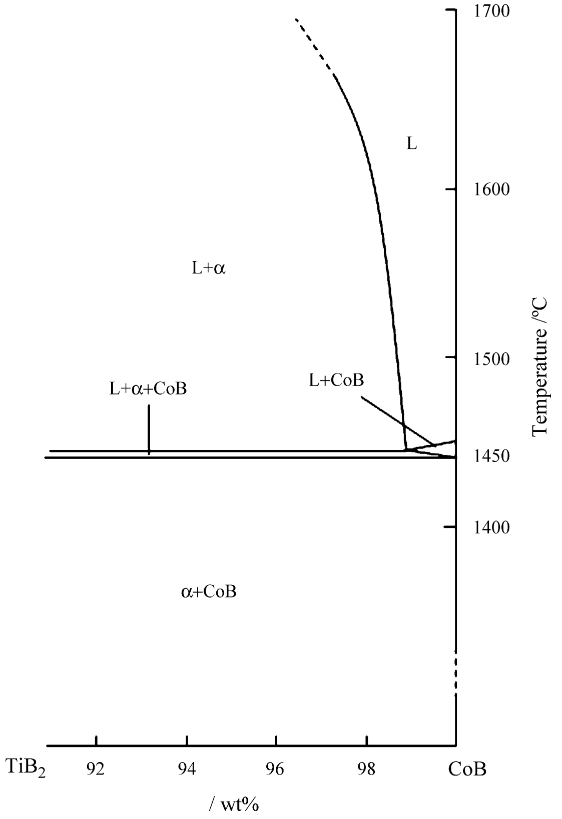

Fig. 6. Estimated pseudobinary phase diagram of TiB_2–CoB system: after Ref. 24.

cient for general liquid sintering. However, the particles of TiB_2 would be activated for sintering because the surface of the TiB_2 particles is melted by low amount of molten CoB, so-called pseudobinary eutectic reaction.[27] The eutectic temperature for the rich side of CoB drastically decreases as shown in TiB_2–CoB pseudobinary phase diagram[24] of Fig. 6. That is, the sintering temperature is lower than the melting temperature of $(Ti,W)B_2$ and $(W,Ti)B_2$, while, the eutectic temperature between the solid solutions and CoB would be decreased by pseudobinary eutectic reaction just on the surface of the solid solutions. Therefore, this phenomenon leads to an enhancement of the densification by liquid phase sintering. Related to this proposed explanation it has been found that Ni–B coated WC powders easily leads to liquid phase sintering.[19]

This present results show that the addition of cobalt boride into the $(Ti,W)B_2$ phase is effective for the improvement of the densification and phase decomposition enhanced by the pseudobinary eutectic reaction between the solid solutions and cobalt boride.

4. Conclusions

The effect of cobalt boride addition on simultaneous densification and phase decomposition of the TiB_2–WB_2 solid solutions, with a WB_2 content of 50 mol%, by pressureless induction heating was investigated. The densification and the phase decomposition was enhanced by slight CoB addition. With an addition of 0.5 wt.% CoB, the product obtained by induction heating for 600 s is dense with the two phases of $(Ti,W)B_2$ and $(W,Ti)B_2$. The Vickers microhardness and the fracture toughness K_{IC} of the product with a relative density of 95% are 22.0 GPa and 6.0 MPa m$^{1/2}$, respectively. The formation of CoB is suggested as playing a role in the enhancement of the densification and the decomposition of the solid solutions.

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