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Mechanical properties of WC–WB–W_2B composites prepared by reaction sintering of B_4C–W–WC powders

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Abstract

Composites of WC–WB–W_2B with no metallic binder were prepared by the reaction sintering of a B_4C–W–WC (mole ratio 1:5:80) powder mixture at sintering temperatures between 1500 and 1900 °C using resistance-heated hot pressing. WB, W_2B and a part of WC in the composites were formed by the solid-state reaction between B_4C and W. Dense sintered bodies were obtained at and above 1650 °C, in which small aggregates composed of WB and W_2B were scattered in WC matrices. The rapid grain growth of WC occurred over a temperature range between 1650 and 1700 °C, and correspondingly resulted in decreases of both the hardness and fracture toughness. The sintering temperature 1650 °C was the most suitable for preparing dense sintered bodies with combined high values of Young's modulus, hardness and fracture toughness.

Keywords: Composites; Hot pressing; Mechanical properties; Powders-solid state reaction; WB; W_2B; WC

1. Introduction

Transition metal carbides have extremely high hardness. Of these carbides WC has the highest values for Young's modulus and shear modulus,[1] and therefore forms the basis of cemented carbides used for high-performance cutting tools and wear-resistant parts. Conventional cemented carbides are composed mainly of WC and of metallic binder phase, basically Co. Although reducing the amount of metallic binder decreases sinterability, strength and fracture toughness, it brings the benefit of increasing Young's modulus, hardness and corrosion resistance. However, it is not easy to manufacture WC fully consolidated bodies even by pressure sintering. For a cemented carbide containing no metallic binder, named a binderless carbide, which was developed for use in corrosive environments, therefore, TiC and TaC were added as non-metallic binders.[2–4] They form a binder phase, called the γ-phase, and fill up the space between the WC grains as do metallic binders.[5] Although the WC–TiC–TaC material is more sinterable than pure WC, an additional HIP treatment after pressureless sintering was needed for obtaining fully dense bodies.

Recently, a reactive hot-pressing technique in which a displacement reaction proceeds was successfully applied to the consolidation of TiB_2–TiC,[6–10] TiB_2–TiN[11,12] and TiB_2–Ti(C, N)[13] composites with poor sinterability. For example, a TiB_2–TiC composite was synthesized from a B_4C and Ti powder mixture by the solid-state displacement reaction $B_4C + 3Ti = 2TiB_2 + TiC$, and was simultaneously sintered under an applied pressure. The highly deficient phases $TiC_{0.5}$ and Ti_xC formed during the reaction caused fast mass transfer and resulted in consolidation at relatively low temperature.[6] In a previous paper,[14] we succeeded in preparing dense WC–WB–W_2B composites with no metallic binder from WC, B_4C and W powder mixtures using fundamentally the same technique. These composites were synthesized basically by the reaction $B_4C + 5W + xWC = 4WB + (1 + x)WC$ during sintering. Good mechanical properties were obtained at x values between 35 and 130, especially at an x value of 80. As is widely known, the sintering temperature controls the grain size of sintered

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bodies and results in a strong influence on mechanical properties which are themselves related closely to the grain size. In this study, therefore, WC–WB–W_2B composites were prepared at various sintering temperatures by the reaction sintering of a B_4C + 5W + 80WC powder mixture using resistance-heated hot pressing, and the effect of the sintering temperature on the microstructure and mechanical properties was studied.

2. Experimental

The following powders were used as starting materials for reaction sintering: B_4C (Rare Metallic, purity 99 wt.%, average particle diameter 1.5 μm), W (Rare Metallic, purity 99.9 wt.%, average particle diameter 6.0 μm), and WC (Japan New Metals, average particle diameter 0.75 μm, chemical composition (wt.%): total carbon 6.10, free carbon 0.01, Fe 0.01, Mo 0.02, W bal.). The chemical composition of the B_4C used in this study was determined as $B_{4.0}C_{1.0}$ by chemical analysis. The starting powders were mixed to stoichiometrically cause the reaction

$$B_4C + 5W + 80WC = 4WB + 81WC \quad (1)$$

The resistance-heated hot-pressing technique which can heat a sample at a very high heating rate was used for reaction sintering of sample mixtures with sintering equipment named a Spark-Plasma Sintering Machine (Sumitomo Coal Mines, SPS-2080). A graphite die (height: 50 mm, outer diameter: 50 mm, inner diameter: 20 mm) with a sample mixture was surrounded by a graphite insulation felt sheet. The graphite die and sample (electrically conductive) are directly heated by passing pulsating DC current between the upper and lower graphite punches. The temperature at 10-mm depth from the surface of the die was measured through a small hole in the die with an optical pyrometer. Every die with a sample was heated at a rate of 50 °C min^{-1} under an applied pressure of 50 MPa, and was maintained at a given temperature between 1500 and 1900 °C for 20 min.

Sintered bodies were analyzed by powder X-ray diffractometry (XRD) and were examined metallographically with an electron probe microanalyzer (EPMA). Density and mechanical properties were measured for characterizing the sintered bodies. The density was measured by the Archimedean method. The mechanical properties were evaluated for Vickers hardness, Young's modulus, Poisson's ratio, and fracture toughness. Young's modulus and Poisson's ratio were measured by the pulse-echo method. Vickers hardness was measured under a 9.8 N load held for 15 s. Fracture toughness was estimated by the indentation method using Evans and Davis's equation.[15]

3. Results and discussion

3.1. Reaction products

The sintered bodies obtained at temperatures between 1500 and 1900 °C were composed mainly of WC and of small amounts of W_2B and WB. Fig. 1 shows the relative X-ray intensity for the sintered bodies as a function of sintering temperature. Each relative intensity value was calculated from the intensities of the highest diffraction peaks for W_2B (211), WB (112), and WC (100). The relative intensities of the products vary hardly over the sintering temperature range. This suggests that the solid-state reaction already ceased at and above 1500 °C. The stoichiometric reaction Eq. (1) does not accept the formation of W_2B. If the W concentration of the starting WC powder is just a little higher than that in stoichiometric WC, excessive W produces W_2B, because the molar quantity of WC in the powder mixture before reaction is much larger than that of the WB to be produced stoichiometrically according to Eq. (1). The W/C mole ratio of the WC powder is estimated to be 1.006 from the analytical values, on the assumption that the impurities Fe and Mo formed Fe_3C and Mo_2C with C and free C resolved into the WC phase at high temperatures. A precise value for the W concentration of WC phase in equilibrium with W is not clear in the WC phase diagrams reported.[16] Although in this study both WB and W_2B were formed as tungsten borides by the solid-state reaction, it is possible to prevent the formation of W_2B. The further addition of an appropriate amount of C to the powder mixture used will induce the energetically favorable[17] reaction W_2B + C = WB + WC and will provide a WC–WB composite.

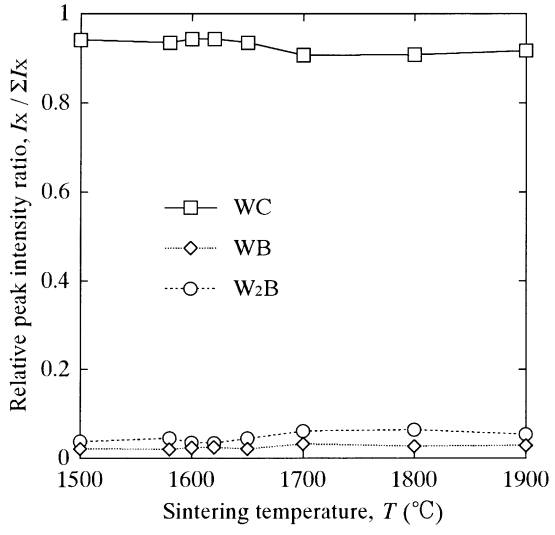

Fig. 1. Change in relative peak intensity ratio, $I_x/\Sigma I_x$, with sintering temperature.

3.2. Microstructure

Fig. 2 shows the microstructures of the sintered bodies obtained at 1650 and 1800 °C. An enlarged microstructure for Fig. 2(b) is shown in Fig. 3. There are small white-colored aggregates in many places. Each of the aggregates is composed of two kinds of grain. Taking into account the XRD results, the outer grains are WB, the inner ones W_2B and the matrix WC. This morphology suggests that the layer sequence of W/W_2B/WB/WC/B_4C was produced in the early stage of the reaction between W and B_4C. The reaction layer sequence for carbide and boride formed in a transition metal–B_4C reaction system is dependent on the transition metal. In the reaction system Ti–B_4C, the sequence is reverse to that in W–B_4C: Ti/TiC_{1-x}/[TiC_{1-x} + TiB + Ti_3B_4]/TiB_2/B_4C.[6–10] Reaction layers in the reaction system Ti–BN are similar to the Ti–B_4C has the sequence of Ti/TiN/TiB_2/BN.[11,12]

Grains of WC in the sintered bodies obtained at 1650 °C were small, but grains for 1800 °C were much larger as shown in Fig. 2. Aggregates of WB and W_2B grew little with increasing grain size of WC. They were left inside the grown WC grains, and had little effect in pinning migrating grain boundaries and preventing the resultant grain growth of WC. Fig. 4 shows the average grain size as measured by the intercept method.[18] The average grain size of WC grains for 1600 and 1650 °C, both 0.80 μm, is close to that of the starting WC powder, 0.75 μm. The grain growth rate changed abruptly between 1650 and 1700 °C, and above 1800 °C WC grains grew up to 24 μm.

There were many pores in the sintered body obtained at a sintering temperature of 1500 °C. Pores were reduced with increasing sintering temperature, and few

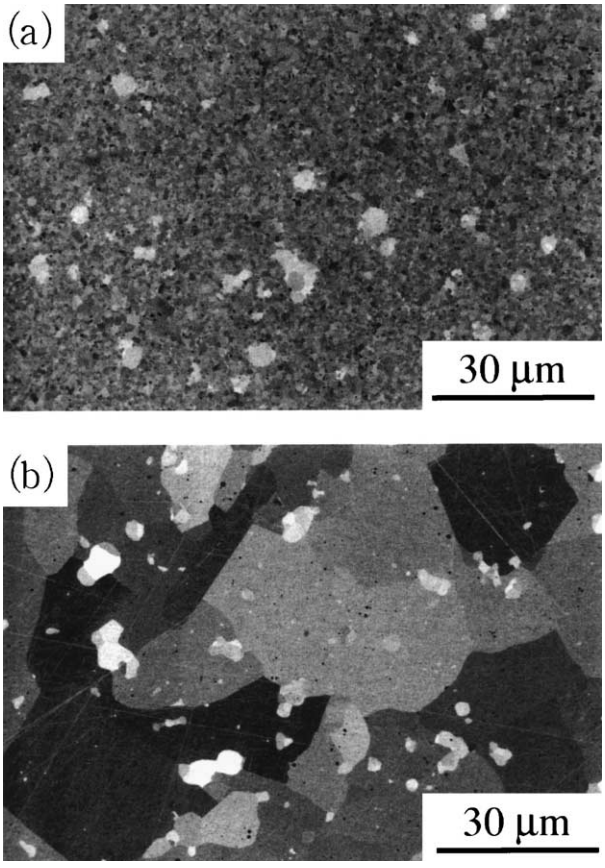

Fig. 2. Microstructure (backscattered electron images) of composites obtained at (a) 1650 °C and (b) 1800 °C.

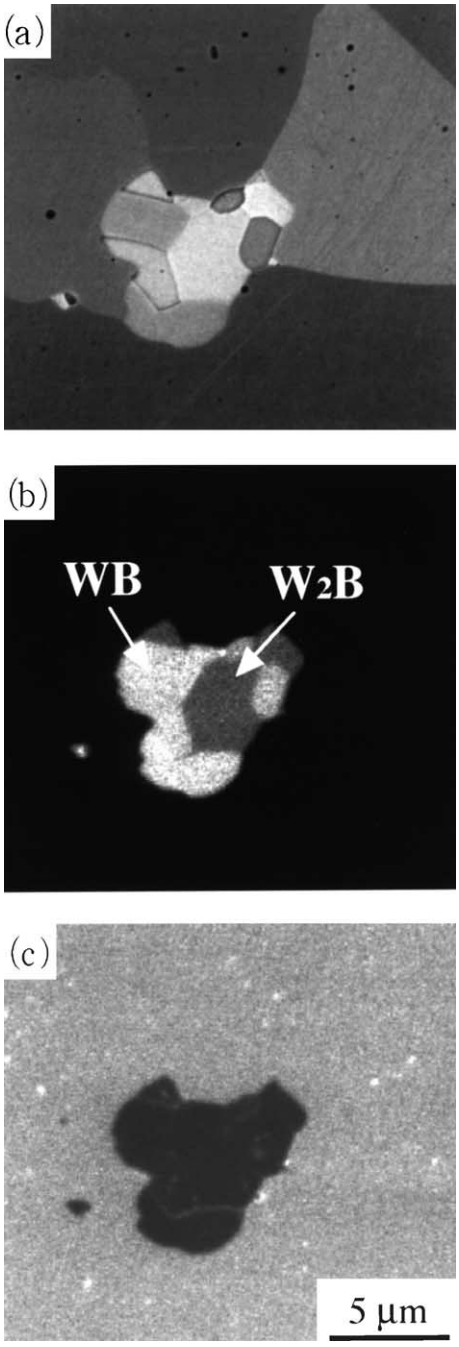

Fig. 3. Microstructure of a composite obtained at 1800 °C. (a) backscattered electron image, (b) distribution of boron and (c) distribution of carbon.

pores were found above 1700 °C (Fig. 2). Fig. 5 shows the bulk density of the sintered bodies. The bulk density increased with sintering temperature, and reached a constant value of 15.60 Mgm^{-3} at and above 1650 °C. The sintering temperature 1650 °C is the lowest one suitable for densification and the highest one without substantial grain grow.

3.3. Mechanical properties

The Young's modulus, Poisson's ratio, Vickers hardness and fracture toughness of the sintered bodies were measured to evaluate their mechanical properties. Fig. 6 shows the Young's modulus and Poisson's ratio of the sintered bodies. The former increased with sintering temperature and reached an almost constant value at and above 1650 °C. The change in Young's modulus with sintering temperature is very similar to that in the bulk density shown in Fig. 5. As shown in Fig. 7, the modulus values follow a straight line as a function of the bulk density:

$$E = 99.82(d_b - 8.58) \quad (2)$$

where E is the Young's modulus (GPa) and d_b is the bulk density (Mg m^{-3}). The Poisson's ratio had a nearly constant value independent of the sintering temperature. The values for the typical refractory carbides TiC, ZrC, HfC, VC, NbC, TaC and WC range from 0.18 to 0.24.[12] The composites TiB_2–TiC, TiB_2–TiN and TiB_2–Ti(CN) have values of 0.17–0.25.[7,9,12] The Poisson's ratio of WC/W_2B/WB is close to those of the above carbides and composites.

Fig. 8 shows the Vickers hardness of the sintered bodies. The hardness increased with sintering temperature

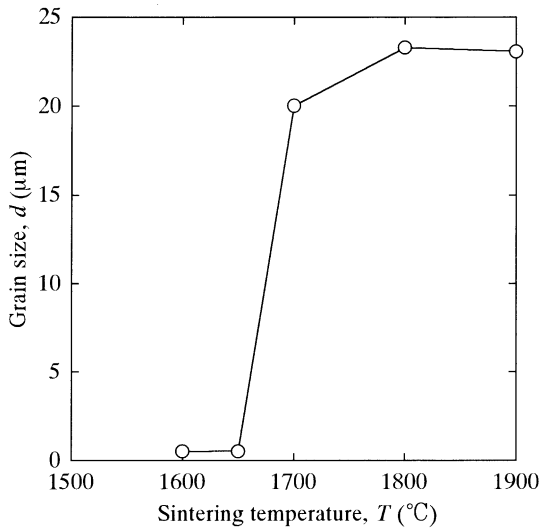

Fig. 4. Change in grain size with sintering temperature.

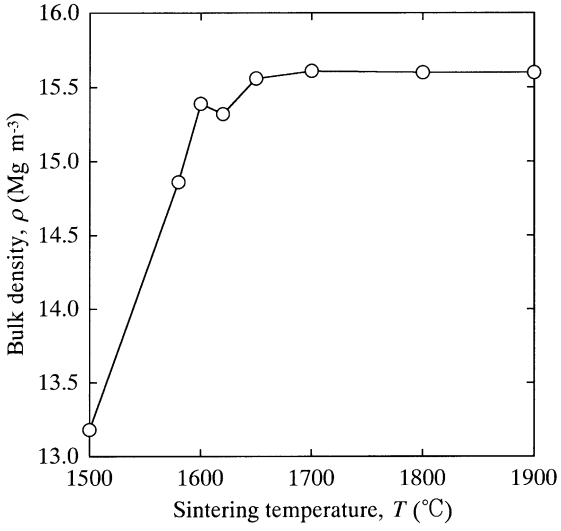

Fig. 5. Change in bulk density with sintering temperature.

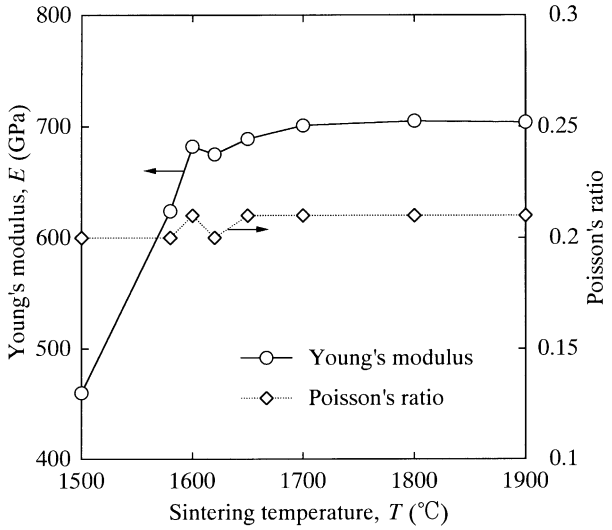

Fig. 6. Change in Young's modulus and Poisson's ratio with sintering temperature.

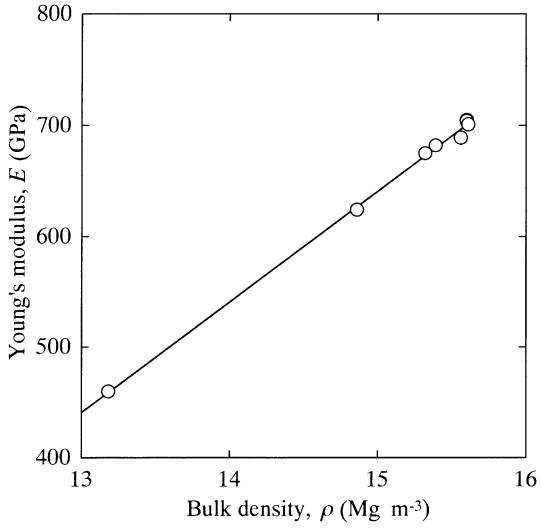

Fig. 7. Relation between Young's modulus and bulk density.

up to 1600 °C, had a constant value of 22.6 GPa from this temperature to 1650 °C, decreased sharply between 1650 and 1700 °C, and decreased much moderately above 1700 °C. The increase in the hardness up to 1600 °C is due to the decrease in the porosity. The change in the hardness of the dense sintered bodies obtained at and above 1650 °C corresponds to that in the grain size shown in Fig. 4.

Fig. 9 shows the relation between the hardness and the grain size. As widely known from the Petch equation,[19] for metallic materials the upper and lower yield stress and the rupture strength for low-temperature brittle fracture are proportional to (grain size)$^{-1/2}$. This relation holds also for various oxide ceramics.[20] Thus the strength of brittle materials decreases with increasing grain size. In brittle materials, hardness reflects a degree of resistance to fracture, and consequently decreases with increasing grain size. In the binderless cemented carbide WC-3 wt.% TiC-2 wt.% TaC,[3] similarly, the hardness decreased as the particle size of the starting WC powders and the resulting grain size in the sintered bodies increased. For densely sintered WC–Co cemented carbides also, the hardness decreased with the grain size of WC.[21]

Fig. 10 shows the fracture toughness calculated from the results of the Vickers indentation test and the density values by Evans and Davis's equation,[15] which is recommended as valid for the fracture toughness of cemented carbides.[22] The change in the fracture toughness with the sintering temperature much resembles that in the Vickers hardness. For the dense sintered bodies, the fracture toughness decreased with increasing grain size as shown in Fig. 11, reflecting the strength decrease with grain size.

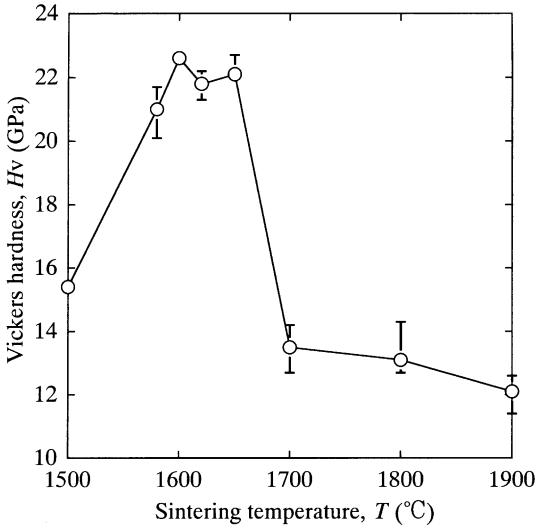

Fig. 8. Change in Vickers hardness with sintering temperature.

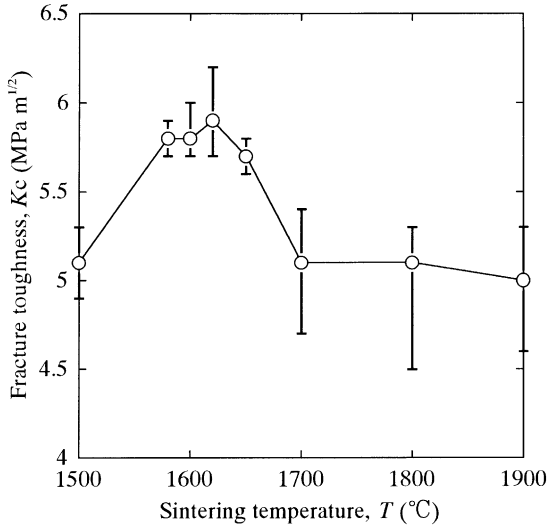

Fig. 10. Change in fracture toughness with sintering temperature.

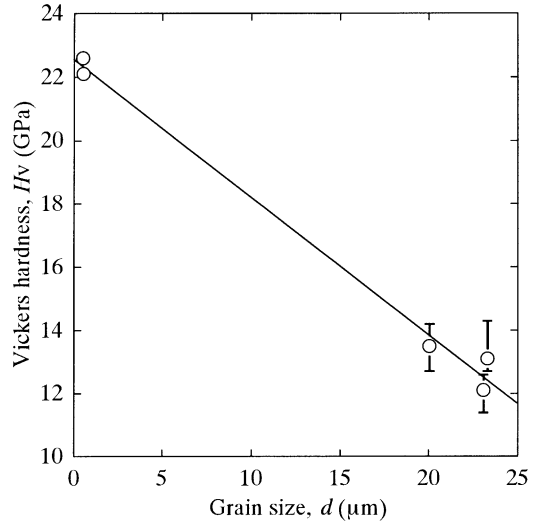

Fig. 9. Relation between Vickers hardness and grain size.

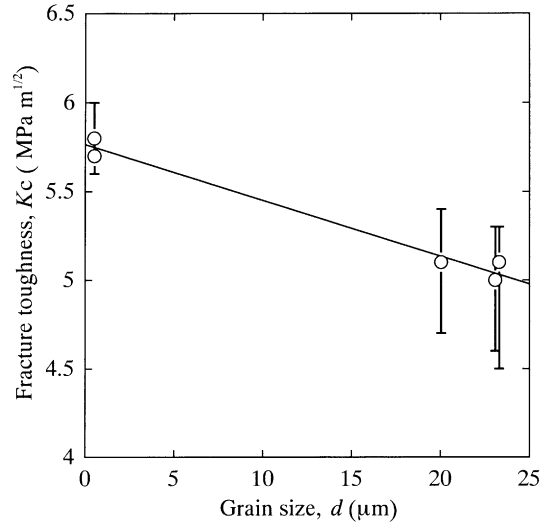

Fig. 11. Relation between fracture toughness and grain size.

As described above, sintering temperatures near 1650 °C are suitable for obtaining high combined values for Young's modulus, Vickers hardness and fracture toughness. However, after raising the sintering temperature by only 50 °C, good properties for hardness and fracture toughness are lost due to rapid grain growth. Therefore, the addition of compounds to avoid the grain growth of WC, for example, VC and Cr_3C_2 which act well on WC–Co[23,24] and WC–TiC–TaC,[3] is potentially attractive for widening the sintering temperature range appropriate for obtaining good mechanical properties.

4. Conclusions

The synthesis of WC–WB–W_2B composites from a B_4C–W–WC (mole ratio 1:5:80) powder mixture and their simultaneous consolidation were performed by reactive resistance-heated hot pressing over the sintering temperature range of 1500–1900 °C. Although the powder was prepared at the mole ratio to cause the reaction $B_4C + 5W + 80WC = 4WB + 81WC$, W_2B was formed due to a slight W excess in the W powder used. The bulk density increased with sintering temperature, and reached a constant value at and above 1650 °C where the samples were fully consolidated. As the bulk density increased, the Young's modulus increased linearly. In every dense sintered body, small aggregates composed of W_2B and WB were scattered in a WC matrix. Grains of WC rapidly grew over 1650 °C. The aggregates were left inside the grown WC grains and did not pin the grain boundaries of the WC. The increase in the grain size of WC had no influence on Young's modulus and Poisson's ratio, but resulted in decreases in the hardness and the fracture toughness. The sintering temperature 1650 °C was found to be suitable for obtaining dense composites with the good mechanical properties.

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