Highly dense binderless WC was obtained by hot press sintering (HP) and then treated by hot isostatic pressing (HIP). Compositional and phase analyses of the products were carried out using field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). The mechanical properties were evaluated, and the location of the inhibitors was studied by transmission electron microscopy (TEM). The sub-micron (0.53 μm) powders of WC (doped with 0.33 wt % VC and 0.54 wt % Cr₃C₂) were HP sintered at 1800, 1900, and 2000°C. WC with a relative density of 97.9% and a grain size of approximately 0.73 μm was obtained after sintering at 2000°C for 30 min under a pressure of 28 MPa. The Vickers hardness and fracture toughness were 24.15 ± 0.33 GPa and 4.40 ± 0.10 MPa·m¹/₂, respectively. After treatment by HIP at 1750°C for 120 min under a pressure of 150 MPa, the relative density of the samples was increased to 99.4%, the hardness was over 26.00 GPa, and the grain size was 0.75–0.81 μm. The grain growth inhibitors were also characterised by TEM and energy dispersive X-ray spectroscopy (EDX); the results show that the grain growth was effectively suppressed by the inhibitors of VC and Cr₃C₂ as a result of the segregation of the inhibitors at the grain boundaries.

Key-words : Binderless WC, Hot pressing, Hot isostatic pressing, Hardness, Inhibitors

1. Introduction

WC–Co cemented carbides have been widely used as wear-resistant components, cutting tools and dies due to their excellent wear resistance, fracture toughness and high hardness.¹ The cobalt binder phase not only facilitates densification but also increases the fracture toughness. However, the binder phase decreases the hardness and corrosion resistance of the materials, which limits their industrial application.² Therefore, the development of binderless tungsten carbides, such as pure WC,³–⁶ WC–Mo₄C⁷) and WC–TiC,⁸ has been widely investigated in recent years.

The properties of binderless tungsten carbides produced by powder metallurgy can be improved by decreasing the grain size and improving the density of the sintered bodies. Due to the high melting point of pure WC, it is difficult to sinter binderless WC to a high density and fine grain using the conventional sintering process. Therefore, many new technologies such as spark plasma sintering¹¹,¹²,¹⁶,¹⁹ and high-frequency induction heated sintering¹³,¹⁴,¹⁷,¹⁸,¹⁹ have been used to consolidate binderless WC. The high heating rate and shot holding time of these new technologies allows the preparation of binderless tungsten carbides with high density and fine grains. However, the mechanism is not well understood, and the processing limits the product size; consequently, the application of these techniques in industry is limited.

Conventional sintering techniques include pressureless sintering or low pressure sintering, hot pressing, and hot isostatic pressing.¹¹ These methods involve high temperatures and long holding times, which facilitate grain growth. However, the grain growth can be restrained by adding some inhibitors. Transition metal carbides that have free energies of formation lower than that of WC can be used as inhibitors, e.g., VC, TiC, SiC, Cr₃C₂ and ZrC.¹³,¹⁴ Among those carbides, VC and Cr₃C₂ are most commonly used as grain growth inhibitors, and VC is considered to be more effective than Cr₃C₂ in WC–Co cemented carbides when added in equal amounts. It is believed that the inhibitors dissolve preferentially into the metallic binder and hinder the dissolution of W and C, suppressing grain growth by dissolution/replication.¹⁴ In the case of binderless WC with little (less than 0.5 wt %) or no metallic binder, the inhibition of the dissolution/replication in WC–Co may not be sufficient.

In this work, binderless sub-micron WC powders with 0.33 wt % VC and 0.54 wt % Cr₃C₂ were sintered by hot pressing and then treated by hot isostatic pressing. The microstructure, phase, and mechanical properties were studied. The location of the inhibitors and the inhibition mechanism of grain growth were also investigated.

2. Experimental procedure

Commercially available WC was used as a raw material (Xiamen Golden Egret Special alloy Co. Ltd., China), with a grain size of 0.53 μm, as measured by a Fisher sub-sieve sizer (FSSS), doped with 0.33 wt % VC, 0.54 wt % Cr₃C₂, a total carbon content of 6.18 wt % (free carbon content of 0.04 wt %) and other minor impurities given in weight percent: 0.29% O, 0.0015% Ni, 0.0023% Co, and 0.0018% Fe. Initially, the powders were poured into a graphite die with an inner diameter of 60 mm and a height of 100 mm and then pre-pressed under a pressure of 17 MPa. Subsequently, sintering was performed under vacuum pressure below 10 Pa. The heating process was as follows: The powders were firstly heated to 800°C at a heating rate of 5°C/min, then...
heated to 1600°C at a heating rate of 10°C/min, and finally heated to the sintering temperature at a heating rate of 3°C/min. When the sintering temperature was reached, a pressure of 28 MPa was applied and held for 30 min. After the retention time, the pressure was removed and the sample was cooled to 1000°C at a rate of 10°C/min, and then the power was turned off and the sample was cooled with the furnace. To optimise the sintering process, the following three sintering temperatures were used: 1800, 1900 and 2000°C. In order to obtain fully dense WC materials, the samples sintered by HP at 1900 and 2000°C were further treated by HIP at 1750°C for two hours under a pressure of 150 MPa.

The relative density of the sintered samples was measured by the Archimedes method. Compositional and phase analyses of the products were conducted by FE-SEM (SM-7001F, Japan) and XRD (X-pen pro-MPD x-Ray, Netherlands). The location of the inhibitors was determined by a 200 kV TEM (Tecnai G2 F20 S-TWIN, America) with EDX. The TEM samples were obtained by mechanical grinding and ion-milling.

The micro-hardness of the samples was measured by a Vickers micro-hardness machine (HVS-30, China). A 98.1 N load was applied on each sample for 15 s using a standard micro-Vickers indenter. Five different locations of each sample were measured, and the average was taken as the measured value. The fracture toughness, \( K_{IC} \), of the sample was calculated with the following equation:

\[
K_{IC} = 0.016 \left( \frac{E}{H} \right)^{1/2} \cdot \frac{P}{C^{1/2}}
\]

Where \( E \) is Young’s modulus, \( H \) is the Vickers hardness, \( P \) is the indentation load, and \( C \) is the mean crack length as measured from the centre of the indentation.

3. Results and discussion

3.1 Phase structure analysis

The XRD patterns of the initial powders and samples sintered by HP at different temperatures are shown in Fig. 1. It can be seen that only WC peaks were observed in the pattern of the initial powders, without sub-carbide \( W_2C \) or other impurities. However, all the samples sintered by HP contained minor amounts of \( W_2C \). According to the vendor specifications, the carbon content in the initial WC powders was stoichiometric, and the oxygen content was 0.29 wt%. The presence of \( W_2C \) may be attributed to the reduction of surface oxides, which consumed carbon within the carbide powders.9 In addition, when the powders are exposed to the reducing atmosphere of graphite die and vacuum, \( W_2C \) may also form because some of the surface oxides are reduced by C or CO produced from the die at high temperatures. The existence of minor amounts of \( W_2C \) (less than 3.5 wt%) has no significant effect on the hardness and fracture toughness. However, as the amount of \( W_2C \) is increased, the hardness and other mechanical properties decreased distinctly.16 The amount of \( W_2C \) in all the sintered samples is nearly the same, as seen in Fig. 1, suggesting that \( W_2C \) was obtained from the reduction of the surface oxides in the initial powders and that the surface oxides were completely consumed.

3.2 Mechanical properties analysis

Table 1 lists the mechanical properties of the samples that were HP sintered and treated by HIP at different temperatures. The results show that the relative density of the sample increases with increasing HP sintering temperature. The relative density of sample A (HP sintered at 1800°C) was only 83.9%; however, it reached 95.9% for sample B (HP sintered at 1900°C) and 97.9% for sample C (HP sintered at 2000°C). The highest density was obtained for the samples that were HP sintered and treated by HIP (samples D and E), which had a relative density of 99.4%. The density of the sample is closely related to the temperature and holding time, as the distance of mass transportation increases with increasing temperature and longer retention time.3 The density of samples D and E was almost the same, which may be attributed to a sufficiently high pressure and long holding time.

The hardness of the HP sintered samples also increased with increasing sintering temperatures. A higher hardness of 24.15 GPa was determined for sample C. After treatment by HIP, the hardness of samples D and E was greater than 26.00 GPa. The highest hardness of 26.77 GPa obtained in sample D is close to or higher than those of reported binderless WC, i.e., \( H_v = 27.05 \) GPa,19 \( H_v = 23.14 \) GPa,17 \( H_v = 25.40 \) GPa.18 It is worthwhile to note that the hardness of the sample depends on the

![Fig. 1. XRD patterns of the initial powders and samples HP sintered at different temperatures.](image)

| Sample | Sintering condition* | Relative density† (%) | Hv (GPa) | \( K_{IC} \) (MPa m\(^{1/2}\)) | Grain size (μm) |
|--------|---------------------|-----------------------|----------|------------------|----------------|
| A      | HP: 1800°C          | 83.9                  | 13.13 ± 0.33 | —                | 0.57           |
| B      | HP: 1900°C          | 95.9                  | 22.95 ± 0.20 | 4.89 ± 0.18      | 0.65           |
| C      | HP: 2000°C          | 97.9                  | 24.15 ± 0.33 | 4.40 ± 0.10      | 0.73           |
| D      | HP: 1900°C and treated by HIP | 99.4 | 26.77 ± 0.22 | 4.84 ± 0.22 | 0.75 |
| E      | HP: 2000°C and treated by HIP | 99.4 | 26.00 ± 0.13 | 4.54 ± 0.23 | 0.81 |

*HP: at different temperatures for 30 min under a pressure of 28 MPa; treated by HIP: at 1750°C for 120 min under a pressure of 150 MPa.

†The theoretical density of pure WC is 15.70 g/cm\(^3\).
applied indentation load; the higher the applied indentation load, the lower the hardness. 2)

The fracture toughness of the samples was also evaluated, excepting sample A due to its low density, and the results are listed in Table 1. For the HP sintered samples, the fracture toughness varied in a range of 4.40–4.89 MPa·m$^{1/2}$ and tended to decrease with increasing Vickers hardness. After treated by HIP, the fracture toughness was 4.54–4.84 MPa·m$^{1/2}$, a little decrease compared with the sample C, and the sample D has higher fracture toughness than the sample E although its higher hardness. Sample E had lower hardness and fracture toughness compared with the sample D might be attributed to grain growth.

3.3 Microstructure analysis

The FE-SEM micrographs of the initial powders are shown in Fig. 2(a). It can be seen that the initial powders were generally faced or round and contained few agglomerates. In addition, most of the particles were less than 0.5 μm, with a minor amount of large particles close to 1 μm. Figures 2(b)–2(f) show the fracture surface images of the samples that were HP sintered and treated by HIP at different temperatures. The shape of the WC grains of sample A was similar to that of the initial powders, and many open pores can be obviously seen in Fig. 2(b). However, the WC grains of samples B–E were highly faced. Moreover, most of the pores were filled, and the rest of the pores were consolidated to form closed pores, as shown by the arrow in Fig. 2(f). Because of the existence of the closed pores, it was difficult to obtain an accurate density. Although the samples were treated by HIP at high pressure for a long holding time, the relative density was only 99.4%.

The average WC grain sizes of samples A, B, C, D, and E were approximately 0.57, 0.65, 0.73, 0.75, and 0.81 μm, as determined from the SEM micrographs by the linear intercept method. 19) Generally, grains grow easily at high temperatures, especially for ultrafine WC powder with high surface energy. However, the grain growth can be inhibited effectively when the powders contain a certain amount of grain growth inhibitor. Despite the high temperature of 2000°C, a fine microstructure was obtained, which may be attributed to the presence of VC and Cr$_3$C$_2$ in the initial powders. The fracture mode of all the samples was mainly intergranular, with a small amount of transgranular fracture, as shown by the arrow in Fig. 2(d).

Fig. 2. FE-SEM micrographs of the initial powders and sintered samples: (a) initial powders; (b) sample A; (c) sample B; (d) sample C; (e) sample D; and (f) sample E.
with its point group, which is the determining factor in the shape of the crystal. The space group of WC is P6m2, and the ratio between the \( a \)-axis and \( c \)-axis in the unit cell is approximately 0.976. \(^{21}\) Therefore, the point group of WC is \( \text{P}6m2 \). According to the relationship among the point group, early face and monomorphour, when the early face is \((10010)\), the monomorphour is triangular prismatic, and the predicted shape of the WC grains is plate-like because the \( a \)-axis is longer than the \( c \)-axis; when the early face is \((0001)\), the morphology is parallel double face, and the predicted shape of the WC grains is triangular. The crystallographic facets reflect the anisotropy of the crystal, which was caused by the difference in surface energy. Thus, the plate-like shape was attributed to the difference in the surface energy of the \((0110)\) and \((1000)\) planes. \(^{5,8,22}\)

The TEM micrograph and the corresponding electron diffraction pattern of a single WC grain of sample E are shown in Figs. 4(a) and 4(b). The shape of the WC grain [shown in Fig. 4(a)] was plate-like, and the faceted grain boundary was also observed, as indicated by the arrow. The possible outside surface of the WC grain was \( \{1010\} \) according to the point group. Therefore, it can be deduced that the faceted grain boundary was along the \( \{1120\}\text{WC} \) direction. The TEM electron diffraction pattern [show in Fig. 4(b)] confirms that the grain was pure WC and the zone axis direction was \([1210]\).

**Figure 5** shows the images of the crystal defects in sample E. A number of defects were observed, including dislocation arrays, dislocation networks, twins, and stacking faults. Figure 5(a) shows nearly parallel dislocation arrays and nearly vertical dislocation networks in the WC grains and grain boundaries, while extended faults can also be seen in the WC grains, as indicated by the arrow in Fig. 5(a). The dislocation cells were observed near the grain boundary, as seen in Fig. 5(b). The twin can also be observed in the WC grain in Fig. 5(c). Dislocation arrays, dislocation networks, and dislocations cells may be produced by plastic deformation of WC grains at high temperature under high...
pressure. When movement of the dislocations is hindered by grain boundaries, dislocations pile up near the grain boundaries to form dislocation arrays. If two or more dislocation arrays encounter each other in the grains or at the grain boundaries, dislocation networks and cells are easily formed. Extended faults may be produced by a perfect dislocation that decomposes into two imperfect dislocations and a fault between the two imperfect dislocations to reduce the free energy. The width of the extended fault was approximately 40 nm, or 130 interatomic distances; therefore, it can be inferred that the stacking fault energy in the WC grains was very low. The locations of the VC and Cr3C2 were determined by TEM and EDX, as seen in Figs. 6 and 7. Representative images and the EDX spectra of sample E at the grain triple junction are shown in Fig. 6. As seen in the micrograph shown in Fig. 6(a), the grain boundaries were smooth and curved. Both V and Cr were detected in the small grain (indicated by the arrow) near and at the grain triple junction, as shown in Figs. 6(c)–6(e). However, no V or Cr was detected in the bigger WC grain, as seen in Fig. 6(f). Figure 7 shows representative micrographs and the EDX spectra of the sample E at the boundary steps. Figure 7(a) shows the image of the boundary steps, from which it can be obviously seen that the boundary was faceted. Figure 7(c) shows that no V or Cr was detected in the WC grain. Figure 7(d) shows that both V and Cr were segregated at the faceted boundary. However, no V or Cr was detected at the curved boundary, as shown in Figs. 7(e) and 7(f).

The Cr3C2 was expected to be liquid, whereas the VC was solid at the sintering temperature of 2000°C because the melting points
of Cr₃C₂ and VC are approximately 1800 and 2650°C, respectively. The small WC grains may be preferentially dissolved in the Cr₃C₂, as the solubility of WC increases with decreasing particle radius, and the VC near the liquid may also dissolve in the Cr₃C₂. Therefore, the bigger WC grain was free of V and Cr, while the smaller grain contained both V and Cr, as seen in Figs. 6(c)–6(f). Moreover, it also can be inferred that the growth of the WC grain occurred partly through the dissolution/reprecipitation process of the Cr₃C₂, which was liquid at high temperature and can act as a binder. However, the density of sample A was low, indicating that the dissolution/reprecipitation process was slow. Both V and Cr were observed near or at the grain boundary [shown in Figs. 6(e) and 7(d)], from which it can be concluded that the migration of the grain boundaries was hindered by the segregation of V and Cr. Therefore, a fine microstructure was obtained despite the high temperature and long holding time.

The smoothly curved grain boundaries indicate that they are atomically rough, and the faceted grain boundaries are straight on the atomic scale. Grains experienced normal growth when the grain boundaries were curved. However, the existence of the faceted boundaries would cause the abnormal grain growth (AGG). AGG has been observed in WC-Co, Ni-based superalloys, and alumina owing to the existence of faceted boundaries. Although the faceted boundaries were found in the binderless WC, no AGG was observed. Previous research

![Fig. 7. Micrographs and EDX spectra of sample E at the boundary steps: (a) image of the boundary steps; (b) location of the point and areas; (c) point 1; (d) area 1; (e) area 2; and (f) area 3.](image-url)
showed that when the content of Cr$_3$C$_2$ in samples sintered by gas pressurised sintering (GPS) was equal to or greater than 0.5 wt%, AGG was completely inhibited. Therefore, the absence of AGG may possibly be attributed to the appropriate amount of doped Cr$_3$C$_2$ (0.54 wt%) in the initial powders and the segregation of the inhibitors at the faceted boundary, as shown in Fig. 7(d).

4. Conclusions

In this study, sub-micron (0.53 μm) powders of WC (doped with 0.33 wt% VC and 0.54 wt% Cr$_3$C$_2$) was sintered by HP and treated by HIP and the highly dense sub-micron WC materials were successfully produced. The following conclusion can be drawn:

1) The dense binderless sub-micron WC materials with a relative density greater than 96% were produced by HP at 1900–2000°C for 30 min under a pressure of 28 MPa using the sub-micron powders.

2) The extremely dense WC materials with a relative density up to 99.4% were obtained after treatment by HIP at 1750°C for 30 min under a pressure of 150 MPa.

3) For the HP sintered dense materials, the hardness and fracture toughness were 22.95–24.15 GPa and 4.40–4.89 MPa·m$^{1/2}$ respectively. After treatment by HIP, the hardness was over 26 GPa, and the fracture toughness was 4.54–4.84 MPa·m$^{1/2}$.

4) The grain growth inhibitors could effectively inhibit grain growth and abnormal grain growth due to the segregation of the inhibitors at the grain boundaries.

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