Effect of the combined addition of TaC and NbC on the dispersity of cubic phase in ultra-fine WC–10Co–0.5Cr cemented carbides

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Abstract

TaC and NbC have different effects on the dispersity of precipitated cubic phase, which acts as an important role in regulating the mechanical properties of ultra-fine cemented carbides. In this work, the influence of the combined addition of TaC and NbC on the microstructure evolution and mechanical properties in ultra-fine WC–10Co–0.5Cr cemented carbides was systematically investigated through the thermodynamic calculations and experiments. With the guide of thermodynamic calculations, the ultra-fine WC–10Co–0.5Cr cemented carbides with the combined addition of TaC and NbC were prepared. By replacing TaC with NbC, the dispersity of cubic carbidies can be improved significantly from large-size honeycombed to small-size isolated cubic particles, which is explained by thermodynamic calculations. The brittle cubic phase results in the degradation of crack propagation resistance, and thus deteriorates the mechanical properties. Therefore, both the hardness and fracture toughness increase with the improvement of dispersity of cubic phase in cemented carbides.

1. Introduction

WC–Co based cemented carbides have been used widely for machining, mining, cutting, drilling and wear resistant parts due to the excellent combination of hardness and toughness [1–3]. Compared with the traditional cemented carbides, the hardness and strength can be improved by reducing the WC grain size to submicrometer or nanometer scale [6–10]. During the sintering process, the most effective way to control the grain growth is through adding small amount of grain growth inhibitors, such as VC, Cr3C2, TaC or NbC [11–18]. Among these, VC and Cr3C2 are the most effective inhibitors. TaC and NbC, as the refractory carbides, can inhibit heterogeneous grain growth and improve the high-temperature mechanical and physical properties [19, 20]. However, the limited solubility of TaC or NbC in the binder phase leads to the precipitation of the coarse cubic (W, Ta)C [15, 21, 22] or (W, Nb)C [20, 23–25] solid solution. The poor dispersity of the large-sized brittle cubic phases can deteriorate the mechanical properties of the ultra-fine cemented carbides [20, 21, 25].

Although TaC and NbC have the similar physical and chemical properties, the dispersity of precipitated (W, Ta)C and (W, Nb)C cubic phases is inconsistent during sintering. As our previous studies [21, 22], the alloys with excessive TaC addition tends to form the honeycombed (Ta, W)C cubic phase. The size of the honeycombed cubic carbides within a range of several tens microns is depended on the composition of the alloys. Interestingly, the alloys with excessive NbC addition prefer to form the isolated (Nb, W)C grains with the size of several microns [20, 23–25]. However, the mechanism of this phenomenon is not clarified from the aspect of experiments or theoretical calculations. Meanwhile, no systematic research has been carried out to investigate if the replacement of TaC can improve the dispersity of cubic particles and related mechanical properties in the ultra-fine cemented carbides by NbC addition.
Therefore, the ultra-fine WC–10Co–0.5Cr–0.5Ta cemented carbides with the combined addition of TaC and NbC were prepared in the current work. Small amount of Cr3C2 addition can obtain better inhibition effect and more homogenous WC particles than that doped alone [14, 15, 26]. By the integration of calculations and experiments, the influence of TaC and NbC additives on the dispersity of cubic phase in the WC–10Co–0.5Cr alloys is investigated.

2. Experimental procedure

Carbon content is of critical important to control the reasonable phases in cemented carbides. Thermodynamic calculations were carried out before the experiment to select the alloy composition. The phase diagrams of the different combined addition of TaC and NbC in the WC–10Co–0.5Cr (in wt.%) were calculated according to the thermodynamic database CSUTDCC1 [27]. The phase equilibria of WC–10Co–0.5Cr–0.2Ta–0.3Nb alloy was selected as an example in figure 1. Based on the calculations, the 5.52 wt. % C content was confirmed to ensure the reasonable phase composition (no M6C, M7C3 and graphite phases) with the different TaC and NbC addition. The composition of the WC–10Co–0.5Cr–xTa–(0.5–x)Nb was designed according to the thermodynamic calculations, as listed in table 1. By comparing these five alloys, the impact of TaC and NbC additions on the dispersity of cubic phase in the WC–10Co–0.5Cr alloys is verified.

WC (0.88 μm), Co (0.83 μm), Cr3C2 (1.25 μm), TaC (1.25 μm) and NbC (2.33 μm) powders were used as the raw materials. The powders were ball-milled for 30 h using alcohol as the milling medium with the addition of 2 wt.% paraffin. The ball to powder weight ratio of 10:1 and a mill rotation rate of 290 r min−1 were employed. The mixed powders were dried, pressed and sintered at 1410 °C for 1 h. After sintering, the alloys were sectioned, ground and polished. Scanning electron microscopy (SEM, Nova NanoSEM 230, USA) was used to observe the

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![Figure 1. Calculated phase equilibria of the WC–10Co–0.5Cr–0.2Ta–0.3Nb cemented carbides.](image)

Table 1. The chemical compositions of the WC–10Co–0.5Cr–xTa–(0.5–x)Nb cemented carbides.

| Sample | Co | Cr | Ta | Nb | C   | W   |
|--------|----|----|----|----|-----|-----|
| 1#     | 10 | 0.5| 0.4| 0.1| 5.52| Bal.|
| 2#     | 10 | 0.5| 0.3| 0.2| 5.52| Bal.|
| 3#     | 10 | 0.5| 0.2| 0.3| 5.52| Bal.|
| 4#     | 10 | 0.5| 0.1| 0.4| 5.52| Bal.|
| 5#     | 10 | 0.5| —  | 0.5| 5.52| Bal.|

Therefore, the ultra-fine WC–10Co–0.5Cr cemented carbides with the combined addition of TaC and NbC were prepared in the current work. Small amount of Cr3C2 addition can obtain better inhibition effect and more homogenous WC particles than that doped alone [14, 15, 26]. By the integration of calculations and experiments, the influence of TaC and NbC additives on the dispersity of cubic phase and related mechanical properties has been investigated.
microstructure. Electron probe microanalysis (EPMA, JXA-8230, JEOL, Japan) was used to analyze the distributions of the elements. The orientation of cubic phase was analyzed by electron backscattered diffraction (EBSD, Helios Nanolab 600i, FEI, Hillsboro) fitted with the HKL system and the HKL Channel 5 software. Hardness was determined by Vickers hardness tester (HVS-50, China) using a load of 30 kg. The fracture toughness (KIC) was calculated by the following equation [7]:

\[
K_{IC} = 0.15 \sqrt{\frac{HV_{30}}{\sum_{i=1}^{4} l_i}}
\]

where \(HV_{30}\) is the Vickers indentation load of 30 Kg, \(l_i\) is the length of the crack tip from the hardness indent in mm. At least five individual samples were prepared for the measurements of each property.

Figure 2. SEM images of WC–10Co–0.5Cr–(a) 0.4Ta–0.1Nb, (b) 0.3Ta–0.2Nb, (c) 0.2Ta–0.3Nb, (d) 0.1Ta–0.4Nb, (e) 0.5Nb cemented carbides.
3. Results and discussion

Figure 2 presents the micrographs of the WC–10Co–0.5Cr alloys with different TaC and NbC additions after sintering at 1410 °C for 1 h. As shown, the finer WC particles distribute uniformly and without abnormal grain growth. Among the samples, there is no obvious change of WC grain size. However, the obvious difference in the microstructure is the distribution of cubic phase. In order to clearly observe the cubic phase, the distribution of the elements (Ta, Nb and Cr) is detected in the investigated alloys, as illustrated in figures 3–5. It is found that the cubic solid-solution is enriched in Ta and Nb, but depleted in Cr. As presented in figure 6, the composition of cubic phase mainly consists of Ta, Nb, W and C based on the thermodynamic calculation, which agrees with the experiment observation. During the liquid sintering, the elements dissolve in the liquid binder and react to form the complex (Ta, Nb, W)C cubic solid-solution. Figure 7 shows the EBSD maps of the inverse pole figure (IPF) coloring orientation of the cubic phase superimposed on WC phase shown in a band contrast map.

As shown in figures 2(a), (b) and 3, the alloys with 0.1 and 0.2 wt.% Nb additions have the large honeycombed cubic particles. The same IPF color proves that the honeycombed cubic particles have the same orientation, as presented in figure 7(a). The size of the individual cubic phase segregation is approximately 33 μm of sample 1 (0.1 wt.% Nb), but it decreases to about 16 μm of sample 2 with 0.2 wt.% Nb content. The honeycombed cubic phase disappears and the small isolated cubic particles (about 3 μm) form in samples with
Figure 6. Calculated composition of cubic phase of the WC–10Co–0.5Cr–xTa–(0.5–x)Nb cemented carbides with the change of Nb content at 1410°C.

Figure 7. EBSD maps of (a) WC–10Co–0.5Cr–0.3Ta–0.2Nb and (b) WC–10Co–0.5Cr–0.2Ta–0.3Nb with the IPF coloring orientation of the cubic phase superimposed on WC phase shown in a band contrast map. The same IPF color scale is used to show the orientation of the cubic phase.
0.3 and 0.4 wt. % Nb additions, as shown in figures 2(c), (d) and 4. Figure 7(b) indicates that the isolated cubic particles with different orientations are the different small particles in the microstructure. When the Nb content reach 0.5 wt. % (figures 2(e) and 5), the very small cubic phase particles disperse homogeneously in the microstructure. It should be noted that the different color scale bar is used to facilitate the observation of the element distributions. Therefore, the dispersity of cubic phase has an obvious improvement with the increasing of the Nb content.

To further understand the microstructure evolution, the mole percent of undissolved cubic phase at 1410 and 1100 °C is thermodynamically calculated with the different TaC and NbC additions, as shown in figure 8. Replacing the TaC with NbC can improve the amount of undissolved cubic particles, which act as the precipitation sites of the cubic phase during the sintering process. Moreover, the proportion of dissolved cubic phase drops from 56.0 to 40.8% with the increasing of NbC content. Partial cubic phase dissolve into the liquid binder during liquid sintering, especially the small particle size. The dissolved elements (Ta, Nb and W) in the oversaturated liquid Co precipitate onto the undissolved cubic phase to form the complex (Ta, Nb, W)C cubic solid-solution. If more undissolved cubic phase as the precipitation sites at the sintering temperature, the dispersity of cubic particles can be improved and the segregation size of the cubic phase can be reduced.

Meanwhile, the wettability of cubic particles and liquid binder is of vital importance to effect the dispersity of cubic phase and its morphology. For the poor wettability, the growth of cubic phase can shove the liquid binder
and combine with the surrounding WC phase, and form the large honeycombed cubic particle [22]. Therefore, the extent of the dispersity of cubic phase depends on the amount of the undissolved cubic carbides and the wettability of cubic carbides and liquid binder. As indicated in figure 8, the amount of the undissolved cubic carbides increases with the increased Nb. Meanwhile, the wettability of NbC with liquid Co is better than that of TaC [28]. As a result, the dispersity of cubic phase in the microstructure can be improved by replacing the Ta with Nb.

Figure 9 shows the mechanical properties of samples with different Ta and Nb addition. It is found that both the hardness and fracture toughness of alloys have the ascending tendency as the increased Nb content. The distribution of cubic carbides is the main factor to impact the mechanical properties. Compared with WC, TaC and NbC show a higher hardness at the room temperature [29]. The small size of uniformly distributed cubic particles can enhance the hardness compared with partial large honeycombed cubic phase. The alloy with the 0.5% Nb addition obtains the best dispersity of cubic particles (figure 2), which leads to the maximum value of

Figure 10. SEM images of the crack propagation of the WC–10Co–0.5Cr–(a) 0.3Ta–0.2Nb, (b) 0.2Ta–0.3Nb and (c) 0.5Nb cemented carbides.
hardness. The better dispersity of cubic phase can provide more grain boundaries among the WC, Co binder and cubic phases. This increases the fractions of the crack path and amount of fracture energy [30], and thus improve the fracture toughness of alloys. Besides, cubic carbides (TaC and NbC) have a much lower Young’s modulus than the WC phase (>700 Gpa) [31, 32], which results in the degradation of crack propagation resistance, especially for the non-uniformly distributed cubic particles. According to the microstructure in figure 2, higher Nb content provides the better dispersity of cubic phase, which is the primary motivator to improve the fracture toughness. Therefore, the addition of 0.5% Nb into the WC–10%Co–0.5%Cr alloy can obtain the best fracture toughness.

Figure 10 presents the SEM images of the crack propagation with the different Ta and Nb content. As shown in figure 10, both intergranular and transgranular cracks can be observed in the alloys. The crack propagation mode of the WC/WC interface is dominated by intergranular fracture. It is found that high ratio of transgranular cracks can pass through the large brittle honeycombed cubic phase easily and degrade of fracture toughness, as shown in figure 10(a). With the increased NbC content, the intergranular fracture can be observed along the WC–Cubic interface, and the transgranular fracture is also found in small isolated cubic particles, as shown in figure 10(b). The reduced size of brittle cubic phase may inhibit the crack propagation to a certain extent and improve the fracture toughness. More intergranular cracks appear with refined WC and uniform cubic phase distribution in figure 10(c). Therefore, these positive effect makes the simultaneous improvement of the hardness and fracture toughness.

4. Conclusions

By integrating of thermodynamic calculation and experimental investigation, the effect of the combined addition of TaC and NbC on the microstructure evolution and mechanical properties in ultra-fine WC–10Co–0.5Cr cemented carbides has been systematically studied. The microstructure evolution indicates that the dispersity of cubic phase has a visible difference with the different TaC and NbC additions. By replacing TaC with NbC, the large-size honeycombed cubic particles have gradually decreased and transformed into the small-size isolated ones. The mechanism for the dispersity of cubic carbides has been explained with the assistance of the thermodynamic calculations. The amount of the undissolved cubic phase and the wettability of cubic carbides and liquid binder are two key factors to impact the cubic phase distribution. The micro cracks can propagate through the coarse brittle cubic phase easily and deteriorate the mechanical properties. With the increased NbC content, the improved dispersity of cubic phase can restrain the cracks propagation and increase the hardness and fracture toughness simultaneously.

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