Effect of secondary carbides on the core-rim structure evolution of TiC-based cerments

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Abstract

Herein, the effect of adding VC with different contents and Mo2C, WC and TaC on the core-rim structure evolution of TiC-based cerments was investigated using x-ray diffraction, scanning electron microscopy and energy-dispersive spectroscopy. Results show that the added secondary carbides exhibiting the same crystal structure as TiC are prone to solid dissolution in TiC grains and change the core-rim structures of TiC-based cerments. With the addition of only VC, (Ti,V)C is the main component in the black core-grey rim structure and increasing the VC content is beneficial for promoting the dissolution process of cores. With the addition of multiple carbides, the core-rim structure in cermet Ta-7 is effectively improved, showing a high percentage of white core-grey rim structures, and the mechanical properties are improved.

1. Introduction

Because TiC-based cerments offer many advantages such as good high-temperature hardness and excellent thermal deformation resistance, they can be used as low-cost substitutes for WC–Co cemented cerbides to achieve good surface smoothness of a workpiece in a high-speed cutting environment [1–3]. However, owing to the poor wettability of TiC by the metal binders in contrast to WC grains, abnormal TiC grain growth occurs in the liquid-state sintering stage and the strength of TiC-based cerments is hardly to meet the cutting requirements [4, 5].

Secondary transition metal carbides, such as WC, Mo2C, TaC, NbC, VC and Cr3C2, are added to the TiC-based cerments to inhibit TiC grain growth and improve the mechanical properties, and core-rim surrounding structures are formed because of the dissolution–precipitation process [6–11]. The crystal structures of the cores and rims are identical; however, their lattice parameters and components are different. The lattice misfit within the core-rim interfaces induces internal stress, which affects the mechanical properties [12, 13]. Because the difference in the lattice parameters between TiC and VC are smallest among the secondary transition metal carbides, VC is the most effective additive for reducing the lattice misfit. However, VC in small amounts is often viewed as the grain growth inhibitor [14, 15]. For the exerting the solution strength effect, Arenas et al investigated the impact of high VC contents on the microstructure and properties of TiC-based cerments [16]. They proposed that the formation of (Ti,V)C is beneficial for improving wear resistance. However, higher amounts of VC resulted in the thickening of the surrounding rims and a sharp decrease in the mechanical properties. Xiong et al studied effect of VC on the microstructure and properties of Ti(C,N)-based cerments with a VC content of less than 6.4 wt%. They found that the increased number of submicron white core-grey rim grains and newly formed ultrafine rimless grains improved the mechanical properties of the cerments [17].

Therefore, controlling of core-rim structure is crucial for increasing the mechanical properties of cerments. Rim coarsening via the Ostwald ripening mechanism adversely affects the mechanical properties and should be avoided [18]. Furthermore, the addition of transition metal carbide compounds is an effective approach for controlling the coarsening of cores by hindering the direct aggregation of TiC particles [19]. However, few
studies have examined the effect of only VC addition and the addition of compounds on the grain control of core-rim structures in TiC-based cermets. In this study, the effect of adding VC at less than 18 wt% and transition carbides, such as Mo₂C, WC and TaC, on the core-rim structure evolution of TiC-based cermets was investigated. First, to determine the optimum VC content, only VC was added to TiC-based cermets. Next, Mo₂C, WC and TaC were added and changes in the microstructure evolution and mechanical properties of TiC-based cermets were evaluated. For varying amounts of added Mo₂C, WC and TaC contents, TiC and VC additions were fixed at an optimised proportion.

2. Materials and methods

The raw materials used in this study were TiC, VC, Mo₂C, WC, TaC, Co and Ni powders, which were commercially available with a purity of more than 99% and an average particle size of 2–3 μm. Compositions of all specimens are listed in table 1. The powders were subjected to the wet-mill process using a planetary mill with ethanol at 200 r min⁻¹ for 72 h. WC–Co cemented carbide balls (Ø10 mm and Ø6 mm) were used with a ball-to-powder weight ratio of 10:1. The powders were dried and then mixed with 10% SD-2X rubber; thereafter, they were dissolved in 120°F solvent oil via stirring. Then, the mixtures were again dried in a vacuum atmosphere. All specimens were pressed into compacts with the dimensions of 25 mm × 8 mm × 8 mm at 175 MPa. The TiC-based cermets were vacuum sintered at 1400 °C and the holding time was 1 h.

For mechanical tests and microstructural observations, the sintered cermets were ground and polished. Using a three-point-bending method with a loading velocity and span of 0.5 mm min⁻¹ and 17-mm, respectively, the transverse rupture strength (TRS) was measured on a WDW-50A testing machine. The hardness was tested on a THV-50DX Vickers hardness tester with a load and holding time of 40000 N and 15 s, respectively. The fracture toughness (KIC) was calculated according to the indentation method proposed by Shetty et al [20]. The microstructure of TiC-based cermet was observed using scanning electron microscopy (SEM; TESCAN VEGA II LMU) in the back-scattered electron (BSE) mode and energy-dispersive spectroscopy (EDS; OXFORD INCA Energy 350). The average grain size was measured by image analysis (IA) method [21]. Moreover, phase identification was performed with a step length of 0.02° in a D/MAX-2500PC-type x-ray diffractometer equipped with a Cu radiation source. The operating voltage was 40 kV.

3. Results and discussion

3.1. Microstructure evolution

The BSE microstructures of TiC-based cermets are shown in figure 1. The black core-grey rim surrounding structure was embedded in the binder with distinct colour contrast. Interestingly, the large core-rim structure exhibited a regular shape with thick surrounding rims. When the VC content was increased from 5 wt% to 10 wt%, the microstructure was refined. As the VC content was further increased to 16.6 wt%, some regular-shaped rimless structures appeared in figure 1(d) (red circles). With the addition of the highest VC content, the contrast disparity between the composition of cores and rims decreased. To investigate the effect of VC content on the change in the composition of the core-rim structures, EDS was performed and the results are shown in table 2. The main component in the cores was (Ti,V)C and the percentage of V atomic ratio increased gradually as the VC content increased. This is different from the previously reported core components of TiC- or Ti(C,N)-based cermets [22, 23]. The black cores were considered to be the undissolved TiC or Ti(C,N) grains. The detected (Ti,V)C indicated that the added VC underwent solid dissolution in the TiC grains.

Furthermore, the rims exhibited a higher V content and the changing trend of the V atomic ratio was the same as that in the cores. TiC and VC share the same crystal structure. When a high amount of VC was added, more VC underwent solid dissolution in the black cores and the average atomic numbers between some cores

| Specimen | TiC | VC | Mo | WC | TaC | Co+Ni |
|----------|-----|----|----|----|-----|-------|
| V-1      | Balance | 5 | / | / | / | 20 |
| V-2      | Balance | 8.4 | / | / | / | 20 |
| V-3      | Balance | 10 | / | / | / | 20 |
| V-4      | Balance | 16.6 | / | / | / | 20 |
| Mo-5     | Balance | 10 | 6 | / | / | 20 |
| W-6      | Balance | 10 | 6 | 6 | / | 20 |
| Ta-7     | Balance | 10 | 6 | 6 | 6 | 20 |
and rims were similar; thus, the colour contrast in the BSE mode was not obvious and rimless structures formed. The detected elemental distribution in rimless grain and grey rim of cermet V-4 are similar. W detected in the core-rim structure was introduced by the milled WC-Co balls in the high-energy milling process, which aggravated the colour contrast in the core-rim structure.

The x-ray diffraction patterns of cermet V-3 as a function of the corresponding milled mixture are shown in figure 2. Only two types of phases with a cubic crystal structure are observed in the diffraction peaks, corresponding to $(\text{Ti},\text{V})\text{C}$ and the metal binder. The lattice parameters of the cores and rims showed slight variations, and the diffraction curves were intertwined. WC accounted for a small proportion of the milled powder. However, the diffraction peaks of WC and VC were not observed in the sintered cermet V-3, indicating that WC and added VC dissolved in the binder during the liquid-state sintering stage. Because the atomic radius of Ti $(\text{RTi} = 0.1467 \text{ nm})$ is larger than those of V $(\text{RV} = 0.1338 \text{ nm})$ and W $(\text{RW} = 0.1394 \text{ nm})$, the diffraction peaks of $(\text{Ti},\text{V})\text{C}$ slightly shifted to higher angles owing to the solid dissolved V and W atoms [17]. The binder diffraction peaks shifted to lower angles corresponding to Co-Ni-X, where X refers to the dissolved metals. Because the atomic radii of Ti and V were larger than those of Co and Ni, the distortion of the binder unit cell increased, shifting the diffraction peaks to the left.

The core-rim structure formation depends on the dissolution-precipitation process [24, 25]. The effect of VC content on the dissolution rate and precipitation dynamics of carbides can be estimated based on the change in the core grain size and rim thickness, which was shown in figure 3. When the VC content was increased from 5 wt% to 16.6 wt%, the average core grain size globally exhibited a decreasing trend, indicating that increasing

| Element (at.%) | Ti | V | W | Co | Ni | C |
|---------------|----|---|---|----|----|---|
| Black cores   |    |   |   |    |    |   |
| Cermet V-1    | 51.97 | 1.81 | 1.08 | /   | /   | 45.14 |
| Cermet V-2    | 49.57 | 3.54 | 0.89 | /   | /   | 46.01 |
| Cermet V-3    | 46.47 | 4.16 | 1.14 | 0.54 | 0.72 | 46.97 |
| Cermet V-4    | 35.87 | 8.24 | 1.47 | 2.44 | 9.22 | 42.77 |
| Grey rims     |    |   |   |    |    |   |
| Cermet V-1    | 49.63 | 2.57 | 1.16 | 0.58 | 1.85 | 44.21 |
| Cermet V-2    | 48.11 | 4.84 | 1.24 | /   | /   | 45.81 |
| Cermet V-3    | 45.35 | 5.13 | 1.55 | /   | 0.59 | 47.42 |
| Cermet V-4    | 34.32 | 5.58 | 1.36 | 2.35 | 8.4  | 44.99 |
| Rimless grain |    |   |   |    |    |   |
| Cermet V-4    | 35.85 | 5.05 | 1.38 | 2.73 | 9.85 | 45.15 |

Figure 1. SEM (BSE) micrographs of TiC-based cermets with different VC contents: (a) cermet V-1, (b) cermet V-2, (c) cermet V-3, (d) cermet V-4.

Table 2. EDS results of core-rim structures in TiC-based cermets (at.%).
the VC content promoted the dissolution of cores. Furthermore, additional liquid forms with increasing VC content because the solubility of VC in binder is higher than TiC [26]. The frequency distribution of the core grain size is shown in figure 4. The percentage of cores with grain size of less than 1 μm increased when more than 10 wt% VC was added. Based on the principle that smaller carbides undergo preferential dissolution, a higher dissolution rate was beneficial for accelerating the dissolution of small TiC particles [27].

With the VC content increasing to 10 wt%, the average rim thickness increased slightly first and then decreased. The dissolved carbides in binder preferentially precipitate around the larger cores. Thus, the large core-rim structure increased the average rim thickness. When 10 wt% VC was added, the distribution of cores was relatively concentrated within a small range of less than 1 μm and the microstructure was improved, showing the smallest average rim thickness. Cermet V-4 exhibited the maximum average rim thickness at the highest VC content. This maximum value was mainly attributed to the rimless grains, which were wholly counted owing to the same colure contrast and similar composition as the rims. The surrounding rim is brittle, and an excessively thick rim is harmful to improving mechanical properties. The aforementioned analysis of the cermets showed excessively thick rims that do not meet the performance requirements under high-speed cutting conditions, which must be further decreased for improved mechanical properties.

Transitional metal carbides are beneficial for improving the wettability of TiC by the metals and effectively inhibit core grain growth. Compared with cermet V-3, the microstructures of cermets Mo-5, W-6 and Ta-7 with added Mo_{2}C, WC and TaC, respectively, are shown in figure 5. With the addition of transition metal
carbides, the regular shape of surrounding rims gradually disappeared, and the rim thickness decreased. The morphology of the core-rim structure was significantly varied.

White cores with a small grain size were observed in the cermets in figure 5, and the number of grain sizes noticeably increased with the addition of multiple carbides (red arrows). Mo$_2$C, WC and TaC diffused into the centre of fine TiC grains during the solid-state sintering process. (Ti,M)C was formed with solid-dissolved heavy

![Figure 4. Grain size distribution of the black cores of TiC-based cermets: (a) Cermet V-1, (b) Cermet V-2, (c) Cermet V-3, (d) Cermet V-4.](image)

![Figure 5. SEM (BSE) micrographs of TiC-based cermets: (a) cermet V-3, (b) cermet Mo-5, (c) cermet W-6, (d) cermet Ta-7.](image)
metal elements, where M denotes Mo, W and Ta. In the BSE mode, a heavier atomic number was associated with a brighter corresponding area. Therefore, the colour contrast of fine TiC particles turned white \[25\]. The formation energy of (Ti, M)C solid solution increased, and the dissolution rate of small white grains reduced during liquid-state sintering stage. When the percentage of small white cores increased, the average rim thickness decreased. However, for large TiC grains, the added Mo\(_2\)C, WC and TaC diffused into the surface and formed thin inner rims. Further, thick grey rims were formed via a selective dissolution–reprecipitation process during the liquid-state sintering stage. Therefore, two types of white core-grey rim and black core-grey rim surrounding structures were observed.

The number of white cores noticeably increased with the addition of TaC (figure 5\((d)\)). This phenomenon indicates that the added transition metal carbides exhibiting the same crystal structure as TiC easily solid-dissolved into the TiC cores. Owing to the significant difference in the average atomic numbers of TaC and TiC, the colour contrast in microstructure of cermet Ta-7 was more distinct.

### 3.2. Mechanical properties

The mechanical properties of TiC-based cermets are shown in figure 6. Carbides were assumed to mainly contribute to the hardness, and the total content of VC and TiC in cermets V-1–V-4 was constant. Therefore, the hardness of cermets V-1–V-4 showed slight fluctuations with increasing VC content. TRS and \(K_{IC}\) increased to their peak values when the VC content was increased by 5–10 wt% and subsequently decreased for a further increase in the VC content. Increasing the VC content was beneficial for promoting the dissolution process and increase the wettability, thereby increasing TRS and \(K_{IC}\). When the VC content was increased to 16.6 wt%, the largest average rim thickness was achieved and the brittleness of cermet V-4 increased. When cracks propagated to the adjacent ceramic grains, they were prone to propagate along the thicker rim boundary, decreasing the TRS and \(K_{IC}\). When 10 wt% VC was added, the grain refinement of the core-rim structure was beneficial to for improving the mechanical properties, thus, optimal hardness, TRS and \(K_{IC}\) values were obtained for cermet V-3 with only VC addition.

In metal binders, Mo\(_2\)C and WC exhibited higher solubility than TiC and VC. When Mo\(_2\)C and WC were added, more carbides dissolved in the binder, the wettability of carbides by metals was improved and the core-rim structure was further enhanced, thereby increasing the TRS and \(K_{IC}\). Because the hardness of WC is higher than Mo\(_2\)C, the hardness of Cermet W-6 increased. When TaC was multiple added, the microstructure was
further enhanced and the number of white core-grey rims remarkably increased. The rims surrounding the white cores were thinner than those surrounding the black cores. The white core-grey rim surrounding structure is beneficial for improving the mechanical properties of cermets [28]. Therefore, cermet Ta-7 with the addition of multiple carbides exhibited best mechanical properties with a TRS, $K_{IC}$ and hardness of 1543 MPa, 8.1 MPa $m^{-1/2}$ and 1508 N mm$^{-2}$, respectively.

4. Conclusions

(1) The black core–grey rim structure in TiC-based cermets with addition of VC was mainly composed of (Ti, VC). The dissolution process was enhanced when the VC content was increased, and the core-rim structure was improved with the addition of 10 wt% VC. Some grains with rimless structures were observed when the added VC content was the highest, and the composition contrast was similar to that of the rims.

(2) With the addition of Mo$_2$C, WC and TaC compounds, the microstructure of TiC-based cermets revealed two types of white core-grey rim and black core-grey rim structures. With the addition of multiple carbides, the percentage of white core-grey rim structures increased and the number of white cores was highest when TaC was added.

(3) Thick rims were not beneficial to the TRS of TiC-based cermets. In cermet Ta-7, the rim thickness obviously decreased and the core-rim structure showed improvements, exhibiting the best mechanical properties with a TRS, $K_{IC}$ and hardness of 1543 MPa, 8.1 MPa $m^{-1/2}$ and 1508 N mm$^{-2}$, respectively.

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