Effect of Cooling Rate on the Formation and Morphology of (W,V)C_x in VC-doped WC–Co Cemented Carbide

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Abstract The grain growth retardation mechanism and the effect of cooling rate on VC-doped WC–Co cemented carbides were investigated in this work. WC–30Co and WC–30Co–VC were prepared by powder metallurgy, liquid-phase sintering at 1400 °C and followed by water quenching (>150 °C/s) or furnace cooling (~0.083 °C/s). Based on the results of electron probe microanalysis (EPMA), we found that WC concentration in the Co binder was independent of VC doping during liquid-phase sintering, hence barely contributing to the retardation of WC grain growth. In contrast, the (W,V)C_x phase formed at the WC/Co interfaces played a major role in retarding WC grain growth during liquid-phase sintering. The effect of cooling rate on the morphology of (W,V)C_x was revealed by high-resolution transmission electron microscopy (HRTEM) and energy-dispersive spectroscopy (EDS). In the water-quenched WC–30Co–VC, (W,V)C_x precipitates were found as thin layers at the WC/Co interfaces. In contrast, both thin layers of similar thickness and nanoparticles of (W,V)C_x were observed in the furnace-cooled counterpart. These observations listed above suggested that thin (W,V)C_x layers were stable structures effectively suppressing the growth of WC grains and their thickness remained independent of the cooling rate. The (W,V)C_x nanoparticles, however, may be inhibited through rapid cooling, ensuring the VC-doped WC–Co cemented carbides desired toughness.

KEY WORDS: WC–Co; VC doping; (W,V)C_x; Water-quenched; Furnace-cooled

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1 Introduction

WC–Co cemented carbides have been widely used as cutting tools, mining tools, and many other wear parts, due to their unique combination of high hardness, excellent wear resistance and good fracture toughness [1–3]. After sintering, WC–Co cemented carbides exhibit the composite structure of hard WC grains embedded in the tough Co binder phase. Strong correlations between the mechanical properties of this material and the WC grain size have been widely reported [4–6]. Typically, the smaller the WC grain size, the higher the strength and hardness of the material. So far, the addition of grain growth inhibitors such as TiC, VC, TaC, Cr₂C₃ and NbC have been discovered to be an effective method in controlling the grain size of WC during high-temperature sintering [7]. Among these transition metal carbides, VC is the only inhibitor which remains

equally effective in the range of 1300–1575 °C and has been proved to be the most powerful in restricting discontinuous grain growth [8].

Meanwhile, the underlying retardation mechanism of VC doping on WC grain growth is still under investigation. It is generally acknowledged that the growth of WC grains proceeds through the dissolution/re-precipitation reactions at the WC–Co interfaces, and three hypotheses have been proposed for interpreting the role of VC during this process so far. According to Ref. [9], VC doping gives rise to reduced WC concentration in the liquid Co phase, which hinders the re-precipitation of WC at existing grain surfaces. Hayashi [10] and Kawakami *et al.* [11, 12] have proposed different views. The authors believed that WC grain growth is inhibited by the adsorption of dopant atoms at steps/kinks on the WC grain surface, which prevents the precipitation of W atoms at these locations. It was considered that (W,V)C_x precipitates formed at WC/Co interfaces can be regarded as diffusion barriers for W atoms, which then suppressed the growth of WC grains [13–19].

A key challenge on these hypotheses is that most compositional analysis and microstructural characterization were performed after the samples studied were sintered or cooled. Hence, it would not be possible to identify the corresponding stages (*i.e.* heat-up, solid-/liquid-phase sintering, cooling) of the material upon the solubility of W in the Co phase, the segregation of V at interfaces, the formation of (W,V)C_x and so on. Reliable confirmation of these would be crucial on the interpretation of the retardation mechanism. In this regard, several groups have adopted rapid cooling treatments, in order to freeze the microstructures representative of elevated temperatures. Take the precipitation of (W,V)C_x for example, a threshold nucleation temperature of >1100 °C has been reported [20], in agreement with the temperature range where VC is considered effective in grain growth retardation [5]. Many researchers [17, 18, 21] quenched WC–12Co–0.5VC in oil (>100 °C/s) and confirmed that (W,V)C_x precipitates were present during liquid-phase sintering, and accumulated on the {0001} and {10 $\bar{1}$ 0} planes of triangular-prism-shaped WC grains [22]. Lattice misfit (or carbon content [19]) was discovered to be a controlling factor on the morphology and density of (W,V)C_x on WC/Co interfaces. A misfit of ~8% has been found to be the most effective in blocking the mass transport near WC surfaces, hence, prohibiting the growth of WC grains [18, 23].

In this work, we aim to investigate the effect of water quenching with a cooling rate of >150 °C/s on VC-doped WC–Co-based cemented carbides. In parallel, furnace-cooled samples will also be examined, giving rise to a cooling rate of ~0.083 °C/s. Based on high-resolution transmission electron microscopy (HRTEM) observations

and energy-dispersive spectroscopy (EDS) analysis, the effect of cooling rate on the growth kinetics, morphology and spatial distribution of (W,V)C_x will be studied and the retardation mechanisms upon the WC grain growth will be evaluated. Furthermore, we chose WC–30wt%Co as the baseline composition. The resulting size of Co pools in the microstructure is about 2 µm, which is appropriate for collecting chemical composition data by electron probe microanalysis (EPMA), where the typical resolution limit would be ~1 µm. Following this approach, the local chemistries measured would be of statistical significance, serving as an important complement to data obtained from TEM–EDS [16], energy-filtered transmission electron microscopy (EFTEM) [14, 15] and atom probe tomography (APT) [24].

2 Experimental

In this investigation, WC–30wt%Co and WC–30wt%Co–1wt%VC were designed to demonstrate the effect of VC doping on the as-sintered microstructures in WC–Co. Fabrication of these two materials was performed following a standard powder-processing route. The starting powders of WC, Co and VC were sourced from Zhuzhou Cemented Carbide Group Co. Ltd., and they were wet-milled in ethanol for 48 h, dried and cold-pressed into blocks of 5 mm × 5 mm × 20 mm at 150 MPa. The finishing green compacts were then sintered at 1400 °C for 2 h in H₂ atmosphere. Finally, the specimens were divided into two batches: one for furnace cooling (~0.083 °C/s) and the other for immediate water quenching (>150 °C/s) from 1400 °C. Microstructures and local chemistries were characterized by scanning electron microscopy (SEM, FEI SIRION 200), EPMA (JXA-8230), conventional TEM and HRTEM-EDS (Tecnai G² F20; 200 kV). Specimens for TEM observation were prepared from mechanical polishing (finishing foil thickness ~30 µm) and subsequent ion milling (5 keV Ar⁺ ions, 30 µA).

3 Results

3.1 Chemical Analysis of the Co Binder Phase

Chemical analysis was carried out on the Co binder phases in the water-quenched and furnace-cooled WC–Co alloys by EPMA. Figure 1 illustrates the measurement set-up in a water-quenched WC–30Co sample, where the electron beam size is ~1 µm, about half of the size of the probed Co pools. All results of EPMA analysis are listed in Table 1, averaged among at least 10 probed areas.

In the water-quenched WC–30Co and WC–30Co–VC, the compositions in the Co phase during liquid-phase sintering (1400 °C, 2 h) were preserved to room temperature. The mass fractions of W in the Co phase were found nearly the same, suggesting that VC doping had no significant effect on the solubility of W in the Co phase during sintering. According to the nominal composition WC–30wt%Co–1wt%VC, the ratio of V (wt%)/Co (wt%) gives 0.027. However, the results of EPMA on the Co phase show only 0.013, implying that about 48% of V was dissolved in the Co phase. These agree well with the fact that V exhibits a large segregation tendency in the WC/Co interface [14, 24]. Finally, a small increase in C wt% found in WC–30Co–VC was probably associated with the addition of VC, which introduced more C into the alloy.

In the furnace-cooled WC–30Co and WC–30Co–VC, the mass fraction of W in the Co phase of WC–30Co–VC was 14.9% lower than that of WC–30Co, indicating that VC doping could facilitate the precipitation of W out from the Co phase during slow cooling. According to the nominal composition and the results of EPMA, the ratio of V (wt%)/Co (wt%) is 0.027 and 0.014, respectively, similar to that of the water-quenched case. However, the C in these alloys was found at least 10wt% lower than their water-quenched counterparts, which was probably as a result of the decreased solubility of C in the Co binder phase at low temperatures.

Fig. 1 Illustration of microstructural features and the position of EPMA probe on the Co phase in the water-quenched WC–30Co alloy (SEM, 15 kV)

3.2 Microstructural Characterization of WC–30Co and WC–30Co–VC

Microstructural characterization by TEM was carried out on water-quenched WC–30Co and WC–30Co–VC, as well as furnace-cooled WC–30Co–VC. The comparison between water-quenched WC–30Co and WC–30Co–VC demonstrates the role of VC doping in the morphology of WC/Co interface and the grain size of WC, while the comparison between water-quenched and furnace-cooled WC–30Co–VC reveals the effect of cooling rate on (W,V) C_x formation and morphology. Owing to the scope and main purpose of this work, we did not perform TEM analysis on the furnace-cooled WC–30Co.

3.2.1 Water-quenched WC–30Co and WC–30Co–VC

Figure 2 shows the microstructural features of water-quenched WC–30Co and WC–30Co–VC. The areas of light and dark contrasts represent the WC grains and the Co phase, respectively. In WC–30Co, most WC grains appear faceted and some of them have undergone abnormal grain growth. These large grains of WC were most likely formed from the merging of several small neighbouring grains. In WC–30Co–VC, the WC grains are much smaller in size and the distribution of WC and Co phases is more homogeneous. On average, the WC grains were measured as $\sim 0.84 \mu\text{m}$ for WC–30Co and $\sim 0.36 \mu\text{m}$ for WC–30Co–VC, indicating that a small amount of VC addition may effectively suppress the grain growth of WC. In addition, the doping of VC gives rise to fine step-like profiles of WC grains (shown in circled regions in Fig. 2b). No such interface morphology was observed in WC–30Co, where the profiles appeared plateau-like.

Detailed structures at the WC/Co interface are revealed in Figs. 3 and 4. In Fig. 3a, an abnormally grown WC grain near $z = 1\bar{2}10$ is shown in a water-quenched WC–30Co sample. A WC(0001)/Co interface is labelled with a white arrow and the atomic arrangements are shown in the HRTEM image of Fig. 3b. The WC/Co boundary was clean and sharp, and no precipitation phases were observed. In Fig. 4a, a WC grain in a water-quenched WC–30Co–VC sample is shown and the imaging direction was also taken from $1\bar{2}10$. The

Table 1 EPMA results of Co binder phase in four alloys sintered at 1400 °C

Alloy	W (wt%)	Co (wt%)	C (wt%)	V (wt%)
WC–30Co WQ	24.89 ± 0.35	74.26 ± 0.76	0.41 ± 0.07	
WC–30Co–VC WQ	24.13 ± 1.22	74.29 ± 1.26	0.58 ± 0.15	1.00 ± 0.11
WC–30Co FC	21.25 ± 0.74	78.07 ± 0.62	0.34 ± 0.09	
WC–30Co–VC FC	18.09 ± 1.26	79.53 ± 1.05	0.50 ± 0.16	1.13 ± 0.21

WQ water-quenched, FC furnace-cooled

Fig. 2 TEM micrographs of **a** WC–30Co, **b** WC–30Co–VC alloys, sintered at 1400 °C for 2 h and followed by water quenching. The WC/Co interfaces in Fig. 2b were faceted with fine multi-steps, shown in *white circled regions*

Fig. 3 WC/Co interface in water-quenched WC–30Co alloy: **a** TEM micrograph of a WC crystal observed along the $1\bar{2}10$ direction, **b** HRTEM image of the WC(0001)/Co interface, as labelled in *white arrow* in Fig. 3a

white arrows b and c indicate the regions of step-like profiles, and the corresponding WC–Co interfacial structures from $(0001)_{\text{WC}}$ and $(10\bar{1}0)_{\text{WC}}$ habit planes are shown in Fig. 4b, c, respectively. In Fig. 4b, thin layers of $(\text{W,V})\text{C}_x$ were detected at the WC(0001)/Co interface and the range of which was spanned over 3 atomic planes. According to the literature [13–15, 25], the precipitation phase $(\text{W,V})\text{C}_x$ is in fact the solid solution of W in VC and features a rock-salt structure. This phase tends to hold an energetically favoured $\{111\}_{(\text{W,V})\text{C}_x} // \{0001\}_{\text{WC}}$ orientation relationship with the neighbouring WC grain, which is in good agreement with Fig. 4b. In Fig. 4c, pile-ups of this precipitation phase was found, forming small islands of $(\text{W,V})\text{C}_x$. Note that at the

WC(0001)/Co interface, the spread of $(\text{W,V})\text{C}_x$ layers was homogeneous and their coverage upon the $(0001)_{\text{WC}}$ habit plane was both complete and continuous. In contrast, the $(\text{W,V})\text{C}_x$ phase was restricted to 1–2 atomic layers at the WC(10 $\bar{1}0$)/Co interface, featuring an orientation relationship of $\{1\bar{1}0\}_{(\text{W,V})\text{C}_x} // \{10\bar{1}0\}_{\text{WC}}$. The spatial distribution of $(\text{W,V})\text{C}_x$ was intermittent across the $(10\bar{1}0)_{\text{WC}}$ habit plane.

3.2.2 Furnace-Cooled WC–30Co–VC

Figures 5, 6, 7 indicate the microstructure characterizations in furnace-cooled WC–30Co–VC. In Fig. 5a, a WC grain is imaged along the $1\bar{2}10$ direction. Similar to the water-quenched

Fig. 4 WC/Co interface in water-quenched WC-30Co-VC alloy: **a** TEM micrograph of a WC grain surrounded by Co pools. The white arrows **b**, **c** indicate the magnified area shown in Fig. 4b and c, respectively; **b** HRTEM image of the WC(0001)/Co interface, **c** HRTEM image of the WC(10 $\bar{1}$ 0)/Co interface

Fig. 5 WC/Co interface in furnace-cooled WC-30Co-VC alloy: **a** TEM micrograph of a WC grain, **b** HRTEM image of the WC(0001)/Co interface as indicated in Fig. 5a with a white arrow. The black dots represent columns of W atoms in WC, while the white dots represent columns of W atoms in the (W,V) C_x phase

state, small step profiles consisting of (0001)_{WC} and (10 $\bar{1}$ 0)_{WC} habit planes were found. On the (0001)_{WC} habit plane, a ~ 1 nm layer of (W,V) C_x phase is identified, as shown in Fig. 5b. This

suggests that the layer-structured precipitate (W,V) C_x remained stable after nucleation in the liquid sintering phase and did not gain in thickness during the slow cooling process.

Fig. 6 Precipitation behaviour of (W,V) C_x in furnace-cooled WC–30Co–VC alloy: **a** TEM micrograph illustrating the hemispherical geometry of (W,V) C_x at the intersecting corners of (0001)WC and (10 $\bar{1}$ 0)WC habit planes in a WC grain, as shown in the *white circled region*, **b** HRTEM image of this region, featuring a preferred pile-up of (W,V) C_x on (0001)WC to (10 $\bar{1}$ 0)WC. The stacking of (W,V) C_x on (0001)WC was featured of small atomic-scale steps so as to relieve misfit strain, as shown in the *white boxed region*

The precipitation of (W,V) C_x at the intersecting corners of (0001) $_{WC}$ and (10 $\bar{1}$ 0) $_{WC}$ habit planes behaved otherwise. Island-like (hemispherical) (W,V) C_x precipitates were found in these corners, as demonstrated in Fig. 6a. According to Fig. 6b, it can be further concluded that this (W,V) C_x phase preferred to stack on (0001) $_{WC}$, resulting in preferred pile-up on (0001) $_{WC}$ and incomplete coverage on (10 $\bar{1}$ 0) $_{WC}$. In addition, the stacking of (W,V) C_x on (0001) $_{WC}$ was characteristic of small atomic-scale steps. Similar phenomenon was also reported in Ref. [15]. The authors attributed this to the accommodation of interfacial misfit, i.e. small atomic-scale steps (misfit dislocations) must be introduced to relieve the local strain at the interface.

Continued growth of the (W,V) C_x phase could lead to the formation of small islands of (W,V) C_x , which were eventually coalesced into nanoscale particles. Figure 7a demonstrates an example of this process with a 50 nm wedge-shaped (W,V) C_x particle, discovered at the triple point of two WC grains (WC1 and WC2) and the Co binding phase. Results of EDS in Fig. 7b confirm its composition consisting of $\sim 8\text{at}\%$ W, which falls within the solubility limit of W in VC ($T = 1500^\circ\text{C}$, max. W content = 23at%) [26]. Figure 7c, d illustrates the fine details of orientation relationship in WC1–(W,V) C_x –Co (labelled in black box) and WC1–(W,V) C_x –WC–2 (labelled in white box) regions, respectively. In Fig. 7c, an

orientation relationship of $\{111\}_{(W,V)C_x} // \{0001\}_{WC}$ was identified, similar to that of the water-quenched WC–30Co–VC. In Fig. 7d, the (W,V) C_x particle extends to the corner between WC grains 1 and 2. In addition to the WC(0001)/(W,V) C_x interface identified for WC1, a WC(10 $\bar{1}$ 0)/(W,V) C_x -type interface was identified for WC2, exhibiting an orientation relationship of $\{110\}_{(W,V)C_x} // \{10\bar{1}0\}_{WC}$. The contrast sharpness near the interface boundary seemed significantly reduced. According to the literature [15, 18], the lattice mismatch between (W,V) C_x and WC was estimated to be 3.9% for $\{111\}_{(W,V)C_x} // \{0001\}_{WC}$ and 14.9% for $\{110\}_{(W,V)C_x} // \{10\bar{1}0\}_{WC}$, respectively. The high misfit in the latter case was probably the origin of reduced contrast sharpness at the interface boundary.

In summary, thin layers of (W,V) C_x were observed at the WC/Co interface in both water-quenched and furnace-cooled WC–30Co–VC, spreading over a few atomic planes. Meanwhile, the precipitation behaviour of (W,V) C_x at the intersecting corner of (0001) $_{WC}$ and (10 $\bar{1}$ 0) $_{WC}$ habit planes was different. Island-like (hemispherical) (W,V) C_x precipitates were formed, and the thickness of the stacked atoms appeared much thinner in the water-quenched condition than in the furnace-cooled condition. Notably, the thickest area of which was only about 4 nm in the water-quenched state (Fig. 4c) and 8–10 nm in the furnace-cooled state (Fig. 6b). Moreover, (W,V) C_x precipitates

Fig. 7 Formation of nanoscale (W,V)C_x particles in furnace-cooled WC-30Co-VC: **a** TEM image of a 50 nm (W,V)C_x particle located at the triple point of WC grains 1, 2 and the Co binding phase, **b** EDS spectrum of this (W,V)C_x particle, from which the concentration of W was found ~8at%, **c**, **d** demonstrate the orientation relations for WC1-(W,V)C_x-Co (black box region in Fig. 7a) and WC1-(W,V)C_x-WC2 (white box region in Fig. 8a), respectively

could undergo substantial growth in the furnace-cooled condition. In particular, large wedge-shaped (W,V)C_x nanoparticles up to tens of nanometres were found at the triple points of WC grains and the Co phase (Fig. 7). On the contrary, similar observations were not confirmed in the water-quenched WC-30Co-VC.

4 Discussion

A number of previous works [9, 27, 28] believed that adding VC gives rise to the reduction of W solubility in Co during liquid-phase sintering, hence inhibiting the

dissolution/re-precipitation process of W on WC grain surfaces. However, the chemical analysis involved in these works were performed on slow or medium-rate cooled samples, and did not reveal the genuine effect of VC during liquid-phase sintering. In this work, we found that the effect of VC doping on the W solubility in the Co phase was subtle for water-quenched WC-30Co and WC-30Co-VC, based on the results of EPMA. Similar effects have also been reported for Cr addition in WC-Co, which is another promising grain growth inhibitor alongside VC [29]. This suggests that the explanation of WC grain growth retardation based on WC dissolution may be inappropriate.

Fig. 8 Schematic diagram of step profiles at the corner of two WC grains in WC–30Co–VC: **a** as-sintered; **b** as-cooled

Some studies [11, 12, 24] supported the retardation mechanism based on the adsorption/desorption process of V atoms on the surface kink/step sites of WC grains. A key basis of their argument is that they have attributed the formation of $(W,V)C_x$ to the cooling process, during which $(W,V)C_x$ would not have participated in grain growth retardation. However, Kawakami *et al.* [11] claimed that the $(W,V)C_x$ phase is formed continuously near the Co solid–liquid interface, whereas Weidow *et al.* [24] proposed that it is formed in the temperature range of 900–930 °C during solidification. Two important points should be noted here. On one hand, the cooling rates involved were either not specified or estimated at around 50 °C/s [11, 24], and so may not be sufficient in freezing the microstructures from elevated temperatures. As a result, discrepancies were introduced on the nucleation temperature range of the $(W,V)C_x$ phase. On the other hand, the amount of VC dopants is usually small, about 0.3–0.5 wt%, therefore their impact alone may not sufficiently reproduce the degree of overall suppression on WC grain growth ([16]; this work). In fact, according to recent *ab initio* study, the dopant adsorption and desorption mechanism probably operates during solid phase sintering of WC–Co cemented carbides [30]. As for liquid-phase sintering, the precipitation of $(W,V)C_x$ layers at WC/Co interfaces most probably dominates the grain growth retardation.

The characteristics of $(W,V)C_x$ layers formed in water-quenched WC–30Co–VC in this work were similar to that

of oil-quenched WC–12Co–0.5VC, reported by Sugiyama *et al.* [17, 18]. The same types of orientation relationship were identified between the rock-salt structured $(W,V)C_x$ precipitate and the {0001} or {10 $\bar{1}$ 0} habit planes of WC, for water-quenched, oil-quenched and furnace-cooled specimens.

The level of lattice misfit was the controlling factor for such relations as well as the observed morphologies of these precipitates, theoretically proven in Ref. [25]. The authors therein predicted that during rapid cooling, there are two layers in the basal {0001}_{WC} and 0–2 layers in the prismatic {10 $\bar{1}$ 0}_{WC} interface at high-temperature equilibrium. In fact, since $(W,V)C_x$ is nonstoichiometric, varied carbon contents may simply result in different lattice constants, hence different misfit values with the habit planes of WC. It is reported in Refs. [19, 21] that due to low lattice mismatch, thin layers of $(W,V)C_x$ easily form and may fully cover the {0001} basal planes of WC. However, owing to high lattice mismatch, the morphology of $(W,V)C_x$ on {10 $\bar{1}$ 0} prismatic planes becomes highly dependent of the carbon content. In low carbon grades, the morphology of $(W,V)C_x$ remains planar, while in high carbon grades, $(W,V)C_x$ loses wettability with the WC grain surfaces and favours the accumulation of islands-like precipitates and nanoparticles. In this work, more C has been essentially introduced in WC–30Co–VC compared to the literature [19, 21], resulting in thin layers of $(W,V)C_x$ on {0001}_{WC} and island-like precipitates of $(W,V)C_x$ on {10 $\bar{1}$ 0}_{WC} in the water-quenched sample. The rapid

cooling rate did not allow further growth of $(W,V)C_x$ phases on $\{10\bar{1}0\}_{WC}$. In the furnace-cooled sample, not only thin layers and small islands of $(W,V)C_x$ were found, but also large $(W,V)C_x$ nanoparticles were identified, giving rise to rough surface topology on $\{10\bar{1}0\}_{WC}$.

On the basis of previous discussion, we summarize the retardation mechanism of WC grain growth involved in this work during liquid-phase sintering in Fig. 8. Figure 8a shows the precipitation of $(W,V)C_x$ on basal $\{0001\}$ and prismatic $\{10\bar{1}0\}$ planes of WC. Depending on the level of lattice mismatch, thin layers of $(W,V)C_x$ of varied thickness will form ([17, 25]; this work). On the basal $\{0001\}$ plane of WC, $(W,V)C_x$ layers typically appear thicker and more uniformly laid out than on $\{10\bar{1}0\}$, thus resulting in stronger suppression of WC grain coarsening in $\langle 0001 \rangle$ direction than in $\langle 10\bar{1}0 \rangle$. When the amount of precipitates accumulate at the junctions of two WC habit planes, $(W,V)C_x$ of island-like (hemispherical) morphology appears. These phases may also inhibit WC grain growth, i.e. along $\langle 10\bar{1}0 \rangle$, providing that they can achieve sufficient density at the junction sites [18]. Figure 8b illustrates the case during (slow) cooling. The $(W,V)C_x$ phase at the corner of multi-steps on WC surface becomes larger and grows almost beyond the steps. Their thickness on the basal $\{0001\}$ planes does not change much during this process. Beyond a critical layer thickness (or lattice mismatch level), the morphology of $(W,V)C_x$ deviates from planar and increasing amounts of island-like (hemispherical) $(W,V)C_x$ precipitates accumulate at the corner of multi-step profiles [18]. These precipitates undergo remarkable growth and finally merge into a single large $(W,V)C_x$ particle located at the triple point between two WC grains and the Co phase.

Note that the grain growth retardation effect of $(W,V)C_x$ nanoparticles will be limited to those WC grains in direct contact with. Hence, they will not function as effective as the thin layers and small islands of $(W,V)C_x$. What is worse, these particles may serve as brittle second phases, susceptible to crack initiation and propagation [31]. As a result, suppressing the growth of these precipitates during cooling is crucial. In this work, the detrimental $(W,V)C_x$ nanoparticles have been successfully eliminated through water quenching, where the time scale of sufficient $(W,V)C_x$ accumulation at WC grain junctions is typically several orders of magnitude higher than the cooling process (<10 s).

5 Conclusions

In this study, we investigated the formation and morphology of $(W,V)C_x$ at the WC/Co interfaces in water-quenched and furnace-cooled VC-doped WC–30Co. According

to EPMA and HRTEM results, we have drawn the following conclusions.

1. VC doping had no significant impact on the solubility of W in the Co phase during liquid-phase sintering, but favoured the precipitation of W from Co during cooling process.
2. In WC–30Co–VC water-quenched from 1400 °C, thin layers of $(W,V)C_x$ were observed, suggesting their presence during liquid-phase sintering. In the furnace-cooled case, thin layers and small islands of $(W,V)C_x$ precipitates were found at the WC/Co interfaces, and nano-size $(W,V)C_x$ particles were observed at the WC grain junctions.
3. The inhibition of WC grain growth involved thin layers and small islands of $(W,V)C_x$, serving as effective diffusion barriers. Lattice misfit affected the morphology of $(W,V)C_x$ as well as its orientation relation with WC and Co.
4. Rapid cooling can be an effective means of suppressing the formation of large $(W,V)C_x$ brittle nanoparticles in the VC-doped WC–30Co cemented carbides.

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