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Fabrication and characterization of ultrafine WC–8Co–xCeB$_6$ cemented carbides

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Abstract

Nanocomposite WC–8Co (mass%) powders with different CeB$_6$ contents were prepared using the planetary ball milling method. Effects of CeB$_6$ on the microstructures and mechanical properties of WC–8Co cemented carbides were investigated by X-ray diffraction, scanning electron microscope and mechanical properties testing. The results show that the grain growth and regularization of WC particles occur simultaneous with the addition of CeB$_6$. CeB$_6$ addition improves the density and fracture toughness and decreases the volume fraction of the η (Co$_3$W$_3$C) phase in the materials.

Keywords: Ultrafine cemented carbides; CeB$_6$; Microstructure; Fracture toughness

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1. Introduction

Cemented carbides are widely used in machining, drilling, cutting, forming and mining tools, as well as high-performance construction and wear resistant parts due to their high hardness and strength [1]. The hardness, strength and toughness of cemented carbides can be substantially increased by decreasing the grain size to the range of submicron or nanometer scales [2,3]. Cemented carbides are processed from WC and Co powders by liquid phase sintering process, during which the WC grain growth may occur [4]. Such a microstructure evolution during sintering is detrimental to the mechanical properties and can be diminished by adding some transition metal carbides such as VC, Cr$_3$C$_2$, NbC, TaC or their mixtures [5–8]. Although commercial processes are now available to produce sintered WC–Co with ultrafine grained size, the optimal control on grain growth during sintering still remains a critical technique challenge.

A German study of rare earth elements doped hard metals was initiated in the early 1960s [9]. China started the research and application of rare earth elements in cemented carbides in the late 1960s. A study [10] showed that after the addition of rare-earth elements in YT14, YT15, and YG16 cemented carbides, the densities of these cemented carbides barely change, while the porosities are decreased. It was found that the introduction of rare earth elements can lead to the refinement and homogenization of the WC particles [11–16]. Chen et al. [15] reported that the addition of 0.5 mass% yttrium in WC–Ni cemented carbides result in the density increase from 13.95 to 14.33 g/cm^3, the flexural strength from 1735 to 2117 MPa with an increment of about 22% and the hardness from 84.5 to 85.5 HRA. It was also reported that adding the rare-earth additives can reduce the friction coefficients, increase α-Co contents, enhance bending strength/impact toughness by 10% and dramatically improve the service life [17].

In this study, nanocrystalline WC–8Co powders with CeB$_6$ were consolidated to full density through low pressure sintering at high temperatures. The effects of CeB$_6$ on the density, microstructures, and fracture toughness of the materials were compared to the samples without CeB$_6$ additions.

2. Experimental

Table 1 shows the *nominal composition* of the cemented carbides. The average sizes of the WC, Co and CeB$_6$ powders

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Table 1
The nominal composition of alloys (mass%).

Sample	WC	Co	CeB_6
Sample 1	92	8	0
Sample 2	91.5	8	0.5
Sample 3	91	8	1.0
Sample 4	89.5	8	1.5

are 0.4, 3 and 3 μm, respectively. Minor CeB_6 was added to WC–8Co powders before milling. Mechanical milling was carried out for 72 h in 4 planetary ball milling system in alcohol under argon cover, using WC–8 mass% Co with a diameter of 5 mm as the milling bodies and media. The ball to powder weight ratio was 6:1 and the milling speed was 450 rpm. The post-milling pulp was dried in a vacuum oven at 80 °C for 12 h and 0.5 mass% polyethylene glycol was added as the pressing aid. The mixed powders were granulated and pressed to compacts of 25 mm in diameter under a pressure of 250 MPa. Dewaxing of green compacts was conducted in a separated cycle in flowing hydrogen, followed by sintering in an industrial vacuum sintering furnace. *The sintering cycle* included the following steps: heat to 600 °C at a speed of 10 °C per min, then heat to 1200 °C with a speed of 20 °C per min, followed by heating to 1400 °C with a heat rate of 20 °C per min in the vacuum condition. The holding time at 1400 °C was 60 min and the pressure in the dwell time was 5 MPa in argon atmosphere to avoid the prominent evaporation of cobalt during the liquid phase sintering. After sintering, the cemented carbides were cooled down to room temperature in the vacuum sintering furnace.

The density of the sintered cemented carbides was measured by the Archimedes method, while a Micro-Plus laser diffraction particle size analyzer was employed to measure the powder particle size. The microhardness was measured using an HD9-45 optical surface Vickers hardness tester with a load of 100 g. The D/max2550pc X-ray diffractometer with Cu Ka radiation ($k = 0.154$ nm) was used to identify the phases in the materials and determine the crystal size of the composite powder through Williamson–Hall method [18]. The microstructural observation of the cemented carbides as well as the compositional analysis of some certain phases was conducted using a FEI Nano230 scanning electron microscope (SEM) equipped with an EDAX X-ray energy dispersive spectroscopy (EDS) system. The mean grain size of the sintering samples was determined using quantitative microscopy techniques.

The fracture toughness (K_{IC}) of the sintered cemented carbides was determined by measuring the crack length from the tip of the indentation generated by Vicker's indentation load of 30 kg, and the Palmqvist indentation toughness was calculated as follows [19]

$$K_{IC} = 0.15\sqrt{\frac{\mathrm{HV30}}{\sum_{i=1}^{4} l_i}} \tag{1}$$

where l_i is the length of the crack tip from the hardness indent in mm. For sake of accuracy in measures, the specimen was polished to near-mirror finish and checked for face parallelism before testing. Crack lengths measurement was carried out using an optical microscope.

3. Results

3.1. Microstructures of the starting powders and composite powders

The morphologies of the WC, Co, CeB_6 powders and the prepared WC–8Co composite powders are shown in Fig. 1. It

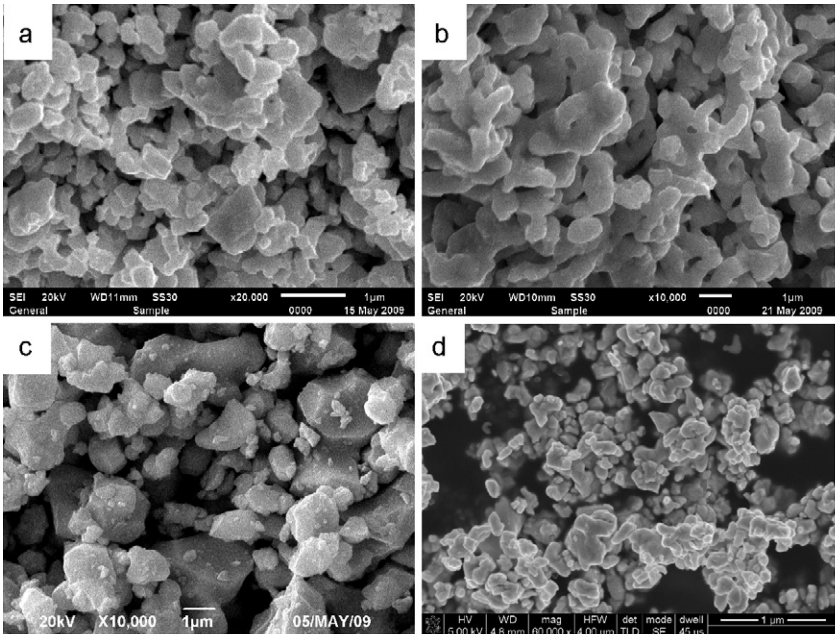

Fig. 1. SEM images of the starting powders WC (a), Co (b), CeB_6 (c) and the composite powder of the sample 3 (d).

can be seen that the original WC particle size is small. It should be noted that the distribution of WC particle size is narrow without distinctively large particles, which is especially beneficial to generate a uniform microstructure. SEM observation confirms that the prepared WC–8Co–xCeB$_6$ composite powders are small and uniform. The average particle size is about 150 nm. The WC particles show a spherical morphology. The X-ray diffraction tests show that the main phases of the composite powders are WC and Co. The mean grain size of WC crystal of the composite powders is determined about 41 nm by Williamson–Hall method. The typical SEM morphology of the nanocrystalline composite powders is shown in Fig. 1d.

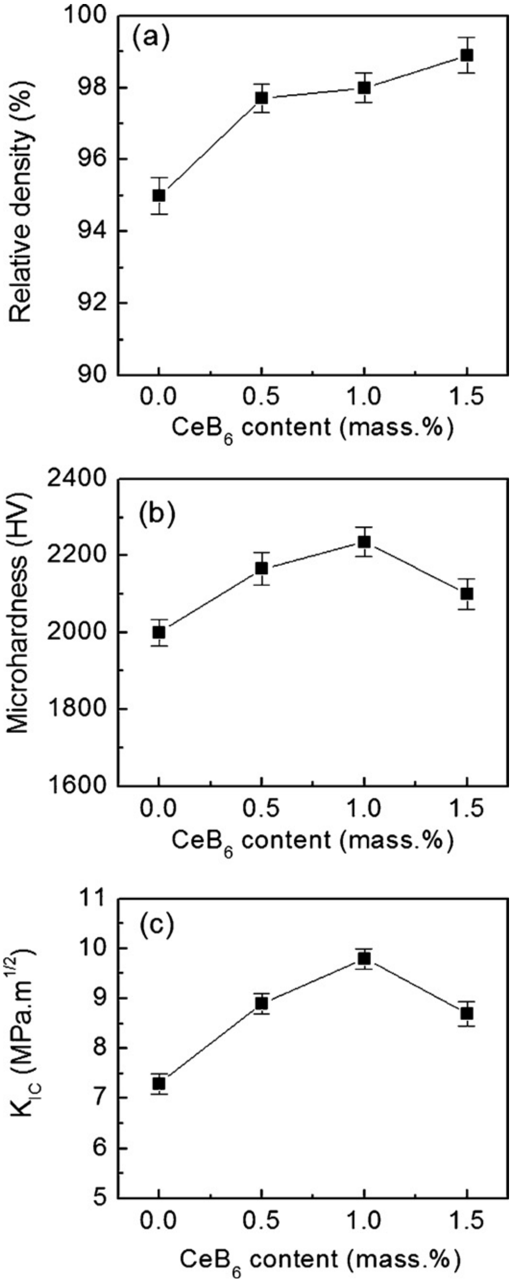

Fig. 2. Relative density and mechanical properties of cemented carbides after sintering at 1400 °C (a: relative density; b: microhardness; c: fracture toughness).

3.2. Density and mechanical properties of the sintered cemented carbides

Fig. 2 shows the relative densities, microhardness and fracture toughness of the cemented carbides with different CeB$_6$ contents after sintering. It shows that the addition of CeB$_6$ substantially increases the sintered relative density of the cemented carbides (Fig. 2a). The addition of 1 mass% CeB$_6$ results in an increase of the relative density of about 3%, while the addition of 1.5 mass% CeB$_6$ results in an increase of the relative density of about 4.1%.

It is noted in Fig. 2b that the micro-hardness of the cemented carbides with CeB$_6$ addition is higher than that of the cemented carbides without CeB$_6$ addition. However, adding excess CeB$_6$ lead to the decrease in the micro-hardness of cemented carbides. For 0.5 mass% CeB$_6$ doped cemented carbides, the average increase of micro-hardness is up to 166 HV, while for sample 3 doped with 1 mass% CeB$_6$ has the highest micro-hardness. However, the microhardness of the cemented carbides doped with 1.5 mass% CeB$_6$ decreases by an extent of 105–141 HV.

Fig. 2c presents the effect of CeB$_6$ addition on the fracture toughness of the based cemented carbides. It shows that there is a significant improvement in the fracture toughness for the cemented carbides with CeB$_6$ additions, compared to CeB$_6$-free samples. The increase of fracture toughness in sample 2 is about 21.9%, and the addition of 1 mass% CeB$_6$ (sample 3) can increase the fracture toughness of the based sample by 1.6–2.7 MPa m$^{1/2}$. However, it should be noted that the fracture toughness of the cemented carbides with 1.5 mass% CeB$_6$ addition decreases by 0.8–1.3 MPa m$^{1/2}$ compared to sample 3.

3.3. Microstructures of the sintered cemented carbides

Fig. 3 shows the XRD patterns of various samples of the cemented carbides. It is found that the CeB$_6$ addition decreases the formation of η (Co$_3$W$_3$C) phases and promotes the formation of CoWB, W$_2$Co$_{21}$B$_6$ and CeBO$_3$ phases. In addition, with the increase of the CeB$_6$ content, the intensity of the peak of η phase in sample 2 is lower than that in sample 1, which disappears in samples 3 and 4. However, the intensities of the peaks of CoWB, W$_2$Co$_{21}$B$_6$ and CeBO$_3$ phases in sample 4 are higher than those in samples 3 and 2. The disappearance of

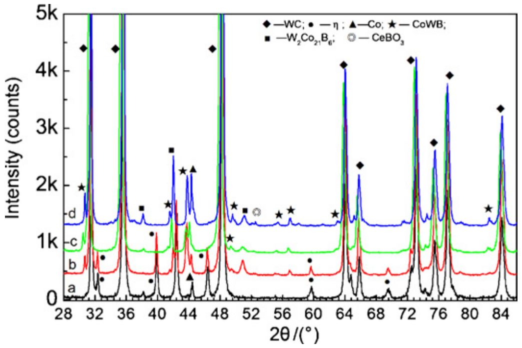

Fig. 3. XRD patterns of the cemented carbides 1, 2, 3 and 4 after sintering at 1400 °C (a: sample 1; b: sample 2; c: sample 3, d: sample 4).

η phase and the formation of CoWB phase can improve the hardness and fracture toughness of the sintered cemented carbides due to the brittleness of η phase and high hardness of CoWB phase.

Fig. 4 shows the SEM images of the cemented carbides. Without CeB_6, the abnormal growth of WC particles and the larger Co lakes have generally been observed. In the samples with CeB_6, the continuous and discontinuous growth of the WC particles are inhibited with the addition of 1.0% CeB_6, hence the WC particles are refined, with the size decreasing from 370–450 nm to 274–315 nm. With the addition of 1.5% CeB_6, however, the average size of the WC particles grows evidently. Moreover, it should be noted that the addition of CeB_6 results in more homogeneous distribution of Co, *decreases* in the grain size of cobalt binding phase and the amount of η phases, as showed in Fig. 4.

Fig. 5 shows the SEM images of the fracture surfaces of the cemented carbides. It can be seen that most of the WC particles are around 275–384 nm. The addition of CeB_6 increases the uniformity of the WC particle sizes and decreases the total porosity and the large B-type pores. The fracture mode can be described as brittle and intergranular fractures, with obvious cleavage and dimple characters. No obvious plastic deformation can be detected, with the crack initiated from the pores and a few coarse WC grains.

4. Discussion

Fig. 2 shows that the addition of CeB_6 leads to the increase of the relative densities of the cemented carbides and the decrease in the total porosity and the large B-type pores in the cemented carbides. It can also be obviously seen from Fig. 4 that the cemented carbides without the CeB_6 addition have a wide distribution grain size of the WC particles. On the other hand, the distributions of the grain sizes for WC particles with the CeB_6 addition are very narrowly distributed. Therefore, we can expect that the cemented carbides with the CeB_6 additions have better performance. One should note that pores are the primary fracture sources of the cemented carbides. Since the cemented carbides are brittle powder metallurgy materials, pores can cause the intense build-up of the internal stress, and nucleate cracks during deformation. Due to the close relationship between the strength and the porosity, less pores and smaller pore size will result in higher strength and hardness. During the sintering cycle, the gaseous impurities (such as oxygen) in the sample will be partially released in the gaseous form. If these impurities are not immediately removed, pores will generally be formed. Because the rare earth elements are highly active, the impurities like oxygen will react with the rare earth elements first. The appearance of the rare earth phase, $CeBO_3$, which are stable at high temperature, tells us that the gaseous impurities are thus reduced and the possible formation of the pores are decreased.

The main mechanisms of the WC particles growth include [20]: (1) diffusion during solid sintering process, (2) dissolution and reprecipitation of WC in Co phase during liquid phase sintering. In both of the processes, diffusion plays a critical role. The processes of dissolution and separation of carbides *are* that: smaller grains dissolve due to their higher dissolution potential (increased chemical potential), while coarser ones grow by

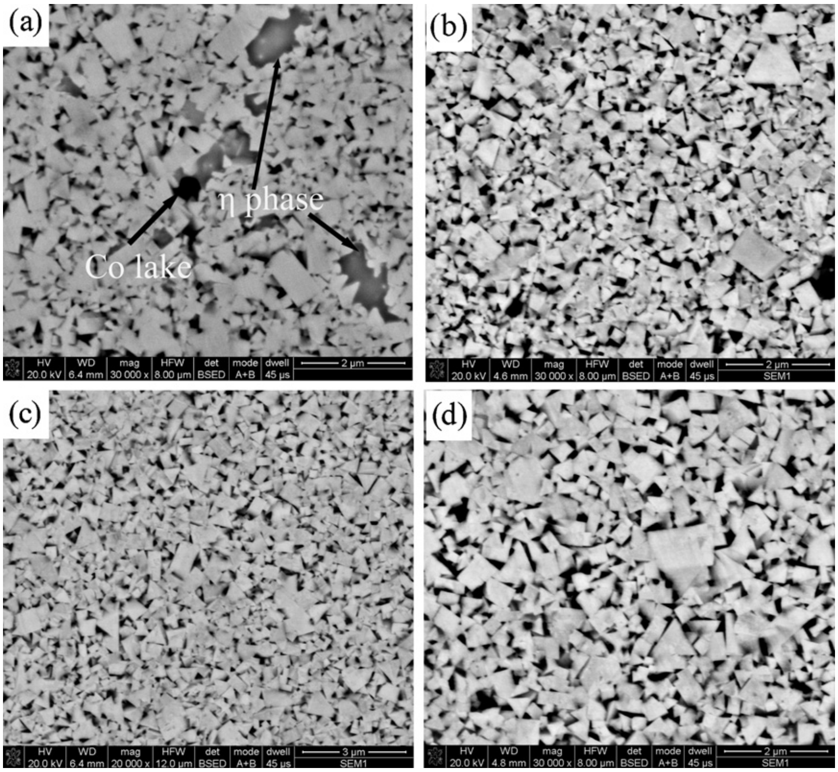

Fig. 4. SEM microstructures of the cemented carbides after sintering at 1400 °C (a: sample 1; b: sample 2; c: sample 3, d: sample 4).

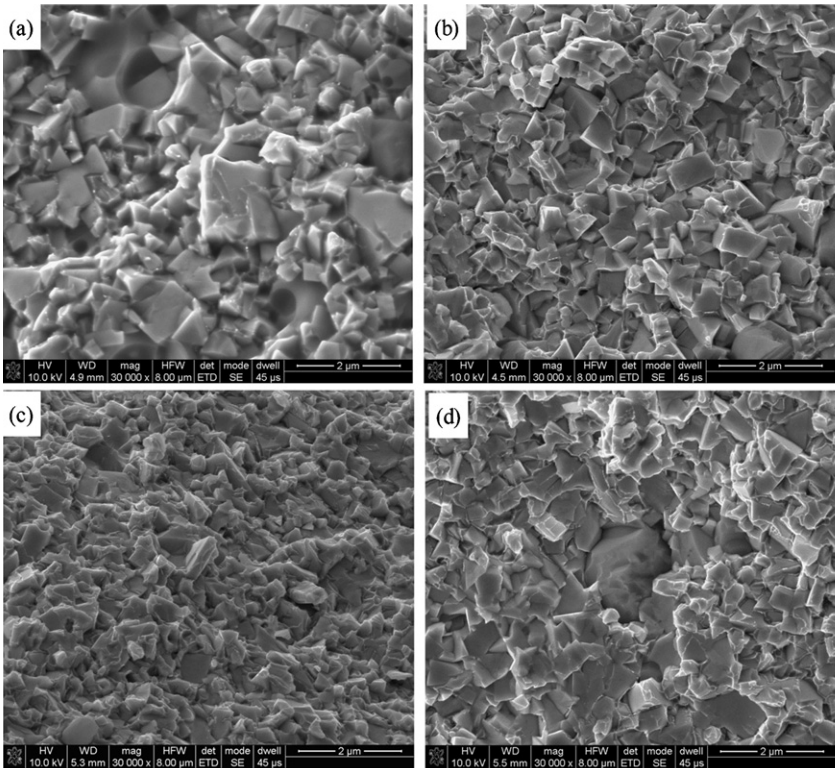

Fig. 5. SEM fractures surfaces of the cemented carbides after sintering at1400 °C (a: sample 1; b: sample 2; c: sample 3, d: sample 4).

material re-precipitation, thereby reducing the interface area of the system. Therefore, reducing the diffusion rate is very important in controlling the WC grain size.

It can be seen from Fig. 4, without the addition of CeB_6, that the WC particles growth is obvious and some abnormal large grains can be observed in the cemented carbides. With 0.5% CeB_6 addition, the number of abnormal coarse grains decreases and the WC particles are much smaller. The possible explanation is that the addition of CeB_6 may cause a decrease in the surface tension, and thin films are formed at the interfaces of liquid cobalt and carbide phase. Moreover, the rare earth elements might reduce the sintering temperature of the cemented carbide and decrease the content of liquid phase [16]. Thus, the diffusing process is slowed down and the WC particles growth through dissolution–reprecipitation coarsening in the presence of liquid phase is hindered.

However, it should be noted that with the addition of 1.5% CeB_6, the average size of the WC particles grows evidently. Some mini-pores, formed during the process of coalescence of the grains, can be clearly observed. It is concluded that the rapid grain growth occurs by the coalescence of the grains. Coalescence of the grains shows a unique way of grain growth through the mass transport mechanisms. The possible mechanisms for coalescence of the grains may include various diffusion processes, or even grain rotations.

Hardness and fracture toughness are the two most important mechanical properties of the cemented tungsten carbides. It can be seen from Fig. 2 that adding suitable CeB_6 improves the microhardness of cemented carbides. The evolution of the microhardness is most likely due to the structural parameters, especially the finer sizes of WC grains. For WC–Co hard metals, the hardness depends mainly on the WC grain size and Co content. According to the Hall–Petch relation, the hardness of the cemented carbides will be enhanced if the grain size decreases. The hardness of cement materials is inversely proportional to the grain size and the fracture toughness is inversely proportional to the hardness, although the relationship between the hardness and fracture toughness may not be linear when the grain sizes are extremely small. It is observed from Fig. 2 that the microhardness is not inversely proportional to the fracture toughness. Thereby, adding a suitable amount of CeB_6 in the sintered WC–Co, with ultrafine grain sizes can obtain both high hardness and strong fracture toughness.

There are three possible mechanisms, by which the mechanical properties of WC–Co can be improved by decreasing the grain size. The first mechanism is based on the effect of defects. It is expected that the defect size (such as pore size) in the sintered material with ultrafine grain size is drastically reduced, compared to that in the conventional bulk WC–Co with coarse grain size. In our cemented carbides, the total porosity and large B-type pores are decreased with increasing the CeB_6 content. Hence, this could be a reason for the significant improvement in the fracture toughness for the cemented carbides with CeB_6 additions. The second mechanism is based on the effect of the interfaces. The total amount of the interfacial area between the WC grains and the Co binder will be substantially increased as the grain size decreases. The increase in the fractions of the crack path through binder/carbide interfaces will contribute to a significant amount of the fracture energy and in turn enhance the overall toughness of the material. The third possible mechanism is also related to the interface related deformation mechanisms. As pointed out by Gleiter et al. [21] and Richter and Ruthendorf [22], the conventional dislocation generation and migration become increasingly difficult as the grain size down to the ultrafine and nano scales. The more possible mechanisms for the deformation of the cemented carbide with ultrafine and nano scaled grains might mainly be due to the grain boundary sliding and short range diffusion assisted mechanisms such as grain rotation and grain shape accommodation.

Therefore, interfaces play a critical role in improving the fracture toughness of the cemented carbides. The significant increase in the fracture toughness for the cemented carbides with CeB_6 additions can be seen from Fig. 2. The possible reason might be due to the aggregation of the $CeBO_3$ at the interfaces of the cobalt/carbide phase boundaries and the carbide/carbide interfaces. Since the rare earth elements are highly active, the impurities like oxygen are gathered around the rare earth elements, and correspondently, the WC–Co grain boundaries and phase boundaries are thus purified. As a result, the interfaces of the cobalt/carbide phase boundaries and the carbide/carbide interfaces can be strengthened.

The existence of rare earth element can also inhibit the transformation from α-Co (fcc) to ε-Co (hcp) [15]. In general, the fcc phase is more ductile, compared to the hcp phase. Therefore, it is important to preserve more α-Co by inhibiting the harmful phase transformation. The transformation is realized through the nucleation and extension of the faults with the help of the dislocation movement. The rare earth phase ($CeBO_3$) can pin the dislocations and impede their movement. As a result, the α-Co → ε-Co transformation is hindered. Since α-Co is equipped with more sliding systems than ε-Co, the dislocations in α-Co are easier to slide when external stress are applied, and thus higher toughness and strength can be achieved.

One should note that the increase of the fracture toughness could be related to the disappearance of the η (Co_3W_3C) phases and the information of $CeBO_3$ and WCoB phases. It can also be seen from Figs. 3 and 4 that the formation of η phases decreases with the CeB_6 addition, but disappears in the cemented carbides 3 and 4. The fracture toughness of sample 3 increases due to the inhibition of the cracks propagation. However, the fracture toughness of sample 4 obviously decreases due to the large size of the rare earth phases, which act as crack initiators during deformation. It is implied that adding suitable amount of CeB_6 is critical for the improvement of the mechanical properties of the cemented carbides. Thus, the cutting performance of the present cemented carbides with the suitable amount of CeB_6 could be better than that of conventional CeB_6-free cemented carbide cemented carbides.

5. Conclusions

Nanocrystalline composite powder of WC–8Co with the mean grain size of 41 nm was fabricated by planetary ball milling of conventional powder. The addition of small amount of the CeB_6 (less than 1 mass%) can inhibit the continuous and discontinuous growth of WC grains. Although the addition of CeB_6 can increase the relative densities and fracture toughness of cemented carbides, adding excess CeB_6 can lead to the decrease of micro-hardness and toughness of cemented carbides. The CeB_6 addition decreases the formation of η (Co_3W_3C) phases and promotes the formation of CoWB, $W_2Co_{21}B_6$ and $CeBO_3$ phases.

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