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Effects of deep cryogenic treatment on microstructure and properties of WC−11Co cemented carbides with various carbon contents

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Abstract: The effects of deep cryogenic treatment on the microstructure and properties of WC−11Co cemented carbides with various carbon contents were investigated. The results show that after deep cryogenic treatment, WC grains are refined into triangular prism with sound edges via the process of spheroidization, but WC grain size has no evident change compared with that of untreated alloys. The phase transformation of Co phase from α-Co (FCC) to ε-Co (HCP) is observed in the cryogenically treated alloys, which is attributed to the decrease of W solubility in the binder (Co). Deep cryogenic treatment enhances the hardness and bending strength of the alloys, while it has no significant effects on the density and cobalt magnetic performance.
Key words: WC−Co cemented carbide; deep cryogenic treatment; phase transformation; microstructure; properties

1 Introduction

WC−Co cemented carbides, also commonly referred to as hard-metals, consist of a matrix of hard faceted WC grains embedded in a tough Co binder. They have been extensively used in the cutting and mining tools due to the exceptional combination of strength, toughness and wear resistance [1,2]. In recent years, a large number of cemented carbides with excellent performance have been developed by changing the composition or the microstructure. The properties can be modified owing to the fact that the composition depends on the carbon content and the microstructural morphology can be changed by heat treatment. Deep cryogenic treatment (DCT), as the extension of traditional heat treatment, has been applied in the industry of cemented carbides.

Deep cryogenic treatment is the process of submitting a material to subzero temperature (−196 °C) to enhance the service life through morphological changes. For the traditional ferrous materials, DCT can convert the retained austenite into martensite. The subjected metals also develop a more uniform, refined microstructure with greater density. Thus, the mechanical properties of ferrous materials are improved [3]. For the WC−Co cemented carbides, REDDY et al [4] concluded that the precipitation and distribution of the η-phase after DCT improved the flank wear resistance by observing the cryogenically treated P-30 tungsten carbide inserts. STEWART [5] postulated that DCT had an effect on the cobalt binder by changing phase or crystal structure in the study of C2 tungsten carbide (WC−6%Co). Many scientific researchers have also reported the effects of cryogenic treatment on WC−Co cemented carbides. WC grains are refined into their most stable state via the spheroidization. The martensite phase transformation in the cobalt binder is also observed during the DCT, and the mechanical properties of cemented carbides can be greatly improved, such as rupture strength, hardness and wear resistance [6].

The effects of carbon content on WC−Co cemented carbides have been investigated in some literatures on the basis of Co−W−C phase diagram [7]. Carbon content affects the type, amount and distribution of η-phase, WC shape and mechanical properties of cemented carbides. When carbon content is higher than the theoretical value, the free carbon in the cemented carbides can wreck the

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continuity of the Co matrix and then influence the toughness, strength and abrasion resistance of the material. When carbon content is lower than the theoretical value of the two-phase region, the brittle η-phase ($M_{12}C$, M_6C) formed in the composite material can lower the strength of material [8,9]. Therefore, carbon content plays a decisive role in WC−Co cemented carbides.

In this work, the effects of deep cryogenic treatment on WC−11Co cemented carbides with various carbon contents were investigated. The experimental results were analyzed with respect to the phase composition and microstructure and W solubility of the binder by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), respectively. The mechanical properties were also presented.

2 Experimental

2.1 Materials

In the present study, WC−11Co cemented carbides with certain concentration gradient of carbon content were prepared from the mixtures of WC and metallic Co powders. A series of carbon contents ranged from the formation of η-phase (M_6C or $M_{12}C$) in the carbon-poor alloys to a carbon content of the formation of free carbon in the carbon-rich alloys by evenly mixing carbon black into the powder mixtures. The properly blended mixtures were subjected to compaction, pre-sintering and final liquid phase sintering at 1450 °C for 1 h. Then, the inserts with different carbon contents were manufactured into the shape of tool inserts with dimensions of 6.5 mm × 5.25 mm × 20 mm. The untreated (UT) three inserts were labeled by UT-1, UT-2 and UT-3, all of which represented different carbon contents of 4.45%, 4.92% and 5.25%, respectively. The cryogenically-treated inserts were labeled by DCT-1, DCT-2 and DCT-3.

2.2 Deep cryogenic treatment

In the deep cryogenic treatment, the inserts labeled by DCT-1, DCT-2 and DCT-3 were slowly cooled in the refrigerator for sufficient time before submitting them directly to the liquid nitrogen (−196 °C). The inserts were held at this temperature for 3 h and then brought back to room temperature at a rate of 2 °C/min.

2.3 Microstructure and properties analysis

The microstructure and phase composition of the inserts were investigated by SEM (Sirion 200) and XRD with Cu K_α (D/max−2500), respectively. The measurement of mean grain size of WC was carried out by the linear intercept method with SEM. The concentration of W dissolved in the Co binder phase was measured by EPMA (JXA−8230). Physical and mechanical properties including density, hardness, cobalt magnetic performance and bending strength of the inserts were measured and compared before and after different deep cryogenic treatments. The density of the inserts was measured by the Archimedes method. The hardness was measured by a Rockwell hardness instrument. The cobalt magnetic performance was measured by the cobalt magnetism meter. The bending strength was measured on the inserts according to three-point bending experiment method.

3 Results and discussion

3.1 Phase composition and microstructure

WC−11Co inserts were examined to understand whether any composition changes would take place or not after DCT using X-ray diffraction method. In order to exclude WC factor, all inserts were etched in the certain etchants (mixture of equal quantities of 10% aqueous solutions of $K_3Fe(CN)_6$ and sodium hydroxide) before XRD examination. The phase compositions are shown in Fig. 1 and Table 1. Cryogenically-treated inserts show almost the same trend as that of UT inserts. Therefore, deep cryogenic treatment has a little effect on phase composition.

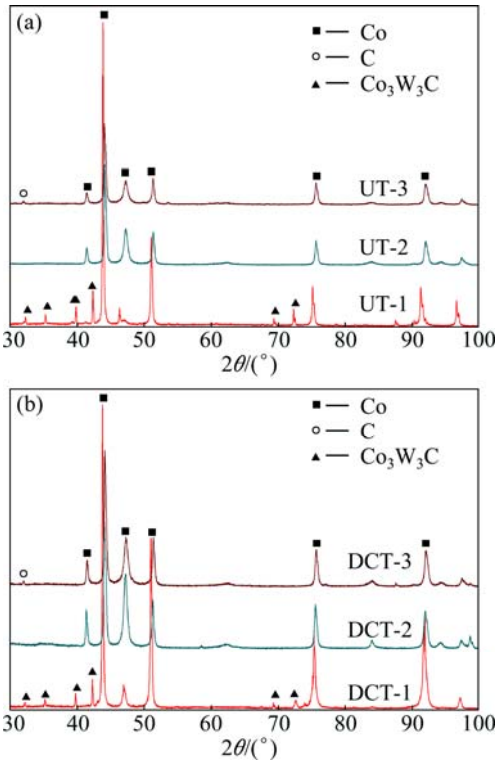

Fig. 1 XRD patterns of WC−11Co cemented carbides (etched WC) with various carbon contents before (a) and after (b) deep cryogenic treatment

Table 1 Compositions of WC−11Co cemented carbides with various carbon contents after deep cryogenic treatment

Sample	Mass fraction of carbon/%	Composition	Mean grain size of WC/μm
UT-1	4.45	WC+Co+Co_3W_3C	2.2
UT-2	4.92	WC+Co	2.5
UT-3	5.25	WC+Co+graphite	2.5
DTC-1	4.45	WC+Co+Co_3W_3C	2.3
DTC-2	4.92	WC+Co	2.5
DTC-3	5.25	WC+Co+graphite	2.6

Figure 2 shows the microstructures of the inserts with various carbon contents before and after deep cryogenic treatment. In the carbon-poor alloys, it can be seen from Figs. 2(a_1) and (b_1) that η-phase, Co_3W_3C, is formed in both UT and DCT inserts, but the amount of η-phase in the DCT inserts is more than that in the UT ones. It can be explained that the clustering of carbon atoms acts as nuclei for the η-phase around the defects, which are induced by martensite phase transformation in the DCT [10,11]. In the carbon-rich alloys, as shown in Figs. 2(a_3) and (b_3), free carbon is formed while the η-phase disappears in the inserts.

In addition, the morphology characteristics of WC grains should be mentioned. As can be seen from Fig. 2 and Table 1, there is a slight increase for WC grain size in the DCT inserts as compared with the UT ones. The mechanism of WC coarsening can be explained on the basis of activation energy, which has a sensitive

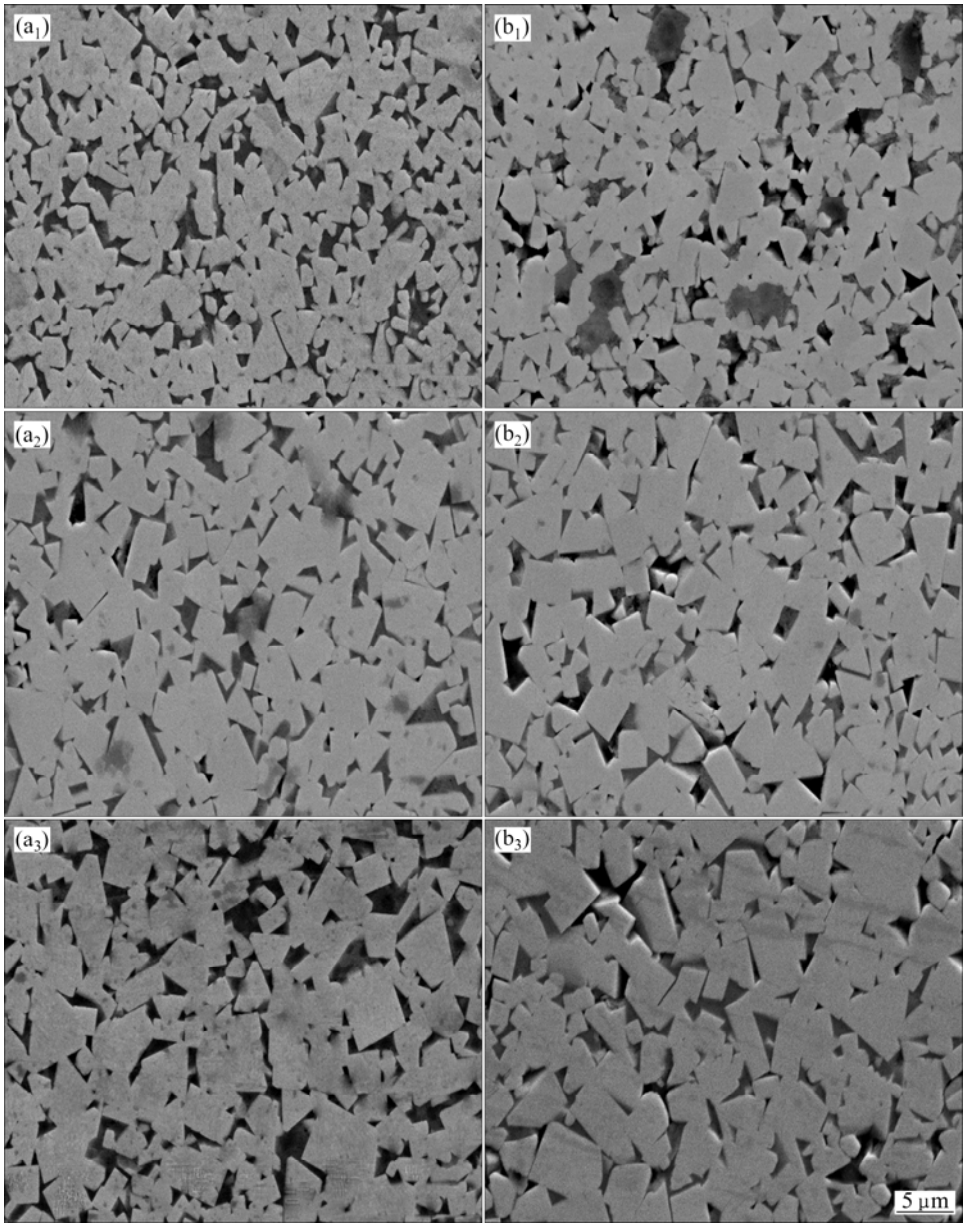

Fig. 2 SEM images of WC−11Co cemented carbides with various carbon contents before and after deep cryogenic treatment: (a_1) UT-1; (b_1) DCT-1; (a_2) UT-2; (b_2) DCT-2; (a_3) UT-3; (b_3) DCT-3

relationship with carbon content. So, the coarsening of WC grains is influenced by η-phase and carbon self-diffusion at the interface between WC and Co phases [12,13]. And cobalt densification due to deep cryogenic treatment also has a significant effect on the WC coarsening. It can also be seen from Fig. 2 that WC grains with the characteristics of truncated trigonal prism shape are refined into triangular prism with sound edges via spheroidization after the DCT, which is in good agreement with what GILL et al [3] observed. The possible reason is that cryogenic temperature acts as the catalyst for preferential growth of three of the six prismatic tungsten carbide planes [14,15].

3.2 W solubility of Co binder

In order to further study the martensite phase transformation of the Co phase, EPMA analysis of the W content in the Co phase was performed, as shown in Fig. 3.

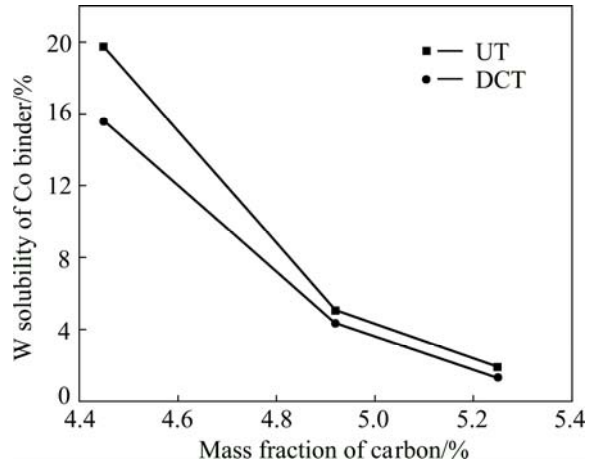

Fig. 3 Effect of deep cryogenic treatment on W solubility of Co binder in inserts

W solubility in Co binder is a significant factor determining the structure and transformation of the Co binder phase. It is influenced by many related factors including temperature, carbon content and so on. As can be seen from Fig. 3, there is a slight decrease for W solubility in the cryogenically-treated inserts compared with untreated ones. And W solubility decreases with increasing the carbon content in the inserts [16,17]. It is important to note that Co phase consists of α-Co (face-centered cubic structure) and ε-Co (close-packed hexagonal structure), and W only acts as the stabilizers for α-Co phase. It has been reported that the content of ε-Co is obviously higher than that of α-Co in cryogenically-treated cemented carbides due to the non-diffusion phase transformation. On the basis of thermo-dynamics, the equilibrium concentration of W in α-Co is higher than that in ε-Co at the same temperature [18]. Therefore, W solubility of the binder in the deep cryogenically treated inserts decreases compared with the untreated ones.

3.3 Properties

The results of measured physical and mechanical properties of WC–11Co cemented carbides with various carbon contents are listed in Table 2.

Table 2 Properties of WC−11Co with various carbon contents before and after deep cryogenic treatment

Sample	Density/ ($g \cdot cm^{-3}$)	Cobalt magnetic/%	Hardness (HRA)	Bending strength/MPa
UT-1	14.49	9.25	87.9	1040
UT-2	14.33	6.55	87.15	2860
UT-3	14.24	6.67	87.01	2260
DCT-1	14.52	9.10	88.25	1070
DCT-2	14.31	6.65	87.20	2930
DCT-3	14.21	6.60	87.25	2320

The cobalt magnetic performance can be expressed by the fraction of ferromagnetic cobalt binder phase, which is suppressed by carbon content to some degree. It can be clearly seen from Table 2 that the cobalt magnetic in DCT inserts shows a slight decrease compared with UT ones, which is attributed to larger amount of ε-Co in the DCT inserts. ε-Co has lower saturation magnetization than α-Co [19].

The density mainly depends on WC, Co phase, η-phase or graphite. Therefore, deep cryogenic treatment has little effect on the density of WC−11Co cemented carbides.

According to Hall−Petch relationship, the hardness of the inserts can be enhanced with decreasing the WC grain size. It can be seen from Table 2 that compared with untreated ones, the hardness values in the cryogenically-treated inserts are increased by 0.39%, 0.06% and 0.28%, respectively. These results can be explained by the following two mechanisms. The first mechanism is attributed to the compressive residual stress, which is induced by the large difference of thermal expansion coefficient between WC and Co phases during the DCT progress. The other is that densification of Co phase has an important effect on the hardness in the inserts.

Bending strength has the intimate relationship with the inherent performance of WC−Co cemented carbides, which is characterized by Co content, WC grain size, carbon content and other chemical elements [20]. As can be seen from Table 2, bending strength in the DCT inserts shows an obvious increase compared with that of UT ones. LIU [21] hold the view that the bending

strength of cemented carbides mainly depended on the Co content and distribution, nevertheless, which is determined by the Co mean free path relevant with WC grain size and Co content to some extent. In this work, therefore, the possible mechanism for increasing bending strength can be attributed to the increase of Co mean free path resulting from the WC coarsening. In addition, the residual stress on the surface of alloys possibly exerts a certain impact on the bending strength due to the cryogenic treatment.

4 Conclusions

1) Although deep cryogenic treatment has a little effect on phase composition, the amount of η-phase increases compared with untreated ones. WC grain shape shows triangular prism with sound edges via the process of spheroidization.

2) W solubility in the Co phase slightly decreases due to phase transformation of Co phase during the cryogenic treatment progress.

3) The hardness and bending strength after deep cryogenic treatment are higher than those of untreated ones and the cobalt magnetic slightly decreases, while the density shows no significant changes.

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深冷处理对不同碳含量 WC−11Co 硬质合金显微组织及性能的影响

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摘　要：研究深冷处理对不同碳含量 WC−11Co 硬质合金显微组织和性能的影响。结果表明：经深冷处理后 WC 晶粒的形状通过球化方式变成具有圆滑过度角的三角菱柱状，但其尺寸无明显变化。在经深冷处理后的合金中，W 在 Co 中的固溶度减小，且 Co 相发生了从面心立方 α-Co 到密排六方 ε-Co 的转变。此外，深冷处理提高了合金的硬度与抗弯强度，但是对于合金的密度与钴磁性能影响不大。

关键词：WC−Co 硬质合金；深冷处理；相变；显微组织；性能

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