Enhancement on the transverse fracture strength of functional graded structure cemented carbides

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Coated cemented carbides have been widely used in machining ferrous and nonferrous metal components, for their advantages in wear resistance, chemical stability, service lifetime and cutting efficiency over traditional uncoated cemented carbides [1,2]. Usually there are mainly two kinds of coating techniques for cemented carbides: physical vapor deposition (PVD) and chemical vapor deposition (CVD) [3, 4]. PVD techniques include sputtering, ion implanting, ion plating and activated reactive evaporation. Comparatively, CVD has been more widely used than PVD for coating cemented carbides, as it provides coatings of higher bonding strength, and hence endows hard alloy with more excellent service properties. However, typical CVD requires reactions at a relatively high temperature (~1000 °C), and leads to microstructure change in the surface of cemented carbides and even bulk distortion problems. The further problems involve possible grain growth and carbon-deficient phase formation in the surface layer close to the coating, deteriorating the bonding strength and stress relaxation between the coating and the substrate [5, 6].

Recently there is an innovation on the coated cemented carbides inserts. A gradient layer lack of brittle cubic phase and enriched in ductile binder phase was formed between the coating and the substrate [6–9]. This ductile gradient layer could prevent the crack propagation from the brittle coating to the substrate, hence toughens the insert and prolongs the service life. This kind of gradient layer forms by a process called as "gradient-sintering." Firstly a cemented carbide containing nitrogen is sintered in a usual manner, then it is sintered again in a nitrogen-free atmosphere. During the second step, an outward diffusion of nitrogen occurs. Titanium-rich cubic phases dissolve, and due to strong thermodynamic coupling between nitrogen and titanium, this leads to an inward diffusion of titanium, and a surface zone depleted in cubic phases forms. The thermodynamics and kinetics of the formation of the surface gradient zone have been studied extensively by many materials scientists [6–9]. In this work the transverse fracture strength of the cemented carbides after presintering, gradient sintering and coating were studied, and an enhancement of the transverse fracture strength during the above processes was found for the first time.

The cemented carbide alloys studied in this work were based on the mixtures of WC, Ti(C,N) and Co powders. The content of cobalt was 6, 8 and 10 wt% respectively, while that of Ti(C,N) varied from 2.0 to 4.0 wt%. TaC in amount of 6.0 wt% was also added to improve the high temperature wearability of hardalloys. In order to compensate for the carbon loss in sintering and CVD process, about 0.3 wt% carbon powder was added. The powder mixture was milled for 24 hr in a ball mill with cemented carbide milling balls, and alcohol was added to increase milling efficiency. The powders were then dried at about 80 °C for 10 hr, and then pressed into 6 mm × 6 mm × 25 mm bars at a pressure of 100 MPa. The compacts were sintered in a vacuum furnace by two steps. Firstly, the compacts were dewaxed at 500 °C for 2 hr, and then sintered at 1380 °C. The controlled atmosphere was a low-pressure N_2 at about 3500 Pa. The gas was introduced when the sintering temperature of 1380 °C was reached and was present during the whole process to prevent the evacuation of nitrogen from the compacts. After sintering for 1 hr, the compacts were cooled in the furnace. The first sintering step was called pre-sintering. In order to eliminate surface defects, the samples were ground before subsequent sintering. At the second step, the samples were re-heated to 1420 °C and held for 2 hr in a nitrogen free atmosphere, consisting mainly of Ar, in order to develop a composition gradient structure. The second sintering step was called gradient sintering. The sintered parts were then coated with TiN, Al_2O_3, and Ti(C,N) hard coatings in sequence in a CVD furnace at 1000 °C. Before CVD coating, elaborate precautions were taken to ensure the surface to be exceptionally clean and to avoid the discontinuities or diminished adhesion at the interface, which is detrimental to the mechanical properties of the coated materials.

The transverse rupture strength was tested on specimens of size 6 mm × 6 mm × 25 mm. The microstructures of polished samples after different stage sintering and coating were observed with a scanning electron microscope (SEM). The SEM was operated in a backscattered mode.

Fig. 1 indicates that the transverse fracture strengths of all the cemented carbides were significantly improved after gradient sintering and coating. For example, the WC-6Co added with 2.0 wt% Ti(C,N) had
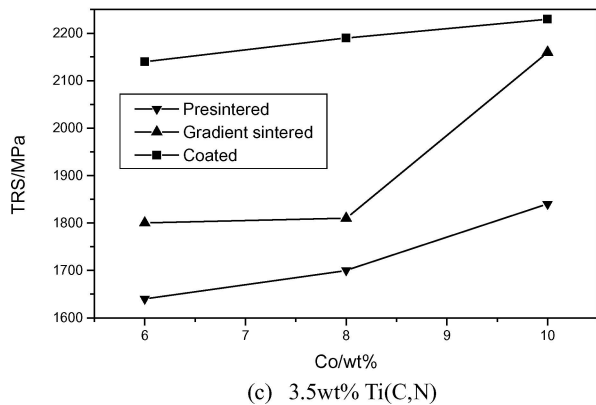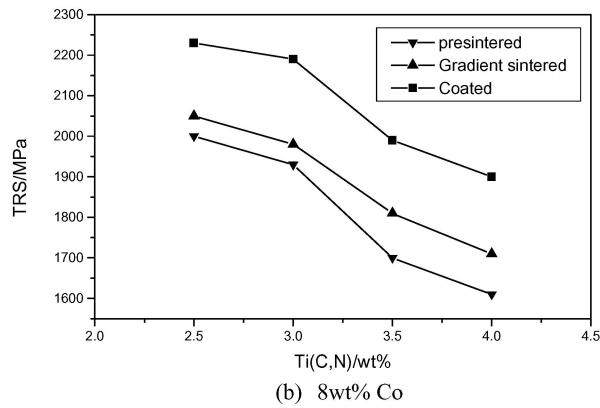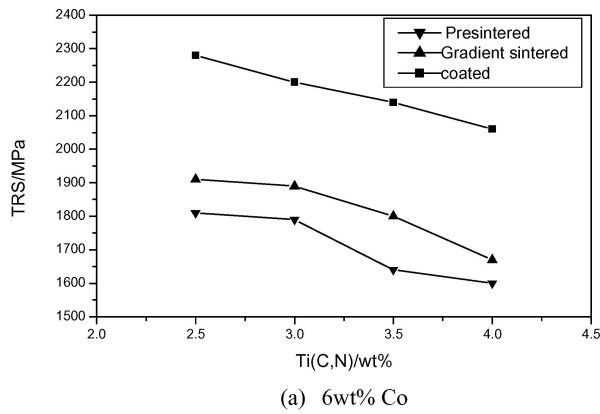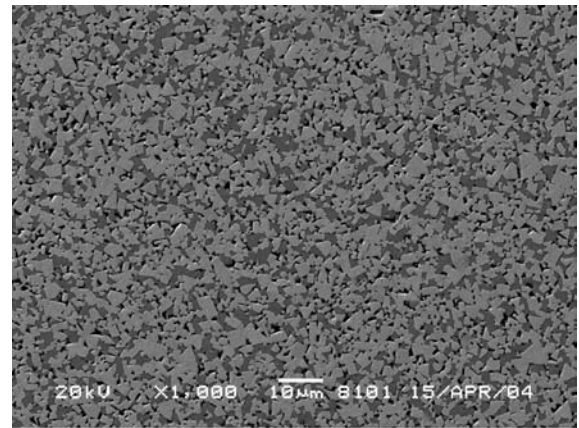
(a) 6wt% Co

(b) 8wt% Co

(c) 3.5wt% Ti(C,N)

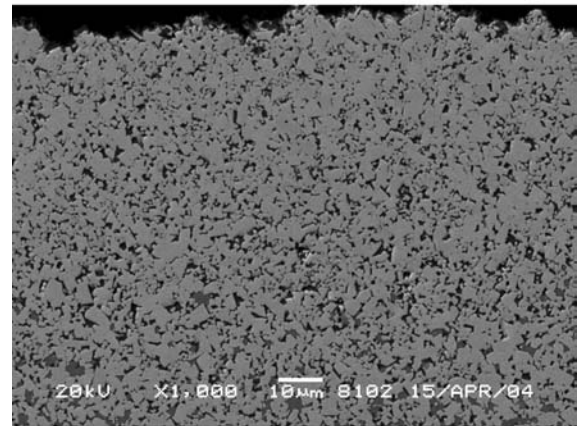*Figure 1* Transverse fracture strength of graded cemented carbides with different compositions and at different processing stages.

(a) the presintered microstructure

(b) the gradient sintered microstructure

(c) the coated microstructure

Figure 2 The microstructures of WC-6 wt%Co-3.5 wt% Ti(C,N) alloy at different processing stages.

a transverse rupture strength (TRS) of 1800 MPa in presintered state, but after gradient sintering the TRS increased to about 1900 MPa and finally increased to 2300 MPa after coating, as indicted in Fig. 1(a). Fig. 1 also shows that the TRS of cemented carbides decreased with the content of Ti(C,N) due to the brittle nature of Ti(C,N); while the TRS increased with the content of Co due to the good toughness of metal binder. In order to understand the improvement of TRS, the microstructures of a WC-6 wt%Co-3.5 wt% Ti(C,N) alloy were studied.
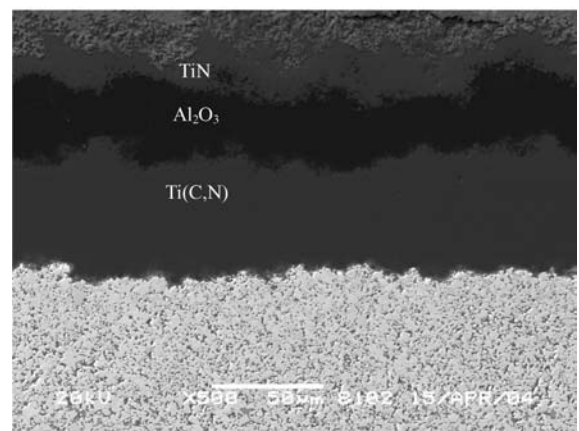
The microstructures were observed with backscattered electron images, which clearly reflected the composition distribution of phases. Thus the bright phase is attributed to WC, the grey phase is (Ti,W)(C,N), or the β phase, and the dark phase is the binder, Co solid solution. As shown in Fig. 2(a), after presintering the microstructure of cemented carbides consisted of WC (in white), Co solid solution (in dark) and β phase (in grey). After gradient sintering, a composition gradient layer in depletion of β phase and rich in Co formed in the surface (only white and dark phases can be found in a depth of nearly 60 μm to the surface). Coating seldom affected the bulk microstructure, except that there were three hard layers with compositions of TiN, Al$_2$O$_3$, and Ti(C,N), respectively on the surface, as shown in Fig. 2(c). No carbon-deficient phase was found between the coating and the substrate.

As the microstructure of the substrate varied little 100–200 μm below the surface, it then seems that the TRS of cemented carbides could be closely related to its surface microstructure. TRS is a combination of shear

strength, compressive strength, and tensile strength and is used as a general measure of the toughness of the sintered cemented carbides. For cemented carbides with homogeneous microstructure, the TRS is a function of both the intrinsic strength and the nature and distribution of the defects with the structure. However, the surface condition plays an even more important role in TRS of cemented carbides with gradient surface layer. As has been indicated in Fig. 2(b) the surface gradient layer was depleted in β phase and rich in Co solid solution, β phase is so brittle that cannot withstand the propagation of cracks, while Co binder phase has a better ductility and can release stress concentration in the tip of cracks by plastic deformation. Therefore, the surface gradient layer is much more tougher than the bulk, and can effectively hinder the propagation of surface cracks. This might be the main cause of the TRS improvement after gradient sintering. Coatings usually provide cemented carbides with higher surface hardness and wear resistance than uncoated ones. The effect of coatings on TRS of cemented carbides is still uncertain. CVD usually deteriorate the TRS of cemented carbides by introducing residual tensile stress and carbon-deficient phases [10, 11]. However results in this work shows that CVD improves TRS of cemented carbides. It could be due to the suppression of the formation of carbon-deficient phase and release of residual stress between the coating and the substrate by the gradient layer. As has been described previously, during gradient sintering, nitrogen and titanium in β phase diffuses outwards and inwards respectively. In this process, carbon previously in β phase was left, so the surface gradient layer was rich in carbon. Besides, as has been mentioned above, a slight excess of carbon was also added to the raw materials. The enrichment of carbon in the surface could compensate for the depletion of surface carbon in subsequent CVD process, hence suppressed the formation of carbon-deficient phase, a brittle phase in nature, thus, the mechanical properties of the coated cemented carbides could be improved. As the surface gradient layer was much tougher than the bulk, through plastic deformation of cobalt-rich phase it could release the stress occurred in CVD process and decrease the residual stress between the coatings and the substrate. As

the coatings usually have a high hardness, and the load for inducing formation of surface cracks could be promoted. With the two shortcomings overcome, coatings could then significantly increase the TRS of cemented carbides.

In conclusion, the transverse fracture strength of cemented carbide with graded structure is significantly improved by gradient sintering and coating. The improvement of TRS could be attributed to the formation of a surface gradient layer, which can hinder the propagation of surface cracks in presintered sample and can suppress the formation of carbon-deficient phase and release residual stress in coated samples.

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