Formation mechanism of cobalt-gradient structure in WC-Co hard alloy

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Cemented carbides are one of the most important tooling materials, owing to their high hardness and outstanding wear resistance [1–3]. The combination of properties results from their composite nature, wherein, a brittle refractory carbide (WC, TiC, TaC etc.) is combined with a tough binder metal (mostly Co, sometimes Ni or Fe). However, the hardness (or the wear resistance) and the toughness are two properties of cemented carbides, which usually cannot be improved at the same time in a single alloy.

In the 1980s and 1990s Sandvik introduced new materials that were described as "the most significant innovation in the history of cemented carbide since the early 1950s [4–7]." The patented dual phase (DP) technology permits a simultaneous increase in both the wear resistance and toughness of cemented carbide, or either property independently. The DP materials were achieved by changing the distribution of the cobalt within the insert, i.e., the formation of a cobalt-gradient structure. There was a low cobalt content of around 3% at the surface to provide the high wear resistance required to penetrate the rock; a middle layer with a cobalt content of around 10% to give the insert high toughness; and a core with around 6% cobalt to give a balance of properties. This gives a hardness distribution across the button which is high at the outside and the core, falling off in the middle, cobalt rich zone. The DP grade cemented carbides showed an increase of 40% in service lifetime compared with conventional materials. However, the formation mechanism of the cobalt-gradient has seldom been reported [8–11].

In this paper, a WC-6Co hard alloy with a cobalt-gradient was prepared by a two-step sintering process. Firstly, WC-6Co alloy with a carbon content lower than equilibrium was presintered to introduce a η-phase containing homogenous microstructure. Then the hard alloy was carburized in a carbon atmosphere to form cobalt-gradient. The effected processing parameters such as carbon content and carburizing temperature on the formation of the cobalt-gradient structure were investigated and a possible composition gradient formation mechanism is presented.

The raw materials were Co powder ($\sim$2.12 μm), WC powder ($\sim$2.37 μm) and, W powder ($\sim$1.12 μm). The above powders were firstly mixed in alcohol for 24 h, then dried and granulated with wax. The nominal composition of the mixed powder was WC-6 wt%Co, and pure W powder was added to adjust the carbon content. The carbon content of the mixed powder is showed in Table I.

The granulated powder was cold pressed at 100 MPa. The compacts were dewaxed at 900 °C for 2 h in H_2 atmosphere, and presintered at 1420 °C for 60 min in vacuum. The presintered samples were covered with graphite powder and then carburized at 1420, 1440, and 1460 °C for 60 min respectively in H_2 atmosphere.

Fig. 1 shows the optical microstructure of YG6-A sample after being presintered. It was found that the microstructure of the presintered sample was mainly composed of WC, γ, and η phase. The microstructures of YG6-B and YG6-C were almost the same, except that the size and the content of η phase, which is gray in color in the microstructure, varied in samples of different initial carbon contents. η phase consisted of such complex carbides as Co_2W_4C, Co_3W_3C, and Co_4W_2C, and was formed only when the gross carbon content of the alloy was below the equilibrium level. The addition of W powder would decrease the gross carbon content as it dissolved in liquid Co during sintering, and hence make the following reactions possible:

$$4W + C + 2Co \rightarrow Co_2W_4C \quad (1)$$

$$3W + C + 3Co \rightarrow Co_3W_3C \quad (2)$$

$$2W + C + 4Co \rightarrow Co_4W_2C \quad (3)$$

Fig. 2 shows the microstructure of YG6-A carburized at 1420 °C for 60 min, Co content was different at different positions in the sample. At the surface, the microstructure was rich in WC, with η phase absent, the Co content was about 4%. The middle layer was rich in Co with a content of 8%, also without η phase. The microstructure of the core alloy was almost the same as that of the as-presintered sample except some angular WC grains were found, with η phase present. The thickness of the gradient layer, including both the outer layer and the middle layer, is shown in Fig. 3. It was found that the thickness of the gradient layer increased with the gross carbon content increasing and the carburizing temperature decreasing, thus the sample with the highest C content and the lowest carburizing temperature, had the thickest gradient layer.

During liquid phase sintering, carbon dissolved in Co phase. In an atmosphere rich in carbon, carbon atoms diffused through the Co phase from the surface to the inner parts of the sample, and reacted with η phase to form more liquid Co and WC:

$$Co_2W_4C + 3C \rightarrow 4WC + 2Co \quad (4)$$

$$Co_3W_3C + 2C \rightarrow 3WC + Co \quad (5)$$

$$Co_4W_2C + C \rightarrow 2WC + Co \quad (6)$$

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TABLE I Carbon content of WC-6Co samples

Sample	C (wt%)
YG6-A	5.32
YG6-B	5.24
YG6-C	5.14

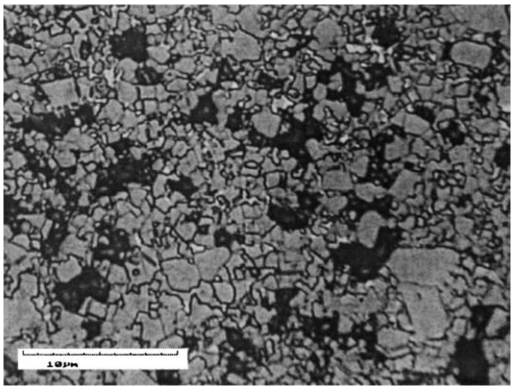


Figure 1 Microstructures of YG6-A after being presintered.

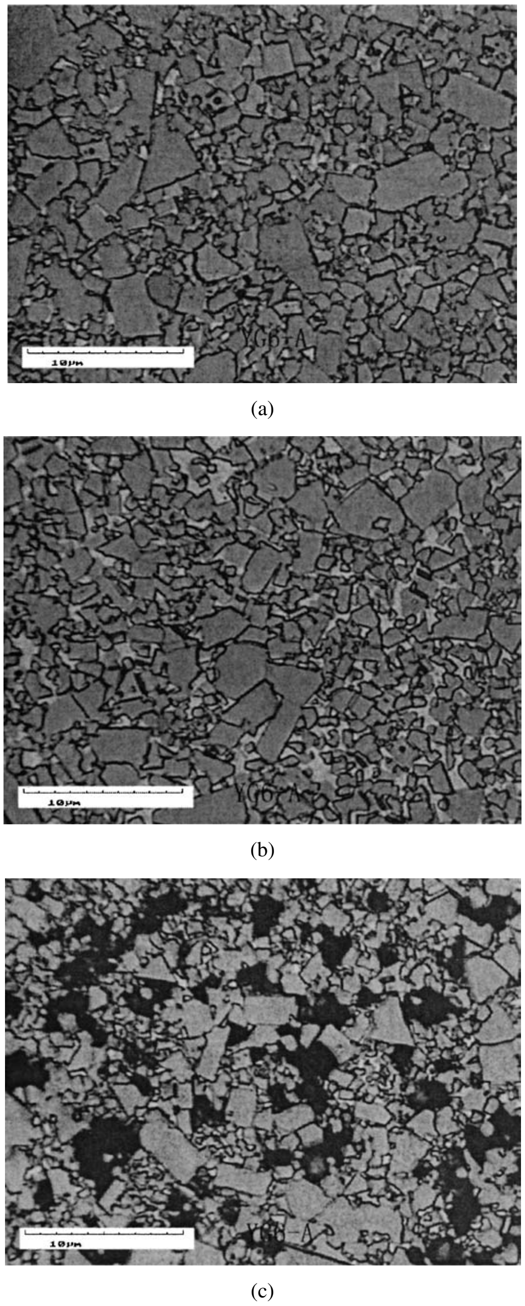


Figure 2 Microstructure of YG6-A, carburized at 1420 °C for 60 min: (a) at the surface, (b) in the middle layer, and (c) in the core.

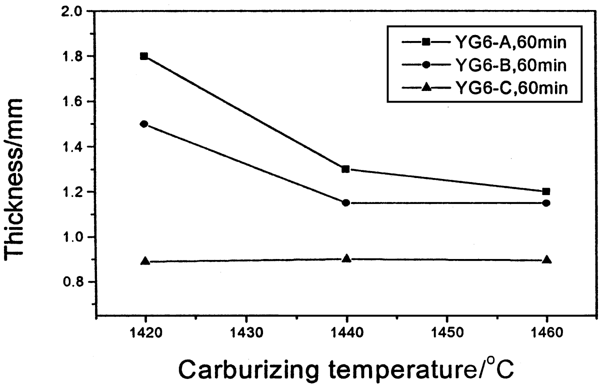
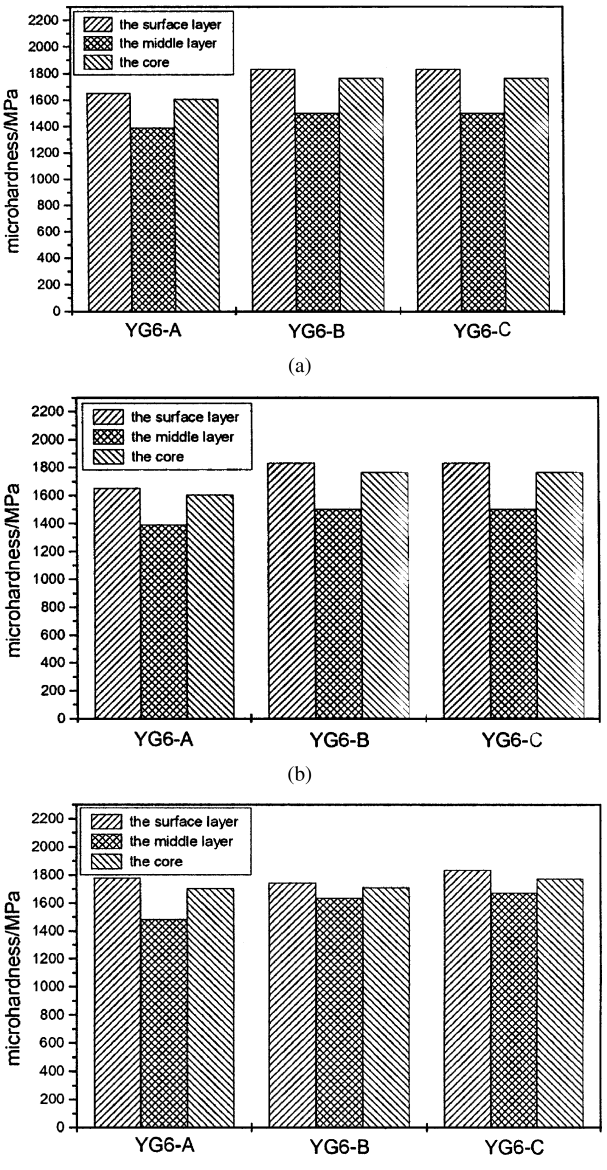


Figure 3 The thickness of the gradient layer vs. carburizing temperature.

WC, which is the resultant of the above reactions precipitated on the primary WC grain in the surface layer, leading to coarsening of WC grains. WC in the alloy forms a rigid skeleton, accounting for about 90% in volume, while Co phase disperses in the rigid skeleton. The precipitated WC increased the skeleton volume in the surface layer [12]. As a result, the Co liquid was driven inward, finally forming a Co gradient structure in the alloy. Therefore, the formation of Co gradient is mainly attributed to two factors: the carbon diffusion and the flow of liquid phase during carburizing.

The formation of η-phase in the presintering step consumes Co phase. The more η-phase forms, the less Co liquid would remain in subsequent carburizing. Thus high carbon content leads to less but finer η-phase, and hence retains more cobalt liquid during sintering. As Co is the main channel for carbon diffusion, a large amount of Co would enhance the carbon diffusion. So the lower the carbon content in cemented carbides, the less thick the gradient would be, as shown in Fig. 3. Another phenomenon shown in Fig. 3, which should be noted, is that for the samples YG6-A and YG6-B, the thickness of the gradient decreased with the carburizing temperature increasing, while the thickness of gradient layer in the sample YG6-C was almost constant. Quantitative metallographical microscopy analysis showed that the WC mean grain size at the surface of samples YG6-A, YG6-B, and YG6-C, which were carburized at 1420 °C for 60 min were about 2.5, 4, and 5 μm, respectively. It was possible that the coarsening of WC grains decreased the thickness of Co layer, i.e., the diffusion channel of carbon, hence hindered the carbon diffusion and further growth of the gradient layer. From the discussion above, it can be concluded that high carbon content favors large gradient thickness due to the following two reasons: (1) The lower the carbon content, the more η-phase formed after presintering. Thus, more carbon is needed to diffuse into the sample to react with the η-phase and to form the same gradient layer thickness; (2) During carburizing, carbon diffuses mainly through Co liquid, and low carbon content associated with large WC grain size and low Co content



(a)

(b)

(c)

Figure 4 Microhardness in the different layer of the gradient cemented carbide: (a) carburized at 1420 °C, (b) carburized at 1440 °C, and (c) carburized at 1460 °C.

in the surface, so, it was more difficult for carbon atoms to diffuse into the sample of low carbon content.

Fig. 4 shows the microhardness in the different layers of the gradient-cemented carbides, which were carburized at 1420, 1440, and 1460 °C for 60 min, respectively. It clearly indicates that the surface layer has the largest microhardness, the middle layer has the lowest microhardness, and the value of the core is intermediate. The microhardness result was in good accordance with the gradient microstructure. Since the surface had a low content of cobalt and large WC grains, it had the highest hardness.

In conclusion, by a two-step sintering process, cemented carbides with a Co gradient can be achieved, composed of WC-rich surface, Co-rich middle layer, and a η-phase containing core. Without regard to holding time in this work, the thickness of the cobalt-gradient layer was found to be closely related to such factors as gross carbon content of the samples and sintering temperature. The lower carbon content favored the formation of η-phase in presintered alloys; however, the higher the carbon content, the finer the η-phase. In the subsequent carburizing step, WC-6Co hard alloy with a higher carbon content and sintered at a lower temperature had the thickest cobalt-gradient layer. This study indicates that a higher carbon content leads to less but finer η-phase, and the retention of more cobalt liquid. Carburizing temperature has a great influence on the formation of the gradient layer. At an excessively high sintering temperature, the diffusion rate of carbon would be so fast that it would lead to severe coarsening of surface WC grain and hinder the further diffusion of carbon atom into the hard alloy body. Therefore, in order to achieve a cobalt gradient layer of enough thickness, the carbon content and the carburizing parameters should be carefully controlled.

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