Copyright © 2014 Tech Science Press CMC, vol.41, no.2, pp.153-161, 2014

Fabrication of Functionally Gradient Cemented Carbide with Ultrafine Grains

Xiangkui Zhou[1], Kai Wang[1], Zhifeng Xu[1], Qiang Wang[2], Guojian Li[1] and Jicheng He[1]

Abstract: At present, the functionally gradient cemented carbide (FGCC) substrate with enrich cobalt on surface is mainly formed from medium grained WC grains. In order to further improve the properties of gradient cemented carbides, the ultrafine powder was chosen in this study and the functionally gradient cemented carbide with ultrafine grains was prepared by a two-step process, where the cemented carbide is first lower pressure pre-sintered and then subjected to a gradient sintering. The results show that it is possible to form gradient layer with enriched cobalt on surface by this method and also the grain growth can be inhibited by low pressure pre-sintering. Ultrafine grain gradient cemented carbide was fabricated after the gradient sintering, the thickness of gradient layer was about 43μm and the average grain size of WC is about 0.42μm. The formational mechanism of the functionally gradient cemented carbide with ultrafine grains are discussed through analyzing the influence of ultrafine microstructure, which was obtain by lower pressure pre-sintering, on atomic diffusion and grain growth during gradient sintering process.

Keywords: ultrafine grains, functionally gradient cemented carbide, sintering, grain size.

1 Introduction

Functionally gradient cemented carbide with the surface enriched in ductile binder is usually used as the substrate of coated tool. The surface gradient layer with higher toughness can prevent crack propagation from the coating into the substrate,

[1] Key Laboratory of Electromagnetic Processing of Materials (Ministry of Education), Northeastern University, Shenyang 110819, China.

[2] Corresponding author. Key Laboratory of Electromagnetic Processing of Materials (Ministry of Education), Northeastern University, No. 3-11 Wenhua Road, Heping District, Shenyang, Liaoning Province, 110819, P. R. China. Tel: +86-24-83681726; Fax: +86-24-83681758; Email: wangq@mail.neu.edu.cn

which may extend the service lifetime of coated tool [Andrén (2011); Walter et al. (2002)]. Suzuki et al [Suzuki et al. (1981)] found that an enriched binder gradient layer at the surface of nitrogen-containing cemented carbides could be formed by sintered in a denitriding atmosphere. Nowadays, functionally gradient cemented carbide is mainly prepared by a two-step sintering, in which the cemented carbide is first pre-sintered in vacuum furnace with negative pressure N_2 gas and then subjected to a gradient sintered in a nitrogen free atmosphere [Ekroth et al. (2000)]. However, the functionally gradient cemented carbide prepared by this method usually has larger WC grain, which will reduce to a certain extent the service lifetime of the coated tools with th is kind of substrate.

According to the Hall-Petch formula, the smaller the grain is the higher properties the alloy has. Cemented carbide with ultrafine grain is the major development trend in the future for its excellent mechanical properties [McCandlish et al. (1993); Zhang et al. (2003); Milman et al. (1999)]. The key point of preparing the ultrafine grain cemented carbide is to control the grain growth in sintering process. Now the grain growth can be inhibited to a certain extent by using the sintering technologies that can accelerate the heating rate, shorten the holding time and decrease the sintering temperature, such as hot pressing sintering [Azcona et al. (2002)], microwave sintering [Breval et al. (2005); Agrawal et al. (2000)], spark plasma sintering (SPS)[Jia et al. (2005); Cha et al. (2003); Sivaprahasam et al. (2007)] and hot isostatic pressing sintering (HIP sintering)[Azonna et al. (2002)]. Evolved form HIP sintering, low pressure sintering technology only introduces no more than 20MPa inert gas during liquid phase sintering. Low pressure sintering is better to control the grains growth and is not limited by the size of product, so it can reduce the production cost and widely used in practical production.

If the ultrafine crystalline gradient cemented carbide with the surface enriched in binder could be prepared, the service lifetime of coating tool with such substrate might be further prolonged. Ultrafine WC power used to prepare ultrafine crystalline cemented carbide has higher surface energy, so WC grains easily grow in the process of pre-sintering. Therefore, the pre-sintering method which could control grain growth is very important for fabricating the ultrafine crystalline gradient cemented carbide. Thus vacuum pre-sintering and low pressure pre-sintering were used in this paper to prepare ultrafine cemented carbide and the effects of these two pre-sintering technologies on the microstructures of cemented carbide were studied. And then ultrafine crystal gradient cemented carbide with surface enriched in binder were prepared by gradient sintering and the effects of microstructures obtained by two pre-sintering methods on the gradient layer formation and grain growth of ultrafine crystalline gradient cemented carbide were investigated.

2 Experimental

The cemented carbide used in this paper was based on a mixture of WC, (Ti,W)C, Ti(C,N) powders and metallic Co powder. A small amount of VC and Cr_3C_2 was used as grain inhibitors. Powder mixture and particle sizes for the cemented carbide are given in Table 1.

Table 1: Powder mixture and particle sizes for the cemented carbide.

	WC	**Co**	**Ti(C,N)**	**(W,Ti)C**	**VC**	**Cr_3C_2**
Content (wt%)	77	12	4	6	0.35	0.65
Fsss (μm)	0.4	1.0	1.5	1.5	1.0	1.0

The sintering was divided into two steps: pre-sintering and gradient sintering. Two kinds of pre-sintering methods (Vacuum pre-sintering and low pressure pre-sintering) were used. In the process of the vacuum pre-sintering, N_2 gas about 50KPa was introduced when the raising temperature reached 1350°C. Then the specimens were heated up to 1390°C and held for 15 min before furnace cooling to room temperature. In the process of the low pressure pre-sintering, Ar_2 gas about 9 MPa was introduced when the raising temperature reached 1350°C. Then the specimens were heated up to 1410°C and held for 30 min before furnace cooling to room temperature. The two kinds of pre-sintered specimens were then underwent gradient sintering, in which the specimens were heated up to 1430°C and then kept for 1h in a nitrogen free atmosphere before furnace cooling to room temperature.

The sintered specimens were cut perpendicular to the original surface so as to make a cross section visible, embedded in resin and polished according to standard metallographic sample preparation method. The thickness of the gradient layer was measured by scanning electron microscopy (SEM). A field-emission scanning electron microscopy (FESEM) was used to observe the morphology of the prepared cemented carbide bulks. The measurement of WC mean grains size was carried out by use of the Win ROOF software. Average grain size of WC in different shapes and areas was measured according to equivalent diameter method from the FESEM images. These measurements were made on about 600 grains randomly selected for each specimen.

3 Results and discussion

3.1 Pre-sintering

Figure 1 shows the microstructure of cemented carbide sintered with different pre-sintering ways. The microstructures under all the experimental conditions are composed of WC phase (bright areas), Co rich binder phase (dark areas) and cubic (Ti,W)C or Ti(C,N) phases (grey areas). There is no obvious gradient layer formed after these two kinds of pre-sintering ways. The grains size of WC is not uniform and a lot of coarse WC grains with rectangular or triangular shape appear in the alloy sintered by vacuum pre-sintering. Some of the cubic phases formed a complex core-rim structure, as shown in Fig. 1(a). However, after low pressure sintering, the grains size of WC is small, only a little of abnormal WC grains appear and the grains of cubic phase is also small, as shown in Fig. 1(b).

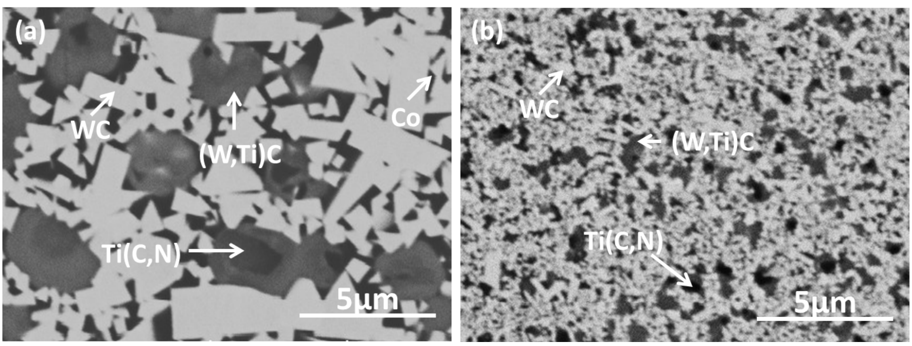

Figure 1: The microstructure of carbide cemented after (a) vacuum pre-sintering and (b) low pressure pre-sintering.

In order to analyze the influence of pre-sintering ways on the grain growth of cemented carbide, the graphical analysis software were used to measure the WC grain size. Figure 2 shows the WC grain size distribution of the specimens prepared by vacuum pre-sintering and low pressure pre-sintering. After vacuum pre-sintering, the WC grains have a size distribution mainly in a range of 0.6-1.2μm. Moreover, a lot of coarse WC grains exist and the largest WC grains can be up to 3μm. The average WC grain is about 0.91μm. Compared with the raw material size of WC powder, the WC grain has high growth rate during vacuum pre-sintering. In the specimen prepared by low pressure pre-sintering, more than 90% fraction of the WC grains distribute statistically in a range of 0.3-0.5μm. Only a little of abnormal WC grains which are more than 0.6μm appear and the average grain size of WC grains are about 0.35μm. The low pressure pre-sintered specimen has a finer grain than the specimen prepared by vacuum pre-sintering.

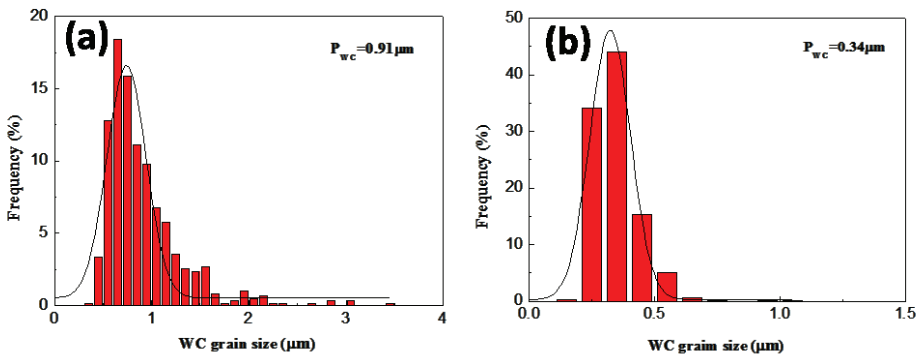

Figure 2: The WC grain size distributions of specimens prepared by (a) vacuum pre-sintering and (b) low pressure pre-sintering.

3.2 Gradient sintering

Figure 3 shows the microstructures of the alloy prepared by gradient sintering in a nitrogen-free atmosphere after two different pre-sintering ways. Gradient layer on the surface zone free from cubic carbides was formed after gradient sintering. The microstructure in the surface is different form that of interior. There are no cubic carbides phases in the surface, where only the WC phase and binder phase appear. In the process of the gradient sintering, the specimens were sintered in an N-free atmosphere, leading to an outward diffusion of N. The gradient in N-activity created by diffusion will lead to an inward diffusion of Ti. In this way a surface zone free of the hard carbonitride phase, and enriched in Co and WC, is created[Schwarzkopf et al. (1988); Gustafson et al. (1994); Frykholm et al. (2013)].

It can be seen from Fig. 3 that the same gradient sintering process forms different thickness of gradient layer for the different pre-sintering methods. The thickness of gradient layer in the alloy prepared by low pressure pre-sintering is 43μm, which is 26.4% thicker than the thickness (34μm) in the alloy prepared by the vacuum pre-sintered. Thickness variation is related to the microstructure of alloy prepared by pre-sintering. After vacuum pre-sintering, the WC grains become coarse and the distribution of binder is uneven. Ti and N atoms need to bypass the coarse WC grains, which increase the diffusion distance during gradient sintering. However, the WC grains of alloy prepared by low pressure pre-sintering are very small and the amount of binder is more in unit area, which may shorten the diffusion distance and increase the diffusion paths for the diffusion of Ti and N during gradient sintering.

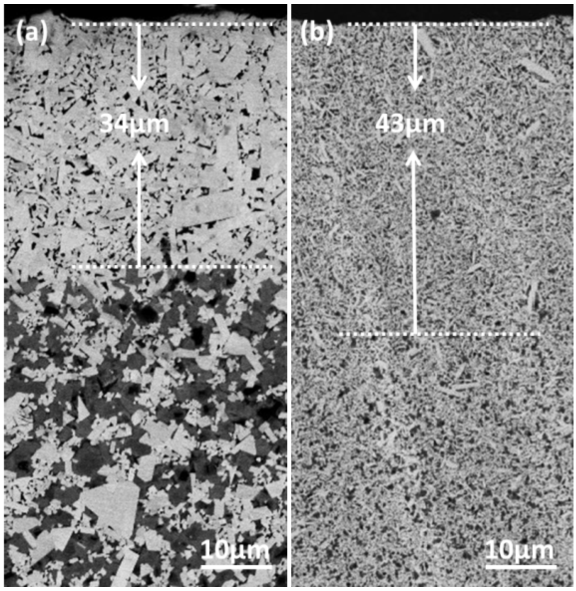

Figure 3: Microstructure at the surface of cemented carbide prepared by gradient sintering after (a) vacuum pre-sintering and (b) low pressure pre-sintering.

Figure 4 shows the inside microstructure of alloy prepared by gradient sintering after different pre-sintering. The morphology of WC grain in the alloy prepared by vacuum pre-sintering is manly rectangular after gradient sintering. There is a great difference in the WC grain size and some large WC grains grow closely together. The cubic phase is also coarse and coarse cubic phases appear from grey at edge to dark at center gradually for the different content of nitrogen [Frykholm et al. (2001)], as shown in Fig. 4(a). There are a little of rectangle plate WC grains in the alloy prepared by gradient sintering after low pressure pre-sintering and most of WC grains are relatively small.

In order to determine the WC grain growth during gradient sintering, the WC grain size distribution of alloy prepared by gradient sintering after different pre-sintering ways were measured, as shown in Fig. 5. In the specimen underwent vacuum pre-sintering, more than 90% of WC grains have sizes in a range of 0.6-1.8μm, about 5% of grains are more than 2μm and the largest WC grains reach to 4.5μm. The average WC grain size (1.03μm) after gradient sintering increase by 0.12μm than that before gradient sintering, which means that the WC grains grow up about 13% during gradient sintering. While, the distribution of WC grain size of alloy underwent low pressure pre-sintering is concentrated. More than 95% of the WC grains have sizes in a range of 0.3-0.6μm and the largest WC grain only reaches

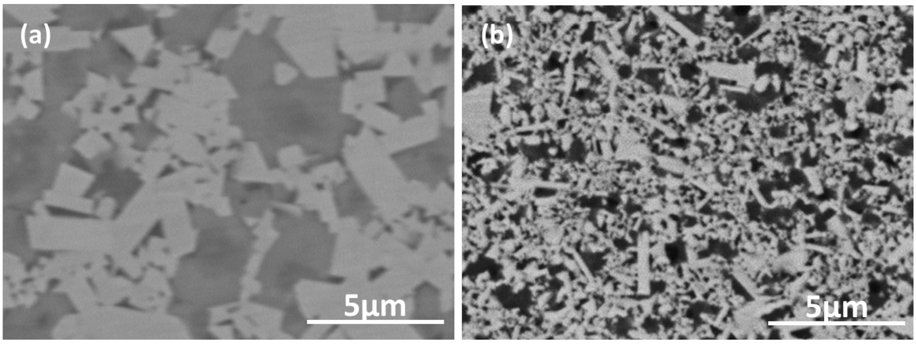

Figure 4: The inside microstructure of carbide cemented prepared by gradient sintering after (a) vacuum pre-sintering and (b) low pressure pre-sintering.

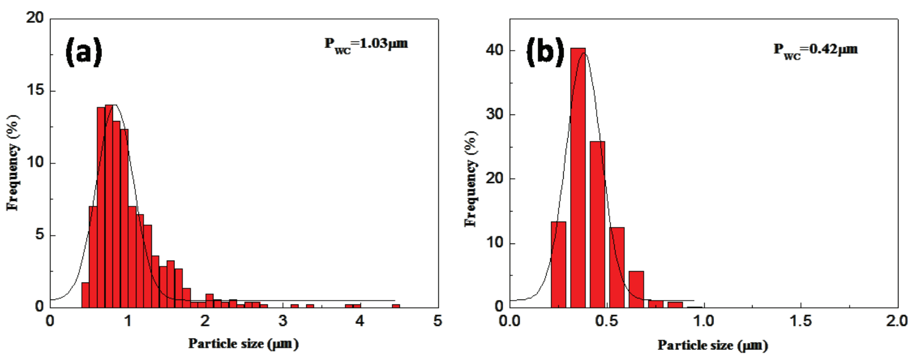

Figure 5: Distribution of WC grain size in the alloys prepared by gradient sintering after (a) vacuum pre-sintering and (b) low pressure pre-sintering.

to 0.8μm. The average WC grain size is 0.42μm, which has increased by 0.08μm than that before gradient sintering.

The WC grains of alloy prepared by different pre-sintering ways have different growth rate during gradient sintering. According to Ostwald ripening theory [Voorhess (1985)], for the great difference in the WC grain size of alloy underwent vacuum pre-sintering, the larger WC grains can easily swallow the smaller grains during the gradient sintering process. While, the alloy underwent low pressure pre-sintering has homogeneous grain size distribution and the WC grains have slow growth rate during gradient sintering. Therefore, Low pressure pre-sintering can suppress the WC grain growth and obtain ultrafine grain cemented carbide and then the ultrafine grain gradient cemented carbide with surface enriched in binder can be obtained by the following gradient sintering.

4 Conclusions

A two-step process, low pressure pre-sintering and gradient sintering, was tried out for the preparation of functionally gradient cemented carbide with ultrafine grains, and the effect of microstructures obtained by low pressure pre-sintering or vacuum pre-sintering on the gradient structure formation and grain growth was studied. Cemented carbide with ultrafine grains can be prepared by low pressure pre-sintering and the average WC grain size is about 0.34μm. The microstructure with fine WC grains and the uniform distribution of binder phase can form thicker gradient layer during gradient sintering for its being benefit to diffusion of N and Ti atoms. Moreover, in the microstructure with homogeneous WC grain size distribution, the WC grains have slow growth rate during gradient sintering. Finally, ultrafine grain gradient cemented carbide with the thickness of gradient layer of 43μm and the average WC grain size of 0.42μm is fabricated by the two-step process.

Acknowledgement: This work was financially supported by the National Science and Technology Major Project of the Ministry of Science and Technology of China (Grant Nos. 2012ZX04003061) and the National Natural Science Foundation of China (Grant Nos. 51101032, 51061130557) and the Fundamental Research Funds for the Central Universities (Grant Nos. N110809001, N120509001).

References

Andrén, H. O. (2011): Microstructure development during sintering and heat-treatment of cemented carbides and cermets. *Mater. Chem. Phys.*, vol. 67, pp. 209-213.

Azcona, I.; Ordóñez, A.; Sánchez, J. M.; Castro, F. (2002): Hot isostatic pressing of ultrafine tungsten carbide-cobalt hardmetals. *J. Mater. Sci,.* vol. 37, pp. 4189-4195.

Agrawal, D.; Cheng, J.; Seegopual, P.; Gao, L. (2000): Grain growth control in microwave sintering of ultrafine WC–Co composite powder compacts. *Powder Metall.,* vol. 43, pp. 15-16.

Azonna, I.; Ordonez, A.; Sanchez, J. M.; Castro, F. (2002): Hot isostatic pressing of ultrafine tungsten carbide-cobalt hardmetals. *J. Mater. Sci.*, vol. 37, pp. 4189-4195.

Breval, E.; Cheng, J. P.; Agrawal, D. K.; Gigl, P.; et al. (2005): Comparison between microwave and conventional sintering of WC/Co composites. *Mat. Sci. Eng. A,*. vol. 391, pp. 285-295.

Cha, S. I.; Hong, S. H.; Kim, B. K. (2003): Spark plasma sintering behavior of nanocrystalline WC–10Co cemented carbide powders. *Mater. Sci. Eng. A,.* vol. 351, pp. 31-38.

Ekroth, M.; Frykholm, R.; Lindholm, M.; Andrén, H. O. (2000): Gradient zones in WC-Ti(C,N)-Co-based cemented carbides: experimental study and computer simulations. *Acta,.* Vol. 48, pp. 2177-2185.

Frykholm, R.; Ekroth, M.; Jansson, B.; Agren, J.; Andren, H. O. (2013): A new labyrinth factor for modeling the effect of binder volume fraction on gradient sintering of cemented carbides. *Acta. Mater.*, vol. 51, pp. 1115-1121.

Frykholm, R.; Andren, H. O. (2001): Development of the microstructure during gradient sintering of a cemented carbide. *Mater. Chem. Phys.*, vol. 67, pp. 203-208.

Gustafson, P.; Ostlund, A. (1994): Binder-Phase Enrichment by Dissolution of Cubic Carbides. *Int. J. Refract. Met. Hard. Mater.*, vol. 12, pp. 129-136.

Jia, C. C.; Tang, H.; Mei, X. Z.; Yin, F. Z.; Qu, X. H. (2005): Spark plasma sintering on nanometer scale WC-Co powder. *Mater Let,.* vol. 59, pp. 2566-2569.

McCandlish, L.E.; Kear, B. H.; Kim, B. K. (1993): Carbothermic reaction process for making nanophase WC–Co powders. *US patent* 5230729.

Milman, Yu. V.; Luyckx, S.; Northrop, I.T. (1999): Influence of temperature, grain size and cobalt content on the hardness of WC-Co alloys. *Int. J. Refract. Met H,.* vol. 17, pp: 39-44.

Suzuki, H.; Hayashi, K.; Taniguchi, Y. (1981): The β-free layer formed near the surface of vacuum-sintered WC-β-Co alloys containing nitrogen. *Trans Jpn Inst Met*, vol. 22, pp. 758-764.

Sivaprahasam, D.; Chandrasekar, S. B.; Sundaresan, R. R. (2007): Microstructure and mechanical properties of nanocrystalline WC–12Co consolidated by spark plasma sintering. *Int. J. Refract. Met. Hard. Mater.,* vol. 25, pp. 144-152.

Schwarzkopf, M.; Exner, H. E.; Fischmeister, H. F. (1988): Kinetics of compositional modification of (W,Ti)C-WC-Co alloy surfaces. *Mater. Sci. Eng. A,.* vol. 105/106, pp. 225-231.

Voorhess, P. W. (1985): The Theory of Ostwald Ripening. *J. Stat. Phys.*, vol. 38, pp. 231-250.

Walter, L.; Klaus, D. (2002): Functionally graded hardmetals. *J. Alloy. Compd.*, vol. 338, pp. 194-211.

Zhang, F. L.; Wang, C. Y.; Zhu, M. (2003): Nanostructured WC/Co composite powder prepared by high energy ball milling. *Scripta Mater,.* vol. 49, pp: 1123-1128.