Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 689–692
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Sintering of binderless tungsten carbide

Kuo-Ming Tsai, Chung-Yu Hsieh, Horng-Hwa Lu *

Department of Mechanical Engineering, National Chin-Yi University of Technology, Taiping City, Taichung County 411, Taiwan, ROC

Received 9 January 2009; received in revised form 27 June 2009; accepted 2 October 2009
Available online 3 November 2009

Abstract

The most widely used mold materials for optical glass molding processes are cemented tungsten carbide and silicon carbide. In this research, tungsten carbide with minor addition of TiC and TiN as the second phase has been studied. The powders were ball-milled and pre-formed under a temperature of 200 °C and a pressure of 130 MPa. The specimens were sintered in a graphite lined furnace at a temperature of 1600 °C. A density of 15.43 g/cm^3, a Vickers hardness number of 23.14 GPa, and a fracture toughness of 6.56 MPa m$^{1/2}$ was found for the sintered specimen fabricated by this process. The result of X-ray analysis revealed no trace of precipitated graphite during sintering, nor the brittle eta-phase as a result of decarburization. Through scanning electron microscopy, spherical air bubbles have been found to precipitate inside the grains, because the activation energy for grain-boundary diffusion is lower than that of the air inside the grains. Therefore it is advisable that the pre-form process is carried out in vacuum.
Crown Copyright © 2009 Published by Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Sintering; Tungsten carbide; Mold material; Binderless

1. Introduction

With the advancement of optical industry, manufacturing processes for polymer lenses are well documented and the materials involved are readily available, however the fabrication technology of mold material for glass molding is still a research in progress. In glass molding processes, optical grade glass globules are heated to 500–600 °C, and compressed in a multi-stage molding machine into lenses with specified aspheric profiles. The mold materials used are generally binderless tungsten carbide or silicon carbide. The form precisions of lenses will be degraded as a result of the difference in thermal expansion coefficients between cobalt binder and the substrate in commercial tungsten carbides. Therefore binderless tungsten carbide has become a crucial material when high-end optical components are required.

A number of transition metal carbides such as WC, TiC and TaC are frequently used in the optical industry. These materials are characterized by their high melting temperature, hardness, abrasive resistance, electrical and thermal conductivity as well as chemical stability. Among these cemented carbides, tungsten carbide is the most widely used because of its high melting point (2785 °C) and hardness (16–22 GPa) [1,2].

Cobalt is often employed in sintering processes for tungsten carbide as the binder phase because of its low melting temperature. The liquid phased cobalt binder provides the sintered product with higher density and toughness. The sintering process for WC will be much more difficult without cobalt or other lower melting-point metals as the binder phase [3]. On the other hand, excessive binder phase lowers the corrosion and oxidation resistance of the cemented carbide [4]. Therefore much research endeavor had been devoted to characterizing the effects of binder concentration on properties of these carbides [4–7]. Composite carbides such as WC–TiC–TaC have found applications in sliding mechanical parts and cushions because of the high resistance to corrosion and wear [4]. Although TiC and WC tend to form solid solution during sintering and strengthen the final product, the abrasive resistance and toughness are lowered because of the precipitated carbon in sintered WC–TiC–TaC composites along WC/TiC boundaries [6,7].

Excessive carbon contents tend to result in precipitated graphite phase which produces cavities and pores in the sintered products. Therefore the mechanical properties of these sintered hard metals are dictated by their carbon content. High carbon content results in low density, low hardness cement carbides.

* Corresponding author. Tel.: +886 4 23924505x7179; fax: +886 4 23930681.
E-mail address: hhlu@ncut.edu.tw (H.-H. Lu).

0272-8842/$36.00. Crown Copyright © 2009 Published by Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2009.10.017

The carbon content is also known to affect grain size of tungsten carbide. Kim et al. [8] reported that for sintered WC–Co, the shape of WC grain is dominated by carbon content. With saturated carbon, triangular WC phase was produced in the sintered WC–Co samples.

Sintering temperature and hence the mechanical properties of the final product are controlled by particle size of the constituents. The activation energy is lowered for nano-scale powders, and hence a low sintering temperature is needed, and cemented carbide with better physical and mechanical properties can be obtained [9,10].

Presently, the sintering processes for WC–Co are extensively studied, whereas less research endeavors are devoted to developing binderless tungsten carbide process technology. This paper primarily discusses the sintering process parameters of tungsten carbide with minor addition of TiC and TiN as the secondary phase.

2. Experimental

2.1. Sample preparation and sintering process

The experimental procedure in this study is shown in Fig. 1. Powders of WC, TiC and TiN together with proper amount of tungsten-steel balls were first filled into a cylindrical container. The container was then placed in a horizontal ball-mill grinder and the powders were dry-milled for 72 h. Volatile solvent was then added to wash the ground powder from the steel balls. The powder mix was then dried and sieved, and was blended in a heated water bath with 2% paraffin. Exactly 30 g of the powder were placed in a hot pressing mold and pressed under a temperature of 200 °C and a pressure of 130 MPa into a circular parison of 30 mm diameter. After hot pressing the sample was degreased in high temperature graphite lined furnace, at a heating rate of 3 °C/min, to 300 °C for 60 min, and then sintered at 1600 °C for 30 min at the same heating rate. The specimen was then cooled in the furnace to room temperature. The heating curve is shown in Fig. 2.

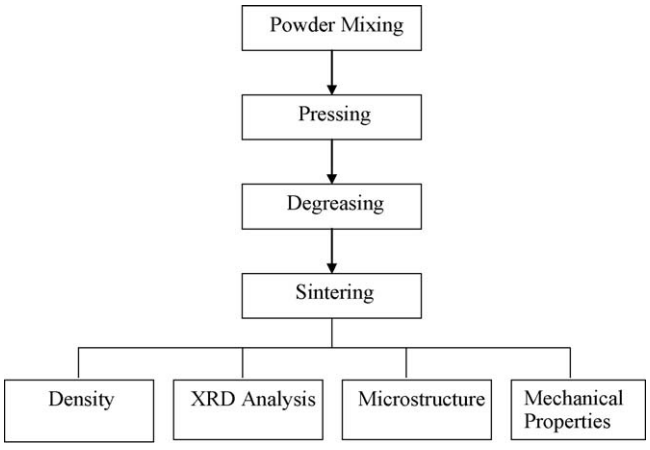

Fig. 1. The flow chart of experimental procedure.

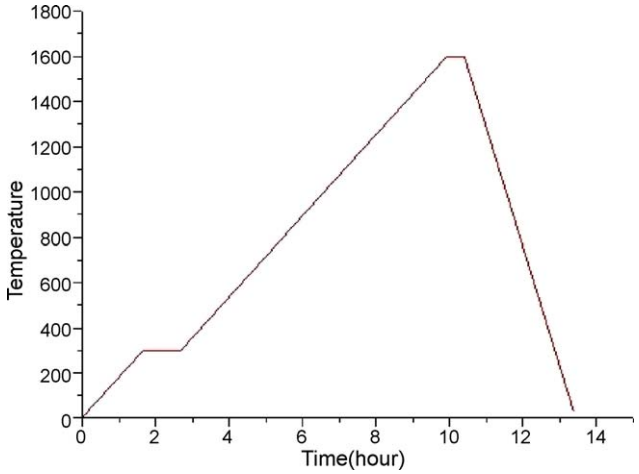

Fig. 2. The heating curve for sintering process.

2.2. Properties measurement

The density measurement was implemented in an electronic microbalance (Sartorius, Model BP221S, German) with a precision of 10^{-4} g, according to ASTM B311-93 standards, based on Archimedes principle. The hardness of the sample was measured in a Vickers hardness machine (Future Tech, FV-700e, Japan). A 98.1 N load was applied on the surface for 15 s using the pyramid shaped Vickers diamond indenter. The measurements were implemented at three different locations on each sample, and the average was taken as the measured value. Vickers indentation test was also used to measure the fracture toughness, K_{IC} (MPa $m^{1/2}$), of samples. All the cracks take Palmqvist form where crack-tips propagate in radial direction, originated from each corner of the indentation [11]. The fracture toughness is known to be inversely proportional to the square root of the overall crack length, therefore K_{IC} of each sample can be determined by measured data.

2.3. OM and SEM micrograph

In order to investigate the microstructure of the surface of sintered specimens, the samples were mounted, grounded in diamond grinding machine from 45 μm down to 0.5 μm, and then polished and observed in optical microscope for surface porosities. The specimens were then etched in a Murakami solution (10 g $K_3Fe(CN)_6$ + 10 g NaOH + 100 ml H_2O) to observe the grain-size distributions of the sintered samples. Also, scanning electron microscope (Topcon SM200) was operated at 20 kV to observe the ball-milled powders as well as the microstructure of sintered product.

2.4. X-ray analysis

X-ray diffraction was used to perform qualitative analysis of the samples. The operating conditions chosen were copper target with a voltage of 40 kV and a current of 100 mA, scanned from 20° to 80° at an increment of 1°/min. JCPDS cards were used to identify the peaks on the diffraction data to determine the phases in the samples.

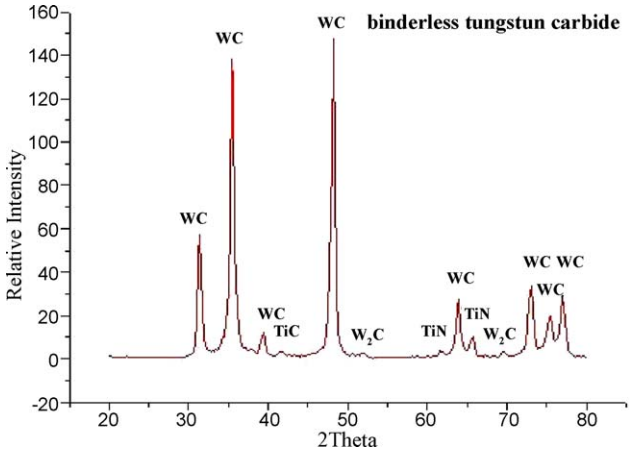

Fig. 3. X-ray diffraction pattern of sintered specimen.

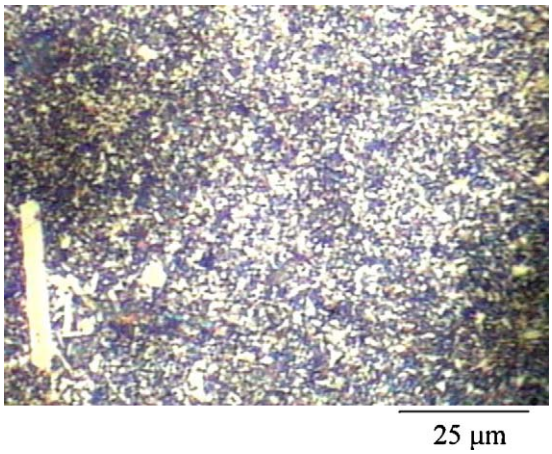

Fig. 5. Metallography for etched specimen shows localized grain growth.

3. Results and discussion

The results of diffraction analysis of sintered products are shown in Fig. 3. No precipitated crystalline carbon has been observed in the samples, whereas the presence of W_2C and few W phase has been identified. The existence of few metallic tungsten impurities in the powder is owing to long grinding time and decarbonization behavior in the sintering process. Tao et al. [12] reported that the presence of oxygen in the chamber consumes carbon and hence lower the carbon content. Metallic tungsten reacts with WC at a temperature of 1250 °C to form W_2C. Also, the amount of W_2C generated is related to the diameter of WC powders. Finer particles possess higher surface energy, and hence are more easily reacted with oxygen during the sintering process. As for the mechanical properties, excess W_2C phases lower the hardness of the sintered samples. This is consistent with the observations of Cha and Hong [13].

Fig. 4 shows the SEM micrograph of pure tungsten carbide where surface porosities are presented. From SEM micrograph, the shapes of the pits are found to be spherical. During the sintering process, without the presence of stresses the porosities will be spherical in shape.

Localized abnormal grain growth has been observed on the etched specimens, as shown in Fig. 5. The rate of abnormal grain growth is generally so fast that it is very difficult to control the microstructure of the cemented carbide. Non-uniform grain growth can arise from inhomogeneous distribution of the particle size. However, further research is needed to determine whether the conglomeration of fine powders is responsible for the abnormal grain growth in binderless tungsten carbide. Sommer et al. [14] postulated that localized deficiency of carbon triggers chemical reactions which result in twining, and the twin boundaries accelerate grain growth. Morton et al. [15] reported that addition of coarse WC particles incurs incongruous grain growth, and that no apparent grain growth was observed with TiC as the inhibitor. In this study TiC was added to verify Morton's study, and the result confirmed that TiC is not an effective grain growth inhibitor.

The Vickers hardness test revealed that the hardness of the sintered product is 23.142 GPa, based on the conditions described in Section 2.3. Fig. 6 shows the micrograph of an indentation where crack-tips initiate from the corners of indented pit and propagate in radial directions. The fracture toughness of the samples is 6.56 MPa $m^{1/2}$, calculated from the data of crack-length measurements. The results of hardness and

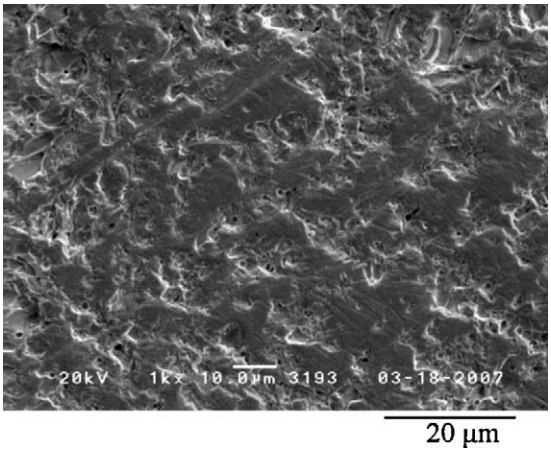

Fig. 4. SEM micrograph of sintered sample.

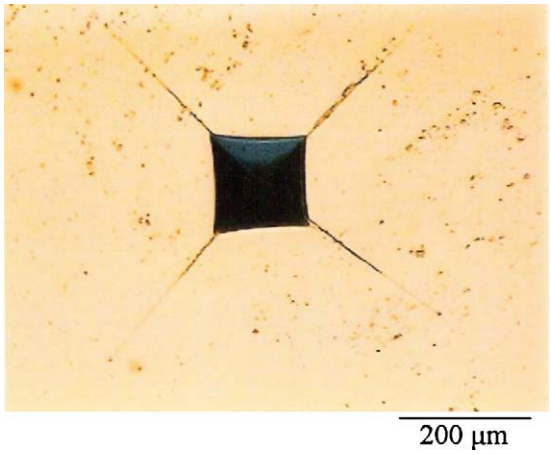

Fig. 6. Indentation of Vickers hardness test (100×).

Table 1
Comparison of the mechanical properties of sintered WC among researches.

Composition	Density (g/cm^3)	Hv (GPa)	K_{IC} (MPa m$^{1/2}$)	Literature
90WC–10Co	–	17.658	6	[16]
95WC–3TiC–1.5TaC–0.5NbC	14.6	18.639	8	[17]
WC–2.9Co	–	19.757	6.5	[18]
WC	–	24.328	6.6	[19]
Binderless WC	15.4	23.142	6.56	This work

fracture toughness from former researchers on various WC materials are listed in Table 1 for comparison [16–19]. It is apparent that the density of sintered WC is improved with appropriate addition of carbides, however it awaits experimental confirmation as to their applicability to ultra-precision machining of optical molds where pure binderless tungsten carbide is often used as the mold material and bulk diamond blade as the cutter. The hardness and the fracture toughness of cemented carbide in this study agree perfectly with the data reported for pure binderless tungsten carbide in Kim's work [19], and are superior to these of the other studies where cobalt is added.

4. Conclusion

In this study binderless tungsten carbide for mold material in optical glass molding is sintered through traditional powder metallurgy process technology. Pure tungsten carbide with minor addition of TiC and TiN as the secondary phase was sintered to a density of 15.4290 g/cm^3, Vickers hardness number of 23.142 GPa, and fracture toughness of 6.56 MPa m$^{1/2}$. X-ray diffraction pattern showed no trace of precipitated graphite or the presence of any brittle eta-phase as a result of decarburization. Localized pits of trapped air was observed in scanning electron micrograph suggesting the mobility of grain-boundary migration is higher than that of porosities during the sintering process of pure tungsten carbide.

References

[1] P. Schwartzkopf, R. Kieffer, Refractory Hard Metals—Boride, Carbide, Nitride and Silicide, MacMillan, New York, 1953.
[2] L.E. Toth, Transition Metal Carbides and Nitrides, Academic Press, New York, 1971.
[3] A. Hirata, H. Zheng, M. Yoshikawa, Adhesion properties of CVD diamond film on binder-less sintered tungsten carbide prepared by the spark sintering process, Journal of Diamond and Related Materials 7 (1998) 1669–1674.
[4] H.C. Kim, I.J. Shon, J.E. Garay, Z.A. Munir, Consolidation and properties of binderless sub-micron tungsten carbide by field-activated sintering, International Journal of Refractory Metals and Hard Materials 22 (2004) 257–264.
[5] S. Imasato, K. Tokumoto, T. Kitada, S. Sakaguchi, Properties of ultra-fine grain binderless cemented carbide 'RCCFN', International Journal of Refractory Metals and Hard Materials 13 (1995) 305–312.
[6] H. Engqvist, G.A. Botton, N. Axen, S. Hogmark, A study of grain boundaries in a binderless cemented carbide, International Journal of Refractory Metals and Hard Materials 16 (1998) 309–313.
[7] H. Engqvist, G.A. Botton, N. Axén, S. Hogmark, Microstructure and abrasive wear of binderless carbides, Journal of the American Ceramic Society 83 (2000) 2491–2496.
[8] S. Kim, S.H. Han, J.K. Park, H.E. Kim, Variation of WC grain shape with carbon content in the WC–Co alloys during liquid-phase sintering, Scripta Materialia 48 (2003) 635–639.
[9] M. Sherif El-Eskandarany, Structure and properties of nano-crystalline TiC full-density bulk alloy consolidated from mechanically reacted powders, Journal of Alloys and Compounds 305 (2000) 225–238.
[10] L. Fu, L.H. Cao, Y.S. Fan, Two-step synthesis of nanostructured tungsten carbide–cobalt powders, Scripta Materialia 44 (2001) 1061–1068.
[11] D.K. Shetty, I.G. Wright, P.N. Mincer, A.H. Clauer, Indentation fracture of WC–Co cermets, Journal of Materials Science 20 (1985) 1873–1882.
[12] L. Tao, L. Qingfa, J.Y.H. Fuha, P.C. Yu, C.C. Wu, Effects of lower cobalt binder concentrations in sintering of tungsten carbide, Materials Science and Engineering 430 (2006) 113–119.
[13] S.I. Cha, S.H. Hong, Microstructures of binderless tungsten carbides sintered by spark plasma sintering process, Materials Science and Engineering 356 (2003) 381–389.
[14] M. Sommer, W.D. Schubert, E.B. Zobet, P. Warbichler, On the formation of very large WC crystals during sintering of ultra-fine WC–Co alloys, International Journal of Refractory Metals and Hard Materials 20 (2002) 41–50.
[15] C.W. Morton, D.J. Wills, K. Stjernberg, The temperature ranges for maximum effectiveness of grain growth inhibitors in WC–Co alloys, International Journal of Refractory Metals and Hard Materials 23 (2005) 287–293.
[16] V. Richter, M.V. Ruthendorf, On hardness and toughness of ultra-fine and nano-crystalline hard materials, International Journal of Refractory Metals and Hard Materials 17 (1999) 141–152.
[17] H. Engqvist, G.A. Botton, N. Axén, S. Hogmark, A study of grain boundaries in a binderless cemented carbide, International Journal of Refractory Metals and Hard Materials 16 (1998) 309–313.
[18] C.D. Park, H.C. Kim, I.J. Shon, Z.A. Munir, One-step synthesis of dense tungsten carbide–cobalt hard materials, Journal of the American Ceramic Society 85 (2002) 2670–2677.
[19] H.C. Kim, I.J. Shon, J.K. Yoon, J.M. Doh, Consolidation of ultra fine WC and WC–Co hard materials by pulsed current activated sintering and its mechanical properties, International Journal of Refractory Metals and Hard Materials 25 (2007) 46–52.