Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 23(2013) 372−376
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Effects of microwave sintering temperature and soaking time on microstructure of WC−8Co

Rui BAO[1], Jian-hong YI[1,2], Yuan-dong PENG[1], Hao-ze ZHANG[1]

1. State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China;
2. School of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

Received 16 November 2011; accepted 14 May 2012

Abstract: WC−8Co cemented carbide samples were processed via microwave irradiation in a 2.45 GHz, high-power multi-mode microwave cavity. The densification of the compacts and the microstructures of the prepared alloys were studied. The results demonstrate that the liquid phase is formed around 1300 °C and nearly full densification is obtained at 1450 °C for 5 min via microwave irradiation. The microstructures of microwave sintered samples have finer and more uniform WC grains than those of vacuum sintered samples. Besides, the WC grain size and distribution are only decided by the sintering temperature. Holding time has negligible effects on them. No matter how holding time is, the mean grain size is 2.7 μm when the sintering temperature is kept at 1450 °C.

Key words: tungsten carbide; microwave sintering; cobalt binder; microstructure; grain size

1 Introduction

To resolve the contradiction of hardness and strength, tungsten carbides which consist of a high volume fraction of the hard hexagonal WC phase embedded within a ductile and tough Co hinder phase are invented by the powder metallurgical method [1]. However, more carbides with excellent and integrated properties are advanced to adapt to the harsh demands and working environment nowadays. Hence, nanocrystalline [2], ultrafine [3] and extra coarse cemented carbide, gradient cemented carbide [4,5] and coated carbide [6] are prepared to further relax the conflict of hardness and strength.

However, it is hard to improve the properties by using conventional sintering methods due to the low heating rate and long holding time. For example, WC−10Co carbide produced by vacuum sintering (the most popular sintering method in carbide industry) will lead to the abnormal growth of WC grains and widen the grain distribution. These are not beneficial to performance improvement. Consequently, some novel processes have been put forward, such as microwave sintering [7,8], spark plasma sintering [9] and high frequency induction-heated sintering [10,11]. Though most of them still have some problems, they show the unlimited potential and application value.

Microwave sintering has been used in powder metallurgy due to the unparalleled characteristics such as accelerated heating rate, shortened processing cycle, high energy efficiency, fine and homogeneous microstructure, and enhanced mechanical performance [12]. Up to now, some work has been reported about carbide preparation by microwave processing. According to BREVAL et al [7], microstructural investigation by TEM showed that in microwave sintered material nearly no tungsten dissolved in the cobalt phase, whereas in conventionally sintered samples up to 20% tungsten was dissolved in the cobalt binder phase. Besides, microwave sintered samples have better properties such as excellent resistance and uniform shrinkage. But, they did not account for the effect of processing conditions on the dissolution behavior of WC in the Co binder. Microwave reaction sintering of a powder mixture of metallic tungsten, carbon and cobalt was explored by RDÖIGER et al [13], and obtained finer microstructures than by the conventional route. SUNIL et al [14] reported that

Foundation item: Project (51274107) supported by the National Natural Science Foundation of China
Corresponding author: Jian-hong YI; Tel: +86-731-88877328; Fax: +86-731-88710855; E-mail: yijianhong2007@sohu.com
DOI: 10.1016/S1003-6326(13)62472-3

microwave sintering of raw crystalline WC−12Co compacts yielded samples with slightly better properties. Limited experimental investigations, however, can be found in the processing of tungsten carbide.

In this work, we focused on the microwave sintering of WC−8Co carbide by a multi-mode microwave furnace with frequency of 2.45 GHz and discussed the effects of sinter temperature and holding time on sintered samples.

2 Experimental

Samples with a composition of 92WC−8Co (mass fraction, %) were prepared from WC and Co powders. Sodium-butadiene rubber (2.0%) was mixed to ensure the good forming property. No grain growth inhibitors were premixed in the WC−8Co powder. The compacts were shaped into cylindrical and sintered in a microwave furnace with frequency of 2.45 GHz and maximum power of 5.5 kW after removing the sodium-butadiene rubber in a conventional furnace. Temperature is measured using an infrared pyrometer (RaytekMM2MH, US) with an emissivity of 0.75. The compacts were placed in the center of alumina-fiber insulations with SiC serving as a susceptor. The SiC susceptor was used and mounted, encircling the compact to inhibit the heat loss. The stage supporting the insulations turns clockwise at a speed of 5 r/min. The heating rate is adjusted by changing the input power of magnetron [15]. The entire processing was carried out in pure N_2 atmosphere.

The sintered samples were vertically cut and polished to a 1.0 μm finish. The microstructures of the samples were observed under a scanning electron microscope without chemical etching in order to obtain more reliable grain size data. The average grain size of a cross-section was measured using analytical software. At least 1000 grains were examined for each sample with different fields and averaged. The three-dimensional average grain size was obtained from the measured two-dimensional data by multiplying the latter by 1.5, and are presented as the grain size data [16]. The degree of sintering is characterized by densification (η) as

$$\eta = \frac{\rho_s - \rho_g}{\rho_t - \rho_g}$$

where ρ_t, ρ_s and ρ_g are theoretical, sintered and green densities of sample, respectively.

3 Results and discussion

In our work, heating rates were controlled in the range of 30−40 °C/min. Most samples were held for 5 min when a given temperature was reached by microwave sintering. Then, the microwave heating system was cut off and cooled to the room temperature in the furnace. The entire processing requires only one-sixth time of that in the vacuum sintering.

Compared with the vacuum sintering, microwave sintering can optimize the microstructures of the prepared samples. The geometrical shape of all obtained samples was well maintained, and no bubbling or distortion was observed. The microstructures of samples prepared by different sintering methods are given in Fig. 1.

It can be seen from Fig. 1 that the mean grain size prepared by microwave irradiation is much smaller compared with that prepared by vacuum sintering. By analysis the microstructures with the mean chord intercept method, the mean grain sizes were obtained, which are 2.7 μm by microwave irradiation and 3.7 μm by vacuum sintering, respectively. Also, samples obtained by microwave sintering have more uniform grain size. Smaller grains and narrower grain distribution give the microwave sintered samples more superior mechanical properties.

The temperature measure during the microwave processing is usually paid the most attention. A pyrometer which is based on the temperature sensing optical properties is always used in microwave processing. Some authors believe that this optical device can be sensitive to the emissivity of the target material, which can lead to temperature measurement errors [14]. In our work, the emissivity of an infrared detector is set at 0.75. As shown in Fig. 2, a sudden increase in densification turns up near the temperature of 1300 °C from 22% to 48%. During the liquid phase sintering, once liquid forms, the densification can be improved quickly. By the way, this temperature is very close to the eutectic temperature of carbides. Hence, we speculate that the liquid forms at this temperature. This shows that the measurement error using infrared pyrometer must be small and the emissivity we set is suitable. Moreover, the response time of pyrometer is 2 ms, which is helpful to reduce the measurement errors of temperature by avoiding the transient disturbance.

Figure 2 shows the densification of microwave sintered WC−8Co samples as a function of the temperature. Nearly full densification is obtained when the sintering temperature reaches 1450 °C holding for 5 min. Additionally, we also can see from Fig. 1 that the WC grains are all transformed to well-defined angular shaped platelets even the samples are obtained at such a high heating rate and short holding time by microwave processing. Atoms may accelerate diffusion when samples are exposed in the microwave fields and the densification can be enhanced in a short holding time [17].

The effects of soaking time on microstructure of WC−8Co samples are also studied. It can be seen from

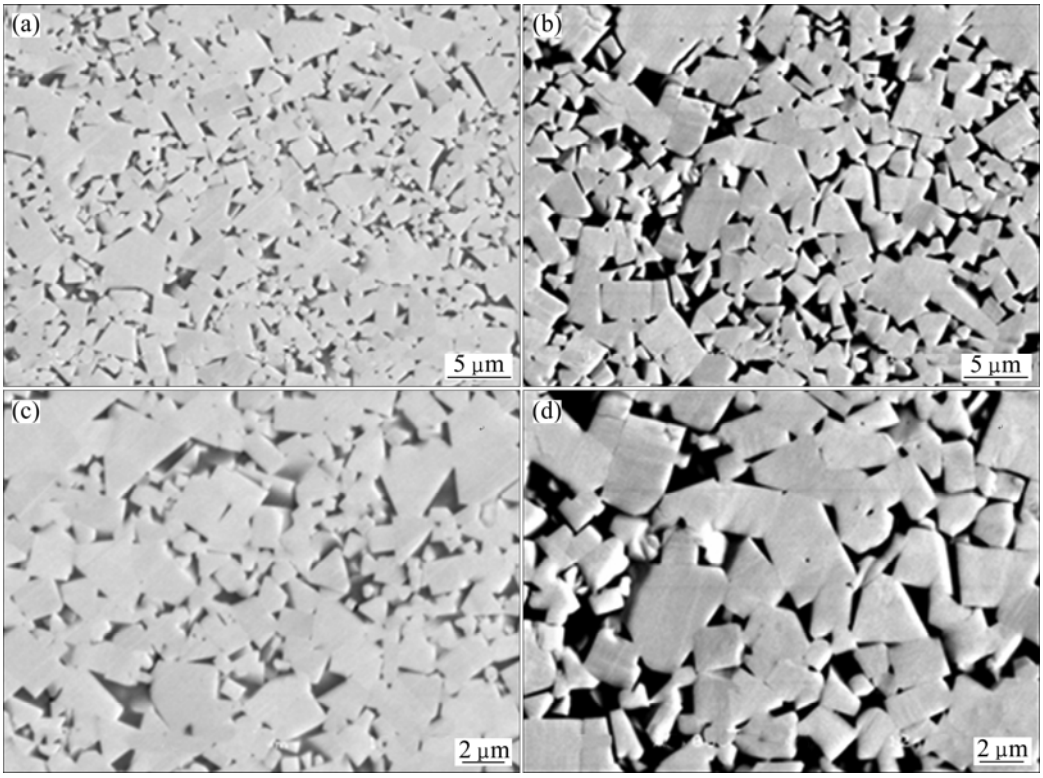

Fig. 1 SEM micrographs of sintered WC−8Co samples by different preparation methods: (a, c) Microwave irradiation (1450 °C, 5 min); (b, d) Vacuum sintering (1450 °C, 120 min)

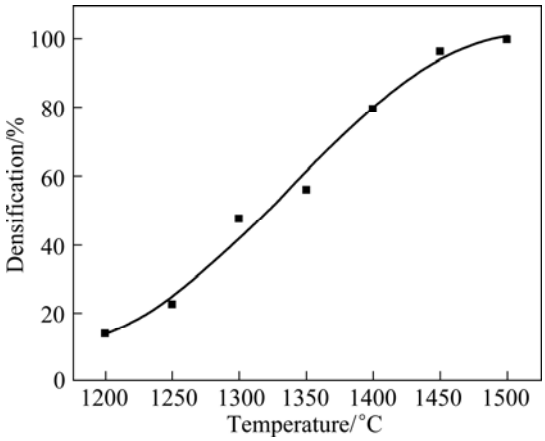

Fig. 2 Densification of microwave-sintered WC−8Co samples as function of temperature (holding time: 5 min)

Fig. 3 (microstructures of microwave sintered samples with different holding time) that there is no obvious difference on grain size and shape between holding time of 5 min and 60 min.

In order to verify the result from the observation above, samples sintered at 1450 °C for 0, 5, 10, 30, and 60 min, respectively are prepared. The mean grain sizes of them are shown in Fig. 4.

From Fig. 4 the WC mean grain size of the microwave prepared samples does not increase as the soaking time increases. All the mean grain sizes of

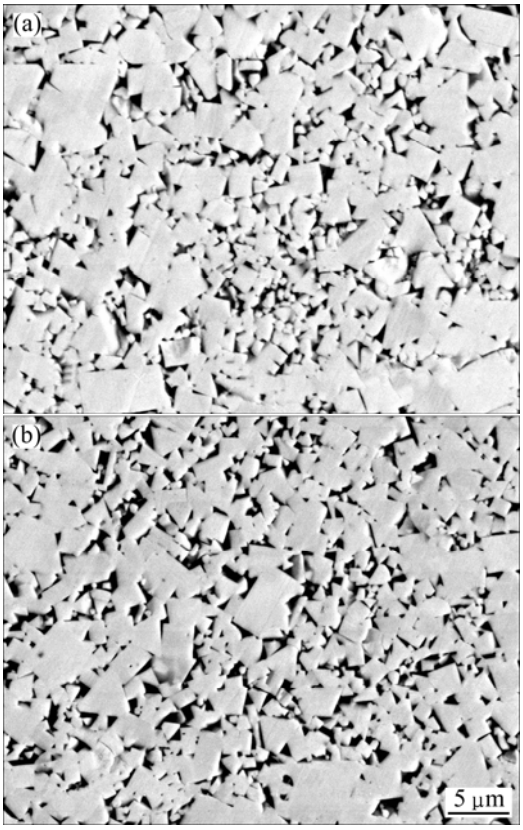

Fig. 3 Microstructures of microwave-sintered WC−8Co samples at 1450 °C for different soaking time: (a) 5 min; (b) 60 min

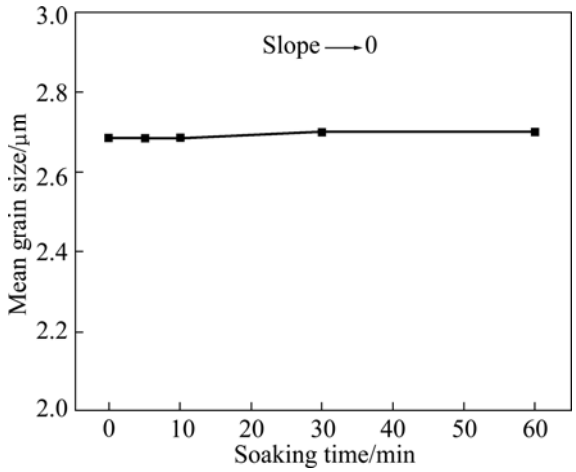

Fig. 4 WC mean grain sizes of microwave sintered WC−8Co samples at 1450 °C for different soaking time

samples with different soaking time are close to 2.7 μm. This finding is important for preparing tungsten carbides because it might offer hope to control WC grain size and distribution. The more uniform microstructure might improve the mechanical properties.

The mechanism of this finding is not clear yet. BREVAL et al [7] compared the WC−Co samples sintered by microwave and conventional methods and reported that in the microwave sintered material the cobalt phase dissolved nearly no tungsten, whereas in conventional sintered samples up to 20% was dissolved in the cobalt binder phase [7]. If they are correct, the dissolution-reprecipitation mechanism of WC−Co will not happen. This means that the growth of WC grains is mainly related to coalescence of grain-to-grain contacts, and non-continuous growth does not exist during the microwave processing.

In our study, however, in microwave sintered samples the tungsten content dissolved in the cobalt binder phase is much higher than that in vacuum sintered samples (see Fig. 5). A TEM study and EDS analysis show that the tungsten dissolved in the region *A* is about 16.8% higher than that in region *B*. The solubilities of W in regions *A* and *B* are 30.41% and 13.61%, respectively.

The solubility of tungsten in the cobalt binder phase depends on the sintering temperature. In order to compare the solubility of samples prepared by two different sintering methods, both of them have the same sintering temperature. The cause of higher tungsten solubility may be due to the microwave effect, which is considered to promote the atom diffusion. A possible explanation for the finding of no grain growth with soaking time is that only dissolution of W and C atoms in the cobalt binder phase happens, no precipitation occurs during the microwave processing. Furthermore, this discovery is very essential for producing tungsten

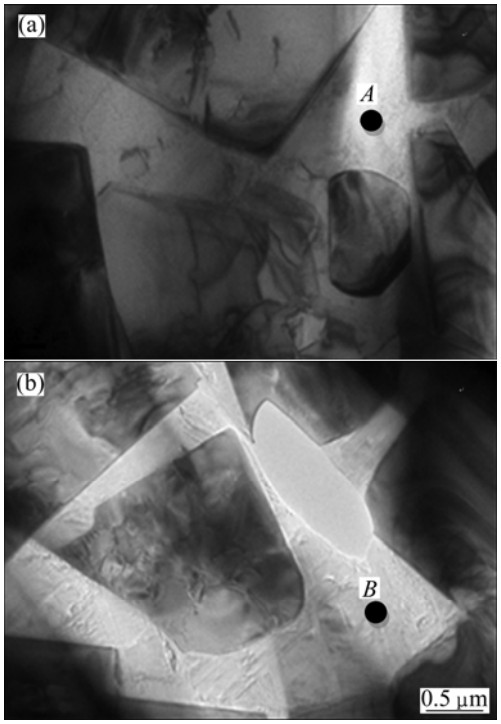

Fig. 5 TEM bright-field images of WC grain and Co binder phase of sintered WC−8Co samples by different sinter methods: (a) Microwave irradiation (1450 °C, 5 min); (b) Vacuum sintering (1450 °C, 120 min)

cemented carbide with nanometer or coarse crystalline WC grains. Both of them are the main research directions of cemented carbide industry.

In existing condition, preparing nanocrystalline tungsten cemented carbide powder is not a problem. According to the reports, using the chemical vapor synthesis and spray conversion process can produce nanosized WC or WC_{1-x} powder with particles size mostly less than 100 nm [2]. For preparing bulk nanostructured WC−Co cements, rapid growth of WC crystal grains is extremely difficult to control with the increase of sintering temperature and soaking time owing to the high surface energy [18]. Using microwave sintering only the influence of sintering temperature could be taken into account because there is no grain growth with the soaking time. As long as we choose an optimum sintering temperature, the WC grain growth will decrease to the largest degree. Moreover, the heating rate under microwave irradiation is 3−12 times higher than that under the conventional heating treatment (about 10 °C/min), which makes the effect of sinter temperature on grain growth relatively small.

Coarse grain carbides are widely used for the instruments because of their excellent performance of hardness and strength. But, due to the dissolution-precipitation mechanism, the grain distribution

broadened during the sintering processing. If the sample is prepared by microwave sintering, more uniform microstructure will be expected. The only thing to do is choosing the coarse powder with a narrow size distribution. This will lead to uniform microstructure by microwave processing, which makes the sample have more excellent performances.

4 Conclusions

1) Nearly full densification of WC−8Co cemented carbide can be obtained at 1450 °C holding for 5 min by microwave irradiation.

2) Compared with vacuum sintered samples (3.7 μm), finer grains (2.7 μm) and more uniform grain size have been found in the microwave prepared ones.

3) There is no obvious relationship between the holding time and grain size of the prepared cemented carbide using microwave irradiation. No matter how holding time is, all of the mean grain size are 2.7 μm when sintering temperature reaches 1450 °C.

4) The solubility of tungsten in cobalt phase of microwave sintered samples is almost 16.8% higher than vacuum sintered ones.

References

[1] KIM H C, OH D Y, SHON I J. Sintering of nanophase WC–15vol.%Co hard metals by rapid sintering process [J]. International Journal of Refractory Metals & Hard Materials, 2004, 22: 197−203.

[2] FANG Z Z, WANG X, RYU T, HWANG K S, SOHN H Y. Synthesis, sintering and mechanical properities of nanocrystailline cemented tungste carbide−A review [J]. International Journal of Refractory Metals & Hard Materials, 2009, 27: 288−299.

[3] SUN L, YANG T E, JIA C C, XIONG J. VC, Cr_3C_2 doped ultrafine WC−Co cemented carbides prepared by spark plasma sintering [J]. International Journal of Refractory Metals & Hard Materials, 2011, 29: 147−152.

[4] FAN P, GUO J, FANG Z Z, PRICHARD P. Design of cobalt gradient via controlling carbon content and WC grain size in liquid-phase-sintered WC−Co composite [J]. International Journal of Refractory Metals & Hard Materials, 2009, 27: 256−260.

[5] FANG Z Z, ESO O O. Liquid phase sintering of functionally graded WC−Co composites [J]. Scripta Materialia, 2005, 52: 785−791.

[6] DUCROSA C, BENEVENTB V, SANCHETTEB F. Deposition, characterization and machining performance of multilayer PVD coatings on cemented carbide cutting tools [J]. Surface and Coatings Technology, 2003, 163−164: 681−688.

[7] BREVAL E, CHENG J P, AGRAWAL D K, GIGL P, DENNIS M, ROY R, PAPWORTH A J. Comparison between microwave and conventional sintering of WC/Co composites [J]. Materials Science and Engineering A, 2005, 391: 285−295.

[8] AGRAWAL D, CHENG J, SEEGOPAUL P, GAO L. Grain growth control in microwave sintering of ultrafine WC−Co composite powder compacts [J]. Powder Metallurgy, 2000, 43: 15−16.

[9] SIVAPRAHASAM D, CHANDRASEKAR S B, SUNDARESAN R. Microstructure and mechanical properties of nanocrystalline WC−12Co consolidated by spark plasma sintering [J]. International Journal of Refractory Metals & Hard Materials, 2007, 25: 144−152.

[10] KIM H C, SHON I J. Rapid sintering of ultra-fine WC−10 wt% Co by high-frequency induction heating [J]. Journal of Materials Science, 2005, 40: 2849−2854.

[11] KIM H C, OH D Y, GUOJ J, SHON I J. Synthesis of WC and dense WC−5vol.% Co hard materials by high-frequency induction heated combustion [J]. Materials Science and Engineering A, 2004, 368: 10−17.

[12] GUO Y L, YI J H, LUO S D, ZHOU C S, CHEN L F, PENG Y D. Fabrication of W−Cu composition by microwave infiltration [J]. Journal of Alloys and Compounds, 2010, 492: L75−L78.

[13] RÖDIGER K, DREYER K, GERDES T, WILLERT-PORADA M. Microwave sintering of hardmetals [J]. International Journal of Refractory Metals & Hard Materials 1998, 16: 409−416.

[14] SUNIL B R, SIVAPRAHASAM D, SUBASRI R. Microwave sintering of nanocrystalline WC−12Co: Challenges and perspectives [J]. International Journal of Refractory Metals & Hard Materials, 2010, 28: 180−186.

[15] ZHOU C S, YI J H, LUO S D, PENG Y D, LI L Y, CHEN G. Effect of heating rate on the microwave sintered W−Ni−Fe heavy alloys [J]. Journal of Alloys and Compounds, 2009, 482 (1−2): L6−L8.

[16] YANG D Y, KANG S L. Suppression of abnormal grain growth in WC−Co via pre-sintering treatment [J]. International Journal of Refractory Metals & Hard Materials, 2009, 27: 90−94.

[17] DEMIRSKYI D, RAGULYA A, AGRAWAL D. Initial stage sintering of binderless tungsten carbide powder under microwave radiation [J]. Ceramics International, 2011, 37: 505−512.

[18] BAO Rui, YI Jian-hong, PENG Yuan-dong, ZHANG Hao-ze, LI Ai-kun. Decarburization and improvement of ultra fine straight WC−8Co sintered via microwave sintering [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(4): 853−857.

烧结温度和保温时间对微波制备 WC−8Co 硬质合金显微组织的影响

鲍 瑞[1]，易健宏[1,2]，彭元东[1]，张浩泽[1]

1. 中南大学 粉末冶金国家重点实验室，长沙 410083；2. 昆明理工大学 材料科学与工程学院，昆明 650093

摘 要：采用 2.45 GHz 高功率多模腔微波炉制备 WC−8Co 硬质合金，对压坯的收缩率和合金的显微组织进行研究。结果表明：液相温度出现在 1300 °C 附近；在烧结温度 1450 °C 下保温 5 min 能获得几乎全致密的合金试样。微波烧结法制备的合金晶粒要比真空烧结制备的合金晶粒尺寸细小且分布更均匀。另外，WC 晶粒的尺寸和分布主要取决于烧结温度；保温时间对合金晶粒的影响很小，无论在 1450 °C 下保温多长时间 WC 平均晶粒的尺寸始终保持在 2.7 μm。

关键词：硬质合金；微波烧结；钴相；微观结构；晶粒尺寸

(Edited by Xiang-qun LI)