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Materials

Manufacture of the Ultrafine Grain WC/Co Cemented Carbides by Combined Sintering Processing

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Abstract: A new kind of sintering process, combined sintering process, *i.e.* vacuum sintering plus hot isolate pressure sintering (HIP), was introduced for producing ultrafine WC-10%Co (mass fraction, so as the follows) cemented carbides. The effects of some processing parameters on the microstructure and mechanical properties of the obtained cemented carbides were studied. The results show that the rapid shrinkage and the pronounced densification of the cemented carbides took place during the vacuum sintering stage, which is intimately correlated with the local liquid sintering occurred during this early sintering stage for the high surface activity of ultrafine WC-Co powder. The way of high pressure imposing, isothermal treatment cycle during vacuum sintering and HIP sintering stage directly influence the densification of compacts and the mechanical properties of the produced WC-10%Co cemented carbides.

Keywords: ultrafine WC-Co cemented carbides; vacuum sintering; HIP sintering

1 Introduction

Over the years, the research on ultrafine WC-Co cemented carbides has attracted much attention all over the world for the materials were acknowledged to possess excellent mechanical properties such as high fracture strength, high hardness, high toughness and good wear-resistance, *et al.* [1–3]. To produce ultrafine WC-Co cemented carbides, the conventional sintering techniques such as vacuum sintering, H_2-sintering have become limited owing to the fact that the densification of compacts during these processes always has to resort to high sintering temperature and long sintering cycle, which inevitably results in the pronounced growth of WC grains. Therefore, even with the proper addition of WC grain growth inhibitor, the ultrafine structure of WC-Co cemented carbides can not be obtained by the methods. While hot pressed sintering and high isolate pressure (HIP) sintering techniques can accelerate the densification of compacts with the aid of exterior stress provided by gas medium, and significantly shorten sintering cycle and lower sintering temperature, and thereby have been widely used for manufacturing ultrafine-grained materials. However, mono-axially imposed strain involved in hot pressed sintering always leads to non-uniform shrinkage and densification of compacts. On the other hand, although HIP sintering process can provide enough large and uniform driving force for densification, the high pressure and requirements of high pressure resistance of equipment involved in HIP sintering make it unfeasible to scale up to the industrialized production.

In this article, a new kind of combined sintering technique was undertaken to produce ultrafine WC-Co cemented carbides, in which vacuum sintering and HIP sintering were reasonably integrated. The vacuum sintering was performed at a low temperature and the HIP sintering was conducted at a high temperature and a relatively low pressure (5MPa). The integrating vacuum sintering with HIP sintering is based on the fact that the residual gas remained in compacts can be efficiently expelled at vacuum atmosphere and the densification of compacts can be accelerated by HIP sintering. The detailed characteristics of the combined sintering process will be discussed in the following.

2 Experiment

The raw powder, ultrafine WC-10%Co (mass fraction, so as the follows) composite powder was synthesized by reducing and carbonizing the composite of tungsten and cobalt oxides in a fluidized reactor [4]. As shown in **figure 1** (a), the raw powder contains lots of large agglomerates, which will definitely affect the sintering of compacts. Therefore, in order to obtain the uniform-structured cemented carbides, it is necessary to break these agglomerates. First, the powder was added with 0.2% vanadium carbide (VC) which can act as

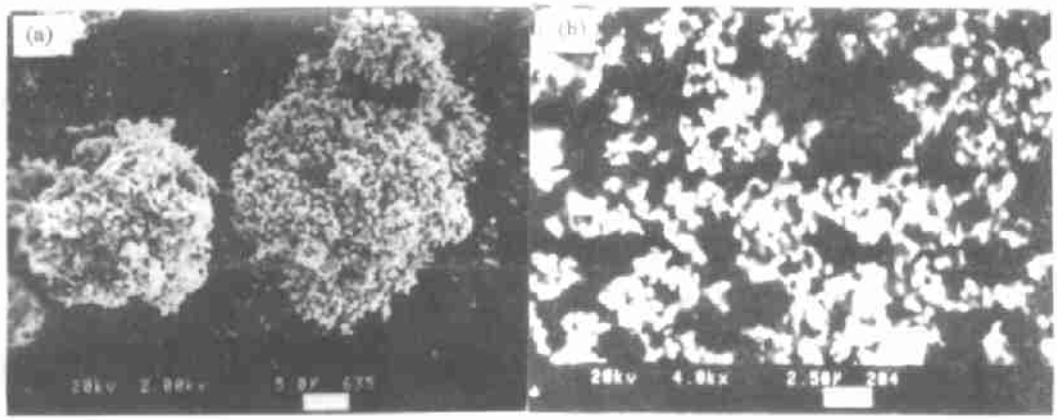

Figure 1 The SEM photograph of ultrafine WC-10%Co composite power, (a) before the ball-milling; (b) after 27 h ball-milling.

the WC grain growth inhibitor during sintering [5], and then was ball-milled in a planetary mill for 27 h at the rotating rate of 120 r/min. The ball-milling medium was alcohol free of water. The SEM (Scanning Electron Microscope) photographs of the ball-milled powder was shown in figure 1 (b), which suggested that the large agglomerates were effectively pulverized into small particles with relatively uniform size distribution. The powder were shaped into 6 mm×6 mm×30 mm compacts by the combined shaping process, *i.e.* shearing shaping and dry pressing process [6].

The compacts were firstly put in a vacuum sintering furnace for wax expelling at 400 ℃ for 40 min, then were sintered in a combined sintering furnace for the combined sintering. Four different experimental runs R1–R4 were carried out for studying the effects of sintering processes on the mechanical properties of the produced cemented carbides. The detailed processing parameters of these four experimental runs are listed in **table 1**. The curves of temperature raising, high pressure imposing and shrinkage during the run R1 are shown in **figure 2**, while for the run R2–R4, the curves are shown in **figure 3** and **figure 4** respectively.

Table 1 The relation between the processing parameters and mechanical properties of the ultrafine WC-10%Co produced by combined sintering

Experimental runs	Processing parameters of the combined sintering							Mechanical properties of samples		
	Vacuum sintering stage			HIP sintering stage						
	P / Pa	T / ℃	τ / min	t_1 / ℃*	P / MPa	t_2 / ℃*	τ / min	Fracture strength/MPa	Hardness HRC	ρ g·cm^{-3}
Run 1	20	1 240	10	1 240	5	1 340	20	1 230	80.1	12.90
Run 2	20	1 240	30	1 240	5	1 340	20	1 470	83.3	13.85
Run 3	20	1 240	30	1 300	5	1 340	20	1 750	87.0	14.01
Run 4	20	1 240	30	1 300	5	1 340	40	1 890	92.4	14.18

* t_1: the temperature at which Argon gas of high pressure was puffed into the furnace;
* t_2: the temperature at which HIP sintering was conducted.

The sintered samples for measuring fracture strength and Vickers hardness were cut into the size of 4 mm× 4 mm × 30 mm, and the tests were carried out with MTS ceramic mechanical testing machine and Vicks hardometer respectively. The density was measured by Archimedes methods. The mechanical properties of the WC-Co cemented carbides produced under the different sintering conditions were listed in table1. The fracture surface of the carbides was observed by SEM (Cambridge instrument, S-250), as shown in **figure 5**

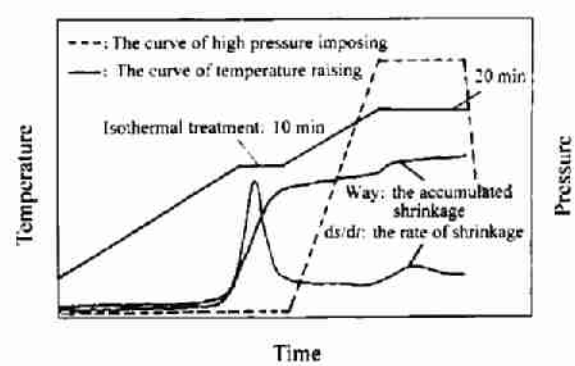

Figure 2 The curves of sintering process and shrinkage of ultrafine WC-10%Co cemented carbides during the experimental run R1

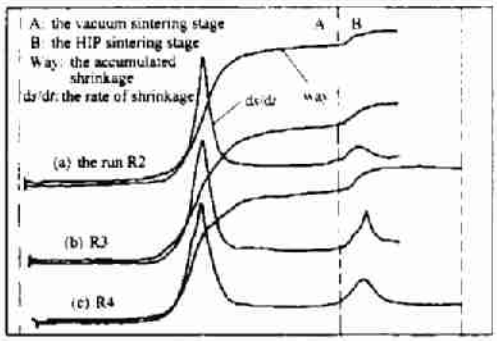

Figure 3 The curves of shrinkage of ultrafine WC-10%Co cemented carbides sintered by the experimental runs R2–R4

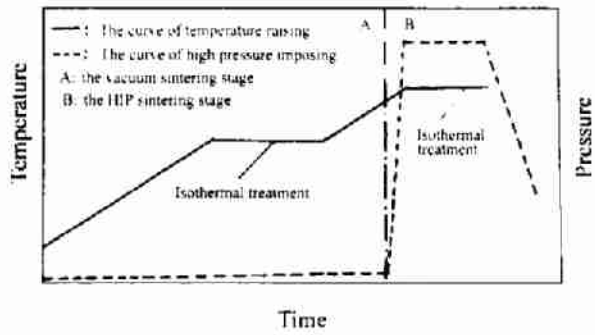

Figure 4 The curves of sintering processing during the experimental runs R2–R4. (Note: the time and temperature during the HIP sintering of the experimental runs R2–R4 are listed in table 1).

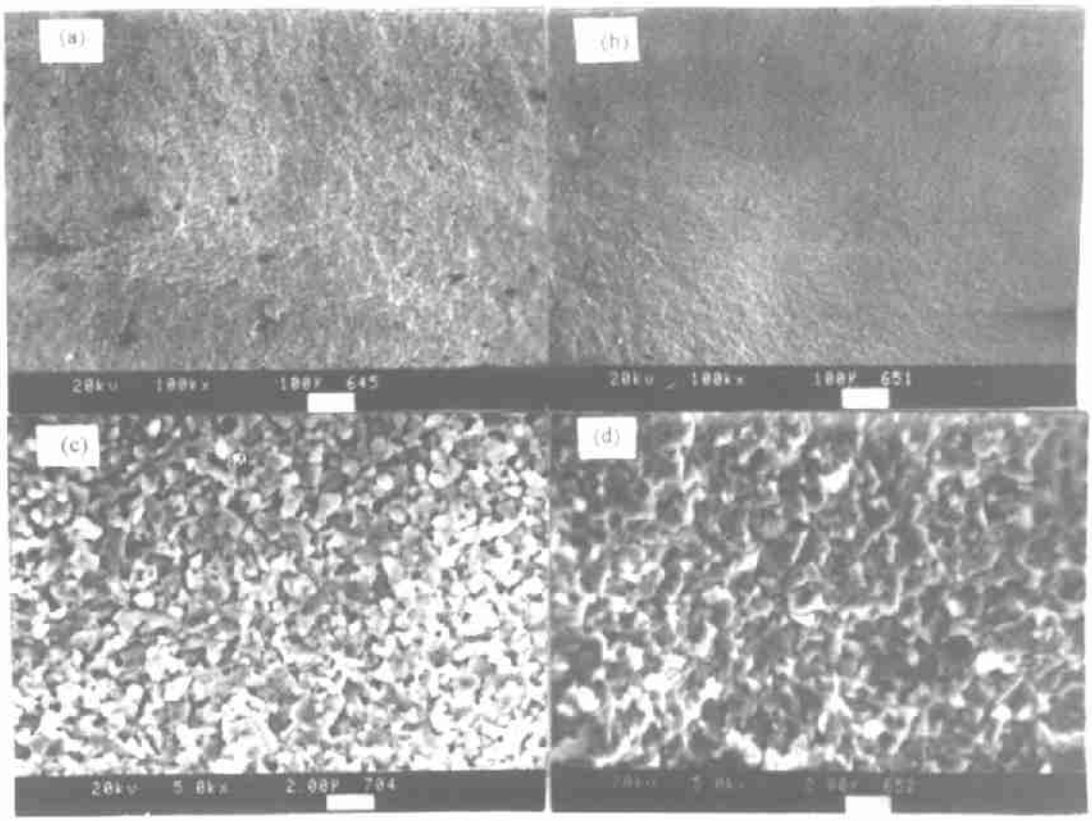

Figure 5 The SEM photographs of the fracture surface WC-10%(+0.2%VC) cemented carbides produced by the combined sintering, (a) Produced by the run R1; (b) Produced by the run R2; (c) Produced by the run R3; (d) Produced by the run R4.

(a), (b), (c) and (d). The average WC grain size was estimated from about 100 particles in SEM photographs, and the numerical error of which was below 5%.

3 Results and Discussion

In this study, the combined sintering was carried out in two steps. Firstly, vacuum sintering was conducted at a relatively low temperature of 1 240 ℃; Following the vacuum sintering, the HIP sintering was performed at 1340 ℃ and at the pressure of 5 MPa imposed by Argon gas. Because the liquid sintering of ultrafine WC-Co cemented carbides occurred at 1 280 ℃ [7], the vacuum sintering involved in the combined sintering is virtually the solid state sintering, while the HIP sintering pertains to the liquid sintering.

3.1 The early rapid shrinkage of ultrafine WC-Co cemented carbides during solid state sintering (*i.e.* vacuum sintering) stage

As regards ultrafine WC-Co cemented carbides, the shrinkage during solid state sintering can be up to 90% of the total shrinkage, as suggested by Scubert [7], apparently larger than that of the standard-sized cemented carbides, 80% of the total shrinkage. Our experimental

results also suggest the same tendency, as shown by the curves of the accumulated shrinkage (way curves) in figures 2 and 3. Therefore, the classical mechanism of solo solid mass transferring involved in solid state sintering of standard-sized WC-Co cemented carbides can not reasonably interpret this phenomenon. Schubert proposed a new coarsening mechanism of WC grains during solid state sintering of ultrafine WC-Co cemented carbides, in which the "coalescence" of ultrafine WC particles was realized by thin film (solid/liquid) migration or by thin film-aided solution-reprecipitation [7]. However, the argument didn't provide a clear interpretation how the liquid film could form.

During solid state sintering, the atoms of W and C will dissolve into cobalt phase by solid mass transferring mechanism and formed as γ phase, *i.e.* Co(W, C) solid solution. The interfacial reaction can be shown by the following equation:

$$WC + 2Co = Co(W) + Co(C) \quad (1)$$

As to ultrafine WC-Co composite powder, the WC grains possess high surface activity, which endows W and C atoms with high self-diffusion activity. Therefore, the activation energy of the interfacial reaction (1) can be remarkably decreased, which significantly accelerates the dissolution of W and C atoms into cobalt phase. As a result, the eutectic composition of WC-Co binary system can be rapidly achieved at relatively low temperature such as 1 280 ℃ or even lower, which consequently leads to liquid sintering. As a result, when vacuum sintering was conducted at 1 240 ℃ in this study, even if liquid sintering hasn't occurred throughout the compacts, it is possible that local liquid sintering would have taken place beforehand in some micro regions where extremely fine WC particles assemble. **Figure 6** (a)–(d) illustrates the process of the

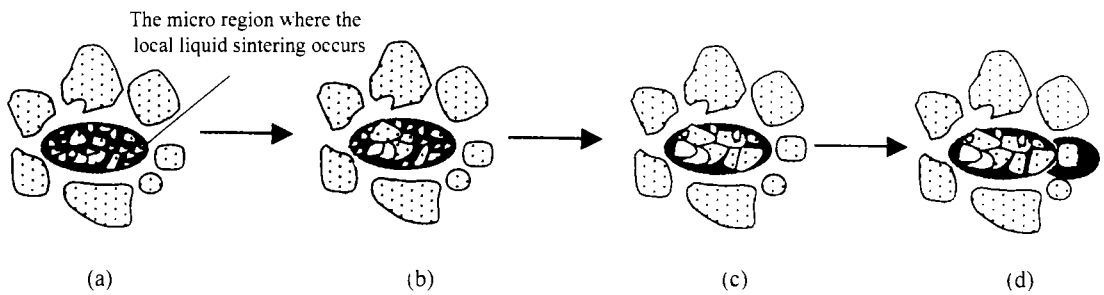

Figure 6 The schematic drawing of the process of local liquid sintering

local liquid sintering.

The existence of local liquid sintering lies in two facts. First, it is impossible to obtain mono-dispersed WC-Co powder by mechanical pulverizing method; thus, there always assemble some particles of relatively small size in some micro regions where they adhere together for the high surface energy, as shown in figure 6 (a). Second, the high surface activity of these relatively small particles enables W and C atoms diffuse into cobalt binder at high rates. As a result, the local liquid sintering occurs beforehand in these micro regions.

Once the local liquid sintering takes place, it will greatly accelerate mass transferring between WC and Co phases through the local liquid mass transferring and consequently result in the rapid coarsening of these fine particles as shown in figure 6 (b) and (c). During the subsequent sintering, the resulted coarse particles can readily act as seed crystals for further grain coarsening by solid/liquid mass transferring between these coarsened particles and other neighbored particles [7], as shown in figure 6 (d). The local liquid sintering is also well demonstrated by the curves of shrinking rate, *i.e.* ds/dt curves in figure 2 and figure 3 (a)–(c). The greatest shrinking rate of ultrafine WC-10%Co compacts during the combined sintering occurred at 1240 ℃, which was apparently correlated with the occurrence of the local liquid sintering.

Therefore, the local liquid sintering remarkably accelerated the mass transferring between WC grains and cobalt binder, and hence greatly accelerated the growth of WC grains and the densification of compacts. As a result, up to 90% of shrinkage occurred during the solid state sintering stage, *i.e.* the vacuum sintering stage. On the other hand, the coarsening of WC grains also weakened the local liquid sintering. As suggested by ds/dt curves in figure 2 and figure 3 (a)–(c), the rate of shrinkage was not constant during the vacuum sintering. After reaching the greatest value, the rate of shrinkage slows down rapidly. It suggested that, after the coarsening of WC grains, the dissolution rate of W and C atoms into cobalt phase decreased, and the local liquid sintering can't continue to be dominant for the limited amount of liquid phase at 1 240 ℃.

3.2 The effects of processing parameters on the mechanical properties of the produced ultrafine WC-CO cemented carbides

(1) The effects of isothermal treatment cycle during the vacuum sintering stage.

The experimental results show that, under otherwise identical condition, the time of the isothermal treatment during the vacuum sintering greatly affects the mechanical properties of the produced cemented carbides, which can be demonstrated by the experimental runs R1 and R2. It is well recognized that , at the temperature above 1 100 ℃, some quantity of the gas will be generated for the reaction between free carbon and oxides in WC-Co compacts [3]. The gas together with the residual gas jumbled during shaping should be effectively expelled in order to get compacts fully densified. However, the reaction and gas expelling are relatively slow processes, for which an isothermal treatment for a certain time is necessary. In this case, if the isothermal treatment is too short, a large quantity of residual gas will be inevitably left in compacts. With the following liquid sintering, the residual gas will be wrapped by liquid phase and formed as small pores, which will consequently lower the density and worsen the mechanical properties of the sintered compacts. The fact is well corroborated by the results of the experimental runs R1 and R2. In the run R1, as indicated by table 1, the time of the isothermal treatment during vacuum sintering was only for 10 min, while in the run R2, it was for 30 min. Therefore, the fracture strength, hardness and density of the samples produced by the run R1 were apparently lower than that of the samples produced by the run R2. As shown in figure 5 (a) and (b), some micro pores can be clearly observed in the fracture surface of the cemented carbide produced by the run R1, while for the sample produced by the run R2, a more densified structure appears, no micro defects can be observed at this resolution.

(2) The effects of isothermal treatment cycle and the way of high pressure imposing during the HIP sintering.

Generally, the driving force for densification during vacuum sintering is limited, although the vacuum atmosphere can ameliorate the moistening between WC grains and cobalt binder. Therefore, the following HIP sintering appears to be a necessary and effective way to get the compacts further densified with the aid of exterior stress imposed by the gas of high pressure. In this study, three different HIP sintering processes, *i.e.* the experimental runs R2, R3 and R4, were conducted for studying the effects of the processing parameters of HIP sintering. The processing parameters of these experimental runs are listed in table 1. According to the experimental results, both the isothermal treatment time and the way of high pressure imposing substantially affect the mechanical properties of the produced WC-Co cemented carbides.

1) The effects of isothermal treatment cycle during the HIP sintering.

As to the effects of the isothermal treatment, it is well understood that the longer the thermal treatment, the higher the density of the obtained sample is expected. The curves of the shrinking rate (ds/dt curves) in figure 3(c) suggested that the detectable shrinkage of compacts only occurred during the first 20 min, while during the following 20 min, no shrinkage can be detected. Therefore, the ds/dt and way curves in figure 3 (c) appeared as smooth level lines for the late 20 min of the HIP sintering. The fact indicated that a large majority of the micro defects in WC-Co compacts such as pores, crackles were effectively and rapidly eliminated after the first 20 min HIP sintering and only very small quantity of micro defects were left. As expected, the shrinkage during the subsequent sintering became so weak that is undetectable. Nonetheless, the weak shrinkage during the late 20 min sintering was still beneficial to improving the mechanical properties of WC-10%Co cemented carbides.As indicated in table1, the density, fracture strength and hardness of the samples that were HIP sintered at 1 340 ℃ for 40 min (by the run R4) are all higher than that of the carbides sintered at 1 340 ℃ for 20 min (by the run R3). The tendency was also demonstrated by the SEM photographs of the fracture surface in figure 5 (c) and (d). As illustrated by SEM observations, the samples produced by the experimental run R4 have a more densified structure than that of the samples produced by the run R3. The reason for this can be well apprehensively ascribed to the continuance of eliminating micro defects during the late 20 min of HIP sintering. On the other hand, photographic analysis shows that the average WC grain size of the ultrafine cemented carbides shown in figure 5 (c) and (d) are all less than 0.5 μm. Therefore, although the cycle of the HIP sintering during the experimental run R4 is twice as long as that during the run R3, no obvious enhanced growth of WC grains can be observed. The reason for this can be ascribed to the effects of the grain growth inhibitor, VC.

2) The effects of the way of high pressure imposing during HIP sintering.

In this study, two different ways of high pressure imposing were undertaken. As indicated by table 1, for the

experimental run R2, the argon gas of high pressure was puffed into the furnace at the temperature of 1 240 ℃ (t_1), while for the experimental run R3, the high pressure was imposed at 1 300 ℃. The different ways of high pressure imposing result in different mechanical properties of the sintered cemented carbides. For the samples produced by the run R2, the mechanical properties such as fracture strength, hardness are all obviously lower than those of the samples produced by the experimental run R3, as suggested by table 1.

At 1 240 ℃, although the local liquid sintering took place, the wholly liquid sintering hadn't occurred. If the gas of high pressure is imposed at 1 240 ℃, some quantity of gas will easily leak into compacts through the access formed by some interlocked micro pores that haven't been eliminated during the vacuum sintering. Therefore, with the subsequent temperature raising and the appearance of large quantity of liquid phase, these pores saturated with the gas of high pressure will be consequently wrapped by liquid phase. Although HIP sintering can provide enough large driving force of densification, it is very difficult to eliminate these closed pores suspending in the liquid phase. As a result, the sintered WC-Co cemented carbides are of high porosity and poor mechanical properties as indicated by table 1.

4 Conclusions

(1) Up to 90% shrinkage and the substantial densification of ultrafine WC-Co cemented carbides occurred during the vacuum sintering stage. The rapid shrinkage and densification of compacts during this early sintering stage is closely correlated with the local liquid sintering, which occurs in some micro regions where assemble extremely fine WC grains. It is the high self-diffusion activity of W and C atoms of these fine particles that enables the local liquid sintering to take place beforehand in these micro regions.

(2) The isothermal treatment during the vacuum sintering stage should be long enough to expel the residual gas in compacts. Otherwise, the residual gas will be wrapped by liquid phase and lower the density of sintered compacts.

(3) Lengthening the isothermal treatment during the HIP sintering is conductive to improving the mechanical properties of the produced ultrafine WC-Co cemented carbides. Because of the effects of the grain growth inhibitor (VC), no obvious grain growth can be observed, although the isothermal treatment during the HIP sintering is prolonged.

(4) The way of high pressure imposing has great effects on the densification of compacts. To avoid the gas of high pressure leaking into compacts, the high pressure should be imposed when solely liquid sintering has taken place.

Acknowledgment

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