研 究

New Design of Microstructure of WC-Co/TiC-Al₂O₃ Composite Materials
by Mechanical Coating of Particles

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SYNOPSIS

In order to design a microstructure of a sintered composite material as uniform as possible, an experimental investigation was carried out by preparation of WC particles coated with Co, Al₂O₃, and TiC by high-speed rotational impact blending. The composite material was then fabricated by spark plasma sintering. The compositions were changed with different ratios of TiC to Al₂O₃. The comparatively uniform microstructure was obtained corresponding to the coated particle model. The composition of 55WC-10Co-30TiC-5Al₂O₃ yielded the highest values of Vickers hardness and transverse rupture strength due to uniform dispersion of each component and generation of Al₂O₃ particulate reinforcement effect with less pores than other compositions.

KEY WORDS

coated particle, microstructure, cemented carbide, rotational impact blending, spark plasma sintering

1 Introduction

WC-Co cemented carbides are currently the most important hard materials in a wide range of hardness and toughness combinations. And they are used in various applications, such as metal cutting, stone cutting, rock drilling, and wear tools. Many attempts have been made to create WC-Co composite by dispersing several ceramic phases into the WC-Co matrix. The kind of additive materials, sintering methods and particle sizes have been investigated to improve the mechanical properties.

Nevertheless, in reality, when a material is fabricated, not only those things are important and influence mechanical behavior of materials, but also the morphology of the microstructure such as uniform dispersion of additives or particle arrangement in the powder mixture becomes predominant for final properties of sintered products.

A mechanically coated particle is a process which may constitute a suitable starting point in the preparation of new composite materials. The properties of the sintered materials will depend on the degree of dispersion of the constituting particles throughout the formed material block. A highly uniform particle mixture can be obtained from mechanical mixing or coating of core particles with fine ones¹⁾.

The purpose of the present study is to attempt to design a uniform microstructure of WC-Co/TiC-Al₂O₃ composite

materials by preparation of coated particles by means of a high-speed rotational blending machine for various compositions to obtain high mechanical properties.

2 Experimental Procedures

2.1 Apparatus

Usually, cemented carbides have been prepared by mixing particle components with an ordinary ball mill. Recently, authors¹⁾ adopted a high-speed rotational blending machine, Hybridizer (Type NHS-1; Nara Machinery), schematically shown in Fig. 1, for the preparation of surface composite particles, for the higher mechanical properties of the sintered materials should stem from higher uniformity of each component in the microscopic scale as compared with the case of the ball mill. The coating chamber is surrounded with a jacket in which coolant is circulated. This processing can be summarized as follows: particles inside the casing of Hybridizer are mixed and circulated in a high-speed air stream caused with a rotor, and are hit repeatedly among other particles, the wall of a stator and the blades of the rotor. As a result of these mechanical actions, small particles become fixed on the surface of large ones. Hybridizer can be operated by changing the rotational speed for a certain period of treatment time²⁾.

2.2 Particle samples

Table 1 lists the size and true density of starting particles.

Fig.1 Experimental apparatus of Hybridizer for fabricating surface composite particles.

WC coarse particles (WC60-41400N) are core ones, Co is binding or matrix phase after sintering (UM Cobalt & Energy Products), and high purity TiC (Wako Pure Chemical Industries, Ltd) and Al₂O₃ (AL-160 SG-3, Showa Dekiko K.K.) are fine coating particles. WC-Co/TiC-Al₂O₃ coated powder contained 0–30 wt% TiC, and 0–30 wt% Al₂O₃ with fixed percentage of 55WC-10Co. For comparison, mixtures of 55WC-10Co-35TiC, and 55WC-10Co-35Al₂O₃ by weight percentage were also prepared by the same method with Hybridizer, as listed in Table 2.

2.3 Powder preparations

2.3.1 Mixing ratio

When the surface of a coarse particle is coated with a monolayer of fine particles, the number of fine particles, N , depends on their arrangement. The maximum value, N_m , corresponding to the hexagonal close packing on a plane (and) is given by³⁾

$$N_m = \frac{2\pi}{\sqrt{3}} \left(\frac{D}{d_i} + 1 \right)^2 \quad (1)$$

where D is the diameter of coarse particle, and d_i is the diameter of fine particle of component i .

The mixing ratio of component i , M_{ri} , is defined as the ratio of the net volume of fine particles in mono-layer based on Eq. (1) to the total volume of mixed particles.

$$M_{ri} = \frac{N_{mi} d_i^3}{\sum_{i=1}^n N_{mi} d_i^3 + D^3} \quad (2)$$

2.3.2 Surface coating

The preparation of surface composite particles was

Table 1 Starting particles with Hybridizer.

Components	Average size (μm)	Particle density (g/cm^3)
WC	6	15.60
Co	1.4	8.84
TiC	0.9	4.90
Al ₂ O ₃	0.5	3.97

Table 2 Compositions of WC-Co composites.

Composition (wt%)	TiC content (wt%)	Al ₂ O ₃ content (wt%)
55WC-10Co	-	35
	5	30
	10	25
	15	20
	20	15
	25	20
	30	5
	35	-

carried out by two steps to form multi-layer coated particles designed⁴⁾, as shown in Fig. 2. At first, WC core particle was coated with Co particles, and then TiC and Al₂O₃ particles were added to be fixed on the surface of WC core ones with Co binding layer by means of Hybridizer at rotational speed of 8,000 rpm for treatment time of 10 min for each step.

2.4 Sintering process

The coated powder prepared were sintered under vacuum at pressure of 50 MPa for 5 min at 1680 °C in graphite dies by means of spark plasma sintering apparatus (SPS), (Sumitomo Coal Mining, DR.SINTER, SPS-1050). Sintered disks thus obtained (by SPS) were 25 mm in diameter and 5 mm thick.

2.5 Microstructures and mechanical properties

All the disks formed were ground with diamond grinder with 400-grit and 1000-grit and polished with diamond paste of particle size 3, 1 and 0.25 μm by turns. The polished disks were cut into bars of 1.5 mm $\times$ 2.0 mm $\times$ 30 mm for strength, hardness and fracture toughness measurements. The bars were polished with a 1000-grit diamond finish on one side and were leveled parallel to their lengths in order to eliminate edge flaws for strength testing. The transverse rupture strength (TRS) was measured with a material testing

Fig.2 Preparation steps of WC-Co/TiC-Al₂O₃ surface composite particles.

Fig.3 SEM photographs of (a) individual WC-Co/TiC-Al₂O₃ coated particle prepared by means of Hybridizer and of (b) the surface of coated particle.

machine (SHIMADZU, Autograph-DSS10TS) applying three-point bending test with a span length of 20 mm and a crosshead speed of 0.05 mm/min. The microstructures were observed by means of scanning electron microscopy (SEM), (JEOL, JSM-5410). Vickers hardness (HV) was measured with a Vickers indenter under the load of 294 N and loading duration of 15 s. Each test was repeated at least six times.

X-ray diffraction (XRD) (JEJO, JDX-3500) measurement was conducted to determine the phase composition of the sintered samples using Cu-K α radiation. The chemical compositions of the samples were analyzed by Energy Dispersive X-ray Spectrometer (EDX).

3 Experimental Results and Discussion

3.1 WC-Co/TiC-Al₂O₃ composite particles

Fig. 3 (a) illustrates individual WC-Co/TiC-Al₂O₃ coated particles. The surface of WC particle was coated with Co and embedded with TiC and Al₂O₃ fine particles by means of Hybridizer, as shown in Fig. 3 (b), which corresponds to the coated particle model in the Fig. 2 satisfactorily.

3.2 Formation of uniform microstructure of WC-Co/TiC-Al₂O₃ composite

3.2.1 Influence of compositions on microstructure

In order to obtain a uniform microstructure of sintered materials corresponding to the coated particle model in Fig. 2,

coated particles of various compositions were prepared and then the microstructures were observed with SEM.

Fig. 4 shows the microstructure of the composites. In case of the composite of 55WC-10Co-35Al₂O₃ without TiC in Fig. 4(a), WC particles were aggregated, connected with Co binding phase and presented in Al₂O₃ matrix. Aggregation of WC particles occurred in the sintering stage and they precipitated in Co liquid phase which has the high surface tension as a driving force to solder WC particles together. Furthermore, the addition of 35wt% Al₂O₃ into cemented carbide was associated with diffusion of carbon from WC towards Al₂O₃⁵⁾. In this case, CO evolved and produced the pores inside the material⁵⁾, as shown in Fig. 4(a). However, the formation of a small amount of carbon excess could be attributed to the diffusion of carbon within the graphite dies during sintering, even though the dies had been coated inside with BN. In addition, to find the cause of the formation of carbon excess, only Al₂O₃ powder and the Al₂O₃ powder containing methanol and ethylene glycol were sintered in the graphite dies⁶⁾. From the XRD study the presence of carbon peaks was indicated in XRD pattern,

as shown in Fig. 5 (a).

Fig.5 XRD patterns of sintered materials of (a) 55WC-10Co with 35Al₂O₃, (b) 55WC-10Co with 35TiC, (c) 55WC-10Co with 20TiC-15Al₂O₃ and (d) 55WC-10Co with 30TiC-5Al₂O₃ composites.

Fig.4 SEM photographs of (a) 55WC-10Co with 35Al₂O₃, (b) 55WC-10Co with 35TiC, (c) 55WC-10Co with 20TiC-15Al₂O₃ and (d) 55WC-10Co with 30TiC-5Al₂O₃.

○ WC ● TiC-WC ● Al₂O₃

In the composite of 55WC-10Co-35TiC without Al_2O_3 in Fig. 4(b), WC particles were dispersed in the TiC to form TiC-WC or β -phase, which was confirmed by EDX analysis, as shown in Fig. 6. The proportion of β -phase is to be increased with higher TiC contents⁷⁾. However, TiC-WC system might produce the carbon excess as free carbon peaks, as shown in XRD pattern of Fig. 5(c). Since TiC and TiC-WC solid solutions mostly contain TiO or TiN contaminations, they should produce macro- or micropores⁷⁾ depending on their amount of free carbon and TiO, as high porosity appeared in Fig. 5(c).

Fig. 4(c) shows the microstructure of composite of 55WC-10Co with the addition of 20TiC-15 Al_2O_3 . WC grains were non-uniformly dispersed and surrounded by the β -phase and presented in Al_2O_3 phase with less pores. As the result, this composition generates different microstructure from the coated particle model in the Fig. 2 in comparison with the case mentioned below.

Fig. 4(d) shows the microstructure of composite of 55WC-10Co-30TiC and 5 Al_2O_3 . WC gains were uniformly dispersed in TiC-WC matrix phase and surrounded with Al_2O_3 grains to generate particulate reinforcing effect. In spite of Al_2O_3 lower sintering temperature than β -phase, the grain growth of Al_2O_3 will be controlled due to hard β -phase⁸⁾ Furthermore, a part of WC was dissolved and uniformly dispersed in the solid solution of β -phase, which suppressed the coarsening of Al_2O_3 grains and thus acted as a grain growth inhibitor for less pores. This TiC-WC system may also produce the carbon excess, as shown in XRD pattern as carbon peaks in Fig. 5(d).

Here, we can conclude that this composition of 55WC-10Co-30TiC and 5 Al_2O_3 yielded the ideal microstructure with uniform dispersion of each component corresponding to the coated particle model in comparison with other

compositions, as shown in Figs. 2, 6 and 7.

3.2.2 Effect of compositions on mechanical properties

Fig. 8 shows Vickers hardness of WC-Co/TiC- Al_2O_3 composites. The hardness increased with higher amount of TiC from 5 up to 30 by weight percentage. With a sample of 35TiC without Al_2O_3 addition, the hardness got lower. As a result, the highest hardness was obtained from the combination of 30TiC and 5 Al_2O_3 addition due to generation of Al_2O_3 particulate reinforcing effect around WC gains with uniform dispersion in TiC-WC matrix phase, as mentioned in the above section.

Fig. 9 shows the changes in the transverse rupture strength (TRS) of WC-Co/TiC- Al_2O_3 composites as a function of TiC- Al_2O_3 addition. The TRS was increased with increasing TiC content up to 30% and decreasing Al_2O_3 because of the higher uniform dispersion of Al_2O_3 or the greater particulate reinforcing effect with decreasing amount of pores, as shown in Figs. 4 and 7. Increase in Al_2O_3 additions

Fig. 7 Cross-section of individual coated particle in WC-Co/TiC- Al_2O_3 sintered composite.

Fig. 6 EDX pattern of 55WC-10Co-30TiC-5 Al_2O_3 composite.

Fig. 8 Vickers hardness as a function of TiC-Al₂O₃ additive content.

yielded high porosity due to gas products, as mentioned before and also with the composite of 35TiC without Al₂O₃ addition. The highest TRS was obtained with the composition of 55WC-10Co with 30TiC and 5Al₂O₃ addition due to more uniform dispersion of WC and Al₂O₃ grains in TiC-WC matrix phase.

4 Summary

The uniform dispersion of each component was attained with coated particles prepared by means of Hybridizer. As a result, the designed microstructure of the sintered composite corresponding to the coated particle model was obtained with the composition of 55WC-10Co-30TiC-5Al₂O₃ to yield the highest values of Vickers hardness and transverse rupture strength.

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Fig. 9 Transverse rupture strength as a function of TiC-Al₂O₃ additive content.

References

- 1) S.Kangwantrakool and K.Shinohara: "Preparation of New WC-Co/TiC-Al₂O₃ Composite Materials with Mechanically Coated Particles", J. Chem. Eng. Japan, 34(2001)1486-1492.
- 2) K.Shinohara, H.Liang and T.Uchiyama: "Mixing and Lightness Characteristics of Fine particles Coated by High-Speed Rotational Impact Blending", J. Ceram. Soc. Jpn., 108(2000)402-406.
- 3) T.M.Jones and N.Pilpel: "Some Physical Properties of Lactose and Magnesia", J. Pharm. Pharmacol., 17(1965) 440-448.
- 4) M.Koishi, H.Honda, T.Matsuno and O.Hoojiro: Biryushi-Ultra Fine Particle, Tekku Pub.Co.Ltd., Tokyo, (1989).
- 5) W.Acchar, A.E.Martinelli, F.A.Vieira and C.A.A.Cairo: "Sintering Behavior of Alumina-Tungsten Carbide Composites", Mater. Sci. Eng., A28(2000)84-87.
- 6) W.P.Tai and T.Watanabe: "Fabrication and Mechanical Properties of Al₂O₃-WC-Co Composites by Vacuum Hot Pressing", J. Am. Ceram. Soc., 81(1998)1673-1676.
- 7) S.Paul and K.Richard: Cemented Carbides, Macmillan, New York, (1960).
- 8) L.Wang, J.L.Shi, Z.L.Hua, J.H.Gao and D.S.Yan: "The Influence of Addition of WC Particles on Mechanical Properties of Alumina-Matrix Composite", Material Letters, 50(2000)179-182.