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Application of Recycled Tungsten Carbide Powder for Fabrication of Iron Based Powder Metallurgy Alloy

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Abstract**—**Tungsten carbide is widely used as a tool material in metal manufacturing process. Since tungsten is typical rare metal, establishment of recycle process of tungsten carbide tools and restore into cemented carbide material bring great impact to metal manufacturing industry. Recently, recycle process of tungsten carbide has been developed and established gradually. However, the demands for quality of cemented carbide tool are quite severe because hardness, toughness, anti-wear ability, heat resistance, fatigue strength and so on should be guaranteed for precision machining and tool life. Currently, it is hard to restore the recycled tungsten carbide powder entirely as raw material for new processed cemented carbide tool. In this study, to suggest positive use of recycled tungsten carbide powder, we have tried to fabricate a carbon based sintered steel which shows reinforced mechanical properties with recycled tungsten carbide powder. We have made set of newly designed sintered steels. Compression test of sintered specimen in density ratio of 0.85 (which means 15% porosity inside) has been conducted. As results, at least 1.7 times higher in nominal strength in the amount of 7.0 wt.% was shown in recycled WC powder. The strength reached to over 600 MPa for the Fe-WC-Co-Cu sintered alloy. Wear test has been conducted by using ball-on-disk type friction tester using 5 mm diameter ball with normal force of 2 N in the dry conditions. Wear amount after 1,000 m running distance shows that about 1.5 times longer life was shown in designed sintered alloy. Since results of tensile test showed that same tendency in previous testing, it is concluded that designed sintered alloy can be used for several mechanical parts with special strength and anti-wear ability in relatively low cost due to recycled tungsten carbide powder.

Keywords**—**Tungsten carbide, recycle process, compression test, powder metallurgy, anti-wear ability.

I. Introduction

TUNGSTEN carbide (WC) is widely used as raw material for tool in several metal working process because of its excellent hardness. Since high precision machining demands in manufacturing industry lead to mass consumption of cobalt (Co) cemented WC tool, mass scraps of used WC tools are formed day by day. As a result, recycling process of WC has been established to save resources of tungsten which is typical rare material [1]-[4].

Japan has imported tungsten about 5,000 ton/year. About 2,500 ton has been supplied to manufacture WC tools for domestic use by year [5]. Japanese tool makers have made effort to collect their branded products which are spent by customer [3], [4]. Such branded used tools are able to recycle as raw material powder for brand new WC products because its Co content can be easily clarified from specifications in collection. In other words, since the demands for quality of WC tool are quite severe [6], there is a lot of effort that must be paid by tool maker in order to achieve the mechanical properties such as hardness, toughness, anti-wear ability, heat resistance, fatigue strength, which are dependent on Co content. However, since there are huge number of off-bland tools and non-standardized tools in manufacturing industry, it is hard to classify them, and identify their Co content [7]. As a result, about 70% of used WC tools can be collected from Japanese industry and be processed into recycled WC-Co powder by refinery, nevertheless only 850 ton is restored but 900 ton cannot be re-used due to difficulty of separation or classification with Co content [5]. Thus, there is a lot of used tungsten material in Japan but currently it is hard to re-use the recycled WC-Co powder into new processed WC tool entirely. In this study, to suggest positive use of such recycled WC-Co powder which is improper for re-use, we have tried to fabricate an iron based Powder Metallurgy (PM) alloy which shows reinforced mechanical properties with recycled WC-Co powder. Japanese PM Industries have manufactured 90,000 ton/year of iron based sintered alloy as mechanical steel parts such as gear and bearing in automotive industry [8]. These PM steel products demand higher strength, stiffness and anti-wear ability, however unstable amount of ingredient does not necessarily affect such mechanical properties in contrast with WC tools, because the demands in such mechanical properties are comparatively low level.

We have made set of newly designed sintered steels with recycled WC-Co powder as ingredient. To estimate amount of recycled powder appropriate for existent powder compaction facilities, compressibility of powder mixture was confirmed by uniaxial closed-die compaction test. Then, true stress - true strain curve of sintered specimens in density ratio of 0.85 (which means 15% porosity inside) was measured by axial compression test. Tensile test and ball-on-disk type wear test were also performed in selected compositions to confirm its ductility and anti-wear ability.

II. Experimental Procedure

A. Recycled WC-Co Powder

Recycled WC-Co powder has been provided by ONS Co., Ltd. Table I shows chemical compositions of powder. Note that composition measurement was conducted several times as several samples were randomly extracted from processed recycled powder in same lot. Mean particle size of the powder is about 5 μm.

As shown in Table I, Co content varied from 7.0 to 12.5

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mass.% because the provided WC-Co powder consists of off-bland and non-standardized used tools as a reason why it is improper to recycle into new WC tools. Therefore, content of WC also varied, and other carbides such as TiC are detected a little amount due to thin hard coating on tool surface.

TABLE I
CHEMICAL COMPOSITIONS OF RECYCLED WC-CO POWDER

Mass.%	WC	Co	Ni	Cr	TaC	TiC	NbC
Max.	82	7.0	0	0	0	0	0
Min.	93	12.5	1.0	1.0	1.0	1.0	1.0

B. Powder Mixtures for Newly Designed Sintered Steel

We prepared five kinds of powder mixture with different amount of recycled WC-Co powder as additive for iron (Fe) powder (KOBE STEEL Co., Ltd., Atomized Iron Powder, 300M). Mean particle size of Fe powder is about 100 μm. 0.5 wt.% of graphite (G) powder has been added before mixing with WC-Co powder to fabricate sintered steel after compaction and sintering. Furthermore, we also prepared powder mixtures which additionally includes 3.0 wt.% of copper (Cu) powder (FUKUDA METAL FOIL & POWDER Co., Ltd., Electrolytic Pure Copper Powder, CE-15). Mean particle size of Cu powder is about 40 μm. Table II shows compounding ratio between powders and theoretical density for all prepared powder mixtures. Note that density was estimated on the assumption that ratio of WC and Co in recycled WC-Co powder is 10:1 roughly according to chemical compositions.

TABLE II
COMPOUNDING RATIO OF POWDER MIXTURES

Addition for PM steel (%)	Fe	G	WC-Co	Cu	Density (g/cm^3)
0[WC-Co]	99.500	0.5	-	-	7.84
3.0[WC-Co]	96.515	0.485	3.0	-	8.06
5.0[WC-Co]	94.525	0.475	5.0	-	8.20
7.0[WC-Co]	92.535	0.465	7.0	-	8.34
10.0[WC-Co]	89.550	0.450	10	-	8.55
15.0[WC-Co]	84.575	0.425	15	-	8.90
0[WC-Co]-3.0Cu	96.515.	0.485	-	3.0	7.87
3.0[WC-Co] -3.0Cu	93.530	0.470	3.0	3.0	8.09
5.0[WC-Co] -3.0Cu	91.540	0.460	5.0	3.0	8.23
7.0[WC-Co] -3.0Cu	89.550	0.450	7.0	3.0	8.37
10.0[WC-Co] -3.0Cu	86.565	0.435	10	3.0	8.59
15.0[WC-Co] -3.0Cu	81.590	0.410	15	3.0	8.94

C. Uniaxial Closed-Die Compaction Test in Powder Mixture

Compressibility of powder mixture is very important factor because it is significantly related to quality of PM product. Higher compaction force causes higher frictional force between die wall and powder, leads to galling, ultimately followed by poor die life or unexpected fracture occurrence. Density distribution in powder compact which is also arisen from die wall friction causes not only inhomogeneous mechanical properties but also dimensional change during sintering process. Compaction pressure to get enough compact density which is about 0.85 in density ratio should be under 700 MPa for sintered steel [9]. To identify compaction pressure to get 0.85 density ratio in all tested powder mixture, compaction test has been conducted by using 10 mm diameter cylindrical die under several compaction force; 2.5 tonf (24.5 kN) to 12.5 tonf (123 kN).

D.Sintering

Conventional lab type electric furnace as shown in Fig. 1 has been used for sintering process. Argon gas was supplied in furnace to prevent oxidation of specimen during sintering. Fig. 2 shows temperature - time diagram for sintering. Note that 1.0 wt.% of zinc stearate powder which is typical lubricant for metal powder die compaction has been added for all powder mixtures to prevent galling occurrence during compaction. Therefore, sublimation of zinc stearate is carried out at 320 ºC, and then sintering is conducted at 1150 ºC for 3 hours.

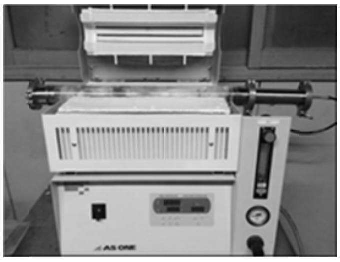


Fig. 1 Lab type electric furnace for sintering process

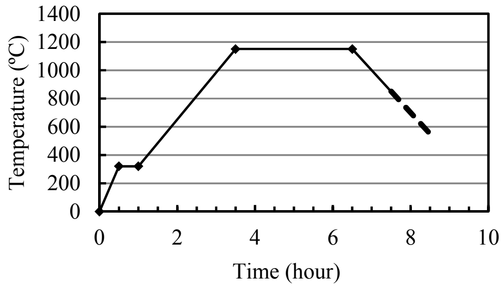
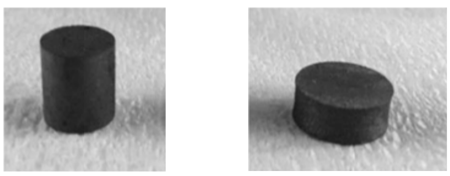


Fig. 2 Temperature - time diagram in sintering

E. Axial Compression Test for Sintered Specimens

Strength of sintered steel specimens in 0.85 of density ratio was identified by true stress σ - true strain ε curve. Shape of specimen is cylinder with 10 mm diameter and height, which is compacted by using same die-set with compaction test. Specimen was pressed axially until its height decreases to about 4 mm in several steps by using universal testing machine with flat die. Solid lubricant sheet was supplied in every step to avoid barreling occurrence. Fig. 3 shows appearance of a specimen before and after pressurizing.



(a) Before compression (b) After Compression

Fig. 3 Appearance of a sintered steel specimen in compression test

True stress - true strain curve was formulated according to *n*-power law [10]:

$$\sigma = F\varepsilon^{n} \tag{1}$$

where *F* is strength index and *n* is strain hardening exponent. These are materials constant to express flow stress respectively. According to knowledge in instability condition in tensile stress-tensile strain curve,

$$\frac{d\sigma}{d\varepsilon} = \sigma \tag{2}$$

is given at maximum tensile force. Using (2) for (1), we obtain

$$\varepsilon = n \tag{3}$$

This fact indicates that tensile strength σ_B which is defined as nominal stress can be estimated as:

$$\sigma = \sigma_B e^{n} = Fn^{n} \tag{4}$$

$$\sigma_B = F\left(\frac{n}{e}\right)^{n} \tag{5}$$

where *e* is Euler's number (=2.718). Thus, *F* value, *n* value and estimated tensile strength σ_B have been calculated and investigated with WC-Co powder amount.

F. Wear Test

Anti-wear ability of designed sintered steel was simply estimated by wear mark on specimen after friction test with conventional ball-on-disk type tribometer shown in Fig. 4. 5.0 mm diameter ball (SUJ2 in JIS) is used as counter material and indented with 2.0 N of normal force on disk shape sintered specimen. Rotational radius is 7.0 mm and speed is 410 rpm (0.3 m/s). Depth of wear mark on the disk and diameter of counter ball after 1.0 km running in dry condition were measured.

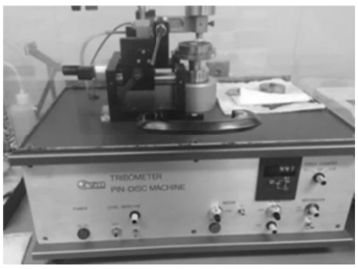


Fig. 4 Ball-on-disk type tribometer for wear test of sintered specimen

G. Tensile Test

Tensile test has been additionally conducted. Shape of specimen is plate with 2.0 mm width and thickness at tensile region.

III. Experimental Result and Discussion

A. Compressibility

Fig. 5 shows relationship between compaction pressure and density ratio for 0%, 7.0% and 15%WC-Co of powder mixtures. With increasing WC-Co amount, compressibility is significantly decreases due to hardness of WC particle. For example, compaction pressure necessary to get 0.85 of density ratio becomes about 650 MPa for 7.0%WC-Co powder as about 450 MPa is necessary for case of Fe-G powder only. In case of 15%WC-Co, more than 1,000 MPa of pressure is necessary to fulfill 0.85 of density ratio. Cu powder addition caused little increase of compressibility; thus, its effect was negligible. It is concluded that over 10% addition will be improper to uniaxial die compaction facilities for manufacturing PM steel parts.

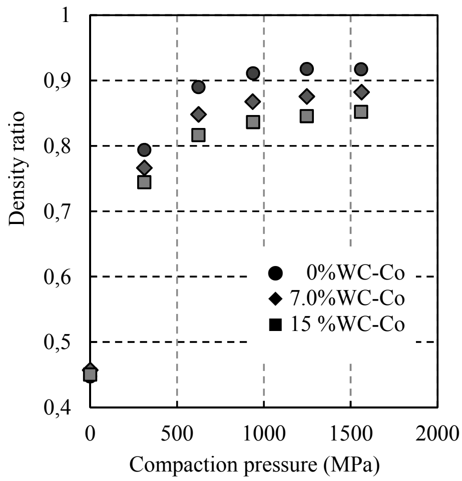


Fig. 5 Relationship between compaction pressure and density ratio

B. Strength of Sintered Specimens

Fig. 6 shows example of true stress - true strain curve of sintered specimen. WC-Co addition causes significant increase in flow stress from small to large strain.

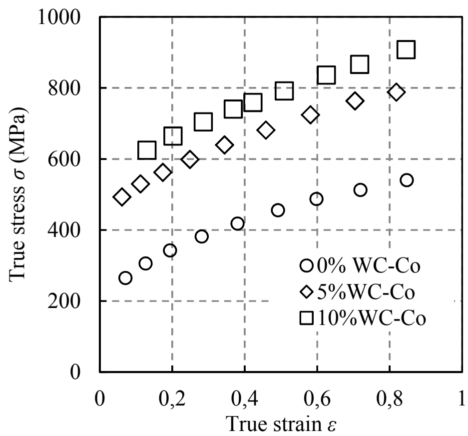


Fig. 6 Relationship between compaction pressure and density ratio

Fig. 7 shows variation of evaluated tensile strength σ_B with

WC-Co amount. σ_B increases with WC-Co amount, however, reinforcement becomes negligible after 7.0% addition which shows about 1.7 times higher strength from original Fe-G sintered steel (0%WC-Co).

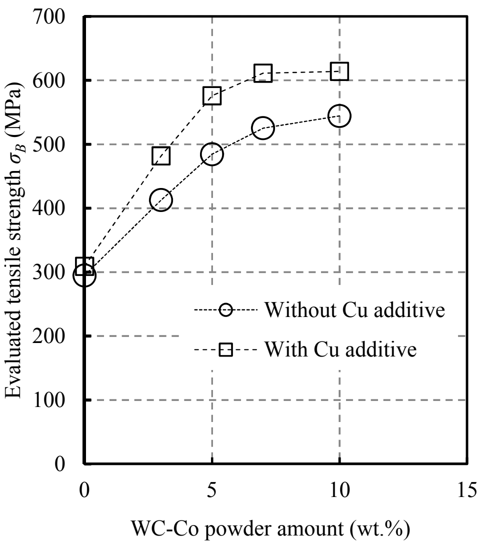


Fig. 7 Variation of evaluated tensile strength σ_B with WC-Co amount

WC phase in crystalline exists around parent phase which is formed by Fe particles, and dispersion strengthening will be expected. In case of 10% addition, about 400 particles must be allocated on surface of a Fe particle, as particle size of WC-Co is 20 times smaller than Fe. According to simple area evaluation, maximally 650 particles can be expected to allot, however it is hard to arrange particles homogeneously in practice due to aggregation of WC-Co particles. Therefore, it seems that effect of dispersion strengthening was saturated in tested conditions. It is concluded that 7.0% to 10%WC-Co amount will be preferable in designed PM steel.

Sintered steel made from 3.0%Cu additive powder mixture shows 70 to 90 MPa higher strength and reach to over 600 MPa. It indicates that precipitation of Cu phase occurs from solid solution and reinforce parent phase.

C. Anti-Wear Ability

Fig. 8 shows wear depth of disk specimens which are made from original Fe-G powder, 7%WC-Co powder mixture and 7%WC-Co -3%Cu powder mixture. It indicates that anti-wear ability significantly is improved as wear depth becomes about 1.5 times lower value in designed PM steels. However Cu additive shows negative effect although it increases strength as mentioned at Fig. 7.

Fig. 9 shows diameter of wear mark on counter ball. Comparing with original Fe-G and 7%WC-Co -3%Cu, little increase can be observed. It is considered that Cu phase was partly remains and acts to prevent massive galling instead of some wear amount in dry conditions.

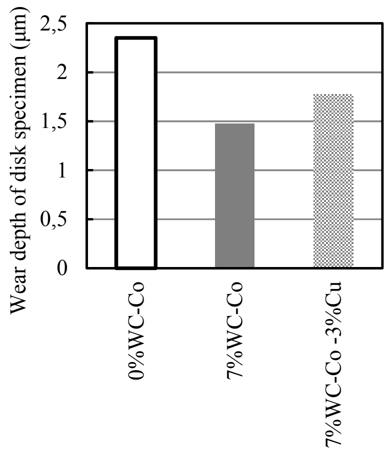


Fig. 8 Wear depth of sintered disk specimens

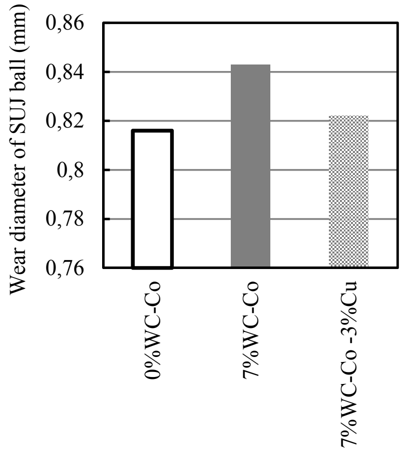


Fig. 9 Diameter of wear mark on counter ball

D. Strength in Tensile Test

Fig. 10 shows tensile strength measured by tensile test. The values are quite lower than the results evaluated from axial compression test because unfortunately only about 0.5% of elongation was observed in all tested specimens. For example, according to tensile property of commercial Fe-Cu-C type sintered alloy, tensile strength is 360 MPa as its elongation is 1.0%. Since all specimens were fractured without necking occurrence in this study, it seems that there was inhomogeneous density distribution in tensile axis. Furthermore, the flow stress of PM parts decreases in tensile axis due to its porosity. Even so, the same reinforce tendency has been clearly recognized as relative strength increment seems to be the same. Tensile strength reaches to over 300 MPa for designed sintered steels although poor elongation. It seems that the almost same strength as compression test result is acquired when elongation reaches to 1.0% and specimen break with necking occurrence.

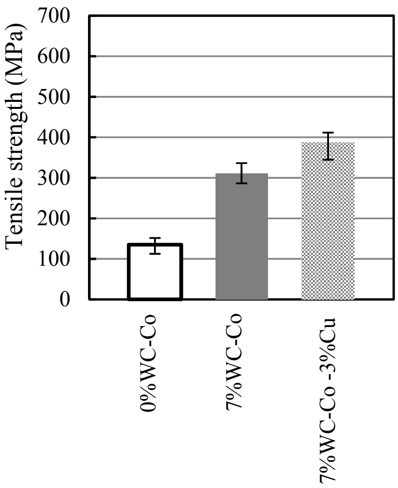


Fig. 10 Tensile strength of designed sintered steel at 0.5% elongation

IV. Conclusion

In this study, to suggest positive use of recycled WC-Co powder which is improper to restore to bland new cemented carbide tools, we have made set of newly designed sintered steels with different WC-Co amount. Compressibility of the powder mixtures, strength and anti-wear ability of designed sintered steels have been investigated by powder compaction test, compression test, tensile test and wear test. Results are concluded as follows:

1) With increasing WC-Co amount, compressibility of powder mixture is significantly decreases. Over 10% addition should be avoided to fulfill 0.85 of compact density ratio.
2) In the compression test, WC-Co addition causes significant increase in flow stress from small to large compression strain. Evaluated tensile strength σ_B shows 1.7 times higher from original Fe-G sintered steel and reach to over 600 MPa for 7%WC-Co -3%Cu.
3) Wear depth after 1.0 km running becomes about 1.5 times lower value in designed sintered steels.
4) In the tensile test, tensile strength reaches to over 300 MPa for designed sintered steels although only about 0.5% of elongation was observed.

Japan has enough amounts of used WC-Co tools as a relatively cheap resource. Since designed iron based PM alloy shows higher strength and good anti-wear ability which is favorable for conventional PM mechanical parts, re-use of recycled WC-Co powder for PM steel will become feasible way to decrease waste of used WC tools and save tungsten. Compressibility of powder mixture expected to be improved by some kinds of powder processing technique such as ball milling. Study in other subjects such as heat resistance, tribological properties, fatigue properties and so on will expand re-use of recycled WC-Co powder more.

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