B. *Physical Properties*

1) Hardness Test: The surface of carbide specimen is polished before hardness test. A Vickers hardness (Hv) test is chosen to identify the hardness of test specimens. The indenting load is 0.5 Kg in order to get a suitable indentation for hardness calculation. The hardness of different specimens are listed in Table II。

TABLE II Hardness of four series carbide specimens.

Specimen	Hardness (Hv)	Specimen	Hardness (Hv)
W8A	Hv1519	T12A	Hv1600
W8B	Hv1570	T12B	Hv1604
W15A	Hv1271	WTA	Hv1502
W15B	Hv1275	WTB	Hv1565

2) Density Ratio: Density ratio is defined as the ratio of sintered specimen density to theoretical density, which is used to investigate the interaction between WC and binders or TiC and binders during sintering process. Furthermore, the influences of density ratio on the ability of wear resistance are also evaluated. Firstly, all of opening pores on the surface are sealed with wax. Then, densities of specimens are measured based on Archimedes' Principle. Finally, the sintering density ratio of the sintered specimen is calculated with measured weights in atmospheric environments. The density ratios of four series of specimens are shown in Table III.

TABLE III Density ratios of four series carbide specimens.

Specimen	Density Ratio	Specimen	Density Ratio
W8A	87%	T12A	98%
W8B	86%	T12B	99%
W15A	86%	WTA	87%
W15B	86%	WTB	97%

3) X-Ray Diffraction: This inspection is to ensure the constituent phases of carbide specimens after sintering. The copper target is chosen under 40 kV with 100 mA condition. The range of diffraction angles is from 20° to 100° with a scan rate of 12° per minute. Constituent phases of those four series specimens are shown in Table IV. Some carbon element are detected on the surfaces of W15A, W15B and WTA specimens, which came from a layer of carbon powder that has been pre-laid on the bottom of the specimens box during sintering process. Similarly, Mo_2C is also detected in W15 series specimens, too. Except these phenomena, there is no abnormal reaction in the others specimens. This result shows that the sintering parameters are suitable.

TABLE IV X-Ray diffraction results.

Specimen	Composition	Specimen	Composition
W8A	WC	T12A	TiC
W8B	WC, Co_3W_3C	T12B	TiC
W15A	WC, Mo_2C, C	WTA	WC, TiC, C
W15B	WC, Mo_2C, C	WTB	TiC

C. *Tribological Behaviour*

1) Wear volume: A Pin-on-disk mode is used for investigating the wear behaviour of each set of specimen. The schematic diagram of specimens setting is shown in Fig. 2. Wear test condition is set load 1 Kg with relative sliding speed 3 m/s. The total sliding distance for each test set is 10800 m. After wear test the width of worn scar on carbide specimen is measured and then transferred to wear volume. The wear volume of each test specimen is shown in Table V.

2) Friction Behaviors: The average of coefficient of friction is calculated from the normal loading and the friction force with a sampling rate of 0.5 Hz. The value of each group is shown in Table VI.

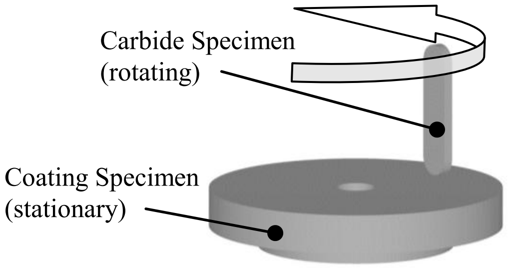

Fig. 2 Schematic diagram of pin on disk wear test.

TABLE V Wear volume of carbide specimens.

Specimen	Wear volume (mm^3)	Specimen	Wear volume (mm^3)
W8A/Nitride	0.0086	T12A/Nitride	0.0159
W8B/Nitride	0.0291	T12B/Nitride	0.0126
W8A/DLC	0.0040	T12A/DLC	0.0017
W8B/DLC	0.0043	T12B/DLC	0.0002
W15A/Nitride	0.0070	WTA/Nitride	0.0168
W15B/Nitride	0.0116	WTB/Nitride	0.0187

TABLE VI Coefficient of friction between specimens.

Specimen	COF	Specimen	COF
W8A/Nitride	0.15	T12A/Nitride	0.22
W8B/Nitride	0.15	T12B/Nitride	0.22
W8A/DLC	<0.048	T12A/DLC	<0.048
W8B/DLC	<0.048	T12B/DLC	<0.048
W15A/Nitride	0.17	WTA/Nitride	0.24
W15B/Nitride	0.17	WTB/Nitride	0.24

3) Worn Surface Analysis: After wear test, some typical carbide and steel specimens are observed under Optical Microscope (OM) and Scanning Electron Microscope (SEM) in order to identify wear mechanisms. Additionally, the Energy Dispersive X-ray Spectroscopy (EDS) is used to confirm the composition on a specific position.

III. DISCUSSION

A. *Effect of Binders on Hardness of Sintering Specimen*

In this work nickel is the major binder. In order to find the effect of metallic binders on hardness of sintering specimens, the composition of Ni, Co and Mo are adjusted to different ratio. The hardness of the four series of sintering specimens is shown in Fig. 3. The results show that hardness of series B is higher than that of series A for W8, W15 and T12 specimens, separately. In fact, binder of series B is composed by three metal elements. There are two reasons that series B specimen hardness is higher than that of series A. Firstly, the hardness of cobalt is Hv250, which is higher than the other two metals, Ni and Mo, in the binder. Secondly, the amount of nickel and cobalt in the binder of series B reaches 15 wt%, which enhances the wetting effect more than other specimens, during liquid phase sintering; then, a more uniform structure can be obtained after sintering. However, the effect is limited because the amount of cobalt is only 5 wt%. On the other hand, the particle size of WC in W15 series is larger than in W8. Therefore, hardness of W15 series is lower than that of W8 series, according to Hall-Petch relationship. Even so, the high hardness of TiC powder added to the sintering specimen can compensate the drawback of coarse particle size of WC. Therefore, hardness of WT series is equivalent to W8 series. Moreover, in WT series, the hardness of WTB specimen is also higher than WTA specimen that because WTB contains higher ratio of TiC powder.

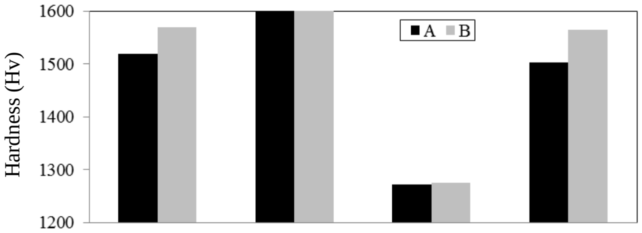

Fig. 3 Hardness of four series sintering carbide specimens.

B. Effect of Compositions on Density Ratio

Comparing these series specimens, sintering TiC specimens have high density ratio among all series specimens, showing as Fig. 4. In sintering TiC specimen, the core-shell structure is formed by TiC and Ni chemical reaction during sintering. That is the main contribution to high density ratio. Nevertheless, this effect is insufficient in WTA specimen because it contains TiC only 10 wt%.

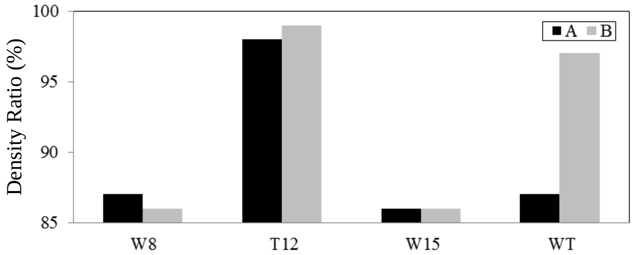

Fig. 4 Density ratio of four series sintering carbide specimens.

C. Tribological Behavior between Sintering Carbide and Nitriding SKD61 Steel

1) Effect of Variety and Amount of Binders on Wear Resistance of Sintering Specimen: The wear volume of each series specimen is shown in Fig. 5. Because of the excellent diffusibility of molybdenum, alloying process can be enhanced to form high strength bonding for every particle and yield a uniform structure. Additionally, molybdenum can promote the WO_3 and MoO_3 forming that makes adhesive and wear loss being reduced. Therefore, the wear volume of W8A and W15A is much less than W8B and W15B respectively. However, the mechanism that has mentioned above does not dominate the promotion of wear resistance in T12 series, even though the hardness of TiC is higher than WC. It is obvious that the wear volume of T12A is not only much more than that of W8A and W15A, but also more than T12B. This phenomenon implies that the effect of overall amount of nickel and cobalt is stronger than the effect of Mo for enhancing the wear resistance of titanium carbide. Finally, the interaction and interfere between these two mechanisms, the contribution of Mo in WC versus the effect of Ni/Co in TiC, let WTA and WTB posses a similar wear performance.

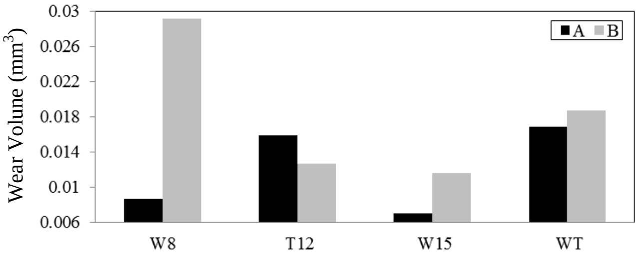

Fig. 5 Wear volume of sintering carbide specimens/nitride layer.

2) Effect of Particle Sizes on Wear Resistance of Sintering Specimen: Molybdenum plays an important role in W8 series. The reduction of Mo directly relates to the decline of wear resistance, see Fig. 5. This change is not so severe in W15 series because the particle size of WC dominates this phenomenon. Sintering specimens with smaller particle size have much more interfaces. For high binder content (>16%) sintering carbide, plastic deformation will occur in the interfaces because the interface strength is less than that of the bonded particles. Therefore, when the loading is over the strength of the interfaces, plastic flow will occur in the interfaces. That leads to hardness of W15 is higher than W8. Moreover, the gripping effect of the large particle is higher than that of the small one due to the geometric effect. In a same penetrating depth, a smaller particle does not have enough wrap and support so that it is easier to be drawn away from the binder. On the other hand, a different mechanism dominates the tribological behaviour in T12 series, in which interactions between TiC and binders influence wear behaviors more significant than effect of particle size and hardness of TiC.

3) Analysis of worn Surface of Sintering Carbides: There are three-stage in wear process for all sintering carbide specimens. Run-in process is the first period. In this period, a polished region is formed, showing in Fig. 6. There is no scratch in the region because the hardness of sintering carbide is higher than nitride layer. The second stage is adhesive wear process. Nitride layer is wearing down, and debris of SKD61 substrate adhesive on carbide specimen, showing in Fig. 7. The third stage is a peel-off period. Accumulating thick adhesive layers is stripped from the carbide specimen. Meanwhile, the stripped layer brings some carbide particles away. This phenomenon is verified from the composition detection of wear debris.

4) Analysis of Worn Surface of Nitride Layer: For steel specimens, the wear behaviors are similar to carbide specimens doing, and can be categorized three-stage. In first stage, the nitride layer is scratched by carbide specimen. Meanwhile, carbide specimen is also polished by nitride layer. During second stage, the SKD61 substrate is exposed and then oxidized due to the heat of friction. This is verified by EDS analysis. Finally, the nitride layer is nearly scratched over in the third stage. Moreover, the periodic stresses acting on the rubbing surface of SKD61 steel cause surface fatigue, and the friction force leads to the fatigue cracks propagation being perpendicular to the sliding direction, showing in Fig, 8.

D. Tribological Behavior between Sintering Carbide and DLC Coated 52100 Steel

1) Effect of Variety and Amount of Binders on Wear Resistance of Sintering Specimen: The wear behaviors between sintering carbide and DLC coating film has the different results, comparing with nitride layer. For this counter part (DLC), TiC specimen has a better wear resistance than WC specimen, showing in Fig. 9. Furthermore, the wetting effect of cobalt in TiC specimen can promotes the hardness and uniformity of sintering carbide so that reducing the wear loss of T12B. However, the behaviour is not shown in W8 series. Therefore, it is reasonable to evaluate the ability of wear resistance of sintering titanium carbide by its hardness under this wear condition.

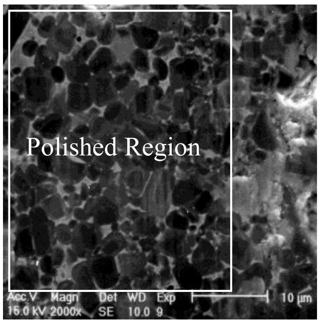

Fig. 6 SEM image of a polished region on a sintering carbide specimen.

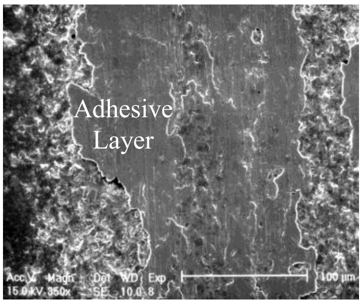

Fig. 7 SEM image of an adhesive layer on a sintering carbide specimen.

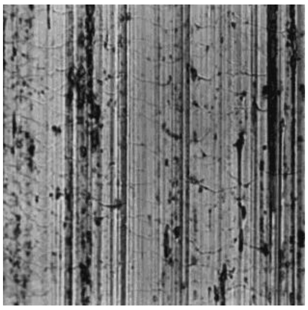

Fig. 8 OM image of fatigue crackson the surface of SKD61 steel.

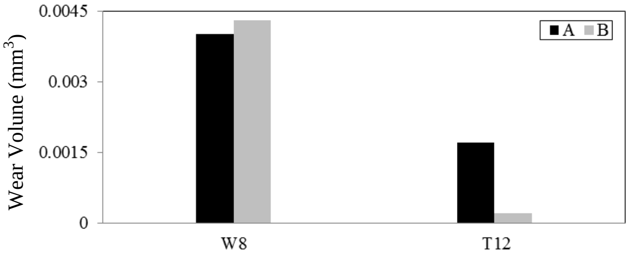

Fig. 9 Wear volume of sintering carbide specimens/DLC film.

2) Analysis of Worn Surface of Sintering Carbides: Sliding on DLC film, a typical worn surface of the sintering specimen is shown in Fig. 10. The worn surface shows micro scratch and local region binder lost by diffusion. Furthermore, there is no adhesive wear and no observable wear debris.

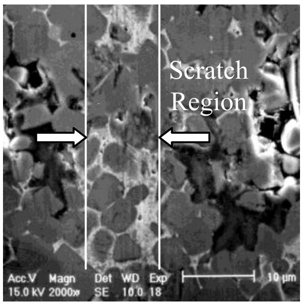

Fig. 10 SEM image of a polished carbide specimen with a scratch region.

3) Worn Surface of DLC Film: DLC film has a high hardness and exhibits no adhesive wear. Therefore, the coefficient of friction is very small when rubs on sintering carbide. On the other hand, the SAE52100 steel is a heat absorber, which avoids rising the temperature of DLC film during the wear period. Hence, the DLC film maintains an excellent wear performance during the whole wear test.

IV. CONCLUSION

According to the experimental results and the above discussion, five conclusions are listed as follows:

1) There was no negative effect on the wear performance *D*ensity ratios between 86% and 99% of sintering carbides did not have negative effects on the wear performance with a lower density.

2) Molybdenum binder could enhance the wear resistance of sintering tungsten carbides.

3) For TiC/DLC friction pair, the hardness of sintering titanium carbides could be used to evaluate the wear performance.

4) The coefficient of friction between sintering carbide and DLC film was very low, which resulted in low wear loss.

5) SAE52100 steel could avoid the failure of the DLC coating film and maintained the wear performance when sliding against sintering carbides.

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