Ion Implantation Modification and Induced Ultra Low Friction of WC-Co

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Various ion species including C, N, O and Ar are implanted into WC-6.5%Co cermet samples to study surface modification of tribological properties for industrial applications of the cermet tools. Ultra low friction coefficient down to 0.04 is found under high-load WC-self wearing for low-beam-current high-dose C-ion implanted samples. In order to achieve an excellent compromise of a combination of low friction, high hardness and high wear resistance for WC-Co tooling applications with superior performance of tooling harder materials, C-ion implantation using low beam currents and to higher doses is found to be the best choice. The C-ion-implantation induced modifications of the mechanical properties of the cermet have been attributed to physical interactions such as microstructural fining.

Key Words : Ion Implantation, Surface Modification, Friction Coefficient, WC-Co

1. Introduction

Cobalt-cemented tungsten carbide cermet, WC-Co, is among the few most important strategic materials in the world. Any processes which can substantially improve the material properties are therefore sought after. Ion implantation has a number of advantages over other surface processing techniques¹⁾ in treating valuable precision tools²⁾ used in high-technology fields. Surface modification of tungsten carbide by ion implantation particularly for improving mechanical properties has widely and constantly been investigated (e.g. 3)~5)) and put into industrial applications as well 6)~8)). However, most of the previous work has been focused onto improvements of the hardness and wear resistance, while few particularly on reduction of friction (e.g. 9)). High-performance tools are required to possess combined superior mechanical properties, which could yet hardly be achieved. Instead, for a particular application area, some features may be considered to be dominant and stressed but others not to be weakened. One of the areas is the low-friction application, where hardness and wear resistance would still be expected to be maintained as highly as possible. The present study provides a unique illustrated case of ion implantation modification of surface friction for WC-Co. In the study, various ion species such as common active carbon, nitrogen and oxygen were used in order to search for the optimal modification while inert argon was used for investigating related mechanisms.

2. Experiment

C, N, O and Ar ions were implanted into surface-

mirror-finished WC-6.5% Co samples (grain size about $2.5\mu\text{m}$) at energies around 100 keV to varied doses with higher or lower beam currents, as shown in Table 1. During ion implantation, the sample temperature was monitored using a thermo-couple (Chromel-Alumel) buried behind the sample. After ion implantation, microhardness in the Knoop scale of the samples was measured using a digital microhardness tester (Matsuzawa, MXT- α) under a load of 5g. The tribological behaviors of the implanted and unimplanted samples were studied using a pin-on-disk tribometer (ISC-200, Implant Sciences) with WC balls (thus a self-wearing) under a load of 500 g (in some cases, 750 g, 150 g, and 50 g), a sliding speed of 5 cm/s in an open-air (tropic atmosphere, humidity about 60-70%) room-temperature (about 25°) environment. The friction coefficients and wear rates were measured and calculated according to the international standard¹⁰⁾. More details of the experiments have been described elsewhere⁹⁾. The sample surfaces were examined using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

3. Results and Discussion

The measured data for friction coefficient, Knoop microhardness and wear rate are listed in Table 1. The data are plotted as functions of the ion dose in Figure 1.

3. 1 Results of various ion species implantation

Lower-current C-ion implantation continuously reduced friction coefficient μ with increasing dose down to about 17% of that of the unimplanted surface when the dose was near 10^{18} ions/cm². The highest hardness value was observed at a dose of about 4×10^{17}

Table 1 Ion implantation conditions, results of the measured friction coefficient, hardness and wear rate and a study on the combination effect from the three factors. E : ion energy, I : ion beam current. The dose unit is ions/cm². " $F. C.$ " : friction coefficient, " HK " : Knoop microhardness number in kg/mm², " $W. R.$ " : wear rate in mm². The subscript 0 represents the data from the unimplanted sample. Σ represents $\mu/\mu_0 + HK_0/HK + W. R./W. R_0$, which is an index of the combination effect, the lower value, the better the compromise. $\Sigma=3$ is the index for unimplanted result, while $\Sigma<3$ indicates a total improvement and $\Sigma>3$ a total worsening.

Ion	E (keV)	I (μ A)	Dose (10 ¹⁷)	$F. C.$ μ	$\frac{\mu}{\mu_0}$	HK	$\frac{HK_0}{HK}$	$W. R.$ (10 ⁻⁹)	$\frac{W. R.}{W. R_0}$	Σ
—	0	0	0	0.26	1	3300	1	2.7	1	3
C	120	5-10	0.5	0.20	0.77	3563	0.93	2.5	0.93	2.63
			1.5	0.20	0.77	3765	0.88	1.2	0.44	2.09
			4	0.15	0.58	3938	0.84	3.1	1.15	2.57
			4.5	0.12	0.46	3820	0.86	0	0	1.32
			6	0.08	0.31	3407	0.97	0	0	1.28
			8	0.045	0.17	3024	1.09	0	0	1.26
		30-40	3	0.23	0.88	3169	1.04	0	0	1.92
			8	0.27	1.04	2632	1.25	30	11.11	13.4
		10-20	2	0.17	0.65	3612	0.91	5.5	2.04	3.6
			4	0.12	0.46	2478	1.33	10	3.7	5.49
N ₂	140	40	0.5	0.26	1	3613	0.91	2.7	1	2.91
			2	0.27	1.04	4458	0.74	0	0	1.78
		20	0.5	0.24	0.92	3586	0.92	0.5	0.19	2.03
			2	0.2	0.77	3106	1.06	5.8	2.15	3.98
O ₂	140	20	4	0.2	0.77	2052	1.61	33	12.22	14.6
			2	0.24	0.92	3365	0.98	0.5	0.19	2.09
		40	1	0.21	0.81	2941	1.12	24	8.89	10.82
			1	0.24	0.92	2756	1.2	0.4	0.15	2.27
Ar	130	40-50	4	0.3	1.15	2639	1.25	1	0.37	2.77

ions/cm². This high hardness was maintained for doses up to 8×10^{17} ions/cm². For the cases of higher doses, ultra low friction coefficients and near-zero wear losses were observed. Higher-current C-ion implantation softened the cermet, and increased both friction coefficient and wear rate. These changes developed with increasing dose.

Low-current N-ion implantation increased hardness at lower doses but decreased hardness at high dose levels. Although it produced lower friction, it lowered down wear resistance pronouncedly. High-current N-ion implantation increased hardness drastically with increasing dose, but did not improve friction, which turned worse at higher dose levels.

O-ion implantation did not basically improve friction. Low-current implantation achieved the highest hardness at low doses but decreased both hardness and wear resistance significantly with increasing dose. High-current implantation could achieve higher increases in both hardness and wear resistance than the low-current implantation.

Ar-ion implantation, whether using low or high beam current, decreased hardness and did nearly not improve friction. High-current implantation reduced hardness more than low-current implantation but brought about lower wear rate.

3. 2 Effects from various conditions

Ion species : C exhibited the most significant effect on reducing friction coefficient with low-current ion im-

plantation, especially, at high doses. N showed a similar effect for the low-current ion implantation, however, the hardness drastically decreased with dose. This is in disagreement with some previous observation⁴⁾, which claimed a complete similarity between N and C ion implantation effects in WC. Our results indicate that N cannot compete with C when both low friction and high hardness are required.

Dose : As shown in Figure 1, C and N ion implantations pronouncedly reduced friction coefficient with increasing dose. However, the ion-implantation-induced hardness change depended on dose. There generally existed an optimum dose that produced the highest increase in hardness for a certain ion species. A compromise between acceptable high hardness and low friction showed that C was better than N at an appropriate higher dose. A study on the combination effect for friction, hardness and wear is shown in Table 1. A combination effect index is introduced in such a way that it is the sum of the reduction of the friction coefficient, reduction of the wear rate, and the reciprocal of the increase in hardness. A decrease in each term represents an improvement in the corresponding physical property, and the sum represents a probability sum of all property improvements. Thus, the lower the index value is, the better the compromise. The index of 3 is for the unimplanted result, smaller than 3 a total improvement and greater than 3 a total worsening. From the table it is seen that the

Fig. 1 Friction coefficient, Knoop microhardness and wear rate as a function of ion dose for all ion implanted samples, compared with the data from the unimplanted samples (dose=0). In the legend, (l) : low current implantation, and (h) : high current implantation.

best compromise, represented by the lowest index value, is achieved from the high-dose C-ion implantation.

Beam current : Ion beam current, thus the sample temperature, has inevitable effect on the results, and this effect, whether positive or negative, depends on ion species. The sample-temperature monitoring showed that the lower beam currents, 5-20 μA , slightly raised the sample temperatures, less than 10°C high than room temperature, while the higher beam currents, normally 40-50 μA , could lead to temperatures around 100°C. It is noted that as the temperature was measured at the back of the sample, the temperature in the ion-implanted area near the surface should be much higher. The low-current implanting of C and Ar ions produced higher hardness increases and more friction decreases than the high-current implanting, whereas implanting of N and O ions did the opposite in general. The literatures only mentioned that higher temperatures of the ion-implanted WC sample worsened the tribological properties⁴⁾, but did not notice the ion species dependence. From our observation summarized above, it can be postulated that chemical interaction dominates the N- and O- ion implantation effect, while physical interaction does

the C- and Ar- ion implantation effect. The chemical interaction refers to forming compounds such as nitride and oxide for the cases of N and O ion implantations^{e.g. 11)}, as the process is favored by elevated temperatures due to the higher beam current. In contrast, the physical interaction process does not lead to compound formation but only physical changes, which can more easily occur and be maintained at lower temperatures. For Ar, it is obvious, but for C it is unexpectedly interesting. Nevertheless, X-ray diffraction (XRD) analysis showed that no new phase was formed after C-ion implantation in WC-Co¹²⁾.

Wear testing load : The interesting friction behavior only occurred at high loads. A load of 750 g was applied to test the friction of the C-implanted sample and an ultra low friction coefficient down to 0.04 was observed.

3. 3 Ultra low friction coefficient

C-ion implantation to the dose of 8×10^{17} C-atoms/ cm^2 produced the ultra low friction coefficient while still maintained the acceptable high hardness and zero wear rate. None of other ion-species implantation was able to compete. The ultra low friction coefficient, 0.04, is unusual in the solid-wear-pair condition without lubricants compared with known data such as 0.05 for MoS₂¹⁵⁾, which has been known as the best solid lubricant material. We compared our result with previously reported results⁴⁾, which showed a friction coefficient of 0.027 on WC-Co after N-ion implantation under conditions of WC pin (0.5 mm in diameter), a load of 75 N, a sliding speed of 1 m/s, and a light hydrocarbon spirit flowing and cooling environment. Limited by the setting load capacity of our wear tester, 750 g is the maximum load we can apply. However, we can use the friction theory to estimate the friction coefficient under high loads. For ceramics, $\mu L^{1/3}$ (L : load) is approximately constant¹⁶⁾. With our data of $\mu = 0.04$ when $L = 750$ g, we obtain $\mu = 0.019$ when $L = 7500$ g. Specially, the previous result was obtained under a lubrication condition and a much faster sliding speed whereas ours was in the dry air environment and with the much slower sliding speed (normally, the slower the speed, the higher the friction coefficient¹⁷⁾). Therefore, the friction coefficient we observed is indeed ultra low.

3. 4 Discussion on mechanisms

It has been suggested that the low friction might be due to a thin graphite layer stemming from implanted carbon formed between two contacting surfaces and the graphite plays the role of high lubrication¹⁸⁾. The friction coefficient of pure graphite under the same testing conditions such as the load, sliding speed and atmosphere as used for testing ion-implanted WC-Co (the graphite surface was rougher, but it was found to have a negligible effect on friction under the load used) was checked to be about 0.1 at the steady state. This indicated that the idea on the graphite lubrication effect was untenable or at least the effect was fairly minor. The observed C-ion implantation induced ultra increase in nanohardness and decrease in

Fig. 2 AFM images of the surfaces of (A) unimplanted WC-6.5% Co sample, and (B) C-ion-implanted sample (120 keV, 6×10^{17} ions/cm²).

friction of small-grain WC-10% Co have been studied by the authors and attributed to ion-beam-induced formation of near-surface nanostructure¹²⁾. Our AFM study on the surfaces of the samples (WC-6.5%Co) observed formation of nanosized (about 50-200 nm) particle structures on the C-ion implanted surface, compared with the smoother unimplanted surface, as shown in Figure 2. The surface microstructures inside and outside the wear track were also examined using SEM, as shown in Figure 3. A comparison shows that the carbide grain size inside the wear track is smaller than that outside and more inter-spaces among carbides inside the wear track than outside. It is proposed that the physical interaction induced by C-ion implantation may build the potential for the transgranular fracture¹³⁾. The stress and temperature imposed by the wearing lead to the fracture of the grains easily. This is because of almost no strong chemical interaction brought by C-ion implantation compared with that induced by other active-ion-species (such as N and O) implantation, and thus the fining of the grains eases sliding and reduces friction. But, owing to the carbon atoms still interacting with the carbide phase¹⁴⁾ and decorating the dislocations, the material is still hard enough. As the implanted Ar ions have no such interaction, they simply destruct

Fig. 3 SEM photographs of the surface microstructures of the C-ion implanted samples. (a) The structure inside the wear track. (b) The structure outside the wear track.

carbides and even Co binders⁷⁾ (in this case, the preferential sputtering yield of Co is about 3 times of that of WC¹⁹⁾) and eventually bring about weakening of the material. High-current C or Ar ion implantation basically speeds up and extends the process of the destructing, and hence the high-current implantation even worsens the surface properties.

4. Conclusions

In order to achieve an excellent compromise between low friction, high hardness and high wear resistance for WC-Co tooling applications, C-ion implantation using low beam currents and to higher doses is the optimal treatment of the cermet. The ultra low friction coefficient under the WC-self wearing at high loads (≥ 500 g) incorporated with high microhardness and wear resistance induced by low-current high-dose ($\sim 8 \times 10^{17}$ C-atoms/cm²) C-ion implantation has been observed. This interesting tribological behavior has been attributed to fining of the surface microstructure. Effects from C and N ion implantation of WC-Co are different on modification of tribological properties. The mechanisms causing the effects are also different, the physical interaction dominating the C-ion implantation case but the chemical interaction doing the N-ion implantation case.

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