Article ID: 1003- 6326(2000)01- 0064- 05

Effects of intermixing process on bonding strength of IBED CrN coatings①

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Abstract: The coating-substrate bonding strengths under different intermixing processes were evaluated by scratch and spherical rolling contact fatigue methods. The results show that for low bombarding energy of N ions dynamic recoiling at 10keV and 20keV, the coating layers are of excellent bonding strengths. The bonding strength of CrN coating with 40 keV static recoiling is higher than that of low energy(20keV). On the other hand, the bonding strength of coating with 40keV dynamic recoiling is much lower than that of static recoiling at the same energy and even less than that of dynamic recoiling intermixings at 10keV and 20keV energy. The results of scratch and spherical rolling contact fatigue methods exhibit the same trend for each group of recoiling methods, yet the results of the scratch and fatigue tests for two groups do not agree with each other.

Key words: IBED; CrN coating; inter-mixing processes; bonding strength **Document code: A**

1 INTRODUCTION

High energy particles recoiling is usually used to strengthen the interface in order to increase the coating-substrate adhesion property[1,2]. Basically, the IBED (ion beam-enhanced deposition) intermixing processing includes dynamic recoil mixing (IDR) and static recoil mixing (ISR). Dynamic recoil mixing means that the high energy N ions and the deposited Cr atoms, sputtered from target, arrive at the sample surface simultaneously. The static recoil intermixing applies the high energy N ions bombarding on the pre-deposited layer to form an interface mixing. An appropriate intermixing process will leads to an excellent bonding strength of coating-substrate system. Generally, the higher the bombarding energy, the better the bonding strength will be. But our previous experimental results showed that high energy N ion dynamic recoiling leads to decrease the coating substrate bonding strength by selective sputtering effect of energetic particles[3]. So it is important to study the effects of different energies and recoiling method for the coating adhesion. In this paper bonding strength is evaluated by scratch and spherical rolling contact fatigue tests, and the results are compared with each other for different intermixing processes.

2 EXPERIMENTAL

It is well accepted that scratch test is rather a load carrying property than adhesion, and contact fatigue is appreciable to evaluate the real interface conditions[4]. In this paper spherical rolling was selected to compare the different coating-substrate bonding strengths. The sample material was AISI52100 steel with a standard heat treatment, and the hardness was HRC61~ 62. The steel samples were ground and polished to an average surface roughness less than 0. 1 μm and then cleaned with propanone in an ultrasonic container. Prior to deposition, the samples were sputter etched with an argon ion beam for about 10 min. The interface mixing processes with IBED are shown in Table 1. After the interface mixing, CrN was deposited with the same parameters, which were, N partial pressure $p_N = 1.0 \times 10^{-2}$ Pa, N ion enhanced bombarding energy $E_r = 4$ keV, Cr atom deposition rate 2.5×10^{15} $cm^{-2} \cdot s^{-1}$, N ions/Cr atoms ratio 1.45×10^{-2}, deposition time 4h. The thickness of all CrN coatings was 1.5 μm.

In order to compare the evaluating method of bonding strength , scratch and spherical rolling con-

Table 1 Coating-substrate interface mixing processes and parameters

Sample	Pre-deposited Cr layer/μm	N ions energy/keV	N ions rate /($cm^{-2} \cdot s^{-1}$)	N ions recoiling time/s
IDR10	No	10	1.0×10^{14}	1200
IDR20	No	20	1.0×10^{14}	1200
IDR40	No	40	1.0×10^{14}	1200
ISR20	0.25	20	1.0×10^{14}	1200
ISR40	0.25	40	1.0×10^{14}	1200

① **Foundation item:** Project 59671064 supported by the National Natural Science Foundation of China
Received date: Oct. 20, 1998; **accepted date:** Apr. 29, 1999

tact fatigue tests were used. The critical debonding loads L_c and $\Delta\tau$ were defined as coating-substrate bonding strengths. The parameters of scratch test were: scratching rate $10 \pm 1\,mm \cdot min^{-1}$, loading rate $20 \sim 40\,N \cdot min^{-1}$, loading deviation 0.03 N, standard Rockwell diamond indenter.

The spherical rolling contact fatigue was measured with self-made contact fatigue tester, as shown in Fig. 1, the diameter of spherical rolling ball $d = 4.75\,mm$, $Ra = 0.05\,\mu m$. Contact zone was immersed in lubricating oil; the rotation rate was 2 800 r/min. When the debonding area reaches 5% of the contact zone after 5×10^6 cycles, the maximum shear stress amplitude $\Delta\tau$ is defined as coating-substrate fatigue strength and regarded as the dynamic bonding strength.

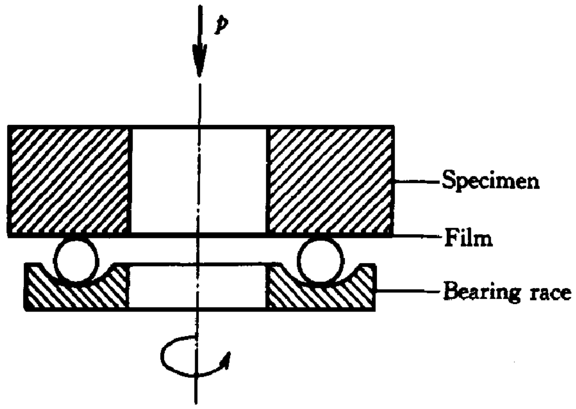

Fig. 1 Sketch of spherical rolling contact fatigue test

The normal loads applied on the spherical rolling ball were 23.1, 27.7, 32.6 and 36.9 N, and the running cycles for 5% area spalling were recorded respectively. The Young's modulus of CrN $E_1 = 330$ GPa, the Poisson ratio $\upsilon_1 = 0.2$. For AISI52100 steel: $E_2 = 219$ GPa; $\upsilon_2 = 0.3$. On the basis of Hertzian theory, the shear stress amplitudes under the above mentioned loads were 320, 330, 340 and 347 MPa, respectively.

3 EXPERIMENTAL

3.1 Results of scratch testing

The scratch test results of coating systems with 10, 20 and 40 keV bombarding energy dynamic recoiling interfaces are shown in Fig. 2. With the increase of bombarding energy the acoustic emission (AE) signal was sharply jumped at the loads of $L =$ 16, 21 and 37 N. The SEM micrograph of the scratch track for 10 keV IDR showed that the coating does not delaminate at the coating/substrate interface, only a few cracks are regarded as intrinsic CrN cracking (see Fig. 3). From the scratch morphology of coating with different energies (IDR) at 80 N ~ 100 N loads (see Fig. 4), show only slight delaminating of the coatings with 10 keV and 20 keV IDR near the end of the track (100 N). Optical micrograph showed significant delaminating for coating with 40 keV IDR occurs at 87 N and the debonding started at 36 N. Obviously, the SEM observation does not agree with the critical force L_c detected by scratch test. The critical value of L_c is associated with the threshold of the acoustic signal which may come from different sources. On the other hand, the SEM clearly indicates where the spalling occurs and it is more reliable than the AE signal in terms of bonding strength evaluation. The SEM observation also shows a large amount of cracks vertical to the scratch direction prior to spalling. This crack may refer to the inherent fracture of the coating layer during sliding and AE signal emission. It seems that the higher the bombarding energy, the larger the inherent fracture strength and so does the AE signal. However, with the increase of

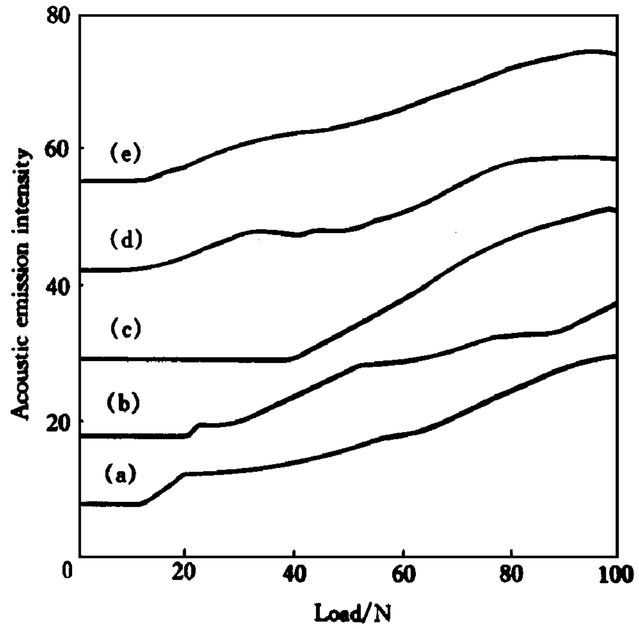

Fig. 2 Scratch testing load-AE curves with different interfaces
(a) —IDR10; (b) —IDR20; (c) —IDR40; (d) —ISR20; (e) —ISR40

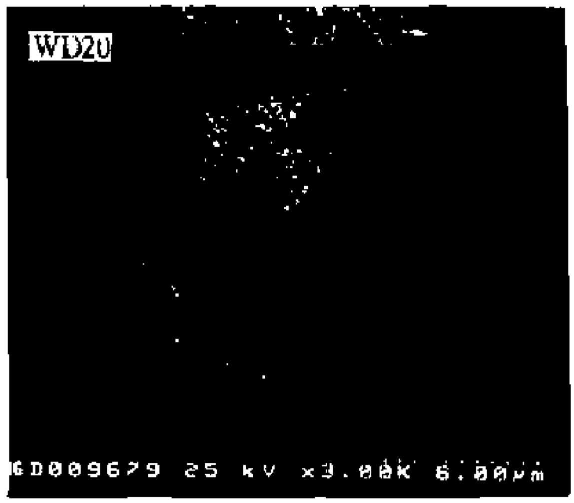

Fig. 3 Scratch morphology of IDR10 sample ($L = 20\,N$)

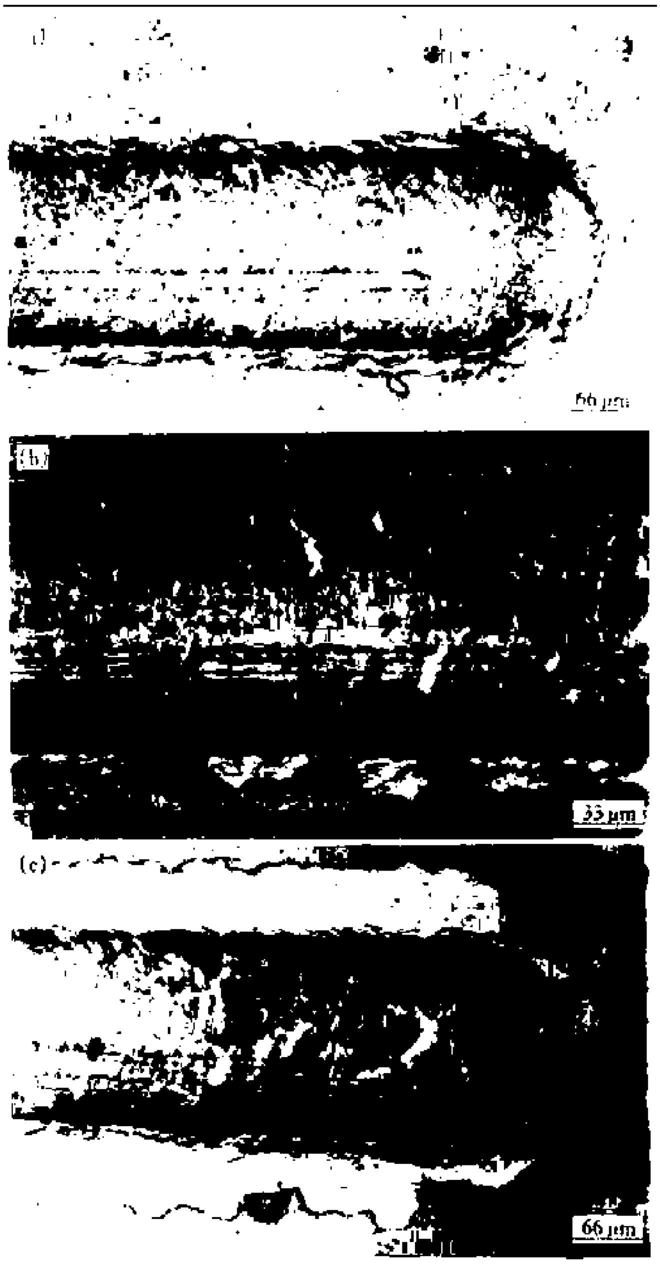

Fig. 4 Scratch morphologies of coatings under different dynamic recoil intermixing processes
(a) —IDR10; (b) —IDR20; (c) —IDR40

the dynamic recoiling voltage as well as the inherent fracture strength, the threshold of AE vs strength takes another rule, i. e. it decreases with increasing energy.

The AE vs load curves of (e) and (d) in Fig. 2 are the scratch results for ISR interface. The threshold of AE signals occurred at around 10 N to 12 N loads.

The optical scratch morphology shown in Fig. 5 indicates that only a few patches of delamination occurred at 100 N and their morphology is somewhat different from that of IDR ones. The bonding strength with ISR interface should be evaluated as 95 N to 100 N loads, and is much higher than that with IDR process.

On the basis of results in Refs. [5, 6], the high bombarding energy IDR process will lead to an nonuniform sputtering for heterogeneous material. The carbide segregated at the interface of high carbon steel AISI52100 and XPS analysis results indicated that the carbon was in the graphite state. This selective sputtering effect is pronounced with the increase of impact energy and results in a low interface adhesion with high bombarding energy interface mixing. For ISR interface, a pre-deposited pure Cr layer with a thickness around 0. 25 μm on the base material, then bombarded by the high energy N ions, can effectively keep from selective sputtering and avoid carbon to segregate at the interface. Table 2 summarizes the critical loads of scratch test evaluated by micrography.

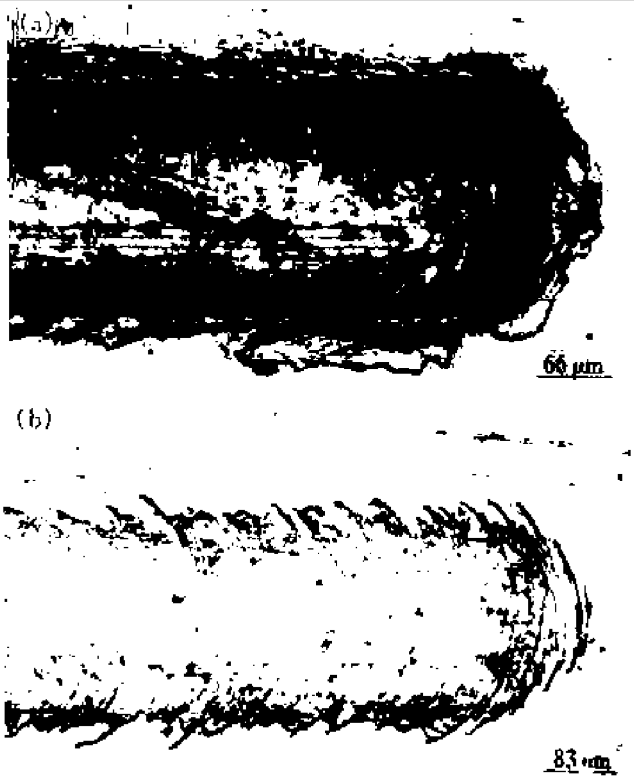

Fig. 5 Scratch morphologies of coatings under different static recoil intermixing processes
(a) —ISR20; (b) —ISR40

Table 2 Summarization of critical loads of scratch test evaluated by micrography

Sample No.	Critical load L_c/N
IDR10	90
IDR20	86
IDR40	36
ISR20	95
ISR40	100

3.2 Results of contact fatigue test

Fig. 6 shows the results of bonding strengths evaluated by rolling contact fatigue test with IDR and ISR processing. The bonding strength of ISR 40 keV being much higher than that of ISR 20 keV indicates that the higher the bombarding energy, the better the adhesion for the static intermixing. But for the IDR interface, high energy N ions bombarding results in a low bonding strength and both 10 keV and 20 keV reach the maximum value. Because of the limitation of the capacity of the testing machine, the bonding strengths for IDR10 and IDR20 cannot be compared further. Basically, the scratch and contact fatigue tests show the same order within the group of each intermixing method. Comparing of the ISR and IDR results, it is noticed that in this study the coating substrate adhesion with IDR intermixing is superior to that of ISR ones.

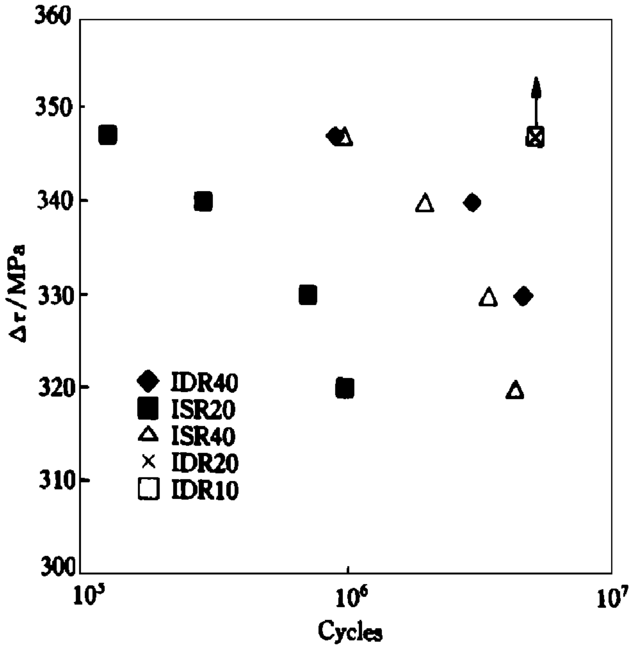

Fig. 6 Δτ—N curves of different coating systems

The delamination morphology of static intermixing after contact fatigue test shown in Fig. 7 indicates the delamination edge with ISR 40 keV processing is more uniform than that with ISR 20 keV ones. This uniform edge may be related to good combination of strength and ductility by high energy ion impact and lead to lower delaminating crack propagation rate and higher adhesion.

4 DISCUSSION

During scratch test, the diamond stylus is penetrating into the coating with the increase of the normal force and produces a complex stress strain field. The critical load L_c will be affected by many factors, such as coating thickness, hardnesses of coating and base material, coefficient of friction, and roughness[4,7]. For instance, for the same interface processing, the thicker the coating, the higher the L_c, even the interface condition is the same. Its result may not reflect the reality of coating adhesion. The critical load L_c should be an evaluation of a synthetical endurance for the coating substrate system under the scratch load. The scratch test may indicate the difference of adhesion for the same coating substrate system with similar deposition processing parameters. But it should be careful to measure the different coating substrate system.

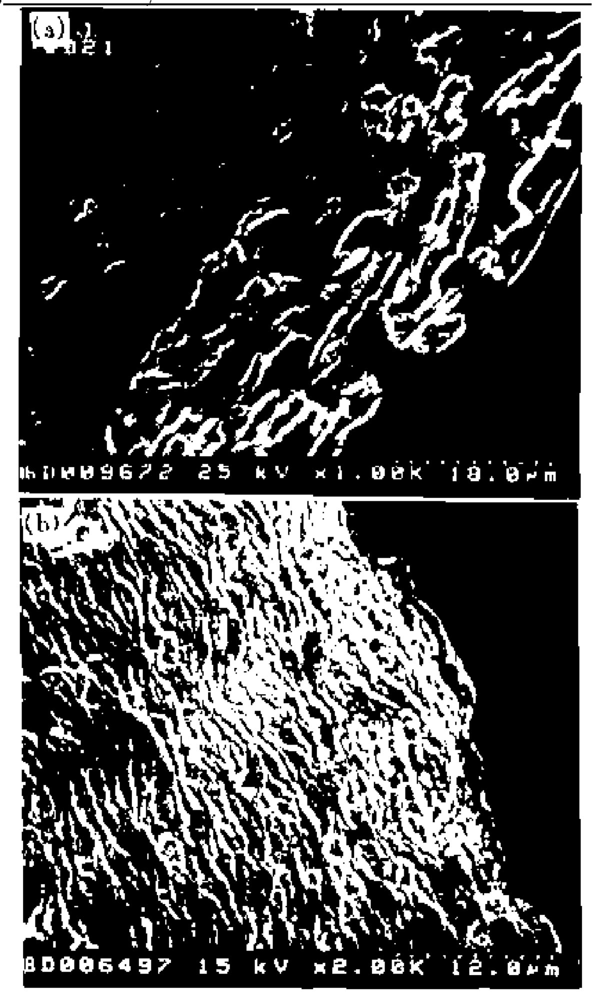

Fig. 7 Morphologies of spherical rolling contact fatigue tests
(a) —ISR20; (b) —ISR40

According to Hertzian theory, the stress and strain tensors under a normal force can be easily calculated. For rolling contact of a coated piece, the cyclic shear stress at the coating substrate interface is responsible for the delamination[8]. Normally, the shear strength is lower than the shear strength of the substrate itself. Crack is easy to form and propagate at the interface even it's not the site of maximum shear stress. In the elastic regime, the shear stress is only associated with the elastic modulus of the substrate and the coating layer. The layer thickness effect can be easily corrected. So Δτ can be employed as an index of the bonding strength, and is more appreciable than the critical load L_c for the evaluation of coating system adhesion.

Because of excellent adhesion for the IDR 10keV and IDR 20keV samples, the coatings did not delaminate at the interface after 5×10^6 cycles if $\Delta\tau > 347$ MPa. It is presumed to increase normal load (p), yet it won't be an effective way.

According to Hertzian theory,

$$\sigma_0 = \left[\frac{6E^2}{\pi^3 R^2}p\right]^{\frac{1}{3}},$$

$$a = \left[\frac{3R}{4E}p\right]^{\frac{1}{3}}, \qquad (1)$$

$$\frac{1}{E} = \frac{1-\upsilon_1^2}{E_1} + \frac{1-\upsilon_2^2}{E_2}$$

where σ_0 is maximum contact stress;

a is radius of contact area;

υ_1, υ_2 are Poisson's ratios of coating and substrate;

E_1, E_2 are Young's modulii of coating and substrate;

R is radius of bearing ball;

p is contact load.

When the thickness of coating is 1.5 μm, p = 23.1 N, σ_0 = 2.25 GPa and a = 0.07 mm, calculation shows that $\Delta\tau$ at the interface is 320 MPa, but the $\Delta\tau_{max}$ at 25.5 μm beneath the interface is 1210 MPa, which is higher than that at the interface. When the load is 36.9 N, $\Delta\tau$ only increases to 347 MPa at the interface, but the maximum alternating shear stress will increase to 1410 MPa at a depth of 30 μm. This may cause fatigue failure to initiate at the $\Delta\tau_{max}$ position in the substrate but not at the coating-substrate interface. Calculation shows that when the normal load is 23.1 N, $\Delta\tau$ can reach 650 MPa at the coating-substrate interface as the diameter of bearing ball decreases from 4.7 mm to 2 mm. Therefore, an effective way for the high bonding strength evaluation is to decrease the radius of the bearing balls and make the $\Delta\tau_{max}$ distribute at the shallow layer of the substrate beneath the interface and keep the base material from cracking.

5 CONCLUSIONS

1) For ion beam enhanced deposition of CrN, using dynamic recoiling intermixing, low bombarding energy as 10 keV and 20 keV exhibit an excellent adhesion. High energy (40 keV) N ions dynamic recoiling will decrease the coating-substrate bonding strength by selective etching effect of the energetic particles.

2) For static recoiling intermixing, 40 keV N high-energy ion impact reaches higher adhesion than that of 20 keV ones. However, the static recoiling ones are not as good as 10 and 20 keV dynamic intermixing.

3) Micrograph observation gives better delamination criterion than the acoustic emission signal in scratch test.

4) For high bonding strength as IBED CrN coating substrate system, spherical rolling contact fatigue test is the best way to evaluate the bonding strength of the coatings.

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(Edited by PENG Chao-qun)