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Hardness, toughness and electrochemical properties of Cr-N coating by ion beam enhanced deposition①

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Abstract: The hardness, toughness and electrochemical properties of the Cr-N coatings were studied by the method of Ion Beam Enhanced Deposition(IBED). The results show that the fraction of CrN phase and its hardness increase with increasing N_2 partial pressure and N ions bombarding energy in a certain range, but the toughness decreases. When the N ions : Cr atoms ratio changes from 1.45×10^{-2}, 3.67×10^{-2} to 5.87×10^{-2}, Cr_2O_3 is produced. In terms of corrosion resistance, the coated specimen shows a slight improvement in comparison with substrate 52100 steel. The Cr-N coated specimen is characterized with pitting corrosion by penetrating the agent through the defects involved very thin coating layer .

Key words: Cr-N; coating; hardness; toughness; electrochemistry **Document code**: A

1 INTRODUCTION

The mechanical properties of materials such as tensile strength, plasticity and wear resistance are closely related to their hardness[1, 2]. In order to improve the wear and corrosion resistances of machine parts, various hard coatings were used. However, a very thin coating layer(0.5 ~ 1.5 μm) deposited by Ion Beam Enhanced Deposition (IBED) technique is usually not match for the required depth of various macro/micro indentation tests[3~5], in this case it's appreciable to use the nano-indentation method, with which less than 1 μm thick layer can be measured. Usually, the wear mechanism for a hard coating on a hard substrate are micro-ploughing and spalling. With increasing the coating hardness, the micro-ploughing decreases and the wear resistance improves. But an excessive hardness of the coating layer will associate with a decrease of toughness and deteriorate debonding resistance and tribological properties. So it's important to optimize the hardness and toughness of a coating layer. To improve the coating properties, the relation of the processing parameter, structure of Cr-N coating and its hardness, toughness and electrochemical properties are studied in the present work.

2 EXPERIMENTAL

The base materials were Si(111) chip and AISI52100 steel (HRC61), their average surface roughness(Ra) was less than 0.05 μm. To obtain an appropriate interface mixing, 20 keV N ion dynamic recoiling was processed; its deposition parameters are listed in Table 1.

Nano Tester 550 was used to measure the hardness of the coatings with different deposition processings. The indenting load range was 0.05 ~ 76 mN, the loading and unloading rate was 0.65 mN/s, loading was held 30 s and a standard Berkovich diamond tip was used. The toughness of the coating was measured by Micrometer-II tester with Vicker indenter at 1N load and the loading lasted 15 s. The fracture toughness (K_{IC}) of the coatings were calculated by the following equation[6].

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$$K_{IC} = 0.129\left(\frac{Ha^{1/2}}{\phi}\right)\left(\frac{E\phi}{H}\right)^{0.4}\left(\frac{L}{a}\right)^{-3/2} \quad (1)$$

where H is the hardness of coating; a is the half length of opposite angle; Φ is the limited factor, equals 3; E is the elastic modulus; L is the summation of four corners crack length.

Table 1 Cr-N coating deposition parameters

Samples	p_N/Pa	E_N/keV	N ions:Cr atoms
P1	1.5×10^{-3}	4	1.45×10^{-2}
P2	4.0×10^{-3}	4	1.45×10^{-2}
P3	1.0×10^{-2}	4	1.45×10^{-2}
E1	1.0×10^{-2}	4	1.45×10^{-2}
E2	1.0×10^{-2}	8	1.45×10^{-2}
E3	1.0×10^{-2}	12	1.45×10^{-2}
I1	1.0×10^{-2}	8	1.45×10^{-2}
I2	1.0×10^{-2}	8	3.67×10^{-2}
I3	1.0×10^{-2}	8	5.87×10^{-2}

p_N represents N_2 partial pressure;
E_N means N ion bombarding energy;
N ions:Cr atoms is the ratio of N ions to Cr atoms.

The electrochemical properties of Cr-N coatings with different N ion energies were tested on AISI 52100 steel substrate and operated with 0.5 mol/L H_2SO_4 and 0.5 mol/L NaCl solution. The structure, component and element state of the films were investigated by XRD and PSI 5702 XPS/AES.

3 RESULTS AND DISCUSSION

3.1 Hardness of coatings

With different nitrogen partial pressures, the hardness values evaluated by nano-indentation are listed in Table 2. The thickness of the coatings with different p_N and E_N was about 1.5 μm, for the indentation depth was required less than 1/7 to 1/10 of the coating thickness, the indenting load was controlled under 8 mN. In this case, these hardness data can be regarded as intrinsic hardness of the coatings[7, 8]. Fig. 1 is the load p(mN)—depth h(nm) curve with $p_N = 1.0\times10^{-2}$Pa.

When the N_2 partial pressure increases from 1.5×10^{-3}Pa to 4.0×10^{-3}Pa and 1.0×10^{-2} Pa, the N contents (mole fraction, %) of coatings amount to 8 %, 40 % and 45 % respectively. CrN will become a dominant phase and Cr/Cr_2N structure will reduce. Meanwhile, the hardness will increase from 12.30 GPa, 17.10 GPa to 18.72 GPa. When N ion bombarding energy changes from 4 keV, 8 keV to 12 keV, the coating hardness will increase from 18.72 GPa, 20.34 GPa to 22.34 GPa. The results indicate that the N ion bombarding energy affects the hardness of the Cr-N coatings significantly, although the chemical compositions and structures of the coatings observed by AES and XRD analysis show little difference. With N ions:Cr atoms ratio changing from 1.45×10^{-2}, 3.67×10^{-2} to 5.87×10^{-2}, the thicknesses of the coatings are 1.5 μm, 1.0 μm and 0.5 μm. As N ions:Cr atoms = 1.45×10^{-2}, the Cr-N coating only consists of CrN phase. When the N ions : Cr atoms ratio exceeds 3.67×10^{-2}, a 5.87×10^{-2} N ion flux of bombarding will result in an acceleration of re-sputtering of the coated Cr-N layer. In the meantime Cr_2O_3 is easy to be produced through decomposition of CrN in the layer. So

Table 2 Hardness and toughness results from different deposition parameters

Samples	Hardness/GPa	K_{IC}/(MPa·m$^{1/2}$)
P1	12.30	—
P2	17.10	—
P3	18.72	—
E1	18.72	2.50
E2	20.34	1.80
E3	22.34	1.50
I1	22.34	1.80
I2	22.64	1.45
I3	24.05	1.40

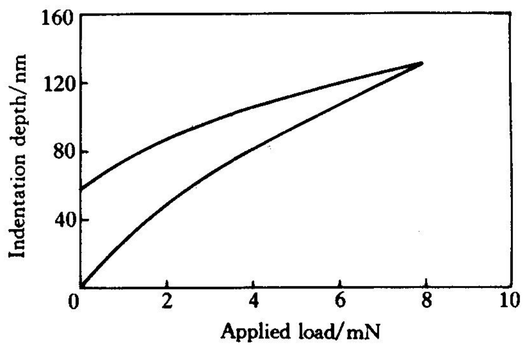

Fig. 1 Loading and unloading curves

the coating is composed of CrN and Cr_2O_3, and its hardness will change from 20.34 GPa, 22.64 GPa to 24.05 GPa. As the hardness of Si(111) chip is softer than that of coating and the indenting depth for 0.5 μm thick coating is not less than that of 1/7~1/10 coating layer, the absolute hardness of Cr_2O_3 must be higher than that of experimental results. These results indicate that the hardness of the coatings is closely related to its structure, particularly when the structure changes sharply by the deposition parameters.

3.2 Toughness(K_{IC}) of coatings

With different N ion bombarding energies and N ions : Cr atoms ratios, the toughness (K_{IC}) of the Cr-N coatings are listed in Table 2. The high energy N ion bombarding results in irradiation defects and vacancies, and the coating density is decreased[9]. Usually high energy bombardment leads to a dense coating layer, however if the energy is too high, the toughness of the coating layer is decreased and will deteriorate the properties of the Cr-N coating[10]. With increasing N ions: Cr atoms ratio, Cr_2O_3 will become a predominate structure and lower down the coating toughness even the hardness is high. So it is important to adjust hardness and toughness of the coating layer.

3.3 Electrochemical properties

Fig. 2 shows the potential dynamic current curves of the Cr-N coatings bombarded at 4 keV, 8 keV and 12 keV nitrogen ions on AISI52100 steel substrate, and measured in 0.5 mol/L H_2SO_4 water solution. The depassivation potential shifts to the negative direction with increasing N ion bombarding energy and all coated layers show better corrosion resistance than the naked substrate. An increase in the current at potentials below the potential of depassivation for the existence of two phases structure system(Cr + CrN) indicates alloy corrosion[10]. The current of all samples increase rapidly in the same manner when the potential reaches a definite level. The electrochemical curves of Cr-N coatings with different bombarding energies measured in 0.5 mol/L NaCl solution are shown in Fig. 3, which is similar to those of in 0.5 mol/L H_2SO_4. The coated specimens show a slight improvement in comparison with the AISI52100 steel substrate. The Cr-N coated specimens are characterized in pitting corrosion by penetrating the agent through the defects. The morphology of coating defects and pitting corrosion are shown as Fig. 4 and Fig. 5. SEM observation shows a number of corrosion pits distributed on the surface, yet the coating is partly attached at the bottom of the pit. So the coating has remarkable

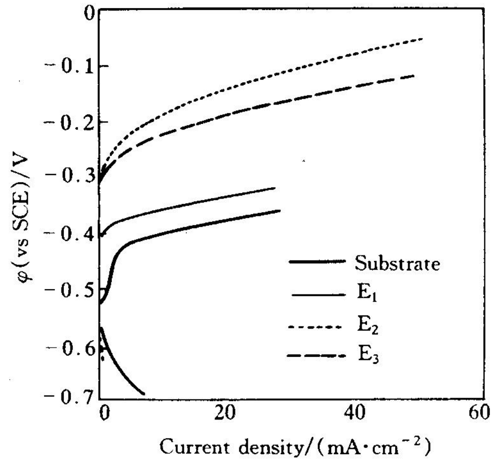

Fig.2 Anodic polarization curves in 0.5 mol/L H_2SO_4 for Cr-N coatings

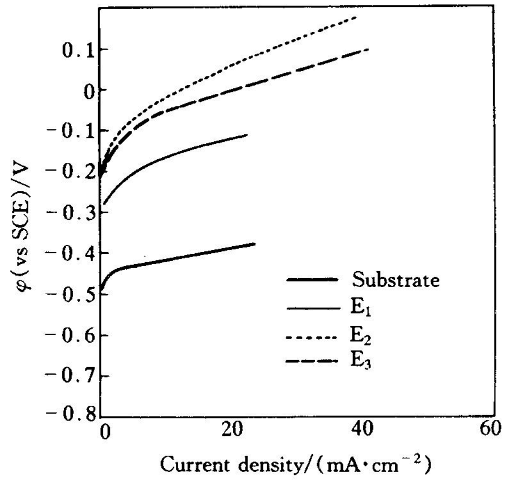

Fig.3 Anodic polarization curves in 0.5 mol/L NaCl for Cr-N coatings

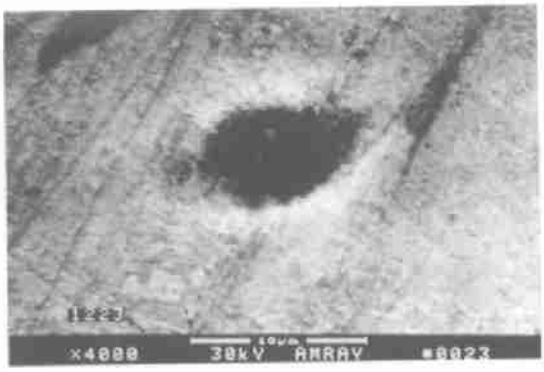

Fig. 4 Morphology of coating surface defect

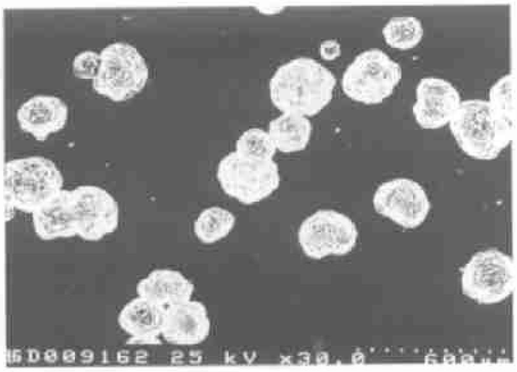

Fig. 5 Corrosion morphology of Cr-N coating

corrosion resistance (Fig. 6). Under the condition of electrochemical corrosion, the corrosion occurs at the defect position and makes the surface exposed to the solution. The corrosion potential of the substrate is lower than that of coating. A small cathode with a large positive anode will make the base material corrode rapidly and result in pitting corrosion. It's important to reduce the size and number of the defects by adjusting deposition parameters.

4 CONCLUSIONS

(1) With increasing N_2 partial pressure, the content of CrN will increase and lead to increase of Cr-N coating hardness. High N ion bombarding energy results in increasing of Cr-N coating hardness.

Fig. 6 Morphology of pitting corrosion

(2) When the ratio of N ions : Cr atoms changes from 1.45×10^{-2}, 3.67×10^{-2} to 5.87×10^{-2}, the structure of the coating will change from CrN, CrN + Cr_2O_3 to Cr_2O_3. The hardness of the film becomes higher and the coating toughness (K_{IC}) is reduced.

(3) The corrosion resistance of the Cr-N coating is improved in comparison with those of the base material AISI52100 steel. Cr-N deposited specimen is characterized in pitting corrosion in electrochemical corrosion by the penetrating agent through coating defects.

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