EFFECT OF ADDITIONAL ELEMENTS ON MICRISTRUCTURE AND PROPERTIES OF CR-N BASED COMPOSITE COATINGS[1]

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Abstract

CrMoN and CrWN composite coatings were deposited unsing closed field unbanlanced magnetron sputter ion plating system. The microstructure, preferred orientation and morphology of coatings were determined by X-ray diffraction analysis and SEM observation. Influence of additional elements on the microstructure, adhesion, mechanic and tribological properties have been investigated. XRD Results showed that preferred orientation of CrMoN and CrWN coatings changed obviously as compared with the pure CrN coating. All of the new compostie coatings exhibited excellent adhesion due to the gradient interface layer design. By introducing Mo and W elements into the CrN-based structure, the coating hardness improved in comparision with the pure CrN coatings. Results also showed the wear resistance of CrMoN and CrWN coatings increased clearly. The steady-state dry friction coefficients measured against a WC-6%Co ball for the new compostie coatings are about 0.3, which were significant dropped than that of pure CrN coaing of 0.5. It is expected that these advantageous properties can enable these new compsite coatings for a wide range of applications such as dry high-speed cutting.

Key words: CrN based compsite coating; Microstructure; Hardness; Tribological behaviour.

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1 INTRODUTCITON

Cr-N based coatings deposited by magnetron sputtering have been reported to have good hardness, excellent wear and corrosion resistance. A further improvement of mechanical properties and tribological behaviour is still asked for if a hard coating layer is to meet the needs of diverse service conditions. Alloying is one of usually used processes in the modification of the bulk material. The basic strengthening mechanisms of alloying processes included of solid-solution strengthening, and dispersion strengthening. Quoting the materials strengthening principle in bulk materials, therefore, many reports on compound formation by reactive co-sputtering of two metals were published. And the properties of composite coating also dependents upon the species of addition elements co-deposited into the coatings.

An incorporation of other elements into the Cr-N based coatings to produce a composite coating have been confirmed to be effective to improvement their mechanical and tribological performance.[1-3] Properties of these composite coatings depend not only on their elemental and phase composition and but also on the size, shape and crystallographic orientations of grains from which they are composed.[4] Many authors have discussed the enhanced mechanism of these kinds of incorporation coatings. P. Hones[5] indicated that the different hardness values of the CrTiN, CrMoN and CrNbN ternary compounds coatings are mainly due to changes in the bonding character. For CrMoN coating, it was concluded that the coatings having the Mo content less than 30.4 at.% must be a substitutional solid solution of (Cr, Mo)N.[6] J. Musil[7] demonstrated that sputtered nitrides containing a small amount (≤15 at.%) of the added element, such as Cr–Ni–N, could be a very efficient method to produce nanocomposite films based on nitrides because of the formation of a solid solution in coatings. Literatures also found that the addition of Al, Ti elements could not only significantly improve the hardness, but also, both Cr and Al form a passive oxide layer, improving overall oxidation resistance at high temperature.[8-10] Although many authors have demonstrated and discussed the mechanisms of hardness improvement and enhance of wear resistance, there are still a rather unexplored means for strengthening of composite coating.

In this paper, the aim of combining chromium with molybdenum and tungsten elements as the additional metal is to enhance the wear resistance of the coating and to increase high hardness by utilizing the composite effect. The influences of added elements on the microstructure, morphology, adhesion, mechanic and tribological behaviour have been investigated.

2 EXPERIMENTAL DETAILS

The Cr-N based coatings were deposited on the high speed steel substrates in an industrial Closed Field Unbalanced Magnetron Sputter Ion Plating system. The substrates were Ar plasma ion cleaned using pulsed DC bias prior to deposition and a Cr interlayer of approximately 200-300 nm was first deposited. Then, nitrogen was introduced into the chamber to produce a ramp Cr-N coating of about 1μm thickness after deposition of the initial Cr interlayer. The last stage is the deposition of Cr-*Me*-N (*Me* is the additional elements of Mo and W) composite coatings at a bias of -60 V and OEM setting of 55%. Concentration of the coating was controlled using a closed-loop Optical Emission Monitoring (OEM) system. Coating thicknesses were assessed using the ball crater tester. Adhesion was measured using a 0.2-mm tip radius Rockwell diamond indenter applied a 150-kgf load. Pin-on-disc sliding wear tests were performed on the coated samples against a 5-mm WC-5%Co ball. Each sample type was tested at a normal applied force of 80 N giving a maximum contact pressure at the end of the test. A sliding speed of 0.2 m s^{-1} was used for all the tests. The tests in air were carried out for a sliding distance of 360 m (0.5 h). The frictional force generated by the sliding was recorded. Optical microscopy was used to examine and measure the wear trace of coatings. The microstructure, preferred orientation and morphology of coatings were determined by X-ray diffraction analysis and SEM observation.

3 RESULTS AND DISCUSSION

3.1 Effect of Additional Elements on Microstructure and Morphology

Fig.1 is the XRD patterns of CrN、Cr-Mo-N、Cr-W-N coatings. CrN coating exhibited strongly CrN(111) and CrN(200) peaks with traces of CrN(220) and CrN(311) orientation. CrWN coating showed mainly a (200) orientation with the weak peaks of the CrN(111) or CrN(220) orientations. For CrMoN coating, only the diffraction peak corresponding to the CrN(200) and weak of CrN(111) can be observed. The relative intensities of the diffraction peaks of CrN(111) tended to decrease obviously after doping of Mo and W in the composite coatings. All of the diffraction peaks detected in CrMoN and CrWN coatings were found to broaden, and, shifted to lower diffraction angle than that in CrN coating. Its might be caused by the addition of Mo and W to form fine crystal or induced the internal stress in the coatings. But the diffraction peaks of MoN or WN phase did not detected in XRD patterns of CrMoN and CrWN coatings. This result demonstrated that added Mo and W atoms would be dissolved into CrN lattice by substitutional replacements of bigger Mo (1.363Å) and W (1.371Å) atoms for Cr (1.249Å) sites, respectively. It was agreement with the other author's publicized literatures. [6,11]

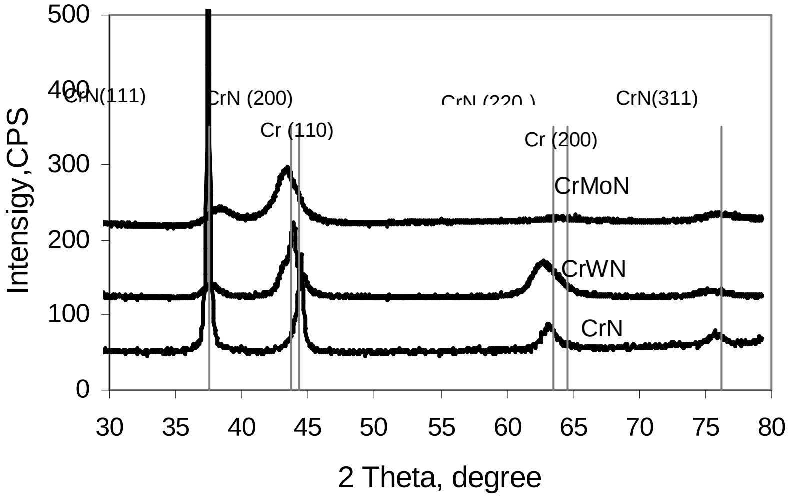

Figure 1. XRD patterns of CrN, CrMoN and CrWN coatings.

SEM observation results of CrN, Cr-Mo-N and Cr-W-N coatings showed in Fig.2. Section morphology exhibited typical columnar microstructure for all coatings. From the surface topographic features, the coatings with addition of Mo content exhibited much denser and smoother.

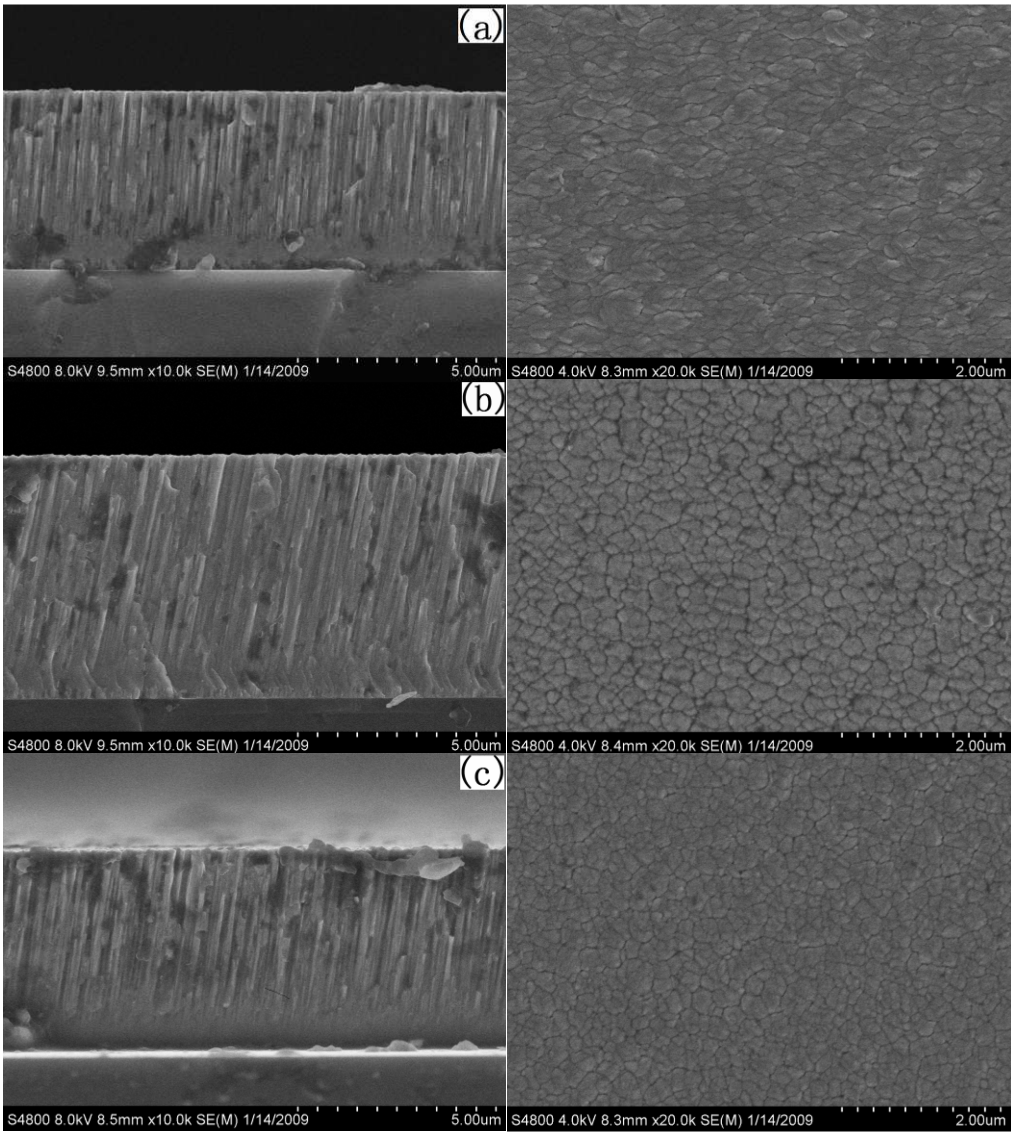

Figure 2. Cross-section and surface morphologies of CrN, CrMoN and CrWN coatings.

3.2 Effect of Additional Elements on Mechanical Properties of Coatings

3.2.1 Hardness, modulus and adhesion of coatings

Fig.3 is the hardness and modulus of CrN, CrMoN and CrWN coatings deposited at same bias and OEM setting. Results showed that the added elements of Mo and W are benefit of the improvement of hardness of coatings. Cr atoms in the NaCl f.c.c structure of CrN coating were substitutional replaced by Mo and W with bigger atomic radii might induce a disruption of the initial crystal structure. This crystal mismatch leads to a increasing of resistance to dislocation motion. Consequently, hardness of CrMoN and CrWN coaings increased because of this solid-solution strengthening effect. Modulus of coatings exhibited a tendency of tiny drops. Because of not enough amounts of added elements in the coatings, modulus could not be changed in greater levels. The H/E ratio has been presented by a number of authors to be a suitable parameter for predicting wear resistance of coating material than is hardness alone.[12,13] The higher H/E ratio of Cr-N based coatings of molybdenum and tungsten co-deposition should be of benefit to improve the wear resistance of coatings. Adhesion of various coatings of CrN, CrMoN and CrWN were evaluated using

Rockwell indentation under a load of 150 kgf. Excellent coatings adhesion were demonstrated in the Rockwell adhesion test on the M42 high speed steel substrates with no delamination and only slight radial cracking (Fig. 4).

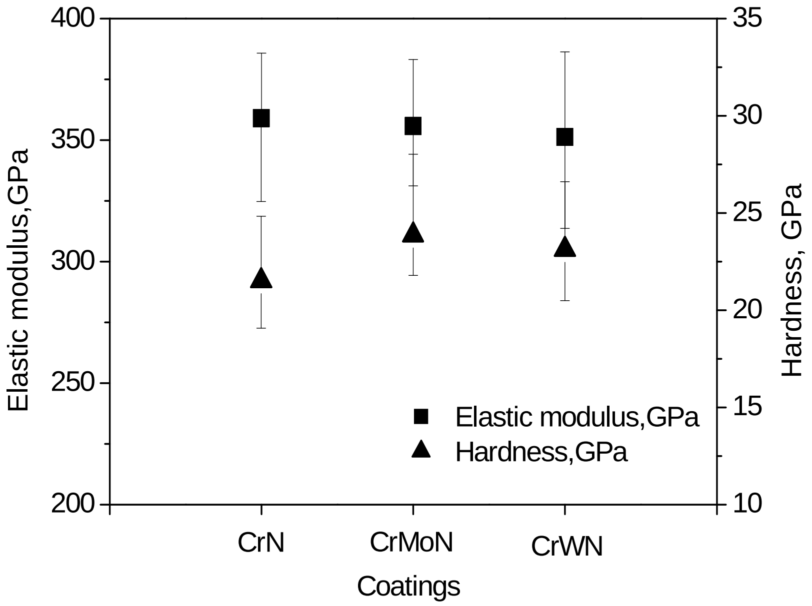

Figure 3. Hardness and modulus of CrN, CrMoN and CrWN coatings.

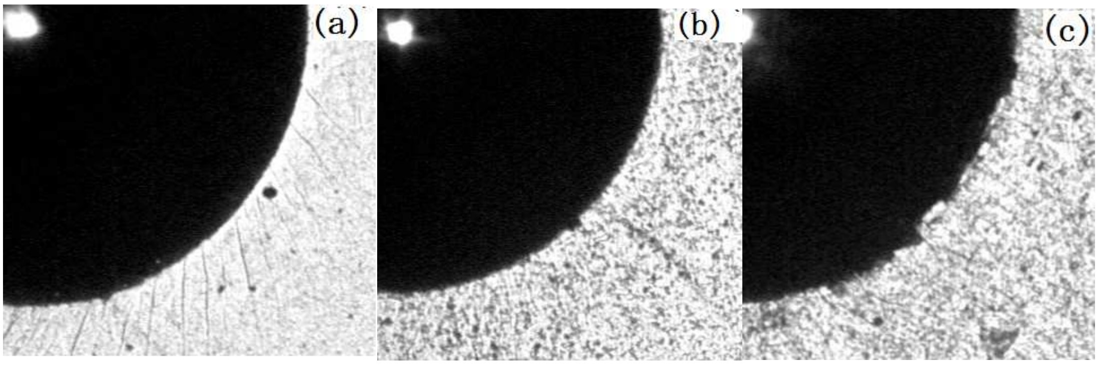

Figure 4. Adhesion of (a) CrN, (b) CrMoN, (c) CrWN assessed using Rockwell indenter.

3.2.2 Tribological behaviour

Fig.5 showed the friction coefficient of CrN, CrMoN and CrWN coatings in dry sliding against WC ball using ball-on-disc tester under a load of 20N at ambient temperature. The average friction coefficient decreased from 0.5 for CrN coating to about 0.3 for CrMoN and CrWN coatings. The friction coefficient of CrN based coatings was dropped because of additions of W and Mo. Decreasing of friction coefficient with addition of Mo content in coating can be explained by a tribo-chemical reaction, where the coating layer reacts with ambient H_2O to produce MoO_3 thin layer during sliding process. These products like MoO_3 tribo-layer were known to function as self-lubricant layer. [11] The reason for the friction coefficient of CrWN coatings was lower than that of CrN coating cannot be solely explained by the tribo-chemical reaction. Other mechanisms might be involved. Fig.6 was the SEM morphologies of the wear tracks (Figure 6.a, b, c) and the wear scars on the counter ball surface (Figure 6.a1, b1, c1) of various coatings. It can be found that obverse wear was detected for pure CrN coating deposited at the same bias and OEM setting. The wear resistance of CrMoN and CrWN coatings significantly improved because of the high hardness and lower friction coefficient.

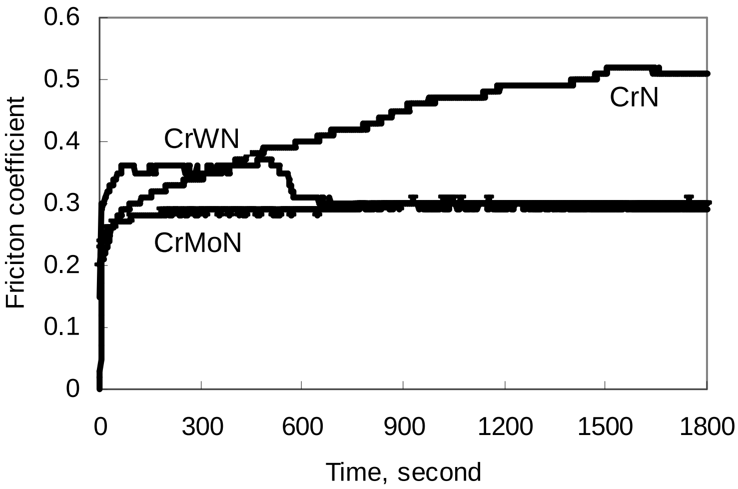

Figure 5. Friction coefficients of CrN, CrMoN and CrWN coatings.

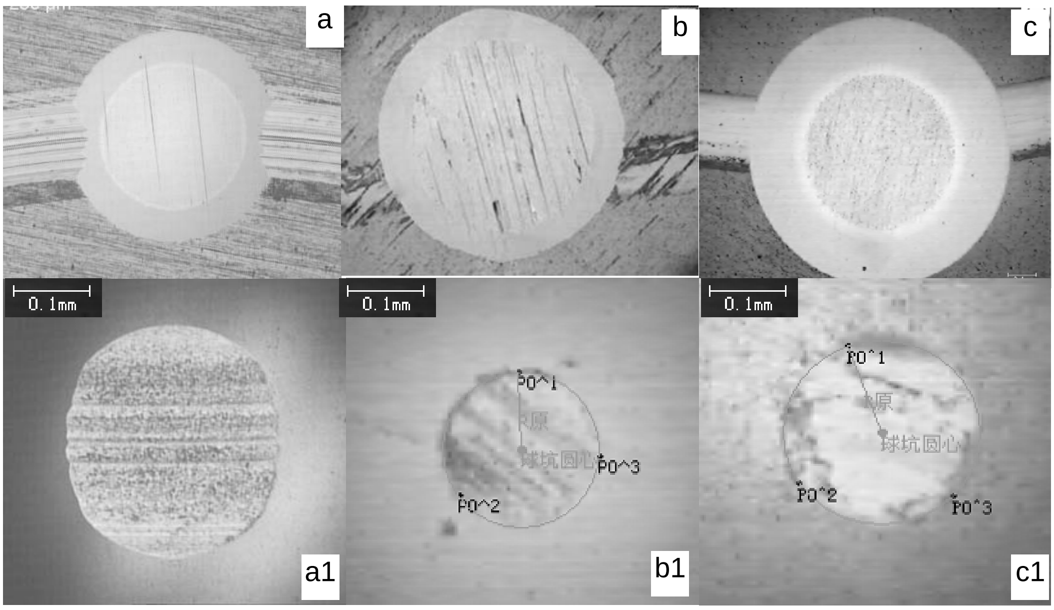

Figure 6. Wear tracks of (a) CrN, (b) CrMoN and, (c) CrWN.

4 CONCLUSIONS

(1) Preferred orientation of CrN based coating added Mo and W elements changed obviously compared with the pure CrN coating under the same bias voltage and OEM setting. CrN(111) texture turns to weak, CrN(200) diffraction peaks increased. But the MoN and WN phase can not be detected in the CrMoN and CrWN composite coatings.
(2) The CrMoN and CrWN composite coatings exhibited excellent adhesion with the high speed steel substrate, because gradient layer was designed between the interface Cr layer and top layer.
(3) Hardness of CrMoN and CrWN composite coatings increased clearly in comparison with pure CrN coating. Modulus of composite did not change due to the limited additional element of Mo and W elements.
(4) Friction coefficient of CrMoN and CrWN dropped from 0.5 to 0.3 than that of pure

CrN coatings. Wear resistance of composite coatings have been improved significantly.

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