Effect of Mo Content on Microstructure and Properties of CrMoN Composite Coatings Postprint

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Abstract

CrMoN composite coatings with different Mo contents were prepared on M2 high-speed steel substrates by direct current reactive magnetron sputtering, and the influence of Mo content variation on the composition, phase structure, chemical valence state, cross-sectional morphology, microhardness, and tribological properties of the CrMoN composite coatings was investigated. The results show that with increasing Mo content, the phase structure of the CrMoN composite coatings first transforms into a (Cr,Mo)N substitutional solid solution based on the fcc-CrN phase, and subsequently into a mixed phase dominated by the fcc- -Mo2N phase; when the Mo content reaches 69.3 at%, a small amount of bcc-Mo phase is generated; the microhardness of the CrMoN composite coatings first increases and then decreases, reaching its maximum at a Mo content of 45.4 at%; when the Mo content exceeds 45.4 at%, a large amount of MoO3 phase forms during friction with the counterface, reducing the friction coefficient and wear rate.

Full Text

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Abstract

Ceramic coatings are widely used as protective layers to enhance the performance and durability of tools and components. Compared with conventional TiN-based hard coatings, CrN-based coatings such as Cr-X-N (X=Ti, Al, Si, C, B, Ta, Nb, Ni) represent a more attractive alternative due to their low friction coefficient, superior oxidation resistance, and excellent corrosion resistance under severe environmental conditions. Among these, CrMoN coatings are particularly promising because the self-lubricating MoO phase may form during tribological processes. However, the effect of Mo content on the structure and tribological properties of CrMoN coatings remains unclear.

In this study, CrMoN composite coatings with varying Mo content were deposited on M2 high-speed steel (HSS) substrates by DC reactive magnetron sputtering. The influence of Mo content on microstructure and properties was systematically investigated, including chemical composition, phase structure, chemical valence, cross-sectional morphology, microhardness, and tribological behavior. The results showed that the phase structure evolved with increasing Mo content, first transforming into a (Cr, Mo)N substitutional solid solution based on the fcc-CrN phase, then into a mixed phase dominated by fcc- -Mo N. When the Mo content reached 69.3 at%, a small amount of elemental bcc-Mo phase appeared. The microhardness of CrMoN composite coatings initially increased, reaching a maximum at 45.4 at% Mo, then decreased. When the Mo content exceeded 45.4 at%, a relatively low friction coefficient was obtained compared with CrN coating due to the formation of substantial MoO lubricating phase during the friction process.

KEY WORDS CrMoN composite coatings, magnetron sputtering, microhardness, friction coefficient

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1. Introduction

M2 high-speed steel substrates measuring 20 mm × 20 mm × 2 mm were used in this study. The substrates were ground sequentially to 2000-grit sandpaper, polished with diamond paste, ultrasonically cleaned in acetone and absolute ethanol for 15 minutes each, dried with cool air, and then placed in a JGP560 ultra-high vacuum magnetron sputtering system. [Figure 1: see original paper] shows a schematic of this apparatus, with independently positioned Cr and Mo targets (both >99.9% purity) located at the bottom of the vacuum chamber. The target-to-substrate distance was 60 mm for both targets, and the substrate holder oscillated above them during deposition.

Prior to deposition, the chamber was evacuated to 5×10   Pa and the substrates were heated to 200°C. Argon gas was then introduced to maintain a pressure of

0.5 Pa. Substrate pre-sputtering cleaning was performed at a DC bias of -200 V and Cr target current of 0.4 A for 5 minutes. Subsequently, a metallic Cr adhesion layer was deposited to improve coating-substrate bonding at a DC bias of -100 V and Cr target current of 0.4 A for 5 minutes. The CrMoN composite coatings were then deposited using two independent mass flow controllers to regulate N and Ar flow rates, both set at 30 mL/min, maintaining a pressure of 0.5 Pa. Different Mo contents were achieved by adjusting the Cr and Mo target currents while keeping the substrate temperature at 200°C throughout the 120-minute deposition process, followed by cooling to room temperature under vacuum. Specific deposition parameters are summarized in .

TiN-based hard coatings have been widely applied in industrial production due to their high hardness, excellent wear resistance, and low friction coefficient. In particular, TiN, TiCN, and TiAlN coatings have become mature and dominant in the tool coating field. However, TiN hard coatings suffer from weak adhesion, high brittleness, and easy spalling. In contrast, CrN coatings exhibit superior thermal stability, corrosion resistance, and wear resistance, with significantly better high-temperature oxidation resistance than TiN coatings, attracting considerable attention. Nevertheless, the hardness of CrN coatings is lower than that of TiN. Researchers have improved CrN performance through compositional modification and nanostructuring, such as adding other elements to form ternary chromium-based nitride coatings Cr-X-N (X=Ti, Al, Si, C, B, Ta, Nb, Ni). Since Mo-containing hard coatings can generate MoO lubricating phases during friction and wear processes, Mo doping is expected to enhance the hardness and wear resistance of CrN coatings. However, the lubricant content significantly affects the tribological performance of self-lubricating materials: insufficient lubricant supply cannot compensate for consumption during wear, potentially increasing friction; optimal lubricant content forms effective lubricating films that reduce friction; while excessive lubricant content degrades mechanical strength. Currently, detailed reports on the effect of Mo content on the friction properties of CrMoN composite coatings are scarce. Therefore, this work prepared CrMoN composite coatings with different Mo contents by DC reactive magnetron sputtering to investigate the influence of Mo content on composition, phase structure, chemical valence, cross-sectional morphology, microhardness, and friction properties, aiming to optimize the Mo content in CrMoN coatings.

2. Experimental Methods

The phase composition of the coatings was analyzed using a D/MAX-RA X-ray diffractometer (XRD) with Cu K radiation at 50 kV and 100 mA, scanning from 15° to 85° at 0.02° step size and 4°/min speed. Cross-sectional morphology and coating thickness were examined using an INSPECT-F50 scanning electron microscope (SEM), and chemical composition was qualitatively analyzed with an attached ISIS energy-dispersive spectrometer (EDS). Chemical valence states were investigated using an Escalab250 X-ray photoelectron spectrometer (XPS) with Al K radiation (1486.6 eV) at 150 W and 15 kV. Microhardness was measured with an LM 247AT automatic digital microhardness tester at 10 g load for 15 seconds. Tribological properties in ambient atmosphere were evaluated using an MS-T3000 friction and wear tester with a 4 mm diameter Al O ball counterpart under 2 N load, 200 r/min rotation speed for 30 minutes. Wear track cross-sectional area was measured with an Alpha-Step IQ surface profilometer to calculate volumetric wear rate, and worn surfaces were observed by SEM.

2.1 Composition, Phase Structure, and Cross-Sectional Morphology

EDS analysis results of metallic elements in CrMoN composite coatings with different Mo contents are presented in , showing Mo content varying from 0 to 69.3 at%. [Figure 2: see original paper] displays the XRD patterns of CrMoN coatings with different Mo contents. Without Mo addition, the coating exhibited a NaCl-type fcc-CrN phase with weak diffraction peaks on (200) and (220) planes. All Mo-containing CrMoN coatings showed diffraction peaks on (111), (200), (220), and (311) planes with preferred orientation along the (200) plane. As Mo content increased to 45.4 at%, the (200) diffraction peak gradually shifted slightly to lower angles, while above 45.4 at%, a significant shift occurred. [Figure 3: see original paper] shows the fcc lattice constant calculated from the (200) plane spacing. The lattice constant increased linearly with Mo content from 0 to 45.4 at%, following Vegard' s law, indicating that larger Mo atoms (0.1454 nm) substituted for smaller Cr atoms (0.1267 nm) in the CrN lattice, forming a (Cr, Mo)N substitutional solid solution based on the fcc-CrN phase. When Mo content exceeded 45.4 at%, the lattice constant increased sharply, deviating from Vegard' s law due to the formation of more fcc- -Mo N phase with a larger lattice constant (0.417 nm) than CrN (0.414 nm), reducing the relative CrN content and shifting the dominant phase from the (Cr, Mo)N solid solution. At 69.3 at% Mo, weak diffraction peaks of elemental Mo appeared, indicating a small amount of bcc-Mo phase.

[Figure 4: see original paper] presents cross-sectional SEM images of CrMoN coatings with different Mo contents. The single-phase CrN coating exhibited a columnar grain structure. With increasing Mo content, the columnar grains refined and nearly disappeared at 45.4 at% Mo. Further Mo addition caused the columnar structure to reappear. This phenomenon likely resulted from the high sputtering currents of both targets, which imparted high energy to incident particles, enabling sufficient diffusion of deposited atoms to form uniform dense structures. High deposition rates and doping both contributed to grain refinement. The columnar grain size first decreased to a minimum at 45.4 at% Mo, then increased again. Grain sizes calculated using the Scherrer formula, listed in , showed consistent trends with these observations.

2.2 XPS Analysis of Coating Surfaces

[Figure 5: see original paper] shows the Cr 2p, Mo 3d, and N 1s XPS spectra of CrMoN coatings with 20.4 at% and 69.3 at% Mo, fitted using Gaussian-

Lorentzian iteration. The Cr 2p / spectrum in [Figure 5a: see original paper] was fitted with two peaks corresponding to CrN (575.04 eV) and Cr O (576.82 eV). With increasing Mo content, the Cr 2p / binding energy position remained unchanged while peak intensity decreased, indicating unchanged Cr valence but reduced relative content. The Mo 3d / spectrum in [Figure 5b: see original paper] was fitted with two peaks for -Mo N (228.25 eV) and MoO (228.93 eV). The Mo 3d / binding energy also remained constant with increasing Mo content, while peak intensity increased, suggesting unchanged Mo valence but increased relative content. Although elemental Mo formed, its binding energy (228 eV) is very close to that of -Mo N (228.25 eV) and its content was low, thus not affecting the overall Mo valence state. Cr O and MoO formed through chemical reactions between Cr/Mo and residual oxygen in the vacuum chamber during deposition. The N 1s spectrum in [Figure 5c: see original paper] was fitted with peaks for CrN (396.55 eV) and -Mo N (397.33 eV). With increasing Mo content, the N 1s peak shifted to higher binding energy and intensity decreased, indicating increased -Mo N phase and reduced relative nitrogen content.

2.3 Microhardness Analysis

The microhardness of CrMoN composite coatings increased from 1802 HV to a maximum of 2714 HV, then decreased to 2206 HV with increasing Mo content (). This hardness enhancement can be attributed to two mechanisms: (1) Solid solution strengthening, where Mo dissolution in the CrN lattice caused lattice distortion and strengthening, improving hardness. However, above 45.4 at% Mo, hardness decreased due to the appearance of mixed phases. (2) Grain refinement strengthening, where the relationship between grain size calculated from XRD results and hardness followed the Hall-Petch equation. Reduced grain size increased grain boundary area, effectively impeding dislocation motion and intergranular slip, thereby enhancing hardness.

2.4 Friction and Wear Properties

[Figure 6: see original paper] shows the friction coefficient and wear rate of CrMoN coatings with different Mo contents. The friction coefficient initially increased then decreased with Mo content. The increased hardness of CrMoN coatings raised the yield strength and energy required for plastic deformation, leading to higher friction coefficients. According to Blau’ s theory, when solid lubricants exist in friction pairs and discontinuous lubricating films form during friction, the total friction force F comprises two components: friction between the counterpart and coating, and friction between the counterpart and lubricating film:

$$F = F_m + F_l \tag{1}$$

where X and X are the contact areas between the counterpart and the coating and lubricating film, respectively, while F and F are the corresponding friction forces. Assuming normal load distributes uniformly over the contact area, the friction coefficient can be expressed as:

$$\mu = (1 - X_l)\mu_m + X_l\mu_l \tag{2}$$

where and are the friction coefficients between the counterpart and the coating and lubricating film, respectively. Equation (2) indicates that larger lubricating film contact area yields lower friction coefficient. Therefore, higher Mo content generates larger MoO lubricating film area during friction, resulting in lower friction coefficient. The wear rate followed a similar trend to the friction coefficient with increasing Mo content.

[Figure 7: see original paper] and [Figure 8: see original paper] present wear track profiles and surface SEM images of CrMoN coatings with different Mo contents. All wear tracks were shallow and narrow. At Mo contents below 45.4 at%, wear track profiles showed protrusions at both edges, indicating debris accumulation. At high Mo contents, the wear track profiles became smooth with minimal wear, demonstrating improved wear resistance. The CrN coating exhibited a relatively smooth worn surface with debris mainly distributed at the track edges, indicating abrasive wear as the primary mechanism ([Figure 8a: see original paper]). CrMoN coatings with low Mo content showed debris within the wear tracks; EDS analysis revealed substantial oxides, suggesting abrasive, adhesive, and oxidative wear mechanisms ([FIGURE:8b-c]). At high Mo contents, CrMoN coatings displayed smooth, shallow wear tracks with only slight scratching, with abrasive wear remaining the dominant mechanism due to the formation of substantial MoO lubricating phase during friction.

4. Conclusions

(1) CrMoN composite coatings with different Mo contents were prepared on M2 high-speed steel substrates by DC reactive magnetron sputtering. After Mo addition, all composite coatings exhibited preferred orientation growth along the (200) plane. With increasing Mo content, the phase structure transformed from a (Cr, Mo)N substitutional solid solution based on fcc-CrN phase to a mixed phase dominated by fcc- -Mo N. At 69.3 at% Mo, a small amount of bcc-Mo phase formed.

(2) Compared with CrN coating, the microhardness of CrMoN composite coatings increased with Mo addition. The hardness first increased then decreased with Mo content, reaching a maximum at 45.4 at% Mo.

(3) With increasing Mo content, the friction coefficient and wear rate of CrMoN composite coatings first increased then decreased. When Mo content exceeded 45.4 at%, substantial MoO lubricating phase formed during friction, reducing both friction coefficient and wear rate.

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