Effect of Ni doping on the microstructure and toughness of CrAlN coatings deposited by magnetron sputtering

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Abstract
This study determines the effects of nickel (Ni) doping on the composition, phase structure, chemical valence state, hardness, and toughness of CrAlNiN coatings. CrAlNiN coatings with various Ni contents (0.00 at%–27.71 at%) were deposited on the surfaces of M2 tool steel and monocrystalline silicon (Si) using unbalanced magnetron sputter ion plating. The results showed that the CrAlNiN coatings possess a nanomultilayer structure, maintaining the face centered cubic crystal structure of the chromium aluminum nitride (CrAlN) coatings. The Ni in the coatings acts as a toughening phase to ease stress, to increase resistance to crack growth, and to delay the generation of cracks, thereby having an obvious toughening effect. At an Ni content of approximately 20.33%, the Ni toughening phase in the modulation layer tends to saturate and the effect of continuing the increase in Ni content is limited from the viewpoint of improving the toughness.

1. Introduction

Hard nitride coatings have limited applications due to their poor toughness, regardless of their excellent hardness and wear resistant properties [1–6]. Researches on increasing the toughness of hard nitride coatings while maintaining their hardness has attracted considerable attention globally [7, 8]. Currently, nitride coatings have been toughened via the ductile phase, gradient and multilayer structures, phase transformations, and nanocrystalline structures [9–12]. Hybrid materials comprising hard and soft phases possess both high hardness and toughness, such as MeN–M, where MeN represents hard nitride that possesses high hardness (such as CrN or TiN), and M represents the soft phase that provides excellent toughness properties [13]. The soft phase is selected from metals that do not easily react with nitrogen, such as Cu [14] and Y [15]. Musil et al prepared a ZrCuN coating using DC magnetron sputtering technology. Their results showed that the coating primarily comprised ZrN and Cu, where Cu and Zr are insoluble elements. Due to the soft phase of Cu, ZrCuN showed a good toughness while maintaining a high hardness [16]. The same effect was achieved by adding Y to ZrN, where the elastic recovery of the coating was 83% and plastic deformation resistance was 0.75 [15].

In recent years, MeN–Ni series of soft-phase coatings have increasingly attracted attention [17–22]. Yang et al doped different contents of nickel (Ni) into tungsten nitride (WN) and found that, with an increase in the Ni content, the hardness of the coatings first increased and then decreased; when the Ni content was sufficiently high, the soft Ni phase increased and hard phase decreased, showing a decreased hardness and enhanced toughness [8]. Karvankova et al found that a small amount of Ni doping into Zr–N could improve the hardness and result in preferential growth along the NaCl (200) plane [19]. Adding Ni as a toughening element is expected to improve the mechanical properties of CrAlN coatings.

Currently, there are few reports on the preparation and study of CrAlNiN coatings; in addition, the magnetron sputtering deposition process for such coatings still needs to be studied. Accordingly, herein, five groups of CrAlNiN coatings with different Ni contents were prepared by controlling the sputtering current of an
Ni target. The influence of Ni doping on the microstructure, hardness, and toughness of the CrAlN coatings was then studied.

2. Experimental details

The CrAlNiN coatings were prepared using a Teer-650 closed field unbalanced magnetron sputter ion plating instrument. An Al and Ni targets and and two Cr targets with purities of 99.99% were adopted, as shown in figure 1. The substrates were monocrystalline Si and M2 high-speed steel. The M2 high-speed steel sample was gradually ground using successive grades of sandpaper until a grade of #1500 was achieved; then, it was polished using a diamond spray, followed by successive ultrasonic cleaning with acetone and ethanol for 15 min. After being dried with hot air, the sample was placed in the rotating base of a vacuum chamber with vacuum degree prior to deposition was $5 \times 10^{-4}$ Pa. The Ni content in the coating was controlled via the current of Ni target. The deposition process parameters, i.e., the OEM (optical emission monitor), substrate bias voltage, target currents, and time, are listed in table 1. Using these process parameters, five groups of CrAlNiN coatings with different Ni contents were prepared by changing the sputtering current of the Ni target; these groups are denoted CrAlN–xNi, where x represents the intensity of the Ni target current.

![Figure 1. Schematic of the CrAlNiN coating target setting.](image)

Table 1. Deposition parameters of the CrAlNiN coatings.

| Deposition Parameters | OEM | Bias voltage(V) | Target current (A) | Time (s) |
|-----------------------|-----|-----------------|--------------------|----------|
| Substrates Preclean   | 0   | −450            | Cr 0.3 Al 0.3 Cr 0.3 Ni 0.3 | 1800     |
| Cr                    | 0   | −100            | Cr 4 Al 4 Cr 4 Ni 3 | 300      |
| CrN                   | 90 ~ 75 | −75          | Cr 4 Al 4 Cr 4 Ni 3 | 500      |
| CrAlNiN               | 60 ~ 55 | −75          | Cr 4 Al 8 Cr 4 Ni 0–8 | 7200     |

The coating phases were analyzed using the Bruker D8 ADVANCE x-ray diffraction (XRD) system using Cu–Kα radiation operated at 40 kV and 100 mA with a scan rate in the 2θ range of 20°–80°. The coating surface morphologies were observed using SIGMA field emission scanning electron microscopy (SEM) and coating components were analyzed using energy disperse spectroscopy attached to the SEM. A transmission electron microscope (TEM) was employed to analyze the crosssection multilayer morphology of the coating and was operated at 300 kV with 0.24-nm-point resolution. The bonding structure of the Ni elements in the coatings was detected using x-ray photoelectron spectroscopy (XPS, Axis Ultra) with a monochromatic Al–Kα radiation source at 164 W. The XPS analysis was conducted at a base pressure of $3 \times 10^{-7}$ Pa and test depth was approximately 15 nm. The hardness and Young’s modulus were measured via a G200 nanoindentation instrument using a Berkovich diamond indenter tip at a maximum load of 400 mN and indentation depth of 150 nm. A constant Poisson ratio of $\nu = 0.25$ was assumed. To ensure the measurement accuracy, each sample was measured ten times and the average value was taken. An HT-5001 scratch instrument was used to analyze the toughness of the CrAlNiN coatings with different Ni contents with a loading range of 0–60 N.
3. Results

3.1. Chemical and microstructural characterization

The thickness and composition of the surface elements of the CrAlNiN coatings deposited using different Ni target currents are shown in Table 2. The coating thickness increased with increasing Ni target current. On the surfaces of the CrAlNiN coatings, the Ni content increased from 0 at% to 20.33 at%; at its highest, the Ni target current was 6 A. The atomic fraction of Cr and N showed a decreasing trend (from 44.97 at% at 0 A to 34.57 at% at 8 A), and the Al content changed from 9.8 at% at 0 A to 7.33 at% at 8 A, which was not an obvious change.

The XRD patterns of the CrAlNiN coatings with different Ni contents are shown in Figure 2. The four groups of coatings display obvious diffraction peaks at 37.3°, 43.6°, and 63.8°. Compared to the JCPDS card, these coatings show a face centered cubic (FCC) structure similar to NaCl. This indicates that Ni doping does not change the original crystal structure of the CrAlN coating; conversely, with the increase in the Ni content, the CrAlNiN coating preferentially grew along the (111) plane. This is due to the nanocolumnar structure, which is related to the adsorption atom mobility in the growth direction; as a result, the Ni doping results in an increased mobility of the adsorbed atoms on the (111) plane. There is no Ni-related diffraction peak in the XRD pattern, the nitride formed by Ni and N may be very close to the peak location of CrN in the deposition process, forming overlapping diffraction peaks.

Figure 3 shows the TEM morphology of the functional layer, where the topmost CrAlNi coating has an Ni content of 20.33 at% and corresponding selective diffraction pattern (SADP). The TEM morphology (figure 3(a)) shows that the CrAlNiN coating contains a nanoscale multilayer structure with the thickness of each layer being approximately 5 nm and modulation cycle being approximately 10 nm. The SADP (figure 3(b)) shows that the CrAlNiN coating is an FCC-structured polycrystal. The diffraction ring results for (111), (200), and (220), which do not have any redundant diffraction signals, are consistent with the XRD pattern. The (111) plane has the strongest diffraction signal, indicating that the growth of the coating showed a preferential orientation.

| Coating       | Ni target current [A] | Cr   | Al  | Ni  | N   | Coating thickness [μm] |
|---------------|-----------------------|------|-----|-----|-----|------------------------|
| CrAlN         | 0                     | 44.97| 9.80| 0   | 45.23| 2.924                  |
| CrAlN–2Ni     | 2                     | 41.53| 9.59| 7.12| 41.76| 3.318                  |
| CrAlN–4Ni     | 4                     | 39.49| 9.11| 13.57| 37.83| 3.554                  |
| CrAlN–6Ni     | 6                     | 38.94| 8.28| 20.33| 32.45| 3.743                  |
| CrAlN–8Ni     | 8                     | 34.57| 7.33| 27.71| 30.22| 3.796                  |

Figure 2. XRD patterns of the CrAlNiN coatings with different Ni contents.

Table 2. Surface compositions and thicknesses of the CrAlNiN coatings deposited with different Ni target currents.
3.2. Mechanical properties

Figure 4 shows the nanoindentation test results for the CrAlNiN coatings with different Ni contents. Figure 4(a) shows that the hardness of the CrAlN coatings increased slightly with a small addition of Ni. As the Ni content continued to increase, the hardness of the CrAlNiN coatings decreased sharply and became smaller than that of the CrAlN coating. The elastic modulus (figure 4(b)) shows the same trend as the hardness and indicates that significant Ni doping can reduce the hardness and the elastic modulus of the CrAlN coating. When the Ni content was 7.12 at\%, the hardness and elastic modulus of the CrAlNiN coating reached maximum values of 21.5 and 301.6 GPa, respectively.

3.3. Toughness of the CrAlNiN coatings

The toughness of the CrAlNiN coatings with different Ni contents was studied using the crack propagating (CPR) method. The evaluation formula for the coating scratch toughness CPR is as follows:

\[ \text{CPR} = L_{c1} \times (L_{c2} - L_{c1}), \]  

where \( L_{c1} \) is the critical load at crack initiation and \( L_{c2} \) is the critical load at complete failure of the coating due to spalling. Larger values of \( L_{c1} \) indicate a greater resistance of the coating to cracking. However, only cracks are not sufficient to cause a coating to break; \( L_{c2} - L_{c1} \) characterizes the ability of a coating to bear a load after cracking and peeling off.

Acoustic emission curves automatically generated by the CrAlNiN coatings with different Ni contents during scratch testing are shown in figure 5. Combined with the CPR calculation results listed in table 3, for an undoped-Ni CrAlN coating, the \( L_{c1} \) and \( L_{c2} \) values for crack initiation are 27 and 30 N and CPR value is 81. With
Ni doping, the $L_{c1}$ and $L_{c2}$ values of the CrAlNiN coatings were greater than those for the CrAlN coating. With increasing Ni content, the $L_{c1}$, $L_{c2}$, and $(L_{c2} - L_{c1})$ values showed an increasing trend. When the Ni content reached 20.33 at%, the CPR value of the coating increased to 352, indicating that increasing the Ni content can significantly improve the toughness of the coating. A continuous increase in the Ni content to 27.72 at% reduced the possibility of a change in the CPR value of the coating, indicating that the toughening effect is limited when the Ni content exceeds a certain value.

To verify the CPR values, the morphologies of the five groups of CrAlNiN coatings with different Ni contents were analyzed after the scratch test, as shown in Figure 6. Large areas of cracks and spallation occurred in the tails of the CrAlN coating scratches without Ni, and toughness was poor (figure 6(a)). With Ni doping, only continuous cracks appeared in the scratch morphologies of the CrAlNiN coatings with an Ni content of 7.12 at%; no large area spalling was observed (figure 6(b)), indicating that the resistance of the coating to crack generation improved. With a further increase in the Ni content, the cracks in the scratch morphologies of the coating were further reduced, and at higher Ni content, an increase in the toughness became more obvious. When the Ni content reached a maximum value of 27.71 at%, only a few microcracks could be found in the scratch morphology of the CrAlNiN coating and no obvious coating peeling was observed (figure 6(c)). The morphology of the scratches further verified that Ni doping can improve the toughness of CrAlN coatings. Experimental data of the comprehensive plasticity index and scratches indicated that, with an increase in the Ni content, the ability of CrAlN coatings to resist crack nucleation and fracture was significantly improved, i.e., the toughness of the coating was significantly improved.

4. Discussion

The experimental results show that doping with Ni can improve the toughness of CrAlN coatings. According to the CrAlNiN microstructure, the toughening mechanism with Ni doping can be discussed as follows.

To further explore the influence of Ni doping on the hardness and toughness of CrAlN coatings, the valence states of Ni in CrAlNiN coatings with Ni contents of 7.12 and 20.33 at% were compared and analyzed. The XPS
Fitting results are shown in figure 7. Figure 7(a) shows that the diffraction peak of 852.98 eV in the CrAlNiN coating with low Ni content was very weak, indicating that the Ni in the coating was primarily in the form of nitride (855.84 eV). However, strong diffraction peaks from Ni elements appeared in the CrAlNiN coating with high Ni content (figure 7(b)), indicating that, with an increase in the Ni content in the coating, more Ni existed as a simple substance due to the weak binding ability of Ni and N.

Although the soft phases caused by the doping of Ni reduced the hardness and elastic modulus, the increase in the Ni content significantly improved the toughness of the CrAlNiN coatings. Metal Ni particles are often used as binder toughening ceramic materials to absorb external loads owing to their good plasticity. CrAlN coatings comprised the brittle hard phases of CrN and AlN. Due to the poor plasticity of these hard phases, stress cannot be relaxed during the process of scratch loading and severe deformation occurs at defect positions in the coating, leading to crack growth at the tip, which expands and aggregates to form a main crack. After doping with a second Ni phase, Ni primarily exists in the form of a mixture of simple substances and nitride. In the process of scratch loading, the soft phase can consume some energy via shear deformation and therefore play a
role in easing the stress. Because a crack tip is difficult to form and cracks do not easily diffuse due to the interface when the loading force is increased, a delay in the propagation significantly improves the toughness of coatings [9]. When the Ni content reaches a certain level, the Ni toughening phase tends to be saturated; therefore, continuing to increase the Ni content has a limited effect on improving the toughness of the coating.

5. Conclusions

Herein, by controlling the current of an Ni target, CrAlNiN coatings with different Ni contents were prepared and influences of different amounts of Ni doping on the microstructure and toughness of CrAlN coatings were studied. The main conclusions of the study are as follows:

(1) The FCC crystal structure of CrAlN coatings remained unchanged even with Ni doping, and the CrAlNiN coatings had a nanomultilayer structure. The thickness of the modulation layer of the CrAlNiN coating with an Ni content of 20.33 at% was approximately 5 nm and modulation cycle was approximately 10 nm.

(2) With an increase in the Ni content, more Ni elements in the CrAlNiN coatings participated in the toughening phase, thereby alleviating stress, increasing the resistance of the coating to crack growth, delaying the propagation of cracks, and playing an obvious role in toughening the material. When the Ni content reached a certain level, the Ni toughening phase became saturated and continuing to increase the Ni content had a limited effect on improving the toughness of the coatings.

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