Microstructure and Properties of the Cr–Si–N Coatings Deposited by Combining High-Power Impulse Magnetron Sputtering (HiPIMS) and Pulsed DC Magnetron Sputtering

Tie-Gang Wang^{1,2} · Yu Dong¹ · Belachew Abera Gebrekidan¹ · Yan-Mei Liu¹ · Qi-Xiang Fan¹ · Kwang Ho Kim²

Received: 25 March 2017 / Revised: 14 April 2017 / Published online: 15 June 2017
© The Chinese Society for Metals and Springer-Verlag GmbH Germany 2017

Abstract The Cr–Si–N coatings were prepared by combining system of high-power impulse magnetron sputtering and pulsed DC magnetron sputtering. The Si content in the coating was adjusted by changing the sputtering power of the Si target. By virtue of electron-probe microanalysis, X-ray diffraction analysis and scanning electron microscopy, the influence of the Si content on the coating composition, phase constituents, deposition rate, surface morphology and microstructure was investigated systematically. In addition, the change rules of micro-hardness, internal stress, adhesion, friction coefficient and wear rate with increasing Si content were also obtained. In this work, the precipitation of silicon in the coating was found. With increasing Si content, the coating microstructure gradually evolved from continuous columnar to discontinuous columnar and quasi-equiaxed crystals; accordingly, the coating inner stress first declined sharply and then kept almost constant. Both the coating hardness and the friction coefficient have the same change tendency with the increase of the Si content, namely increasing at first and then decreasing. The Cr–Si–N coating presented the highest hardness and average friction coefficient for an Si content of about 9.7 at.%, but the wear resistance decreased slightly due to the high brittleness. The above phenomenon was attributed to a microstructural evolution of the Cr–Si–N coatings induced by the silicon addition.

KEY WORDS: Cr–Si–N coating; High-power impulse magnetron sputtering (HiPIMS); Pulsed DC magnetron sputtering; Mechanical property; Friction coefficient

1 Introduction

Transition metal nitride coatings, such as TiN, CrN, and ZrN, were applied as hard coatings because of their high hardness, excellent wear resistance and chemical stability

[1–3]. Among them, chromium nitride (CrN) coatings were widely used as protective coatings for various tribological forming and casting applications [4, 5]. The CrN coatings also show excellent corrosion resistance under severe environmental conditions [6] and good oxidation resistance [7]. Moreover, chromium nitride (CrN) thin films have already been widely used on cutting tools due to their superior corrosion and wear resistance and low internal stress [8]. Recently, many researchers doped Si or B into the chromium-based nitride coatings to significantly improve the coating hardness, toughness and thermal stability by forming nanocomposite structures [9–11] because the dislocation activity is absent in the thermally highly stable nanocomposite coatings that consist of a few-nanometer small crystallites of hard transition metal nitrides (or carbides, borides, etc.) “glued” together by about one-monolayer-thin layer of an amorphous covalent nitride such as Si₃N₄, BN. The

Available online at <http://link.springer.com/journal/40195>

✉ Tie-Gang Wang
sygtwang@163.com

✉ Kwang Ho Kim
kwhokim@pusan.ac.kr

¹ Tianjin Key Laboratory of High Speed Cutting and Precision Manufacturing, Tianjin University of Technology and Education, Tianjin 300222, China

² Global Frontier R&D Center for Hybrid Interface Materials, Pusan National University, Busan 609-735, South Korea

segregation of the above two phases, i.e. nanocrystallites and amorphous layer, is driven by thermodynamics and results in the formation of sharp and strong interfaces that provide the nanocomposite coatings with high hardness and strength. In these hetero structures, a large number of interfaces between nanometer thin epitaxial layers with a big difference in elastic shear moduli hindered the dislocation motion and the grain boundary sliding, so that a large stress is needed to initiate and propagate a crack in such systems [12]. However, the performance of chromium-based nanocomposite coatings has poor repeatability, which usually is attributed to the following reasons: low purity of the raw target material, oxygen impurities introduced in coating, difficult control of the deposition conditions, etc.

As an advanced physical vapor deposition (PVD) technology, high-power impulse magnetron sputtering (HiPIMS) is famous in the deposition of dense coatings as well as in the enhancement of interface adhesion by metal ion etching prior to coating deposition, because of its significantly high ionization ratios compared with conventional magnetron sputtering processes. Moreover, hard coatings grown by HiPIMS are known for having smooth surfaces and dense structures [13, 14]. However, the HiPIMS technology is associated with substantially lower deposition rates when compared with other magnetron sputtering techniques [15, 16]. To improve the deposition rate, recent efforts have been mainly focused on either adjusting the HiPIMS power input to moderate levels [17] or developing hybrid deposition processes [18, 19]. In the latter approach, HiPIMS is introduced to a multi-target deposition system to combine with other deposition technologies having higher deposition rates, which is the reason why we preferred to combine HiPIMS with pulsed DC magnetron sputtering which has relatively higher deposition rates.

In this work, Cr–Si–N coatings were synthesized by a hybrid coating system with a HiPIMS using a Cr source and a pulsed DC magnetron sputtering using a Si source, which allow an easy control of the coating composition and ensure purity, because the impurities in the simple substance targets are less than those in the alloy targets. The influence of the Si content in Cr–Si–N coatings on the coating growth process, phase constituents, microstructure, hardness, internal stress, adhesion and friction behavior was investigated in detail. Accordingly, the mechanisms of coating growth and strengthening were also discussed.

2 Experimental

2.1 Deposition of the Cr–Si–N Coatings

The Cr–Si–N coatings with different Si contents were prepared by HiPIMS and pulsed DC magnetron sputtering co-

sputtering technique. The (100)-oriented single-crystalline Si wafers (sample size: 30 mm × 20 mm × 0.7 mm) and SUS 304 stainless steel sheets were used as substrates for coating microstructure analysis and performance testing. The HiPIMS and pulsed DC magnetron sputtering were connected to the Cr target and Si target, respectively. The power setting of the pulsed DC source was manipulated to adjust the silicon content in the coating. A rotating sample holder was located at the center of a vacuum chamber and kept at a distance of 70 mm from the target. A direct current bias power supply was connected to the sample holder. All the substrates were ultrasonically cleaned in acetone and ethanol sequentially for 30 min, and fixed on the holder after being blown dry by pure nitrogen. The chamber was evacuated to a base pressure below 5.0×10^{-3} Pa using a rotary and turbomolecular pump. Before deposition, plasma etching was conducted by Ar glow discharge for 5 min with a DC bias of −800 V at 2 Pa. Then, ion bombardment was also conducted by the HiPIMS Cr target for 10 min with a gradually reduced DC bias from −800 to −200 V at the working pressure of 7.0×10^{-1} Pa. To improve the adhesion between the coating and the substrate, a Cr interlayer was deposited for 20 min. Then, starting with the Si target, the Cr–Si–N coatings were deposited. The working pressure was maintained at 7.0×10^{-1} Pa and the volume ratio of the reactive gas N₂ to the inert gas Ar was kept at 1:1. The frequency of HiPIMS and duty cycle of the DC pulse power were maintained at 180 Hz and 50%, respectively. All the coating thickness in this work was kept at about 3.5 μm by strictly controlling the deposition time. The detailed deposition parameters for the Cr–Si–N coatings are listed in Table 1.

2.2 Characterization and Tests of the Cr–Si–N Coatings

An electron-probe microanalysis (EPMA, Shimadzu, EPMA 1600) was carried out to determine the chemical

Table 1 Detailed deposition parameters for the CrN and Cr–Si–N coatings prepared by co-sputtering technique

Parameters	Value
Base pressure (Pa)	3.0×10^{-3}
Working pressure (Pa)	7.0×10^{-1}
Deposition temperature (°C)	300
HiPIMS average power/Cr target (kW)	1.0
Pulsed DC power/Si target (kW)	0, 0.4, 0.6, 0.8, 1.0
N ₂ /Ar gas flow ratio (Scm)	20:40
Substrate rotation speed (rpm)	20
Film thickness (μm)	~3.5
Distance between the target and substrate (mm)	70

compositions of the Cr–Si–N coatings. The crystal structure of the coatings was determined by an X-ray diffractometer (XRD, D8-Discovery Brucker, Cu K α , 40 kV, 40 mA). A locked couple θ – 2θ mode with a 0.02° step size and a 0.2 s step time was employed. The diffraction patterns were collected from 20° to 80° . The coatings thickness was measured using an α -step stylus profilometer (part of the Si substrate was masked in order to get a step), and then their deposition rates were calculated according to the individual deposition time. The coating morphologies of surface and cross section were observed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800) coupled with an energy-dispersive X-ray spectroscopy (EDS, Oxford ISIS).

The hardness was evaluated by a micro-hardness tester with a Knoop indenter (Matsuzawa, MMT-7) under a load of 25 g. The inner stresses of the coatings were calculated based on the Stoney's equation [20] by measuring the curvature of the coated Si-substrates using a laser scanning profilometer. The values of hardness and residual stress were average values of 10 respective measurements. The adhesive strength between the coating and the substrate was evaluated by using a scratch tester (J&L Tech, Scratch test JLST022) with a Rockwell C diamond stylus (cone apex angle: 120° tip radius: 200 μm) moving across the sample surface. During the scratch tests, the normal load was increased gradually up to 100 N at a loading rate of 1 N/s and a translation speed of 0.2 mm/s, and the scratch length was set as 20 mm. The friction force, friction coefficient, and acoustic emission signals were also recorded during the scratch tests in order to measure the critical load. These investigations were complemented by observing the scratch track with an optical microscope (OM, Olympus PMG3-613U W/Acc) to confirm the starting point of the adhesion failure. The values of the critical load presented in this paper are the average of five measurements made on the same specimen.

The tribological behavior of the Cr–Si–N coatings was evaluated using a ball-on-disk sliding wear apparatus. The friction tests were conducted at an ambient temperature of $20 \pm 2^\circ\text{C}$, relative humidity of $25 \pm 3\%$ under a load of 5 N with an Al_2O_3 ball (diameter 6.0 mm, average hardness 22 GPa) as a counterpart material. The sliding speed, radius of wear track and total sliding distance were 0.1 m/s, 3.0 mm and 226 m (12,000 laps), respectively. The friction coefficients were continuously recorded during the testing process by a computer. Before testing, both the specimen and the counterpart in turn were ultrasonically cleaned in acetone and ethanol solution. Each sample was tested repeatedly three times, and no coating perforation occurred. According to Archard's classical wear equation, the specific wear rate k can be calculated by the following equation [21]:

$$k = \frac{V}{SL} \quad (1)$$

where V is the wear volume of the Cr–Si–N coatings calculated by the dimensions of the wear tracks, and S , L are the total sliding distance and the applied load, respectively. In addition, the film worn tracks after wear tests were evaluated using an FE-SEM.

3 Results and Discussion

3.1 Compositions and Microstructure

Figure 1 shows the variation of the Cr, Si, and N contents in the Cr–Si–N coatings as a function of Si sputtering power, whereas the average sputtering power of the HiPIMS Cr target was fixed at 1.0 kW. It can be seen that the N content in the coating increased slightly with the increase of the Si sputtering power, being about 60 at.% to 65 at.%. As expected, the Si content in the Cr–Si–N coatings increased monotonously from 0 to 11.4 at.% and the Cr content decreased from 40 at.% to 25 at.% with an increase of the Si sputtering power from 0 to 1.0 kW. Similar results had also been reported by Wang and Kim [9] and Huang *et al.* [22]; namely, the higher sputtering power applied on the Si target had the effect that the higher fraction of material was received from magnetron sputtering during the deposition process, which resulted in higher Si contents in the Cr–Si–N coatings. The sum of the Cr and Si contents was almost invariable, about 40 at.%. Therefore, the incorporation of Si into the Cr–N coatings had little effect on the N content.

The X-ray diffraction patterns of the Cr–N and Cr–Si–N coatings with different Si contents are shown in Fig. 2. The Cr–N coating free from Si shows the characteristics of nanocrystallized CrN. The two observed diffraction peaks

Fig. 1 Chemical composition (obtained by EPMA) of the CrN and Cr–Si–N coatings as a function of Si sputtering power

Fig. 2 X-ray diffraction patterns of the CrN and Cr-Si-N coatings with different Si contents

located at $2\theta = 43.65^\circ$ and 63.10° correspond to the (200) and (220) crystal planes of CrN, respectively. The significant broadening of the above diffraction peaks was attributed to the diminution of grain size playing an important role [23]. Because HiPIMS employed short intense power pulses, it led to dense plasma and high fraction of ionized sputtered species. Such a high level of ion bombardment and high energy influx to the growing coating altered the plasma chemistry and refined the grain size [13, 24].

As Si was incorporated into the coatings, all the XRD patterns showed similar features. The CrN (200) diffraction peak became wider and weaker with an increase of the Si content, while the CrN (220) diffraction peak disappeared, indicating a decreased crystallinity of the CrN phase. Similar results had been reported by Wang *et al.* using arc ion plating and magnetron sputtering joint technology [9]. The above phenomenon can be explained by the formation of heterogeneous nanocomposite coatings due to the addition of Si; namely the face-centered cubic CrN nanocolumns were partially or/and fully enveloped by an amorphous SiN_x tissue phase [25]. In addition, it was very interesting that the three Si diffraction peaks corresponding to the (111), (220) and (311) crystal planes of Si, respectively, were detected in all Cr-Si-N coatings, even if the Si content was only 2.7 at.%. The above results are very different from those published by other researchers [9, 22]. There are two possible explanations for the above phenomenon. A first one is the limited solubility of Si in the CrN lattice, which is also influenced by the grain size of CrN crystals, with less Si being dissolved in finer CrN crystals or/and amorphous SiN_x phase that has been mentioned above. A second one is the higher sputtering efficiency from pulsed DC magnetron sputtering than from HiPIMS [15], so that the sputtered polysilicon did not fully react with nitrogen prior to deposition. Some Si atomic clusters sputtered from the target were deposited into the

Fig. 3 Dependence of deposition rate of the CrN and Cr-Si-N coatings on the Si content

coating, which formed the polysilicon phases. Furthermore, the peak intensity of Si became slightly more intense as the Si content increased and showed a preferred growth orientation of the (111) crystal plane. In addition, all the XRD patterns of the Cr-Si-N coatings exhibited a broad hump in the range of 65° – 74° . This could be explained by the fact that the addition of Si resulted in formation of an amorphous SiN_x tissue phase.

The dependence of the deposition rate of the CrN and Cr-Si-N coatings on the Si content under the deposition conditions described above is plotted in Fig. 3. It can be observed that the deposition rate increases approximately linearly with the increase of the Si content. In the case of absence of Si doping, the HiPIMS CrN coating possesses the lowest deposition rate of about 7.5 nm/min. The sputtered Si by pulsed DC played an important role on the coating thickness, which was attributed to the higher sputtering efficiency from pulsed DC magnetron sputtering than from HiPIMS [15], although the latter has a higher ionization rate. The typical surface morphologies of the CrN coating and Cr-Si-N coatings with an Si content of 9.7 and 11.4 at.% are shown in Fig. 4a–c. It can be seen that the coating surface becomes more and more smooth with the increase of the Si content. There are many quasi-circular or elliptic nanoscale bumps uniformly distributed on the coating surface, which corresponds to the tops of short columnar units. These bumps also decrease gradually with increasing Si content. The above trend is consistent with the results reported by Huang *et al.* [22]. Because larger amounts of amorphous SiN_x phase were formed as the Si content increased, that refined the grain size and resulted in a denser microstructure and smoother surface.

Figure 5a–c shows the typical fractured cross-sectional SEM images of the CrN and Cr-Si-N coatings with different Si contents. It can be seen that all the Cr transitional layers adhere well to the substrates and coatings. Neither

Fig. 4 Typical surface morphologies of the CrN coating and Cr–Si–N coatings with different Si contents, **a** 0, **b** 9.7 at.%, **c** 11.4 at.%

Fig. 5 Typical fractured cross-sectional SEM images of the CrN and Cr–Si–N coatings with different Si contents: **a** 0, **b** 9.7 at.%, **c** 11.4 at.%

pinholes nor pores can be observed in these microstructures. For the CrN coating, a dense and fine columnar microstructure with uniform columns is revealed in Fig. 5a. The columnar units grow outward from the Cr interlayer and throughout the whole coating thickness. With increasing Si content in the Cr–Si–N coatings (Fig. 5b, c), the width and length of the columnar units decrease gradually and the microstructure becomes more compact. When the Si content is equal to 11.4 at.%, the coating possesses the densest microstructure, and no units grow throughout the entire coating thickness. The above tendency is in good agreement with the XRD spectra shown in Fig. 2. In conclusion, doping Si into the Cr–N coatings had significant effects on the microstructure, namely the columnar grain growth was suppressed and the nanocomposite structure was formed. The growth pattern changed from continuous columnar to discontinuous columnar and quasi-equiaxed crystals when the Si content increased. Similar results had also been reported for nanocomposite nitride coatings, for which the addition of Si or B in mixed Ar–N₂ discharge was prone to form an amorphous matrix which was able to segregate to grain boundaries and act as grain refiner, resulting in a reduction of the grain size [26].

3.2 Mechanical Properties

The hardness variation of the CrN and Cr–Si–N coatings with different Si contents is presented in Fig. 6. As shown in this figure, the hardness of all the Cr–Si–N coatings is higher than that of the CrN coating. As the Si content increases from 0 to 2.7 at.% and to 6.4 at.%, the coating hardness increases continuously and keeps on increasing at

Fig. 6 Hardness variation of the CrN and Cr–Si–N coatings with different Si contents

a much faster rate as the Si content increases to 9.7 at.%. On the one hand, the increased hardness could be attributed to the formation of nc-CrN/a-SiN_x nanocomposite crystalline state [27]. The above tendency was due to the grain boundary strengthening, the phenomena created by strong cohesive energy of interphase boundaries [28] and by the Hall–Petch relation derived from crystal size refinement [29]. Both the formation of strong interphase boundaries and the refinement of crystallites resulted from the percolation of amorphous SiN_x phase into the grain boundaries of CrN. On the other hand, some Si atoms existed in the form of interstitial atoms, which would cause lattice distortion to produce solid solution strengthening. It was also suggested that the Si content plays a critical role in the nanocomposite coatings [30].

The hardness of the Cr–Si–N coatings reached a maximum when the silicon content was 9.7 at.%. A further increase of the Si content made the coating soft and the amorphous SiN_x phase became dominant over the CrN phase, so that the coating hardness decreased again. Hence, we have to find the optimum Si content for its most effective performance. When the Si content exceeded 9.7 at.%, the hardness enhancement mainly depended on the property of the amorphous SiN_x phase which is softer. Although some polysilicon phases in the coating were also precipitated, they were not helpful for hardness enhancement. So, the hardness of the Cr–Si–N coating decreased sharply when the Si content varied from 9.7 to 11.4 at.%. In another similar study [31], the hardness value of (Cr_{0.5}Al_{0.5})_{1-x}Si_xN coatings decreased very strongly after adding more than 11.5 at.% Si. In terms of coating hardness, the optimal Si content in this study was 9.7 at.%.

Figure 7 shows the internal stress variation of the CrN and Cr–Si–N coatings with increasing Si content. It can be seen that all the coatings possess a compressive internal stress, which is attributed to HiPIMS employing short intense power pulse. The dense plasma caused a high level

of ion bombardment and high energy influx to the growing coatings that induced compressive stresses [24]. Usually, the stress sources in the coated specimen include peening stress, solidification stress, quenching stress and cooling stress [20]. Due to the high ionization rate of HiPIMS, the sputtered species in negative bias field were accelerated to impact on the substrate or previously deposited layers at high velocity. The kinetic energy of the sputtered particles led to significant peening on the underlying material, thereby inducing compressive stresses into the specimen. The magnitude of the compressive stress depended on the particle velocity and mass as well as on thermophysical properties [32]. During the subsequent cooling to ambient temperature, cooling stresses arise in the coated specimens. The thermophysical property mismatch between the coating and substrate, mainly the difference of thermal expansion coefficient, resulted in compressive cooling stresses into the specimen [33]. These stresses mentioned above superimposed each other and changed the internal stress situation of the whole specimen.

After doping Si into the Cr–N coatings, the internal stress decreased sharply even if the Si content was only 2.7 at.%. In this work, the Cr–Si–N coatings consisted of CrN and Si nanocrystallites as well as of amorphous SiN_x layers. There are a large number of interfaces between nanometer thin epitaxial layers with a big difference in elastic shear moduli, which can effectively release the internal stress [12]. Moreover, the soft amorphous SiN_x matrix can also buffer and release partial stress, because it is prone to deformation under the action of stress. With the increase of the Si content in coatings, the internal stress decreased slightly and eventually maintained at around –100 MPa. The reason is that more and more soft amorphous SiN_x matrix released most of the coating growth stress and kept the Cr–Si–N coatings at a low compressive stress state. In a previous study [20], we had reported that the appropriate compressive stress in the coating could improve its mechanical properties.

The adhesion between the coating and the substrate is another key index for evaluating its comprehensive performance. This is normally defined as the energy to separate the coating from the substrate. This energy is very difficult to measure, and thus the separation force is often considered as an indicator of adhesion. In general, the critical load is defined as a burst and rising friction force that emerges due to a series of damages and detachment of coating layers from the substrate surface [34]. Figure 8 shows the test results of critical load for the CrN and Cr–Si–N coatings with different Si contents. It is evident that all the coatings present good adhesion and that the critical load first gradually decreases and then rapidly increases again with increasing Si content. The critical load reaches the minimum value of about 65 N when the Si content is

Fig. 7 Internal stress variations of the CrN and Cr–Si–N coatings with different Si contents

Fig. 8 Critical load for the CrN and Cr-Si-N coatings with different Si contents

9.7 at.%. The above trends were attributed to the microstructure evolution, composition variation as well as phase transformation that have been discussed in the previous sections. In addition, the fewer defects in HiPIMS coatings are also helpful to inhibit the propagation and expansion of micro-cracks, which can promote a strong adhesion. The HiPIMS CrN coating possessed a higher critical load, because its dense nanocolumnar structure and small crystal size presented an excellent interfacial shearing resistance. It had been reported that the small grains could slide and deflect slightly under the combined stresses which would buffer and release partial stresses applied to the interface [35]. In this case, it was difficult to crack and peel off the coating from the substrate, and thus a strong adhesion was achieved. Although more and more amorphous SiN_x matrix further restricted the grain growth, the critical load decreased gradually with an increase of the Si content until it reached 9.7 at.%. This can be explained by the fact that the coatings became more and more brittle with an increase of the hardness, so that they were prone to crack and peel off from the substrate under the joint action of shear and compressive stresses, which eventually resulted in the shear failures at the interfaces and reduced the adhesion. Conversely, the sharp increase of the critical load as the Si content exceeded 9.7 at.% may be due to the decreased hardness which enhanced the toughness and adhesion.

3.3 Tribological Behaviors

Figure 9 presents the average friction coefficient of the CrN and Cr-Si-N coatings with different Si contents, which was calculated from the tribological process entered the steady-state to the end of the friction test. As can be seen that the average friction coefficient of the Cr-Si-N coatings increases gradually with increasing Si content, reaching the maximum value 0.51 with an Si content of

Fig. 9 Average friction coefficient of the CrN and Cr-Si-N coatings with different Si contents

9.7 at.%, and then decreases again as the Si content exceeds 9.7 at.%. The above tendency is same as that of the hardness. The CrN coating shows the lowest average friction coefficient. The addition of Si to the Cr-N coatings resulted in an increment of the average friction coefficient, which was attributed to the microstructure evolution, composition variation, and occurrence of tribo-chemical reaction at the friction interfaces [36]. Although the average friction coefficient increased, the variation range was still acceptable. Moreover, the behavior of the friction coefficient with the addition of Si was in accordance with that reported in the literature [37].

Figure 10 shows the typical friction coefficient-sliding time curve of the Cr-Si-N coating with an Si content of 9.7 at.%. It can be seen that the friction coefficient rapidly increases during the initial running-in period, which is a transition of the contact condition from two-body abrasion to interfacial sliding. The transition from the running-in period to steady-state period is fast, and the running-in phase lasts less than 50 s. This was attributed to the smooth

Fig. 10 Typical friction coefficient-sliding time curve of the Cr-Si-N coating with the Si content of 9.7 at.%

surface of the Cr–Si–N coating prepared by HiPIMS. After entering the steady-state period, the friction coefficient has slight fluctuations and gradually increases slightly with the sliding time. This can be explained by the flakes falling off from the coating involving the friction process as third-body abrasives and by the gradually increased interfacial contact area between the coating and the counterpart due to the occurrence of wear [38].

To compare the wear resistance among the coatings, the wear rate of the Cr–Si–N coatings with different Si contents is presented in Fig. 11. As the Si content increases, the wear resistance of the coatings is improved gradually until the Si content reaches 6.4 at.%. This is because the formation of nanocomposite structure enhances the coating hardness and toughness, which is closely related to the microstructure evolution. When the Si content is 9.7 at.%, the wear rate increases slightly which is due to the higher hardness. In this case, the Cr–Si–N coating is very brittle and prone to crack and peel off from the substrate, so that it leads to a reduced wear resistance. Combined with the results in Fig. 6, the coating hardness decreases again as the Si content increases further because this enhances the toughness and wear resistance. A typical worn morphology of the Cr–Si–N coating with a Si content of 9.7 at.% is presented in Fig. 12. It can be seen that some micro-ploughs are formed by transferring the spalled wear debris into the interface between the coating and the friction pair. The hard wear debris acted as a third body to be involved in the friction process, and scratched the friction interface like a blade. The main wear mechanism of the Cr–Si–N coatings was plastic deformation, crack initiation and propagation under the high contact stresses, inducing the local film to flake off, and eventually leading to the formation of micro-ploughs on the wear scar. Similar mechanisms had also been discussed by Chang *et al.* [31].

Fig. 11 Wear rate of the Cr–Si–N coatings with different Si contents

Fig. 12 Typical worn morphology of the Cr–Si–N coating with the Si content of 9.7 at.%

4 Conclusions

1. Applying HiPIMS and pulsed DC co-sputtering technique, Cr–Si–N coatings containing polysilicon phase were prepared. With increasing Si content, the coating microstructure gradually evolved from continuous columnar to discontinuous columnar and quasi-equiaxed crystals. The optimal Si content was 9.7 at.%.
2. Doping Si into the Cr–N coatings significantly improved the hardness, which was attributed to the solid solution strengthening and grain boundary strengthening by forming the nanocomposite coatings. As the Si content increased, the coating inner stress first declined sharply and then kept almost constant, while the hardness first increased and then decreased, which was contrary to the trend of the adhesion between the coating and substrate.
3. The addition of Si to the Cr–N coatings resulted in an increment of the average friction coefficient and wear resistance, which was attributed to the microstructure evolution, mechanical property variation, and tribo-chemical reactions at the friction interfaces. Although the friction coefficient increased, the variation range was still acceptable. The variation of the friction coefficient with the Si content was the same as that of hardness.

Acknowledgements This work was supported by the Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (No. 2013M3A6B1078874). In addition, it was also funded by the National Nature Science Foundation of China (No. 51301181), the Tianjin Key Research Program of Application Foundation and Advanced Technology (No. 15JCZDJC39700), the Tianjin Science and Technology correspondent project (No. 16JCTPJC49500), and the Innovation Team Training Plan of Tianjin Universities and colleges (No. TD12-5043).

References

- [1] X.Y. Guan, Y.X. Wang, G.A. Zhang, X. Jiang, L.P. Wang, Q.J. Xue, *Tribol. Int.* **106**, 78 (2017)
- [2] Q.X. Fan, T.G. Wang, Y.M. Liu, Z.H. Wu, T. Zhang, T. Li, Z.B. Yang, *Acta Metall. Sin. (Engl. Lett.)* **29**, 1119 (2016)
- [3] X.S. Wan, S.S. Zhao, Y. Yang, J. Gong, C. Sun, *Surf. Coat. Technol.* **204**, 1800 (2010)
- [4] Y.X. Ou, J. Lin, H.L. Che, J.J. Moore, W.D. Sproul, M.K. Lei, *Thin Solid Film* **594**, 147 (2015)
- [5] L. Shan, Y.X. Wang, J.L. Li, X. Jiang, J.M. Chen, *Tribol. Int.* **82**, 78 (2015)
- [6] A. Gilewicz, P. Chmielewska, D. Murzynski, E. Dobruchowska, B. Warcholinski, *Surf. Coat. Technol.* **299**, 7 (2016)
- [7] Z.T. Wu, Z.B. Qi, D.F. Zhang, B.B. Wei, Z.C. Wang, *Surf. Coat. Technol.* **289**, 45 (2016)
- [8] J.J. Roa, E. Jiménez-Piqué, R. Martínez, G. Ramírez, J.M. Tarragó, R. Rodríguez, L. Llanes, *Thin Solid Film* **571**, 308 (2014)
- [9] Q.M. Wang, K.H. Kim, *Acta Mater.* **57**, 4974 (2009)
- [10] J.L. Lin, B. Wang, Y.X. Ou, W.D. Sproul, I. Dahan, J.J. Moore, *Surf. Coat. Technol.* **216**, 251 (2013)
- [11] Q.Z. Wang, F. Zhou, M. Callisti, T. Polcar, J.Z. Kong, J.W. Yan, *J. Alloy. Compd.* **708**, 1103 (2017)
- [12] S. Veprek, M.G.J. Veprek-Heijman, P. Karvankova, J. Prochazka, *Thin Solid Films* **476**, 1 (2005)
- [13] P. Souček, J. Daniel, J. Hnilica, K. Bernátová, L. Zábranský, V. Buršíková, M. Stupavská, P. Vašina, *Surf. Coat. Technol.* **311**, 257 (2017)
- [14] Q.S. Ma, L.H. Li, Y. Xu, J.B. Gu, L. Wang, Y. Xu, *Appl. Surf. Sci.* **392**, 826 (2017)
- [15] T. Konishi, K. Yukimura, K. Takaki, *Surf. Coat. Technol.* **286**, 239 (2016)
- [16] A. Anders, *Surf. Coat. Technol.* **257**, 308 (2014)
- [17] I.L. Velicu, V. Tiron, G. Popa, *Surf. Coat. Technol.* **250**, 57 (2014)
- [18] L.D. Giudice, S. Adjam, D.L. Grange, O. Banakh, A. Karimi, R. Sanjinés, *Surf. Coat. Technol.* **295**, 99 (2016)
- [19] H. Zhou, J. Zheng, B.H. Gui, D.S. Geng, Q.M. Wang, *Vacuum* **129**, 191 (2017)
- [20] T.G. Wang, S.S. Zhao, W.G. Hua, J.B. Li, J. Gong, C. Sun, *Mater. Sci. Eng., A* **527**, 454 (2010)
- [21] J.F. Archard, *J. Appl. Phys.* **24**, 981 (1953)
- [22] L.L. Huang, C.W. Zou, W. Xie, F. Peng, L.X. Shao, *Ceram. Int.* **42**, 5062 (2016)
- [23] T.G. Wang, Y.M. Liu, T.F. Zhang, D.I. Kim, K.H. Kim, *J. Mater. Sci. Technol.* **28**, 981 (2012)
- [24] M. Balzer, M. Fenker, *Surf. Coat. Technol.* **250**, 37 (2014)
- [25] S. Veprek, M.G.J. Veprek-Heijman, *Surf. Coat. Technol.* **201**, 6064 (2007)
- [26] S. Veprek, *J. Vac. Sci. Technol.* **31**, 050822 (2013)
- [27] C.C. Chang, H.W. Chen, J.W. Lee, J.G. Duh, *Surf. Coat. Technol.* **284**, 273 (2015)
- [28] S. Veprek, S. Reiprich, L. Shizhi, *Appl. Phys. Lett.* **66**, 2640 (1995)
- [29] A. Lasalmonie, J.L. Strudel, *J. Mater. Sci.* **21**, 1837 (1986)
- [30] S. Liu, R. Raghavan, X.T. Zeng, J. Michler, *Appl. Phys. Lett.* **104**, 081919 (2014)
- [31] C.C. Chang, H.S. Chen, J.W. Lee, J.G. Duh, *Thin Solid Films* **584**, 46 (2015)
- [32] P. Bansal, P.H. Shipway, S.B. Leen, *Acta Mater.* **55**, 5089 (2007)
- [33] R. Gadow, M.J. Riegert-Escribano, M. Buchmann, *J. Therm. Spray Technol.* **14**, 100 (2005)
- [34] V.V. Le, T.T. Nguyen, S.K. Kim, K.H. Pham, *Surf. Coat. Technol.* **218**, 87 (2013)
- [35] T.G. Wang, D. Jeong, Y.M. Liu, Q.M. Wang, S. Iyengar, S. Melin, K.H. Kim, *Surf. Coat. Technol.* **206**, 2638 (2012)
- [36] R. Bajwa, Z. Khan, H. Nazir, V. Chacko, A. Saeed, *Acta Metall. Sin. (Engl. Lett.)* **29**, 902 (2016)
- [37] T. Polcar, A. Cavaleiro, *Surf. Coat. Technol.* **206**, 1244 (2011)
- [38] Y.S. Hong, S.H. Kwon, T.G. Wang, D.I. Kim, J. Choi, K.H. Kim, *Trans. Nonferrous Met. Soc. China* **21**, s62 (2011)