Coatings based on chromium carbide fabricated by an arc sputtering of graphite and Cr-Al(Si) targets

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Abstract. Single CrAlC, CrAlSiC and multilayer [CrAlC/a-C]ₙ, [CrAlSiC/a-C]ₙ coatings have been fabricated and investigated. Joint use of arc plasma source with Cr-Al(Si) cathode and pulsed arc plasma source with graphite cathode was applied to single coatings deposition. Diamond-like a-C layers alternate with CrAl(Si)C in multilayer coatings. The doping of CrAlC with silicon is accompanied by an increase in their crystallinity due to the formation of silicon carbide particles. Structural changes make CrAlSiC films harder with a low friction coefficient and a high resistance to plastic deformation. The multilayer coatings are crack resistant.

1. Introduction

Recently, extensive studies have been carried out to improve the tribological performances of carbon coatings using element doping, architecture design, and new deposition technology [1]. Doping with carbide-forming metals (Ti, Mo, W, Cr) leads to the formation of ultrafine carbide nano-grains increasing coating hardness. Cr, Mn, Fe, Co, Ni carbides films have mainly amorphous structure with nanocrystalline inclusions [2, 3]. The strong metal-carbon bonds increase internal stresses, reduce ductility and viscosity of coatings. Metals that do not form strong bonds with carbon (Cu, Al) contribute to the formation of metal phases improving the viscosity, but reducing the hardness [5, 6]. Nevertheless, it is possible to obtain a thermally stable coating with a low residual stress, high hardness, and high toughness by doping several elements, including metal atoms that form strong bonds with carbon, metal atoms that do not form strong bonds with carbon, and non-metal atoms [7].

The multilayer coating design has an important role in the fabrication of materials having the optimal mechanical and tribological properties. Multilayer coatings, characterised by high hardness, crack, and friction wear resistances, are technologically prospective materials. The advanced mechanical properties of such coatings can be tailored through unique phase combinations and interfacial architecture. The interfaces and possible grain boundaries deflect or reduce the cracks propagation and stresses concentration. Various multilayer coatings, such as a-C/a-C:Ti, TaN/a-CNₓ, Mo₂N/CrN, (TiCₓ/TiC)/a-C, and CrN/diamond-like carbon (DLC)/Cr-DLC have been intensively studied [1,6-11]. However, the multilayer coatings consisting of CrAlC, CrAlSiC layers and diamond-like carbon (a-C) have not been well studied. In this study we focus our attention on the properties of single CrAlC, CrAlSiC and multilayer [CrAlC/a-C]ₙ, [CrAlSiC/a-C]ₙ coatings.
2. Materials and methods

Single CrAlC, CrAlSiC and multilayer [CrAlC/a-C]n, [CrAlSiC/a-C]n coatings were deposited using UVNIPA-001 machine. GCr15 tool steel, 9Cr18 stainless steel and Si plates were used as substrates for coating deposition. The substrates cleaned with distilled water and ethanol in an ultrasonic bath following by ion etching in vacuum. An arc plasma source with the Cr0.5Al0.5 or Cr0.35Al0.55Si0.08 cathode and pulsed arc plasma source with a graphite cathode were used to deposit the CrAlC and CrAlSiC. The same conditions were used for the deposition of the corresponding layers in multilayer coatings. The arc pulse frequency of 3 Hz and the discharge voltage of 300 V have been applied to conduct the deposition of coatings. The times of deposition of the separate layers in the multilayer coatings have been set so that the layer thickness does not exceed 50 nm.

Scanning electron microscopy (SEM, QUANTA 200), transmission electron microscopy (TEM, JEM-200), and Raman spectroscopy were used to study the structure of coatings. The Cr, Al, and C contents in the coatings were determined by energy-dispersive X-ray spectroscopy using a QUANTA 200 microscope equipped with an EDAX analyser. The characteristic hardness ($H$) and reduced modulus ($E$) were measured using the nanoindentation technique (NanoTest 600) at a depth where they were not affected by the substrate. A coating-cracking test was performed using Ø50-µm diamond ball under loads of 100–1500 mN in steps of 100 mN. The indenter pass length (scratch) was 100 µm. The load of start coating cracking ($P_{cr}$) was determined using SEM images of scratches.

3. Results and discussion

Figure 1 shows TEM images with corresponding selected-area electron diffraction (SAED) patterns of the CrAlC and CrAlSiC coatings. The structural ordering in coatings depends on their composition. CrAlC is amorphous with the broad diffuse rings according to the SAED pattern (figure 1a). Amorphous matrix of this coating contains separate spherical inclusions having sizes of 5–20 nm and inclusions in the form of plates (~ 50 nm). The spherical inclusions belong to nanocrystalline chromium carbide. The plates are, most likely, the sets of graphite planes. In CrAlSiC coating against the background of no uniform amorphous matrix, many nano-grains having sizes of 10–30 nm are visible (figure 1b). The broad diffuse rings and narrow rings with separate spots in the SAED pattern of CrAlSiC (figure 1b) indicate that its structure is also amorphous with nanocrystalline inclusions. The doping of CrAlC with silicon accompanied by improving their crystallinity owing to the formation of silicon carbide grains. Presence of the SiC grains in CrAlSiC was detected early by X-ray diffraction (XRD) (data in press). Accurate identification the phases using SAED patterns spectra is not possible. The presence of Cr$_x$Al(Si)$_{1-x}$C and metastable CrC phases is also feasibly in both coatings.

![Figure 1. TEM images (bright field) of (a) CrAlC and (b) CrAlSiC. SAED patterns are shown in the upper left corner of TEM images.](image-url)
The Raman spectra of CrAlC and CrAlSiC are shown in figure 2. The Raman peaks in the range of 1000–1700 cm\(^{-1}\) indicate carbon clusters in both coatings. However, the Raman spectra of CrAlC and CrAlSiC are different. The spectrum of CrAlC has three separate peaks at 820 cm\(^{-1}\), 1316 cm\(^{-1}\) (D-peak) and 1531 cm\(^{-1}\) (G-peak). The separate peaks at 1316 cm\(^{-1}\) and 1531 cm\(^{-1}\) are inherent in nanocrystalline graphite. Peak in the range 700–800 cm\(^{-1}\) is, most likely, associated with the Me-C bonds. The spectrum of CrAlSiC has a wide band with maxima at 780 cm\(^{-1}\), 1274 cm\(^{-1}\) (D-peak) and 1566 cm\(^{-1}\) (G-peak). A wide band in the range 1000–2000 cm\(^{-1}\) is characteristic of amorphous carbon with large amount of \(sp^2\)-bonded carbon. Large intensive band in the range 500–1000 cm\(^{-1}\) appeared owing to the silicon carbide formation.

Thus, in CrAlC along with the amorphous matrix, chromium carbide, and Cr\(_{x}\)Al\(_{1-x}\)C nanograins, clusters of nanocrystalline graphite as spherical inclusions and plates were observed. The structure of CrAlSiC includes the amorphous matrix, clusters of nanoscale amorphous carbon with large amount of \(sp^2\)-bonded carbon, and large amount of silicon carbide nano-grains.

![Figure 2. Raman spectra of (a) CrAlC and (b) CrAlSiC. Black line is the baseline corrected Raman data; red lines are the baseline corrected Raman data fitted with a sum of Gaussian peaks ((a) three peaks for CrAlC and (b) three peaks for CrAlSiC).](image)

The characteristics of single CrAlC, CrAlSiC and multilayer [CrAlC/a-C]\(_{20}\), [CrAlSiC/a-C]\(_{20}\) coatings listed in table 1. The content of aluminum (\(C_{Al}\)) in CrAlSiC is higher. Despite this, its hardness (\(H\)) is higher owing to the presence of silicon carbide nanograins. Moreover, doping with silicon reduces the friction coefficient (\(f\)) by more than five times.

|                      | \(h\)  | \(C_{Cr}/C_{Al}\) | \(H\)    | \(E\)  | \(H^2/E^2\) | \(P_{cr}\) | \(f\)   |
|----------------------|--------|-------------------|----------|--------|-------------|------------|--------|
| CrAlC                | 1600   | 0.7               | 12.5±1.3 | 214±38 | 0.04        | 600        | 0.22   |
| CrAlSiC              | 2500   | 0.4               | 15.8±0.6 | 232±12 | 0.07        | 700        | 0.04   |
| [CrAlC/a-C]\(_{20}\) | 1600   | –                 | 13.3±0.9 | 166±90 | 0.08        | 1200       | 0.15   |

\(a\) Film thickness.

\(b\) Elastic modulus.
The hardness of multilayer [CrAlC/a-C]_20 is close to the hardness of corresponding single CrAlC; $H/E^2$ ratio is higher of 2.0 times. The hardness of [CrAlSiC/a-C]_20 is slightly higher of the hardness of CrAlSiC; $H/E^2$ ratio is higher of ~ 1.4 times (table 1). Thus, the introduction of diamond-like carbon (a-C) increases the $H/E^2$ ratios characterizing the resistance to plastic deformation. However, the hardness of both multilayer coatings are considerably lower than those of the a-C coating [11]. This effect could be attributed to the decreases in the hardness of the a-C layers due to their graphitisation under the bombardment by Cr⁺ and Al⁺ ions during the deposition of the CrAlC or CrAlSiC layer. Friction coefficient of the [CrAlC/a-C]_20 is lower of CrAlC as the upper layer in the multilayer is a-C having a smooth surface [11].

Although the hardness of the multilayer coatings are not increased, they are more crack-resistant compared with the single coating. The critical load of crack appearance ($P_{cr}$) is more than 1.9–2.0 times higher (table 1). Owing to the cracks propagation, the spalling of large fragments destroys the coating. We observed such effect during the cracking test of CrAlC under load of 700 mN that exceed the load of start cracking (figure 3a). High value of $H/E^2$ in CrAlSiC characterizes the resistance to plastic deformation. Destroy of CrAlSiC under load of 700 mN did not happen owing to the higher value of $H/E^2$. Only the crack network observed in the SEM image (figure 3b). In a multilayer coating when the cracks propagate into the deep regions of the coating, they reach the first interlayer boundary, and thus only small fragments of the upper layer spall. The destruction of the coating over the entire depth does not occur (figure 3c). As follows from the above, the structural features of the layers affect the physical-mechanical properties of multilayer coatings.

Figure 3. SEM images of the scratches formed after the pass of the diamond indenter: (a) CrAlC, (load: 700 mN), (b) CrAlSiC (load: 700 mN), and (c) [CrAlC/a-C]_20 (load: 1200 mN).

4. Conclusion
The structures, mechanical, and tribological properties of the CrAlC, CrAlSiC, and multilayer [CrAlC/a-C]_20, [CrAlSiC]/a-C]_20 coatings, fabricated using PVD technology were studied. The arc plasma source with the Cr-Al(Si) cathode and pulsed arc plasma source with the graphite cathode were used to deposit the coatings.

Transmission and scanning electron microscopies (TEM, SEM), and Raman spectroscopy were employed to investigate the coatings structures. Along with the amorphous matrix, chromium carbide, and CrₓAl₁₋ₓC nanograins, clusters of nanocrystalline graphite existed in CrAlC. The doping of CrAlC coatings with silicon accompanied by improving their crystallinity due to the formation of silicon
carbide grains. The structure modification of CrAlC by Si doping makes them harder with a higher resistance to plastic deformation and lower friction coefficient. The multilayer structure significantly increased the resistance to plastic deformation and crack resistance.

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References
[1] Sui X, Lui J, Zhang S, Yang J and Hao J 2018 App. Surf. Sci. 439 24
[2] Rubshtein A P, Vladimirov A B and Plotnikov S A 2018 Sol. Stat. Phenom. 279 153
[3] Jansson U and Lewin E 2013 Thin Solid Films 536 1
[4] Dai W, Wang A and Wang Q 2015 Surf. Coat. Technol. 272 33
[5] Dai W, Gao X, Liu J and Wang Q 2016 Diam. Relat. Mat. 70 98
[6] Rubshtein A P, Vladimirov A B and Plotnikov S A 2018 Sol. Stat. Phenom. 279 160
[7] Kuo Y C, Wang C J and Lee J W 2017 Thin Solid Films 638 220
[8] Cai J B, Wang X L, Bai W Q, Wang D H, Gu C D and Tu J P 2013 Surf. Coat. Technol. 232 403
[9] Chen R, Tu J P, Liu D G, Yu Y L, Qu S X and Gu C D 2012 Surf. Coat. Technol. 206 2242
[10] Bouaouina B, Besnard A, Abaidia S E and Haid F 2017 Appl. Surf. Sci. 395 117
[11] Gavrilov N V, Mamaev A S, Plotnikov A S, Rubshtein A P, Trakhtenberg I S and Uglov V A 2010 Surf. Coat. Technol. 204 4018