Structure and mechanical characteristics of CrAlC films doped with silicon

A P Rubshtein, A B Vladimirov and S A Plotnikov

M.N. Miheev Institute of Metal Physics, Ural Branch of Russian Academy of Sciences, 620990, Ekaterinburg, Russia

E-mail: rubshtein@imp.uran.ru

Abstract. CrAlC and CrAlSiC films have been obtained and investigated. Simultaneous sputtering of graphite and Cr$_{0.5}$Al$_{0.5}$ or Cr$_{0.35}$Al$_{0.55}$Si$_{0.08}$ targets was used for films deposition. The structure of the films is amorphous-nanocrystalline. The doping of CrAlC films 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 higher resistance to plastic deformation.

1. Introduction

Doping of coatings with other elements is one of the ways improving their functional characteristics. Doping with carbide-forming metals (Ti, Mo, W, Cr) leads to the formation of ultrafine carbide inclusions, which can significantly increase the hardness of coatings [1]. Cr, Mn, Fe, Co, Ni carbides films have either completely amorphous or mainly amorphous structure with nanocrystalline inclusions [2]. In the case of joint sputtering of chromium and carbon targets or composite Me-C target coating with an amorphous structure is formed [3]. However, the strong metal-carbon bonds increase internal stresses, reduce ductility and viscosity of coatings. In contrast, doping of carbon coatings with metals that do not form strong bonds with carbon (Cu [4], Al [5]) is accompanied by the formation of metal phases in the carbon matrix, which improve the viscosity, but reduce the hardness. Nevertheless, it is possible to obtain thermally stable coatings with low residual stress, high hardness and toughness by doping with non-metallic elements, for example, silicon [6]. This paper presents the results of study of CrAlC and CrAlSiC films deposited with PVD technique.

2. Materials and methods

The films were deposited in a vacuum chamber of ion-plasma machine. The vacuum chamber is equipped with a gas ion source, an arc source for sputtering metal targets and a pulsed arc source for sputtering a graphite target. Graphite, Cr$_{0.5}$Al$_{0.5}$ or Cr$_{0.35}$Al$_{0.55}$Si$_{0.08}$ targets were used for the deposition of CrAlC or CrAlSiC films. A joint sputtering of Cr$_{0.5}$Al$_{0.5}$ or Cr$_{0.35}$Al$_{0.55}$Si$_{0.08}$ and graphite targets by arc and pulsed arc (frequency of 3 Hz, discharge voltage of 300 V) techniques were used to conduct the deposition of the CrAlC or CrAlSiC films.

The thickness and composition of the films were determined using QUANTA 200 scanning electron microscope with EDAX analyser. Hardness and elastic modulus were measured by nanoindentation method (NanoTest 600, Micro Materials Ltd, UK). The phase composition of the films was studied by X-ray diffraction on an Empyrean diffractometer (PANalytical B.V., PHILIPS).
using CuKα radiation. A sliding beam at an angle of incidence of 5 degrees have been used to examine the coating crystal structure.

3. Results and discussion

The composition of the films is given in Table 1. As can be seen from the table, the Cr/Al ratio in the films is lower than in the sputtered targets. It may be due to the different sputtering rates of chromium and aluminum or screening of chromium ions with carbon ions. Previously the decrease of Cr/C ratio in films with an increase in the content of carbon ions in the plasma was established. In addition, Al atoms prevent the formation of chromium carbides, which can lead to poor crystallization and an increase in amorphous components [7].

Table 1. Composition and mechanical characteristics of CrAlC and CrAlSiC films.

|       | h (nm)  | C_Cr (at.%) | C_Al (at.%) | C_Si (at.%) | C_C (at.%) | H (GPa) | E (GPa) | H^3/E^2 (GPa) |
|-------|---------|-------------|-------------|-------------|------------|---------|---------|---------------|
| CrAlC | 1600    | 34.2±1.1    | 56.0±1.3    | -           | 12.6±3.3   | 125±1.3 | 214±38 | 0.04          |
| CrAlSiC | 2500   | 22.1±1.8    | 56.4±1.5    | 7.2±1.1     | 12.4±4.3   | 158±0.6 | 232±12 | 0.07          |

a Film thickness.
b Element content in film.
c Hardness.
d Elastic modulus.

At the close carbon content in the films, the content of aluminum in CrAlSiC is higher. Despite this, the hardness of CrAlSiC is higher of the hardness of CrAlC ~1.3 times, H^3/E^2 ratio is higher of ~1.7 times. The doping of CrAlC films with silicon for 7.2 at. % leads to a change in their structure. Figure 1 shows the X-ray diffraction spectra of CrAlC and CrAlSiC. Both spectra include a wide peak in the range of 2θ from 27 to 52°. The diffuse character of the peaks indicates the amorphous-nanocrystalline structure of the films. A wide diffuse peak is a result not only existence of amorphous component in films, but also an overlap of lines of nanograins having the different composition and structure. The lines centers were found after fitting XRD spectra with a linear combination of Gaussian and Lorentzian curves. Table 2 shows the experimentally values of the interplanar distances and the reference data for the intensive lines of the phases Cr_3C_2, Cr_2AlC, Al_2O_3 and SiC. The experimental values with an accuracy of ± 3% coincide with the values from literature.

The shift of the maximum towards smaller angles, observed on the X-ray spectrum of the CrAlSiC film (figure 1(b)), occurs due to the formation of silicon carbide in the film. The line with a center of 2θ =35.36° was found after fitting of the diffraction spectrum. This line is close to the intense (102) line of silicon carbide, having a maximum at 2θ =35.75°.

Nanograins of silicon carbide with a size of up to 30 nm were detected in CrAlSiC using transmission electron microscopy. However, chromium carbide and alumina also have the intense lines at 2θ = 35.25° and 2θ =35.17°, respectively. The existence of these phases in both CrAlC and CrAlSiC is confirmed by the presence of other lines at 2θ =39.06° and 2θ =57.54° belonging to Cr_3C_2 and Al_2O_3, respectively. Accurate determination of the phase composition and phase ratio using obtained X-ray spectra is not possible. The formation in the films of Cr_2Al, Cr_{1-x}Al_{x}SiC and the metastable CrC phases is also possible. Cr_{1-x}Al_{x}SiC phase is a result of Cr atoms partially replacement by Al due to the large its amount in films.

Despite the increase in hardness due to the presence of silicon carbide nanograins, CrAlSiC film has a higher value of H^3/E^2 ratio. This ratio characterizes the film resistance to plastic deformation. Increase of H^3/E^2 ratio means, that doping of CrAlC film with silicon should increase their wear resistance during tribological exposure. Aluminum oxide, found in both films, makes their corrosion-resistant (test results will be published).
Figure 1. XRD spectra of CrAlC (a) and CrAlSiC (b).

Table 2. Phase composition of CrAlC and CrAlSiC films.

| Phase      | CrAlC film | CrAlSiC film |
|------------|------------|--------------|
|            | $2\theta_{\text{exp.}}$(deg.)$^a$ | $d_{\text{exp.}}$(nm)$^b$ | $d_{\text{ref.}}$(nm)$^b$ | (hkl)$^c$ | $2\theta_{\text{exp.}}$(deg.) | $d_{\text{exp.}}$(nm) | $d_{\text{ref.}}$(nm) | (hkl) |
| Cr$_3$C$_2$ | 35.8       | 0.2930       | 0.2747       | (011)  | 35.4       | 0.2536       | 0.2546       | (104)  |
|            | 40.4       | 0.2231       | 0.2306       | (112)  | 43.3       | 0.2086       | 0.2135       | (113)  |
|            | 45.6       | 0.1988       | 0.1949       | (211)  | 53.7       | 0.1704       | 0.1696       | (115)  |
|            | 53.8       | 0.1702       | 0.1696       | (115)  | 56.5       | 0.1627       | 0.1601       | (116)  |
| Cr$_2$Al(Si)C | 42.7       | 0.2115       | 0.2139       | (103)  | 43.3       | 0.2865       |             | (103)  |
| Al$_2$O$_3$ | 35.8       | 0.2508       | 0.2551       | (104)  | 35.4       | 0.2536       | 0.2551       | (104)  |
| SiC        |            |              |              |        | 56.5       | 0.1627       | 0.1601       | (116)  |
|            | 56.5       | 0.1627       | 0.1601       | (116)  | 35.4       | 0.2536       | 0.2509       | (102)  |

$^a$ Diffraction angle.
$^b$ Interplanar distance.
$^c$ Miller indices.
4. Conclusion
Thus, the doping of CrAlC films with silicon is accompanied by improving their crystallinity due to the formation of silicon carbide grains. The structure modification of CrAlC makes them harder with a higher resistance to plastic deformation.

Acknowledgments
The results of study of mechanical characteristics of films of part “Results and discussion” were obtained within the state assignment of Minobrnauki of Russia (theme “Function” No AAAA-A19-119012990095-0). The results of study of structure of films of part “Results and discussion” were obtained within the RSF grant (project No. 17-12-01002).

References
[1] Rubshtein A P, Vladimirov A B and Plotnikov S A 2018 Sol. Stat. Phenom. 279 153–9
[2] Jansson U and Lewin E 2013 Thin Solid Films 536 1–24
[3] Gassner G 2005 Surf. Coat. Technol. 200 1147–50
[4] Dai W, Wang A and Wang Q 2015 Surf. Coat. Technol. 272 33–8
[5] Dai W, Gao X, Liu J and Wang Q 2016 Diam. Relat. Mat. 70 98–104
[6] Kuo Y C, Wang C J and Lee J W 2017 Thin Solid Films 638 220–9
[7] Fu N C and Li G W 2006 Appl. Surf. Sci. 253 1260–4