Tribological properties of CrAlSiC coatings fabricated under various conditions for generating carbon plasma

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Abstract. There were investigated tribological properties of CrAlSiC coatings deposited by two techniques. In both techniques a plasma source of a cathode-arc discharge with Cr-Al-Si composite target served the source of Cr, Al, and Si atoms during coating deposition. A plasma source of a pulsed cathode-arc discharge with graphite cathode and a gas discharge device to generate a non-self-sustained discharge in argon-acetylene mixture have been used for generating carbon plasma in first and second techniques, correspondingly. First coating has a low coefficient of friction. Under frictional action, coating wears out uniformity without chipping. Second coating is less resistant to frictional action.

1. Introduction

The scientific and commercial interest in the development of nanostructured materials, which exhibit enhanced physical properties over their polycrystalline counterparts, is driven by increasing practical demands on the mechanical performance, the wear and corrosion resistance of industrial components [1]. A wide variety of production techniques, including mechanical alloying, rapid solidification, sintering of nanopowder etc. are all being developed. In parallel with the manufacturing of bulk materials, technologies of vacuum plasma deposition of coatings, in particular, multicomponent and multilayer, are being intensively developed. The physical nature of the formation of the structure of such coatings, depending on the deposition conditions, thermal stability of coatings, and the wear mechanisms are being investigated [2, 3]. Among them, the transition-metal carbides and nitrides, such as TiN, CrN, and CrC, are the most popular materials for coatings owing to their high hardness, excellent wear resistance, and thermal stability [4]. The doping by metals that do not form bonds with the carbon matrix (Cu, Al) is accompanied by the formation of metal phases, that improve the viscosity. Nevertheless, it is possible to obtain thermally stable coatings with low residual stresses, high hardness, and high toughness through doping by nonmetal atoms such as Si [5].

In this paper, there were investigated CrAlSiC coatings deposited by two techniques. In both techniques a plasma source of a cathode-arc discharge with a Cr-Al-Si composite target served the source of Cr, Al, and Si atoms during the coating deposition. A plasma source of a pulsed cathode-arc discharge with a graphite cathode have been used for generating carbon plasma in first technique, gas discharge device to generate a non-self-sustained discharge in an argon-acetylene mixture have been used as source the carbon in the second technique. The main goal of the work was to study the tribological properties of coatings under frictional action.
2. Materials and methods

CrAlSiC coatings were fabricated using UVNIPA-001 machine. Si plates were used as substrates. The Si plates cleaned with distilled water and ethanol in an ultrasonic bath following by ion etching in vacuum. A plasma source of a cathode-arc discharge plasma source with a \( \text{Cr}_{0.35}\text{Al}_{0.55}\text{Si}_{0.08} \) cathode and a plasma source of a pulsed cathode-arc discharge with a graphite cathode were used to deposit the CrAlSiC(I) coating. The arc pulse frequency of 15 Hz and the discharge voltage of 300 V have been applied to conduct the deposition this coating. A plasma source of a cathode-arc discharge plasma source with \( \text{Cr}_{0.35}\text{Al}_{0.55}\text{Si}_{0.08} \) target and gas discharge device to generate a non-self-sustained discharge in an argon-acetylene mixture were used for the depositions of the CrAlSiC(II) coating. Decomposition of acetylene in an argon–acetylene mixture (30% Ar, 70% \( \text{C}_2\text{H}_2 \), \( P = 0.2 \) Pa) was performed in a non-self-sustained hollow-cathode pulsed-direct-current-(DC) discharge (\( U = 300 \) V, \( I = 3 \) A).

The coating thickness was measured using a scanning electron microscopy (SEM) image of the cross section of the coating–substrate. The Cr, Al, Si and C contents in the coatings were determined by energy-dispersive X-ray spectroscopy (EDX) using a QUANTA 200 microscope equipped with an EDAX analyzer.

The tribological behaviours of coatings were investigated with a high-speed reciprocating friction and wear tester (MFT-R4000) at 25 °C and relative humidity of 33% under dry sliding conditions. A GCr15 ball (Ø 6 mm) was used as the mating material. All tests were carried out at a sliding velocity of 20 mm/s and applied load of 3 N. A scratch test was performed using 050-μm diamond ball under loads of 100–1500 mN in steps of 100 mN (NanoTest 600 device). The indenter pass length (scratch) was 100 μm. The load of start coating cracking was determined using SEM images of scratches.

3. Results and discussion

The thickness and chemical composition of CrAlSiC(I) and CrAlSiC(II) coatings are presented in table 1. In addition of Cr, Al, Si and C, oxygen was detected at a level of several at.% in both coatings. Besides the CrAlSiC(II) contains argon. The presence of argon indicates the formation of closed micropores. In this coating Cr/Al ratios are lower than that in the Cr–Al–Si cathode (0.6). The increase in Al content can lead to a low crystallization and increases in amorphous components [6]. Moreover, the screening of chromium ions with carbon ions in the plasma could reduce the chromium content [7].

| Coating      | Carbon source | \( h \) (nm) | \( C_{\text{Cr}} \) (at.%) | \( C_{\text{Al}} \) (at.%) | \( C_{\text{Cr}}/C_{\text{Al}} \) | \( C_{\text{C}} \) (at.%) | \( C_{\text{Si}} \) (at.%) | \( C_{\text{O}} \) (at.%) | \( C_{\text{Ar}} \) (at.%) |
|--------------|---------------|--------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| CrAlSiC(I)   | graphite      | 4000         | 27.3           | 48.0           | 0.6           | 14.6           | 5.9            | 4.2            | -              |
| CrAlSiC(II)  | acetylene     | 3800         | 16.7           | 42.3           | 0.4           | 17.6           | 7.8            | 9.0            | 6.6            |

The surface morphology of the coatings is different. Defects of various shapes and sizes are visible in SEM pictures (figure 1 a,b). Protrusions with sharp edge of 2-4 μm in size are inherent for CrAlSiC(I) (figure 1a). Bubble-like defects and holes of 5-15 μm in size are inherent for CrAlSiC(II) (figure 1b). Density of defects is higher in the CrAlSiC(I). Higher level of chromium and oxygen content in the protrusions-like defects was detected by EDX. The bubble-like defects have the same composition as the coating. It can be observed that separate bubble-like defects detached, possibly, due to internal stresses that develop as the coating grows.

The formation of the defects depends on the deposition conditions. A plasma source of a pulsed cathode-arc discharge with a graphite cathode is used to deposit the CrAlSiC(I). In this process, graphite microparticles are formed on the cathode surface under the action of a pulsed-arc. Microparticles falling on the growing surface of coating cause local overheating and can thus initiate the diffusion growth of energetically favorable elongated pyramidal structures (protrusions) [8]. In a plasma-assistant chemical vapor deposition process (CrAlSiC(II) coating) decomposition of acetylene
in an argon–acetylene mixture is performed in a non-self-sustained pulsed-direct-current-discharge. The walls of working chamber serve as a cathode. May be proposed, that the discharges concentrate on the imperfections of the surface, including growing nanograins of carbides. In these places the coating grows by another mechanism, creating channels and defects in the bubble-like shape [9].

Figure 1. SEM images of (a) – CrAlSiC(I) and (b) – CrAlSiC(II) coatings

Figure 2 shows the variation of the friction coefficient versus sliding time at 3 N load. The variation of friction coefficient in CrAlSiC(I) coating is small (f_{average} = 0.04, f_{max} = 0.05). Chipping protrusion-like defects in this coating act as the polishing particles under the friction, that leads to decrease of friction coefficient and abrasive wear dominance. The uniform wear of the CrAlSiC(I) coating material itself occurs. The variations of friction coefficient in CrAlSiC(II) coating after 6 min of sliding have sinusoidal behavior. The range of friction coefficient peaks is wide (f_{average} = 0.13, f_{max} = 0.29). This is because of the destroying of the coating due to the detach of bubble-like defects.

Figure 2. Friction coefficient vs. sliding time.

A scratch test was performed using Ø50-µm diamond ball under loads of 100–1500 mN in steps of 100 mN. Visible scratches in both coatings are shown in figure 3. Scratches in the CrAlSiC(I) are uniform without chipping at the edges (figure 4a). There are slightly visible traces of abrasive action of solid particles (chipping protrusions) inside the scratch. Scratches in the CrAlSiC(II) at loads of more than 700 mN have round-shaped chips 5-15 µm in size (figure 4b). The chip’s size corresponds to the size of bubble-like defects (figure 1b). Uniform wear of the CrAlSiC(I) is confirmed by the linear relationship f = d(P), where d is the maximum scratch depth, P is the load (figure 5, black squares). The curve f = d(P) for the CrAlSiC(II) (figure 5, open squares) coincides with the curve for the CrAlSiC(I) in the load interval 100-700 mN. At loads over 700 mN, a curve jump is observed, because the process of chipping off the bubble-like fragments of the coating begins. It should be noted, that the maximum depth of scratches at a load of 1500 mN is less coating thickness. Complete wear of the coatings does not occur.
4. Conclusions
A comparative analysis of CrAlSiC coatings fabricated under various conditions for generating carbon plasma (graphite sputtering or hydrocarbon destruction) has been carried out. The deposition conditions affect the formation of the coating surface morphology. The CrAlSiC(I), fabricated by joint using both a plasma source of a cathode-arc discharge with CrAlSi cathode and a plasma source of a pulsed cathode-arc discharge with graphite cathodes, has a low coefficient of friction; under frictional action, coating wears uniformly without chipping. The CrAlSiC(II), fabricated by joint using both a plasma source of a cathode-arc discharge with CrAlSi cathode and a gas-discharge source with an argon-acetylene mixture, is less resistant to frictional action. With an increase in the time of frictional action (reciprocating test) or the load during scratching, the coating is destroyed by chipping off fragments.

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