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Thermal stability and high-temperature oxidation behavior of Si–Cr–N coatings with high content of silicon

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ABSTRACT

Si–Cr–N coatings are promising candidates for protective coatings for materials with a poor resistance to oxidation at elevated temperatures. In this article, we examine and present the thermal stability and high temperature oxidation behavior of reactively magnetron sputtered $Si_xCr_yN_z$ coatings with high content of silicon (>30 at.%) and N/metal ratios of 0.48 and 1.1. These coatings are investigated under isothermal and dynamic conditions using differential scanning calorimetry and thermal gravimetric analysis for temperatures of up to 1400 °C. The structure and morphology of the oxidized coatings are studied by X-ray diffraction, and electron microscopy. As-deposited $Si_xCr_yN_z$ coatings represent a composite system consisting of two chemically separated amorphous phases: a-SiN_x phase and a-SiCrN phase. The decomposition process connected with N_2 release occurs in $Si_xCr_yN_z$ coatings at an annealing temperature $T_a \geq 1000$ °C in an Ar atmosphere and involves a formation of nanocrystalline hcp-Cr_2N, Cr_5Si_3, hcp-Si_3N_4 and hcp-$CrSi_2$ phases. These structural changes are reflected in an increase in hardness from 13.2 GPa and 19.3 GPa to 34 GPa and 25.6 GPa for $Si_{0.66}Cr_{0.34}N_{0.48}$ and $Si_{0.66}Cr_{0.34}N_{1.1}$ coatings, respectively. $Si_xCr_yN_z$ coatings exhibit considerable oxidation resistance due to the formation of stable and dense Cr_2O_3 scales. The rapid oxidation of $Si_xCr_yN_z$ coatings starts as temperature T_a reaches ~1090 °C. The dense oxide scale of ~0.4 µm is formed during isothermal oxidation of $Si_{0.66}Cr_{0.34}N_{1.1}$ coatings at the temperature of 1100 °C for 48 h.

1. Introduction

Excellent mechanical properties and high temperature oxidation resistance of hard coatings represent the most important parameters in the machining industry, where the emphasis is on the increase of the cutting rate and of the lifetime of the tool. Hard coatings also provide a convenient way to protect high-temperature structural materials with a poor resistance to oxidation at elevated temperatures. Illustrative examples are titanium aluminides based on γ-TiAl, which are promising candidates to be used in automotive and aerojet engines because of their low density, high stiffness and good creep properties [1–4]. However, these intermetallic alloys lose toughness after they are exposed to temperatures above 850 °C, because of the formation of mixed Ti and Al-oxides in the structure.

Conventional TiN and CrN hard coatings are widely used to improve the lifetime of cutting tools, but their use at high temperatures is limited because of the onset of rapid oxidation at ~600 °C. Ternary TiAlN coatings exhibit higher oxidation resistance with the start of oxidation in the range of 870–950 °C depending on the Al content [5]. The oxidation of $Ti_{0.5}Al_{0.5}N$ proceeds by outward diffusion of Al to form Al-rich oxide at the surface and inward diffusion of O to form Ti-rich oxide at the interface to TiAlN [6].

Rovere et al. [7,8] reported on the promising oxidation resistance properties of $Cr_{1-x}Al_xN$ films based on the formation of dense and adherent $(Al,Cr)_2O_3$ mixed oxide scales during exposure to air at elevated temperatures. The excellent protection of unoxidized films by oxinitride layer ended when the decomposition occurs at ~1100 °C, resulting in enhanced oxidation and subsequent failure of the film. The addition of yttrium further improved the oxidation behavior of these nitride coatings. Yttrium segregation to the oxide scale grain boundaries blocked fast diffusion paths [1,9,10].

Musil [11] presented two new classes of non-oxide hard amorphous nanocomposite coatings based on nitrides with a thermal stability of above 1000 °C. 1. a-(Si_3N_4/MeN_x) composite coatings with high (≥50 vol.%) content of a-Si_3N_4 phase; here Me = Ta, Zr, Ti, Al, Mo, W, etc. [12,13]. 2. a-(Si–B–C–N) coatings with strong covalent bonds [13,14]. The absence of grains in these coatings prevents a direct diffusion of the external atmosphere to the substrate through grain boundaries. Their thermal stability is determined by the

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crystallization of the amorphous material and is dependent upon several factors including the thermal stability of individual phases, the interdiffusion of elements from the substrate and the chemical composition of the annealing atmosphere [11].

Zeman et al. studied [15] Ta–Si–N coatings with a high (>20 at.%) Si content. Oxide layer based on orthorombic Ta_2O_5 formed a thin barrier to oxygen penetration on the top of Ta–Si–N films during high-temperature exposure at temperatures in the range of 800 °C to 1080 °C. W–Si–N coatings, described by Musil et al. [16], with a high (>60 vol.%) Si_3N_4 content, X-ray amorphous character and containing over-stoichiometric $WN_{x>1}$ phase exhibited a high oxidation resistance of up to 800 °C. Kim et al. [17], reported an oxidation behavior of Cr–Si–N coatings with a low content of Si ranging from 0 to 15 at.%. The increased oxidation resistance of the Cr–Si–N coatings was attributed to the formation of amorphous SiO_2 layer together with a Cr_2O_3 layer on the surface of the coating.

In this article, we present the analysis of the Si–Cr–N coatings with a high (>30 at.%) Si content prepared by reactive magnetron sputtering. Their high-temperature behavior was investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Thermal stability, structure evolution and mechanical properties of the coatings annealed at temperatures of up to 1400 °C were examined using X-ray diffraction (XRD), transmission electron microscopy (TEM) and nanoindentation measurements.

2. Experimental details

Si–Cr–N coatings were grown on negatively biased substrates by unbalanced magnetron sputtering from $CrSi_2$ target (100 mm in dia., 99.5% purity) in reactive Ar + N_2 discharges. The magnetron-power density was fixed at 7.2 $W \cdot cm^{-2}$ yielding a deposition rate R of approximately 3.3 $\mu m \cdot h^{-1}$ depending on the partial pressure of nitrogen. Substrates were placed opposite to the target at a distance of 80 mm. No additional heating besides the thermal effect due to the contact with plasma was used during deposition. All depositions were carried out at a negative substrate bias $U_s = -50$ V. The base pressure in the chamber was below 5×10^{-4} Pa and the total working gas pressure during the depositions was kept at 0.53 Pa with a N_2 partial pressure in the range of 0.08 Pa to 0.2 Pa.

Different substrates and coating thicknesses were used for the individual analyses. Polished low alloyed steel plates (16MnCr5) were coated with a 8.3 μm thick coating for DSC measurement. To exclude the influence of the substrates, the analyzed coatings were separated from the substrates. The poor adhesion of thick Si–Cr–N coatings to the low alloyed steel substrates allows for the easy separation of the coating from the substrate. Subsequently, free-standing coatings were mechanically ground to a powder and put into the sample holder of the measuring equipment. Coated mirror-polished Si(001) and Al_2O_3 plates (sapphire, c-cut, $8 \times 8 \times 0.3$ mm^3) were used for TGA, chemical composition, chemical bonds and structure analysis of Si–Cr–N coatings. Prior to the deposition all substrates were cleaned in an ultrasonic acetone and isopropyl alcohol bath.

Phase and structural changes of Si–Cr–N coatings annealed at up to 1400 °C in flowing Ar (purity 99.9999%, 10 sccm flow rate) at atmospheric pressure with a heating rate of 10 $°C \cdot min^{-1}$ were monitored by simultaneous DSC and TGA in the thermal analysis apparatus Netzsch STA 409 CD.

The high-temperature oxidation resistance was tested in a pure synthetic air with a flow rate of 1 l/h under TGA mode. The annealing temperature was increased from room temperature up to 1300 °C at the heating rate of 10 $°C \cdot min^{-1}$. Furthermore, Si–Cr–N coatings deposited on Si(001) substrates were isothermally oxidized at 900 °C and 1100 °C for 48 h during TGA measurement.

The chemical composition of the as-deposited and the annealed Si–Cr–N coatings was determined during the electron microscopy studies by means of energy-dispersive X-ray spectroscopy (SEM-EDX, INCA Oxford Instruments Analytical, Bruker Nano for EDX mapping). Information related to the chemical bonds of Si–Cr–N coatings was obtained by X-ray photoelectron spectroscopy (XPS, Omicron Nanotechnology). The morphology and thickness of the Si–Cr–N coatings were studied by a Tescan Lyra dual-beam scanning electron microscope (DB-SEM).

Structural investigations of the as-deposited Si–Cr–N coatings as well as of the oxidized coatings were performed by grazing incidence X-ray diffraction (GI-XRD) or Bragg-Brentano X-ray diffraction (XRD) measurements in a PANalytical X'pert PRO MRD diffractometer with Cu Kα radiation ($\lambda = 1.5418$ nm) with the angle of incidence set to 1.5° in GI-XRD. Transmission electron microscopy and high resolution transmission electron microscopy (TEM, Jeol 200 kV; HR-TEM Jeol JEM-2100) were also conducted to study the structure of the as-deposited and the annealed Si–Cr–N coatings.

The indentation hardness (H) and effective Young's elastic modulus (E^*) of Si–Cr–N coatings were measured using a nanoindenter (Hysitron, TI Ubi 750 equipped with a Berkovich diamond indenter) at a constant indentation depth of 120 nm. The presented results are the averages of 16 measurements (4×4 pattern) on three different places of each sample. Standard deviations for the measurements are presented in the form of error bars.

3. Results and discussion

3.1. Chemical composition and structure

Chemical analysis by SEM-EDX revealed several different compositions of our $Si_xCr_yN_z$ coatings depending on the partial pressure of nitrogen during deposition. For further investigation, two coatings with the following compositions were selected: $Si_{0.66}Cr_{0.34}N_{0.48}$ and $Si_{0.66}Cr_{0.34}N_{1.1}$ with N/metal ratios of 0.48 ± 0.02 and 1.1 ± 0.02, respectively. A small amount of impurities of carbon and oxygen not exceeding 3 at.% in total was detected as well.

Typical DB-SEM cross-sectional images of as-deposited $Si_xCr_yN_z$ coatings are displayed in Fig. 1a and b. The coatings exhibited dense, nonporous, featureless morphology on the fracture with no apparent defects. The surface of all $Si_xCr_yN_z$ coatings was very smooth (average roughness Ra ~3 nm as measured by AFM). The as-deposited $Si_xCr_yN_z$ coatings exhibited an X-ray amorphous structure with a high level of atomic disorder (Fig. 2). TEM investigation of the coatings provided an additional insight into the microstructure. High-resolution bright-field TEM (HR-TEM) image (Fig. 1c) revealed an amorphous character of $Si_{0.66}Cr_{0.34}N_{1.1}$ coating and the contrast difference indicated the presence of two chemically distinct phases. This result is in agreement with the selected area electron diffraction (SAED) pattern acquired (Fig. 1d) during dark-field XTEM analysis, which showed two diffusion rings suggesting an amorphous structure of the coatings.

XPS Si2p, N1s and Cr2p core level spectra of as-deposited $Si_{0.66}Cr_{0.34}N_{0.48}$ coatings are presented in Fig. 3. In the Si2p spectra only one peak located at around 101.7 eV was observed, which corresponds to Si – N bond. These results indicate that the SiN_x phase forms during the deposition of the coatings. This has been confirmed by the N1s spectra, where the peak located at approx. 397.5 eV corresponds to the N – Si bond. The peak at binding energy of approx. 583.5 eV was found in the Cr2p spectra and belongs to free non-binding Cr. Residual oxygen is bonded to Cr, which is indicated by the peak at approx. 576.8 eV corresponding to the Cr – O bond. On the basis of HR-TEM and XPS analysis, we can conclude that the as-deposited $Si_xCr_yN_z$ coatings represent a composite system consisting of amorphous a-SiN_x phase and an amorphous a-SiCrN phase.

3.2. Thermal stability

The results of the simultaneous DSC and TGA measurements of $Si_xCr_yN_z$ coatings are shown in Fig. 4. The baseline corrected dynamical