Phase Composition, Thermal Stability, Physical and Mechanical Properties of Superhard on Base Zr–Ti–Si–N Nanocomposite Coatings

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Abstract – Zr–Ti–Si–N coating had high thermal stability of phase composition and remained structure state under thermal annealing temperatures reached 1180 °C in vacuum and 830 °C in air. Effect of isochronous annealing on phase composition, structure, and stress state of Zr–Ti–Si–N ion-plasma deposited coatings (nanocomposite coatings) was reported. Below 1000 °C annealing temperature in vacuum, changing of phase composition is determined by appearing of siliconitride crystallites (B–Si3N4) with hexagonal crystalline lattice and by formation of ZrO2 oxide crystallites. Formation of the latter did not result in decay of solid solution (ZrTi)N but increased in it a specific content of Ti-component.

Vacuum annealing increased sizes of solid solution nanocrystallites from (12 to 15) in as-deposited coatings to 25 nm after annealing temperature reached 1180 °C. One could also find macro- and microrelaxations, which were accompanied by formation of deformation defects, which values reached 15.5 vol.%.

Under 530 °C annealing in vacuum or in air, nanocomposite coating hardness increased. When Ti and Si concentration increased and three phases nc-ZrN, (Zr, Ti)N-nc, and α-Si3N4 were formed, average hardness increased to 40.8 ± 4 GPa. Annealing to 500 °C increased hardness and demonstrated lower spread in values H = 48 ± 6 GPa and E = 456 ± 78 GPa.

1. Introduction

Recently, nanocomposite coatings of new generation composed of at least two phases with nanocrystalline and/or amorphous structures are of great interest. Due to very small size (10 nm) of their grains and more important role of boundary zones surrounding single grains, nanocomposite materials behave unlike traditional materials with grain size higher than 100 nm and display quite different properties. Novel unique physical and functional properties of nanocomposites promote rapid development of nanocomposite materials [1–5]. Films with H < 40 GPa and H > 40 GPa hardness are currently described as hard and superhard, correspondingly [5]. As is known, there are two groups of hard and superhard nanocomposites with nc-MeN/hard phase and nc-MeN/soft phase [3–5]. Moreover, bicrystalline phases and/or phases with different crystallographic grain orientations of the same material are distinguished in nanocrystalline and/or amorphous phases. Experimental data of a number of authors demonstrated that Zr–Si–N system was composed of two phases ZrN and (Si, Zr)N [6]. It is possible to assume that Ti addition to this system, would allow one to obtain several phases: nc-ZrN/a-Si3N4 and nc-Ti3N with definite Si and N concentrations. As it is known from works [7, 8], properties of solid α – Si3N4/McN strongly depend on phase composition and thermal stability of individual phases composing the total coating. It was demonstrated that Zr–Si–N films with ZrN, (x = 0.8) composition were thermally stable till 1130 °C. Those of ZrN, (x = 1.2) composition, i.e. having higher Zr concentration, like (α – Si3N4/MeN) Si3N4 + ZrN, (x = 1.2), were crystallized under higher temperature of 1530 °C (x = N/Zr in ZrNx phase). However, when Si3N4 phase was amorphous and took more than 50 vol.% of the coating, hardness ranged from 20 to 40 GPa, i.e. did not transit superhardness limit of 40 GPa [5, 8, 9].

We should like to note works [6], in which the authors studied structure stability and mechanical properties of Ti–Zr–N films deposited by vacuum-arc source (Cathodic Arc Vapor Deposition – CAVD) under various plasma densities from metallic cathodes Ti and Zr.

Also we should like to note theoretical works [3, 4], which studied electron structure, stability, decohesion mechanism, shear of interfaces in superhard and heterostructures nc-TmN/α-Si3N4.

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Therefore, the purpose of this work was to study formation of superhard coatings on Zr–Ti–Si–N base and their properties including thermal stability.

2. Experimental

Coatings were fabricated using vacuum-arc deposition from unit-cast, Zr, Zr–Si, and Zr–Ti–Si targets. Films were deposited in nitrogen atmosphere. Deposition was carried out using standard vacuum-arc and HF discharge methods. Bias potential was applied to substrate from HF generator, which produced impulses of convergent oscillations with $\leq 1\, \text{MHz}$ frequency, every impulse duration being $60\, \mu\text{s}$, their repetition frequency – about $10\, \text{kHz}$. Due to HF diode effect, value of negative autobias potential occurring in substrate increased from 2 to 3 kV at the beginning of impulse (after start of discharger operation). Coatings of 2 to 3.5 µm thickness were deposited to steel substrates (of 20 and 30 mm diameter and 3 to 5 mm thickness). Deposition was performed without additional substrate heating. Zr–Ti–Si–N coatings were deposited to polycrystalline steel (St.3 – 0.3 wt.%C, Fe the rest). Molecular nitrogen was employed as a reaction gas (Table 1).

Table 1. Physical-technological parameters of deposition

<table>
<thead>
<tr>
<th>Evaporated materials</th>
<th>Coating</th>
<th>$I, \text{A}$</th>
<th>$P_N, \text{Pa}$</th>
<th>$U_{RF}, \text{V}$</th>
<th>$U, \text{V}$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>ZrN</td>
<td>110</td>
<td>0.3</td>
<td>–</td>
<td>200</td>
<td>Standard technology</td>
</tr>
<tr>
<td>Zr</td>
<td>ZrN</td>
<td>110</td>
<td>0.3</td>
<td>200</td>
<td>–</td>
<td>HF deposition</td>
</tr>
<tr>
<td>Zr–Si</td>
<td>(ZrSi)N</td>
<td>110</td>
<td>0.3</td>
<td>200</td>
<td>–</td>
<td>HF deposition</td>
</tr>
<tr>
<td>Ti–Zr–Si</td>
<td>(Ti–Zr–Si)N</td>
<td>110</td>
<td>0.3</td>
<td>200</td>
<td>–</td>
<td>HF deposition</td>
</tr>
</tbody>
</table>

$I_c$ is the cathode current in A; $P_N$ is the pressure of atomic nitrogen in Pa units; $U_{RF}$ is the bias voltage of $H_\text{f}$ discharge; $U$ is the bias voltage under conditions of vacuum-arc discharge. Annealing was performed in air medium, in a furnace SNOL 8.2/1100 (Kharkov, Ukraine), under temperature $T = 300$, 500, and 800 °C, and in a vacuum furnace SNVE-1.3, under $5 \cdot 10^{-4}$ Pa pressure, and $T = 300$, 500, 800, and 1180 °C. Studies of phase compositions and structures were performed using X-ray diffraction devices DRON-3M, under filtered emission Cu–K$_\alpha$,

3. Experimental results and discussion.

The coatings prepared by sputtering from the Zr–Si–Ti target.

Figure 1 shows energy spectra of ion backscattering measured for steel samples with deposited Zr–Ti–Si–N coatings. Since Zr and Ti concentration was high, these spectra could hardly help to determine Si and N background concentration. Measurements of Si and N concentration using eating away of the RBS spectra gave higher error than for Zr and Ti. But still, Si concentration was not less than 7 at.%, while that of N might reach more than 15 at.%.
formation $\varepsilon$, microdeformation $<\varepsilon>$, and concentration of packing defects $\alpha_{\text{def.pack.}}$. The data were obtained both for samples after coating deposition and for those annealed in vacuum and air under various temperatures.

Crystallites of solid (Zr, Ti)N solution underwent compressing elastic macrostresses occurring in a “film-substrate” system. Compressing stresses, which were present in a plane of growing film, indicated development of compressing deformation in a crystal lattice, which was identified by a shift of diffraction lines in the process of angular surveys (“sin$^2\psi$ – method”) and reached – 2.93% value (Table 2). With $E \approx 400$ GPa characteristic elastic modulus and 0.28 Poisson coefficient, deformation value corresponded to that occurring under action of compressing stresses $\sigma_c \approx –8.5$ GPa. We should also note that such high stresses characterize nitride films, which were formed under deposition with high radiation factor, which provided high adhesion to base material and development of compression stresses in the film, which was stiffly bound to the base material due to “atomic peening”-effect.

At substructure level, microdeformation was still high, and amounted 1.4%. With a relatively small average crystallite size ($L \approx 15$ nm), development of such high microdeformation indicated significant contribution of crystallite deformed boundaries.

Phase composition of ion-plasma films under temperature of vacuum annealing lower than 1000 °C remained practically unchanged, corresponding to post-deposition state. An average crystallite size of solid solution (Zr, Ti)N also remained practically unchanged. Under this temperature range (300–1000 °C), microdeformation at substructure level typically decreased from 1.4 to 0.8% (Table 2), which indicated decreasing amount of lattice defects.

Compressing macrodeformation partially relaxed when annealing temperature increased within 25 to 1000 °C range. Practically, it decreased by a factor of three, reaching a value $\varepsilon \approx –1.1%$ under $T_{an} = 1000$ °C. We should note that $\varepsilon \approx –1%$, which was close to that obtained under annealing, was reached in the case of pure, ordered ZrN ion-plasma deposited coatings. A lattice period $d_0$ defined for non-stressed cross-section (under sin$^2\psi_0 = 0.43$) decreased with decreasing annealing temperature (Table 2). If one would relate such decreased period to ordering of titanium atoms with lower atomic radius, which were built-in into metallic sublattice instead of Zr atoms, then using Vegard’s rule, the decrease from 0.4552 to 0.4512 nm corresponded to 8.5 to 19.5 at.% increase of titanium atom content.

Shift of diffraction lines to various directions corresponding to planes taken at 0–20 (according to Bregg-Brentano scheme) seems to be explained by packing defects, which are present in metallic fcc-sublattice. Concentration of packing defects may be evaluated by comparison of shifting (222) and non-shifting (333) peak positions[10]. After condensation, average packing defect concentration in a lattice of (Zr, Ti)N solid solution was 5.7%. As a result of annealing, packing defect concentration increased and reached 15.5% under $T_{an} = 800$ °C.

Qualitative changing of phase composition was observed in films under vacuum annealing at $T_{an} > 1000$ °C. Figure 2, a shows characteristic diffraction curve, which was taken under 30 min annealing at $T_{an} = 1100$ °C. Under high-temperature annealing, in addition to (Zr, Ti)N nitrides (which period was close to ZrN lattice) and (Ti, Z)N (which period was close to TiN lattice), we observed diffraction peaks from zirconium oxide crystallites (ZrO$_2$, according to JCPDS Powder Diffraction Cards, international Center for Diffraction Data 42-1164, hexagonal lattice) and titanium oxide (TiO, JCPDS 43-1296, cubic lattice), and, probably, initial amorphous β-Si3N4 phase crystallites (JCPDS 33-1160, hexagonal lattice).

Appearance of zirconium and titanium oxides was related to oxidation relaxation under coating surface interaction with oxygen atoms coming from residual vacuum atmosphere under annealing. Under annealing temperatures below 1000 °C, coatings phase composition remained practically unchanged (Figs. 2, a, b). One could note only changed width of diffraction lines and their shift to higher diffraction angles. The latter characterizes relaxation of compressing stresses in coatings. Changed diffraction lines were related to increased crystalline sizes (in general) and decreased micro-deformation.

Figure 3, a shows the film cross-section, which demonstrates that in the course of deposition, no cracks were found, that indicated good quality of the coating. Figure 3, b shows chemical composition over coating cross-section. Spectra indicate that N concentration (for second series) changed from 3.16 to 4.22 wt.% Si concentration was about 0.98 to 1.03 wt.%, Ti was 11.78 to 13.52 wt%. and that $Z_r = 73.90$ to 77.91 wt.%. These results indicated that amount of N is essentially high, and this allowed it to participate in formation of nitrides with Zr, Ti, or (Zr, Ti)N solid solution. Si concentration was low,
Intensity, arb. unit

20, degree

Fig. 2. Region of X-ray diffraction spectra taken for the coatings of Zr–Ti–Si–N system after deposition (1); after 30 min annealing in vacuum, under $T_{\text{an}} = 500^\circ \text{C}$ (2), and under $T_{\text{an}} = 800^\circ \text{C}$ in air (3). Three peaks, which are not designated in the curve, are for an oxide of Fe$_2$O$_3$ substrate (JCPDS 33-0664) (a). XRD diffraction patterns for Zr–Ti–Si target in 0.3 Pa nitrogen atmosphere (vacuum-arc source with HF discharge): 1 – for initial (as-received) samples; 2 – for annealed at 500$^\circ \text{C}$ (30 min in vacuum); 3 – for annealed at 800$^\circ \text{C}$ (30 min in vacuum) (b)

However, results reported by Veprek et al. [3, 4] indicated Si concentration as high as 6 to 7 at.% which was enough to form siliconitride phases.

Changes occurred under macrodeformation of crystallites of basic film phase – (Zr, Ti)N solid solution. Compressing deformation of crystallite lattices increased, which seemed to be related to additional new crystalline components, which appeared in film material: oxides and siliconitrides. In the lattice itself, a period decreased corresponding to increased Ti concentration. Ordered atoms in metallic (Zr/Ti) sublattice of solid solution increased from 8.5 to 21 at.%. In this temperature range, crystallite size increased from 15 to 25 nm, crystallite lattice microdeformation increasing non-essentially up 0.5 to 0.8% [10, 11]. Table 2 summarizes substructure characteristics of (Zr, Ti)N solid solution crystallites.

Figure 4, a shows XRD-diffraction patterns, and lower (b), a histogram of volume phases for nanostructured Zr–Si–N coating with 10 to 12 nm grain
sizes for nc-ZrH phase (where nc is a nano-structured phase). These data demonstrate 17% volume fraction of quasi-amorphous α-Si3N4 phase, 54% of nano-composite nano-structured phases, and the rest was α-Fe from samples substrates.

Figure 5 shows nano-hardness vs annealing temperatures for coatings fabricated using vacuum-arc source with HF discharge (hardness values for Zr–Ti–N (see Fig. 6) and Zr–Si–N systems are presented for comparison with Zr–Ti–Si–N coating). We should like to note that “self-hardening effect” was observed for those nano-structured coatings, which were deposited to substrates under low temperatures (not exceeding 120 to 150 °C) [11]. Therefore, the process of spinodal segregation along nano-grain boundaries was not terminated because of energy deficit for diffusion rate. When annealing temperature came close to 550 to 600 °C range [12], the process of spinodal segregation was over, i.e. all nano-grains were totally surrounded by an interlayer of several α-Si3N4 nano-layers (quasi-amorphous phase).

In initial state, after deposition, those samples (second series), which phase composition included three phases (Zr,Ti)N-nc, ZrN-nc, and α-Si3N4, hardness was $H = 40.6 \pm 4$ GPa; $E = 392 \pm 26$ GPa (Figs. 7, 8). 500 °C annealing increased $H$ and $E$ and decreased spread in hardness values, for example, $H = 48 \pm 6$ GPa and $E = (456 \pm 78$ GPa).

In such a way, hardness, which was increased in the process of annealing, seems to be related to incomplete spinodal phase segregation at grain boundaries resulting from deposition of Zr–Ti–Si–N- (nano-composite). Annealing stimulated spinodal phase segregation [3, 4], forming more stable modulated film structures with alternating in volume concentration of phase components (ZrN; (Zr,Ti)N; Si3N4).

4. Conclusion

In such a way, decreased concentration of active oxygen atoms coming from annealing atmosphere increased stability of film phase composition from 500 to 1000 °C. Changing crystalline phase composition was determined by crystallization of siliconitrides and formation of β-Si3N4 crystallites with hexagonal lattice, as well as low ZrO2 concentration formed in the film surface.

High macro- and microdeformation occurring in the coating seems to be related to an “atomic peening” effect resulting to non-ordered distribution of titanium atoms implanted to the film during its growth. In the course of annealing, the macro- and micro-deformation relaxed. The relaxation was accompanied by formation of deformation packing defects in a metallic sublattice of (Zr, Ti)N solid solution. This can be revealed by X-ray scanning, which demonstrated shift and broadening of diffraction peaks. Highest content of packing defects indicated shift of most closely packed planes in a fcc-sublattice (111) with respect to each other [1, 4, 8, 11] and became pronounced under vacuum annealing at $T_{an} = 800$ to 1100 °C reaching 15.5 vol.%.
deposition state, Zr–Ti–Si–N film (as received) had 40.8 GPa nanohardness. After annealing (a dark dotted curve) at 500 °C in vacuum, coating nanohardness reached \( H = 55.3 \) GPa (see Fig. 5).

In Zr–Ti–Si–N coatings, increased Ti concentration, formation of three phases: \((Zr, Ti)N\)-nc-57 vol.\%, TiN-nc-35 vol.\%, and \(\alpha-Si_3N_4\) ≥ 7.5 vol.\%, as well as changes of grain size, which decreased to (6 to 8) nm in \((Zr, Ti)N\) and (10 to 12) in TiN in comparison with first series resulted in increased nanohardness and decreased difference in hardness values. Annealing in vacuum below 500 °C finished the process of spinodal segregation at grain boundaries and interfaces. Annealing stimulated segregation processes and formed stable modulated coating structure [1, 4, 8].

**References**