

Study of a variable deposition angle effect on the structure of Ti-Pb composite coatings

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Abstract. The results of a study on a variable deposition angle effect on the structure of TiPb / TiPbN composite coatings sprayed on titanium alloy (VT6) substrates by magnetron sputtering are presented. The structures of coatings deposited on immobile and rotating substrates and obtained by co-sputtering a mosaic target of Ti and Pb are compared. It is shown that the differences in the incidence angles of the flow particles deposited on the substrates result in different mechanisms for coating structures formation.

In spite of certain environmental difficulties in production use of lead, thin Pb films are of increasing interest due to a wide range of applications including tribology [1, 2], aerospace industry [3], thin-film metallic photocathodes [4, 5] and electron-beam guns [6, 7], electrode contacts [7, 8] as well as various compounds and composites [9, 10]. Magnetron sputtering and pulsed laser deposition (PLD) have been effectively used to fabricate thin Pb films. With the help of PLD high-quality thin films are obtained at room temperature [11]. However, for this purpose the problem of droplets in the deposited flow must be solved when spraying, which substantially interferes with the solution of various problems set by the researcher [12–14]. Therefore, in this work the priority was given to magnetron sputtering.

To co-precipitate several components of thin films by magnetron sputtering, several magnetrons with targets of different compositions [15] or so-called "mosaic" targets are used which consist of a base metal matrix with inserts of other metals [16], which allows using only one magnetron whose target design is produced according to a special program [17].

In this work, the second variant was used. Pb inserts (2 mm diameter bars) in the Ti target were placed in holes located along the axis of the target sputtering zone at the intervals of 18 mm.

Thus, the thin-film metal composition was obtained by magnetron sputtering of Ti and Pb in a single process cycle; the chamber had been previously evacuated using a diffusion pump (with cooling the trap in liquid nitrogen) to a pressure of $P = 3 \cdot 10^{-4}$ Pa. The coatings were deposited on specimens with the sizes of 20×15×10 mm made of VT6 titanium alloy. Once the shutter was opened, the specimens was heated to the temperature of 160–170 °C (20–30 minutes) which grew up to about 180 °C with the magnetron being turned on.

The substrates were immobile and located opposite the magnetron or rotated in front of the magnetron during deposition. The distance between the magnetron and the targets equalled 100 mm. Before being installed into the chamber the specimens were washed in an ultrasonic bath with gasoline



and alcohol and then dried. The surface of the grounded substrate in the chamber was purified with Ar ions using an ion source for 20 minutes with the following process parameters: $P_{Ar} = 5 \times 10^{-2}$ Pa, current of $I = 0.5$ A, ion energy of the order of $E \approx 1.5$ keV. Argon was used as the atomizing gas for the magnetron.

Sputtering on immobile and rotating substrates was applied in one mode. The ion source was not turned off after purification, which thus provided ion-stimulated deposition of coatings during the whole process. First, at a pressure in the chamber of $P_{Ar} = 5 \times 10^{-2}$ Pa a Ti + Pb layer with 50 nm thickness was deposited for 3 minutes using a pulse mode (50 kHz) of the magnetron operation at a discharge current of $I_d = 4$ A and a discharge voltage of $U_d = 525$ V and a bias voltage on the substrate of 75 V. Nitrogen was then introduced into the chamber, and the second TiN + Pb layer with 1,5 μ m thickness (immobile substrate) and 1 μ m thickness (the substrate rotates) (figure 2) was deposited for 85 minutes under the same discharge parameters at a pressure of $P_{Ar+N_2} = 2 \times 10^{-1}$ Pa.

The quantitative phase composition and the crystallographic texture of multicomponent coatings on a titanium alloy substrate were studied by X-ray diffraction analysis using a DRON-4 diffractometer in filtered $CuK\alpha$ radiation [18–22]. The texture was evaluated by the method of inverse pole figures, and the pole density of the reflections was determined by the ratio of the reflections intensities in textured samples to the intensities of the corresponding reflections in the textureless standard which was estimated by calculation of all the intensity factors [23]. The fractions of the phases presented in the coating were evaluated on the basis of the mean pole densities of the reflections for each phase, i.e. taking into account the texture.

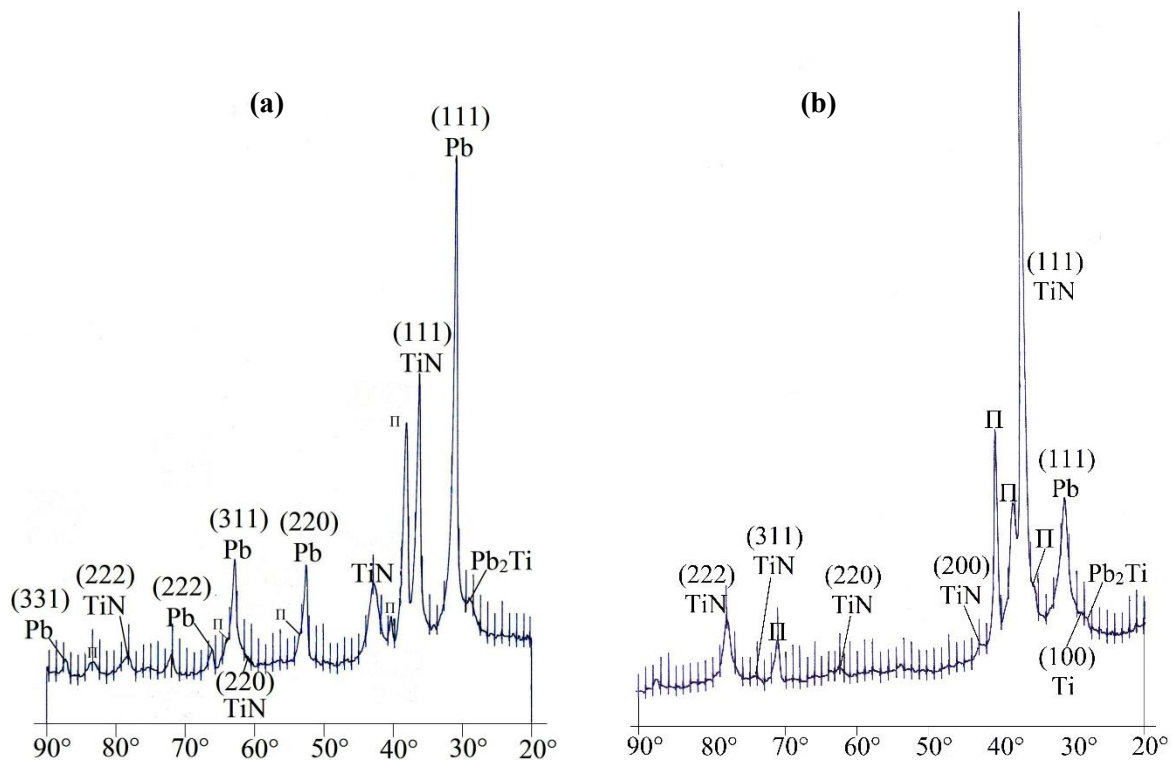


Figure 1. Diffraction patterns for coatings of samples № 1 – (a) and № 2 – (b); Π – substrate.

Figures 1(a), (b) show the diffraction patterns of two coatings obtained by deposition on an immobile substrate (№ 1) and a rotating substrate (№ 2). The phase compositions of both coatings are the same and are characterized by the presence of three phase reflections: α -Ti with hexagonal close-packed crystal lattice, δ -TiN titanium nitride with NaCl-type lattice, and Pb with FCC lattice. Reflections of α -Ti are the total reflections of the coating and the titanium substrate since the thickness (1–1.5 μ m) of coatings is less than the penetration depth of X-rays. Therefore, to evaluate the texture of titanium in

the coating and to estimate its volume fraction in the coating, the coatings were also deposited on a nickel alloy substrate simultaneously with the coating deposition on titanium substrate. These coatings showed that titanium in the coating had a pronounced basal texture, and its volume fraction was $\sim 10\%$ of titanium nitride fraction.

Table 1. Pole densities of Pb reflections.

	hkl	№ 1 P_{hkl}	№ 2 P_{hkl}
1	111	0.15	0.075
2	200	0	0.075
3	220	0.13	0.075
4	311	0.13	0.075
5	331	0.04	0.075
$P_{average}$		0.113	0.075

Table 2. Pole densities of TiN reflections.

	hkl	№ 1 P_{hkl}	№ 2 P_{hkl}
1	111	2.50	5.9
2	200	1.25	0.23
3	220	0.32	0.24
4	311	0.52	0.33
$P_{average}$		1.147	1.673

Tables 1 and 2 show the values of the pole densities for TiN and Pb reflections for the two coatings, and table 3 gives the phases ratios in coatings which differ in a variable deposition angle. The differences are found in the volume ratio of the phases as well as in the texture. The texture of Pb in coating № 2 could not be estimated due to the small amount of Pb in the coating (3.9 %, see table 3); to calculate the quantitative ratio of the phases in this coating, we assumed that lead in this coating is textureless (table 1), therefore, the values of the pole density for all the reflections were assumed to be identical and equal to the pole density of the single reflection (111) which we were able to detect (figure 1(b)). This assumption is correct since the lead texture in coating № 1 is also close to the textureless state.

Table 3. Average values of pole densities and volume fractions of phases in coatings.

№№	α -Ti	TiN	Pb	$V_{\alpha-Ti}$	V_{TiN}	V_{Pb}
	$P_{average} \%$					
1	0.115	1.147	0.113	8.4	83.4	8.2
2	0.167	1.673	0.075	8.7	87.4	3.9

It was found that the variable deposition angle affects the texture of TiN and α -Ti differently. The type of titanium texture for both coatings is the same and characterized by parallel location of the basal plane to the substrate. Conditions for titanium nitride (table 2) are different – the texture of the immobile sample is much weaker, and in addition to the typical for ion-vacuum coatings $\{111\}$ texture being parallel to the substrate a weak component of the cubic texture is present in the sample (see table 2). This indicates different formation mechanisms of the (α -Ti) solid solution structure and the (TiN) interstitial phase in the coating.

The obtained results show that varying geometric and, undoubtedly, energy conditions of the multicomponent coatings deposition one can obtain a controlled phase composition and phase orientations to which a certain set of service properties corresponds. Thus, in coating № 1 (immobile substrate) Pb is almost twice as much and TiN is correspondingly less than in coating № 2 (rotating substrate), which makes it possible to vary the phase composition of the coating depending on the required functional properties, e.g. tribological characteristics or wear resistance. An important result is the possibility of a quantitative evaluation of the phase composition on the basis of X-ray diffraction data, which makes it possible to search for quantitative correlations with properties. Quantitative textural results can also be used to optimize functional properties.

The fact that a two-component $\{111\} + \{001\}$ nitride texture is found in coating № 1, and one-component $\{111\}$ intensive texture is present in coating № 2 can be also used for practical purposes since a strong one-component $\{111\}$ texture are generally associated with the columnar structure formation in ion-vacuum coatings that is optimal for providing high wear resistance but characterized

by higher permeability compared to coatings with an equiaxed microstructure which multicomponent less pronounced texture usually corresponds to.

It is also been found that the mechanisms of texture formation in a solid solution (α -Ti) and interstitial phase (TiN) differ. This gives additional possibilities for creating a controlled texture in Ti / TiN / Ti / ...multilayer coatings, since in this case it is possible to realize different variants of orientation of the components of the multilayer coating and thereby change the structure of interphase boundaries that largely determine the properties of multilayer coatings.

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