High Temperature Material Processes 20(1), 85–92 (2016)

EFFECT OF THERMAL ANNEALING AND DEPOSITION CONDITIONS ON THE STRUCTURE AND MECHANICAL PROPERTIES OF A MULTILAYER NITRIDE COATING BASED ON Ta

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An analysis of the structure and mechanical properties of multilayer nitride coatings based on Ta depending on the deposition conditions and thermal vacuum-free annealing was conducted. Ta/TaN is a multylayer structure with alternate deposition of a polycrystalline layer of Ta of high ductility and a layer of TaN of high strength. TaN is a coating deposited by magnetron sputtering with the ratio $N_2/Ar = 0.4$*, exhibiting a high degree of crystallinity that leads to a high adhesive strength and hardness of Ta/TaN multilayer coatings. For nitride coatings based on refractory elements of the V–VI period, the general patterns consisting in the formation of the NaCl structure, and the predominant orientation of the planes (111) were identified. The application of heat treatment decreases the microhardness of the Ta/TaN multilayer coatings from 2600 to 1200 kgf/mm*^{2}*, and leads to deterioration of the adhesive strength between the layers. In the process of mechanical testing, the tribological coefficient for the considered protective coatings was 0.1–0.25, the volume of surface wear was 14.3 mm*^{3}*.*

KEY WORDS: *multilayer nitride coatings, nanostructures, annealing, thermal stability, wear*

1. INTRODUCTION

The use of nitride multilayer systems is the best compromise for obtaining coatings with high hardness, toughness, good adhesion of monolayer interfaces, and resistance to abrasion. TiN is one of the most widely known and studied coatings that are used effectively in aerospace, military, and automotive industries for producing such items as helicopter gearboxes and compressor blades, the transmission parts and compressor blades of engines with a high ratio of thrust to power. The use of TiN as a protective coating makes it possible to increase the interval of service, improve the level of mechanisms reliability, and to ensure their complete recovery, however, the industrial interest still aims at increasing the wear resistance, hardness, and fracture toughness (Pogrebnjak, 2013; Pogrebnjak et al., 2007). Since the refractory elements of the V–VI period, in particular Ta, are often used as alloying elements in multielement systems, it is useful to consider the nitride coating based on this element. Sufficiently considered solid multilayer coatings such as Ti/TiN, (TiZrNbTaHf + Mo)N, MoN/CrN, TiN/MoN, and TiN/ZrN were widely studied and described in (Misaelides et al., 2004; Lavrentiev and Pogrebnjak, 1998; Maksakova et al., 2015; Pogrebnjak et al., 1987).

As the compounds of this period have high melting points to provide coatings based on them, the methods of vacuum-arc deposition and magnetron sputtering are the most frequently used ones.

In considering the nitride coatings based on a refractory metal (TiN, HfN, TiN/ZrN, TiN/MoN, WN, etc.), it was noted that by changing the deposition conditions, the formation of the texture plane growth (111) at compositions close to stoichiometric can occur. Thus, it can be assumed that the physical process of the formation of nanostructures for nitride coatings based on Ta obeys the general laws (Pogrebnjak et al., 2001, 2015; Ivashchenko et al., 2014; Pogrebnjak et al., 2013; Kumar et al., 2010; Pogrebnyak and Proskurovskii, 1994).

The aim of this study is to analyze the structural regularities that occur as a result of the change in the deposition parameters of coatings based on Ta and in conducting temperature annealing of Ta/TaN coatings.

2. METHODS AND EXPERIMENTS

The Ta/TaN multilayer coating was deposited on a substrate from an SKH 9 high-speed tool steel by magnetron sputtering in an N_2/Ar atmosphere with a Ta target. The flow ratio F_{N_2}/F_{Ar} ranged from 0.1 to 0.5. The substrate of the SKH 9 tool steel was cut into several small samples with dimensions $20 \times 20 \times 2$ mm^3 and exposed to heat treatment to minimize surface oxidation. In the next purification stage, the substrate surface was sanded and polished with 1 mm diamond paste, and then cleaned with trichloroethylene and acetone and also was ultrasonically treated to remove organic contaminants. During the coating application, the pressure in the spray chamber was maintained at 5×10^{-3} Torr, a main parameter in the process of magnetron sputtering was the ratio of N_2 stream to Ar (F_{N_2}/F_{Ar}) stream that ranged from 0 to 0.15, with the compositional modulation wavelength (Λ) ranging from 20 to 200 nm. Thermal annealing of samples was carried out at a temperature from 200 to 800°C for 2 h.

An analysis of the structure and substructure of the Ta/TaN multilayer coating was made with the help of a DRON-4 X-ray diffractometer in the CrK_α radiation and an RINT-2500 V using a position-sensitive proportional counter (PSPC/MDGT). The

XRD spectra were recorded at the angles 20°, 30°, 40°, ..., 80°. The Vickers method was used for the microhardness measurement. The chemical composition of the coating layers was analyzed by AES (Auger electron spectroscopy) at the profile depth, the tribological characteristics were measured using a scratch tester (Kanga et al., 2000; Ma et al., 2013).

3. RESULTS AND DISCUSSION

Ta/TaN multilayer coatings were deposited by alternately applying Ta and TaN layers. The first Ta layer was deposited in an argon atmosphere, and then N_2 was supplied. The total thickness of the examined coatings was 1 μm. The changes in the microhardness of the Ta/TaN coatings by varying the N_2/Ar ratio are shown in Fig. 1.

The microhardness increases with the N_2/Ar stream to 0.4, but decreases at higher ratios. The growth of the microhardness is associated with the changes in the coating structure. It is confirmed by X-ray diffraction (XRD) in Fig. 2. When the N_2/Ar ratio is equal to 0.1 and 0.2, the spectrum planar position, width, and intensity prove the nonstoichiometric composition of the coating. For $x < 1$, at $F_{N_2}/F_{Ar} = 0.3$, the TaN (111), TaN (200), TaN (220), and TaN (311) diffraction spectra are broad and weak, reflecting the poor crystallinity of the deposited TaN coatings.

As shown in Fig. 2, with the F_{N_2}/F_{Ar} ratio the polycrystalline TaN coating exhibits a high degree of crystallinity, as all planar spectra are pronounced. As expected, for the Ta/TaN nitride coating, the pattern forming a preferential texture of growth of the plane (111), with compositions close to the stoichiometric one, is conserved.

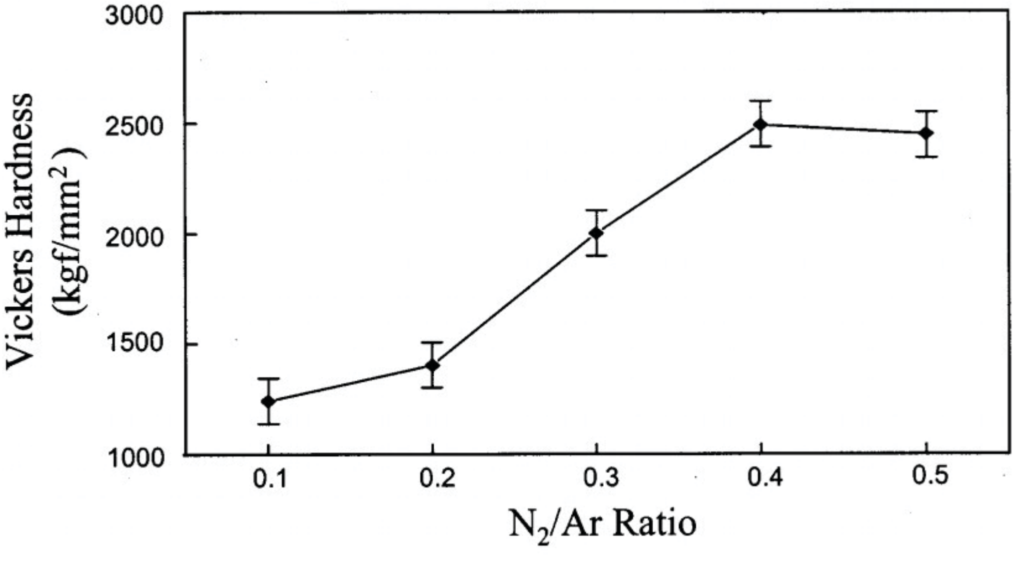

FIG. 1: Microhardness of the Ta/TaN multilayer coating as a function of the N_2/Ar flow ratio

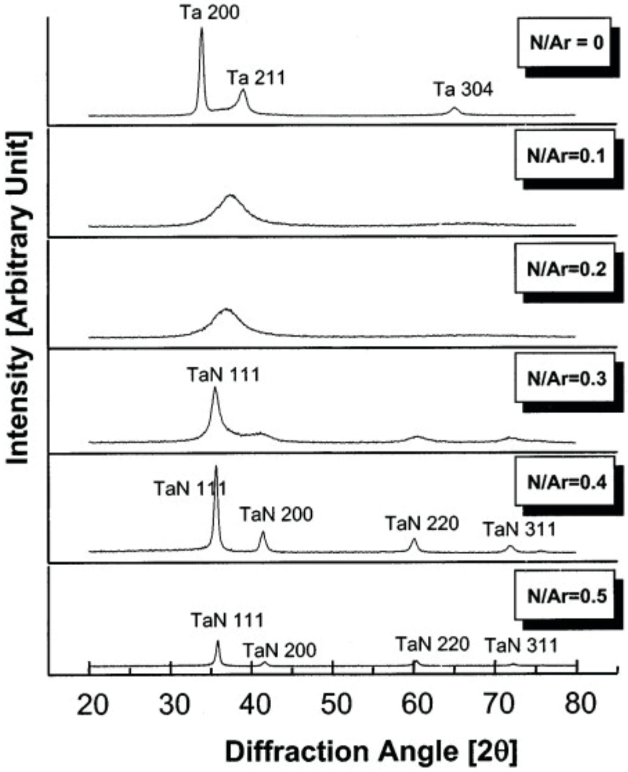

FIG. 2: XRD patterns for the TaN film as a function of the N_2/Ar ratio

Figure 3 shows the dependence of the microhardness of the Ta/TaN multilayer coating (F_{N_2}/F_{Ar} = 0.4) on the temperature of thermal annealing in vacuumless environment. The microhardness of the Ta/TaN multilayer coating decreases with increase in the annealing temperature. The reducing of the microhardness at higher annealing temperatures is likely to occur due to the formation of oxides, since Ta is easily oxidized (Gibbs free energy of formation ΔG_f° at 298 K = –457 kcal/mol^{-1} for Ta_2O_5). Ta–Ta with a binding energy of 88 kcal/ mol^{-1} is less than Ta–N (146 kcal/mol^{-1}), therefore it is easier to oxidize.

Besides oxidation during the thermal annealing, the diffusion of TaN atoms in the Ta layer occurs, so that TaN has the composition Ta:N = 5.5:4.5. Being the most active, this process occurs at 800°C. Therefore, the annealing at temperatures reaching 800°C will decrease the microhardness of the layer and change the multilayer at almost the monolithic film (Fig. 4), which is undesirable, since it impairs the physical and mechanical properties of the coating, such as the toughness and adhesive strength.

The atmosphere in which the annealing was made has a significant impact on the structure and properties of TaN coatings. When vacuumless thermal annealing of $TaN_{1.00}$ is made, the zone of interdiffusion in the adhesive area is formed, so there

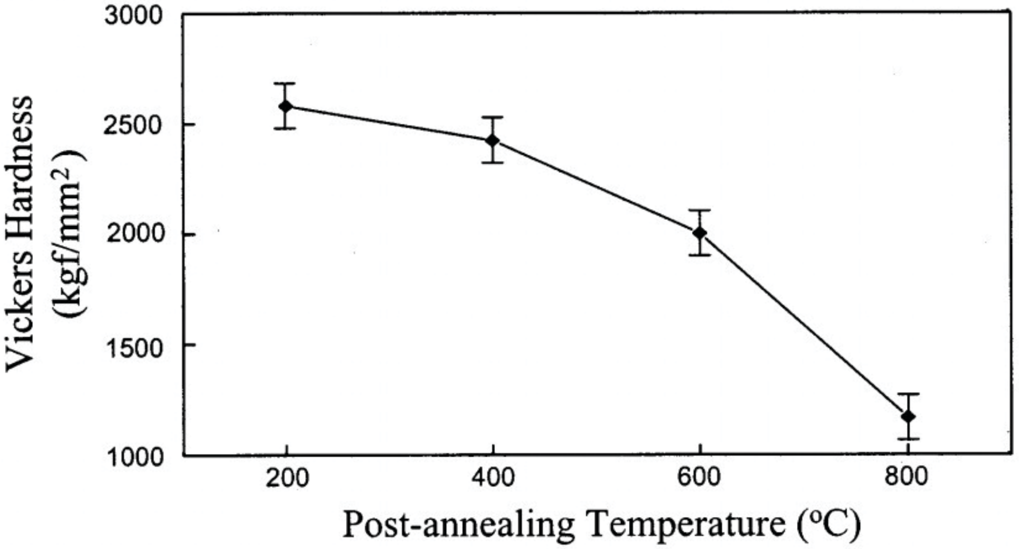

FIG. 3: Microhardness of the Ta/TaN multilayer coating as a function of the post-annealing temperature (N_2/Ar = 0.4)

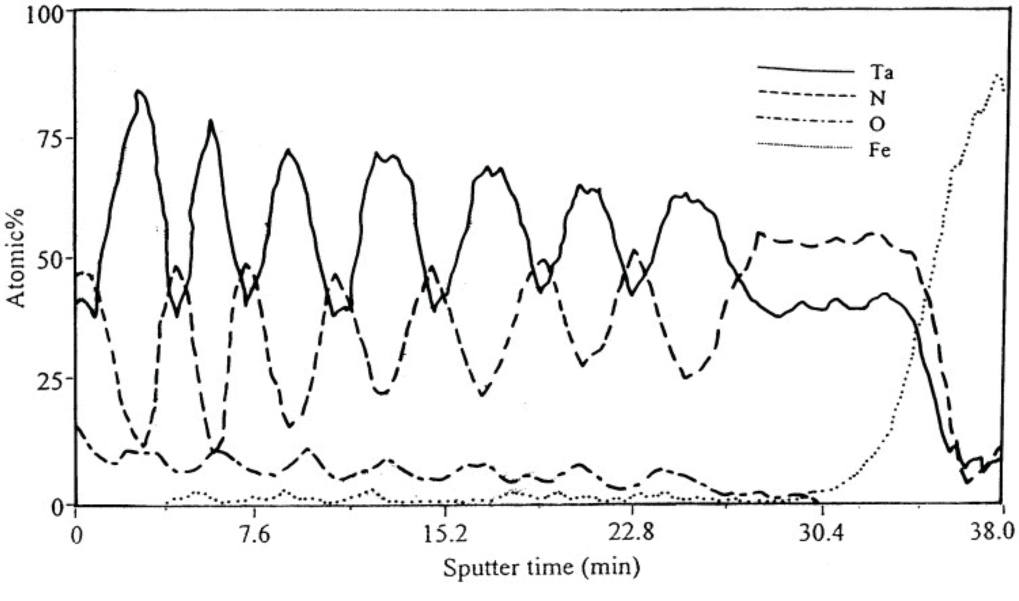

FIG. 4: Auger electron spectroscopy profiles of Ta and N elements obtained after thermal annealing at 600°C (Λ = 20 nm, N_2/Ar = 0.4)

are a drop in the Ta concentration to 20 at.% over the entire region of diffusion and the presence of large oxygen concentration of 50 at.%. The appearance of the zone of mutual diffusion in the adhesive area impairs the coating indications. A characteristic feature of nitride coatings based on Ta is that after thermal annealing in vacuum, there is a high concentration of Ta and N, in contrast to the vacuumless annealing, wherein the concentration of N is reduced to nearly 0 at.% over the whole depth of the coating. Vacuum annealing at a pressure of 3 Pa eliminates the possibility of formation of the zone of mutual diffusion and distribution of the oxygen concentration in the depth of the coating.

An analysis of the tribological properties of the Ta/TaN multilayer coating was made using a scratch tester, the measurement results are shown in Fig. 5. The friction coefficient was 0.1–0.25, the volumetric wear of the coatings was 14.3 mm^3. According to Fig. 5, the tribological process is accompanied by vibrations of frictional signals, and when a tribo-indenter load exceeds a critical value of 35 N, adhesive rupture or delamination of the coating occurs. The increase in the adhesive strength

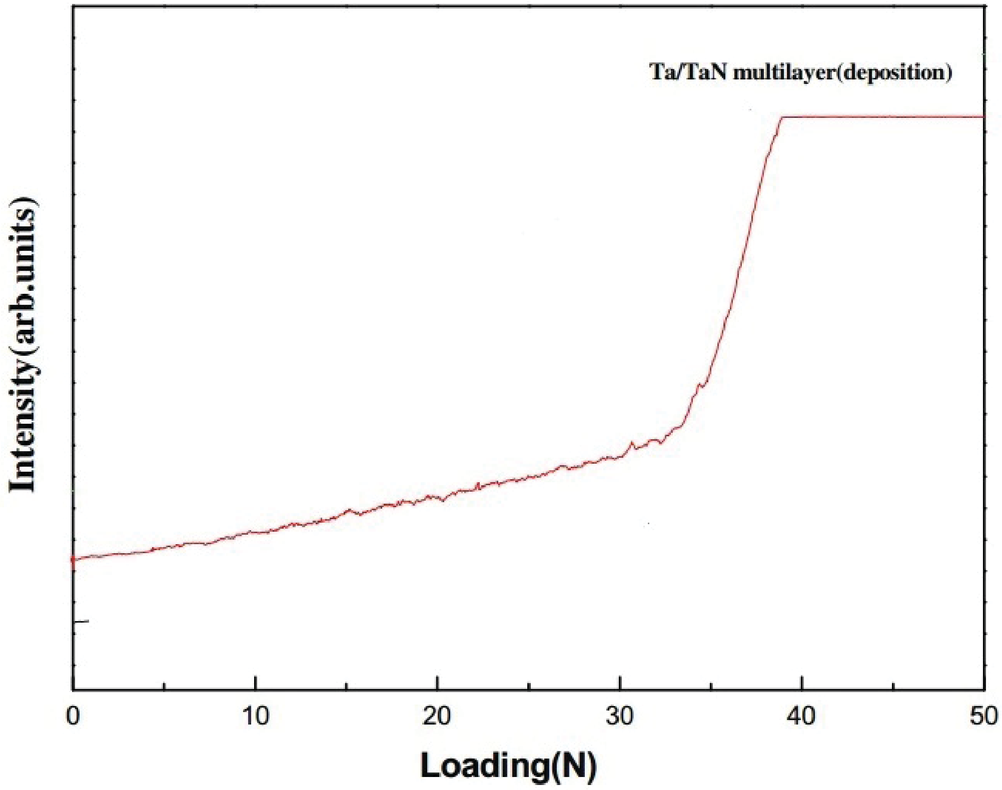

FIG. 5: The results of tribological measurements of the Ta/TaN multilayer coating depending on tribo-indenter load

and improvement of the coating tribological characteristics are likely to be achieved by reducing the internal stress and improving the ductility by alternating Ta and Ta/N layers.

4. CONCLUSIONS

The analysis of the structure and mechanical properties of nitride coatings based on Ta, depending on the conditions of deposition and vacuumless thermal annealing has been reviewed. The investigated coatings were prepared by magnetron sputtering at a fixed substrate temperature (room temperature) and at a pressure of 5×10^{-3} Torr. It is indicated that nitride coatings based on refractory elements of V–VI period with the structure of the NaCl, the (111) plane is a predominant growth texture.

According to the results of the analysis, it has been revealed that for producing Ta/TaN coatings with a high degree of crystallinity and excellent mechanical characteristics, the optimal ratio of the N_2/Ar stream should be 0.4. The use of thermal vacuumless annealing reduces the values of the microhardness of Ta/TaN multilayer coatings from 2600 to 1200 kgf/mm^2, and leads to deterioration of the adhesive strength between the layers.

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