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Solid Solution Hardening of Reactively Sputtered Nanolaminate ZrN-TiN Coatings

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The development of nanocomposite coatings has opened new possibilities for the fabrication of functional and protective coatings with unusual combinations of mechanical, tribological and chemical properties such as stability at elevated temperatures, high hardness and toughness, wear and corrosion resistance. In this study, nanolaminate structures consisting of ZrN and TiN layers were prepared using various modulation periods during pulse-dc magnetron sputtering. The coatings were deposited on nitrided Ti-6Al-4V alloys (duplex treatment) and simultaneously on (100) silicon wafers. The Zr and Ti targets (both 51 mm diameter), were pulsed in asynchronous mode at 300 kHz and 1.1 μ s reverse time (duty cycle \sim 70%). Two types of coatings of a total thickness of approximately 1 μ m and 4 μ m were prepared by adjusting the deposition time. The structure of the coatings was studied by X-ray diffraction and High-Resolution Scanning Electron Microscopy, and the hardness (H) and the reduced Young's modulus (E), were determined by depth-sensing indentation (Hysitron Inc.) using a Berkovich pyramidal tip. In the case of the nanolaminate coatings, various individual modulation periods, L, were explored. The nanolaminate coatings with L ranging from 1 to 10 nm displayed a single phase of solid solution with a Zr-rich composition, Ti_{0.35}Zr_{0.65}N. This finding indicates mixing or diffusion between the two phases which occurred during the growth. The grain size was found to vary with the value of L. The grain size of the solid solution Ti_{0.35}Zr_{0.65}N was \sim 8-12 nm, while that of the laminate structure was \sim 10-25 nm. The solid solution structure was found to be the main cause of the hardening of the nanolaminate structure; H values of the solid solution coatings were between 32 and 35 GPa, significantly higher than those of the single-layer coatings (21 GPa for TiN and 18 GPa for ZrN). The hardness and the grain size varied with the modulation period of the multilayer coating, which was also found to affect the wear resistance and other tribological characteristics related to the friction coefficient, μ , to the resistance to plastic deformation, H₃/E₂, and to toughness, H/E.

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