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Nanomechanical and electrochemical properties of ZrN coated NiTi shape memory alloy

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ABSTRACT

Zirconium nitride (ZrN) thin films were deposited on NiTi and Si substrates in the 23–570 °C temperature range by direct current reactive magnetron sputtering using N_2/Ar gas mixture. The film hardness, corrosion behavior, phase composition, and texture were determined. The deposited films were composed mainly by the cubic ZrN phase, whose texture varies with substrate temperature, changing progressively from (111) to (200) texture as the temperature increases. The hardness of the films is influenced by the texture and has a linear relationship with the ratio of the texture coefficients P(111)/P(200). The higher hardness is obtained for ZrN thin films with (200) texture. Electrochemical tests show that NiTi coated with (200)-oriented ZrN films has higher tendency to passivation and greater stability of the passive film as compared to (111)-oriented ZrN films, despite no abrupt changes was observed when the texture changes from (111) to (200).

1. Introduction

Thin film coatings and plasma treatment are well known to improve the mechanical, chemical and magnetic properties of steels and tools [1–3]. Zirconium nitride (ZrN) is a transition metal (TM) nitride, similar to titanium nitride (TiN), applied to improve the surface properties. Its physical characteristics resulting from both metallic and covalent bonds can combine good electrical and thermal conductivity with high hardness, high melting temperature and chemical inertness. Thin films composed of binary nitrides can present a well-known NaCl type crystalline structure and, like TiN have mechanical properties depending on the crystallographic texture of the deposited film [4]. In all the applications, the lifetime and performance of the coatings are influenced by the control of the microstructure and texture. Despite all the research efforts, the physical mechanisms concerning the evolution of texture and grain growth of the films are not completely clarified. In particular, the texture in polycrystalline TiN and ZrN thin films has different explanations in many published works. Some authors proposed that the texture evolution is governed by the strain energy minimization during the growing process [5–8]. On the other hand, several authors report that the texture is related with the adatom mobility and the kinetic-driven mechanisms [9–12]. Other authors found that both the strain energy and the surface energy act in a competition mode during the grain growth. Also, it was suggested for TiN thin films that in the initial stage of growth, the (002) planes were aligned to the substrate surface axis to minimize the surface energy. Furthermore, at later stages, the (002) growth front tilted away from the surface by about 60° to relax the strain, causing the change of the preferred growth direction favoring the (111) planes [13]. Therefore, the explanation of the leading process for the texture of TM nitride thin films remains an issue to be addressed. Besides the mechanical properties that are related with crystallographic texture, the chemical inertness of thin films would also be related with this feature. The chemical inertness in aggressive media is a mandatory feature for biocompatibility of TM nitride thin films. In particular, ZrN thin films have the potential to be used as coating for biomaterials and for bioelectronic devices, due to its biocompatibility together with good electrical, thermal and mechanical properties [14,15]. Generally, the choice for a biomaterial is made by taking into account its corrosion resistance. However, even with the corrosion protection feature of such materials, the dissolution process that occurs in aggressive media containing chlorine ions can lead to the contamination of the organism with metal ions, affecting the biocompatibility and mechanical properties of a prosthesis [16]. As a consequence, in such applications, as in biomedical implants, severe restrictions are imposed on the materials to be used concerning stability in aqueous solutions with high concentrations of electrolytes. For these reasons, it is mandatory to understand the corrosion behavior of the

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ZrN thin films on different substrates used as biomaterials and to correlate the chemical inertness with the texture and with the deposition parameters to obtain high corrosion protection maintaining the mechanical resistance. The aim of the present work is to investigate the corrosion resistance and hardness of ZrN thin films deposited at different temperatures on NiTi, C and on Si substrates. We focused in the microstructure in relation with the corrosion and mechanical properties.

2. Experimental

In order to prepare and characterize the ZrN films, which involves the preparation of the samples for X-ray diffraction analysis (XRD) and electrochemical tests, we choose Si(100) wafer and NiTi as substrates, respectively. The NiTi samples were grounded after being cut and then polished with an alumina suspension up to 0.1 μm of particle size. The samples were then cleaned with acetone in an ultrasonic bath for 30 min. The ZrN thin films were deposited using direct current reactive magnetron sputtering, applying a power of 100 W on a Zr target in Ar/N_2 atmosphere. It was used floating potential bias during deposition and the current density was 0.60 mA/cm^2. The base pressure in the chamber was 10^{-7} mbar. The substrate temperature was varied from 25 to 570 °C maintaining a total pressure of 2×10^{-2} mbar with a flux of 5.0 sccm for Ar and 0.88 sccm for N_2. After the deposition, the samples were slowly cooled in vacuum inside the deposition chamber. In order to study the corrosion behavior of the ZrN coated-NiTi samples, open-circuit potential (OCP) measurements and potentiodynamic polarization tests were performed in a VoltaLab PGZ100 potentiostat/galvanostat. The electrochemical tests were carried out at 37 °C in non-deaerated solutions. The electrolyte was an artificial saliva solution AFNOR S90-701 prepared using analytical grade reagents without previous purification. ZrN-coated- or uncoated-NiTi substrate of circular geometry was employed as the working electrode. For the corrosion tests, the thin film area to be studied was defined by partially covering the sample with an insulating resin. A 0.95 cm^2 area of the sample was exposed to the electrolytic solution. Before each experiment the working electrode was degreased with acetone, cleaned with ethanol, and rinsed with distilled and deionized water. A graphite rod was used as auxiliary electrode and a saturated calomel electrode (SCE) was the reference connected to the cell by a salt bridge and a Luggin-Haber capillary. All potentials mentioned in the text are quoted versus this reference electrode. Potentiodynamic polarization curves were obtained at 1 mV s^{-1} scan rate, after 60 min recording the open-circuit potential (OCP). The potentiodynamic polarization started at the value of 250 mV more negative than the OCP and followed to the positive direction of potentials. The breakdown potential-E_b (the potential where the passivating film begins to break down) was taken as the value at which the current density sharply increases during the positive potential scan. The hardness and reduced elastic modulus measurements were accessed by nanoindentation tests using a NanoTest-600 equipment manufactured by Micro Materials Ltd., equipped with a three-sided pyramidal diamond tip (Berkovich indenter). The unloading portion of load–depth curves was analyzed, allowing estimating values for film hardness [17]. Nanoindentation tests were performed at a load rate of 0.01 mN.s^{-1} and a constant indentation depth of 20 nm. The substrate effect on hardness measurements appears when the indentation depth reaches between 10% and 20% of the total thickness. In order to avoid this effect, we chose the lower limit (10%) to perform our measurements. The elastic modulus was calculated by using a Poisson ratio of 0.16 for ZrN [18]. The crystalline structure of the ZrN films was studied by X-ray diffraction at room temperature with a grazing incidence of 0.6° on an X-ray diffractometer (Shimadzu XRD-6000) with Cu-Kα (λ = 1.54064 Å) radiation (U = 40 kV and I = 30 mA), using as reference XRD data files from ICSD (Inorganic Crystal Structure Database) [19]. On the study of the thickness and the microstructure, scanning electron microscopy (SEM) analysis was used on the cross-section of the samples with a Shimadzu SSX-550 electron microscope. The thickness of the thin films was directly measured from the SEM images.

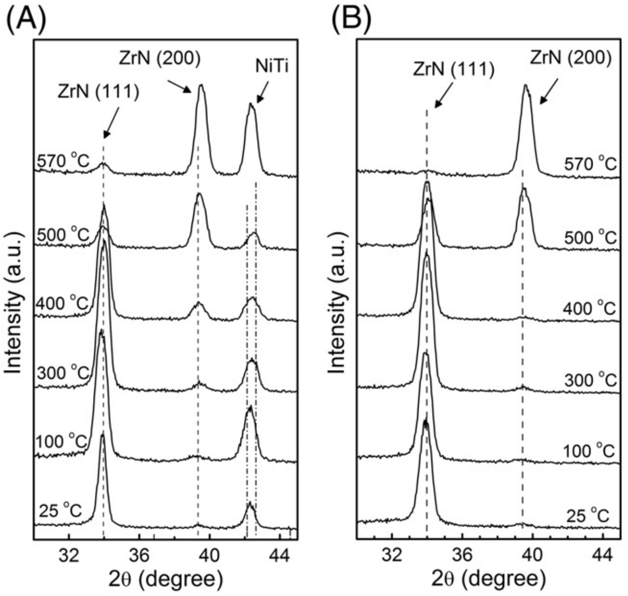

Fig. 1. XRD patterns for ZrN thin films deposited at different temperatures (A) on NiTi substrate and (B) on Si substrates.

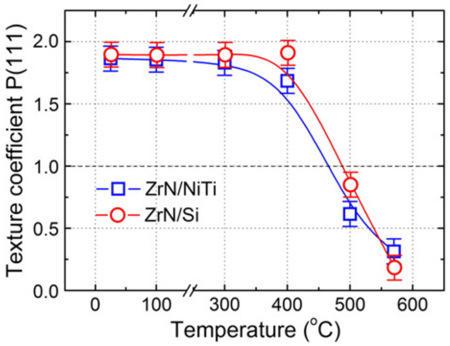

Fig. 2. Texture coefficient P(111) obtained by Harris method for ZrN thin films deposited at different temperatures on NiTi and on Si substrates. The dashed line at P(111) = 1.0 represents the situation where no texture is present. For values below 1.0, the texture is on (200) direction.

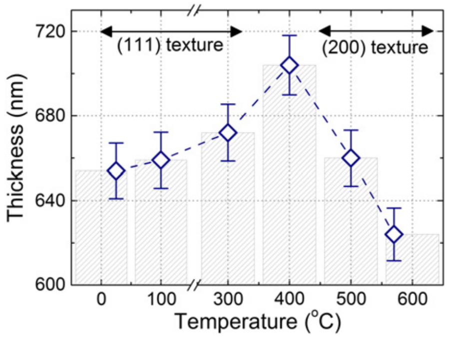

Fig. 3. Thickness of ZrN thin films deposited on NiTi substrates as measured by SEM analysis. The thin films were deposited at different temperatures.