



## Surface Modification of NiTi shape memory alloy using HA-Ag-ZrO<sub>2</sub> nanocomposite coating: Structure and performance

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Nickel–titanium (NiTi) shape memory alloys exhibit super elasticity, shape recovery, and favorable mechanical compatibility; however, their biomedical applications remain limited by surface corrosion, nickel release, insufficient bioactivity, and susceptibility to implant-associated infection. This study investigated the effect of dip-coated nano-hydroxyapatite (nHAp), silver nanoparticles (AgNPs), and zirconium dioxide nanoparticles (ZrO<sub>2</sub> NPs) coatings, applied individually and in combination, on the surface and corrosion properties of NiTi alloy. Eight conditions are evaluated: uncoated NiTi, AgNPs, nHAp, ZrO<sub>2</sub> NPs, AgNPs–nHAp, AgNPs–ZrO<sub>2</sub> NPs, nHAp–ZrO<sub>2</sub> NPs, and AgNPs–nHAp–ZrO<sub>2</sub> NPs. Coating thickness and surface characteristics are examined using optical microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). Functional performance is assessed through water contact angle measurements, Vickers hardness, and potentiodynamic polarization testing. Coating thickness ranged from 44.5860 to 66.0207  $\mu\text{m}$ . All coated surfaces exhibited markedly improved wettability, with contact angles of 7.364–19.409°, compared with 76.533° for uncoated NiTi. The ZrO<sub>2</sub> NPs coating achieved the highest hardness of 521.8 HV, representing a 126.6% increase over the substrate, while the ternary AgNPs–nHAp–ZrO<sub>2</sub> NPs coating reached 383.2 HV. All coatings improved corrosion resistance relative to uncoated NiTi. The ternary coating exhibited the lowest corrosion current ( $9.082 \times 10^{-8}$  A) and corrosion rate ( $8.893 \times 10^{-4}$  mm/year), compared with  $2.808 \times 10^{-6}$  A and  $2.745 \times 10^{-2}$  mm/year for the uncoated substrate, corresponding to a protection efficiency of 96.76% and an approximately 30.87-fold reduction in corrosion rate. The nHAp–ZrO<sub>2</sub> NPs and AgNPs coatings also exhibited high protection efficiencies of 95.08% and 94.94%, respectively. Overall, the AgNPs–nHAp–ZrO<sub>2</sub> NPs coating provided the most favorable balance of corrosion resistance, wettability, and hardness, whereas ZrO<sub>2</sub> NPs showed superior performance when maximum surface hardness is prioritized.

**Keywords:** NiTi; Shape memory alloy; Dip coating; Hydroxyapatite; Zirconia.

## 1. INTRODUCTION

Near-Equi atomic NiTi is a technologically important shape memory alloy because thermoelastic martensitic transformation enables shape recovery and superplastic strain. These characteristics, together with a comparatively low apparent elastic modulus and good fatigue response, support applications in orthodontic arch wires, stents, guidewires, bone fixation devices, and other minimally invasive or load-responsive implants. The same high nickel content that enables the transformation response, however, makes surface stability a central biomedical issue. Damage, defects, or localized breakdown of the native titanium-rich oxide may facilitate corrosion and nickel release, particularly under chloride-containing, mechanically disturbed, or inflammatory conditions [1-3].

Surface coatings can decouple the bulk mechanical function of NiTi from the biological and electrochemical requirements at the tissue interface. nHAp,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , is attractive because its calcium-phosphate chemistry resembles the mineral component of bone and can support interfacial mineralization. Its limitations include brittleness, cracking, and imperfect barrier continuity when applied as a stand-alone layer.  $\text{ZrO}_2$  NPs contributes chemical stability, hardness, and crack resistance, and has consequently been combined with nHAp to improve mechanical integrity and corrosion performance. Qiu et al. demonstrated that HA/ $\text{ZrO}_2$  composite coatings can improve the corrosion behavior of NiTi, while later work has continued to show the value of reinforced calcium-phosphate layers on NiTi and related implant alloys [1,4,5].

silver nanoparticles (AgNPs) is incorporated into biomedical surfaces primarily to introduce antimicrobial functionality. Nevertheless, the benefits of Ag depend strongly on particle distribution, dose, release rate, and the surrounding matrix. Excessive or poorly controlled silver exposure may compromise mammalian-cell compatibility, while discontinuous silver-rich islands can alter electrochemical microcells. A composite strategy is therefore more defensible than evaluating silver as an isolated additive: nHAp can provide bioactive chemistry,  $\text{ZrO}_2$  NPs can reinforce the barrier, and AgNPs can supply potential antimicrobial action if release is controlled. Antibacterial behavior must still be measured directly; the presence of Ag by itself is not proof of efficacy [6].

Dip coating offers a simple and scalable route for depositing particulate or sol-gel-derived layers on geometrically complex substrates. The withdrawal stage converts suspension rheology, particle stability, surface energy, and drainage into a wet film, while drying and thermal treatment determine shrinkage, cracking, adhesion, phase stability, and final thickness. Repeated dipping can build thickness but may also accumulate residual stress. Consequently, coating performance cannot be predicted from nominal composition or thickness alone; it must be linked to phase constitution, morphology, elemental distribution, wettability, mechanical response, and electrochemical behavior.

The present study compares seven coating chemistries on NiTi: AgNPs, nHAp,  $\text{ZrO}_2$  NPs, AgNPs–nHAp, AgNPs– $\text{ZrO}_2$  NPs, nHAp– $\text{ZrO}_2$  NPs, and a ternary AgNPs–nHAp– $\text{ZrO}_2$  mix. The objective is to establish how single-phase and hybrid architectures affect (i) coating thickness, (ii) crystalline signatures, (iii) surface morphology and elemental coverage, (iv) water wettability, (v) Vickers hardness, and (vi) corrosion kinetics. The working hypothesis is that the ternary layer will provide a more favorable multifunctional balance than any single constituent because its performance can emerge from complementary barrier, bioactive, and Ag-containing domains.

## 2. MATERIALS AND METHODS

### 2.1. Experimental design and specimen groups

A controlled comparative design is used in which a common NiTi substrate is evaluated without coating and after deposition of seven coating systems. Table 1 defines the specimen codes used throughout the manuscript. The term “Mix” is used for the ternary AgNPs–nHAp–ZrO<sub>2</sub> layer to maintain consistency with the experimental specimen labeling.

**Table 1** Experimental surface conditions.

| Code                       | Surface system                               | Functional design intent                                 |
|----------------------------|----------------------------------------------|----------------------------------------------------------|
| Base                       | Uncoated NiTi                                | Reference surface and native oxide                       |
| AgNPs                      | Nano Silver-containing layer                 | Ag-bearing surface; antibacterial potential to be tested |
| nHAp                       | Nano Hydroxyapatite                          | Bioactive calcium-phosphate surface                      |
| ZrO <sub>2</sub> NPs       | Nano zirconium dioxide                       | Hard, chemically stable ceramic barrier                  |
| AgNPs–nHAp                 | Nano Silver + nano hydroxyapatite            | Ag-bearing bioactive composite                           |
| AgNPs–ZrO <sub>2</sub> NPs | Nano Silver + nano zirconium dioxide         | Ag-bearing reinforced barrier                            |
| nHAp–ZrO <sub>2</sub> NPs  | Nano Hydroxyapatite + nano zirconium dioxide | Bioactive reinforced ceramic composite                   |
| Mix                        | AgNPs–nHAp–ZrO <sub>2</sub>                  | Ternary multifunctional coating                          |

### 2.2. NiTi substrate preparation

A near-equitoxic nickel–titanium alloy with a nominal composition of 50 at. % Ni and 50 at. % Ti is used as the substrate material. The nominal austenite finish temperature of the alloy is approximately 20–25 °C. The NiTi alloy sheet is cut using abrasive water-jet cutting into two sets of square specimens. The first set had dimensions of 10 × 10 × 1 mm, whereas the second set had dimensions of 20 × 20 × 1 mm. The prepared specimens are subsequently used as substrates for dip-coating deposition. The specimen surfaces are mechanically ground using silicon carbide abrasive papers, with P600 used as the final abrasive grade. Grinding is continued until a macroscopically uniform surface finish is obtained to improve surface–coating mechanical interlocking. The final surface condition is therefore reported as P600-ground. The arithmetic means surface roughness, Ra, should be reported as Ra = 0.6 μm if profilometry measurements are available. Following mechanical grinding, the specimens are ultrasonically cleaned in acetone for 15 min to remove grease, abrasive particles, and other surface contaminants. The specimens are then dried at room temperature. Before dip coating, the NiTi surfaces are chemically activated using a phosphoric acid solution prepared by mixing 78 mL of 88 wt.% H<sub>3</sub>PO<sub>4</sub> with 10 mL of deionized water. Based on the volumes and nominal reagent density, the resulting solution had an estimated phosphoric acid concentration of approximately 81.8 wt.%. The specimens are immersed in the phosphoric acid solution for 5 min at room temperature. After acid activation, the specimens are thoroughly rinsed with deionized water and dried. They are subsequently immersed in 99% ethanol for 5 min to remove residual water and surface contaminants. The specimens are then allowed to dry completely at room temperature before the dip-coating process. A total of eight independent NiTi specimens are prepared. Seven specimens are subjected to dip-coating deposition,

whereas one specimen is retained in the uncoated condition as the control substrate. Thus, the experimental set consisted of seven coated specimens and one uncoated NiTi specimen (total N = 8).

### *2.3. Coating suspension preparation*

The coating suspensions are prepared using nano-hydroxyapatite (nHAp), silver nanoparticles (AgNPs), and zirconium dioxide nanoparticles (ZrO<sub>2</sub> NPs) as the coating constituents. Distilled water is used as the dispersion medium, while gelatin and gum acacia are employed as polymeric binding agents. A 3% (w/v) gelatin solution is prepared by dissolving 3 g of gelatin in 100 mL of distilled water. Separately, a 3% (w/v) gum acacia solution is prepared by dispersing 3 g of gum acacia in 100 mL of distilled water. Each solution is stirred on a magnetic hot plate for 2 h while maintaining the temperature below 50 °C to obtain homogeneous polymeric solutions. Subsequently, 10 mL of the gelatin solution is mixed with 5 mL of the gum acacia solution to obtain 15 mL of the polymeric coating medium. The nano powders are then incorporated into the prepared polymeric medium according to the required coating composition. For each single-component coating, 0.3 g of the corresponding nano powder is dispersed in 15 mL of the polymeric medium, corresponding to a concentration of 2% (w/v). Thus, the AgNPs, nHAp, and ZrO<sub>2</sub> NPs single-component suspensions each contained 2% (w/v) of the respective nanoparticle phase. For the binary coating systems, 0.3 g of each constituent nano powder is incorporated into the same 15 mL polymeric medium. Accordingly, the AgNPs–nHAp, AgNPs–ZrO<sub>2</sub> NPs, and nHAp–ZrO<sub>2</sub> NPs formulations each contained 2% (w/v) of each nanoparticle component, corresponding to a total nanoparticle loading of 4% (w/v). For the ternary formulation, designated as the “Mix” coating, 0.3 g each of AgNPs, nHAp, and ZrO<sub>2</sub> NPs is dispersed in 15 mL of the polymeric medium. Therefore, each constituent is present at 2% (w/v), giving a total nanoparticle loading of 6% (w/v). Following nanoparticle addition, each suspension is stirred for 1 h at a temperature below 50 °C to promote uniform dispersion of the particles within the polymeric medium. The suspensions are subsequently subjected to ultrasonic treatment for 30 min to reduce nanoparticle agglomeration and improve suspension homogeneity prior to the dip-coating process.

### *2.4. Dip-coating deposition and post-treatment*

Prior to the dip-coating process, the NiTi specimens are subjected to surface preparation to remove surface contaminants and improve coating adhesion. The specimen surfaces are mechanically ground and polished to obtain a uniform surface condition. They are subsequently cleaned with distilled water and ethanol to remove residual polishing debris, grease, and other surface contaminants. The cleaned specimens are then chemically treated with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) to activate the NiTi surface and enhance its interaction with the coating suspension. Following acid treatment, the specimens are thoroughly rinsed with distilled water and dried before coating deposition. The prepared NiTi specimens are then coated using the dip-coating technique. Each specimen is completely immersed in the corresponding nanoparticle-containing coating suspension for 20 s. After immersion, the specimens are withdrawn from the suspension and allowed to air-dry under ambient conditions. Three consecutive dip-coating cycles are performed for each coating system to increase surface coverage and build a continuous coating layer. A drying interval of 10 min is maintained between successive coating cycles to allow stabilization of the deposited layer before application of the subsequent coating. The same deposition procedure is applied to all seven coating systems. After completion of the third coating cycle, the coated specimens are allowed to air-dry completely before subsequent surface

characterization and performance testing. Identical surface-preparation and deposition conditions are maintained for all specimen groups to minimize processing-related variations and enable direct comparison of the different coating compositions.

### 2.5. Coating thickness

Average coating thickness is obtained by optical microscopy. The reported values are 44.5860-66.0207  $\mu\text{m}$ . Cross-sectional images of the coated NiTi specimens are examined, and the coating thickness is determined by measuring the perpendicular distance between the NiTi substrate-coating interface and the outer coating surface. Measurements are taken at different locations along the coating cross-section to account for local variations in layer thickness, and the average coating thickness is calculated for each coating system. The obtained thickness values are subsequently compared among the different single-component, binary, and ternary coatings.

### 2.6. X-ray diffraction

The crystalline characteristics and phase constitution of the uncoated and coated NiTi specimens are investigated using X-ray diffraction (XRD) with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The diffraction patterns are recorded over a  $2\theta$  range of approximately  $15\text{--}80^\circ$  using a step size of  $0.05^\circ$ . The X-ray generator is operated at 40 Kv and 30 Ma. The resulting diffraction patterns are analyzed by comparing the positions and relative intensities of the observed diffraction peaks with reference diffraction data to identify the characteristic crystalline phases associated with the NiTi substrate and the deposited nHAp, AgNPs, and ZrO $_2$  NP-containing coatings.

### 2.7. SEM and EDS

The surface morphology of the uncoated and coated NiTi specimens is examined using a TESCAN VEGA3 scanning electron microscope (SEM). Micrographs are acquired at an accelerating voltage of 20 Kv and approximately  $500\times$  magnification, with a scale bar of 100  $\mu\text{m}$ . SEM examination is used to evaluate the general surface coverage and morphological characteristics of the deposited coatings, including particle distribution, agglomeration, surface porosity, and the presence of cracks or other morphological defects. Energy-dispersive X-ray spectroscopy (EDS) is performed in conjunction with SEM to investigate the elemental composition of the specimen surfaces. Area analyses are obtained from selected rectangular regions of the examined surfaces to provide representative elemental information. The detected elemental signals are used to verify the presence and distribution of the principal elements associated with the NiTi substrate and the nHAp-, AgNP-, and ZrO $_2$  NP-containing coating systems.

### 2.8. Wettability

The surface wettability of the uncoated and coated NiTi specimens is evaluated by static water contact angle measurements using deionized water. A droplet of approximately 2  $\mu\text{L}$  is carefully deposited onto the specimen surface, and its behavior is recorded using a CCD camera connected to the contact-angle measurement system. Images are acquired at intervals of 5 s to monitor the interaction and spreading of the water droplet on the surface. The contact angle is determined using the associated image-analysis software based on the profile of the droplet at the solid-liquid interface. Three measurements are performed for each experimental condition, and the average contact angle is

calculated for comparison among the uncoated and coated specimens. Lower contact-angle values are interpreted as indicating greater surface wettability.

## 2.9. Vickers hardness

The surface hardness of the uncoated and coated NiTi specimens is evaluated using the Vickers indentation method. A load of 200 g is applied to the specimen surface for a dwell time of 15 s. Three indentations are performed at different locations on each specimen to account for local variations in surface hardness. The corresponding Vickers hardness values (HV) are determined, and the average of the three measurements is calculated for each specimen. Identical loading and dwell-time conditions are maintained for all uncoated and coated specimens to ensure consistent comparison among the investigated coating systems.

## 2.10. Electrochemical corrosion testing

Potentiodynamic polarization is performed using a CH Instruments CHI 604E electrochemical workstation and an exposed specimen area of 1 cm<sup>2</sup>. Open-circuit potential (OCP), anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ), corrosion potential ( $E_{corr}$ ), corrosion current ( $I_{corr}$ ), and corrosion rate are reported. For the NiTi conversion, the supplied calculation used a density of 6.45 g/cm<sup>3</sup> and an equivalent weight of 19.303. Corrosion rate is calculated according to Eq. (1), consistent in form with ASTM G102 [7].

$$CR \text{ (mm/year)} = 3.272 \times 10^3 \times I_{corr} \text{ (}\mu\text{A)} \times EW / (A \times \rho)$$

where EW is equivalent weight, A is exposed area in cm<sup>2</sup>, and  $\rho$  is density in g/cm<sup>3</sup>. Protection efficiency is calculated as  $\eta = [(CR_{base} - CR_{coated})/CR_{base}] \times 100$ . The electrochemical measurements are performed in simulated body fluid (SBF), and the composition and concentration of its constituents are presented in Table 2. The SBF solution is maintained at the specified test temperature throughout the measurements. The electrochemical cell is configured using the appropriate working, reference, and counter electrodes in accordance with the adopted electrochemical protocol. Prior to polarization testing, the specimens are allowed to stabilize at open-circuit potential (OCP) for the prescribed period. Potentiodynamic polarization is subsequently conducted over the specified potential range and scan rate. Uncompensated solution resistance is treated according to the applied measurement procedure, and the anodic and cathodic Tafel regions are selected from the linear portions of the polarization curves for determination of the corrosion parameters. [7,8].

**Table 2** Chemical composition of the simulated body fluid used for electrochemical testing.

| Item | Description                          | Quantity gm/l |
|------|--------------------------------------|---------------|
| 1    | NaCl                                 | 8.036         |
| 2    | KCl                                  | 0.225         |
| 3    | CaCl <sub>2</sub>                    | 0.293         |
| 4    | NaHCO <sub>3</sub>                   | 0.352         |
| 5    | K <sub>2</sub> HPO <sub>4</sub>      | 0.230         |
| 6    | MgCl <sub>2</sub> .6H <sub>2</sub> O | 0.311         |
| 7    | NaSO <sub>4</sub>                    | 0.072         |

## 2.11. 2.11 Data analysis

The experimental results are analyzed descriptively to compare the surface and electrochemical performance of the uncoated and coated NiTi specimens. Where repeated measurements are

performed, the arithmetic mean is calculated and used as the representative value for each specimen. Comparisons among the investigated coating systems are based on the measured coating thickness, contact angle, Vickers hardness, and electrochemical corrosion parameters. No inferential statistical tests are applied.

### 3. RESULTS AND DISCUSSION

#### 3.1. Coating thickness

All coating systems formed micrometre-scale layers, with average thicknesses ranging from 44.5860 to 66.0207  $\mu\text{m}$  (Table 3). AgNPs-ZrO<sub>2</sub> NPs produced the thickest layer (66.0207  $\mu\text{m}$ ), followed by the ternary AgNPs-nHAp-ZrO<sub>2</sub> NPs coating (62.2181  $\mu\text{m}$ ) and AgNPs-nHAp (59.7941  $\mu\text{m}$ ), whereas nHAp-ZrO<sub>2</sub> NPs produced the thinnest layer (44.5860  $\mu\text{m}$ ). The difference between the maximum and minimum values is 21.4347  $\mu\text{m}$ , or 48.1% of the minimum thickness.

**Table 3** Average optical thickness of the single, binary, and ternary nanoparticle coatings on NiTi.

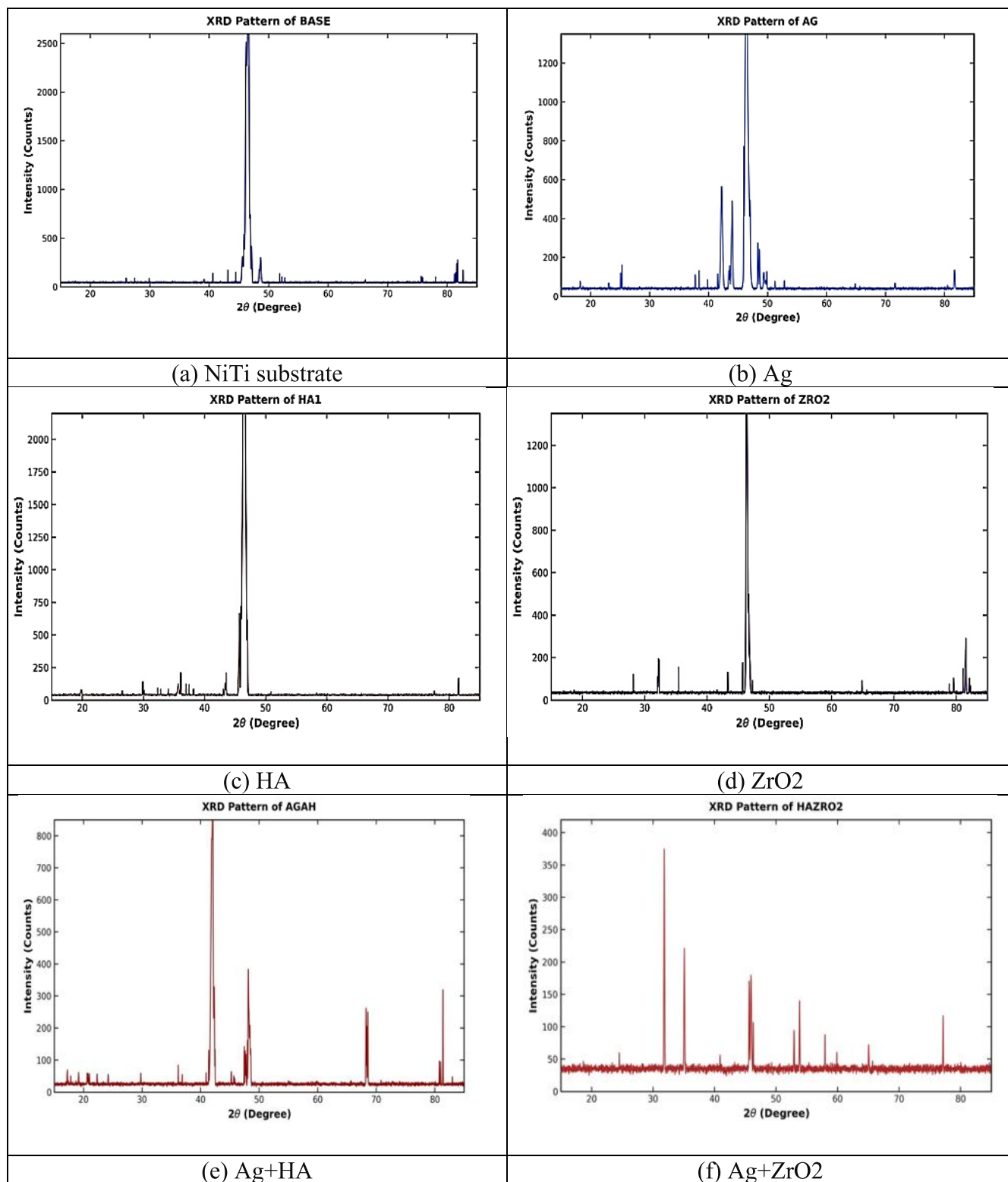
| samples | Coating             | Thickness ( $\mu\text{m}$ ) |
|---------|---------------------|-----------------------------|
| 1       | Ag                  | 51.1966                     |
| 2       | HA                  | 55.5082                     |
| 3       | ZrO <sub>2</sub>    | 55.3193                     |
| 4       | Ag-HA               | 59.7941                     |
| 5       | Ag-ZrO <sub>2</sub> | 66.0207                     |
| 6       | HA-ZrO <sub>2</sub> | 44.5860                     |
| 7       | Mix                 | 62.2181                     |

Because all specimens received the same three-cycle dip-coating schedule, the thickness variation is attributed mainly to composition-dependent suspension viscosity, particle packing, drainage, and drying shrinkage. Total solids loading alone does not explain the result: the two binary systems AgNPs-ZrO<sub>2</sub> NPs and nHAp-ZrO<sub>2</sub> NPs had the same nominal nanoparticle loading but yielded the highest and lowest thicknesses, respectively. More importantly, thickness did not control corrosion protection. The thickest coating achieved 89.52% protection, while the thinnest achieved 95.08%; therefore, continuity, pore connectivity, phase distribution, and interfacial integrity are more influential than nominal thickness.

#### 3.2. XRD phase signatures

The available XRD patterns confirmed crystalline contributions from the NiTi substrate and the deposited phases (Figure 1). The substrate is dominated by the principal NiTi reflection in the low-40° 2 $\theta$  region. Ag-containing coatings showed additional reflections consistent with face-centred-cubic metallic Ag, while nHAp-containing coatings exhibited calcium-phosphate reflections near 25.9° and across 31-33°. Zirconia-related peaks are superimposed on the NiTi background in ZrO<sub>2</sub>-containing coatings, and the available composite patterns contained overlapping reflections from their constituent phases. Residual substrate peaks are expected because X-rays can penetrate the coating and sample the alloy through locally thin or heterogeneous regions. These phase signatures show that dip coating retained identifiable Ag-, nHAp-, and ZrO<sub>2</sub>-containing constituents rather than producing a fully amorphous surface. The supplied figure does not include patterns for AgNPs-ZrO<sub>2</sub> NPs or the ternary coating; these panels should be inserted before submission if those conditions are discussed structurally. In addition, the available patterns do not support reliable crystallite-size calculation,

quantitative phase fractions, or unambiguous discrimination between tetragonal and monoclinic zirconia. Any claim concerning secondary calcium-phosphate phases or NiTi precipitates should therefore be based on the original diffraction files, background correction, and reference-card matching.



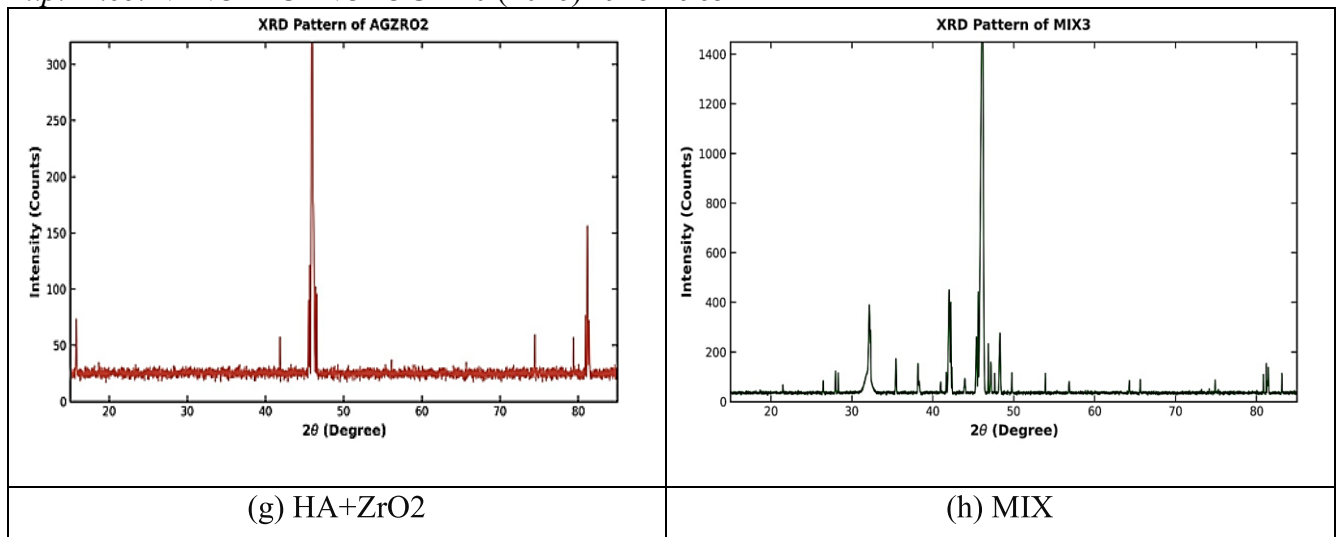
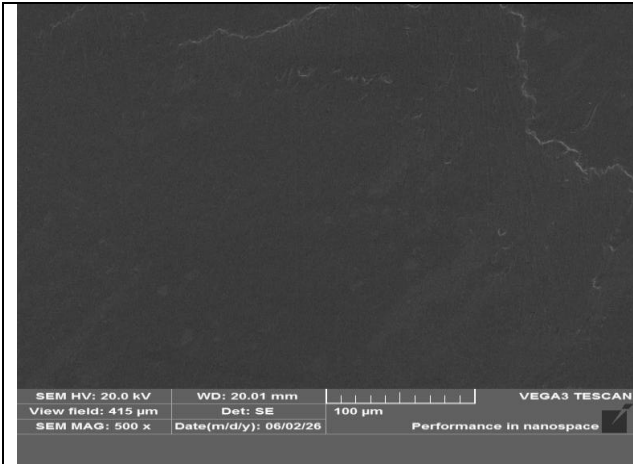


**Figure 1** XRD patterns of uncoated NiTi and the AgNPs-, nHAp-, ZrO<sub>2</sub> NPs-, binary-, and ternary-coated specimens.

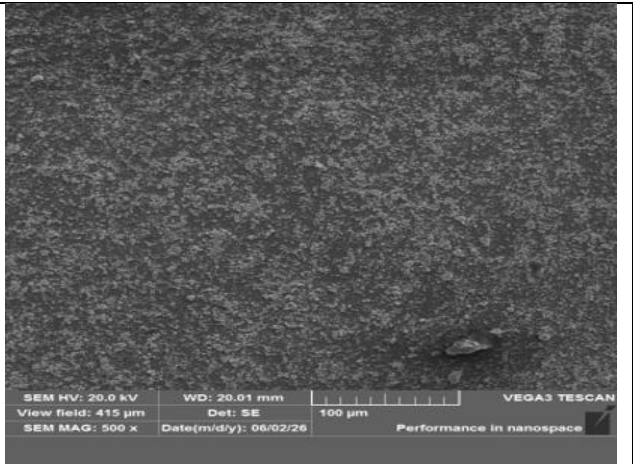
### 3.3. Surface morphology

The uncoated NiTi surface is comparatively smooth at the examined magnification and retained preparation traces with few discontinuities (Figure 2). The AgNPs coating formed a fine, densely populated surface, whereas nHAp contained larger bright agglomerates over a finer background. ZrO<sub>2</sub> NPs produced a relatively compact fine-particle layer with fewer large agglomerates than nHAp.

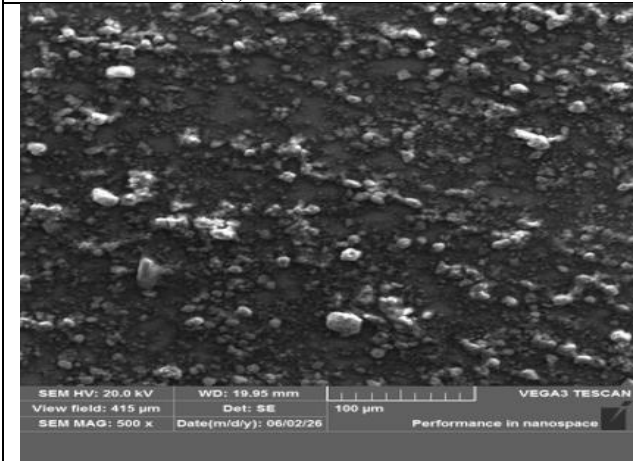
The binary coatings showed composition-dependent morphologies. AgNPs-nHAp contained isolated coarse particles on a smoother matrix, indicating preferential agglomeration or incomplete homogenization. AgNPs-ZrO<sub>2</sub> NPs produced a denser granular surface with both fine and coarse features, while nHAp-ZrO<sub>2</sub> NPs appeared relatively continuous with localized agglomerates. The ternary coating displayed the broadest coverage and the most interconnected granular texture.



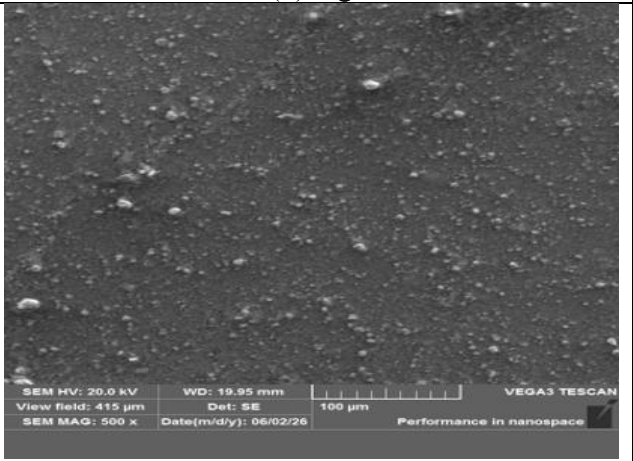
(a) NiTi substrate



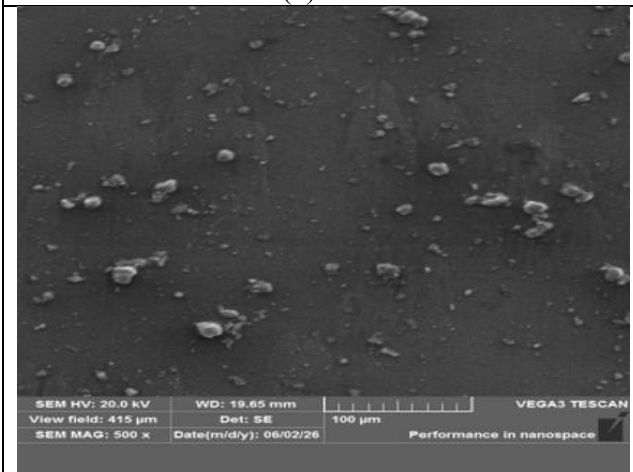
(b) Ag



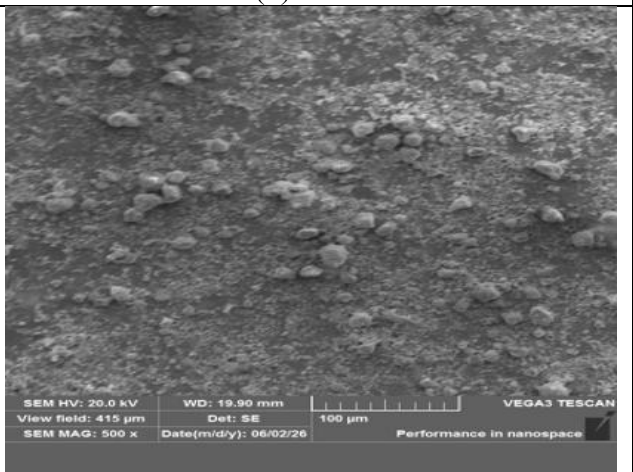
(c) HA



(d) ZrO<sub>2</sub>



(e) Ag+HA



(f) Ag+ZrO<sub>2</sub>

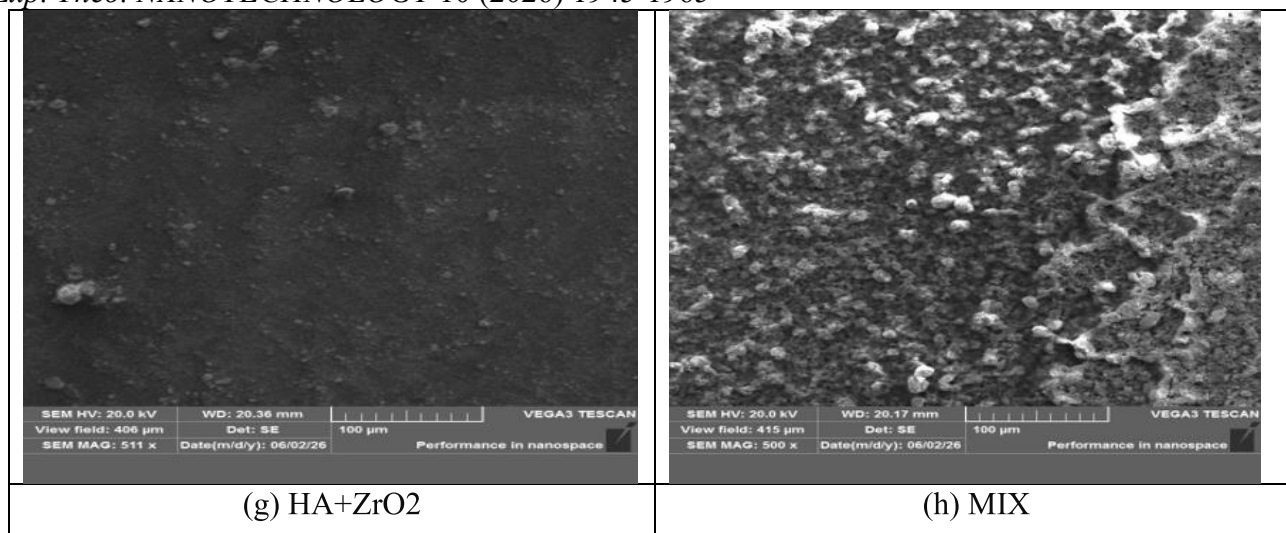


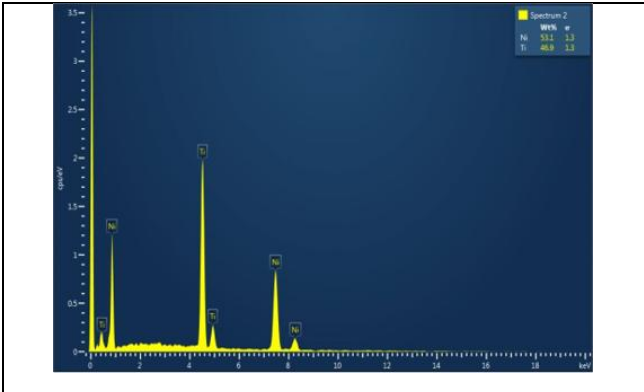
**Figure 2** SEM surface morphologies of uncoated and coated NiTi specimens at approximately 500x and 20 kV; the original scale bars are retained.

The dense, multiphase texture of the ternary coating is consistent with a more tortuous path for electrolyte transport, which helps explain its low corrosion current. Zirconia can reinforce weak calcium-phosphate regions and reduce effective permeability, whereas Ag-containing domains may modify interparticle packing. The comparatively lower protection of nHAp alone is consistent with the sensitivity of stand-alone hydroxyapatite layers to pores, microcracks, and dissolution pathways; the improved response of nHAp-ZrO<sub>2</sub> NPs agrees with previous corrosion studies of reinforced hydroxyapatite coatings on NiTi [1,3,4]. This interpretation remains morphological because 500x images cannot resolve nanoscale porosity or confirm the absence of through-thickness defects.

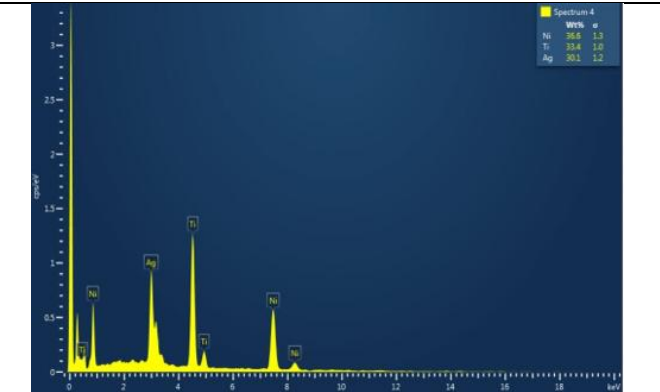
### 3.4. Elemental constitution by EDS

The EDS spectrum of uncoated NiTi is dominated by Ni and Ti, with O and C signals attributable to the native oxide, surface contamination, mounting, or the electron interaction volume (Figure 3). The coated specimens showed the expected qualitative elemental signatures: Ag in AgNPs-containing coatings; Ca, P, and O in nHAp-containing coatings; and Zr and O in ZrO<sub>2</sub>-containing coatings. The binary and ternary spectra therefore support coexistence of their intended constituents.

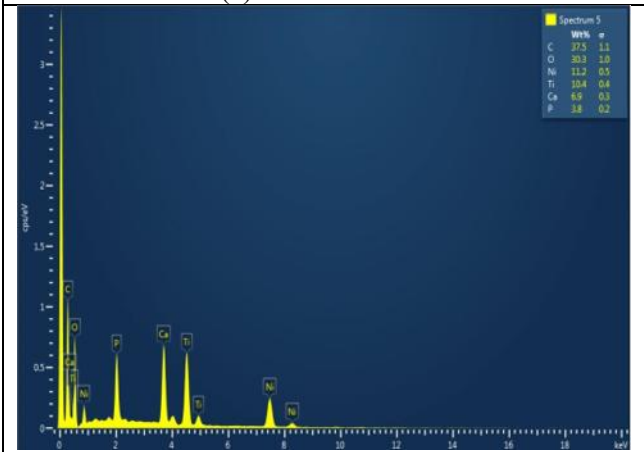
Residual Ni and Ti signals from coated surfaces indicate that the interaction volume reached the substrate through the coating or sampled locally thin, porous, or incompletely covered regions. They do not, by themselves, quantify coating continuity. Exact weight and atomic percentages, Ca/P ratios, Ag content, and coating-to-substrate signal ratios should be obtained from the original EDS exports and averaged over several regions. Elemental maps are also required to determine whether Ag and ZrO<sub>2</sub> NPs are uniformly distributed within the nHAp-containing matrix.



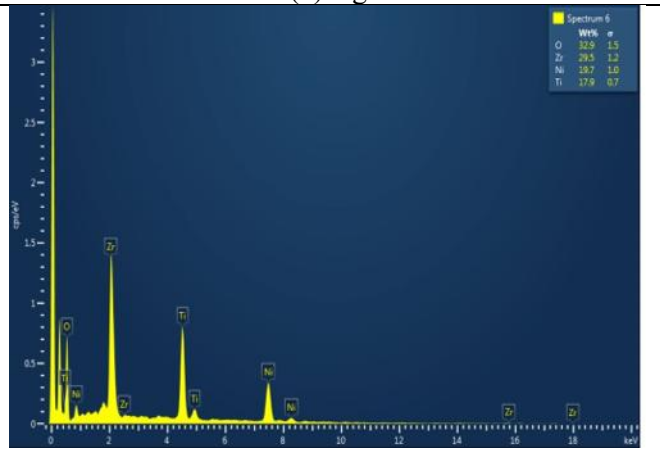
(a) NiTi substrate



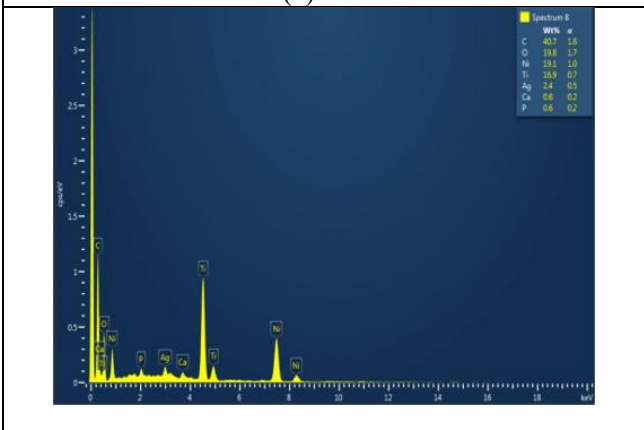
(b) Ag



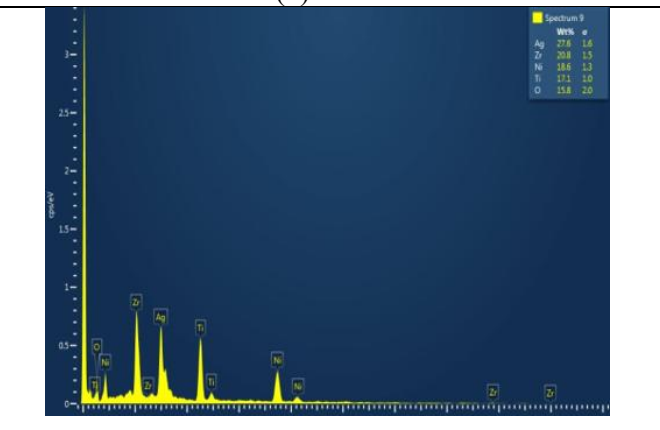
(c) HA



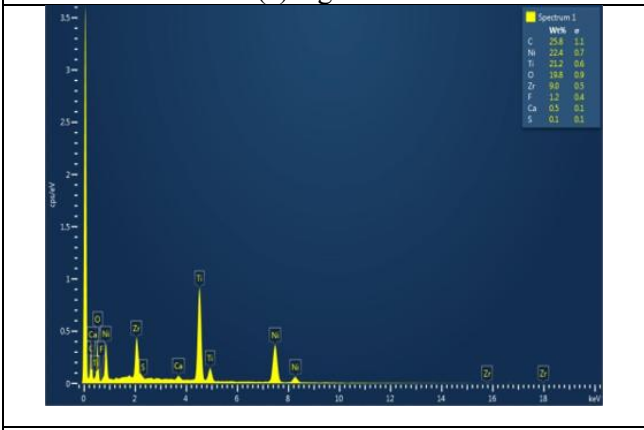
(d) ZrO<sub>2</sub>



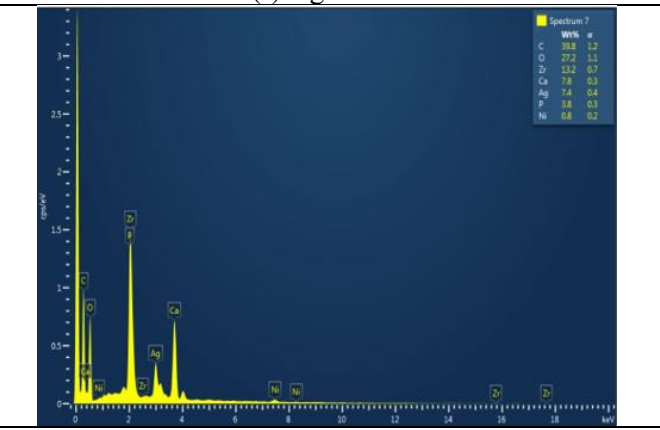
(e) Ag+HA



(f) Ag+ZrO<sub>2</sub>



(g) HA+ZrO<sub>2</sub>



(h) MIX

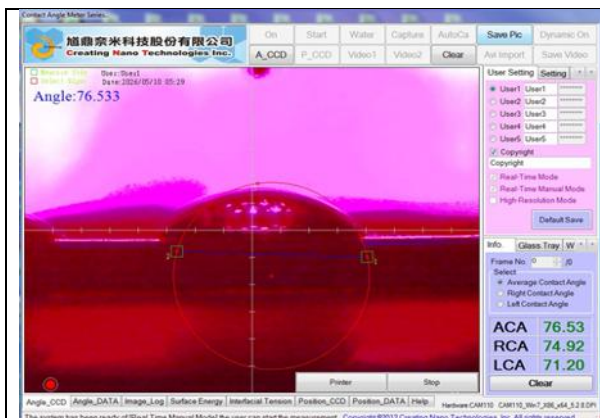
**Figure 3** Representative EDS acquisition regions and spectra of uncoated and coated NiTi specimens, showing the qualitative elemental constituents of each surface.

### 3.5. Wettability

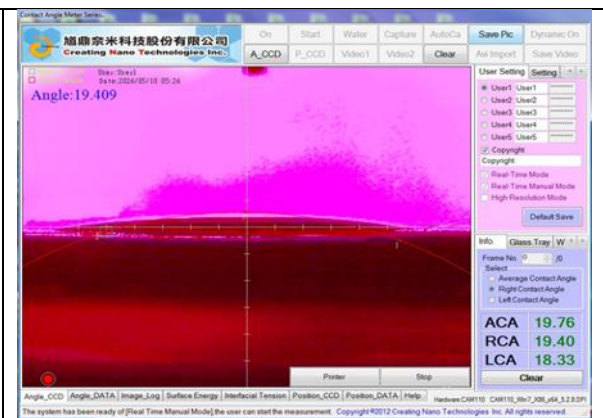
The water contact angle decreased from 76.533° for uncoated NiTi to 7.364-19.409° after coating (Table 4 and Figure 4), confirming a marked increase in wettability. nHAp produced the lowest angle (7.364°), followed by the ternary coating (8.381°) and AgNPs-nHAp (9.497°). Even AgNPs, which had the highest angle among the coated surfaces (19.409°), reduced the contact angle by 74.6% relative to the substrate.

**Table 4** Static water contact angles and percentage reductions relative to uncoated NiTi.

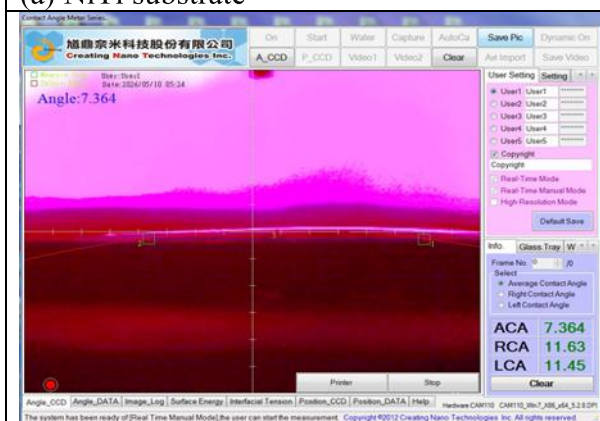
| Surface   | Contact angle (°) | Reduction vs substrate (%) | Wetting classification |
|-----------|-------------------|----------------------------|------------------------|
| Substrate | 76.533            | 0.0                        | Hydrophilic            |
| Ag        | 19.409            | 74.6                       | Hydrophilic            |
| HA        | 7.364             | 90.4                       | Hydrophilic            |
| ZrO2      | 16.339            | 78.7                       | Hydrophilic            |
| Ag-HA     | 9.497             | 87.6                       | Hydrophilic            |
| Ag-ZrO2   | 15.672            | 79.5                       | Hydrophilic            |
| HA-ZrO2   | 18.082            | 76.4                       | Hydrophilic            |
| Mix       | 8.381             | 89.0                       | Hydrophilic            |



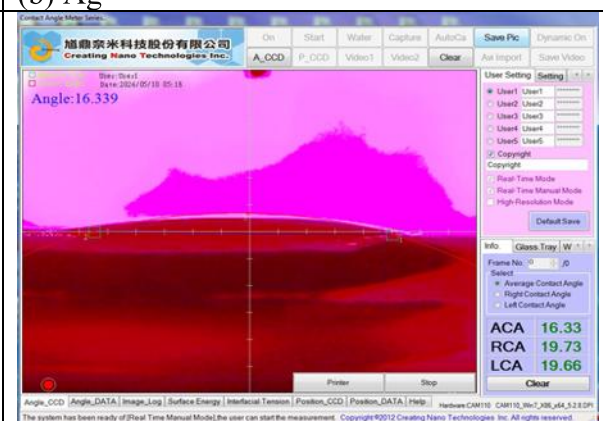
(a) NiTi substrate



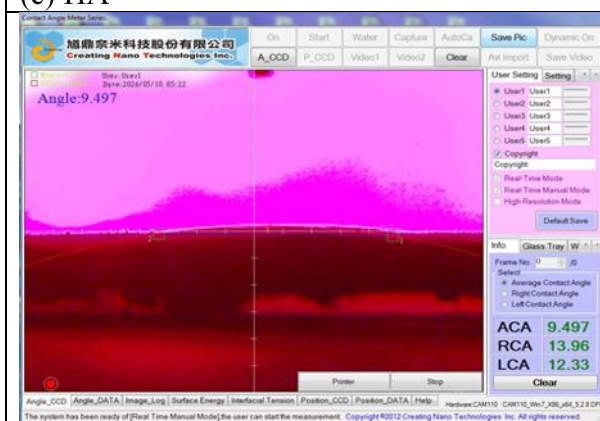
(b) Ag



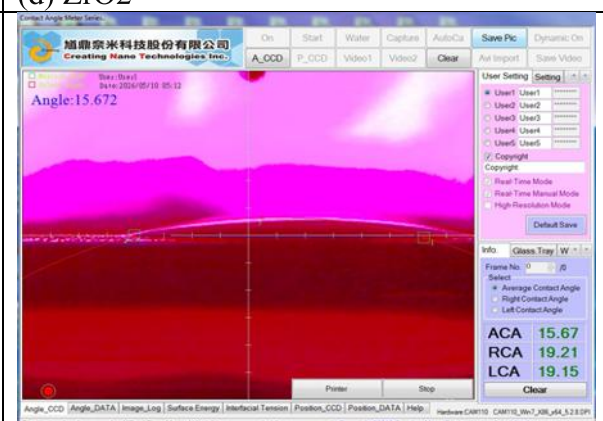
(c) HA



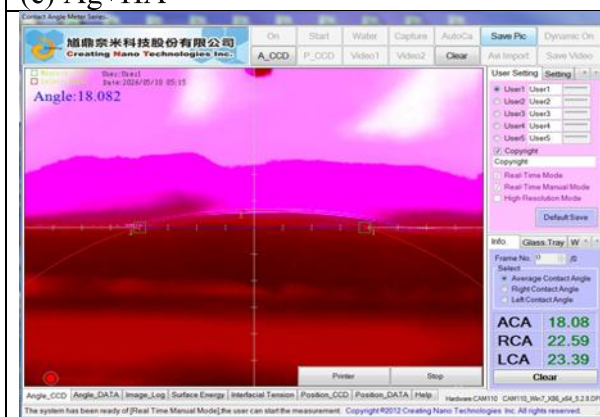
(d) ZrO2



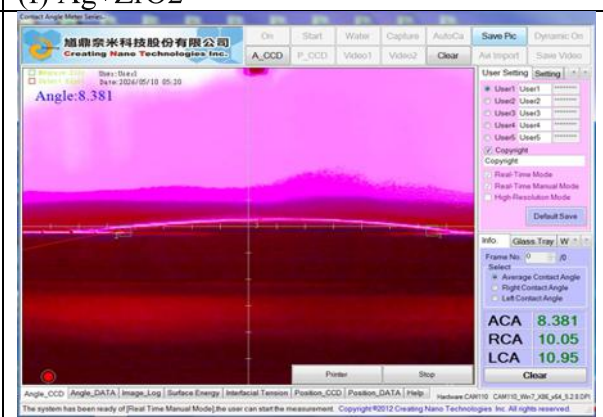
(e) Ag+HA



(f) Ag+ZrO2



(g) HA+ZrO2



(h) MIX

**Figure 4** Static water-droplet profiles used to determine the contact angles of uncoated and coated NiTi specimens.

The strong wettability of nHAp-containing surfaces is attributed to polar calcium, phosphate, and hydroxyl groups combined with coating microtexture, consistent with earlier studies of calcium-phosphate-modified implant alloys [2,4,5]. The ternary coating is especially notable because it combined a contact angle of  $8.381^\circ$  with the best corrosion resistance. High wettability can accelerate electrolyte entry when connected pores are present; the simultaneous decrease in corrosion current therefore suggests that the ternary layer maintained a hydrophilic outer surface while restricting through-thickness transport. Cross-sectional SEM, roughness, open-porosity, and water-uptake measurements are needed to verify this mechanism. Contact angle alone does not demonstrate cytocompatibility, osseointegration, or in vivo bioactivity.

### 3.6. Vickers hardness

Surface hardness depended strongly on coating composition (Table 5). ZrO<sub>2</sub> NPs produced the highest value, 521.8 HV, which is 126.6% above the uncoated NiTi value of 230.3 HV. AgNPs-ZrO<sub>2</sub> NPs (386.7 HV), the ternary coating (383.2 HV), and nHAp-ZrO<sub>2</sub> NPs (318.3 HV) increased hardness by 67.9%, 66.4%, and 38.2%, respectively. In contrast, AgNPs (191.1 HV), nHAp (187.8 HV), and AgNPs-nHAp (218.8 HV) remained below the substrate value by 17.0%, 18.5%, and 5.0%, respectively.

**Table 5** Vickers hardness and percentage change relative to uncoated NiTi at a load of 200 g and a dwell time of 15 s.

| Surface             | Hardness (HV) | Change vs substrate (%) | Relative response |
|---------------------|---------------|-------------------------|-------------------|
| Substrate           | 230.3         | +0.0                    | Reference         |
| Ag                  | 191.1         | -17.0                   | Decrease          |
| HA                  | 187.8         | -18.5                   | Decrease          |
| ZrO <sub>2</sub>    | 521.8         | +126.6                  | Increase          |
| Ag-HA               | 218.8         | -5.0                    | Decrease          |
| Ag-ZrO <sub>2</sub> | 386.7         | +67.9                   | Increase          |
| HA-ZrO <sub>2</sub> | 318.3         | +38.2                   | Increase          |
| Mix                 | 383.2         | +66.4                   | Increase          |

The high hardness of the ZrO<sub>2</sub> NPs coating and the increases measured for AgNPs-ZrO<sub>2</sub> NPs, nHAp-ZrO<sub>2</sub> NPs, and the ternary system are consistent with reinforcement by a zirconia-containing ceramic network. The lower values of AgNPs, nHAp, and AgNPs-nHAp may reflect coating porosity, weakly supported agglomerates, the softer Ag phase where present, and the combined response of coating and substrate during indentation. These values should be interpreted as composite surface responses rather than intrinsic coating hardness because the coatings are only 44.5860-66.0207  $\mu\text{m}$  thick. Reporting indentation diagonals and measurement dispersion would strengthen compliance with the microindentation method [13]. Hardness also cannot substitute for adhesion or fracture testing: a hard, relatively thick coating may crack or delaminate during the recoverable deformation of superelastic NiTi. Scratch, bend, and cyclic-strain tests with post-deformation microscopy are therefore required.

### 3.7. Electrochemical corrosion behavior

All coatings reduced the corrosion current and corrosion rate relative to uncoated NiTi (Table 6). The substrate exhibited  $I_{corr} = 2.808 \times 10^{-6}$  A and a corrosion rate of  $2.745 \times 10^{-2}$  mm/year. The ternary AgNPs-nHAp-ZrO<sub>2</sub> NPs coating produced the lowest  $I_{corr}$  ( $9.082 \times 10^{-8}$  A) and corrosion rate ( $8.893 \times 10^{-4}$  mm/year), corresponding to 96.76% protection and a 30.87-fold reduction in corrosion rate. nHAp-ZrO<sub>2</sub> NPs and AgNPs are the next most protective conditions, with efficiencies of 95.08% and 94.94% and corrosion-rate reductions of 20.32- and 19.78-fold, respectively. Although nHAp alone showed the smallest improvement, it still reduced the corrosion rate by 69.76%.

**Table 6** Potentiodynamic polarization parameters, corrosion rates, protection efficiencies, and fold reductions for uncoated and coated NiTi in SBF.

| Surface             | OCP (V) | $\beta_a$ | $\beta_c$ | E <sub>corr</sub> (V) | I <sub>corr</sub> (A) | CR (mm/y) | $\eta$ (%) | Fold  |
|---------------------|---------|-----------|-----------|-----------------------|-----------------------|-----------|------------|-------|
| Substrate           | -0.501  | 0.193     | 0.163     | -0.543                | 2.808e-06             | 2.745e-02 | 0.00       | 1.00  |
| Ag                  | -0.465  | 0.219     | 0.207     | -0.218                | 1.418e-07             | 1.388e-03 | 94.94      | 19.78 |
| HA                  | -0.400  | 0.963     | 0.222     | -0.116                | 8.477e-07             | 8.300e-03 | 69.76      | 3.31  |
| ZrO <sub>2</sub>    | -0.371  | 0.294     | 0.258     | -0.133                | 4.443e-07             | 4.350e-03 | 84.15      | 6.31  |
| Ag-HA               | -0.297  | 0.238     | 0.159     | -0.565                | 3.698e-07             | 3.621e-03 | 86.81      | 7.58  |
| Ag-ZrO <sub>2</sub> | -0.211  | 0.384     | 0.167     | -0.289                | 2.938e-07             | 2.876e-03 | 89.52      | 9.54  |
| HA-ZrO <sub>2</sub> | -0.120  | 0.439     | 0.219     | -0.289                | 1.380e-07             | 1.351e-03 | 95.08      | 20.32 |
| Mix                 | -0.051  | 0.221     | 0.196     | -0.354                | 9.082e-08             | 8.893e-04 | 96.76      | 30.87 |

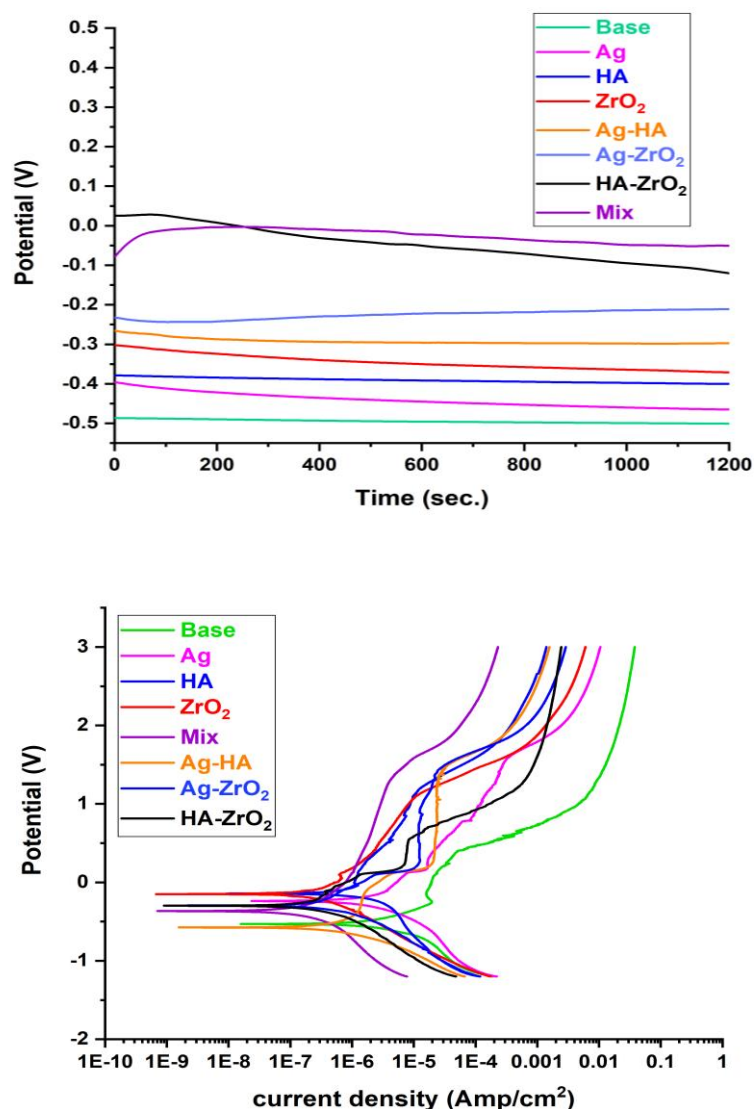


**Figure 5** Open-circuit potential curves and potentiodynamic polarization curves of uncoated and coated NiTi specimens in SBF.

**Table 7** Open-circuit potential, stabilization time, corrosion potential, and corrosion current density of uncoated and coated NiTi specimens in SBF.

| Samples               | EOCP (V) | Time (s) | Ecorr (V) | Current density, $i_{corr}$ (A cm <sup>-2</sup> ) |
|-----------------------|----------|----------|-----------|---------------------------------------------------|
| Base NiTi             | -0.501   | 1200     | -0.543    | $2.808 \times 10^{-6}$                            |
| Ag                    | -0.465   | 1200     | -0.218    | $1.418 \times 10^{-7}$                            |
| HAp                   | -0.400   | 1200     | -0.116    | $8.477 \times 10^{-7}$                            |
| ZrO <sub>2</sub>      | -0.371   | 1200     | -0.133    | $4.443 \times 10^{-7}$                            |
| Ag-HAp                | -0.297   | 1200     | -0.565    | $3.698 \times 10^{-7}$                            |
| Ag- ZrO <sub>2</sub>  | -0.211   | 1200     | -0.289    | $2.938 \times 10^{-7}$                            |
| Hap- ZrO <sub>2</sub> | -0.120   | 1200     | -0.289    | $1.380 \times 10^{-7}$                            |
| MIX                   | -0.051   | 1200     | -0.354    | $9.082 \times 10^{-8}$                            |

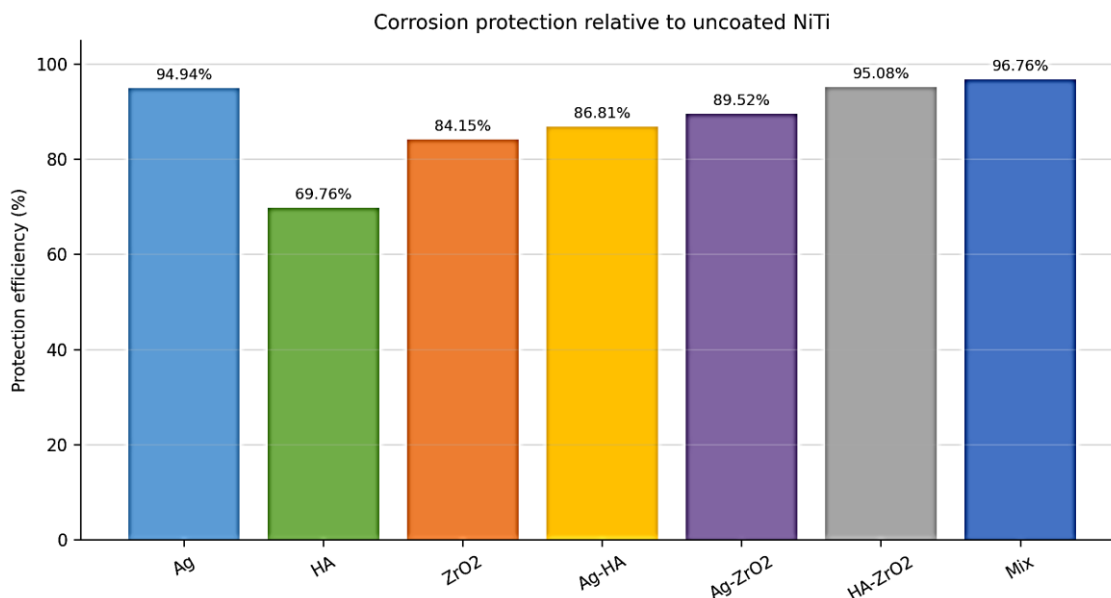


**Figure 6** Corrosion protection efficiencies of the nanoparticle coatings calculated from the reported corrosion rates relative to uncoated NiTi.

The electrochemical ranking confirms that coating thickness is not the controlling variable. AgNPs-ZrO<sub>2</sub> NPs is the thickest layer but reached 89.52% protection, whereas the thinner nHAp-ZrO<sub>2</sub> NPs layer reached 95.08%. The superior ternary response is instead consistent with broad surface coverage and a compact multiphase network that reduced the electrochemically exposed area and increased the tortuosity of ionic transport. Zirconia can improve chemical stability and constrain defects in the nHAp-rich phase, while AgNPs may occupy interparticle regions. Similar improvements have been reported for reinforced calcium-phosphate coatings on NiTi [1,3,4]. The AgNPs-only result should nevertheless be evaluated over longer immersion periods because Ag dissolution, galvanic heterogeneity, and defect growth may change with time.

The open-circuit potential became less negative for several coated specimens and reached -0.051 V for the ternary coating, indicating a nobler stabilized surface under the reported conditions.  $E_{corr}$  did not follow the same order and is most negative for AgNPs-nHAp (-0.565 V). This difference is expected because  $E_{corr}$  is a mixed potential and does not independently measure the corrosion rate;  $I_{corr}$  and passive-region stability provide the more relevant kinetic comparison. The interpretation remains descriptive because inferential statistics are not applied. The original polarization plots, Tafel fitting windows, replicate curves, reference-electrode identity, and uncertainty values should be reported before drawing stronger comparative conclusions [7, 8].

### 3.8. Integrated performance and biomedical considerations

The preferred coating depends on the required function. ZrO<sub>2</sub> NPs is the leading condition when maximum surface hardness is prioritized, and nHAp provides the lowest contact angle. For corrosion protection, the ternary coating ranks first, followed by nHAp-ZrO<sub>2</sub> NPs and AgNPs. When corrosion resistance, wettability, and hardness are considered together, the ternary coating provides the most balanced measured response: a corrosion rate of  $8.893 \times 10^{-4}$  mm/year, 96.76% protection, a contact angle of  $8.381^\circ$ , and a hardness of 383.2 HV. Its thickness of 62.2181  $\mu\text{m}$ , however, makes adhesion, flexibility, and cyclic durability decisive requirements for further development.

The present physicochemical and electrochemical results do not establish clinical suitability or antibacterial activity. Silver-containing coatings require Ag-release kinetics, direct tests against relevant Gram-positive and Gram-negative organisms, and mammalian-cell cytotoxicity assessment [6,9,11]. NiTi surfaces require Ni-release measurements during static immersion and mechanically assisted exposure, while nHAp-containing coatings require dissolution stability, apatite-forming ability, and osteoblast-response testing. Biological evaluation should follow the risk-based framework of ISO 10993-1 and the in vitro cytotoxicity procedures of ISO 10993-5 [9,10]. Until these tests are completed, the ternary system should be described as the best-performing candidate in the present dataset rather than as a clinically validated or antibacterial coating.

#### 4. CONCLUSIONS

Dip coating successfully produced Ag-, HA-, and ZrO<sub>2</sub>-containing single and composite layers on NiTi with thicknesses of 44.5860-66.0207  $\mu\text{m}$ . The coatings generated distinct crystalline signatures, transformed the surface morphology, and introduced the expected constituent elements qualitatively by EDS. All coatings markedly increased hydrophilicity and reduced the corrosion rate. The ternary Ag-HA-ZrO<sub>2</sub> mix provided the best measured overall performance, with a contact angle of 8.381°, hardness of 383.2 HV, corrosion current of  $9.082 \times 10^{-8}$  A, corrosion rate of  $8.893 \times 10^{-4}$  mm/year, and protection efficiency of 96.76%. Its corrosion rate was approximately 30.87 times lower than that of uncoated NiTi. ZrO<sub>2</sub> provided the highest hardness (521.8 HV), while HA provided the lowest contact angle (7.364°). HA-ZrO<sub>2</sub> achieved 95.08% corrosion protection despite being the thinnest coating, confirming that coating integrity and multiphase architecture were more important than thickness alone. The ternary coating is therefore the preferred candidate for subsequent optimization, but it cannot yet be designated as a biomedical or antibacterial coating without adhesion and cyclic-strain testing, quantitative phase and elemental analysis, Ni and Ag release studies, cytotoxicity assessment, bioactivity measurements, and direct antibacterial evaluation. Overall, the investigated coatings demonstrate potential for biomedical surface engineering; however, the present physicochemical and electrochemical results do not establish clinical suitability. Further biological evaluation should include in vitro cytotoxicity testing in accordance with ISO 10993-5 and a broader risk-based assessment following ISO 10993-1 [9, 10].

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