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Meeting-report

Electrochemical Comparison Between HEA Films in Different Deposition Conditions

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Introduction

Newly discovered structural and functional materials [1], high-entropy alloys (HEAs) are already being utilized in the development of numerous new and significant high-tech applications on account of their exceptional properties, including enhanced abrasion resistance, corrosion resistance, and high hardness [2,3]. Additionally, protective coatings have been fabricated from HEA thin films for comparable high-tech applications. One advantage of the pulsed laser deposition (PLD) method is that it only requires targets with a small area, which simplifies the optimization of the growth process. Utilizing Energy Dispersive X-ray Spectroscopy (EDS) with a scanning electron microscope (SEM), elemental analysis confirmed that the PLD technique effectively transferred stoichiometric information from the target to the thin film [4]. The targets were fabricated using an alloy produced through Vacuum Arc Remelting (VAR) from high-purity primary materials. The deposited thin films were subjected to analysis regarding their physical structure, chemical composition, microhardness, and corrosion behavior subsequent to the growth process. These investigations are necessary for investigating the potential medical applications of HEA thin films.

Experimental

Target manufacturing and thin film deposition

Experimental alloy with a high entropy was produced via the VAR method using an MRF ABJ 900 VAR apparatus from the ERAMET Laboratory (www.eramet.wixsite.com/eramet), which is affiliated with the University Politehnica of Bucharest.

ASTM B214-16-classified granular raw materials of the highest purity were utilized in the production of the metal units. The masses of the molten components (34.92g) and the raw materials (35g) for the batch were determined by weighing them on a high precision weighting balance. Subsequently, the metallurgical process efficiency was computed as 99.77%. Chemical composition for each element (in grams) is: Al (3.03), Cr (5.83), Fe (6.28), Co (6.62) and Ni (13.24).

EDS analysis, at.% is Al = 10.19; Cr = 17.54; Fe = 18.34; Co = 18.40; Ni = 35.53 and the chemical molar composition is AlCrFeCoNi2.0. The variation in elemental concentration detected through EDS measurements can be attributed to several factors: the analysis being conducted in random micro-zones, which may not accurately reflect the alloy's overall composition; losses that occur during the melting process, such as evaporation and metal splashes; or measurement errors. Additionally, the variations may stem from the chemical composition and purity levels of the materials purchased.

Optical microscopy (Olympus GX 51, Tokyo, Japan) and scanning electron microscopy (Inspect S, FEI, Holland) analyses of the alloy's microstructure revealed that it has a dendritic structure characterized by grain refinement and the appearance of acicular geometric formations that grow preferentially in particular directions.

Hardness assessments were conducted in all characteristic areas utilizing a Shimadzu HMV 2T microhardness instrument (Tokyo, Japan). For conducting measurements, the Vickers method was selected, employing a force value of 1.961N and an indentation duration of 10 seconds. Achieving low values for the hardness variation coefficient signifies that the alloys are highly homogeneous.

For physical and chemical characterization, films were grown at room temperature on Si substrates; for electrochemical characterization, films were grown on highly polished Ti disks. Just before being inserted into the deposition chamber, the substrates underwent a five-minute sonication process followed by a final drying step utilizing high purity nitrogen. A KrF laser (=248 nm, pulse duration 25 ns) operating at a fluence of 3 J/cm2 and a repetition rate of 40 Hz ablated the HEA target for 10-12 minutes. The depositions were performed under N2 (1×10-4 mbar), films denoted as HEN.

Samples characterization

Film structure, surface morphology, and chemical composition were examined by grazing incidence X-ray diffraction (GIXRD) with a diffractometer (Empyrean, Malvern) programmed to work in a parallel beam geometry after deposition. The surface chemical composition of the film was examined using ESCALB Xi+ XPS equipment with monochromatic AlKα radiation. Survey and high-resolution scans were taken for core regions of Ni, Fe, Cr, Al, Co, O, C, and N. Binding energies were based on the adventitious C1s location at 284.8 eV.

In our case, Grifols Ringer's solution from Laboratorios Grifols, Barcelona, Spain, was used for all electrochemical measurements. A rectangular cell with 250 ml electrolyte was used for electrochemical measurements at 25°C.

The working electrode (sample to be examined) potential was recorded against a saturated KCl-calomel reference electrode (SSCE) and a Pt cylindrical grid counter electrode. ZSimpWin software was used to examine AC impedance spectra from a PAR 263 A potentiostat and PAR 5210 lock-in amplifier.

Results and Discussion

The GIXRD patterns acquired from film exhibited only the peaks corresponding to the bcc phase (see Fig.1). Surface morphology analyses were carried out by SEM and a typical surface image acquired from thin film is displayed in Fig.2. Regardless of the deposition factors, thin films consistently display micrometer-sized droplets, which is a common occurrence when using the PLD technology. Furthermore, one can observe areas where droplets that were formerly attached have suddenly become disengaged. Furthermore, it was found that droplets were layered on top of each other. In addition, several droplets underwent a hydrodynamic effect upon impact with the substrate, resulting in their transformation into donut-shaped formations during subsequent cooling. No notable alterations in morphology were observed when comparing pictures obtained from thin HEA and HEN film.

Due to a passive layer of titanium dioxide, TiO2, which is protective and inert in Ringer's solution, the pure Ti sample displays little change.

For all samples, a near capacitive response [5] was detected and characterized in Nyquist plots, as one can see in Fig.3.

The Bode-IZI diagrams (Fig.4a) illustrate constant values (horizontal line) of log |Z| versus log (f) at high frequencies. The phase angle approaches 0°, which represents the response of the simulated body fluid impedance within the higher frequency band of 1–100 kHz.

The Bode-phase plots exhibit a linear trend with a slope of approximately -1 in log |Z| as the frequency decreases, as illustrated in Fig.4b. Conversely, the phase angle values approach 80° across a broad range of low and mid-frequency values. It should be noted that the aforementioned behavior is indicative of a compact passive film capacitor.

Conclusions

The high-entropy alloy AlCoCrFeNi2 was synthesized by melting in a controlled environment of pure argon, ensuring minimum loss of the component chemical elements during the manufacturing process. The HEA material was employed as a target in a PLD system for the purpose of film growth, either in a high vacuum or a nitrogen (N2) atmosphere. The deposited films exhibited a high degree of fidelity to the chemical composition of the targets but did not accurately replicate their phase structure. The films that were produced under a nitrogen environment contained nitrogen atoms within their crystal structure, forming chemical bonds with metal atoms to create nitride compounds. These films demonstrated superior electrochemical characteristics compared to the films deposited under high vacuum conditions.

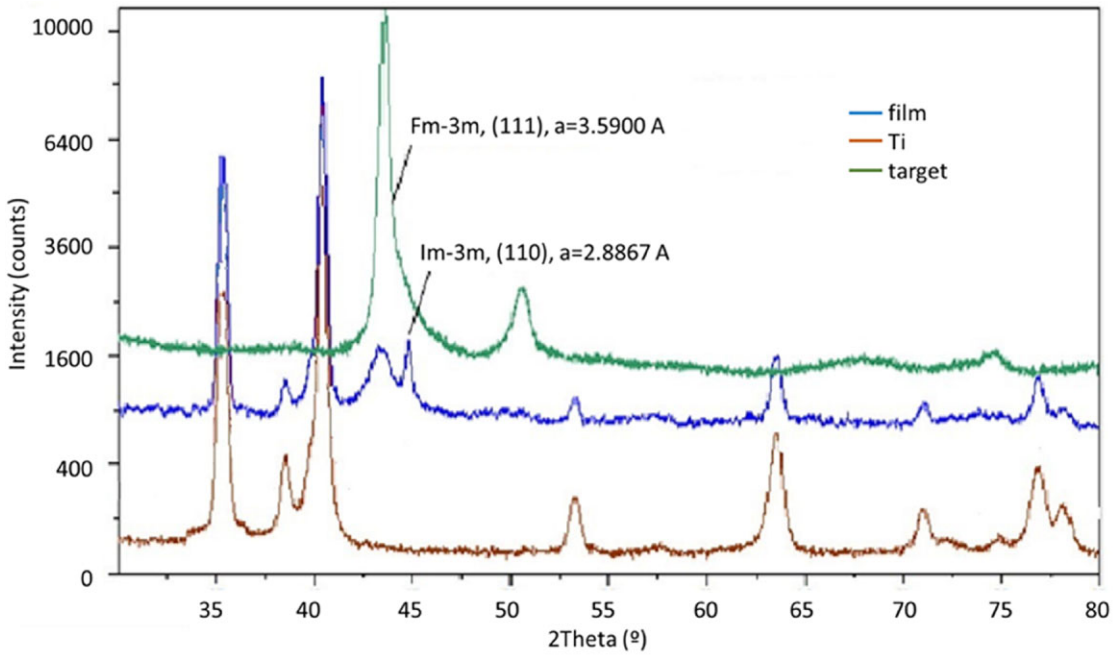

Fig.1. XRD patterns of the analyzed thin film, the target and Ti substrate.

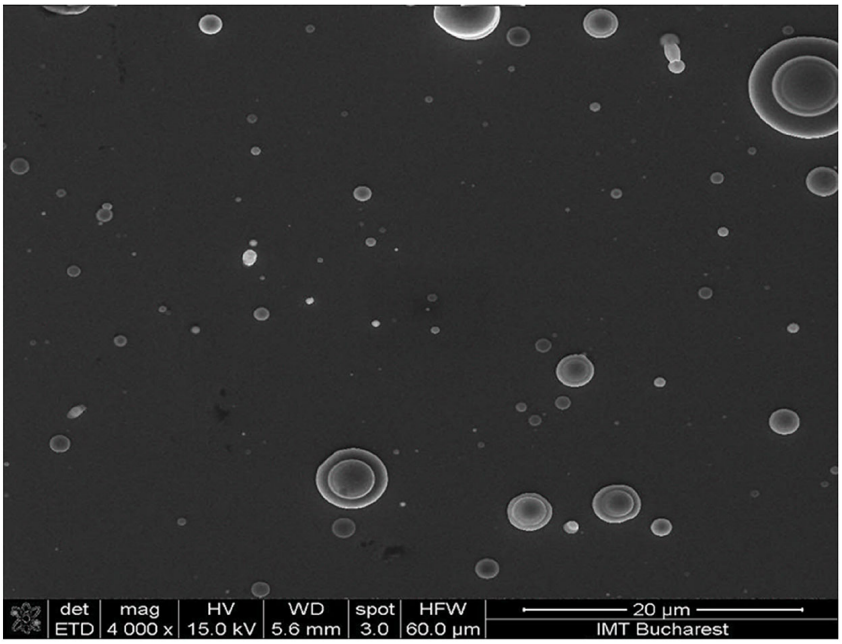

Fig.2. SEM image of the morphology of the thin film.

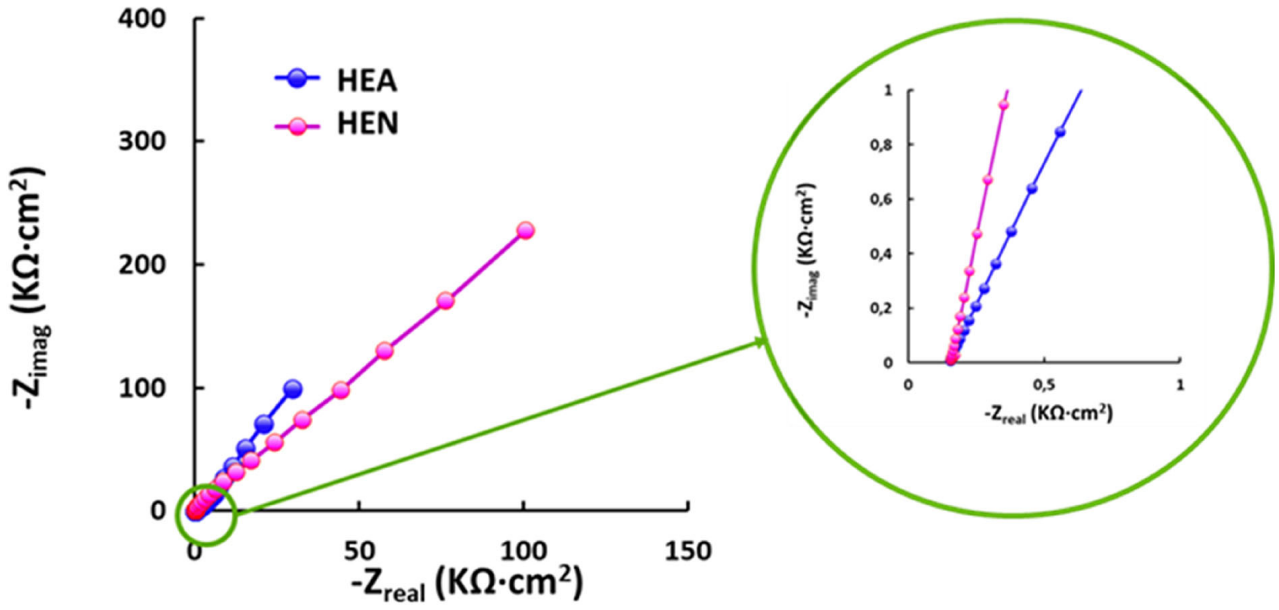

Fig.3. Nyquist plots for the two samples at corrosion potential in Ringer solution.

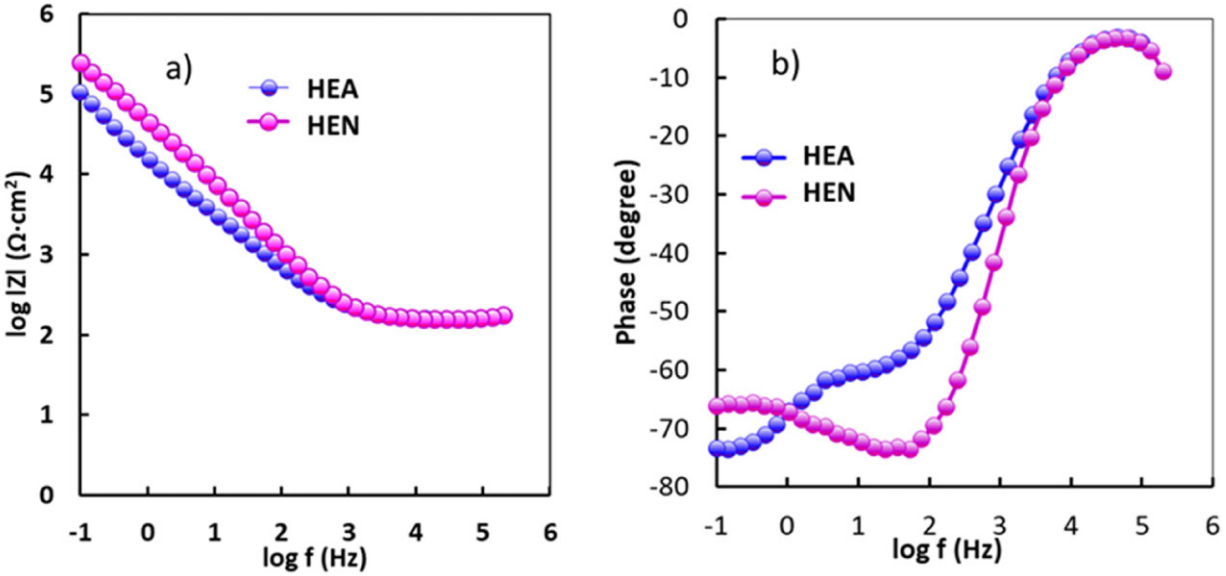

Fig.4. a) Bode-|Z| and b) Bode-phase for the samples in Ringer solution.

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