Codeposition of inorganic fullerene-like WS$_2$ nanoparticles in an electrodeposited nickel matrix under the influence of ultrasonic agitation

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** ABSTRACT **

The effects of ultrasound (US) agitation (at different intensities of ultrasound) on the codeposition of inorganic fullerene-like (IF) WS$_2$ in a metallic Ni matrix are investigated. The wt.% of IF-WS$_2$ particles in the nanocomposite coatings increases from 4.5 wt.% (in films grown under mechanical stirring but without US agitation) up to about 7 wt.% (in films prepared under US agitation at the optimum intensity of ultrasound). While composite coatings obtained only under mechanical stirring exhibit a rather irregular surface morphology, with pronounced 3D multimodal protrusions, a more uniform and compact coating is attained under application of US agitation. In turn, the introduction of WS$_2$ particles significantly modifies the growth of Ni, inducing grain size refinement, increasing the stacking fault probability and causing a drastic change of crystallographic texture. These microstructural features act in a synergistic manner to simultaneously increase the hardness of the composite coatings while causing the expected decrease in the friction coefficient (due to the presence of WS$_2$ solid lubricant particles), therefore enhancing the wear resistance, particularly when the coatings are deposited under the presence of US.

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1. Introduction

Transition-metal (TM) dichalcogenides (MoS$_2$, WS$_2$, NbS$_2$, etc.) are amongst the most commonly used solid lubricants for a wide range of applications, including aerospace and automotive technology, load bearing and release mechanisms, cutting tools, etc. [1–4]. These materials exhibit outstanding lubrication properties owing to a layered structure in which adjacent layers are weakly bonded by van der Waals forces. These two-dimensional layered compounds are not stable in the planar form and they tend to fold into closed-cage or tubular structures (i.e., inorganic fullerene-like particles, which were first described in 1992) [5]. Their unique morphology, spherical and closed structure without dangling bonds, confers them a chemical inertness and a high elasticity. Due to these exceptional characteristics, inorganic fullerene-like particles, such as IF-WS$_2$, have been established as a promising material to provide lower friction and wear [6,7]. Originally, these materials were prepared by mixing powders with organic or inorganic binders. This procedure was unsuitable for applications requiring the use of high-vacuum because of pronounced outgassing from the films. Later, coatings with analogous compositions were prepared by spray deposition or sputtering, which overcame the outgassing problem [8,9]. However, deposits consisting solely of TM dichalcogenides suffer from the drawback that they are mechanically soft, exhibit low endurance and oxidize relatively easily. Hence, self-lubricating composite coatings, constituted of IF particles embedded in a mechanically hard matrix (such as a metallic matrix), have emerged as alternative materials that combine excellent wear resistance with high strength and reasonably good corrosion resistance. In most cases, these composites are fabricated by sputtering and other physical vapour deposition techniques and contain relatively large amounts of TM dichalcogenide phases [10].

However, these techniques often require high temperatures, elevated pressures or expensive equipment, and the degradation of some particles takes place easily. Because of these restrictions, electrodeposition techniques have been established as a suitable method to prepare these materials [11–13]. The use of electrodeposition techniques to produce this type of composite coatings has been demonstrated more recently and has been much less...
exploited. In particular, the incorporation of IF-WS₂ nanoparticles into electrodeposited metallic matrices has been scarcely reported [14–16]. Interestingly, good combination of properties can be obtained with relatively low amounts of IF particles in the films, making it a promising technique to obtain self-lubricating surfaces [17].

On the other hand, the electrodeposition technique and, as a consequence, the properties of the coating, depend on several variables, such as electrolyte formulation, temperature, current density and hydrodynamic conditions, being the dispersion of particles in the electrolyte one of the most critical parameters [18,19]. To promote a homogeneous dispersion of particles, several strategies have been attempted, such as the incorporation of additives as chemical dispersion agent [20–22], or the application of ultrasonic energy. In particular, the deposition of composites under the influence of ultrasounds has received significant attention due to its potential benefits, which include deagglomeration of particles, enhancement of the particle codeposition rate and improvement of the content and uniformity of particles in the metal matrix [23–26].

Remarkably, although metal/IF-WS₂ systems are promising composite coatings that can find wide range of applications, there are very few works studying the electrodeposition process in a systematic manner. In particular, the role of ultrasound agitation on the codeposition of IF-WS₂ in an electrodeposited nickel matrix has not been investigated yet. Thus, in this work, attempts have been made to analyze the effect of ultrasound agitation (different US intensities) on the morphological, structural and functional properties of the Ni/IF-WS₂ coatings.

2. Experimental

Ni/IF-WS₂ nanocomposite coatings were electrolytically deposited from a standard nickel Watts bath to which industrial grade IF-WS₂ nanoparticles (NanoMaterials, Ltd.) were added. Nickel Watts bath was selected as it is one of the most popular electrolytes for functional applications.

First attempts performed in order to obtain Ni/IF-WS₂ composite coatings from Ni Watts electrolyte without additives at low WS₂ concentrations (0.1–1.0 g L⁻¹), led to irregular nickel coatings with no incorporation of WS₂ nanoparticles. When higher WS₂ concentration (5–100 g L⁻¹) were tested, a black film on the surface of the substrates was observed after electrodeposition, formed by loosely adhered WS₂ nanoparticles that were removed after ultrasound water cleaning. Under these conditions, no nickel coating was detected which would indicate that high concentration of conductive WS₂ nanoparticles in the electrolyte provokes their deposition by electrophoretic forces, inhibiting the electrodeposition of the nickel.

In order to enhance the codeposition of the WS₂ nanoparticles and improve the quality of the composite coating, a cationic surfactant was used. In particular, the surfactant CTAB (cetyl trimethyl ammonium bromide) was chosen as it is a cationic surfactant with a high ability to strongly bond to nanoparticles surface [27].

The results indicated that the incorporation of the cationic surfactant promoted the codeposition of the WS₂ nanoparticles. Current density, additive concentration and nanoparticle loading were selected based on non-published preliminary results. The detailed bath composition and experimental process parameters are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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</tr>
<tr>
<td>Temperature, °C</td>
<td>55</td>
</tr>
<tr>
<td>Current density, A dm⁻²</td>
<td>5.0</td>
</tr>
<tr>
<td>Electrodeposition time, h</td>
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</tr>
<tr>
<td>Agitation system</td>
<td>Mechanical stirring (300 rpm)</td>
</tr>
<tr>
<td></td>
<td>ultrasonic stirring (24 kHz)</td>
</tr>
<tr>
<td></td>
<td>(20, 30 and 40 W cm⁻²)</td>
</tr>
</tbody>
</table>

IF-WS₂ was added to the nickel Watts electrolyte and the suspensions were intensively stirred using a magnetic stirrer (300 rpm) for at least 24 h at room temperature prior to the codeposition experiments. Immediately before the electrodeposition process, the suspensions were submitted to a 10-min ultrasonic pretreatment to avoid agglomeration. The ultrasonic irradiation was given by means of an UP200S ultrasonic processor horn type (24 kHz, maximum nominal power 180 W, Hielsher Ultrasonics GmbH) equipped with a sonotrode S14 (14 mm tip diameter) adjusted at 55% vibration amplitude.

Cylindrical glass cells with volumes of 200 mL were used for the codeposition experiments. Coatings were deposited on flat commercial mild steel (grade St37) cathodes of 3 cm². The anode was a pure nickel foil (3 cm²) positioned on the side of the vessel, face to face to the cathode. The distance between anode and cathode was 4 cm. The substrates were degreased, rinsed in cold distilled water, activated in a 15% HCl solution (1 min) and rinsed in distilled water again. Electrocodeposition was carried out at a constant current density of 5.0 A dm⁻² during 1 h using a DC power supply (5 A/30 V, BLAUSONIC FA-350). In order to maintain a uniform particle concentration in the bulk solution, two agitation methods were used during the electrodeposition process: mechanical agitation by a magnetic stirrer (ω = 300 rpm) located at the bottom of the cell, and ultrasonic energy by an ultrasonic probe which was directly immersed into the solution from above and accurately positioned between the working and counter electrodes in a way that there was no shielding. The ultrasonic irradiation was given by means of the same ultrasonic processor horn type and sonotrode. The intensity of the ultrasound directed to the electrochemical system was varied by controlling the amplitude of the vibration tip. In this study, vibration amplitude was adjusted to 25, 55 and 75% in a continuous mode, corresponding to an ultrasonic intensity of 20, 30 and 40 W cm⁻² respectively, measured by a processor connected to an ultrasonic power meter (Hielsher Ultrasonics). The experimental set-up is described in more detail in previous works [28]. The electrolyte temperature was maintained at 55 °C using a thermostat (Polyscience, 9106 model). Temperature was measured before and after each experiment. Temperature increase due to ultrasonic energy did not exceed 2–4 °C. After electrolysis, the samples were ultrasonically cleaned in ethanol for 1 min to remove loosely adsorbed particles from the surface.

The morphology of the surface and cross-section of the coatings were examined by scanning electron microscopy (SEM and FE-SEM) (JEOL JSM 5500LV and CARL ZEISS ULTRA PLUS, respectively). The weight percentage of IF-WS₂ incorporation was determined from cross-sections photomicrographs using an energy dispersive X-ray (EDX) microanalyser coupled to the SEM. The amount of WS₂

Table 1 Bath composition and deposition conditions for Ni/IF-WS₂ composite coatings.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration/g L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulphate (NiSO₄·6H₂O, Sigma–Aldrich ACS reagent 99%)</td>
<td>250</td>
</tr>
<tr>
<td>Nickel chloride (NiCl₂·6H₂O, Sigma–Aldrich 99.9%)</td>
<td>45</td>
</tr>
<tr>
<td>Boric acid (H₃BO₃, Sigma–Aldrich ACS reagent 99.5%)</td>
<td>40</td>
</tr>
<tr>
<td>CTAB (cetyl trimethyl ammonium bromide, Sigma–Aldrich, 99%)</td>
<td>0.2</td>
</tr>
<tr>
<td>IF-WS₂ (NanoMaterials, Ltd.)</td>
<td>1</td>
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Deposition conditions

<table>
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<th>Parameters</th>
<th>Value</th>
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<td>(20, 30 and 40 W cm⁻²)</td>
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</table>
was examined at five different locations of each coating and the average weight percentage of these particles was calculated.

The phase percentages and microstructural parameters of the different coatings were evaluated by X-ray diffraction (XRD), using Cu Kα radiation, in the Bragg–Brentano geometry operating in a step scan mode (Panalytical X’Pert PRO MRD). The values of cell parameters, crystalite sizes (i.e., average coherent diffraction length, <D>, microstrains (\(\varepsilon^2\)), and stacking fault probability (\(\alpha_{sf}\)) were quantified by means of data analysis program based on a full pattern fitting procedure (Rietveld method) [29–31]. Crystalite sizes and microstrains were determined using the Delft model while stacking fault probabilities were evaluated according to the Warren formulae [32]. According to Warren, 1/\(\alpha_{sf}\) indicates the average number of layers between two consecutive stacking faults.

TEM characterization was carried out on a JEOL JEM-2011 microscope operated at 200 kV. For the TEM observations, the substrates were removed by grinding with SiC paper (grit 1000 and 4000) and the films were subsequently thinned by ion milling, which was performed from both sides of the deposits in order to remove any surface contamination.

The mechanical properties (hardness, reduced elastic modulus and elastic recovery) were evaluated by means of nanoindentation, using an UMI device from Fischer–Cripps Laboratories equipped with a Berkovich pyramidal-shaped diamond tip, operating in the load control mode. Nanoindentation tests were performed on the cross sections of the coatings, after careful polishing using SiC paper and diamond paste. The maximum value of applied load was 30 mN to ensure that the lateral size of the indentation imprint was smaller than the film thickness. The thermal drift during nanoindentation was lower than 0.05 nm/s. Proper corrections for the contact area (calibrated with a fused quartz specimen), instrument compliance, and initial penetration depth were applied. The hardness (H) and reduced elastic modulus (\(E_r\)) values were evaluated from the load–displacement curves using the method of Oliver and Pharr [33]. From the initial unloading slope, the contact stiffness, S, was determined as:

\[
S = \frac{dP}{dh}
\]  

where \(P\) and \(h\) denote the applied force and the penetration depth during nanoindentation, respectively. The reduced Young’s modulus was determined based on its relationship with the contact area, \(A\), and contact stiffness [34]:

\[
S = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A}
\]

where \(\beta\) is the King’s factor, that depends on the geometry of the indenter (\(\beta = 1.034\) for a Berkovich indenter). The reduced modulus takes into account the elastic displacements that occur in both the specimen, with Young’s modulus \(E\) and Poisson’s ratio \(\nu\), and the diamond indenter, with elastic constants \(E_1\) and \(\nu_1\) (for diamond, \(E_1 = 1140\) GPa and \(\nu_1 = 0.07\)):

\[
\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_1^2}{E_1}
\]

The hardness was calculated from the following expression:

\[
H = \frac{P_{\text{max}}}{A}
\]

where \(P_{\text{max}}\) is the maximum load applied during nanoindentation. Finally, the elastic recovery was evaluated as the ratio between the elastic and the total (plastic + elastic) energies during nanoindentation, \(W_{\text{el}}/W_{\text{tot}}\). The values of \(W_{\text{el}}\) were calculated from the area between the unloading curve and the displacement axis. In turn, \(W_{\text{tot}}\) is the area between the loading curve and the displacement axis [35]. The results presented in this work are the statistical average of a set of 25 indentations for each sample.

Friction coefficients were measured using a ball-on-disk tribometer (CSM, model THT) at room temperature. A 100Cr6 steel ball with a diameter of 6 mm was used as counterface material. The tests were conducted under a normal load of 1 N, with a rotation diameter of 3 mm at a sliding distance of 1600 m and a sliding speed of 17 cm s\(^{-1}\). The calculated initial Hertzian contact pressure was 3.8 GPa [36].

3. Results and discussion

3.1. Characterization of the particles

Fig. 1 shows a SEM micrograph of the WS\(_2\) nanopowder. The particles possess an irregular spherical shape and a broad size distribution (from 40 to 120 nm). Moreover, the nanoparticles were prone to agglomerate due to attractive van der Waals forces and, while nanometer features were still observable, the clusters acquired sub-micron size spherical shapes (about \(\Omega = 600\) nm).

The TEM image of an IF-WS\(_2\) nanoparticle (Fig. 2(a)) tends to feature the typical hollow closed-cage structure. However, the morphology is not that of a perfect onion–like sphere and, in some cases, semispherical or polyhedral-shaped particles are observed. The average size of the particles is 50 nm, whereas the interlayer spacing is \(\sim 0.62\) nm [37], characteristic of hexagonal WS\(_2\) (S.G.: P63/mmc, PCPDF: 08-0237). The corresponding Fast Fourier Transform (FFT) shows spotty rings belonging to \((002), (1 0 1)\) and \((1 0 3)\) crystallographic planes (inset of Fig. 2(b)).

3.2. Characterization of the Ni/IF-WS\(_2\) composite coatings

3.2.1. Composition analysis

In order to analyze the effect of ultrasound agitation on the WS\(_2\) content in the composite, Ni/IF-WS\(_2\) composite coatings were obtained from nickel Watts electrolytes under mechanical and ultrasonic agitation at different US intensities. Fig. 3 shows that US agitation has significant effect on the weight percentage of the particles incorporated into the metal deposit. The results indicate that the wt.% of WS\(_2\) particles in the nickel matrix increases with ultrasound intensity up to 30 W cm\(^{-2}\) and slightly decreases at higher intensity values. Thus, the mean wt.% of particles incorporated in the nickel matrix ranges from about 4.5% under mechanical agitation (with no US) to about 7% when the composite coatings are obtained under US agitation (30 W cm\(^{-2}\) US intensity). The enhancement on particle incorporation observed under ultrasonic agitation might be due to the combined effect of forced convection of the electrolyte suspension that promotes the particle transport to the cathode and the increase in the number of individual particles produced by ultrasound. In this sense, the effective particle
dispersion and the deagglomeration effect obtained through the application of ultrasound to the electrolytic bath would lead to an increase in the density of particles. The smaller the agglomerated WS$_2$ particle groups, the higher the opportunity for attraction by the electric field, making the adsorption stronger and more effective [24] and leading to an increase in the particle incorporation. On the other hand, the slight decrease of the wt.% of WS$_2$ incorporated in the nickel matrix at the largest US intensity studied (40 W cm$^{-2}$) would indicate that too much agitation negatively affects particle codeposition, probably because the intense force convection of solution and large cavitation volumes (bubble size and/or number) tends to remove the loosely adsorbed WS$_2$ nanoparticles from the cathode surface before they are built in [38–40].

3.2.2. Morphology and structure

The surface morphology of the composite coatings obtained under mechanical and ultrasonic agitation was analyzed by SEM and is illustrated in Fig. 4. In the case of silent electrodeposition, the Ni/IF-WS$_2$ composite coatings does not show a coherent coating, but severe irregular surfaces characterized by 3D multinodal protrusions (WS$_2$-rich, as determined by EDX) were observed. As a consequence of the big size and broad distribution of these protrusions, the surface of these coatings presents a high roughness ($R_a \approx 3.19 \pm 0.20 \mu$m). Among these protrusions, the typical pyramidal structure of pure nickel growth is sometimes distinguished [28].

When applying ultrasonic agitation, a change in the topography of the composite coatings is induced. Namely, there is an enhancement of the compactness of the nickel film accompanied by a reduction in the grain size of nickel. The roughness of the surface decreases, although high values of $R_a$ (from 2.54 to 1.88 μm) compared to those of pure Ni ($R_a = 0.71 \pm 0.04 \mu$m) are still attained, as a result of the presence of WS$_2$ agglomerates on the surface of the films. The most compact coatings were obtained under ultrasonic agitation at 30 W cm$^{-2}$ US intensity.

The cross-section analysis of the composite coatings provided more information about the growth mechanism of the Ni/IF-WS$_2$ films (Fig. 5). Under mechanical agitation, the Ni/IF-WS$_2$ composite coatings consist of an initial Ni-rich layer (∼10 μm thick) well adhered to the substrate, containing a small percentage of WS$_2$ nanoparticles (Fig. 5(a)). From this initial uniform layer, irregular 3D protuberances of nickel with a higher proportion of IF-WS$_2$ adsorbed particles grow outwards until ∼40 μm. As the film thickness increases, the width of these structures increases. Finally, these protuberances gradually merge leaving voids of irregular shaped pores with sizes of about 15 μm. This growth mechanism, very different to that we have observed for the codeposition of other nanoparticles (e.g., Al$_2$O$_3$, SiC) [28,41], has also been described for the electrodeposition of Co/IF-WS$_2$ [14] and Ni/WC composite coatings [40]. These systems have in common that the codeposited particles are all electrically conductive. Thus, the way metal grows around particles during the electrodeposition process greatly depends on the properties of their surface. Because IF-WS$_2$ nanoparticles are electrically conductive, particles in contact with the electrode probably have a potential close to the potential of the electrode. Therefore, metal deposition occurs both on the particle and the electrode, and hence, the growth profile follows the shape of the particle [42], giving rise to the multinodal protrusions. By the application of ultrasound agitation, a more uniform and compact coating was obtained (Fig. 5(b)). Thus, grain coalescence and two-dimensional growth were encouraged and denser deposits of approximately the same thickness (∼40 μm) were observed. Good adhesion between coating and substrate was observed both under silent and ultrasound agitation at 30 W cm$^{-2}$ US intensity.

TEM characterization of the composites unambiguously reveals the incorporation of WS$_2$ particles within the Ni matrix for the

![Image](https://example.com/image1.png)

**Fig. 2.** (a) TEM and (b) HRTEM images of IF-WS$_2$ nanoparticles. The corresponding FFT is shown as an inset in (b).

![Image](https://example.com/image2.png)

**Fig. 3.** Effect of ultrasound agitation (different US intensities) on the wt.% of IF-WS$_2$ particles in the nickel composite coating.
coatings prepared both without and with the assistance of ultrasound. Fig. 6(a) shows the TEM image of the composite prepared without ultrasound, revealing the presence of WS$_2$ nanoparticles embedded in the Ni matrix (as pointed by the white arrow). Fig. 6(b) shows a magnified detail of another region of the composite. The corresponding selected area electron diffraction (SAED) pattern is shown in the inset. The spotty rings can be assigned to Ni fcc and hexagonal WS$_2$, as indicated in the figure. The same holds for the composite prepared with ultrasonic agitation (Fig. 6(c)). The FFT performed at different locations of the composite film demonstrated that the IF-WS$_2$ nanoparticles had been successfully codeposited with Ni.

The influence of WS$_2$ particles on the structure of the nickel electrodeposits was investigated by XRD methods. Fig. 7 shows the XRD patterns of the different coatings, where the main peaks, corresponding to fcc Ni, have been Miller indexed. Plotting the data in root mean square scale reveals the presence of some additional small peaks (see Fig. 8), which match the angular positions of the hcp WS$_2$ and bcc Fe phases, the latter coming from the steel substrate. From Fig. 7 it can be inferred that incorporation of the WS$_2$ particles causes important microstructural changes during the growth of the composite coatings. First, the Ni film prepared from the Watt’s solution grows preferentially along the (2 0 0) direction. When WS$_2$ particles are incorporated to the coating, a change in the crystallographic texture is observed and the intensities of the (1 1 1), (2 2 0) and (3 1 1) peaks increase at the expense of the (2 0 0) reflection. A change in the preferred texture has been observed in pure Ni films as a function of the applied current density during electrodeposition [43] but also in Ni/Al$_2$O$_3$ and Ni/TiO$_2$ composite films with the incorporation of the ceramic particles [44].

Additional microstructural effects can be obtained from Rietveld refinements of the XRD patterns. One of the curves generated from the full pattern fitting procedure is shown in Fig. 8, together with the experimental XRD data and the corresponding Miller indexes. Rietveld calculations indicate that the WS$_2$ phase percentage is around 5–7 wt.% for all the composite coatings, in agreement with the results from EDX compositional analysis (Fig. 3). Average values of microstrains for the WS$_2$ phase are around $3 \times 10^{-3}$, for all deposition conditions. The incorporation of the WS$_2$ particles drastically reduces the crystallite size of fcc Ni, from 200 nm in pure Ni to values around 85–100 nm in the Ni/IF-WS$_2$ composites (see Table 2). Grain size refinement can be understood on the basis that uniformly distributed WS$_2$ particles could restrain the growth of Ni crystals during electrodeposition. Nevertheless, the modifications that the CTAB itself can partially induce on the Ni matrix cannot be ruled out as has been pointed in the literature [45]. An increase of the stacking fault probability is observed after incorporation of the WS$_2$ particles in the coating. Furthermore, the microstrains increase when the WS$_2$ particles are introduced in the coating in absence of US agitation. While no pronounced influence of the US agitation is observed

![Fig. 4](image-url). SEM micrograph presenting the surface morphology of Ni/IF-WS$_2$ composite coatings obtained under (a) mechanical agitation and ultrasound agitation (b) at 20 W cm$^{-2}$ US intensity, (c) at 30 W cm$^{-2}$ US intensity, and (d) at 40 W cm$^{-2}$ US intensity.

![Fig. 5](image-url). SEM cross-sectional image of Ni/IF-WS$_2$ composite coating obtained under (a) mechanical agitation and (b) US agitation (30 W cm$^{-2}$ US intensity).
on the crystallite size, a progressive decrease of microstrains in fcc-Ni is found with the increase of the US intensity.

3.2.3. Physical properties
3.2.3.1. Mechanical properties. Representative load–displacement nanoindentation curves corresponding to the several investigated films are shown in Fig. 9. The maximum depth at the end of the loading segment is larger for pure Ni than for any Ni/IF-WS2 sample. This is indicative that the presence of WS2 particles in the coating brings about an increase of the hardness. Interestingly, the US agitation tends to further reduce the maximum penetration depth. The overall dependence of H on the US intensity is shown in Fig. 10(a). An increase of H is indeed observed when the composite coating is grown under US agitation. A two-fold increase in H (from 3.5 GPa for pure Ni up to almost 7 GPa for Ni/IF-WS2 US 30 W cm$^{-2}$ and Ni/IF-WS2 US 40 W cm$^{-2}$) is achieved. The influence of WS2 on the

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**Table 2**

Structural parameters corresponding to the Ni phase, as obtained from Rietveld refinements of the XRD patterns. Note that $<D>_{>0}$, $<\varepsilon^2>_{>0}^{1/2}$ and $\alpha_{WS2}$ denote the average coherent diffraction length (or crystallite size), the microstrains and the stacking fault probability (see text for details).

<table>
<thead>
<tr>
<th>Material</th>
<th>$&lt;D&gt;_{&gt;0}$ (±10 nm)</th>
<th>$&lt;\varepsilon^2&gt;_{&gt;0}^{1/2}$ (±5 $\times$ 10$^{-5}$)</th>
<th>$\alpha_{WS2}$ (±1 $\times$ 10$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>200</td>
<td>6.0 $\times$ 10$^{-4}$</td>
<td>3 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>Ni/IF-WS2</td>
<td>140</td>
<td>8.4 $\times$ 10$^{-4}$</td>
<td>3.5 $\times$ 10$^{-3}$</td>
</tr>
<tr>
<td>Mechanical agitation</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ni/IF-WS2</td>
<td>100</td>
<td>5.5 $\times$ 10$^{-4}$</td>
<td>2.5 $\times$ 10$^{-3}$</td>
</tr>
<tr>
<td>US (20 W cm$^{-2}$)</td>
<td>85</td>
<td>4.3 $\times$ 10$^{-4}$</td>
<td>3.0 $\times$ 10$^{-3}$</td>
</tr>
<tr>
<td>Ni/IF-WS2</td>
<td>90</td>
<td>3.2 $\times$ 10$^{-4}$</td>
<td>2.0 $\times$ 10$^{-3}$</td>
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<td>US (30 W cm$^{-2}$)</td>
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<tr>
<td>Ni/IF-WS2</td>
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<tr>
<td>US (40 W cm$^{-2}$)</td>
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</table>
hardness of the deposits is also evident in panels (b) and (c) of Fig. 9, which reveal that the lateral size of the indentation imprints, obtained after applying a maximum load of 30 mN, is much smaller in the Ni/IF-WS2 US 30 W cm$^{-2}$ composite than for pure Ni films.

The hardness of IF-WS2 is rather low, generally lower than 3 GPa [1]. That is why WS2 particles (and other solid lubricants, such as MoS2 or graphite) are often considered as soft materials and their presence cannot explain, by itself, the observed increase of hardness in the investigated Ni/IF-WS2 composite coatings. In fact, a reduction of hardness has been reported in certain metal–WS2 composite films (e.g., Ni–P/WS2 electroless deposited coatings) as a consequence of the introduction of the soft WS2 particles in the hard Ni–P matrix [46]. Hence, the observed increase of hardness in the herein investigated films is ascribed to the microstructural changes (mainly, the crystallite size refinement and the change of preferred orientation) accompanying the incorporation of the WS2 particles in the deposits. With the decrease in the crystallite size, the motion of dislocations is progressively hindered to a higher extent by the larger amount of grain boundaries, hence leading to piling up of dislocations and the consequent increase of stress concentration (Hall–Petch strengthening) [47]. The increase of the stacking fault probability (Table 2) can also contribute to the enhancement of hardness, since this type of planar defects impose barriers for dislocation propagation in a similar way as high-angle grain boundaries [30]. Besides crystallite size refinement, the changes observed in the crystallographic texture of the films can also partially account for the increase of hardness. In fcc metals, like Ni, there are twelve slip directions (i.e., the three $<110>$ directions along the four $\{111\}$ slip planes). During nanoindentation, a net compressive stress is applied perpendicular to the sample plane ($z$ direction). If the film shows a preferred $\{200\}$ texture, then the $<110>$ directions are oriented at $45^\circ$ with respect to the $z$-direction, which is the ideal case for plastic flow, according to the Schmidt’s law. Hence, from the textural point of view, a lower hardness is indeed expected in pure Ni film, which exhibits a $\{200\}$ texture [43].

Fig. 10. Dependence of (a) hardness, $H$, (b) reduced Young's modulus, $E_r$, (c) elastic strain to failure, i.e. $H/E_r$ ratio, and (d) elastic recovery, $W_r/W_{tot}$, as a function of the intensity of the ultrasound signal. Note that the values corresponding to the Ni coating are indicated with discontinuous lines.
Contrary to what is observed for the hardness, the influence of WS2 on the Young’s modulus of the coatings is more modest (Fig. 10(b)). According to Eq. (3) and assuming a Poisson’s ratio of 0.31 [48], the Young’s modulus of pure Ni film is 152 GPa (close to the Er value). Values of Er ~ 150 GPa are obtained for all the Ni/IF-WS2 composite films, which closely match the Young’s modulus for pure Ni. This result could be expected bearing in mind the low phase percentage of WS2 in the films.

Nanoindentation data also provide information about the so-called elastic recovery of the films, which is proportional to the \( W_{el}/W_{tot} \) ratio. This parameter is of particular interest in applications such as impact loading since it indicates how much energy is elastically released from the material after it has been loaded. In general, there is no direct correlation between \( H \) and the elastic recovery. However, a relationship has indeed been established between \( W_{el}/W_{tot} \) and \( H/E_r \) with the aid of finite element simulations performed on a wide variety of elastic–plastic materials [49,50]. As shown in Fig. 10(d), the \( W_{el}/W_{tot} \) ratio tends to increase with the incorporation of WS2 particles in the coatings and is also roughly proportional to the US intensity. The higher elastic recovery of the composite coating can be possibly attributed to the elastic nature of the WS2 nanoparticles, in contrast to the rather plastic nature of the nickel film.

3.2.3.2. Tribological properties. Preliminary ball-on-disk tests were performed to evaluate the friction properties of the electrodeposited composite coatings. Fig. 11 presents the variation of the friction coefficient of pure Ni and Ni/IF-WS2 composite coatings obtained under mechanical and ultrasound agitation as a function of the sliding distance. It is observed that the incorporation of IF-WS2 particles significantly decreases the friction coefficient of the pure nickel coatings, which becomes further reduced with the increase of the US intensity (an overall reduction of about 40% is attained), confirming that application of this solid lubricant improved lubricity of the coating. Codeposition of moderate amounts of IF-WS2 particles on the coatings surface is considered the main reason for the reduced friction coefficient. Indeed, the agglomerates of IF-WS2 are very soft and can split into individual nanoparticles under light loads and shear movement [51]. The IF-WS2 nanoparticles can provide an effective rolling friction mechanism and serve as spacers, preventing asperity contact between the mating surfaces. Although the incorporated nanoparticles in the Ni/IF-WS2 composite coating are not free to offer rolling friction, some IF nanoparticles can be released to the mating interface under the testing conditions, thus providing a lubricating effect and reducing the friction. These results are similar to those observed for other composite coatings containing solid lubricants [1,51–53].

Since the volume of matter removed from the coating is proportional to the frictional coefficient [54], a higher wear resistance for the Ni/IF-WS2 films prepared using US agitation with higher intensity is expected. Besides the low friction of WS2, which originates from the weak van der Waals’ forces between the basal planes of the hcp layered structure of the crystal lattice [17,46], the microstructural changes that occur in Ni and the concomitant increase of hardness (Fig. 10(a)), can also contribute to the improvement in the wear resistance. To some extent, ball-on-disk tests can be correlated with the results from nanoindentation. Actually, the wear resistance of a thin film not only depends on its hardness (typically harder materials exhibit a higher wear resistance) but also on the reciprocal of the reduced Young’s modulus. Namely, the elastic strain to failure, which is related to the \( H/E_r \) ratio, has been sometimes shown to be a suitable parameter to describe the wear resistance of a coating from nanoindentation results, rather than \( H \) itself [55,56]. As shown in Fig. 10(c), the \( H/E_r \) ratio increases with the intensity of the US signal and it is also larger for Ni/WS2 composites than for pure Ni films.

4. Conclusions

In this study, a comprehensive investigation of the effect of mechanical and ultrasound agitation (at different US intensities) on the properties of electrodeposited Ni/IF-WS2 nanocomposite coatings has been performed.

It has been shown that Ni/IF-WS2 composite coatings obtained only under mechanical agitation stirring (with no ultrasound) present an irregular surface formed by 3D multinodular protrusions, connected to the electrically conductive nature of the IF-WS2 nanoparticles. By the application of ultrasound agitation, a more uniform and compact coating is achieved. Moreover, the application of ultrasound agitation has a significant effect on the weight percentage of the particles incorporated in the metal deposit. Thus, the wt.% of IF-WS2 particles in the nickel matrix increases from 4.5 wt.% (in films grown under mechanical agitation only) to about 7 wt.% (in films prepared under ultrasound agitation at 30 W cm\(^{-2}\) of US intensity).

Usually, because of the inherent properties of IF-WS2 particles, their inclusion into metallic coatings results in lower friction coefficient but also in lower mechanical strength, as compared to the metallic film without particles. However, our results reveal that the introduction of WS2 particles also significantly modifies the growth of Ni, inducing grain size refinement, increasing the stacking fault probability and causing a drastic change of crystallographic texture. These microstructural modifications act in a synergistic manner to simultaneously increase the hardness while causing a decrease in the friction coefficient, therefore enhancing the wear resistance. These effects are more pronounced if US agitation is used during electrodeposition.

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References


