Synthesis and corrosion resistance of Cu-Al-N nanostructured thin films deposited through magnetron sputtering

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Abstract

Cu-Al-N thin films were deposited by means of the unbalanced magnetron cosputtering technique, varying the pulsed DC source power that is associated with the aluminum target. The structural characterization, done through x ray diffraction (XRD) and transmission electronic microscopy (TEM), showed that the films were nanocrystalline, with a crystallite size of an order of magnitude of 10 nm. According to the chemical composition results, they consisted of a Cu-Al phase, copper nitride and aluminum nitride, that depended on the deposition power. The electrochemical characterization was performed by means of Tafel extrapolation and electrochemical impedance spectroscopy (EIS). The Tafel results showed a decrease in the corrosion current with an increase in the power, and the electrochemical impedance results showed an inductive behavior at low frequencies.

Introduction

Copper is one of the most important industrial materials, because it has a wide variety of applications due to its properties, such as its good electrical and thermal conductivity. Copper mixed with several elements opens up the possibility for thousands of alloys, of which many are technologically and industrially relevant [1, 2]. An alloy with other elements can modify some properties, such as the mechanical strength, wear resistance, and corrosion resistance [1, 2]. Copper alloys are included in the preferred alloys for marine applications due to their corrosion resistance in marine and seawater environments, but they corrode under specific conditions, such as selective corrosion, erosion corrosion, cavitating, etc [3]. That is why copper and its alloys are widely used in the electronic industry, pipes, heat exchangers, valves, steel-coated plates for small ship hulls, etc [3]. On the other hand, the study of nanocrystalline materials has demonstrated that they can afford an enhancement of its properties, such as mechanical ones, in comparison with the bulk material, so there is a growing interest in the production of nanocrystalline materials [4, 5]. Due to the easy management of the growth parameters using the sputtering technique and the capacity to obtain phases far from the solubility equilibrium, this technique is one of the most efficient for the deposition of nanocrystalline materials in the form of coatings or thin films [5]. An example of the versatility of the sputtering technique is the research of Jianyun Zheng et al [6–9] in which TiN/TiCN multilayers were deposited via DC magnetron sputtering and the effect of different parameters, as thickness and plasma treatment after deposition, was studied. Jianyun Zheng et al [6, 7] found that for the films without treatments the hardness increase with the number of bilayers, but its value is close to the hardness of TiCN and TiN/TiCN films, despite the greater thickness of the TiN/TiCN multilayers. The wear resistance did not vary significantly in comparison with others hard coatings, but the service life increased because of the greater thickness. With a argon plasma treatment [9] the films experience a recrystallization process, so that its density increased, the thickness decreased and the interface between layers become blurred. The hardness of the multilayers increased with the treatment time, and the friction coefficient decreased. Finally, with a plasma nitriding treatment [8] a change in the composition of the uppermost layer of the films was observed, forming C–N bonding, and TiN phase with the disociation of the TiC phase. This cause a lower
hardness in comparison with the films without treatment but a better tribologic behavior was observed. On the other hand, several researchers have reported on the study of Cu-Al-N type films; for example, J Musil et al [10] deposited Al-Cu-N films through DC reactive unbalanced magnetron sputtering and studied their microstructure and hardness. The results show that a nanocomposite material is obtained with a grain size smaller than 10 nm, high hardness, and a relatively low Young’s modulus. M Shariati et al [11] studied the effect of the annealing process at different temperatures on the structure, morphology, and optical properties of Al-Cu-N coatings deposited via DC magnetron sputtering, finding that the crystallite size increases along with the annealing, as does the grain size, which in turn generates greater roughness and decreases reflectance. Li Xing’ao et al [12] found that the addition of Al to Cu3N films generates a change in the preferred orientation, a decrease in electrical resistivity, and an improvement in hardness.

In the present investigation, the structure, the chemical composition, and the electrochemical behavior of Cu-Al-N thin films deposited through unbalanced magnetron cosputtering at different powers of the source associated with the aluminum target are studied.

**Experimental details**

Thin films were deposited on phosphor bronze substrates through unbalanced magnetron cosputtering, using two targets, one of engineering-grade copper (99.9%) and the other of aluminum with 99.99% purity. The copper target was connected to an RF source and the aluminum one to a pulsed-DC power source. With the aim of varying the aluminum content in the films, four different degrees of pulsed-DC power were used: 15 W, 18 W, 21 W, and 26 W, keeping the rest of the parameters constant. A combination of Ar and N2, with flows of 5 sccm and 2.5 sccm, respectively, was used as the growth environment. The substrate temperature was kept at room temperature. A summary of the growth conditions is shown in Table 1 and a scheme of the sputtering system can be seen in Figure 1. The average thickness of the deposited thin films was approximately 112.9 ± 5.1 nm, which was measured by means of scanning electron microscopy (SEM).

| Sample Name | Cu-2Al-N | Cu-4Al-N | Cu-6Al-N | Cu-10Al-N |
|-------------|----------|----------|----------|-----------|
| Power: pulsed DC source (W) | 15 | 18 | 21 | 26 |
| Power: RF source (W) | 50 | 50 | 50 | 50 |
| Environment | Ar-N | Ar-N | Ar-N | Ar-N |
| Base pressure (Torr) | 6 × 10⁻⁶ | 6 × 10⁻⁶ | 6 × 10⁻⁶ | 6 × 10⁻⁶ |
| Working pressure (Torr) | 9 × 10⁻³ | 9 × 10⁻³ | 9 × 10⁻³ | 9 × 10⁻³ |
| Time (min) | 30 | 30 | 30 | 30 |
For the structural characterization, x-ray diffraction was used, with a Panalytical Empyrean diffractometer and a JEOL JEM 2200FS + CS transmission electron microscope. The compositional characterization, before and after the corrosion test, was done with an Escalab 250Xi x-ray photoelectron spectroscopy (XPS) that uses a monochromatic aluminum x-ray source and a JSM7401F SEM and EDS, in order to complement the post-corrosion analysis. The electrochemical characterization was carried out in an electrochemical cell with three electrodes, where the reference electrode was a saturated calomel electrode, the counter electrode was made of platinum, and the reference electrode was the substrate-film system. Potentiodynamic techniques were applied using Tafel extrapolation and electrochemical impedance spectroscopy (EIS) in an aqueous solution of NaCl at 3.5% using Gamry software.

Results and discussion

The XRD structural characterization showed that only the samples deposited at 15 W exhibited reflections (figure 2), which corresponded to the cubic structure of the Al_{0.6}Cu_{3.4} compound with a preferential orientation (1 1 1) and a crystallite size of 15.08 ± 0.001 nm. The films deposited at higher powers (18 W, 21 W, and 26 W)
did not show XRD peaks, which would indicate that the samples deposited at powers greater than 15 W can be amorphous or nanocrystalline. This will be complemented by means of TEM analysis.

For the majority of the Cu-Al-N films, no XRD signals were observed, so it was decided to carry out the analysis through transmission electron microscopy (TEM). Figure 3 shows that the electron diffraction pattern of the film deposited at 18 W consisted of circles, which were determined to be polycrystalline. This confirms that the films were nanocrystalline. The micrographs obtained with HRTEM (figure 4) reveal that the crystallites had a size of around 7–10 nm.

The analysis of the electron patterns showed that the film at 18 W was composed of AlN, Cu3N, Cu3Al, and metallic copper, all of them with a cubic structure. The reference PDFs used in order to determine the lattice planes were: 00-047-1088, 98-010-1641, 00-004-0836, and 00-034-0679. In the case of the films at 21 W, the results showed that they consisted of AlN, Cu3N, Cu3,4Al0,6, and metallic copper. From this it was inferred that an increase in power does not affect the formation of nitrides. The difference is in the appearance of Cu3,4Al0,6, so the power mainly affects the appearance of phases Cu-Al.

According to these results, the films were composed of two nitrides: AlN and Cu3N. Their identification is relevant, because in this case there are two poorly polarizable elements, aluminum and nitrogen, and a polarizable one, copper. In other words, nitrogen has more affinity with aluminum than with copper, which makes aluminum nitride formation more likely than copper formation. Nevertheless, the sputtering technique is known for allowing unstable phases to be obtained at room temperature and atmospheric pressure conditions. Because of this, the obtaining of Cu3N through the sputtering technique is not rare; several papers report it...
As mentioned in [17], copper has three locations in its matrix for non-metallic elements: in the net interstices, in the grain frontiers, and as compounds. Equally, a threshold is reported for the nitrogen quantity, below which the effect of nitrogen is to decrease the size of the material’s grain and above which nitride begins to form, decreasing the nitrogen’s effectiveness in reducing the grain size [17]. Therefore, aluminum and nitrogen addition generates a decrease in the grain size, making the films nanocrystalline.

Figure 5 shows the Cu2p2/3 and N1s signal spectra, and figure 6 shows the Al2s and O1s signal spectra of the films at 15 W and 21 W. The observed signal at ≈933.0 eV confirms the presence of copper nitride, and the ≈397.4 eV signal is associated with aluminum nitride. At the same time, Cu2p3/2 and Cu2p1/2 peaks can be seen, which indicates a mixed oxidation state. Furthermore, in the Cu2p3/2 signal, two contributions are evident, where the lower binding energy corresponds to Cu and the Cu–Al bond [18–22]. The one with the highest binding energy is the copper nitride one [23–28]. AlN is evident because of the aluminum signal’s shift towards higher binding energies, which has already been observed in other studies [29–31], and that explains the higher nitrogen electronegativity. The nitrogen signal has four contributions: the one in which the binding energy is around 399.7 eV is from Cu3N. It can be seen that at ≈398.7 eV there is a signal that is from Al-N-O in which, as mentioned in the paper by Leland Rosenberger et al. [29], nitrogen is in an intermediate environment of electron extraction and is denominated aluminum oxinitride. This is usually formed using two methods: The first consists of aluminum nitride oxidation, either by heating or by AlN barrage on the surface with argon ions, both cases in an oxygen atmosphere, and the second consists of aluminum oxide nitriding by several means, including reactive magnetron sputtering. In the N1s signal, there is a contribution from the nitrogen species dissolved in the coating, which, due to the rapid deposition, can be located between the grains by physisorption or adsorbed on the surface [25, 27, 28, 32]. Finally, the O1s signal has four contributions, two of them from the copper oxides and the aluminum oxides [18, 19, 29, 33], one due to the CuAl2O4 phase [22], and another due to the pollutants, such as observed oxygen species, for example O–N, or hydroxyls groups [19, 31, 34].

The XPS results for the rest of the thin films are similar, so that the binding energies do not exhibit a significant shift with the %Al variation. The same interactions are still observed: Cu, Cu-Al, Cu3N, AlN, CuO,
Al₂O, and CuAl₂O₄. However, the phase that is not defined is the one corresponding to the bond between the copper and the aluminum, which happens due to the signals' closeness. From other investigations [18, 20, 35], it is known that the Cu₂p copper peak exhibits a continuous shift towards higher binding energies as the aluminum quantity increases in a Cu-Al alloy, that is to say, there is electron cloud displacement towards the copper from the aluminum, due to copper’s higher electronegativity. Furthermore, previous investigations indicate that metallic copper signals are around the values of 932–932.6 eV, and for a Cu-Al alloy, depending on the quantity of the aluminum and other alloys, it is between 932.6 and 932.8 eV, where the higher value belongs to the CuAl₂ phase. Therefore, the observed slight shift (0.1–0.27 eV) of the Cu₂p signal for the films deposited at 26 W may be due to a shift of the Cu₃,₄Al₀,₆ to the Cu₃Al phase. The as-deposited composition obtained with XPS of the samples deposited at 15 W y 21 W is shown in the table 2.

From the XPS analysis, it can also be concluded that there is a variation in the phase’s proportions: the higher the aluminum power, the higher the percentage of Cu₃N, AlN, copper oxides, and aluminum oxides the films exhibit. On the other hand, the areas corresponding to the Cu-Al alloys do not vary significantly. Similarly, there is a decrease in the aluminum nitride quantity when establishing the Cu₃Al stoichiometric phase in the 26 W films. Conversely, the copper nitride proportion is independent of the Cu-Al compounds formed, and it increases along with the Al target power.

The electrochemical characterization results through TAFEL are shown in figure 7(a), in which it can be seen that the behavior of all the powers is similar. In the 21 W and 26 W films, it can be seen that they have corrosion currents very close to each other, being statistically the same (figure 7(b)). On the other hand, the corrosion current for these thin films is lower than the 15 W and 18 W power currents. Likewise, It can be seen that for the 15 W case, the electrochemical behavior does not show an improvement with respect to the substrate, since their Icorr are statistically equal, but for higher powers there is a decrease in this parameter with respect to the phosphor bronze.

The decrease in the corrosion current with the power increase can be explained by their morphology. The samples exhibited a nodular morphology, which has a nodule size that decreases with the power. A smaller size

| Signal | % Atomic |
|--------|----------|
| Al₂s   | 2.97     |
| Cu₃s   | 41.93    |
| N₁s    | 3.75     |
| O₁s    | 10.78    |
| Cu₂p   | 40.56    |

### Table 2. As deposited XPS composition of the 15 W and 21 W samples.

| % Atomic |
|----------|
| 15 W     |
| 21 W     |
| 3.29     |
| 42.46    |
| 3.62     |
| 9.34     |
| 41.29    |

Figure 8. Scanning electron microscopy pictures of the samples' surfaces after the corrosion test. (a) 15 W, (b) 21 W. An elemental characterization of the corrosion products was done through EDS. The results are similar for all the samples; therefore, the results for only one sample are shown. For the 21 W film.
grain decreases the possibilities for direct paths to the substrate for the electrolyte, which contributes to the films deposited at 21 W and 26 W exhibiting the lowest corrosion current density. On the other hand, in the XPS composition analysis, it can be seen that by increasing the power applied to the target Al, a greater proportion of copper and aluminum nitrides was able to be obtained. These are compounds that are characterized by having good corrosion resistance, which also contributes to the enhancement of the electrochemical behavior. In summary, the higher corrosion rate (which is directly related to the current density, \( \text{I}_{\text{corr}} \)) for the lower powers is explained by a more direct path, due to the morphology with bigger nodules, and by the lowest proportion of nitrides in its composition.

Figure 7(b) shows a comparison of the densities of the corrosion currents, measured for each of the films along with the reference samples (Cu-N and substrate). From this it can be concluded that except for the 15 W case, all the thin films exhibited better electrochemical behavior than bronze. The \( \text{I}_{\text{corr}} \) is an order of magnitude less than those of 21 W and 26 W. Thus the films exhibit better corrosion resistance than the substrate, but not better than Cu-N, having an \( \text{I}_{\text{corr}} \) close to that of the latter.

Figure 8 shows the corroded surface of the films deposited at powers of 15 W and 21 W. In these micrographs, taken at 1000X magnification, it can be seen, in addition to the corrosion residues, that some processes of localized corrosion or pitting are exhibited. This is confirmed upon analyzing the anodic part of the potentiodynamic polarization graph (figure 7), in which the pitting process and the passivating tendency to higher powers can be seen.

Table 3 shows the elemental composition results for the corrosion residues. It can be concluded that the corrosion residues are mainly composed of copper, oxygen, and carbon. Aluminum is, according to this result, consumed preferably in the corrosion process, while just a small quantity of it is observed in some surface regions [36, 37].

An XPS analysis of the corrosion products was done in order to better identify the compounds. Figure 9 shows the Cu2p3/2 signal of a coating at 15 W. The results are similar for all samples. The presence of satellite signals is evident; they are common for copper oxide. This oxide is the main corrosion product of copper and its alloys in aqueous solutions and allows the formation of the ions’ diffusion through the layer on the surface. The contribution to the CuCl signal can also be seen during the corrosion process that happens during the production of this oxide, following the reaction:

\[
\text{Cu} - e^- + 2\text{Cl}^- \rightarrow \text{CuCl}_2^-
\]
In conclusion, the typical corrosion residues of copper and its alloys were present: Cu$_2$O, CuCl, and CuCl$_2$, which matches the information obtained in the EDS elemental composition. The preferred aluminum dissolution was corroborated in the XPS analysis, since the aluminum signal was very weak (figure 9(b)). The N1s signal only has two contributions, one for each nitride present, so that the one with lower energy corresponds to AlN and the higher energy one to Cu$_3$N. From this it can be deduced that the aluminum observed in the composition analysis comes mainly from AlN. The composition obtained with XPS of the samples deposited at 15 W y 21 W after corrosion test is shown in the table 4.

For the intermetallic compounds between copper and aluminum, the corrosion reactions are the following:

$$\text{CuCl}_2^{-} \rightarrow \text{CuCl} + \text{Cl}^-$$

$$2\text{CuCl}_2^- + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} + 4\text{Cl}^-$$

Table 4. XPS composition of the 15 W and 21 W samples after corrosion test.

| Signal | % Atomic 15 W | % Atomic 21 W |
|--------|---------------|---------------|
| Al2s   | 0,75          | 0,14          |
| C1s    | 69,07         | 68,7          |
| N1s    | 1,09          | 0,88          |
| Cu2p   | 3,72          | 4,88          |
| O1s    | 25,38         | 25,41         |

In conclusion, the typical corrosion residues of copper and its alloys were present: Cu$_2$O, CuCl, and CuCl$_2$, which matches the information obtained in the EDS elemental composition. The preferred aluminum dissolution was corroborated in the XPS analysis, since the aluminum signal was very weak (figure 9(b)). The N1s signal only has two contributions, one for each nitride present, so that the one with lower energy corresponds to AlN and the higher energy one to Cu$_3$N. From this it can be deduced that the aluminum observed in the composition analysis comes mainly from AlN. The composition obtained with XPS of the samples deposited at 15 W y 21 W after corrosion test is shown in the table 4.

For the intermetallic compounds between copper and aluminum, the corrosion reactions are the following:

$$\text{Al}_2\text{Cu} + 6\text{Cl}^- \rightarrow \text{Cu} + 2\text{AlCl}_3 + 6\text{e}^-$$

$$\text{AlCu} + 3\text{Cl}^- \rightarrow \text{Cu} + \text{AlCl}_3 + 3\text{e}^-$$

$$\text{Al}_4\text{Cu}_9 + 12\text{Cl}^- \rightarrow 9\text{Cu} + 4\text{AlCl}_3 + 12\text{e}^-$$

Through these reactions, the aluminum is preferably dissolved. The results did not vary significantly between the thin films, so in all the cases the same reactions and the same corrosion products are presented.

The EIS results for the sample deposited with 15 W of power to the aluminum target are shown in figure 10 in the form of Bode and Nyquist plots. From the module graph it can be observed that there is a constant increase in the magnitude of the impedance with the immersion time. At all the times at low frequencies, the diagram does not end with a typical horizontal line of a purely resistive behavior. For the two hours there is a slight module decrease, and for the longer times the slope is still negative. This implies that at the shortest time there can be an inductive behavior, and at longer the diffusive processes are dominant at low frequencies. In the case of the phase diagram, there is a verified phenomenon at low frequencies at 2 h, since two valleys are observed, that is to say, two time constants, one at low frequencies and another at intermediate frequencies. For 48 h and 72 h, there is only one time constant observed, which implies the coupling phenomena associated with them. Finally, for the longest time, two time constants can be seen. In the Nyquist plot, the inductive phenomenon is indentified by its tendency to ‘bend inwards’ in the diagram at low frequencies.
The observed behavior at low frequencies and at 2 h of immersion is associated with an inductive phenomenon \([38–40]\). At times longer that 2 h, the diffusive processes are dominant at lower frequencies. They are modeled with a Warburg-type impedance. Other investigations have studied the various causes of the inductive behavior, the first being the change in stoichiometry in the interface due to ion accumulation, which affects the its resistance, and the second being the competition among the reaction sites. In summary, processes that imply changes in the surface conditions, such as desorption, pitting, absorption, and formation of a passivating layer or oxide layer, are able to carry out the formation of this inductive response at low frequencies.
Taking into account that this case has at least two interfaces, coating and substrate, there must be two minimum time constants, which in equivalent circuit terms are two RC elements. However, in the composition results it was observed that the coatings exhibit a surface oxide layer (copper and aluminum oxide). Therefore, there is another RC element associated with this oxide, so the equivalent circuits are shown in figure 11, in which the one corresponding to the shortest immersion time includes an inductance, in order to model the low frequency phenomena. For times longer than 2 h, an RC element associated with an oxide layer was also included.

In the EIS test results for the films at powers higher than 15 W, the inductive behavior is still seen at 2 h of immersion, but with a greater intensity than the previous cases, so this inductive behavior is becoming more intense as the Al target power increases. This can be perceived in the largest loop or hook in the Nyquist plot as well as in the greater decrease in the module at low frequencies, for example the results for the 26 W samples (figure 12).

It is possible that the existence of several phases generates inductive behavior at low frequencies, since its presence can produce ion accumulation that changes the stoichiometry or the competition for the reaction or absorption sites. This translates to changes in the surface conditions by pitting, absorption, or oxide accumulation. From what was observed in the micrographs of the corroded surfaces, this can be generated by the formation of a more resistant oxide layer or by the failure of the same.

Polarization resistance (figure 13) of the deposited films at 15 W and 18 W continually increases with the immersion time; at 21 W it is practically constant, and finally at 26 W the polarization resistance exhibits a large increase, followed by a slow decrease. Polarization resistance is related to the charge movement opposition, or current flow, generated by the electrochemical reactions that can happen on the surface of an electrode while being polarized. In this way, the current is controlled by the kinetic reactions and by the diffusion, and its value, which combines the high- and low-frequency phenomena, is given by the addition of all the circuit resistors. Therefore, this parameter represents a mixture of the pore resistance and the charge transfer resistance, (designated ‘substrate resistance’).

Pore resistance (figure 14(a)), which represents opposition to ionic movement through the coatings’ pores, of the 15 W film exhibits a less desirable behavior. It starts out being the highest, but undergoes an abrupt decrease, after which it maintains a relatively low value. This $R_{pore}$ behavior happens in spite of this film’s having the greatest polarization resistance at all the immersion times. In brief, this parameter exhibits the best behavior in the 21 W and 26 W samples, which matches the potentiodynamic polarization (Tafel) results. Finally, the variation in the charge transfer resistance that is associated with the substrate is shown in figure 14(b). It can be seen that at all times the 15 W sample has the highest $R_{tc}$, and the films with the best behavior are deposited at 21 W and 26 W, in that order.

It can be concluded that the 21 W and 26 W samples exhibit the best behavior, because they show better behavior with respect to the pore resistance, which is related to the coating, and the substrate resistance, which is associated with the substrate metal dissolution, does not exhibit abrupt decreases, so the result is a thin film with good resistance.
Conclusions

The deposited thin films are polycrystalline, with a crystallite size that decreases with an increase in the power and with the presence of nitrogen in the growth atmosphere. So the Cu-Al-N films deposited at a power greater than 15 W are nanocrystalline, with crystallite sizes below 10 nm. The effect of power variation is observed in the Cu-Al phase formed and in the quantities of copper and aluminium nitrides within the films. It was possible to obtain thin films with a corrosion current density lower than the corrosion current density of phosphor bronze. The electrochemical characterization carried out through EIS showed that there are characteristic behaviors at low frequencies, which are associated with the diffusion and inductive processes. In general, there are diffusion processes in all the coatings, but when there are abrupt changes in the surface conditions, such as localized corrosion processes, inductive behavior is the dominant one. Electrochemically, the best films were deposited at a power of 21 W.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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