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Impact of Cu and Ce on the Electrochemical, Antibacterial, and Wear Properties of 316L Stainless Steel: Insights for Biomedical Applications

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Abstract

This study provides a comprehensive investigation of the tribological, electrochemical, and antibacterial characteristics of austenitic stainless steel, type 316L, doped with Ce and Cu. The samples were doped with varying concentrations of Ce (0.5, 1.5, and 3 wt%) and Cu (1.5, 2.5, and 3.5 wt%). The initial measurements focused on determining the final density values of each sample. Subsequently, friction wear tests were conducted under both dry and wet conditions, shedding light on the wear resistance of the materials. In addition, electrochemical polarization tests were employed to assess the influence of Ce and Cu on the corrosion resistance of AISI 316L. Furthermore, antibacterial assessments were conducted against bacterial cultures of *Staphylococcus aureus* (ATCC 29213) and *Escherichia coli* (ATCC 25922). The findings of this study illuminate several noteworthy outcomes. Namely, the results showed that all Ce and Cu-doped samples exhibited an increase in final density values when compared with the as-received AISI 316L. The wear test results revealed that samples doped with 0.5 wt% Ce and 2.5 wt% Cu exhibited the highest wear resistance, in both dry and wet environments. Polarization curve analysis indicated that Ce was more effective in enhancing the corrosion resistance of AISI 316L than Cu. Notably, Ce and Cu modifications endowed the material with antibacterial properties, effectively inhibiting bacterial growth in both *S. aureus* and *E. coli* cultures. In summary, this study demonstrates that the addition of even trace amounts of Ce and Cu to AISI 316L leads to noticeable improvements in the material's tribological, electrochemical, and antibacterial performance, underscoring its potential for diverse biomedical applications. The enhanced mechanical strength, corrosion resistance, and antibacterial activity make the doped material promising for use in various medical devices, implants, and other biomedical applications.

Keywords:

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[1],[2] authors contributed equally to this work.

Stainless steel, doping, cerium, copper, tribology, corrosion, antibacterial activity, biomaterials

1. Introduction

Joints often deteriorate because of various factors such as trauma, accidents, ageing, and obesity, leading to the use of bone prostheses. With increasing life expectancy and advancements in technology, the incidence of bone fractures is on the rise. For instance, hip fractures, which were 1.66 million in 1990, are projected to reach 6.26 million by 2050 and potentially even 21.3 million, according to recent estimates [1-3]. Therefore, there is a need for prompt action to provide materials that are biocompatible and mechanically stable to support bone function, ensuring long-lasting effects. Simultaneously, there is a need to offer additional functionalities such as antibacterial properties or the leaching of beneficial compounds to enhance compatibility and acceptability within the body.

To meet the growing demand for long-lasting implants, intensive research on biomaterials is underway. Metallic biomaterials currently dominate the implant market, constituting 70-80% due to their exceptional biological and mechanical properties. Among these, AISI 316L stainless steel (SS 316L) alloy is a common choice for biomedical applications, recognized for its corrosion resistance, formability, biocompatibility, and mechanical strength [4-7]. In addition to its exceptional properties, the cost factor stands out as one of the primary competitive advantages of SS 316L over its main rivals, including titanium-based materials and Co-Cr alloys [8]. However, the relatively low tribological properties of SS 316L can render it susceptible to the corrosive effects of bodily fluids, ultimately leading to implant loosening over time and necessitating revision surgery [9, 10]. Furthermore, SS 316L presents a significant microbiological drawback as it provides an environment conducive to the survival of bacteria and the formation of biofilms on its surface [11]. Wear, corrosion, and infection-related challenges are the primary barriers to the use of SS 316L in the fabrication of functional biomaterials.

To address these issues, alternative biomaterials [12-16] have been explored. There are different approaches to enhancing the value of traditionally used biocompatible materials, such as doping, blending, mixing, melting, or ion implantation [17, 18]. In addition, various substances or elements such as Cu, Zn, Zr, Ag, Ce, Ga are considered as dopant materials that could enhance the functionality of traditionally used biocompatible materials like stainless steel, titanium, or magnesium alloys [19-21]. Taking this into consideration, copper (as a more explored material) and Ce (as a less explored material) were chosen for this study to compare their antibacterial and other activities in the same base material, such as SS 316. Copper (Cu) is a widely adopted solution for addressing complications such as implant loss due to infection. It imparts antibacterial and angiogenic properties to the material while promoting osteogenesis. Additionally, the antibacterial activity of Cu-doped biomaterials provides an alternative to the extensive use of prophylactic antibiotics, thereby helping to mitigate the development of antibiotic resistance [19, 22-24]. In recent years, the development of Cu-containing austenitic stainless steel as a novel structural/functional material has garnered significant attention for its potential to mitigate the risk of bacterial infection. It also holds great promise as a biomaterial for implant devices, offering improved corrosion resistance and tribological properties [25]. Hence, copper emerges as a promising dopant, given its outstanding antibacterial properties and minimal cytotoxicity [26, 27]. In addition, upon analyzing the literature, it becomes evident that elements from the lanthanide series display comparable performance to copper concerning biocompatibility and antibacterial properties [28]. Hence, the use of elements from this group in the realm of medicine is steadily expanding, driven by their pharmacological and biological properties [29]. For instance, Cerium (Ce), a rare earth element, has exhibited cytotoxic effects on cancer cells and has the potential to inhibit the growth of various bacteria [19, 30, 31]. However, it is widely recognized that the addition of small quantities of cerium to steels can significantly enhance their corrosion resistance [32, 33].

This study aims to investigate the electrochemical, antibacterial, and tribological properties of AISI 316L stainless steel, with a focus on enhancing these properties by incorporating copper and cerium dopants. The study will examine wear mechanisms, antibacterial efficacy against various bacterial cultures, and corrosion resistance of stainless steel with varying Cu and Ce dopant concentrations, and the results will be compared with those of AISI 316L.

2. Materials and Methods

2.1 Materials

Austenitic stainless steel alloy, type 316L, alloyed with both Ce and Cu in various quantities, was prepared using specific procedures and equipment. The Ce content was varied to 0.5, 1.5, and 3 wt%, corresponding to samples labelled as 1.1, 1.2, and 1.3, while the Cu content ranged from 1.5, 2.5, and 3.5 wt%, denoted as samples 2.1, 2.2, and 2.3, respectively. Table 1 provides the chemical composition of the alloys, with stainless steel supplied by Camex, Měšice, Czech Republic.

The Cu-modified stainless steel samples were created by melting the stainless steel alloy along with Cu and Ce lumps in a MAM-1 arc melter (Edmund Buehler). The melting process occurred in a high-purity argon atmosphere (99.9999 vol.%). To eliminate residual oxygen, a piece of Ti was initially melted as an oxygen getter. Subsequently, pre-weighed stainless steel pieces containing Cu or Ce lumps were placed on a water-cooled Cu mould and instantly melted by striking an arc from a tungsten cathode. The samples underwent three re-melting cycles to ensure melt homogeneity.

The resulting ingots were homogenized at 1100 °C for 2 h in an argon environment, followed by cold-rolling and recrystallization annealing at 1100 °C for 30 min. The steel was then cut into smaller disks using a diamond saw. These stainless steel alloy disks were embedded in a non-conductive resin, ground using 1200-grade sandpaper, and polished with diamond suspension to achieve a surface roughness of 1 μm. After the polishing step, the final density values of the samples were measured at room temperature according to the Archimedes principle using an AND GR-200 precision balance.

Microstructural analysis of the steel was performed using a JEOL JSM 7600F scanning electron microscope, operating in secondary electron and backscatter electron imaging modes at an accelerating voltage of 15 kV and a working distance of 15 mm. The chemical composition of the materials was determined through energy-dispersive spectroscopy (EDS) analysis, facilitated by INCA software [34].

2.2 Methods

To determine the tribological properties of the samples, a ball-on-disc dry friction wear test was conducted following the ASTM G99 standard. This process employed a TURKYUS brand POD/HT/WT wear device. The dry friction wear test involved a 50-meter sliding distance, a 10 N load, and a rotational speed of 150 rpm. As a counter surface, 100Cr6 steel with a diameter of 6mm was used. In contrast, wet friction wear tests were conducted in simulated body fluid (SBF). The sliding distance, load, rotational speed, and abrasive type parameters selected for the wear test in wet conditions were chosen to be the same as those for dry friction wear for comparison purposes. This allowed for a comparison of the wear results under wet and dry conditions, assessing the impact of Ce and Cu doping on the performance of AISI 316L in 0.9% NaCl. After the wear test, wear track images were captured using a JEOL scanning electron microscope (SEM), model JSM-6060.

Table 1. Amounts of Ce and Cu Added to SS 316L

Sample Name	Base Material	Dopant	Amount (wt.%)
1.1	AISI 316L	Cerium	0.5
1.2			1.5
1.3			3
2.1		Copper	1.5
2.2			2.5
2.3			3.5

The polarization test was conducted in a three-electrode cell, which was controlled by the AMETEK brand VersaSTAT 4 model potentiostat/galvanostat. In this setup, the samples served as the working electrode, while platinum functioned as the reference electrode. Before the polarization test, the samples were immersed in SBF for 1 h to reach equilibrium. The Tafel extrapolation method was employed to estimate the corrosion current density (i_{corr}) and corrosion potential (E_{corr}). The test covered a voltage range from -250 mV to +250 mV, vs. Saturated calomel electrode (SCE) with a scan rate of 1 mV/s. Furthermore, the area of the samples in contact with the 0.9% NaCl solution was standardized to 1 cm^2. Before antibacterial testing, all 316L samples were sterilized under UVC light.

Antimicrobial testing against Gram-positive *Staphylococcus aureus (S. aureus)* strain ATCC 29213 and Gram-negative *Escherichia coli (E. coli)* strain ATCC 29213 was carried out following the ISO 22196 standard with certain modifications [35]. Bacteria were cultured on Mueller-Hinton agar for 24 h at 37 °C. The bacteria were then suspended in a 1/500 dilution of nutrient broth to achieve a concentration of $1x10^8$ CFU/ml, as measured by a spectrophotometer (OD600nm). Serial dilutions of the bacterial inoculum were prepared using 1/500 nutrient broth to reach a final bacterial concentration of 1×10^4 CFUs/mL. Subsequently, 1000 µL of this prepared bacterial suspension was pipetted into sterile test tubes. Pre-sterilized SS 316L samples were placed into these tubes and incubated for 24 h at 37 °C. As a control, a tube containing the bacterial growth medium without a 316L sample was also incubated. After the incubation period, the tubes were vortexed, and 100 µL of the bacterial solution was spread on the surface of Mueller-Hinton agar plates using a sterile Drigalski spatula. The plates were incubated for 24 h at 37 °C, and the results were observed.

3. Results and Discussion

3.1 Density Results

Fig. 1a and 1b shows the final and relative density values of the Ce and Cu-doped samples, respectively. As can be seen, both Ce and Cu doping results in an increase in the density of 316L. Notably, the highest density value among the Ce-doped materials was observed in the 316L sample with 3 wt% Ce. It was also observed that the addition of 0.5 wt% Ce resulted in a greater increase in material density compared to adding 1.5 wt% Ce. The implications of these density changes on the material's mechanical properties will be discussed in subsequent sections.

Conversely, among Cu-doped 316L samples, the highest density value was attained in the sample doped with 2.5 wt% Cu. Interestingly, increasing the Cu doping level from 2.5 to 3.5 wt% led to a decrease in the final density value. Nevertheless, all samples doped with both Ce and Cu by weight exhibited higher density values than the reference sample. It is well-established that increased porosity within a material adversely affects its mechanical properties. For instance, as demonstrated by Kurgan et al. [36], who examined the microstructural and mechanical properties of sintered AISI 316L stainless steel implant materials prepared through powder metallurgy (P/M), the amount of porosity plays a crucial role. In their study, 800 MPa cold-pressed samples were sintered at temperatures of 1200 °C, 1250 °C, and 1300 °C for 30 min under a nitrogen atmosphere. Various mechanical tests, including tensile, fatigue, and microhardness tests, were conducted to investigate the correlation between porosity and mechanical properties. As the material density increased, all mechanical test results showed improvement. Hence, the observed increase in density in the doped samples is expected to have a positive influence on the mechanical properties of AISI 316L.

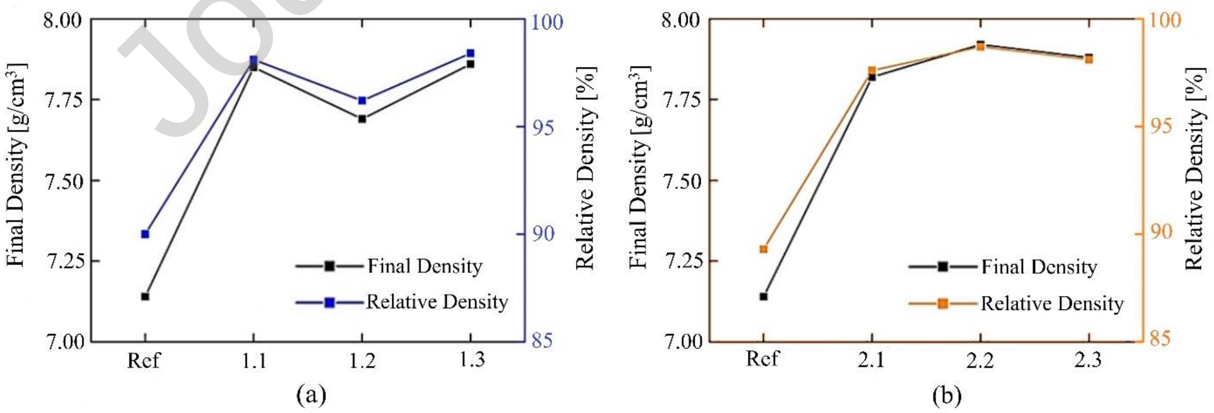

Fig. 1. Effect of Cu and Ce doping on 316L density value; a) Ce doped 316L and b) Cu doped 316L

3.2. Dry Friction Wear Test Results

Wear resistance is a pivotal attribute when considering the service life of metallic biomaterials. Wear-related issues can lead to osteolysis, prompting inflammatory responses within the body and, consequently, implant loosening. Aseptic loosening, largely due to the degradation of implants and bone, is the primary cause (accounting for 80%) of revision surgery. Another significant issue arising from wear is the release of ions from the material into bodily fluids. The toxic effects of these ions - once concentrated in the lymph nodes and bone marrow - can lead to the formation of carcinogenic tissues. Metallic biomaterials used in hard tissue applications are expected to exhibit exceptional wear resistance, especially during prolonged implantation processes [37]. In the case of AISI 316L, its low carbon content hinders carbide formation within the microstructure, resulting in low hardness and wear resistance. Moreover, the austenitic structure of 316L precludes toughening by heat treatment, which poses challenges for enhancing wear resistance [38]. Consequently, the utilization of 316L in the metal components of hip and joint prostheses is restricted due to its comparatively higher wear rate compared with alternatives such as CoCr alloy. Literature studies have underscored the extensive susceptibility of 316L to body-related damage, including scratching, abrasion, oxidation, and adhesion, primarily because of its inherent low wear resistance [39, 40]. To ameliorate the low wear resistance of stainless steel, various elements can be incorporated into its structure.

Fig. 2 shows the wear rates and coefficient of friction values for Ce-doped 316L. As depicted in Fig. 2a, the lowest wear rate was observed in the 0.5 wt% Ce-doped sample. However, with an increase in the Ce content from 0.5 wt% to 1.5 wt%, the material's wear resistance declined, even surpassing that of the reference sample. Remarkably, the wear resistance of the sample containing 3 wt% Ce once again improved, and the wear rate was lower than that of the reference. The introduction of Ce into 316L resulted in an enhancement of the material's wear resistance.

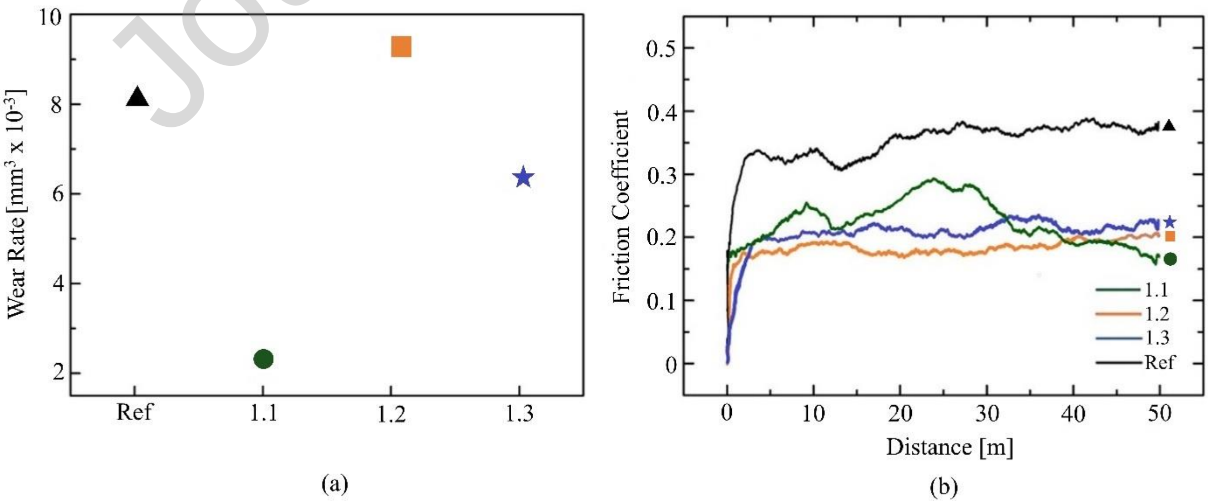

Fig. 2. Dry friction wear test results for Ce-doped samples; a) wear rate, and b) coefficient of friction diagram

The wear rate results obtained were substantiated by the SEM images of the wear track shown in Fig. 3. A careful inspection of these images revealed delamination zones, microcracks, and adhesive wear traces on the wear surface of the reference sample. In addition, areas of agglomeration, caused by fragments breaking away from the material's surface and subsequently adhering back onto the surface, were observed.

Upon examining the wear track images of the 0.5 wt% Ce-doped sample, it became evident that the amount of material removed from the surface had significantly decreased. Conversely, the microstructure images vividly illustrated the lower wear resistance of the sample with 1.5 wt% Ce doping. The width of the wear scar was measured to be greater than that of the reference sample, and an increased occurrence of delamination and plastic deformation zones was observed.

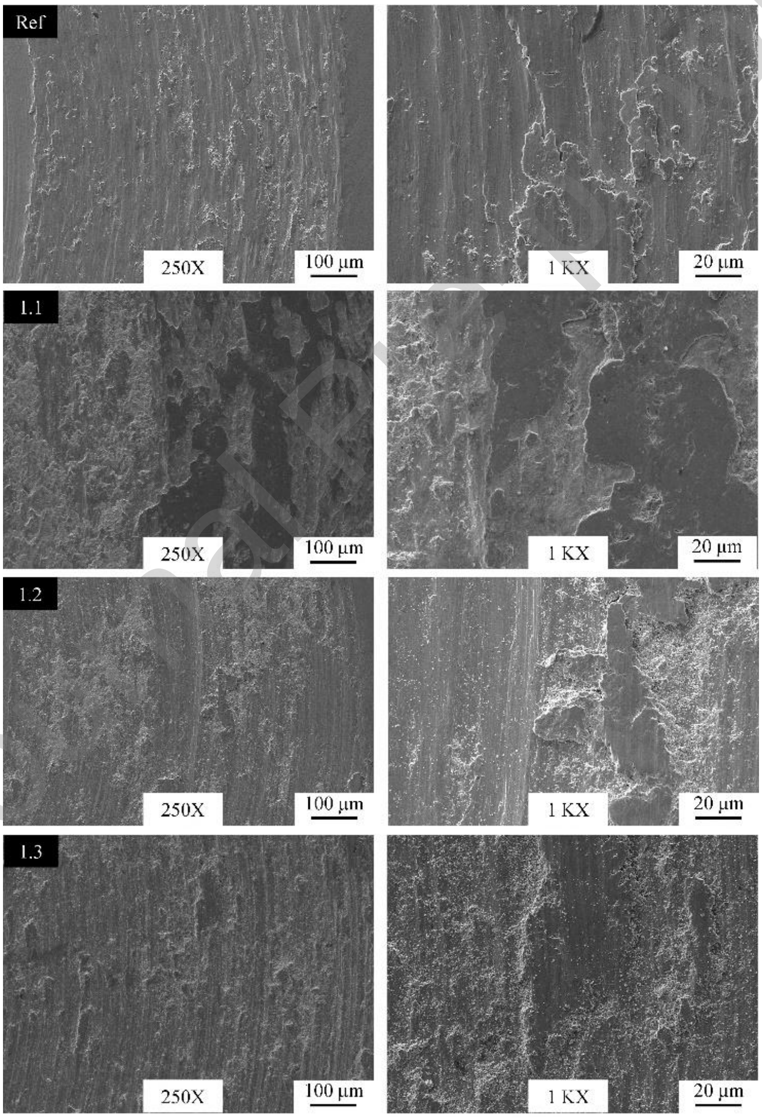

Fig. 3. SEM images of wear track of Ce doped samples: the reference, 1.1, 1.2 and 1.3.

On the other hand, upon analyzing the friction coefficient graph of Ce-doped 316L samples, it became evident that all values exhibited a consistent range, fluctuating between 0.25 and 0.4, which aligns with the findings in the literature [9]. Remarkably, the reference sample displayed the highest coefficient of friction value, and this value decreased as Ce doping was introduced into the material's structure. This phenomenon can be attributed to the adhesive wear characteristics of the material.

Noteworthy that oxidative, adhesive, and abrasive wear are the primary mechanisms responsible for material removal in stainless steel and other alloys. Specific wear characteristics vary significantly based on factors such as normal loads, composition, temperature, and wear environment [41, 42]. Consequently, the introduction of Ce into the material structure led to an enhancement in its anti-wear performance, with the highest wear resistance observed in the 0.5 wt% Ce-doped sample.

Conversely, while this holds for the Ce-doped samples, the wear resistance results and the friction coefficient graph for Cu-doped 316L are presented in Fig. 4. Notably, all Cu-doped samples exhibited a lower wear rate than the reference sample, with the sample containing 2.5 wt% Cu doping displaying the maximum wear resistance. These wear rate findings were substantiated by the SEM images of the wear track, as illustrated in Fig. 5. As evident, the widest wear track was measured in the reference sample. However, the introduction of Cu into the material structure led to a reduction in the wear track width. Moreover, the addition of Cu resulted in a decreased frequency of delamination zones compared with the reference sample. This reduction in the delamination zones contributed to a decrease in the removal of particles from the material surface. Furthermore, it's noteworthy that no microcracks were identified in any of the Cu-doped 316L samples.

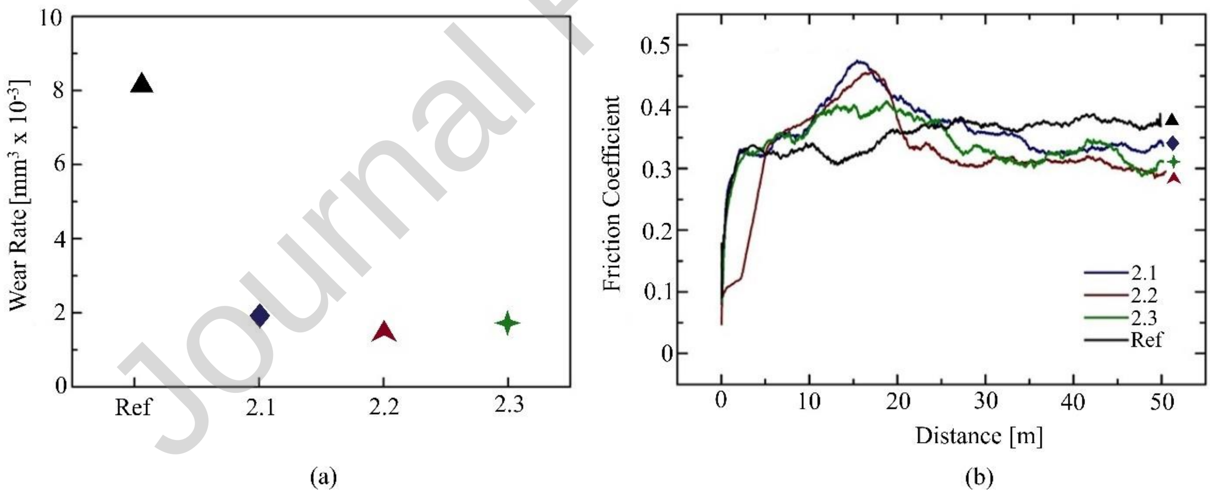

Fig. 4. Dry friction wear test results for Cu doped samples; a) wear rate, and b) coefficient of friction diagram

Cu doping of 316L did not change the friction coefficient graph. In other words, the coefficients of friction for all Cu-doped 316L samples remained identical to the reference sample. Considering this information, it can be concluded that both Ce and Cu doping of 316L enhances the wear performance of the material. As a result, slight adjustments in the chemical composition positively impacted the dry friction wear properties of the material across all aspects. However, it's important to note that these materials will be employed in environments with aggressive and corrosive body fluids, rendering the dry friction wear test alone insufficient for a comprehensive evaluation of wear properties. Consequently, the wear resistance of Ce and Cu-doped 316L in a simulated body fluid environment is explored in the following section.

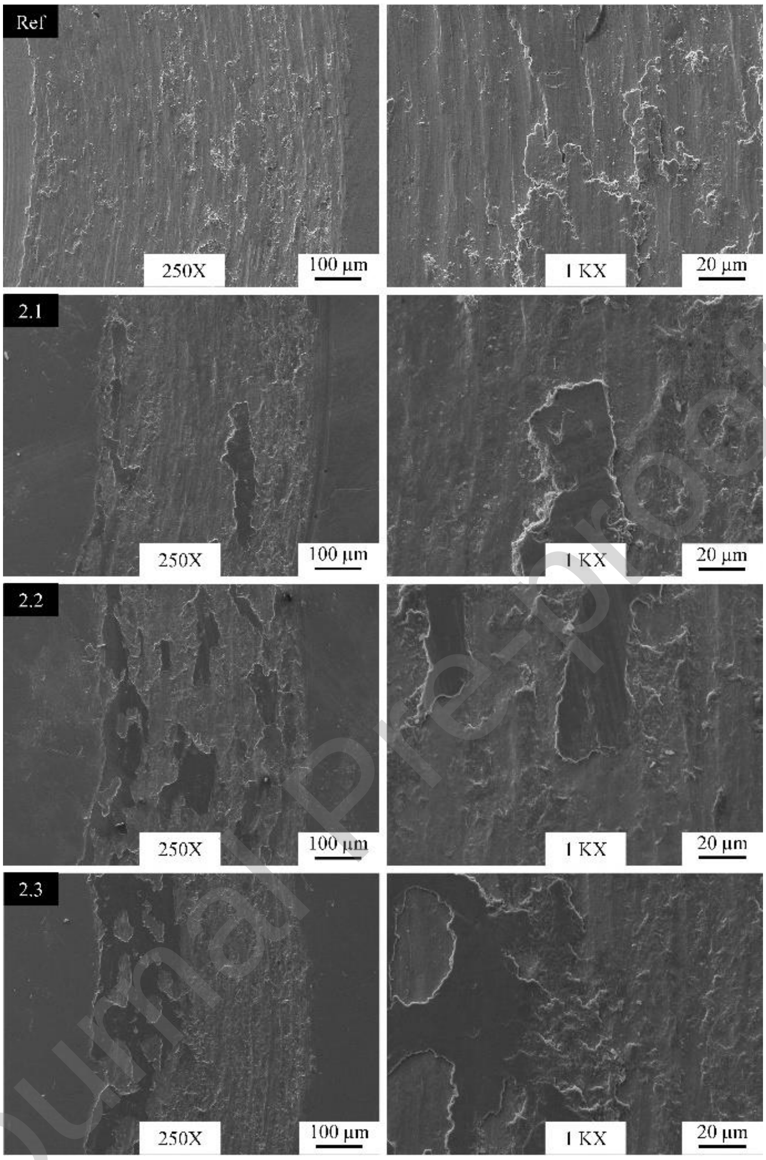

Fig. 5. SEM images of wear track of Cu-doped samples: the reference, 2.1, 2.2, and 2.3.

3.3. Wet Friction Wear Test Results

Upon implantation into the human body, the implant encounters an environment considerably more hostile than mere saltwater. Factors such as elevated temperature and sodium chloride concentration, along with changes in pH, abrasion, and substantial loading, can hasten the corrosion of the implant throughout its service life. Moreover, it's essential to recognize that the chemical composition and fluid concentration surrounding an implant can differ significantly within different anatomical regions [8]. For instance, a dental implant is primarily exposed to saliva, whereas hip, knee, and cardiovascular implants are immersed in blood plasma. In the realm of in-vitro research, artificially engineered fluids such as Ringer's solution, simulated body fluid, artificial saliva, and phosphate buffer saline solution are commonly employed. It's crucial to note that the composition of these fluids can adversely affect the tribological properties of the material [43]. Consequently, relying solely on results from dry friction wear testing is insufficient for a comprehensive assessment of the tribological properties of a biomaterial candidate. In this study, we conducted wet friction wear testing of Ce and Cu-doped 316L samples in SBF. This allowed us to measure the tribological performance of the materials under controlled in vitro conditions. Fig. 6 presents the wear rate and coefficient of friction graph for Ce-doped 316L, allowing for a comprehensive evaluation.

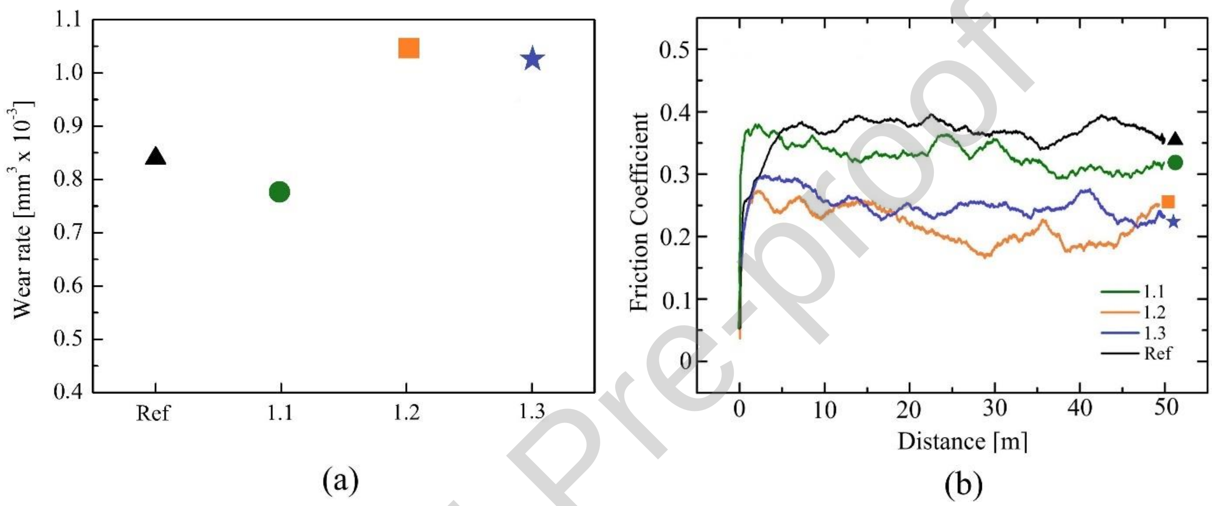

Fig. 6. Wet friction wear test results for Ce-doped samples; a) wear rate, and b) friction coefficient diagram

As observed, the wear rate for all samples, including the reference, decreased when tested in SBF compared with dry friction wear. However, in contrast to dry friction wear testing, the reference sample exhibited stronger wear resistance than 316L with 1.5% and 3% Ce doping by weight in the SBF environment. Nevertheless, the lowest wear rate was recorded for 316L with 0.5 wt% Ce doping. In this context, the most favourable outcome in both dry and SBF friction wear tests for Ce-doped materials was achieved with the sample containing 0.5 wt% Ce. The friction coefficient graph presented in the same figure reveals that the values decreased compared with dry friction wear. The presence of a liquid in the SBF caused a lubricating effect, leading to a reduction in the friction coefficient. However, it's important to note that the maximum coefficient of friction was still observed in the reference sample. Therefore, the incorporation of Ce led to a decrease in the friction coefficient of the material.

It's worth mentioning that the coefficient of friction is influenced by factors such as the type of abrasive ball and the characteristics of the material's surface [44]. In other words, the oxide film structure, material hardness, surface roughness, and ductility values directly affect the wear and friction coefficients [45].

Therefore, it is essential to acknowledge that establishing a single parameter-dependent relationship between friction coefficients and wear rates may not be feasible. On the other hand, Fig. 7 displays the wear rate and coefficient of friction graph for Cu-doped 316L samples. Notably, all samples exhibited reduced wear rates and friction coefficient values compared with the dry friction wear test results. Furthermore, all Cu-doped samples displayed enhanced wear resistance compared to the reference sample, with the lowest wear rate observed in the sample with 2.5 wt% Cu addition. It's important to note that an increase in the Cu content from 2.5 to 3.5 wt% resulted in an upturn in the wear rate. In summary, the inclusion of Ce and Cu significantly contributed to improving the wear resistance of 316L in both wet and dry environments. The enhancement of low wear resistance, a key limitation of stainless steel, is regarded as one of the study's most noteworthy achievements.

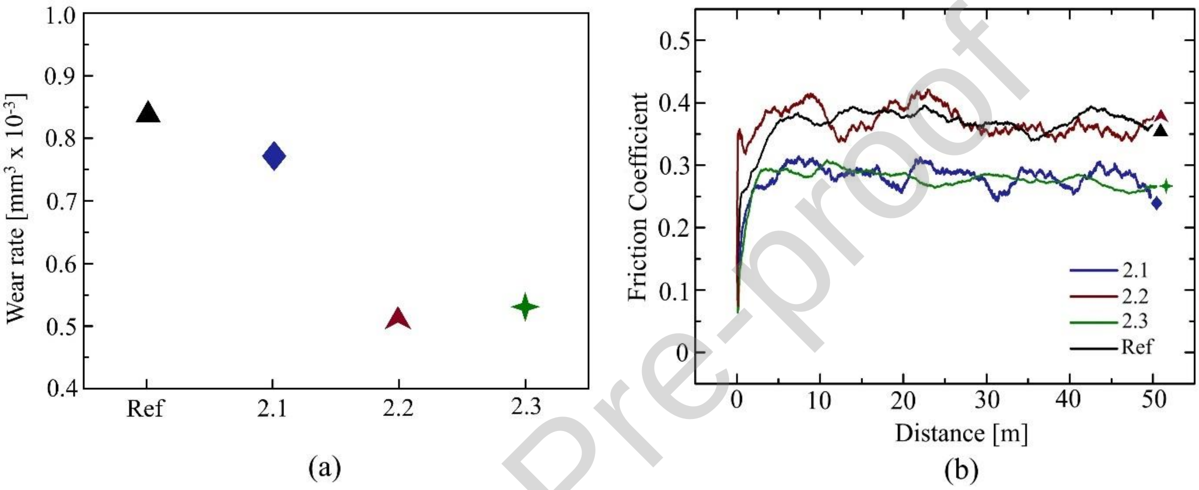

Fig. 7. Wet friction wear test results for Cu-doped samples; a) wear rate, and b) friction coefficient diagram

3.4. Electrochemical Analysis

Biological fluids within the human body are known to be corrosive and aggressive, leading to ongoing adverse interactions with metallic implants. These reactions result in various forms of corrosion, including pitting and cracking, on the surface of the material. The corrosion of metallic biomaterials leads to alterations in pH within biological environments, reduced dissolved O_2 levels, and the release of ions into the body fluid [46]. Consequently, the responses generated by the body's interaction with metallic implants and the material's degradation process are crucial factors influencing biocompatibility [47]. Stainless steels are generally considered to exhibit exceptional resistance to both general and localized corrosion due to their chromium content, which meets or exceeds the critical atomic concentration of 13%. The uniform distribution of chromium throughout the microstructure forms a thin amorphous chromium oxide (Cr_2O_3) layer, typically measuring between 10 and 50 Å, on the steel's surface. This ionic bond within the layer shields the surface from electrochemical degradation [48]. Notably, studies by Hanawa [49] have identified small quantities of Ni, Mo, and Mn oxides, in addition to chromium oxide, on the surface of the oxide layer composition on austenitic stainless steels. These oxides, in conjunction with Cr_2O_3, enhance the oxide film layer formed on the stainless steel's surface. However, literature sources suggest that when 316L is employed in metal-on-metal load-bearing systems, the oxide layer may be penetrated due to wear. The primary reason for the material's medical concerns, such as severe friction and abrasion within the body, is its inadequate hardness. Consequently, the material is prone to corrosion, releasing Ni, Cr, and Fe ions into body fluids [50]. Research conducted to assess the impact of Cr and Ni ions on the human body has revealed that these metals can trigger severe allergic reactions and even cancer at critical concentrations [51, 52]. Considering this information, it is reasonable to assert that stainless steel is susceptible to tribo-corrosion when used for permanent implant applications due to the corrosive body environment. To address this issue, which leads to implant failure and necessitates revision surgery, 316L SS was doped with Ce and Cu, and the influence of these elements on corrosion resistance was investigated. It is widely recognized that the addition of small amounts of lanthanide group elements with a strong affinity for oxygen, such as Ce, to steels can enhance their corrosion resistance by facilitating the formation of oxides within the structure [32, 53]. The polarization curves of Ce-doped 316L are illustrated in Fig. 8. In the Tafel diagram, the anodic polarization curve provides insights into the passivity of the oxide layer on the metal surface [54]. The corrosion potential on the diagram is the potential of the corroding surface in an electrolyte relative to a reference electrode. This value is derived from the Tafel extrapolation of the anodic and cathodic curves in the potentiodynamic polarization diagram.

The current density at the corrosion potential is also obtained from the potentiodynamic polarization curves and is directly linked to the corrosion rate. Lower i_{corr} values indicate superior corrosion resistance of the material [55, 56]. As depicted in Fig. 8, the i_{corr} value for the sample with 1.5 wt% Ce addition exceeded that of the reference sample, and the Tafel plot shifted to the right. Conversely, when the Ce addition was increased to 3 wt%, the corrosion current density approached the value of AISI 316L, and there was no discernible change in corrosion resistance. Interestingly, the polarization curve for the sample with 0.5 wt% Ce addition shifted to the left when compared with the reference sample. This indicates that an increase in the Ce content within the structure led to a decrease in the material's corrosion resistance, with the maximum corrosion resistance measured in the sample containing 0.5 wt% Ce. Similarly, Junping et al. [57] assessed the impact of Ce addition on the corrosion characteristics of 316L and found that the addition of small amounts of Ce enhanced corrosion resistance. In this regard, the study's findings align with existing literature.

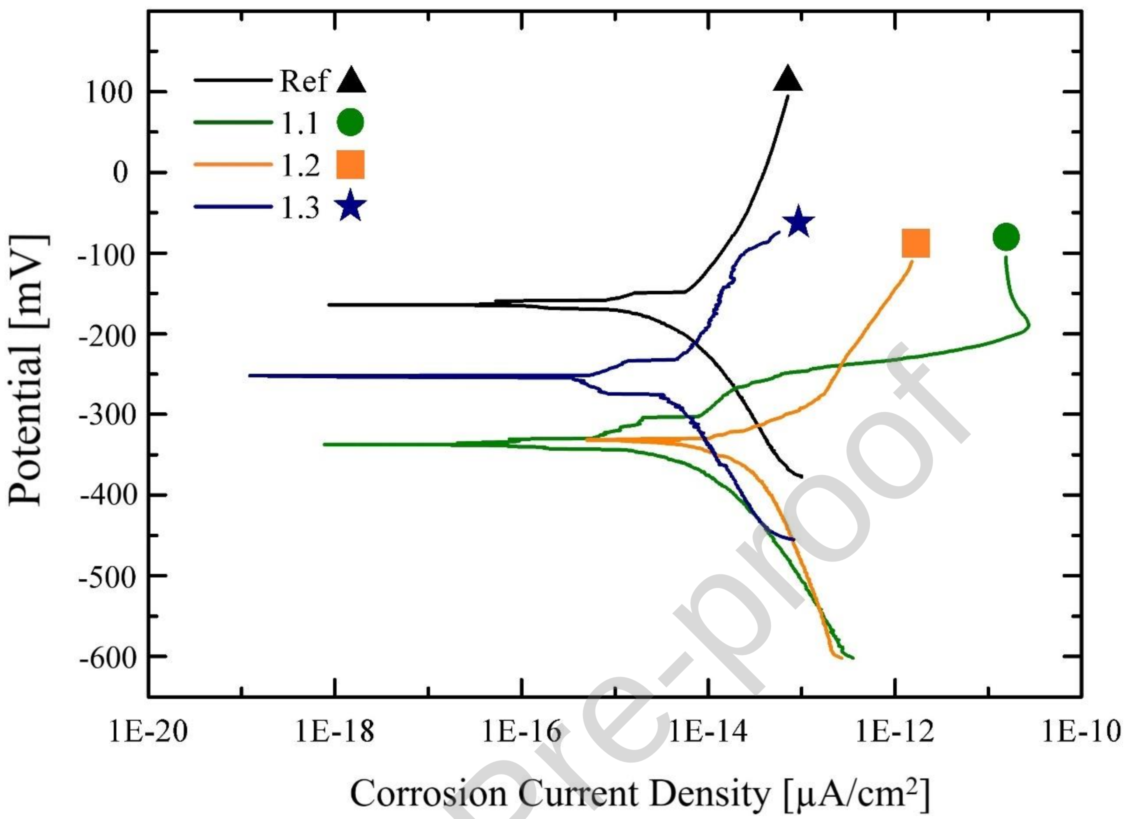

Fig. 8. Tafel extrapolation diagram of the reference and Ce-doped samples

The influence of Cu on the corrosion behaviour of stainless steel has generated conflicting data in the literature. Some studies [25] The influence of Cu on the corrosion behaviour of stainless steel has generated conflicting data in the literature. Some studies suggest that Cu's addition can prevent the dissolution of soluble sulfur residues in stainless steel by facilitating the re-deposition of previously dissolved Cu on the steel surface, leading to the formation of a protective $CuCl_2$ layer that reduces the corrosion rate. However, other research indicates that Cu alloys can have adverse effects on localized corrosion, affecting passivation, pitting potential, and intergranular corrosion. It has been observed that Cu may decrease chromium enrichment on the passive film during the initial stages of passivation, thereby reducing the stability of the passive film and the material's resistance to pitting [10].

In this study, polarization curves for Cu-doped 316L stainless steels were generated, revealing a decrease in corrosion current density with the addition of Cu. The polarization curves of Cu-doped 316L are given in Fig. 9. The lowest i_{corr} value was observed in a 316L sample doped with 3.5 wt% Cu. When comparing the effects of Ce and Cu on corrosion resistance in 316L, it became evident that Ce had a more pronounced impact on enhancing corrosion resistance than Cu.

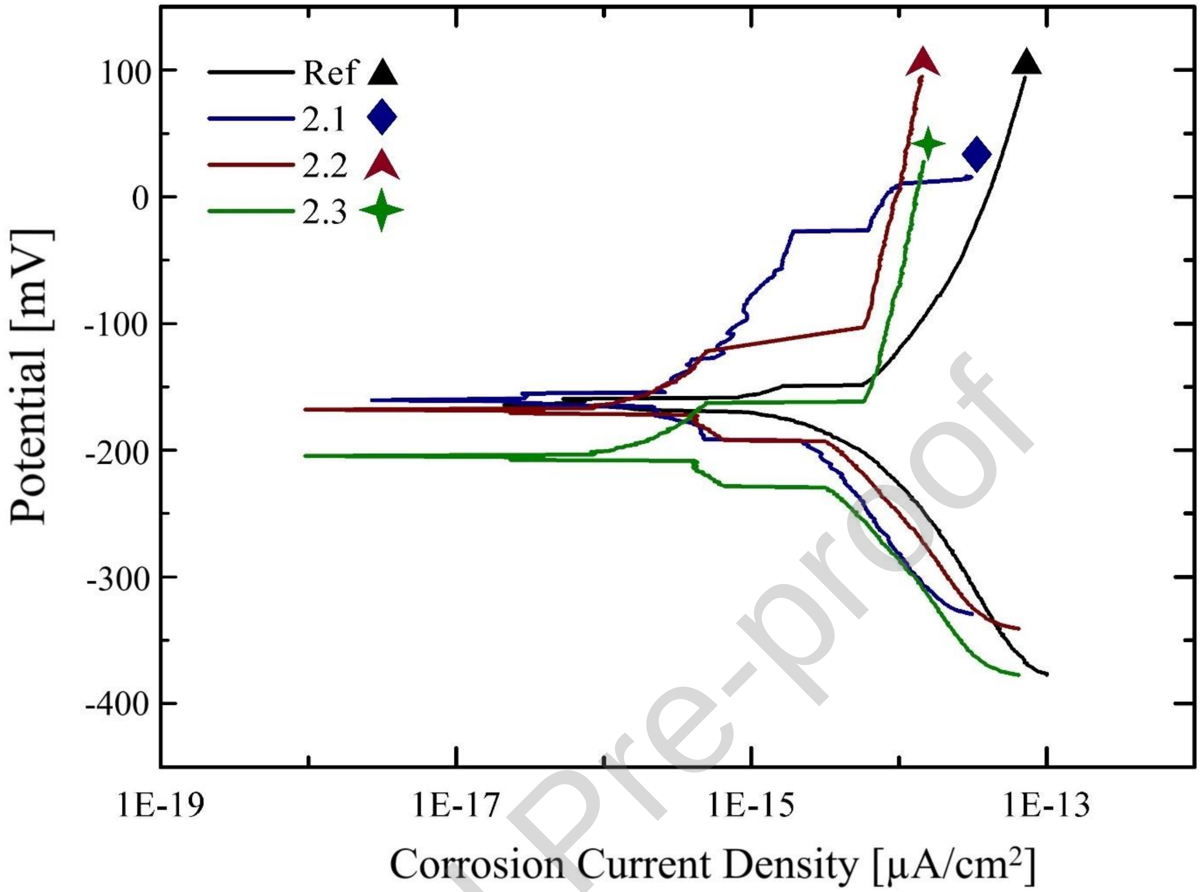

Fig. 9. Tafel extrapolation diagram of the reference and Cu-doped samples

3.5. Antibacterial Analysis

In the realm of modern medicine, despite significant strides in aseptic techniques and the availability of effective broad-spectrum antibiotics, postoperative infections persist as a common and formidable complication in surgical procedures [58]. The incidence of infections following surgeries can fluctuate and has been documented to range between 0.7% and 4.2%. In more severe cases, such as third-degree open fracture surgeries, infection rates may surge to as high as 30% [59]. When an infection arises, the body recognizes implanted materials as foreign entities, inciting a response that may culminate in bone sequestration [60]. Consequently, the repercussions of infection are magnified in terms of patient health, frequently necessitating revision surgery, extended hospitalization, and augmented healthcare costs. To mitigate this issue, there is an escalating demand for long-term implant materials endowed with antibacterial properties to preclude postoperative infections.

Stainless steel alloys have served as a high-performance metallic biomaterial in various domains for nearly a century, encompassing fields such as dentistry and orthopedics. However, AISI 316L, while proffering numerous advantages, manifests pronounced microbiological limitations, notably the survival of bacteria on its surface and the development of biofilms [11]. Consequently, recent research initiatives have been undertaken to fabricate antibacterial joint prostheses distinguished by heightened resistance to infection. In the contemporary literature, diverse studies have explored the antibacterial attributes of metallic biomaterials through the infusion of minute quantities of antibacterial metals, including Ag, Cu, Zn, and Ce [22, 57].

The antibacterial potential of Cu and Ce-doped AISI 316L against two distinct bacterial cultures and compared the outcomes with those of the reference sample were scrutinized. The results of the antibacterial analysis against the *S. aureus* bacterial culture are outlined in Table 2. The quantitative data in Table 2 are accompanied by the visual representations in Fig. 10, where Fig. 10a delineates the number of bacterial colonies that emerged when bacteria did not come into contact with the metal samples following an incubation period of 18-24 h.

Table 2. Colony counts of *S. aureus* plates, and alteration percentages according to the growth control.

Sample	1. experiment		2. experiment		Average
	CFU/ml	Alteration (%) *	CFU/ml	Alteration (%) *	Alteration (%) *
1.1	25	-99,94	70	-99,24	-99,59
1.2	0	-100	10	-99,89	-99,945
1.3	0	-100	0	-100	-100
2.1	210	-99,55	480	-94,81	-97,18
2.2	40700	-14,31	950.000	10170	5077,845
2.3	650	-98,63	170	-98,16	-98,395
Reference	53000	11,57	635.000	6764	3387,785

* Colony count alteration according to growth control
CFU/ml: Number of colony forming units in one millilitre of liquid (CFU: Colony forming unit)

Table 2 and Fig. 10 show a notable reduction in the number of bacterial cultures proliferating in the medium with an increase in the Ce concentration. Even in the sample doped with 0.5 wt% Ce, there was a remarkable 99.94% decrease in the number of colonies produced compared to the reference sample. Notably, as the amount of Ce was further augmented from 0.5 wt% to 1.5 wt%, a complete bacterial suppression was achieved. It was similarly ascertained that the addition of 3 wt% Ce led to the demise of all *S. aureus* bacterial colonies. Indeed, it is established that minute quantities of Ce confer antibacterial and anti-inflammatory properties upon biomaterials [57].

In this context, Junping et al. [57] conducted an exploration into the antibacterial effectiveness of four distinct 316L compositions containing varying Ce concentrations, namely 0.04, 0.12, 0.29, and 0.38 wt%. Upon analysis of the findings, it was apparent that Ce-modified 316L exhibited antibacterial activity against *S. aureus*, and this antibacterial efficacy was augmented with increasing Ce content. Hence, it is plausible to assert that the impact of Ce on the *S. aureus* bacterial culture aligns with existing literature.

Conversely, when evaluating the influence of Cu-doped AISI 316L on *S. aureus* bacterial growth, a 99.55% and 98.63% inhibition of bacterial proliferation was observed at Cu additions of 1.5 wt% and 3.5 wt%, respectively. However, the antibacterial activity was negligible in the sample with 2.5 wt% Cu doping. Nonetheless, all Cu-doped samples exhibited a reduction in the number of bacterial colonies compared to the reference sample.

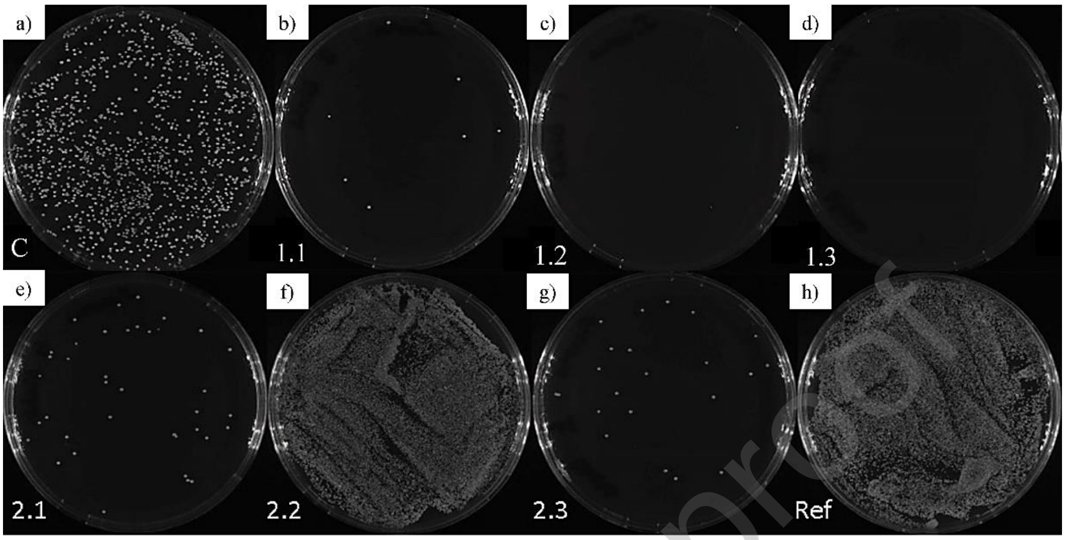

Fig. 10. Photographs of *S. aureus* plates after incubation; a) C: Control, b) 1.1, c) 1.2, d) 1.3, e) 2.1, f) 2.2, g) 2.3 h) Reference (316L)

Researchers [61, 62] have elucidated that the carboxyl group present in lipoproteins imparts a negative charge to the bacterial surface, thereby making bacteria attract positively charged Cu ions. Upon interaction with Cu ions, bacterial cell membranes change permeability, leading to the inactivation of enzymes. Consequently, the leakage of DNA, RNA, proteins, and cytoplasm ensues, resulting in bacterial death [63, 64]. In this study, the antibacterial effect of copper was demonstrated, aligning with the findings in existing literature. For instance, Ren et al. [65] developed developed Cu-bearing 316L SS containing 3.77 wt% Cu to mitigate implant-related infections (IRI). The results of their investigation revealed that 316L-Cu SS exhibited broad-spectrum antibacterial activity against Staphylococcus aureus, Escherichia coli, and Staphylococcus epidermidis, with in vitro bacteriostatic rates of 95.2%, 94.8%, and 94.1%, respectively. In another study, Akhtar et al. [66] coated 316L stainless steel with Cu-chitosan complexes and evaluated their antibacterial properties against E. coli and S. aureus. Cu-chitosan compounds demonstrated significant efficacy against both bacterial strains, preventing bacterial growth, and this effect persisted even after 24 hours. In contrast, the sample coated with chitosan alone did not exhibit antibacterial activity. Furthermore, Zhang et al. [67] reported that Cu-containing stainless steel displayed remarkable antibacterial activity against both gram-positive S. aureus and gram-negative E. coli.

Table 3. Colony counts of E.coli plates, and alteration percentages according to the growth control.

Sample	1st Exp.		2nd Exp.		Average
	CFU/ml	Alteration (%)*	CFU/ml	Alteration (%)*	Alteration (%)*
1.1	695000	-95,99	45.500	-98,25	-97,12
1.2	215	-99,99	0	-100	-99,995
1.3	0	-100	0	-100	-100
2.1	860000	-95,04	156.000	-94	-94,52
2.2	15650000	-9,79	527.000	-79,73	-44,76
2.3	0	-100	850	-99,96	-99,98
Reference	15250000	-12,1	514.000	-80,23	-46,165

* Colony count alteration according to growth control

The results of the antibacterial analysis against the E. coli bacterial culture are presented in Table 3. These numerical findings are complemented by the images of the cultivated media with E. coli, as illustrated in Fig. 11. Notably, there was no antibacterial effect observed in the reference sample against E. coli. However, the antibacterial efficacy of the material improved in correlation with an increase in the wt% Ce content. At this juncture, the bacterial inhibition rates for 0.5, 1.5, and 3 wt% Ce-doped 316L samples were measured at 95.04%, 99.99%, and 100%, respectively.

The bacterial inhibition rates for the 1.5, 2.5, and 3.5 wt% Cu-doped 316L samples were 95.04%, 9.79%, and 100%, respectively. Notably, the antibacterial activity substantially decreased with an increase in Cu concentration from 1.5 wt% to 3.5 wt%. However, complete bacterial suppression was achieved when the Cu additive quantity was raised to 3.5 wt%. Consequently, the highest level of antibacterial activity against the *E. coli* bacterial culture was observed in 316L doped with 3 wt% Ce and 3.5 wt% Cu. In summary, it became evident that the antibacterial properties against both *E. coli* and *S. aureus* bacteria increase with rising cerium concentration and remain highly effective on both bacterial cultures, even at low doping ratios. In this light, the results obtained in this study align with existing literature and research data [57, 68, 69].

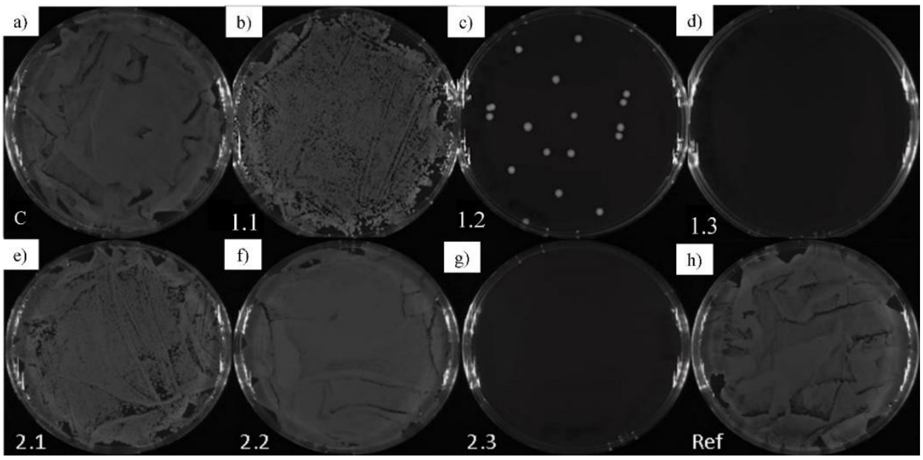

Fig. 11. Photographs of *E.coli* plates after incubation. a) C: Control, b) 1.1, c) 1.2, d) 1.3, e) 2.1, f) 2.2, g) 2.3 h) Reference (316L)

4. Conclusions

Based on the comprehensive experimental investigation conducted, the following conclusions have been drawn:

- The introduction of Ce and Cu into AISI 316L resulted in a notable increase in the material's final density values, with all doped samples achieving densities of 90% and above, as opposed to the 87% relative density of the reference sample.
- Wear test results revealed that 0.5 wt% Ce and 3 wt% Cu doped samples exhibited superior wear resistance in both dry and wet conditions. These two compositions demonstrated the lowest wear rates in the tests performed in SBF, indicating that Ce and Cu additions significantly enhance the wear resistance of AISI 316L.
- A reduction in the coefficient of friction was observed in both Ce and Cu-doped samples, with lower coefficient values measured in SBF for both material groups.
- Electrochemical analysis of polarization curves showed that both Ce and Cu doping led to lower corrosion current densities compared to the reference sample. Ce, in particular, demonstrated notable success in enhancing the corrosion resistance of stainless steel, although Cu also contributed to improved corrosion resistance.
- Antibacterial testing indicated that the reference sample had no inherent antibacterial properties against both *S. aureus* and *E. coli*. In contrast, the incorporation of Ce and Cu resulted in significant antibacterial activity against both bacterial cultures, thereby enhancing the biocompatibility of AISI 316L.
- The study concludes that the addition of Ce and Cu to AISI 316L leads to an overall improvement in the material's mechanical, electrochemical, and antibacterial properties, making it a promising candidate for various biomedical applications.

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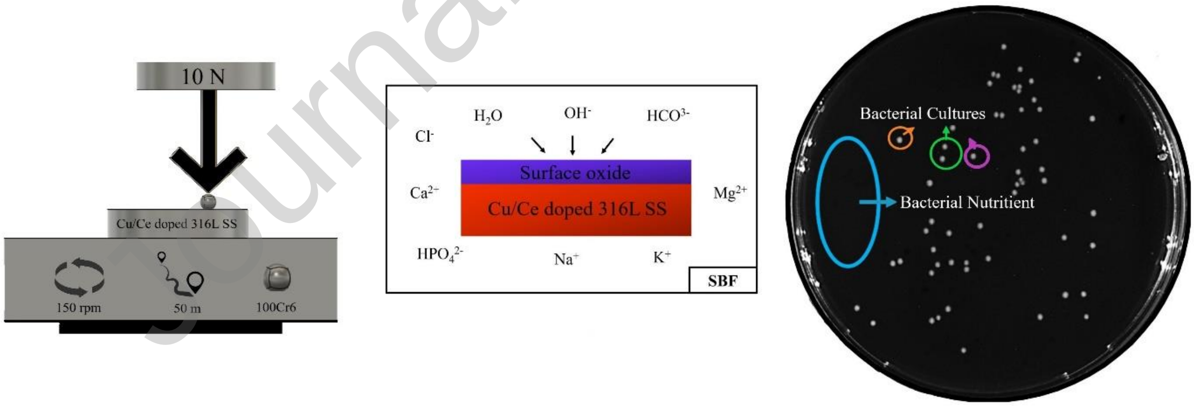
Graphical abstract



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We, the authors of the manuscript titled "Effect of Cu and Ce on the Electrochemical, Antibacterial, and Wear Properties of 316L," hereby declare that this manuscript is an original work and has not been published nor submitted for publication elsewhere, in whole or in part.

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