A STUDY OF THE SURFACE FREE ENERGY OF STAINLESS STEEL SURGICAL INSTRUMENTS

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Surgical instruments include a diverse range of components with distinct shapes and forms, specifically designed to execute certain surgical operations and methods. In the life cycle of a surgical instrument cleaning, disinfection, rinsing and drying are repeatedly performed to ensure hygiene and asepsis. The disinfection and rinsing are performed mostly in water (used as basis in a solution where cleaning other process chemicals are dissolved, mechanical cleaning and temperature agent for the surface, solvent for water soluble contaminations, rinsing of other chemicals used in the disinfection process) and other chemicals (used for disinfection and cleaning - chemicals from the aldehyde, formaldehyde and glutaraldehyde class, neutralizing agents - citric or phosphoric acids or maintenance - paraffin oil for surfaces that come in contact) that prove to be aggressive to the metal surface of the instrument leading to corrosion.

A study regarding the changes in surface free energy of stainless steels used as surgical instruments in various stages of use is appropriate since it can be related to corrosion behavior and the life cycle of the product.

Keywords: stainless steel, surgical instruments, surface free energy.

1. Introduction

Stainless steel is an excellent biomaterial due to its high resistance to corrosion which is one of the main reasons why it is used in the manufacture of a wide range of medical surgical instruments [1, 2]. Corrosion is the gradual

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degradation and disintegration of metals due to their electrochemical interaction with the surrounding environment. Stainless steel used for medical purposes requires superior corrosion resistance compared to that used in other fields [3]. Precisely for this reason, improving the quality of stainless steel with even better corrosion resistance is still a matter of great interest to scientists. Orthopedic implants have been manufactured using austenitic stainless steel type 304, (18% Cr and 8% Ni), since 1920. The presence of chromium (Cr) in stainless steel enhances its resistance to corrosion by creating a protective coating of chromium oxide (Cr_2O_3) on its surface. The inclusion of nickel (Ni) in the material decreases the likelihood of galvanic corrosion by minimizing the formation of pores that may occur during phase transitions [4-7]. Austenitic stainless steel type 316 (2% Mo) has enhanced resistance to pitting corrosion. The creation of this particular steel was needed for its use in the medical sector due to the presence of Cl^- ions in bodily fluids, which facilitate the occurrence of pitting corrosion [5, 8-12]. Austenitic stainless steel type 316L was developed with enhanced resistance to intergranular corrosion by decreasing the carbon percentage to below 0.03% [13, 14]. Stainless steel type 316L continues to be the primary metallic biomaterial used in the production of medical implants and surgical tools. Significant advancements have been achieved in using nitrogen-based steels (HNS) as a substitute for nickel, thereby mitigating the possible hazards linked to this element, such as allergic reactions [15, 16]. Hygiene and asepsis procedures are crucial in ensuring the effectiveness of surgical operations and preventing potential post-operative problems, particularly in the context of implanted medical devices and surgical instruments. In the past century, surgical interventions were considered impressive displays of skill and were performed in unsanitary conditions with an audience. However, due to the poor outcomes that were observed, modern surgical practices now prioritize strict hygiene measures and the sterilization of surgical instruments as essential [3, 17-24]. Although the surgical equipment may get contaminated during the surgery, the sterilizing step effectively breaks the epidemiological cycle. Hence, it is essential for the instruments to be manufactured from materials that fulfill the technical specifications of the instrument and can endure the sterilizing conditions, including high temperatures, pressure, and chemical cleaning agents. The surface characteristics of the material have a crucial role in both the contamination of the instrument and its effective sterilization. The contamination of surgical instruments must consider crucial parameters such as the surface's free energy, roughness, and contact angle with water [25, 26]. The connection between surface free energy and corrosion resistance of stainless steels has received little research attention and lacks discussion [27, 28].

The lifespan of a surgical tool is determined particularly by the corrosion characteristics of the material it was manufactured from [29]. The aim of this research was to investigate the modifications in surface free energy of stainless steels used in the production of surgical instruments at various phases of product utilization.

2. Materials and methods

A set of used surgical tools, coded as S1 - chisel, S2 - forceps, S3 - chisel, S4 - retractor and S5 - scissors are used for the study.

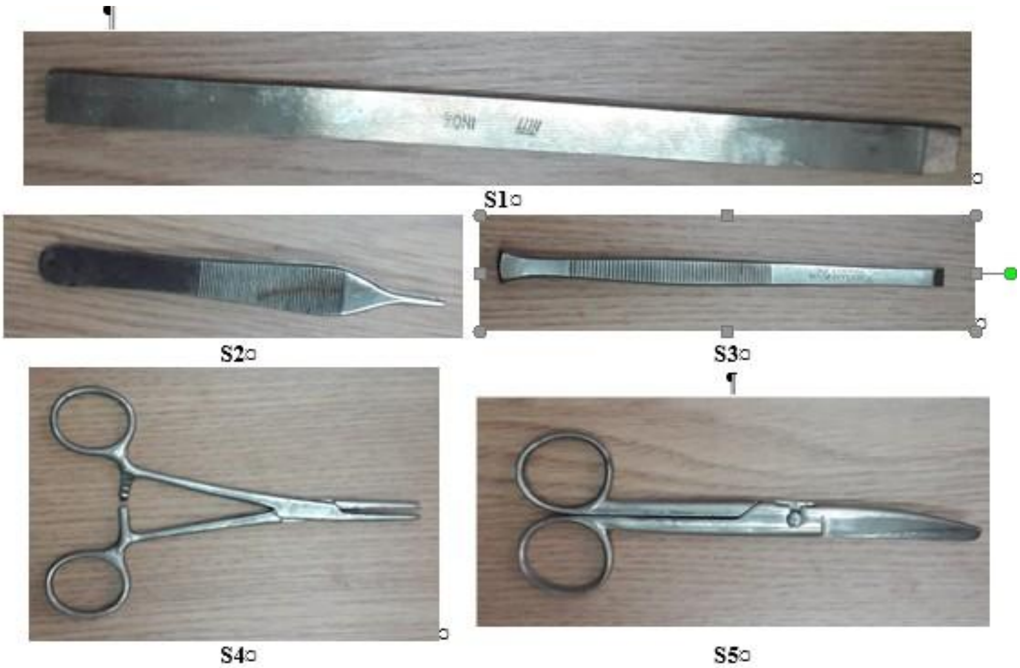

Fig. 1. Macro images of the investigated surgical instruments: S1 - chisel, S2 - forceps, S3 - chisel, S4 - retractor and S5 – scissors

The samples were first tested by energy dispersive spectroscopy using JEOL JED-2300 Analysis Station to determine the chemical composition, then contact angle measurements were performed using a KRUSS DSA30 Drop Shape Analyzer using three liquids, water, diiodomethane and ethylene glycol to determine the surface free energy of the samples using the Fowkes, Wu and OWKR methods.

The above tests were performed on the samples as received, and, to study the wear effect on the surface free energy, the samples were processed as follows: a set of samples were mirror polished using a BUEHLER PHOENIX BETA GRINDER/POLISHER equipment and passivated by immersion in nitric acid. Contact angle measurements were performed on as passivated surfaces (coded with letter P) that were later submerged in saline solution (3.5%NaCl) and a 400mV potential was applied to enhance corrosion speed. The immersion time was 8h. Contact angle measurements were performed on the corroded surface.

The three methods used to determine the surface free energy, i.e. Fowkes, Wu and OWKR use various premises that depend upon polar and dispersive interactions between the solid and liquid [30-34]. This concept was introduced by Fowkes and modified by Owens and Wendt which define differently the concept of polar interactions. The Wu method uses the Owens - Wendt premises, but consider the harmonic means of the interactions. Given the influence of the chemical composition and roughness on the measured contact angle the decision of using simultaneously these three methods seems appropriate to evaluate a crucial parameter for corrosion resistance, the surface free energy.

3. Results

3.1. Chemical composition and steel grades

As stated, the samples in as received condition were first tested by EDS to determine the chemical composition. In table 1 the chemical composition is presented, along the steel grade.

Table 1

The chemical composition of the tested samples, in weight percent, remainder is iron

Sample	%C	%Mn	%Si	%Cr	%Ni	Others	Grade
S1	0.11±0.02	1.52±0.14	0.56±0.1	18.50±0.7	9.23±0.63	0.52±0.12Mo	303
*303**	*Max. 0.12*	*Max. 2.00*	*Max. 1.00*	*17.00-19.00*	*8.00-10.00*	*Max. 0.70Mo*	
S2	0.05±0.002	1.73±0.22	0.76±0.13	17.95±0.63	8.63±0.68	-	304
S3	0.065±0.004	1.68±0.27	0.66±0.18	18.23±0.33	7.95±0.48	0.43±0.06Mo	304
*304**	*Max. 0.07*	*Max. 2.00*	*Max. 1.00*	*17.00-19.00*	*8.00-10.00*	*Max. 0.10N*	
S4	0.18±0.026	0.92±0.08	0.49±0.05	13.65±0.68	0.96±0.05	-	420A
*420A**	*0.16-0.25*	*Max. 1.00*	*Max. 1.00*	*12.00-14.00*	*Max. 1.00*	*Max. 1.00 Ni*	
S5	0.32±0.063	0.92±0.06	0.63±0.086	12.96±0.35	0.68±0.08	-	420B
*420B**	*0.26-0.35*	*Max. 1.00*	*Max. 1.00*	*12.00-14.00*	*Max. 1.00*	*Max. 1.00 Ni*	

*Composition according to ASTM F899 - 12b

The chemical composition of the steels is in accordance to ASTM F899 specifications for wrought stainless steels for surgical instruments and in agreement with the intended use as specified by ISO 7153. The chromium and nickel equivalents were computed using the average values from table 1 and the corresponding points placed on the Schaffler diagram, as depicted in Fig. 2 [35-37].

Samples S1, S2 and S3 predict a mixture of ferrite (F) and austenite (A) in the structure, when the structure expected would be fully austenitic. The Schaeffler diagram predicts a mixture of martensite (M) and ferrite (F) for sample S4, while for sample S5 a mixture of martensite (M) and austenite (A). The expected structure for both would be a martensitic one.

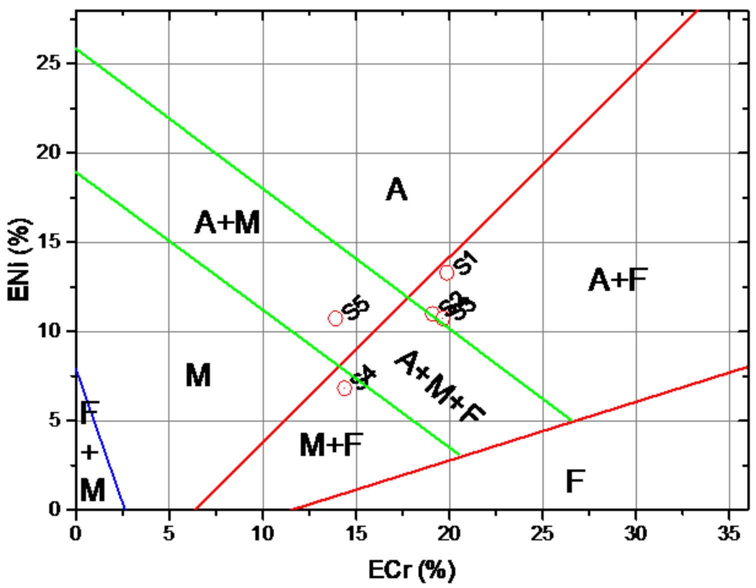

Fig. 2 Schaeffler diagram showing with chromium and nickel equivalents plotted for the experimental samples

The use of the Schaffler allows estimating the structure of austenitic stainless steels, and as observed above, the predictions were sufficiently accurate.

3.2. Surface wetting

The use of the contact angle value permits a qualitative appreciation of the wetting characteristics of the surface. In following paragraphs, a global comparison on the contact angles for water, diiodomethane and ethylene glycol on the used (U), passivated (P) and corroded surfaces (C) is presented. Sample coding used depicts first the sample name followed by the state of the surface, as example S1P reflects the characteristics of the sample S1 with a passivated surface. In Fig. 3 a comparison of the contact angles for water (W) is presented.

On the as received surface (U) the contact angle values for water are lowest, reflecting a good wetting of the surface - an undesirable behavior for surgical instruments. On a freshly passivated surface (P) the contact angle for water increases, the surface becomes more hydrophobic. The surface of the corroded samples (C) shows a mild decrease of the contact angle, the surface becomes more hydrophilic.

The same pattern was observed for all samples: on a fresh passivated surface the behavior is hydrophobic and the contact angle values decrease as the surface becomes more degraded, by corrosion and usual wear. It is obvious that a normal use in service, along with possible corrosion, wear is another phenomenon that needs to be accounted for.

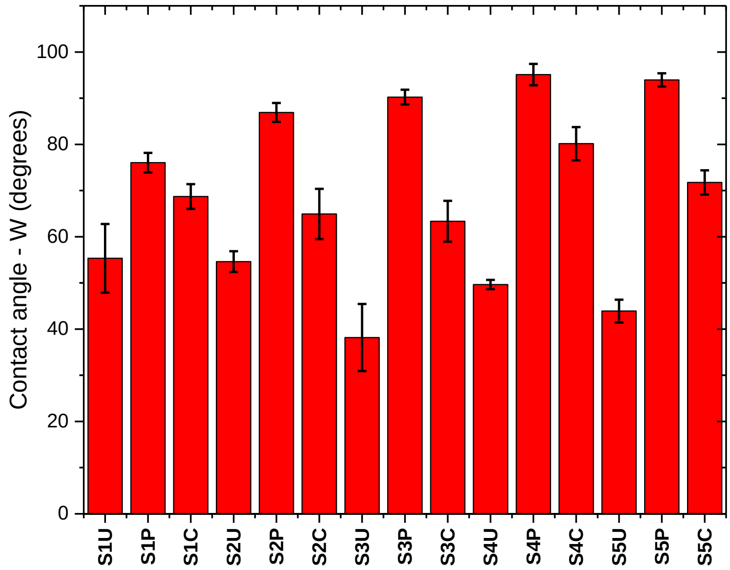

Fig. 3. Comparison of the contact angles for water

Surface roughness affects wetting behavior, thus the as received samples show the most hydrophilic surface, caused by a cumulated effect surface corrosion - roughness change.

The mixed effect corrosion - roughness variation can be inferred from the spread of contact angle values on the as received surface. Five measurements were performed on random locations on the surface that was considered to be most active during use and a great spread of contact angle values were observed.

As an example, for sample S1U, the measured contact angles ranged from 42.36° to 63.89°, the box-plot and water drop presented in Fig. 4 a. and b. reflect the situation.

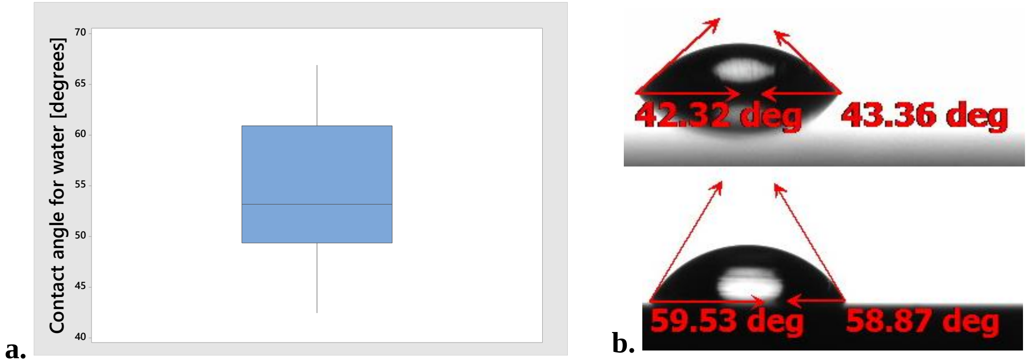

Fig.4 Spread of contact angle values for water, sample S1U showing: a. the boxplot; b. water drops showing large and small angles

Analyzing the surface behavior against diiodomethane (D), as presented in Fig. 5, it can be stated that a similar trend as for water appears, yet the change in contact angle values shows a lesser variability.

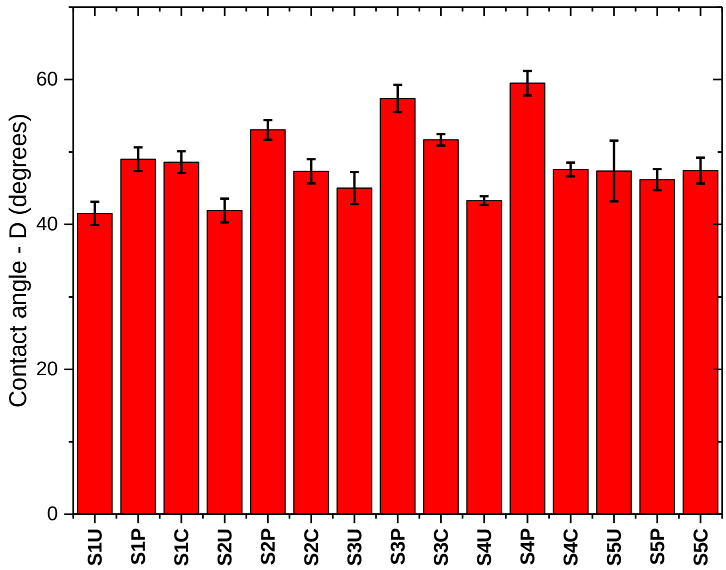

Fig. 5 Comparison of the contact angles for diiodomethane

The passivated samples show a lesser wetting for diiodomethane, similar to water, except sample S5 where no statistically significant difference was observed. The comparative analysis for contact angle for ethylene glycol (E) is presented in Fig. 6.

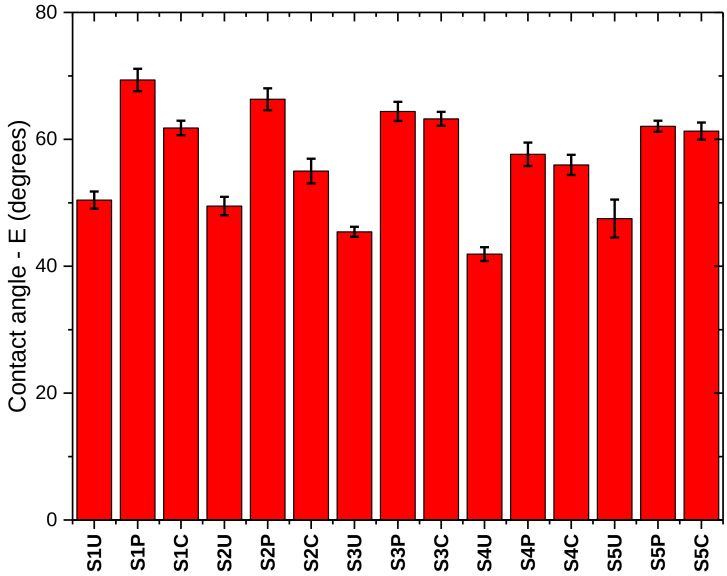

Fig. 6 Comparison of the contact angles for ethylene glycol

The behavior of ethylene glycol strongly resembles the one of water, the passivated samples are less wetted than the corroded samples, the lowest contact angles are observed on the as received surfaces, indicating an enhanced wetting.

Regarding surface wetting based upon contact angle values it can be observed that freshly passivated samples reveal lesser wetting, and, as the surface becomes more affected by corrosion and roughness changes, the contact angle values decrease enhancing wetting, an undesirable aspect.

3.3. Surface free energy

Strongly related to contact angle values are the surface free energies, parameters determined based upon previous contact angle measurements. The Fowkes, Wu and OWKR methods are used to determine the surface free energy of the samples. Since each method uses its own assumptions, it is interesting to observe the eventual discrepancies regarding the results regarding the surface free energies obtained. In Fig. 7 the results obtained for the surface free energy computed by Fowkes's method are plotted.

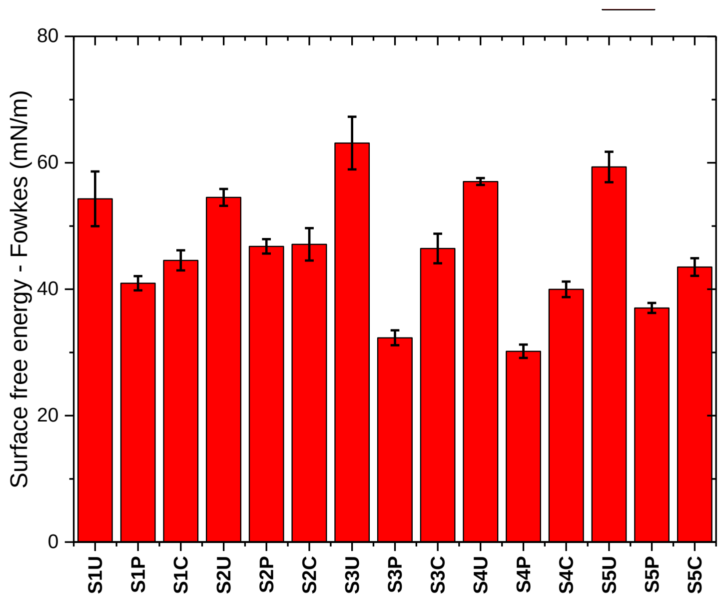

Fig. 7 Surface free energy values obtained using the method proposed by Fowkes

The highest surface energies are observed for the samples in as received condition, while the lowest appear on the fresh passivated ones. The corroded ones show intermediate values. Large discrepancies appear for the samples S3, S4 and S5, the chisel, retractor and scissors. It would be expected to observe a significant variation on S4 and S5, given the martensitic grades of steels, given the lower Cr content and higher C content, yet S3, given that it is a 304 steel, a behavior similar to S1 and S2 would be expected. Currently our inference relates the stresses and strains at the surface resulting from intensive use. The results obtained for the surface free energy determined according to Wu method are presented in Fig. 8.

The surface free energies determined by the Wu method shows a similar trend as the ones determined by Fowkes method. The passivated surfaces show lowest surface free energies, the corroded surface intermediate ones, while as received highest ones.

According to this method, the surface free energies are higher when compared to the ones predicted by Fowkes method, except sample S2, where the surface free energy on the passivated sample is less. Generally, the trend is unchanged, the differences in energies are of maximum 5mN/mm.

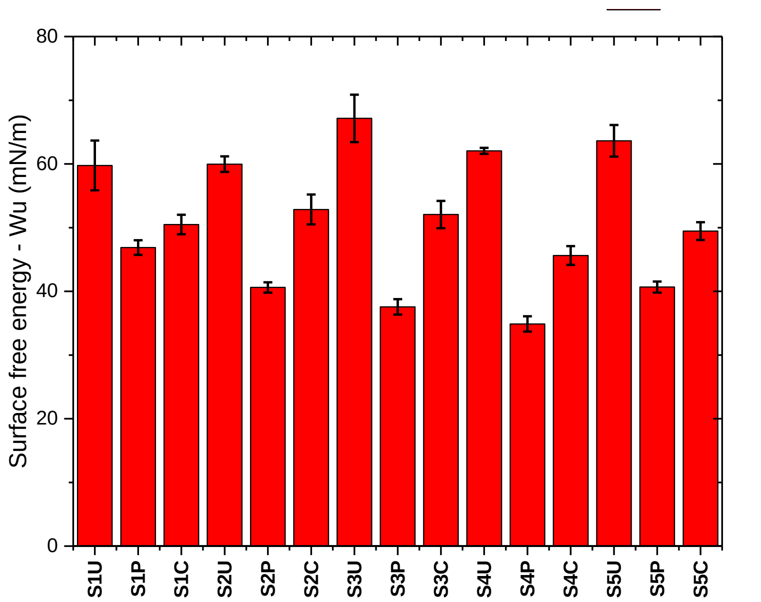

Fig. 8 Surface free energy values obtained using the method proposed by Wu

The results regarding the surface free energy obtained by applying the OWKR method are presented in Fig. 9.

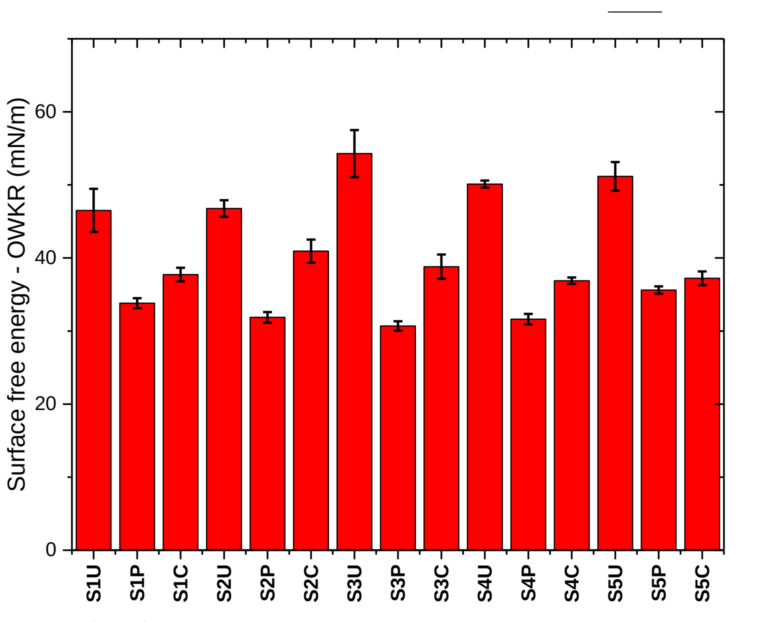

Fig. 9 Surface free energy values obtained using the OWKR method

The same trend for the surface free energy is obtained using the OWKR method. The passivated samples show lowest surface free energies and begin to increase as the surface becomes more and more degraded. As values, the OWKR method predicts lower values than previous methods, a global comparison is presented in Fig. 10.

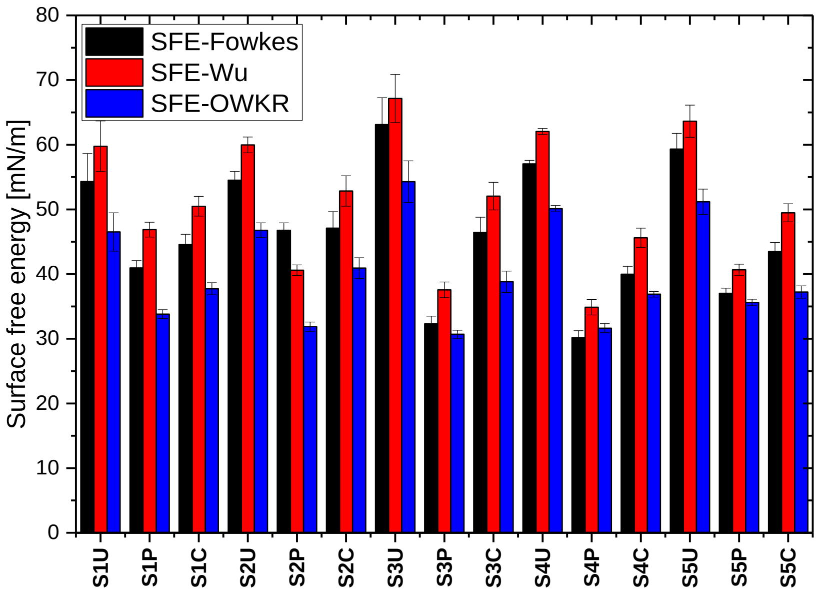

Fig. 10 Comparison of surface free energies determine by the three methods

Regardless of the method used, a similar trend was observed in the variation: as the surface becomes more and more degraded, its surface free energy tends to increase.

4. Conclusion

The surface free energy can be regarded as a crucial parameter for corrosion resistance, as a surface with higher energy will be more prone to interactions with the environment to reduce it.

The study regarding the surface free energy on surgical instruments comprised samples selected from the cutting (chisels and scissors) and non-cutting instruments (forceps and retractors). As previous information regarding the steel grades was unavailable, the selection was random, the chemical composition revealed that three instruments were made of austenitic stainless steel (the chisels and the retractor) and two of martensitic stainless steels (scissors and retractors). It would be beneficial to extend the study in a comparison of a steel from the austenitic, ferritic, martensitic and precipitation hardening grades, as specified by ASTM F899.

Despite this limitation, it was found to have a direct correlation between surface condition and surface free energy. The fresh passivated surfaces have the lowest surface free energy, and as the surface becomes degraded (by corrosion) the energies increases. In the normal use of surgical instruments, along corrosion phenomena, surface roughness is modified (mostly by scratches during transportation and use), the contributions of both factors show a significant increase in the surface free energy.

Regardless of the method used to determine the surface free energy, Fowkes, Wu and OWKR, a similar trend was observed, which leads to the conclusion that the change in chemical composition does not greatly affect the estimation. According to the results corrosion alone does not cause a large increase in surface free energy, rather the associated effect corrosion - increase in surface roughness.

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