**ORIGINAL ARTICLE** 



# Corrosion Resistant Support Materials (CRSM) as Potential Development of Technical Parameters for Biocompatibility Testing of Bone Implant Products: A Review

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**ABSTRACT** – This study aims to describe the risk of bone implant material 316L-SS by identifying the material or materials or methods that can withstand the rate of corrosion or anti-corrosion. The method used is a literature study supported by tabulation data processing instruments, mind mapping, and fishbone diagrams. All journal literature is collected, grouped, carefully identified, and scored to obtain information regarding its anti-corrosive material. The results show that corrosion of 316L can be coated with an anti-corrosive support material as follows: 1) alumina sol-gel, 2) silane, 3) parylene, 4) niobium oxide (Nb<sub>2</sub>O<sub>5</sub>), 5) 0.01%SS, 6) MgO/Tb,Eu-HAp, 7) Ti-6AI-4V coated HAp 40 micrometers, 8) HAp+HNO<sub>3</sub>, 9) nano-HA, 10) samarium-gadolinium-HAp (Sm/Gd-HAp), 11) nano-thin film hydroxyapatite polylactic acid (nHA-PLA), 12) multiwall carbon nanotube, 13) f-MWCNT, 14) Ag-HA/f-MWCNT nanocomposite, 15) nano HAp, 16) nano TiO<sub>2</sub>, 17) double-HA, 18 ) titanium ions, 19) superhydrophilic TNT, 20) superhydrophobic TNT, and 21) Ti-Nb-Zr-Ta6. Each element that coats 316L-SS has different characteristics of advantages. Unfortunately, all existing literature does not explain the technical advantages of each type of CRSM. The advantages are explained by comparing the coating elements with one another.

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## **KEYWORDS**

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# INTRODUCTION

The government's policy to seek the availability of domestic bone implants is becoming more evident with the establishment of a consortium of bone implants as a result of Agency for the Assessment and Application of Technology (Badan Pengkajian dan Penerapan Teknologi, BPPT) (now has been merged into one institution, National Research and Innovation Agency [Badan Riset dan Inovasi Nasional, BRIN], under Research Center of Advance Materials. The choice of materials used is quite large, but BPPT chooses to use 316L-SS steel and titanium as raw materials. This is because in the market, it is quite widely used, and quite a lot of ISO standards regulate it.

This innovative work of bone implants made from 316L-SS certainly requires progress toward maturity, which increasingly requires support in the form of national standards. With standards, this product will have more measurable potential risks that will arise.

Among the potential risks that can arise from this bone implant product is the capability of bone implant materials to become chemical resistant (inhibitors) contained in human body tissues. Of course, the level of risk will vary greatly because it depends on which part of the body to be implanted. The development of science and technology related to supporting materials to increase the durability of 316L-SS and titanium alloy bone implants has been rapid. Identification of supporting materials to increase the resilience of bone implants is very important, considering that this is part of the effort to guarantee the safety and health of consumers within the framework of standardization of 316L-SS bone implant products by taking into account a number of material variants that can overcome corrosion which will become a problem. Part of the endurance test validation in the process of developing bone implant product standards later. The research was conducted to analyze the identification of materials that can be used as anti-corrosion for 316L-SS as bone implant material.

# **EXPERIMENTAL METHOD**

# Materials and Instruments

This study uses the literature review method with a number of journal references, as many as 68 international journals from 1977 to 2024. The data search process is using the Google Scholar application using search keywords, namely: 1) "corrosion resistance, 316L-SS", 2) "corrosion resistance, 316L-SS, Hydroxyapatite (HA)", 3) "corrosion resistance, 316L-SS, Ti", 4) "corrosion resistance, 316L-SS, CoCr", and 5) "corrosion resistance, 316L-SS, Mg alloys" with the composition of the latest referencesshown in Figure 1.



Figure 1. Up-to-date reference sources in the literature study

This research was conducted using data processing using the Microsoft Excel application. For the 68 international journals, data processing was carried out by tabulating the data in a table with columns named data information, including the title of scientific paper (Eng), title of papers (Eng), paper author/researcher, year of paper, corrosion resistant support materials (CRSM) name grouping, bone implant designation, simplification of bone implant designation, abstract paper, paper citation. After being tabulated, the amount of CRSM information collected related to the dominant CRSM used by researchers is calculated, then the results are tabulated in a table according to the most to the smallest number. Data/information tabulation is also carried out based on the year the paper was published. Table 1 shows the draft tabulation.

	Table 1. Draft of data abbilition										
No	Title of Paper (Eng)	Author	Theme	Year	Corrosion Resistant Support Materials	Materials	Grouping1 (316L-SS + what?)	Allotment Bone Implants	Grouping2 (common use/special use)	DOI	Abstract of Paper
1	Stress corrosion cracking of bone implants	G Bombara, M Cavallini	Corrosion 316L SS	1977	High Cr ferritic stainless steel	SS feritic High Cr	316L SS + others alloy	femur fracture	common use	-	-

# Table 1. Draft of data tabulation

#### **Method and Procedure**

The results of the data processing were analyzed to obtain information about the supporting materials to increase the corrosion resistance of 316L-SS by literature review. The results are described using mind-mapping diagrams and tables of CRSMs and their references in an exploratory-descriptive manner. The analysis explains the material's name as additional material, the technical method process used, the claim of anti-corrosion, and the type of human body purpose for use. This study uses a causal effect analysis method based on literature studies related to the corrosion of 316L-SS bone implants.

The research used a descriptive exploratory analysis method design in the form of tracing all references related to 316L-SS-based bone implants with a research design namely focusing on the output of corrosion resistant support materials (CRSM), then the focus was further detailed into five anti-corrosive materials including details: 316L-SS + alloys (x), Hydroxyapatite + alloys (x), Titanium + alloys (x), 316-SS + CoCr and finally Mg + alloys (x). The data source is secondary data originating from a number of related research literature with a total of 68 papers (Table 2). The analytical method used is by explaining the name of the additional material that is claimed to be CRSM, then explaining the processing technique used, then explaining what anti-corrosion claims were found, and finally, for general body needs or specifically for the use of the bone implant.

Output of research	Material Anti-corrosive	Type of Purpose of bone implant	Type of Data	Sum of Data	Analysis Method				
Corrosion Resistant	316L-SS + x	Common use	Secondary	24	Literature review with mind-map				
Support Materials (CRSM) as Potential Development		Special use	-		<ul> <li>with explanation</li> <li>about:</li> <li>1. the material names as additional;</li> <li>2. the technical method process</li> <li>using:</li> </ul>				
of Technical Parameters	Hydroxyapatite + x	Common use	Secondary	21					
for Biocompatibility Testing of Bone Implant		Special use							
Products: A Review	Titanium + x	Common use	Secondary		3. claim of anti-corrosion; and				
		Special use			4. type of human body purpose				
	316L-SS + CoCr	Common use	Secondary	8	-				
		Special use			_				
	Mg Alloy	Common use	Secondary	3					
		Special use							

## Table 2. Research design (n=68)

# **RESULT AND DISCUSSION**

Based on the results of data processing, the results obtained are a number of anti-corrosion supporting materials, which are mostly used by researchers for bone implants, as shown in Table 3.

Table 3.	Corrosion-resistant st	support materials (	(CRSM)	data tabulation results (	68 t	papers	)
rabie o.	Corrobion resistant s	apport materials (	CIUSINI	autu tuoutution results		pupers	1

No	CRSM	Sum of papers
1	316L SS plus	24
2	hydroxyapatite (HAp)	21
3	titanium	12
4	316L SS + CoCr	8
5	Mg alloys	3

# Anti-corrosion material 316L-SS + x (n=24)

The first anti-corrosion identified was an alloy between 316L-SS with a certain support material made in the form of layers, alloys, or with certain material treatment techniques. In Figure 2, there were 23 variants of CRSM 316L-SS + x consisting of 13 types for general-use bone implants and 14 for special-use bone implants. Specific uses are specified for use only for certain body parts and cannot be used for other body parts—for example, dental implants and skull/face bone implants.



Figure 2. Mapping CRSM literature study (316L-SS+x) for general and specific body areas

#### Bone implant for common use (n = 10)

Based on research by Nielsen [1], it was explained that the best alloys for boneimplants were titanium alloys, cobaltnickel alloys, cobalt-cromium alloys, and 316L-SS. This is because all these materials have the best potential breakdown value. If sorted, they include Ti-4,5Al-5Mo-1,5Cr (+2.4 SCE), titanium (pure) (+2.4 SCE), tantalum (+2.25 SCE), Ti-6Al-4V (+2.0 SCE), Ti-Ni (+1.14 SCE), Co-Ni-Cr (+0.42 SCE), Co-Cr-Mo (+0.42 SCE), 316L-SS (+ 0.2 to +0.3SCE). The greater the saturated colomel electrode (SCE) value, the better the biocompatibility.

On the other hand, Wigginton [2] explained that 316L-SS as bone implants can improve its mechanical properties and fatigue resistance to corrosion by the cold forging method. Cold forging 316L-SS can increase the ASTM grain size index by 8 to the ASTM grain size index by 14. In addition to the cold forging method, 316L-SS can improve its mechanical properties and corrosion fatigue resistance by eliminating material stress after cold forging. The hallmark of the cold-forged 316L-SS is the appearance of a non-slip material surface at a visual magnification of 600 times.

Sivakumar [3] reported that the composition of bone implant materials followed the ASTM standard with the composition of chemical components, including Cr (16.5–18.5%), Ni (10.5–13.5), Mn (2.00 max), Mo (2.00–2.50%), C (0.01–0.03%), P (0.045% max), Si(1.00% max), S (0.03% max), and Fe (balance). The principle is that no material components should be outside the ASTM limits. In his research, Silvakumar [3] explained that the element Mo was the main cause of cracking.

Another potential for corrosion in 316L-SS is (pitting corrosion), which is generally caused by (fatigue corrosion). The method of preventing fatigue corrosion is to increase the corrosion resistance of pits. One of the ways to increase pitting corrosion power is by using surface nitrogen ion implantation methods and heat treatment. The impact is that fine prior-prior grain size is produced in the preparation of the material structure so that it is more resistant to fatigue corrosion [4].

Increasing the corrosion resistance of 316L-SS can also be done using alumina sol-gel coating deposited by the dipcoating method. Silica coats the center of the coating. The coating results must be homogeneous, free of cracks, and contain low  $Al_2O_3$  crystals through the Boehmite phase. This method has succeeded in providing evidence of increasing pitting corrosion protection by 470 mV and reducing passive current by  $10^{-9}$  ampere.cm<sup>-2</sup> [5].

Another method of increasing the corrosion resistance of 316L-SS is by coating two polymer layers, namely silane and parylene. Silane is an inorganic compound with the chemical formula  $SiH_4$ , which makes it a group 14 hybrid. Meanwhile, parylene is a conformal polymer film used as a protective conformal layer for more than 25 years. Coating silane and parylene of 2 m can effectively provide corrosion resistance protection. Another coating method is to use Nb and SS coatings. Nb coatings are usually in the form of niobium oxide (Nb<sub>2</sub>O<sub>5</sub>) and stainless steel (SS) coatings. Coating with niobium oxide material on 316L-SS has a positive effect on improving corrosion behavior. In addition, the coating has a significant effect on decreasing the corrosion current density [6].

A study conducted by Pathote et al. [7] shows that 316L-SS is very susceptible to corrosives in the human body. This was proven when the steel surface was soaked for 270 minutes and 60 minutes with simulated body fluids (SBF) experiencing a corrosion rate that was in line with long soaking. So, Yahyaoui et al. [8] showed research results where using a TiN PVD coating would provide additional protective effects related to physiological corrosion.

In the struggle between bone implants and the rate of corrosion that occurs, there is a potential layer that can inhibit the rate of corrosion, namely the bioactive glass layer. El-Baakili [9] conducted research showing that bioglass 15-7510P has the highest acellular bioactivity, as evidenced by the rapid formation of a thick and continuous apatite layer.

#### Bone implant for special use (n = 14)

Based on the results of research by Bombara and Cavalinni [10], it was explained that hydrochloric acid in the treatment process for the restoration of femoral fractures causes pitting in stress corrosion cracks. 316L-SS material with high Cr ferritic condition and extra low interstitial elements are much more resistant to pitting corrosion. Coating 316L with stainless steel as much as 0.01% SS resulted in no detectable biological effect, while 0.1% SS interfered with the behavior of osteoblasts, and 1% SS resulted in the death of body cells [11].

Another coating method is the surface polishing method with the electro method. This method can provide the best resistance to crevice corrosion [12]. Crevice corrosion is corrosion that occurs in metals that are attached to other metals, such as crevices that can hold dirt and water [10]. Treatment of implants for knee and hip joints often requires CRSM, which can reduce its corrosion but still maintain the hardness of the material [13].

According to Dadfar et al. [14] research, other methods to increase corrosion resistance, particularly in orthopedic parts, such as mono-block hip bars, can be done using the post-weld heat treatment (PWHT) method. In the PWHT method, materials that have been welded using special tools are reheated to reduce residual stress due to welding so that metal resistance increases against stress corrosion cracking (SCC) [15]. The corrosion behavior of weld metal (WM) is better than that of base metal (BM). This phenomenon is associated with the secondary phase present in BM. The secondary phase in the weld metal dissolves when the base metal melts due to the welding process. As a result, the coupling corrosion rate is greater than that of other parts, but as for the heat affected zone (HAZ), the adjacent zone of the weld metal is generally less resistant to corrosion, so corrosion occurs in that zone and PWHT reduces the corrosion rate of both BM and WM [14].

On the other hand, according to Yang et al. [16] research, he explained that increasing the corrosion resistance of 316L-SS can be done by adding 0.01% lanthanum (La). The effect is that there is the widest passive region and the best resistance to pitting corrosion attack in the range of 0.01%-0.08%, where the La reaction occurs in steel refining, inclusion modification, and passive film formation in simulated body fluids [16].

In a part of the body called a hip prosthesis, a lot of what happens is called a loosening of the hip prosthesis. Most of the significant loosening of the hip prosthesis was due to corrosion of the fretting between the 316L-SS femoral shaft and bone cement [17].

Muley [18] suggests that there is a method that can improve the performance of femoral bone implants (locking compression plates on fractured femurs, locking screws, and compression screws) from pitting corrosion by refining metal grains with plastic deformation. This metal grain refinement exhibits good specific strength against corrosion. Materials 316L-SS are forged by heat of 600°C with multi-axial heat [18].

The grain size of the metal was smoothed from 30 m to 0.86 m after 9 straining steps. The combination of Hall-Petch reinforcement and strain hardening increases hardness and better shear wear resistance [18]. Screw corrosion is often a problem in the world of bone implants. One of the methods to increase the resistance of the pit structure from corrosion is by drilling a micro laser system using argon gas [19].

A study conducted by Li et al. [20] shows that the frequency laser melting (SLM) method is very effective in producing oral alveolar implants (OAI) that are resistant to corrosion by changing the scanning speed. The results showed that corrosion resistance increased with a scanning speed of 800 mm/s with pH 4 and 6 in artificial saliva.

A study by Pellier et al. [21] revealed that fretting corrosion wear on 316L-SS contact with poly-methyl-metaacrylate (PMMA), but that mechanical wear could be measured and that corrosive wear was minimal by applying a higher cathodic potential of E = -800 mV (SCE). However, from an engineering perspective, implant design and installation techniques may be adjusted to lessen the stress concentration that forms close to the fracture site, according to research by Gervais et al. [22]. Some of the greatest methods to prevent surface corrosion from vigorous contact with bodily fluids—which often fail and finally break due to corrosion—are summarized in research by G. Manivasagam et al. [23]. Therefore, the general coating process makes use of nanoparticles' superior qualities to achieve improved mechanical properties and bicompatibility. Furthermore, studies conducted in 2014 by Karamian et al. [24] showed that nanoscale coating with NHA/Zircon. As a consequence, there seems to be apatite crystal formation on the surface, and the greatest bioactivity happens on the same sample, which has 10% by weight of zircon because of the lowest Xc. According to research by Kajzer et al. [25], mechanical damage may be estimated using stereoscopic and scanning electron microscope (SEM).

#### Hydroxyapatite Materials + x (HAp) (n = 21)

The next anti-corrosion identified was an alloy of 316L-SS with hydroxyapatite (HAp) or arranged in layers and certain material treatment techniques. As a result (Figure 3), there were 21 CRSM variants, hydroxyapatite + x alloy group consisting of 12 for general use of bone implants and 9 CRSM for special use of bone implants.



Figure 3. CRSM (hydroxyapatite) literature mapping for general and specific body areas

#### Bone Implant for common use (n = 12)

A study conducted by Kannan et al. [26] explained that the treatment of adding a supporting material in the form of hydroxyapatite + HNO3 by the passivation method to increase the corrosion resistance of 316L-SS with a better level of biocompatibility [26]. The method uses an artificially induced passivation layer on the metal surface before coating to increase the implant's corrosion resistance properties. The results show the efficiency of HAp coating on the HNO<sub>3</sub>-treated surface [26].

Another 316L-SS coating by hydroxyapatite (HAp) is studied by Aksakal et al. [27]. The coating method was carried out using the hydroxyapatite (HAp) method, which was coated with Ti-6Al-4V and 316L-SS substrates using the solgel method. In his research, Aksakal explained that if 316L-SS was coated with HAp 72 m, it had the highest corrosion susceptibility, while Ti-6Al-4V coated with HAp 40 m showed the highest corrosion resistance. This indicates that adhesion and corrosion resistance decrease with increasing thickness of the second layer of substrate [27]. It is proven to provide significant corrosion protection. The trial showed that the OCP (open circuit potential) value was getting smaller and smaller in 316L-SS bone implants coated with hydroxyapatite (HAp). OCP is the potential that exists in an open circuit. That is, the voltage exists when the terminal ends of a circuit are detached, and there is no external load, for example, in bone implants [28].

When hydroxyapatite coating is used with nano-sized materials, then nano-HA deposition using medium stress and high sintering temperature will modify the HA structure, produce a denser layer, and increase the corrosion resistance of 316L-SS [29]. However, to further improve protection against several bacteria, such as Staphylococcus aureus and Escherichia coli, and assist in the application of bone tissue cell regeneration to be spliced, a hydroxyapatite (Sm/Gd-HAp) coating can be used, which is substituted with samarium.gadolinium on 316L-SS which is passivated in boric fluid [30].

Another CRSM is by coating a sol-gel-derived nano-hydroxyapatite polylactic acid (nHA-PLA) thin film method on 316L-SS. The result is that cytotoxicity assays confirm the normal growth and viability of human fibroblast cells (HFFF2), showing a fairly good bio-resistance ability [31]. On the other hand, alloy coating can also be done using nanohydroxyapatite (HAp) powder mixed with electrical discharge machining (PMEDM). This coating material can improve the morphological properties of bone implants, along with a 79% increase in microhardness (HV) of the modified 316L-SS bone implant surface [32]. Another innovative development related to hydroxyapatite is HA coating using HA bioactive composite, called carbon nanotube multiwall with spray pyrolysis technique. Spray pyrolysis is one of the important techniques for synthesizing nanomaterials and coating the substrate with a thin film layer [33]. The X-ray diffraction (XRD) results showed an increase in surface area and a decrease in the crystal size of the 316L-SS bone implant coated with HA or f-MWCNT composites, while the SEM results showed that round meso HA crystals grew evenly on the f-MWCNT wall. These nanoflake meso crystals are beneficial for bioactivity. When compared, the HA or f-MWCNT composite showed an increase in antibacterial activity with an inhibition zone of12 mm against Escherichia coli. This composite also had a higher corrosion resistance performance in stimulated body fluids with a decrease in current density from 7.3 A cm to 6.5 A. cm — 2 after MWCNT incorporation [34]. Another CRSM result of research by Sivaraj and Vijayalakshmi [34] is coating using Ag-HA/f-MWCNT nanocomposite (multi-wall carbon nanotube) on 316L-SS provides quite a lot of benefits, namely: 1) decreased minimum inhibitory concentration (MIC) from 0.25 mg to 0.125 mg with Ag concentration, 2) corrosion efficiency shows a decrease in current density from 3.9 to 3.5 A, and 3) 3 wt% Ag substituted composites are non-hemolytic which are very suitable for orthopedic implants [34].

A study by Manonmani [35] stated that the coating of bone implants using nano HApand nanoTiO<sub>2</sub> proved that corrosion resistance could be increased by enhanced cell attachment and proliferation in nano biocomposite coated samples so that they are ideal candidates for biomedical applications [35]. A trial of the use of the drug calcium hydrogen phosphate (CaHPO<sub>4</sub>) was carried out with concentrations of  $1 \times 10^{-5}$  and  $1 \times 10^{-3}$ . The results showed that a CahPO<sup>4</sup> concentration of  $1 \times 10^{-3}$  was the most protective for 316L-SS bone implants [36].

#### Bone Implant for Special Use (n = 9)

CRSM for specific body areas has also experienced significant development, based on research by Aksakal et al. [37] proving that the failure of bone implant products is caused by four types of failure, namely: a) 42% of failures occur due to corrosion coupled with erosion-corrosion, b) 16.5% due to inclusions and gap stresses correlated with fatigue, c) 16.5% failure due to having traces of production impurities, and d) 25% indicating fatigue through ductile type failure. Ductility is a level of ductility of the material structure, where the structure can experience post-elastic deviation when it reaches the state on the verge of collapse, which is the largest ductility factor value of 5.3 (SNI 03-1726-2002). So, the results of the study concluded that the main reasons for failure were corrosive attacks, manufacturing defects, and failures caused by non-standard materials [37].

Aksakal's research [37] also revealed that in the case of hip bone implants, there are fractures in many locations. This may be due to manufacturing defects on both tool surfaces and associated with incompatible component designs, in addition to the failure of the titanium plate femoral compression. Stainless steel is formed by corrosion fatigue mechanisms triggered by the presence of intense localized corrosion and intergranular cracking. There is also a failure of the vertebral column to experience cavities caused by the formation of intense pitting corrosion during use [37].

A study revealed that the 15% H<sub>2</sub>SO<sub>4</sub> treatment was very efficient in corrosion resistance, meaning that the process of dissolving the H<sub>2</sub>SO<sub>4</sub> alloy in the hydroxyapatite layer could save 15% for the 316L-SS coating [38]. Another interesting thing is that anti-corrosion can also be made by coating using hydroxyapatite, which is double substituted with MgO/Tb, Eu-HAp with electrodeposition method, and the results show good anti-corrosion performance, better bioactivity, and biocompatibility [39].

The study of Fathi et al. [40] reaffirmed the use of HA as the best coating for orthodontic 316L-SS bone implants. The results show that double or double HA coating will significantly increase the corrosion current density, which is much lower than the value obtained for single-coated HA specimens [40]. Coating with other HA was also proven by Assdian et al. [29] using Nano-HAp material with  $H_2SO_4$  concentration treatment. With such treatment, the results showed that the nano-HA deposition using moderate stress and the appropriate time span gave a smooth and almost cracked-free layer, thereby increasing the corrosion resistance of the sample. Increasing the sintering temperature changes the HA structure, resulting in the formation of a denser layer and increasing the corrosion resistance of the sample [29].

Another CRSM is hydroxyapatite ceramic (HAp) in the form of calcium phosphate deposited on 316L-SS stainless steel by pulsed laser deposition method. Another sample is HAp calcium phosphate deposited on a Ti-6Al-4V alloy. After comparison, the results show that HAp-coated Ti-6Al-4V provides higher corrosion protection than HAp-coated 316L-SS stainless steel [41].

As explained in the general body section above, Sivaraj and Vijayalakshmi's research [34] in the form of CRSM Ag-HA, or referred to as f-MWCNT, can also be used for orthodontic body parts [26]. Similarly, the same-based Cu-HA nano-composite layer, namely f-MWCNT, found that the 316L-SS coating using Cu-HA nano-composite showed high crystalline properties with P63mc space groups and spherical morphology. The corrosion current density showed a remarkable decrease from 6.8 to 3.8 A, indicating that the hydrospatite composite layer provided higher barrier properties for the corrosion protection of 316L-SS bone implants. Also, the antibacterial ability of Cu-hydroxyapatite/f-MWCNT nanocomposite is effective against Escherichia coli compared to other microorganisms. However, this material is non-toxic, biocompatible, and suitable for biomedical applications [42].

A study conducted by Gnanavel et al. [41] showed that the corrosion resistance of HAp-coating Ti-6Al-4V provided higher corrosion protection than HAp-coated 316L-SS stainless steel substrates. This method is called the pulsed laser deposition technique.

Apart from that, there is another coating technique put forward by Sivaraj and Vijayalakhsmi [34], namely Cuhydroxyapatite/f-MWCNT coating, with a new spray pyrolysis technique. The results show that the Cu-substituted hydroxyapatite/f-MWCNT composite coating provides higher barrier properties, which are beneficial for achieving higher corrosion protection of 316L-SS implants, in addition to the presence of better Escherichia coli antibacterial ability, the coated material is non-toxic and biocompatible.

#### Titanium material (n = 12)

The next anti-corrosion that has been identified is an alloy of 316L-SS with titanium (Ti) or arranged in layers and certain material treatment techniques. The result (Figure 4) is that there are 9 CRSM variants, 316L-SS+Titanium alloy group consisting of 4 for using bone implants in general and 5 CRSM for using special bone implants.



Figure 4. CRSM (titanium) literature mapping for general and specialized body areas

#### Bone Implant for common use (n = 8)

The results of the research by Seah et al. [43] stated that for the case of the implant product containing gaps, the 316L-SS stainless steel bone implants showed weak resistance to crevices and experienced pitting corrosion from metal biomaterials rather than titanium alloys. The excellent corrosion resistance of solid and porous titanium is due to the strong affinity of the metal even for small amounts of oxygen in aqueous environments, resulting in a highly resistant and self-regenerating passive film [43].

A study by Aziz-kerrzo et al. [44] compared the level of corrosion resistance between Ti, Ti-6Al-4V, and Ti-45Ni. Corrosion resistance test using buffered salt solution using anodic polarization and electrochemical impedance measurement. Anodic polarization is a shift of polarization in the "positive" direction (above corrosion potential  $[E_{corr}]$ ), whereas electrochemical impedance is a method for analyzing the response of a corroded electrode to an AC potential signal at low amplitude (~10mV) over a very wide frequency range. The results show that Ti and Ti-6Al-4V have high resistance to local corrosion initiation, and Ti-45Ni has susceptibility to local corrosion attack [44].

Research conducted by Feng et al. [45] proved that 316L-SS without titanium ion implantation had a polycrystalline structure containing inclusions of the second phase. This condition is very susceptible to pitting corrosion and intergranular corrosion, as observed by SEM. As for 316L-SS, after the implantation of Ti ions, the outer surface was deformed and homogenized, and the area underneath was partially irregular. As a result, local corrosion is avoided, and the sample is subjected to general corrosion. This proves that coating using titanium increases the corrosion resistance of 316L-SS bone implants [45].

Asri et al. [46] in his research suggested that there are two techniques for improving the corrosion resistance of bone implants, namely: 1) surface modification techniques, which include deposition of layers, development of passivation oxide layers, and surface modification of ion beams; and 2) surface texture techniques which include plasma spraying, chemical etching, blasting, electropolishing, and laser treatment. However, Asri et al. [46] concluded that the biocompatible metal surface modification technique is the best solution from others because of 3 advantages: a) it is able to improve corrosion resistance performance, b) it is able to achieve superior biocompatibility, and c) it promotes osseointegration of biocompatible metals and alloys [46].

A research conducted by Wathanyu et al. [47] shows that coating using the cold spray method and with a high porosity gradient when layers 2 and 3 are very significant shows a very stable passive film at the interface layer, which increases the level of corrosion at a lower level. The structure of the Ti layer stimulates the ingrowth of bone cells.

In research conducted by Puraditya et al. [48], it was shown that the  $TiO_2$  and  $ZrO_2$  thermal spray coating method on HA materials 316L-SS and Ti-6Al-4V was able to reduce the corrosion rate to a greater extent than HA coating alone. A study conducted by Atmaca et al. [49] stated that a coating using physical vapor deposition (PVD) in the form of a TiNbTaZr alloy provides superior corrosion resistance and reduces wear under SBF conditions. This is because the resulting layer structure is nano-sized without delamination or cracking and consists of a stable  $\beta$  phase.

Recent research by Naser and Anaee [50] showed that coating using Gd-Ni-Ti for 316L-SS stainless steel using the sputtering technique was able to provide an increase in surface roughness from 25.2 nm to 47.2 nm, and this resulted in an increase in durability and efficiency equivalent to 78.38%. On the other hand, the development of research on increasing the corrosion resistance of 316L-SS for bone implants by Nabeel et al. [51] is using the AM 316L-SS method, namely 316L-SS, the manufacturing process of which is given additional treatment to modify the mechanical, corrosive, and biological. The results show that AM is better when compared with wrought 316L-SS because of its unique and smooth microstructural features. However, when compared with SLM 316L-SS, the SLM method is superior.

#### Bone Implant for special use (n = 4)

Another interesting coating technique for strengthening orthodontic 316L-SS bone implants that of Huang et al. [52] who performed coatings with 2 types of titanium dioxide ( $TiO_2$ -nano-tube (TNT) using superhydrophilic TNT and superhydrophobic TNT by considering 2 phases.  $TiO_2$  crystals, namely the amorphous phase and anatase phase) so that the results are as follows: a) for superhydrophilic amorphous TNT, failed to protect 316L-SS from corrosion; b) for super hydrophobic amorphous TNT, slightly increased corrosion of 316L-SS, c) for superhydrophilic anatase TNT and superhydrophobicity, significantly improves corrosion resistance, d) for superhydrophilic amorphous TNT, minimizes platelet adhesion and activity, e) for superhydrophilic anatase TNT, activates fibrin network formation and can be applied as a promising permanent biomaterial in blood contact biomedical devices wherein reduction of platelet adhesion/ activity and increased corrosion resistance can be combined effectively, and f) for both types of superhydrophobic TNT, both amorphous and anatase were able to significantly reduce platelet adhesion and increase corrosion resistance regardless of the crystalline phase [52].

The first strengthening technique is as studied by Samuel et al. [53], in which 316L-SS is coated with Ti-Nb-Zr-Ta alloy or the use of Ti-Nb-Zr-Ta alloy alone. The method is a deposition process using a laser, where the corrosion resistance produced is better than the commercially pure titanium grade 2 and Ti-6Al-4V ELI (CP) alloy. In vitro studies showed comparable cell proliferation but increased cell differentiation properties compared to Ti-6Al-4V ELI [53]. In their research, Afzali et al. [54] confirmed that there is the most important corrosion that must be considered in the new generation of titanium alloys (the type with low modulus), namely electrochemical corrosion, where the impact is very detrimental to the human body due to the release of toxic metal ions and corrosion products [54].

Aparicio et al. [55] conveyed the results of their research specifically for dental implants made of pure commercial Ti. It is important to pay attention to the extent of surface corrosion, which is the problem of residual compressive surface tension caused by shot blasting. Another thing is the coating using Ti-15Mo alloy; the results of Kumar and Narayanan's [56] research prove that there is passivity in the anodic potential of all tested fluoride ion concentrations. This means that although a number of molybdenum (Mo) ions are released, they are not harmful, so this alloy is very biocompatible for dental implant applications [56].

#### 316L-SS + CoCr material (n = 7)

The transformation-induced-plasticity (TRIP) steel is a high-strength and ductile stainless steel. The research results of Syrett and Wing [57] showed that TRIP steel was able to withstand fretting corrosion and corrosion fatigue quite well. So, this steel can be a priority candidate for future implants. Another study, X. Huang et al. [58] shows that the alloy between 316L-SS and CoCrMo has a lower level of corrosion if the gap created is larger. It is stated that a joint gap width of 0.05 mm is more prone to leaks than a gap with width 0.1 mm.

On the other hand, Li's research, Bolin et al. [59] shows that the addition of 10% by weight of Co-Cr-Mo-W to 316L-SS stainless steel powder will increase its yield strength from 731.96 MPa to 784.09 Mpa, no cracking and fracture failures were seen in the tensile test, corrosion resistance was also increased, shown at a lower corrosion current density pitting potential ( $E_{pit}$ ) of 277mv. Chemically, this occurs because adding the Cr element will form a passive film around the powder pores around the hole and expand outward so that the stress increases.

A study conducted by Morsiya [60] stated that the CoCrMo alloy has the advantage of a fairly high chromium content, which is able to form a passive oxide layer on the surface, protecting the alloy from the body's environment.

Another study by Wang et al. [61] states that the entropic alloy  $Co_{36}Fe_{36}Cr_{18}Ni_{10}$  slows down or inhibits pitting corrosion, restoring pitting corrosion. Twin boundaries are very effective in reducing the formation of corrosion holes and minimizing the expansion of corrosion cracks. The main cause is the formation of a passive film, which produces more insoluble substances with lower enthalpy, making it more stable. In research by Mace and Gilberth [62], crevice corrosion is typical for CoCrMo alloys compared to those without such guidelines.

In research by Manaka et al. [63], it is stated that if Ti-6Al-4V extra low interstitial (ELI) is combined with CoCrMo, the results do not show local corrosion and maintain a temporary local passive layer. Another study by Murugan et al.

[64] stated that the TiCoCr alloy that coated 316L-SS with a coating duration of 90 minutes had much better surface characteristics than TiO, and TiN.

## Magnesium (Mg) material (n = 3)

A study conducted by Palanisamy et al. [65] shows that the corrosion rate of 316L-SS can be reduced by providing a Mg-Alloy (AZ80) alloy oxy-fuel (HVOF) coating but using the response surface methodology (RSM) method, namely optimizing parameters. HVOF spray to achieve higher levels of hardness and reduce porosity. The results show that the minimum porosity volume is inversely correlated with the micro-hardness volume, where the minimum porosity is 0.21  $\pm$  0.013 vol% and the maximum micro-hardness is  $367 \pm 4$  HV0.3.

There is another interesting thing in the research conducted by Singh et al. [66] which stated that by carrying out a new family of bioactive glass (BAG) method on one of them, namely MgO via sol-gel route, resulted in the finding that both of them could be used as anti-aging coatings. Corrosion with increasing adhesion strength values, in terms of surface texture, shows a corrosive resistance density between 35 nA/cm<sup>2</sup> and 353 nA/cm<sup>2</sup>. This shows the potential of the synthesized BAG as a coating material for 316L-SS implants.

In general, the use of medical Mg alloy coating materials has several critical points, as stated by Wei and Gao [67] as follows: 1) surface coating materials with Mg alloys must have the characteristics of biocompatibility and long-term protection against corrosion by being able to inhibit the release of hydrogen directly, excessive during the degradation process; 2) the corrosion rate of Mg alloys in the blood environment is much higher than corrosion in the bone environment, so it is necessary to develop various types of coatings; and 3) the coating material must be able to be absorbed by the body safely when biodegradation takes place, particularly in the main human organs.

# CONCLUSION

Based on the results of the discussion, conclusions can be drawn as follows:

- 1. Corrosion is an absolute condition that occurs in a bone implant product, even if it is made of titanium and its alloys, particularly those made of 316L-SS. Corrosion that occurs is due to chemical activity in the body, especially blood which contains a number of mineral salts, ferum, calcium, chemical drug elements and so on.
- 2. The corrosion of 316L-SS as bone implant material can be minimized in the best way according to the coating element, namely through: 1) coating with other elements or alloys, 2) coating with hydroxyapatite (HAp), and 3) coating with titanium elements or their alloys.
- 3. The corrosion of 316L-SS as bone implant material can be minimized through 3 main techniques: 1) material engineering modification, 2) casting engineering, and 3) coating technique.
- 4. There are several techniques or methods of minimizing the corrosion process, namely: 1) cold forging, 2) dipcoating, 3) electrodeposition, 4) passivation method, 5) deposition, 6) passivation oxide coating, 7) modification ion beam surface, 8) plasma spraying, 9) chemical etching, 10) blasting, 11) electropolishing, and 12) laser.
- 5. The corrosion of 316L can be coated with an anti-corrosive support material (CRSM) as follows: 1) alumina sol-gel, 2) silane, 3) parylene, 4) niobium oxide (Nb<sub>2</sub>O<sub>5</sub>), 5) 0.01%SS, 6) MgO/Tb,Eu-HAp, 7) Ti-6Al-4V coated HAp 40 micrometers, 8) HAp+HNO<sub>3</sub>, 9) nano-HA, 10) samarium-gadolinium-p (Sm/Gd-HAp), 11) nano-thin film hydroxyapatite polylactic acid (nHA-PLA), 12) multiwall carbon nanotube, 13) f-MWCNT, 14) Ag-HA/f-MWCNT nanocomposite, 15) nanoHAp, 16) nano-TiO<sub>2</sub>, 17) double-HA, 18) titanium ions, 19) superhydrophilic TiO<sub>2</sub>-nano-tube (TNT), 20) superhydrophobic TNT, and 21) Ti-Nb-Zr-Ta.
- 6. Each element that coats 316L-SS has different characteristics of advantages. Unfortunately, all existing literature does not explain the technical advantages of each type of CRSM. The advantages are explained by comparing the coating elements with one another.

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