

# A Review on Corrosion of Lean Duplex Stainless Steel in Ringer Solution

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## Abstract

Biomaterials should have desired qualities such as great corrosion resistant, osseo-integration, great wear resistant, mechanical compatibility, and biocompatibility to provide safe implantation with a long lifespan and without eliciting rejection. Metallic implantation corrosion seems to be significant because it may compromise mechanical and biocompatibility integrity. This study presents a basic introduction of leaner duplex stainless steel implantation corrosion, varieties of DSS corrosion in Ringer solutions, and the function of alloying components in implant failure.

## Introduction

Duplex stainless steels contain a biphasic of austenite and ferrite, both of which are present in about equal proportions in the material. In all continents, new varieties of DSS with a notable quantity of nitrogen (near to 0.2 percent), no Mo, and extremely low Ni (less than 2percent) have been developed. The creation of lean duplex, which has much fewer allowed features than regular duplex, has become the primary goal. The goal is to replace 316 and even 304 grades in biomedical applications that are great cost-effective replacements to 304L and 316L [1]. Once metals and alloys have been utilized as implantation in the human body, corrosion is among the most common difficulties. It will be accomplished by electrochemical processes. It is indeed vital to remember that biomaterial corrosion isn't merely a chemistry and physics experiment [2].

Once a metal is implanted in the human body, corrosion happens slowly due to an electrochemical reaction. Crevice and Because of the restricted corrosion behavior and metallic ion leakage from implantation, corrosion resistant must be improved by altering the SS surface [3]. Once a metal implantation has been put in the milieu of the human body, corrosion is the slow destruction of materials caused by electrochemical assault. Apart from fracture toughness and fatigue strength, a bioimplant should have extremely good corrosion and wear resistant in a greatly corrosive body environment and under variable loading circumstances. Anions including bicarbonate, phosphate, and chloride ions, as well as cations including Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and others, make up the aqueous solution in the human body. The predicted rate of corrosion for metal implants was  $2.5 \times 10^{-4}$  mm/yr, or 0.01 mil/yr [4].

## 1.1 Mechanisms of Corrosion in Vivo Applications

Hank's solution, Ringer's solution, or simulated body fluid (SBF) are utilized to replicate the corrosion behavior of implantation in a human body milieu. The many types of corrosion that occur in vivo and result in excessive metallic ions being released into the environment have been described below [5]–[10]:

Table 2.2 Corrosion Kinds in Biomaterial Implantation that Made of Traditional Materials [2].

Type of corrosion	Material	Implant location	Shape of the implant
Pitting	304SS	Orthopedic/ Dental alloy	
Crevice	316 L SS	Bone plates and screws	
Corrosion fatigue	316 SS	Bone cement	
Galvanic	304SS, 316SS	Oral Implants Screws and nuts	
Fretting	Ti6Al4V CoCr SS	Ball Joints	
Selective Leaching	Mercury gold	Oral Implants	

## 1. *General Corrosion*

Throughout localized corrosion, the whole surface of the metals are subjected to the cathodic reaction, resulting in general (uniform) corrosion. Potentially, the uniform corrosion mechanism implicated two critical stages: a) initial surface of metal bombardment via chemical solutions resulted in the creation of a beginning stages in which the cathodics and anodics locations were being nearly appended to one another, and b) the uniform corrosive engine propagated a corrosion nucleus all around sample surface of the metal. Uniform corrosion is also defined as corrosion that occurs at a consistent pace over an exposing surface of the metal [5][2].

## 2. *Localized Corrosion*

### - *Pitting Corrosion*

Pitting corrosion happens when a tiny surface pit is inserted in a solution in an implantation. The accompanying negative charge from the freed electrons should be dispersed via the metal of the implant when the metal around the pit dissolves or lose positive ions from its surface. If the right substance and surface situations aren't in place, this sort of corrosion may move quickly, aggressively destroying metallic implantation [11]. For stainless steel implanted instruments, pitting corrosion seems to be a common occurrence. Localized corrosion may develop under physiological settings as a consequence of flaws in the oxide passivation layer. These isolated areas will erode aggressively, forming pits on the material's surface [12].

### - *Crevice Corrosion*

Corrosion of Crevice is a kind of corrosion that occurs only in limited places (crevices). Corrosion occurs within the crevices as a result of the creation of a disproportionate aeration cells. To rate a material's resistant against Corrosion of crevice, an essential corrosion of crevice temp has been typically utilized [11]. Corrosion of Crevice is a kind of corrosion, which happens at the bone-implantation interface or on an implantation tool when an overlaying or composites kind surface takes place on a metal material in a tissue/fluids environment with limited space and little or no oxygen [12]. Even in settings when steady pitting would not occur, the presence of fissures on the surface may cause localized corrosion (for example, at lower amount of halides). Failures in this process were found in medical devices at the contact between the plates of bone and stainless steel screws [13].

### - *Galvanic Corrosion*

The corrosion of galvanic happens when two dissimilar alloys or metals make contact. One of the metals would act as an anode, while the other one will act as a cathode, owing to the variation in electrical potential. As a result, ions dissolved in the bodily fluid are displaced, and corrosion emerges on both metals, simulating the action of an electrical battery, particularly in acidic environments. In orthopedic surgery, using various alloys or metals in the same operative region is not suggested [12]. The corrosion of galvanic may develop in surgical implantation if the plate of bone and bones screws have been constructed of different metals or alloys. Corrosion is more likely to develop between the plates and the screw holes' bottom surface [2].

### - *Intergranular Corrosion*

The corrosion of Intergranular (IGC), also called as inter - granular attacking (IGA), was a type of corrosion in which the outsides of crystallites seem to be more vulnerable to corrosion than the insides of the crystallites. Inter-granular corrosion occurs at grains boundaries as a result of the existence of a second stage, pollutants, or atom separation. Lower-energy grains boundaries, on the other hand, were not appear to corrode. [13].

### - *Fretting corrosion*

The corrosion of fretting occurs as a result of a mechanical process that destroys the passive layer initially. This type of corrosion may be seen in osteosynthesis devices once that material is fractured and an internal free surface is exposed [12]. Fretting happens when two opposed surfaces in the bodily environment, including the plates of bone and heads of screw of prosthetic devices, come into contact. In a corrosive media, it is caused by minor relative motions between the contacting surfaces [2].

### - *Dealloying*

Dealloying, also known as selected parting or leaching corrosion, seems to be a corrosion processing where the more active metals in an alloy is selectively eliminated, leaving a porous weaker deposits of the really noble metal behind. One of two processes happens during the dealloying processes: (1) alloys dissolutions and replating of the cathodics elements, or (2) selecting dissolution of anodic alloys ingredient. Including in dentistry, selecting leaching was also necessary [13]. This kind of corrosion was caused by chemical changes inside the particles rather than between them [2]. By adding tantalum that forms tantalum carbide rather than stainless steels, chromium carbide may be stabilized towards welding degradation [11].

### - *Stress Corrosion Cracking (SCC)*

SCC is a phenomena that occurs when static tensile tension is combined with a corrosive environment. Generally, the time needed to induce SCC reduces as these stressors rise. The chemical and metallurgical state of the material (precipitates, existence of secondary phases, grains size, thermal situation and chemical composition); environmental situations (mixing, solution viscosity, electrochemical potential, pH, pressure, temp and environmental composition); and crackibg geometry and stress condition are all factors that influence SCC kinetics. Based on the alloy, the microstructure, and the environment, SCC might well be mixed, transgranular, or intergranular. SCC was seen in a number of instances using SS orthopedic implantation. [13].

## - Corrosion Fatigue (CF)

Fatigue corrosion is a kind of metal fracture that arises as a result of the combination of electrochemical processes with cyclic stress [2]. The onset and progression of fractures as a consequence of the synergistic interaction of cyclical stress and a corrosive surroundings has been referred to as fatigue corrosion. The cyclical tension causes localized degradation of surface oxides, resulting in corrosion pits. Corrosion products that normally prevent additional corrosion are also removed by the cyclic stress. Fatigue corrosion most often results in a TG fracture with no branching. Fatigue corrosion affects all metals and alloys, even those that are resistant to SCC, such as stainless steel [13].

### 1.2 Corrosion of Duplex Stainless Steel

Stainless steel's superior corrosion resistant is typically due to its passivation. The defect amount in the passive layer generated at great voltage is substantially lower, and it offers greater protective performance [14]. Proteins were denatured in the bio corrosive environment and turn into a coating on the surface of the metal, preventing corrosion. Rapid or uncontrolled corrosion causes hydrogen and ion emission, as well as significant pH changes that might cause harmful biological responses. The passive layer resistant to corrosion is affected by structural changes in the layer or variations in the ion or electrical resistant of a layer. Chloride ions have a significant impact on the metal implants corrosion because of the great diffusivity, which allows them to quickly permeate the passive coating. Metals corrosion was slowed down by protein adsorption in two ways. The adsorbed protein layer first creates a barrier between the electrolytes and the surface oxide film, causing the surface oxide to develop. Proteins clearly operate as a cathodic corrosion protection. Secondly, the oxide ions on the surface are negatively charged [15].

#### 1.2.1 Corrosion Types of Duplex Stainless Steel

DSS had the least amount of corrosion. The austenite and ferrite phases, on the other side, could not corrode in the same way. N, Mo, Ni and Cr have not been distributed evenly throughout the austenite and ferrite phases in DSSs. This heterogeneity might generate galvanic interactions, resulting in a variation in corrosion behavior between different phases and a preference for corrosion attacking on the weaker phase. Ferrite has a greater activity level than austenite. The increased corrosion resistant of austenite compared to ferrite was due to the greater Ni concentration in this phase. In a selective assault, metal ions were released mostly from ferrite areas [16][17]. The corrosion of galvanic occurs when an electrolyte, including serum or bodily fluid, comes into direct physical contacting with a dissimilar metals, particularly in an acidic pH environment. In comparison to polycrystalline oxide layers, amorphous oxide films have a better corrosion resistant. Corrosion is triggered by crystallographic flaws in the surface coating. Amorphous oxide films with no grain boundaries, flaws, or dislocations have the lowest current density and no breakdown potential. The addition of nitrogen to stainless steels improves their resistant to pitting corrosion [18][19].

## - Pitting and Crevice Corrosion Resistant

DSS is distinguished by a temp over which pitting corrosion begins and spreads. Critical Pitting Temp is the name given to this temp (CPT). Pitting initiation will not happen below this temp for a long time. The CPT is susceptible to tiny alterations, and pit initiation is random. The Essential Crevice Temp is the temp at which crevice corrosion begins to occur (CCT). Greater critical pitting or crevice corrosion temps, in general, imply more resistant to these types of corrosion. All grades of DSS have CPT and CCT that are much greater than Type 316. As a result, DSS is a material that may be used in a variety of applications. (According to IMO rules)  $CPT = \text{Constant} + \text{percent Cr} + 3.3 \times \text{percent Mo} + 16 \times \text{percent N}$  [18]. DSSs' pitting resistant is mostly determined by their Cr, Mo, and N concentrations. As a result, the pitting corrosion resistant may be described in terms of an empirical pitting resistant equivalent number (PREN) calculated as follows:

$$\text{PREN} = \text{wt \% Cr} + 3.3 \text{ wt \% Mo} + x \text{ wt \% N} \dots \dots (9)$$

whereas the  $x$  magnitude ranging from 16 to 30.

Pitting resistant increases as the PREN magnitude increases. The PREN magnitudes of both phases may be affected by the partitioning of Cr and Mo in the ferritic phase and Ni and N in the austenitic phase. Moreover, secondary phase particle precipitation may alter the composition of the  $\alpha$ - and  $\gamma$ -phases, actually results in specific pitting corrosion of such a weak phase. The term "critical pitting temp" (CPT) is a better way to express how susceptible stainless metals are to pitting corrosion. With increasing temp, the ferrite fractional volume rises while the austenite fractional volume drops. With rising temp, Mo and Cr concentration in the  $\alpha$ -phase decreases, whereas N concentration in the  $\gamma$ -phase rises. As a result, the PREN magnitude for the  $\alpha$ -phase calculated with  $x = 20$  falls, whereas the magnitude for the  $\gamma$ -phase grows as the temp rises. Because lean UNS S32101 DSS has a very low Mo concentration, overall pitting potential declines with time, resulting in Cr<sub>2</sub>N precipitates. Pits form around Cr<sub>2</sub>N precipitates in the Cr-depleted zone, and eventually develop into ferritic particles. The development of the  $\gamma$  phase reduces the passivation range, causing substantial pitting attacking in the ferrite phase [18].

As the percentage increased, the resistant to pitting corrosion steadily diminished. In all of the DSSs, the phase fraction ( $\alpha:\gamma$ ) with the strongest resistant to pitting corrosion has been roughly 50:50. Pitting resistant equivalents number (PREN) of  $\alpha$  and  $\gamma$  phases in the DSSs (PREN and PREN<sub>γ</sub>, respectively) have been utilized to illustrate the relationship between pitting corrosion resistant and phase fraction. The two phases' PREN magnitudes begin to diverge. The pitting susceptibility level of the less resistant phase, which is anticipated by the PREN magnitudes of the two phases, determines the total resistant to pitting corrosion of DSS. Pitting corrosion began in the  $\alpha$  phase next to the  $\gamma$  phase and spread to the phase. In all DSS, the more dissolved phase (the less noble phase) was  $\alpha$  phase. The mean corrosion depth reduced as the proportion rose. Between  $\alpha$  and  $\gamma$  phases, pitting corrosion of DSS had a greater association with galvanic corrosion rate. [20].

The pitting resistant equivalence (PRE) magnitude has been utilized in practice to compare the pitting corrosion resistant of stainless steel. For the austenite phase, the PRE number seems to be between 34 and 35, while for the ferrite matrix, it is approximately 41. (without the nitride particles). This shows that austenite, with a lower PRE number, is more susceptible to pitting corrosion than ferrite at temps over the CPT. The austenite phase's lower Cr and Mo content may explain why it is more susceptible to pitting corrosion than the ferrite phase [21].

#### - **Stress Corrosion Cracking**

DSS grades have been used to substitute austenitic grades in situations where there is a reduced danger of SCC. DSS has a strong chloride SCC resistant and strength because of the existence of ferrite. Austenite in DSS improves water corrosion resistant and low-temp impact toughness. Great applied stress, low pH, and great temp limit DSS's resistant to SCC. In hot chloride solutions, the  $\gamma$ -phase is more vulnerable to SCC assault, but in hot alkaline sulfide solutions, the  $\gamma$ -phase is preferentially targeted. Corrosion pits aid fine fracture nucleation, resulting in selective  $\gamma$ -phase dissolution. Owing to the development of  $\gamma$ -phase in these locations, preferential attacking took place at the  $\gamma$ - and  $\alpha$ - borders. Intermetallic phase and Cr-rich-precipitates, on the other hand, are deleterious to DSS corrosion resistant, particularly in greatly alloyed steels. These phases cause IGC, pitting corrosion, and SCC by depleting Cr or Cr/Mo concentration in the matrix close to the precipitates. [18].

#### - **Intergranular Corrosion**

When exposed to corrosive conditions, the development of intermetallic phases, chromium carbides, and chromium nitrides reduces Cr or both Mo and Cr in DSS, resulting in intergranular corrosion. In DSS, detrimental intermetallic phases cause poor corrosion resistant and low toughness. [18].

### **1.2.2 Role of Alloying Elements in corrosion resistant of Duplex**

- Chromium (Cr)–Ferrite Stabilizers – To generate a stable passive layer that protects steel against moderate air corrosion, a minimal of 10.5 percent chromium is required. The corrosion resistant improves as the chromium level rises.
- Molybdenum (Mo)–Ferrite Stabilizers – Molybdenum works with chromium to offer chloride corrosion resistant and pitting corrosion resistant; it also inhibits the formation of harmful intermetallic phases (for example,  $\chi$ ,  $\sigma$ )
- Nickel (Ni)–Upgrades the lattice structure from BCC to FCC; FCC provides great toughness; Ni additives delay the production of intermetallic phases that are harmful. The nickel content of DSS is insufficient to withstand the harsh reduction conditions.
- Nitrogen ( $N_2$ )–Austenite Stabilizers – It prevents the development of the  $\sigma$  phase, improves resistant to crevice and pitting corrosion, and boosts toughness; nitrogen is regulated according to nickel concentration to produce the required phase balance.
- Manganese (Mn) – This stabilizes austenite, although it also might impair pitting corrosion resistant. [18],[22].

### **1.3 Corrosion Resistant of Lean Duplex Stainless Steels**

The breakdown possibilities and pitting damages of lean duplex stainless steel UNS S32101 and ASS 304L were comparable. For the LDX and ASS, there does not seem to be a general link between PRE number and breakdown potential. Lean DSS were often stable, and nitrogen addition causes phases to reform readily [22]. The corrosion resistant of LDX is comparable to that of AISI 316L steel, but it has a yield limit that is two times greater than that of traditional austenitic grades. Because of its lower Mo and Ni concentrations, lean duplex was significantly more vulnerable to martensitic transformation. Steels with a PRE more than 40 were classified as super duplex, whereas those with a PRE less than 40 were classified as duplex or "lean" duplex. Since their Mo concentration is so low, LDSS have a lower PRE than DSS (less than 1.0 percent). The PRE number of 30 is a non-official dividing line between LDSS and DSS. Lean duplex stainless steel austenite had been determined to be as metastable as austenitic AISI 301LN grades and more metastable than AISI 304L grade [23].

Throughout air corrosion, the disintegration of the lean DSS microstructure just seems to propagate preferentially toward the outer layer rather than in depth. Pitting corrosion appeared to be less common in small localized kinds of cavities, suggesting that corrosion was predominantly caused by selective dissolution [24]. Thermal aging mostly generated CrN production at grain boundaries in the 2101 grade due to its great N alloyed concentration. The rate of precipitation for the detrimental Sigma phase was retarded by the low Mo content. Precipitation of Cr compounds resulted in the creation of chromium-depleted regions close to these secondary phases that accelerated pitting corrosion, caused IGC sensitization, and SCC. This resulted from Cr re-diffusion from the grains bulk to the deficient patches at grain borders [25].

Mn has a detrimental influence on 2101 LDSS SCC resistant, but N has a beneficial effect. Adsorbed sulphur has been shown to reduce the corrosion resistant of stainless steel by inhibiting the repassivation of passive film defects caused by chloride ions. SCC was competing with a selective corrosion assault on the ferrite phase. The addition of a substantial quantity of Mo to LDSS boosted its SCC resistant, but the great Mn concentration in LDSS 2101 reduced the alloy's SCC resistant [26]. Localized corrosion occurs in the LDX 2101 matrix's weakest areas. For LDX 2101 to have strong corrosion resistant, it must have equivalent volume fractions of phases, a defect-free microstructure, and no deleterious phases. Because LDX 2101 has a lower Mo content, precipitation of  $\sigma$  is more difficult. The resistant to pitting corrosion reduced as the temp rose from 950 degree centigrade to 1100 degree centigrade [27]. As the temp rises, the chemical composition of each phase changes, causing the PREN of the ferrite phase to decrease and the PREN of the austenite phase to rise. In the alloy UNS S32101, however, there were no PREN magnitudes that were identical in both

stages. As a result, the pits preferentially form in the austenite phase and are restricted by the ferrite phase. The PREN magnitude of the weaker phase determines pitting corrosion resistant [28].

LDSS has been discovered to have greater pitting corrosion resistant and a lower critical pitting temp than normal austenitic kinds. LDSS, UNS S32101 has excellent stress corrosion cracking resistant. The pitting resistant of alloys may also be harmed by erosion, particularly if the re passivation rate is inadequate. The repassivation ratio was increased by increasing the concentration and adding N and Mo. A Mo-containing alloy re-passivates more quickly than a non-Mo alloy. Resulting from adverse impact of Mn in the form of MnS inclusions, the LDSS UNS S32101 with 5wt percent Mn is an alloy of interest (affect the pitting behavior). Mn is present in UNS S32101's passive layer, and it is more likely to be oxidized and absorbed into the passive film produced on the austenite phase than into the dual phase of the lean duplex UNS S32101. [29].

## Conclusions

1. Corrosion resistant of LDX is similar to that of AISI 316L steel.
2. The resistant of DSS to corrosion is decreased by great temps, low pH, and great applied stress.
3. Intermetallic phases and chromium nitrides are harmful to the corrosion resistant of DSSs.
4. DSS corrosion resistant can be improved by adding alloying elements including N and Mo.
5. Lean UNS S32101 DSS has pitting potential that decreases with time.

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