WHITE PAPER: ADVANCED CORROSION MANAGEMENT TECHNOLOGY

Parker SuparShield™

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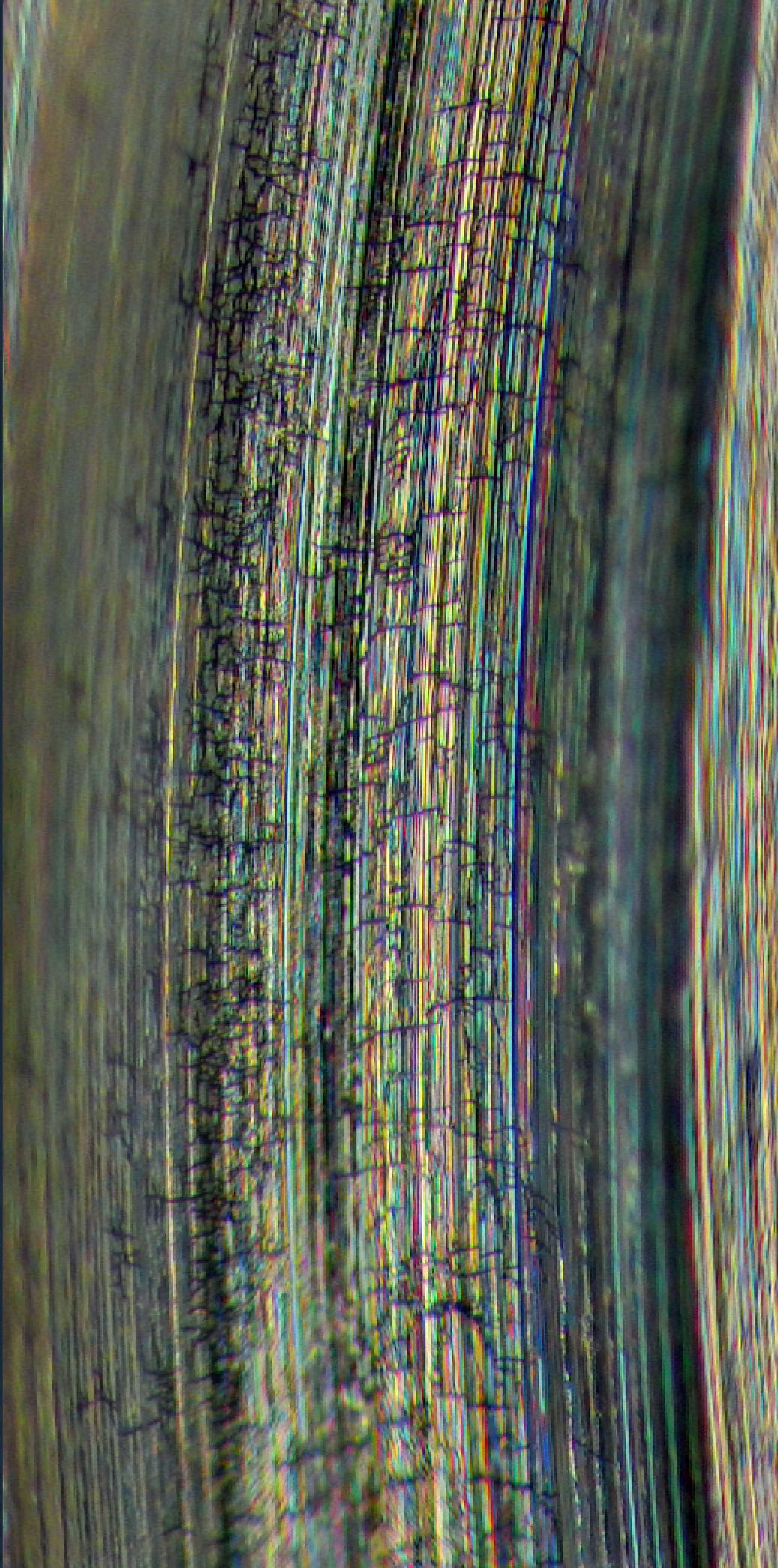


VALUE PROPOSITION

SuparShield™ is Parker's next generation processing technology for performance enhancement of stainless steels, developed to mitigate premature failures caused by:

- Corrosion (Stress Corrosion Cracking, Pitting, Hydrogen Embrittlement etc.)
- Fatigue (Thermal, High Cycle, and Low Cycle Fatigue, such as vibration)

1. Abstract

Conventional austenitic stainless -steel grades such as 316/316L have served as the alloys of choice for several energy markets, including conventional oil and gas. With the advent of clean technology and new alternative fuels, hydrogen and sustainable aviation fuels (SAFs), these applications see increasingly more corrosive environments and critical ranges of pressure and temperature.

This has often led to more frequent and more severe corrosion attacks – especially those related to stress corrosion cracking, hydrogen embrittlement and pitting. The need to mitigate these issues has led to increased adoption of higher alloyed stainless materials. This choice often results in compromises such as significantly higher costs and longer lead times.

Scientists and engineers at Parker have combined our modern understanding of these corrosion failure modes and mechanisms along with years of research and testing and created a novel processing technology for the most demanding of these applications.

This next generation corrosion management technology, called SuparShield™, provides a giant leap in corrosion performance at competitive costs, providing an added option to the end-user looking for the best available – safest solution for their applications.

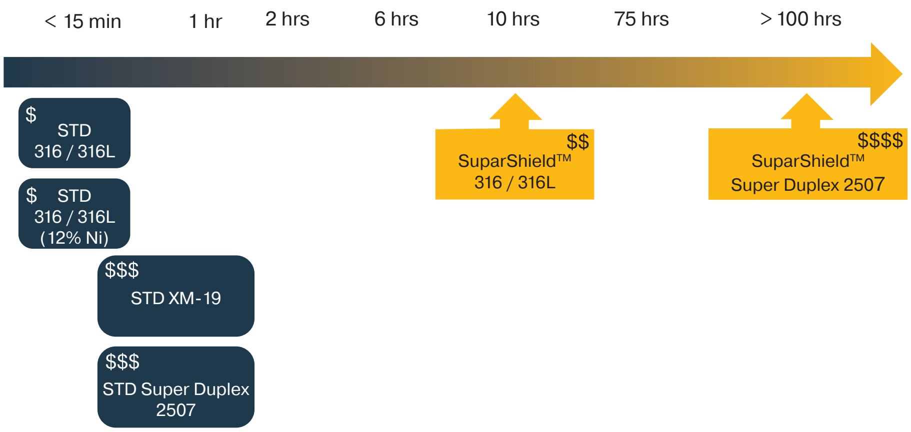


Figure 1: Service Life Extension based on Modified ASTM G36 – G36+ (time to crack, performed on ACTUAL product)

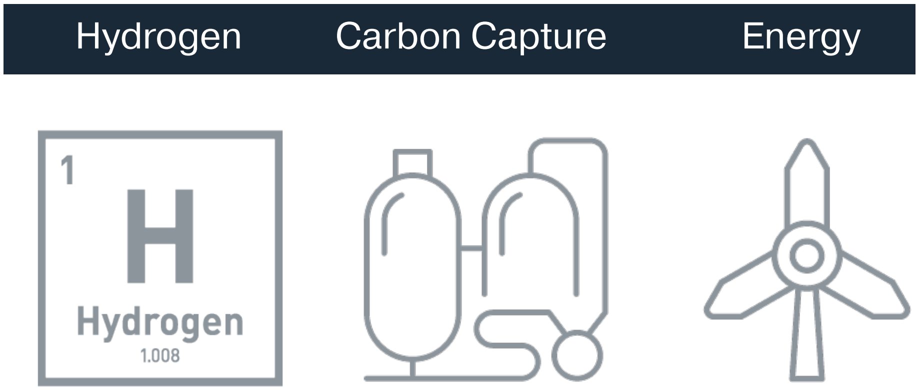


Figure 2: Applications with Corrosive Environments at Critical Ranges of Pressure and Temperature

2. Corrosion

In metals, corrosion is an electrochemical reaction between the atoms on the metal surface and the environment in a way that leads to performance degradation of the metal component.

Corrosion can present a significant safety risk in several applications. Additionally, the financial impact of corrosion due to inspections, maintenance, unexpected downtimes, and environmental impact can be very high.

In fact, the Association of Metal Protection and Performance (AMPP), the worldwide corrosion authority, estimates the global annual cost of corrosion to be about $2.5 Trillion.

Modern applications have put ever increasing demands on materials by subjecting them to increasingly harsher environments and with higher longevity expectations.

This is especially true in the energy sector. For example, the traditional alloys (like austenitic stainless steels) have been subjected to applications where they are expected to withstand pressures exceeding 10,000 psi in offshore chloride rich environments, often in the presence of other corrosive gases such as hydrogen sulfide (H_2S), carbon dioxide (CO_2) and/or hydrogen.

Parker has always been the technology leader in providing material and design solutions for the harshest of these demands from the industry.

While corrosion can occur in several different forms, two of the most severe of these forms are: Pitting Corrosion and Environmentally Assisted Cracking (EAC – Stress Corrosion Cracking, including Hydrogen Embrittlement).

Both are relatively aggressive forms of corrosion leading to creation of localized regions of reduced load bearing capability. These would be the pits in the case of pitting corrosion and cracks in the case of EAC.

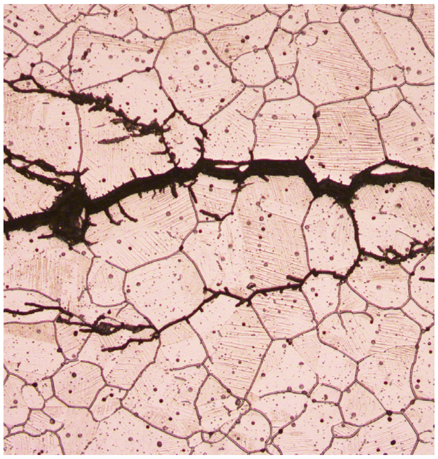


Figure 4: SCC - Offshore Application

The tips of these pits/cracks become regions of stress concentration under application loads and may lead to further propagation of these features, ultimately resulting in leaks or in some cases, catastrophic failures. These corrosion forms are discussed in more detail next.

Tensile Stresses	Corrosive Environment	Material
Strengthening	High Temperatures	Poor Chemitry
Machining	Acids or Caustics	Processing
Installing	Moisture	Inclusion Content
	Chlorides, Sulfides, H_2	

Figure 3: Stress Corrosion Cracking Factors

2.1Pitting

Pitting is a localized form of corrosion that leads to the formation of surface cavities in the material.

The pits can grow progressively deep and often be dangerous because they can penetrate the thickness of the stainless-steel component and reduce the pressure retaining capability of the components. Figure 5 represents a typical example of pitting.

Pitting is more severe in stagnant chloride-rich environments, a condition that is difficult to avoid in offshore applications, for example.

Moreover, pits can also be harmful as they can act as stress risers leading to formation of cracks in components under tensile stresses.

Figure: 5 Pitting Corrosion

2.2 Stress Corrosion Cracking

SCC is described as the initiation and propagation of cracks in an overly stressed component and in the presence of a corrosive environment. No single mechanism to explain SCC has been adopted yet by the scientific community despite several decades of attempts – a testimony to the complexity of the problem. However, it is generally accepted that there are three pre-requisites for the phenomena to occur (*Figure 3*):

- Presence of tensile residual stresses on the exposed surface
- Corrosive environment
- Susceptible material

In offshore environments, the presence of chloride ions can accelerate the rate of SCC in most stainless steels.

Figure 4 shows an example of stress corrosion cracking occurring on a component in an offshore environment.

However, it is generally accepted now that the presence of chlorides is not a mandatory requirement. For applications using high strength or heavily cold worked stainless steels, cracks may also appear in sulfide rich environments (sour service) and/or in environments containing gaseous H_2. These mechanisms are more broadly grouped together as “Environmentally Assisted Cracking (EAC)”.

Under specific conditions, traditional austenitic stainless steels can be especially susceptible to hydrogen embrittlement, a type of stress corrosion cracking. This mode of cracking is often brittle and rapid, even in otherwise ductile materials.

Due to their severe impact, these corrosion mechanisms have been studied for several decades and consequently, several strategies have been adopted by the industry for their mitigation.

3. Current mitigation strategies

One of the most common mitigation strategies used is to choose higher alloyed stainless steels, typically with a higher PREN value, such as super austenitic stainless steels or duplex/super duplex stainless steels. These options are usually much more expensive than traditional austenitic stainless steels.

Another strategy is to use material options with reduced residual stresses or reduced mechanical properties. Residual stresses are the stresses inherently present even in the absence of external loads.

These are formed due to a combination of material manufacturing, and processing techniques, machining, and installation / operation conditions of the final product. This mitigation tactic is often accomplished by using welds or annealing the raw material.

However, for high pressure applications (especially > 10,000 psi), this is not really an option due to the required high tensile / yield strength which ultimately enable the higher working pressures of the product.

Another common corrosion mitigation strategy is to apply inert or semi-inert coating or plating to parts. This has several limitations. Often these options can be very expensive, have limited surface coverage, and only applicable to certain material and environment combinations.

Moreover, coatings or platings often get delaminated or peeled off relatively easily leaving small areas (fissures / scratches / cracks) on component surface making them prone to selective and aggressive attack by corrosive agents.

Reducing the exposure to corrosive agents is another possible strategy. Nonetheless, in most of these critical applications, it is difficult to completely isolate the components from the environment.

Therefore, it is quite apparent that the prevention of pitting and SCC requires combined efforts, including the whole value chain: making the proper material choice, the manufacturing process, the product design, installation, and operation.

It is also clear that all the existing strategies have limitations and that there is a need for a more comprehensive solution.

4. The solution: Parker SuparShield™

Parker has historically played an active part in minimizing the deleterious effects of corrosion by sourcing materials that meet the superior industry standards and strict material specifications, as well as optimizing the product design and manufacturing methods to minimize regions of high “stress x strain” concentration.

With the ultimate goal of pioneering solutions for critical applications, Parker is committed to continue to develop anti-corrosion technologies that prolong product life and provide cost-effective and safe alternatives to its customers, without compromising the best-in-class product performance.

The latest of these solutions is the **Parker SuparShield™ Corrosion Management Technology.**

It is an innovative solution that improves the corrosion resistance without any pressure / temperature de-rating of the product or changes in the assembly procedure.

The corrosion protection is especially significant against pitting and stress corrosion cracking.

Parts processed with the Parker SuparShield™ process have a unique blend of material mechanical and chemical properties, design, and manufacturing techniques that have been especially put together and optimized to deliver the best results.

Specific steps for this corrosion management process have been targeted to deliver extension of service life that compares with or exceeds the corrosion performance of exotic alloys, or CRAs.

For conventional austenitic stainless steels, the material processing techniques that impart these attributes can often also lead to increasing susceptibility to pitting and stress corrosion cracking.

> With careful modifications to various stages of product design and manufacturing, Parker SuparShield™ selectively mitigates the undesirable attributes and provides a solution where the product strength is not compromised and yet, its corrosion and fatigue resistance is significantly improved – a true ‘best of both’.

It is able to achieve this without being an external layer applied to the product: it is not a coating or a plating that can be easily removed from the product surface during handling or installation.

Extensive testing has been conducted to accomplish the optimization and repeatability of this process – this program was created based on the New Technology Qualification Strategy detailed below.

4.1 New Technology Qualification Strategy

The general approach for the SuparShield^{TM} Technology qualification was as follows:

- The process was based on a systematic, risk-based approach and performed by a qualification team possessing all required competencies.
- The new technology was widely screened to identify the novel elements, as these contain the most significant risk.
- The level of the qualification was sufficient to account for the uncertainty associated with the technology and meet the functional specification, reliability, safety, and performance.
- Consideration of QA/QC requirements for manufacturing, assembly, installation, start-up, inspection, commissioning of systems, equipment or components were covered by the qualification if these deviated from the practices given by validated sets of requirements.

The technology qualification program incorporated a testing strategy that showed clearly how the technology should be taken from its development to its final goal. It included seven main phases detailed below:

Phase I: Failure Mode(s) Identification

Phase II: Failure Mode(s) Mitigation Strategies

Phase III: “Manufacturing” Process Parametric Studies (DOE)

Phase IV: Proof of Concept Test Program
- Chemical Composition
- Metallurgical Analysis
- Microscopy Analysis (microstructure characterization)
- Corrosion
  - SCC
  - Pitting
  - Salt Spray
- Product Performance Testing

Phase V: Production and Deployment - Product Qualification Test Program
- Chemical Composition
- Metallurgical Analysis
- Microscopy Analysis (microstructure characterization)
- Corrosion
  - SCC
  - Pitting
  - Salt Spray
- Product Performance Testing (fitting, valve, tubing, etc.)

Phase VI: “Manufacturing” Scalability – MRL_{max}
- Process Optimization
- Expanding the product offering
- Robust QA/QC process in place

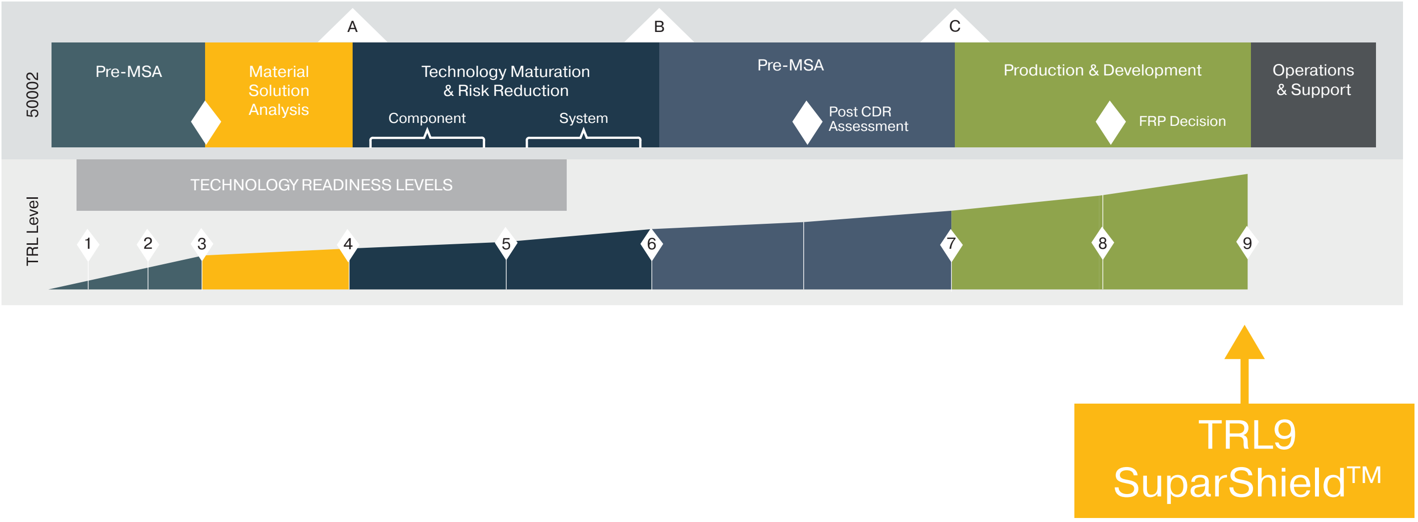
Phase VII: Field Test – TRL_{max}

4.1.1 Premium Performance Validation Process

To validate the SuparShield™ technology, Parker developed an enhanced testing protocol. This validation program was ultimately based on a series of accredited and adopted industry standards, such as:

- ASTM G36 – ‘Standard Practice for Evaluating Stress-Corrosion-Cracking Resistance of Metals and Alloys in a Boiling Magnesium Chloride Solution’. The ASTM G36 standard protocol is a testing program widely adopted to provide a closer correlation to field corrosion conditions. Parker went beyond, developing and adopting an enhanced testing protocol named G36+.
- ASTM G48 – ‘Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution’.
- In addition to these, metallurgical, micrography and surface analysis techniques have been further optimized and used to characterize the applicable failure modes. Specifically, corrosion testing was conducted under various controlled conditions at both Parker laboratories and independent/third-party test facilities.

Figure 6: SuparShield^{TM} Technology Technical Readiness Level (TRL)



- Parker subjected this next generation corrosion technology well beyond the traditional neutral salt spray testing.

Extensive testing has been conducted to accomplish the optimization and repeatability of this process:

- 3+ years of testing
- 500+ parts have gone through the validation testing program
- 4+ types of materials tested, including but not limited to:
    - 316/316L stainless (S31600 / S31603)
    - 316/316L stainless (S31600 / S31603) 12% Ni
    - XM-19 (S20910)
    - Super Duplex 2507 stainless steel (S32750)

4.2 Relevant Test Results

Pitting is one of the most common forms of corrosion in the industry. Its highly localized nature leads to material removal (pit initiation) and consequently reduces the load bearing capability of the instrumentation product. When left unchecked, these pits can get deeper with time and can eventually lead to crack formation.

ASTM G-48 Practice A is the industry accepted test for studying the resistance of an alloy toward pitting corrosion.

Consequently, Parker SuparShield™ processed parts were tested and their performance compared with unprocessed parts. The extent of corrosion was observed in terms of weight loss as shown in Figure 7.

In general, it was observed that the SuparShield™ treatment reduced the weight loss by as much as 50%: Parker SuparShield™ treatment significantly reduced the extent of damage due to Pitting.

Stress Corrosion Cracking has become an increasingly common occurrence in several applications where the performance demands from the material have increased. This may be due to the exposure to increasingly corrosive environments, need for higher pressure ratings and/or presence of higher concentration of harsher chemicals to the media.

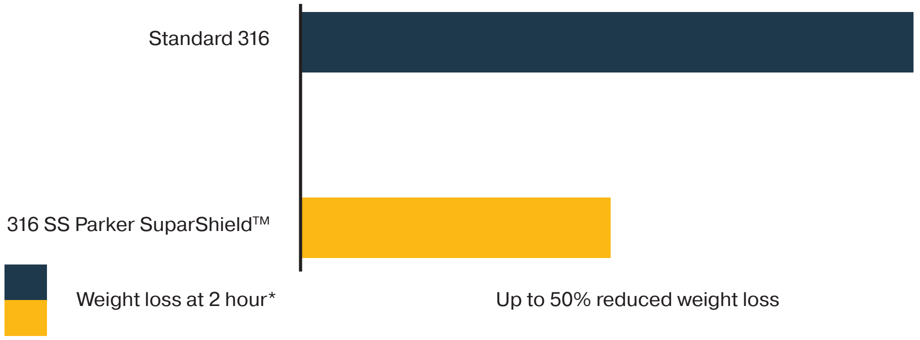


Figure 7: Pitting Weight Loss – SuparShield™ Processed versus Non-Processed 316/316L Parts

*Table 1: Service Life Extension based on Modified ASTM G36 – G36+ (time to crack)**

Alloy	Average Time to Crack ASTM G36 (min)
Annealed 316/316L (benchmark)	4,200
Cold Worked 316/316L	15
Cold Worked 316/316L + SuparShield™	**600**
Cold Worked 316/316L 12% Ni	15
Cold Worked 316/316L 12% Ni + SuparShield™	**600**
Cold Worked 2507	30
Cold Worked 2507 + SuparShield™	**1860**
Cold Worked XM-19	15
Cold Worked XM-19 + SuparShield™	**1240**

G36+ is not performed on raw material coupons, but the actual complete product

** The numbers for the time to crack are average of multiple samples being evaluated at periodic intervals of time per the ASTM G36 test procedure*

ASTM G36 is one of the most common standards that is used to rank the relative susceptibility to stress corrosion cracking for stainless steels and related alloys in aqueous chloride rich environments. The same standard may also be used to evaluate the effect of different processing techniques or heat treat conditions of stainless alloys.

A modified version of the test that uses the same test conditions as the original standard but with an apparatus that allows for stable testing of finished components of varying sizes and shapes to evaluate the performance of the parts processed with the Parker SuparShield™ process.

The test procedure involves immersing the parts in the test solution and evaluating the part surfaces (internal and external) for any visible evidence of stress cracking at fixed intervals of time. The test ends with visible cracks at 20X magnification anywhere on the part surface.

The longer a part / alloy lasts in the solution without any cracking, the better its resistance to stress cracking is expected to be in real world applications.

Several alloys were tested in the standard condition and after SuparShield™ processing. The results are shared in Table 1 (above) and Figure 8 (next page).

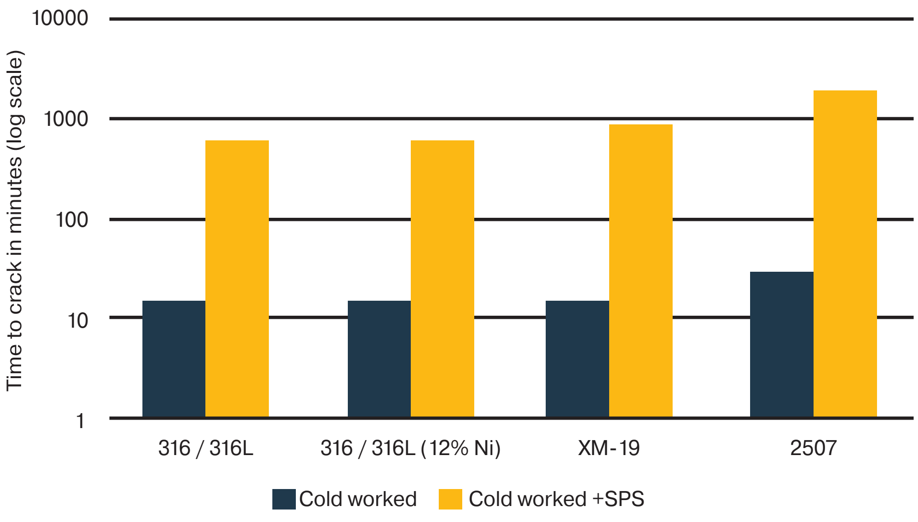


Figure 8: Service Life Extension based on Modified ASTM G36 – G36+ (time to crack) for different alloys in standard versus processed conditions

> The data shows that SuparShield™ provides a true alternative for applications where stress corrosion cracking is a big concern.

It is clear that SuparShield™ processed parts lasted significantly longer than the conventional state for all the alloys tested. The testing revealed that the SuparShield™ processed 316/316L outperformed even the standard cold worked Super Duplex alloy – one of the conventional alloys of choice for high corrosion resistance.

The annealed state of an alloy can be considered as the benchmark when it comes to the best performance toward stress corrosion cracking.

However, using an annealed material is not always an option due to its lower strength, therefore limiting its use in applications that require high pressure ratings.

Figure 9 compares the standard 316 grades with and without the SuparShield™ processing against this benchmark.

SuparShield™ processed parts provided a step improvement in the corrosion performance that compared better with the annealed state of the material than the standard state.

It is important to note SuparShield™ achieved this improvement without ANY reduction in the material strength.

4.2.1 The Role of Nickel Content

Another important aspect that was investigated during this technology qualification process, was the actual role of nickel content in a specific type of stainless steel, grade 316/316L.

ASTM A276 prescribes a range of 10%-14% Ni content for 316/316L. To check the effect of Ni content on SCC, two common variations were analyzed: 316/316L with 10%-12% nickel and 316/316L with 12%-14% nickel.

The main concern was whether a marginal increase in Ni content (2%-4%) would make a significant difference in the corrosion performance

Figure 10 (opposite) shows the Copson curve for several Fe-Ni-Cr alloys in stressed condition in a boiling magnesium chloride environment. The curve plots the nickel content on the horizontal axis and SCC resistance on the vertical axis. It shows an interesting trend: nickel content doesn't always directly improve SCC resistance. The curve dips in the middle, creating a "valley of vulnerability".

The nickel content of both 316/316L (10%-12% Ni) and 316/316L (12%-14% Ni) falls right in this vulnerability zone.

In a chloride rich environment, that extra 2%-4% nickel doesn't offer significant improvement in SCC resistance.

If the application truly needs superior SCC resistance in this environment, the Copson curve suggests two escape routes:

a. Go Lower in nickel (Less than ~ 6%): Stainless steels with low nickel content (<6%) such as Super Duplex 2507 can offer better SCC resistance compared to conventional 316/316L in an aggressive chloride rich environment.

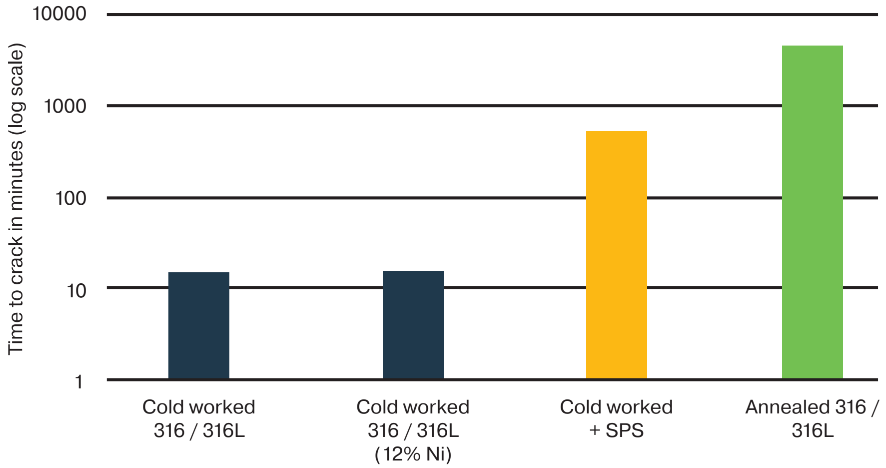


Figure 9: Service Life Extension based on Modified ASTM G36 – G36+ (time to crack) for 316 grade

b. Go Higher in Nickel (More than ~ 20%): Stainless steels with significantly higher nickel content (> 20%) such as super austenitic stainless steels can also climb out of the vulnerability valley and provide superior SCC resistance.

This implies that nickel content is just one piece of the puzzle. While nickel content plays a role, it is not the only factor influencing SCC resistance.

In fact, other factors such as material processing techniques, product design, machining, assembly, and application also play a crucial role.

When it comes to SCC resistance, the difference between 316/316L (10% Ni) and 316/316L (12%-14% Ni) is negligible.

For significant improvement, the conventional choices are to consider steels with much lower or much higher nickel content. Material selection is a critical process, and it is always recommended to consult material selection charts and/or corrosion engineers for specific applications.

The advantage of the SuparShield™ treatment is that it provides an order of magnitude improvement in the stress corrosion resistance of the conventional 316/316L grade stainless steels.

This performance improvement is overlayed on the curve shown in Figure 10.

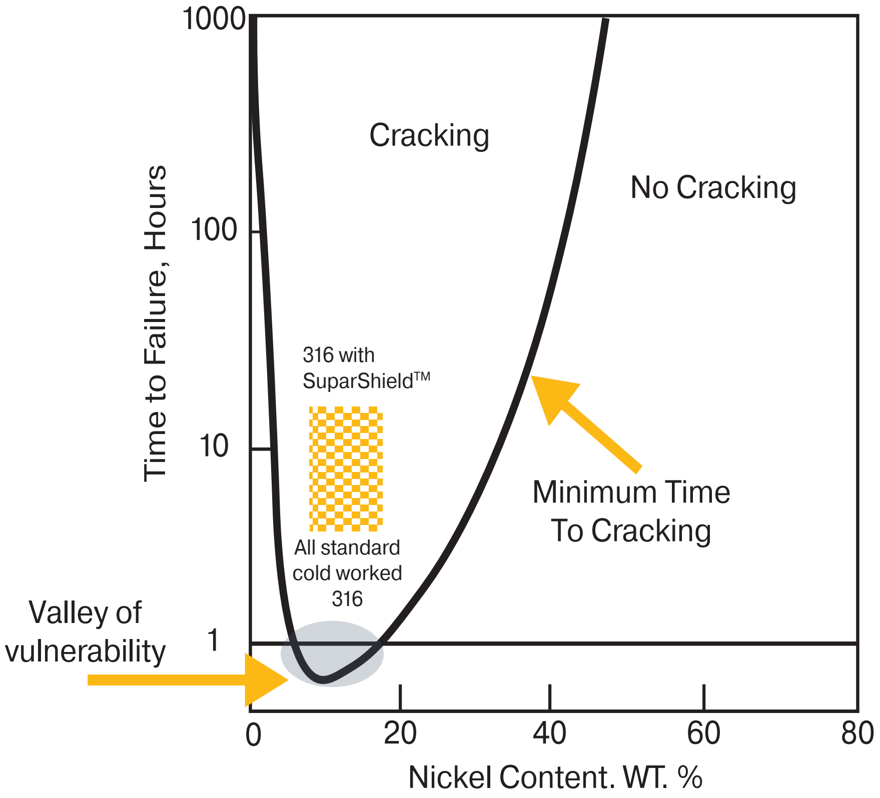


Figure 10: Copson curve for several Fe-Ni-Cr alloys in stressed condition in a boiling magnesium chloride environment

5. Additional benefits

5.1 Improved Surface Finish

As an added benefit, the SuparShield™ process results in a premium surface finish on the parts. The finish is uniform and on all visible surfaces of the part – inside and outside.

This appearance makes the processed parts easily distinguishable from conventional parts available today. At the same time, it ensures that the processed parts have significantly reduced extent of “defects” such as scratches, dings, and dents commonly visible in parts made directly from the bar stock.

5.2 Hydrogen Embrittlement Resistance

The vulnerability of stainless steels to hydrogen embrittlement (HE) can limit their use in environments with hydrogen exposure. HE is a detrimental phenomenon where hydrogen ingress and specific material conditions collaborate to cause premature failure.

This document explores a novel technology with the potential to significantly improve the HE resistance of stainless steels, drawing connections to established knowledge on stress corrosion cracking (SCC).

HE is a complex phenomenon influenced by hydrogen content, microstructure, and various internal material properties.

While being distinct phenomena, HE and aqueous SCC share some intriguing mechanistic similarities[1]. Both involve hydrogen and its interaction with the material’s internal state.

These properties can be influenced by processing techniques and potentially contribute to the degree of susceptibility.

In fact, both hydrogen embrittlement and stress corrosion cracking are considered types of Environmentally Assisted Cracking[2], sharing several commonalities in their mechanisms. SuparShield™ is a novel technology that demonstrably improves the resistance of stainless steels to some forms of corrosion including stress corrosion cracking.

Although the specific details of the technology are proprietary, it offers a promising approach due to the established connection between material properties, stress corrosion cracking and HE susceptibility.

Rationale for HE Improvement

Drawing parallels with the role of internal material properties in SCC, the SuparShield™ technology might influence material properties in a way that discourages detrimental hydrogen interactions. This could potentially:

- Enhance the material's ability to resist hydrogen diffusion and trapping.
- Promote interactions between the material and hydrogen that are less detrimental.
- Improve the overall integrity of the material in the presence of hydrogen.

5.3 Validation

Dedicated experimental investigations are necessary to quantify the impact of this technology on HE resistance in stainless steels in specific environments. These studies would involve exposing processed and unprocessed samples to hydrogen environments and evaluating their mechanical performance. At Parker, we are committed to conducting the necessary testing in partnership with our customers. These results will be made available in the near future.

Building upon the success against stress corrosion cracking and the established understanding of HE and SCC mechanisms, it is expected that SuparShield™ will enhance performance of 316/316L grade stainless steels toward HE as well. However, further research is warranted.

By mitigating HE susceptibility, this technology can broaden the applicability of stainless steels in hydrogen-rich environments.

5.4 Fatigue Resistance

Stainless steels are widely used in various applications due to their excellent mechanical properties. However, they are susceptible to fatigue failure under cyclic loading conditions. Fatigue is a gradual degradation process where repeated cyclic stresses lead to crack initiation and propagation, ultimately resulting in failure. Fatigue is a complex phenomenon influenced by factors such as stress amplitude, frequency, material properties, environment, and microstructure.

In stainless steels, fatigue cracks can initiate at various locations, including surface imperfections, grain boundaries, and internal inclusions. Fatigue crack initiation and propagation are highly influenced by localized stresses within the material especially around sharp corners, edges, or surface defects such as scratches, crevices, and pits. The established knowledge of fatigue mechanisms suggests a strong rationale for the effectiveness of SuparShield™.

SuparShield™ significantly reduces the extent of surface defects such as those mentioned above and thus can influence stress localization in a way that discourages both crack initiation and growth.

By enhancing fatigue resistance, this technology will offer significant benefits, including:

- Extended Component Lifespan
- Reduced Maintenance Requirements

6. Shaping the future of material performance with Parker

At Parker, we are committed to relentless innovation and cutting-edge research to develop solutions that empower our customers. In this white paper, we have discussed SuparShield™, a comprehensive corrosion management technology that exemplifies this commitment.

By significantly improving the corrosion resistance of widely used alloys like 316/316L, this novel approach offers a bridge between conventional alloys and the often more expensive and less readily available corrosion resistance materials. This translates into substantial benefits for our customers, including:

a. Enhanced Asset Integrity

Superior resistance to pitting, stress corrosion cracking, hydrogen embrittlement, and fatigue extends the lifespan of critical energy infrastructure, both offshore and in clean energy applications like hydrogen.

b. Reduced Ownership Cost (OPEX)

By minimizing corrosion-related failures and repairs, this technology translates to significant cost savings over the life cycle of your assets.

c. Operational Efficiency

Improved material performance allows for more efficient operations and reduced downtime.

d. Green and Sustainable Solutions

Extending the life of existing assets promotes environmental sustainability by reducing the need for material replacement and associated manufacturing processes.

We believe this breakthrough technology represents a significant leap forward in corrosion management for our customers. By offering SuparShield™, Parker once again underscores our commitment to understanding our customer's needs and offer the best and safest technological solution.

For further inquiries or to discuss how this technology can benefit your specific needs, please contact Parker today.

Download the MPI™ Medium Pressure Fittings, Adapters, and Valves catalog by scanning the QR code below

Table 2: Definitions & Abbreviations

Acronym	Description
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
CRAs	Corrosion Resistance Alloys
EAC	Environmentally Assisted Cracking
HE	Hydrogen Embrittlement
MRL	Manufacturing Readiness Level
PREN	Pitting Resistance Equivalent Number
SAFs	Sustainable Aviation Fuels
SCC	Stress Corrosion Cracking
SSD	Super Duplex
SS	Stainless Steel
SPS	SuparShield™
TRL	Technical Readiness Level

Table 3: Industry Standards

Reference Number	Document Title	Document Number
1	H. K. D. H. Bhadeshia (2010); "Stress corrosion cracking and hydrogen embrittlement"	-
2	G.G. Leute (2003); "Environmentally Assisted Cracking"	-
3	Hydrogen Piping and Pipelines	ASME/ANSI B31.12
4	Standard Specification for Seamless and Welded Stainless Steel Tubing	ASTM A 269
5	Standard Specification for Stainless Steel Bars and Shapes	ASTM A276
6	Standard Specification for Wrought Stainless Steel Piping Fittings	ASTM A 815/815M-01a
7	Standard Practice for Evaluating Stress-Corrosion-Cracking Resistance of Metals...	ASTM G 36
8	Pitting and crevice corrosion resistance of stainless steel and related alloys	ASTM G 48

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