Stress Corrosion Cracking and Hydrogen Embrittlement of High-Strength Fasteners

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Unexpected, brittle failures of high strength fasteners on aerospace vehicles have been caused by stress corrosion cracking (SCC) and by hydrogen stress cracking (HSC). Confusion exists as to the nature of each phenomenon. The poorly understood failure mechanisms are difficult to differentiate, especially in the field. There is a growing acceptance of the term SCC to cover failures by both mechanisms. Data are given to characterize the classes. For low-alloy carbon steels, heat treated to yield strengths below approximately 160 ksi, stress corrosion is not a problem, nor is hydrogen embrittlement (delayed cracking) very common. Above this stress difficulties can occur. The high-strength precipitation hardening stainless steels have varying degrees of resistance to stress corrosion cracking and hydrogen embrittlement, depending upon strength level and heat treating procedures that influence the microstructure. Use of plane strain fracture toughness K_{IC} and the stress corrosion threshold of K_{ISCC} offers promise of selecting optimum bolting for a specific environment. The attractiveness of plane strain fracture toughness analysis is that it does not differentiate between failure mechanisms; failure can be either SCC or HSC.

Introduction

THE design engineer, alone or in consultation with metallurgical personnel, may or may not be fully cognizant of fastener systems that could result in brittle failures as a result of stress corrosion cracking (SCC) or hydrogen stress cracking (HSC).† The failure of high-strength fasteners in aerospace equipment as a result of SCC and/or HSC occurs infrequently and happens unexpectedly. There is a growing acceptance of the term SCC to cover both mechanisms.

The incidence of fastener failure has been decreasing with time because engineers have learned to avoid materials that have given difficulties in the past. Often, too, a difficulty brings together a roomful of experts who generally come up with a successful solution. Solutions are not always as simple as a material's substitution, but may be complex, involving material changes, use of coatings, redesign, or reduction of stress, sometimes singly but often changing many factors simultaneously.[1]

In aerospace hardware, fatigue of the fasteners has not been a problem mainly because acceptance testing time and flight times have been too short (less than 1 hr) to develop failures with the stress loadings. However, on the space shuttle that aims for 100 flights fatigue of fasteners would become a problem to consider. As higher stressed parts are used more attention must be given to steel cleanliness (inclusions act as crack nuclei), to radiused threads (to reduce notch effect), and to larger head shank fillets (also to reduce notch effect). High-strength fasteners should have threads and head shank fillets rolled on after heat treatment and shanks should be ground and polished. Rolling threads after heat treatment has two benefits. It builds up a residual stress to counteract in part a portion of the applied tensile load and it ensures unbroken grain flow lines through the critical area created by the notch effect of the threads. These considerations have been helpful in increasing fatigue life; they have also been helpful in improving resistance to SCC.

There are other types of fastener failures, e.g., overtorquing and stress-rupture, but failures as a result of stress-corrosion and/or hydrogen embrittlement are most insidious. Because of a lack of a standardized test method for SCC and for HSC, statistical analyses of data are not feasible. The American Society for Testing and Materials is actively working in both areas to develop standardized tests for both phenomena.‡

SCC and HSC, as two fracture mechanisms responsible for delayed failures, have caused many serious and unexpected failures in high-strength fasteners. Failures have occurred in applications at stresses that were considered safe from stress (below the Y.S.) analyses even using generous factors of safety. These occurrences have lead designers to use materials far from their true capability either by using less than optimum strengths of a high-strength steel or using steels heat treated to the maximum strength, but using the steels at very low-strength levels, say 25% of the yield strength.

As the strength level increases above about 160 ksi, both the sensitivity to brittle fracture and the susceptibility to SCC and HSC increases. Although steels with strengths in excess of 300 ksi are available, designers are reluctant to push for this strength level and have settled on levels of 200–260 ksi. Some designers who have had the unfortunate experience of either SCC or HSC have even backed off to strengths of 160–180 ksi.

Shotpeening, plating, and painting of low-alloy, high-strength martensitic fasteners as a means of preventing delayed failures at ambient temperatures has been largely unsatisfactory. Current interest lies in use of HSC or SCC resistant stainless types and superalloys (nickel-base and cobalt-base).

Failures due to Stress Corrosion Cracking or Hydrogen Stress Cracking on the Titan III Family of Vehicles

The Air Force in their Titan III program has had difficulties with high-strength fasteners on the boosters over the past six or seven years. Table 1 lists some of the fastener steels

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† The term, hydrogen stress cracking, is also synonymous with hydrogen embrittlement, hydrogen cracking, and hydrogen induced delayed cracking.

‡ Standard test procedures are being developed in the following areas: G.01.06 SCC and corrosion fatigue; G01.06.01 smooth test specimens; G01.06.02 environments and materials; G01.06.04 precracked growth; E24.04 subcritical crack growth; and F7.01 hydrogen embrittlement.

Table 1 Fastener failures on the Titan III family of vehicles

Material	Hardness, UTS and/or heat treatment	Application	Probable failure mode
15-7 Mo	R_c 46	Shear tie bolt between solid core and liquid core	Stress corrosion cracking
15-5 PH	180–190 ksi	Solid rocket motor frangible bolt	Hydrogen stress cracking from galvanic coupling
17-4 PH	H 950	Fuel and oxidizer valve assemblies	Hydrogen stress cracking from galvanic coupling
440C	R_c 57	Actuator adjustable bolt	Stress corrosion cracking
H-11	R_c 52, 260 ksi	Launch pad baseplate stems	Hydrogen stress cracking from galvanic coupling
431	180 ksi	Marman clamp on hot gas cooler	Stress corrosion cracking Hydrogen stress cracking
Unitemp 212	180 ksi	Solid rocket motor	(?)
17-4 PH	R_c 46; 1 hr 900°F	Pressure valve	Stress corrosion cracking
431	180 ksi	Solid rocket motor	Hydrogen stress cracking (?)

and mode of failure. Failures were all in a marine atmosphere. The precipitation hardening steels have all been slowly replaced by the cold worked type of A286. The 440C and H-11 were continued in service but their heat treatments were modified and/or protection by organic coatings became a requirement. Type 212 was eliminated but Type 431 was continued in service with organic coatings; long range solutions involved substitution of A286.

These failures occurred during the early years of T-III development despite a program of stress corrosion control having been evolved over this period. Tensile stresses (preloads) on the fasteners are now minimized to 40% of yield, where possible, and materials are sought and heat treated where possible to an ultimate tensile strength of 160 ksi. The importance of stress level, environment, and metallurgical structure of the metal in SCC and/or HSC is well recognized by the Program Office. Contact with dissimilar metals is recognized as the most likely source of hydrogen by corrosion and is avoided or protected against. Chemical conversion coatings and anodizing on aluminum often retards such corrosion when high-strength fasteners are used in conjunction with aluminum.

NASA has had a few failures by corrosion in 4330, 4340, AM 355, and 17-7 PH.[2] NASA plans to initiate studies of service influence on fracture behavior, i.e., use of fracture mechanics concepts.

Definition and Differentiation of Stress Corrosion Cracking and Hydrogen Stress Cracking

Despite the effort expended, theories proposed, and data collected, neither fracture mode is well understood. Some of the difficulty arises because the two mechanisms are so much alike. It is only in the laboratory, by electrochemical means, that the two mechanisms can be uniquely differentiated. In the field, it is difficult, if not impossible, to identify which cracking phenomenon was responsible for the failure. However, despite many similarities, the basic mechanisms are different. Stress corrosion theory is not sufficiently advanced to predict failure times; this is also true of HSC. A unifying mechanism of SCC is sorely needed.

Stress corrosion cracking is the phenomenon in which a crack nucleates in a corrosive environment of a susceptible metal while the metal is stressed in tension; the crack then propagates by stress-induced corrosion of the advancing crack tip. Cracking may occur intergranularly or transgranularly depending on the metal and its heat treatment. Failure occurs with little or no plastic deformation; hence the fractures are termed brittle failures. The stresses are generally below the yield stress.

The SCC occurs in specific enivronments and with environmentally sensitive metals. Failures generally occur from inadequate knowledge of environmental conditions. In most cases, there is negligible loss of metal by general corrosion, and at times the corrosion is imperceptible to the eye. Stress corrosion cracking requires highly anodic areas and a localized pH, such as may exist in oxide film cracks, pits, crevices and cold worked areas.

Hydrogen stress cracking is a phenomenon which occurs because of hydrogen penetration into the lattice in the presence of a tensile stress. It is generally agreed that corrosion plays no direct role in this mechanism. However, corrosion often plays an indirect role as being the source of hydrogen.

In classical HSC, the hydrogen goes into solid solution being introduced by electrolytic charging, pickling, heat treatment, and by corrosion reactions. Hydrogen then causes delayed failure under static load in high-strength alloys and the embrittling effect increases with increase in severity of notch, i.e., stress concentration.

The amount of hydrogen which will cause HSC is exceedingly small and is of the order of 4 or 5 ppm. Damage has been reported with hydrogen contents of even less than 1 ppm.

The delayed failure characteristics of 4340 steel,§ exposed to distilled water and failed presumably by HSC, are shown in Fig. 1. Similar failure characteristics are caused by SCC. Note in Fig. 1 the short time-to-failure of the 4340 as the ultimate tensile strength (UTS) of the steel increases and the threshold stresses below which no failure occurs.[3]

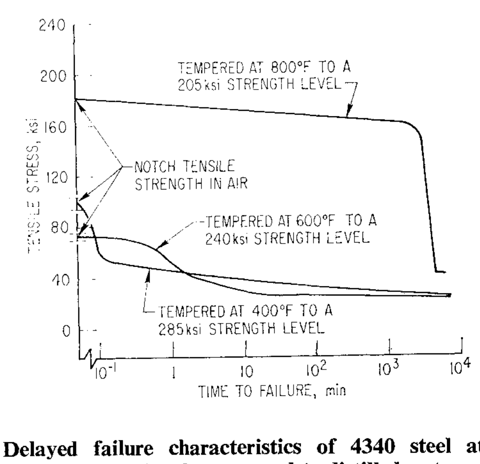

Fig. 1 Delayed failure characteristics of 4340 steel at various strength levels when exposed to distilled water.

§ Nominal compositions of all alloys mentioned in this report are given in appendix.

The important parameters in these delayed failures are strength levels, steel composition and metallurgical structure (microstructure), tensile stresses, environment (i.e., tendency for corrosion or introduction of hydrogen) and time. Temperature seems to increase the likelihood of stress corrosion cracking more so than HSC; the latter occurs around room temperature. The tensile stresses can be applied stresses, residual stresses (as in roll formed threads, heat treatment, welding, straightening, cold rolling) or a sum of these stresses. If residual stresses are present, they are very difficult to measure or estimate so that one does not know of what magnitude they are in a structure. For either SCC or HSC, there exists a stress threshold limit below which the stress will not cause fracture.

In the laboratory, the electrochemical behavior of the metal offers perhaps the best arguments that SCC and HSC are separate, distinct phenomenon. Delayed cracking that occurs under cathodic polarization (hydrogen generation) can hardly be attributed to SCC. Conversely, delayed fracturing in situations where anodic polarization is causing dissolution (corrosion) of the metal can hardly be identified as HSC. The polarization vs time-to-failure curves identify the two mechanisms uniquely. Obviously, such methods have limited field use. There are many test procedures that are used to evaluate susceptibility to SCC and HSC, but only a few of the common ones are mentioned.

A common SCC test to establish susceptibility of bar stock involves loading the specimen to some high percentage of its yield stress, or sometimes UTS, and exposing it to alternate immersion in a 3.5% NaCl solution for 10 min followed by 50 min of drying in forced air. The cycling is continued until the specimen fails or the test is discontinued. The sodium chloride is usually dissolved in distilled water or is acidified (say to a pH of 1.5). Imposed stresses generally vary from 75% to 90% of the fatigue cracked notched tensile strength and from 75% to 90% of their 0.2% yield strengths when unnotched. It is quite common to check austenitic steels for SCC by exposing them to 42% boiling aqueous $MgCl_2$ (154C, 309F) solution; ferritic stainless steels, by contrast, are relatively immune to cracking in $MgCl_2$.

Until recently, SCC tests were conducted on smooth specimens. They are helpful in selection of materials for environments or in development of coatings. They could not be used, however, for establishing safe design loads. Often there is large scatter in these data. The SCC tests on both smooth and precracked specimens used in facture toughness studies provide the designer with tools for material selection on bases of service environments that can be simulated in the laboratory. The testing methods as mentioned need standardization.

For the HSC test to establish susceptibility, a notched specimen is loaded to 75% of its notched yield strength and hydrogen is cathodically charged into the steel while under load. Sometimes a notched specimen is plated with electrolytic cadmium and then loaded. A notched specimen provides more susceptibility to HSC than an unnotched one. Cathodically charging a steel with hydrogen provides considerably more hydrogen than is necessary to produce a delayed failure. Loadings are similar to those used for SCC tests.

High-strength bolts must also pass a stress-durability (static fatigue) test. The bolts are stressed to 72% of the minimum tensile load and are held for 96 hr. If embrittled by hydrogen they will fail.

The potentiostatic procedure is becoming more popular in the study of both types of phenomena. Figure 2 shows how 13-8PH steel can be made to fail by either phenomenon by changing the impressed potential.[4] This type of test can probably be standardized to develop the relative susceptibility of a given steel in various heat treated conditions to either SCC or HSC. The test is definitely a laboratory tool and would not yield design data, only guide lines.

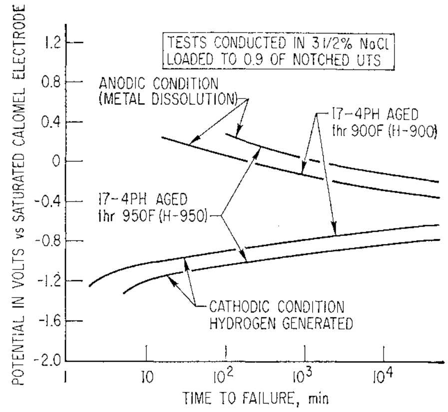

Fig. 2 Curves illustrate the type of data obtained with potentiostatic tests.

In environmental cracking failures at the launch ranges, it is not possible to separate unequivocally HSC from SCC. When there is a question as to whether it is one or the other or possibly a combination, the failures have been referred to as being the result of 1) stress-corrosion cracking (which would include SCC and HSC), or 2) environmental stress cracking. For engineering purposes, this may be sufficient. Pinpointing the actual failure mechanism may be of academic interest only, at least to an engineer.

The appearance of the fracture surface is similar, if not identical, for stress corrosion and hydrogen failures and, hence, the failure modes can't be distinguished from each other. This situation leads some to believe that the mechanisms are identical, whereas to others it just means that fractures are similar. Electron fractography with transmission electron microscope or the newer scanning electron microscope cannot uniquely identify HSC. Electron microscopy is a very useful tool when used in conjunction with other tools. A knowledge of circumstances leading to failure is a valuable adjunct to successful failure analyses. The compilations of electron fractographs by Air Force Materials Laboratory (AFML) are helpful in deciding what the nature of the failure mode may be.[5]

The occurence of intergranular and transgranular cracking or both is the result of hydrogen, a susceptible microstructure, the specimen geometry, and static or dynamic tensile loading. Fidelle, Legrand, and Couderc[6] reviewing 39 studies involving fractography of materials failed by HSC and SCC found 23 instances of fully or predominantly intergranular cracks, 8 fully or predominantly transgranular, 8 mixed, i.e., both types. Intergranular cracking appears to be the most frequent type in both HSC and SCC.

Materials for High-Strength Fasteners

The aerospace industry has emphasized the systems concept of fastener usage for reliability. Design has been improved so that stronger, lighter and more sophisticated fastener systems are available. Lately there has been thought given to environmentally resistant fasteners.

Steel composition is important, as is the metallurgical structure. The time for initiation of the first crack in either HSC or SCC is a reflection of the microstructure resistance to hydrogen diffusion or pit corrosion. Much is known empirically about what compositions and/or structures are susceptible to HSC or SCC, but little is known from so-called first principles about the relation of microstructure to crack initiation and propagation.[7] Most data are basically phenomenological.

Although much ordinarily is not said about nuts and washers, they too must be carefully selected for the fastener system. Careful selection means that the nuts are also tested in a SCC test; the nut is torqued on a bolt and the assembly alternately submerged in salt water. Washers are used to distribute the load. They too should be compatible corrosion-wise. Being loaded in compression they do not fail by HSC or SCC.

Materials for aerospace fasteners are categorized in sevaral ways: 1) by grouping strength levels, 2) by composition and metallographic structure, and 3) by relative susceptibility to SCC and/or HSC. In the future, the steels will be categorized by fracture toughness parameters; some such compilations are already appearing.

Classification by Strength Level

One arbitrary classification of threaded fasteners is by ultimate strength range: low strength—up to 125 ksi; medium strength—125–160; high strength—180–260; ultra high strength—280 and up. Figure 3 gives the strength ranges for some popular alloy steel fasteners. Figure 4 gives the strength ranges for some stainless steels and superalloys.

Classification by Composition and Metallurgical Structure

Another classification by type of alloy is useful in understanding the behavior of these materials to SCC or HSC; these are: martensitic, stainless steels (austenitic and ferritic), precipitation hardening stainless steels, (semiaustenitic and martensitic), superalloys (nickel-base and cobalt-base).

Experience has shown that some types of high-strength steels are quite susceptible to SCC and HSC while others are not. Some change in degree of susceptibility to SCC results from the objectionable precipitation of grain boundary carbides and presence of secondary phases.

Steels used at or above 160 ksi UTS should meet AMS-2300A cleanliness levels. Steels should be vacuum or consumable arc melted to minimize inclusions which can cause pitting. Mechanical properties sometimes can be higher and more uniform, with greater fracture toughness if vacuum melted.

Martensitic Steels

For carbon and low-alloy steels heat treated to strength levels of about 160 ksi or less, SCC is not a problem nor is HSC common. The common martensitic steels are shown in Fig. 3.

The maraging steels can develop strengths over 300,000 psi but so far they have had limited application at this level but at lower strengths are usable alloys. These steels are cooled from the austenitizing temperature forming a soft and weak martensite; aging at 850–950°F hardens and strengthens it.

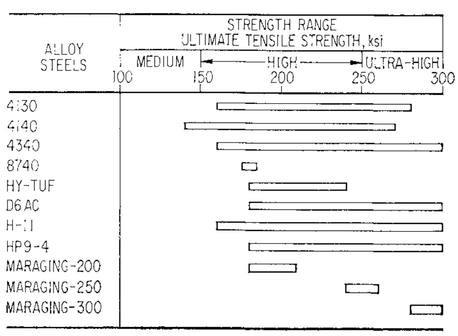

Fig. 3 Classification of low-alloy steels (martensitic types) by strength range. The wide range of some of the steels is obtained by tempering at different temperatures.

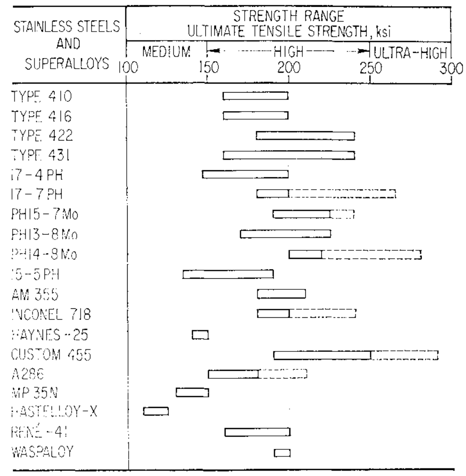

Fig. 4 Classification of stainless steels and superalloys by strength range. Dashed lines indicate strengths obtainable by coldwork and aging.

Stainless Steels (Austenitic and Ferritic)

The austenitic steels of the Type 300 series are much too weak¶ to be considered for high strength fasteners. Only through cold work and stress relief can high strengths be developed in these materials; half-hard material will have an UTS of 150 ksi while full-hard will have one of 185 ksi.

Even though the annealed materials have low strength levels, the alloys can be fractured in environments containing chlorides. Pitting on these steels can occur at emergent slip lines, as well as at inclusions.[7] The annealed materials are very resistant to HSC.

Precipitation hardening austenitic nickel chromium are also available. Alloy A286 is one of the first and is now one of the most popular high strength stainless steels. If the alloy is cold worked (60%) and aged (1200°F), strengths of over 200 ksi are attainable. Alloy A286 has outstanding resistance to SCC and HSC. In poteniostatic experiments it has not been possible to fracture the alloy under anodic or cathodic condition. Field experience confirms the alloy high resistance to these phenomena.[4]

The ferritic stainless steels, Type 400 (e.g., 410, 416, 420, 422, and 431) are heat treatable to strengths of around 200 ksi. Although these steels are martensitic in structure, they are not generally considered in the martensitic class inasmuch as they have relatively high chromium contents, i.e., about 13%. These types have good general corrosion resistance but they are susceptible to SCC. This susceptibility can be removed by tempering at 1100°F or higher, but high strength is sacrificed.

Precipitation Hardening Stainless Steels

These precipitation hardening stainless steels beside imparting excellent general corrosion resistance to the alloy can attain rather high strengths. The objective of obtaining a high-strength, unplated, corrosion resistant alloy appeared to be attainable with the introduction of the precipitation hardening stainless-steel grades. This objective was to circumvent problems such as HSC and/or SCC that had been experienced with plated and unplated martensitic, low- and high-alloy steels in the 200 to 250 ksi range.

These precipitation hardening steels have varying degrees of resistance to SCC and HSC depending, of course, on

¶ MIL-Handbook-5A assigns Types 301, 302, 303, 304, 316, 321, and 347 yield strengths of 30 ksi and ultimate tensile strengths of 75 ksi.

strength level but also on the temperature of the aging treatment. Aging below 1000°F may cause these steels to be susceptible to SCC and HSC, but aging them above this temperature the steels have excellent resistance to these cracking phenomena.

These precipitation-hardening types are of two basic classes: martensitic and semiaustenitic. The martensitic types are 17-4 PH, 15-5 PH, and PH 13-8 Mo. In these alloys the martensitic structure forms on cooling from a solution treatment; subsequent aging between 900°F and 1150°F strengthens the martensite by precipitation hardening and tempering to realize a gamut of strength values. Typical semiaustenitic steels are 17-7 PH, PH 15-7 Mo, PH 14-8 Mo and AM 350. In these alloys, the composition has been adjusted so that the austenite forms on solution treating and is retained at room temperature. In this condition it is readily fabricated (cold worked). The hardening is obtained by reheating the austenite to 1400°F or 1750°F (called conditioning), cooling, and finally aging at 950°F or 1050°F.

If either of these steels is overaged, i.e., beyond highest strength, both the fracture toughness and SCC resistance are improved. The fracture toughness and SCC resistance of martenistic steels are significantly higher than the semiaustenitic types.

Superalloys (Nickel-Base and Cobalt-Base)

In general, as the nickel content increases in the austenitic steels, the more they are resistant to SCC and to HSC. Some high-strength stainless fasteners are also made from superalloys (i.e., high-strength nickel-base and cobalt-base alloys). The nickel-base Inco 718 superalloy, cold worked and precipitation hardened will have strengths in excess of 200,000 psi. The new and highly alloyed MP-35N exhibits the corrosion resistance of the best nickel-base alloys. It has a high resistance to SCC and to HSC in salt environments and marine atmospheres.

Classification by Relative Resistance to Stress Corrosion Cracking

A third classification involves rating SCC according to relative susceptibility and can be used as a rough guide to material selection based on experience and some laboratory work. This classification comprises: 1) alloys and heat treatments that can be used without restriction; 2) alloys and heat treatments that can be used if used with caution; 3) alloys and heat treatments that should not be used.

This information has been abstracted and expanded, on the basis of other aerospace findings, and is given in tabular form, Tables 2–4. The tables apply only to SCC in environments of sodium chloride solutions, salt sprays, alternate immersion (wetting and drying) and marine atmospheres, and are primarily for smooth specimens. Similar tables for HSC are not available.

These ratings are not to be construed as particularly exact because no attempt has been made to evaluate the effect of stress, environment, metallographic structure and time. This type of tabular information represents the type of SCC data that was available before the advent of fracture mechanics. No attempt, incidentally, has been made here to incorporate data obtained by fracture mechanics and given elsewhere. Other environments that are of concern to the aerospace materials engineer are the metal-propellant compatibilities. Cracking with some of the steels has also been reported in phosphate, sulfate, nitrate, and sulfide solutions. None of these are of concern here.

Promise of Fracture Toughness Criteria

Improvement of methods of analyzing fracture in various environments through the use of fracture mechanics allows the fracture process (whether by SCC or HSC) to be studied on a macroscopic basis independent of the influence of

Table 2 Materials with a high resistance to stress corrosion cracking

Materials	Type	Heat treatment[a]	Remarks
300 series stainless types 303, 304, 316, 321, 347	Austenitic	Annealing	Stressed material can crack in chloride solutions. Annealed materials are not of high strength. Cold worked materials can develop high strength but they must be stress relieved.
17-4 PH	Martensitic	H1000 and above	
17-7 PH	Semiaustenitic	CH 900	Strength is developed by cold work (60%) and aging (900°F)
PH 13-8 Mo	Martensitic	H1000 and above	
15-5 PH	Martensitic	H1000 and above	
PH 15-7 Mo	Semiaustenitic	CH 900	Strength is developed by cold work (60%) and aging (900°F)
PH 14-8 Mo	Semiaustenitic	CH 900	As for PH 15-7 Mo above
AM 350	Semiaustenitic	SCT1000 and above	
AM 355	Semiaustenitic	SCT1000 and above	
Custom-455	Semiaustenitic	H1000 and above	
A 286	Austenitic	Solution treated and aged	
A 286 (CW and Aged)	Austenitic	Solution treated and aged	High strength is developed by cold work (60%) and aging (1200°F)
Inconel 718	Face centered cubic	Solution treated and aged	
Inconel X-750	Face centered cubic	Solution treated and aged	
Rene-41	Face centered cubic	Solution treated and aged	
MP 35N	Face centered cubic	Solution treated and aged	Solution annealed and cold worked 60% and aged
Waspaloy	Face centered	Solution treated and aged	
Low Alloy Steels 4130, 4140, 4340, 8740	Martensitic	Quenched and tempered	High resistance to SCC if tempered to attain strength of 160 ksi or lower
Maraging Steel	Martensitic	Solution treated and aged	High resistance if heat treated to 200 ksi or lower

[a] For heat treatments refer to Aerospace Structural Metals Handbook, Metals Handbook ASM, or steel producer's literature.

Table 3 Materials with a high resistance to stress corrosion cracking if used with caution

Materials	Type	Heat treatment	Remarks
Low alloy steels 4130, 4140, 4340, HY-TUF 8740, D6AC,	Martensitic	Quenched and tempered	Good resistance to SCC if tempered to approximately 160–180 ksi
Maraging steel	Martenstic	Solution treated and aged	All three grades; Maraging-200, -250 and -300
400 series stainless 410, 416, 422, 431	Martensitic	Quenched and tempered	Not susceptible if tempered at 1100°F or higher
15-5 PH	Martensitic	H950–H1000	
PH 13-8 Mo	Martensitic	H950–H1000	
17-4 PH	Martensitic	H950–H1000	
AM 355	Semiaustenitic	SCT 950–H1000	

Table 4 Materials with a low resistance to stress corrosion cracking

Materials	Type	Heat treatment	Remarks
Low alloy steels 4130, 4140, 4340, 8740, D6AC, HY-TUF	Martensitic	Quenched and tempered	Very susceptible to SCC if tempered to attain strengths of 180 ksi and higher
H-11	Martensitic	Quenched and tempered	
17-7 PH	Semiaustenitic	All heat treatments except CH 900	
PH 15-7 Mo	Semiaustenitic	All heat treatments except CH 900	
AM 355	Semiaustenitic	Heat treatments below SCT 900	
400 Series stainless 410, 416, 422, 431	Martensitic	Quenched and tempered	Very susceptible in the secondary hardening range, 500°–1000°F

specimen geometry effects and dependent only on stress level and environment. The fracture toughness approach gives for the first time a quantitative knowledge of the effects of a particular environment on a steel stressed below the yield stress. Such quantitative data will be required by the designer once he learns how to use it. The appeal of the method, aside from being quantitative, is that it reflects a metals behavior in an environment which may lead to either SCC or HSC. More importantly, the method does not differentiate between mechanisms leading to failure.

The K_{ISCC} parameter, hence, indicates with good reproducibility, the stress-crack-size threshold below which subcritical cracks will not propagate to a critical size leading to catastrophic failure in a gaseous, liquid or complex environments in a period of usually 500–1000 hr. Both K_{IC} and K_{ISCC} have units of ksi(in.)$^{1/2}$.

To overcome disadvantages with smooth specimens used previously, where long times may be involved for crack nucleation, Brown and others have used specimens with pre-existing cracks. Such specimens eliminate crack initiation periods when surface films break down and pitting starts, removes possibility of drawing erroneous conclusions that alloys are immune to SCC, and specimens with pre-existing cracks permit use of fracture mechanics concepts. Brown[8] introduced the concept of the threshold K_{ISCC}. Very quickly Brown's idea became popular and many investigations have shown the value of this approach.

The use of plane strain** fracture toughness criteria, i.e., K_{IC} and the K_{ISCC}, offer promise of selecting fastener materials that are not susceptible to either SCC or HSC on the launch pad or in any other environment. The fracture mechanics approach can show if a metal is affected by the stress-environment and to what degree. The analysis also shows that where degradation occurs there is a threshold stress below which no SCC or HSC occurs, see Fig. 5. Note how severely the salt environment reduces the stress intensity factor K_I (Ref. 9). Distilled water, as well as moisture, is seldom considered an aggressive environment. Yet moisture can have a controlling influence on the fracture behavior of high-strength steels.[10]

In tough alloys failure occurs at longer time intervals. Crack propagation may be slower and the alloy may tolerate a longer crack before fracturing. A small crack may cause SCC in a material of low toughness whereas a larger crack may be required to fail a tougher material. The tougher material may require a longer time to fail because crack growth is slower in a tougher material and not because SCC or HSC is slower. Failure time then becomes a measure of the rate of crack growth.

By relating the environmental applied stress intensity factor K_{ISCC} to the plane strain fracture toughness K_{IC} the differences in toughness of alloys or their heat treatments

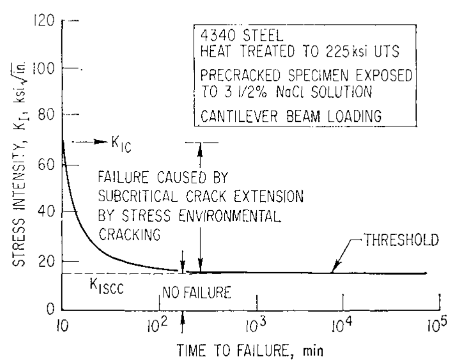

Fig. 5 Typical behavior of a high strength 4340 in a corrosive environment. Note how severely the fracture toughness, K_{IC}, is reduced in the salt solution.

** Plane strain conditions refer to the square fracture produced by SCC or HSC. Plane stress conditions would involve slant or shear fractures; these are not observed with SCC or HSC ordinarily.

Table 5 Fracture toughness rating of alloys and heat treatments on their resistance to salt water environments[12]

Material	Heat treatment	Ultimate tensile strength, ksi	Seacoast test K_{ISCC}	Seacoast test K_{ISCC}/K_{IC}	Accelerated test K_{ISCC}	Accelerated test K_{ISCC}/K_{IC}
Inconel 718[a]	1950°F AC, 8 hr 1350° + FC to 1200°F for 24 hr	189.6	106	0.87	130	0.98
17-4 PH[a]	H 1150	151.6	93.9	0.77	110	0.89
AISI 304	Annealed	84.0	53.5	0.77	59.7	0.86
4340	800°F temp.	204.8	48.3	0.72	29.7	0.44
17-4 PH	H 900	202.4	38.5	0.69	40.3	0.72
H-11 (AM)[b]	1100°F temp.	282.6	39.5	0.62	23.2	0.24
410[a]	1125°F temp.	128.8	52.4	0.55	49.6	0.52
H-11 (AM)	1000°F temp.	300.3	16.7	0.52	8.6	0.27
18Ni(250)Mar.	900°F	269.5	55.6	0.50	72.9	0.65
H-11 (VM)	1000°F temp.		11.4	0.40	10.8	0.38
4340	475°F temp.	267.2	13.3	0.29	11.1	0.24
AM355 (FH)	SCT 1000		33.1	0.28	50.3	0.42
AM355	SCT 1000	169.4	24.5	0.24	36.7	0.43
410	650°F temp.	197.0	22.0	0.24	23.8	0.26
AM355	SCT 850	195.9	10.7	0.22	24.9	0.52
AM355 (FH)	SCT 850		9.7	0.15	6.2	0.10
AISI 304	Sensitized 100 hr. 1100°F	83.9	8.5	0.12	15.2	0.22

[a] Plane strain conditions maintained only at low-stress intensities. Therefore, values are approximate. True plane strain K_{ISCC} could not be obtained.

[b] Explanation of abbreviations: AM—air melt, VM—vacuum melt, FH—fully hardened.

can be normalized. The ratio K_{ISCC}/K_{IC} serves as a normalizing parameter to compare steels and their heat treatments.[10] See Fig. 6.

The most widely used fracture mechanics specimen is the precracked cantilever-beam specimen.[11] By dead-weight loading this specimen in an environment and recording the time to failure, the plane-strain stress-intensity threshold K_{ISCC} can be calculated.

The type of data obtained by fracture mechanics analyses is well-illustrated by the work of Freedman[12] who obtained K_{IC} and K_{ISCC} data on ferrous and nickel alloys. Single edge notched and fatigue cracked specimens were tension loaded in a salt solution for 1000 hr (accelerated test). Identical specimens were tension loaded in racks exposed at the seacoast (Playa del Rey, Calif.). Times to failure at seacoast varied from 49 hr to 7668 hr. Some tests were run 12,843 hr without failure.

Freedman's data (Table 5) gives a rating of susceptibility of various alloys to accelerated (laboratory) and seacoast testing. The ratio of K_{ISCC}/K_{IC} for seawater ranks the alloys from Inconel 718 (most resistant) to sensitized Type 304 (most susceptible). Unexplained differences are to be noted in the ratio for the accelerated test. Variations between the accelerated and seacoast tests can probably be explained by the unappreciated variability of the aggressive environments.

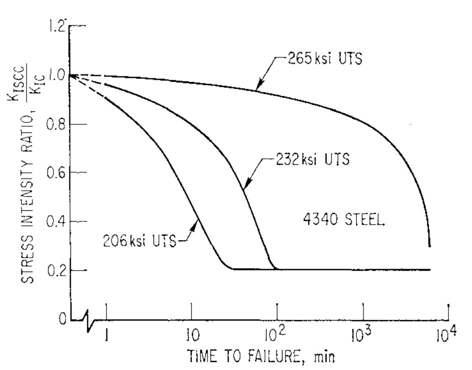

Fig. 6 Delayed fracture characteristics of 4340 steel plotted in a normalized manner using the stress intensity ratio.

Recommendations

Recommendations take on a two-fold aspect. 1) What can the designer and/or metallurgist do about the SCC and HSC problem? 2) What can industry, profession, society or government agency do about test standardization, data accumulation, and dissemination of the information?

What Can the Designer or Metallurgist Do about SCC and HSC?

There are some practical approaches to the problem of failed fasteners by SCC and HSC; some of these are quite obvious.

The first obvious solution is to use alternate materials. There are materials that have good resistance to SCC. On the basis of the fracture toughness criteria K_{ISCC} and the ratio K_{ISCC}/K_{IC} tempered with experience, a selection could be made. Unfortunately fracture toughness criteria are only now being collected and all fastener materials have not been tested. However, there are some highly resistant materials of the stainless steel (so-called corrosion resistant) type available, e.g., A286, A286 CW, Inconel 718 CW, etc.

The second obvious solution is to keep the aggressive environment in the case of SCC, and a hydrogen source in the case of HSC, away from the steel. Although aerospace engineers shy away from coatings, platings of cadmium or aluminum may be helpful on low-alloy steel martensites. Extreme care in electroplating and required subsequent baking must be exercised at high-strength levels to prevent HSC. In some aerospace applications, organic coatings, paints, (Locktite, Lock-safe, greases and even baked-on solid lubricants) can protect against the environments. If torquing and retorquing are done on the bolts, these operations can remove these types of coatings and reapplication of the protection is required.

A less obvious solution to the problem would involve designs that would eliminate or minimize factors that promote SCC. One should, for instance, avoid crevices, deep recesses, sharp corners, notches of any kind, and dissimilar metals unless one metal is insulated from the other in some manner.

In any new design, where new alloys are to be tried and new environments are to be experienced, it is highly recom-

Table 6 Nominal compositions of all alloys mentioned in the text

Material	Elements given in percent									
	C	Cr	Ni	Co	Fe	Mo	W	Cb	Ti	Al	Other
4130	0.3	0.95			bal	0.20					
4140	0.4	0.95			bal	0.20					
4340	0.4	0.8	1.90		bal	0.25					
8740	0.4	0.5	0.55		bal	0.25					
HY-TUF	0.25	0.30	1.80		bal	0.40					1.5 Si
D6AC	0.45	1.00	0.55		bal	1.00					0.07 V
HP 9-4	0.45	0.27	8.00	4.00	bal	0.25					
Maraging-200	0.03		18.5	8.50	bal	3.25			0.20	0.10	
Maraging-250	0.03		18.5	7.50	bal	4.80			0.40	0.10	
Maraging-300	0.03		18.5	9.00	bal	4.80			0.60	0.10	
Type 410	0.15	12.5			bal						
Type 416	0.15	13.0			bal	0.60					
Type 422	0.23	12.0	0.80		bal	1.00					0.25 V
Type 431	0.15	16.0	1.85								
Type 440C	1.10	17.0	0.75		bal	0.55					
H-11	0.40	5.0			bal	1.30					0.5 V
17-4 PH	0.07	16.50	4.0		bal			0.3			0.4 Cu
17-7 PH	0.09	17.00	7.1		bal					1.10	
PH 15-7 Mo	0.09	15.0	12.1		bal	2.50				1.10	
PH 13-8 Mo	0.05	12.75	8.0		bal	2.25					
PH 14-8 Mo	0.05	14.35	8.1		bal	2.50				1.10	
15-5 PH	0.07	14.75	4.5		bal		0.3				0.35 Cu
AM 350	0.10	16.5	4.5		bal	2.9					0.1 N
AM 355	0.12	15.5	4.5		bal	2.9					0.1 N
Inconel-718	0.05	15.0	26.0		bal	1.25			2.15	0.2	0.3 V
Haynes-25 (L605, WF-11)	0.10	20.0	10.0	bal			15.0				
Custom-455	0.05	11.75	8.5		bal	0.5		0.3	1.1		2.0 Cu
A-286	0.05	14.75	25.25		bal	1.3			2.15	0.15	0.3 V
MP 35N		20.0	35.0	35.0		10.0					
Hastelloy-X	0.10	22.0	bal	1.5	18.5	9.0	0.6				
Rene-41	0.09	19.0	bal	11.0	10.0				3.1	1.5	
Waspaloy	0.07	19.5	bal	13.5	2.0	4.3			3.0	1.4	
Inconel-X750	0.04	15.5	bal		7.0			0.95	2.5	0.7	
Type 303	0.15	18.0	9.0		bal						
Type 304	0.08	18.5	9.5		bal						
Type 309	0.20	23.0	13.5		bal						
Type 316	0.08	17.0	12.0		bal	2.25					
Type 321	0.08	18.0	11.0		bal				5 × C		
Type 347	0.08	18.0	11.0		bal			10 × C			
Unitemp 212	0.08	16.0	25.0		bal			0.50	4.0	0.15	

mended that fracture toughness tests be conducted to ascertain the possibility of some susceptibility to degradation, if not complete failure.

What Can Industry, Profession, Society or Agency Do about SCC and HSC?

There is a need for standardization of fracture toughness tests using the precracked specimens. The American Society for Testing and Materials already has a tentative specification on testing. Without standardization, the data that are and are becoming available have limited usefulness in material selection or design. A standard test must be in existence long enough so that sufficient data can be accumulated for statistical study. The accumulating data should be compiled into usable form by industry, the metallurgical profession, government agency or technical society.

Conclusions

The current situation on the use of fasteners in aerospace applications has been appraised. Confusion exists as to the physical nature of HSC and SCC. Examples of fastener failures on the Titan III family of vehicles illustrate the nature of the problem. Although there is a distinct difference between SCC and HSC phenomena on the laboratory scale, it is often difficult if not impossible to differentiate between the two mechanisms in the field. Corrosion theory is not sufficiently advanced to be able to predict dangerous stress-environment structure combinations that could lead to failure.

The high strength fasteners which occasionally fail in service can be divided into three categories: 1) by ultimate tensile strength level, 2) by metallurgical type, and 3) by relative susceptibility to salt solutions or marine atmospheres.

Fracture toughness analysis offers the best hope of obtaining data on SCC or HSC. The analysis does not differentiate between mechanisms. The use of plane-strain fracture toughness K_{IC} and stress corrosion threshold K_{ISCC} offers promise of selecting fastener materials that are not susceptible to SCC or HSC failures. The K_{IC} or K_{ISCC} parameters are becoming more meaningful to the designer than elongation and reduction of area because these "measures of ductility" have little to do with the performance of a structure.

Table 6 gives the nominal compositions of all alloys mentioned in the text.

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Application of an Improved Transpiration Cooling Concept to Space Shuttle Type Vehicles

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In order to reduce coolant requirements transpiration cooled structures should be operated at the maximum possible surface temperature. At high-surface temperature a flow instability can occur, because of the pressure drop characteristics of gases, leading to burnout of the porous structure. This instability can be avoided by overlaying the sintered metallic structure with a ceramic coating of much higher permeability. By applying this design concept to the leading-edge and interference heating regions of a space shuttle type vehicle substantial reductions can be realized in coolant requirement. Since the thickness of the ceramic layer is inversely proportional to the required coolant flow rate, the leading-edge coolant savings are offset by increasing structure weight. For interference heating, however, the ceramic layer is thin and large net savings in weight can be obtained.

Nomenclature

C_p = specific heat, Btu/lbm-°R
D = diameter, ft
g_c = conversion factor, 32.17 lbm-ft/lbf-sec^2
H = enthalpy, Btu/lbm
ΔH = net enthalpy rise in coolant, Btu/lbm
k = conductivity, Btu/ft-sec-°R
L = length, ft
M = coolant molar weight, lbm/lb-mole
$\dot{m}$ = coolant flux, lbm/ft^2-sec
N_C = convective heat-transfer coefficient, lbm/ft^2-sec
P = pressure, lbf/ft^2
Q_c = convective heat flux, Btu/ft^2-sec
R = gas constant, lbf-ft/lb-mole-°R
T = temperature, deg R
α = porous matrix viscous pressure drop constant, ft^{-2}
β = porous matrix inertial pressure drop constant, ft^{-1}
ε = effective emissivity of surface, dimensionless
γ = porous matrix void fraction, dimensionless
Γ = porous matrix tortuosity for heat conduction, dimensionless
μ = coolant viscosity, lbm/ft-sec
ρ = coolant density, lbm/ft^3
σ = Stefan-Boltzmann constant, 0.476×10^{-12} Btu/ft^2-sec-°R^4
$\bar{\sigma}$ = elemental surface area normal vector, ft^2
θ = included angle between $\bar{\sigma}$ and freestream vector, rad

Subscripts

A = value at point A
B = value at point B
C = value for coolant
e = effective value
l = value for coolant liquid phase
o = value without transpiration cooling or value in coolant storage reservoir
pore = value for pore within the porous matrix
r = recovery value
s = value for freestream species evaluated at surface temperature and pressure

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Index categories: Heat Conduction; Boundary Layers and Convective Heat Transfer—Laminar; Structural Composite Materials (Including Coatings).

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