B.9 "Environmental Degradation of High Strength Materials," by Peter M. Scott

Introduction

Many high strength materials are used in PWRs and BWRs for bolts, studs and springs. Typical uses of high strength, martensitic, low alloy steels are for the closure studs and nuts of pressure vessels and manway cover plates, pump casings and support assemblies, valve bonnets and packing glands. They are also used for bolts and tie rods in PWR secondary water in steam generators. High strength stainless steels and nickel base alloys are deployed in many components in the primary coolant circuits of both PWRs and BWRs. Examples include valve stems, internal bolting and springs in main coolant pumps and valves, control rod drive assemblies, core internals, fuel hold down springs, etc.

Failures of internal bolts and springs can give rise to loose parts and loss of essential function of the component concerned. External bolts and studs are clearly critical to maintaining the integrity of the principal pressure boundary. From the very beginning of exploitation of PWRs and BWRs for power production, small but significant numbers of failures of high strength materials have occurred in service. They have usually been attributed to stress corrosion cracking (SCC) or hydrogen embrittlement (HE). A few have also been attributed to corrosion fatigue and in the specific case of low alloy steels used for external bolting in the primary circuit, also to boric acid corrosion by primary water leaks and steam cutting. Recurring themes in the case of high strength low alloy and stainless steels have been the initial unsuitability of the heat treatment and hardness of the as-installed component, or in some cases after thermal aging leading to unacceptable hardness, and the presence of inappropriate lubricants to facilitate assembly. For the nickel base alloys, attention has also been focused on the suitability of the initial heat treatment to obtain the desired mechanical properties but here the in-service problems encountered have been more analogous to those of nickel base alloys in general, particularly in PWR primary water service.

Nickel base alloys

Alloys X750 and 718 are nickel base alloys that are age hardened to precipitate the strengthening phases γ' and/or γ''. Their chemical compositions are given in Table B.9.1. Bolts in alloy X750 can have yield strengths of 115-140 ksi (790-965 MPa) while Alloy 718 can be hardened to higher strengths, for example 170-180 ksi (1170-1240 MPa) for bolts and even over 200 ksi (1380 MPa) for springs dependent on the level of cold work applied before age hardening.[1] Many more components fabricated from alloy X750 have experienced intergranular stress corrosion cracking (IGSCC) in service in both PWRs and BWRs while only a very limited number of similar failures of alloy 718 have been observed in PWR service.[1,2]

Improvements have been made to alloy X750 for PWR primary water service by increasing the solution annealing temperature to 1950-2100°F (1060-1150°C) and with it the resultant grain size, and by the adoption of a single step aging heat treatment at 1300°F (704°C) for 20 hours. Although the main goal of the aging heat treatment is to precipitate the strengthening phase γ', $Ni_3(Ti, Al)$, an added advantage of these particular heat treatment conditions for PWR primary water service is a fine, dense $M_{23}C_6$ carbide

distribution at grain boundaries.[3] In addition, great attention is now paid to keeping the design stresses, including those at stress concentrations, at least below the proportional limit. Surface condition of components is also known to influence the risk of IGSCC, in particular cold work and residual stress. Moreover, the atmosphere used during the aging heat treatment alloy of X750 was found to have a profound influence on initiation times for IGSCC in PWR primary water.[3] This was due to oxidation of surface layers that had to be removed by machining after heat treatment in order to ensure optimum performance in service. The combination of all these improvements has seemingly stopped the previously generic failures of alloy X750 control rod drive split pins, for example, with operating periods presently exceeding 100,000hours without failure.

Alloy 718 is a normally highly reliable high strength alloy for use in PWR primary water although a few failures in PWR service are known.[1,2] Some studies in the literature have implicated the formation during thermal aging of δ phase, the thermodynamically most stable form of the strengthening phases γ," as having an aggravating influence on subsequent IGSCC susceptibility.[4] Others have not observed a major effect of δ phase on product performance.[2] Indeed, δ phase is a necessary feature to avoid excessive grain growth during solution treatment prior to aging.[2] By contrast, intergranular oxidation of the surface during product rolling and heat treatment can have a severe adverse influence on IGSCC initiation in PWR primary water. For optimum IGSCC resistance in plant, it is essential to remove the layer affected by the furnace atmosphere, as observed previously for alloy X750.

Stainless steels

The most commonly used high strength bolting material in PWR primary circuits is cold worked Type 316 stainless steels with strength levels, depending on component diameter, up to 100 ksi (700 MPa), which requires typically 10 to 20% cold work. The NRC position is that strain-hardened austenitic steels shall not exceed 90 ksi (630MPa). Even cold worked Type 304 (not L grade) may be used in PWR primary water although the practical extent of its use is not for the moment clear. With the exception of heavily neutron irradiated core baffle bolts there have been no known failures in service.

Where higher strength levels are required for components such as bolts, springs and valve stems, materials such as A286 precipitation hardened austenitic stainless steel, A410 and similar martensitic stainless steels and 17-4PH precipitation hardened martensitic stainless steel are used (Table B.9.1). Over the years, small numbers of such components have cracked in service usually attributed to stress corrosion or hydrogen embrittlement.

A286, an austenitic, precipitation hardened, stainless steel is strengthened by γ', $Ni_3(Ti,Al)$, formed during aging at 1330°F (720°C). Its use is favored where the expansion coefficient relative to other austenitic stainless steels is an important design factor. Unfortunately, it is susceptible to IGSCC in PWR primary water when loaded at or above the room temperature yield stress, typically 100 ksi (700 MPa).[5-10] Cold work prior to aging in combination with the lower of two commonly used solution annealing temperatures of 900 and 980°C has a particularly adverse effect on IGSCC resistance.[8] Hot heading of bolts, which can create a heat-affected zone between the head and shank, is another known adverse factor. Nevertheless, even if these metallurgical factors are optimized, immunity from cracking cannot be assured unless the stresses are

maintained below the room temperature yield stress, which necessitates strictly controlled bolt-loading procedures. There is also strong circumstantial evidence that superimposed fatigue stresses can lower the mean threshold stress for IGSCC even further. Finally, the role of impurities, including oxygen introduced during plant shut down and possibly consumed only slowly in confined crevices, in helping crack initiation is clear from all the evidence available. Once initiated, cracks grow relatively easily even in well-controlled PWR primary water.[7]

Components such as valve stems, bolts and tie rods requiring rather high strength combined with good corrosion resistance in PWR primary circuit water have been typically fabricated from martensitic stainless steels, particularly Type 410 and 17-4 PH. A significant number of failures of martensitic stainless steels such as Type 410, for example, have occurred.[11] In most cases, the affected components have usually entered service in an overly hard condition due to tempering at too low a temperature but no in-service aging seems to have been involved in these cases, the materials proving susceptible to stress corrosion cracking / hydrogen embrittlement in PWR primary water in the as-fabricated condition. A high tempering temperature above 1100°F (600°C) is preferred to avoid hydrogen embrittlement susceptibility. An additional problem has been caused by pitting/crevice corrosion of Type 410 and similar martensitic stainless steels in contact with graphite containing materials in the packing glands of valves, sometimes leading to valve stem seizure. The preferred replacement material has often been 17-4 PH with its higher chromium and molybdenum content conferring better resistance to crevice corrosion.

A significant number of service failures of 17-4 PH precipitation hardening stainless steel have also occurred in PWR primary water.[11-14] Initially, intergranular cracking by stress corrosion/hydrogen embrittlement was associated with the lowest temperature aging heat treatment at 900°F (480°C) designated H900. This gives a minimum Vickers hardness value of 435HV well in excess of the limit of 350HV commonly observed to limit the risk of hydrogen embrittlement. The H1100 (593°C) aging heat treatment was subsequently widely adopted and normally yields a hardness value below 350HV. Nevertheless, a small number of failures, due either to brittle fracture or stress corrosion / hydrogen embrittlement, have continued to occur. The origin of these failures appears to be thermal aging in service.

Two main thermal aging mechanisms of martensitic stainless steels are recognized. The first "reversible temper embrittlement" is related to the diffusion of phosphorus (and arsenic, antimony and tin) to grain boundaries at aging temperatures generally above 750°F (400°C) and can occur in both Type 410 and 17-4 PH stainless steels. The grain boundaries are consequently embrittled and are particularly susceptible to intergranular hydrogen embrittlement but no general increase in hardness is observed. It can be reversed by heat treating around 1100°F (600°C) and avoided by reducing the phosphorus content and by small (1%) alloying additions of molybdenum.

The second thermal aging embrittlement mechanism is relevant only to precipitation hardened stainless steels such as of 17-4 PH. It arises from an intra-granular decomposition of the martensitic matrix into two phases, α which is rich in iron, and α' which is chromium rich. Further hardening arises from additional precipitation of the copper rich ε phase. A generalized increase in hardness is observed with corresponding increases in strength and ductile / brittle transition temperature and loss of fracture toughness. This hardening cannot be reversed without re-solution annealing. French

studies have shown that this aging mechanism can occur in 17-4 PH steels on time scales relevant to the design lives of PWRs at temperatures exceeding 485°F (250°C) and quantitative models for component assessment have been developed.[12,13] Mechanical fractures occur by cleavage although those involving corrosion can also be intergranular. Both types of failure have been associated with hardness values after in-service aging significantly exceeding 350HV. Corrosion related failures have also been aggravated by impurities coming from valve packing gland materials.

Low alloy martensitic steels

High strength martensitic and maraging steels are used in many external fastener applications in nuclear power reactors and a significant number of failures of this class of component have occurred.[15] Most have been described as corrosion related failures. The problems encountered with external bolting have affected both support bolting and pressure boundary fasteners. Support bolting, in particular, can be affected by severe localized corrosion at interfaces with concrete where water may accumulate and protective plating or a polymeric coating system is often necessary.

Cracking of low alloy (AISI 4340 and 4140) and maraging steel support bolting has been attributed mainly to hydrogen embrittlement. Steels with ultra high yield strengths greater than 150 ksi (1035 MPa) have failed due to a combination of too high applied stresses and humid or wet environments collecting around the bases of components. Steels with lower yield strengths have also failed due to poor heat treatment or material variability. Consequent on these failures, a review of environmental cracking properties of high strength steels exposed to water or salt water at low temperatures was carried out and regulatory guidelines based on this information were published in the USA.[16] Acceptability of high strength bolting was based on a lower bound approach to KISCC as a function of yield strength. This fracture mechanics based approach may have some attractions for defining a quality assurance procedure and for defect assessment. However, hydrogen cracks can start from surfaces, usually in crevices or from pits. Consequently, it is advisable also to have an upper hound strength limit (such as 150 ksi given in the EPRI Materials Handbook as the upper limit below which no service failures have been observed) to avoid this type of cracking.

The second category of bolt failures is concerned with the integrity of the primary pressure boundary at locations such as the flanges of manway covers, pump casings and valves. Most of these incidents have been caused by boric acid corrosion or steam cutting (erosion-corrosion) due to PWR primary water seal leaks. A small number of failures among this category of bolts have, however, been associated with stress corrosion cracking/hydrogen embrittlement rather than wastage.[16] The ferritic bolting steels involved were not out of specification but had been in contact with molybdenum disulfide lubricants. It has been postulated that the lubricant dissociated on contact with hot water to yield hydrogen sulfide, which is a severe hydrogen embrittling agent for ferritic steels. Consequently sulfide containing lubricants are no longer permitted. More generally, the main remedy for this category of high strength bolting failures is to avoid leaks at flanges seals by improved gasket design.

References for B.9

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Table B.9.1 Composition of Some Common High Strength Nickel Base Alloys and Stainless Steels

Element	Alloy X750	Alloy 718	A-286	17-4PH
Nickel	>70.0	50-55	24-27	3.0-5.0
Chromium	14-17	17-21	12-15	15-17.5
Iron	5-9	Bal.	Bal.	Bal.
Titanium	2.25-2.75	0.65-1.15	1.55-2.0	
Aluminum	0.4-1.0	0.2-0.8	≤0.35	
Niobium plus Tantalum	0.7-1.2	4.75-5.50		0.15-0.45
Molybdenum		2.8-3.3	1.00-1.50	
Carbon	≤0.08	≤0.08	≤0.08	≤0.07
Manganese	≤1.0	≤0.35	≤2.0	≤1.0
Sulfur	≤0.010	≤0.010	≤0.030	≤0.030
Phosphorus			≤0.040	≤0.040
Silicon	≤0.5	≤0.35	≤1.0	
Copper	≤0.5	≤0.30		3.0-5.0
Vanadium			0.10-0.50	