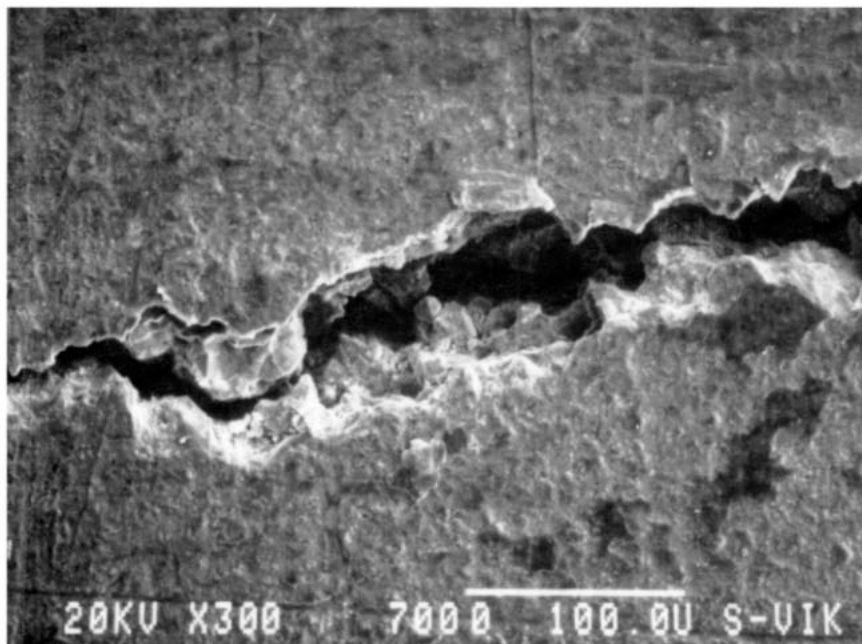


CORROSION IN THE NUCLEAR INDUSTRY A NORDIC SURVEY



IGSCC CRACK IN INCONEL 600

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CORROSION IN THE NUCLEAR INDUSTRY
A NORDIC SURVEY

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Abstract

Experience with corrosion in Nordic nuclear power plants is compared with worldwide experience. Corrosion in seawater systems and its prevention are discussed. Accelerated corrosion tests on stainless steels for use in seawater are evaluated. Some of the work described is part of larger national research programs, such as dealloying of aluminium bronzes and stress corrosion cracking of high strength nickelbase alloys. Finally some alternative materials for nuclear power applications are presented.

Key words

Corrosion in nuclear power plants
Corrosion in seawater systems
Nordic countries
Dealloying
Aluminium bronzes
Stress corrosion cracking
Nickelbase alloys
Accelerated testing

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SUMMARY

Corrosion in nuclear power plants is a well known problem both in the Nordic countries and worldwide. Corrosion occurs in many different forms, such as general corrosion, crevice corrosion, pitting, stress corrosion cracking and erosion corrosion.

The corrosion damages in the operating Nordic nuclear power plants vary in both form and extent. The effects on plant availability have so far been small, and all corrosion effects have been recognized before they have become of any significance to plant safety. It should however be recalled that corrosion in most cases does not produce a uniform attack on the material. Thus, in principle, intergranular stress corrosion cracking and crevice corrosion could cause serious deterioration in a short time.

These are some of the reasons behind a joint project that has been performed from 1982 to 1985, the NKA/SÅK-4 project.

In the project a compilation of corrosion experiences in the Nordic countries and worldwide is made. The most serious problem in boiling water reactors is intergranular stress corrosion cracking in stainless steel piping. In pressurized water reactors serious corrosion has occurred in steam generators, due to a combined effect of construction practice, materials characteristics and operating conditions.

The compilations shows that so far the corrosion experience in the Nordic countries is considerably more favourable than in the rest of the world.

Corrosion in seawater with varying salinity, typical for the Nordic countries, is one of the topics in this project. Experience from nuclear power plants as well as from conventional power plants has been compiled. The investigation deals with pumps, heat exchangers, valves and pipes. It turns out that a proper choice of material, different for each type of component, can decrease the corrosion in the seawater systems and therefore increase plant availability and safety. Aluminium bronzes are commonly used materials in seawater systems. A study made on dealloying of such materials shows that heat treatment of cast aluminium bronzes increases the dealloying resistance and also improves mechanical properties.

Corrosion of stainless steel in salt water can be evaluated by means of accelerated tests. A critical review has been made of tests available to study pitting and crevice corrosion. It turns out that international standards have frequently been modified at individual laboratories in order to improve the testing procedure. Although this yields better results, it makes it difficult to compare results from one laboratory to another.

Nickelbase alloys are sensitive to intergranular stress corrosion cracking in the environments prevailing in both boiling water reactors and pressurized water reactors. In another part of this project the influence of heat treatment and microstructure on stress corrosion cracking of nickelbase alloys is studied. The results show that the corrosion susceptibility is affected by heat treatment and microstructure. There are however still many questions to solve and more work is requested in this area.

Finally this report gives a brief outline of the alternatives to the materials employed today in power plants, both nuclear and conventional. A number of alternative materials is available. The condensers in Swedish nuclear power plants are now manufactured from titanium. Other materials under development for power plants include a number of stainless steels (e.g. the new Swedish steel 254 SMO with increased contents of molybdenum and the titanium stabilized ferritic steel Monit). They are now being tested in power plant environments and in seawater.

Generally speaking, a number of methods are available in order to control corrosion in nuclear power plants, ranging from a proper choice of material to using adequate water chemistry. The results obtained in the project show that the corrosion experience from the nuclear industry is valuable in conventional industry, and vice versa.

Apart from developing and testing new materials, current experimental work is concentrated on the understanding of microstructure and on corrosion protection through controlled water chemistry. It is one conclusion from the project that different Nordic laboratories have unique knowledges and competences which can be combined for mutual benefit through joint action.

SAMMANFATTNING

Korrosion i kärnkraftverk är ett välkänt problem i såväl de nordiska länderna som i resten av världen. Korrosion uppträder i olika former, såsom allmän korrosion, spaltkorrosion, grovfrätning, spänningskorrosions sprickning och erosionskorrosion.

De korrosionsskador som förekommit i de nordiska kärnkraftverken varierar i både form och omfattning. Kraftverkens drift har hittills bara påverkats i liten utsträckning, då alla korrosionsangreppen har upptäckts i god tid innan de har fått någon betydelse för säkerheten. Man bör emellertid komma ihåg att korrosion i många fall inte orsakar ett jämnt angrepp på materialet, t ex kan interkristallin spänningskorrosion och spaltkorrosion lokalt orsaka allvarliga skador på kort tid.

Detta är några av de bakomliggande orsakerna till det nordiska samarbetsprojektet, NKA/SÄK-4, som har drivits under åren 1982 till 1985.

I projektet har gjorts en sammanställning av korrosionserfarenheter dels från nordens och dels från resten av världen. Man har funnit att det allvarligaste problemet i kokarreaktorer är sprickor i rostfria rör orsakade av interkristallin spänningskorrosion. I tryckvattenreaktorer finner man att de allvarligaste angreppen förekommer i ånggeneratorerna och beror på en kombinerad effekt av konstruktion, materialval och driftförhållanden. Sammanställningen visar också att hittills har problemen med korrosion i de nordiska kärnkraftreaktorerna varit mindre än i resten av världen.

Korrosion orsakad av havsvatten, med de olika salthalter som förekommer i nordens, är en av delstudierna inom projektet. Erfarenheterna från såväl kärnkraftverk som konventionella kraftverk har sammanställts. Undersökningen behandlar havsvattnets inverkan på pumpar, värmeväxlare, ventiler och rör och visar att lämpligt materialval för de olika komponenterna i havsvattensystemen kan minska korrosionen och därmed öka kraftverkens tillgänglighet och säkerhet. Aluminiumbronser är ett vanligt material i havsvattensystem. En studie gjord på selektiv (upplösnings-) korrosion av sådant material visar att värmebehandling av gjutna aluminiumbronser ökar motståndet mot selektiv korrosion och förbättrar de mekaniska egenskaperna.

Korrosion hos rostfritt stål i saltvatten kan studeras med accelererade försök. En litteraturstudie har gjorts på de experiment av groppfrätning och spaltkorrosion hos rostfria stål som är tillgängliga för studier. Den visar att många laboratorier, i syfte att förbättra provningsprocedurerna modifierar internationella standards. Det ger i och för sig ett bättre resultat, men försvårar jämförelsen av resultaten mellan olika laboratorier.

Nicklebaslegeringar är känsliga för interkristallin spänningskorrosion både i kokarvattenmiljö och i tryckvattenmiljö. I en del av projektet studerades vilken inverkan värmebehandling och mikrostruktur (metallkornens utseende och form) har på känsligheten för spänningskorrosion hos nickelhaslegeringar. Resultaten visar att korrosionskänsligheten påverkas av både värmebehandling och mikrostruktur. Det återstår emellertid ett stort antal frågor att besvara och ytterligare insatser behöver göras på detta område.

Slutligen ger den här rapporten en kort översikt över alternativen till de material som idag används i både kärnkraftverk och konventionella kraftverk. Flera alternativa material finns tillgängliga. Kondensatorerna i svenska kärnkraftverk är idag gjorda av titan. Andra material under utveckling är ett antal rostfria stål (t ex de nya svenska stålen 254 SMO med förhöjd molybdenhalt och det titanstabiliserade ferritiska stålet Monit). De testas nu både i kraftverkmiljö och havsvatten.

Det finns idag flera tillgängliga metoder för att begränsa korrosion i kärnkraftverk, från ett riktigt materialval till lämplig vattenkemi. Resultaten från projektet visar att korrosionserfarenheterna från kärnkraftindustrin är värdefulla för konventionell industri och vice versa.

Vid sidan om utveckling och provning av nya material bedrivs också forskning som syftar till att förstå mikrostrukturen och för att förbättra korrosionsskyddet genom kontrollerad vattenkemi. En av projektets slutsatser är att olika nordiska forskningslaboratorier har unika kompetenser och kunskaper, som genom samarbete kan kombineras och ge ömsesidiga fördelar.

1. Introduction

Different forms of corrosion have considerably affected the operation of nuclear power plants all over the world. In general, corrosion becomes more extensive the older the plant is. Consequently this problem has to be watched carefully, like in other power plants and process industries.

The 16 nuclear power plants in operation in the Nordic countries show a great variety of damages induced by corrosion. In general, the overall effects on plant availability have been small, and all corrosion effects have been well recognized before they have become of any significance of plant safety. The largest number of damages have affected turbine plants and seawater cooling systems. More severe cases of corrosion that have been experienced are caused by intergranular stress corrosion cracking (steam generators, stainless steel piping, high strength bolts and screws) and erosion corrosion (structural steels in turbine plants).

In a worldwide perspective the corrosion problems in the Nordic nuclear power plants have been of manageable extent. However, some plants have been shut down for considerable periods due to repair of damages caused by corrosion. The costs of these shutdowns can be very high.

Efforts to prevent corrosion can of course start when designing plants or components, but the corrosion damages are often discovered much later when the plant has been in operation for a considerable time.

Corrosion is of equal interest to authorities, utilities and vendors. From the authorities point of view, a good prevention of corrosion means high safety, to the utilities it means high availability, and for the vendors it is important to demonstrate a proper choice of material and manufacturing technology.

For the last three years a Nordic joint project on corrosion has been performed. The project was a part of the Safety Research Programme sponsored by the Nordic Liaison Committee for Atomic Energy (NKA) during the period 1982-1985.

The purpose of this project was to compile and evaluate the corrosion experiences in the (nuclear) power industry in the Nordic countries. Corrosion is a large subject and this project could not cover all interesting questions in the field.

The following objects were studied in the NKA/SÄK-4 project:

- Corrosion experience in light water reactors
- Corrosion in seawater systems
- Stress corrosion cracking in nickelbase alloys
- New materials in nuclear power plants.

This report is a short survey of the work carried out in the project. A list of technical reports can be found at the end of the report.

2 Compilation of experience of corrosion in (Nordic) nuclear power stations.

Worldwide, different types of corrosion in light water reactors (LWR) have caused shutdowns and created serious problems of plant availability and economics to the utility industry. Well-known examples are intergranular stress corrosion cracking (IGSCC) in austenitic stainless steel piping of BWRs and a variety of corrosion related phenomena in PWR steam generators. In the Nordic countries there are presently sixteen LWRs in operation, eleven BWRs and five PWRs.

2.1 Worldwide corrosion problems in LWRs.

Many LWRs have, despite several years of operation, not experienced any serious corrosion problems. In other cases, corrosion is, and has been, a problem that has significantly affected the performance of both BWRs and PWRs. In some cases damages have appeared after only a very short period of operation.

In 1980-1982 in the USA different corrosion problems together caused a capacity factor loss of about 7% as an average for all units.

Today the two major problem areas in nuclear systems are

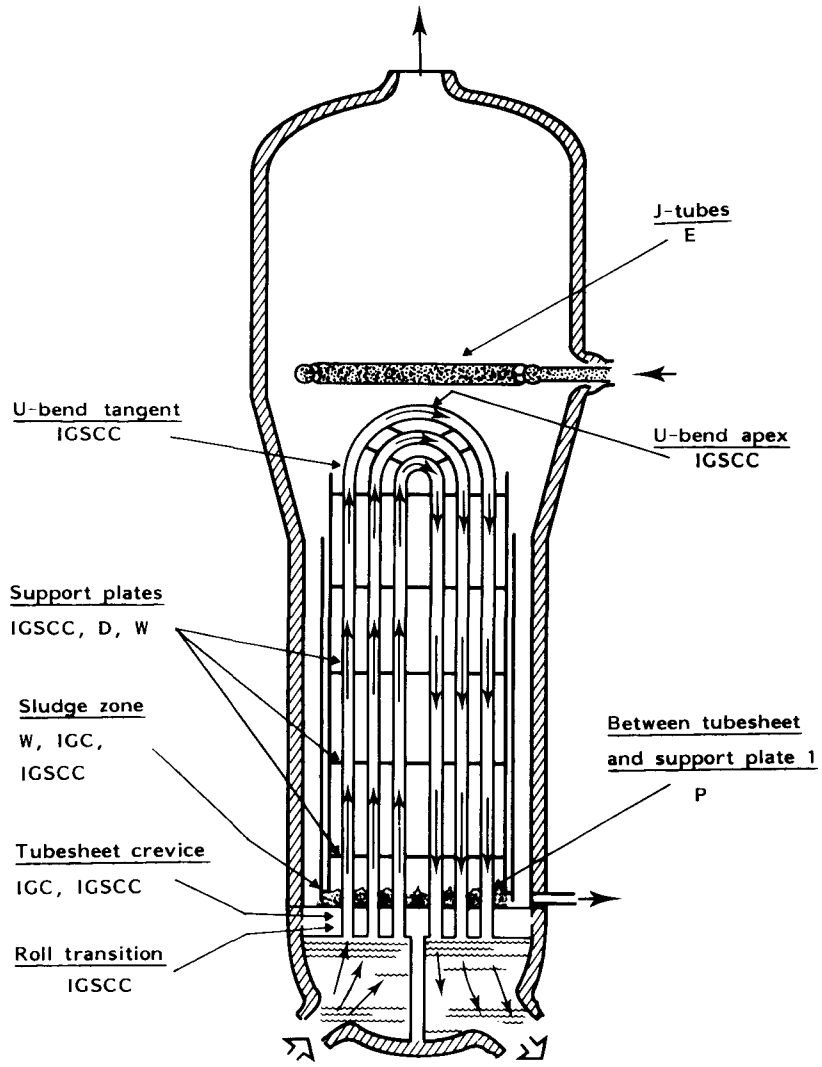
- in BWRs:
IGSCC in the weld heat affected zones of austenitic stainless steel piping and

in PWRs:
different forms of corrosion (e.g. wastage, intergranular corrosion (IGC), denting, IGSCC from both the primary and secondary side, pitting) in steam generators.

IGSCC in BWR stainless steel piping came to public attention in 1974. Since then it has been a chronic problem, and today more than 650 cases have been reported.
mitigate it are:

<u>Prerequisite</u>	<u>Effects in BWR piping</u>	<u>Remedies</u>
Metallurgical	Grain boundary chromium depletion in weld heat affected zones (HAZ)	Use of stainless steel with less than 0.02% C.
Stress	Tensile residual stresses	Compressive residual stresses on the inside at the HAZ
Environment	High purity water with 100-400 ppb dissolved oxygen	Oxygen content below 5-10 ppb by hydrogen injection

A large number of PWRs have experience damages in steam generator tubes. More than 90% of these failures are caused by corrosion.



- IGSC = intergranular stress corrosion cracking
- IGC = intergranular corrosion
- D = denting
- W = wastage
- P = pitting
- E = erosion - corrosion

Fig. 1: Types of corrosion encountered in PWR steam generators

In several units these problems have been halted or delayed. However, at present seven units have completed steam generator replacements, six in the USA (Surry 1 and 2, Turkey Point 3 and 4, Point Beach 1, and Robinson) and one in Germany (Obrigheim). Some others are considering replacement in order to solve their steam generator problems, or have already decided to do so.

2.2 Experiences in Nordic LWRs.

In an international perspective the corrosion damages experienced in the Nordic nuclear power plants have been of a manageable extent. Among other things this is illustrated by capacity factors of Nordic BWRs that are considerably higher than the average for other BWRs in the world. The main reason why the PWRs in Sweden have not obtained the same fine results is the problems with steam generators at the Ringhals power station.

The sixteen Nordic reactors in operation exhibit a great variety of corrosion induced damages. The most commonly experienced types of corrosion problems are stress corrosion cracking (stainless steel piping, steam generator tubes in nickel base Alloy 600, bolts and screws in high strength stainless steel and nickel base Alloy X-750) and erosion corrosion (structural steels in the turbine plant). The largest number of corrosion damages have affected turbine plants and seawater cooling systems (see 3.1).

Examples of incidents (apart from problems in seawater cooling systems) that have attracted attention are (1):

- IGSCC in core grid bolts at Forsmark and the TVO power station in Finland
- IGSCC in stainless steel piping at Ringhals 1.
- Steam generator problems at Ringhals 2.
- Erosion-corrosion in turbine plants.
- IGSCC in screws (X-750) in the top tie-plate on the fuel bundle.
- Chloride induced SCC in moisture separator reheaters.
- Irradiation induced IGSCC at Oskarshamn 1.

2.3 What to expect in the future.

In the course of time corrosion of different forms has considerably affected the operation of nuclear power plants all over the world. In general corrosion becomes more extensive as the age of the equipment increases.

Today only a few Nordic nuclear units are older than ten years while their designed lifetime is thirty to forty years. On the other hand large efforts are made to eliminate or slow down the existing problems and to avoid them in future plants.

For BWRs, a number of remedies to mitigate IGSCC in stainless steel piping have been developed and are currently being implemented. Research has revealed a phenomenon known as low temperature sensitization, LTS, i.e. sensitization at normal BWR temperatures. It is not known today whether the lifetime of a reactor is long enough to raise problems due to LTS.

As far as PWRs are concerned one corrosion problem has succeeded the other in steam generators using nickelbase Alloy 600 (like in Ringhals 2, 3 and 4). Individual efforts made have been successful but new problems have often arisen in plants in operation, in the form of wastage, denting, IGSCC, intergranular corrosion, and pitting. The prospects for new steam generators (new PWRs or replacement of steam generators) are better. In these structures more resistant alloys may be used, like thermally treated Alloy 600 or Alloy 690. In general the need for a better control of the secondary water chemistry has been recognized.

For PWRs with stainless steel tubing in their steam generators (like Loviisa 1 and 2) the main threat is ingress of chlorides through leaking condenser tubes. These chlorides may cause transgranular stress corrosion cracking of the steam generator tubes.

IGSCC in high strength, precipitation hardening alloys (e.g. X-750, 718 and A286) is a problem common to both BWRs and PWRs. A number of reactor components have been affected. At present the causes for component degradation are not understood. Thus, an increasing amount of failures is to be expected all over the world, in spite of the fact that remedial actions are being implemented.

3. Corrosion in seawater

In the Nordic countries most power plants, both nuclear and conventional, are seawater cooled. Corrosion in pumps, valves, heat exchangers and pipes caused by seawater is therefore a well known problem.

In the project some investigations in this field has been performed, the work is described below.

3.1 Experience of corrosion and corrosion protection in seawater systems in the Nordic countries.

In order to collect the power plants knowledge of corrosion in seawater, experience from Denmark, Finland, Norway and Sweden has been collected (2). The investigation concerns pumps heat exchangers, valves and pipes. The main emphasis was on pumps and heat exchangers.

The most common pumps in the seawater cooling systems of power plants are vertically extended shaft pumps. To counteract corrosion on column and casing with organic surface coating and corrosion on stainless steel shafts and impellers under shutdown conditions, these pumps should be provided with internal and external cathodic protection. The experience with tin bronzes and aluminium bronzes in impellers and shafts in such pumps has been so poor - erosion and cavitation damage - that a change has usually been made to preferentially ferritic-austenitic Mo-alloyed stainless steels. The combination of stainless steel/Ni-Resist 2 D has been unsatisfactory owing to the occurrence of galvanic corrosion on the latter material.

For heat exchangers, both tube and plate, titanium has proved to be by far the best choice. In the optimal solution for a titanium heat exchanger the tubes are seal-welded to tube sheets of explosion-bonded titanium clad steel. For retubing of old condensers a similar procedure with tubes of high-alloy stainless steel in tube sheets of stainless clad steel is of economic interest. However, certain questions, among which the effect of chlorination of the cooling water, remain to be clarified before such a procedure can be unreservedly recommended.

Pipings of rubber-lined carbon steel or with thick coatings of solvent-free epoxy resin have shown good corrosion resistance in the seawater systems of power plants.

Tar-epoxy-resin-coated pipes, however, should usually be provided with internal cathodic protection. Cement-lined carbon steel pipes are used with varying results in the offshore industry. Recently, promising results have been noted with pipes of the high alloy stainless steel 254 SMO which have come into use for similar purposes.

Valves in seawater cooling systems have been affected, in particular, by corrosion due to defectively applied or damaged organic coatings on cast iron. Different seawater-resistant bronzes (gunmetal, tin bronze and aluminium bronze) are therefore preferable as valve material.

3.2 Dealloying of aluminium bronzes

Aluminium bronzes are frequently employed in components which have to operate in seawater. Generally these alloys are used in as-cast condition. As part of the SAK-4 project, an attempt was made to demonstrate that heat treatment would improve the mechanical properties and corrosion resistance. The major corrosion problem of the alloys in seawater applications is dealloying at crevices. Therefore two aluminium bronzes were studied under seawater conditions (3,4). Their properties have been evaluated by microstructural studies, as well as by mechanical and corrosion testing in as-cast and heat treated conditions.

The materials were a nickel aluminium bronze (Cu-Al-Fe-Ni) and an aluminium bronze with iron and manganese additions (Cu-Al-Fe-Mn) obtained from failed components from a nuclear power plant. The two alloys were tempering heat treated in as-cast condition and after water quenching at 450, 600 and 700° C for 3 hours.

Water quenching and tempering increased the hardness in both materials compared with slow cooling. In general the nickel aluminium bronze was harder than the other material. The dealloying resistance was best after tempering at high temperatures between 600 and 700° C. At the same temperatures good mechanical properties were also obtained.

3.3 A critical evaluation of accelerated corrosion testing of stainless steels for seawater applications.

During the last years new stainless steels for seawater applications have been developed. As practical experience with these new steels in seawater systems is limited, accelerated laboratory tests have been used to demonstrate their corrosion resistance. How good are these accelerated tests with respect to their ability to predict corrosion resistance in practice, and is their reproducibility satisfactory?

In the project a critical evaluation of the tests has been made, also including recommendations for test procedures (5). One problem is that international standards are seldom followed in all details. Individual improvements of standard tests make it difficult to compare results from one laboratory to another. However, these modifications of the tests sometimes have given more valuable results.

Crevice corrosion tests, however, suffer from difficulties with controlling the crevice geometry. Another problem is related to the corrosion tests in practice. In accelerated pitting corrosion tests there is an uncontrolled variable because crevice corrosion occurs at the edges of the masks used to define the working area. It turns out that the advanced stainless steels are more likely to suffer from crevice corrosion, so shortcomings in the pitting corrosion tests may not be too serious.

Corrosion under stagnant conditions is a problem with stainless steels in many seawater applications. In some cases behaviour under stagnant condition is the main basis for material selection. Nevertheless, tests for corrosion resistance under such conditions have not been developed, probably because environmental factors causing the problems are different from case to case (oxygen gradients, acidification due to hydrolysis, deposits, and hydrogen sulphide produced by bacteria).

4 Stress corrosion cracking of high strength nickel base alloys

It has been reported that components made of high strength nickelbase alloys have failed to an increasing extent. Such failures can cause serious damage or affect plant availability, for example stress corrosion cracking in bolts and guide pins. The effect of different heat treatments on the susceptibility of intergranular stress corrosion cracking of Inconel X-750 was therefore studied in the project (6,10).

A literature survey (7) on microstructure studies and corrosion properties showed that there are contradictory observations concerning stress corrosion cracking of Inconel X-750 in both boiling and pressurized water reactors. According to literature the most resistant structure is obtained by solution annealing at a relatively high temperature (about 1100°C) followed by a single tempering treatment (about 700°C/20 h). It is said that through this heat treatment the most appropriate microstructure is obtained: a small grain size, a high ratio of $M_{23}C_6/MC$ precipitation and a uniform distribution of gamma prime phase.

Based on the outcome of the literature survey the following experimental work was carried out:

- The relationships between different heat treatments and resulting microstructures was studied.
- The dependence of stress corrosion cracking susceptibility on heat treatment was examined.
- The influence of metallurgical structure on stress corrosion susceptibility in boiling water reactor environment was examined.

Two charges of Inconel X-750 were investigated. The material was heat treated at temperatures that are normal for commercial use and then studied by electron microscopy. Different forms of intergranular corrosion tests and a stress corrosion test were performed in order to study the corrosion susceptibility.

The experiments showed that the microstructure of Inconel X-750 depends on the heat treatment and that the corrosion susceptibility is governed by a number of factors such as e.g. charge dependence and microstructure.

The work carried out has thrown some light on Intergranular Stress Corrosion Cracking of Inconel X-750, but much work remains still to be done.

5. New materials in nuclear power applications

Corrosion problems, in general, can be solved in different ways, e.g. through design, or choice of environment. One radical way of avoiding difficulties encountered with corrosion would be to replace the material in question with a more corrosion resistant type. Economic considerations may even warrant a change from Copper-alloys to titanium. This has been the case in condensers in some Swedish nuclear power plants. In the future the same solution may be used for other components such as intermediate superheaters and steam generators.(8)

Ferritic austenitic or duplex stainless steels have recently obtained increasing application in the process industry. These steels have a better resistance to general corrosion than carbon or low alloyed steels, and they are less susceptible to stress corrosion cracking than ordinary austenitic stainless steels. They also have a good weldability and excellent properties in e.g. bending. Duplex materials have been tested in environments similar to those prevailing in nuclear power plants with good results. The question is whether the corrosion properties are good enough for e.g. intermediate superheaters. More studies on the behaviour of duplex stainless steels in nuclear environments are necessary before these steels can be used in nuclear applications.

Austenitic stainless steels with high contents of chromium, nickel and molybdenum (e.g. Sanicro 28) are promising alloys for use in seawater applications. Comparing corrosion test results of this type of alloys to AISI 316 steel it can be observed that they have a much better resistance against crevice and pitting corrosion. Full scale condenser tests have been carried out with a recently introduced stainless steel (254 SMO) in Finnish and Swedish power plants. The results are very promising.

Titanium stabilized ferritic stainless steel with 25% Cr, 4% Ni and 4% Mo (MONIT) has excellent corrosion resistance in seawater and good weldability and manufacturing properties. It has also been tested in seawater cooled condensers with good results.

The alloys mentioned above are examples of materials that in the future could be commonly used in the power industry. The preliminary experience with these materials is quite promising, but additional tests are still required.

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