INTERGRANULAR STRESS CORROSION CRACKING (IGSCC) SUSCEPTIBILITY OF INCONEL X-750: STATE OF THE ART

B. Remartínez, J.I. Pastor and J. Santamaría

IBERDROLA GENERACIÓN-SETEG-Tecnología de Materiales,
Pº Virgen del Puerto, 53 28005 Madrid Spain
Email: bremartinez@iberdrola.es

ABSTRACT

INCONEL alloys have been widely used in light water reactors for internal structural components, where high mechanical properties and excellent corrosion resistance at high temperatures are required. These age hardenable nickel-chromium-iron alloys have been showing an excellent behaviour during their life service.

One of the most important Nickel based alloy is INCONEL 600, which is containing about 76% Ni, 15% Cr, 8% Fe and 0.5% Ti. Its microstructure is formed of a majority matrix of γ phase, in which some small precipitates appears inside the grains, as well as in the grain boundaries. As its mechanical properties at temperatures about 300ºC were so excellent, this alloy has been used to for internal components, including springs, bolts, guide tube pins, etc. But, in spite of its excellent creep strength behaviour, some Intergranular Stress Corrosion Cracking (IGSCC) phenomena have been appeared in both pressurised and boiling water reactors, showing that this alloy is susceptible to suffer IGSCC.

In order to avoid the possible failures caused by this susceptibility, a new nickel base alloy was proposed, INCONEL-750, which was supposed to be free of this kind of corrosion. In this alloy, IGSCC behaviour was improved by adding some minor alloy elements and changing some parameters in the heat treatment. In some nuclear power plants, this alloy was chosen for the tie rods used to repair the shroud of the reactor vessel in which some microcracks had appeared.

Although up to now the experience of the INCONEL-750 alloy behaviour inside the reactor vessel is quite limited, the first data showing susceptibility to IGSCC in this alloy have already appeared. Therefore, some investigations are being carried out in order to determine the real behaviour of this alloy under the reactor operation conditions.

At the same time, several developments to improve the corrosion resistance behaviour of these alloys inside the reactor are being carried out. In this way, for example, INCONEL-718 alloy has been manufactured; this alloy is highly resistant to crack initiation in aqueous environments in most heat-treated conditions, but several heat treatments exhibits high crack propagation rates. Up to now, the developed studies has demonstrated that the IGSCC behaviour of these alloys, which highly depends on crack initiation and propagation resistance, is significantly affected by microstructure. Further studies have to be developed in order to determine if the behaviour of this new alloy under real operation conditions is correct in both BWR and PWR environments.

INTRODUCTION

Nickel-base alloys are used extensively in Light Water Reactor (LWR) nuclear power systems due to their excellent corrosion resistance and strength in high temperature aqueous environments. Alloy 600, a solid solution strengthened nickel-base alloy, is used for Pressurised Water Reactor (PWR) Steam generator tubing for the majority of PWR nuclear power stations. Alloy 600 is also used in Boiling Water Reactor (BWR) systems for safe ends and other components.

For applications requiring very high strength and superior corrosion resistance, age hardenable nickel-base alloys such as Alloy X-750 are often used. Specific applications include fuel assembly hold down springs. BWR Jet Pump components and high strength bolts for core and other structural components.

In spite of their generally excellent general corrosion resistance, the above mentioned alloys have been found to be susceptible to localised forms of corrosion attack such as stress corrosion cracking, corrosion fatigue, and intergranular attack. Susceptibility to these forms of damage is a function of prior thermomechanical treatment and service environment. For Alloy 600, from an economic standpoint, the most severe impact has resulted from instances of intergranular attack and denting related cracking. There have, however, been several instances of cracking in PWR primary environments. In some of these cases fatigue could not be ruled out as a contributing factor. For certain environments and heat treatments Alloys X-750 is susceptible to environmentally assisted fatigue and stress corrosion cracking.

Failures of components in service, while few in number, have resulted in significant economic impact. These failures have provided impetus for the development of materials with improved resistance to these environmental effects but the available data is limited. For this reason a research program, has been initiated with the goal of achieving a mechanistic understanding of the stress corrosion cracking behaviour of Ni-Cr-Fe alloys used in nuclear power systems.

MICROSTRUCTURE

Age hardenable Ni-Cr-Fe alloys are complex alloys, and a wide range of thermal treatments can modify their properties. In the heat-treated condition, the microstructure of these alloys consists of several intermetallic precipitates surrounded by a metallic matrix. These intermetallic phases strengthen the metallic matrix, and the magnitude of these strengthening is related to the particle size and spacing.

The most prevalent phases are the FCC matrix phase (γ phase), followed by intermetallic precipitate γ' phase, and also precipitated carbides MC and $M_{23}C_6$, where the M letter represents a metal. The γ' phase precipitates coherently with the matrix. Additional strength can be achieved by the presence of solid solution elements such as Cobalt, Iron, Chromium, Titanium and Aluminium, and by changing either composition or heat treatment, other intermetallic phases may appear inside the metallic matrix [8].

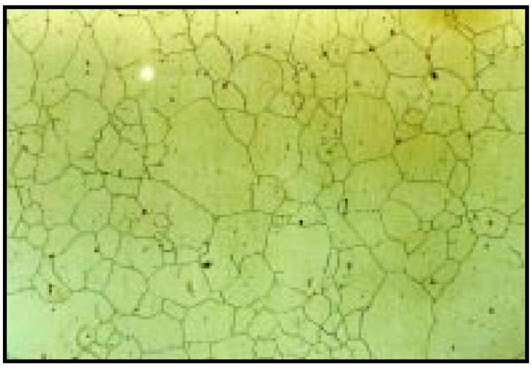


Figure 1: (x100) INCONEL 600 microstructure after the heat treatment

Figure 1 shows the microstructure of an INCONEL 600-specimen alloy after a solution and quenching thermal treatment. In the micrograph there are middle size γ phase grains (Ni-Cr-Fe solid solution) containing precipitated particles, which are identified as Titanium and Aluminium carbides. These precipitated particles exhibits a characteristic orangish colour, as it can be seen in detail in Figure 2; their chemical composition was confirmed by an electron dispersive spectroscopy (EDS) analysis, and they were identified as Titanium and Aluminium carbides [1].

Figure 2: (x1000) Orange poligonal precipitated phases (10% Oxalic acid)

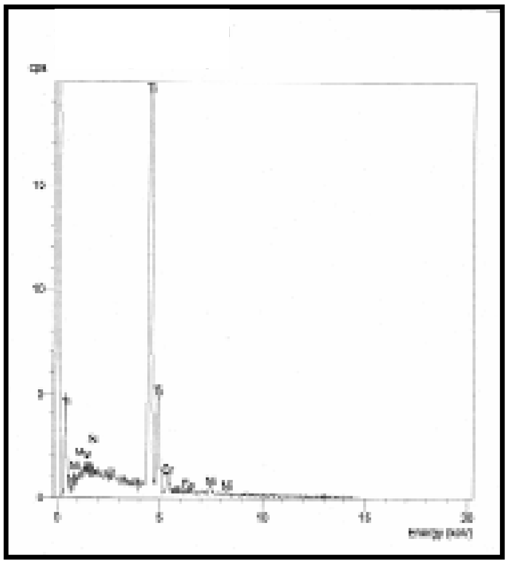


Figure 3: EDS Spectrum of the Orange poligonal precipitated phases

IGSCC IN INCONEL 600

Despite the good mechanical properties at high temperatures that this alloy has exhibited, some intergranular stress corrosion failures have taken place in several components made of this alloy. These failures have proved that these alloys are susceptible to environmental degradation in aqueous environments. Several crack growth tests have been performed, and it has been found that crack growth rates in air saturated water are faster than for dearated water. It has also been found that sensitisation in alloy 600 appears to have very little effect on its fatigue behaviour in dearated environments, but the crack grow rate of sensitised material is significantly higher when the amount of dissolved oxygen is gradually increased.

The observed differences between the SCC behaviour in deaderated and air saturate water would suggest that the electrochemical potential play an important role in cracking development. Some experiments have shown that stress corrosion cracks could be inhibited when alloy 600 was electrically coupled to gold, while cracking was accelerated when the alloy was coupled to iron.

Since the time needed to initiate SCC in pure water is very long, accelerated tests in hot caustic media are also used to determine the stress corrosion characteristics of alloy 600. Deaerated 10% NaOH solutions were used, and it was found that aged material performed better than mill annealed in its resistance to SCC. Other tests also showed that ageing mill annealed tubing at 600ºC for 4 hours improved the cracking behaviour of alloy 600 in deaerated NaOH (0.2 to 0.75M) over that of mill annealed material.

NEW DEVELOPMENT: INCONEL 750

In order to avoid the possible failures caused by IGSCC INCONEL 600 susceptibility, a new nickel base alloy was proposed, INCONEL-750, which is an alloy 600 base-modified alloy. In this alloy, IGSCC behaviour was improved by adding some minor alloy elements (Titanium, Aluminium, and small quantities of Niobium) and changing some parameters in the HTH heat treatment. HTH thermal treatment is the most commonly heat treatment recommended for this alloy in nuclear applications and consists of a solution annealing at about 1090 ºC, water quench, and then ageing for 20 hours at 704 ºC approximately. Variations in the cooling rate after annealing, and changes in the age hardening heat treatment leads to a different stress corrosion cracking behaviour during the life service. For example, it has been found that the ageing conditions that give high yield strength also give a high SCC susceptibility [4].

The microstructure of the X-750 HTH material is characterised by a majority γ matrix phase, with a uniform distribution of γ' phase with MC type carbide, in which M is mainly Ti) and grain boundaries decorated with a semicontinuous carbide phase (see Figures 4 and 5) [2].

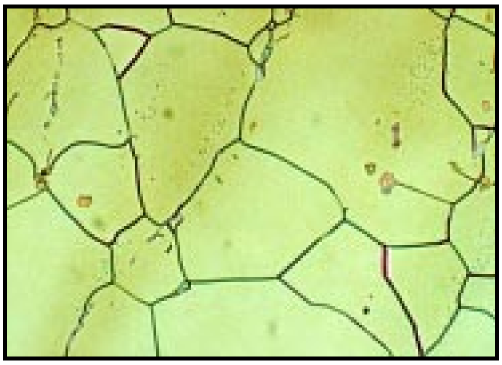


Figure 4: (x200) INCONEL 750 microstructure (Orange precipitated carbides can be observed)

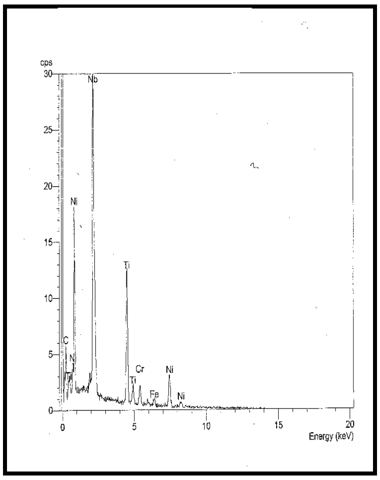


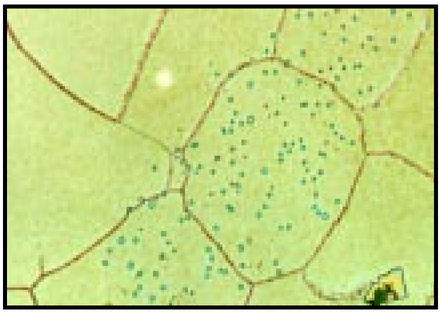
Figure 5: EDS Spectrum of the Orange polygonal precipitated phases

Further STEM analysis indicated a significant degree of Chromium depletion in the regions adjacent to the grain boundaries in this HTM material, which was not observed in other heat treatments. This Chromium depletion produced by the formation of $M_{23}C_6$ along the grain boundaries during ageing was identified by energy dispersive X-ray analysis (EDXA) and it was found that the precipitate carbides contained nearly 90% Cr (typically, the composition of the carbides is (in wt. %):

TABLE 1
CHEMICAL COMPOSITION OF RICH CHROMIUM GRAIN BOUNDARY CARBIDES

Element	Al	Si	Nb	Ti	Cr	Fe	Ni	P and S
wt %	0.13	0.48	0.63	0.21	88.99	2.13	7.39	Not detectable

Furthermore, the Chromium profile perpendicular to the grain boundary was obtained by EDXA analysis (figure 7), and the typical Chromium depletion surrounding the grain boundaries could be observed [7]. Some experiments with different ageing conditions (and also with different amount of precipitated Chromium phase) were carried out, and it could be observed that the greater wide and deep Chromium depletion (associated with the higher yield strength obtained) was associated with the highest IGSCC susceptibility.



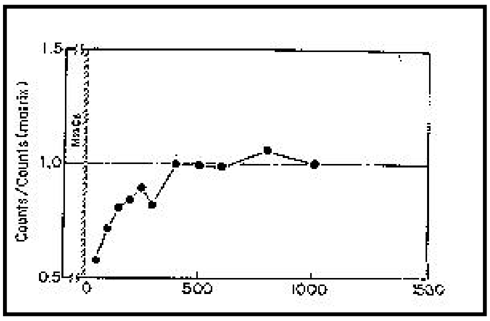


Figure 6: Detailed grain boundaries Chromium precipitates

Figure 7: Typical Chromium profile perpendicular to the grain boundary

So, that experiments showed that the Chromium depletion near the grain boundary associated with the Chromium Carbide formation at the grain boundary causes the IGSCC susceptibility of INCONEL X-750, and moreover, by studying different ageing treatments, it such a poor IGSCC property coincides with the ageing that gives a high yield strength.

The three-step heat treatment was also selected for IGSCC behaviour examination. This treatment consists of a first solution step (T~1100ºC for 4h.), followed by a stabilisation step (T~850ºC for 24h.) and ending by a last ageing step (T~700ºC for 20h.). The results showed that these heat-treated alloys were more susceptible to IGSCC in high-temperature water than the HTM treated alloys, in spite of the smaller corrosion rate in a modified ASTM standard corrosion test. EDXA revealed Titanium segregation and formation of Titanium-rich phases along the grain boundary (carbides, γ' and η phase -Ni_3Ti_7-), and it is thought that the poor resistance to IGSCC after a three-step heat treatment might be caused by formation of a local cell between the grain boundary and the matrix. Next figure shows the Chromium and Titanium typical profile perpendicular to a grain boundary. It can be observed that no clear Chromium depletion is created near the grain boundary, even perpendicular to the $M_{23}C_6$ carbides. But the Titanium profile shows that the Titanium rich-phase on the grain boundary may result from the Titanium segregation to the grain boundary, contrasting with the Chromium depletion by the formation of Chromium carbides.

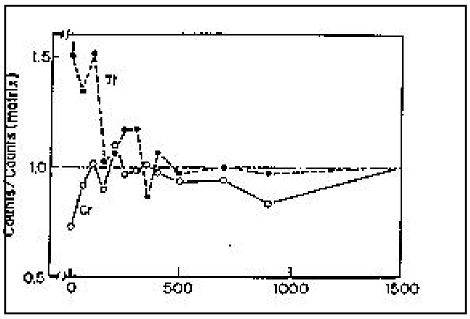


Figure 8: Chromium and Titanium profile perpendicular to a grain boundary

The different Titanium-rich phases and the $M_{23}C_6$ precipitated along the grain boundaries, covered the grain boundaries with a chemically inhomogeneous state, and this absence of homogeneity causes local cell reactions between the precipitates and the matrix, which are the rootcause of the IGSCC observed in these three-step heat treated X-750 alloys.

The results of all the studied cases go in the same direction: thermal treatment and microstructure plays an important role in the behaviour of Alloy X-750, and IGSCC susceptibility strongly depends particularly on the carbide formation on the grain boundaries. So, in spite of X-750´s exceptional high temperature mechanical properties, it has been found to be susceptible to intergranular stress corrosion cracking in relatively low temperature aqueous environments such as those that exist in LWR systems [5], and for this reason new developments in INCONEL alloys are now being carried out.

INCONEL DEVELOPMENTS

INCONEL 718 alloy seems to be one of the most important nickel-based alloy candidates to substitute the X-600 and X-750 alloy. This alloy is highly resistant to crack initiation in aqueous environments in most heat-treated conditions, but several heat treatments exhibits high crack propagation rates. Heat treatments designed to minimise the formation of δ phase at the grain boundaries are also the ones which presents the highest resistance to crack growth, with rates comparable with the same alloy X-750 material [6].

Anyway, up to now, the developed studies has demonstrated that the IGSCC behaviour of these alloys, which highly depends on crack initiation and propagation resistance, is significantly affected by microstructure. The data show that a commercial ageing treatment, preceded by a high temperature solution anneal (1038ºC), can retain the excellent resistance to crack initiation and significantly improve the crack grow resistance. But further studies have to be carried out in order to determine the real behaviour of this new alloy under the reactor operation conditions.

CONCLUSIONS

The most important conclusion of this article is that, although the performance of high-strength, age -hardened NiCrFe alloys is generally good, there are some evidences which shows that they have some IGSCC problems in aqueous environments when they are exposed to conditions which are similar to the LWR operation conditions.

It has also been shown that microstructure, which strongly depends on the thermal treatment, has a great influence in the stress-corrosion behaviour of these alloys. So, it is very important to fix the parameters of the heat treatment in order to achieve the best conditions that may postpone both the initiation and the growing of the stress-corrosion cracks in the nuclear components made of these materials.

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REFERENCES

1. Santamaría, J. and Pastor, J.I. Informe TEMAT - 99.052. Madrid 1999
2. Santamaría, J. and De Luis, J. Informe TEMAT - 100.464. Madrid 1999
3. “The Effect of Thermal Treatment on the fracture properties of alloy X-750 in aqueous environments”. Informe EPRI TR-102437s
4. “The Effects of Heat Treatment and Environment on corrosion fatigue: Alloy 600”. Informe EPRI TR-102436 Vol.2
5. “The Effects of Heat Treatment and Environment on corrosion fatigue: Alloy 750”. Informe EPRI TR-102436 Vol.1
6. “Improved Stress Corrosion Resistance of NiCrFe Alloys”. Informe EPRI NP-6908-M
7. M. Tsubota, K.Hattori and T. Kaneko. “Study on SCC susceptibility of INCONEL X-750 in High-Temperature pure water: effects of ageing temperature and time”. National Association of Corrosion Engineers. Vol. 44. Nº2, Febr.1988
8. Saarinen,K., Hänninen,H. And Ehrnsten,U. “SCC of INCONEL X-750 in LWR environments”. 12Th Scandinavian Corrosion Congress. Eurocorr´92