

SUPERALLOY APPLICATIONS IN THE NUCLEAR FIELD

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ABSTRACT

The process conditions in the areas of nuclear fuel processing, fabrication, utilization, reprocessing and disposal are severe, demanding therefore the use of materials with high temperature mechanical strength and corrosion resistance. A number of refractory metal containing superalloys have found application in the different areas of the nuclear field. The main aspects of the microstructure, strengthening mechanisms and corrosion resistance of 3 superalloys, namely Incoloy 825, Inconel 718 and Hastelloy C have been discussed. The role of the refractory metal elements in influencing the mechanical strength and corrosion resistance of superalloys has been emphasised.

INTRODUCTION

The increase in the living standard of mankind has been accompanied by a steady growth of utilization of energy in all forms; from about 2700 to 20 000 million tons of coal equivalent between the years 1950 to 1980. The three main sources of energy now available for large scale generation of electricity at an economic price are fossil fuels (coal, oil and natural gas), water with an available head and nuclear fuels. Nuclear power has provided an increasing proportion of the energy utilized in a number of countries. The flowsheet of operations of a fossil fueled power plant is fairly straightforward: fuel is transported from mine or well to the plant, conveyed to burners, and the ashes or residues are disposed off or dispersed with or without prior treatment. On the other hand, the flowsheet of a nuclear power plant is much more complex (figure 1). The basic steps are essentially the same whether the fuel is uranium, thorium or plutonium or a mixture of them. The energy producing stage is the fission of uranium (or plutonium)

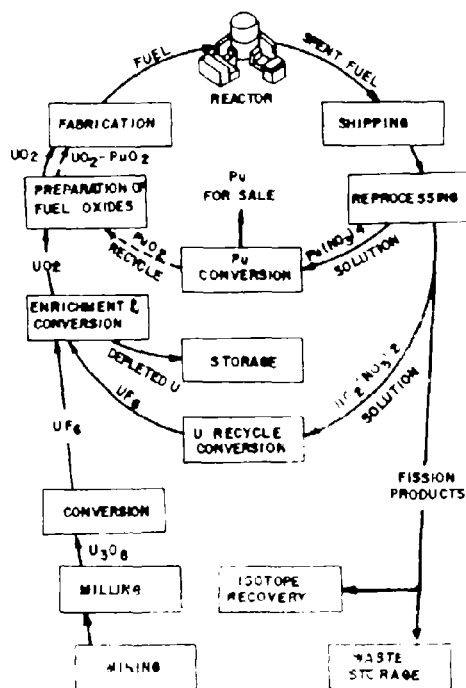


FIG 1 Nuclear Fuel Cycle for Light Water Reactors [1]

nuclei under neutron bombardment. The unique feature of a fuel "cycle" arises from the fact that complete combustion of all available fissile fuel in the reactor core is not practical. The fuel is withdrawn after 25-30% of the fuel has been consumed and reprocessed to remove unwanted fission products and purify the remaining fissile material for reuse. The fuel cycle which roughly demarks the nuclear field, consists of the following stages:

1. mining and milling of U ore,

2. refining
3. conversion,
4. enrichment of U^{235} content,
5. fuel preparation and fabrication,
6. power generation,
7. spent fuel transportation,
8. reprocessing and waste recovery,
9. waste storage and disposal.

The process conditions encountered in stage 1 through 5 are substantially similar to comparable processes in the chemical industry or in a specialized metallurgical plant, however the composition and process conditions

encountered in stages 3 and 4 are severe and unique in the nuclear field. Stage 6 constitutes the reactor. Parameters such as fuel, coolant, core, power plant characteristics etc, vary with the type of reactor, as shown in Table I. In stage 7, 8 and 9, the process material is highly radioactive and reactive. The chemical nature of the process in stage 8 though similar to those in stages 3 and 4, is far more aggressive to structural materials and components.

TABLE I - Typical Parameters for Reactors of about 500 MW

REACTOR TYPE	Magnox	AGR	BWR	PWR	CANDU	SGHW (Saturated)	Fast reactor
FUEL							
Fuel material	U	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	PuO ₂ UO ₂
Can material	Mg	SS	Zr	Zr	Zr	Zr	SS
Feed enrichment (% U ²³⁵ or Pu)	Natural	2.0-2.4	2.5	3.0	Natural	2.0	15
Reject enrichment(%)	-	0.6	0.9	0.9	-	0.6	
COOLANT							
Composition	CO ₂	CO ₂	H ₂ O	H ₂ O	D ₂ O	H ₂ O	Na
Pressure (2) (psi)	385	435	1000	2100	1350	1000	Zero
Inlet temperature (°C)	247	290	275	277	250	274	400
Outlet temperature (°C)	414	675	286	300	294	283	600
CORE							
Dia. X ht. (ft)	57X30	31X27	14X12	11X11	21X16	23X12	6.5X3
Ave. power density (KW/litre)	0.9	2.2	33.6	65	9.7	12	380
MODERATOR	Graphite	Graphite	H ₂ O	H ₂ O	D ₂ O	D ₂ O	None
PRESSURE VESSEL	Concrete	Concrete	Steel	Steel	Zr tubes	Zr tubes	SS tank
Inside dia. X ht (ft)	96X96	63X59	17.75X64	12X42	0.35 ft dia.	0.42 ft dia.	
Wall thickness (in.)	132	144	5.7	7.5	0.2	0.2	0.5
TOWER PLANT							
Steam press (2) (psi)	665	2300	965	725	565	900	2300
Temp. (°C)	400	566	282	260	255	280	537
Station net thermal efficiency	31.4	41.5	33.1	33	30	33	43

Note: SS - Stainless Steel - D₂O - heavy water

TABLE II - Application of Refractory Metal containing Superalloys in the Nuclear field

ALLOY	COMPOSITION	APPLICATIONS
Hastelloy B	Ni-28Mo-2Fe	1. Isotope separation by chlorination
Hastelloy C	Ni-16Cr-1Co 15.5 Mo-6Fe	1. Batch process of UF ₆ production 2. Stirred bed process of UF ₄ production 3. Isotope separation by chlorination 4. UCl ₄ purification by sublimation 5. Perflex process of core dissolution 6. Waste calcining 7. Chloride waste handling
Hastelloy N	Ni-7Cr-16.5Mo-5Fe	1. Aqueous and nonaqueous processing of transuranium elements
Hastelloy X	Ni-22Cr-1.5Co-9Mo -0.6W-18.5Fe	1. Light water cooled reactors 2. High temperature gas cooled reactors 3. Fast breeder reactors
Alloy 79-4	Ni-4Mo-17Fe	1. Nonaqueous processing of transuranium elements
BMI-HAFO-20	Ni-25Cr-6Mo -16Fe-1Ti-1Cu	1. Fuel reprocessing - cladding removal 2. Waste handling
Inconel 750X	Ni-15.5Cr-1Nb- 2.5Ti-0.7Al-7Fe	1. Liquid metal cooled reactors
Inconel 718	Ni-20Cr-3Mo-18Fe 5Nb-1Ti-0.5Al	1. Light water cooled reactors and gas cooled reactors
Incoloy 825	Fe-21.5Cr-42Ni-3Mo	1. Light water cooled reactors
Carpenter 20	Fe-29Ni-20Cr-2Mo-2Cu	1. Aqueous fuel reprocessing and coredissolution
Haynes-25	Co-20Cr-10Ni-15W 3Fe	1. Isotope separation by chlorination 2. Waste handling

The nature of the process conditions in the nuclear field being both thermally and chemically aggressive, a large number of superalloys have found applications, because of their well known high temperature mechanical strength and corrosion resistance. Table II lists the different refractory metal containing Ni, Fe and Co base superalloys that have been used in the nuclear field. Among these,

Incoloy 825, Inconel 718 and Hastelloy C are considered important, since they find application as critical components. This paper discusses certain aspects of the microstructure, strengthening mechanism and corrosion resistance of these 3 alloys to throw more light on the behavior of these alloys in specific nuclear environments.

TABLE III. Typical Compositions

Element	Alloy	Incoloy 825	Inconel 718	Hastelloy		
				C	C-276	C-4
Ni		38.0-46.0	50.0-55.0	57.4	56.3	67.6
Fe		balance	balance	6.0	6.1	0.3
Cr		19.5-23.5	17.0-21.0	15.1	16.1	16.1
Mo		2.5-3.5	2.8-3.30	16.1	16.0	15.6
W		-	-	3.4	3.6	0.04
Nb		-	4.75-5.50	-	-	-
V		-	-	0.05	0.11	0.03
Ti		0.6-1.2	0.65-1.15	-	-	0.43
Mn		1.0 max	0.35 max	0.6	0.4	0.10
Si		0.5 max	0.35 max	0.6	0.06	0.04
Co		-	1.0 max	1.3	0.85	0.17
Al		0.2 max	0.2-0.8	-	-	-
Cu		1.5-3.0	0.3 max	-	-	-
C		0.05 max	0.08 max	0.08	0.01	0.006
B		-	0.006 max	-	-	-

MICROSTRUCTURE AND STRENGTHENING MECHANISMS

Alloys suitable for high temperature applications can be classified into 2 basic groups; (i) body centered cubic refractory metal base alloys (V, Nb, Ta, Cr, Mo and W) and (ii) austenitic Fe, Ni and Co base alloys, otherwise known as superalloys. In general, the factor that limits the utilization of refractory alloys at high temperatures is their low resistance to oxidation, whereas the maximum temperature for the utilization of superalloys is limited not by oxidation resistance but by mechanical strength. The strengthening of superalloys occurs by one or a combination of the following mechanisms:

- i. Solid solution hardening, caused mainly by the presence of W, Mo, Ta, Nb and Cr. Besides these elements, Co helps reduce the stacking fault energy in Ni base superalloys.
- ii. Dispersion hardening, caused by carbides (such as M_7C_3 , $M_{23}C_6$, M_6C and MC, where in Cr, Nb, Ta and Ti are the more common carbide formers) and by incoherent particles of stable oxides (such as ThO_2) obtained through powder metallurgical techniques.
- iii. Grain boundary strengthening, that occurs upon addition of small quantities of Zr and/or R.
- iv. Precipitation hardening, caused by coherent phases such as f.c.c. γ' ($Ni_3(Al, Ti)$) or b.c.c. γ'' (Ni_3Nb). The presence of Co also helps raise the solvus temperature of γ' . Precipitation hardening is the most effective mechanism in Ni base superalloys.

The main aspects of the microstructure and strengthening mechanism in Incoloy 825, Inconel 718 and Hastelloy C are:

Incoloy 825: Upon solubilizing at 1100-1200°C the microstructure of this alloy presents gross ($\sim 10\mu m$) and incoherent precipitates of TiC and TiN dispersed in an austenitic matrix. The Mo in the alloy (see Table III for typical compositions) brings about solid solution hardening. However upon aging the alloy at temperatures below 815°C a small amount of hardening occurs depending upon the Al and Ti content of the alloy, due mainly to precipitation of γ' . Also in this temperature range, precipitation of metastable carbides such as $M_{23}C_6$ takes place. Aging for longer times could result in the precipitation of undesirable σ phase.

Inconel 718: The microstructure of solubilized Inconel 718 basically contains dispersed particles of TiN, Nb (C,N) and TiC in an austenitic matrix. The free Mo and Nb bring about solid solution hardening. The main hardening mechanism in this alloys is by precipitation of γ'' although hardening by precipitation of γ' also occurs. The presence of Fe in this alloy is essential for γ'' to precipitate. The precipitation of undesirable phases such as Laves, or the transformation of γ'' to orthorhombic Ni_3Nb upon overaging could take place. The precipitation of small quantities of M_6C type carbides have also been known to occur.

Hastelloy C: This is basically a solid solution

TABLE IV. Corrosion Resistance of Hastelloy C and Incoloy 825 in Acidic Solutions [2]

ACIDIC SOLUTIONS	ALLOY	HASTELLOY C	INCOLOY 825
H ₂ SO ₄		A 0-96%, 65°C	A 0-5%, 80°C
		B 0-10%, BP	B 0-45%, BP B 40-80%, 100°C
H ₃ PO ₄		A 0-85%, 65°C	A 0-20%, BP
		A 0-50%, BP	B 20-80%, BP A 0-80%, 75°C
HNO ₃		A 0-70%, RT	A 0-30%, BP
		A 0-30%, 65°C	B 30-70%, BP A 0-70%, 75°C
HCl		B 30-70%, 65°C	
		B 0-10% BP	
HF		A 0-37%, RT	
		A 0-2%, 65°C	
Acetic acid		B 2-37%, 65°C	
		B 0-1%, BP	
Formic acid		A 0-5% RT	B 38-70%, 60°C
		B 5-45% RT	
Oxalic		A 0-100%, BP	
		A 0-90%, 65°C	
		B 0-90%, BP	
			A 0-10% BP B 10-50% BP

A- < 0.1 mm/year, B- 0.1 - 0.5 mm/yr, % -concentration W/W

RT- Room temperature, BP - Boiling Point

hardening alloy, due mainly to the high Mo and W contents. These alloying elements also cause the precipitation of M₆C. An undesirable intermetallic Mu-phase (Ni, Fe, Co)₃(W,Mo,Cr)₂ also forms, which along with precipitation of M₆C, locally depletes the matrix of Mo. In order to reduce the effects of localized corrosion (discussed in the next section) the

Si and C contents of this alloy were reduced to 0.06% and 0.01% respectively. This new alloy was called Hastelloy C-276. In spite of the reductions in Si and C contents, μ phase precipitates were nevertheless observed after prolonged exposure of the alloy to aging temperatures. Hence, the Fe, W, Co and Mn contents of the alloy were also reduced giving rise to Hastelloy C-4 (see Table III)

CORROSION/OXIDATION RESISTANCE

The corrosion/oxidation behavior of metals in general depend to a large extent on the conditions of the environment, which vary considerably, depending on the stage in the fuel cycle. Historically, Ni base superalloys have been frequently used when resistance to highly corrosive process conditions are required, combined with adequate resistance to pitting and stress corrosion. Table IV lists the corrosion resistance of Hastelloy C and Incoloy 825 in various acids. These 2 alloys have found application in various acidic environments encountered in fuel recovery, enrichment and reprocessing. Besides the good resistance to general corrosion, the 3 alloys have however demonstrated susceptibility to specific forms of localized attack or sensitivity to stress corrosion

Incoloy 825: The Mo content in Incoloy 825 greatly improves its corrosion resistance to HCl, H₃PO₄, a number of organic acids and increases the pitting and stress corrosion resistance in chloride solutions. Although Monel-400 (Ni-Cu alloy) is much more resistant in F containing environments, equipment that normally cannot be stress relieved, are often made of Incoloy 825, due to its enhanced resistance to stress corrosion cracking in F containing environments.

Incoloy 825 however becomes sensitive to intergranular attack upon exposure to temperature in the range 650-760°C, due to the presence of Cr depleted regions adjacent to grain boundaries. This region is caused by cellular precipitation of Cr rich M₂₃C₆ [3]. The presence of Ti imparts partial stabilization, but for complete stabilization, the M₂₃C₆ is precipitated in the range 927-982°C, where in Cr diffusion is sufficiently rapid to prevent the formation of continuous Cr depleted regions.

Inconel 718: One of the main application of this alloy is as fuel rod spacer grids in power reactors, where it is exposed to high temperature water. In typical pressurized water reactor (PWR) and off nominal environments anticipated during reactor operation, this alloy exhibits good general corrosion, but suffers intergranular stress corrosion cracking in ammoniated reference water at 315°C when stressed above the yield strength. Braze heat treated alloys (fuel rod spacer grids are fabricated by brazing) are also sensitive to stress level in ammoniated reference water [4]. On the other hand Inconel 718 suffers stress corrosion cracking in hot potassium tetraborate (used in P.W.R. during chemical shut down) even at stresses below the yield stress after relatively short exposure times (-72 hours). The stress corrosion failures were believed to be related to () the presence of numerous very small closely spaced NbC precipitates at grain

boundaries that had formed prior to age hardening, and (ii) the pickled surface of the alloy.

In an evaluation programme of the effects of reactor environments on the properties of reactor structural materials for nuclear superheat and gas cooled reactor, Inconel 718 revealed significant intergranular attack and internal oxidation in oxidising environments of He and water vapour at 815°C [5].

Hastelloy C: The excellent corrosion resistance of this alloy in a wide range of acids can be seriously impaired by certain thermal treatments during its processing and fabrication. Exposure of Hastelloy C, C-276 and C-4 in the range 650-1200°C results in the formation of Mo rich carbide precipitates that impairs the resistance of the alloys to intergranular, crevice and stress corrosion. The susceptibility of alloys C and C-276 to crevice corrosion and to stress corrosion cracking in chloride solutions has been attributed to galvanic action between the anodic matrix and cathodic Mo rich carbide precipitates at the grain boundaries [6]. In contrast, the Mo rich intermetallic compound (μ phase) impairs the resistance only to intergranular cracking in oxidising acids. The formation of Mo rich carbide precipitates is prevented in alloy C-4 by maintaining the C low and by addition of Ti. Formation of the μ phase is also minimized by adjustment of the alloy content. In spite of these changes to the composition of C-4, it is susceptible to intergranular attack in oxidising acids. An unidentified Ti rich phase was reported at grain boundaries after heating for one hour at 870°C. The reduction in the W content also causes crevice corrosion of alloy C-4 in the annealed condition in 10% ferric chloride which does not normally occur in alloys C or C-276. The deleterious effect of the absence of W can be circumvented by increasing the Mo content from 16 to 18%, rendering the alloy resistant to all 3 forms of corrosion [6].

FINAL COMMENTS

Other refractory metal bearing superalloys not discussed in this paper also exhibit good corrosion resistance and high temperature mechanical strength; the former due primarily to the presence of Cr and the refractory metals. Upon considering Zr together with the refractory metals, it can be observed that these elements play a significant role in the 4 principal strengthening mechanisms in superalloys. However, addition of W, Mo, Ta, Nb, V and Cr to superalloys has to be in controlled quantities, since they are also formers of intermetallic phases σ, χ, μ and Laves, whose presence has deleterious effects, both on mechanical properties and corrosion resistance.

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