EXPERIENCE WITH INCONEL-625 IN CRACKER SERVICE IN HEAVY WATER PLANTS

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In ammonia based Heavy Water Plants working on monothermal process enriched ammonia is cracked into its individual constituents for further processing. The cracking of ammonia, which is an endothermic process, takes place in cracker tubes filled with a catalyst which are fired inside a furnace. The design pressure of the tube is 160 kg per sq.cm. and the design temperature 765 deg. C.

At around 600 deg. C temperature, the phenomenon of creep sets in any material. 'Creep' in metals can be considered to be a time and temperature dependent process of plastic deformation. When stress is accompanied by heat, strain progresses leading to rupture of the material. The hotter the metal, greater the stress, the creep damage will occur more quickly. Thermal cycling can also lead to acceleration of creep damage. The rupture due to creep is understood to be caused by travel of creep dislocation through the matrix first in the form of creep voids accumulating into creep fissures eventually leading to failure by creep rupture.

Significant factors that are considered in the design for high temperature application in the creep range are creep stress to rupture or limiting strain for the design life, i.e.limit the design stress to maintain dimensional stability of the components for the intended life or work on the basis of stress to rupture for design life hours of 100,000 hours.

In our application, the allowable design stress value for the components at the design metal temperature is based on rupture stress at that temperature for design life. This is generally based on the results of short term tests of about 10,000 hours with extrapolation/projection at much higher temperature and stresses than the design values. This is generally 67% of the mean value or 80% of the minimum value of stress time curve, whichever is less.

In view of high output efficiency in the modern industrial process in high temperature range there is a need for heat resisting alloys, such as stabilised high chromium nickel steels, that are in use in the petro-chemical, fertiliser and other similar industries.

In Heavy Water Plants such application is of crackers where the material of high creep strength with good resistance to oxidation, carburisation and nitriding is required. It is seen that most of the family of nickel-chromium alloys have better heat resistance characterstics eventhough they also loose significantly the creep resistance and strength with increase in temperature. However Inconel-625 both wrought and cast type meet the requirements in the temperature range of operation of the cracker, i.e. around 720 deg. C. and therefore Inconel-625 is the best suited material for the cracker design on the basis of stress rupture strength of 100,000 hrs.

Inconel-625

		Wrought	Cast
a)	**Chemical Composition :**		
	Ni ...	61/58	60
	C ...	0.1 max	0.06 to 0.1
	Si ...	0.5 Max	.05 Max
	Mn ...	0.5 Max	0.5 Max
	Cr ...	20/23	20/23
	Mo ...	8/10	8.5/9.5
	Nb ...	(Nb+Ta) 3.15/4.15	3.15/4.15
	S ...	0.015 Max	0.015 Max
	P ...	0.015 Max	0.015 Max
	Fe ...	5.0	4.0
	Sn ...	Nil	0.01 Max
	Pb ...	Nil	0.01 Max
	Al ...	0.40 Max	Nil
	Ti ...	0.40 Max	Nil
	Co ...	1.00 Max	Nil
b)	**Condition :**	Solution Annealed at 1150 deg. C & air cooled	Solution Annealed at 1100/1170 deg.C & air cooled
c)	Grain size -	2 to 5	

d) **Mechanical Properties :**

At room temp. specified

YP (N/sq.mm)	...	276 Min	275 Min
UTS (N/sq.mm)	...	690 Min	615 Min
% Elongation [lo = 5d]	...	50 Min	25 Min

At rooom temp. available

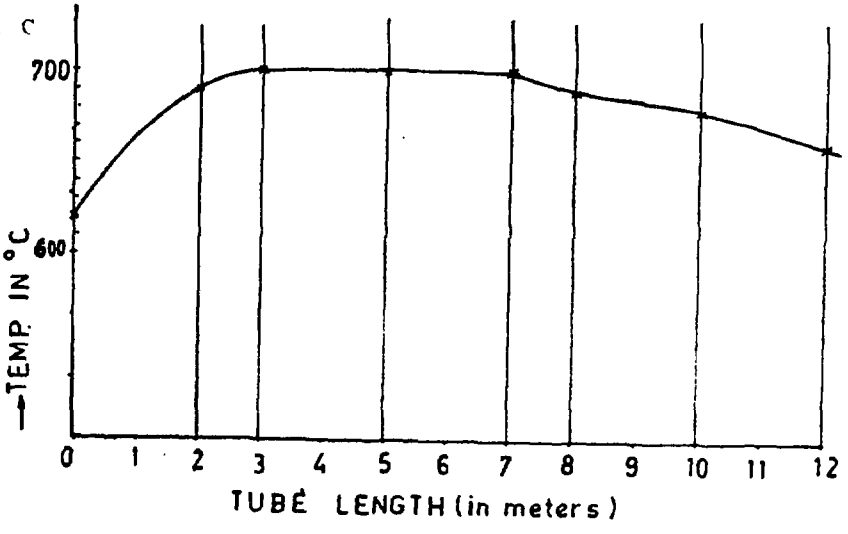
YP (N/sq.mm)	...	342 - 426	301
UTS (N/sq.mm)	...	734 - 803	680
% Elongation [lo = 5d]	...	53.69	29

e) **Hardness : (H.V. - Scale)**

a) Unused	...	248 to 387	117 to 198
		(9100 hrs)	(25000 hrs)
b) Exposed	...	350 to 450	366 to 554

Skin temperatre profile of cracker tube outer wall

From Bottom	deg. C
0 meters	620
2 meters	690
3 meters	700
5 meters	700
7 meters	700
8 meters	690
10meters	680
12meters	660



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5 meters	700
7 meters	700
8 meters	690
10meters	680
12meters	660

Design Limitation

Wrought Inconel tubes have been in use in cracker service since early 70's, the same material in cast form has also been tried as alternatives since early 80's. From the cracking point of view eventhough cracker operation is desirable at lower pressure and higher temperature, the same has not been considered due to the need for additional energy and capital cost and therefore the operating pressure has been kept at 146 kg/sq.cm. but the temperature of operation has been reduced to 660/650 deg. C as none of the suppliers could offer stress rupture value of 82.35 N/sq.mm at design temperature of 765 deg. C for 100,000 hours, the values reduced through extrapolation on the basis of short time, high stress on cast and wrought tubes were 65 N/sq.mm and 62 N/sq.mm respectively. As inconel material shows steep fall in stress to rupture values with increase in temperature this lower operating temperature for the fixed thickness would mean lowering of stresses and extending the service life of the cracker tube. In consideration of this the operating temperature is desired to be limited to 660/650 deg. C, this also means reduced cracking of ammonia and to match up the demand installation of additional cracker tubes.

HISTORY OF FAILURE IN CRACKERS

i) After about 24,000 hours of operation in HWP (Tuticorin) there were failures in two tubes. These were due to formation of continuous grain boundary precipitates resulting in reduction in ductility at room temperature as well as at high temperature with the increasing strength. The deterioration in the mechanical properties were highest in the middle region of the tubes exposed to maximum temperature in the cracker. Also carburised/oxidised layer observed contributed to reduced stress rupture strength.

ii) In case of Thal where cast Inconel tubes are installed, after 10000 hours of operation there was a failure in three tubes. The failure was attributed to high temperature transformation in the material resulting in formation of precipitates along the boundaries with initiation of cracks at the inner surface of the tube with oxidised/carburised layer in the bottom region of the tubes. The mechanical properties of the exposed tubes varied indicating exposure to different temperature zones in the furnace and also recovery in the ductility at elevated temperatures was poor (6%).

iii) After 30,000 hours of operation of cracker in Baroda, study conducted on a specimen tube showed nitriding on the inner surface due to reaction with ammonia, forming of creep microvoids and carbide precipitates at the grain boundary and embrettlement associated with phase transformation with temperature.

WROUGHT MATERIAL INCONEL-625

Exposed time	Temperature exposed	Reasons of failure	Microstructure	Mechanical properties (UTS in N/sq.mm)	REMARKS
24000 hrs	Bottom: 515/696 deg. C Top : 552/650 deg. C	Formation of continuous grain boundary precipitates with deterioration in ductility at room & high temp. in the presence of flaw in material	Intragranular fracture * Excessive grain boundary as well as matrix carbide precipitation. Also numerous small cracks both on inner & outer tube surfaces.	Room Tem.bottom % Elongation: Min.2, Max.7 UTS: Min.607, Max.641 Room Temp.(Top) % Elongation: Min.26, Max.44 UTS: Min.869,Max.938 At 600 deg. C Bottom % Elongation: Min.14, Max.15 UTS: Min.538, Max.545 At 600 Deg. C (Top) % Elongation: 43 UTS: 689	1. Two tubes cracked. Three tubes bulged Location about 700 mm from furnace lower level 2. Bottom & middle portion of the main cracker tubes have suffered reduction in ductilities at room & elevated temp. due to continuous grain boundary precipitate 3. Oxidising/ carburising reaction observed.

CAST MATERIAL = INCONEL-625

Exposed time	Temperature exposed	Reasons of failure	Microstructure	Mechanical properties (UTS in N/sq.mm)	REMARKS
9100 hrs	Top: 700/788 deg. C Middle: 790 deg.C Bottom: 649/688 deg. C	Exposure to high temp. resulting in formation of precipitates along the boundaries	Continuous chain of carbide precipitates at the grain boundaries as well as within the matrix	Room.Temp.(Top) % Elongation: 19.25-26.5 UTS: 552 - 636.65 Room Temp. (Bottom) % Elongation: 6.5 - 15 UTS: 628 - 640 At 600 Deg.C (Top) % Elongation: 24.25 - 31.25 UTS: 474 - 512 At 600 Deg.C (Bottom) % Elongation: 10 - 15 UTS: 640 - 602	Three tubes cracked. Cracks at weld location in two tubes and closure to the weld in the third tube.

Mechanical properties of exposed material = wrought

	Room Temperature		600 deg. C	
	UTS (N/sq.mm)	% Elongation	UTS (N/sq.mm)	% Elongation
Bottom	517-641	2 - 30	538-800	16-47
Middle	572-586	23 - 24	565	47-52
Top	869-924	26 - 44	689	43

Mechanical properties of exposed material - cast

	Room Temperature		600 deg. C	
	UTS (N/sq.mm)	% Elongation	UTS (N/sq.mm)	% Elongation
Bottom	628-640	6.5 - 15	540-602	10-15
Middle	580-676	14 - 25	444-557	17.5-28.5
Top	553-636	19.2 - 26.5	474-512	24-31

It is observed that the recovery in ductility for cast material at elevated temp. is not as much as the wrought product.

From the history of the failures in the plants it is indicative that Inconel-625 subjected to long time exposure between 650 - 700 deg. C (less than 10,000 hours) or short time exposure at about 760 deg. C. Causes formation of gamma and other carbide precipitates leading to deterioration in the mechanical properties at room and elevated temperatures promoting failures in presence of existing unnoticed flaw.

Counter-measures

1. In order to reduce the rate of damage it is necessary that -

a) Proper temperature profile is maintained in the furnace by burner management

b) Proper distribution of process vapour over catalyst bed.

c) Evolve procedure to gauge creep damage and set limits for replacements of tubes.

2. To bring into focus progressing defects, cracker tubes during planned shut-downs should be checked for -

a) By DP for surface defects.

b) Enlargement of diameter (bulge) by gauges

c) Increases in hardness.

d) Ultrasonic checks for subsurface defects

e) Microstructural studies at representative locations

f) Soap bubble test with nitrogen gas for pin holes/tight cracks

3. Sample tubes pressure loaded be kept at appropriate location to closely simulate the conditions of cracker tubes for metallurgical studies and mechanical tests.

4. Improvement Potentialities :

a) Modification of metallurgical composition of inconel 625 tubes.

i) To improve stress to rupture strength at temperature of interest i.e. around 650 to 750 deg. C by micro-alloying.

ii) To retard the precipitation tendencies in the temperature range of operation.

b) Examine the possibilities for metallurgical reversion of precipated material.

c) Look for lower order. Cheaper Ni - Cr alloys suitably modified by micro-alloying appropriate for application with service life of 50,000 hours.