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Application Of Superalloys In Petrochemical And Marine Sectors In India

M. Nageswara Rao
Emeritus Professor, Department of Metallurgical and Materials Engineering, National Institute of Technology Warangal
Warangal 506021 Andhra Pradesh, India
E-mail: mnr@nitw.ac.in
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ABSTRACT

Around the world, oil and gas development activities are increasing due to the growing demands for energy. Increasingly hostile environments involving deep offshore wells, higher pressure and temperature conditions, sour wells etc are encountered during exploration / development. This necessitates use of construction materials with high strength and resistance to corrosion in the severe conditions associated with production/refining. Superalloy grades such as 825, 625 and 718 have been deployed with success to meet these challenges. Technology to produce various millforms / critical components of superalloy grade 718 for aeronautical applications has been established in India. Work has also been carried out in the Country to develop superalloy grades 825 and 625 with no specific reference, however, to petrochemical applications.

The high strength nickel-base superalloy grades 686 and 725 have proved to be excellent candidate materials for a variety of marine applications – fasteners, springs etc. The Ni-base superalloy grade C276, exhibiting excellent corrosion resistance to seawater especially under crevice corrosion conditions, is similar to superalloy grade 686. Superalloy grade C276 has been successfully produced in India in different millforms.

The paper gives an overview of the development work done in India on superalloy grades 718, 625, 825 and C276 and prospects of using these materials in petrochemical and marine sectors in the country.

NOMENCLATURE OF SYMBOLS USED

OD	:	Outside diameter
ID	:	Inside diameter
HT	:	Height
L	:	Length
AMS	:	Aerospace Material Specification
VIM	:	Vacuum Induction Melting
ESR	:	Electroslag Remelting
VAR	:	Vacuum Arc Remelting

1. INTRODUCTION

Around the world oil and gas development activities are increasing due to the growing demands for energy. The exploration and development activities have to be carried out in increasingly hostile environments involving deep offshore wells, higher pressure and temperature conditions, sour wells etc. This necessitates use of construction materials with high strength and resistance to corrosion in the severe conditions associated with production / refining challenges. Specific superalloy grades developed in the country can be put to use to face these challenges.

Essentially two types of superalloys have been deployed for oil and gas applications. First type is solid solution strengthened nickel-base alloys. These are often deployed in cold-worked condition, to realize high strength levels. The second type is age-hardened nickel-base alloys. Particularly for offshore applications, weight considerations can affect the economic viability of the project and hence is the importance of using high strength alloys.

Fe-Ni based superalloy grade 825 (UNS N 08825) and Ni-based grade 625 (UNS N 06625) are the two most important alloys belonging to the first type. Grade 825 is the workhorse of the modern oil and gas industry and is widely applied in flowlines and pipelines. It is used in cold-worked condition in sour gas wells. Grade 625 shows excellent behavior in large majority of oil and gas environments and, with its good weldability, has become designer's choice for applications involving welding. Grades 825 and 625 have been successfully produced in India in small quantities under the name Superni 825 and Superni 625 respectively.

Different items of equipment facing hostile environments in the petrochemical sector involve heavy cross sections. Strengthening by cold work cannot be employed in such cases. For such applications the second type of alloys (age-hardened nickel-base alloys) is selected by the designers. 718 (UNS N07718) and X750 (UNS N07750) are two among these age-hardened superalloy grades. These two alloys have been successfully produced in India under the name Superni 718 and Superni X750 respectively, though not for petrochemical applications.

In a similar manner there are marine environments which are highly aggressive in nature. Materials such as stainless steels, monels and even the superalloy grade 625 known for its high degree of corrosion resistance have been found to be inadequate in such environments[1,2]. It has been demonstrated that superalloy grade 686 shows corrosion resistance superior to these grades[1,2]. Superalloy grade C276 developed in the country (Superni C276) also shows promise in this regard.

In the following an overview is given of the experience gained in India with respect to production of those superalloy grades which promise to serve as excellent candidate materials to withstand the severe most service conditions encountered in petrochemical and marine sectors. Processing and evaluation of various superalloy grades for creep and fatigue resistant applications in gas turbine engines has been reviewed earlier[3] by Nageswara Rao and Mayadeo.

2. MATERIALS AND METHODS

2.1 Superalloy grades developed which have potential application in oil & gas and marine sectors

Development work on a number of superalloy grades with potential application in petrochemical and marine sectors has been carried out at Mishra Dhatu Nigam Limited, Hyderabad. Prominent among them are Superni 825, Superni 625, Superni 718 and Superni C276.

The grades belong to one of the two superalloy families – Nickel base superalloys, and Nickel-Iron base superalloys. The nominal chemical composition of these grades is given in Table 1. Superni 825 and Superni 718 are Ni-Fe base superalloys; Superni 625 and Superni C276, in contrast, are Ni base superalloys. Superni 825, Superni 625 and Superni C276 are essentially solid solution strengthened superalloys. In contrast, Superni 718 is a precipitation strengthened superalloy.

2.2 Melting and refining

All the alloys have been processed through two-stage melting. The first stage involved vacuum induction melting (VIM). VIM lowers the gas content (hydrogen, nitrogen and oxygen) and drives away through evaporation trace elements such as Pb, Bi, Cd, Te, As, Sb and Se, whose presence can adversely affect workability of ingots and mechanical properties of finished products. These elements, even when present in only trace amounts, can adversely affect the service life.

The second melting was by vacuum arc remelting (VAR) or electroslag remelting (ESR); in majority of instances, VAR was adopted. Remelting in VAR furnace refines the metal by further removal of gases and volatile impurities and removal / fragmentation of non-metallic inclusions. Equally importantly it enables production of large ingots with freedom from macrosegregation and severe microsegregation.

Careful choice of input raw materials was done to restrict the levels of several undesirable residual elements known for their deleterious effect, even when present at only trace levels, on service performance of superalloys[4]. On the other hand controlled additions at trace levels of elements such as boron, zirconium were made to derive the benefits of improved hot workability and mechanical property enhancement, a subject reviewed by Holt and Wallace[6].

2.3 Hot working

Hot working of ingots was carried out in a servohydraulically driven forge press to billet /flat sizes suitable for subsequent hot rolling to bar, sheet or strip forms. When material is to be converted to tube form by hot extrusion, as was the case for Superni 625, forging was done to a billet size corresponding to input size for the extrusion press. Similarly when Superni 718 was to be produced in the form of rings and discs, forging was done to the billet size which corresponds to the input size for ring rolling mill and roll forming machine respectively. Superalloys are in general difficult to work; they have very limited forgeability range compared to e.g., stainless steels. Strict control on hot working parameters was accordingly exercised.

2.4 Development of specific superalloy grades

2.4.1 Superni 718

Many heats of Superni 718 were processed. Large majority of them were for aeronautical application. It has been reported that elements like sulfur, phosphorus are surface active in superalloy grade 718[5]. Accordingly the levels of these elements were closely controlled during making heats of Superni 718 to attain acceptable high temperature mechanical properties in the finished product. The material has been produced in several mill forms – hot forged billets, hot rolled bars, cold rolled sheets and strips. In addition, different types of critical components have been manufactured starting with Superni 718 feedstock – blades, rings and discs all for aeroengine applications. Blades have been produced through forging route. Rings were made using ring rolling mill. Discs were formed through the roll forming process.

Table 1

Compositions of indigenously produced superalloy grades of interest to oil & gas and marine Sectors

UNS Number	Alloy Name	Composition							
		Cr	Ni	C	Mn	Si	P	S	Mo	Others
N08825	825	19.5-23.5	38-46	0.05	1.0	0.5	0.03	0.03	2.5-3.5	Ti 0.6-1.2, Cu 1.5-3.0, Fe 22.0 Min
N06625	625	20-23	58 Min	0.1	0.5	0.5	0.015	0.015	8-10	Nb 3.15-4.15, Fe 5
N07718	718	17-21	50-55	0.08	0.35	0.35	0.015	0.015	2.8-3.3	Nb 4.75-5.50, Ti 0.65-1.15, Fe Bal
N10276	C276	14.5-16.5	Bal	0.02	1.0	0.08	0.03	0.03	15-17	Co 2.5, W 3.0-4.5 V 0.35, Fe 4-7

Single values are maximum values, unless otherwise noted.

2.4.2 Superni C276

Unlike the case of Superni 718, only few heats of Superni C276 were produced. They were made for non-aeronautical applications. The material has been produced in essentially two mill forms - hot rolled bars and cold rolled sheets.

2.4.3 Superni 825 and Superni 625

Superni 825 and Superni 625 have been produced in relatively small quantities – only one heat of each of these grades was processed. These grades have been produced in the form of forged billets and / or hot rolled bars. Attempt was made to produce tubes of Superni 625 using the extrusion route.

3. RESULTS AND DISCUSSION

3.1 Development of Superni 718 for aeronautical applications

3.1.1 Millforms

Among the different superalloy grades mentioned above, Superni 718 has been produced in the largest quantity. Accordingly much experience has been gained with reference to its production and characterization and a large volume of property data has been generated.

Evaluation of the material has been done as per the relevant Aerospace Material Specification (AMS 5662 / 5663 for bars, forgings & rings). Table 2 gives the minimum longitudinal tensile properties of the superalloy grade 718 in solution treated and aged condition as specified by AMS. The tensile properties at room temperature and 922 K have been evaluated for all batches after the standard heat treatment and material from each one of the batches was found to conform to the requirements of the governing AMS.

Since the fabricated structures may have deliberate or accidental stress concentrations, an important acceptance criterion for this material in the solution treated and aged condition is the notched stress rupture testing. The governing AMS (5662 / 5663 for bars, forgings & rings) stipulates a minimum life of 23 hours, when stress rupture testing is done on specimens with a combined notched and unnotched test section at 922 K and stress level of 689 MPa. Table 3 gives the details. It has been established that δ phase morphology, volume fraction and distribution importantly influence the notch stress rupture life of the superalloy grade 718[5]. Accordingly microstructures that occur in the superalloy grade 718 have been classified into acceptable and unacceptable categories based on the nature of presence of δ phase in the microstructure. Hot working practice and the ensuing heat treatment have a profound effect on the nature of occurrence of δ phase in the microstructure[4]. Solution heat treatment for all the batches was carried out at 1223 K. Microstructure after heat treatment was always falling under the 'acceptable" category.

Table 2

Aerospace Materials Specification for tensile properties of bars of superalloy grade 718

Property	Room Temperature	922 K
Longitudinal Tensile Strength(MPa) min.	1275	999
Yield Strength, 0.2% Offset(MPa) min	1034	862
Elongation (Longitudinal Direction)(%) min	12	12
Reduction of Area (Longitudinal Direction)(%) min	15	15

Table 3

Aerospace Material Specification for notch rupture life of bars of superalloy grade 718

Test conditions		Acceptance criteria	
Stress	689 MPa	Life (min)	23 hours
Temperature	922 K	Elongation % (min)	4

3.1.2 Rings

Ring rolling process was successfully employed for making rings of Superni 718. The cast ingot was forged to the required billet size and turning of the billet carried out to the required diameter. The machined billets were then cut into the required unit lengths. Individual pieces were then subjected to upset forging and piercing to obtain upset cheese of the required size. The cheese was then ring rolled to the required rolling dimensions. The ring thus obtained was then machined to the required profile. The processing flow chart for production of rings 471 OD x 370 ID x 40 HT (dimensions in millimeters) is shown in Fig. 1, for the purpose of illustration[7].

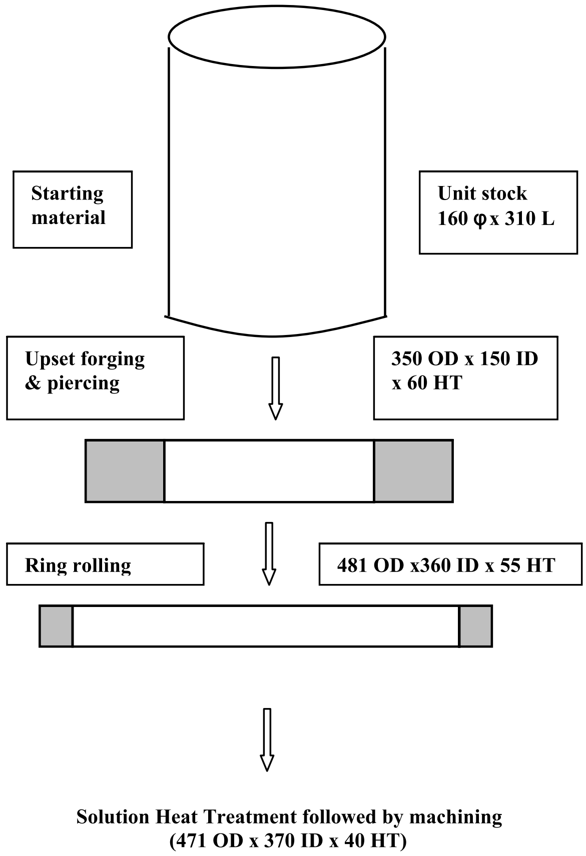

Fig. 1 : Schematic showing the processing flow chart for rolling of rings of Superni 718.

3.1.3 Discs

Roll forming process was employed for manufacture of discs of Superni 718. Forged billets 190 mm ϕ x 420 mm height were upset in three stages in the temperature range 1203 – 1223 K to a height of 75-80 mm and ~510 mm diameter using isothermal hydraulic forge press of 1600 tons capacity and employing flat dies. The upset pancakes were machined to dimensions of 420 mm ϕ and 70 mm height. After microstructural examination and sonic evaluation, the pancakes were subjected to roll forming in the temperature range 1223 – 1253 K on a roll forming machine. Figure 2 shows schematically the process flow steps followed for roll forming the disc. The mechanical properties of the formed disc were evaluated and the product was found to meet the specification in all respects[8]. Table 4 compares the results obtained with the specified values.

Table 4

Mechanical properties of roll formed discs made of Superni 718

Property	Measured value	Specified value
Ultimate Tensile Strength (MPa) at Room Temperature	1291	1240
0.2% Proof Stress (MPa) at Room Temperature	1106	1035
% Elongationat Room Temperature	23	12
% Reduction in Area at Room Temperature	28	15
Ultimate Tensile Strength (MPa) at 922 K	1005	1000
0.2% Proof Stress (MPa) at 922 K	920	860
% Elongationat 922 K	14	12
% Reduction in Area at 922 K	30	15
Low Cycle Fatigue life with trapezoidal cycles σ_{max} =650 MPa 15-90-15 sec at 863 K	Not fractured after 100 hours	72 hours
Notched stress rupture life at 689 MPa and 922 K	Not fractured after 100 hours	23 hours
Creep life at 590 MPa at 923 K	Not fractured after 110 hours	100 hours

3.2 Development of Superni 625

The efforts made to produce tubing of Superni 625 starting with forged billets and adopting hot extrusion process were not successful. The extrusion trials were carried out at Nuclear Fuel Complex, Hyderabad using the hot extrusion press available there. The billets got stalled. In contrast, tubes of superalloy grades 800 and 600 could be successfully produced using the same extrusion press.

Figure 3 shows the variation of 0.2% proof stress and ultimate tensile strength of superalloy grades 625, 600 and 800 as a

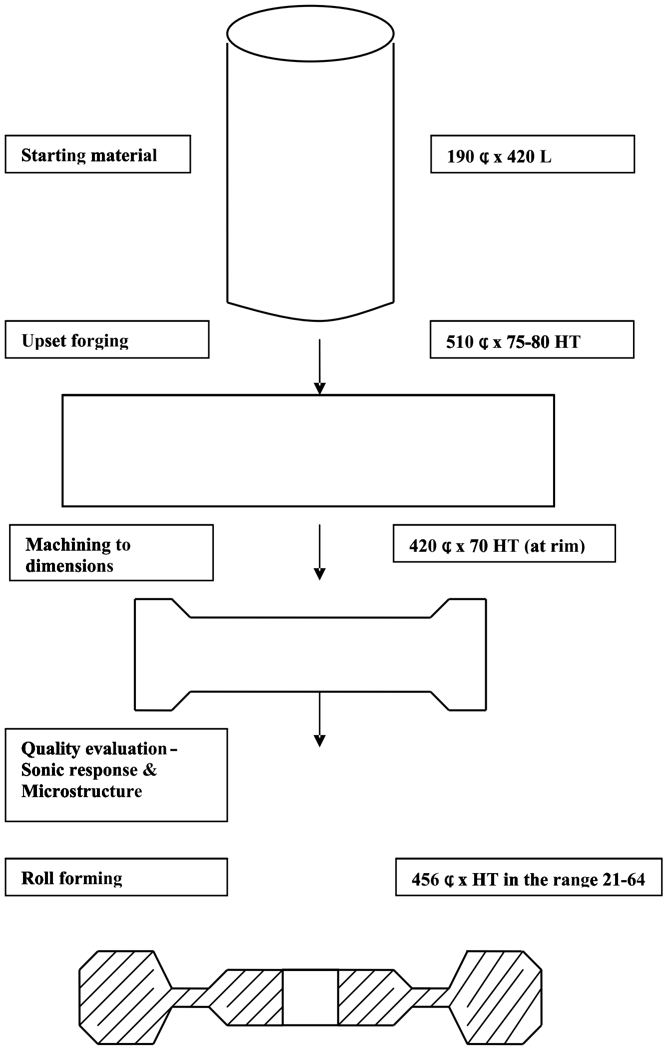

Fig. 2 : Process flow chart for manufacture of discs of Superni 718 through roll-forming route.

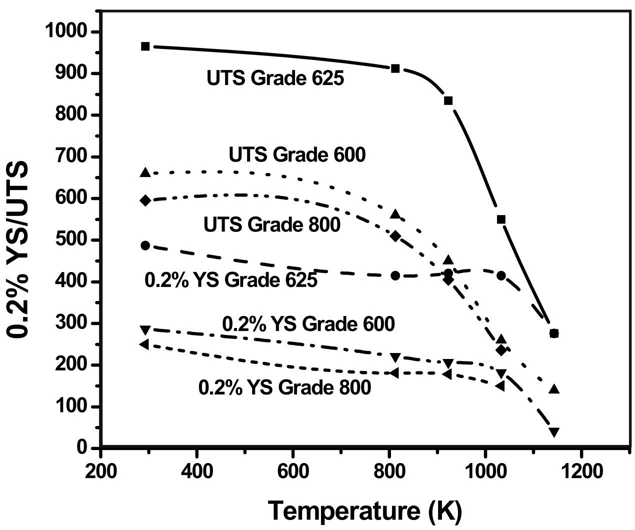

Fig. 3 : Strength vs temperature for three superalloy grades

function of temperature. It is obvious from the figure that grade 625 requires much higher pressure for extrusion. Production of tubes of grade 625 thus requires an extrusion press of higher capacity and this capability remains to be established in the country. In contrast forged billets and hot rolled bars of Superni 625 could be successfully manufactured using the facilities at Mishra Dhatu Nigam Limited.

3.3 Spin-offs of superalloy technologies developed

3.3.1 Oil & gas sector

There are immense possibilities to use the experience gained as detailed above for catering to the requirements of superalloy products in important non-aeronautical sectors, e.g., petrochemical and marine sectors. For example the superalloy grades 825, 625 and 718 have found important applications in oil and gas sector. Grade 825 is the workhorse of the modern oil and gas industry and is widely applied in flow lines and pipelines. It is used in cold worked condition in sour gas wells. Grade 625 shows excellent behavior in large majority of oil and gas environments. In addition Grade 625 serves as welding wire. It is a very stable alloy, not causing any detrimental effects during welding. Grade 625 has therefore become the workhorse for the oil and gas welding industry. Grade 718, a precipitation strengthened superalloy, is used for petrochemical applications requiring high strength and involving heavy cross sections where strengthening by cold work is not possible.

Processing and evaluation has to be tailor made to the intended application. For example, Superni 718 has been developed in India for aeronautical application. To use the material for petrochemical application, the heat treatment is to be done differently. Grade 718 is solution treated in the range 1193 – 1273 K for aeronautical applications. For oil field applications, however, solution treatment is to be carried out at a higher temperature lying in the range 1283 – 1311 K. Similarly there are differences in the precipitation-hardening treatment adopted for the two applications. Testing also is to be tailor-made to the particular application. For example, evaluation of 718 for petrochemical applications requires mechanical testing in corrosive environments simulating those expected to be encountered in service in oil and gas sector.

3.3.2 Spin-offs in marine sector

Similarly the development work done on superalloys in the country can have useful spin-offs with respect to their application in marine sector. For example, the nickel base alloy Superni C276, developed and used in India for essentially chemical engineering applications, exhibits excellent corrosion resistance to sea water, especially under crevice corrosion conditions. The alloy is very similar in chemical composition to superalloy grade 686. Developed by M/s Special Metals Corporation, Grade 686 has been demonstrated to be an excellent material for a variety of marine applications – fasteners, springs etc. Superni C276 is thus expected to bridge an important gap in the availability of materials for severely aggressive marine applications. We have not evaluated Superni C276 for hydrogen embrittlement and galvanic corrosion behavior in seawater environments. These issues are of great relevance for use of the alloy in marine sector. Studies have been initiated at National Institute of Technology Warangal, with funding from Naval Research Board, to carry out this evaluation.

4. CONCLUSIONS

(i) Capabilities have been established in the country for production of various grades of superalloys to cater primarily to the aeronautical sector; non-aeronautical applications have not been in the foreground. There can be useful spin-offs in terms of use of some of these superalloy grades with advantage for non-aeronautical applications, e.g., in oil and gas and marine sectors.

(ii) There are demanding applications in oil and gas sector, marine sector etc., necessitating design with high duty superalloys.

(iii) Some modifications in production technology and evaluation / testing would be involved while adopting the superalloys developed primarily for aeronautical sector to non-aeronautical applications, e.g., in oil & gas and marine sectors.

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