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Advances in nickel-based cast superalloys

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Abstract

Nickel-based superalloys have served as the most competitive high temperature structural materials under highly stressed and aggressive operating conditions in a variety of applications for more than 60 years. The most demanding among all the applications has been the gas turbine aerofoil castings of modern aero-engines. These turbine parts operate in extremely aggressive environment of high velocity hot combustion gas-air mixture carrying highly corrosive ingredients at high pressure. Gas turbine aerofoil materials should therefore possess adequate resistance to creep, fatigue and aggressive environment. Materials design for such application therefore has been extremely challenging, particularly since the engine designers always aim at higher turbine entry temperature (TET) in order to achieve greater engine thrust and better fuel efficiency. In spite of enormous efforts made in the recent past towards developing ceramics and their composites, Ni-based superalloys continue to be most reliable blade and vane materials offering always the highest TET. This has been possible through better alloy design, improved blade cooling schemes, protective coatings and directional solidification (DS) of either columnar grains or single crystals (SC) along the most favorable $\langle 001 \rangle$ texture. During the last six decades, TET has gone up by about 500K. This article covers recent advances in cast Ni-based superalloys, including our own efforts in this direction. Extensive research at DMRL has led to the development of new generation Ni-based superalloys, designated as DMD-4 and DMS-4 for DS and SC processing, respectively. Simultaneously, expertise has been developed to cast DS and SC components for aero-engines. Technology has also been established for pilot scale production of these components.

1. Introduction

Materials development for gas turbine engines has been largely driven by military requirements since their introduction to the propulsion of high performance aircraft. Steadily increasing demands for higher engine thrust, thrust to weight ratio and fuel efficiency have pushed engine operating temperatures and stresses progressively higher. For this reason, material development for turbine blades and vanes which extract useful power from high velocity, highly corrosive hot flame has been mainly directed towards improving creep resistance, although high temperature corrosion resistance and other relevant properties also required attention. Nickel-based superalloy with FCC (γ) matrix and ordered FCC (γ') coherent precipitates has proved to be the right candidate to meet the challenging combination of properties. The first commercial nickel-based alloy developmental work, undertaken by the British in the early 1940s, led to the development of wrought Nimonic-75 and Nimonic-80 alloys. The introduction of vacuum induction melting (VIM) and vacuum investment casting in the early 1950s provided further opportunities to exploit full potential of γ' strengthening. Several nickel-based alloys were developed during 1960s, as shown in Fig.1. Alloy development continued through the 1970s, though moderately, while more attention was paid to process development with specific interest towards DS technology for turbine blades and vanes. A number of nickel-based alloys were designed during early 1980s up to late 1990s, specifically for DS and SC cast components, which offered opportunities to tailor and trim grain boundary strengthening elements.

Table 1 shows the alloy chemistry of industrially successful cast nickel-based super alloys, which helped to maintain blade and vane performance abreast with many advances in engine design. TET has improved by $\sim 500^\circ\text{C}$ over the last six decades. About 250°C of this improvement is due to more efficient serpentine and film cooling and about 100°C is due to the use of advanced thermal barrier ceramic coatings on platform and full airfoil. The balance 30% is due to improved superalloys and DS/SX casting process [1]. The purpose of the present paper is to scan through the progress made in this field of cast Ni-based superalloy development within the broader context of superalloy metallurgy, and offer comments on future possibilities.

2. Cast superalloy design

Nickel-based superalloys owe their performance superiority over all other high temperature structural alloys to coherent precipitation of ordered FCC γ' phase in an austenitic FCC matrix which can be strengthened by solid solution alloying and precipitation of carbides. The γ' phase is stable up to temperatures well above 1000°C (close to 1200°C for recent alloys) and can directionally coarsen for enhanced creep resistance under operating conditions (Fig. 2). Design of these Ni-based superalloys involves optimization of not less than 10 to 12 elemental constituents as can be seen from Table 1. All these elements can broadly be classified into four major groups:

- I. Those which preferentially partition to the γ' -phase and substitute therein for Al-sites such as Ti, Nb, Ta and Hf

Table 1: Composition (wt.%) of Cast Nickel-base Super alloys for Gas Turbine Airfoil Parts

Sl No.	Alloy	Ni	Cr	Co	Mo	W	Re	Ta	Hf	Nb	Ti	Al	Zr	C	B	Other	Total Refractory Element	Density (gm/cc)	140 MPa / 100Hrs creep rupture Temp. (°C)
1	IN 713C	74.2	12.5	-	4.2	-	-	-	-	2	0.8	6.1	0.1	0.12	0.01	-	6.2	8.25	
2	Nimocast 95	57.5	19.5	18	-	-	-	-	-	-	2.9	2	0.02	0.07	0.015	-	-	8.2	
3	IN 100	60.5	10	15	3	-	-	-	-	-	4.7	5.5	0.06	0.18	0.014	1.0 V	3	7.75	1010
4	Rene 100	62.6	9.5	15	3	-	-	-	-	-	4.2	5.5	0.06	0.15	0.015	1	3	7.75	
5	Udimet 700	59	14.3	14.5	4.3	-	-	-	-	-	3.5	4.3	0.02	0.08	0.015	-	4.3	8.1	960
6	IN 731	67.7	9.5	10	2.5	-	-	-	-	-	4.6	5.5	0.06	0.18	0.015	1.0 V	2.5	7.75	
7	B 1900	64.5	8	10	6	-	-	4.3	-	-	1	6	0.08	0.1	0.015	-	10.3	8.2	
8	C 1023	58.5	15.5	10	8	-	-	-	-	-	3.6	4.2	-	0.15	0.006	-	8	-	
9	Udimet 710	54.8	18	15	3	1.5	-	-	-	-	2.5	5	0.08	0.13	-	-	4.5	8.02	
10	Rene 41	56	19.0	10.5	9.5	-	-	-	-	-	3.2	1.7	0.01	0.08	0.005	-	9.5	-	
11	Rene77	53.5	15	18.5	5.2	-	-	-	-	-	3.5	4.25	-	0.08	0.015	-	5.2	7.91	
12	Rene 80	60.3	14	9.5	4	4	-	-	-	-	5	3	0.03	0.17	0.015	-	8	8.16	
13	Mar-M 421	62.6	15.8	9.5	2	3.8	-	-	-	-	1.8	4.3	0.05	0.14	0.015	-	5.8	8.08	
14	Mar-M 200	59.5	9	10	-	12.5	-	-	-	1.8	2	5	0.05	0.15	0.015	-	14.3	8.53	1020
15	Mar-M 002	69.8	9	10	-	-	-	2.5	1.5	-	1.5	5.5	0.05	0.15	0.015	-	4	-	
16	Mar-M 246	59.8	9	10	2.5	10	-	1.5	-	-	1.5	5.5	0.05	0.14	0.015	-	14	8.44	1036
17	IN 792	60.8	12.7	9	2	3.9	-	3.9	-	-	4.2	3.2	0.1	0.21	0.02	-	9.8	8.25	
18	M 22	71.3	5.7	-	2	11	-	3	-	-	-	6.3	0.6	0.13	-	-	16	8.63	
19	Mar-M 001	59	10	15	3	-	-	-	1.5	-	4.7	5.5	0.06	0.18	0.014	1.0 V	4.5	7.75	1010
20	Mar-M 004	73.6	12	-	4.5	-	-	-	1.3	2	0.6	5.9	0.1	0.05	0.01	-	7.8	-	
21	Mar-M 005	59	9	10	2	7	-	3.8	1.6	-	2.6	4.8	0.05	0.1	0.015	-	14.4	-	
22	Mar-M 006	58.4	9	10	2.5	10	-	1.5	1.4	-	1.5	5.5	0.05	0.15	0.015	-	15.4	8.56	1048
23	Mar-M 007	63	8	10	6	-	-	4.3	1.5	-	1	6	0.08	0.1	0.015	-	11.8	8.25	
24	Rene 80+ Hf	59.8	14	9.5	4	4	-	-	0.8	-	4.7	3	0.01	0.15	0.015	-	8.8	8.3	
25	Mar-M 432	50.2	15.5	20	-	3	-	2	-	2	4.3	2.8	0.05	0.15	0.015	-	7	8.16	
26	Mar-M 009	58.4	9	10	-	12.5	-	-	2	1	2	5	-	0.14	0.015	-	15.5	-	
27	IN 713LC	74.8	12	-	4.5	-	-	-	-	2	0.6	5.9	0.1	0.05	0.01	-	6.5	8.25	990
28	IN738C	61.4	16	8.5	1.75	2.6	-	1.75	-	0.9	3.4	3.4	0.1	0.17	0.01	-	7	8.11	
29	IN738LC	61.5	16	8.5	1.75	2.6	-	1.75	-	0.9	3.4	3.4	0.04	0.11	0.01	-	7	8.11	
30	Mar-M 247	59.6	8.5	10	0.65	10	-	3	1.4	-	1	5.6	0.04	0.16	0.015	-	15	8.53	
31	PWA 1422	59.2	9	10	-	12	-	-	1.5	1	2	5	0.1	0.14	0.015	-	14.5	8.53	
32	DZ- 4	67.2	9.5	5.8	3.8	5.5	-	-	-	-	2	6	-	0.14	0.015	-	9.3		
33	CM 247 LC	61.7	8.1	9.2	0.5	9.5	-	3.2	1.4	-	0.7	5.6	0.01	0.07	0.015	-	14.6	8.5	1050
34	Nasair 100	68.7	9	-	1.5	10.5	-	3.3	-	-	1.2	5.8	-	0.01	-	-	15.3		
35	Alloy 444	73.2	8.6	-	-	11.1	-	-	-	-	2	5.1	-	-	-	-	11.1		
36	RR 2000	62.5	10	15	3	-	-	-	-	-	4	5.5	-	-	-	1.0 V	3	7.87	
37	RR2060	63	15	5	2	2	-	5	-	-	2	5	-	0.02	-	-	9		

Table 1: Composition (wt.%) of Cast Nickel-base Super alloys for Gas Turbine Airfoil Parts—*contd.*

<i>Sl No.</i>	<i>Alloy</i>	<i>Ni</i>	<i>Cr</i>	<i>Co</i>	<i>Mo</i>	<i>W</i>	<i>Re</i>	<i>Ta</i>	<i>Hf</i>	<i>Nb</i>	<i>Ti</i>	<i>Al</i>	<i>Zr</i>	<i>C</i>	<i>B</i>	<i>Other</i>	<i>Total Refractory Element</i>	<i>Density (gm/cc)</i>	<i>140 MPa / 100Hrs creep rupture Temp. (°C)</i>
38	SRR 99	66.3	8	5	-	10	-	3	-	-	2.2	5.5	-	-	-	-	13	8.56	
39	PWA 1480	62.5	10	5	-	4	-	12	-	-	1.5	5	-	-	-	-	16	8.7	1080
40	CMSX 2	66.2	8	4.6	0.6	8	-	6	-	-	1	5.6	-	-	-	-	14.6	8.6	
41	CMSX 3	66.1	8	4.6	0.6	8	-	6	0.1	-	1	5.6	-	-	-	-	14.7	8.6	
42	SC 16	70.5	16	-	3	-	-	3.5	-	-	3.5	3.5	-	-	-	-	6.5	8.21	
43	AF56	61.4	12	-	3	-	-	5	-	-	4.2	3.4	-	-	-	-	11	8.25	
44	Rene N4	62	9.8	7.5	1.5	6	-	4.8	0.15	0.5	3.5	4.2	-	0.05	0.004	-	13	8.5	
45	MXON	64.9	8	5	2	8	-	6	-	-	-	6.1	-	-	-	-	16	8.6	
46	AM 1	62.6	8	6	2	6	-	9	-	-	1.2	5.2	-	-	-	-	17	8.6	
47	AM 3	67.8	8	5.5	2.2	5	-	3.5	-	-	2	6	-	-	-	-	10.7	8.25	
48	MC 2	64.5	8	5	2	8	-	6	-	-	1.5	5	-	-	-	-	16	8.63	
49	DD 3	68.2	9.5	5	4	5.5	-	-	-	-	2	5.8	-	-	-	-	9.5	8.2	
50	CMSX 11B	62.1	12.5	7	0.5	5	-	5	0.04	0.1	4.2	3.6	-	-	-	-	10.6	8.6	
51	CMSX 11C	64.5	14.9	3	0.4	4.5	-	5	0.04	0.1	4.2	3.4	-	-	-	-	10	8.36	
52	CMSX 4	61.7	6.5	9	0.6	6	3	6.5	0.1	-	1	5.6	-	-	-	-	16.2	8.7	
53	PW 1484	59.4	5	10	2	6	3	9	-	-	-	5.6	-	-	-	-	20	8.95	1120
54	Rene N5	63.1	7	7.5	1.5	5	3	6.5	0.15	-	-	6.2	-	0.05	0.004	0.01 Y	16.1	8.63	
55	SC 180	60.2	5.3	10	1.7	5	3	8.5	0.1	-	1	5.2	-	-	-	-	18.3	8.84	
56	TUT 92	68	10	-	1.2	7	0.8	8	-	-	1.2	5.3	-	-	-	-	17		
57	DD 6	61	4.3	9	2	8	2	7.5	0.1	0.5	-	5.6	-	-	-	-	20.1	8.83	
58	CM 186 LC	62.6	6	9	0.5	8	3	3	1.4	-	0.7	5.7	0.005	0.07	0.015	-	15.9	8.7	1070
59	PWA 1426	60.7	6.5	10	1.7	6.5	3	4	1.5	-	-	6	-	0.1	0.015	-	16.7		
60	Rene 142	57.7	6.8	12	1.5	4.9	2.8	6.4	1.5	-	-	6.2	0.02	0.12	0.015	-	17.1		
61	CM SX10	69.6	2	3	0.4	5	6	8	0.03	0.1	0.2	5.7	-	-	-	-	19.53	9.05	1140
62	Rene N6	57.3	4.2	12.5	1.4	6	5.4	7.2	0.15	-	-	5.8	-	0.05	0.004	-	20.1	8.97	
63	TMS 75	59.9	3	12	2	6	5	6	0.1	-	-	6	-	-	-	-	19.1		
64	TMS 80	58.2	2.9	11.6	1.9	5.8	4.9	5.8	0.1	-	-	5.8	-	-	0.5	3.0 Ir	21.5		
65	DMS 4	67	2.4	4	-	5.5	6.5	9	0.1	0.3	-	5.2	-	-	-	-	21.4	9.08	1142
66	DMD 4	66.8	2.4	4	-	5.5	6.5	8	1.2	0.3	-	5.2	-	0.07	0.01	-	21.2	9.07	1090
67	PWA 1483	60.3	12.2	9	1.9	3.8	-	5	0.5	-	4.1	3.6	-	0.07	0.008	-	10.7		
68	TMD 103	59.8	3	12	2	6	5	6	0.1	-	-	6	-	0.07	0.015	-	19.1		
69	NHK 71	67.5	12.2	-	0.5	7.8	-	5.8	-	-	1.2	5	-	-	-	-	14.1		
70	YH 61	65.8	7.2	1	0.9	8.8	1.4	8.8	0.25	0.8	-	5	-	0.07	0.02	-	20.9		
71	TMS 82+	62.4	4.9	7.8	1.9	8.7	2.4	6	0.1	-	0.5	5.3	-	-	-	-	19.1		1127
72	MC-NG	70.3	4	<0.2	1	5	4	5	0.1	-	0.5	6	-	-	-	4.0 Ru	19.1	8.75	1102
73	TA	56.7	6.0	11.0	-	6.0	4.8	6.8	0.12	-	1.4	5.4	-	-	-	3.0 Ru	20.72		1127
74	TMS138	63.7	3.2	5.8	2.9	5.9	5	5.6	0.1	-	-	5.8	-	-	-	2.0 Ru	21.5	8.95	1136
75	TMS 196	59.7	4.6	5.6	2.4	5.0	6.4	5.6	0.1	-	-	5.6	-	-	-	5.0 Ru	24.5	9.01	1151

from the IV and V group of the periodic table of elements.

- II. Those which preferentially partition to the γ -phase and substitute for the Ni-sites in the γ -phase such as Co, Rh, Ir, Ru, Os from the VIII group of the periodic table of elements.
- III. Those which generally partition to the γ -phase and substitute for the Al-sites in the γ -phase such as Mo, W, Re from the VI and VII group of the periodic table of elements.
- IV. Those which tend to segregate to grain boundaries such as B, C, Zr.

Some of these elements can also be sub-classified as the carbide formers, such as Cr, Mo, W, Nb, Ta, Ti and Hf. Another sub-class can be the oxide formers, such as Cr and Al, which develop adherent diffusion-resistant oxides to protect the substrate from aggressive environment. Five generations of Ni-based cast superalloys have been developed so far with the following guidelines of alloy design:

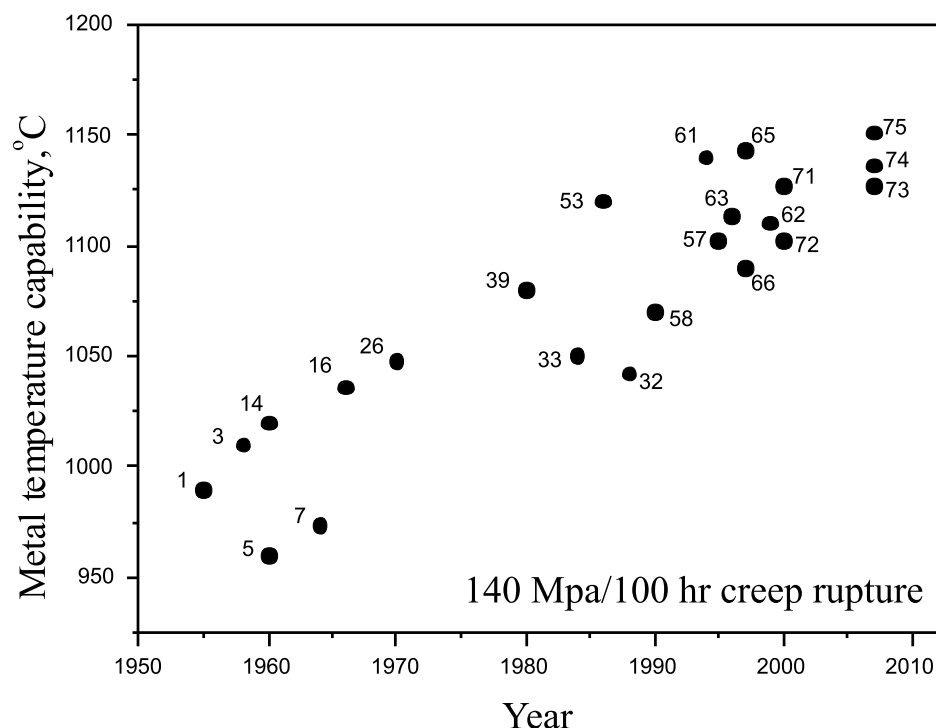
- Solid solution strengthening γ and γ'
- Increase volume percent of γ'
- Increase liquidus (T_L), solidus (T_S), incipient melting (T_I) and solvus temperatures
- Decrease solidification range ($T_L - T_S$)
- Increase stacking fault energy of γ'
- Increase coherent strains for application under 0.6 T_{Melting}
- Decrease ripening rates for application above 0.6 T_{Melting}
- Minimize formation of η , Ni_3Nb , Laves, σ and μ phases
- Control carbides to prevent denuded zones, M_{23}C grain boundary films and Widmanstätten M_6C for better tensile properties
- Control carbides and grain boundary γ' to enhance rupture strength

3. First generation superalloys

These alloys were derived initially from wrought superalloys to take advantage of vacuum melting and casting introduced in the early 1950s. All these cast superalloys can be grouped in to conventionally cast (CC), directionally solidified (DS) and single crystal (SC) superalloys.

3.1 Conventionally cast superalloys

IN713 C is one of the earliest alloys in this category where Al and Nb were used rather than Ti for γ' strengthening. Industrial experience of cracking in this alloy around massive carbides formed during solidification led to a low carbon variant IN713 LC later with improved ductility but retaining sufficient carbon to preserve grain boundary strength. The possibility of increasing γ' volume fraction in cast superalloys through vacuum melting and casting at around 10 wt.% of Ti and Al content led to relatively low density alloy IN100 and Rene100 where large additions of solid solution strengthening elements were not necessary because of as high as 70% of γ' volume fraction. IN100, however, was prone to embrittlement after prolonged exposure at about 850°C due to deleterious phase formation such as σ , μ , χ , π or Lave phases. Phase computation (PHACOMP) techniques of calculating average electron vacancy number (N_v) for given alloys were evolved to predict and avoid these topologically close packed (TCP) intermetallic compounds. Tailoring of IN100 composition on the basis of N_v calculation has led to the alloy IN731 that is free from TCP-phase formation. Alloy design through PHACOMP control became standard practice for most of the highly alloyed nickel based superalloys [2-4]. B1900 is an alloy favoured by Pratt & Whitney in the late 1960s, wherein high γ' strengthening of IN100 was maintained with improved castability by replacing Ti with Ta. Increased amount of refractory solid solution strengtheners such as W and Mo were added to alloys later in order to impart higher temperature capability even though such additions increased



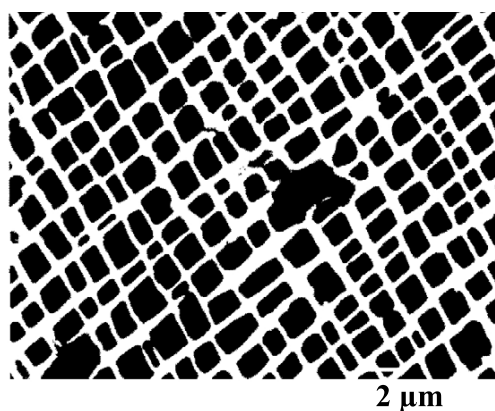
S. No.	Alloy
1	IN 713C
3	IN 100
5	Udimet 700
7	B 1900
14	Mar M 200
16	Mar M 246
26	Mar M 009
32	DZ- 4
33	CM- 247
39	PW 1480
53	PW 1484
57	DD- 6
58	CM 186LC
61	CM SX10
62	Rene N6
63	TMS 75
65	DMS 4
66	DMD 4
71	TMS 82+
72	MC-NG
73	TA
74	TMS138
75	TMS 196

Fig. 1 : Chronological development of cast Ni-base superalloys (S. No. as listed in Table 1)

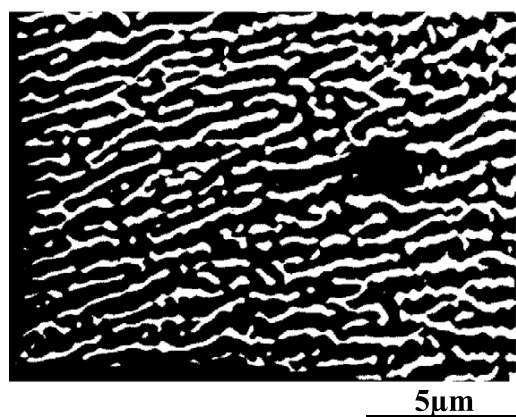
alloy density. Mar-M200, Mar-M246, IN 792 and M22 are such alloys, which in their original form gave inconsistent creep life and inadequate ductility at around 760°C. Addition of 2 wt.% of Hf to Mar M200 improved ductility and minimized porosity through the increased amount of low melting eutectic. A series of new alloys emerged with Hf addition. These include Mar-M009 (= Mar-M200 + Hf), Mar-M001 (= IN100 + Hf), Mar-M004 (= IN713 + Hf), Mar-M007 (= B1900 + Hf), Mar-M006 (= Mar-M246 + Hf) and Mar-M005 (= Rene125 + Hf). General Electric pursued their own alloy development with Rene41, Rene77, Rene80 and Rene80Hf having relatively higher Cr content for improved corrosion resistance at the cost of some high temperature strength. Other similar alloys with high Cr content are C1023, IN738C, IN738LC, Nimocast-95, Udimet700, Udimet710, Mar M 421 and Mar M432 [5].

3.2 Directionally solidified superalloys:

Creep failures of gas turbine airfoils along transverse grain boundaries in number of running engines revealed that the major operating stress experienced in blades and vanes along airfoil stacking axis finds relatively easy fracture path along transverse grain boundaries through nucleation and growth of cavities, grain boundary sliding and interconnection of existing shrinkage pores. Elimination of transverse grain boundaries (Fig. 3), through directional solidification of turbine blades and vanes, therefore led to further increase in temperature capability as shown in Fig. 1. Although transverse grain boundary elimination was the original motivation for DS, it was the favoured [100] growth

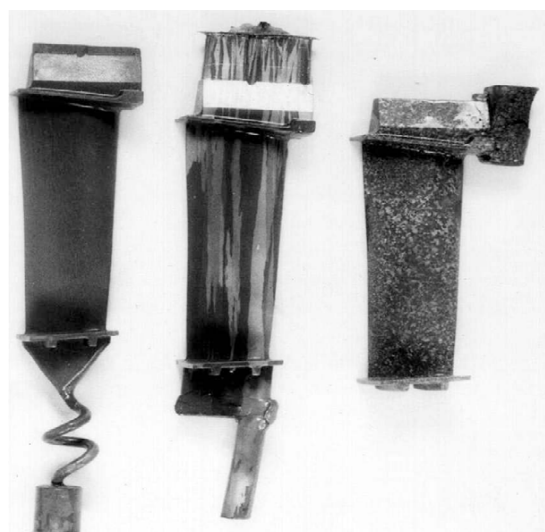


(a)

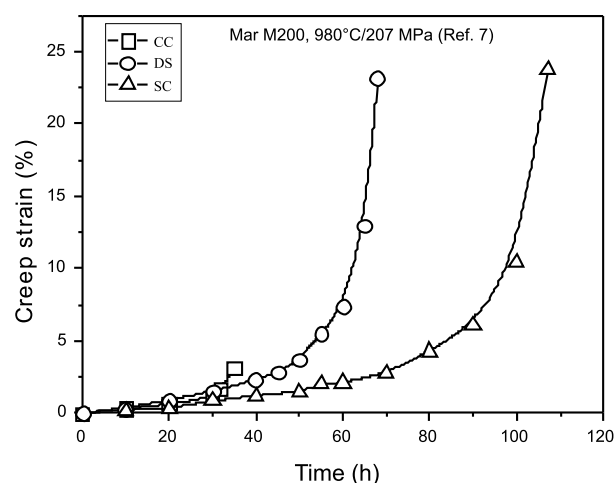


(b)

Fig. 2 : (a) Cubic γ precipitates of superalloy DMD4, aged at 1150°C after dissolving at 1330°C; (b) Rafted γ structure in creep ruptured superalloy DMD4.



(a)



(b)

Fig. 3 : (a) Conventionally cast, directionally solidified and single crystal gas turbine blades. (b) Creep curves of equiaxed, directionally solidified and single crystal super alloy.

direction and improved heat treatment characteristics from which most benefit had occurred. Alignment of [100] along blade axis not only provided intrinsically high creep resistance, but also improved thermal fatigue life by several orders. The low Young's modulus associated with [100] direction kept thermal stresses, caused by temperature gradients across the blade, to a minimum (6). Continuing improvements in airfoil cooling techniques resulted in significant gains in gas turbine operating efficiencies. The cooling techniques usually resulted in very complex cored, thin wall (0.5 mm to 1 mm) airfoil designs (Fig. 4) which are susceptible to grain boundary cracking during DS casting of high creep strength alloys. Other problems associated with DS processing of Hf-modified conventionally cast alloys are metal/core reaction and freckle formation. Attempts were made therefore to develop DS alloys, which would overcome these problems. CM247LC is one such alloy [7] derived from the base Mar-M247 composition reducing C to improve carbide microstructure, stability and alloy ductility; tailoring Zr and Ti contents to improve DS grain boundary cracking resistance; reducing W, Mo and Cr levels to minimize the formation of deleterious secondary M_6C platelets, η phase,

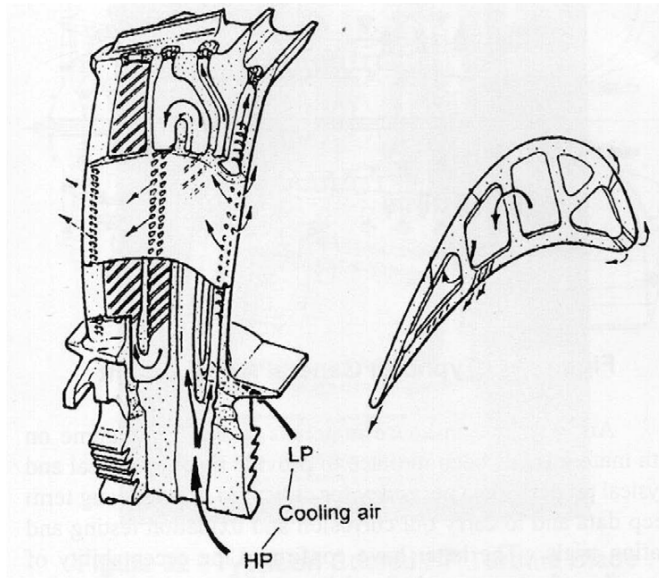


Fig. 4 : Complex airfoil design with serpentine cooling channels and film cooling holes.

α -W phase and σ phase and also reducing Hf level to a moderate 1.4% in order to avoid HfO_2 inclusion problem. The equivalent DS alloy from Pratt and Whitney is PWA1422 that has been derived by removing W and Hf by only half wt.% each from Mar-M009 to reduce HfO_2 inclusion during DS processing and α -W phase formation during service [8]. All these carefully designed columnar grained DS superalloys could improve turbine blade metal temperature capability by about 14°C relative to the conventionally cast superalloys. This much increase in metal temperature capability could push TET by about 60°C through blade cooling for higher engine efficiency or roughly double the component life [9].

3.3 Single crystal superalloys

Logical extension of eliminating transverse grain boundaries in DS technology was to remove grain boundaries altogether by employing in the DS shell mold a grain restrictor that would allow only one grain to grow into the mold cavity as a single crystal turbine blade/vane (Fig. 5). Absence of grain boundaries in single crystals then required no grain boundary strengtheners such as C, B, Zr, and Hf, which were actually the melting point depressants in these alloys. A number of SC alloys such as Nasair-100 [9-11] and Alloy-444 (12) were developed by stripping off C, B, Zr, and Hf that elevated the alloy incipient melting point well above γ' solvus to achieve effective dissolution of all the as-cast γ' and chemical homogeneity so as to produce homogeneous and uniform distribution of cubic γ' leading to better creep strength. Despite the high temperature homogenization treatment, the creep advantage of these single crystals over their columnar equivalents was small and they were prone to a number of processing defects such as freckles and re-crystallization which could be catastrophic in the absence of grain boundary strengtheners. Full potential of SC alloys could be exploited only through more specific modifications to the matrix and γ' strengthening contributions. Rolls Royce introduced a low-density SC superalloy RR2000 with minimum γ - γ' mismatch to replace IN100 [13]. A SC nozzle guide vane alloy RR2060 with high Al and Ta contents, while keeping Cr levels above 10wt%

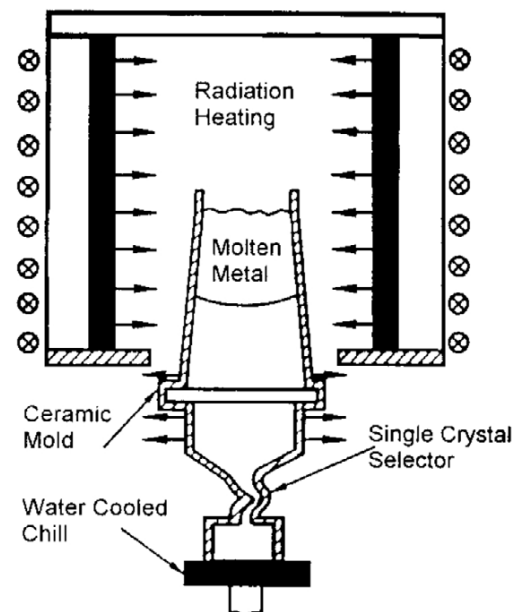


Fig. 5 : Schematic of single crystal grain selector in a DS/SC casting furnace.

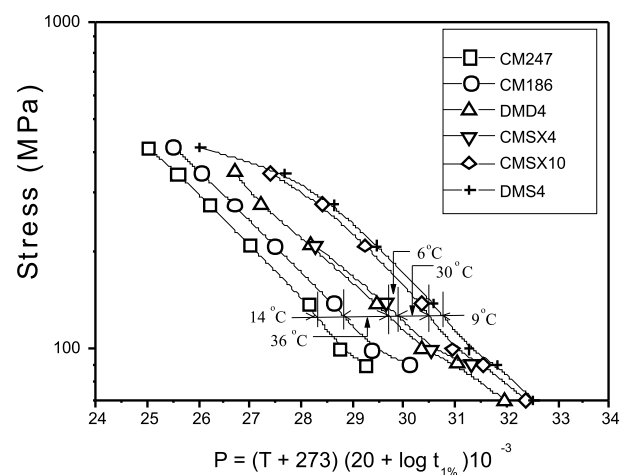


Fig. 6 : Average Larson-Miller 1.0% creep strength of cast Ni-base super alloys.

was designed to exhibit improved resistance to oxidation, hot corrosion and thermal fatigue [13]. A high strength SC alloy SRR99 was developed in Britain to exploit the differing deformation mechanisms that can operate as dislocations shear the γ' precipitates [14,15]. Pratt and Whitney developed SC alloy PWA1480 keeping very high (12wt%) Ta [16]. Cannon Muskegon has derived CMSX2 and CMSX3 SC alloys from Mar M247 by removing B, Hf, Zr and C; partial substitution of W by Ta to impart castability; maintaining about 60% of γ' volume fraction with lower Co for increased solid solubility and freedom from a, m, and s phases [7]. Other first generation SC alloys developed were ReneN4 by GE [17,18] and MXON [19], AM1, AM3, MC2 in France and DD3 in China [20]. These SC alloys provided about 20°C of metal temperature advantage over the existing DS alloys (Fig. 6).

4. Second generation superalloys

Turbine engine experience with the first generation SC superalloys has resulted in further alloy development with

basic design goal of about 30°C increase in metal temperature. This required a significant increase in refractory alloying elements while maintaining γ' volume fraction above 60%. Rhenium was known (21) to partition mainly to the γ -matrix, retard γ' coarsening and increase γ/γ' misfit. Atom probe micro-analyses of Re modified PWA1480 and CMSX2 alloys revealed small Re clusters of $\sim 10^\circ \text{\AA}$ size in the γ -matrix (22). These Re clusters would act as more efficient obstacles to dislocation movement in the γ -matrix compared to isolated solute atoms in γ solid solution and thereby improve strength remarkably. Studies conducted on long-range order in γ' also showed that about 20% of Re, Mo and W partition to and occupy the Al-site in the ordered γ' structure. Re was found to be the potent alloying element for the required ultrahigh strength levels with its ability to strengthen both γ and γ' , retard diffusion and reduce γ' coarsening. Superalloy PWA1484 [23] was designed with 20wt% total refractory elements, lower Cr from 10 wt% of PWA1480 to 5wt% and incorporating 3wt.% Re. CMSX4 (24), Rene5 and SC180 [25] are the other 2nd-generation SC superalloys having 3wt% Re and similar metal temperature capabilities. CMSX4 turbine blades have been flight qualified for maximum metal temperature approaching 1130°C at maximum engine power during accelerated, simulated mission endurance test (ASMET) [26]. Alloy design through d-electron concepts [27, devised on the basis of the molecular orbital calculations of electronic structures, led to another 2nd generation SC super alloy TUT92 employing only 0.8wt% Re that exhibited excellent combination of creep-rupture properties, hot corrosion resistance and low density relative to other 2nd generation alloys.

5. Third to fifth generation superalloys

Encouraged by 30°C metal temperature capability improvement of 2nd generation SC super-alloys with 3 wt% Re over the first generation SC super alloys, yet higher levels of Re were pursued due to its dual role of improving creep strength as well as environmental resistance in spite of low Cr level. Definition of next generation superalloys emerged with another 30°C improvement in metal temperature capability, which was partly stimulated by the needs identified during new engine design for the recently introduced Boing-777 wide body, twin-engine aircraft, and the industrial TRENT 800 engine. Cannon Muskegon corporation, USA optimized their third generation single crystal alloy CMSX10 employing total refractory elements of about 20wt.% with 6wt.% Re after tailoring Cr, Co and W level to 2, 3 and 5 wt% respectively [28]. Complete absence of TCP phase formation for this alloy has been confirmed at 913°C even after 5000 hours exposure. Rolls Royce has already demonstrated increased turbine efficiency of industrial TRENT 800 engine by replacing cooled blades with un-cooled, hollow IP blades of CMSX10 whose castability is comparable to CMSX4 as has been confirmed by casting components of a variety of engines such as, first stage HPT cooled and solid second stage blades of Allison Engine T56, first stage Solar Turbines MARS engine blades [29,30]. CMSX10 has 21°C heat treatment window to completely dissolve coarse γ' and γ/γ' eutectic at final soak temperature of 1366°C. Aging at 1152°C gives regular array of γ' cubes of 0.5mm edge. Secondary aging at 871°C/24 hours and 760°C/30 hours gives finer γ' within alloy matrix channels for additional tensile and creep strengths at lower temperature, particularly beneficial in the root sections of turbine blades. GE designed their third generation single

crystal superalloy Rene-6 where the composition was optimized to have good balance between creep rupture strength and microstructural stability as compared to CMSX10 with relatively higher Co, Cr and Mo, relatively lower Ta and Re while incorporating C, B and Hf in trace amount for improved tolerance to low angle grain boundaries, and also Y to improve adherence of the protective Al_2O_3 layer that forms during service. More than 98% eutectic γ/γ' solutioning at mere 1320°C/ 6hr has been possible with Rene-6 as against 45hr solutioning up to 1365°C for CMSX10. Longer solutioning time (~ 30 hours) however provides higher creep rupture life and better phase stability. Rene-6 has also undergone extensive engine testing in a variety of engines ranging from small (F414) to large (GE90) airfoils. Two other third generation single crystal alloys TMS75 and TMS80 were designed with the help of Cluster Variation Method (CVM) of computing alloy composition (31, 32) based on statistical thermodynamics using Lennard-Jones inter-atomic potentials at the National Research Institute for Metals (NRIM), Japan [33]. Alloy TMS75 is very close to Rene-N6 in terms of major alloying elements, except Cr and Ta being less by 1wt.% each and Co and Re being less by 0.5wt% each, while the alloy TMS80 has additional 3wt.% of Ir unlike TMS75 and Rene-N6. Both TMS75 and TMS80 could be fully solutionised with a 40°C heat treatment window through 1300°C/ 1hr + 1320°C/ 5hr and aged through 1150°C/ 4hr + 870°C/ 20hr for uniform γ' precipitates of 0.5 mm cube edges and superior phase stability, environmental resistance and creep rupture property at higher temperature and lower stress regime. Phase stability of TMS80 with 3wt% Ir in fact, is superior to TMS75 [31,32].

A third generation single crystal superalloy DMS4 [34] was developed at DMRL by pushing the total refractory elements to about 22wt% with about 6.5wt.% Re and removing Mo and Ti altogether. This alloy could be fully solutionised in a stepped manner between 1315°C -1360°C in about 24 hours with about 20°C of heat treatment window. Homogeneous distribution of γ' precipitates in uniform size of about 0.5 mm cube edges could be achieved in this alloy through 1160°C/ 4hr aging followed by 1140°C/ 4hr of simulated coating treatment and final aging at 870°C/20hr. This alloy exhibited superior 1% creep strength (Fig. 6) and creep rupture life comparable to CMSX10 together with good castability, alloy phase stability and environmental resistance even though its alloying parameters Md and Bo values of 0.97 and 0.648 were far away from their respective optimum target of 0.98 and 0.67 suggested by CVM. Recent Monte Carlo Simulation and 3-D atom probe study of fully aged single crystal alloy DMS4 shows [35] the partitioning behavior of various alloying elements to be in good agreement, except for Re. The simulations have shown that Cr and Co partition to γ while Al, Ta and Re partition to γ' . In contrast, atom probe experiments show that Re partitions strongly to γ . The disagreement may be due to the inaccuracy of the interatomic potentials used in the simulations. The atom probe results [35] suggest that Ni, Nb and W exhibit only weak partitioning (Table 2). A columnar-grained superalloy DMD4 [36] has also been derived from the DMS4 alloy for cost effective production of complex turbine airfoil parts, which are difficult to cast in single crystal form. Alloy composition has been tailored by replacing some of the Ta with Hf and incorporating C and B for grain boundary strengthening. Complete dissolution of as-cast coarse γ' and 95% of eutectic γ/γ' without incipient melting could be achieved in this alloy by solutionising in a stepped manner between 1300°C-1330°C in about 30 hours. Aging for optimum

Table 2 : Composition of γ and γ' and partition coefficients (k) in DMS4, obtained from atom probe and Monte Carlo simulations (35).

Element	3D Atom Probe			Monte Carlo simulations		
	$c_{\gamma'}$, at. %	c_{γ} , at. %	k	$c_{\gamma'}$, at. %	c_{γ} , at. %	k
Ta	5.42	0.64	8.47	3.71	1.74	2.13
Al	16.63	2.47	6.73	13.99	6.92	2.04
Ni	70.81	67.75	1.05	71.08	78.74	0.90
Nb	2.02	1.93	1.05	Not considered		
W	2.39	3.03	0.79	2.07	1.36	1.52
Co	1.31	6.89	0.19	3.92	5.62	0.70
Cr	0.97	8.40	0.12	2.37	4.79	0.49
Re	0.29	8.79	0.04	2.85	0.82	3.48

γ' structure was 1150°C/6hr followed by 870°C/20hr. This alloy showed excellent castability with respect to wide chord and thin walled blades and vanes with overhanging shrouds and complex cooling channels of advanced gas turbine engines together with good phase stability, environmental resistance and creep rupture properties (Fig. 6) close to the second generation single crystal superalloy CMSX-4 [36].

ONERA in France developed a single crystal superalloy MC-NG [37,38] with total refractory metal content of 19.1 wt% incorporating Re and Ru of 4 wt% each for turbine blades of future turbo-shaft engines. Alloy chemistry of MC-NG was optimized through a number of multiple regression analyses of existing data and experimental validations, aimed for the best combination of high γ' -solvus, high γ/γ' mismatch, low density, good phase stability and acceptable resistance to hot corrosion and high temperature oxidation along with creep strength comparable with the third generation superalloys. Alloy MC-NG could be fully solutionised using a two-step treatment of 1310°C/3hr followed by a 3°C/hr ramp to 1340°C/3hr. Aging at 1100°C/4hr plus 850°C/24hr could produce a homogeneous distribution of γ' precipitates of about 0.5 mm cube edges. This alloy exhibited best balance of overall properties with a density of 8.75g.cm⁻³ and a specific creep strength comparable with that of CMSX10 and Rene-6 but without any propensity to form Re-rich TCP phases. It was designated by ONERA as their fourth generation single crystal alloy.

Very recently, the National Institute of Materials Science (NIMS), Japan developed a Ni-base single crystal superalloy TMS-196 by incorporating further ruthenium (Ru) and chromium (Cr) over the compositions of all the previous Ni-based superalloys [39]. Enhanced phase stability of this alloy with further Ru additions allowed higher content of refractory elements and Cr content that resulted in superior high temperature creep (under conditions of 800-1100°C/137-735MPa) and oxidation resistance along with thermo-mechanical fatigue (TMF) resistance over the current commercial superalloys, such as CMSX-4, CMSX-10, PWA1484 and Rene N5. The surface of oxidized TMS-196 exhibited continuous alumina layer indicating good oxidation resistance similar to that of Rene N5. The high refractory content (24.5 wt.%) in TMS-196 results in large negative lattice misfits and fine interfacial dislocation networks between γ and γ' at elevated temperatures leading to improved resistance to creep and TMF. The casting yield of TMS-196 is in the range of commercial 2nd generation superalloys.

This alloy is designated by NIMS as their fifth generation single crystal alloy being a promising candidate alloy for turbine blade applications to further enhance engine performance.

6. Alloys for advanced IGT buckets and vanes:

The land based Industrial Gas Turbine (IGT) industry is experiencing tremendous growth as the electric power generation using IGT in combine cycle mode has become increasingly efficient (>50%) together with less emission of CO₂ into air as compared to less than 35% efficiency of either steam turbines or combustion turbines working in simple cycle. The combine cycle power plant mainly comprises gas turbines, steam turbines and heat recovery steam generators. Thermal efficiency of combine cycle power plants has been greatly improved in the last decade by increasing engine firing temperatures after introducing better airfoil materials such as single crystal alloys CMSX11B, AF56 and PWA1483. These alloys were developed with about 12wt% Cr for long-term environmental resistance together with C, B, Hf addition to enhance alloy tolerance for low angle boundaries. A number of single crystal superalloys such as CMSX11C, SC16 have also been developed (40) for industrial gas turbine applications, where hot corrosion and oxidation resistance demanded higher Cr levels (above 12wt%). Long term phase stability was ensured in such alloys by keeping moderate level of Mo, Ta and increasing Ti/Al ratio to maintain reasonable strength. Both CMSX11B and CMSX11C alloys could be solution treated by 1227°C/1hr + 1249°C/1hr + 1260°C/2hr + 1264°C/4hr to dissolve all γ' and eutectic $\gamma-\gamma'$. Primary aging of 1121°C/5hr results in regular array of γ' precipitates of about 0.4 to 0.5 cube edge. The secondary and tertiary aging of 871°C/20hr and 760°C/30hr result in fine γ' precipitates in the γ -matrix channels increasing low temperature strength for the root section. Long term creep rupture properties of these alloys are equivalent or superior to the second-generation single crystal superalloys. Further, these alloys have attractive blends of bare hot corrosion and oxidation resistance. Pratt and Whitney have designed single crystal alloy PWA 1483 [41] for IGT airfoil applications incorporating 12.2wt.% Cr to impart environmental resistance and B, Hf, C to impart tolerance to low angle boundary (LAB) and high angle boundary (HAB) defects. The alloy showed good castability towards IGT airfoil components. Partial solutionising at 1204°C/4hr/AC was carried out to avoid

incipient melting and minimize re-crystallization. Primary aging was carried out at 1079°C/4hr/AC and secondary aging at 870°C/20hr/AC.

The DS alloy TMD-103 for IGT airfoil casting was derived from the single crystal superalloy TMS75 by simply adding 0.07wt.% C and 0.015wt.% B for grain boundary strengthening (42). This alloy was solutionised through 1225°C/1hr + 1275°C/5hr leaving the eutectic and grain boundary γ which would otherwise melt at 1300°C. Ageing of this alloy was accomplished at 1150°C/4hr/AC + 870°C/20hr/AC. The long term creep rupture strength of this alloy was found to be equivalent of second generation single crystal superalloy CMSX-4. Its hot corrosion resistance was equivalent of IN792Hf (12.5wt% Cr) in spite of low (3 wt. %) Cr level. Its oxidation resistance is equivalent of CMSX-4 and its temperature advantage over second-generation DS alloy CM186LC is about 36°C. This alloy could be directionally solidified in the form of a large hollow blade for a 2000kW IGT without any defect [43]. TMS82+ is another alloy that has been designed [44] with less Re (2.4wt %) than second-generation superalloys but with better creep strength than that of third generation superalloys. Complete solutionising could be achieved by 1300°C/1hr + 1320°C/5hr/AC with about 40°C heat treatment window. Aging was accomplished at 1150°C/4hr/AC + 870°C/20hr/AC. Superior creep strength could be realized with TMS82+ than that of the third generation superalloys such as TMS75 due to larger negative misfit of -0.24 (relative to -0.08 of TMS75), which accelerate γ -rafting and result in very fine dislocation network at γ - γ' interface relative to TMS75.

7. Future Direction

Development of gas turbine airfoil materials all over the world is being focused towards highest-ever metal temperature capability well above 1150°C with reasonable environmental resistance. Current level of temperature capability in cast Ni-base superalloys has been achieved by pushing total refractory element content beyond 20wt.% as in alloy Rene N6, DMS4, TMS80 and TMS196. Further rise in metal temperature capability and environmental resistance may come by alloying with platinum group of metals in place of Mo and W which are known to form TCP phases and also have poor environmental resistance. Alloy chemistry of IGT buckets/vanes differs greatly from that of aero-engine blade/vane alloys, both on account of altered operating scenario and DS processing difficulties encountered due to their large size resulting in a number of casting defects such as freckles, low and high angle grain boundaries and re-crystallization. Therefore, SC casting acceptance standards and post casting processing are major factors to affect casting yield and design performance of IGT components. The inevitable increase in total number of defects and variation in properties with increasing component volume imparts additional cost and performance penalties. Elastic modulus being a fourth-rank tensor does vary significantly with crystal orientation. Crystallographic slip dependent plastic properties, such as creep and tensile strength, are not only an-isotropic, but also the extent of anisotropy is a strong function of alloy compositions. This anisotropy of tensile properties is due to competition between octahedral and cube slip behavior and therefore is also a complex function of γ' size, shape, distribution and alloy composition. Low temperature tensile properties and associated low cycle fatigue life are very critical for the durability of root attachment in turbine blade design.

High temperature creep resistance in single crystal superalloys depends on a complex diffusion controlled slip-climb mechanism that is highly sensitive to alloy chemistry and crystal orientation. Typically, grain boundary mis-orientation beyond 10° is known to result in a precipitous drop in creep strength due to order of magnitude increase in diffusion relative to trans-granular diffusion. Some of the single crystal IGT bucket/vane alloys have been recently designed with increased alloy tolerance to grain boundary mis-orientation up to 25 by incorporating sufficient level of grain boundary strengtheners such as C, B, Hf but at the cost of some amount of creep strength. Similarly, partial γ' solutionising has been adopted in a number of IGT alloys to control the extent of re-crystallization with the help of undissolved γ' network. This is again at the cost of not using full potential of the costly and heavy refractory alloying additions. Stronger the alloy, greater is the extent of re-crystallization and hot tear cracking. It is also necessary to have longitudinal and transverse grain orientation control in single crystal IGT buckets/vanes since these are an-isotropic and large variation in properties along different directions are encountered due to their large size. All these need to be tackled through careful selection of shell mold strength/collapsibility and process/equipment innovations employing high temperature gradient across thin wall-molds with crystal selectors having three dimensional control on crystal orientation (45) together with alloy design for optimum combination of creep strength, ductility, environmental resistance, to achieve performance superiority.

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