Superalloys 2004
Edited by K.A. Green, T.M. Pollock, H. Harada,
T.E. Howson, R.C. Reed, J.J. Schirra, and S. Walston
TMS (The Minerals, Metals & Materials Society), 2004

IMPROVED SINGLE CRYSTAL SUPERALLOYS, CMSX-4®(SLS)[La+Y] and CMSX-486®

Ken Harris, Jacqueline B. Wahl
Cannon-Muskegon Corporation [A PCC Company], Box 506, Muskegon, MI 49443-0506 USA

Keywords: Single Crystal, Oxidation, Defect Tolerance

Abstract

Single crystal superalloys and casting technology offer a combination of attractive properties for advanced gas turbine engine components. The alloys are designed to produce superior properties for a challenging combination of requirements: high temperature creep-strength, fatigue resistance, oxidation resistance, coating performance and retention of performance in thin-walled configurations. Application of this technology to new components has only been restricted by the competing criteria of affordability for first time introduction.

The development of improved single crystal superalloys, CMSX-4 (SLS)[La+Y] and CMSX-486 provide an appealing combination of enhanced performance and production affordability for demanding, high temperature applications in advanced gas turbine engines.

Introduction

Modern turbine engine designs require the use of single crystal (SX) superalloy turbine airfoil, seal and combustor components to obtain performance and life cycle objectives. The benefits of SX castings have been well documented: single crystal alloys offer improved creep-rupture, fatigue, oxidation and coating properties, resulting in superior turbine engine performance and durability [1,2,3,4,5]. In addition, single crystal alloys retain a higher fraction of their thick section rupture life as wall thickness is reduced [6].

Due to the attractive combination of properties and performance, applications of single crystal technology have been extended to a variety of components with widely divergent requirements. The most stringent applications, such as 1st stage turbine blades, require optimum high temperature properties and the use of highly reactive element additions, such as La and Y, ideally without the expense of non-reactive (alumina/yttria) foundry ceramics. Complex configurations, such as multi-vane segments and large industrial gas turbine (IGT) airfoils, require generous grain specifications to obtain the high manufacturing yields necessary for meeting cost objectives.

This paper will discuss the development of two improved single crystal superalloys, CMSX-4® Super Low Sulfur (SLS)[La+Y] and CMSX-486® [7], which were driven by the industry call for advanced technology SX castings at affordable production costs.

CMSX-4 (SLS)[La + Y] Alloy

Background

CMSX-4 is a second generation, Re-bearing nickel-base SX superalloy which has been extensively investigated and documented in the literature [3,4,8,9,10]. The nominal chemistry is provided in Table I. CMSX-4 alloy has been successfully used in numerous aero and industrial gas turbine applications since 1991. These applications, such as high pressure turbine blades and seals, have demonstrated an impressive combination of high temperature strength, good phase stability and oxidation, hot corrosion and coating performance in extensive engine service [11,12,13]. Close to five million pounds (650 heats) of CMSX-4 alloy have been manufactured to date.

Table I. CMSX-4 Alloy Nominal Composition

Element	Wt.%	Element	Wt%
Cr	6.5	Al	5.6
Co	9.6	Ti	1.0
W	6.4	Ta	6.5
Re	3	Hf	0.1
Mo	0.6	Ni	Balance

CMSX-4 [La+Y] alloy was subsequently introduced to meet ever-increasing engine design requirements for hot section turbine components. Of particular interest was improvement in bare alloy oxidation performance to minimize blade tip and internal oxidation and improve thermal barrier coating (TBC) adherence. Evaluation of reactive element additions demonstrated the oxidation behavior of bare CMSX-4 alloy (sulfur content ≤2 ppm) could be dramatically improved by the addition of lanthanum (La) and yttrium (Y) (Figure 1) [14].

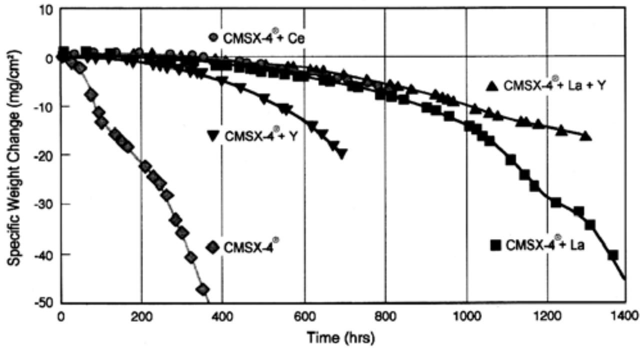


Figure 1. 1093°C (2000°F) Dynamic Cyclic Oxidation Test Results for Bare CMSX-4 Alloy with and without Reactive Element Additions

---

CMSX-4®, CMSX-486®, CM 186 LC®, CM 247 LC®, CMSX-3® and CMSX® are registered trademarks of the Cannon-Muskegon Corporation

It was also shown that control and retention of reactive element additions was improved when a combination of La and Y were used, compared to either element individually. However, realization of these improvements for turbine components was dependant upon the use of expensive, non-reactive alumina or yttria core materials [14]. It should also be noted that, in addition to being more costly, core materials such as alumina are much more difficult to remove following casting, resulting in long, expensive autoclave processing.

New Developments

CMSX-4 (SLS)[La+Y] alloy is an improved version of CMSX-4 which is pre-alloyed with La and Y and has consistent low sulfur content of 1 ppm. Initial development work included production of several R&D-size heats on the Cannon-Muskegon (CM) V-5 250 lb. vacuum induction melting (VIM) furnace to demonstrate 1 ppm sulfur content capability and La + Y control. Subsequently, the manufacturing technology was scaled to 4000 lb. heats on the CM V-6 VIM furnace without negative impact on critical heat chemistry (Table II). CMSX-4 (SLS)[La+Y] has excellent alloy cleanliness in terms of stable oxide inclusions, as represented by 1-2 ppm oxygen content over multiple heats.

Table II. CMSX-4 (SLS)[La+Y] Production Heats – Critical Chemistry

Heat	La ppm	Y ppm	S ppm	Mg ppm	Zr ppm	Si	[N] ppm	[O] ppm
5V0114	363	339	1	<180	<10	<.01	1	2
5V0115	500	490	1	<180	<10	.01	1	2
5V0128	430	410	1	<180	<10	<.01	1	2
6V2451	142	142	1	<180	<10	<.01	1	1
6V2461	747	620	1	<180	14	.01	1	2

The highly reactive elements La and Y tie up the residual sulfur in the alloy as stable La+Y sulfides, preventing the migration/diffusion of sulfur to the free surface. Sulfur segregation has been shown to destroy the strong Van der Waals bond between the α alumina scale layer and the base alloy/coating/bond coat, resulting in premature coating/TBC spallation [15,16,17,18].

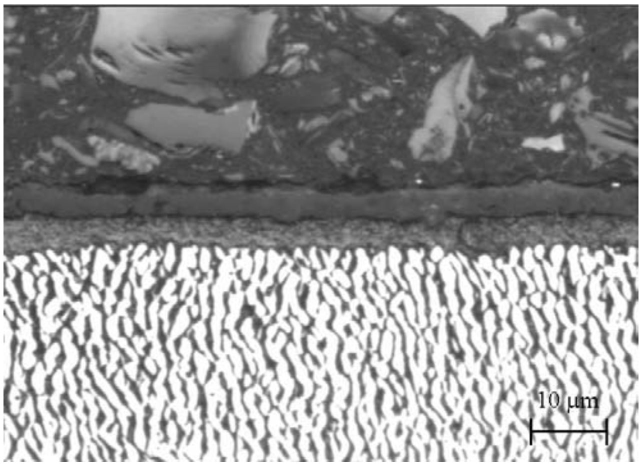


Figure 2. Surface Microstructure on CMSX-4 (~39 ppm La+Y) following 1389 hours creep-rupture testing at 1050°C/125 MPa (1922°F/18 ksi) [Courtesy Rolls-Royce plc]

An example of the benefit of La + Y additions is shown in the remarkable surface microstructure observed following creep-rupture testing at 1050°C (1922°F) (Figure 2) [19]. After 1389 hours there was an 8 micron thick, 2-layer oxide film and no evidence of gamma prime depletion at all. Without the La+Y addition, significant γ' depletion would be expected from extended exposure at this temperature. This behavior translates to substantial improvement to EB-PVD TBC life, as demonstrated in (Figure 3) [20].

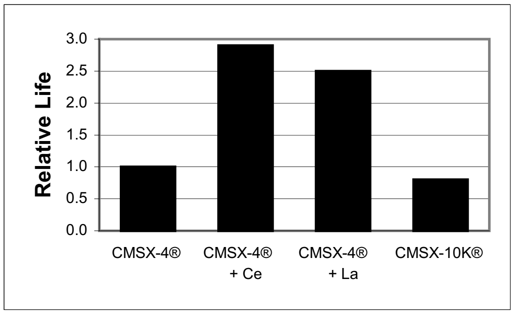


Figure 3. Reactive Element Effects on EB-PVD TBC Life 1093°C (2000°F)/10 hr Thermal Exposure Cycles [Courtesy Solar$^{®}$ Turbines]

Benefits

Casting trails with pre-alloyed CMSX-4 (SLS)[La+Y] ingot have demonstrated improved control and retention of La+Y content compared to traditional Ni-foil-wrapped add packets attached to the charge increment at the casting furnace. The effectiveness of add packets is dependent upon melt-in and subsequent induction stirring prior to pour. Pre-alloying the ingot provides greater consistency of the reactive additions within the molten alloy and reduces the hold time at temperature needed to tie up the residual sulfur, minimizing reactive element loss during remelt. In addition, due to the consistent, low sulfur content of CMSX-4 (SLS)[La+Y], smaller La+Y retentions are needed to obtain the same superior bare oxidation properties and coating/TBC life.

The ability to reduce the reactive element addition for CMSX-4 (SLS) [La+Y] has further benefits: Smaller reactive element additions preclude excessive retention of La and Y in the thicker (root) sections of the castings. This minimizes the potential for incipient melting problems during solution heat treatment, which can have adverse effects on fatigue properties [19]. Smaller retentions also ensure that full solutioning can be achieved and the mechanical property and stability characteristics of CMSX-4 will be maintained in CMSX-4 (SLS)[La+Y] alloy.

Lower La+Y adds also offer the option of using less costly, conventional foundry ceramics (shell and core). Extensive component casting trials have demonstrated CMSX-4 (SLS)[La+Y] alloy can be cast with silica-containing single crystal foundry ceramics and achieve high SX grain yield. Figure 4 demonstrates minimal reactivity observed at the internal surface adjacent to the silica-base core body [21]. Excellent top to bottom (root to airfoil) microchemistry control (retained La + Y content) has been achieved for cored SX airfoil castings. The retained La and Y content for a series of cored airfoil casting trials with varying reactive element additions is shown in Table III [21].

These trials were run to determine the optimum La + Y addition for a desired retention of ~5ppm [La+Y].

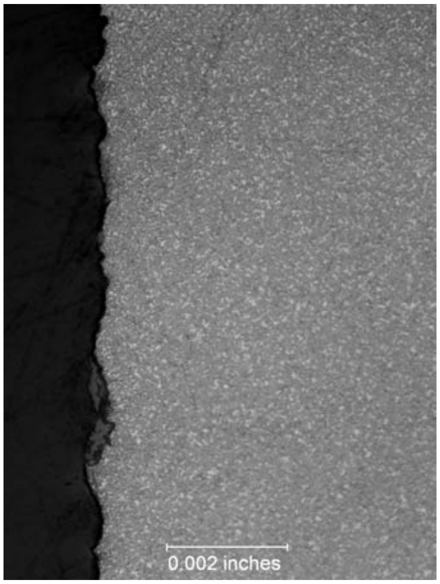


Figure 4. Internal Surface Microstructure following SX Casting of CMSX-4 (SLS) [La+Y] with Silica-base Core Body, showing Minimal Reactivity. [Courtesy Rolls-Royce Corporation]

Table III. Retained La and Y – Cored SX Casting Trials

ID	La (ppm)	Y (ppm)
32470 Tip	1	1
32470 Root	2	1
32472 Tip	1	1
32472 Root	2	1
32354 Tip	3	2
32354 Root	5	1
31479 Tip	5	5
31479 Root	2	1
31749 Tip	10	8
31479 Root	4	1

Composite remelt charge blending from high and low La+Y content heats has been used to obtain La+Y additions ranging from 300-1370 ppm and CMSX-4 (SLS) [La+Y] components are currently operating in production turbine engines. Manufacturing flexibility, inventory cost control and convenience for reactive additions are further advantages of the CMSX-4 (SLS)[La+Y] alloy development program.

CMSX-486 Alloy

Background

Single crystal superalloy vanes have demonstrated improved performance and durability compared to equiaxed (EQ) or directionally solidified (DS) components. This is due not only to the improved properties of SX alloys, but also the absence of transverse boundaries in complex stress regions such as the airfoil leading edge and trailing edge, and the inner and outer shrouds of multi-vane segments. However, these components often have low angle and high angle boundaries (LAB/HAB) defects in the 12°-15° misorientation range which occur during the single crystal solidification process. The highest temperature capability (carbon and boron free) SX alloys are typically limited to 6° LAB defects in critical, high stress regions. C and B-containing SX alloys can accommodate 9°-12° defects with some sacrifice of mechanical properties.

The concept of single crystal casting an alloy with full grain boundary strengthening elements to obtain SX cast components which could accommodate a generous grain defect specification was explored in a collaborative program with Rolls-Royce Corporation (RRC) using the second generation, Re-bearing DS alloy CM 186 LC® [22]. This work demonstrated significant retention of mechanical properties for low angle and high angle boundaries exceeding 20° misorientation [23,24]. In addition, SX CM 186 LC alloy is used as-cast, eliminating solution heat treatment-induced recrystallization (RX) defects due to residual casting stresses. The laboratory testing justified evaluation of relaxed grain inspection criteria, culminating in successful implementation of SX CM 186 LC in the 2nd stage vane segment for the Rolls-Royce AE 3007 A1 and A1E engines flown on regional jets, including the Embraer 135, 140, 145, 145 XR and Legacy family of aircraft, Cessna Citation X and Global Hawk UAV. Total flight experience for this application as of April 2004 is 10 million hours/10 million cycles with demonstrated component life of at least 15, 000 hours [25].

This successful application also identified the opportunity for an optimized grain boundary strengthened (GBS) SX alloy, with improved creep-rupture strength over SX CM 186 LC while retaining the lower cost manufacturing achieved through generous grain inspection criteria and minimal heat treatment.

Alloy Development

The chemistry of CMSX-486 alloy (Table IV) was established following detailed studies of the effect of tantalum (Ta) and hafnium (Hf) chemistry variations on creep strength and mechanical property retention across LAB/HAB grain defects.

Table IV. Nominal Alloy Chemistry (Wt. %)

Alloy	C	B	Al	Co	Cr	Hf	Mo	Ni	Re	Ta	Ti	W	Zr
CM 247 LC	.07	.015	5.6	9.3	8	1.4	.5	Bal	--	3.2	0.7	9.5	.010
CMSX-3	--	--	5.6	4.8	8	0.1	.6	Bal	--	6.3	1.0	8.0	--
CM 186 LC	.07	.015	5.7	9.3	6	1.4	.5	Bal	3	3.4	0.7	8.4	.005
CMSX-681	.09	.015	5.7	9.3	5	1.4	.5	Bal	3	6.0	0.1	8.4	.005
CMSX-486	.07	.015	5.7	9.3	5	1.2	.7	Bal	3	4.5	0.7	8.6	.005
CMSX-4	--	--	5.6	9.6	6.5	0.1	.6	Bal	3	6.5	1.0	6.4	--

Table V. Typical CMSX-486 Creep-Rupture Properties

Test Condition	HT Condition	Life, hrs	Time to 1% Creep	Time to 2% Creep	Elong, %	RA, %
982°C/ 248 MPa (1800°F/36.0 ksi)	Partial Sol'n + Double Age	168.1	51.7	74.8	39.7	47.0
		172.0	56.4	80.9	35.4	45.1
	As Cast + Double Age	143.0	48.0	66.3	35.7	48.1
		138.3	42.9	61.0	46.1	47.0
1038°C/ 172 MPa (1900°F/25.0 ksi)	Partial Sol'n + Double Age	114.3	39.4	59.8	28.4	52.5
	As Cast + Double Age	119.2	39.5	57.8	41.7	49.2
		110.9	37.3	56.1	16.1	17.2
1093°C/83 MPa (2000°F/12.0 ksi)	Partial Sol'n + Double Age	472.0	218.7	315.9	33.9	36.1
		474.2	145.8	289.1	35.2	43.4
	As Cast + Double Age	643.9	357.7	462.1	33.0	37.0
		673.9	360.2	495.5	25.4	40.0

Partial Solution: 1 hr/1238°C + 1 hr/1243°C + 1 hr 1249°C AC/GFC; Double Age: 4 hrs/1080°C AC/GFC + 20 hrs/871°C AC

Creep-Rupture Properties. Conventional 6.35 mm (1/4") diameter near net shape single crystal test bars were cast at Rolls-Royce Corporation (SCFO) from two heats of CMSX-486 alloy for comparative creep-rupture testing. Early results established the optimum balance of creep properties are attained in the as-cast + double aged condition, particularly for aero turbine vane applications where 1093°C (2000°F) metal temperatures are critical (Table V). Similar to SX CM 186 LC alloy, this is advantageous from a manufacturing standpoint as it reduces the post-cast processing requirements and precludes the formation of solution heat treatment-induced recrystallization. Both of these factors have a positive impact on cost of manufacturing.

Table VI. Comparison of Stress-Rupture Life, hours

Alloy	HT Cond.	982°C/ 248 MPa	1038°C/ 172 MPa	1093°C/ 83 MPa
DS CM 247 LC	98% Soln.+ Double Age	43	35	161
CMSX-3	98% Soln + Double Age	80	104	1020
SX CM 186 LC	As-cast + Double Age	100	85	460
CMSX-681	As-cast + Double Age	113	--	528
CMSX-486	As-cast + Double Age	141	115	659

The creep-rupture test results for CMSX-486 compared to SX CM 186 LC and first generation alloys, DS CM 247 LC® and CMSX-3® are shown in Table VI. Consistent with the original development goals, longitudinal creep-rupture properties of CMSX-486 alloy demonstrated the intended improvement in rupture life compared to SX CM 186 LC alloy across a range of temperature/stress conditions. In addition, CMSX-486 alloy is tronger than the first generation SX alloy CMSX-3 at 982° C (1800°F) and comparable at 1038°C (2000°F).

An alternative developmental single crystal alloy composition, designated CMSX®-681 (Table IV), was also evaluated early in this program. CMSX-681 alloy showed lower stress-rupture life compared to CMSX-486 alloy at both the 982°C (1800°F) and 1093°C (2000°F) test conditions, possibly due to less favorable γ/γ’ mismatch at high temperatures. The higher Ti content in CMSX-486 alloy compared to CMSX-681 will expand the lattice of the γ’ probably giving a smaller γ/γ’ misfit. There also is significantly higher Ta content in CMSX-681 (6.0%) which likely partitions to the γ phase, resulting in a higher (less desirable) γ/γ’ misfit compared to CMSX-486 alloy [26,27]. As a result of the less favorable test results, the alternate CMSX-681 alloy chemistry was not pursued further in favor of the CMSX-486 alloy.

The results of long term creep-rupture property testing for CMSX-486 alloy using SX-cast test bars are shown in Figure 5 [28], extending beyond 10,000 hours at each test temperature. It is apparent the desired linear relationship exists out to these time periods. This indicates adequate alloy phase stability in terms of both γ’ and TCP phase formation. The microstructure of post-test stress-rupture specimens confirms the stability of CMSX-486 alloy (Figures 6-8). Some precipitation of acicular looking TCP phases (Re, W & Cr rich) are apparent, though not of sufficient volume fraction to de-alloy the material or nucleate creep cracking. Even so, the Cr content of CMSX-486 alloy has been slightly reduced in subsequent heats to further inhibit TCP phase formation during long term, stressed high temperature exposure.

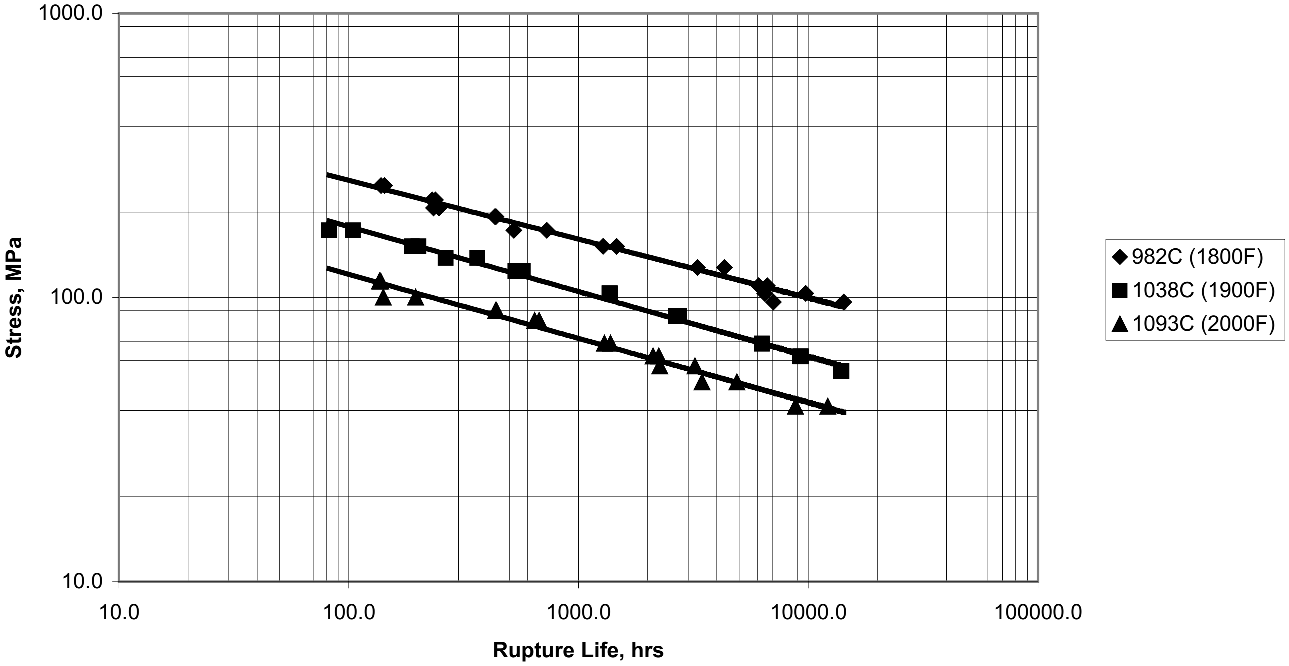
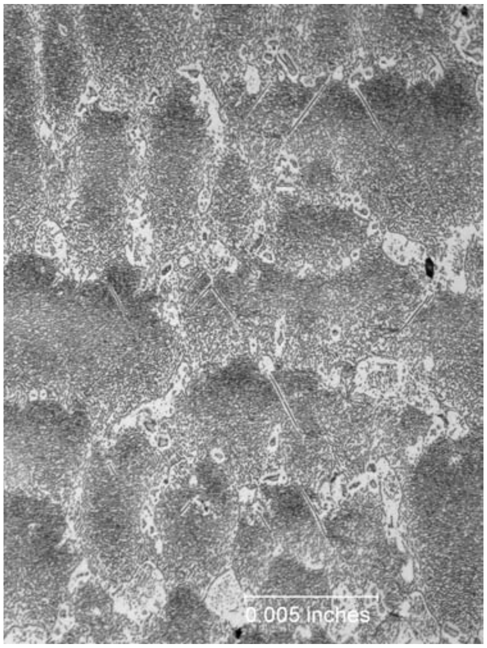


Figure 5. CMSX-486 Alloy Stress-Rupture Life at 982°C, 1038°C and 1093°C.



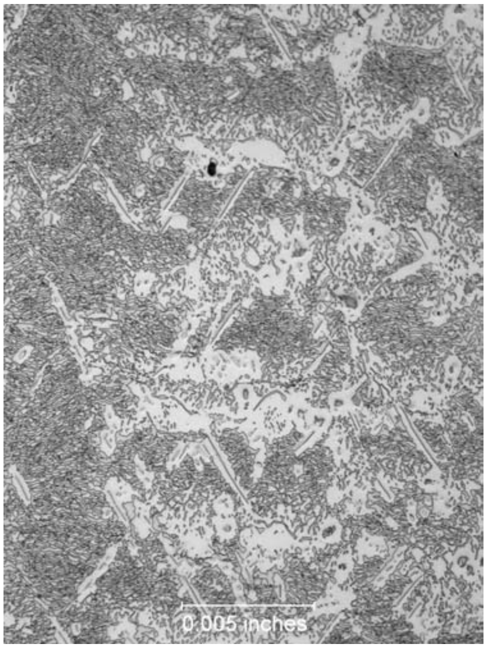


Figure 6. CMSX-486 Alloy Post Creep-Rupture Test Specimen following 14281.1 hours at 982°C/96 MPa (1800°F/14.0 ksi).

Figure 7. CMSX-486 Alloy Post Creep-Rupture Test Specimen following 13881.1 hours at 1038°C/55 MPa (1900°F/8.0 ksi).

Figure 8. CMSX-486 Alloy Post Creep-Rupture Test Specimen following 12150.5 hours at 1093°C/41 MPa (2000°F/6.0 ksi).

<u>Grain Defect Tolerance.</u> To evaluate the potential accommodation for grain defects, bicrystalline slabs were cast using "seeding" techniques to determine the mechanical properties of CMSX-486 alloy across LAB/HAB grain defects (Figure 8). Creep-rupture testing was undertaken over a matrix of temperature and stress conditions. This data indicates retention of baseline (defect-free) properties exceeding 15° degrees misorientation [28]. Examples of rupture life plots vs. LAB/HAB misorientation are shown in Figures 10-12.

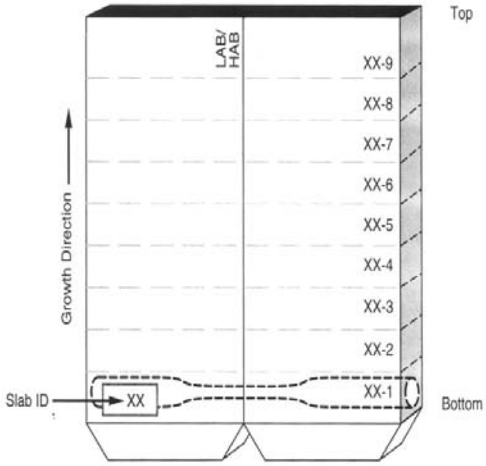


Figure 9. Sketch of Bi-Crystal Slab and Specimen Orientation

In comparison to alternative SX alloys, the benefits of GBS alloy CMSX-486 are significant. At 982°C (1800°F), CMSX-486 alloy demonstrates a distinct advantage over CMSX-3 alloy, which contains no GBS elements (Figure 10). Although Rene' N4 (an SX alloy containing C & B) shows accommodation to 10° misorientation [5], indicating some tolerance for grain defects, CMSX-486 alloy with full grain boundary strengthening elements (C, B, Hf & Zr) shows no reduction in properties to 18° misorientation (Figure 11). As would be expected, the greatest fall-off in LAB/HAB properties occurs at 1093 °C (2000 ℉) (Figure 12) due to degradation of grain boundary boride and carbide microstructure and Hf partitioning at this temperature over time.

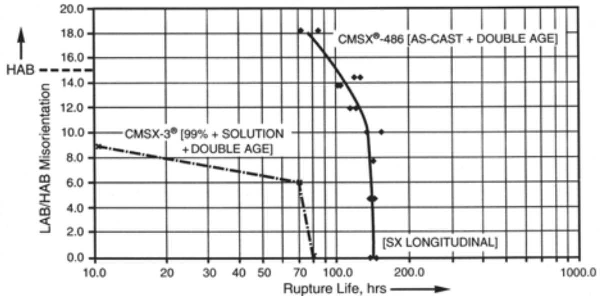


Figure 10. CMSX-486 and CMSX-3 Rupture Life vs. LAB/HAB Misorientation (982°C/248 MPa [1800°F/36.0 ksi])

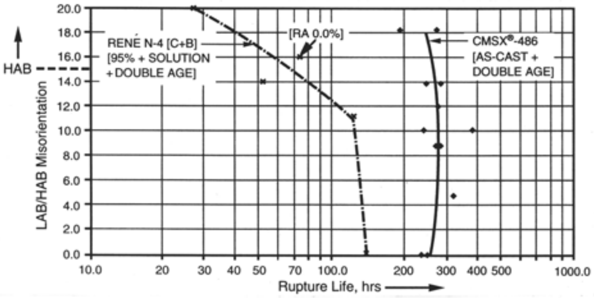


Figure 11. CMSX-486 and Rene' N4 Rupture Life vs. LAB/HAB Misorientation (982°C/207 MPa [1800°F/30.0 ksi])

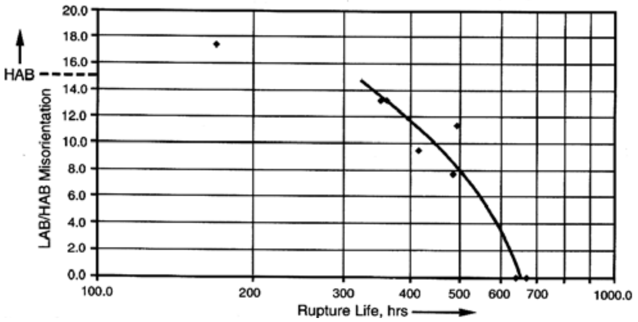


Figure 12. CMSX-486 Rupture Life vs. LAB/HAB Misorientation (1093°C/83 MPa [2000°F/12.0 ksi])

There is an expected decrease in stress-rupture ductility for LABs exceeding 10 . However, at 982 ℃/207 MPa (1800 ℉/30.0 ksi) test conditions with a HAB of 16 , the rupture reduction in area (RA) for CMSX-486 alloy is approximately 8%, whereas René N4 is 0%. Actual grain defect acceptance criteria will be based on component-specific design.

Castability. Castability has been evaluated at multiple casting sources for a variety of configurations. A mold of RRC AE 3007 A1 engine HP2 vane segments (Figure 13) was cast at Rolls-Royce [SCFO] using the same SX casting parameters as the production alloy, CM 186 LC. The casting yield and quality results were assessed by SCFO as good and quite similar to the production alloy. Additionally three molds of outer turbine seal segments were SX cast at a second casting source using a stable alumina prime coat as part of the shell composition. The data show excellent casting yield and quality results. It should be noted that with the relatively high Hf, B and C content for a SX alloy (more similar to a DS alloy), CMSX-486 may well require different casting parameters than those developed for a traditional second generation SX alloy, such as CMSX-4. A stable alumina prime coat approach is also advisable due to the 1.2% Hf content of the alloy.

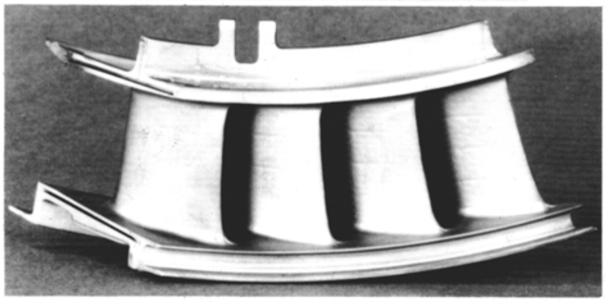


Figure 13. Rolls-Royce AE 3007 A1 SX HP2 Vane Segment

Environmental Properties. CMSX-486 alloy is derived from experience gained in the development of previous Cannon-Muskegon proprietary alloys, and the relationships in the alloy "family" provide additional benefits: CM 186 LC alloy has been extensively tested for oxidation/hot corrosion performance (Figures 14-16 [29,30]). Based on similarities of alloy chemistry, the environmental properties of CMSX-486 alloy are expected to be comparable.

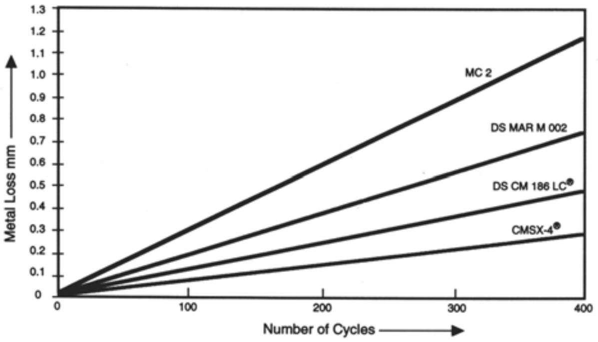


Figure 14. Burner Rig Cyclic Bar Oxidation (1100°C[2012°F], 15 min. cycles, 0.25 ppm NaCl, Mach 0.7)
[Courtesy Rolls-Royce plc]

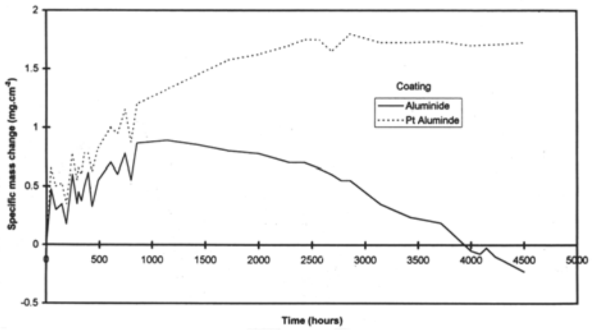


Figure 15. Burner Rig Dynamic Cyclic Oxidation of Coated DS CM 186 LC (1038°C [1900°F], Mach 0.45, JP-5 Fuel, 60 min. cycles) [Courtesy Rolls-Royce Corp]

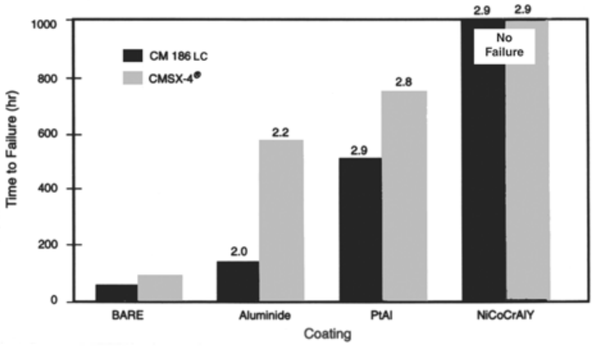


Figure 16. Life of Bare and Coated CMSX-4 and CM 186 LC in Type 1 Hot Corrosion Conditions (899°C [1650°F], 1% S in Fuel, 10 ppm Salt) [Courtesy Rolls-Royce Corp.]

Manufacturing Advantages. Similarly, the "family" nature of CMSX-486 alloy chemistry presents the opportunity to utilize CM 186 LC or CMSX-4 home scrap and/or foundry revert for blend heats. This has been demonstrated in the manufacture of production-size heats, providing a method to reduce initial alloy cost.

Conclusions/Summary

The attractive properties of single crystal alloys have presented the opportunity for many new and challenging applications. However, successful applications development requires not only superior alloy performance, but also cost-effective introduction of new technology. The development of improved single crystal superalloys, CMSX-4 (SLS)[La+Y] and CMSX-486 provide an appealing combination of enhanced performance and production affordability for demanding, high temperature applications in advanced gas turbine engines.

References

1. M. Gell, D.N. Duhl and A.F. Giamei, "The Development of Single Crystal Superalloy Turbine Blades," *Superalloys 1980* (Metals Park OH: American Society for Metals, 1980), 205-214.

2. A.D. Cetel and D.N. Duhl, "Second Generation Nickel-Base Single Crystal Superalloy," *Superalloys 1988* (Warrendale, PA: The Metallurgical Society, 1988), 235-244.

3. P.S. Burkholder et al., "Allison Engine Testing CMSX-4 Single Crystal Blades and Vanes," *Proceedings of 3rd International Charles Parsons Turbine Conference* (London, UK: IOM, 1995).

4. K.P.L. Fullagar et al., "Aero Engine Test Experience with CMSX-4 Alloy Single Crystal Turbine Blades," *Transactions of the ASME,* Vol. 118 (April 1996) 380-388.

5. E.W. Ross and K.S. O'Hara, "Rene' N4: A First Generation Single Crystal Turbine Airfoil Alloy with Improved Oxidation Resistance Low Angle Boundary Strength," *Superalloys 1996* (Warrendale, PA: The Minerals, Metals & Materials Society, 1996), 19-25.

6. D.N.Duhl, *Superalloys, Supercomposites and Superceramics,* (Academic Press Materials Science Series, 1989) 149-182.

7. European Patent Application No. 03254456.1

8. M.C. Thomas et al., "Allison Manufacturing, Property and Turbine Engine Performance of CMSX-4 Single Crystal Airfoils," (Presented at COST 501 Conference, Liege, Belgium, 3-6 Oct. 1994).

9. K. Harris et al., "Development of the Rhenium Containing Superalloys CMSX-4 & CM 186 LC for Single Crystal Blade and Directionally Solidified Vane Applications in Advanced Turbine Engines," *Superalloys 1992* (Warrendale, PA: The Minerals, Metals & Materials Society, 1992), 297-306.

10. D.J. Frasier et al., "Process and Alloy Optimization for CMSX-4 Superalloy Single Crystal Airfoils," (Presented at COST 501/505 Conference, Liege, Belgium 24-27 Sept. 1990).

11. K.G. Kubarych and J.M. Aurrecoechea, "Post Field Test Evaluation of an Advanced Industrial Gas Turbine First Stage Turbine Blade," (Presented at TMS/ASM Materials Week, PA 17-21 Oct. 1993).

12. W.D. Brentnall et al., "Extensive Industrial Gas Turbine Experience with Second Generation Single Crystal Turbine Blades," (Presented at International Gas Turbine & Aeroengine Congress & Exhibition, Orlando, FL, 2-5 Jun 1997), 97-GT-427.

13. R.W. Broomfield et al., " Development and Turbine Engine Performance of Three Advanced Rhenium Containing Superalloys for Single Crystal and Directionally Solidified Blades and Vanes," *Transactions of the ASME,* Vol. 120 (1998) 595 (97-GT-117).

14. D.A. Ford et al., "Improved Performance CMSX-4 Alloy Turbine Blades Utilising PPM Levels of Lanthanum and Yttrium," *Transactions of the ASME,* Vol. 121 (Jan 1999) 138-143.

15. J.G. Smeggil et al., "Reactive Element-Sulfur Interaction and Oxidation Scale Adherence," *Met. Trans.,* 16A (1985), 1164-1166.

16. J.G. Smeggil, A.W. Funkenbusch and N.S. Bornestein, "A Relationship Between Indigenous Impurity Elements and Protective Oxide Scale Adherence Characteristics," *Met. Trans.,* 17A (1986), 923-932.

17. R.T. McVay et al., "Oxidation of Low Sulfur Single Crystal Nickel-Base Superalloys" *Superalloys 1992* (Warrendale, PA: The Minerals, Metals & Materials Society, 1992), 807-816.

18. J.L Smialek et al., "The Control of Sulfur Content in Nickel-Base Single Crystal Superalloys and Its Effects on Cyclic Oxidation Resistance," *Superalloys 1996* (Warrendale, PA: The Minerals, Metals & Materials Society, 1996), 71-80.

19. Courtesy Rolls-Royce plc Internal Data (Private)

20. Courtesy SOLAR® Turbines Internal Data

21. Courtesy Rolls-Royce Corporation [SCFO, M. Kush], May 2004.

22. K. Harris and G.L. Erickson, U.S. Patent #5,069,873 Low Carbon DS Alloy (CM 186 LC), 3 Dec 1991.

23. P.S. Burkholder et al., "CM 186 LC Alloy Single Crystal Turbine Vanes,"(Presented at ASME TURBO EXPO 1999, Indianapolis, IN 7-10 Jun 1999), 99-GT-379.

24. K. Harris and J.B. Wahl, "New Superalloy Concepts for Single Crystal Turbine Blades and Vanes," *Proceedings of 5th International Charles Parsons Turbine Conference* (London, UK: IOM, 2000), 832-846.

25. Rolls-Royce Corporation Service Data [T. Moore], April 2004.

26. B.H. Kear and D.P. Pope "Role of Refractory Elements in Strengthening of Gamma Prime Precipitation Hardened Nickel-Base Superalloys," *Refractory Elements in Superalloys,* (Metals Park, OH: ASM Press, 1987), 135-152.

27. R. Curick, "Strengthening Mechanisms in Nickel-Base Superalloys," (Ph.D. thesis, University of Minnesota, 1972).

28. K. Harris and J.B. Wahl, "CMSX-486, A New Grain Boundary Strengthened Single Crystal Superalloy," (Presented at ASME TURBO EXPO 2002, Amsterdam, the Netherlands, 3-6 Jun 2002), GT2002-30487.

29. P.S. Korinko, M.J. Barber and M. Thomas, "Coating Characterization and Evaluation of Directionally Solidified CM 186 LC and Single Crystal Alloy CMSX-4," (Presented at ASME TURBO EXPO 1996, Birmingham, UK, 10-13 Jun 1996).

30. Courtesy Rolls-Royce plc Internal Data