THE DEVELOPMENT OF THE CMSX® -11B AND CMSX® -11C ALLOYS FOR INDUSTRIAL GAS TURBINE APPLICATION

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Abstract

Two different, non-Re containing single crystal (SX) superalloys are defined primarily for industrial turbine application. The alloys, CMSX®-11B and CMSX®-11C, contain respective chromium levels of about 12.5% and 14.5%. Both materials develop unique and extremely good blends of hot corrosion and oxidation resistance. They exhibit extremely good castability, employ relatively simple solution heat treatments and provide creep strength which is as good or better in comparison to other first generation SX materials such as CMSX-2/3®, PWA 1480 and René N4. Moreover, at certain engine-pertinent temperature/stress conditions, and particularly in long-term tests, the alloys appear to exhibit density corrected strengths which are similar or better than CMSX-4® and other second generation SX casting superalloys.

Introduction

The land-based, combustion turbine industry is experiencing tremendous growth, in part due to public utility commission rulings and environmental considerations. Prevailing rulings appear inconsistent with the long term, high capital expenditure associated with coal and nuclear power projects, thereby making the utility industry increasingly reliant on combustion turbine technology for its power generation requirements.

The General Electric Company forecasts that base-load electric power generation combustion turbines (CT) and combined cycle (CC) plants will account for about 45% of the new global orders and 66% of the new orders placed in the United States through the year 2001 (1). Advances in turbine design, materials, cooling technology and coatings have helped develop this market. Current advanced combustion turbines typically achieve more than 35% efficiency in the simple cycle mode and greater than 50% efficiency in the combined cycle mode. For example, the recent definition of its new gas turbine machine characteristics by Asea Brown Boveri (ABB) reveals that a simple cycle efficiency of 37.8% and combined cycle efficiency of 58.5% are anticipated for their GT 26 model; this being achieved through increasing power density and mass flow by doubling the pressure ratio (up from 15.0 in the GT 13E2 to 30.0) combined with sequential combustion at a relatively low maximum firing temperature (2).

And still another industry giant, Siemens, appears to rely on a more moderate increase to engine pressure ratio (eg., 16.0 for the Siemens V84.3 model versus 10.8 in its V84.2 machine) albeit in tandem with increased firing temperature, mass flow, compressor and turbine efficiencies. It's reported that the V84.3 firing temperature is expected to be 1310°C (2350°F) in contrast to the model V84.2 at 1120°C (2050°F). Furthermore, vane cooling increases from three to four stages while blade cooling is similarly increased from two to three stages. Further design improvements incorporated in the Siemens V84.3A engine are reported to allow an additional increase to firing temperature of about 22°C (40°F) while continuing to maintain acceptable NOx level. (4)

In order to achieve these increased firing temperatures which result in thermal efficiency improvement, large industrial turbine designers are beginning to utilize higher technology materials in their respective engine hot sections than previously applied. Where alloys such as IN 738 LC and IN 939 were previously employed, the search for greater engine efficiency has led the industrial turbine community to adopt technologies which have already been commercially applied within the aero-turbine and small industrial engine community, eg., directionally solidified columnar grain and single crystal components, serpentine and film cooling designs, as well as certain advanced coatings technology. While Siemens is apparently the first large frame turbine producer to announce the usage of SX components within their new turbines (5), it is also accepted that most other large turbine producers have designed SX components into their new products.

Complementary to the internal engine company R&D efforts toward improving industrial turbine efficiencies, industry collaborative programs targeted toward developing and commercializing ultra-high efficiency, environmentally superior, cost-competitive gas turbine systems for base-load applications [with a 1427°C (2600 °F) or greater firing temperature] such as the U.S. Department of Energy (DOE) Advanced Turbine Systems (ATS) Program (6) are extremely active. While the ATS Program continues on target toward achieving the goals of greater than 60% net efficiency for utility scale combined cycles and a 15% jump in efficiency for small industrial machines (7), similarly aimed activities of the Collaborative Advanced Gas Turbine (CAGT) Program

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encompassing joint efforts between 17 parties in North America and Europe (8) further complement the the efforts of the COST program in Europe and the DOE sponsored ATS program.

To similar end, this narrative reports on the development of two single crystal casting alloys exhibiting characteristics which are hoped attractive to the industrial turbine community. Specifically, both alloys provide 738 LC - type hot corrosion resistance in tandem with CM 186 LC level oxidation resistance. The alloys' capability to exhibit good hot corrosion resistance concurrent to providing extremely good oxidation resistance is thought unique in the industry, as most alloys exhibit only one or the other. Combined with this positive characteristic, the alloys exhibit extremely good castability (in small or large components), are able to be solution heat treated in a relatively short period and provide extremely good creep-rupture strength. In certain engine-significant temperature/stress conditions, the alloys exhibit creep-strength, on a density-corrected basis, which is similar to second generation Re-containing alloys such as CMSX-4 and PWA 1484. Furthermore, the alloys appear to exhibit greater long-term rupture strength than CMSX-4 alloy. Moreover, since the alloys do not contain Re, they are at least 50% cheaper per pound of alloy purchased, in comparison to 3 wt.% Re-containing alloys.

Alloy Design

Industrial gas turbine engines have historically operated in temperature/pressure regime where Type II hot corrosion attack was the dominating environmental issue (Fig. 1). However, as the industry has sought to improve engine efficiency, engine firing temperatures have generally increased, thereby creating need for materials more able to endure exposures where a blending of Type I hot corrosion and oxidation predominates.

Figure 1: The Protection Scene (9).

To best achieve the perceived environmental need, moderate alloy chromium levels must be utilized in an alloy's design. As it appears that each turbine producer requires different blends of hot corrosion/oxidation/strength characteristic, two different chromium levels were used as starting points for the CMSX-11B (12.5%) and CMSX-11C (14.5%) alloy designs.

Along with relatively high chromium contributing to alloy environmental properties, other considerations applied to the designs include the selection of low molybdenum level, moderate Ta and elevated Ti: Al ratio. Relatively high Al+Ti levels are employed,

which in tandem with moderate alloy Ta level, helps provide the high strength achieved.

Similarly, the alloy systems employ moderate tungsten levels for solid solution strengthening, however, the alloys also engage Ta: W ratios greater than unity to assist with SX component castability. Partly necessitated by the relatively high chromium levels employed, and the desired levels of W + Ta content, alloy cobalt levels are set relatively low to ensure adequate microstructural stability.

An overview of these alloy design considerations are provided in Figure 2, while more specific chemistry detail is provided in Table I, where the CMSX-11B and CMSX-11C alloy nominal compositions are compared to other first, second and third generation SX superalloys which have gained some commercial significance, albeit mostly in aero-turbine application. Note that the CMSX-11 derivatives do not rely on Re additions for strength attainment and that the alloys may, therefore, exhibit more desirable long-term lives and utility in certain components due to their inherently lower tendency for phasial instability in the temperature regime where Re containing alloys tend to form Topologically-Close-Packed (TCP) phase.

Figure 2: Alloy design criteria.

Table I Nominal Compositions of Three Generations of Single-Crystal Superalloys (Wt%)

Alloy	Cr	Co	Mo	W	Ta	Re	V	Nb	Al	Ti	Hf	Ni	Density (kg/dm ³)	Ref.
First Generation														
PWA 1480	10	5	—	4	12	—	—	—	5.0	1.5	—	Bal.	8.70	10
PWA 1483	12.8	9	1.9	3.8	4	—	—	—	3.6	4.0	—	Bal.	—	31
René N4	9	8	2	0	4	—	—	0.5	3.7	4.2	—	Bal.	8.50	11,12
SRR 99	8	5	—	10	3	—	—	—	5.5	2.2	—	Bal.	8.56	13,14
RR 2000	10	15	3	—	—	—	1	—	5.5	4.0	—	Bal.	7.87	13,14
AM1	8	6	2	6	9	—	—	—	5.2	1.2	—	Bal.	8.59	15
AM3	8	6	2	5	4	—	—	—	6.0	2.0	—	Bal.	8.25	16
CMSX-2*	8	5	0.6	8	6	—	—	—	5.6	1.0	—	Bal.	8.56	17
CMSX-3*	8	5	0.6	8	6	—	—	—	5.6	1.0	0.1	Bal.	8.56	17
CMSX-4*	10	5	3	—	2	—	—	—	4.8	4.7	0.1	Bal.	7.98	18
AF 56 (SX 792)	12	8	2	4	5	—	—	—	3.4	4.2	—	Bal.	8.25	19
SC 16	16	—	3	—	3.5	—	—	—	3.5	3.5	—	Bal.	8.21	20
CMSX*-11B	12.5	7	0.5	5	5	—	—	0.1	3.6	4.2	0.04	Bal.	8.44	21
CMSX*-11C	14.9	3	0.4	4.5	5	—	—	0.1	3.4	4.2	0.04	Bal.	8.36	22
Second Generation														
CMSX-4*	6.5	9	0.6	6	6.5	3	—	—	5.6	1.0	0.1	Bal.	8.70	23
PWA 1484	5	10	2	6	9	3	—	—	5.6	—	—	Bal.	8.95	24
SC 180	5	10	2	5	8.5	3	—	—	6.2	1.0	0.1	Bal.	8.84	25
MC2	8	5	2	8	6	—	—	—	5.0	1.5	—	Bal.	8.53	26
René N5	7	8	2	5	7	3	—	—	6.2	—	0.2	Bal.	NA	27
Third Generation														
CMSX*-10	2	3	.4	5	8	6	—	.1	5.7	.2	.03	Bal.	9.05	28
René N6	4.2	12.5	1.4	6	7.2	5.4	—	—	5.75	—	.15	Bal.	8.98	29

The CMSX-11 alloy derivatives are moderate density materials due to their high chromium and Al+Ti levels. The density of CMSX-11B is 8.44 kg/dm³ while it is 8.36 kg/dm³ for CMSX-11C; this in comparison to CMSX-3 at 8.56 kg/dm³, CMSX-4 at 8.70 kg/dm³ and CMSX-10 at 9.05 kg/dm³.

Alloy Manufacture

The CMSX-11B and CMSX-11C alloys are VIM produced according to the process consideration detailed in Reference 30. Due

to the relatively high alloy chromium contents employed, judicious Cr raw material selection is required to achieve the low levels of residual sulfur and phosphorus desired in the alloy product. Similarly, since low master alloy gas contents are always preferred, and high chromium and titanium containing alloys notoriously exhibit higher residual nitrogen levels, careful raw material selection in tandem with proper VIM procedure development are paramount to quality attainment.

Approximately twenty developmental 136 kg. heats have been produced through the development process. Consistency of major element heat chemistries are easily achieved, and typical tramp element levels prevailing in the CMSX-11 derivatives are illustrated in Table II. The levels achieved, except for gas content, are typical of those predominating in other SX alloys, such as CMSX-4 and CMSX-10. The abnormally high level of nitrogen in the CMSX-11 derivatives (4 ppm vs. 1 ppm) is a function of alloy chromium content, while the 4 ppm oxygen level (vs. 1 ppm in other CM product) is thought attributable to the alloys' relatively high Ti content. Although the developmental heat gas contents are higher than the other CM experience, they nonetheless have not adversely affected SX casting yields when measured in terms of defect formation tendency and/or non-metallic inclusion content. Furthermore, production alloy manufacture will likely provide improvement to each characteristic.

Table II Typical Tramp Element Levels in Development Heats of the CMSX-11B and CMSX-11C Alloys

Alloy	Element/Concentration						Si wt. %
	C ppm	B ppm	Zr ppm	S ppm	N ppm	O ppm	
CMSX®-11B	20	<20	<10	1	4	4	<.01
CMSX®-11C	20	<20	<10	1	4	4	<.01

Foundry and Heat Treatment Characteristics

Through February 1996, the CMSX-11B and CMSX-11C alloys have been cast successfully in six investment casting foundries located throughout the world. Items cast include test bars to 26 mm diameter, test slabs of varying size, plus both aero-turbine and industrial turbine blade components. Better than forty investment cast molds have been produced.

Through this experience, it is clear that both CMSX-11 alloy derivatives provide excellent SX castability. The alloys are not prone to formation of SX process defects such as freckles, slivers, high or low angle boundaries and/or stray grain formation. High production product yields are anticipated since every developmental mold produced has output nearly 100% satisfactory product. Moreover, no cleanliness problems, as measured through zygo dye penetrant inspection and metallographic observation, have been experienced. An example of one of the test casting configurations utilized in the development is provided in Figure 3. The industrial turbine blade test configurations are considerably larger, with heavy platform/root-section blades to about 250mm length being successfully cast.

The test articles and components produced are solution heat treated and given a three step aging treatment. Slightly different peak solution heat treatment temperatures are employed for the CMSX-11B and CMSX-11C alloys. Both treatments, however, can be

accomplished in 10 hours or less. Primary aging (pseudo coating treatment aging) is undertaken at 1121°C/5 Hr./AC condition for both alloys. Similarly, both alloys are further aged at 871°C/24 Hrs./AC + 760°C/30 Hrs./AC condition.

Allison AE 2100 2nd Stage Blade.

Figure 3: One of the several turbine blade configurations used to characterize the CMSX-11B and CMSX-11C alloy castability.

The typical CMSX-11B and CMSX-11C fully heat treated microstructures are illustrated in Figures 4 and 5, as well as the specific respective solution heat treatments currently utilized. The respective solution heat treatments effect nearly 100% γ' and eutectic $\gamma-\gamma'$ dissolution, while the primary aging treatments result in γ' growth and arrangement into fairly regularly aligned, cubic γ' precipitates of about 0.4 - 0.5 μm edge dimension. The secondary and tertiary aging treatments, as shown in Figure 6 for CMSX-11B, tend to promote the formation of relatively fine matrix channel γ' precipitates which likely enhance strength in blade root sections, since root section temperature exposures are generally lower than 760°C.

Solution: 1227°C/1 Hr. + 1249°C/1 Hr. + 1260°C/2 Hrs. + 1264°C/4 Hrs./AC.

Age: 1121°C/5 Hrs./AC,
871°C/24 Hrs./AC,
760°C/30 Hrs./AC.

Figure 4: Two views of fully heat treated CMSX-11B alloy.

Solution: 1204°C/1 Hr. + 1227°C/1 Hr. + 1250°C/2 Hrs. + 1256°C/4 Hrs./AC.

Age: 1121°C/ 5 Hrs./AC.

871°C/24 Hrs./AC.

760°C/30 Hrs./AC.

Figure 5: Two views of fully heat treated CMSX-11C alloy.

Figure 6: The CMSX-11B alloy aged at (a) 1121°C, (b) 1121°C + 871°C, and (c) 1121°C + 871°C + 760°C.

Mechanical Properties

Fairly extensive creep-rupture tests with temperature ranging 760-1038°C confirms the CMSX-11B and CMSX-11C alloys develop impressive respective strength levels. Alloy strengths are at least as good as commercialized SX casting alloys such as CMSX-2/3, PWA 1480 and René N4, plus as good or better, in certain tests, than creep-rupture strengths typically exhibited by the second generation, 3 wt. % Re containing CMSX-4, PWA 1484 and René N5 alloys.

Figure 7 illustrates the typical CMSX-11B/11C alloy strength in comparison to the DS René 80 and equiaxed IN 939 alloys. For a running stress of about 138 MPa, the CMSX-11 derivatives exhibit about 92°C greater strength than IN 939. Also indicated are the 871°C and 982°C capabilities of the PWA 1483 alloy (Ref. 31).

Figure 7: Average longitudinal Larson-Miller stress-rupture strength of several alloys.

While Figure 7 compared the CMSX-11B/11C materials to IN 939, DS René 80 and PWA 1483, Figure 8 illustrates the materials' advantage over the SC 16 alloy, an IN 738 SX alloy derivative developed by ONERA for the European Community Collaborative COST program (20). At about 207 MPa stress, the SC 16 alloy deficit is about 44°C and at 138 MPa, approximately 64°C. If compared on the basis of 1% creep strength, the SC 16 alloy exhibits an even greater deficit. Others have shown the SC 16 creep strength to be similar to equiaxed IN 738 (Ref. 32).

Figure 8: Average longitudinal Larson-Miller stress-rupture strength of three alloys.

As illustrated in Table I, the densities of the CMSX-11B and CMSX-11C alloys are moderately low in comparison to other commercially utilized DS and SX casting alloys. Figure 9 illustrates the specific or density corrected strengths of several commercial alloys in comparison to the CMSX-11 materials. Perhaps of most significance, the CMSX-11B alloy's strength is shown to equal or exceed that of CMSX-4, while the higher Cr containing CMSX-11C alloy appears superior to CMSX-4 only at higher temperatures such as 982-1038°C.

Figure 9: Density corrected stress-rupture strength of several alloys.

Along this line, non-density-corrected log stress vs. log time rupture strength comparison of the IN 738 LC, DS CM 247 LC, CMSX-4 and CMSX-11B alloys at 982°C is shown in Figure 10. Interestingly, the non-Re containing CMSX-11B alloy is shown to exceed the CMSX-4 alloy's rupture strength for tests run to between 1500-2000 hours life. Although not shown, the CMSX-11B alloy 1% average creep strengths demonstrated in these tests were not quite as good as the averaged CMSX-4 capability, however, they did not lag significantly. Similarly, Figure 11 compares the log stress vs. log rupture life of CMSX-4 and CMSX-11B for tests performed at 1038°C (also without density correction), and illustrates a significant advantage occurring with CMSX-11B for a test run to about 3000

hours. As comparative CMSX-4 alloy creep data is not available for the given test, future efforts will define the CMSX-4 alloy's creep-rupture characteristic, as well as expand the CMSX-11B data base in the 1038°C - 1100°C temperature regime.

Figure 10: 982°C stress-rupture strength of several alloys.

Figure 11: 1038°C stress-rupture strength comparison of CMSX-11B and CMSX-4.

Figure 12 illustrates the CMSX-11B γ' structure for a specimen tested at 1010°C/103 MPa condition and which ruptured at 17,278.8 hours. Fracture and thread section views are presented, with both illustrating an absence of TCP phase. This absence of TCP is significant since Re-containing alloys generally form TCP under similar condition and exposure time. Interestingly, this individual rupture result is near the extrapolated life prediction which could be made for the CMSX-10 alloy tested at identical condition.

Figure 12: Two post-test views of a CMSX-11B alloy specimen tested at 1010°C/103 MPa condition to rupture at 17,278.8 hrs.

A review of superalloy 10,000 hour rupture strength capability, on the basis of alloy chromium content, is presented in Figure 13. While traditional superalloy experience suggests that higher alloy chromium levels are accompanied by lower alloy strength, the CMSX-11B and CMSX-11C materials are shown to exhibit uniquely

high relative strengths for their 12.5 and 14.5% respective Cr levels. Of particular significance is the positive strength comparison with the second generation, 3 wt. % Re containing superalloys such as PWA 1484 and CMSX-4. The data also illustrates that Re containing SX superalloys don't necessarily provide long-term rupture strength advantages since other non-Re containing SX alloys such as René N4, CMSX-2 and PWA 1480 apparently perform similarly for 10,000 hour rupture life at the 160 MPa stress level, as determined through 1000 to 3000 hour rupture data extrapolation undertaken by a collaborating gas turbine engine producer.

Figure 13: 10,000 hour rupture strength of several alloys.

Environmental Properties

Environmental tests performed on superalloy materials often give rise to varied results, depending on methods employed and sources employed. In this investigation, four different turbine producers performed both hot corrosion and oxidation tests on the CMSX-11 alloy derivatives. The tests performed were undertaken by both burner rig and crucible evaluation methods, with the significance of the results comparing favorably between three of the four investigative sources, thereby lending credibility to the results achieved.

Figure 14 illustrates the derivative alloys' 500 hour hot corrosion characteristics determined in comparative crucible tests undertaken at 750°C, 850°C and 900°C. Similarly, Figures 15 and 16 present results of hot corrosion tests performed at 732°C and 899°C, with comparison to the IN 738 LC alloy capability. The results appear to confirm that the CMSX-11 materials behave similar to the IN 738 LC material with exposure at around 750°C, and that with long term exposure at about 900°C, the higher Cr containing derivative, CMSX-11C, exhibits an advantage vs. the CMSX-11B alloy, while continuing to perform as well as IN 738 LC to at least 2400 hours.

Figure 14: Hot corrosion of various alloys at 750, 850 and 900°C.

Figure 15: 732°C cyclic hot corrosion of several alloys.

Figure 16: 899°C cyclic hot corrosion of several alloys.

The results of extremely aggressive burner rig hot corrosion tests performed to 500 hour duration at 1050°C are shown in Figure 17. Hot corrosion results are presented through comparison to other widely used gas turbine alloys such as FSX-414, DS René 80 H, DS IN 738 LC, DS IN 939 and DS CM 186 LC. The actual corrosion results are presented in terms of test specimen thickness loss, while the respective material's strength capabilities are expressed on the figure's y-axis as creep-rupture temperature capabilities for 1000 hour lives with a testing stress of 284.4 MPa. For this testing, the figure illustrates that the CMSX-11C alloy develops DS René 80 - type hot corrosion resistance with an attendant 25°C strength advantage. The CMSX-11B alloy doesn't provide quite as good hot

Figure 17: Alloy strength and 1050°C/500 hour burner rig hot corrosion comparison of several alloys.

corrosion capability in the test, but is significantly better than the DS CM 186 LC alloy, a material also considered for some industrial turbine applications.

Burner rig oxidation test results are shown in Figure 18. The alloys compared (along with the result presentation methods employed) are identical to those presented in Figure 17. For this run at 1200°C and exposure of 500 hours, the CM 186 LC alloy is shown to exhibit the best alloy oxidation resistance, with the CMSX-11B and CMSX-11C materials behaving quite similarly; a unique capability for materials exhibiting IN 738/IN 792/ René 80 type corrosion resistance. To that point, Figure 18 also exhibits the reduced oxidation resistance of the René 80 and IN 738 LC alloys in comparison to CMSX-11.

Figure 18: Alloy strength and 1200°C/500 hour burner rig oxidation comparison of several alloys.

Confirmation of the CMSX-11 oxidation characteristic is provided in Figure 19 where the results of a cyclic crucible test performed at 1000°C on the CMSX-11B, CMSX-11C and IN 738 LC alloys are presented. While the IN 738 LC alloy oxidation resistance is low, the two CMSX-11 alloy derivatives exhibit relatively good oxidation characteristic for the duration of the test, ie., 3000 hours. While not presented, the Figure 19 test data source has developed unpublished data at identical conditions for the PWA 1483 alloy which show its capability appearing between the IN 738 LC and CMSX-11C test results. Similar oxidation testing undertaken at 1010°C at another turbine builder shows similar results for the CMSX-11 alloys, as illustrated in Figure 20.

Figure 19: 1000°C cyclic oxidation of three alloys.

Figure 20: 1010°C cyclic oxidation of three alloys.

The alloys, therefore, provide surprisingly good oxidation characteristics, as confirmed through both burner rig and crucible tests performed by multiple gas turbine engine manufacturers. At the same time, similar multiple source testing confirms both alloys exhibit very good hot corrosion capabilities (IN 738 LC/René 80/IN 792 level). The ability of the CMSX-11B and CMSX-11C alloys to provide good hot corrosion and oxidation characteristics, in tandem, is thought unique among available turbine materials.

Summary

Two unique single crystal casting superalloys have been developed for gas turbine engine blade and/or vane application where demanding strength and environmental issues prevail. The non-rhenium containing alloys, CMSX-11B and CMSX-11C, exhibit short-term creep rupture strengths which are as good or better than other lower chromium-containing, first generation SX superalloys. Moreover, both alloys develop long-term creep-rupture strengths which are as good or better than Re-containing second generation SX alloys at conditions pertinent to gas turbine blade and vane component operation. Furthermore, the CMSX-11B and CMSX-11C alloys also provide uniquely attractive blends of bare hot corrosion and oxidation resistance; a characteristic thought unique among superalloys commercially available.

Acknowledgment

The invaluable assistance of several turbine engine companies, who wish to remain unidentified at this point, is gratefully acknowledged.

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