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NEW SINGLE CRYSTAL SUPERALLOYS, CMSX®-7 AND CMSX®-8

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Abstract

Single crystal (SX) superalloys have wide application in the high pressure turbine section of aero and industrial gas turbine engines due to the unique combination of properties and performance. Since introduction of single crystal casting technology, SX alloy development has generally focused on increased temperature capability, and major improvements in alloy performance have been associated with the introduction of new alloying elements, including rhenium (Re) and ruthenium (Ru). 3% Re-containing second generation alloys, such as CMSX-4®, PWA 1484 and Rene' N5 have seen the greatest market utilization and have become the benchmark alloys for comparing new alloy developments. However, Re and Ru are rare elements and have limited production/availability and commensurate high costs, which has resulted in significant escalation of SX alloy costs. Consequently, there has been much interest in the development of improved SX superalloys with no Re or lower Re content compared to second generation alloys.

Cannon-Muskegon® has developed two new SX superalloys: CMSX®-7 alloy, which contains no Re, and low Re CMSX®-8 alloy, as alternatives to first and second generation alloys for applications which require slightly lower temperature capability compared to CMSX-4 alloy. This paper details development and characterization of these new, proprietary SX alloys.

Introduction

Since introduction in the late 1970's, single crystal (SX) alloy development has generally focused on increased temperature capability, and major improvements in alloy performance have been associated with the introduction of new alloying elements, including rhenium (Re) and ruthenium (Ru)[1,2]. Rhenium has been widely used in advanced single crystal superalloys for turbine blade, vane and seal segments due to its potent effect in slowing diffusion and hence creep deformation and fatigue crack initiation under high temperature operating conditions [3]. High temperature creep resistance and fatigue properties are directly related to the useful service life of gas turbine components and turbine engine performance such as power output, fuel burn and carbon dioxide emissions. Re-containing second generation alloys, such as CMSX-4®, PWA 1484 and Rene' N5 have seen the greatest market utilization and have become the benchmark alloys for comparing new alloy developments. Typical Re content for 2nd generation SX alloys is 3%, and 6-7% for 3rd generation CMSX-10K® and CMSX-10N® alloys.

However, Re is a rare element by-product from the mining and processing of copper and/or copper and molybdenum. Ru is a precious metal by-product principally from platinum production. As a result, both elements have limited market availability and commensurate high cost which has resulted in significant escalation of SX alloy costs. In addition, use of Re presents a supply chain risk both economically and strategically. Consequently, there has been much interest in the industry in exploring development of improved SX superalloys with no Re or lower Re content compared to second generation alloys.

Cannon-Muskegon has concurrently developed two new, proprietary SX superalloys: CMSX®-7 alloy, which contains no Re, and low Re CMSX®-8 alloy. CMSX-7 is an improved version of non-Re bearing alloys, such as CMSX-2/3®, PWA 1480 and PWA 1440, with improved properties surprisingly similar to Rene' N5 (3% Re) and Rene' N515 (1.5% Re) alloys. CMSX-8 is an alternative to second generation CMSX-4 alloy for applications which can accommodate somewhat lower maximum temperature capability.

CMSX-7 Alloy

The nominal chemistry of CMSX-7 alloy is provided in Table I. Development goals were to improve alloy mechanical properties compared to existing non-Re-bearing SX alloys, while balancing the solution heat treatment window, castability, alloy stability and oxidation properties/coating adherence. Refractory elements Ta, Mo and W have been balanced to target improved creep-rupture properties; Cr and Co have also been adjusted to ensure good alloy phase stability. The high Ta content is designed for SX castability and freedom from freckling defects; Al, Ti and Ta content will attain approximately 70% volume fraction (Vf) γ' phase. High Al, low Mo content plus the small Hf addition improves bare alloy oxidation resistance and coating adherence. The density of CMSX-7 alloy is approximately 8.8 gms/cm^3.

Table I. CMSX-7 Nominal Chemistry

Element	Wt%	Element	Wt%
Cr	6	Re	--
Co	10	Al	5.7
Mo	0.6	Ti	0.8
Ta	9	Hf	0.2
W	9	Ni	Balance

Microstructure

Heat treatment development studies have established a multi-step solution/homogenization and double age cycle which produces the microstructure shown in Figures 1 and 2. This depicts complete γ' solutioning with some remnant γ/γ' eutectic, no incipient melting and approximately 0.5µm average cubic aligned γ' phase following the high temperature age. This indicates appropriate γ/γ' mismatch and γ/γ' interfacial chemistry.

Mechanical Property Characterization

Extensive creep-rupture, stress-rupture, tensile and strain-controlled low cycle fatigue (LCF) property testing has been conducted on CMSX-7 alloy.

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Figure 1. CMSX-7 casting microstructure following solution + double age heat treatment

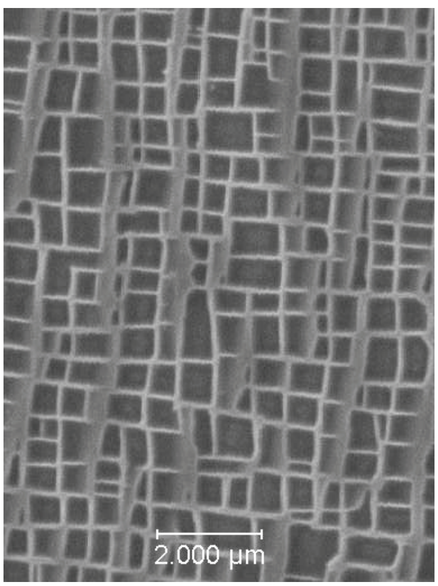

Figure 2. CMSX-7 casting microstructure following solution + double age heat treatment

Larson-Miller rupture life of CMSX-7 compared to CMSX-2/3 alloy are shown in Figure 3 [4] and demonstrate improved properties to approximately 1038ºC (1900ºF), and similar properties above that temperature to 1121ºC (2050ºF). Surprisingly, the CMSX-7 rupture life is quite similar to Rene'N5 (3% Re) and Rene' N515 (1.5% Re) alloy data [1,5,6] (Figure 4), despite the absence of Re in this new SX alloy. Post creep-rupture metallography shows excellent phase stability with negligible (or no) topologically close packed (TCP) phase formation, as shown in Figure 5 following 1176 hours stress-rupture testing at 1093ºC (2000ºF).

In addition to standard 4.52 mm (0.178 inch) diameter test bar creep and stress rupture data, stress-rupture testing was also run on mini-bar and mini-flat specimens machined from a solid single crystal turbine blade casting, as shown in Figures 6 and 7. Mini-bar data (1.52 mm/0.060" diameter) is indicative of the retention of thick section properties for thinner wall designs. Comparing the full size test bar data (diamonds) and the sub-size mini-bar data (squares) shows no discernible degradation in alloy rupture life due to section thickness (Figures 3-4). Mini-flat specimens (0.51 mm/0.020" thick) give an indication of the influence of bare oxidation degradation to thin wall properties. Stress-rupture lives show excellent thin-wall property retention and suggest good high temperature bare oxidation resistance for this alloy. Post-test metallography confirms this observation, as there is minimal surface depletion following 880 hours testing at 1093ºC (2000ºF) (Figure 8).

Burner rig dynamic, cyclic oxidation testing at 1000ºC (1832ºF) and 1100ºC (2012ºF) and Type I hot corrosion (sulfidation) testing at 900ºC (1652ºF) is scheduled at a major turbine engine company. In addition, CMSX-7 alloy is under evaluation at Oak Ridge National Laboratory (ORNL) to further characterize the resistance to environmental degradation. The ORNL evaluation will include polished bare, polished and CVD (chemical vapor deposition) aluminized [7], and/or grit-blasted and HVOF (high velocity oxygen fuel) coated superalloy coupons. The HVOF coated specimens use a commercial-type process and commercial NiCoCrAlYHfSi powder [8]. Coupons will be tested for 1000, 1hour cycles at 1050°C (1922ºF), 1100°C (2012ºF) and 1150°C (2102ºF) in dry and/or wet air with 10 min cooling between cycles. For the wet air tests, water is atomized into a flowing air stream and controlled to 10 vol.% based on the rate of water injection. Standard procedures are used so that the results can be compared to prior results on other superalloys.

CMSX-7 alloy tensile properties from 20ºC (70ºF) to 1038ºC (1900ºF) are shown in Figure 9. The alloy exhibits very high tensile strength, peaking at 1318 MPa (190 ksi) yield strength, 1379 MPa (200 ksi) ultimate tensile strength at 760ºC (1400ºF) while maintaining good ductility (13% elongation/17% reduction in area). The exceptionally high UTS/0.2% YS indicate strain hardening at this temperature, possibly due to further secondary or tertiary γ' precipitation in the γ channels, impeding dislocation movement.

Strain-controlled low cycle fatigue (LCF) testing of CMSX-7 alloy is currently in progress. Typical S-N curves at 1038ºC (1900ºF) and 1093ºC (2000ºF), with R-ratio = 0 or -1 are shown in Figure 10. Each test was run at 20 cpm to fracture or 120,000 cycles. In those cases where crack initiation did not occurred by 120,000 cycles, the test was switched to load control (at 10 Hz) and run to failure or 1,000,000 cycles (runout). Cycles to initiation were calculated based on when the stabilized tensile load starts to decrease. This indicates that the sample has cracked. Of note, the crack initiation data at 1038ºC (1900ºF) is surprisingly similar to CMSX-4 data for hot isostatically pressed (HIP'ed) and heat treated specimens [9].

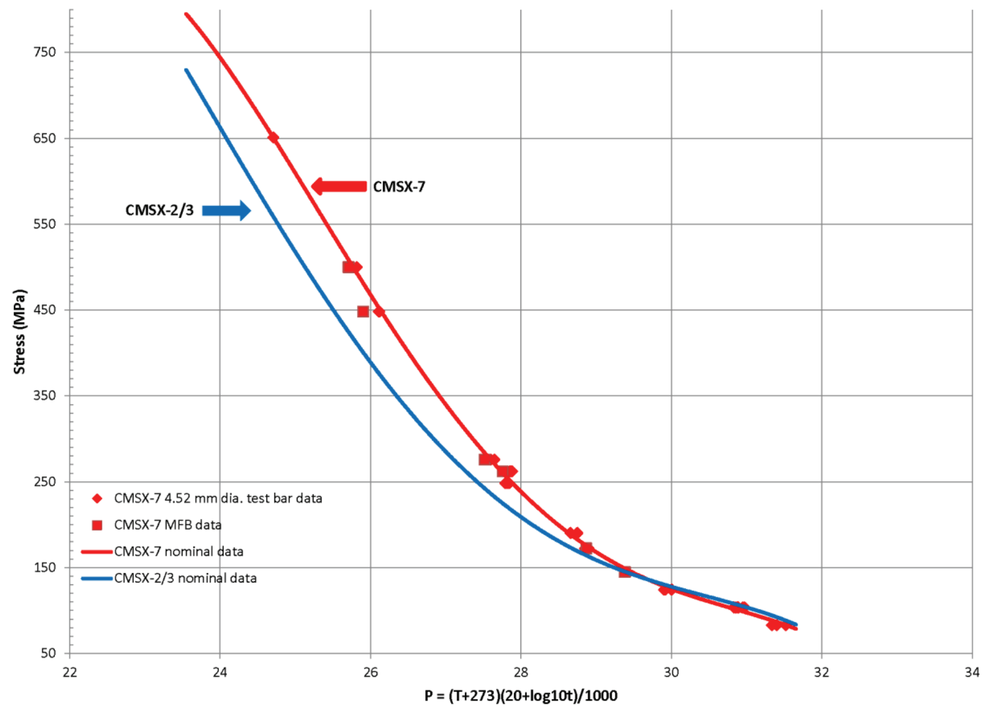

Figure 3. Larson-Miller Rupture Life of CMSX-7 vs. CMSX-2/3

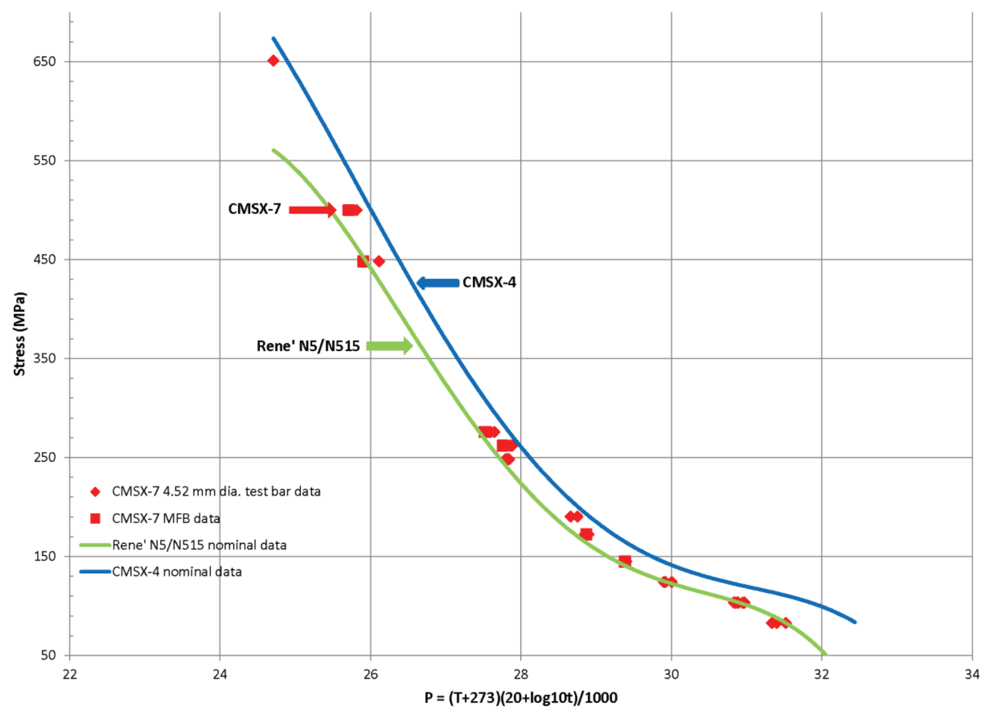

Figure 4. Larson-Miller Rupture Life of CMSX-7 vs. CMSX-4 and Rene’ N5/Rene’ N515

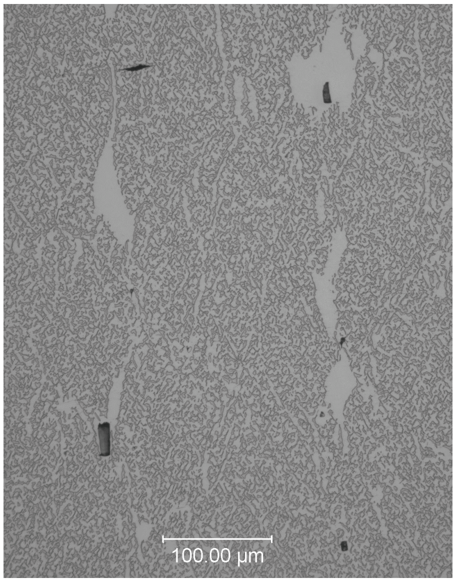

Figure 5. CMSX-7 microstructure following 1176 hours stress-rupture testing at 1093ºC/82.7 MPa (2000ºF/12 ksi)

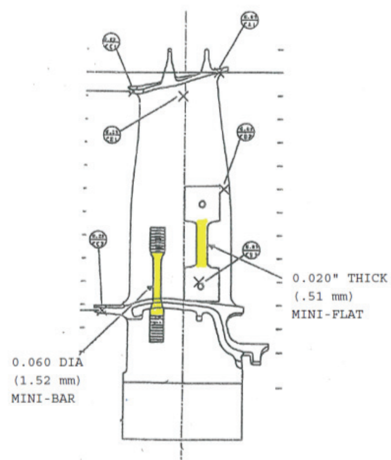

Figure 6. Schematic drawing of machined from blade specimens

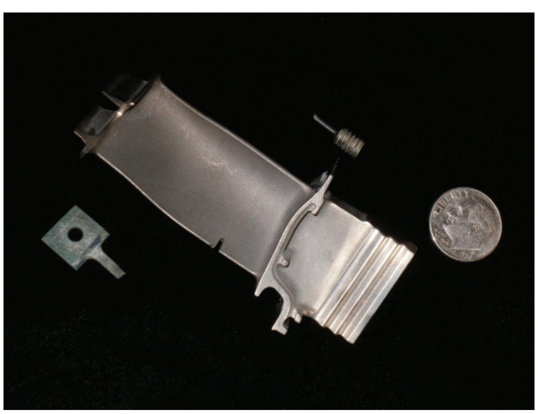

Figure 7. Casting and tested remnants of MFB specimens

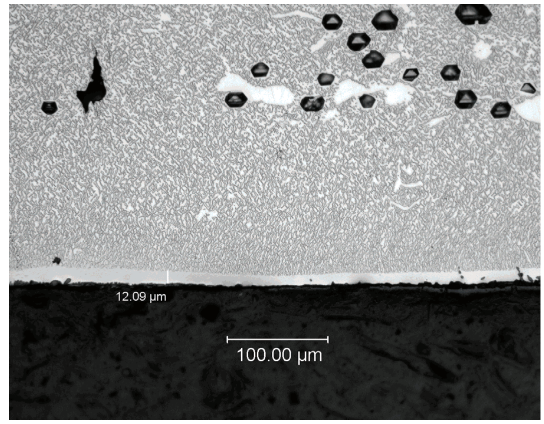

Figure 8. CMSX-7 mini-flat surface denuded zone after 880 hours stress-rupture testing at 1093ºC (2000ºF) showing minimal oxidation/depletion

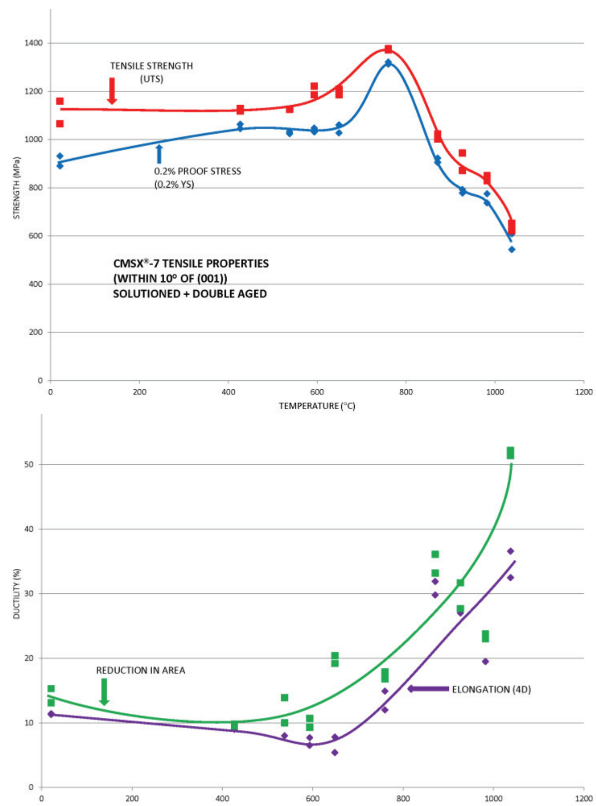

Figure 9. CMSX-7 Tensile Properties

<u>Castability</u>

Initial SX castability assessments for CMSX-7 alloy have been excellent with 95%+ yield for primary orientation and grain defects on test material. DSC solidus and liquidus results for this alloy are 1325ºC (2417ºF) and 1381ºC (2517ºF), respectively.

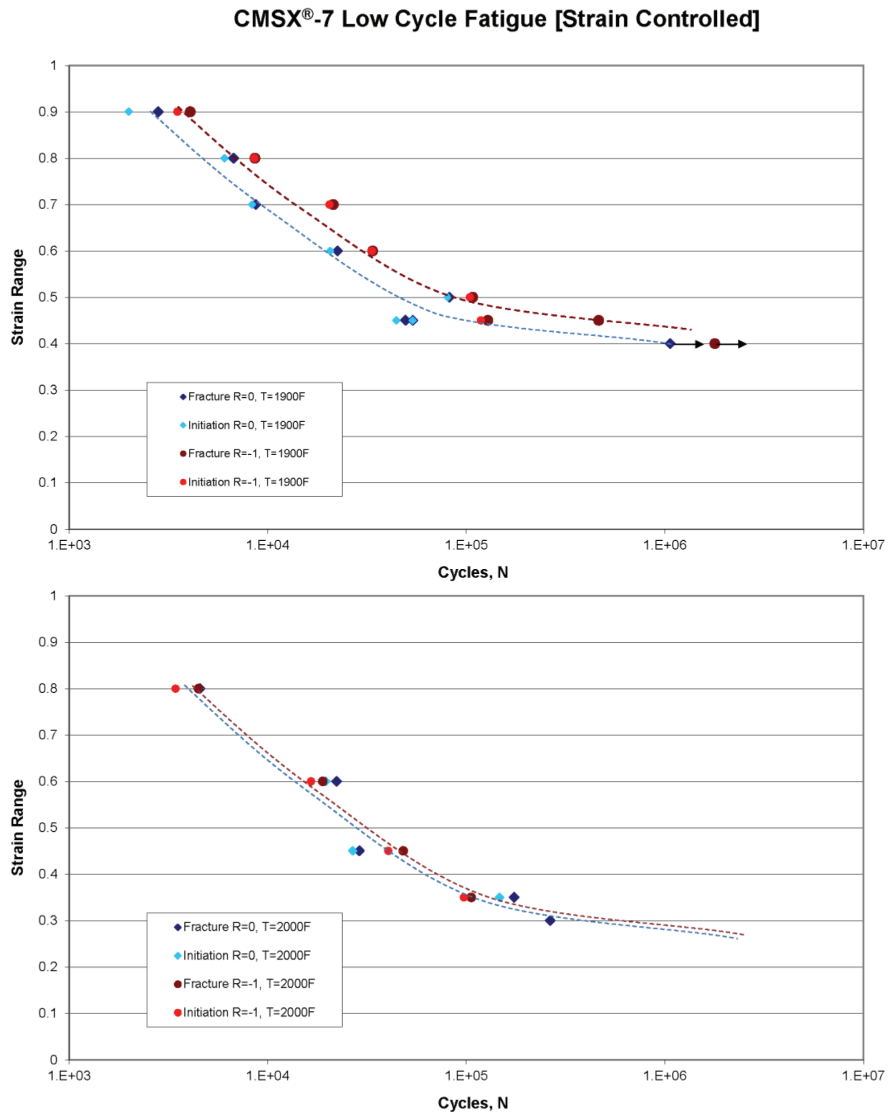

Figure 10. CMSX-7 Strain-controlled LCF at 1038ºC (1900ºF) and 1093ºC (2000ºF)

CMSX-8 Alloy

In a parallel effort, similar development and characterization of low Re CMSX-8 alloy has been undertaken. Development goals were to achieve excellent high temperature creep and low cycle fatigue properties (targeting 2nd generation alloy CMSX-4), along with good oxidation properties/coating adherence, castability and phase stability, but with significantly reduced Re content.

The nominal chemistry of CMSX-8 alloy is provided in Table II. Refractory elements Ta, W, Re and Mo were balanced to achieve good creep-rupture properties (with low Re content), along with acceptable phase stability. Cr and Co content were targeted to ensure phase stability. Similar to CMSX-7 alloy, the high Ta content is designed for SX castability and freedom from freckling defects; Al, Ti and Ta content will attain approximately 70% volume fraction (Vf) γ' phase. High Al, low Mo content plus the small Hf addition improves bare alloy oxidation resistance and coating adherence. The density of CMSX-8 alloy is about 8.85 gms/cm^3.

Table II. CMSX-8 Nominal Chemistry

Element	Wt%	Element	Wt%
Cr	5.4	Re	1.5
Co	10	Al	5.7
Mo	0.6	Ti	0.7
Ta	8	Hf	0.2
W	8	Ni	Balance

Microstructure

Heat treatment development studies have established a multi-step solution/homogenization and double age cycle which produces the microstructure shown in Figures 11 and 12. This depicts complete γ' solutioning with some remnant γ/γ' eutectic, no incipient melting and approximately 0.45µm average cubic aligned γ' phase, indicating appropriate γ/γ' mismatch and γ/γ' interfacial chemistry following the high temperature age.

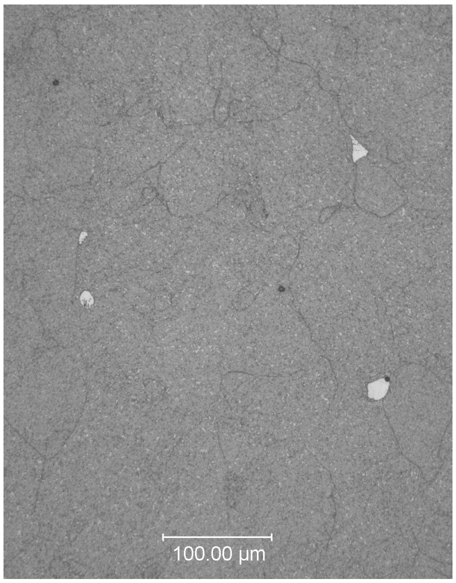

Figure 11. CMSX-8 casting microstructure following solution + double age heat treatment

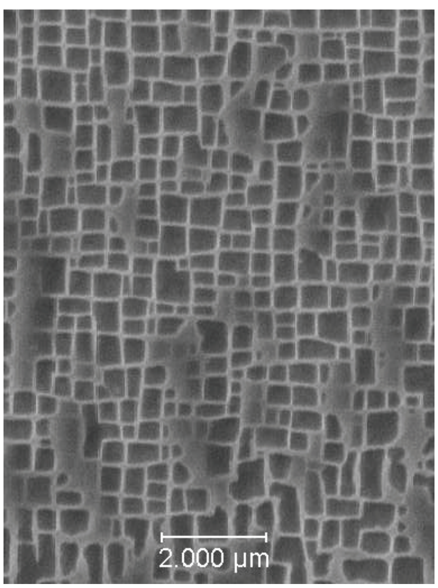

Figure 12. CMSX-8 casting microstructure following solution + double age heat treatment

Mechanical Property Characterization

Extensive creep-rupture, stress-rupture and tensile property testing has been conducted on CMSX-8 alloy. Strain-controlled low cycle fatigue (LCF) property testing is currently in progress.

Larson-Miller rupture life and time to 1% creep for CMSX-8 and CMSX-4 alloys are shown in Figures 13 and 14, respectively [1]. CMSX-8 alloy has similar creep strength and rupture life properties as CMSX-4 alloy (3% Re) up to approximately 1010-1038ºC (1850-1900ºF). CMSX-8 properties fall-off at 1094ºC (2000ºF) and 1121ºC (2050F) due to the lower Re content, as the diffusion inhibiting characteristics of higher Re content become more prevalent. Nevertheless, CMSX-8 rupture life is significantly improved over Rene' N5/Rene' N515 alloys at all temperature/stress conditions [5,6]. Manufactured from blade mini-bar testing confirm excellent retention of thick section properties for thinner-wall applications. Post stress-rupture metallography following 1980 hours at 1093ºC (2000ºF) shows excellent phase stability with negligible TCP phase formation (Figure 15).

Similar to CMSX-7 alloy, post-test metallography on a CMSX-8 mini-flat specimen (0.51 mm/.020" thick) exhibits minimal surface depletion following stress-rupture testing at 1093ºC (2000ºF) (Figure 16). This suggests excellent bare oxidation performance, which will be further assessed in the turbine engine OEM oxidation/hot corrosion testing and ORNL bare and coated oxidation testing previously discussed.

CMSX-8 alloy tensile properties as a function of temperature are shown in Figure 17. The alloy exhibits excellent tensile strength, while maintaining good ductility across the range of temperature.

Strain-controlled low cycle fatigue (LCF) testing of CMSX-8 alloy is in progress. The matrix will include testing both fully heat treated and HIP'ed + heat treated specimens at 1038ºC (1900ºF) and 1093ºC (2000ºF) to establish typical S-N curves, with R-ratio = 0 or -1. Results to data at 1038ºC (1900ºF) are shown in Figure 18.

Physical Property Testing

CMSX-8 physical properties have been characterized in collaboration with the National Physical Laboratory (NPL) in the United Kingdom. Density as a function of temperature (computed from room temperature density and thermal expansion) is shown in Figure 19; Young's and shear moduli (averaged and expansion-corrected) vs. temperature is provided in Figure 20; thermal diffusivity as a function of temperature compared to CMSX-4 alloy in Figure 21; and thermal conductivity vs. temperature in Figure 22. (The thermal conductivity data was estimated from experimental thermal diffusivity and density and estimated specific heat based on data for CMSX-4 alloy.)

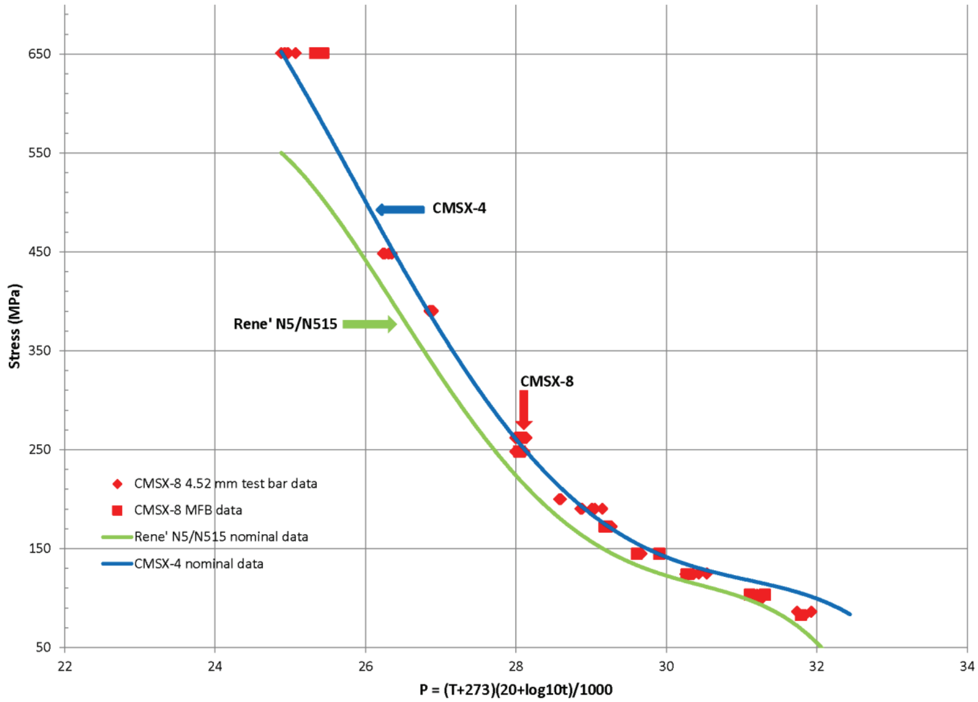

Figure 13. Larson-Miller Rupture Life of CMSX-8 vs. CMSX-4 and Rene' N5/Rene' N515

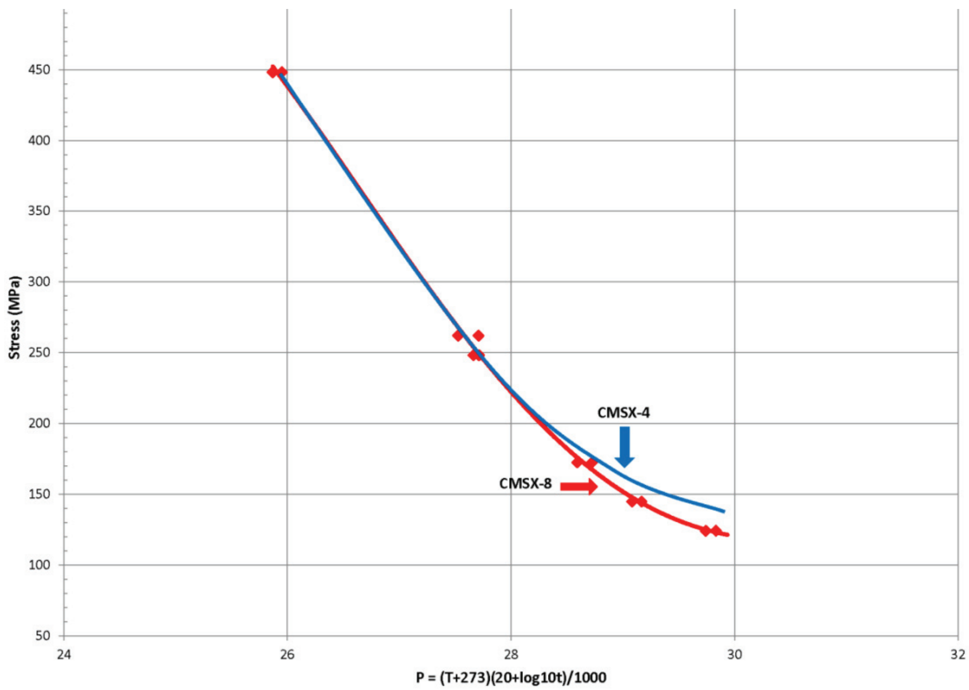

Figure 14. Larson-Miller Time to 1% Creep of CMSX-8 vs. CMSX-4

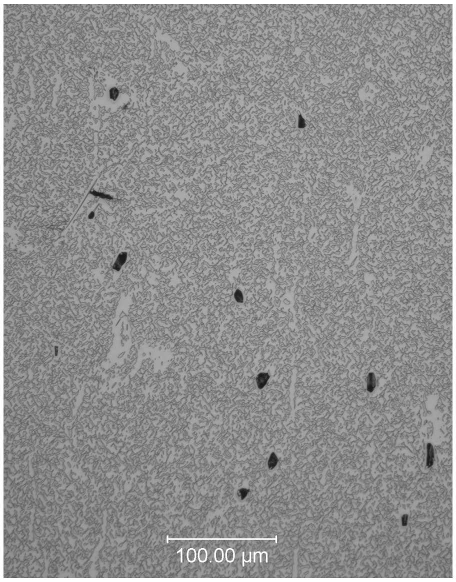

Figure 15. CMSX-8 microstructure following 1980 hours stress-rupture testing at 1093ºC/82.7 MPa (2000ºF/12 ksi)

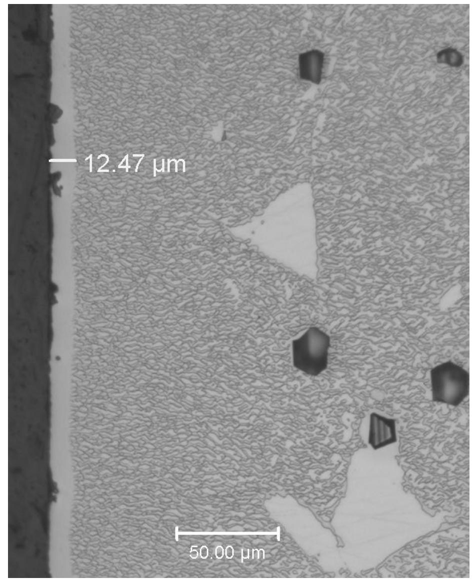

Figure 16. CMSX-8 mini-flat surface denuded zone after 1240 hours stress-rupture testing at 1093ºC (2000ºF) showing minimal oxidation/depletion

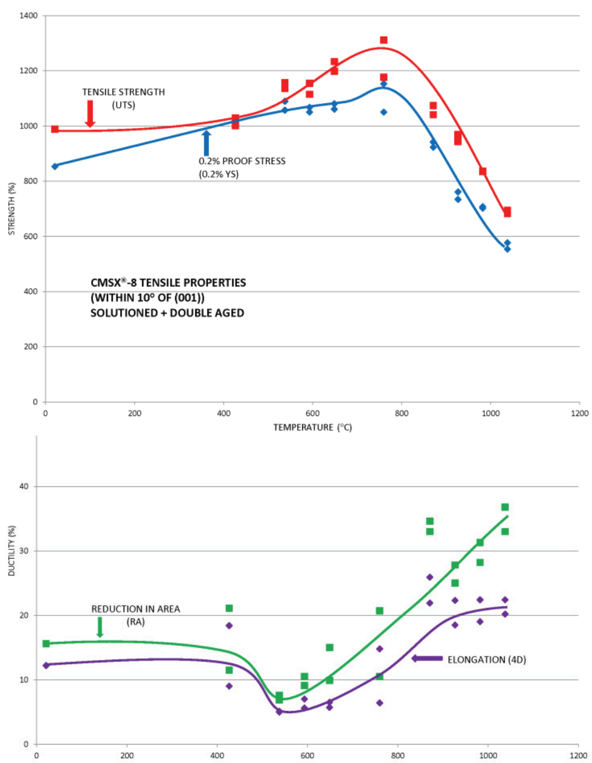

Figure 17. CMSX-8 Tensile Properties

In addition, physical property calculations using a well-established ONERA methodology provide the following estimations for CMSX-8 alloy: γ' solvus, approximately 1284ºC (2343ºF); calculated γ' Vf is 74%. Md values, calculated based on the method originally proposed by Morinaga in 1984 [10] and later applied by the ONERA methodology are as follows: Md_{total} - 0.993, and the Mdγ - 0.893 [11, 12]. This data is indicative of the highly alloyed nature of CMSX-8 alloy. However, as previously indicated, testing to date does not indicate any significant deleterious TCP phase formation.

Castability

Initial SX castability assessments have been excellent with 95%+ yield for primary orientation and grain defects on test material. DSC solidus and liquidus results for this alloy are 1338ºC (2440ºF) and 1389ºC (2532ºF), respectively. Additional castability evaluations are underway at multiple SX foundries for comparison to production components.

Alloy Enhancements/Modifications

Consistent with prior work on advanced single crystal components, there are at times application requirements for enhanced oxidation resistance and/or thermal barrier coating life. In these instances, limiting the maximum sulfur content below 0.5 ppm, along with the addition of reactive elements lanthanum (La) and yttrium (Y) have been shown to improve oxidation and coating properties [13]. Follow-on evaluations of alloys CMSX®-7(SLS)[La+Y] and CMSX®-8(SLS)[La+Y] to characterize these effects are planned.

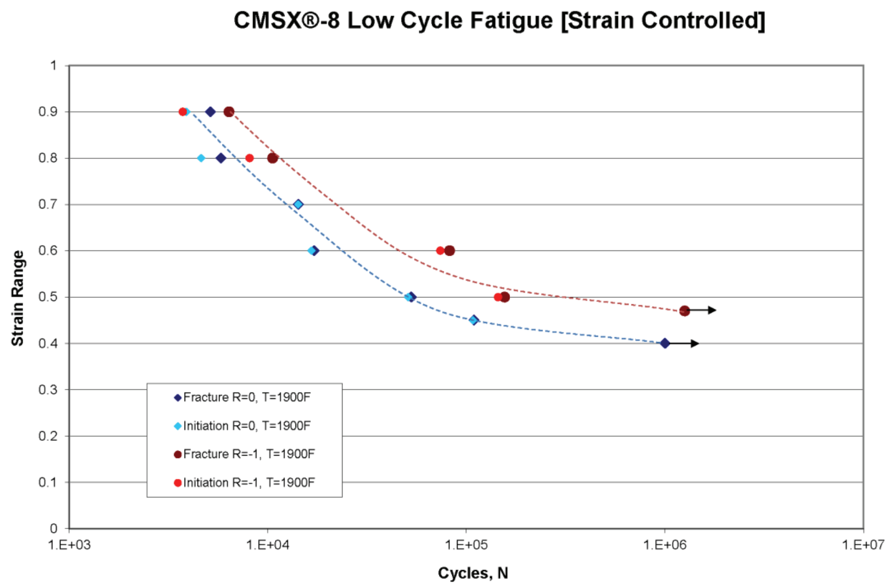

Figure 18. CMSX-8 1038ºC (1900ºF) Strain Controlled LCF

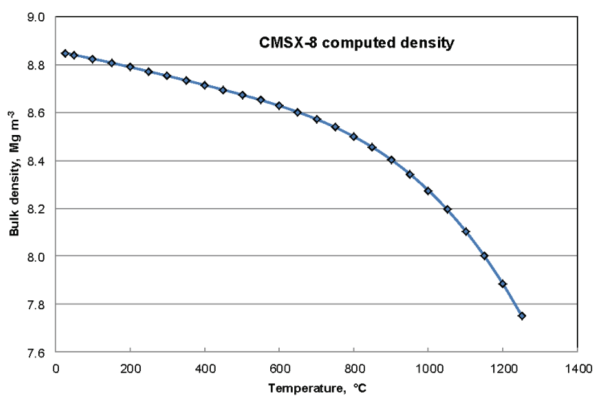

Figure 19. CMSX-8 Density as a function of Temperature

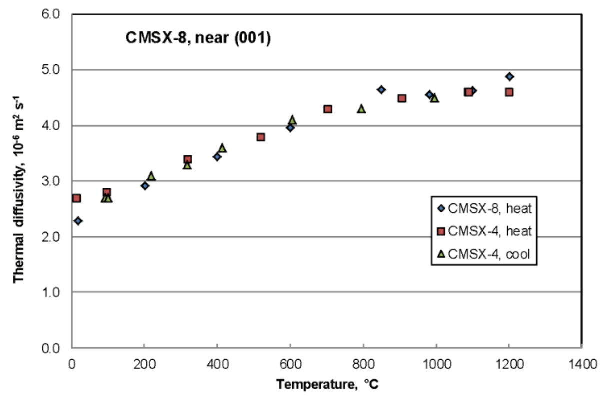

Figure 21. Thermal Diffusivity of CMSX-8 and CMSX-4 vs. Temperature

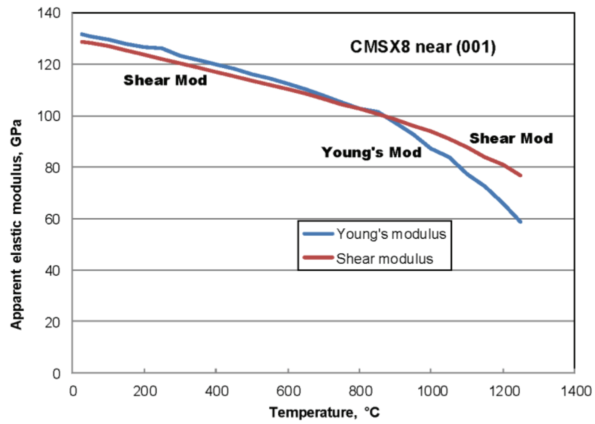

Figure 20. Young's Modulus and Shear Modulus vs. Temperature for CMSX-8

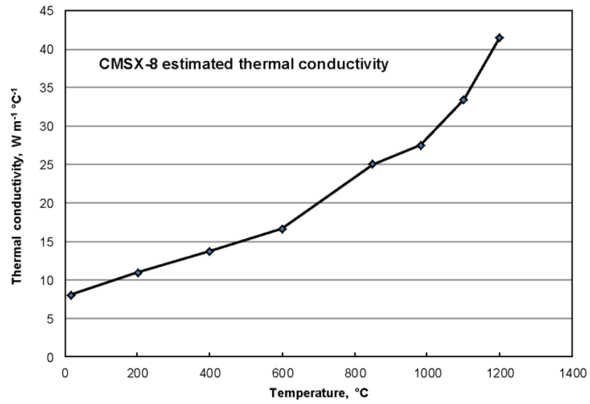

Figure 22. CMSX-8 Thermal Conductivity vs. Temperature

Similarly, it has been shown that additions of grain boundary strengthening elements carbon (C) and boron (B) improve the low angle boundary (LAB) grain defect accommodation for large, difficult to cast industrial gas turbine (IGT) SX components, with some reduction in maximum alloy temperature capability [14]. There is also a greater risk of recrystallized grain formation nucleating at the carbides during solution heat treatment. Assessment of the modified alloy CMSX-8(B/C) solution heat treatment, microstructure, alloy properties, LAB/HAB grain defect accommodation and castability is currently in progress.

Summary

Cannon-Muskegon has developed two new single crystal alloys, CMSX-7, containing no Re, and low Re CMSX-8, which offer exciting opportunities for lower alloy cost applications for new and existing aero and industrial gas turbine components.

CMSX-7 alloy demonstrates improved properties over existing non-Re-bearing SX alloys such as CMSX-2/3 and are remarkably competitive to Re-containing alloys Rene' N5 and Rene' N515. Initial 1038ºC (1900ºF) LCF properties for CMSX-7 are similar to nominal CMSX-4 alloy results. CMSX-7 has demonstrated excellent castability and phase stability. Further characterization of mechanical properties, oxidation and castability for CMSX-7 alloy are in progress.

CMSX-8 alloy (1.5% Re) is comparable to CMSX-4 (3% Re) in terms of creep/stress-rupture properties to at least 1010ºC (1850ºF), with properties that exceed Rene' N5 (3% Re)/Rene' N515 (1.5% Re) alloys at all temperature/stress conditions. Further creep/stress-rupture, LCF, oxidation and component castability evaluations are ongoing.

In addition, alloy modifications for enhanced oxidation resistance and improved grain defect accommodation are also under evaluation.

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Bob Plecki - Joliet Metallurgical
Aaron Stephenson – Mar-Test, Inc.
Roger Morrell - NPL
Tom Versalle – Cannon-Muskegon

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