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Improved Performance Rhenium Containing Single Crystal Alloy Turbine Blades Utilising PPM Levels of the Highly Reactive Elements Lanthanum and Yttrium.

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ABSTRACT

Turbine inlet temperatures have now approached 1650°C (3000°F) at maximum power for the latest large commercial turbofan engines, resulting in high fuel efficiency and thrust levels approaching or exceeding 445 kN (100,000 lbs.). High reliability and durability must be intrinsically designed into these turbine engines to meet operating economic targets and ETOPS certification requirements.

This level of performance has been brought about by a combination of advances in air cooling for turbine blades and vanes, computerized design technology for stresses and airflow and the development and application of rhenium (Re) containing, high γ' volume fraction nickel-base single crystal superalloys, with advanced coatings, including prime-reliant ceramic thermal barrier coatings (TBCs). Re additions to cast airfoil superalloys not only improve creep and thermo-mechanical fatigue strength but also environmental properties, including coating performance. Re slows down diffusion in these alloys at high operating temperatures.(1)

At high gas temperatures, several issues are critical to turbine engine performance retention, blade life and integrity. These are tip oxidation in particular for shroudless blades, internal oxidation for lightly cooled turbine blades and TBC adherence to both the airfoil and tip seal liner. It is now known that sulfur (S) at levels < 10 ppm but > 0.2 ppm in these alloys reduces the adherence of α alumina protective scales on these materials or their coatings by weakening the Van der Waal's bond between the scale and the alloy substrate. A team approach has been used to develop an improvement to CMSX-4® alloy which contains 3% Re, by reducing S and phosphorus (P) levels in the alloy to < 2 ppm, combined with residual additions of lanthanum (La) + yttrium (Y) in the range 10-30 ppm. Results from cyclic, burner rig dynamic oxidation testing at 1093°C (2000°F) show thirteen times the number of cycles to initial alumina scale spallation for CMSX-4 [La + Y] compared to standard CMSX-4.

A key factor for application acceptance is of course manufacturing cost. The development of improved low reactivity prime coats for the blade shell molds along with a viable, tight dimensional control yttrium oxide core body are discussed. The target is to attain grain yields of single crystal CMSX-4 (ULS) [La + Y] turbine blades and casting cleanliness approaching standard CMSX-4. The low residual levels of La + Y along with a sophisticated homogenisation/solutioning heat treatment procedure result in full solutioning with essentially no residual γ/γ' eutectic phase, Ni (La, Y) low melting point eutectics and associated incipient melting pores. Thus, full CMSX-4 mechanical properties are attained. The La assists with ppm chemistry control of the Y throughout the single crystal turbine blade castings through the formation of a continuous lanthanum oxide film between the molten and solidifying alloy and the ceramic core and prime coat of the shell mold. Y and La tie up the < 2 ppm but > 0.2 ppm residual S in the alloy as very stable Y and La sulfides and oxysulfides, thus preventing diffusion of

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the S atoms to the alumina scale layer under high temperature, cyclic oxidising conditions. La also forms a stable phosphide.

CMSX-4 (ULS) [La + Y] HP shroudless turbine blades will commence engine testing in May 1998.

NOMENCLATURE

Ce = cerium
ETOPS = extended over water, twin engine certification requirements
k cal/g mol = kilo calories/per gram mol
kj/g mol = kilo joules/per gram mol
kN = kilo Newton
La = lanthanum
LCF = low cycle fatigue
m bar = milli bars
mg = milligram
mm = millimeter
Ni = nickel
O = oxygen
P = phosphorus
ppm = part per million
Re = rhenium
RE = reactive elements
S = sulfur
SFC = specific fuel consumption
SX = single crystal
TBC = thermal barrier coating
ULS = ultra low sulfur
Y = yttrium
Zr = Zirconium
α = alpha
μm = micro meters
γ = gamma phase
γ' = gamma prime phase
ΔG = free energy of formation

INTRODUCTION

The assumption that S is the dominant element in degrading the protective aluminum oxide scale is supported by a number of researchers (1, 2, 3, 5, 6, 7, 8, 9, 10 and 11). The beneficial effect of Y additions has been identified by Aimone and McCormick (5) and is considered to be due to the combination of this element with S, forming Y oxysulphide ($Y_2O_2S_2$). The available data for the Gibbs standard free energy of formation at 1100°K gives the following values. (12)

$$\Delta G \quad Y_2O_2S = -354 \text{ k cal / g mol (4)}$$
$$\Delta G \quad YS = -97.4 \text{ k cal / g mol (5)}$$

The suppression of the detrimental effect of S will therefore require the addition of Y to a level at least 6 times the S content based stoichiometrically on the ratio of atomic weights viz. S 32, Y 89. For superalloys containing a nominal 5 ppm of S, an addition of at least 30 ppm of Y is required. At this level, which exceeds the solubility limit in CMSX-4 alloy, there is a significant risk of internal incipient melting since Y forms a series of eutectics with nickel from 1285°C to 805°C (Fig. 1).

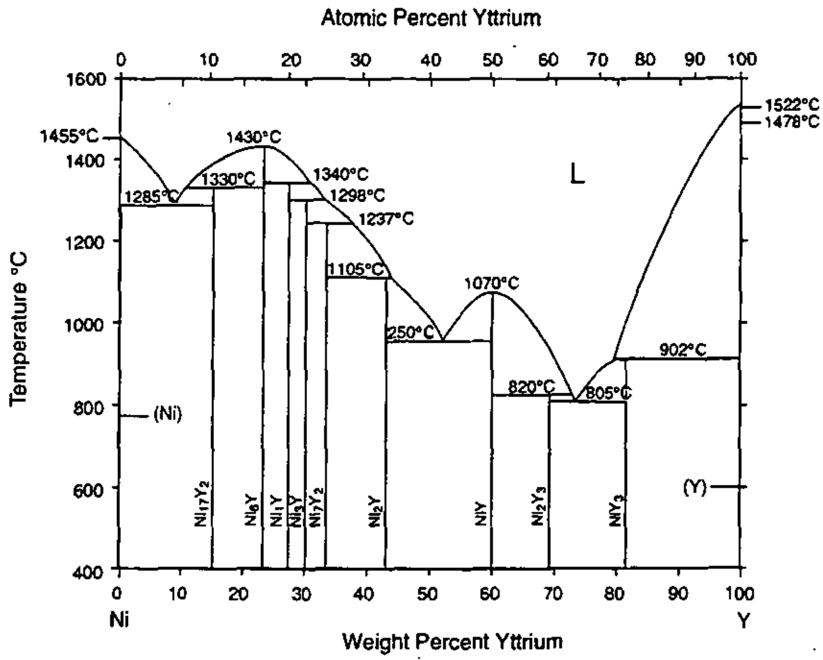


Figure 1

MANUFACTURING TECHNOLOGY

The manufacturing difficulties associated with Y additions are well known (4) and it is necessary to make significant Y additions to the alloy charge to give sufficient residual Y in the SX casting. Work reported by Aimone (5) suggest that only 10% at best is retained in round test bars. Turbine blades with high surface area/volume ratios and containing cores will be expected to retain significantly less than round bars.

The reason for this loss of Y includes evaporation from the melt, reaction with the mold and reaction with the core material. Considering loss by evaporation, the equilibrium vapor pressure of Y at 1475°C is 7.4 x 10^{-4} m bar and 1.6 x 10^{-3} m bar at 1525°C (15). Since a typical casting vacuum is around 5 x 10^{-4} m bar there is a possibility of evaporation, particularly if the vacuum pressure is dynamic.

Turning to Y loss through shell and core reaction, both materials contain silica and from thermodynamic considerations (11) it is clear that Y will reduce silica to yttria, which in turn will form Y_2O_3 $2SiO_2$ (Fig. 2).

$$\Delta G \; SiO_2 = -538 \text{ kj / g mol (1727°C)}$$
$$\Delta G \; Y_2O_3 = -1348 \text{ kj / g mol (1727°C)}$$

and

$$3SiO_2 + 4Y \rightarrow 2Y_2O_3 + 3Si$$

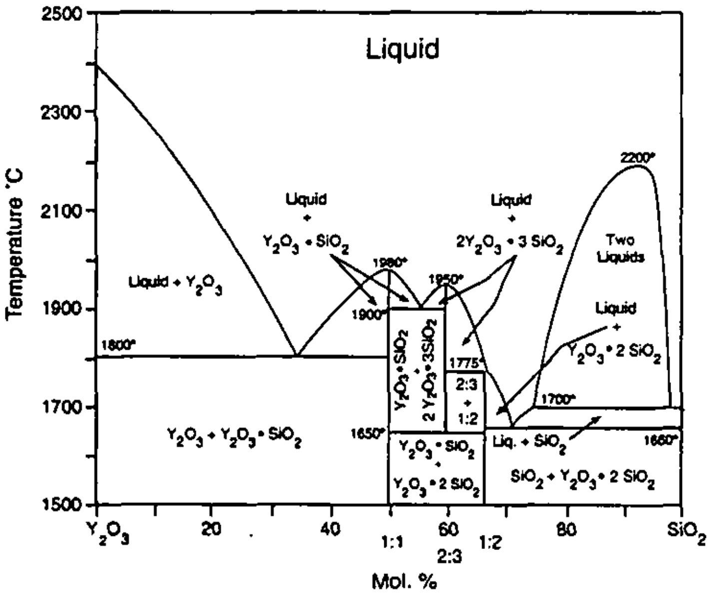


Figure 2

A practical solution is to vacuum induction melt and refine the SX alloy using high quality, low S and P virgin raw materials and ultra-low S and P containing refractories. The evaluation and development work at RR to establish a low cost manufacturing method for Y additions used CMSX-4 (nominal composition shown in Table I) melted by CM with a nominal S level of approximately 1.5 ppm. To achieve the required combination with Y, 7-10 ppm of this element is needed to be retained in the single crystal (SX) castings.

CMSX-4 Alloy
Nominal Composition Wt %

Ni	Base
Cr	6.5
Co	9
Mo	.6
Ta	6
W	6
Re	3
Al	5.6
Ti	1.0
Hf	.1

Table I. Density 8.70 kg/dm^3

Evaluation work has been carried out by the RR research foundry to investigate the extent of Y loss in the manufacture of SX turbine blades. The work involved the casting of turbine blades with and without ceramic cores under different casting conditions and analyzing the residual Y in the casting and the ceramic mold. The following variables were investigated, using constant conventional molding materials based on silica, zircon and alumina.

(i) Y charge additions of 400 ppm and 500 ppm
(ii) Mold/cast temperatures of 1475°C and 1525°C

The results are shown in Figures 3, 4, 5 and 6 and the relationship between the amount of retained Y and the volume to surface area relationship shown in Figure 5. These results clearly show that the loss of Y is due to reaction with ceramics used in the casting process. However, provided the casting temperature can be kept to a minimum, it is possible to retain sufficient Y in low S alloys without resorting to special ceramics such as yttria molds.

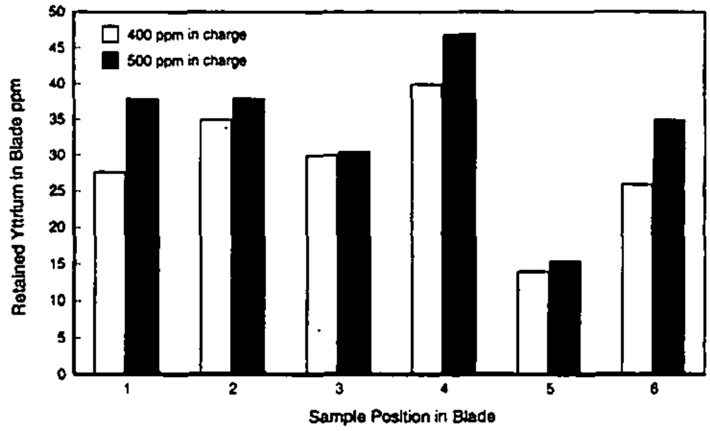


Figure 3 - Retained yttrium in solid blades.

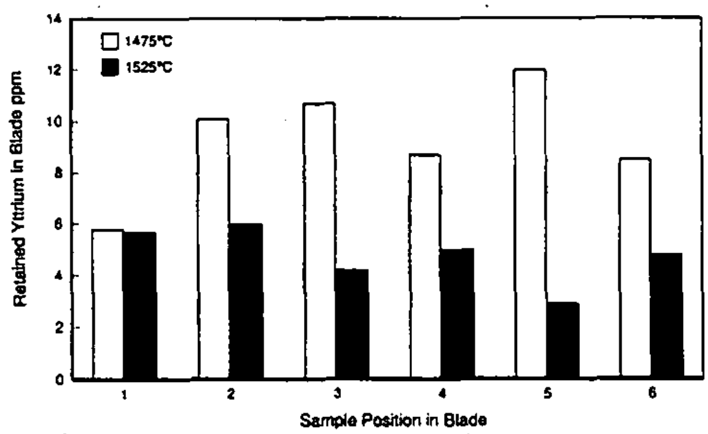


Figure 4 - Retained yttrium in cored blades.

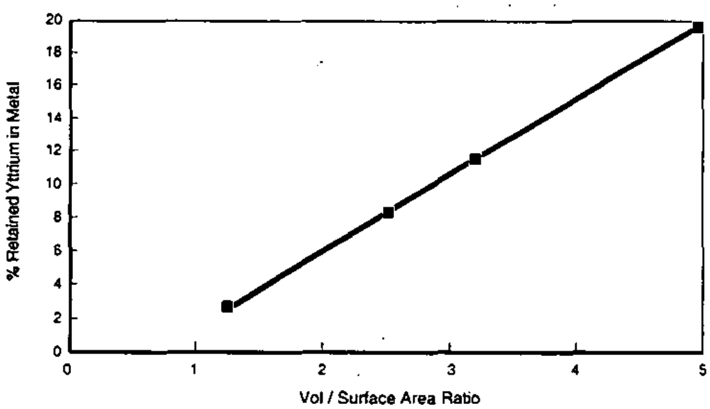


Figure 5 - Effect of surface area on level of retained yttrium.

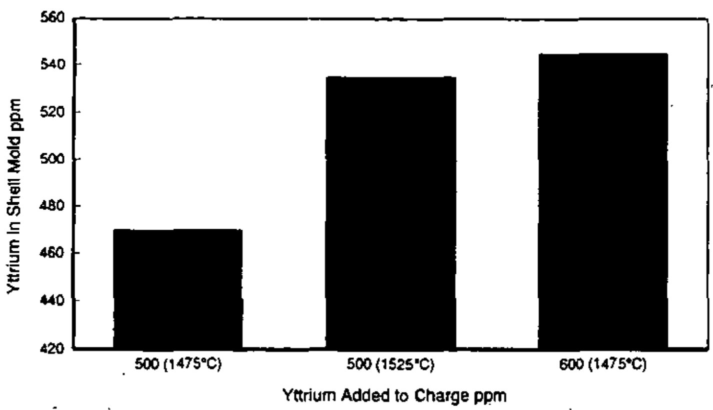


Figure 6 - Yttrium in shell molds cast a different temperatures.

Additions of La were carried out to establish if this element could be retained in SX castings at a higher level than an equivalent amount of Y. The results of analysis from round test bars showed a retention level of approximately twice that of Y. Further trials with additions of both Y and La gave similar results. The amount of La added was the same atomic percentage of Y. The results from these trials are summarised in Figure 7.

Test Piece (25 mm dia)	Residual Quantity ppm	
	Yttrium	Lanthanum
CMSX-4 + Y (400 ppm)	30	-
CMSX-4 + La (500 ppm)		70
CMSX-4 + La (180 ppm)		26
CMSX-4 + La (100 ppm) + Y (75 ppm)	5	9

Figure 7 - Comparitive Retention of Y, La and La + Y in round SX test bars.

To establish if the results from the test bars could be applied to actual turbine blades, a number of the same design as used for the Y trials were SX cast. The aim was to produce the same levels of Y and La in the blades. To achieve this, 200 ppm of Y and 160 ppm of La were added to the remelt bar charge. Typical results from the analysis of the castings are shown in Figure 8.

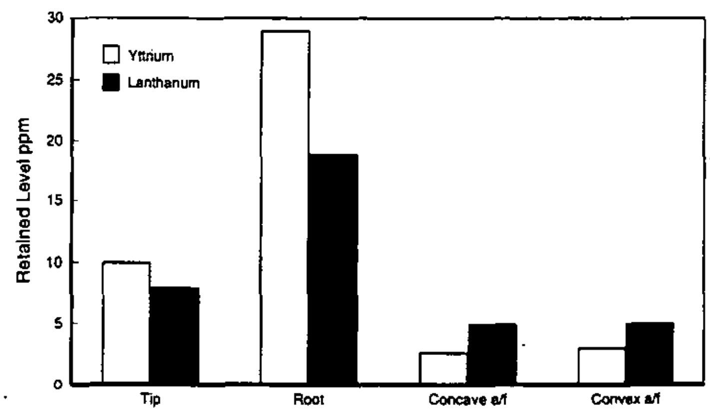


Figure 8 - Retained yttrium and lanthanum in turbine blades.

The results from both the CMSX-4 + Y and CMSX-4 + Y + La trials show that it is possible to retain these elements at a level sufficient to reduce the detrimental effect of S using conventional foundry materials and practice. However, the effect of cores is significant as this material appears to be responsible for most of the dilution of Y and La (Figs. 3 and 4). This problem has been addressed through the development of core materials and cores have been manufactured in both alumina and yttria. Of these two materials, yttria offers the most advantage due to its chemical inertness and ease of removal (16) by core leaching. Work to further investigate this material with respect to Y and La ppm chemistry control and minimisation of grain defects in the SX cored airfoil castings is continuing.

BURNER RIG OXIDATION TESTING

Test Procedure

To initially evaluate the potential benefits for oxidation performance of CMSX-4 with highly reactive element (RE) additions, cyclic dynamic oxidation tests were conducted. Samples of 5.5 mm diameter by 115 mm long were machined from SX test bars. The CMSX-4 alloy used to produce the test bars with and without RE additions contained < 2 ppm S. The samples were lightly grit blasted prior to testing. The samples were tested in a Becon burner rig which is comprised of a modular combustor in which the JP-5 fuel is injected into the primary region, mixed with air and ignited. Secondary air is used to dilute the combustion products to control the burner outlet temperature. The total pressure of the air used in the primary was fixed, yielding approximately the same gas Mach number.

During the test, the pins were removed from the flame and blasted with room temperature air for five minutes following every hour of flame testing.

The oxidation progression was monitored visually and gravimetrically. The samples were photographed after intervals during which significant amounts of oxidation had occurred. The samples were also weighed to the nearest 0.01 mg. The mass change from the initial mass was determined and divided by the areas which were exposed to the hottest portion of the flame, a length of approximately 25 mm. The specific mass change was plotted with a microscopic examination of the test articles occurring after the final exposure. Tests with La doped CMSX-4 were conducted at 1038°C, 1093°C and 1149°C (1900°F, 2000°F, and 2100°F), while the other reactive element additions were tested at 1093°C and 1149°C.

Oxidation Results

CMSX-4 + La tested at 1038°C (1900°F) exhibits approximately a 15 times increase in life to zero crossover of specific weight change compared to conventional CMSX-4; no comparison can be made regarding the life to a fixed mass loss since the RE doped sample was not tested for a sufficiently long enough time to reach sizable mass losses. These results are shown in Figure 9. The doped sample did not exhibit significant amounts of surface roughening after 3000 hours of exposure compared to the localized attack which occurred on the standard CMSX-4 alloy surface after only 1000 hours.

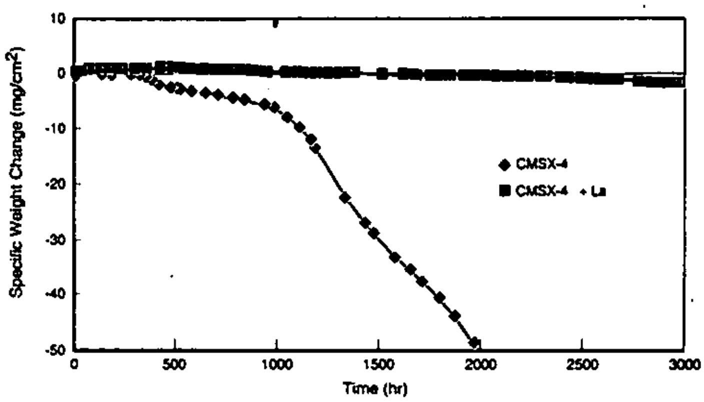


Figure 9 - 1038°C (1900°F) dynamic oxidation test results for Bare CMSX-4 with La addition and without.

The trend of increased life of the RE doped alloys over the conventional chemistry alloy can further be seen in Figure 10 which shows the plot of the gravimetric results for the 1093°C (2000°F) test. All of the reactive element doped samples are included on this plot. These samples include CMSX-4 + Y, La, (La + Y), and Ce in addition to the conventional CMSX-4 alloy. The data clearly reveal increased oxidation resistance with the addition of the RE. The lives relative to a sample loss of approximately 25 μm of metal, calculated based on the density of the alloy, are presented in Table II. The benefit of reactive elements also depends on the type of RE that is added. At 1093°C the Y or La additions alone are not as potent as the Y + La dopants combined. The effect of the Ce addition cannot be ascertained due to the short time the sample was exposed (<400 hrs.).

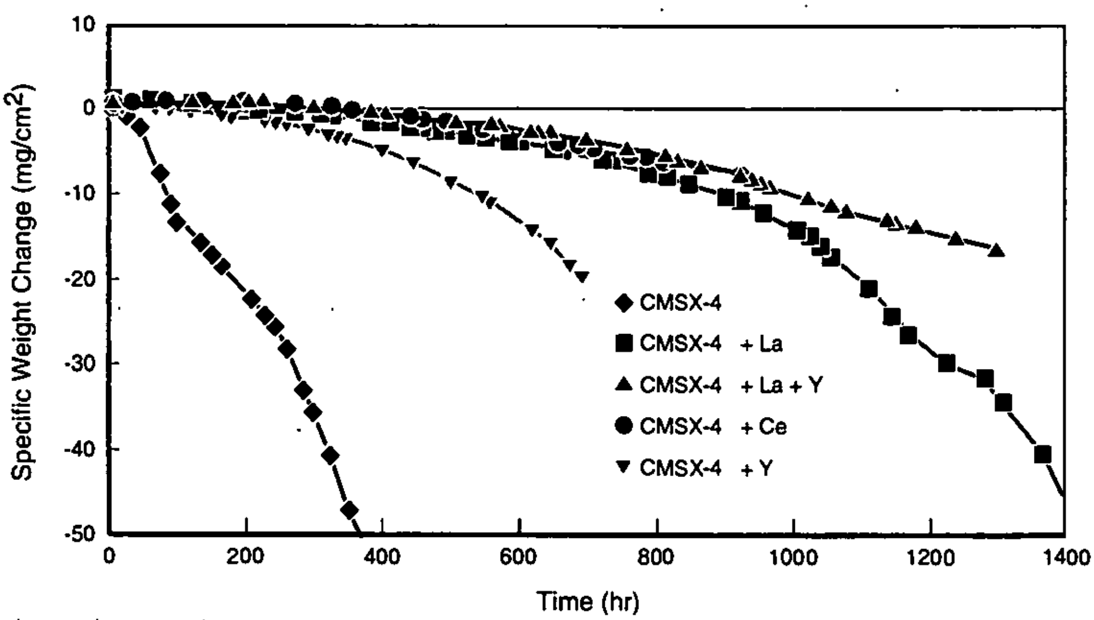


Figure 10 - 1093°C (2000°F) dynamic oxidation test results for Bare CMSX-4 with RE additions and without.

CMSX-4 and reactive element addition	Time (hours) to reach 10 mg/cm^2 (25μm)
1038°C (1900°F)	
None	1100
La	>3000
1093°C (2000°F)	
None	100
La	950
Y + La	1100
Ce	>300
Y	600
1149°C (2100°F)	
None	30
La	~520
La + Y	350
Ce	410

Table II. Life of oxidation tested CMSX-4 with and without reactive element additions. Life is based on the time to lose approximately 10mg/cm², which corresponds to roughly 25μm based on density considerations.

Oxidation of the samples at 1149°C (2100°F) reveals a slightly different result regarding the benefits of RE dopants, as shown in Figure 11. Conventional CMSX-4 clearly does not have adequate oxidation resistance at this temperature in this test as evidenced by its loss of approximately 25μm in less than 30 hours. Samples with RE additions exhibit lives at least ten times greater than conventional CMSX-4. As indicated in the graphs and Table II. The ranking of the additions from worst to best is as follows: (La + Y), Ce and La at 1149°C.

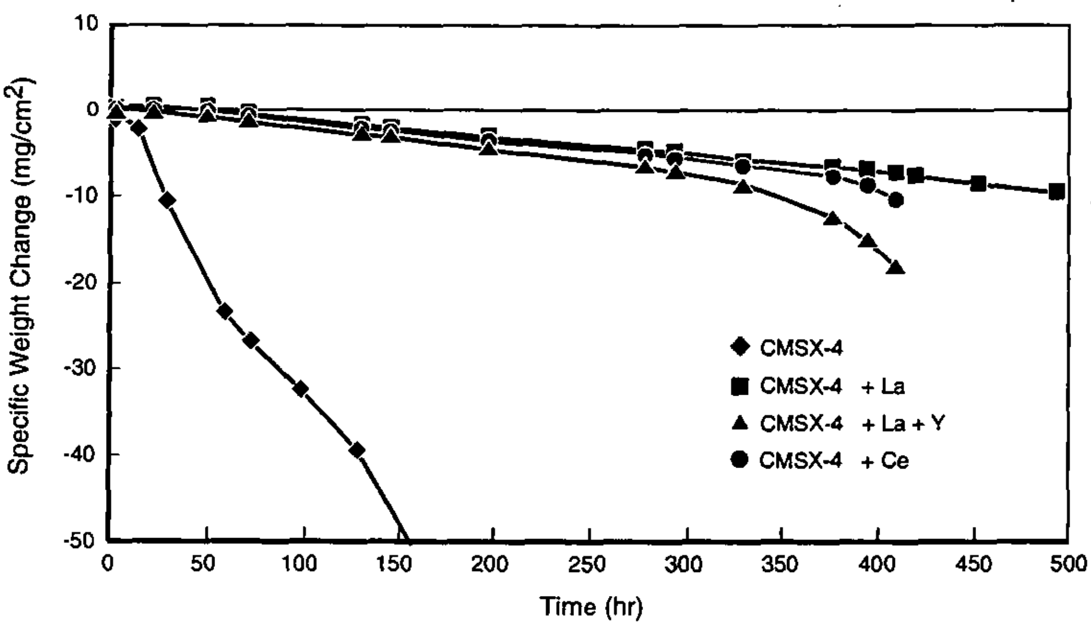


Figure 11 - 1149°C (2100°F) dynamic oxidation test results for Bare CMSX-4 with RE additions and without.

Summary

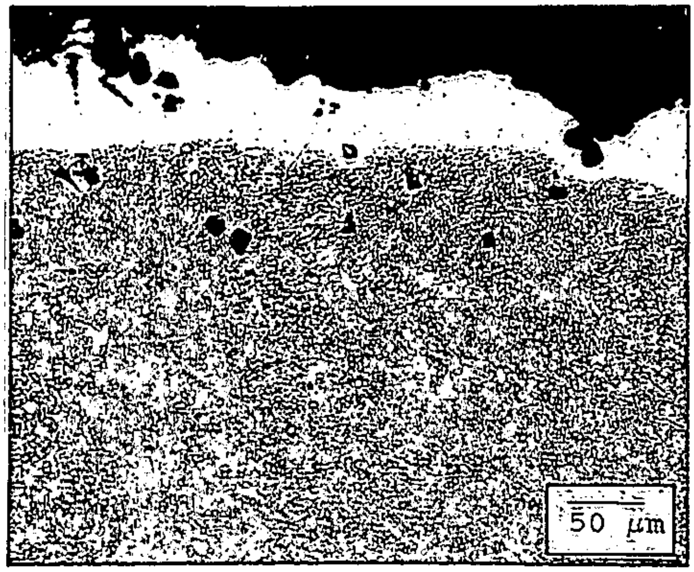
The oxidation behavior of bare CMSX-4 can be dramatically improved by the addition of highly reactive elements (REs). The factor of improvement varies from in excess of 3 to approximately 13 depending on the elemental addition and exposure temperature. There is some variability of the effect of the RE. This could be due to minor variations in the actual RE content in the test pieces. Only one sample from each mold was analyzed for chemistry.

Figure 12 shows the change in sample surface morphology of CMSX-4 and CMSX-4 + La following burner rig cyclic oxidation testing at 1038°C (1900°F) for 3000 -3500 hrs. These micrographs clearly demonstrate that fewer voids and pores are present in the La doped sample. In addition , the amount of surface region alloy depletion is appreciably less.

TURBINE ENGINE APPLICATION AND TESTING

The design of commercial turbofan engines continues to improve in response to the needs of the extremely competitive airline market. Designs that weigh less and have higher fuel efficiencies are required to keep a competitive advantage and thus during recent years both the compressor delivery and turbine rotor inlet temperatures have continued to rise. While improved cooling schemes are employed, the demand for higher fuel

3500 hrs
CMSX-4 1038°C (1900°F)



3000 hrs
CMSX-4 + La 1038°C (1900°F)

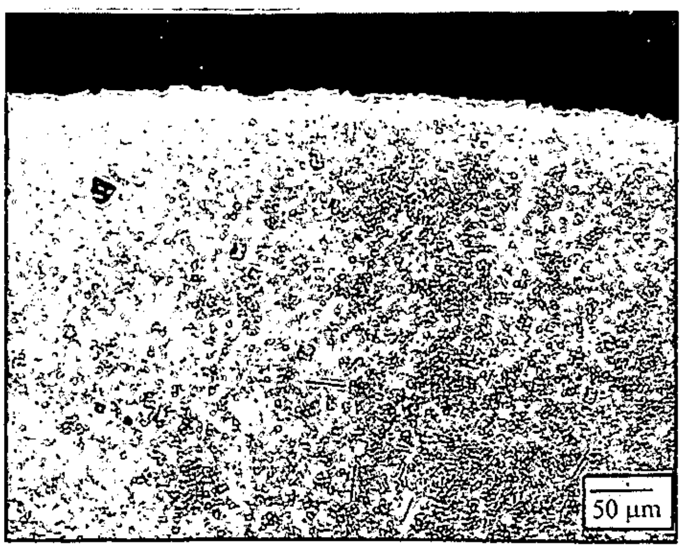


Figure 12: Burner Rig Post-Test Microstructures

efficiencies quickly dictates the minimum required cooling air for the turbine blades and as a result blade metal temperatures have been pushed to new levels.

In addition to fuel efficient, light weight engines, the military and commercial aero turbine engine markets also need engines that will remain on wing for extended overhaul intervals and drive down operating cost. As a result the design must carefully consider durability and specific fuel consumption (SFC) (temperature margin) deterioration rates. One of the single most dominating factors in turbine performance is high pressure turbine blade tip clearance and this clearance can easily be impacted by the oxidation of the blade tip (16) in case of the shroudless blades and of tip seal liners for both shrouded and shroudless blades. Tip coatings are often used to provide environmental protection but they can present bonding and durability problems particularly if the blade and the tip seal liners touch. The optimum cost effective solution is to develop a method of improving the oxidation characteristics of the bare blade alloy itself, thus providing full oxidation protection for the entire tip configuration. The addition of La + Y to CMSX-4 shows intriguing promise of accomplishing this goal by reducing base metal oxidation rates by an order of magnitude combined with improved SX castability and product casting yield compared to the use of Y alone. Additionally, the application of CMSX-4 to the tip seal liners has enabled the plastic deformation of the component to be minimized, resulting in small tip clearances and resultant improved engine efficiency.

Internal oxidation of air-cooled turbine airfoils also represents a technical challenge in modern gas turbine engines. The cooling air temperatures have risen with increased pressure ratio engines and the second generation single crystal alloys are allowing higher metal temperatures before being limited by creep or stress rupture strength. This can lead to internal oxidation, since many turbine blades operate with protective coatings only on the external surfaces of the airfoil. Coating internal passages is possible; however, there are several unique challenges: (1) blocking and plugging of small passageways, (2) embrittlement due to the coating leading to low cycle fatigue (LCF) failures, (3) verification of coating coverage and consistency inside the component. A more robust, lower cost and consistent design can be accomplished if the base material has high inherent oxidation protection as shown with CMSX-4 with La + Y.

Further advances are being made today in commercial turbofan engines by the addition of thermal barrier coatings. A recent design modification to an existing Allison turbofan engine realized 125°C (225°F) temperature reduction to the airfoil metal temperature without any increase in the cooling air. In another Rolls-Royce application, the prime-reliant use of TBC has enabled both a reduction in the cooling air flow and effective metal temperature. However, chipping and spallation of the ceramic coating can become critical failure modes if the airfoil cooling levels have been determined relying on the TBC. This concern has forced several engines to use TBCs as a non-prime-reliant system. While this can offer significant durability enhancements it does not allow the engine cycle temperature to be raised and thus the full benefits of the TBC are not realized. CMSX-4 with La + Y has demonstrated improved adherence with coatings and therefore may be instrumental in allowing thermal barrier coatings to be used on CMSX-4 as prime-reliant with greater confidence.

Finally, in either prime or non-prime-reliant application, there is always the possibility of local loss of TBC due to foreign object damage. The local heat transfer to the damaged area is enhanced due to surface roughness and out-of-wind step. In this event it is essential that the substrate possesses excellent high temperature oxidation properties to enable the engine to stay on-wing for an interval to suit the airline or military operator and yet be repairable.

Single crystal HP turbine blades in CMSX-4 with La + Y will commence engine testing in May 1998.

CONCLUSIONS

The RE combination ppm addition of La + Y to CMSX-4 alloy has shown the best combination of manufacturability, RE ppm chemistry control throughout the SX turbine blade and burner rig cyclic oxidation results where the life of bare CMSX-4 can be improved by a factor as large as approximately 10.

Turbine engine testing in several different applications scheduled for 1998 and 1999 will determine the value of this technology to turbine engine performance and life cycle costs.

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