DEVELOPMENT OF EXOTHERMICALLY CAST SINGLE-CRYSTAL MAR-M 247 AND DERIVATIVE ALLOYS

T. E. Strangman, G. S. Hoppin III
AiResearch Manufacturing Co. of Arizona
A Division of The Garrett Corporation

C. M. Phipps
Jetshapes, Inc.

K. Harris, R. E. Schwer
Cannon-Muskegon

A low-cost, exothermic directional-solidification (DS) process was successfully developed to produce single-crystal (SC) Mar-M 247 high-pressure turbine blades.

Stress-rupture data indicated that SC Mar-M 247 provides only marginal improvements in longitudinal strength relative to the columnar grained DS material. Removal of grain boundary strengthening elements (B, C, Zr, Hf) from the Mar-M 247 com-position--which are also melting point depressants--permitted the alloy to be solutioned at significantly higher temperatures. An order of magnitude improvement in rupture life relative to SC Mar-M 247 was observed for several derivative alloys at 103.5 MPa (15 KSI) and 1093°C (2000°F). Rupture lives of the modified SC alloys were significantly affected by both alloy purity and heat treatment.

Critical aspects of vacuum induction refining, exothermic casting technology, alloy development and heat treatment, which contributed to this new class of turbine blades, are reviewed.

I. INTRODUCTION

Stronger turbine blades for more fuel-efficient aircraft engines were successfully developed using single-crystal (SC) casting technology and alloys specifically tailored for SC applications. Due to the absence of grain boundaries, alloy compositions were freed of the requirement for grain boundary strengthening elements. This paper reviews the vacuum induction refining technology (Cannon-Muskegon), and the NASA-sponsored exothermic casting process (Jetshapes) and SC alloy (AiResearch) development program (1), which contributed to the development of this new class of turbine blades.

II. VACUUM INDUCTION REFINING

In general, the principal difference between conventional superalloys and advanced SC alloys is that grain boundary strengthening elements such as B, Zr, C, and Hf are deleted in SC alloys. These differences in composition are illustrated with the chemistries of Mar-M 247 and NASAIR 100 and three other derivative SC alloys in Table I. (Benefits associated with this modification are discussed in Section IV.) As indicated in the following paragraphs, optimization of the vacuum induction melting procedure was required to produce alloys of the desired chemistries (i.e., alloys with very low C, S, [N], and [O] contents).

TABLE I. Chemistries of Mar-M 247 Modifications.

Element	Mar-M 247 Range	Alloy Compositions (Weight Percentages)			
		Modification No.			
		NASAIR 100	2	3	4
Mo	0.50 — 0.80	1.0	0.8	0.8	1.7
W	9.50 — 10.50	10.5	10.3	10.0	10.2
Ta	2.80 — 3.80	3.3	3.3	3.2	3.0
Ti	0.90 — 1.20	1.2	1.2	1.1	1.1
Cr	8.00 — 8.80	9.0	9.1	8.7	8.8
Co	9.00 — 11.00	----	----	5.1	----
Al	5.30 — 5.70	5.75	5.5	5.4	5.5
C	0.13 — 0.17	<0.01	0.02	0.01	0.02
Hf	1.20 — 1.60	----	0.6	0.6	----
Zr	0.03 — 0.08	----	----	----	----
B	0.01 — 0.02	----	----	----	----
Ni	Balance	Bal	Bal	Bal	Bal

The importance of low [O] in producing remelt bar product essentially free of stable oxide inclusions is obvious. It has been shown (2) that [N] induces microporosity in cast superalloys. Hence, it is important to keep the [N] content of the remelt alloy as low as possible in order to minimize microporosity and to provide the best alloy feeding characteristics.

Basic thermochemical principles were applied to vacuum induction melting to minimize the [N] and [0] content in the remelt bar product in SC alloys. Elements such as Ni, Cr, Co, W, and Mo (whose oxides are relatively easily reduced by carbon under vacuum conditions) were initially charged with a small, tightly controlled carbon addition. Vacuum melting and refining of these elements to conditions of minimum equilibrium [0] content was accomplished using a carbon "boil" reaction; i.e.;

$$[C] + [0] = CO_{(g)}$$

$$\Delta G = \Delta G° + RT\ell n \ \frac{P_{co}}{a_{[c]} \cdot a_{[o]}}$$
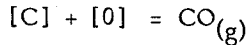
Where:

ΔG	=	Free energy of the reaction
$\Delta G°$	=	Standard free energy of the reaction
T	=	Absolute temperature
P_{co}	=	Partial pressure of CO
$a_{[c]}$	=	Activity of carbon
$a_{[o]}$	=	Activity of oxygen

This reaction was thermodynamically favored to the right by low pressure (vacuum) conditions. The bath was continuously stirred during the refining period to ensure exposure of the molten alloy to the most favored nucleation sites for the CO bubbles, i.e. the molten metal/lining/vacuum interface (3). The reaction was also favored to the right by increasing temperature (4). However, the necessary, very low carbon addition tends to impede the reaction to the right.

Increasing temperatures favor dissociation of the chromium nitrides (5), and desorption and removal of [N] at the melt-vacuum interface. Chromium is a major source of [N] in the raw materials. Since oxygen is surface active and impedes the mass transfer of nitrogen into the gas phase (6), nitrogen was most effectively removed from the nonboiling molten bath of a vacuum induction furnace when the bath was deoxidized. During meltdown and initial refining under vacuum, the CO bubbles acted as a scavenging gas and assisted in removal of [N] as N_2 and [S] as SO_2.

A relatively unreactive $MgO - Al_2O_3$ pre-reacted spinel furnace lining, new to vacuum induction melting, was used to produce the SC alloys. This relatively hard (high bond strength), erosion and attrition resistant lining minimized the occurrence of lining nonmetallic inclusions within the melt and on the melt surface. Although the spinel furnace lining acted as a source of [O], optimization of refining temperature, time, and pressure permitted the alloy to be refined to the desired low levels of [O] and C.

The addition of reactive elements Al and Ti was made after refining was complete. The final pouring operation (under high vacuum conditions) was controlled through a tundish system in the furnace, which ensured near-laminar flow conditions in the final separation and pouring compartments.

Table II shows the C, S, [N] and [0] contents of a series of 400-pound heats of the NASAIR 100 alloy. The carbon contents on all the heats were controlled to <60 ppm, combined with [O] at ≤4 ppm and [N] at ≲8 ppm. This SC alloy vacuum induction refining (VIR) technology was successfully scaled up from the 400-pound development furnace to the 8500-pound production furnace with excellent results for another SC alloy composition.

TABLE II. C, S, [N], and [0] Contents of NASA 100 Alloy Ingots.

Furnace (400 lb. 100% Virgin Heats)				
Heat No.	C ppm	S ppm	[N] ppm	[0] ppm
VF-154	34	8	4	2
VF-219	19	6	8	2
VF-220	24	5	4	4
VF-223	24	13	7	2
VF-225	28	6	4	2
VF-230	24	8	5	1
VF-231	24	8	4	1
VF-232	24	4	4	1
VF-223	20	5	3	3
VF-234	54	10	4	2
VF-235	45	6	5	2
VF-236	52	7	5	4
VF-237	42	6	6	1

III. SINGLE CRYSTAL CASTING PROCESS

The low-cost, nonproprietary exothermic directional-solidification process (7) was successfully developed to produce Mar-M 247 and NASAIR 100 SC high-pressure turbine blades (1) for the Garrett TFE731 turbofan engine. Process development involved evaluation of SC starters, blade orientation, blade density and spacing within the mold, investment mold material, melting crucible materials, exothermic burn conditions, and alloy-pouring temperatures.

Experimentation with different SC selector designs recognized that, as the alloy solidified against the copper chill, a multitude of columnar (001) oriented grains were formed. The requirement of the selector system was delivery to the turbine blade one grain, with a (001) primary orientation, which was properly oriented with respect to the blade stacking axis. Two

selector geometries, a helix and a right-angle selector, were evaluated during initial SC blade casting trials (Figure 1).

Fig. 1. Single-Crystal (SC) Selector Designs.

In the initial evaluation with the Mar-M 247 alloy, approximately 33 percent of the SC blades cast with the helix selector had the desired (001) ±10 degrees orientation. In contrast, about 72 percent of the blades cast with the right-angle selector exhibited the desired orientation. This difference in selector performance was attributed to sidewall nucleation and exothermic process requirements. Specifically, a selector design must allow sufficient room between the mold base and its cross members in order to achieve sufficient exothermic briquette packing for proper mold preheat. In this aspect, the helix selector design is deficient. To minimize sidewall nucleation, the cross members of the right-angle selector must be at a slight upward angle with respect to the mold base.

Blade orientation in the mold was varied to position the root toward and away from the chill block with the selector at the stacking axis or at the end of the root and parallel or perpendicular to the blade root plane. Best results were attained with the selector joined to the front end of the blade root.

Tests were conducted with investment shells of colloidal silica-bonded zircon and alumina shell systems that are standard at Jetshapes. Neither shell system showed any appreciable tendency toward excessive casting inclusions or mold deformation. The alumina system produced a somewhat thinner shell of greater thermal conductivity, which allowed better exothermic packing and resulted in a hotter mold/metal interface with less sidewall nucleation.

Evolution of the exothermic pack process resulted in use of a mold preheat oven for exothermic ignition and firing. The preheat oven was set at a temperature of 1010° - 1038°C (1850° - 1900°F) to promote mold inner surface preheat, as well as exothermic ignition. Ignition and burn in the preheat oven also eliminated problems with the slight amount of smoke generated by the exothermic reaction. Mold temperature at the conclusion of the burn was approximately 1593°C (2900°F).

After the exothermic burn, the mold was transferred from the oven to a water-cooled copper chill in the vacuum casting furnace. Melting of the alloy charge was performed concurrently with the exothermic burn. Metal is typically poured within 6 to 7 minutes after the mold has been removed from the preheat furnace.

For the Mar-M 247 alloy, superheats (temperatures above the freezing plateau, P) are considerably higher for directional-solidification P+236°C (P+425°F) and single-crystal castings P+278°C (P+500°F) relative to conventional equiaxed castings P+111°C (P+200°F). The optimum superheat for casting SC NASAIR 100 components was still higher at P+320°C (P+575°F). High pour temperature for SC blades were used to inhibit grain nucleation on mold walls. No significant investment mold-superalloy reactions were observed as a result of the higher superheats required for SC castings.

High superheat and vacuum conditions did, however, adversely affect the magnesia stabilized zirconia crucible during melting of NASAIR 100 and similar alloys. Partial decomposition of the zirconia crucible resulted in an undersirable addition (up to 0.5 percent) of zirconium to the alloy. This problem was alleviated by using a magnesia crucible for melting these alloys. Magnesium pickup in the SC alloys was 2 to 12 ppm, which was innocuous.

IV. SC ALLOY DEVELOPMENT

Development work was initiated with the Mar-M 247 alloy. However, stress-rupture capability of (001) orientation single crystals was essentially the same as that for longitudinal DS Mar-M 247. Consequently, it was necessary to modify the composition of the alloy in order to obtain a significant improvement in mechanical properties.

Based on the work of Jackson (8), it is known that stress-rupture life is a strong function of the volume fraction of fine γ' in the microstructure. Gamma prime in Mar-M 247--even when heat-treated at (or near) the incipient melting temperature--is only partially solutioned; i.e., substantial amounts of eutectic γ' remain. Thus, the melting point limitation inhibits realization of the full strengthening potential of the γ' in this alloy.

For the Mar-M 247 alloy, it was found that removal of grain boundary strengthening elements such as B, Zr, Hf, and C (which are also melting point depressants) resulted in an increase in the incipient melting point from about 1240°C (2264°F) to 1330°C (2425°F). As shown in Figure 2, this increase was sufficient to permit the γ' to be almost completely solutioned. These results are consistent with similar alloy modifications developed by Boone (9), Duhl (10) and Gell (11) for other nickel-base superalloys.
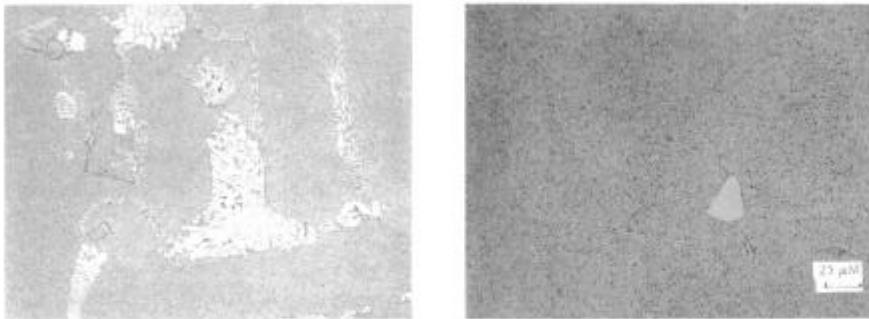
Mar-M 247   1246°C/2 Hr.   NASAIR 100   1324°C/4 Hr.

Fig. 2. Solution Heat-Treated Microstructures of Mar-M 247
and SC NASAIR 100.

In order to reduce alloy cost, cobalt was removed from 3 of the 4 SC alloy modifications of Mar-M 247 (Table I). Cobalt was retained in alloy 3 at the 5-percent level in order to evaluate its effect on the γ' solvus.

SC alloys 2 and 3 retained hafnium at a level of 0.6 percent to evaluate potential strengthening effects and to enhance oxide scale adhesion of diffusion aluminide coatings. However, this modification reduced the incipient melting point of these alloys to about 1294°C (2363°F). Only the alloy with 5 percent Co (alloy 3) could be adequately solutioned at this temperature. These results were consistent with the work of Nguyen-Dinh and Duhl (10) which indicates that cobalt reduces the γ' solvus of nickel-base superalloys.

Improved stress-rupture capabilities of the modified alloys were most evident at low stresses and high temperatures such as 103.5 MPa (15 KSI) and 1093°C (2000°F). This comparison is shown graphically in Figure 3. As indicated in Figure 3, SC NASAIR 100 and SC alloys 2 and 4 are significantly stronger than SC Mar-M 247 and SC alloy 3.
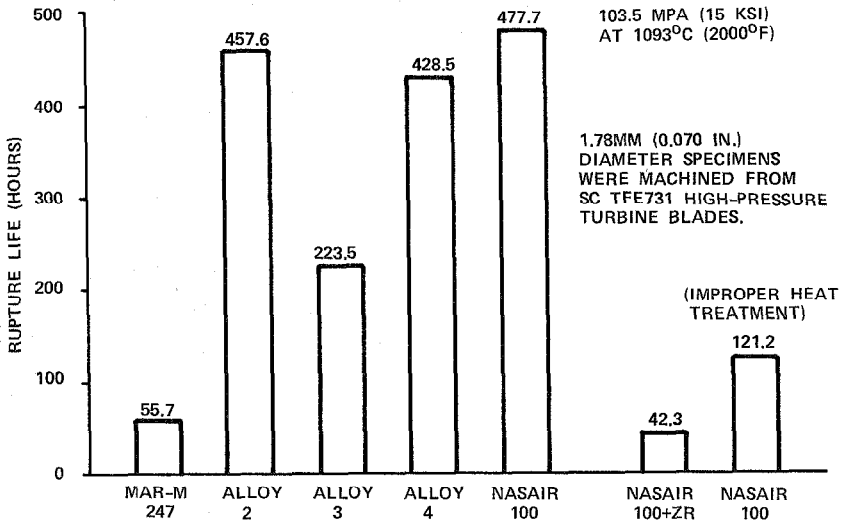
Fig. 3. Average Stress-Rupture Life of Single-Crystal
Alloys (SC) with 001 Orientation [103.5 MPA (15 ksi)
at 1093°C (2000°F)].

Post-test examination of SC NASAIR 100 and SC alloys 2 and
4 indicated that a μ secondary phase precipitated during the stress-
rupture test. The significance of this secondary phase precipita-
tion is currently under investigation. No significant degradation in
ductility has been observed to date. In contrast, SC alloys 3 and
Mar-M 247 have thus far been free of a μ phase.

It was found that the stress-rupture strength of SC alloys
such as NASAIR 100 is highly sensitive to both impurities (intro-
duced during melting) and heat treatment. The following examples
clearly illustrate this characteristic.

As noted in the previous section, the NASAIR 100 alloy
picked up 0.27-percent zirconium during melting in a zirconia
crucible. This addition reduced the incipient melting temperature
of the alloy and, consequently, limited the solution heat treatment
to 1260°C (2300°F). Under these conditions, solutioning of the
eutectic γ' was incomplete, and the SC NASAIR 100 + Zr alloy
exhibited stress-rupture lives similar to SC Mar-M 247.

Following the 1361°C (2400°F)/2-hour + 1324°C (2415°F)/
2-hour vacuum solution heat treatment, the SC NASAIR 100 tur-
bine blades were fan argon-quenched from 1324°C (2415°F) to
816°C (1500°F) in approximately 1.7 minutes. After quenching, the
SC blades were precipitation heat-treated at 982°C (1800°F)/5
hours, followed by 871°C (1600°F)/20 hours in air.

In one instance, the fan argon quench was not activated until the blades had cooled to 1038°C (1900°F). In this case, it took the blades 4.4 minutes to cool from 1234°C (2415°F) to 816°C (1500°F). The delayed argon quench resulted in a significantly coarser γ' particle size relative to standard processed material. Consequently, the number of γ' particles per unit area was about half that of the normally processed material. As indicated in Figure 3, the stress-rupture life capability of the slow-cooled (improperly heat-treated) SC NASAIR 100 was only one-fourth that of properly heat-treated SC NASAIR 100.

Effects of the above heat treatments were also apparent in 760°C (1400°F) tensile test results. Properly heat-treated speci-mens exhibited average yield and ultimate strengths of 1313 MPa (190.5 KSI) and 1393 MPa (202.0 KSI), respectively. In comparison, yield and ultimate strengths of the improperly heat-treated blades were 1128 MPa (163.5 KSI) and 1173 MPa (170.1 KSI), respectively.

Finally, it should be noted that the rupture life advantage of SC NASAIR 100 relative to Mar-M 247 is highly dependent on stress, as indicated in a stress versus Larson-Miller parameter graph (Figure 4). Therefore, high-taper-ratio (low-stress) designs, such as the TFE731 high-pressure blade developed in the NASA-MATE DS blade development project (7), are required to extract maximum benefit from the SC alloys.
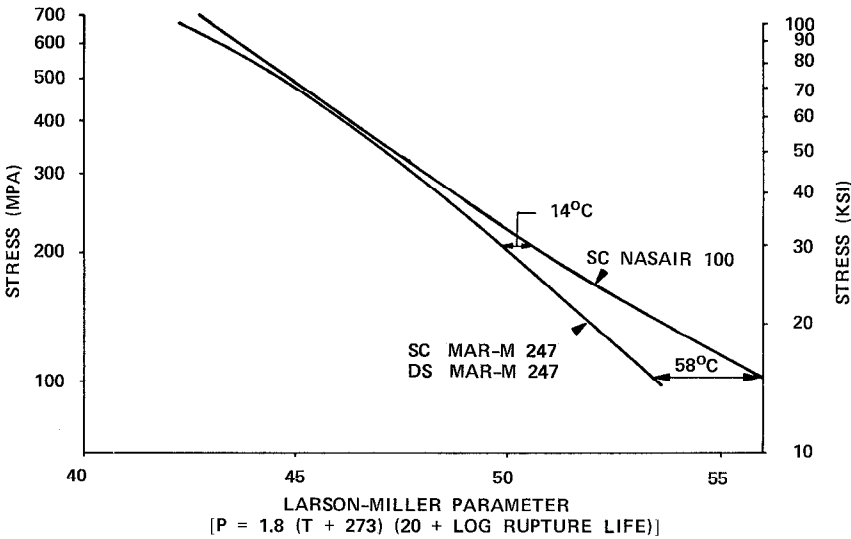

Fig. 4. Stress-Rupture Capabilities of Single-Crystal (SC) Alloys.

V. SUMMARY

Single-crystal turbine blades with significantly improved stress-rupture lives, relative to DS Mar-M 247, have been produced using the exothermic directional-solidification process. Due to the absence of grain boundaries, removal of grain boundary strengthening elements from the Mar-M 247 composition permitted the SC alloy derivatives to be optimally heat treated. At low stresses, 103.5 MPa (15KSI), several alloys exhibited an order of magnitude improvement in stress-rupture life. Smaller improvements in life were also noted at higher stresses.

ACKNOWLEDGEMENT

REFERENCES

(1) G. S. Hoppin III, M. Fujii, and T. E. Strangman, "Low-Cost Single-Crystal Turbine Blades," NASA-Lewis Research Center Contract NAS 3-20073, July 1977-December, 1979.

(2) K. Harris, R. E. Schwer, G. W. Brown, and D. C. Valentine, "The Influence of Nitrogen and Oxygen on the Castability or IN-100," Proc. AVS Conference, June, 1977.

(3) J. F. Elliot, "Metal Refractory Reactions in Vacuum Processing of Steel and Superalloys," MIT, AIME Electric Furnace Conference, 1971.

(4) F. D. Richardson and J. H. F. Jeffers, "Standard Free Energy of Formation of Oxides as a Function of Temperature," J. Iron and Steel Institute, 160, (1948) pp. 261.

(5) C. J. Smithells, "Standard Free Energy of Formation of Nitrides," Metals Reference Book, Vol. II, pp. 588-589, Interscience, NY, 1955.

(6) V. M. Antipov, "Refining of High-Temperature Nickel Alloys in Vacuum Induction Furnaces," Stal, February, 1968, pp. 117-120.

(7) L. Sink, G. S. Hoppin III, and M. Fujii, "Low-Cost Directionally Solidified Turbine Blades - Volume I," NASA CR-159464, January, 1979.

(8) J. J. Jackson, M. J. Donachie, R. J. Henricks, and M. Gell, "The Effects of Volume Percent of Fine γ' on Creep in DS Mar-M 200 + Hf," Metallurgical Transactions A, 8A (1977) pp. 1615-1620.

(9) D. H. Boone, D. N. Duhl, and G. W. Goward, "Nickel-Base Superalloy Resistant to Oxidation-Erosion," U.S. Patent 3,754,902, August 28, 1973.

(10) D. N. Duhl and X. Nguyen-Dinh, "Evaluation of Single-Crystal Superalloys," presented at AIME Annual Meeting, Las Vegas, February 24-28, 1980.

(11) F. L. Snyder and M. Gell, "New Directions in Alloy Design for Gas Turbines," pp. 209-227, Fundamental Aspects of Structural Alloy Design, Editors: R.I. Jaffee and B.A. Wilcox, Plenum Publishing Corp., 1977.