Development of Single Crystal Superalloys: A Brief History

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An industry pioneer shares a historical overview of the early days of single crystal superalloy development.

The 1960s were exciting times, especially in the aircraft industry. By late 1966, the Pratt & Whitney JT3D turbofan engine was a big success in powering the Boeing 707 and the Pratt & Whitney JT8D was in development to power the Boeing 727 and 737. To understand the history of superalloy development, it is important to first have a basic grasp of a gas turbine or "jet" engine.

Figure 1 shows a cutaway of a modern gas turbine engine. As air flows from front to back, it passes through the fan, low pressure compressor, high pressure compressor, combustor, high pressure turbine, and finally the low pressure turbine. The fan, compressor, and turbine are comprised of several stages. As air moves through the fan and compressor, pressure gradually increases, and in the turbine, pressure gradually decreases. As air flows, it alternately moves through both static parts (stators or vanes) and rotating parts (blades). Vanes direct the airflow into the optimum angle for the rotating blades that are attached to discs, which are in turn attached to a shaft. There may be two or three concentric shafts. The low pressure turbine is connected by an inner shaft to the fan and the low pressure compressor, and the high pressure turbine is connected through the outer shaft to the high pressure compressor. Most of the air entering the fan goes around the outside of the engine and is referred to as "bypass" air. The various sections are housed in "cases" that form the pressure vessel.

The energy source that makes this machine work is the combustor, consisting of one or more "cans" where fuel is mixed with high pressure air and ignited: Hot gas flows into the turbine where it spins the turbine blades, as in a pinwheel. The fan and the various compressor stages get their power from the turbines via the shafts. Discs and shafts are mounted in a bearing structure. Temperatures and pressures increase inside the compressor and decrease throughout the turbine as energy is extracted.

Recall that the overall efficiency of a thermodynamic cycle increases as the maximum temperature increases. This leads to one of the primary problems in engine development—how to cope with increased temperature. Generally, the fan is composed of aluminum, the compressor is titanium based, and the turbine is nickel based. Nickel alloys are referred to as "superalloys" due to their excellent combination of mechanical properties and environmental resistance[1]. The combustor exhaust temperature is near or above the melting point of the nickel alloys as well as the cobalt-based alloys, which have been used in the combustor or as first-stage turbine vanes. Early turbines used alloys such as IN718 and parts were made from forgings or castings. However, component life was limited by oxidation, corrosion, strength, creep, and cyclic properties. As engine temperatures continued to rise, three things had to evolve:

- Alloys for high strength and improved creep resistance
- Interior cooling passages
- Better coatings

Path to progress

All of these improvements came to pass, especially throughout the 1970s. Alloys were upgraded to IN792, U700, B1900, and Mar-M200. See Table 1. Phase stability considerations became commonplace, to guard against topolog-

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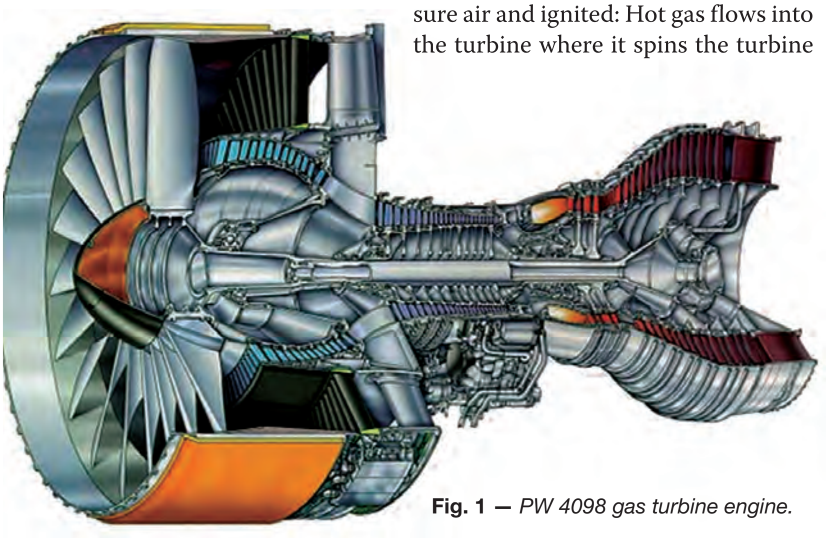


Fig. 1 — *PW 4098 gas turbine engine.*

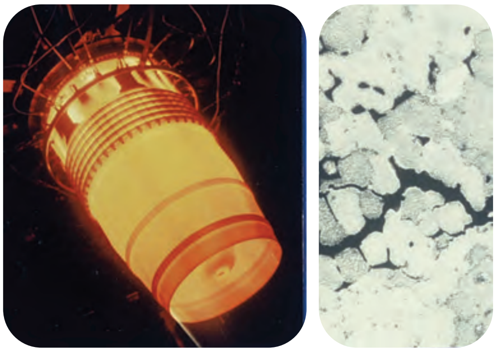


Fig. 2 — *Grain boundary failure. Under jet engine operating conditions, failure occurs at crystal boundaries.*

TABLE I — NICKEL BASE SUPERALLOY COMPOSITIONS [wt%]

Alloy	Cr	Co	W	Ti	Al	C	B	Zr	Nb	Hf	Mo	Ta	Other
Udimet-700	15.0	15.3	—	3.4	4.30	0.070	0.016	—	—	—	4.4	—	—
IN-718	19.0	—	—	0.9	0.60	0.060	—	—	*	—	3.0	*	18.0 Fe
IN-792+Hf	12.2	9.0	3.8	4.1	3.50	0.120	0.015	0.100	—	0.5	1.9	3.9	—
IN-100	9.5	15.0	—	4.8	5.50	0.180	0.015	0.060	—	—	3.0	—	1.0 V
B-1900+Hf	8.0	10.0	—	1.0	6.00	0.110	0.015	0.080	—	1.2	6.0	4.3	—
Mar-M200+Hf	9.0	10.0	12.5	2.0	5.00	0.150	0.015	0.050	1.0	2.0	—	—	—
PWA 1480	10.0	5.0	4.0	1.5	5.00	—	—	—	—	—	—	12.0	—
PWA 1484	5.0	10.0	5.9	—	5.65	—	—	—	—	0.1	1.9	8.7	3.0 Re

*Nb+Ta 5.1 wt%

ically close packed (TCP) phases[2]. Cooling passages were introduced, starting with simple lengthwise holes, then "S" shaped internal cavities, larger internal cavities (and the related thinner walls), pedestals, and other intricate designs. In vanes—and later in some blades—tiny transverse holes were introduced to form a thin wall of cool air (from the compressor) to shield the metal from hot gasses. Hf was added to suppress solidification cracking[3] in these thin walled components.

In the early days, castings were only tolerated where necessary due to a history of cracks associated with casting defects. However, as alloy strength requirements increased, castings were the only choice because high strength alloys such as MAR-M200 could not be forged. Yet castings remained troublesome due to shrinkage porosity and stress rupture originating at grain boundaries (Fig. 2).

Around this time, M.E. ("Bud") Shank convinced Pratt & Whitney that they needed an Advanced Materials Laboratory to meet some of these challenges and he obtained a funding commitment for about 10 years. He hired Frank VerSnyder from General Electric. VerSnyder had the idea that transverse grain boundaries could be eliminated from turbine blades by a process—yet to be perfected—known as directional solidification. This was demonstrated in a laboratory environment in copper. Shank and VerSynder hired Herb Hershenson to develop coatings to provide improved oxidation resistance. These three men then hired talented people from technicians to PhDs in areas such as mechanical properties, oxidation and corrosion, processing (wrought alloys, castings, powder metallurgy), refractory metals, ceramics, chemistry, x-ray diffraction, microscopy, and several other technical areas. Employees were encouraged to think long term, publish papers, and attend conferences. I was hired as one experienced with cobalt alloys, phase transformation kinetics, and x-ray diffraction.

As engineers struggled to make directional solidification a viable production process, the scientific types started thinking about eliminating *all* grain boundaries, as in a single crystal. Metallic single crystals were notoriously weak (recall "easy glide"), but the materials of interest had coherent precipitates that developed at very high temperatures. Even so, many challenges were associated with high temperature vacuum casting processes. VerSnyder advised deemphasizing cobalt alloys and instead embracing the opportunity to improve processes such as directional solidification (DS) used to make columnar grained superalloys and possibly single crystals. Columnar grained alloys seemed ideal for turbine blades, as the primary stress was axial due to centrifugal stress from high speed rotation. And single crystals would address more complex states of stress associated with ever increasing shape complexity.


Fig. 3 — *Trepanned single crystal ingot showing "freckle" trails.*

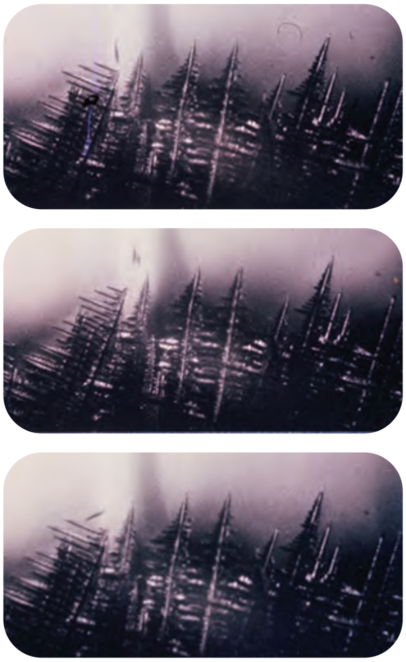


Fig. 4 — *NH_4Cl dendrites, convection plume, and fragmentation.*

Changing course

It was soon discovered that one thorny issue was "freckles," narrow chains of equiaxed grains within an otherwise aligned grain structure. The exact formation mechanism was not understood, although the most credible theory centered on something changing in the inner mold surface as the ceramic shell mold was being dewaxed. This lead to the following action plan:

- Check the chemistry and microstructure of the freckle trails
- Determine the thermal conditions during solidification
- Look for correlations between mold design variables and the incidence of freckling

It was discovered that after carefully machining out freckle trails as shown in Fig. 3, freckles were loaded with eutectic and all the elements with a distribution coefficient less than 1, such as Al and Ti. They also exhibited significant shrinkage. Next, the processing group needed to instrument a few molds to get cooling curves at known positions. This involved writing a computer program to reduce the data into thermal gradients, growth rates, cooling rates, mushy zone height, and other variables. Conditions were marginal at best, with the worst part orientation exhibiting trailing edge (thin) out and root (thick) down. This provided a strong clue that interface curvature was playing an important role.

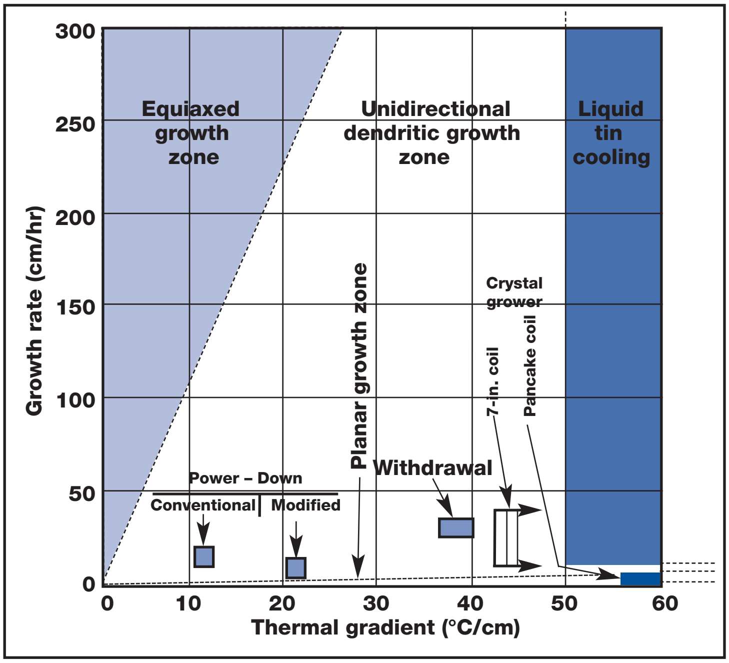


Fig. 5 — *Parameters associated with various directional solidification processes.*

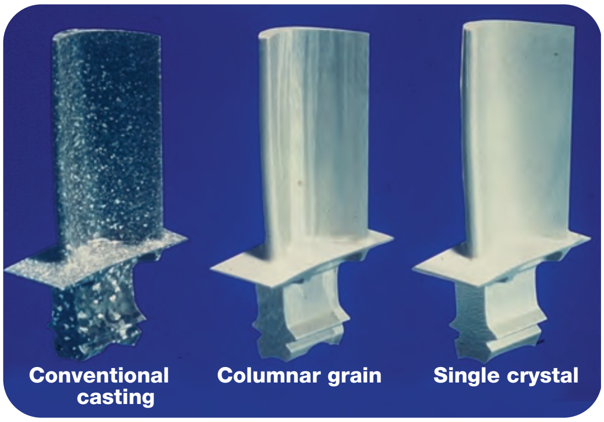


Fig. 6 — *Advances in turbine airfoil materials. Three grain configurations are shown here for the same component.*

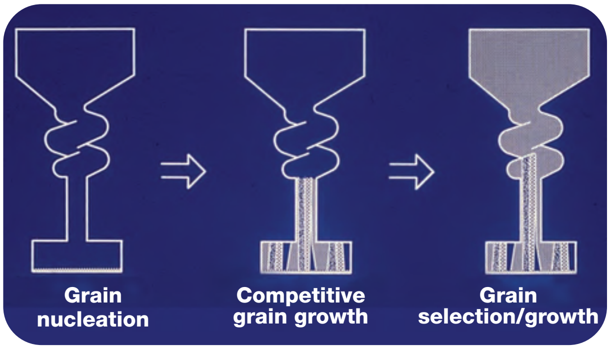


Fig. 7 — *Critical steps in single crystal formation. Shown here is a grain selector schematic with spiral (pigtail).*

Meanwhile, the team continued to study phase diagrams, effects of trace elements, particle coherency, dislocation configurations, antiphase boundaries, stacking faults, dislocation dynamics, precipitation chemistry and kinetics, particle coarsening, interphase partitioning, microsegregation, grain boundaries, carbide chemistry and morphology, competitive growth, elastic anisotropy, and other factors. Researchers needed additional expertise, but it was hard to hire new people in the mid-1970s. The team argued for several years about having summer students as interns. One of the students hired was Stan Johnson. He worked in our group (under Bernard Kear) along with Steve Copley, a ceramist. Copley was interested in dendrites, so an experiment was designed to solidify a solution of NH_4Cl and water from a liquid nitrogen-cooled copper chill plate directionally into a quartz cylinder, so that the process could be filmed by Mert Hornbecker.

Most superalloys have complex chemistries, wide melting ranges, and form dendrites as they solidify; however NH_4Cl was considered to be a reasonable "model" system. During a break in the experiment, the liquid nitrogen supply was shut off. After the break, Johnson noticed that the mushy zone had lengthened due to a reduction in thermal gradient and jets had formed in the mushy zone. The jets were throwing out dendrite fragments and this seemed to have something to do with freckles in superalloys.

Copley was an analysis expert and reasoned that the jets (plumes, Fig. 4, formed by channel convection) were an outcome of constitutional convection due to a density inversion. The liquid at the bottom of the mushy zone was less dense than the liquid above. This came about as the rejection of water away from the NH_4Cl dendrites created a lower density in the interdendritic liquid, which outweighed the normally higher density contribution due to the lower temperatures deep within the mushy zone. He also reasoned that the same might be true for superalloys with Al being rejected to the liquid and elements such as W (distribution coefficient >1) segregating toward the dendrites. A literature search regarding superalloy defects possibly related to segregation revealed many examples of "A" and "V" segregates in nickel alloy ingots. These defects were correlated with alloy chemistry and poor thermal conditions.

A critical experiment was then devised, attempting to make Ni-Al and Ni-Ta single crystal castings with the same atomic percent solute. We predicted defects for the Ni-Al case and no defects for the Ni-Ta ingot and that is *exactly* what happened: The Ni-Al ingot was loaded with equiaxed grains scattered about and the Ni-Ta ingot appeared to be flawless. This 25-lb ingot was the largest metal alloy crystal ever grown by man. Presenting these results at a conference resulted in much skepticism because everybody "knew" that fluid flow does not occur through a metallic dendrite field. A water-based system was considered to be a poor analog due to large differences in density, viscosity, and other variables.

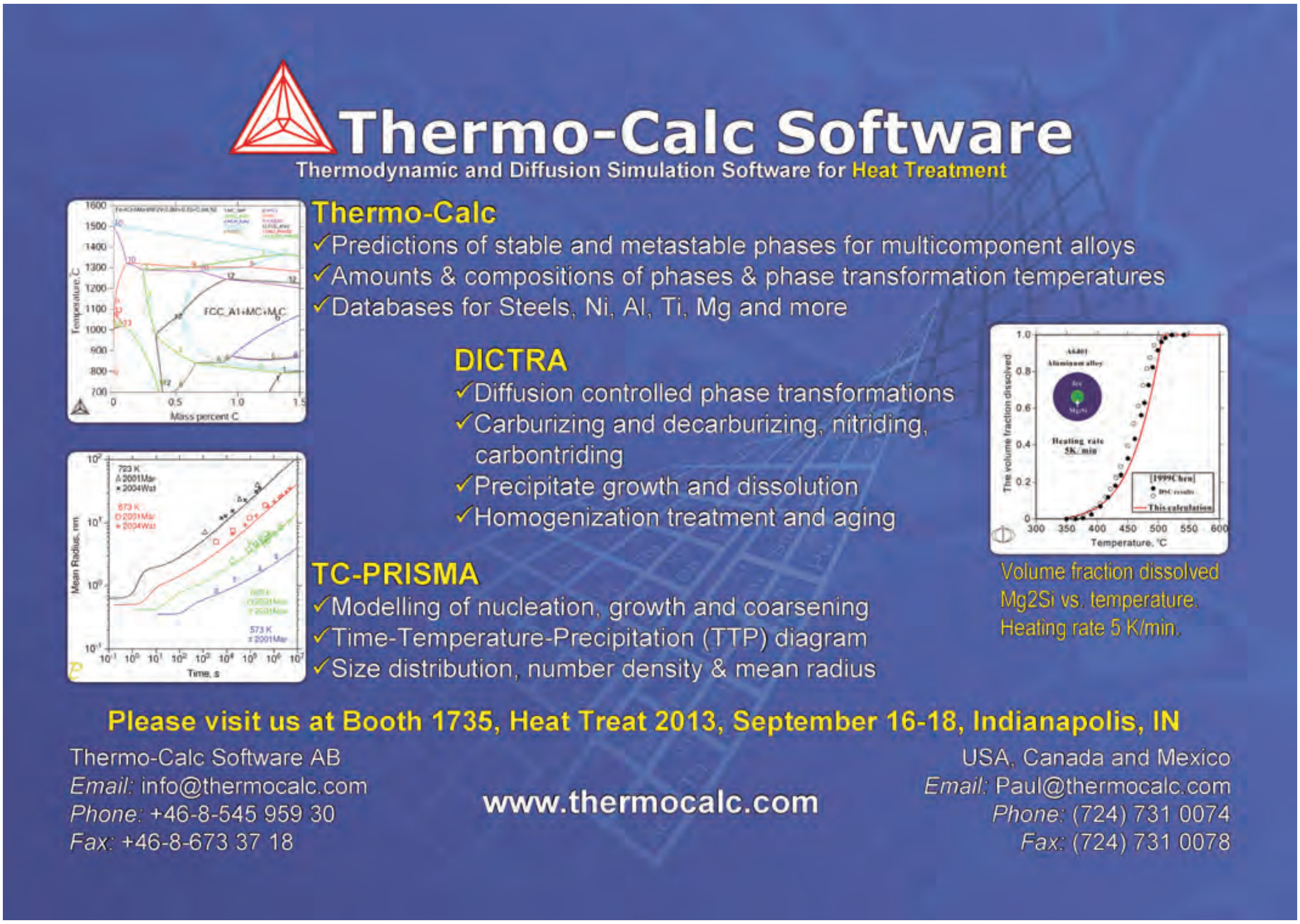
The team continued to try to improve thermal conditions. Progress was remarkable, as shown in Fig. 5. Freckles were disappearing. Results were published in two papers[4,5] and designers now had three choices in grain structure, as shown in Fig. 6. We worked with casting vendors to improve the process and DS yields were soon above 90%. The vendors also continuously improved and developed better core formulations to create the cooling passages. By the next scientific conference, Dr. Fred Weinberg of the University of British Columbia, Canada, had added small particles of W to a metallic dendrite field and showed by radiography that they were indeed moving about. The results were now accepted by the scientific community.

Superalloys continue making strides

With regard to single crystals, physicists argued that materials formed from dendrites (rather that planar front growth) were not true single crystals. This is a fine point. Superalloy "single" crystals were actually ideally imperfect crystals, which is to say that the slight substructure eliminated double diffraction or "extinction." In fact, Copley was very interested in elastic anisotropy and wanted to make a single crystal spring. In analyzing these attempts, a nearly complete lack of asterism in Laue patterns was evident. This led to the belief that a helix would make an ideal single crystal grain selector, as shown in Fig. 7. This worked and quickly became known as the "pigtail."

At times it was hard to convince casting engineers of the extent to which mold composition and thickness, baffle design, part geometry, part orientation, and process parameters [such as superheat and withdrawal rate] could influence interface curvature and solidification parameters such as thermal gradient. One answer was computer simulation. The research team used all the tools available at the time, including analog, closed form, finite difference, and finite element analysis[6]. We worked through the Defense Advanced Research Projects Agency (DARPA) to try to add microstructural predictors as well.

With funding becoming scarce, Maury Gell convinced the Naval Air Development Center (NADC) to grant a contract to evaluate a directionally solidified eutectic (DSE) test in a PT6 engine [a small engine used on some helicopters]. It was running very hot at the time and better materials were needed. The test was interrupted part way through, and it was obvious that the DSE parts were not going to satisfy the life requirements. Gell convinced NADC to try single crystals. Our group had made the DSE parts and was called upon to make a set of PT6 single crystal turbine blades: The engine test ran to completion and the parts looked great. By 1981, single crystals were being tried in both military and large commercial engines[7]. The casting vendors again tweaked the process and casting



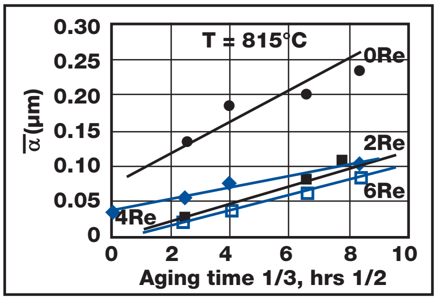


Fig. 8 — *Gamma prime coarsening data for Re modified 1444 Ni alloy.*

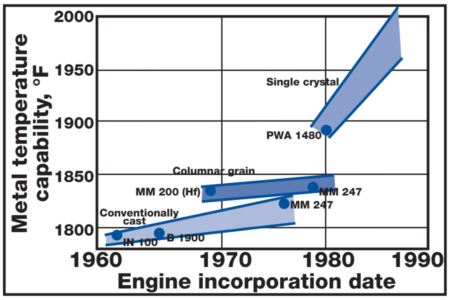


Fig. 9 — *Relationship between materials and temperature capability.*

yields climbed steadily upward. This was crucial to keeping costs under control.

The single crystal alloys that were developed were simpler because the Zr, C, and B grain boundary strengtheners were no longer needed. (A small amount of C is now used to help reduce sulfur, which can be detrimental to oxide adhesion, and to provide a bit of strength to any subboundaries.) Mo was found to be a bad actor with respect to hot corrosion, so B1900 was not the preferred choice, although it had great castability. Ta was a great element all around, as it provided good strengthening, castability, and oxidation resistance. The alloy developed to fit the bill was PWA1480. Fortunately, improved coating chemistries and processes were developed as well.

The Air Force Office of Scientific Research also played a role as the team was allowed to redirect another contract from studying fatigue to studying creep, especially to characterize the role of rhenium. Re had a poor reputation due to an early PM disc failure. However, in a casting, Re has a distribution coefficient >1 (like W), raises the melting "point," and should be a slow diffuser. One of the reasons that cast superalloys are "super" is that they contain a high volume fraction of gamma prime, a fairly coherent precipitate, and this low diffusivity slows down particle coarsening. Researchers were able to establish limits for Re additions and document improved creep resistance and slower coarsening, as shown in Fig. 8[8]. After this work was complete, the PWA1484 alloy was developed.

All of these developments lead to greatly improved component and engine capabilities, as shown in Fig. 9. Thrust increased from 3000 to more than 100,000 lb, while the TBO (time between overhaul) increased from several hundred to several thousand hours. It all happened due to a combination of good management, teamwork, some good fortune, and a can-do attitude.

Future considerations

Despite the advances briefly outlined here, there is much more work to be done to further develop this field. Here is a glimpse of what may lie ahead:

- Faster computers will enable faster model building; widespread use of computer simulation will include pour dynamics, improved microstructural predictors, as well as stress state and strain fields
- More accurate multicomponent phase diagrams
- Better life prediction
- Improved inspection methods
- Better molds and cores
- Improved repair methods
- More complete recycling for Ta, Re, Cr, Hf, and others
- Right-sized automated casting facilities

In addition, as Integrated Computational Materials Engineering tools become more widespread, they could have a noticeable impact on alloy development timelines. ❍

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