ON THE RAPID SOLIDIFICATION OF SUPERALLOYS

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ABSTRACT

A method to produce bulk quantities of rapidly solidified powder has been developed and is being used for the study of superalloy compositions. The method involves rotary atomizing of a molten metal stream and subsequent quenching of the atomized particles in a high velocity, high mass flow helium environment. Results of study to date show that it is possible to attain cooling rates in excess of 10^5 °C/sec for superalloys. The effect of this fast cooling has been one of significant phase suppression, which can lead to the ability to alloy beyond presently defined limits.

Introduction

The performance improvements of today's military gas turbine, such as the Pratt & Whitney F100, over earlier engines were made possible through advancements in design technology and materials processing. Better alloys, by virtue of chemical composition, played only a minor role in achieving present day capability. Future engine projections, nowever, are demanding that better materials be developed in order that still higher levels of performance can be achieved.

The turbine module is especially dependent on improvement in alloy properties such as higher temperature capability, better stability, and better corrosion resistance. The alloys presently being used in this section were developed more than 15 years ago. It has not been that a lack of development interest has existed since then that these alloys are still in use. Rather, it has been the inability to improve the nature of alloying under conditions now imposed for subsequent processing and component fabrication. Precision casting alloy compositions are limited because of such constraints as crucible and mold interactions and massive phase occurrence. Forging alloys are limited because of constraints of segregation during ingot processing.

Superalloy powder metallurgy studies conducted at the P&WA/Florida facility have shown that the use of powder, particularly powder solidified at very high rates of cooling, can eliminate the constraints noted and can enable more effective alloying for the improvement of basic material properties. Several examples which support this statement are as follows. Chemical segregation in fast cooled superalloy powders can be controlled to a submicron level. Massive phases can be eliminated. Solubility of alloying elements can be extended without deleterious phase reaction. None of these can be achieved in ingot or precision casting.

Further, the inherent homogeneity of the powder is such that subsequent processing and heat treatment can be used very effectively to promote maximum material utilization. Abnormal grain growth, for example, can be achieved in superalloy powder materials for optimization of mechanical properties above 1/2 T_M. Mar M 200 alloy powder, processed and reacted in this manner, is, in fact, stronger than and as ductile as the same composition cast in a directional mode.

Our objective is the development of better superalloy compositions and the cooling rates which appear most promising for this purpose are those in excess of 10^5 °C/sec. This range is typically referred to as the range of "splat" cooling. Rates of this magnitude can only be obtained in very thin sections and by necessity, only some form of processing involving the principles of powder metallurgy will apply for large, solid bodies. Numerous techniques are known whereby these fast cooling rates can be attained, but, for the most part, they are set up for laboratory study. In our case, our interest is being directed not only to laboratory studies of fast quench phenomena on superalloys but also toward a means whereby bulk quantities can be attained should implementation be desirable. This paper presents our recent work on the development of a method for rapid solidification of superalloys and presents some of the findings relative to superalloy compositions.

Rapid Solidification

In early work conducted at P&WA/Florida, analytical and experimental studies were carried out in an effort to define a means for production of fast quenched powders that could be implemented with a minimum amount of technological development. Several prerequisites were apparent. First, the approach would have to be capable of providing materials in significant quantities; second, the material produced should adapt itself to simple screening techniques for uniformity of cooling rate; third, the material should be easily handled; and, fourth, the material should have inherently high pour density and good flow characteristics for subsequent operations.

Initial work paralleled that of many investigators in attempting to attain high quench rates by conductive heat removal from the solidifying bodies. Although the results showed the attainment of desired cooling speeds, the material thus produced could not be controlled with respect to quality or uniformity of cooling and the techniques we used could not achieve steady state operation.

Concurrent analytical work, however, showed that forced convection cooling, adequately controlled, could be used to produce powders quenched at fast rates. In fact, the rates possible were analytically determined to be within an order of magnitude of the theoretical limit for "splat" (1-dimensional heat transfer) and within about 2-3 orders of magnitude of the the theoretical limit for any method (3-dimensional heat transfer). This relationship is shown in Figure 1.

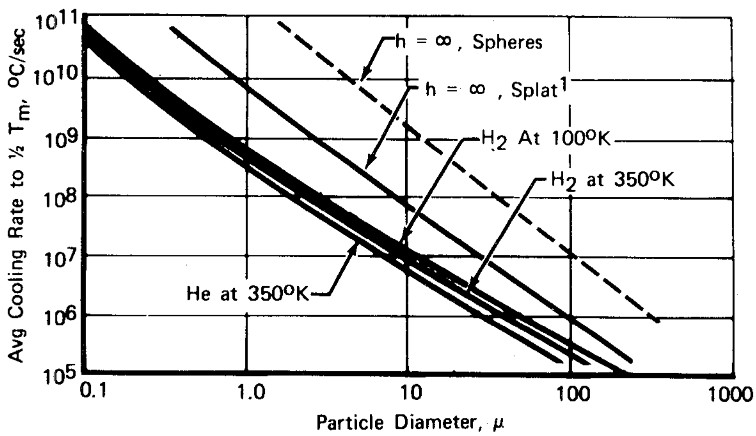


Figure 1. Cooling Rates Possible by Forced Convection Compared to Theoretical Limits

The model used for this analysis was based on the use of an independent particle generator that was itself capable of producing spherical particles and accelerating them into a quenching environment. Under this circumstance, the instantaneous particle cooling rate can be expressed as

$$\frac{dT_p}{dt} = \frac{6K\ Nu(T_p - T_g)}{C_p d_o^2 \rho} + \frac{6\sigma\epsilon(T_p^4 - T_w^4)}{\rho C_p d_o^2}$$

where

- K = thermal conductivity of gas
- Nu = Nusselt number
- T_g = gas temperature
- ρ = material density
- C_p = material heat capacity
- d_o = particle diameter
- σ = Stefan-Boltzmann constant
- ϵ = material emissivity
- T_w = background temperature

The first expression on the right of the equality relates cooling by convection while the second relates cooling by radiation. This latter term accounts for less than 1% of total cooling and, for practical purposes, was ignored.

Convection cooling accounts for >99% of particle cooling and examination of this term implies that the important parameters for fast cooling are particle diameter, gas conductivity, and particle to gas Δ T.

The Nusselt number, of the form

$$Nu = a + bPr^m Re^n$$

where Pr = Prandtl number
Re = Reynolds number,

was not found to vary to any degree of significance for cases of material value. The data used for the curves in Figure 1 did, however, account for changes in relative motion between the particle and gas. An undercooling of 0.075 the normal liquidus was presumed and mean cooling rates were calculated to 0.5 that temperature.

The analysis was taken a step further to determine whether cooling rates would vary from surface to center under these conditions of forced convection. The results showed insignificant differences for the particle size range being considered. This is due to the fact that the film transfer coefficient is low compared to the conductivity of the metal. For 50μ particles, the maximum temperature difference at any given time during cooling between surface and center was calculated to be about 10°C.

From an engineering point of view, maintenance of a high ΔT between the particle and the gas does not pose fundamental problems, nor does the use of a high conductivity gas such as helium. Effort was, therefore, directed toward study of a particle generation system which could be implemented under conditions satisfying the above criteria.

The particle generator ultimately selected was a central, rotary atomizer. In other industry usage, generators of this type have proved to be effective for steady-state production of particles and can produce narrow size distributions, a desirable feature from a high yield point of view. Most work to date with rotary atomizers has been directed toward production of coarse powder, but only because of physical limitations with respect to speed and mass flow rate.

Empirical relations have been derived for rotary atomizers that take the form

$$d = K\left(\frac{M^{.2}}{r^{.3}\ \omega^{.6}}\right)\left(\frac{\sigma^{.1}\ \mu^{.2}}{\rho^{.5}}\right)$$

where
d = mean particle diameter (surface/volume)
K = constant
M = mass flow rate
r = atomizer radius
ω = rotational speed
σ = surface tension
μ = viscosity
ρ = density

Examination of this term suggests that rotational speed is the single most important factor in generation of fine particles with density and atomizing radius having lesser, but significant, effects. It is interesting to note the relative independence of mean particle diameter on mass flow rate.

From experimental work conducted for wetted (coupled) surface, K = 1/3.

For IN100 superalloy type material, the relationship of anticipated mean particle size to tangential velocity, $f(r, \omega)$, is shown in Figure 2. The three flow rates shown were selected on the basis of ease of operation with respect to subsequent gas quench requirements of mass flow and recirculation capacity. For the size of atomizers and mass flow being considered, calculated horsepower to accelerate the liquid metal is small, on the order of 10 HP or less. For these conditions, then, it can be seen that particle sizes of interest (i.e., those capable of cooling at greater than 10^5 °C/sec) fall into a rotational speed range of 15000-35000 rpm and a drive system with this capacity is well within today's state-of-the-art for turbomachinery.

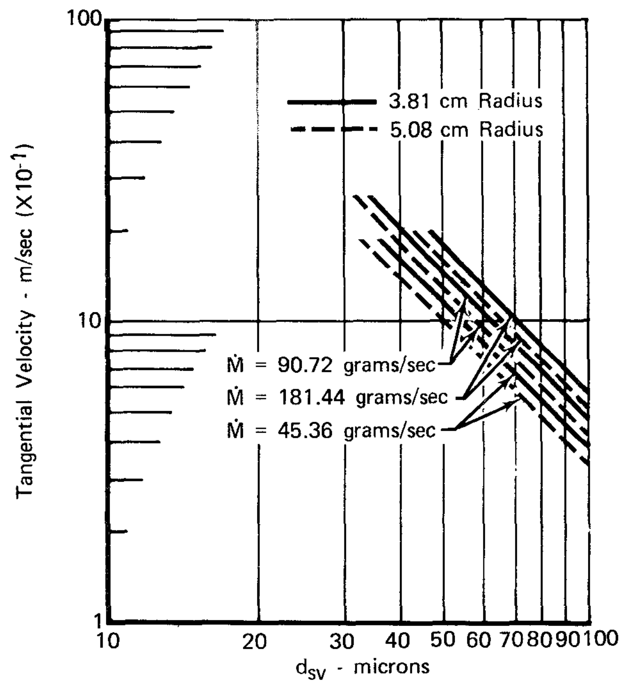


Figure 2. Predicted Tangential Speed vs Resultant Particle Size for IN100-Type Material

These principles of forced convection cooling and central atomization were combined in the design of a prototype rig to test the feasibility of fast quenching in a gaseous medium. The rig, designated AGT400000, is illustrated in Figure 3. It is presently capable of handling metal charges up to 23 kilograms (based on nickel). The unit has 3 annular gas nozzles which are sized to gas mass flow and velocity commensurate with maintenance of high ΔT from calculated heat flux profiles and particle trajectories. For 0.18 Kg/sec metal flowrate this requirement translates to 0.9 Kg/sec He at velocities up to 0.5 Mach. A radial impulse turbine was installed for the atomizer drive. The unit is provided with conventional vacuum induction melting and tundish metering. The sequence of operations include vacuum melting, He backfilling and gas injection, and, finally, pouring and atomization. The device has been operational since January of this year and results are in excellent agreement with the analytical and empirical predictions. The tangential velocity range investigated to date has been within 40-100 m/sec and subsequent screen analyses show that the predicted mean particle size is achieved. A typical distribution is shown in Figure 4 for 94 m/sec atomization.

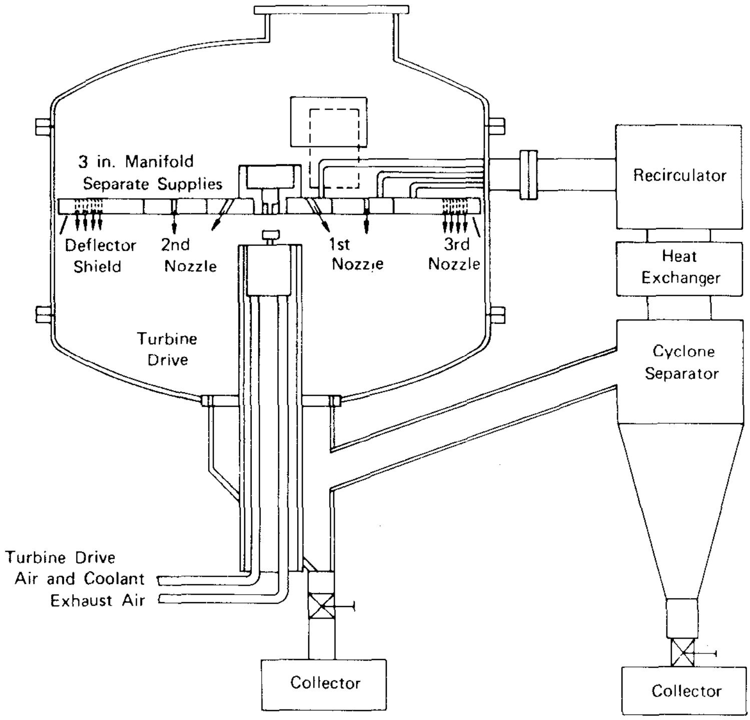


Figure 3. Experimental Powder Rig

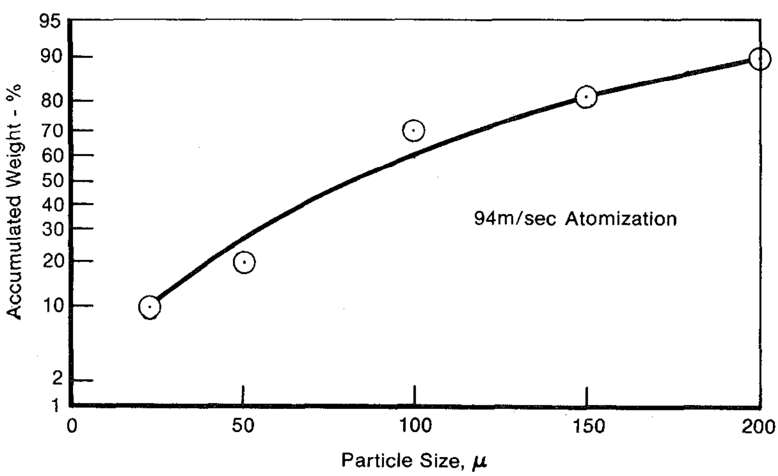


Figure 4. Characteristics of Yield

Dendrite arm spacing has been used by numerous investigators[2,3] as a measure of cooling rate and we did likewise in order to relate actual cooling rate with the analytical predictions. The results are shown in Figure 5. Again, the correlation between experiment and theory is good and it confirms that 10^5 °C/sec rates and higher are possible by forced convection.

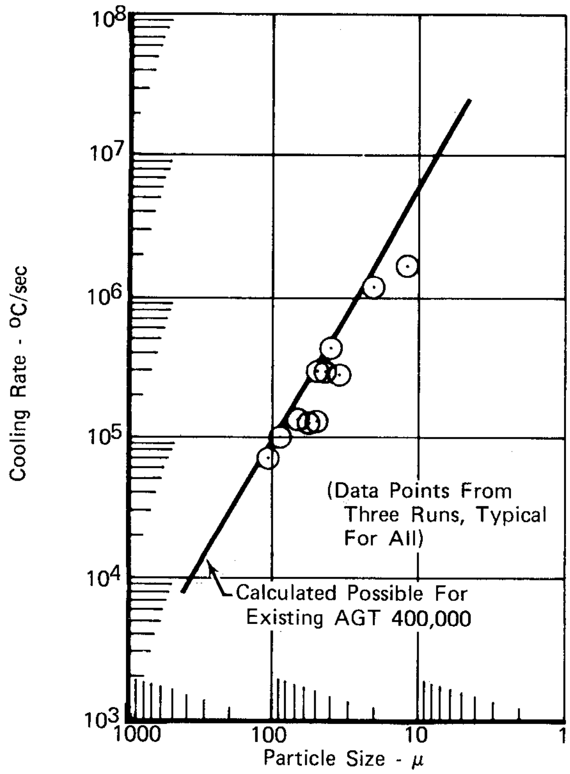


Figure 5. Experimentally Determined Cooling Rates

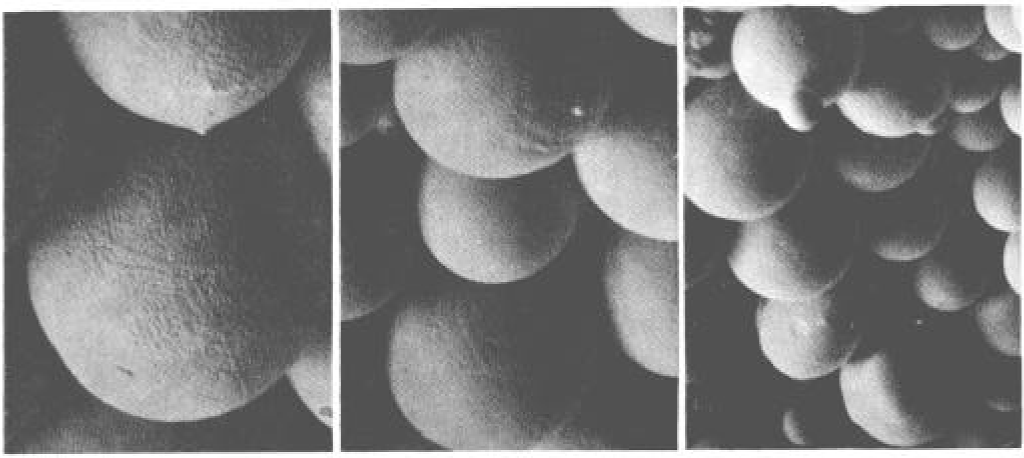
Powder Evaluation

All work to date has been done with IN100 alloy. The composition of this material is nominally 9.5% Cr, 15% Co, 4.5% Ti, 5.5% Al, 3% Mo, 0.17% C, 1% V, 0.015% B, 0.060% Zr, balance Ni.

The typical appearance of IN100 powder produced as described in the previous paragraphs is shown in Figure 6. The powder is spherical and free from aggregate formation like that which occurs when molten particles impact one another. This is an important characteristic since local heat balances for high rate solidification can only be established for particles cooling independently of one another. As is evident, the finer particles exhibit finer surface structures, indicating faster cooling.

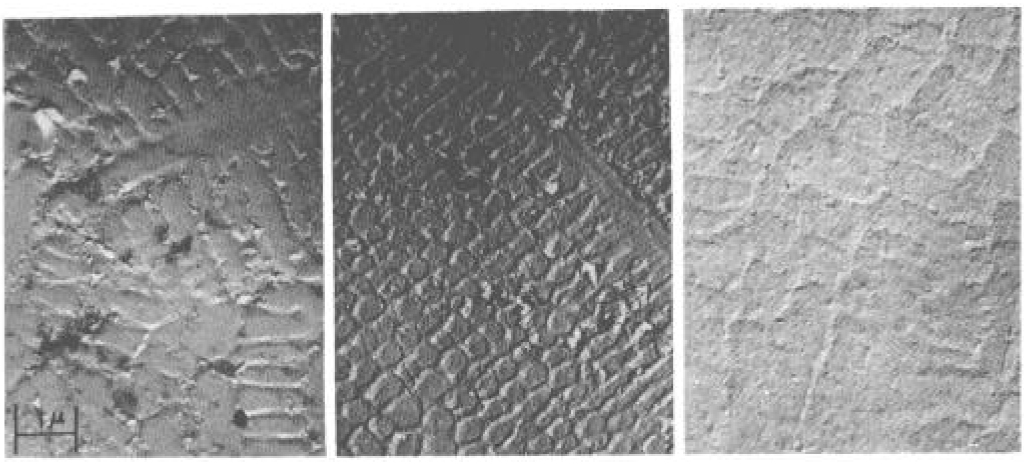
Typical microstructures of the IN100 alloy powder are shown in Figure 7. In the coarse material, which is probably representative of about 3 x 10^4 °C/sec cooling, a fine dendritic structure and second phase (TiC) can be observed. In the intermediate powder range, considered to be representative of about 10^5 °C/sec, the dendritic structure is finer and the second phase reduced in concentration. In the fine powder range, which is near 8 x 10^5 °C/sec, a cellular structure has occurred and essentially total second phase suppression has resulted.

Physical measurements showed that the size of precipitates in these powders varied from about 0.5 μ in the coarse to less than 0.1 μ in the fine. Elemental x-ray analyses showed that the extent of segregation coinsided well with measurements of dendrite arm spacing. For the coarse powders, segregate features were typically on the order of 1-1.3 μ, for the finer, typically 0.4-0.6 μ.



65μ - 105μ 45μ - 65μ <45μ

Figure 6. Surface Appearance of IN100 Alloy Powder



65μ - 105μ 45μ - 65μ <45μ

Figure 7. Microstructure of IN100 Alloy Powder

The contrast of microstructure of fast cooled powder to ingot is, of course, dramatic. There are no massive phases in the powder, as in ingot; segregation effects are reduced more than two orders of magnitude and, for the powder, a supersaturated solid solution has been obtained.

At this time of writing, alloying studies and mechanical testing are being prepared. However, the implication from the work already done strongly supports the contention that better alloy compositions are possible through rapid solidification of powder from the melt. Suggestive are the possibilities of increased concentrations and more effective alloying of the principle and secondary γ' phases, better control in the use of interstitial elements, such as C and B, and the introduction of new phases and new elements which here-to-fore have been avoided because of deleterious reaction. Combined with the inherent qualities of powder from a subsequent working and heat treating point of view, one can envision a new generation of alloys evolving for the improved performance of the gas turbine.

Acknowledgments

This work is presently being sponsored by the Advanced Research Projects Agency under ARPA Order 3152. The monitoring agency is the Air Force Materials Laboratories, Wright-Patterson Air Force Base, Ohio.

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Advanced Research Projects Agency or the U. S. Government.

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