The Effect of Cooling Rate on High-Temperature Precipitation in a Powder-Metallurgy, Gamma/Gamma-Prime Nickel-Base Superalloy

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The effect of cooling rate in the range of 10 K/s to 250 K/s (10 °C/s to 250 °C/s) on the precipitation of secondary gamma prime following supersolvus solution treatment of the powder-metallurgy superalloy LSHR was determined *via* a suite of critical experiments, analytical and FEM analysis of local temperature transients in test samples, and fast-acting numerical simulations based on classical (homogeneous) nucleation and growth. Using high-resolution scanning-electron microscopy, average 2D precipitate diameters were found to range from approximately 10 to 100 nm in various regions of small cubes that had been water quenched, oil quenched, or air cooled. After applying a stereological correction to estimate the equivalent 3D diameters, the precipitate sizes were plotted as a function of cooling rate deduced from analytical/numerical heat-transfer simulations that had been validated using selected thermocouple measurements. This plot revealed an approximately linear dependence of size on the inverse square root of the cooling rate within the temperature range for which nucleation was initiated and essentially completed. However, the present size-dependence on cooling rate was approximately 60 pct *higher* than that based on an extrapolation of the trend deduced from previous measurements for slower cooling rates and precipitation simulations over the entire cooling-rate range. Several sources of this difference, including the effect of small local plastic straining on nucleation, were hypothesized. The effect of stored work on precipitation was also underscored in a comparison of laboratory observations and the size of precipitates developed near the joint in inertia-friction-welded LSHR samples whose cooling rate after local supersolvus exposure had been of the order of 150 K/s (150 °C/s).

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I. INTRODUCTION

GAMMA-PRIME strengthened, nickel-base superalloys are among the most common materials used for high-temperature applications in land-based and aerospace power and propulsion systems. As such, understanding and control of precipitation behavior is very important. The size and volume fraction of gamma-prime precipitates play a key role in controlling strength, fatigue resistance, and other properties.^[1–3]

The synthesis of nickel base superalloys hardened by the fcc gamma-prime phase (based on Ni₃(Ti, Al)) is usually accomplished by one of three distinct routes based on ingot casting, powder production, or part casting. The ingot-metallurgy (IM) route is typically applied to alloys having low-to-moderate amounts (~ 10 to 30 pct) of gamma prime in the fully-hardened state and for which macrosegregation and thermal cracking can be avoided. In such materials, precipitation is often minimal during cooling following solution treatment at temperatures either high in the gamma + gamma-prime phase field or above the gamma-prime solvus. Hardening relies therefore on a final aging heat treatment.

In contrast to IM superalloys, more-highly-alloyed, powder-metallurgy (PM) superalloys (having ~ 40 to 65 pct gamma prime) often decompose *during* cooling following solution treatment. For material that is supersolvus solution treated, for example, precipitation usually occurs in several “bursts”. At a relatively-small undercooling relative to the gamma-prime solvus, secondary gamma prime (so-called to differentiate it from

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the coarse, *primary* gamma-prime dispersion developed during subsolvus extrusion or isothermal forging) nucleates over a narrow temperature interval. During continued cooling, the secondary gamma prime grows *via* diffusion to a size typically in the range of 100 to 500 nm. At temperatures several hundred kelvins below the solvus, diffusional growth becomes sluggish, matrix supersaturation increases again, and an additional burst of gamma-prime precipitates, typically referred to as tertiary (with a size of approximately ~ 10 to 50 nm), is formed. Following cool-down, an isothermal aging treatment at a temperature approximately 50 K to 200 K (50 °C to 200 °C) above the service temperature is common. This aging treatment produces additional fine (~ 10 to 20 nm) gamma-prime precipitates.

Cooling following the solution treatment of *large* PM components must be carefully controlled to avoid thermal (quench) cracking; the propensity for such cracking increases with gamma grain size and solvus temperature.^[4] Thus, the problem is most severe for alloys having a high volume fraction of gamma prime and a high solvus temperature. During heating above the solvus temperature, noticeable gamma grain growth occurs, and quench-cracking susceptibility increases. Cooling techniques such as oil quenching and forced convection are most common. The cooling rates thus imparted *within* bulk components are usually of the order of 0.1 K/s to 4 K/s (0.1 °C/s to 4 °C/s).

A number of solid-state joining and additive-manufacturing processes have been investigated for high-gamma-prime nickel-base superalloys. These include techniques such as inertia- and linear- friction welding^[5–11] and several variants of powder-bed and metal-deposition additive manufacturing/repair.^[12–14] For these operations, temperature transients often include excursions into and/or cooling from the supersolvus temperature range at rates of the order of 100 K/s (100 °C/s) or more,^[15–18] *i.e.*, rates that far exceed those typically encountered during conventional processing of large PM forgings.

Various aspects of the nucleation, growth, and coarsening of model gamma/gamma-prime systems, usually with 2, 3, or 4 components heat treated under *isothermal* conditions, have been investigated.^[19–23] With respect to commercial gamma/gamma-prime PM superalloys, a modest amount of research has been conducted to quantify precipitation behavior experimentally under *continuous cooling conditions*^[24–28] as well as to model such observations.^[29–32] Despite this prior work, the precise effect of cooling rate is not well defined for several reasons. First, many of the experimental measurements involving high cooling rates (i) made use of samples for which an average cooling rate was specified without regard to the ranges in which nucleation and growth are important or (ii) did not address possible errors in the temperature measurements *per se*. Second, most of the model investigations focused on predictions for relatively-slow cooling rates typical of those for large forgings.

The present work was undertaken to assess the applicability of classical nucleation-and-growth models for precipitation under high-cooling-rate conditions.

For this purpose, small cubes of a typical PM superalloy (LSHR) were supersolvus solution treated and cooled *via* free convection, oil quenching, or water quenching. Gamma-prime-precipitate sizes were determined at various locations within each cube and compared to the predictions of a fast-acting model developed and validated previously for the same alloy under slow-cooling-rate conditions.^[33] The existence of accurate thermodynamic and kinetic data for LSHR^[33–35] enabled the determination of the accuracy of the model *per se* without introducing uncertainties that may arise from general-purpose methods for estimating important input material parameters.

II. MATERIAL AND EXPERIMENTAL PROCEDURES

A. Material

The PM superalloy LSHR (denoting “low-solvus, high refractory”), a material typical of multi-component gamma/gamma-prime superalloys used for high-temperature applications, was used to determine precipitation behavior at high cooling rates and to establish the accuracy of a previously-developed fast-acting model. Originally developed by NASA, LSHR provides an attractive balance of properties in forgings subjected to a graded-microstructure heat treatment.^[36]

The as-received material consisted of 230-mm-diameter extruded billet produced by Special Metals (Princeton, KY). This was the same material as that used in previous investigations of the processing of LSHR.^[33,34,37–40] The composition of this material is given in Table I; its processing history has been summarized in detail in the previous papers. In brief, the microstructure of the as-received LSHR billet comprised a fine, micro-duplex structure of equiaxed gamma grains and gamma-prime precipitates, each of whose average diameter was $\sim 2 \mu\text{m}$, and ~ 0.33 volume percent of uniformly-distributed carbide/boride particles with an average diameter of 315 nm. The gamma-prime solvus, $T_{\gamma'}$, was 1430 K (1157 °C).

B. Experimental Procedures

A series of supersolvus solution heat treatments followed by cooling at various rates was performed to obtain a dataset that could be used to validate simulations of precipitation in LSHR at rates higher than those typically experienced during final heat treatment of large forgings. To this end, $10 \times 10 \times 10$ mm cubes were electric-discharge machined (EDM’ed) from the as-received billet. Following EDM, the recast layer on each surface was removed by grinding to a $\sim 0.8\text{-}\mu\text{m}$ surface finish. For instrumented samples, a hole was drilled to the centroid of the cube and a tight-fitting, 1.5-mm diameter, type-K thermocouple was inserted. The diameter of the chromel and alumel thermocouple wires was 0.25 mm; a thin thermocouple junction had been formed by abrading the wires at the tip of the thermocouple. Several other samples were left un-instrumented to

Table I. Composition (Atomic Pct) of Program Material

	Co	Cr	Al	Ti	Mo	W	Nb	Ta	C	B	Ni
LSHR	20.1	13.7	7.61	4.18	1.64	1.35	0.93	0.49	0.218	0.142	bal.
γ' in LSHR*	11.2	2.11	12.0	7.86	0.75	1.24	1.61	0.96	—	—	bal.

*Determined *via* phase extraction.^[35]

Fig. 1—Testing arrangement and metallography used in present work: (a) Photograph illustrating heat-treatment fixture and thermocoupled test sample, (b) sectioning plane for heat-treated cube, and (c) locations at which microstructures were determined.

determine if the cooling rate and hence the microstructure developed during heat treatment were affected by the thermocouple well and thermocouple itself.

Each cube was mounted in a home-made fixture that allowed uniform heat transfer from each of its six surfaces (Figure 1(a)); sample motion during cooling was prevented by the thermocouple (instrumented samples) or a series of fine nichrome wires (un-instrumented

samples). Heat treatment consisted of solutioning in a large box furnace at 1463 K (1190 °C) for 30 or 15 minutes followed by removal and air cooling, oil quenching, or water quenching. The latter two cooling methods involved gentle, but rapid, insertion into the quench medium to avoid agitation. For each cooling method, experiments were performed in duplicate or triplicate.

Following heat treatment, each sample was sectioned along a diagonal plane (Figure 1(b)) to determine the microstructure at locations which had been experienced the widest possible range of cooling rates. Metallographic preparation comprised grinding with SiC papers down to 800 grit, rough polishing with diamond, final polishing with colloidal silica, and etching in a solution of 33 pct nitric acid, 33 pct glacial acetic acid, 33 pct deionized water, and 1 pct hydrofluoric acid. The area fraction of *intragranular* γ' precipitates was determined *via* point counting on secondary-electron (SE) micrographs taken at magnifications between 50 kX and 200 kX at the locations indicated in Figure 1(c) using a Zeiss Gemini scanning electron microscope (SEM). Imaging was performed using an accelerating voltage of 0.5 kV, working distance between 3 and 4 mm, and aperture size of 20 μ m. At least 2 typical images (superimposed with $\sim$ 3000 point-count grid intersections) were each “read” independently by two individuals for each heat treatment/location. With this approach, the scatter in the measurements of the gamma-prime fraction was approximately ± 0.02 or less.

The number of precipitates per unit area was also determined manually for each heat-treatment condition and location. From the precipitate area fraction and number-density results, the average two-dimensional (2D) circle-equivalent diameter (CED) was determined; the uncertainty in this quantity was estimated to be less than 10 pct of the values reported below.

To establish the applicability of laboratory trials to infer microstructure evolution during a transient industrial process, secondary-gamma-prime sizes developed in LSHR during previous inertia friction welding trials were also determined^[11,40] and compared to those developed during the cube heat treatments.

Last, the correlation of 2D precipitate observations and 3D predictions from numerical simulations was facilitated using a series of sectioning simulations using MATLAB[®]. For this purpose, a number of hypothetical distributions of spherical particles, each with a specified volume fraction and standard deviation, were instantiated into a cubic box. For each instantiation, a number of arbitrarily-oriented sections through the box was taken, and the average diameter of the 2D circular sections through the particles determined and compared

to the average 3D diameter. By this means, it was determined that the average 3D diameter was approximately 1.15 times the 2D circle equivalent diameter observed in metallographic sections.^[41]

III. RESULTS AND DISCUSSION

The key results of this investigation comprised measurements of secondary-gamma-prime diameters and corresponding cooling rates at the center of each LSHR cube. Using the measured temperature-transient data, analytical and finite-element-method models were validated and used to estimate the cooling rates at other locations within each cube. These cooling rates were then used to compare measured gamma-prime sizes as a function of cooling rate to fast-acting-simulation predictions.

A. Measured Precipitate Sizes

For a given cooling method, metallographic observations revealed that very similar gamma-prime sizes were found in cubes with or without thermocouples. In addition, the sizes were essentially identical irrespective of whether the solution-heat-treatment time was 15 or 30 minutes. Hence, attention here is focused on thermocoupled samples which were solution heat treated for 30 minutes and then cooled by the various methods.

Typical microstructures developed in the heat-treatment cubes revealed a wide range of sizes for the larger, or secondary, gamma-prime precipitates (Figures 2, 3, 4). In these micrographs (and Table II), the locations (in mm) relative to Cartesian coordinates, whose origin lay at the centroid of the cube, corresponded to LC1 (corner) = (4, -4, -4), LC2 (edge) = (4, -4, 0), LC3 = (4, -4, 4), LC4 (near broad surface) = (0, 0, 4), and LC5 (center) = (0, 0, 0). From a broad perspective, the secondary-gamma-prime sizes were largest for the air-cooled samples (Figure 2), intermediate for the oil-quenched ones (Figure 3), and finest for the water-quenched cubes (Figure 4). Moreover, the precipitate sizes were largest at the center of each cube (LC5), smallest near the corner locations (LC1, LC3), and in-between near the edges and broad surfaces. Smaller (tertiary) gamma prime precipitates were also noted at locations LC4 and LC5 for all three cooling conditions (e.g., Figures 2(b), 3(b), 4(b)). The average 2D diameters of these latter precipitates were approximately 12.5, 7.0, and 7.0 nm for the air-cooled, oil-quenched, and water-quenched samples, respectively. The tertiary gamma-prime observations will be interpreted in a future publication. Suffice it to say for now, however, precipitation simulations indicated that these sizes were slightly or somewhat larger than the estimated critical diameter for a stable gamma prime nucleus, i.e., ~ 5 nm.^[33]

Measurements of the average 2D circle-equivalent diameter of the secondary-gamma-prime precipitates (Table II) provided quantitative insight into the variation in size within each cube as well as that due to

Fig. 2—Microstructure developed in an LSHR cube that was supersolvus solution treated for 30 min and then air cooled: (a) Location LC1 or (b) LC5.

Fig. 3—Microstructure developed in an LSHR cube that was supersolvus solution treated for 30 min and then oil quenched: (a) Location LC1 or (b) LC5.

cooling-method *per se*. In all cases, the measurements at the two corners (LC1 and LC3) were averaged. For air-cooled samples, the sizes ranged from 62 nm at LC1/LC3 to 105 nm at LC5; *i.e.*, an approximately twofold variation in size. A similar two-fold variation (29 to 63 nm) was found for oil-quenched samples. By contrast, water-quenched samples exhibited the finest secondary-gamma-prime precipitates and a threefold variation, *i.e.*, 13 to 39 nm.

Fig. 4—Microstructure developed in an LSHR cube that was supersolus solution treated for 30 min and then water quenched: (a) Location LC1 or (b) LC5.

B. Local Cooling Rates

The interpretation of the spatial variation in secondary-gamma-prime size required estimates of local temperature transients. This was accomplished using both an approximate analytical solution for the heat-transfer problem and detailed finite-element-method (FEM) calculations.

The analytical approach was applied to predict the local temperature field as a function of location and time, $T(x, y, z, t)$, for oil- and water-quenched cubes having dimensions of $2a \times 2a \times 2a = 10 \times 10 \times 10$ mm. It utilized a solution from Reference 42:

$$(T - T_q)/(T - T_o) = \psi(x, a, h)\psi(y, a, h)\psi(z, a, h), \quad [1]$$

in which T_q denotes the (assumed-constant) temperature of the quench medium; T_o is the initial (uniform) temperature of the cube; and h is the ratio of the interface heat transfer coefficient (H) and thermal conductivity (K), both taken to be constant as well. The function $\psi(x, a, h)$ is given by the following relation:

$$\psi(x, a, h) = \sum_{n=1}^{\infty} \frac{2h \cos \alpha_n x}{[(h^2 + \alpha_n^2)a + h] \cos \alpha_n a} \exp(-\kappa \alpha_n^2 t). \quad [2]$$

Here κ denotes the (assumed-constant) thermal diffusivity, and the α_n coefficients are the positive roots of the equation $\alpha \tan(\alpha a) = h$. Similar expressions pertain to the factors $\psi(y, a, h)$ and $\psi(z, a, h)$ in Eq. [1]. Per data in Reference 43 the values of K and κ were 26.0 W/(mK) and 3.88×10^{-6} m²/s, respectively,^[43] at the high temperatures of most importance for the precipitate nucleation-and-growth problem as discussed below. The interface heat transfer coefficient H was taken to be a fitting parameter. The best fit to high-temperature results yielded values of 400 or 800 Nm/(sm²K) for oil or water quenching, respectively.

FEM heat-transfer simulations using the code DEFORMTM were also performed. In these runs, the thermal conductivity and thermal diffusivity/specific heat were assumed to be temperature dependent per Reference 43. In this regard, it should be kept in mind

Table II. Secondary-Gamma-Prime Measurements

Cooling Method	Location	Secondary γ' 2D Dia (nm)	Area Fraction	Cooling Rate (K/s)*
Air Cooled	LC1, LC3	62	0.43	20.2
Air Cooled	LC2	71.5	0.39	17.5
Air Cooled	LC4	93.5	0.38	17.5
Air Cooled	LC5	105	0.41	13.9
Oil Quenched	LC1, LC3	29	0.43	74.1
Oil Quenched	LC2	35.5	0.43	50.6
Oil Quenched	LC4	51.5	0.35	39.6
Oil Quenched	LC5	63	0.34	27.6
Water Quenched	LC1, LC3	12.8	0.33	255.3
Water Quenched	LC2	12.9	0.33	173.9
Water Quenched	LC4	33.8	0.34	87.0
Water Quenched	LC5	39	0.34	73.7

*Colling rate from FEM simulations for the temperature range in which precipitation simulations indicated that nucleation occurs.

that the precipitation of gamma prime during cooling gives rise to a latent heat of transformation which affects the apparent specific heat and hence the thermal diffusivity. The import of this consideration is discussed in Sections III-C and III-D. For the FEM simulations, the interface-heat-transfer coefficient was taken to be 400 Nm/(sm²K) (oil quenching) or 800, 1600, or 2000 Nm/(sm²K) (water quenching). For the air-cool case, the emissivity was assumed to be 0.86 per previous measurements.^[44]

Predicted thermal transients from the analytical and numerical models were compared with corresponding thermocouple measurements at the centroid of each cube for the temperature range in which the nucleation of secondary-gamma-prime precipitates occurred for the cooling rates of interest here, *viz.*, approximately 1385 K to 1405 K (1112 °C to 1132 °C). For each cube, the agreement was reasonably good (Figure 5). For the air-cooled cube, for example, the DEFORM™ prediction was almost identical to the measurement at these temperatures (Figure 5(a)); in fact, even the small retardation at ~ 1390 K (1117 °C) (associated with the latent heat of transformation) was replicated. Similar agreement with measurements was obtained for the analytical and numerical predictions *at high temperatures* for the oil-quenched case (Figure 5(b)), although deviations were noted below ~ 1330 K (1057 °C). Such

differences were likely due to *increases* in the interface heat transfer coefficient (H) with decreasing temperature which were not taken into account in either prediction method. Numerical results with different values of H for the water-quenched cube (Figure 5(c)) suggested that H tended to increase by 2 or 3 times with decreasing temperature.

Using the FEM simulations, the local cooling rates within the temperature range between ~ 1385 K and 1405 K (1112 °C and 1132 °C) were determined for the various locations at which the gamma-prime microstructures were quantified. They are indicated in the final column of Table II.

C. Precipitation Modeling

1. Modeling procedures

Modeling procedures for predicting the size of the intragranular secondary-gamma-prime precipitates observed in the present work were identical to those used previously^[33,34] and thus are summarized only briefly here. The approach was based on classical relations for the rate of homogeneous nucleation and diffusional growth. Because of the rapid cooling conditions in all experiments, coarsening was disregarded.

The rate of nucleation of precipitates, J is given by the following equation^[20,45]:

Fig. 5—Comparison of analytical (green lines) and FEM-simulation (blue lines) predictions of temperature-vs-time transients with measurements (red lines) at the center of LSHR cubes which were supersolvus solution heat treated and then (a) air cooled, (b) oil quenched, or (c) water quenched (Color figure online).

$$J = \frac{2CD}{a_o^4} \sqrt{\frac{\sigma}{k_B T}} \times \exp\left(-\frac{4\pi\sigma r^{*2}}{3k_B T}\right) \times \exp(-\tau/t) \\ = J_o \exp(-\tau/t), \quad [3]$$

in which C denotes the solute content in the matrix expressed as an atomic fraction, D is the solute diffusivity in the matrix phase, a_o is the average lattice parameter of the matrix and precipitate phases (taken to be ~ 0.356 nm), σ is the matrix-precipitate surface energy, k_B is Boltzmann's constant (1.3806 J K^{-1}), T is temperature in kelvins, and t is time. The critical radius of the precipitate, r^* , is a function of σ , the chemical free energy of transformation ΔG^* (taken to be a positive quantity for a decrease in energy), and the elastic strain energy ΔG_p , associated with the difference in lattice parameters of the matrix and precipitate phases, *i.e.*,

$$r^* = \frac{2\sigma}{\Delta G^* + \Delta G_p}. \quad [4]$$

The nucleation rate J in Eq. [3] is related to the steady-state nucleation rate J_o through the term $\exp(-\tau/t)$, which describes the initial nucleation transient during which a metastable distribution of embryos with sub-critical radii are formed. The so-called incubation time constant τ in this exponential term is given by the relation^[20,46]:

$$\tau = \frac{\pi R T r^{*3}}{96 V_M D \sigma}, \quad [5]$$

in which R is the gas constant, and V_M is the molar volume of the precipitate. For the temperatures at which secondary gamma prime nucleates following supersolvus solution treatment (*i.e.*, $\sim 1400 \text{ K}$, or 1127°C), the incubation time constant τ was 0.018 seconds.^[33] For cooling rates of the order of 100 K/s (100°C/s), such an incubation time corresponds to a change in temperature of only 1.8 K (1.8°C). Thus, the nucleation transient was neglected in the present work, and nucleation was assumed to proceed at the steady-state rate J_o .

As is typical, the nucleated precipitates were assumed to be spherical (having a radius of r^*) with subsequent growth controlled by diffusion. The “exact” solution of the diffusion equation for the rate of growth in the presence of a finite matrix supersaturation^[42,47] was applied for this purpose, *viz.*:

$$dr/dt = 2\lambda^2 D/r, \quad [6]$$

in which λ^2 is related to the supersaturation Ω by the following relation:

$$\{\lambda^2 \exp(\lambda^2)\} \times [(\exp(-\lambda^2)) - (\lambda \pi^{1/2} \text{erfc}(\lambda))] = \Omega/2, \quad [7]$$

The supersaturation Ω has its usual definition, *i.e.*,

$$\Omega = (C_m - C_i)/(C_p - C_i). \quad [8]$$

Here C_m , C_i , and C_p represent the compositions of the matrix far from the matrix-particle interface, the matrix at the matrix-particle interface, and the particle at the matrix-particle interface, respectively. The correction to the equilibrium ($r = \infty$) interface composition, C_i , due to the Gibbs-Thompson effect was quantified using the following expression^[48]:

$$C_i(r) = C_i(r = \infty) \left(1 + \frac{2(1 - C_m)\sigma V_M}{(C_p - C_m)RT r} \right). \quad [9]$$

The effect of soft impingement on the ‘far-field’ matrix composition C_m was taken into account using the usual approximation derived from a mass balance^[49]:

$$C_m = (C_o - f C_p)/(1 - f), \quad [10]$$

in which C_o and f denote the overall alloy composition and the volume fraction of the precipitate.

Strictly speaking, Eqs. [3] through [6] apply to nucleation and growth in *two-component* alloys. Methods and assumptions to determine *effective* values for coefficients such as C , D , and ΔG^* of multi-component alloys such as LSHR for use in the relations for nucleation and growth of secondary-gamma-prime precipitates were described in References 33 and 34. These references also outline the specific values for the material coefficients for LSHR as well as the fast-acting spreadsheet method used to perform simulations for this alloy. In most of the simulations, the cooling rate was assumed to be constant. Selected simulations were also run to determine the effect of post-nucleation cooling rate on the average size and volume fraction of secondary-gamma-prime precipitates. For this purpose, simulations in which the post-nucleation cooling rate was one-half, twice, or four times that in the nucleation regime were conducted. Based on observations that tertiary gamma prime nucleates at approximately 1190 K (917°C) in samples that have been supersolvus solution treated, the secondary-gamma-prime simulations were stopped at a temperature of 1173 K (900°C). Selection of a temperature somewhat higher or lower than this did not affect the predictions materially inasmuch as the growth rate of secondary-gamma-prime precipitates is very low below $\sim 1223 \text{ K}$ (950°C).

2. Simulation predictions

Simulation predictions of nucleation behavior and average size of the secondary-gamma-prime precipitates in LSHR for *assumed-constant* cooling rates within the range pertinent to the present work are summarized in Figure 6. In Figure 6(a), the nucleation “start” and “finish” temperatures are those at which the rate of formation (number per unit volume per unit time) was below approximately one percent of the maximum rate. With this operational definition, the simulations revealed that such temperatures are only weakly dependent on cooling rate. Because of the possible influence of the latent heat of transformation on cooling rate *per se*

Fig. 6—Fast-acting simulation predictions for secondary-gamma-prime precipitates in supersolvus-solution-treated LSHR as a function of cooling rate: (a) the temperatures for nucleation start/finish and precipitate volume fractions of 0.02 or 0.05 and (b) the average precipitate diameter.

and hence nucleation, simulation predictions of the cooling-rate dependence of the temperatures at which the volume fraction of precipitates was 0.02 or 0.05 were also estimated and are summarized in Figure 6(a). These latter results indicated that relatively small fractions of precipitate would be expected to have formed (and hence small amounts of transformation heat would have been released) prior to the completion of nucleation. Thus, latent heat effects were surmised to have little effect on nucleation, but could affect subsequent growth behavior.

Figure 6(b) summarizes simulation predictions of the average size of secondary-gamma-prime precipitates over a relatively-wide range of assumed-constant cooling rates. As has been noted before for much lower cooling rates,^[50] the average size follows an inverse-square-root dependence on the cooling rate; *i.e.*, the slope of the line is -0.5 . This behavior can be rationalized on the basis of three facts: (1) nucleation occurs over a very limited range of temperature, even for relatively high cooling rates, (2) the precipitates all have almost exactly the same initial size ($\sim r^*$), and (3) diffusion is rapid enough to maintain comparable supersaturations for all cooling rates. For diffusional growth, the predicted final size is thus dependent primarily on the square root of the cooling time or inversely dependent on the square root of the cooling rate.

The numerical simulations also provided insight into the effect of *non-constant cooling rate* on precipitation

behavior. As noted above, two factors that could have yielded a measurable impact on the cooling rates observed in the experiments were the heat of formation of the precipitates and variations in the interface heat transfer coefficient. Predictions of the average size and volume fraction of precipitates for nominal cooling rates of 5.56 K/s (5.56 °C/s) or 111.1 K/s (111.1 °C/s) are presented in Table III. For the two cases in which the post-nucleation cooling rate was one-half that during nucleation, the predicted final precipitate size was *larger* by 1.5 or 9.5 pct relative to the respective constant-cooling-rate cases and the volume fraction was larger by 0.015. For the cases in which the cooling rate was four times that prevalent during nucleation, the predicted precipitate sizes were *smaller* by comparable percentages, but the volume fractions were lower by 0.06.

D. Comparison of Measured and Predicted Precipitate Sizes

In Figure 7, measurements of the average diameter of secondary-gamma-prime precipitates (after conversion from the 2D values in Table II to 3D) are compared to the constant-cooling-rate model predictions for LSHR (from Figure 6). Here, the data for air-cooled, oil-quenched, and water-quenched cubes are indicated by green, blue, and red squares, respectively. Except for the two data points corresponding to local regions of water-quenched cubes which experienced the fastest cooling rates, the measurements lie above the model-prediction line obtained using material properties (*e.g.*, effective diffusivity) for strain-free (annealed) LSHR (*i.e.*, the lower broken line). Despite being higher by ~ 60 pct relative to the predictions, the measured diameters do lie on a line with a slope of approximately -0.5 . This difference far exceeds that which may be due to a non-constant cooling rate. As described above, the maximum variation that would be expected for post-nucleation cooling rates that are one-half or four times that during the nucleation interval (which bracket observed lower-temperature cooling rates) is of the order of 10 pct or less.

An inspection of the results in Figure 7 may lead one to conclude that the simulation predictions are incorrect. However, these predictions matched not only previous results from slower-heating-rate trials using induction heating,^[33] but also similar slow-heating-rate experiments using direct-resistance heating, as indicated by the datum in purple in the figure. In both the induction and direct-resistance trials, the cooling rate was kept essentially constant by “trimming” the temperature transients associated with radiation heat loss and latent-heat effects using the auxiliary heat source. In addition, it is of interest to note that the measured precipitate size for the highest cooling rates (experienced in the water-quenched cube) also lay approximately on the line corresponding to the model predictions for a strain-free material.

The difference between the measured and predicted precipitate sizes (Figure 7) was mirrored in a similar comparison of number density (derived from number per unit area measurements as in Reference 33) (Figure 8(a)).

Table III. Simulation Predictions of Average Size and Volume Fraction of Secondary Gamma Prime Precipitates as a Function of Cooling Rate*

Cooling Rate, Nucl (K/s)	Cooling Rate, Post-Nucl (K/s)	Secondary γ' 3D Dia (nm)	Area Fraction
5.56	2.78	85.2	0.40
5.56	5.56	83.9	0.385
5.56	11.1	82.1	0.36
5.56	22.2	79.2	0.325
111.1	55.6	19.5	0.395
111.1	111.1	17.8	0.38
111.1	222.2	16.9	0.355
111.1	444.4	16.2	0.32

*Based on completion of secondary gamma prime precipitation and onset of tertiary precipitation at 1173 K (900 °C).

Fig. 7—Comparison of measurements (data points) and predictions (broken lines) for the cooling-rate dependence of the average 3D diameter of secondary-gamma-prime precipitates in LSHR samples that were initially supersolvus solution heat treated.

Specifically, the under-prediction in precipitate size appeared to correlate with an over-prediction in number density. Furthermore, the weak cooling-rate dependence of secondary-gamma-prime volume fraction predicted (and observed) at low cooling rates^[33] was also indicated by the present model predictions for higher cooling rates (Figure 8(b)). The largest consistent difference between the measured and predicted volume fractions was found for the water-quenched cubes. Referring to Figure 5(c), such a difference was probably due to the relatively-high cooling rate below the nucleation temperature range; this higher cooling rate is likely associated with an increase in interface heat transfer coefficient. As shown in Table III, a two- to four-fold increase in cooling rate below the nucleation regime would be expected to lead to a decrease in predicted volume fraction of 0.025 to 0.06 relative to that for the constant-cooling-rate case.

Several factors may be responsible for the differences between the measured and predicted precipitate sizes and number densities shown in Figures 7 and 8(a). These are as follows:

- (i) Non-uniform cooling. Even for the small cubes used here, the cooling rate exhibited moderate-to-large spatial (and temporal) variations (Table II). These variations would have led to small, non-uniform plastic strains which may have increased the effective diffusivity due to pipe-diffusion. In this regard, in an earlier

Fig. 8—Comparison of measurements (data points) and predictions (broken lines) for the cooling-rate dependence of (a) the density (number/volume) and (b) the volume fraction of secondary-gamma-prime precipitates in LSHR samples that were initially supersolvus solution heat treated.

investigation in which LSHR tensile bars were subjected to concurrent cooling and plastic straining at constant rates,^[51] secondary-gamma-prime precipitates whose sizes were 60 pct greater than those found in bars that had been cooled at the same rates but without concurrent straining were developed. Using the same fast-acting simulation method as here and in Reference 33 these larger sizes were rationalized on the basis of an effective diffusivity which was 2.5 times higher than that applicable to a strain free material. Irrespective of such a conclusion, however, the local temperature at which the plastic strain is developed is

important as well. If it occurs *below* the nucleation regime, then the effect of strain on precipitate size would be minimal because the number density (and thus size) is largely fixed during nucleation. Such a behavior may explain the observations for the two data points corresponding to highest-cooling rate locations in the water-quenched cubes.

- (ii) Errors in nucleation rate. As noted in Section III.C, the incubation time to achieve the steady-state nucleation rate was neglected in the simulations. Because such a time was relatively short at ~ 1400 K (1127 °C), O(0.02 seconds), its neglect was concluded to have minimal impact on nucleation predictions. If indeed, it had been considered, the temperature(s) at which the highest nucleation rates would have occurred would have been *lower* resulting in a greater driving force for nucleation and hence higher values of J (Eq. [3]). Correspondingly, the somewhat lower diffusivities at lower temperatures would have retarded precipitate growth and the concomitant depletion of supersaturation. Each of these factors would thus have led to more and finer precipitates, which would contrast to the present observations. In addition, a possible deficiency in estimating the nucleation rate using Eq. [3] (due to concurrent straining or some other source) was quantified. This was done *via* simulations in which J was increased or decreased by a fixed factor; the cooling rate (following supersolvus solution treatment) was 55.6 K/s (55.6 °C/s). It was found that the predicted average diameter of secondary-gamma-prime precipitates after cooling to 1173 K (900 °C) was higher or lower by only ~ 5 pct (relative to the prediction using J given by Eq. [3]) for the cases in which J was lower or higher, respectively, by a factor 10. These variations are much lower than those suggested by the comparison shown in Figure 7.
- (iii) Latent-heat considerations. The results in Figure 6(a) indicated that a rather small volume fraction of transformation and hence heat release occurs during the nucleation of precipitation. From a formal standpoint, such a conclusion would apply strictly to an isolated material point. On the other hand, if the latent heat released at a given point were to be conducted away to another, adjacent material element prior to its transformation, the cooling rate at this latter point could be retarded and thus its nucleation rate could be reduced. Such an occurrence would lead to larger precipitate sizes in qualitative agreement with the trend observed here. A more-complete analysis of such an effect would require a fully-coupled precipitation-FEM simulation beyond the scope of the present research.
- (iv) Mean-field assumption. As for the majority of fast-acting precipitation codes, the present simulation results relied on a so-called

“mean-field” assumption in which the details of the concentration field in the matrix are neglected. Future work to assess this assumption for high cooling-rate conditions is also warranted.

E. Comparison with IFW Observations

Last, it is of considerable interest to compare the present observations under well-controlled laboratory conditions to measurements for inertia-friction welding (IFW) of the same PM nickel-base superalloy, *i.e.*, LSHR. Specifically, attention was focused on regions near the joint at which all of the coarse primary gamma prime (which had been present prior to joining) had been dissolved. In such regions, the supersolvus temperature had been exceeded and the workpiece material had undergone discontinuous dynamic recrystallization (DDRX). Here, the volume fraction of secondary gamma prime (formed during cooling) was found to be ~ 0.355 and its average size (converted to 3D) was 21.3 nm. From FEM simulations of IFW, the local cooling rate near the joint was estimated to 150 K/s (150 °C/s) just below the solvus temperature. This datum, plotted as a black circle on the figure summarizing the laboratory observations (Figure 7), lies close to the data for the highest-cooling-rate results for the water-quenched cubes.

IV. SUMMARY AND CONCLUSIONS

A series of $10 \times 10 \times 10$ mm cubes of the PM nickel-based superalloy LSHR were supersolvus solution heat treated and then air cooled, oil quenched, or water quenched. The size of secondary-gamma-prime precipitates was determined at various locations in each cube at which the local cooling rate was estimated *via* FEM simulations; the cooling rates lay in the range between ~ 10 K/s to 250 K/s (~ 10 °C/s to 250 °C/s). The observations were compared to model predictions based on a classical, homogeneous-nucleation-and-growth analysis. The following conclusions were drawn from this work:

1. The average diameter of secondary-gamma-prime precipitates formed during cooling at rates between ~ 10 K/s and 250 K/s (~ 10 °C/s and 250 °C/s) follows an approximate inverse-square-root dependence on cooling rate.
2. Model predictions of the secondary-gamma-prime precipitate size for cooling at such high rates also show an inverse-square-root dependence on cooling rate.
3. Unlike prior low-cooling-rate precipitate-size measurements which evidenced excellent agreement with model predictions, the present comparisons for high-cooling rates revealed measured sizes approximately 60 pct higher than predicted, except for those corresponding to the highest cooling-rate locations of water-quenched cubes.

4. The higher-than-expected measured precipitate sizes can be rationalized on the basis of small levels of plastic strain developed during non-uniform cooling of the cube samples. Other factors, such as latent heat considerations which can confound the estimation of the cooling rate through the regime in which precipitates nucleate, may also play a role in the precipitation process.
5. From an application standpoint, the efficacy of the laboratory trials has been demonstrated by the good agreement of measurements for inertia-friction-welded LSHR samples and model predictions at corresponding high cooling rates.

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