Using Variant Selection to Facilitate Accurate Fitting of γ'' Peaks in Neutron Diffraction

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γ'' diffraction peaks are hard to discern in neutron/X-ray diffraction patterns, hindering studies on the γ'' -strengthened superalloys using *in-situ* diffraction. In this study, we propose a variant selection method to increase the intensity of γ'' peaks and to facilitate accurate fitting. The specific variants of γ'' are controlled by applying a 300 MPa tensile stress during aging at 790 °C for 5 hours. The interaction energy between the applied stress and the transformation strain of each γ'' variant differs, leading to an increase in the amount of the variants with a greater energy reduction at the expense of other variants. The enhanced variants result in greater γ'' peak intensities in neutron diffraction patterns, allowing both the Pawley refinement and single peak fitting to be performed. Lattice parameters of γ'' and γ phases, and lattice misfit between the two phases and volume fraction of γ'' are acquired. The uncertainties associated with the fitting maintain an acceptable level corresponding to 150 microstrains. The proposed variant selection method shows potential for studying the role of γ'' phase in Ni-base superalloys.

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I. INTRODUCTION

IN-SITU neutron/synchrotron diffraction techniques have been commonly used in studies of engineering materials by measuring the lattice spacings of the major constituent phases.^[1–6] Such techniques have become important approaches when investigating the role/behavior of γ' phase in Ni-base superalloys^[6–10] since the successful separation of the overlapping γ – γ' through the deconvolution method was first reported by Stone *et al.*^[6] Regarding the γ'' strengthened Ni-base superalloys such as Inconel 718 (IN718), most of the reported *in-situ* diffraction experiments on these alloys have measured the lattice spacings of the γ matrix phase but not the γ'' phase. Hence, the role/behavior of γ'' phase in these alloys has rarely been studied using *in-situ* diffraction due to the difficulties in analysis of gamma double prime peaks.

The challenges of using this technique arise from the fact that the γ'' peaks are hard to discern or separate from the overlapping γ – γ'' peaks in a neutron diffraction pattern.^[11,12] The diffraction behavior of the γ'' phase is dependent on its features such as volume fraction, crystallographic structure, precipitate size, and morphology. The features of γ'' phase and its relation to the γ matrix are illustrated in Figure 1. The γ phase is a solid-solution phase with an fcc structure, while the γ'' phase has an ordered D0₂₂ tetragonal structure which is analogous to two cubes stacked upon each other (Figure 1(a)). The lattice parameters of the two phases exhibit $a_{\gamma''} \approx a_{\gamma}$, and $c_{\gamma''} > 2a_{\gamma}$, where the latter gives rise to a large lattice misfit along the c -axis.^[13] The embedded γ'' particle is constrained by the surrounding γ matrix, generating compressive strains in that particle. The compressive strains are much larger along the c -axis than those along the a -axis (Figure 1(b)) due to the larger lattice misfit along c -axis.^[14] In order to accommodate the large compressive strains, a disc-shaped γ'' particle is formed with its habit plane normal to the c -axis during precipitation process (Figure 1(c)).^[15,16] The γ'' phase maintains a cube-to-cube relationship with the γ matrix, thus three variants of γ'' precipitates with the c -axis along different $\{100\}$ directions exist (Figure 1(d)). The size of the γ'' particle is typically less than 100 nm in diameter and less than 20 nm in thickness after the aging heat treatment, while the volume fraction of γ'' phase is less than 15 pct as reported in literature.^[17–25]

In order to utilize the *in-situ* neutron diffraction technique related to the γ'' phase in Ni-base superalloys,

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Fig. 1—(a) The lattice structures of γ and γ'' phases, (b) compressive strain generated in the γ'' particle along the c -axis (indicated by the thick arrows) due to the large misfit, (c) the γ'' displays a disc-shaped particle with its c -axis normal to the disc plane, (d) three variants (illustrated in three different colors) exist with their c -axis along different $\{100\}$ directions (Color figure online).

an accurate fitting to the γ'' peaks is necessary. Therefore, an approach to obtain γ'' diffraction peaks with satisfying quality is required. The deconvolution method, which has been successfully employed in separating the overlapping γ - γ' peaks,^[6–10] is not suitable for the separation of the overlapping γ - γ'' overlapping peaks. The critical idea of deconvolution method is to deduce the fundamental γ' peak position (i.e., $\{200\}$ γ' peak) from the corresponding superlattice γ' peak (i.e., $\{100\}$ γ' peak).^[6] This requires an accurate peak position to be obtained by fitting a superlattice peak of sufficient intensity. The intensity of a superlattice peak depends on $(b_{\text{center}} - b_{\text{corner}})^2$, where b_{center} and b_{corner} are the averaged atomic neutron scattering length of atoms at the face centers and corners of a unit cell, respectively.^[6] In the case of the γ' phase, Ni atoms occupy the face centers, whereas Al/Ti atoms are at the corners. The difference between the neutron scattering lengths ($b_{\text{Ni}} = 1.03 \times 10^{-12}$ cm for Ni, $b_{\text{Al}} = 0.345 \times 10^{-12}$ cm for Al and $b_{\text{Ti}} = -0.344 \times 10^{-12}$ cm for Ti^[26]) is large and leads to a relatively high intensity superlattice peak. However, for the γ'' phase, the face center atoms are Ni, whereas the corner atoms are Nb with $b_{\text{Nb}} = 0.705 \times 10^{-12}$ cm,^[26] giving the difference in scattering length significantly small and resulting in low intensity of γ'' superlattice peaks. Therefore, the deconvolution method cannot be applied to separate the γ - γ''

overlapping peaks since no satisfying γ'' superlattice peaks occur.

An alternative option is to obtain intensity-enhanced γ'' peaks in a neutron diffraction. Since the lattice parameters of γ'' along a -axis and c -axis are different, the three γ'' variants contribute to diffraction peaks at different d -spacings. As the GSAS-II^[27] simulated diffraction peaks in Figure 2(a) show, the $\{200\}$ γ'' peak and $\{004\}$ γ'' peak at different positions originate from different variants in the $[100]$ -oriented grains. By increasing the amount of the variant with c -axis parallel to the diffraction vector at the expense of the amount of the variant with a -axis parallel to the diffraction vector, the intensity of $\{004\}$ γ'' peak is enhanced (Figure 2(b)). The variant selection induced by an applied stress to the material or by residual stresses in a material during heat treatment has been reported,^[15,28–30] providing confidence to this potential method for obtaining intensity-enhanced γ'' peaks. Based on our theoretical and experimental studies, we propose a stress-induced variant selection method to obtain γ'' diffraction peaks with satisfying intensities that can be directly observed in a neutron diffraction pattern. Both the Pawley refinement and single peak fitting were successfully performed to the diffraction pattern acquired from a bulk IN718 sample in a neutron diffraction experiment. Lattice parameters of both the γ'' and γ phases, lattice misfit and

Fig. 2—Neutron diffraction peaks from a material consisting of γ and γ'' phase with volume fraction 87 and 13 pct, respectively, calculated using GSAS-II. The γ'' particle is set to be ellipsoidal shape with $a = b = 70$ nm and $c = 16$ nm. Lattice parameters are set to be $\gamma'' = \gamma = 3.6$ Å, and $\gamma'' = 7.44$ Å. (a) Without variant selection, $\{200\} \gamma''$ and $\{004\} \gamma''$ peaks exist; (b) with variant selection, only $\{004\} \gamma''$ exists with enhanced intensity.

volume fraction of γ'' were obtained with acceptable uncertainties. The variant selection method proposed in this study shows a promising method that may be employed in *in-situ* neutron diffraction experiments to study mechanical properties related to γ'' phase in γ'' -strengthened Ni-base superalloys.

II. VARIANT SELECTION BY STRESS AGING

Oblak *et al.*^[15] reported the method of applying stresses on single crystal alloy 718 bars during aging treatment to obtain γ'' variant-selected microstructure samples. In their experiment, when the tensile stress was applied along the $[001]$ crystal direction, only the γ'' variant with c -axis parallel to the stress axis appeared, whereas the other two variants did not occur. Further systematic studies on the platelet particles variant selection effect by applied stresses were carried out on different polycrystalline alloys including IN718.^[30–32] Qin *et al.*^[28,29] have reported variant selection effect by residual stresses in IN718 ingot during aging heat treatment. These studies concluded that during aging or creep at high temperatures, interactions between the applied stress or residual stresses and the local strains in different variants lead to different strain energy reduction. The favored growth occurs to the variant that experiences the most reduction in strain energy. By neglecting the small strain along a -axis and only considering the strain along c -axis, the change in strain energy due to the interaction between the applied stress and strain can be simplified as Reference 30:

$$\Delta E = -\sigma \times \varepsilon_c \times \cos^2 \theta \times V, \quad [1]$$

where σ is the applied stress, ε_c is the transformation strain along c -axis, θ is the angle of the c -axis to the stress axis, and V is the volume of the variant, as illustrated in Figure 3. The signs of σ and ε_c are defined as positive for tension.

Fig. 3—The angle θ between an arbitrary stress axis and the c -axis of a γ'' particle.

From Eq. [1], we can predict that the growth of a variant is favored if the angle θ is smaller compared to other variants in the same grain. The angle θ for each variant can be calculated once the grain orientation is known and the tendency for preferential growth of the variants under stress can also be determined. Table I lists the angle θ and the tendency for preferential growth of each variant that is represented by different colors in the grains oriented along $[111]$, $[100]$, $[110]$, and $[311]$ directions. Figures 4(a) through (d) give schematic illustrations of the variant distribution in the four grains after stress-free aging, while Figures 4(e) through (h) illustrate the variant distribution after tensile-stress aging, all viewed at the cross-section normal to the stress axis. A cube is used to display the grain orientation and the relationship to each γ'' variant. Compared to the variant distributions after stress-free aging, the variant distributions after tensile-stress aging demonstrate the following features: (i) in the $[111]$ -oriented grain, all three variants exist due to the same angle θ of the variants to the stress axis; (ii) in the $[100]$ - and $[311]$ -oriented grains, the growth of the blue variant is favored at the expense of the green and red variants due to the smaller angle θ of the blue variant; (iii) in the $[110]$ -oriented grain, the growth of the blue and green variants are favored at the expense of the red variant.

III. METHODOLOGY

A. Sample Preparation

In this work, IN718 with nominal chemical composition (wt pct): C (0.02), Cr (19.03), Nb (5.06), Ti (1.00), Al (0.54), Mo (3.06), Ni (52.16), balance Fe was used. 8-mm-diameter rod specimens with gauge length of 67 mm and threaded ends were extracted from forged IN718 bars which were solution heat treated at 1000 °C for 1 hour followed by fan cooling. Then the specimens were subjected to aging heat treatment at 790 °C for 5 hours. During the aging treatment, a 300 MPa tensile stress was applied to the specimens along the axial

direction. After the heat treatment, the specimens were air cooled to room temperature. The microstructures after heat treatment were characterized using a scanning electron microscopy (SEM) (JSM-7800F FE-SEM, JEOL, Japan). The SEM specimen was cut from the cross-section of the bulk specimen, grinded and chemically etched with a mixed solution composited by 5 g CuCl_2 + 100 mL hydrochloric acid + 100 mL ethanol to remove the γ matrix. The observed microstructure displays that the γ grains are about 30 μm , and a small amount of δ phase exists at the grain boundaries. Electron backscatter diffraction (EBSD) characterization was performed to determine the grain orientations. The γ'' variant distribution in differently oriented grains was also characterized.

B. Neutron Diffraction Experiment

Neutron diffraction experiments were carried out using the ENGIN-X neutron diffractometer at ISIS Time-of-flight neutron source, UK.^[33] The rod specimen was mounted on a sample stage with the specimen axial direction oriented horizontally 45 deg to the incident beam. Detectors were fixed at 90 deg to the incident beam. Radial collimators sat between the detectors and the sample, ensuring the detected neutron beams were from the same gauge volume in the sample.^[34] The incident beam slit was set as 4 mm in width and 10 mm in height, the diffracted slit width was 4 mm as defined by the radial collimators. With such a slits setup, the sample gauge volume was maximized in order to gain more diffracted signals, and the pseudo strain arose from the partially filled nominal gauge volume in vertical direction was negligible.^[33] The neutron

Table I. The Angle of Each Variant and Their Tendency for Preferential Growth with Respect to the Stress Axis in the Four Grain Families, and the Enhanced Diffraction Peak from the Preferentially Grown Variants

Grain Orientation	Variant	Angle θ (Deg)	Preferential Growth
111	blue	54.7	—
	green	54.7	
	red	54.7	
100	blue	0	blue
	green	90	
	red	90	
110	blue	45	blue green
	green	45	
	red	90	
311	blue	25.2	blue
	green	72.5	
	red	72.5	

Stress-free aging

Tensile-stress aging

Fig. 4—(a through d) Schematic illustrations of the γ'' variant distribution in grains oriented along [111], [100], [110], and [311] directions on the cross-section of a stress-free aged sample. (e through h) Schematic illustrations of the selected γ'' variant distribution in the four grains on the cross-section of a sample that aged under a tensile stress along the axial axis of the sample. All illustrations viewed along the axial axis of sample.

Fig. 5—Illustration of the schematic experiment setup, the rod specimen was set with its axial axis parallel to the diffraction vector for the bank 1 detector.

scanning was performed at room temperature with acquisition time of about 20 minutes. The experiment setup is illustrated in Figure 5.

IV. RESULTS

A. Microstructures

The γ'' variant distribution was characterized in three grains with their orientations close to [110], [100], and [111] directions which were selected from the EBSD map (Figure 6(a)). Dispersions of small round particles were observed in all three grains with diameter around 33 nm, these particles were γ' particles as discerned from their shape and size. Dispersions of larger particles in all three grains were γ'' particles. The mean diameter of the disc-shaped γ'' particles was determined to be 68 nm using ImageJ. Although the thickness of γ'' particles could not be observed directly in these micrographs, it was estimated to be 16 nm using the reported aspect ratio from literature.^[18,35] The γ'/γ'' volume fraction ratio was estimated to be 0.36 by counting the number of the precipitates in the SEM images, assuming the γ' particles in spherical shape with a diameter of 33 nm and the γ'' particles in ellipsoidal shape with a major axis of 68 nm and minor axis of 16 nm. This rough estimation agrees with the γ'/γ'' volume fraction ratio of an IN718 sample reported by Cozar and Pineau,^[36] which had similar Al+Ti/Nb ratio to the present study. In the grain oriented close to [110] (Figure 6(b)), the γ'' particles all aligned in one direction, these γ'' particles would belong to two variants as indicated by the inset cube. In the grain oriented close to [100] and [311] (Figure 6(c)), only the round shape γ'' particles existed, representing the

only variant in this grain. In the grain oriented close to [111] (Figure 6(d)), the γ'' particles existed in three different orientations, representing the three variants of γ'' . The observed variant distributions in these three grains were consistent with the analysis in Section II, proving that the variant selection manifested after the stress-aging heat treatment.

B. Neutron Diffraction Pattern

Figure 7 shows the illustration of γ'' variants distribution in the four grains viewed along the transverse direction of sample. The cross-section lattice planes of the γ'' variants in the four grains are (112), (004), (204), and (116) planes, respectively. Noted that the axial direction of the rod specimen was set parallel to the diffraction vector, with such a geometry, the {004}, {204}, and {116} γ'' peaks will have larger intensities (as illustrated in Figure 2(b)), since the amount of the variants which contribute to these peaks have increased at the expense of other variants.

The diffraction pattern obtained by the bank 1 detector is shown in Figure 8 with peaks identified. As expected, {004}, {204}, and {116} γ'' peaks show relatively good peak-shaped quality. As explained in Section II, the {200}, {220}, and {312} γ'' peaks would have little intensity since the γ'' variant with their lattice planes {200}, {220}, and {312} normal to the diffraction vector did not exist as confirmed in Figure 6. The {112} γ'' peaks partly overlap with the {111} γ peak, leading to an obvious peak 'shoulder' at the {111} γ peak. In addition, two peaks from δ phase are identified, the existence of δ peaks implies that possible δ peaks would exist at positions that are close to the {004}, {204}, and {116} γ'' peaks. However, the integrated intensity of {211} δ peak is about half of that of {004} γ'' peak, indicating those possible δ peaks that exist close to {004}, {204}, and {116} γ'' peaks would have little intensity, and thus, have little influences to the fitting of {004}, {204}, and {116} γ'' peaks. The low γ'/γ'' volume fraction ratio estimated in Section IV-A indicates that the γ' peaks, which have close positions to the γ peaks, can also be neglected in the fitting procedure. Therefore, the major peaks in Figure 8 can be assumed to be solely γ peaks.

C. Lattice Parameter Determined by Pawley Refinement

The overlapped {112} γ'' / {111} γ peaks lead to a large inaccuracy of fitting. Thus, the refinement and the fitting were only performed to the pattern within the d -spacing range from 0.98 to 2.04 Å for the purpose of a better accuracy. Since a small stress of 5 MPa was applied during the diffraction experiment, a Pawley refinement to the pattern was performed by fitting the peaks from γ , γ'' , and δ phases using GSAS-II as shown in Figure 9. The green line gives the residual between the fitted and measured data and shows a satisfying fitting quality. The lattice parameters of both γ and γ'' phases were obtained and listed in Table III. Although the fitting uncertainties for γ'' phase are larger than that for γ phase, they still maintain an acceptable level

Fig. 6—(a) EBSD map characterized on the cross-section of the sample. (b) through (d) show the γ'' variation distribution in three grains oriented close to [110], [100], [111] directions, respectively. Each grain orientation is displayed by the inset cube, the different γ'' variants are illustrated by different colors on the cube (Color figure online).

Fig. 7—Illustration of γ'' variant distribution in the four grains viewed along the transverse direction of the sample.

corresponding to less than 150 microstrains. Misfit strains between the two phases along a -axis and c -axis were calculated by

$$\varepsilon_a = \frac{(a_{\gamma''} - a_{\gamma})}{a_{\gamma}} \quad [2a]$$

$$\varepsilon_c = \frac{(c_{\gamma''} - 2a_{\gamma})}{2a_{\gamma}}, \quad [2b]$$

respectively, and listed in Table II. As expected, the misfit along c -axis was 3.28 pct, which was significantly larger than 0.44 pct along a -axis.

D. D -Spacing Determined by Single Peak Fitting

In *in-situ* studies of mechanical performance, the plane-specific lattice strain response to an applied stress is commonly investigated by measuring d -spacing evolution of the individual lattice plane.^[9,10,37] Therefore, it is worthy of fitting individual peaks to obtain d -spacing of both γ and γ'' phases. Peaks from γ' and δ phases were neglected due to their low intensities and limited influences. Although the γ'' peaks were discerned separated from the γ peaks in the pattern, their relatively close positions required each set of γ - γ'' peaks to be fitted simultaneously. During the fitting, the tail of the γ peak had a large influence on the fitting to the neighboring γ'' peak since the γ'' peaks were relatively

Fig. 8—Neutron diffraction pattern obtained from the bank 1 detector, showing the major γ peaks and minor γ'' peaks, as well as two peaks from δ phase.

Fig. 9—Pawley-type refinement of the diffraction pattern in d -spacing range 0.98 to 2.04 Å, measured at ENGIN-X diffractometer. The fitted γ , γ'' , and δ peaks are indicated. The refinement quality indices (the weighted profile R-factor (R_{wp}) and the goodness of fit (GoF)) are shown as well.

Table II. Lattice Parameter of Both Phases Obtained by the Pawley Refinement Using GSAS-II and the Misfit Strain Between the Two Phases Along a and c Axes

Phase	Lattice Parameter (Å)	Misfit Strain (Pct)
γ	$a = 3.59723 \pm 0.00007$	—
γ''	$a = 3.61308 \pm 0.00050$	$\varepsilon_a = 0.44 \pm 0.02$
	$c = 7.43027 \pm 0.00103$	$\varepsilon_c = 3.28 \pm 0.02$

small, thus, an accurate fitting to the γ peak was particularly important for the fitting of the γ'' peak. The γ peaks exhibited asymmetric peak shape due to the

moderation process of the time-pulsed neutron source,^[33] so that an asymmetric peak function for the correct fitting of the γ peaks was necessary. The asymmetric peak function used in this study consists of a complementary error function (erfc) convoluted with a Voigt function.^[38]

$$F = \text{erfc}(Z)\text{Voigt}(V). \quad [3]$$

For the fitting of γ'' peaks, a symmetric Voigt function rather than the asymmetric function was used. This is because when both peaks are fitted using asymmetric functions, the correlation effect of asymmetric variables of the two peaks make the fitting difficult to

Fig. 10—Single peak fitting of the three sets of diffraction peaks: (a) {311} γ and {116} γ'' , (b) {220} γ and {204} γ'' , (c) {200} γ and {004} γ'' . The R^2 for the three fittings are 0.9974, 0.9947, and 0.9987, respectively, indicating good fittings are achieved.

Table III. *D*-Spacing of Each Diffraction Peak Determined by Single Peak Fitting Procedure, and Their Corresponding Misfit Strain Between the Two Phases

<i>d</i> -Spacing (Å)		Misfit Strain (Pct)
$d_{200}^{\gamma} = 1.80160 \pm 0.00001$	$d_{004}^{\gamma''} = 1.86138 \pm 0.00022$	3.32 ± 0.02
$d_{220}^{\gamma} = 1.27333 \pm 0.00001$	$d_{204}^{\gamma''} = 1.29751 \pm 0.00016$	1.90 ± 0.02
$d_{311}^{\gamma} = 1.08595 \pm 0.00001$	$d_{116}^{\gamma''} = 1.11626 \pm 0.00011$	2.79 ± 0.02

converge. In addition, the γ'' peak was broadened by the nano-particle sizes and localized strain field, which reduced the peak asymmetry. Therefore, the use of the symmetric Voigt function gave a better γ'' peak fitting as shown in Figure 10.^[33] The *d*-spacings of each lattice plane were determined by the peak positions and the corresponding misfit strain (ε_{hkl}) were calculated using the below expression, results are listed in Table III.

$$\varepsilon_{hkl} = \frac{d_{hkl}'' - d_{hkl}^{\gamma}}{d_{hkl}^{\gamma}}. \quad [4]$$

Different lattice misfit strains existed for different *hkl* planes, which was not unexpected and consistent with the misfit strains in Table II.

E. Volume Fraction of γ''

The volume fraction of γ'' phase can be estimated from the intensity ratio of {004} γ'' to {200} γ peaks. The intensity of diffraction peaks at a time-of-flight diffractometer was expressed as Reference 39:

$$I_{hkl} \propto I_0 \lambda^4 j_{hkl} F_{hkl}^2 \quad [5]$$

where I_0 is the incident intensity, λ the neutron beam wave length, j the multiplicity, and F the structure factor. Considering a two-phase system, the unit cell

volume V_0 and volume fraction f of each phase need to be considered, and thus Eq. [5] can be revised as

$$I_{hkl} \propto I_0 \frac{V_v}{V_0^2} f \lambda^4 j_{hkl} F_{hkl}^2 = I_0 V_v f \lambda^4 j_{hkl} \eta_{hkl}^2, \quad [6]$$

where V_v is the gauge volume, $\eta = \frac{F}{V_0}$ the scattering length density. Following Eq. [6], the relation between intensity and volume fraction was derived^[6]:

$$\frac{I_{004}''}{I_{200}^{\gamma}} = \frac{(\lambda_{004})^4 (\eta_{\gamma''})^2 f_{\gamma''}}{(\lambda_{200})^4 (\eta_{\gamma})^2 f_{\gamma}}. \quad [7]$$

The {004} γ'' /{200} γ peak intensity ratio $I_{004}''/I_{200}^{\gamma}$ is 0.092/0.908 as calculated from the integrated intensities of these two peaks. The scattering length densities of phases, $\eta_{\gamma} = 7.206 \times 10^{10} \text{ cm}^{-2}$ and $\eta_{\gamma''} = 7.328 \times 10^{10} \text{ cm}^{-2}$ were reported in reference,^[25] $\eta_p = \sum_i \frac{b_i x_i}{V_p}$, where b_i is the scattering length of each individual atom, x_i the atomic concentration which was measured by atom probe tomography in their study, and V_p the unit cell volume calculated from lattice parameters. The alloy composition in our study is similar to that used in their study, in addition, they reported chemical compositions of γ'' phase were similar after different aging heat treatments.^[25] Thereby, we assumed the compositions of γ and γ'' phases in our study were similar to those in reference and adopted these scattering length densities to the estimation of γ'' volume

fraction in the current study. The diffracted neutron beam wavelength is proportional to the d -spacing when the diffraction angle is fixed according to the Bragg's law:

$$\lambda = 2d \sin \alpha. \quad [8]$$

Therefore, the volume fraction ratio $f_{\gamma''}/f_{\gamma}$ was calculated to be 0.086 and the γ'' volume fraction $f_{\gamma''}$ was 0.079, the small volume fractions of γ phase and δ phase were not considered. The volume fraction uncertainty was estimated to be about 10 pct from the uncertainty of the γ'' peak intensity which was about 10 pct.

V. DISCUSSION

A. Stress-Induced Variant Selection

Stress-induced variant selection effect has been well studied by many researchers in reported literature,^[15,29–32] which showed that it is a result of interaction between the applied stress and elastic strains of different variants. During nucleation and coarsening, the evolution of morphology of a particle follows a way that the free energy decreases the fastest. The free energy consists of surface energy and elastic strain energy. A study by Li *et al.*^[32] showed that for the θ' precipitates in Al-Cu alloys, the surface energy is dominant at the early stage when particle size is less than around 1 nm. Since the surface energy is isotropic, the particle possesses a spherical shape at the early stage. When the particle size is larger than the critical value, the elastic strain energy, which is anisotropic, becomes dominant and leads to a disc-like shape of the θ' particle. The γ'' precipitates would have a similar critical size since the misfit strains, elastic moduli, and surface energy are not in much difference compared to the θ' precipitates in Al-Cu alloys. The γ'' precipitate forms in a spherical shape at the early stage and then grows into a disc-like shape when the precipitate is larger than the critical size. The critical size is much smaller than the normally observed size of γ'' precipitate (a few ten nanometres), thus it is the elastic strain energy dominant in most cases. When an external stress is applied, the different variants are selected for preferential growth due to the anisotropic elastic strain energy. Qin *et al.*^[29] found that the variant selection effect was not apparent after stress aging for 2 hours, suggesting the variant selection effect is more apparent during the coarsening stage when the elastic strain is dominant compared to the nucleation stage. However, from the simulation by Li *et al.*, variant selection happens at the both the nucleation and coarsening stages. Such an issue may be able to clarify by *in-situ* measurements of evolution of lattice spacing of both the γ and γ'' phases during stress aging of IN718.

An important issue for the applications of IN718 at elevated temperatures is the thermal stability which correlates to the formation of the δ phase. The precipitation of δ phase, as reported by Sundararaman *et al.*^[40] in IN718 and IN625 at temperatures ranged from 750 °C to 950 °C, happened on grain and twin boundaries *via* heterogeneous nucleation, and from

transformation of γ'' to δ . The precipitation kinetic for the δ phase is much slower than that for the γ'' phase, and the transformation follows a well-accepted sequence: super-saturated solid solution – γ'' to δ , as reported by Oradei-Basile and Radavich.^[41] For IN718, a small amount of the δ precipitates at the grain boundaries would be beneficial to the creep resistance. It is the transformation from γ'' to δ that significantly affects the thermal stability, and thereby such a transformation is of great concern. The transformation from γ'' to δ would be related to the formation of stacking faults in the γ'' precipitates according to the studies by Sundararaman *et al.*^[40] The formation of stacking faults can be correlated to the loss of coherency during coarsening when the γ'' precipitates reach a critical size, saying 50 – 100 nm.^[42] Therefore, the formation of δ phase depends on the coarsening kinetic of the γ'' precipitates. The effect on coarsening kinetic of the γ'' precipitates has been reported by Qin *et al.*,^[29] the γ'' precipitate sizes after stress aging are similar to those after stress-free-aging, but the number density of precipitates is higher for the former than the latter, suggesting the applied stress during aging has little effects on coarsening kinetics, but would promote nucleation of the γ'' precipitates. Therefore, the applied stress during aging would have little effects on promoting the precipitation of the δ phase.

Stress partitioning would happen between grains that have different orientations when under loading due to the elastic anisotropy. Thus, the magnitude as well as the direction of the localized stress that experienced by an individual grain would differ from the applied stress, affecting the variant selection effect by the applied stress. In our study, the applied stress was of a magnitude of 300 MPa, which was believed large enough to induce variant selection compared to the 69 MPa tensile stress applied in the experiment by Oblak *et al.*^[15] In fact, it is the direction of the localized stress that would affect the variant selection, since the angle between the c -axis of the γ'' and the stress axis plays the important role in determining which variant is promoted, and which is suppressed by the stress. However, a determination of the direction of the localized stress for each individual grain would be impossible. Consider a microstructure with a weak texture, an individual grain is surrounded by many grains with random orientations, the effect on the localized stress direction would be small for most cases, suggesting the intergranular stress effect would be not significant enough to affect the variant selection in $\{100\}$ and $\{311\}$ oriented grains where the angle θ for the selected variant is much smaller than that for the suppressed variants. For those grains in which the difference in angle θ for different variants is small, for example $\{111\}$ oriented grains, the change in direction of the localized stress may have an apparent influence on the variant selection.

B. The Quality of Fitting

In the Pawley algorithm, the quality of fitting can be assessed by the weighted profile R-factor (R_{wp}) and by the goodness of fit (GoF).^[43] The R_{wp} and GoF of the

Pawley refinement in this study, given by the GSAS-II, are 9.15 pct and 1.00, which are acceptable for a good quality refinement.^[43] From the graphic fitting in Figure 9, the computed intensities agree well with the observed intensities, the only exception being the points around the tip of γ peaks. The visual assessment together with the numerical statistics gives us confidence that a good refinement is achieved. The high R -square coefficients “ R^2 ” and the good agreement between the computed and observed intensities (Figure 10) indicate that good fittings are achieved in terms of single peak fitting.

The measured lattice spacing in Table III can be used to calculate the lattice parameter of both phases since $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2}$ for the γ phase, or $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$ for the γ'' phase. The calculated lattice parameters retain a difference of 0.2 pct compared to the lattice parameters in Table II. The existence of this systematic discrepancy is not surprising since different d -spacing ranges and fitting functions were used, as well as the constraints from other peaks were not the considered in the single peak fitting routine compared to the Pawley refinement. Such discrepancy would not degrade the use of single peak fitting in studies such as elastic moduli and thermal expansion, where the lattice strain is of higher interest than the absolute value of lattice parameters, since the systematic error will be canceled out when calculating lattice strain using the fitting results from the same fitting method.

It is worthy to emphasize that the uncertainty has been kept lower than 150 microstrains, which is acceptable for quantitative strain analysis. An uncertainty of this magnitude is approximately equal to a thermal strain caused by a 10 °C variation in temperature, assuming the thermal expansion coefficient is around 15 microstrains per degree,^[9] or equivalent to an elastic strain response to an applied stress of 24 MPa, assuming the elastic modulus is 160 GPa.^[12] Such small uncertainty combined with the relatively short data acquisition time (20 minutes) allows mechanical properties related to the γ'' phase to be studied *in-situ*.

The small amount of the δ phase along the grain boundaries contributes to the δ peaks in the diffraction pattern. Although the δ peaks have low intensities, the single peak fitting to the γ'' peaks might be affected by those δ peaks which are located near the γ'' peaks. Such influence can be reduced by reducing the fraction of δ phase *via* solution heat treatment at a higher temperature. However, according to the consistency between the results from the single peak fitting and the Pawley refinement, the influence from δ phase is marginal.

Similarly, the γ' peaks are ignored in the fittings since the volume fraction of γ' is small, as analyzed in Section IV–A. In addition, the γ' has a similar lattice parameter to the γ phase, causing the fundamental γ' peaks to completely overlap with the γ peaks. Therefore, the assumption that the major peaks are solely γ peaks is reasonable and the neglect of γ' has little influence on the whole pattern fitting.

C. Measured Lattice Parameters and Volume Fraction

Many of the reported γ'' lattice parameters were measured on extracted residues.^[17,36,44,45] The extraction leads to a relief in the constrain on the γ'' precipitates from the surrounding matrix. The relaxed γ'' lattice parameters would be larger than those of γ'' embedded in the matrix. The current measured lattice parameters of both γ and γ'' phases are comparable to those measured by Slama *et al.*^[17] on extracted γ'' residues from IN718 samples, which had similar chemical composition and was heat treated under similar temperatures to the present study. On the other hand, the lattice parameters of the embedded γ'' in the bulk IN718 sample were measured by Wagner *et al.*^[46] using high-resolution neutron powder diffractometer, leading to $a_\gamma = 3.59592 \text{ \AA}$, and $a_{\gamma''} = 3.59881 \text{ \AA}$. The lattice parameters of γ phase agree well between the two studies; however, the lattice parameter of γ'' in the present study is much larger. The disagreeing γ'' lattice parameters could be due to various reasons, such as a difference in the coherency strain of the γ'' precipitates and/or a difference in the chemical composition of the precipitates.

Volume fractions of γ'' phase in IN718 obtained using diverse measuring approaches or simulations are presented in Table IV. The current measured volume fraction lies within the range of the reported values. The uncertainty of current measurement majorly arises from the fitting of the $\{004\}$ γ'' peak which retains a low height-to-background ratio, and the scattering lengths density which largely depends on the composition and atomic occupancies of γ'' phase. However, compared to other methods, the measurement using neutron diffraction is more straightforward. Furthermore, once the above two measurements become more accurate, the volume fraction measurement will become more reliable.

D. Limitation of the Proposed Method

The deconvolution of the partially overlapped $\{111\}$ $\gamma/\{112\}$ γ'' peaks was not successfully performed using single peak fitting routine. This is due to the large

Table IV. γ'' Volume Fraction Measured/Calculated Using Different Methods

Method	SANS	APT	APT	3D Imaging	Phase Field	ThermoCalc.	Neutron Diffraction
Volume Fraction	3.8 to 6.0 pct	15 pct	11.3 to 14.0 pct	14.2 to 15.5 pct*	16.9 pct	11.6 to 13.5 pct	7.9 pct
Reference	25	23	24	20	14	22	this study

$\gamma' + \gamma''$ combined volume fraction is indicated by *.

number of variables used for the fitting and the low intensity of γ'' peak, and consequently, the d -spacing for $\{112\}$ γ'' peak was not obtained.

The size and the lattice strain of the precipitates have large influences on the mechanical performance of materials and are of great concerns to researchers. The nano-particle size and lattice strain will generate broadening effect to the diffraction peaks. In turn, the mean particle size and the lattice strain can generally be estimated from the peak broadening using the Williamson–Hall relation,^[47] which gives a linear plot of peak width against d -spacing if the precipitate lattice strain distribution is isotropic. However, in this experiment, the disc-shaped γ'' precipitates retain high lattice strain anisotropy, the plot of the peak width against the d -spacing is not linear, resulting in the failure of obtaining the size and lattice strain of the precipitates.

VI. CONCLUSIONS

A variant selection method is developed to facilitate the quantitative analysis of γ'' peaks in neutron diffraction on IN718. The γ'' variants are selectively grown by applying an 300 MPa tensile stress to the sample during the aging heat treatment at 790 °C. Such variant-selected distribution enhances the intensities of non-overlapped γ'' peaks which have good peak shapes and can be observed directly in diffraction patterns. Lattice parameters, lattice spacings, and γ'' volume fraction can be determined from the analysis of the diffraction pattern using Pawley refinement and single peak fitting routines with a fitting uncertainty less than 150 microstrains. The measurement has been successfully performed on a bulk IN718 with a relatively short neutron scanning time (20 minutes), showing the promising potential of this method to benefit the studies on mechanical properties of the γ'' -strengthened Ni-base superalloys including IN718 and its derivatives such as alloy 625, 725, and 706.

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