Effect of Alloying on the Microstructure, Phase Stability, Hardness, and Partitioning Behavior of a New Dual-Superlattice Nickel-Based Superalloy

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A novel $\gamma-\gamma'--\gamma''$ dual-superlattice superalloy, with promising mechanical properties up to elevated temperatures was recently reported by Mignanelli et al. (in: Proceedings of the 9th International Symposium on Superalloy 718 & Derivatives: Energy, Aerospace, and Industrial Applications, pp 679–690, 2018). The present work employs state-of-the-art chemical and spatial characterization techniques to study the effect systematic additions of Mo, W, and Fe and variations in Nb and Al contents have on the phase fraction, thermal stability, elemental partitioning, and mechanical properties of alloys from this system. Alloys were produced through arc melting followed by heat treatment. Multi-scale characterization techniques and hardness testing were employed to characterize their microstructure, thermal stability, and mechanical properties. Alterations in such properties or in elemental partitioning behavior were then explained through thermodynamic modeling. A modest addition of 1.8 at. pct Mo had a strong effect on the microstructure and thermal stability: it minimized microstructural coarsening during heat treatments while not significantly decreasing the $\gamma'$ solvus temperature. A reduction of Nb by 0.6 at. pct strongly reduced the $\gamma''$ volume fraction, without affecting the $\gamma'$ volume fraction. The reduced precipitate fraction led to a significant reduction in alloy hardness. Fe, added to achieve better processability and reduced material cost, decreased the $\gamma'$ solvus temperature and caused rapid microstructural coarsening during heat treatments, without affecting alloy hardness. A reduction of Al by 0.4 at. pct reduced the $\gamma'$ volume fraction and the $\gamma''$ solvus temperature, also without affecting alloy hardness. The addition of 0.9 at. pct W decreased the $\gamma'$ solvus temperature but increased both precipitate volume fractions. These data will be invaluable to optimize current alloy design and to inform future alloy design efforts.
I. INTRODUCTION

There is a global drive to improve engine efficiency and reduce emissions in civil aviation. This motivates the development of new Ni-based superalloys capable of withstanding the higher operating temperatures and increased rotational speeds demanded in the next generation of gas-turbine engine designs.\[1\] Currently, Inconel\[2\] 718 (Ni-20.5Cr-18.85Fe-0.33Co-1.84Mo-1.18Al-3.3Nb-1.23Ti-0.34C-0.02B at. pct)\[2\] remains the most widely used alloy for intermediate temperature applications due to its favorable combination of processability and mechanical strength up to 650 °C. Indeed, it constitutes approximately one-third of the weight of some engines.\[3\] Inconel\[2\] 718 is strengthened by the precipitation of two ordered intermetallic phases, \(\gamma'\) (based on Ni\(_3\)Al with the L1\(_2\) structure) and \(\gamma''\) (based on Ni\(_3\)Nb with the D0\(_{22}\) structure) embedded coherently within the A1 matrix.\[4\] The \(\gamma''\) phase confers additional strengthening over the \(\gamma'\) phase alone (on a normalized volume fraction basis) due to the greater coherency strain resulting from the lattice misfit between the tetragonal \(c\)-axis of the \(\gamma''\) and the \(\gamma\) matrix. However, the \(\gamma''\) phase is also metastable, and rapidly transforms to the thermodynamically stable orthorhombic D0\(_4\) \(\delta\) phase at temperatures above 650 °C, limiting the upper operational temperature \[5,6\].

Alloys with superior temperature capability and strength to Inconel\[2\] 718 have been developed, although such alloys typically rely on higher refractory metal contents and precipitate volume fractions. Consequently, these alloys possess narrow processing windows, exhibit rapid work hardening, are not readily weldable and are susceptible to hot shortness.\[7–11\] While such alloys may be processed using powder metallurgical routes, this significantly increases alloy costs compared to cast and wrought products. As a result, there remains significant interest in developing affordable cast and wrought alloys with superior properties to Inconel 718\[2\], while simultaneously retaining the desirable processability characteristics.

Efforts to enhance the temperature capabilities of 718-type alloys have investigated compositional modifications as well as carefully defined heat treatment schedules to modify the precipitate morphology. Such efforts have been successful, but have only led to relatively modest improvements in thermal stability.\[4,12\] More recently, studies of alloys based on Ni-Cr-Al-Nb have identified the possibility of alloy microstructures containing appreciable volume fractions of both \(\gamma'\) and \(\gamma''\).\[5,13\] These alloys were reported to have yield strengths > 100 MPa higher than many commercial Ni-based superalloys such as 718Plus, Haynes 263, Haynes 282, Haynes 95, RR1000, U720, Rene 220, and Waspaloy. Subsequent work has demonstrated that these alloys retain microstructural stability up to 750 °C\[14\] and that further improvements to their properties may be achieved through judicious alloying.\[15\] However, if these alloys are to be effectively optimized for high temperature service, a detailed understanding must be established of how alloying additions affect the relative stability, morphology and properties of the constituent phases.

The original studies of dual-superlattice superalloys reported that an alloy with composition of Ni-15Cr-4Al-6Nb (at. percent) contained ~25 \(\gamma'\) and ~20 \(\gamma''\). While this alloy demonstrated attractive properties, three alloy development opportunities may be identified based on established superalloy metallurgy. First, the phase fractions are higher than many other superalloys derived from Inconel\[2\] 718. This may
adversely affect the processability of the alloy. It is therefore appropriate to consider alloys with lower Al and Nb contents to determine the extent to which the beneficial properties of a dual-superlattice microstructure may be retained with lower precipitate fractions. Second, the quaternary composition affords comparatively limited solid solution strengthening of the γ matrix. As such, further benefits may be derived from considering the addition of elements such as Mo and W to provide effective strengthening.\[^\text{15}\] Third, the elemental cost of the dual-superlattice alloy is higher than Inconel® 718. It is therefore appropriate to consider the extent to which Fe substitutions may be made as this will significantly reduce alloy cost and ease recycling.

Previous studies have shown that Mo and W additions partition strongly to the γ matrix, where they provide potent solid solution strengthening on a per atomic percent basis.\[^\text{16,17}\] W preferentially sits at Al sites in γ', but if Ta is present in the alloy system, W will instead partition to the γ matrix.\[^\text{18}\] However, these elements are also known to promote the formation of topologically close-packed phases (TCPs) such as σ and μ phase,\[^\text{19–21}\] which are considered deleterious and lead to reduced creep lives. The concentrations of these elements must therefore be carefully controlled to ensure microstructural stability.

In sufficient concentrations, Nb promotes the formation of Ni\(_2\)Nb γ" precipitates, as well as contributing to the γ’ precipitates where it substitutes for Al. As it does not partition strongly to the γ’, Nb additions usually have a limited effect on the γ–γ’ lattice misfit.\[^\text{22}\] Nb also increases the anti-phase boundary (APB) energy of the γ’, as well as acting as a solid solution strengther in both the γ matrix and γ’ precipitates.\[^\text{22,23}\] The addition of Nb has also been reported to reduce precipitate coarsening rates, which has been attributed to its sluggish diffusion kinetics in Ni.\[^\text{24}\]

Fe is an important constituent of Inconel® 718 and related alloys. It significantly reduces raw material costs, while simultaneously improving processability and recyclability. However, if the content is too high, deleterious Laves phases (Ni,Fe,Cr)(Nb,Mo,Ti) can be formed, which compromise the mechanical properties. Fe has also been reported to aid in the formation of γ” precipitates by lowering the electron:atom ratio to values around 2.50 to 2.62, which, as predicted using Engel–Brewer correlations, are preferred for stable D\(_{0_2}\) precipitates.\[^\text{25}\]

The present study involves a combination of microstructural and chemical characterization experiments and thermodynamic modeling, used to understand the properties of the resulting alloys. Six systematic compositional variations of the dual-superlattice alloy were produced to study the effect of Mo, Nb, W, and Fe on the phase stability, solvus temperature, and elemental phase partitioning. The results obtained give insight into the extent to which each of these additions may be accommodated without compromising the alloy microstructure and may therefore help inform future development of these alloys.

## II. EXPERIMENTAL METHODS

A series of six polycrystalline Ni-based superalloys were produced through vacuum arc melting from raw elements of > 99.9 wt pct purity, the alloy designations and nominal compositions of which are shown in Table I. The first alloy in this series, the Base alloy, was designed to contain the same Cr, Al, and Nb contents of the original dual-superlattice superalloy investigated in Reference \[^\text{13}\]. In addition, small concentrations of C, B, and Zr were included to provide grain boundary strengthening, in line with other polycrystalline Ni-based superalloys. The other five alloys were designed with consecutive compositional changes. From the composition of the base alloy, 1.8 at. pct Mo was substituted for Ni to produce the variant + 1.8Mo, having a composition similar to that in Inconel® 718. Next, the Nb composition was reduced to 5.4 at. pct, a reduction of 10 pct of the overall Nb content, to produce the alloy – 0.6Nb. For the third variation + 9Fe, 9 at. pct Fe was added to the composition of 0.6Nb, similar to the composition in AT1 718Plus®. In the – 0.4Al alloy, the Al content was reduced to 3.6 pct, a reduction of 10 pct of the overall Al content. Finally, + 0.9W included 0.9 at. pct W, a composition corresponding to ~ 3 wt pct. In this alloy, Fe was removed in order to avoid complications arising between these two additions. Compositions were measured by SEM–EDX, operated at a voltage of 10 kV. For each alloy, two large area scans over approximately 11mm\(^2\) were taken for 500 s each, the averaged data can be found in Table II. Within the uncertainties that arise from EDX bulk compositional analysis, there is generally a good agreement with the nominal compositions.

All six alloys were prepared for heat treatment by encapsulation in quartz ampoules under vacuum. Solution heat treatments to improve microstructural homogeneity and remove solidification-induced microsegregation were performed at 1200 °C for 24 hours. Subsequent heat treatments were performed

| Name     | Ni | Cr | Nb | Al | Mo | Fe | W | C | B | Zr |
|----------|----|----|----|----|----|----|----|----|----|----|
| Base     | bal| 15 | 6  | 4  | —  | —  | —  | 0.15| 0.16| 0.04|
| + 1.8Mo  | bal| 15 | 6  | 4  | 1.8| —  | —  | 0.15| 0.16| 0.04|
| – 0.6Nb  | bal| 15 | 5.4| 4  | 1.8| —  | 9  | 0.15| 0.16| 0.04|
| + 9Fe    | bal| 15 | 5.4| 4  | 1.8| 9  | —  | 0.15| 0.16| 0.04|
| – 0.4Al  | bal| 15 | 5.4| 3.6| 1.8| 9  | —  | 0.15| 0.16| 0.04|
| + 0.9W   | bal| 15 | 5.4| 3.6| 1.8| —  | 0.9 | 0.15| 0.16| 0.04|

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at 800 °C for 10 and 100 hours to induce precipitation and coarsening of the dual-superlattice γ′ and γ″ microstructures.

The effect of the different alloying additions on the γ′ solvus temperature was determined through differential scanning calorimetry (DSC). DSC thermograms were collected from samples after 100 hours of heat treatment at 800 °C, measuring 5 mm in diameter, and 1 mm thick, using a Netzsch 404 high temperature calorimeter. The heat flux was measured during heating at 10 °C min⁻¹ between 600 and 1400 °C. The tests were performed under flowing Ar to minimize sample oxidation. The resulting data were analyzed according to the NIST guidelines[27] to determine the γ′ solvus temperatures.

Samples were prepared for metallographic examination by sectioning with a Buehler Isomet saw, then mounted in conductive phenolic resin, ground using SiC papers, polished with progressively finer diamond papers, polished with progressively finer diamond, then electro-etched using a 10 vol. pct phosphoric acid solution in distilled water at an applied voltage between 3 and 5 V. Scanning electron micrographs were obtained using an FEI Nova NanoSEM 450 and a Zeiss Auriga SEM, both operated at 5 kV.

X-ray diffraction (XRD) was performed using a Bruker D8 Advance Gen.9 0–20 diffractometer fitted with a LynxEye EX position sensitive detector (PSD). Diffraction data were acquired using Cu-Kα radiation, generated using a 40 kV accelerating voltage, a 40 mA current, and a 2θ collection range of 20°–100°, with an increment of 0.02° and a dwell time of 7 seconds. Diffractograms were analyzed using CrystalDiffract software by comparing them to reference spectra available through the Inorganic Chemical Structures Database (© FIZ Karlsruhe).

Hardness measurements were carried out on a Wilson® VH1202 micro hardness tester using a load of 2 kg and dwell time of 15 seconds. For each sample, 21 measurements were taken from various points spread over the full sample area and the mean values and standard deviations were calculated.

Samples were prepared for Atom Probe Tomography (APT) through cutting and electropolishing of matchsticks, performed using first a solution of 15 vol. pct perchloric acid in acetic acid and a 16–20 V DC voltage, then sharpened using a 2 vol. pct perchloric acid in butoxyethanol at 10 V DC voltage.[28] Samples were analyzed in a Cameca LEAP 5000 XR atom probe, at 50 K, with a pulse frequency of 200 kHz, a detection rate of 1.5 pet, and a pulse fraction of 0.2 for specimens run in voltage mode. Reconstructions were performed using the Cameca Integrated Visualization and Analysis Software (IVAS) 3.6.12 and AP Suite 6, using mainly standard voltage curve reconstruction. Constant shank angle reconstructions were used and compared to the voltage curves. These were only employed in the event the voltage curve reconstruction visibly distorted precipitates due to artifacts (e.g., to mitigate the effect of potential small sample fractures during analysis). Iso-concentration surfaces were created at 7 at. pct Al and 13 to 15 at. pct Nb to identify the different phases present in the alloys. Where a peak overlap was observed (e.g., Cr–Al–Fe at 27 Da, Ni–Nb at 31 Da), it was labeled as the phase with only one isotope, in this case Al and Nb. The reason for this is while Cr, Fe, and Ni have other labeled primary isotope peaks, Al and Nb do not and therefore would not have been included in the reconstruction. Peak decomposition algorithms were then used to obtain phase composition values from isolated single-phase spectra, thereby reducing errors arising from peak overlaps.

Predictions of the phase fractions, phase compositions, and lattice parameters were completed using the Thermo-Calc 2019b software package, with the TCNi8 v8.2 Ni-alloy databases.[29] All compositional predictions were obtained at an isothermal temperature of 800 °C. The simulations were run considering only the γ, γ′, and γ″ phases, consistent with the microstructural observations. Without phase selection, the equilibrium δ phase is predicted over the metastable γ″, in addition to several TCP phases. By excluding δ, the software is forced to calculate with the metastable γ″. The TCP phases were excluded for similar reasons—they may be thermodynamically stable, their formation is typically kinetically inhibited over the short heat treatment durations studied here. Because of this, their exclusion is expected to increase the accuracy of the predictions, as TCP formation significantly depletes the matrix of alloying additions and affects the overall phase compositions and volume fractions.

### III. RESULTS

DSC thermograms from all the alloys revealing the γ′ solvus temperature are shown in Figure 1. Full DSC thermograms taken from 200 to 1400 °C are found in the appendix, Figure A1. Both precipitate phases γ′ and γ″ strengthen the alloy, therefore knowledge of their solvsus is important to understand the limits in operational temperature of the alloys. In this work, we have focused on understanding the effects on γ′ phase
stability, which is particularly useful for high temperature applications. The stability of the γ'' phase will form part of a future work. Some additional phase changes are observed through kinks in the thermograms both below the γ'' solvus temperature and for the – 0.6Nb alloy also above the γ'' solvus temperature. These events are unlikely to be melting events as no intrinsic melting was observed for any alloys after heat treatment of up to 1200 °C. Further investigation as to the exact nature of the events is beyond the scope of this work. The measured γ'' solvus temperature is summarized and compared to thermodynamic predictions in Figure 2 (values also given in appendix Table A-I). The addition of 1.8 at. pct Mo did not significantly alter the γ'' solvus temperature as it led to a reduction of only 1 °C from 1010 to 1009 °C, which lies within the experimental error of the DSC. The reduction of Nb content to 5.4 at. pct reduced it by further 4 °C to 1005 °C and the addition of 9 at. pct Fe resulted in a decrease in γ'' solvus temperature of 17 °C from 1005 to 988 °C. A further 18 °C reduction to 970 °C was observed for the – 0.4Al alloy, which has an Al content of 3.6 at. pct, 10 pct lower than the 4 at. pct of the previous alloys. Al and Nb hence increase the γ'' solvus temperature, whereas Mo and Fe reduce it. Lastly, the + 0.9W alloy exhibited a γ'' solvus temperature of 983 °C. It is not as straightforward to determine the effect of W on the solvus temperature as it was for the other alloying additions. This is because the + 0.9W alloy differs in composition of at least two elements compared with any of the other investigated alloys. The + 0.9W alloy is best compared to either the – 0.4Al alloy with a lower γ'' solvus temperature of 970 °C or to the – 0.6Nb alloy with a higher γ'' solvus temperature of 1005 °C.

First, a comparison between the – 0.4Al alloy and the + 0.9W alloy is undertaken. The difference between these alloys is a removal of the 9 at. pct Fe together with the addition of 0.9 at. pct W. As previously stated, the addition of Fe resulted in a reduction of the solvus temperature. Hence, it is not surprising that the γ'' solvus temperature increases as Fe is removed in the + 0.9W alloy. However, the total difference in solvus temperature from the – 0.4Al to the + 0.9W alloy amounts to only 13 °C, which is substantially less than what was observed for the addition of 9 at. pct Fe to the base alloy (17 °C). Hence, from the comparison of the – 0.4Al alloy and the + 0.9W alloy, it can be suggested that W reduces the γ'' solvus temperature.

The difference between the – 0.6Nb alloy and the + 0.9W alloy is a decrease of the Al content from 4 to 3.6 at. pct alongside the addition of 0.9 at. pct W. A comparison of these alloys reveals a strong reduction in γ'' solvus temperature of 22 °C. Comparing the base alloy and the – 0.4Al alloy, it was found that the reduction of Al led to a reduction of the solvus temperature by 18 °C. Again, the conclusion can be drawn that W led to a further reduction of the γ'' solvus temperature. For both comparisons, the excess reduction attributed to the addition of 0.9 at. pct W amounts to 4 °C.

The results collectively indicate that the γ'' solvus temperature is reduced by Mo, Fe, and W additions, among which W has the relatively strongest effect. However, more pronounced effects are observed for the alloying elements Nb and Al, which both increase the γ'' solvus temperature, with Al being by far the most potent element of all investigated elements. The potencies of these elements are summarized in Table III. The

Table III. Summary of the Potency of the Alloying Additions to Affect the γ'' Solvus Temperatures

| Alloying Element | γ'' Solvus Temperature Potency |
|------------------|-------------------------------|
| Mo               | – 0.6 °C/at. pct              |
| Nb               | + 6.7 °C/at. pct              |
| Fe               | – 1.9 °C/at. pct              |
| Al               | + 45 °C/at. pct               |
| W                | – 4.4 °C/at. pct              |

Fig. 1—DSC thermograms of the alloys showing how individual alloying additions influence the γ'' solvus temperature.

Fig. 2—Comparison of the γ'' solvus temperatures of the alloys as derived from the DSC thermograms and as predicted by Thermo-Calc.
thermodynamic predictions from Thermo-Calc capture the overall trend of $\gamma'$ solvus temperature, particularly the correlation with Al content. However, the predicted effects of Mo and W do not appear to correlate with the experimental observations. Across the entire series of alloys, it is noted that there is an offset of approximately 70 °C between the Thermo-Calc predictions and the experimental values.

A homogenizing heat treatment was chosen for all alloys at 1200 °C in order to dissolve all precipitates, including $\gamma'$ and $\gamma''$, that may have formed during fabrication. This temperature was selected based on the DSC data in Figures 1 and A1 which show the full DSC thermograms up to 1400 °C, thus including the solidus temperature of the alloys. The homogenization temperature was selected to be above all solvus events and temperature of the alloys. The homogenization temperature was selected to be above all solvus events and below the solidus for each alloy. Then, samples were heat treated at 800 °C to induce the controlled levels of precipitation. Figure 3 shows the X-ray diffractograms produced after 100 hours at 800 °C. The base alloy was previously shown to precipitate primarily a combination of $\gamma'$, $\gamma''$, and $\delta$ phases, depending on the heat treatment.[14] After up to 1000 hours at 750 °C, only $\gamma$, $\gamma'$, and $\gamma''$ were observed by synchrotron X-ray diffraction, while at 800 °C $\delta$ precipitation began to occur when the heat treatment exceeded 100 hours in duration.[14]

In the present case, X-ray diffractograms, shown in Figure 3, confirmed that all alloys contained $\gamma$, $\gamma'$, and $\gamma''$ phases. Additional phases are confirmed by XRD in most alloys; the $\delta$ phase and another phase that is likely niobium carbide (NbC). The reduction of Nb may have reduced $\delta$ and NbC precipitation, whereas the reduction in Al and the addition of W promoted the precipitation of these phases. Analysis of the peak location allows to extract lattice parameters of the phases. As the diffraction peaks of the $\gamma$ and $\gamma'$ phase overlap substantially, for most alloys only one lattice parameter for both the $\gamma$ and $\gamma'$ phase was extracted as is presented in Table IV. For the Base and the $-0.4\text{Al}$ alloy, a single value for the lattice parameter was insufficient to match both peaks. It may be that the lower extracted value represents the $\gamma$ lattice parameter and that the larger extracted lattice parameter belongs to the $\gamma'$ phase. Thermo-Calc predicted lattice parameters for the $\gamma$ and $\gamma'$ phases were calculated using molar volumes from the following equation:

$$a = \left(\frac{4V_m}{N_A}\right)^{\frac{1}{2}}$$

where $V_m$ is the predicted molar volume and $N_A$ is Avogadro’s number.

The misfit was calculated according to the following expression:

$$\delta = 2 \left(\frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma'} + a_{\gamma}}\right)$$

The predicted data are also presented in Table IV. Although there is an offset between the experimentally extracted and predicted lattice parameters, where the predicted lattice parameters are consistently larger, the trends in lattice parameter changes roughly coincide. Additions of Mo are found to increase the ($\gamma$) lattice parameter. The reduction of Nb reduces the lattice parameter, and the addition of Fe increases the lattice parameter where Thermo-Calc predicts this change to occur mostly in the $\gamma'$ phase. Thermo-Calc predicts an increase in $\gamma$ and decrease in $\gamma'$ lattice parameter for the removal of Fe and addition of W in the 0.9W alloy, which coincides with the data extracted from XRD. The lattice misfit as predicted by Thermo-Calc effectively decreases for both the addition of Mo and W.

The measured hardness of the alloys is given in Figure 4. The most prominent effect is found for the reduction of Nb by 0.6 at. pct, which led to a reduction in the hardness of over 40 HV. In contrast, the addition of 9 at. pct Fe as well as the reduction of Al by 0.4 at. pct

| Table IV. Lattice Parameters as Extracted from XRD Diffraction Patterns (First Row) and as Calculated by Thermo-Calc (Second and Third Row) |
|-------------------|----------------|----------------|----------------|----------------|----------------|
|                   | BASE           | + 1.8Mo        | $-0.6\text{Nb}$ | + 9Fe          | $-0.4\text{Al}$ | + 0.9W         |
| XRD               | $a_\gamma$/Å   | 3.578 to 3.593 | 3.59           | 3.584          | 3.595          | 3.577 to 3.607 | 3.59          |
| Thermo-Calc       | $a_\gamma$/Å   | 3.611          | 3.620          | 3.619          | 3.620          | 3.619          | 3.623          |
| Thermo-Calc       | $a_\gamma$/Å   | 3.674          | 3.675          | 3.675          | 3.678          | 3.677          | 3.675          |
| Thermo-Calc       | $\delta$/10^{-2}$ | 1.749         | 1.509          | 1.531          | 1.575          | 1.589          | 1.444         |

The calculated lattice parameters were used to calculate the lattice misfit (fourth row).
did not significantly affect the alloy hardness in comparison to their respective previous alloy. Lastly, the addition of the solid solution strengtheners Mo and W seem to have had a positive effect on the alloy hardness, although the relatively large standard deviations reduce the clarity of this observation.

SEM micrographs of the alloys following heat treatment at 800 °C for 10 hours and for 100 hours are presented in Figures 5(a) and (b), respectively. The micrographs were taken from within the grains, away from grain boundaries. The δ phase is not seen in the presented micrographs, as it was found only in small quantities, localized at grain boundaries. NbC particles were also found only in small quantities. The formation of the δ phase with respect to alloying alterations is beyond the scope of the present study and will be part of a future work.

As shown in Figure 5, the 10 hours of heat treatment yielded extremely fine nano-structured microstructures. Heat treating for 100 hours coarsened the precipitates and allowed the effect of individual alloying additions on the precipitate morphology and fraction to become clearer. The micrograph of the base alloy shows the precipitation of two distinct precipitate phases: cuboidal γ' precipitates with rounded corners and thinner, lenticular γ'' precipitates. The two types of precipitates appear in a dual-superlattice and are not connected to each other. Some previous studies on coprecipitation of γ' and γ'' had identified a different, compact morphology where the γ'' phase precipitated on the faces of the cuboidal γ' precipitates and thus helping to reduce γ' coarsening.[4,30,31] The differences in precipitate morphology between those previous studies revealing a ‘compact coprecipitation’ morphology and the current work revealing a precipitate dual-superlattice is likely due to differences in composition and processing, i.e., heat treatments. Besides the Base alloy, the precipitate dual-superlattice can also be observed in all the additional alloys, though slight changes in their morphology and distribution are found for each compositional variation.

The addition of 1.8 at. pct Mo had a refining effect on the microstructure and the 0.6 at. pct reduction of Nb seems to have led to a reduction in the precipitate phase fraction, both of which can be observed after 10 hours and even more so after 100 hours of heat treatment. Allying with 9 at. pct Fe led to substantial coarsening of the microstructure as compared to the −0.6Nb alloy. The formerly cuboidal precipitates are now more irregularly shaped. The clear morphology difference between the γ' and the γ'' precipitates is reduced as these phases seem to have precipitated adjacent to each other instead of being separated from one another by the matrix phase. With the reduction of the Al content in the −0.4Al alloy, the precipitate phase fraction further decreased and the precipitate phases were still clustered together rather than separated by the matrix. Finally, the removal of Fe and the addition of W in the +0.9W alloy restored the more refined microstructure similar to the +1.8Mo alloy, with more distinct precipitate phases than in the Fe-containing alloys. The exact phase fractions of γ' and γ'' of the alloys cannot be calculated from the SEM micrographs due to the similarity in contrast between the precipitates.

Atom probe tomography was utilized to measure accurate chemical compositions and assess the effect of individual alloying additions on partitioning behavior in the γ', γ", and δ phases. The samples heat treated for 10 hours were chosen for this study because the finer microstructure would allow detection of multiple phases within each atom probe needle. In comparison to the SEM analysis, APT allows the unambiguous identification of the precipitate phases by their compositional differences.

An atomistic scale reconstruction of the APT sample of the base alloy is shown in Figure 6(a) in which the γ, γ', and γ'' phases may be separately distinguished. Due to the complex shapes and number of phases present, proximity histograms could not be utilized to analyze their interfaces. Instead, regions of interest (50 × 20 × 20 nm) were selected and located perpendicular to the interface to be analyzed. This method, which provides 1-D composition profiles, is very effective for measuring chemical compositions at the interfaces, although if the selected area is not perfectly parallel to the interface, its width can be artificially inflated. Figure 6(b) shows a 1-D composition profile going through all the phases present. The solid solubility of Nb in the γ' phase is substantially higher than that of Al in γ'', which is consistent with the previous semi-quantitative EDX observations.[13]

The alloy with 1.8 at. pct Mo was also analyzed by atom probe tomography and a reconstruction is shown...
Fig. 5—In-lens SEM images of the microstructure of each alloy after (a) 10 hours of heat treatment and (b) 100 hours of heat treatment at 800 °C.
Fig. 6—(a) Atom probe tomography reconstruction of the base alloy, showing Cr, Al, and Nb atom distributions in the three phases $\gamma$, $\gamma''$, and $\gamma''''$, separated by iso-concentration surfaces of 7 at. pct Al and 15 at. pct Nb; (b) 1-D composition profile going across all the phases present, the location the composition profile was taken from is shown in (a) as a white arrow.

Fig. 7—(a) APT reconstruction of a specimen of the alloy with 1.8 at. pct Mo iso-concentration surfaces of 7 at. pct Al and 15 at. pct Nb envelope the precipitate phases $\gamma'$ and $\gamma''''$; (b) detailed view of crystallographic zone axis from the reconstruction shown in (a); (c), (d), and (e) 1-dimensional composition profiles across all phase interfaces from the reconstruction shown by arrows in (a).
in Figure 7(a), where the cuboidal precipitate morphology of the \( \gamma' \) precipitates can be observed.

One-dimensional composition profiles across the \( \gamma' \)-\( \gamma'' \) phase interfaces are shown in Figures 7(b) through (d). The added Mo is predominantly accommodated within the \( \gamma \) phase as well as in the \( \gamma'' \) phase but is absent in the \( \nu \) phase. Figure 7(d) reveals a depletion in Ni at the \( \gamma' \)-\( \gamma'' \) interface. While the interface between the \( \gamma \) and the \( \gamma' \) phase is clear, the interface between the \( \gamma \) and \( \gamma'' \) phases as well as between the \( \gamma' \) and \( \gamma'' \) phases (Figures 7(c) and (d)) are diffuse, which can be observed through the "serrations" in the iso-concentration surfaces shown in Figure 7(a). The serrations are likely to be an artifact of the data binning algorithm.

The 3D reconstruction of the \(- 0.6\text{Nb}\) APT specimen is shown in Figure 8(a). The lenticular \( \gamma'' \) shape is clearly seen in this specimen. It is also noteworthy that the \( \gamma'' \) precipitate has grown around a \( \gamma' \) precipitate, indicating that the \( \gamma' \) precipitates formed first. 1-D composition profiles through all three phases are presented in Figures 8(b) through (d). No apparent differences to the previous alloy are observed from the reduction of Nb, with the only exception that the \( \gamma' \)-\( \gamma'' \) interface is slightly enriched in Ni, whereas the same interface was depleted in Ni for the previous alloy. The alloying alterations may have caused a change in interfacial energy of the precipitate phase interfaces, leading to decoration or expulsion of Ni at the interface.

The APT reconstruction of the \(+ 9\text{Fe}\) alloy is shown in Figure 9(a). Based on the SEM analysis shown in Figure 5, the presence of Fe coarsened the microstructure and led to more spherical than cuboidal \( \gamma' \) phase precipitates which have grown into one another as well as into the \( \gamma'' \) phase. The spherical shape of the \( \gamma' \) precipitates and their merging are also observable in the APT reconstruction, as can be seen for the irregular
precipitate in the back of the reconstruction, likely having merged from two or three γ’ phase precipitates.

Inspection of the interfacial composition profiles, shown in Figures 9(b) through (d), indicate that Fe segregated preferentially to the γ’ phase, although low levels were found in solid solution both in the γ’ and in the γ” phases. In contrast to the +1.8Mo alloy but similarly to the +0.6Nb alloy, there is an excess Ni segregation at the γ’–γ” interface.

Figure 10(a) shows an APT reconstruction of the 0.4Al alloy. The lenticular nature of the γ” phase is, again, clearly seen and the γ’ phase is found to sit on the side of the γ” phase in accordance with the observations made from the SEM micrographs. One γ’ precipitate is found sitting partially within the γ” phase. This is an observation that the SEM had not been able to provide due to the lack of contrast between the precipitate phases.

Figures 10(b) through (d) show 1-dimensional composition profiles across phase interfaces. There are no apparent differences in the phase compositions and interface segregation of this alloy compared to the +9 Fe alloy.

Figure 11(a) shows an APT reconstruction of the alloy with 0.9 at pct W. The +0.9W alloy does not contain Fe and exhibited phase compositions comparable to the −0.6Nb alloy apart from low levels of W in each phase. W partitioned preferentially to the γ” phase (Figure 11(d)), although low levels (<0.5 at pct) were detected within the γ and γ’ phases as well (Figures 11(b) and (c)). In contrast to the previous alloys, the γ’–γ” interface exhibits neither a depletion nor an enrichment of Ni.

For accurate elemental compositions of the γ, γ’, and γ” phases, peak decomposition analysis was performed on the atom probe tomography data. This analysis
yields more precise phase compositions than the 1-D elemental composition profiles, which are used to analyze the interfaces. The decomposition analysis was performed on spectra from isolated single-phase volumes, which were delineated with the iso-concentration surfaces shown in Figure 11, with the interfacial region excluded due to its data not being representative. This was done by exporting the individual phases as a separate file, then selecting a central region of interest (ROI) within them. The peak decomposed APT compositions are shown in Figures 12(a) through (c), respectively (values also given in appendix Tables A-II, A-III and A-IV). From this, conclusions can be drawn on the effects of the alloying additions on the microsegregation of the elements. The alloying additions changed the composition as follows:

\[ +1.8\text{Mo} \] With the addition of 1.8 at. pct Mo, some compositional changes can be observed compared to the base alloy. In the matrix $\gamma$ phase of the $+1.8\text{Mo}$ alloy, Mo took up to 2.5 at. pct, which is consistent with a reduction of Ni by 2.5 at. pct from the value in the base alloy. This suggests that in the matrix $\gamma$ phase Mo merely substituted for Ni. In the $\gamma'$ phase, the presence of Mo had no apparent effect on the composition, although 0.3 at. pct Mo was found in solid solution. Mo, however, triggered dramatic changes to the $\gamma''$ phase composition by decreasing the Al and increasing the Cr solid solubility. In the base alloy, $\gamma''$ contained 6.3 at. pct Al and 1.5 at. pct Cr, whereas the $+1.8\text{Mo}$ alloy contained 5.9 at. pct Cr and 1.8 at. pct Al. Also, the Nb content was reduced by 2 at. pct and Mo was found at 2.2 at. pct in solid solution.

\[ -0.6\text{Nb} \] As the Nb content was reduced from 6 to 5.4 at. pct, the $\gamma$ phase exhibited a slight increase in Ni (+1.7 at. pct) and a slight decrease in Cr (-1.3 at. pct). The Nb reduction does not seem to have affected the elemental segregation in the precipitate phases $\gamma'$ and $\gamma''$. 

Fig. 10—(a) APT reconstruction of the $-0.4\text{Al}$ alloy with iso-concentration surfaces of 7 at. pct Al and 15 at. pct Nb, (b) proximity histogram showing the elemental composition profile across the $\gamma-\gamma'$ interface, (c) 1-D elemental composition profile across the $\gamma'-\gamma$ interface, and (d) 1-D elemental composition profile across the $\gamma''-\gamma''$ interface. The locations of the 1-D composition profiles are highlighted by arrows in (a).
+ 9Fe The highest content of Fe was found in the γ phase, where it mainly substituted for Ni (Ni - 12.8 at. pct, Fe + 12.4 at. pct) and also resulted in a slight increase of Cr by 1.5 at. pct along with a reduction of Nb by 0.9 at. pct. Only 2 at. pct Fe was found in the γ' phase and the Al content was reduced by 1 at. pct. More dramatic effects were observed for the γ" phase where the solubilities of Nb and Cr were clearly affected. Here, the Nb content increased by 4 at. pct and Cr decreased by 3.3 at. pct. Fe was present in a low amount of 1.5 at. pct.

− 0.4Al The 10 pct reduction of Al did not greatly affect the phase compositions. Only in the γ phase, there were slight variations in the segregation behavior of Ni and Cr: the Ni content increased by 1.4 at. pct while Cr decreased by 1.5 at. pct. In the precipitate phases, there were no visible compositional differences to the + 9Fe alloy.

+ 0.9W The + 0.9W alloy, which does not contain Fe, did not exhibit any strong compositional changes. W was found in all phases with a preferential segregation to the γ" phase (γ: 0.8 at. pct, γ': 0.4 at. pct, γ'': 1.4 at. pct). This alloy had the highest γ' phase Al content (15.1 at. pct) out of all the investigated alloys and the lowest γ" phase Nb content (15.3 at. pct).

Figure 12 also shows the phase compositions as predicted by Thermo-Calc at 800 °C. For the γ matrix, the predicted data matched the experimental data well with only slight deviations, such as the predicted Ni content being slightly above the measured data but following the trends and the Cr prediction being slightly below the measured content. While the prediction of Ni content in the γ' phase matches the experimental data very well, larger deviations are found for the two
precipitate forming elements Al and Nb. It is worth noting that this is likely related to the observed temperature offset in the Thermo-Calc predictions, as has been observed in other studies.\cite{32,33,34} The comparison of the $\gamma'$ solvus temperature as measured by DSC and as predicted by Thermo-Calc (Figure 2) revealed an offset of approximately $-70 \, ^\circ C$. Thermo-Calc predictions of the phase compositions calculated at an isothermal temperature of $700 \, ^\circ C$, i.e., at a temperature which compensates somewhat for the observed offset, are in very good agreement to the measured compositions for the $\gamma$ and $\gamma'$ phase, see appendix Figure A2. For both the compositions calculated at $800 \, ^\circ C$ shown in Figure 12 and those calculated at $700 \, ^\circ C$, the Thermo-Calc predictions for the $\gamma''$ phase showed large discrepancies from the experimentally obtained data. The greatest deviation was found for Nb, followed by Cr, which is likely due to the difficulties in performing calculations involving metastable phases. The deviations may also be a reflection of the fidelity of the thermodynamic databases across this particular region of composition space.

IV. DISCUSSION

Compositional variations to a promising polycrystalline Ni-based superalloy have been investigated to get insights into the role of alloying elements and to further promote the development of new and improved
The yield strength of the alloys was not measured directly but instead hardness data were used as a proxy, allowing alloying effects to be investigated. One key question this work wanted to answer was whether the yield strength could be retained when reducing the Nb and Al content to achieve an improved processability. Such a reduction would reduce the precipitate phase fraction, which may lead to a reduced hardness. Our data show that the Al reduction does not notably affect the alloy hardness, while the Nb reduction significantly reduces the alloy hardness. This effect, which may be putatively attributed to a decreased precipitate fraction, but also due to decreased solid solution strengthening, should be considered for further alloy development.

Mo and W, which are both added for solid solution strengthening, have a positive effect on the hardness, which confirms their role as solid solution strengtheners. This effect of Mo and W has also previously been reported on individual rather than successive alloying additions to the Ni-15Cr-4Al-6Nb (at. percent) system.[13]

B. Alloying Effects on Microstructure and Partitioning

SEM micrographs show that Mo has a refining effect on the microstructure, and Fe additions result in precipitate coarsening and clustering, such that γ′ and γ″ precipitates can no longer be clearly distinguished. While Nb was reported to reduce precipitate coarsening,[24] the slight reduction of 0.6 at. pct does not seem to have a strong effect on the microstructure besides reducing the precipitate volume fraction, similar to the reduction of Al. Comparing this with the previous work by Mignanelli et al.[14] they showed that Mo and Fe had no visible effect on the microstructure when observed by SEM, whereas W lead to a “loss of morphological distinction.” However, in their study alloying elements were added individually (to different alloy samples), whereas in our study, these elements were added successively, which may account for the discrepancies in the observations due to the interplay between elements.

The lattice misfit between matrix and precipitate phases influences alloy microstructures. Besides determining precipitate phase shapes, the decreased interfacial energy that goes along with decreased lattice misfits can enhance coarsening. In our study, however, additions of Mo and W lead to a decrease in the lattice misfits while simultaneously resulting in more refined microstructures. Most likely, the slow microstructure coarsening kinetics are dominated by the slow diffusion of the alloying elements Mo and W in Ni.

Due to insufficient contrast between the precipitate phases, phase volume fractions could not be retrieved from the SEM micrographs. However, it is possible to derive the phase fractions from the APT data, from which compositions for all three principal phases were obtained. As these compositions need to add up to the overall sample composition, a linear equation system can be set up. Due to uncertainties in the compositional values, a solution for the phase fraction can be found by solving a constrained least square problem using linear optimization. Two constraints were applied: (1) all phase fractions need to be between zero and one and (2) all phase fractions must add up to one. The so-derived atomic phase fractions can be converted to volume phase fractions with the knowledge of the volume per unit cell, taken from the XRD measurements, and the number of atoms per unit cell as given by
the well-known crystal structures of the phases. An uncertainty analysis was performed using bootstrapping and is presented in the appendix, Figure A3.

The changes in composition near interfaces are not considered in this calculation and can hence lead to some deviations from the actual volume fractions. However, the so-derived data, presented in Figure 13, can be used for relative comparisons between different alloys and hence can be related to alloying effects of the individual alloying elements. The presence of the \(\delta\) phase in all alloys is not considered to have a noticeable influence on this analysis, as the \(\delta\) phase was only found in small quantities at the grain boundaries, away from the lift-out regions for the atom probe needles.

It has previously been mentioned that the Al/Nb ratio is indicative of the type of phase precipitation in a Ni-based superalloy, with ratios larger than 1 leading to two-phase systems of \(\gamma\) and \(\gamma'\) only\(^{[36]}\) and ratios below 0.3 leading to \(\gamma\) and \(\gamma''\). Therefore, the base alloy was developed with an intermediate ratio in order to achieve the coexistence of all three phases.\(^{[13]}\) For all alloys in this work, the Al/Nb ratio is between 0.67 and 0.74, i.e., intermediate, and all contain the three phases \(\gamma\), \(\gamma'\), and \(\gamma''\). The alloys with a larger ratio show also a reduced \(\gamma''\) fraction which agrees with the above statement that larger Al/Nb ratios lead to the disappearance of \(\gamma''\).

To assess the effect of individual alloying additions and alterations, it is helpful to consider the evolution of the phase volume fractions in conjunction with elemental partitioning and the other results presented.

C. Effect of Mo

Upon addition of Mo to the base alloy, both precipitate volume fractions increase though \(\gamma''\) does so more strongly than \(\gamma'\). The matrix phase volume fraction is reduced accordingly. Looking at the elemental partitioning, Mo is found to partition preferentially to \(\gamma\) and \(\gamma''\) (\(\gamma''\) > 2 at. pct \(\gamma'\) at 0.4 in \(\gamma'\)). It also leads to a change in Al partitioning in the \(\gamma''\) phase. There is a sharp reduction of Al content in the \(\gamma''\) phase after the addition of Mo, and also the Nb content is reduced while Cr is enriched. The reduction of the Nb composition needed for \(\gamma''\) formation may explain, in part, the increase in \(\gamma''\) volume fraction. The Al which no longer partitions to the \(\gamma''\) can instead go to \(\gamma'\) which explains the increase in \(\gamma'\) phase fraction. The increased solubility of Cr in the \(\gamma''\) phase at the expense of Al could be caused by the presence of Mo in this phase. The authors believe that Cr preferentially co-segregates with Mo, as is suggested by the compositions of phases such as the sigma phase and carbides, which are commonly enriched in both Cr and Mo and depleted in Al.\(^{[37,38]}\) Some previous work by Gardner \textit{et al.} has shown that similar effects (reduction of Nb, Al and increase of Mo, Cr) occur during the transition from the desirable, metastable \(\gamma''\) to the undesirable, stable \(\delta\) phase.\(^{[39]}\) This could mean that the addition of Mo would promote that transition, although a more thorough investigation of the behavior of Cr segregation and relative stability of \(\gamma''\) and \(\delta\) falls outside the scope of this work.

An increase in the lattice parameters was extracted from XRD and predicted to occur mostly in the \(\gamma\) matrix by Thermo-Calc. This may be due to Mo, having a slightly larger covalent radius than Ni and partitioning to the matrix.

The + 1.8Mo alloy is found to have the highest total precipitate fraction (\(\gamma' + \gamma''\)) of all alloys. As the SEM micrograph shows a refined microstructure, it can be concluded that the addition of Mo leads to the precipitation of a finer and denser dual-superlattice microstructure.

This change in microstructure and the increase in total precipitate fraction may contribute to the slight increase in hardness observed, additionally to a solid solution strengthening mechanism.

D. Effect of Nb

Nb partitions to both precipitate phases, but more strongly to the \(\gamma''\) phase (around 15 to 20 at. pct vs. 8 to 10 at. pct in \(\gamma'\)). Upon reduction of Nb, the \(\gamma''\) volume fraction is strongly reduced in favor of the matrix phase \(\gamma\), while the \(\gamma'\) volume fraction stays the same. This is consistent with Nb being a strong \(\gamma''\) former. It is, however, also one of the major constituent elements of \(\gamma'\) but clearly does not determine the \(\gamma'\) volume fraction. The fact that the \(\gamma'\) volume fraction is not affected by the reduction in Nb leads to the conclusion that Nb first occupies the \(\gamma'\) precipitates and only when \(\gamma'\) is saturated in Nb, the remaining atoms form \(\gamma''\). This is supported by the fact that \(\gamma'\) forms prior to \(\gamma''\) as has previously been suggested by Pineau and Cozad\(^{[4,39]}\) and later shown through TTT diagrams, and as is suggested by the present atom probe reconstructions in Figures 8, 10, and 11. It is also supported by the previously mentioned
relationship between Al/Nb ratio and prevalent precipitate phases.[13] (see also Section IV—B).

When reducing the Nb composition, due to the reduced γ'' volume fraction, the total precipitate fraction is again at a similar level to the base alloy. The hardness, however, is strongly reduced compared to both the Base and the + 1.8Mo alloy. This could be due to reduced solid solution strengthening with reduced Nb content. However, the observation could also suggest that γ'' may be a more effective precipitate strengthen than γ.

E. Effect of Fe

As Fe is added for improved processability and reduced material cost, it is to be assessed whether the additions lead to any deteriorations in superalloy properties. Fe can trigger the precipitation of detrimental Laves phases. It is a promising result that these phases were not found in the present alloys.

However, Fe had a clear effect on the precipitate morphology, in particular the γ' and γ'' phases which precipitated adjacent to one another. The fact that the γ'' precipitates have nucleated on γ' precipitates reminds of the behavior found in previous studies[4,31] (also mentioned in SEM results section), although there is still a large difference between the current morphology we observed, which we would still consider a dual-superlattice morphology, and the ‘compact coprecipitation’ morphology observed in the aforementioned studies. The alloys investigated in the previous studies all contain Fe, which may suggest that the presence of Fe plays a key role in the change of morphology from a separated precipitate dual-superlattice to compact coprecipitation. Further studies investigating the effect of Fe and heat treatments on precipitate morphology will be required to verify this.

Regarding elemental partitioning to the γ−γ′−γ" phases, Fe clearly partitions to the matrix γ-phase, albeit with low levels found in both the γ' and γ" precipitate phases. While Fe was reported to aid in γ" formation,[25] in our three-phase system it instead leads to an increase in the γ' volume fraction and a reduction in the matrix volume fraction (and slight reduction in γ''). In the case of γ'−γ'' coexistence, Fe additions may aid in the formation of γ', even though the γ' solvus temperature is decreased. Further studies are needed to investigate the underlying mechanisms. In the γ'' phase, the addition of Fe increases the solubility of Nb and decreases the Cr solubility. Excess Ni segregation is observed at the γ'−γ'' interface for both alloys containing Fe. A coarsening of the microstructure and precipitate clustering is observed.

XRD results exhibit an increase in the lattice parameter and Thermo-Calc predicted this to be predominantly in the γ' phase. Fe has a similar covalent radius as Ni and hence is unlikely to cause a change in lattice parameters by itself. However, the partitioning of elements as extracted by APT reveals a slight increase in Nb in the γ' phase. Nb has a slightly larger atomic radius than both Ni and Al and may therefore lead to an increase in the lattice parameter of γ'.

F. Effect of Al

Al partitions strongly to the γ' phase and a reduction in Al leads to a substantial reduction in the γ' volume fraction and concomitant increases in both γ and γ'' fractions. Clearly, Al is a strong γ' former with no apparent additional effects on partitioning or phase precipitation.

G. Effect of W

W is found to partition preferentially to the γ'' phase and is least available in γ', which is a differing observation to that of Amouyal et al.[18] As previously mentioned, they had shown that in γ−γ'-containing Ni-superalloys, W preferentially occupies Al sites in the γ' phase unless driven out into the matrix by Ta additions. The alloys in this work do not contain Ta, although they do contain Nb and γ'' as a second precipitate phase. The covalent radius of W is close to that of Nb, both of which are larger than the radius of Al. It is hence not surprising that W is found preferentially in the γ'' phase, likely substituting for Nb. Taking into account the effect of Fe removal on phase fractions, W leads to the increase of both precipitate volume fractions and hence aids in the formation of preciptates. Critically, neither the addition of W nor the addition of Mo at the concentrations considered have led to the precipitation of detrimental TCP phases during the thermal exposures performed in this work.

V. CONCLUSIONS

In this study, we have assessed the effect of individual alloying additions of Mo, W, Fe and variations of Nb, and Al on the properties of a new dual-superlattice reinforced Ni-based superalloy. Thermal stability, hardness, elemental partitioning, microstructure, and phase fractions were investigated. The results presented lead to the following conclusions:

1. The addition of 1.8 at. pct Mo does not significantly decrease the γ’ solvus temperature and prevents microstructural coarsening during heat treatments. A slight increase in hardness is observed, which can be attributed to solid solution strengthening and an increased precipitate volume fraction, i.e., increased precipitate strengthening. The alloying goal (increased strength) has hence been reached without having any apparent negative effect on the alloy.

2. A reduction of the overall Nb content by 10 pct, i.e., 0.6 at. pct reduction, strongly reduces the γ'' volume fraction, without affecting the γ' volume fraction. The reduced precipitate fraction leads to a significant reduction in alloy hardness. Reductions of Nb for improved processability are hence to be handled cautiously, given its effects on superalloy strength.

3. A reduction of the overall Al content by 10 pct, i.e., 0.4 at. pct reduction, reduces the γ' volume fraction and effectively reduces the γ' solvus temperature, but does not have an apparent effect on the alloy hardness. Both Al and Nb are confirmed as γ' and
forming elements, respectively, and found to stabilize the γ' phase to increasing temperatures. Reduction of Al to improve alloy processability may hence be preferable to the reduction of Nb, although the potency of Al to reduce the γ' solvus temperature needs to be kept in mind.

4. Fe, substituted with Ni for better processability and reduced material cost, decreases the γ' solvus temperature and coarsens the microstructure during heat treatment but does not have an apparent effect on the alloy hardness. It is found mostly in solid solution in the γ phase.

5. The addition of 0.9 at. pct W decreases the γ' solvus temperature but increases the precipitate volume fractions, which in addition to solid solution strengthening causes an increase in alloy hardness, which is the purpose of this alloying addition.

6. Thermo-Calc predictions of γ' solvus temperatures capture some of the effects of compositional variation, but with an offset of approximately 70 °C. Thermo-Calc predictions on elemental partitioning can also capture the effects of compositional variation, albeit with varying precision depending on alloying element and phase. Thermo-Calc predictions using an isothermal temperature of 700 °C that account somewhat for the observed temperature offset have provided improved agreement of predicted and experimentally obtained data.

Further to this study, it will be useful to investigate the role of alloying on the formation of the δ phase. This is part of ongoing work.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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APPENDIX

The γ' solvus temperature was retrieved from the DSC thermograms at the inflection point of the S-shaped curve at around 1000 °C by curve differentiation and peak identification. The so-derived γ' solvus temperatures are listed in Table A-I.

Full DSC thermograms presented in Figure A1 show the onset of alloy melting at around 1250 °C. The homogenization temperature was chosen to be between the solidus temperatures and the γ' solvus temperatures around 1000 °C.

Compositions of the γ, γ', and γ'' phases were taken from APT data by peak decomposition of spectra taken

Table A-I. γ' Solvus Temperature as Obtained from DSC Data

| Composition | T_solvus (°C) |
|-------------|--------------|
| Base        | 1010         |
| + 1.8Mo     | 1009         |
| - 0.6Nb     | 1005         |
| + 9Fe       | 988          |
| - 0.4Al     | 970          |
| + 0.9W      | 983          |

Fig. A1—DSC thermograms for all alloys up to 1400 °C showing the solidus temperature of the alloys at around 1250 °C.
from isolated single-phase volumes and are presented in Tables A-II, A-III, and A-IV.

Figure A2 shows the composition of the three phases \( \gamma, \gamma', \) and \( \gamma'' \) as measured by APT on samples heat treated at 800 °C and as predicted by Thermo-Calc assuming an isothermal temperature of 700 °C. This difference in temperature somewhat compensates for a temperature offset observed for Thermo-Calc predictions.

For the \( \gamma \) matrix and the \( \gamma' \) precipitate phase, the predicted data matched the experimental data well with only slight deviations. For the \( \gamma' \) phase, the predicted Ni content was slightly above the measured data but follow the trends and the Cr prediction was slightly below the measured content of the Fe-free alloys. For the \( \gamma'' \) phase, the predicted Al content was slightly below the measured content of the Fe-free alloy. The Ni predictions showed some excess in the base alloy and the + 0.9W alloy but otherwise coincided very well with the experimental data. For the \( \gamma'' \) phase, however, the Thermo-Calc predictions showed large discrepancies from the experimentally obtained data. This is likely due to the difficulties in performing calculations with metastable phases, but also may have occurred due to the fidelity of the thermodynamic databases across this particular composition space. The greatest deviation was found for Nb followed by Cr.

Comparing the different alloys, the Thermo-Calc predictions deviated most from the experimental data for the alloy containing W. This was especially visible for Ni and Al in \( \gamma' \) and for Nb and W in \( \gamma'' \). The best agreement between the predicted and measured compositions was achieved with the Fe-containing alloys.

### UNCERTAINTY ANALYSIS ON THE PHASE VOLUME FRACTION ANALYSIS

Different to linear regression, linear optimization does not allow for easy estimation of confidence intervals. Especially since we know that all phase fractions have to sum to 1, the uncertainties in our estimates of the phase fractions are not independent from each other. Therefore, to estimate the uncertainty of the calculated phase fractions, we use a bootstrapping approach where we randomly resample the measurement data \( n \) times to recalculate the phase fractions from the resampled dataset. Here, we use a value of \( n = 1000 \) and restrict

| Composition (At. Percent) | Ni   | Cr   | Nb   | Al   | Mo  | Fe  | W  |
|---------------------------|------|------|------|------|-----|-----|----|
| Base                      | 72.37| 21.86| 3.88 | 1.73 | 0   | 0   | 0  |
| + 1.8Mo                   | 69.88| 22.39| 3.22 | 1.76 | 2.51| 0   | 0  |
| − 0.6Nb                   | 71.62| 21.06| 3.37 | 1.57 | 2.2 | 0   | 0  |
| + 9Fe                     | 58.81| 22.51| 2.5  | 1.35 | 2.32| 12.36| 0  |
| − 0.4Al                   | 60.16| 21.02| 2.35 | 1.54 | 2.44| 12.39| 0  |
| + 0.9W                    | 70.42| 21.39| 3.19 | 0   | 2.14| 1.32| 0.8|

| Composition (At. Percent) | Ni | Cr   | Nb | Al  | Mo | Fe | W |
|---------------------------|---|------|----|-----|----|----|---|
| Base                      | 74.06| 1.97 | 9.39| 14.41| 0  | 0  | 0 |
| + 1.8Mo                   | 75.06| 1.72 | 8.52| 14.28| 0.3| 0  | 0 |
| − 0.6Nb                   | 74.43| 1.75 | 8.87| 14.71| 0.32| 0  | 0 |
| + 9Fe                     | 73.32| 1.09 | 9.63| 13.74| 0.21| 2  | 0 |
| − 0.4Al                   | 73.7 | 1.14 | 9.17| 13.45| 0.24| 2.2| 0 |
| + 0.9W                    | 73.3 | 1.68 | 8.66| 15.1 | 0.34| 0  | 0.4|

| Composition (At. Percent) | Ni | Nb   | Cr  | Al  | Mo | Fe  | W  |
|---------------------------|---|------|-----|-----|----|-----|----|
| Base                      | 73.66| 18.36| 1.46| 6.28| 0  | 0   | 0  |
| + 1.8Mo                   | 73.64| 16.32| 5.89| 1.76| 2.24| 0   | 0  |
| − 0.6Nb                   | 73.4 | 16.54| 6.01| 1.72| 2.18| 0   | 0  |
| + 9Fe                     | 72.36| 20.34| 2.76| 1.55| 1.45| 1.46| 0  |
| − 0.4Al                   | 73.18| 19.58| 2.65| 1.49| 1.56| 1.47| 0  |
| + 0.9W                    | 72.77| 15.34| 5.98| 2   | 2.07| 0   | 1.4|
the resampled dataset to containing at least 3 unique datapoints which we need for determining the three unknowns (note, however, that the results are very similar when dropping this requirement). This analysis does not include the atom-probe-specific errors on composition as these are negligible. The results are shown for each alloy individually in Figure A3. We color each presented datapoint according to the local relative density, calculated using a Gaussian kernel-density estimate, to visualize the number of overlapping datapoints. The units are arbitrary as we are only interested in the relative density. The best estimate of the phase volume fractions, obtained from the original dataset and previously presented in Figure 13, is marked in each ternary plot with a red cross. Theoretical predictions obtained from Thermo-Calc are marked with a green star. The best estimate generally overlaps well with the highest density of datapoints from the uncertainty analysis. The Thermo-Calc predicted phase fractions, however, deviate considerably. This is not unexpected, as the Thermo-Calc predictions of the phase compositions also exhibited substantial deviations from the experimentally confirmed compositions, especially regarding the compositions of the precipitate phases (see Figure 12).

Since the Base alloy only contains four elements, our resampling approach only generates three distinct samples which leaves the informative value of this uncertainty analysis limited.

Note that the ternary plots in Figure A3 only cover a range of 0.4 to 1 for the $\gamma$ phase volume fraction (respectively, 0 to 0.6 for $\gamma'$ and $\gamma''$ phase volume fractions). There are no data points outside the presented ranges, with the only exceptions being 3 dark blue data points in the 0.9W alloy, which were all either at $\gamma' = 0$ or $\gamma = 0$, as is also seen for some other...
datapoints in the 0.9W alloy. These outlier data points clearly do not represent the material well: we have confirmed with various experimental techniques such as SEM and APT that all three main phases, $\gamma$, $\gamma'$, and $\gamma''$, are present in all alloys. Leaving these datapoints out of the presentation in Figure A3 is therefore justified.

Fig. A3—Ternary plots showing a resampling analysis on the calculation of phase volume compositions. The color of the datapoints indicates the relative density of datapoints at this position. The red cross indicates the best estimate as presented in Fig. 13. The green star indicates the values as predicted by Thermo-Calc (Color figure online).

REFERENCES

1. R.C. Reed, T. Tao, and N. Warnken: Acta Mater., 2009, vol. 57, pp. 5898–913.

2. www.specialmetals.com: Publication Number SMC-045 Copyright © Special Metals Corporation, 2007 (Sept 07).

3. R. Schafrik, D. Ward, and J. Groh: in Superalloy 718, 625, 706 and Various Derivatives, 2001, pp. 1–11.

4. R. Cozar and D.A. Pineau: Metall. Trans., 1973, vol. 4, pp. 47–59.

5. M. Sundararaman, P. Mukhopadhyay, and S. Banerjee: Metall. Trans. A, 1992, vol. 23, pp. 2015–28.

6. M. Sundararaman, P. Mukhopadhyay, and S. Banerjee: Metall. Trans. A, 1988, vol. 19, pp. 453–65.

7. P. Mignanelli, N. Jones, M. Hardy, and H. Stone: in Proceedings of the 9th International Symposium on Superalloy 718 & Derivatives: Energy, Aerospace, and Industrial Applications, 2018, pp. 679–90.

8. P. Mignanelli, N. Jones, M. Hardy, and H. Stone, On the Effect of Alloying Additions to the Ni-Cr-Al-Nb Dual-Superlattice
