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Supplementary Information

The Effect of Temperature and Mo Content on the Lattice Misfit of Model Ni-Based Superalloys – Supplementary Information

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1. Fitting procedure

The extraction of lattice parameters from diffraction data, and subsequent calculation of lattice misfit, is highly dependent on the nature of the fitting procedure employed. The fundamental reflections contain contributions from both the γ and γ′ phases and so can be subject to errors during fitting, particularly when the lattice misfit is small. To assess the impact of such errors on the data analysis, a number of fitting procedures were tested for these data, to determine which yielded the best fit.

a) *Le Bail fit using the GSAS software (Expgui 1.81, APS, Argonne National Laboratory, Lemont, IL, USA)* – The Le Bail fitting methodology scales the intensity of a diffraction peak to best fit the data before a least squares refinement is carried out on the other parameters. In analyzing the data using this method, the superlattice peaks were fitted first to yield a lattice parameter and peak parameters for the γ′ phase. These were then fixed in the subsequent full pattern refinement, allowing only parameters related to the γ phase to be refined. However, due to inherent arbitrary scaling of peaks in this fitting process, there is the potential for one peak to dominate the fit to the combined fundamental peak, yielding an incorrect lattice parameter for the γ-phase.

b) *Full Rietveld fitting with the GSAS software* – In a Rietveld fit, the calculation of the intensities is done from knowledge of the compositions, site partitioning, phase fraction and preferred orientation etc. Previous work on these samples ([20] in reference list) provided some of this information. However, it became apparent that many of the samples suffered from significant texture. Critically, with a limited number of peaks it is difficult to accurately determine this textural effect and so the quality of the fits obtained using this method was poor. Additionally, the large number of assumptions required (about exact composition and site occupation) reduced the confidence in this method, and so it was deemed unsuitable for the analysis of these data.

c) *Pawley fit using the GSAS-II software (Verson 3970, Argonne National Laboratory, Lemont, IL, USA)* – Like a Le Bail fit, the Pawley fitting algorithm also arbitrarily scales the intensities of diffraction peaks but, unlike a Pawley fit, do so as part of the least squares refinement that refines the other parameters. Consequently, this method will be even more prone to the reduction of the intensity of peaks from one phase, such that it no longer contributes to a fundamental reflection. These fits were attempted, but often found to unphysically reduce the contribution of the γ′ in the fundamental to zero, and so were also considered unsuitable.

d) *Individual peak fitting* – Samples of this nature can suffer from intergranular stresses, resulting in strains causing shifts in the positions of families of peaks, thereby reducing the overall quality of a full pattern fit. This can be accommodated by fitting individual families of peaks, where both the superlattice and the related fundamental can be observed in the diffraction data. In these data, this was possible for the families: (i) (100) and (200); (ii) (110) and (220). For each family of reflections, the superlattice reflection may be fitted with a single peak (corresponding to γ′) and the fundamental with two peaks (corresponding to γ and γ′). The *d*-space positions of the two γ′ peaks are held in the expected ratio of 2:1. An advantage of this method is that it is possible to constrain the relative intensities of the two phases within the fundamental based upon their known compositions, whilst still arbitrarily varying the overall scaling. This allows a more accurate representation of the real contribution of the two phases to the diffraction pattern, whilst still permitting some arbitrary scaling of the intensity to account for effects such as texture.
Using the Igor Pro software (Version 8.02, Lake Oswego, OR, US), a fitting procedure was written to carry out fits on these families of peaks. An Ikeda-Carpenter function was used to model the peak shapes, with parameters determined by fitting the diffraction pattern from a standard, previously measured on the ENGIN-X instrument (ISIS Neutron and Muon source, UK).

2. Results

Individual peak fits were carried out, assuming the intensities of the two contributions to the fundamental reflections were in a fixed ratio of γ:γ′ of 1:0.43. This was estimated from the calculation of the structure factor of the two phases for the fundamental reflections in question, using the compositions of the two phases from STEM-EDX and APT data ([20] in reference list). Site partitioning in the γ′ was assumed to be random.

To determine the effect the ratio of intensities has on the fitted lattice parameters and calculated misfit, a series of fits was carried out varying the ratio from 0.30–0.60 in steps of 0.01. It was found that varying the ratio between these bounds caused an error in the misfit ~±0.02%. This is of a similar order to the error that arises from the variance in the peak parameters when fitting with a fixed value of the ratio. Consequently, the ratio was held during the fitting procedure. This also suggests that, for the Le Bail fits, if the contribution of the γ′ is reduced slightly, then a reasonable estimate of the misfit may still be obtained.

Realistically, the shape of the peaks should predominately be a function of the instrument on which the data were collected. As such, for any given fundamental reflection, the two contributing peaks should have roughly similar peak shapes. Sample effects such as size and dislocation density could potentially affect the peak widths in different ways. However, the size of the secondary γ′ is too large to see any appreciable broadening effects, and in the heat-treated condition the micro-strain of the two phases is likely to be similar and minimal. If the widths of both peaks were allowed to vary during the fitting, it was often found that there was an observed over-broadening of the peaks from one of the phases (normally the γ′). This has a similar effect on the fitting as the arbitrary scaling, effectively resulting in only one phase contributing to the sharp fundamental reflection with the other becoming a broad background. Therefore, the widths of the two peaks contributing to the fundamental in each case were kept equal to one another during the fitting procedure.

The results from the Le Bail fitting method and the individual peak fits are shown in Figure S1.

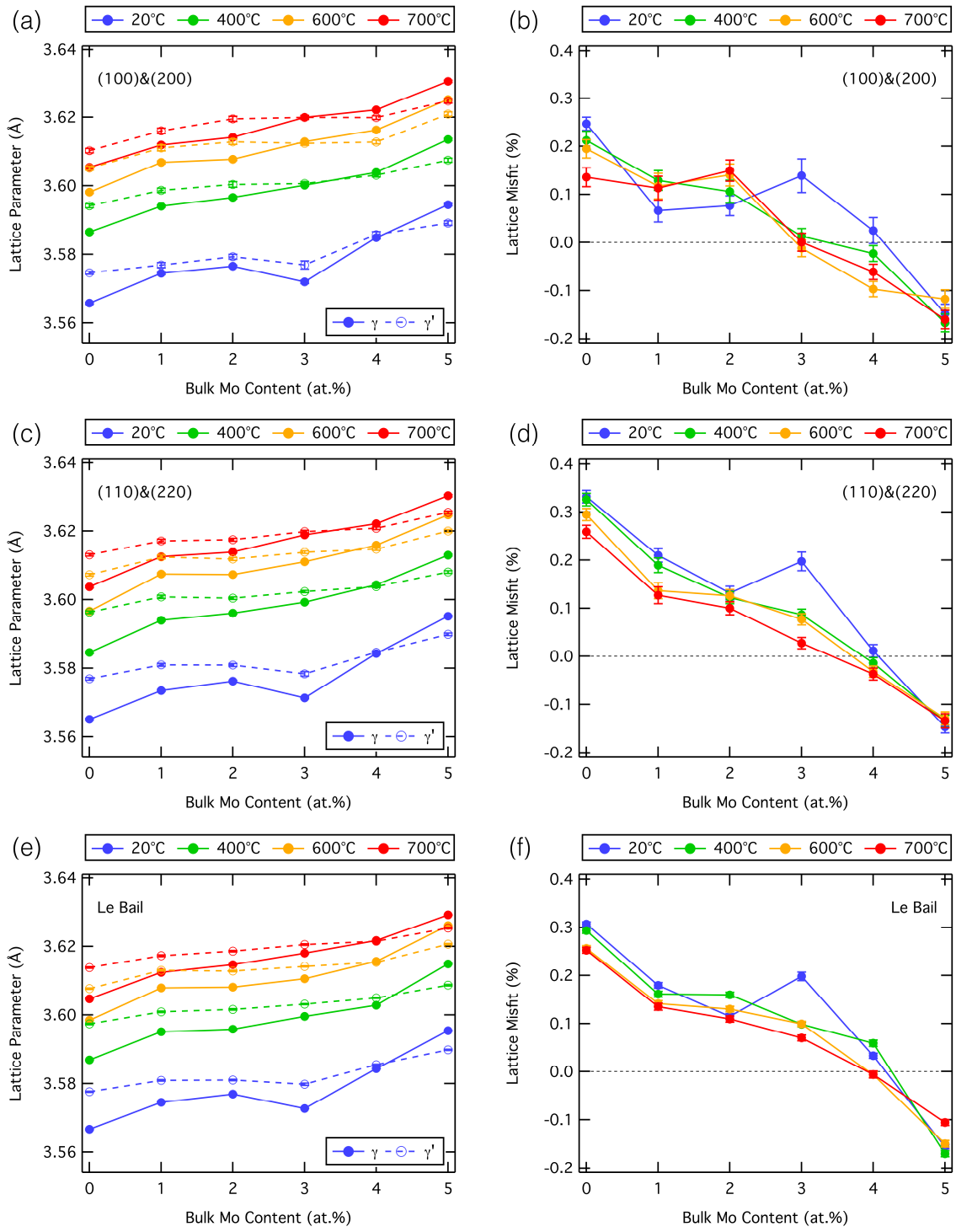

Figure S1. Lattice parameters of the γ and γ′ phases and misfits as a function of nominal bulk Mo content, for different fitting procedures employed. (**a**,**c**,**e**) show the lattice parameters of the two phases, and (**b**,**d**,**f**) the associated misfits. (a) and (b) are for the peak fitting of the family (100) and (200); (c) and (d) are for the peak fitting of the family (110) and (220); (e) and (f) are the results using a full pattern Le Bail fit.

From Figure S1 it is apparent that there are some changes in the fitted lattice parameters, and consequently the calculated lattice misfits, depending on which fitting method and which family of peaks was used. Importantly however, the broad trends observed in the data are the same irrespective of the method. For all methods the lattice parameters and misfits are of a similar order of magnitude. All methods demonstrate that for low Mo there is a high positive misfit. As the Mo

content is increased so the misfit decreases to zero, and then becomes increasingly negative. Both the Le Bail and individual peak fitting of the (110) family suggest this cross-over occurs at around 4 at.% Mo (depending on the temperature). Individual peak fitting of the (100) family suggests that the cross over is between 3–4 at.% Mo. However, overall the quality of the fits obtained in the (100) case are not as good as those in the (110) case, reducing confidence in the results obtained from fitting of the (100) family. This may explain the larger fluctuations and the more significant error bars in Figure S1b, compared with Figure S1(d,f). Overall however, the trends observed in the data are the same for the cases considered. Therefore, it is the Le Bail data that is reported in the main text, as full pattern fits are generally considered to give more accurate values, as they fit to many more peaks than the individual peak fitting case.

3. Conclusions

Several possible diffraction data fitting procedures were considered for the data presented in the main paper. However, despite some fluctuations in the absolute values, it was found that the trends observed were unaffected by the choice of fitting procedure. Consequently, the paper reports the Le Bail data, which is likely to be the most comprehensive, due to the large number of peaks fitted compared with the other methods.