Atom site preference and γ'/γ mismatch strain in Ni–Al–Co–Ti superalloys

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Abstract

The structure and chemistry of Ni–Co–Al–Ti quaternary superalloys are investigated at the microstructural and atomic scale. Atom probe tomography (APT) is used to quantify phase compositions and elemental partitioning behavior. Using aberration corrected electron microscopy, the site occupancy of the atoms within the A_3B structure ($L1_2$ -type) γ' phase is determined via atomic resolution energy dispersive X-ray spectroscopy (EDX). Ni is observed to preferentially occupy the A sub-lattice positions for all alloys, while Al and Ti occupy the B sub-lattice. In contrast, Co's site preference changes from a random distribution to the A sub-lattice as the alloy composition changes, in agreement with theoretical predictions from literature. Finally, the lattice strain across the γ'/γ interfaces is measured as a function of alloy composition.

Keywords: scanning transmission electron microscopy, quaternary superalloy, site preference, strain measurement

1. Introduction

Ni-based superalloys offer superior performance for high-temperature applications such as aircraft engines and power generator turbines due to their high creep and corrosion resistance. These enhanced mechanical properties are attributed to coherent $L1_2$ γ' -Ni₃Al precipitates dispersed in a continuous γ face-centered cubic (fcc) matrix [1, 2]. Through chemical alloying with a wide range of other elements, the chemical and mechanical properties can be further improved. Among

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several alloying elements, Co and Ti are of particular interest because the addition of Ti to Ni-Al increases the volume fraction and solvus temperature of the $L1_2$ phase, while Co increases the creep resistance by reducing the stacking fault energy in the γ matrix [1, 3]. To this end, understanding of phase separation, site occupancy of constituent elements, chemical behavior at local features such as interfaces, etc and their connection with lattice misfit is of essential importance for modern alloy design.

The site preference of solute atoms in the $L1_2$ structure has significant implications on the high-temperature mechanical properties, microstructural stability and resistance to chemical degradation [4]. In the γ' phase, the $L1_2$ -ordered structure consists of two sub-lattices, the Ni sub-lattice or A-site corresponding to the face-centered position and the Al sub-lattice or B-site corresponding to the corner position of the cubic unit cell. A common approach to predicting the site preference behavior of elements in Ni_3Al was derived from the direction of the solubility lobe of the $L1_2$ - Ni_3Al phase in the ternary phase diagram [5]. Further, first-principles calculations have been extensively utilized to study the site preference behavior of ternary alloying elements in $L1_2$ - Ni_3Al at 0 K and elevated temperatures by calculating the defect formation energies [6, 7, 8, 9, 10]. From first-principles calculations, it was observed that most transition metals exhibited a strong Al-site preference, with only a few exhibiting a weak Ni-site preference [9, 11]. However, the site preference for some transition metals in $L1_2$ - Ni_3Al , for example, Co was found to be composition and temperature dependent [6, 9, 10]. Experimentally, Mössbauer effect study [12], atom probe field-ion microscopy (APFIM) [13, 14] and atom location by channeling enhanced microanalysis (ALCHEMI) [15, 16, 17] have been utilized to examine the substitution behavior of solute atoms in Ni_3Al alloys. Nevertheless, site preference study on atom column-per-atom column basis requires methods with enhanced spatial sensitivity.

Lattice misfit and coherency strain between the phases also plays a key role in the precipitate morphology and stability under stress at high temperature [18]. Conventionally, diffraction techniques, such as X-ray diffraction (XRD) [19, 20], neutron diffraction (ND) [3] and convergent beam electron diffraction (CBED) [21, 22, 23], have been employed to quantify lattice misfit measurement in superalloys. These techniques are, however, spatially averaging and do not provide strain on a unit-cell level. In contrast, the recent introduction of revolving scanning transmis-

sion electron microscopy (RevSTEM) enables accurate and precise measurement directly in real space at the atomic scale [24, 25]. Furthermore, this technique has been shown to provide direct nanoscale strain in a ternary superalloy containing Ni, Al, and Cr and offers new opportunities to explore this class of materials [26].

In this article, we perform atomic-scale elemental mapping using aberration corrected scanning transmission electron microscopy (STEM) to explore the site preference behavior of Co atoms at the local atomic scale in the $L1_2$ -precipitates of Ni-Co-Ti-Al superalloy systems with varying composition. The results obtained provide experimental evidence of the influence of alloy composition on site preference in the $L1_2$ - Ni_3Al intermetallic system, confirming theoretical predictions from first-principles calculations. Furthermore, simulated atomic resolution EDX maps are used to confirm the observation of Co random substitution in an alloy by illustrating the effect of interplanar spacing of like atoms on the resolution of the EDX signal. Finally, we explore local strain within the γ' and γ phases as well as their interfaces.

2. Materials and Method

Three Ni-Co-Ti-Al alloys with nominal compositions listed in Table 1 were fabricated and compared in this study. Throughout the manuscript, these are referenced with regard to the Co at%, i.e. 15Co, 30Co, and 55Co alloys. The alloys were directionally solidified via the Bridgman process, as adapted from Ref. [3]. Solution heat treatments were performed in a quartz tube at 1330 °C (15Co & 30Co alloys) and 1245 °C (55Co alloy). Subsequently, all the alloys were aged at 750 °C for 7 days to ensure homogeneity.

Table 1: Nominal composition (at.%) of Ni-Co-Al-Ti superalloy samples

Alloy	Ni	Co	Al	Ti
15Co	70.0	15.0	12.35	2.65
30Co	55.0	30.0	9.71	5.29
55Co	30.0	55.0	5.29	9.71

Atom probe specimens were prepared by electrodischarge machining (EDM) and electropolishing, providing a tip radius of approximately 50 nm. The APT experiments were carried out with a Local Electrode Atom Probe (LEAP 3000X Si) using pulsed-voltage mode. The data collection was performed at a pulse fraction, evaporation rate, specimen temperature, pulse frequency, and gauge pressure of 0.2, 0.002 ions pulse⁻¹, 55 K, 200 kHz, and < 5.0 x 10⁻⁸ Pa respectively. Specimens for TEM were prepared via focused ion beam (FIB) lift-out using a FEI Quanta 3D FEG to minimize magnetic interaction by limiting the sample volume. Bulk sample removal was achieved using a 30 kV Ga⁺ beam, subsequently followed by 5 kV Ga⁺ and 2 kV Ga⁺ milling to reduce surface damage. To minimize surface oxide formation, the specimens were kept in vacuum before being transferred to the microscope within 48 hours after preparation.

Scanning transmission electron microscopy and EDX were performed using a probe-corrected FEI Titan G2 60–300 kV S/TEM equipped with a Schottky field emission gun (X-FEG) source and operated at 200 kV. The probe convergence semi-angle and inner collection semi-angle for HAADF imaging were 13.5 mrad and 77 mrad, respectively. Revolving STEM (RevSTEM) image series were acquired and contained a total of 40 1024×1024 frames with a dwell time of 2 μs/pixel [24]. A 90° rotation was introduced to the scan coordinate system between each frame. Atom column positions in the STEM images were determined by fitting each atom column to a two-dimensional Gaussian function and then projected into a matrix representation using the Atom Column Indexing approach [27]. Sample thickness was measured by comparing position averaged convergent beam diffraction (PACBED) captured at each analysis area to simulations [28]. For the lattice misfit calculation, four image series were analyzed in the γ' and γ regions, respectively for each alloy. EDX maps were generated using the X-ray K-line for each element. These maps were then averaged to a single unit cell using the lattice-averaging method from Ref.[29].

Atomic resolution EDX simulations were performed using the μSTEM software package [30] which utilizes a quantum excitation of phonons (QEP) model [31]. The images were simulated using experimental conditions. Simulated images were convolved with a Gaussian function of 1.3 Å full-width half-max to approximately account for the finite effective source size. Blurred maps were resampled to match the pixel size of the experimental maps. Furthermore, noise was applied to the simulated maps using a Poisson distribution by taking into account the acquisition time,

beam current and detector solid angle from experiment.

3. Results & Discussion

As commonly observed in nickel-based superalloys, cuboidal γ' precipitates are found embedded within the γ matrix as shown from the STEM images in Figure 1. Furthermore, the precipitates' morphology is indicative of substantial lattice misfit between γ' - and γ -phases, consistent with the results reported in Ref. [3]. When the γ' phase is viewed at the atomic scale with HAADF STEM, such as the left half of Figure 1(d), the Ni sub-lattice corresponds to the intense atom columns, while Al-sites corresponds to the weaker columns. In the γ phase, the even atom column intensities are indicative of a random solid solution with the fcc structure. Also, the γ'/γ interface appears to be fairly abrupt with a transition of a few unit cells. This results either from the projection of precipitate surface roughness or a local chemical gradient.

Figure 1: (a) HAADF STEM of cuboidal precipitates in (a) 15Co, (b) 30Co, (c) and 55Co alloy. (d) HAADF STEM of the coherent γ'/γ interface viewed along the $\langle 100 \rangle$ direction. The inset is a schematic illustration of the $L1_2$ - γ' unit cell. The A- (green) and B-sites (red) correspond to the Ni and Al sub-lattices, respectively.

3.1. Elemental partitioning between γ' and γ

Three-dimensional atom probe (3DAP) reconstructions of Ni (green), Co (orange), Al (red) and Ti (blue) are shown in Figure 2(a). As with the HAADF STEM images, two composition regions are observed, corresponding to γ' and γ as indicated. Furthermore, the γ' phase exhibits uniform composition as noted in Ref. [3]. From a concentration profile across a γ'/γ interface in 15Co, Co and Al are observed to segregate strongly to γ and γ' respectively. For each alloy, the average γ' and γ composition quantified from atom probe are presented in Table 2.

Figure 2: (a) Atom probe reconstruction of the 15Co alloy specimen with Ni 2.5% (red), Co 15% (orange), Al 15% (green), and Ti 100% (blue). (b) Proximity histogram depicting the compositional transition across the γ'/γ interface.

The partitioning ratio, κ_i is also calculated to determine the elemental segregation behavior. κ_i is defined as the ratio of the concentration of element i in the γ' phase to the concentration of the element i in the γ phase, i.e. $\kappa_i = C^{\gamma'}_i / C^{\gamma}_i$, where $i = \text{Ni, Co, Al or Ti}$. Elements with $\kappa_i > 1$ preferentially partition to the γ' phase, while $\kappa_i < 1$ partitions to the γ matrix. Based on ratios presented in Table 2, Ni, Al and Ti exhibit γ' partitioning. This is in contrast to Co, which preferentially segregates to the γ phase as noted above.

Table 2: Average phase composition and partitioning ratios for 15Co, 30Co and 55Co alloys as determined using atom probe tomography.

Alloy	Phase	Composition (at%)				Partitioning Ratio			
		Ni	Co	Al	Ti	K_{Ni}	K_{Co}	K_{Al}	K_{Ti}
15Co	γ'	71.0	4.89	18.75	5.37	1.0525	0.1999	2.4582	11.129
	γ	67.67	24.43	7.63	0.48				
30Co	γ'	61.65	12.80	15.97	9.59	1.4968	0.2305	5.5211	21.793
	γ	41.19	55.55	2.89	0.44				
55Co	γ'	42.68	32.72	8.089	16.51	2.112	0.4084	3.7817	11.775
	γ	16.33	80.1	2.14	1.40				

3.2. Site preference investigation in the $L1_2$ - γ' phase

While HAADF STEM images are generally considered to be directly interpretable in terms of type and number of atoms present, the site preference for the atoms in the γ' is not readily determined here [32, 33]. This is due to the number of different atom types present as well as their relatively close atomic numbers. Instead, atomic resolution STEM EDX analysis captures site preference behavior of the γ' precipitates as shown in Figure 3. To avoid the compositional gradient at the γ'/γ interfaces, the EDX maps are acquired at or near the center of γ' precipitates.

For all alloys, it is evident that Al and Ti preferentially occupy the B sub-lattice, and Ni preferentially occupy the A sub-lattice. The site preference of Co, however, is less clear, particularly for 15Co. It is worth noting that despite the relatively low concentration of Co in the γ' phase of this alloy (~ 5 at. %), the total counts of Co- K_α signal detected is roughly the same as that for Ti-K in the same region. In other words, the Co counts are sufficient to produce a signal-to-noise ratio (SNR) comparable to Ti. To aid in the visualization of the site preference, lattice-averaged maps are presented in the inset for each map. In the case of 30Co and 55Co alloys, Co is observed to prefer the Ni-sites, while 15Co shows no clear preference.

To clarify the behavior observed in the atomic resolution EDX maps, simulations are con-

Figure 3: Experimental EDX maps for the $\langle 001 \rangle$ direction of the γ' phase in (a) 15Co alloy (b) 30Co alloy (c) and 55Co alloy. Insets shows lattice-averaged maps with enhanced S/N ratio to enable direct visualization of the site preference.

ducting using three-dimensional supercells of the $L1_2$ - Ni_3Al structure with $10 \times 10 \times 140$ unit cells (56000 atoms). The supercell compositions are designed to closely approximate those of the $L1_2$ phase from APT. For the first supercell, the composition is 71.27Ni-4.875Co-18.5036Al-5.3482Ti at.%, where Ti is located on the B sub-lattice and Co is situated on both A and B. In the second supercell, the composition is 70.01Ni-4.9875Co-19.157Al-5.8429Ti at.%, where Ti atoms are located on the B sub-lattice while Co occupy only A positions. The lattice parameter of the unit cell is 3.57 Å, as measured from the RevSTEM image of the γ' phase of 15Co [24, 27].

Using these supercells, simulated atomic resolution EDX maps demonstrate the effect of atomic site preference on the signal. As shown in Figure 4(a), when Co exists on both A and B sub-lattices, the Co signal is smeared across the map with a low SNR. In contrast, the simulated EDX maps with Co located exclusively on the A sub-lattice, Figure 4(b), show an improved SNR with periodicity corresponding to the A sub-lattice.

Figure 4: Simulated EDX maps of the γ' -L1₂ structure when (a) Co is randomly substituted on the A- and B-sites. (b) Co exclusively occupies the A-sites. Lattice-averaged maps from 15Co and 30Co alloys are displayed in the inset in (a) and (b), respectively. EDX concentration profiles from (c) 15Co alloy and simulation with random distribution of Co. (d) 30Co and 55Co alloys and simulation with Co fixed on A-sites. Each EDX profile is normalized and plotted over two unit cells.

To compare EDX experiments and simulations, the lattice-average maps are replicated and integrated along $\langle 010 \rangle$ to create the concentration profiles in Figures 4(c) and (d). The distinct profile peaks labeled **A** and **A/B** correspond to those integrated locations that include A sub-lattice atom columns and those that contain both A and B sub-lattices, respectively. As a result, the Ni signals peak at **A**, while Ti and Al peak at **A/B** for all alloys.

In all cases, Ni, Al, and Ti signals are in excellent agreement for both experiment and simu-

lation. For the case of Co distributed on both sub-lattices, Figure 4(c), the signal is spread evenly across simulation profile. This is in good agreement with the ^{15}Co EDX maps, supporting the conclusion that Co lacks a site preference in these comparatively low Co concentration alloys. In contrast, when Co is exclusively substituted for Ni, as presented in Figure 4(d), clear peaks are observed that coincide with the A sub-lattice. This is in excellent agreement with the EDX results from experiment for ^{30}Co and ^{55}Co , confirming that the Co preferentially occupies A sub-lattice positions in these alloys.

These results from simulations and experiment indicate that Co undergoes a change in site preference from random across A and B to predominately A with increasing Co concentration. This is in agreement with first-principles calculations by Zhao *et al.* who reported that the strong Al site preference is a result of the co-alloying atoms [34]. Based on these prior results, there are a number of contributing factors including the large difference in atomic radii for Ni, Co, Al, and Ti as well as their local chemical bonding environments as a function of composition.

3.3. $\gamma' - \gamma$ Coherency Strain

The elastic strain between the γ' and γ phases connects directly to the mechanical properties of the alloy. To quantify the elastic strain, the lattice parameters are directly measured from HAADF STEM images. The center of a γ' precipitate is selected to serve as a common reference lattice parameter between different regions of the material. As an example, the analysis of the ^{15}Co alloy is presented in Figure 5. The average ϵ_{xx} and ϵ_{yy} from a γ' -precipitate along path A, Figure 5(a), are parallel and perpendicular to the γ'/γ interface, respectively. Large negative ϵ_{xx} strain is observed across the interface, where the strain suddenly drop from approximately 0.5% in the γ' to -1.6% in the γ . This relationship is reversed along path B, Figure 5(b), where a large negative strain is observed for ϵ_{yy} . Similar trends in the the lattice distortion are observed for all the alloy compositions studied, peaking in the γ channels where the strain is -2.3% and -2.17% for 30 and 55Co, respectively. The observed strain gradient originates from lattice distortion within the alloy due to coherency strain introduced by thermal expansion mismatch between the phases. This behavior is consistent with prior investigations with other techniques characterising γ/γ' interfaces in superalloys [3, 21, 22, 26, 35].

Figure 5: (a) Average lattice strain as a function of distance to the γ'/γ interface along path A in 15Co alloy. (b) Strain variation along path B. Approximate locations of the examined points within the precipitate are shown in the inset.

Beyond strain, lattice misfit, δ , between the γ' and γ phases is another important descriptor of superalloy system, defined as:

$$\delta = \frac{2(a_{\gamma'} - a_{\gamma})}{(a_{\gamma'} + a_{\gamma})} \quad (1)$$

where $a_{\gamma'}$ and a_{γ} are the average lattice parameters measured in the γ' and γ phases, respectively. A prior neutron diffraction (ND) investigation of the present alloy system by Minshull *et al.* showed that the lattice misfit between the γ' and γ phases increases as the Co and Ti contents increases

[3]. Diffraction-based techniques such as neutron diffraction provide highly accurate and precise measurements, thereby, making them ideal reference for our STEM measurements.

For each alloy, δ was calculated from the average lattice parameters from four images in the γ' and γ phase. The average measurement standard deviation across γ' and γ regions range from ~ 4.5 pm to ~ 8.5 pm within each image, corresponding to 1.28% to 2.5% variation. For a direct comparison between the neutron diffraction and STEM results here, δ measured using RevSTEM images are positive for all alloys (i.e. $a_{\gamma'} > a_{\gamma}$), as shown in Figure 6(a). While the δ values measured here are considerably larger than those reported from neutron diffraction, there are a number of contributing factors for this discrepancy. Although the quaternary superalloy system analyzed in this work is adapted from the composition and processing history of the samples reported in Ref. [3], the present alloys were heat treated at 750 °C for 7 days, significantly shorter than the ~ 42 days for Ref. [3]. As a result, the δ derived from elastically deformed phases in the present alloy are representative of the constrained lattice misfit since the lattice parameter of the two phases do not approach their equilibrium values. Thus, the lattice misfit obtained after substantial aging treatment in Ref. [3] is closer to the true unconstrained lattice misfit [21]. Furthermore, strain relaxation in the TEM specimen due to the presence of free surfaces can contribute to the partial relaxation of coherency strain [21, 22, 26]. In addition, the average sample region for RevSTEM analysis is smaller (~ 25 nm²) in comparison to the larger sample area ($\sim$ mm²) for neutron diffraction. Since δ varies at different locations within the alloy, as demonstrated in Figure 5, it is difficult to compare, on an absolute scale, with sample averaging techniques like X-ray and neutron diffraction.

Also in contrast to neutron diffraction, δ from the STEM analysis in 55Co alloy is smaller than in 30Co alloy. A potential origin of this discrepancy lies in the high planar fault density observed in 55Co i.e. semicoherent interface, which was not observed for the other concentrations. A representative HAADF STEM image across the γ'/γ interface of 55Co, where a number of {111} stacking faults in the γ phase are observed, is shown in Figure 6(b). Further, the high planar density is related to the relative increase of Co concentration in comparison to the other alloys. γ partitioning elements, such as Co, are known to lower the stacking fault energy (SFE) of the γ matrix, which dramatically effects the nature of dislocation motion [1]. In the γ phase, deformation

Figure 6: (a) Lattice misfit calculated for alloys. δ for neutron diffraction were obtained from Ref. [3]. (b) STEM image across the γ'/γ interface in 55Co alloy. Disturbance in stacking sequence at the faults are highlighted

occurs on the $\{111\}$ close-packed planes, in the close packed directions $\langle 110 \rangle$. The low SFE causes unit dislocations, $a/2\langle 110 \rangle$ to dissociate into pairs of partial dislocations of type $a/6\langle 21\bar{1} \rangle + a/6\langle \bar{1}21 \rangle$ that are separated by a stacking fault [1, 18]. Such stacking faults can then develop within the γ matrix to compensate for the increased coherency strain within the alloy, and thus provide a pathway for strain relaxation.

4. Conclusions

The microstructure, interfacial strain and chemistry were analyzed for a set of quaternary alloys containing Ni, Co, Al and Ti. Using aberration corrected STEM imaging and spectroscopy, it was shown that all alloys exhibit a two phase microstructure consisting of cuboidal γ' -L1₂ precipitates within a γ -matrix (fcc). Atom probe tomography showed that the Ni, Al and Ti preferentially partitioned to the γ' phase, while Co partitioned to the γ matrix. At low concentrations of Co and Ti, atomic resolution EDX maps revealed that Co occupies both A and B sub-lattices. Co transitions to an A sub-lattice site preference at high concentrations of Co and Ti. Simulated EDX maps for two contrasting site preference behavior of Co atoms provide supporting evidence of our observations. Significant lattice distortion is present in each of the alloys, peaking in the γ matrix, with compressive strain in the γ' /matrix interface. Lattice misfit measured here is generally higher than that obtained from neutron diffraction due to the small sample region examined and stacking faults are observed to compensate for the high coherency strain built up in the 55Co sample. As a next step in the investigation of this alloy system, it is suggested that the thermodynamic driving force for the composition dependent site preference be studied in detailed. In particular, it will also be important to correlate the sample thermal history with site preference and mechanical properties.

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- [1] R. C. Reed, *The superalloys: Fundamentals and Applications*, Cambridge University Press, U.K., 2006.
- [2] M. Durand-Charre, *The Microstructure of Superalloys*, Gordon and Breach Science Publishers, Amsterdam, The Netherlands, 1997.
- [3] J. P. Minshull, S. Neumeier, M. G. Tucker, H. J. Stone, Al-L1₂ Structures in the Al-Co-Ni-Ti Quaternary Phase System, *Advanced Materials Research* 278 (2011) 399–404.

- [4] R. D. Rawlings, A. E. Staton-Bevan, The alloying behaviour and mechanical properties of polycrystalline Ni_3Al (γ' phase) with ternary additions, *Journal of Materials Science* 10 (3) (1975) 505–514.
- [5] R. Guard, J. Westbrook, Alloying behavior of Ni_3Al (γ' -phase), *TRANSACTIONS OF THE AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS* 215 (5) (1959) 807–814.
- [6] C. Jiang, B. Gleeson, Site preference of transition metal elements in Ni_3Al , *Scripta materialia* 55 (5) (2006) 433–436.
- [7] C. Jiang, D. Sordellet, B. Gleeson, Site preference of ternary alloying elements in Ni_3Al : A first-principles study, *Acta Materialia* 54 (4) (2006) 1147 – 1154.
- [8] A. Ruban, H. Skriver, Calculated site substitution in γ' - Ni_3Al , *Solid State Communications* 99 (11) (1996) 813 – 817.
- [9] A. V. Ruban, H. L. Skriver, Calculated site substitution in ternary γ' - Ni_3Al : Temperature and composition effects, *Phys. Rev. B* 55 (1997) 856–874.
- [10] Q. Wu, S. Li, Alloying element additions to Ni_3Al : Site preferences and effects on elastic properties from first-principles calculations, *Computational Materials Science* 53 (1) (2012) 436 – 443.
- [11] O. Andersen, O. Jepsen, D. Glötzel, F. Bassani, F. Fumi, M. Tosi, Highlights of condensed matter theory, in: *Proceedings of the International School of Physics Enrico Fermi*, Vol. 89, 1985, p. 59.
- [12] J. Nicholls, R. D. Rawlings, A Mössbauer effect study of Ni_3Al with iron additions, *Acta Metallurgica* 25 (2) (1977) 187 – 194.
- [13] M. Miller, J. Horton, Site occupation determinations by APFIM for Hf, Fe, and Co in Ni_3Al , *Scripta Metallurgica* 20 (8) (1986) 1125 – 1130.
- [14] N. Wanderka, U. Glatzel, Chemical composition measurements of a nickel-base superalloy by atom probe field ion microscopy, *Materials Science and Engineering: A* 203 (1–2) (1995) 69 – 74.
- [15] D. Shindo, M. Kikuchi, M. Hirabayashi, S. Hanada, O. Izumi, Site Determination of Fe, Co and Cr Atoms Added in Ni_3Al by Electron Channelling Enhanced Microanalysis, *Transactions of the Japan Institute of Metals* 29 (12) (1988) 956–961.
- [16] A. Chiba, D. Shindo, S. Hanada, Site occupation determination of Pd in Ni_3Al by ALCHEMI, *Acta metallurgica et materialia* 39 (1) (1991) 13–18.
- [17] C. Liebscher, J. Preussner, R. Voelkl, U. Glatzel, Atomic site location by channelling enhanced microanalysis (alchemi) in γ' -strengthened ni-and pt-base alloys, *Acta Materialia* 56 (16) (2008) 4267–4276.
- [18] B. Geddes, *Superalloys: alloying and performance*, Asm International, 2010.
- [19] Y. Mishima, S. Ochiai, T. Suzuki, Lattice parameters of Ni (γ), Ni_3Al (γ') and Ni_3Ga (γ') solid solutions with additions of transition and B-subgroup elements, *Acta Metallurgica* 33 (6) (1985) 1161–1169.
- [20] M. Morinaga, K. Sone, T. Kamimura, K. Ohtaka, N. Yukawa, X-ray determination of static displacements of atoms in alloyed Ni_3Al , *Journal of Applied Crystallography* 21 (1) (1988) 41–47.

- [21] D. Lahrman, R. Field, R. Darolia, H. Fraser, Investigation of techniques for measuring lattice mismatch in a rhenium containing nickel base superalloy, *Acta Metallurgica* 36 (5) (1988) 1309 – 1320.
- [22] M. J. Kaufman, D. D. Pearson, H. L. Fraser, The use of convergent-beam electron diffraction to determine local lattice distortions in nickel-base superalloys, *Philosophical Magazine A* 54 (1) (1986) 79–92.
- [23] R. Ecob, R. Ricks, A. Porter, The measurement of precipitate/matrix lattice mismatch in nickel-base superalloys, *Scripta Metallurgica* 16 (9) (1982) 1085 – 1090.
- [24] X. Sang, J. M. LeBeau, Revolving scanning transmission electron microscopy: Correcting sample drift distortion without prior knowledge, *Ultramicroscopy* 138 (2014) 28 – 35.
- [25] J. H. Dycus, J. S. Harris, X. Sang, C. M. Fancher, S. D. Findlay, A. A. Oni, T.-t. E. Chan, C. C. Koch, J. L. Jones, L. J. Allen, D. L. Irving, J. M. LeBeau, Accurate nanoscale crystallography in real-space using scanning transmission electron microscopy, *Microscopy and Microanalysis* 21 (2015) 946–952.
- [26] A. A. Oni, X. Sang, S. V. Raju, S. Dumpala, S. Broderick, A. Kumar, S. Sinnott, S. Saxena, K. Rajan, J. M. LeBeau, Large area strain analysis using scanning transmission electron microscopy across multiple images, *Applied Physics Letters* 106 (1).
- [27] X. Sang, A. A. Oni, J. M. LeBeau, Atom Column Indexing: Atomic Resolution Image Analysis Through a Matrix Representation, *Microscopy and Microanalysis* 20 (2014) 1764–1771.
- [28] J. M. LeBeau, S. D. Findlay, L. J. Allen, S. Stemmer, Position averaged convergent beam electron diffraction: Theory and applications, *Ultramicroscopy* 110 (2) (2010) 118 – 125.
- [29] P. Lu, L. Zhou, M. J. Kramer, D. J. Smith, Atomic-scale Chemical Imaging and Quantification of Metallic Alloy Structures by Energy-Dispersive X-ray Spectroscopy, *Scientific reports* 4.
- [30] L. Allen, A. D'Alfonso, S. Findlay, Modelling the inelastic scattering of fast electrons, *Ultramicroscopy* 151 (0) (2015) 11 – 22.
- [31] B. D. Forbes, A. V. Martin, S. D. Findlay, A. J. D'Alfonso, L. J. Allen, Quantum mechanical model for phonon excitation in electron diffraction and imaging using a born-oppenheimer approximation, *Phys. Rev. B* 82 (2010) 104103.
- [32] S. Pennycook, D. Jesso, High-resolution incoherent imaging of crystals, *Physical Review Letters* 64 (8) (1990) 938.
- [33] J. M. LeBeau, S. D. Findlay, L. J. Allen, S. Stemmer, Standardless Atom Counting in Scanning Transmission Electron Microscopy, *Nano Letters* 10 (11) (2010) 4405–4408. doi:10.1021/nl102025s.
- [34] W. Zhao, Z. Sun, S. Gong, Synergistic effect of co-alloying elements on site preferences and elastic properties of Ni₃Al: A first-principles study, *Intermetallics* 65 (2015) 75–80.
- [35] D. Collins, L. Yan, E. Marquis, L. Connor, J. Ciardiello, A. Evans, H. Stone, Lattice misfit during ageing of a polycrystalline nickel-base superalloy, *Acta Materialia* 61 (20) (2013) 7791–7804.