PLANAR DEFECTS IN Ni$_3$Sn

Under appropriate ageing treatments, supersaturated Ni-rich $\alpha'$ solutions decomposed at an advancing reaction front into alternating lamellae of Sn-depleted fcc $\alpha$ and $D0_{19}$ Ni$_3$Sn. This discontinuous precipitation and the typical defect structures generated within the $D0_{19}$ compound were investigated using conventional and high-resolution transmission electron microscopy. Complete characterisation of defects lying on the basal planes of Ni$_3$Sn lamellae was achieved by HRTEM imaging and Iterative Digital Image Matching. Mechanisms of defect formation are proposed based on energetic considerations and growth features.

4.1 INTRODUCTION

The purpose of the work presented in this chapter was to investigate characteristic defect structures generated in Ni$_3$Sn during its discontinuous precipitation (DP), while aiming at a better understanding of defect formation mechanisms at an atomic level. The co-operative growth of $\alpha$ and $D0_{19}$ Ni$_3$Sn from an Sn-supersaturated solid solution ($\alpha'$) has been extensively evaluated$^{1-8}$. However, the previous studies were mainly focused on the morphology of the reaction products, growth kinetics, and composition profile across the discontinuous front, rather than investigating defect structures generated during the precipitation.

Due to the high defect density present in the Ni$_3$Sn lamellae, complete identification of faults lying on the basal planes was difficult by CTEM. Therefore, these defects have been investigated by a general method of analysis based on HRTEM imaging$^9$, which was described in CHAPTER 2. As a starting point, the possible (close-packed preserving) planar defects were classified in accordance with their visibility on prismatic projections (and magnitude of the displacement vector). Analysis of HRTEM images obtained under two different viewing conditions, followed by matching with optimised simulated images, allowed unambiguous identifications. The types of defects found in Ni$_3$Sn, as well as their spatial arrangement, disclosed important aspects of the defect formation,
which could be related to general growth features of the DP. Hence, it is worthwhile to briefly review here the driving forces and mechanisms operating during nucleation and growth in this type of transformation.

In some alloy systems, decomposition of a supersaturated solid solution involves preferential nucleation of the second phase at grain boundaries (GBs). This type of heterogeneous precipitation can lead to the formation of two-phase colonies that grow behind migrating fronts. The typical resulting morphology is based on decomposition into a lamellar constituent, comprising a solute depleted phase and the precipitate phase, both growing co-operatively into the supersaturated matrix. Since the composition and orientation of the matrix change discontinuously across the reaction front, this particular case of heterogeneous precipitation has been called discontinuous\textsuperscript{10,11}. Many investigations on these purely diffusional transformations were carried out in the past and a few theories have been developed to account for the initiation and growth in DP.

**DP INITIATION MECHANISMS:**

The two basic models established as frequently operative mechanisms for the initiation of DP at GBs are the ‘pucker mechanism’ of Tu and Turnbull\textsuperscript{12,13} and the Fournelle and Clark mechanism\textsuperscript{14} (FIGURE 4.1). Both treat the initiation of DP within a more general framework of GB migration\textsuperscript{11} (GBM). In the ‘pucker mechanism’ an embryo, developing at an angle with respect to a GB, causes the boundary to be locally deflected by the torque term associated with the interfacial tension balance at the triple point. If $\gamma_1 < \gamma_3$, the GB tends to migrate ‘upwards’ until the higher energy broad face is incorporated in the low interfacial energy grain. The process is iterated to form a group of parallel precipitates (FIGURE 4.1 (a)). Here the initial driving force for boundary migration is provided by a reduction in the interfacial energy associated with the precipitate. Although this mechanism has been proven to be operative, it is critically dependent on the crystallographic orientation across the GB ($\gamma = \gamma(\theta)$), and is hence clearly not universal\textsuperscript{11}. In the Fournelle and Clark mechanism, precipitation occurs on an already moving boundary. The GB is locally pinned but still allowed to continue migrating between the precipitates (FIGURE 4.1 (b)). In contrast with the previous, this mechanism does not require any special interfacial energy conditions, and it is probably operating whenever no preferential matrix/precipitate habit plane can be observed, which in general is the case\textsuperscript{11}.  

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The primary driving force for precipitation is reduction in volume free energy (chemical driving force); this however does not justify the discontinuous process as opposed to a continuous one (with its generally more favourable interfacial energy conditions). Sulonen\textsuperscript{15,16} and Hillert\textsuperscript{17} first proposed that the general driving force for initial grain boundary deflection has its origin in the relaxation of strain. This can be the case, if the composition gradients immediately adjacent to the boundary cause significant changes in lattice parameter. There is, however, evidence that at least in some alloy systems, like Al-Ag, coherency strain cannot be the main driving force for the discontinuous process since the lattice misfit is extremely small\textsuperscript{18}. Furthermore, according to Aaronson and Clark\textsuperscript{19}, in those systems, a prior continuous precipitation can deplete the chemical driving force by as much as 98\% (reducing as well any coherency strain available) and still DP can engulf the already decomposed matrix. Nevertheless, these systems, where the interfacial energy contribution may dominate the DP reaction, have been considered as exceptions\textsuperscript{11}.

Due to the complexity of the DP, it has been impossible to assign a unique mechanism to the reaction initiation, valid at all temperature and for all systems. Yet, the relaxation of strain rather than minimisation of surface energy is commonly accepted to be the general driving force for diffusion-induced GBM and DP\textsuperscript{20}. As suggested by Yoon\textsuperscript{20}, chemically induced interface migration (CIIM) is in fact a more general and desirable term to use in these situations because of the associated composition changes.
**DP Growth:**

Co-operative growth with one phase incorporating the atom excess rejected by the other phase is largely a question of mass transport, controlled by diffusion along the boundary layer at the migrating front (Figure 4.2). The interface and the lattice provide parallel competing paths along which transport may occur, and it has since long been established\textsuperscript{21,22} that in interstitial alloys lattice diffusion is predominant, while in substitutional alloys the front interfaces provide a high diffusivity path. Actually, in substitutional alloys, redistribution of solute has been shown to occur on a nanometer scale in the immediate vicinity of the reaction front, in a layer with a typical thickness\textsuperscript{11} ($\delta$) of 5 nm. Actually, as demonstrated by Hillert\textsuperscript{23,24}, enhanced volume substitutional diffusion during the growth of a DP colony tends to equalise the solute distribution on both sides of the boundary, thereby reducing the driving force for a discontinuous reaction and favouring a continuous one. Moreover, at temperatures where lattice diffusion is frozen out, little bulk composition changes (partition between the phases) can occur, unless the GB migrates\textsuperscript{25}. This phenomenological argument has been used to include DP as a particular case of GBM (or CIIM). The steady-state growth of the periodic lamellar structure, which in many respects is similar to a lamellar eutectic structure, has been discussed in a number of investigations starting with the classical paper by Cahn for DP and eutectoid reactions\textsuperscript{23-28}. However, it is worth mentioning that descriptions based only on the diffusional process and interfacial considerations have not yet been able to fully predict the growth rate and the fraction of $\beta$-phase for a given interlamellar spacing (in contrast with eutectic growth)\textsuperscript{29}.

![Figure 4.2](image.png)  
**Figure 4.2** Diffusion field at a DP boundary layer of thickness $\delta$. Alternating lamellae of $\alpha$ and $\beta$ grow behind a reaction front advancing into a supersaturated matrix of composition $C_{\alpha'}$.  

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4.2 EXPERIMENTAL DETAILS AND SIMULATION METHODS

4.2.1 MATERIALS, INSTRUMENTS AND EXPERIMENTAL PROCEDURES

A Ni-Sn alloy containing 8 at.% of Sn was prepared in an arc furnace, where the constituents (with 99.99 wt.% nominal purity) were melted together in a water-cooled copper bed under a protective argon atmosphere. Two sets of samples were aged; one at 600 °C for 24h and another at 700 °C for 48h. Another set was homogenised at 900 °C for 170h and subsequently aged at 600 °C for 48h. All the heat-treatments were performed with a prior encapsulation of the samples in evacuated quartz tubes and were followed by water quenching.

Preliminary observations of the microstructures were made by scanning electron microscopy (SEM) using a Philips XL30-FEG instrument equipped with energy dispersive X-ray spectrometry (EDS). A mixture of nitric acid, acetic acid and water was used to etch the samples prior to SEM observation. Sn concentrations were obtained from the measured integrated peak intensities $I$, using the Cliff-Lorimer equation:

$$\frac{C_{Ni}}{C_{Sn}} = K \frac{I_{NiKα}}{I_{SnLα}}$$

where $C_{Ni}$ and $C_{Sn}$ are the mole fractions of Ni and Sn in the alloy. The factor $K$ was determined experimentally using as standard the $D0_{19}$ Ni$_3$Sn compound (on the Ni-rich side of the intermetallic domain of solubility).

The samples for transmission electron microscopy (TEM) were prepared by grinding, dimpling, and ion milling 3 mm discs to electron transparency. A JEOL 200CX microscope was used for conventional work and a JEOL 4000EX/II microscope was used for both conventional and high-resolution work. The microscopes instrumental parameters can be found in Table 2.1. The Ni-Sn samples were found exceptionally prone to contamination during TEM work. The use of an N$_2$ anti-contamination device partially eased this problem, but contamination was still severe after different diffraction and/or high-resolution conditions had been obtained from the same area.
4.2.2 IMAGE SIMULATION

High-resolution imaging conditions were retrieved with the Iterative Digital Image Matching (IDIM) package program\textsuperscript{31} as described in \textsc{Chapter} 2. The lattice parameters of the $D_0_{19}$ hexagonal cell used to simulate the bulk structure are: $a = 0.529$ nm and $c = 0.424$ nm\textsuperscript{32}. The defect supercells have their (non-relaxed) dimensions based on the bulk cell. At least 6 close-packed atomic layers separated adjacent defects in the supercells and edge regions of 3 atomic layers (0.636 nm) were excluded from the matching process. This was expected to minimise the interference of artefacts introduced by the periodicity boundary conditions on the simulated images. The average intensity and standard deviation of the simulated and experimental images were aligned in the course of the optimisations. Relative lateral positioning was carried out before comparison by alignment in reciprocal-space. The numerical agreement factor used was the cross-correlation factor (eq. 2.27) and the optimisation parameters included defocus, thickness, beam tilt, crystal tilt and achromatic damping. The evolution runs were interrupted at a maximum number of 100 or 200 generations (each corresponding to 20 matching trials).

4.2.3 STRAIN FIELD EVALUATION

Strain fields were evaluated and mapped from experimental HRTEM images using the (geometric) phase analysis routines included in the Digital Micrograph package program\textsuperscript{33}. The method has been described in \textsc{Chapter} 2. Gaussian circular masks have been used and the reference lattice parameters are based on the average $g$. A linear phase ramp was artificially introduced in the phase images (with a 10x magnification) and the inclination of the resulting fringes was chosen to be the same of the corresponding $\pm g$ lattice fringes.

4.3 RESULTS AND DISCUSSION

The planar defects present in the Ni$_3$Sn lamellae result directly from the phase transformations occurring in the system. For this reason, an assessment of the mechanisms responsible for the observed morphologies is essential for a correct understanding of their influence on defect formation. The microstructural analysis starts with the characterisation of the features induced by the solidification process and is followed by a detailed study of the precipitation.
4.3.1 PHASE TRANSFORMATIONS AND RESULTING MORPHOLOGIES

SOLIDIFICATION:

Figure 4.3 presents the microstructures resulting from the heat-treatments as observed by SEM (secondary electrons). The fine scale of the as-solidified microstructure shown in Figure 4.3 (a) reflects the relatively high cooling rate imposed. Since solidification took place under a constrained growth regime (heat flow opposite to growth direction), the dendritic morphology of the primary phase, and the underlying unstable solid/liquid interface, resulted from constitutional undercooling. Deficient back-diffusion in the solidifying α' dendrites led to a Sn excess in the remnant liquid, inducing the formation of interdendritic eutectic at the latest solidification stage for an alloy composition not at the eutectic tie-line (see APPENDIX I). A severe microsegregation (coring) in the α' dendrites was revealed by prolonged polishing and etching, which resulted in a higher rate of material removal at the Ni richer cores, with ≈ 3 at.% Sn, as compared to the edges, with ≈ 9 at.% Sn. The composition measurements at the as-solidified dendrite edges were taken at 1 μm from the interdendritic D019 phase to rule out the possibility of including this phase on the detected signal. This and the averaging of the measuring process contributed to a lower value than it would be expected from the phase diagram (α_\text{eutectic} having 11 at.% Sn\textsuperscript{35}). Averaging should also be considered for the values obtained at the dendrite cores. The composition gradient indicates that the solute excess was redistributed over the remnant liquid (in each interdendritic region) at every step of the solidification process, making it possible to consider the solute redistribution as a long terminal transient beginning at the solidus composition \(C_i\) (Figure 4.3 (e)). Such type of microsegregation, which can be modelled based on “Scheil equation” type of descriptions\textsuperscript{36}, testifies for a reduced mass transport in the solid.

PRECIPITATION:

The supersaturated solid solution α' decomposed behind a moving reaction front into alternating lamellae of α with lower tin content (\(C_\alpha\)) and the intermetallic Ni\textsubscript{3}Sn, according to the reaction: \(\alpha' (\text{fcc}) \rightarrow \alpha (\text{fcc}) + \text{Ni}_3\text{Sn} (D0_{19})\). Due to coring, α' has compositions \(C_{\alpha'}\), lying between \(C_i\) and \(C_f\) in Figure 4.3 (e)). As it can be seen in Figure 4.3 (b), during the 700 °C ageing treatment, the discontinuous process occurred incipiently at the dendrite edges (Sn richest regions). Ageing at
FIGURE 4.3  (a) Cored α’ dendrites and interdendritic α’ + Ni$_3$Sn eutectic. (b) Incipient DP in Sn-rich α’. (c) Extensive DP. (d) Complete dissolution of the eutectic and subsequent integral decomposition of the matrix. (e) Scheme of the coring-precipitation transformations. The equilibrium eutectic temperature is 1130 °C35.
600 °C, on the other hand, resulted in an extensive discontinuous precipitation (Figure 4.3 (c)), which roughly trailed back the composition gradient direction, but could not progress up to the dendrite cores, where the degree of supersaturation did not endorse decomposition. SEM and TEM observations showed that the interfaces between α’ and the interdendritic Ni₃Sn provided heterogeneous nucleation sites for the recrystallization of α and that subsequent solute pile-up led to precipitation of Ni₃Sn at the migrating fronts (Figure 4.4). The discontinuous reaction adapted to the composition variation in the parent phase by an increase in interlamellar spacing (λ), which ranged from 0.1 to about 2 µm. In general, in the early stages of a DP, the reaction fronts are typically curved, and for a constant composition of the matrix there must lamella branching or re-nucleation at the front if the interlamellar spacing is to be maintained. Here, contrarily, the progressive solute depletion in α’ imposed a frequent cessation of growth of Ni₃Sn lamellae behind the reaction front.

\[ \alpha + \text{Ni}_3\text{Sn} \downarrow \text{Interdendritic} \text{Ni}_3\text{Sn} \]

**Figure 4.4** The interfaces between α’ and the interdendritic Ni₃Sn provided heterogeneous nucleation sites for the recrystallization of α. Pile-up of solute at the migrating front leads to a general initiation of DP at 200 to 500 nm from the interdendritic Ni₃Sn.
Homogenisation of the as-solidified structure at 900 °C resulted in a complete dissolution of the irregular eutectic in the fcc matrix, which was fully decomposed (with roughly a constant $\lambda$ of 0.4 μm) during the subsequent ageing treatment at 600 °C (Figure 4.3 (d)). The lattice parameter difference between a supersaturated matrix $\alpha'$ with 8 at.% Sn and the depleted $\alpha$ formed at 600 °C (2.5 at. % Sn) amounts to $\Delta a \approx 0.005$ nm (1.4 %). This relatively high misfit indicates that coherency strain can be an important precipitation driving force.

The qualitative scheme of coring/precipitation presented in Figure 4.3 (e) assumes that the interruption of the discontinuous reaction shown in Figure 4.3 (b) and (c) was due to solute deficiency rather than insufficient time. Furthermore, it was considered that the reaction ceased when the parent phase at the front exhibited the composition corresponding to the solvus line ($C_\alpha$) for each ageing temperature. However, according to the equilibrium phase diagram (Appendix I), the initial solid would be formed with $\approx 3$ at.% Sn, which is a higher concentration than the one corresponding to the solvus composition at 600 °C (2.5 at.% Sn). This would lead to expect the dendrite cores to be able to decompose. The only thermodynamic requirement for the reaction is that it decreases the free energy of the system. Therefore, at relatively low temperatures, where diffusion is slow and the available free energy is large, the system may decompose into a two-phase mixture, which goes only partly towards equilibrium compositions. In fact, it has been pointed out that the DP reaction products are often not at the equilibrium compositions and, as proposed by Cahn, if GB diffusion is controlling the front migration, equilibrium compositions cannot be reached. In the present case, a deviation of the non-equilibrium solvus in the direction of higher solute concentrations, may have occurred to the extent of interrupting the decomposition at the $\alpha'$ dendrite cores. Thus, only a combination of kinetic (hindered diffusion) and free energy (undercooling) considerations would allow a quantitative analysis of the observed behaviour.
For clarity, the $\text{Ni}_3\text{Sn}(\text{eutectic}) \rightarrow \text{Ni}_3\text{Sn}(D0_{19})$ transformation was not included in the description of Figure 4.3 (e). In reality, the $\text{Ni}_3\text{Sn}$ phase forming at the eutectic temperature is not stable at low temperatures$^{35,40}$ (see Appendices I and II). Under equilibrium conditions, the stoichiometric high-temperature (HT) phase transforms congruently at 950 °C to the low-temperature $D0_{19}$ phase. There has been an indication$^{40}$ that, in practice, this transformation is massive, for quenching rates below 200 °C/s$^{40}$. Yet for rates higher than 2000 °C/s, a metastable martensitic phase with an ordered structure of the $\beta$-$\text{Cu}_3\text{Ti}$ type tends to form$^{35,40}$. Furthermore, Pak et al.$^{40}$ observed an extensive number of planar defects on the basal and prismatic planes of a massive $D0_{19}$ $\text{Ni}_3\text{Sn}$ phase obtained at a rate close to 200 °C/s. In the present case, no martensite was detected and no particular planar defects were found in the interdendritic $D0_{19}$ $\text{Ni}_3\text{Sn}$ by the post mortem TEM observations. In addition, the equilibrium Ni-rich HT phase decomposes according to the $\text{Ni}_3\text{Sn}(\text{HT}) \rightarrow \alpha + \text{Ni}_3\text{Sn}(D0_{19})$ reaction at 920 °C, here, however, such eutectoid transformation was suppressed due to the high cooling rate from the liquid state.

The $\text{Ni}_3\text{Sn}$ lamellae grow by extension of the (0002) planes, as it can be seen in the many-beam TEM images shown in Figures 4.5 and 4.6. The general orientation relationship (OR) among co-operating lamellae of $\alpha/\text{Ni}_3\text{Sn}$ was found to be:

\[
(0001)_{\text{Ni}_3\text{Sn}} // \{11\} \alpha, \ (1120)_{\text{Ni}_3\text{Sn}} // \{110\} \alpha
\]

Slight misorientations (of less than 5 mrad) between adjacent $\alpha$ and $\text{Ni}_3\text{Sn}$ lamellae, as well as between consecutive $\text{Ni}_3\text{Sn}$ lamellae, were however regularly present. This worsened the contamination-related problem, since it required optimisation of the imaging conditions to be largely performed at the area of interest. No preferred OR between the parent phase and the lamellae was found and no displacive operations were observed at the $\alpha'/\text{Ni}_3\text{Sn}$ fronts, as could be expected for a purely diffusional transformation. Local changes in growth direction, and undercooling, affected the interface curvature, preventing the reaction fronts from acquiring a regular topology. This is evident from the variation in orientation of the interface plane shown in Figure 4.5, where the depleted solid solution is nearly twin-related to the parent phase.
Planar defects parallel to (0001)

Nearly edge-on reaction front

Inclined reaction front

FIGURE 4.5 (a) HRTEM image taken along [11\bar{2}0] featuring a DP front in a sample aged at 600 °C (JEOL 4000EX/II). The Ni$_3$Sn lamella grows by extension of the (0002) planes. The α/Ni$_3$Sn interfaces are neither parallel to low index planes nor flat. The growth mechanism preserves and extends existing planar defects parallel to (0001).
**FIGURE 4.5 (b)** Detail of **FIGURE 4.5 (a)**. The $\alpha/\alpha'$ interface (b) is close to a $\Sigma 3$ {111} twin-boundary configuration, with $\alpha$ and $\alpha'$ viewed along zone axes of the type $\langle 110 \rangle$. 

Planar defect

$\Sigma 3$

$\overline{d}_{111}$

$\overline{d}_{111}$

$[0001]$  

$[\overline{1}100]$

$\alpha$

$\alpha'$

$\overline{d}_{0001} = 0.424 \text{ nm}$

Ni$_3$Sn
Whenever $\alpha$ and $\alpha'$ had very close crystallographic orientations (as in Figure 4.6), the atomic planes showed continuity across the $\alpha/\alpha'$ interfaces, although some dislocations could be found accommodating the misfit and misorientation. In these specific cases, the $\alpha/\alpha'$ interfaces displayed a particularly diffuse contrast originating only from local strain and from the composition gradient existent in the quenched boundary. Continuity of $\{111\}/(0002)$ planes across the
α'/Ni$_3$Sn interfaces occurred to a less extent. Nevertheless, the existence of a stress field at the fronts resulting from coherency effects could be inferred from the fact that the {111} matrix planes showed local distortions across the Ni$_3$Sn lamellae (see the region across the arrows in Figure 4.6). Such behaviour agrees with the expected lattice parameter changes\textsuperscript{32,37}, which correspond to about 2 % expansion along the $c$ axis.

**Figure 4.6** HRTEM image taken along [1120] featuring a precipitation front in a sample aged at 600 °C (JEOL 4000EX/II). Due to small misorientations, optimal imaging conditions could not be met simultaneously for the three phases. The approximate position of a dislocation at the α/α' interface is indicated.
Moiré fringes indicated that the $\alpha$/Ni$_3$Sn interfaces were generally neither parallel to low index planes nor flat (see Figures 4.5 and 4.6). Overall, the results show that the transformation was unable to take advantage of potentially low interfacial-energy configurations. Consequently, the OR between the precipitating phases is not related to a concurrent tendency to minimise the total interfacial energy of the system, but rather stems from an initially favoured nucleation of Ni$_3$Sn on $\{111\}_\alpha$ planes. The crystallographic relation resulting from this early stage would have been further supported during growth, by kinetic reasons related to a comparable growth rate for $\alpha$ along $\{111\}$ and for Ni$_3$Sn along the prismatic directions. The growth process has some orientation tolerance and the slight misorientation between the phases can be justified by fluctuations during the advancement of the fronts.

Unless the fcc/D0$_{19}$ interfacial energies are highly sensitive to the Sn concentration in the fcc phase, the few particular cases where $\alpha$ and $\alpha'$ were found to have the same (or twinned) crystallographic orientation exclude initiation processes related to a pucker mechanism$^{12,13}$ (at least as the only operating DP initiation mechanism). In fact, in these cases, one can expect $\gamma_3 = \gamma_1$ (see Figure 4.1(a)). Furthermore, since no preferential matrix/precipitate habit plane was found, a DP initiation mechanism of the Fournelle and Clark$^{14}$ type (Figure 4.1 (b)) seems more likely in this system.

The mechanisms operating during initiation and growth could not be observed in situ because the slow kinetics of the transformation required long ageing times in the heating-stage. This eventually led to rounding off the specimen edges, turning it opaque to the electron beam.

It is worthwhile to analyse here some of the general differences and similarities in precipitation behaviour between the Ni-Sn system and the Co-W system (Chapter 3). The enhanced bulk diffusivity in Co-W at 900 °C may render inoperative a discontinuous precipitation in this system, while at lower temperatures
a reduction in volume diffusion generally favours a DP\textsuperscript{23,24}. In effect, the precipitation of Co\textsubscript{3}W at 600 °C has been reported to occur through a discontinuous reaction\textsuperscript{41-43}. Furthermore, the fact that in Ni-Sn, the fcc $\rightarrow$ D\textsubscript{0\textsubscript{19}} transformation does not have any displacive character, in contrast to the transformation described for Co-W, may also be related to the high stacking fault energy in fcc Ni, as stacking faults provide the nucleation sites for Co\textsubscript{3}W. In fact, while the stacking fault energy can be expected to be rather low for the Co-rich fcc solid solution (as discussed in CHAPTER 3), that is not the case for the Ni-rich solid solutions because pure Ni has one of the highest stacking-fault energies of all the fcc metals\textsuperscript{44} (125 mJ/m\textsuperscript{2}). However, as in the Co-W case, in every set of heat-treated samples the Ni\textsubscript{3}Sn lamellae repeatedly exhibited planar defects on (0002) planes (FIGURE 4.7). Although some of these defects were found to start/end inside the Ni\textsubscript{3}Sn lamellae, generally the growth fronts seemed much undisturbed by their presence, and predominantly just extended already existing planar defects (see FIGURE 4.5). The spatial arrangement in Figure 4.7 suggests that annealing out of defects in Ni\textsubscript{3}Sn did not occur extensively during the ageing treatments (compare with FIGURE 3.12) and, contrarily to what was observed for Co\textsubscript{3}W, no disordered hcp phase was found bordering the Ni\textsubscript{3}Sn lamellae.

### 4.3.2 IDENTIFICATION OF PLANAR DEFECTS IN BASAL PLANES OF D\textsubscript{0\textsubscript{19}} Ni\textsubscript{3}Sn

Close-packed preserving displacements at the basal plane of the D\textsubscript{0\textsubscript{19}} structure can generate anti-phase boundaries (APB), complex intrinsic stacking faults (CISF), and a superlattice intrinsic stacking fault (SISF), where $\mathbf{f}_{\text{APB}} = 1/6\langle \overline{1}2\overline{1}0 \rangle$, $\mathbf{f}_{\text{CISF}} = 1/6\langle 01\overline{1}0 \rangle$ and $\mathbf{f}_{\text{SISF}} = 1/3\langle \overline{1}000 \rangle$. Examples of these displacement vectors are represented in FIGURE 2.7. As described in CHAPTERS 2 and 3, besides pure extrinsic faults, displacement vectors involving translations perpendicular to the basal plane can lead to a $\pi$-rotation fault ($\pi$RF) with $\mathbf{f} = 1/6\langle \overline{2}203 \rangle$, (see FIGURES 3.16 and 3.17) which is a superlattice defect, and to complex faults with $\mathbf{f} = 1/6\langle 01\overline{1}3 \rangle$. 

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Figure 4.7 Many-beam image taken along [11\(\bar{2}0\)]/[\(\bar{1}0\)] featuring a typical Ni\(_3\)Sn lamella (JEOL 4000EX/II). The precipitation occurred at 600 °C without previous homogenisation. The lamella exhibits planar defects on (0002) planes.
4.3.2.1 Conventional TEM Analysis

As presented in Chapter 2, contrast experiments in fundamental and superlattice dark-field (DF) enable to discriminate between the above planar defects. According to the dynamical diffraction theory, under two-beam conditions, the difference in phase generated by the planar defects gives rise to the following visibility criteria. Antiphase boundaries present contrast with superlattice reflections and should be invisible in fundamental dark field. Extrinsic stacking faults are visible with general \{hkil\} reflections when \(l\) is odd and invisible when \(l\) is even. All complex and superlattice stacking faults having an intrinsic component exhibit contrast with \{h0\(\overline{h}\)l\} reflections. However, the complex ones are visible with 2 of the 3 superlattice reflections of the \(h - k = 3n\) and \(l\) even type, and invisible with all the corresponding fundamental reflections; while superlattice ones are invisible for all these conditions (see Table 2.3).

Figure 4.8 and 4.9 present fundamental and superlattice dark-field images of Ni\textsubscript{3}Sn lamellae exhibiting typical defect configurations. The frequent planar defects running along the lamellae never exhibited visibility conditions compatible with a complex nature. A strong contrast was displayed under \(g = \overline{2}201\), \(g = 2\overline{2}00\), and \(g = \text{I}000\) diffraction conditions, and invisibility was always obtained under \(g = 1\overline{1}20\) and \(g = 2\overline{2}40\). These visibility characteristics conform to SISF (\(f = 1/3\{\text{I}100\}\)) or \(\pi\)RF (\(f = 1/6\{\text{2}203\}\)). In the case of single edge-on planar defects, the image is a fine line as it could be expected from a rough extrapolation of the fringe pattern of an inclined defect\textsuperscript{45}. The difference in contrast in Figure 4.8 (a) does not correspond to a real difference in the type of planar defect, but rather depends on the thickness and crystal orientation, since it was found to vary with \(s_g\). The termination of such defects inside a Ni\textsubscript{3}Sn lamella was frequently associated with other planar defects, which lied close to \{11\(\overline{2}0\)\} planes and exhibited the contrast of pure-order defects, i.e., visible under \(g = 1\overline{1}20\) and invisible under \(g = 2\overline{2}01\) and \(g = 2\overline{2}40\). Figure 4.8 (b) shows two of these defects, with the one at the top being at a nearly edge-on orientation. Other kind of APBs was also observed (Figure 4.9 (b) and (c)). These last APBs were much undisturbed by the defects on the basal planes and did not have a dense, or even a generalised presence. Such order defects tended to lie on prismatic planes and low order pyramidal planes. Due to the orientation relationship, Ni\textsubscript{3}Sn 2\overline{2}40 reflections coincide with \(\alpha\ 2\overline{2}0\) reflections, for this reason \(\alpha\) is also imaged in Figure 4.9 (c).
Figure 4.8  Ni$_3$Sn precipitated at 600 °C (after homogenisation at 900°C). The DF images (JEOL 4000EX/II) show the same region and were obtained under approximate two-beam conditions (excited systematic row). In (a) the reflection $\mathbf{g} = 2\bar{2}01$ turned visible SISFs or $\pi$RFs. In (b) the reflection $\mathbf{g} = 1\bar{1}\bar{2}0$ revealed two APB segments.

Figure 4.9  Ni$_3$Sn precipitated at 600 °C (without previous homogenisation). The DF images (JEOL 200CX) show the same region and were each obtained under two-beam conditions. The reflections used were $\mathbf{g} = 2\bar{2}01$ (a), $\mathbf{g} = 1\bar{1}\bar{2}0$ (b) and $\mathbf{g} = 2\bar{2}40$ (c). The projected [0001] direction is indicated and a tilt of about 30° separates condition (a) from (b) and (c). An SISF or a $\pi$RF can be seen in (a). Growth APBs display full contrast in (b) and residual contrast in (c).
The images in 4.9 were obtained with 200 kV (JEOL 200CX microscope) under two-beam conditions. However, due to the scale of the microstructure, conventional work at a higher resolution was often found more elucidating. In effect, the images presented in Figure 4.8 were obtained at 400 kV (JEOL 4000EX/II microscope) under approximate two-beam conditions. The flattening of the Ewald sphere at this high accelerating voltage does not allow attaining ideal two-beam conditions due to systematic reflections. However, the conditions $\mathbf{g} \cdot \mathbf{R} = 0$ and $\mathbf{g} \cdot \mathbf{R} = \text{integer}$ (in eqs. 2.33) hold for all the systematic reflections, if they hold for the lowest order reflection. Hence, the presence of systematic reflections does not invalidate the invisibility criteria for stacking faults (or dislocations).

The APBs present in the Ni-rich Ni$_3$Sn phase displayed residual contrast for 2240 reflections (Figure 4.9 (c)). Similar contrast features were observed for thermal APBs present in Co-rich Co$_3$W plates and also reported for Ga-rich bulk Fe$_3$Ga. Fagot et al. suggested that the apparent deviation of the experimental displacements from the vectors derived from purely geometric considerations is due to condensation of excess atoms at the planes adjacent to the defect region. Nevertheless, the observed residual contrast can be simply due to relaxation of the atom positions at the planar defect. The difference in number of fringes displayed by the APBs under superlattice and fundamental reflections can be explained in terms of the difference in extinction distance (eq. 2.7):

$$\xi_{2240}^{200 \text{ kV}} = 231 \text{ nm} \quad \text{and} \quad \xi_{2240}^{200 \text{ kV}} = 51 \text{ nm}.$$ 

A thickness between 100 and 200 nm ($s_n = 0$) can hence be estimated for the specimen in Figure 4.9. The extinction distances tend to be reduced through dynamic interactions with systematic reflections, however the one-fringe image of the inclined order defect in Figure 4.8 (b) points also to a high extinction distance. As a first approximation (using eq. 2.7):

$$\xi_{1120}^{400 \text{ kV}} = 276 \text{ nm}.$$
Differentiation between an SISF and a \( \pi \)RF can be achieved based on the extrinsic component of the latter defect. The additional characterisation requires a comparison of the external fringes resulting from an inclined defect, under two different fundamental dark-field conditions, one for \( l \) even and other for \( l \) odd. However, the stacking faults on the (0002) planes were in general too close together and close to the Ni\textsubscript{3}Sn/\( \alpha \) interfaces for individual contrast experiments. Hence, analyses based on high-resolution imaging were carried out instead.

### 4.3.2.2 HIGH-RESOLUTION TEM ANALYSIS

Due to the projective nature of HRTEM imaging, coherent planar defects can be invisible along certain viewing directions. As described in Chapter 2, this provides the means for an identification approach\(^9\), comparable to the visibility criterion used in conventional TEM. Nevertheless, in ordered structures, projected displacements equivalent to lattice vectors of the underlying disordered structure can only be detectable if disruption of long-range chemical order gives rise to sufficient intensity contrast. For example, in the case of an APB on the basal plane of the \( D_0_{19} \) structure (see Figure 2.7), it is essential to differentiate pure-X atomic columns from X/Y ones, when viewing along \( \langle 1\bar{1}20 \rangle \) and \( \langle 10\bar{1}0 \rangle \) directions. In \( \langle 10\bar{1}0 \rangle \) projections, because the spacing between the atomic columns (0.132 nm along \( \langle 1\bar{1}20 \rangle \) directions) is smaller than the point-resolution of the microscope, the structure is not resolved. However, the image simulations showed that (as for Co\textsubscript{3}W), under the experimental domain of thickness and defocus values used, there is a direct correspondence between contrast maxima and columns of mixed Ni/Sn atoms and, hence chemical contrast is always present. On the other hand, image simulations pointed again to a strong dependence of chemical contrast on defocus and thickness for \( \langle 1\bar{1}20 \rangle \) projections. Chemical contrast in Ni\textsubscript{3}Sn \( \langle 1\bar{1}20 \rangle \) images can be assessed from Figure 4.10, where image simulations for a planar defect, having \( f_{\text{APB}} = 1/6\langle 2\bar{1}0 \rangle \) and being viewed along \( [2\bar{1}0] \), are presented for different values of thickness (\( t \)) and defocus (\( \Delta f \)). The planar defect is invisible in (b) and chemical order is clearly apparent. Nevertheless, the simulations carried out indicated a high sensitivity to those two conditions and, in fact, experimental variations invariably turned the planar defects easily detectable in the observation field, although locally \( t \) and \( \Delta f \) could result in reduced chemical contrast. Consequently, in practice, the identification method could be used with a certain induces a weak contrast variation in (c). Only in (d), disruption of long-range reliability.
Based on a sufficient chemical contrast assumption, planar defects produced by displacements on the basal plane are expected to display the visibility listed in Table 2.4. As it can be seen in this table, differentiation between defects cannot be based solely on the visibility criterion, but can be attained with additional quantification of the projected fault vector. Generally, identification of planar defects on the basal planes of $D0_{19}$ structures requires imaging along one of the $\langle 11\bar{2}0 \rangle$ directions and along a consecutive direction of the $\langle 10\bar{1}0 \rangle$ family. In some particular situations however, the quantification of one projected displacement is enough to pinpoint an APB or a CISF (underlined displacements in Table 2.4). Distinction between purely vs. partly intrinsic defects (see 2.4.2) can be carried out by further image simulation at the level of the disrupted region.
FIGURE 4.11 presents a Ni$_3$Sn lamella bounded by $\alpha$ and containing two typical planar defects parallel to (0002). When imaged along the [11\bar{2}0] direction, these defects induced a strong contrast variation, however along the contiguous [0\bar{1}0\bar{1}] direction no effect was detected. In the [11\bar{2}0] image, the projected displacements parallel to the basal plane were equivalent but opposite for both defects, and corresponded to $\pm \frac{1}{6}[\bar{1}100]$ (or $\pm \frac{1}{6}[\bar{1}\bar{1}00]$) i.e., $\pm 0.132$ nm (or $\pm 0.265$ nm) for a lattice parameter $a = 0.529$ nm$^{32}$. A comparison with the results presented in TABLE 2.4 enables to set the observed defects as either SISFs or $\pi$RFs, in agreement with the conventional TEM analyses. The intrinsic component of complex faults could be associated with the same visibility/displacement conditions but not on consecutive viewing directions, one of the $\langle 1\bar{1}20 \rangle$ type and the other of the $\langle 10\bar{1}0 \rangle$ type. Similar results were obtained in all HRTEM contrast experiments performed on Ni$_3$Sn lamellae exhibiting planar defects parallel to (0002) planes.

The difference in atomic arrangement between the SISF ($f_{\text{SISF}} = 1/3[\bar{1}100]$) and the $\pi$RF ($f_{\text{RF}} = 1/6[\bar{2}203]$), when viewed along [1\bar{1}20], can be evaluated in FIGURE 3.17. The atomic columns are either of pure X or of alternating X and Y. The SISF displacement at the basal plane changes A into C and B into A positions and the displacement involved in a $\pi$-rotation fault brings planes A back to their original position. A, B and C planes possess an $L1_2$ type of bonding configuration. Schematically, a $\pi$RF can be obtained by removing plane C (or equivalently plane B) from an SISF. According to the extension of the contrast variation along the [0001] direction, less planes seem involved at the lower than at the top defect region in FIGURE 4.11. Presupposing a direct correlation between the contrast displayed and the atomic configuration, the top defect was anticipated to correspond to an SISF and the other to a $\pi$RF. Image simulations carried out for Ni$_3$Sn and Co$_3$W showed that the unexpected two-plane periodicity observed along [0001] in $\langle 1\bar{1}20 \rangle$ images is due to beam tilt. Some beam tilt was likely to be present since a voltage-centre alignment, and not a coma-free alignment, was performed before obtaining the experimental images (see 2.3.1). The imaging artefact, generated by the antisymmetric phase shift introduced in the contrast-transfer function by the off-axis misalignment, resulted beneficial because it emphasised the partly extrinsic nature of defects thought to be $\pi$RFs, as it can be detected on a glancing angle observation of FIGURE 4.11.
FIGURE 4.11 Part of a Ni$_3$Sn ($D_{0_{19}}$) lamella containing two stacking faults (JEOL 4000EX/II). The left image was obtained along [11\(\bar{2}0\)] and the right image was obtained at the same region but along the contiguous [01\(\bar{1}0\)] direction. The defects do not induce a contrast variation in the [01\(\bar{1}0\)] image.
4.3.2.3 IMAGE SIMULATION

A high-resolution image of a Ni₃Sn lamella exhibiting two planar defects parallel to (0002) is presented in Figure 4.12. Insets show the result of image simulation optimisations at the locations where the reference images were taken from. The defect supercell used in the simulations corresponded to a πRF. Parameter values obtained after 100 generations can be found in Table 4.1. Cross-correlation factors ($xcf$) of 0.853 were achieved for both the bulk and the πRF. In a quantitative match, it is possible to compare image average intensity (on a scale where the incident intensity is one), image contrast (which can be defined as the standard deviation of the intensity) and image pattern$^{50,51}$. In the present case, because no intensity calibration was carried out and the grey scale of the experimental images was adjusted to the full range of contrast, only pattern matching could be quantified. The image agreement factor used (eq. 2.27) is suitable for the current conditions due to its intensity and grey-scale normalising properties$^{31}$. Typically, convergence was very fast within the first 10 generations (200 images) but effective changes in the conditions still occur in late generations. Furthermore, the late changes did not correspond to refinement around a local optimum, but still involved global optimisation.

The large number of parameters involved in modelling the action of the microscope lens undermines confidence in the uniqueness of this type of fits. It is therefore usually pointed out that no single set obtained from such optimisations should be believed as being an exact solution$^{52,53}$. Effectively, other independent evolutions carried out using different initial conditions converged, within 100 generations and with cross-correlation differences of less than 0.01, to slightly different results. The values displayed in Table 4.1 correspond to the best matches obtained. The calculations showed that in the variable search space, several sets of parameter values lead to nearly equivalent images, however, the independent evolutions tended to converge to the best set of thickness/defocus/beam-tilt values, when the number of generations was increased to 200.
FIGURE 4.12  HRTEM image (JEOL 4000EX/II) of $\text{Ni}_3\text{Sn}$ taken along a $\{1\bar{1}20\}$ zone axis. Two $\pi$RFs are indicated. Insets with optimised image simulations are shown at the locations where the reference images were taken from. The partly extrinsic nature of the faults is revealed by the difference in intensity at alternating (0002) planes, generated by a slight off-axis misalignment of the beam (beam tilt).
TABLE 4.1  Optimised imaging parameters obtained by IDIM\textsuperscript{31}.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bulk 128 atoms</th>
<th>πRF 144 atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defocus (nm)</td>
<td>-11.1</td>
<td>-7.7</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>4.2</td>
<td>4.1</td>
</tr>
<tr>
<td>Beam tilt [0001] (mrad)</td>
<td>0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>Beam tilt [1\bar{1}00] (mrad)</td>
<td>-1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Crystal tilt [0001] (mrad)</td>
<td>-0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Crystal tilt [1\bar{1}00] (mrad)</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$mtf^a$ [0001] (nm)</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>$mtf^a$ [1\bar{1}00] (nm)</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>$xcf$</td>
<td>0.853</td>
<td>0.853</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Variables of an anisotropic modulation transfer function, named as achromatic damping envelope.

Possible differences between the two experimental reference images taken from \textbf{FIGURE 4.12} include small variations in thickness, crystal tilt and defocus (due to an inclination and/or thickness difference), as well as variation in the proportion of the amorphous layers. The results achieved for the two nearby regions indicate, in fact, that the optimisation process could not account for those contributions in a strictly independent manner. However, the thickness values obtained with all the runs were rather consistent (from a 0 to 20 nm allowed range). The $xcf$ values obtained reflect the similar quality of the experimental reference images used and indicate that any relaxation of the atomic positions at the faults was too fine to disturb the matching process. The lack of chemical contrast under the local experimental imaging conditions used is remarkable. Moreover, preferential thinning during sample preparation did not occur at the planar defects. Since the defects did not generate significant diffuse scattering, they are only discernible in \textbf{FIGURE 4.12} because the projected displacement is not a vector of the underlying hcp lattice (as can be seen at a glancing angle observation) and due to the effect of beam tilt. In effect, the partly extrinsic nature of the faults is revealed by the difference in intensity at alternating (0002) planes generated by the slight off-axis alignment of the beam (beam tilt). This extra periodicity along [0001] showed the position of the missing plane, allowing locating the fault precisely. Altogether, the results enabled an unambiguous identification of the defects in \textbf{FIGURE 4.12} as πRFs.
FIGURE 4.13 shows an HRTEM image of the Ni$_3$Sn phase exhibiting a defect expected to correspond to an SISF. An inset with an optimised image simulation is shown at the location where the reference image was taken from. The optimised parameters obtained after 100 generations can be found in TABLE 4.2. The $x_{cf}$ between the simulated and the reference image is 0.597. The quality of the experimental image seems to be responsible for the low cross-correlation obtained. Nevertheless, the qualitative pattern resemblance between the simulated and experimental images enabled to identify the planar defect as an SISF. In effect, the contrast variation observed at the disrupted region was reasonably reproduced and the extent of the perturbation along [0001] was properly simulated. The occurrence of this type of defects on the (0002) planes of the Ni$_3$Sn phase was however occasional; in 85 cases of planar defects studied, only 3 were assigned to SISF, the rest corresponded to πRFs (as, for example, all the defects in FIGURE 4.7).
### Table 4.2  Optimised imaging parameters obtained by IDIM$^{31}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell atom number</td>
<td>(120 atoms)</td>
</tr>
<tr>
<td>Defocus (nm)</td>
<td>-0.5</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>4.0</td>
</tr>
<tr>
<td>Beam tilt [0001] (mrad)</td>
<td>0.8</td>
</tr>
<tr>
<td>Beam tilt [1100] (mrad)</td>
<td>-1.1</td>
</tr>
<tr>
<td>Crystal tilt [0001] (mrad)</td>
<td>-0.1</td>
</tr>
<tr>
<td>Crystal tilt [1100] (mrad)</td>
<td>-0.6</td>
</tr>
<tr>
<td>$mtf_{[0001]}$ (nm)</td>
<td>0.06</td>
</tr>
<tr>
<td>$mtf_{[1100]}$ (nm)</td>
<td>0.07</td>
</tr>
<tr>
<td>$xcf$</td>
<td>0.597</td>
</tr>
</tbody>
</table>

$^a$See footnote to table 4.1.

The treatment of image formation using the concept of contrast-transfer function of the objective lens, $\sin \chi(U)$, relies on the weak-phase-object approximation (see 2.3.1), which for crystals containing heavy atoms is considered not to hold for thickness higher than 0.5 to 1 nm$^{54}$. However, the relatively high $xcf$ values obtained with FIGURE 4.12 suggest that this approximation resulted in a fair description of the electron-object interaction. In fact, the non-linear interference generated did not prevent a direct and simple correspondence between atomic sites even for $\{10\bar{1}0\}$ projections, where the structure could not be completely resolved. Hence, although the actual contrast transfer function of the microscope lens cannot be accurately modelled using conventional simulations, here we have demonstrated that a quantitative image assessment can be used to efficiently retrieve approximated imaging conditions for a phase with heavy atoms. The aim was to provide the best fit to the planar defect images, which could be generated with existent simulation programs.

#### 4.3.2.4 STRAIN FIELD EVALUATION

FIGURES 4.14 and 4.14 present results of the phase analysis performed on the HRTEM images of FIGURES 4.11 and 4.12. Bragg filtered images, which represent real lattice fringes corresponding to the reciprocal vector included in the mask ($+ g$ and $- g$), are also shown in FIGURE 4.14. The displacements involved in the faults were difficult to assess in the real space images, as well as in the Bragg filtered images. However, the bends (phase changes) on the $\bar{1}100$
phase images of both Figures 4.14 and 4.15 act as magnifiers of the rigid-body translations associated with the defects. A constant shear component, which is distorting the whole region in Figure 4.14, can be detected by careful inspection of the real space image (or the 1100 Bragg filtered image), but it is readily inferred from the fact that (aside the bends) the 1100 and 0002 fringes in the phase images are not perpendicular. The difference in intrinsic/extrinsic character of the faults was only revealed in 0001 phase images (not shown), where no noticeable variation in the fringe pattern was induced by the SISF (intrinsic defect) and an 1/3 increase in fringe spacing resulted from the presence of the πRFs (partly extrinsic defects).

The strain mapping images in Figure 4.14 do not reveal any significant variations in the \(c\) lattice parameter \(e_{cz}\) or any localised tangential distortions on (1100) planes \(e_{yz}\). On the other hand, the shear displacements on the (0002) planes \(e_{xy}\) are evident at the fault regions. The magnitude of the phase variation is approximately the same for all the defects and the direction of the projected displacement can be evaluated from the phase and \(e_{xy}\) images, being the same for the defects in Figure 4.14 and opposite for the defects in Figure 4.15. The apparent variation of the (projected) \(a\) lattice parameter at the faults in the \(e_{yy}\) image of Figure 4.14 is however misleading, as the images in Figure 4.15 show. In fact, a local variation in the \(a\) parameter would have to be detected, as well, in the \(e_{yy}\) image obtained with 2110 \(g\). The local variations observed in the \(e_{xy}\) images produced with 1100 vectors (in Figures 4.14 and 4.15) result thus from the steep perturbation in phase caused by the rigid body translation, for which a Fourier analysis of this type breaks down.

The phase analysis, particularly the one carried out with 2110 \(g\), revealed that any lattice distortions at or near the planar defects, resulting from relaxation of the atom positions, cannot be extracted from integrated intensity profiles across the HRTEM images. The phase analysis method has been estimated to be able to detect lattice deformations smaller than one hundredth of the lattice fringe distance\(^{55}\), hence, since the 2110 fringes on the 0110 Bragg filtered image (see also Figure 4.11) are \(a\) apart, any projected atomic displacement at the faults should be smaller than 0.0026 nm.
FIGURE 4.14 Analysis of the strain field around the defects (πRFs) on FIGURE 4.12. The strain images were obtained from 0002 and 1100 phase images.
FIGURE 4.15 Analysis of the strain field around the defects (SISF and πRF) on FIGURE 4.11. The strain component images were obtained (on the left) from 0002 and 0110 phases images and (on the right) from 0002 and 2110 phase images.
4.3.3 DEFECT ORIGIN: CONSIDERATIONS ON ENERGY AND GROWTH FEATURES

4.3.3.1 ENERGETICS

The energy assessments of the order defects in $D0_{19}$ phases vary widely in the literature, whereas the energy involved in superlattice defects seems to not have been given much attention. The energies of the basal APB and the CISF in Ti$_3$Al have been determined from *ab-initio* electronic structure calculations$^{56}$ to be respectively, 300 and 320 mJm$^{-2}$, while APB energies of about 10 mJm$^{-2}$ have been estimated for Mg$_3$Cd from electron microscopy studies$^{57}$.

Although absolute predictions for the Ni$_3$Sn defects are not carried out here, still a comparative study is possible. In contrast to APBs and complex faults, superlattice faults do not disturb bonding configurations at the first- and second-nearest neighbour levels and involve hence less internal energy. The SISF and the SESF (superlattice extrinsic stacking fault) present the same atomic arrangement up to the eighth-nearest neighbour. The $\pi$RF, which is also a superlattice defect, can be schematically produced by removing plane $C$ from an SISF (see Figure 3.17). Since such operation brings back planes $A$ to their original position, it results in a major decrease in number of incorrect higher-order bonds, and the $\pi$RF can be expected to be less disruptive than the SISF or the SESF.

On the grounds of pairwise interactions, Umakoshi and Yamaguchi$^{57}$ carried out an energy assessment for shear faults on the basal plane of a hard-sphere $D0_{19}$ structure. The analysis of the incorrect bonding at the fault up to eighth-nearest neighbours yielded for the SISF$^{57}$:

$$\gamma_{\text{SISF}} = \left[ -3\varphi_{AA}^{(3)} - \varphi_{BB}^{(3)} + 6\varphi_{AA}^{(4)} + 6\varphi_{AB}^{(4)} - 12\varphi_{AA}^{(5)} - 12\varphi_{AB}^{(5)} + 9\varphi_{AA}^{(6)} + 3\varphi_{BB}^{(6)} + 12\varphi_{AA}^{(7)} + 12\varphi_{AB}^{(7)} - 12\varphi_{AA}^{(8)} - 12\varphi_{AB}^{(8)} \right] / \sqrt{3}a_{\text{hcp}}^2$$

where $\varphi_{ij}^{(k)} = \varphi_j(r_k)$ are the pairwise interaction energies between $k$-th-neighbour atoms $i$ and $j$ and $r_k$ is the separation between atoms. Using the same approach, the energies of the SESF and of the $\pi$RF are estimated here to be:

$$\gamma_{\text{SESF}} = \gamma_{\text{SISF}}$$

$$\gamma_{\text{RF}} = \gamma_{\text{SISF}}$$
The experimental departure of the Ni$_3$Sn lattice parameters from the ones corresponding to an ideal hard-sphere model (see Table 2.2), leads to splitting at the levels of the fourth- and seventh-nearest neighbours. Such splitting is however not sufficient to invert the neighbouring order assumed in equations 4.1 to 4.3. Therefore, the presence of non-central forces (denoted by the deviation from the ideal $c/a$ ratio of the underlying hcp lattice, see Table 3.3) should not drastically change the above generic reasoning. In addition, the phase analysis of the HRTEM images showed that the actual atomic position relaxation at the planar defects is extremely fine. Hence:

$$\gamma_{\pi RF} \geq \gamma_{\text{SISF}} / 2$$

Assuming an effect of the fourth-nearest neighbour bonds much smaller than that of the third-nearest neighbours, one can expect:

$$\gamma_{\pi RF} = \gamma_{\text{SISF}} / 2$$

This means that the reduced number of SISF nucleation events at the reaction front cannot be explained based on energy considerations alone, and that the observed defect proportion ($\pi RF:82$, SISF:3, SESF:0) reflects the mechanism of formation, rather than being a measure of the relative energies.

4.3.3.2 GROWTH FEATURES

In principle, in bulk $D_0_{19}$ phases, defects at the basal plane having an extrinsic component, such as the SESF and the $\pi RF$, can be produced by a sequence of shears or by interstitial or vacancy precipitation, which in the case of $\pi$RFs has to be assisted by a single shearing operation. By analogy, in fcc $\rightarrow D_0_{19}$ transformations having a displacive character, those defects can be plausibly produced by faults in a shearing sequence (as described in Chapter 3). Correspondingly, in purely diffusion-controlled transformations, they may be generated at the reaction front, by insertion or removal of an extra basal plane segment (which may be followed by a single shearing operation). Intrinsic faults, on the other hand, only require a single shearing operation.
As shown in Figure 4.5, the faults on (0002) planes of Ni₃Sn are (diffusional) growth defects. Due the low proportion of SISFs, only πRFs were actually observed at the reaction fronts, but it is likely for the former defects to have the same type of origin. The confinement to an unique plane (an apparent shear defect characteristic) is justified by the way in which the faults propagate, in association with growth by (diffusional) extension of the (0002) planes. An initial shearing displacement at the reaction front is however required at the genesis of both types of defects but, due to the fault propagation mechanism, no gliding is actually necessary.

Assuming that a minimum in the γ-surface corresponds to each displacement vector leading to a stable fault⁵⁸,⁵⁹, the stability of shear displacements in the $D0_{19}$ phase can be assessed employing symmetry considerations similar to those used for cubic ordered structures⁶⁰,⁶¹. Based on geometric considerations, Umakoshi and Yamaguchi⁵⁷ established that of the pure shear faults, solely the SISF is absolutely stable and insensitive to the details of the potentials used; the CISF and APB may only be stable if the ordering energy has a minimum at the first-nearest neighbour, i.e., $(dV(r)/dr)_{r=\eta} = 0$ for $V(r_i) = \{\varphi_{AA}^i + \varphi_{BB}^i\}/2 - \varphi_{AB}^i$. This explains why the single shearing operations at the reaction only generated superlattice faults.

The removal of πRFs cannot occur by a single shearing operation, requiring climbing or multiple shearing events on a set of consecutive planes. On the other hand, the transformation of an SISF into a perfect $D0_{19}$ stacking requires only the motion of the glissile superpartial dislocation behind the reaction front, and the number of SISFs may have been reduced by this mechanism. The fact that the fcc → $D0_{19}$ transformation does not have a displacive character is, however, an indication of relatively inoperative extended shearing processes in the Ni-Sn alloy system. Therefore, once formed, SISFs are probably not removed by glide in large proportions (contrarily to what can be expected for Co₃W) and the observed proportion of SISF may result in fact from an original small number of pure shear operations at the fronts.
From the above discussion, it follows that the setting in of the extrinsic character, rather than the local shearing operation, is the critical step behind the high number of events leading to $\pi$RFs. This process should be thermally activated, which results in an entropic term contributing to the free energy of fault formation. However, at 600 °C, such contribution cannot be expected to have a strong effect. The stresses felt by the $D0_{19}$ phase at the reaction front can however provide the explanation for the repeated $\pi$RF nucleation. Removal of an atomic plane segment from an ABAB… stacking leads automatically to a shear displacement if close packing is to be preserved. Insertion of an extra atomic plane segment does not necessarily lead to an intrinsic component, since the extra atoms already occupy a C stacking position. The fact that no purely extrinsic faults were observed may be an indication that the removal of atomic planes was the rule and that the $D0_{19}$ phase at the reaction front was mainly subjected to compressive stresses. A comparison of the atomic volume changes calculated from the lattice parameters of Ni$_3$Sn$^{32}$ and of solid solutions$^{37}$ with 8 and 2.5 at.% Sn provides some support to the above hypothesis ($\Delta V_{a\rightarrow D0_{19}} = +11\%$ and $\Delta V_{a\rightarrow a} = -4\%$). In spite of the fact that the front interfaces are generally not coherent, the volume changes involved in the adaptation to local composition fluctuations may have introduced severe strain parallel to the reaction fronts (of which the bending of the (111)$_{\alpha'}$ planes across Ni$_3$Sn in Figure 4.6 is an indication). In addition, the existence of a concentration profile at the boundary (see Figure 4.2) contributes to form a complex stress state at the $D0_{19}$ fronts since the solute concentration in the parent phase is the lowest across the ‘voluminous’ Ni$_3$Sn lamellae.

The extrinsic operation (collapsing or insertion of a plane segment) may enable the growing system to carry out fast adjustments to the volume fraction of Ni$_3$Sn in order to accommodate local variations in composition. Since faults were observed at the homogenised as well as in the as-solidified samples, this behaviour is general and it is not a particular response to the composition gradient induced by the microsegregation in $\alpha'$. Sudden changes in growth direction, as well as changes in lamella width, were frequently associated with termination/initiation of defects on the (0002) planes, as shown in Figure 4.16. A climbing mechanism leading to the annealing out of faults through migration to the edges, would not justify the abrupt changes in growth direction shown in
CHAPTER 4

FIGURE 4.16. On the other hand, since the lamella width and interlamellar spacing (fraction of Ni₃Sn) are largely dependent on the solute partition occurring at the boundary diffusion field, the conditions governing the co-operative growth cannot be exclusively dependent on the presence of planar defects. In other words, co-operative changes in growth direction cannot be uniquely controlled by fault related mechanisms (indeed, independent occurrences were observed, i.e., abrupt changes of growth direction not connected with fault nucleation/termination). Instead the results indicate that nucleation and termination of faults at the precipitation front are strongly influenced by the local growth conditions. Hence, a local drive to widen the Ni₃Sn lamellae may promote fault nucleation while a decrease in lamella width may be accelerated by a potential fault termination, because both processes can be responsible for stress relieve during the solid-state transformation. Therefore, the faults seem to have assisted the growth mechanisms in controlling lamella width and growth direction, influencing to a certain extent the growth morphology of the Ni₃Sn lamellae and the precipitation mechanisms.

FIGURE 4.16 Dark-field image (JEOL 4000EX/II) of a Ni₃Sn lamella obtained with \( g = \bar{2}201 \). Abrupt changes in growth direction and/or in lamella width (shown by arrows) were frequently associated with termination/initiation of stacking faults on (0002) planes.
This type of behaviour appears to be common to other systems displaying DP. In fact, a concurrent generation of stacking faults on \{111\} planes of the matrix phase along with the DP has been reported for (Fe, Co)_3V alloys\(^\text{62}\) and for an austenitic stainless steel\(^\text{63}\). The phase and the type of planes on which the faults are induced depend on the stress field at the reaction front and on the relative energy of the possible faults. In the present case, the system has accommodated strain by inducing defects in the hexagonal phase, along the growth direction, leaving faultless the high stacking-fault energy matrix. Clearly, the generation of stacking faults and the associated stress field at the reaction front add a component to the variation of the free energy of the system, necessarily affecting the transformation driving force.

As shown in Figure 4.8, termination of faults inside the Ni\(_3\)Sn lamellae was found associated with APB segments lying on \{1120\} planes. The observed APB segments were not strictly confined to the same plane and, as such, were not shear defects resulting from a dissociation scheme, but instead were engendered by growth in association with the faults on (0002) planes. Some of these APB segments were bounded by two faults on (0002) planes (see Figure 4.8). The segments are not likely to be related to climbing of \(\pi\)RFs, because such a process would not result in the straight configurations observed for the last defects, which confirms the growth origin of the APB segments. A geometric model compatible with an APB emanating from a terminating \(\pi\)RF is proposed in Figure 4.17. The change in atomic configuration at planes A and C, induced by a dislocation with \(b = 1/6[\bar{2}023]\), is presented in Figure 4.17 (a). If an APB segment is generated at the reaction front on the \((\bar{1}2\bar{1}0)\) plane (Figure 4.17 (b)), termination of a \(\pi\)RF requires then a dislocation having \(b = 1/6[\bar{1}013]\), which also restores order at the prismatic plane. Alternatively, in the case of an SISF termination, the existence of an APB in \((\bar{1}2\bar{1}0)\) plane requires a dislocation having \(b = 1/6[\bar{1}010]\). Observations of these defect combinations were attempted in HRTEM, but owing to the non edge-on configuration, the presence of the short APBs segments could not be unequivocally detected in \(\{11\bar{2}0\}\) projections. On the other hand, the analysis in \(\{10\bar{1}0\}\) projections turned out to be in practice difficult due to the invisibility of the defects on the basal planes, combined with the unavoidable drifting induced by tilting (no eucentric-plane correction is possible with the top-entry holder configuration of the JEOL 4000EX/II microscope, see Table 2.1).
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FIGURE 4.17  Geometric configurations at a \( \pi \)RF termination. In (a) the bounding dislocation has \( \mathbf{b} = 1/6[2023] \) and lies along \([10\bar{1}0]\). In the stacking sequence, the dot represents the projection of the dislocation line, and the sloping lines indicate that the letter index changes upon passing from the unslipped to the slipped region. The displacement induced on the right side of the prism is represented in projection for the top four planes in the stacking. As indicated in (b), if an APB lying on the \((12\bar{1}0)\) plane is formed at the reaction front, the termination of the \( \pi \)RF requires a dislocation having \( \mathbf{b} = 1/6[10\bar{1}3] \). The asterisk stands for incorrect order and both vectors represented involve a component along \([0001]\).

The APBs observed in the \( D_{019} \) lamellae were “grown in” during the transformation and are not thermal in nature since no disordered intermediate state was found. The growth process did not introduce a strong orientation dependence on the spatial arrangement in the case of the defect type shown in FIGURE 4.9 (b). Furthermore, a strict tendency to minimise the total interfacial energy could not be detected from the crystallographic orientation of the generally smooth domain boundaries. The lower number of these defects in Ni\(_3\)Sn, as compared with Co\(_3\)W (see FIGURE 3.11 (b)), is a consequence of the purely diffusional growth mechanism not dependent on an intermediate disordered state. However, the Ni-Sn system required longer ageing times for detection of an appreciable degree of transformation and this may have led to some annealing out of APBs.
4.4 CONCLUSIONS

- The potential of quantitative HRTEM image simulation was demonstrated for perfect and defect structures involving heavy atoms.

- The extent of discontinuous precipitation in the Ni-Sn alloy containing 8 at.% Sn strongly depends on the thermal history (severity of microsegregation and annealing and ageing cycles).

- The $\alpha'$/Ni$_3$Sn interfaces provided heterogeneous nucleation sites for $\alpha'$ recrystallization and solute pile-up at the $\alpha/\alpha'$ migrating fronts lead to DP initiation.

- The cases where the supersaturated and depleted solution solid solutions had very close crystallographic orientations rule out the Pucker mechanism of DP initiation.

- Under every heat-treatment condition, the discontinuous precipitation engendered frequent stacking faults parallel to (0002) in the Ni$_3$Sn lamellae. These defects were identified by conventional TEM as $\pi$RFs and SISFs. Distinction between these two types of faults was accomplished based on HRTEM and image simulation.

- The planar faults on the Ni$_3$Sn lamellae are a consequence of the diffusional growth by extension of the (0002) planes. The higher fraction of $\pi$RFs as compared to the SISF fraction is not solely dependent on the energy of the defects, but rather seems related to the stress-state at the reaction front.

- Sudden changes in growth direction, as well as changes in lamella width were frequently associated with termination/initiation of defects on the (0002) planes. These results indicate that nucleation of the faults at the precipitation front was strongly influenced by local growth conditions. Furthermore, the faults may have assisted the growth mechanisms in controlling lamella width and growth direction.

- The observed APBs are not of thermal nature, but instead are “grown in” during the direct fcc $\rightarrow$ D0$_{19}$ transformation. These pure-order defects were generally undisturbed by faults on the basal planes. Some APB segments were however found to be bounded by faults on (0002) planes. These segments, which were not strictly confined to a unique plane, were generated by growth in association with the faults.
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