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Ordering and structural transformations in Ni_3Al alloys

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X-ray diffraction profile studies on the filings of stoichiometric and off-stoichiometric compositions of Ni_3Al alloys, with and without boron additions, were conducted to clarify some of the significant anomalies noticed in the literature. The long-range order parameter was estimated as a function of temperature in all the four alloys from (1 0 0)/(2 0 0) and (1 1 0)/(2 2 0) pairs of reflections. The $L1_2$ structure appears to attain a maximum stability at about 600 °C, around which temperature its order parameter was close to the theoretical value. Above 600 °C, this structure becomes less stable and there appears to be formation of an additional structure of a lower symmetry.

1. Introduction

Ni_3Al, an ordered intermetallic compound, is of potential interest for high-temperature structural applications due to its anomalous positive temperature dependence of strength [1, 2]. The inherent brittleness encountered in this alloy has been substantially overcome by small additions of boron [3, 4]. These alloys are considered to belong to the $L1_2$ type of ordered structure [5]. Since X-ray diffraction (XRD) reflections at superlattice locations have been noticed up to very high temperatures (of the order of 1350 °C), it is believed that this ordered structure exists as such up to its melting point.

The values of long-range order parameter S quoted by a number of authors, however, vary widely. Stoeckinger and Neumann [6], working with stoichiometric Ni_3Al single crystals of (h 0 0) orientation annealed at 800 °C (and in a few cases, with short holding times at higher temperatures up to 1385 °C), quote abnormally large and untenable values for S (such as 1.40) which do not appear to vary at all from room temperature up to 1300 °C. They attribute the high value of S to a "systematic error". The values for S quoted by the other authors are more realistic. Corey and Potter [7], in their studies of the order in stoichiometric Ni_3Al, report a value of $S = 0.8$. Stoeckinger and Neumann [6] attribute this "low value" of Corey and Potter to the non-adoption of a dispersion correction by the authors. Clark and Mohanty [8] also quote a similar figure. On the other hand, Aoki and Izumi [9] obtained a near-theoretical value for S (e.g. 0.98 for stoichiometric Ni_3Al) in both stoichiometric and off-stoichiometric compositions, and claim maximum order in all cases. In contrast, Masahashi *et al.* [10] state that perfect ordering is not obtained even with stoichiometric alloys. However, the value of the order parameter is improved when the alloys are doped with carbon (C), boron (B) or beryllium (Be), and they conclude that C and B are particularly effective in stabilizing the $L1_2$ structure.

Some discrepancies have also been noticed in the lattice constants of alloys in the Ni_3Al homogeneity region which have not been satisfactorily explained or accounted for [11]. When the lattice constant for this structure, as obtained by various workers, is plotted against atomic percentage Al, a systematic deviation to lower a values is noticed in most cases [12]. There seems to be a difference between the Ni_3Al and the Ni_3Ga system in this respect. While Ni_3Ga alloys show good agreement and measurement values lie fairly well on the extrapolated linear variation of spacing with atomic percent Ga in the fcc solid solution, considerable scatter of the data for the lattice spacing of the Ni_3Al alloys is noticed. It is possible that the deviations in some cases (especially the older studies) may be because of poor precision in the gadgetry. But even some of the later workers, using more accurate instrumental facilities, have obtained perceptibly lower values for a than can confidently be attributed to poor recording of data.

A careful look into the experimental details of all the work carried out reveals that the homogenization temperatures adopted differ between one work and another, and were generally at 850 °C or higher. In one case [7], a material cooled from a high temperature of 1350 °C and filed thereafter showed a $\Delta 2\theta_{111-200}$ shift resembling a very high density of stacking faults. The authors have quoted a very high stacking fault parameter (SFP) value of 0.044 based on this. (It is interesting to note that the standard material used in the SFP determination was annealed at 900 °C). A SFP of this value (0.044) is abnormally high, since even 70–30 brass and Cu–8% Sn show much lower values (0.029 and 0.021, respectively). An even more

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surprising observation is the difference in lattice constant (about 0.0009 nm) between the as-filed and annealed (at 900 °C) materials.

From the literature, it is evident that significant anomalies exist in lattice and order parameter determinations of Ni_3Al alloys. At this point, it is worthwhile to mention two important observations made related to structural aspects: (i) the above-mentioned observations of Masahashi *et al.* [10] that the $L1_2$ structure gains further stabilization with ternary additions such as carbon and boron, even in off-stoichiometric compositions; and (ii) the observation of Noguchi *et al.* [12] that with an increasing alloying addition in the off-stoichiometric compositions within the phase region of Ni_3Al (23–27 at % Al), the phase stability of an $L1_2$ structure with respect to the DO_{22} as well as DO_{19} structure is likely to be reduced.

A number of questions arise in this situation: can such a structure (DO_{19} or DO_{22}) perhaps also exist at high temperatures even for stoichiometric compositions? Can other closely related ordered structures co-exist which affect the results of different workers? Could it be possible that the anomalous strengthening behaviour noticed in these alloys is related to some structural change?

A careful study at different temperatures might give the answer. Hence the present study was taken up to investigate the onset of ordering, as well as the variation of the ordering parameter with temperature, and to study the changes in the ordered structure, if any, in both stoichiometric and off-stoichiometric composition of Ni_3Al alloys.

2. Experimental procedure

The starting materials used in this work were nickel of 99.9 wt %, aluminium of 99.99 wt % and boron of 99 wt % purity. All the four alloys discussed in this study were prepared by melting in a vacuum induction furnace (Heraeus) and drop casting into copper moulds. They were homogenized at a temperature of 1000 °C for 48 h under a vacuum of 2×10^{-5} torr followed by furnace cooling. The values of nominal and analysed chemical compositions are given in Table I.

An electron micro-probe analysis (EPMA) on all the four alloys revealed the homogeneity of the composition. Filings (325 mesh size) produced from the high temperature (1000 °C, 48 h) homogenized alloys were subjected to 2 h anneals at intervals of 100 °C over the temperature range of 200–800 °C and at 1000, 1200 and 1300 °C. Some samples were also additionally annealed for 24 h at 200 and 1000 °C. The annealing was carried out under a vacuum of 2×10^{-5} torr. Trial samples of nickel filings annealed at 1000 °C for 24 h under the same conditions indicated very little oxidation. For most cases, the high-temperature annealing was followed by furnace cooling to room temperature. In a few cases samples were quenched in water from high temperatures, for reasons that will be discussed below.

TABLE I Alloy compositions used

Alloy code	Alloy compositions	Analysed Al (at %)	Nominal B (wt %)
Stoichiometric compositions			
8B	75 at % Ni–25 at % Al	(24.5)	–
5B	75 at % Ni–25 at % Al + 0.1 wt % B	(24.6)	0.1
Off-stoichiometric compositions			
2.1.A	76 at % Ni–24 at % Al	(23.5)	–
7B	76 at % Ni–24 at % Al + 0.1 wt % B	(23.6)	0.1

2.1. Structure analysis

X-ray diffractometric (chart) recordings of the filings were carried out using nickel-filtered Cu$K\alpha$ radiation and a Philips goniometer operating at 30 kV and 30 mA. A diffractometer slow scanning speed of 1/8° min^{-1} and a paper displacement speed of 10 mm min^{-1} were used. Two superlattice [(1 0 0) and (1 1 0)] and three fundamental [(1 1 1) (2 0 0) and (2 2 0)] reflections were recorded under a lower impulse rate for enhanced accuracy.

The long-range order parameter, S, was estimated based on a comparison of the integrated intensities of superlattice and fundamental reflections, according to the relationship

$$S^2 = \frac{I_s}{I_f} 16 \frac{(X_{Al} f_{Al} + X_{Ni} f_{Ni})^2}{(f_{Ni} - f_{Al})^2} \frac{(L_p)_f}{(L_p)_s} \frac{e_f^{-(2M)}}{e_s^{-(2M)}}$$

where I is the measured integrated intensity; f_{Al} and f_{Ni} are the atomic scattering factors for Al and Ni, respectively; X_{Al} and X_{Ni} are the atomic fraction of Al and Ni, respectively; L_p is the Lorentz polarization factor $(1 + \cos^2 2\theta)/(\sin^2\theta \cos\theta)$; and $e^{-(2M)}$ is the Debye Waller temperature factor. The subscripts s and f refer to the superlattice and fundamental reflections, respectively. The values of the respective scattering factors, together with corrections for anomalous dispersion, were obtained from the international table of X-ray crystallography [13], while those of the Lorentz polarization factor were taken from Cullity [14]. The value of the Debye Waller factor, M, was calculated from the amplitude of vibration ($\bar{u}$) for the Ni_3Al structure quoted by Masahashi *et al.* [10]. In the present study, the order parameter was estimated from the (1 0 0)/(2 0 0) and (1 1 0)/(2 2 0) pairs of reflections.

The possibility of a surface absorption effect due to roughness (in samples of loose filings) affecting the values of the order parameter has been known for some time [15]. In the case of metals of high atomic number, even the relative intensities of the fundamental reflections could be markedly affected due to surface absorption effects (R. Vasudevan, unpublished results). However, in the present case, intensity measurements made on Ni_3Al filings of 325 mesh size did not show any marked surface absorption effects as the plot of $\ln(F_{obs}/F_{calc})$ against $\sin^2\theta$ obtained with Cu$K\alpha$ radiation was in agreement with the expected trend, i.e. decreasing with increasing θ (Fig. 1). No correction was therefore required in the estimation of the order parameter for the present set of alloys. The procedure adopted to determine the surface roughness effects are dealt within detail in an earlier paper [16].

3. Results and discussion

3.1. Long-range order parameter studies

The values of the order parameter obtained on stoichiometric and off-stoichiometric compositions of Ni_3Al (with and without boron additions) alloys over the temperature range (300–800 °C) for a 2 h anneal are shown in Figs 2 and 3, respectively. The theoretical values of the order parameter for both stoichiometric and off-stoichiometric compositions are also indicated in the figures. The order parameter values for the temperatures above 800 °C are not shown, as they were untenable for reasons that will be explained below. It is noticed that the order of the $L1_2$ structure is near perfect at a temperature of 600 °C in all cases. The values quoted from the (1 1 0)/(2 2 0) pair are slightly higher than for the (1 0 0)/(2 0 0) pair, owing perhaps to texture, extinction or other reasons. Such variations are not unusual in order parameter studies. As far as the Ni_3Al alloys are concerned, earlier authors have always quoted results only from the (1 0 0)/(2 0 0) pair. Beyond 600 °C, there is a reduction in the order parameter values, especially as noticed from the (1 1 0)/(2 2 0) pair whose value now goes below that of the (1 0 0)/(2 0 0) pair – in contrast to the earlier situation (Figs 2 and 3). The order parameter estimated on the basis of an $L1_2$ structure for 1000 °C gives untenable values such as 1.159 for an off-stoichiometric composition (alloy 7B) and 1.25 for stoichiometric composition (alloy 5B).

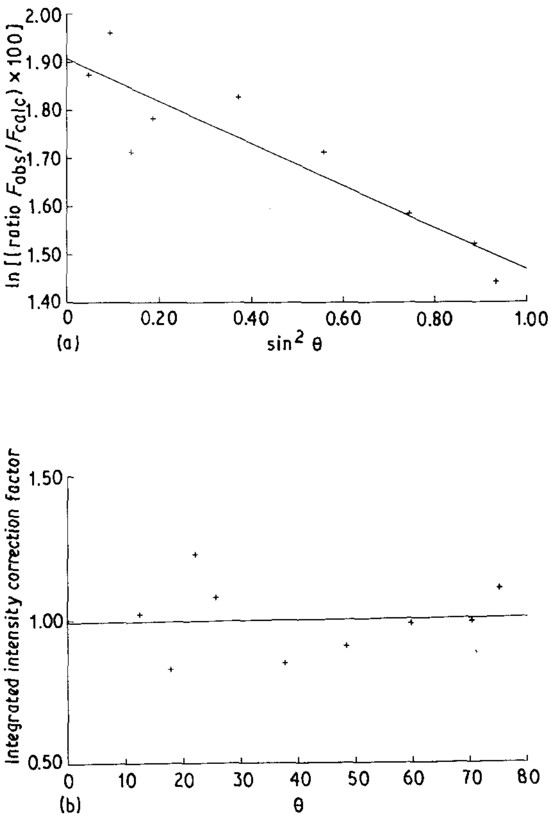

Figure 1 (a) Plot of $\ln(F_{obs}/F_{calc})$ against $\sin^2\theta$ obtained with Cu$K\alpha$ radiation for stoichiometric Ni_3Al (47 μm) filings annealed at 600 °C; +, 75Ni–25Al. (b) Integrated intensity correction curve based on the above plot; +, correction factor.

All these observations indicate that the situation prevailing beyond 600 °C is totally different from the one that exists below this temperature.

3.2. Intensity profile (diffractogram) studies

The observations on intensity profiles are discussed here mainly with reference to one alloy (alloy 7B). Where appropriate, a comparison with other alloys is made. A few diffractograms obtained from the alloy 7B over the range of temperatures are shown in Fig. 4a for the fundamental reflections, namely (1 1 1), (2 0 0)

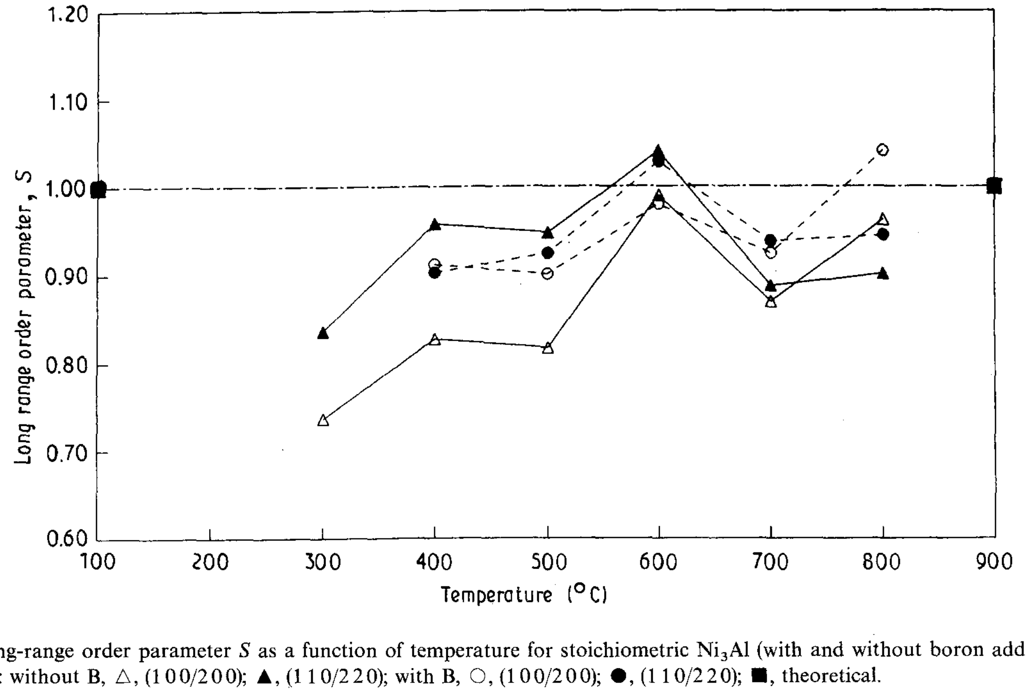

Figure 2 Long-range order parameter S as a function of temperature for stoichiometric Ni_3Al (with and without boron addition). Order parameter, S: without B, △, (1 0 0/2 0 0); ▲, (1 1 0/2 2 0); with B, ○, (1 0 0/2 0 0); ●, (1 1 0/2 2 0); ■, theoretical.

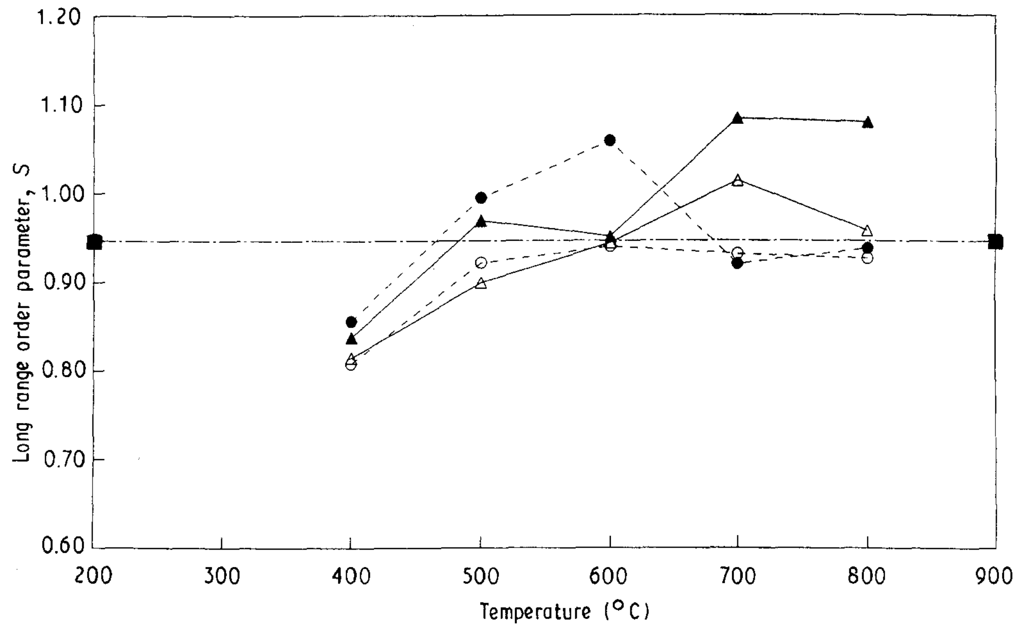

Figure 3 Long-range order parameter S as a function of temperature for Ni-rich off-stoichiometric Ni_3Al (with and without boron addition). Order parameter, S: without B, △, (1 0 0/2 0 0); ▲, (1 1 0/2 2 0); with B, ○, (1 0 0/2 0 0); ●, (1 1 0/2 2 0); ■, theoretical.

and (2 2 0); and in Fig. 4b for the superlattice reflections, namely (1 0 0) and (1 1 0). The diffractograms obtained are of a similar nature in the case of the other alloys studied.

From the intensity profiles, it was observed that ordering starts at a temperature between 200 and 300 °C for a 2 h anneal. When the time was extended to 24 h, a faint ordering was noticed even at 200 °C (Fig. 4b) which is in line with the observations of Corey and Potter [7]. The fundamental reflections at 600 °C are quite sharp with distinctly visible doublet (α_1, α_2) splitting (Fig. 5a and b). The lattice constant of the structure was determined to be 0.35710 nm using a $\cos\theta\cot\theta$ extrapolation of all fundamental lines. Values obtained for all alloys are indicated in Table II. As the temperature is increased beyond 600 °C there is a marked broadening of all the lines, and the clear doublet splitting appears to be vanishing, as shown in Fig. 5a for the (2 2 0) line. There is also a marked shift of peaks towards a higher 2θ (Fig. 4a) which is clearly visible with (1 1 1) as well as (2 0 0) reflections. The superlattice (1 0 0) and (1 1 0) reflections become appreciably weaker (Fig. 4b). As mentioned earlier, there is also a reduction in the order parameter values beyond 600 °C (Figs 2 and 3). All these phenomena together seem to indicate that the $L1_2$ structure is undergoing some distortion, or is being partly replaced by another growing structure.

The intensity profile studies beyond 800 °C are considered below. The superlattice lines become stronger beyond this temperature (Fig. 4b). An important observation was made which is shown in Fig. 6: a 24 h anneal at 1000 °C produces a splitting of the superlattice (1 1 0) line but not the (1 0 0) line which, however, is broadened. At 1200 °C (as also at 1300 °C), a 2 h anneal shows sharp but split reflections at the (1 1 0) as well at the (1 0 0) locations.

Fig. 5b shows the results of the (2 0 0) fundamental line. At 800 °C, there is a noticeable asymmetry while at 1000 °C, a 2 h anneal appears to produce a faint splitting of this line. A 24 h anneal at this temperature clearly brought out the (2 0 0) splitting. There is a clear change in lattice constants determined on samples held at 1000 °C for 2 and 24 h. The latter appears to exhibit clear changes in the two lattice constants, *a* and *c*. At 1200 °C, a 2 h anneal shows a well resolved splitting overlapped by a weak broadened reflection, and the intensity becomes weaker.

TABLE II Experimentally determined lattice parameters of Ni_3Al

Alloy code	Alloy	Lattice parameter (nm)
8B	75Ni–25Al	0.35722
5B	75Ni–25Al + 0.1 B	0.35791
2.1.A	76Ni–24Al	0.35663
7B	76Ni–24Al + 0.1 B	0.35710

Observations made with regard to the (2 2 0) fundamental line were of similar nature (Fig. 5a). At 800 °C, the broadened (2 2 0) line appears to split into two peaks of near-equal intensities, while at 1000 °C a similar splitting overlapped by another broad line was noticed. At 1200 °C, the (2 2 0) reflection also becomes weaker, as for the (2 0 0) reflection. A marked distortion was noticed with regard to the (1 1 1) line, also beyond 800 °C. It is worth pointing out here that all the fundamental peaks move towards a lower 2θ (Fig. 4a) beyond 1000 °C.

Figs 7–9 show the features observed in other alloys, namely 2.1.A, 5B and 8B, respectively, for (2 2 0) locations. It can be seen from these figures that for a 2 h anneal at 1000 °C, there is an overlap of another broad line in all cases. Fig. 10 shows the well-resolved splitting of the (2 0 0) line for all the four alloys when subjected to a 2 h anneal at 1300 °C.

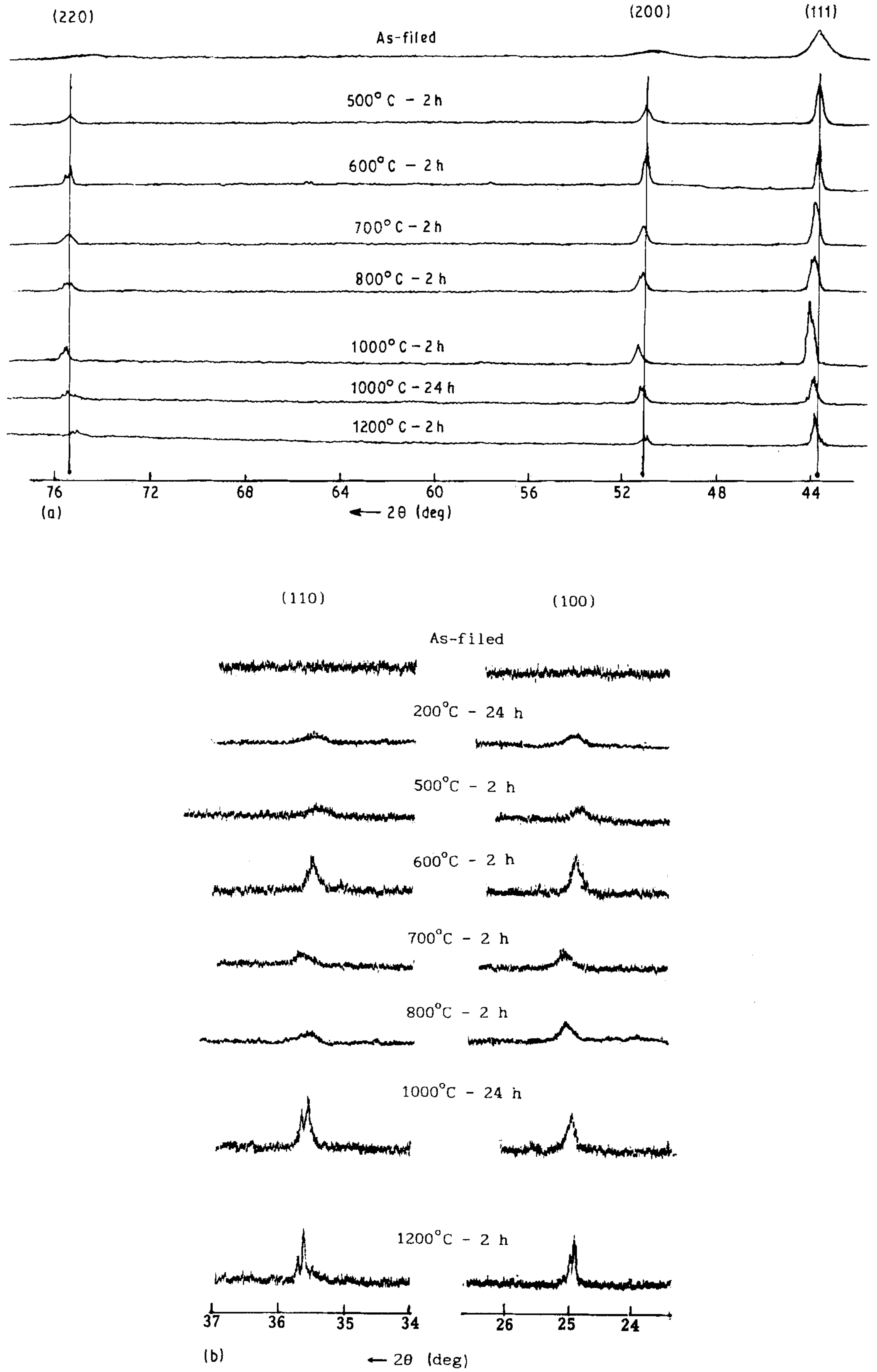

Figure 4 (a) XRD patterns obtained over a range of temperatures for the alloy 7B for the (1 1 1), (2 0 0) and (2 2 0) fundamental reflections. (b) XRD intensity profiles obtained over a range of temperatures for the alloy 7B for the (1 0 0) and (1 1 0) superlattice reflections.

To examine the possibility that these split reflections could be due to impurity lines (due to oxides, nitrides or even borides), a check was carried out based on the information available from the ASTM-JCPDS database for oxides, nitrides and borides of Al, Ni and Al–Ni. None of the phases matched the pattern observed.

The split reflections seen at the (1 0 0), (1 1 0) and (2 0 0) locations allow themselves to be indexed as the (1 0 0) (0 0 1), (1 1 0) (0 1 1) and (2 0 0) (0 0 2) reflections of a tetragonal lattice whose lattice constants are $a \cong 0.35786$ and $c \cong 0.35697$ nm (the values are quoted based on observations made on [(2 0 0)/(0 0 2)]), while the lattice constant of the $L1_2$ structure of this

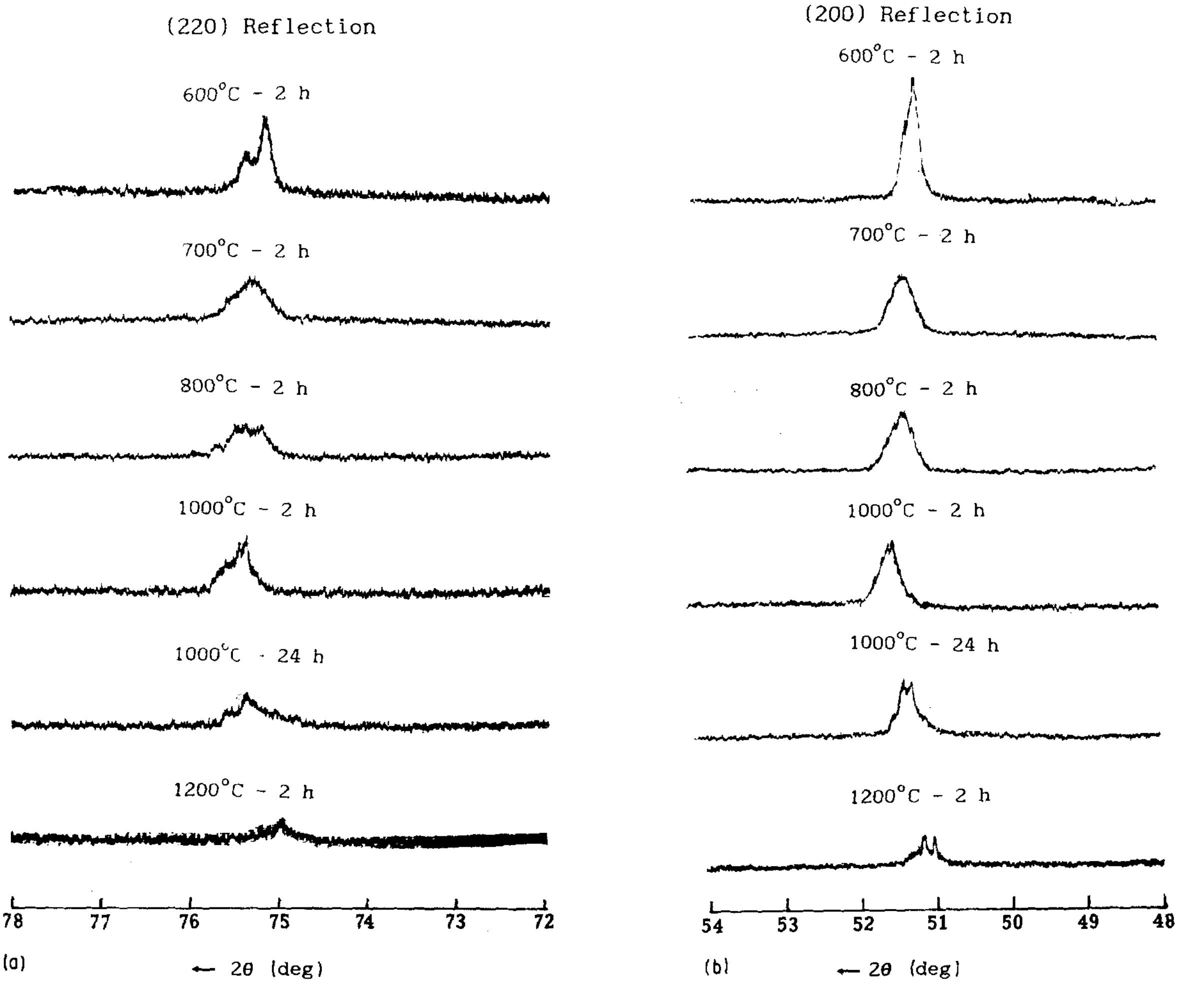

Figure 5 XRD intensity profiles obtained for (a) the (2 2 0) reflection and (b) the (2 0 0) reflection over a range of temperatures for the alloy 7B.

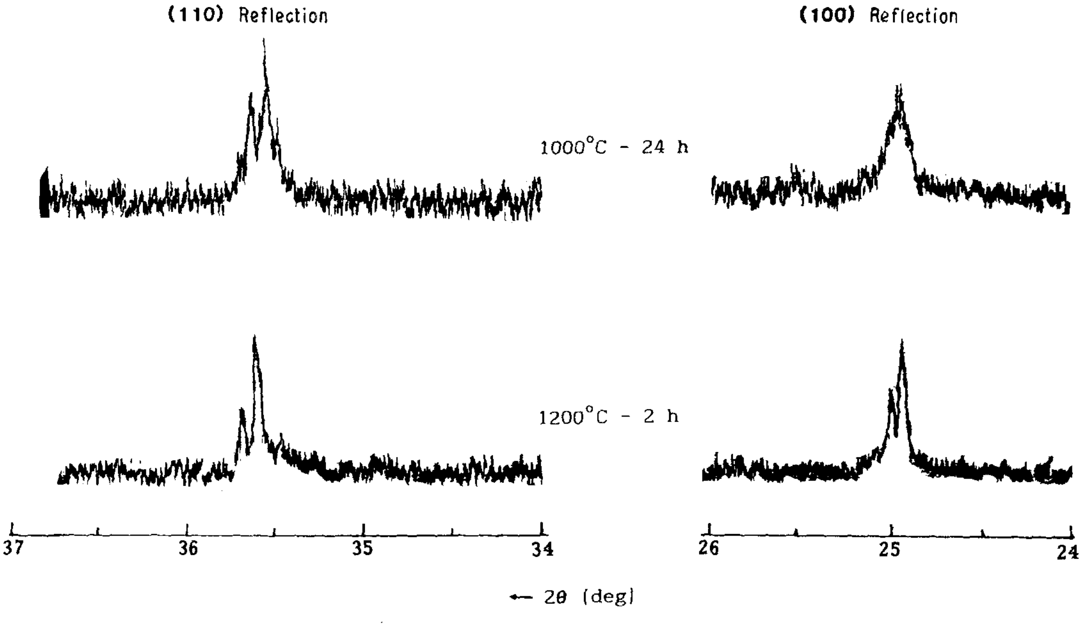

Figure 6 XRD intensity profiles of the (1 0 0) and (1 1 0) superlattice reflections for the alloy 7B when subjected to anneals at 1000 and 1200 °C.

composition (alloy 7B) is 0.3571 nm. Similar indexing was also possible for other alloys. The tetragonal structure identified could perhaps be the DO_{22} structure referred to by Noguchi *et al.* [12]. It appears that this phase is more stable than the $L1_2$, not merely when there is an increased proportion of the minority component as stated by Noguchi *et al.*, but even otherwise when the temperature goes to a value close to 1000 °C. However, the overlapping reflections seen at the (1 1 1), (2 0 0) and (2 2 0) locations could not be

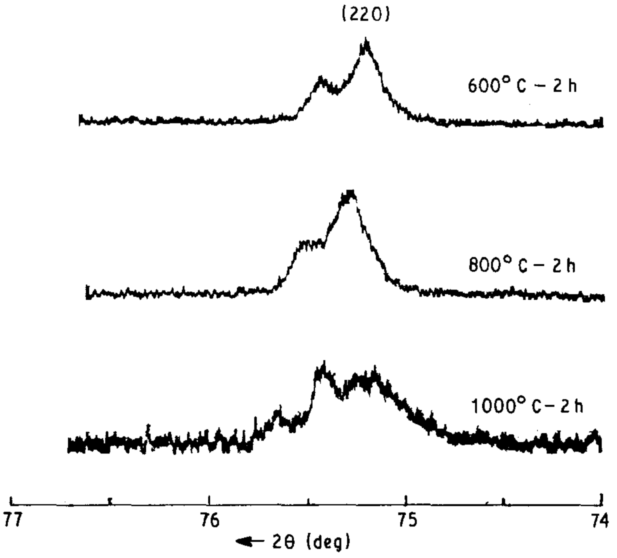

Figure 7 XRD intensity profiles of the (2 2 0) line for the alloy 2.1.A when subjected to a 2-h anneal at 600, 800 and 1000 °C.

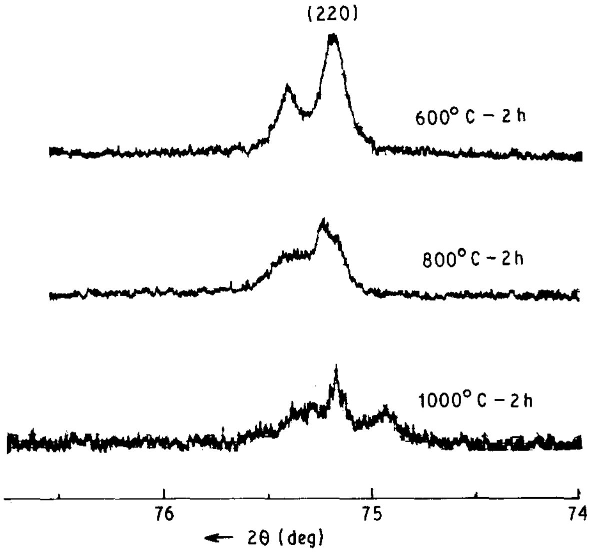

Figure 8 XRD intensity profiles of the (2 2 0) line for the alloy 5B when subjected to a 2-h anneal at 600, 800 and 1000 °C.

accounted for. Hence it is difficult to ascertain the exact crystal structure of this phase at present. The $L1_2$ structure, on the other hand, appears to be uniquely stable at 600 °C.

The existence of these two different structures was confirmed by an experiment in which the samples that were water-quenched after annealing at 1000 °C for 24 h were raised to 600 °C and held for long durations (Fig. 11). The sample subjected to homogenization at 1000 °C and subsequently water-quenched showed many overlapping peaks in addition to the satellite peaks at the (1 1 1) location. When the same sample was taken to 600 °C and held for 2 h, all the overlapping peaks vanished at the (1 1 1) locations. When held for longer durations at 600 °C, the reflections at (1 1 1), (2 0 0) and (2 2 0) become very sharp, which is identical to the earlier situation (Fig. 4a). Again, when the sample was taken back to 1000 °C, all the originally observed anomalies were seen once again. This provides evidence for structural transformation in these alloys at higher temperatures.

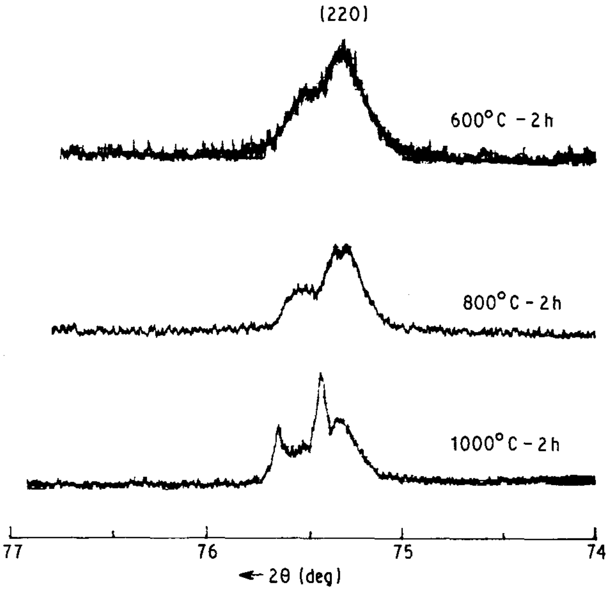

Figure 9 XRD intensity profiles of the (2 2 0) line for the alloy 8B when subjected to a 2-h anneal at 600, 800 and 1000 °C.

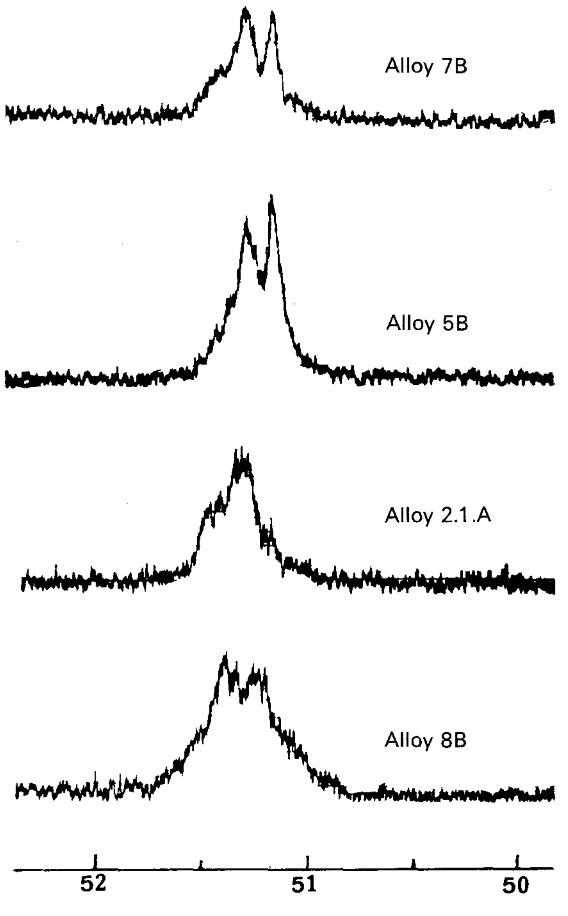

Figure 10 XRD intensity profiles of the (2 0 0) line for all four alloys when subjected to a 2-h anneal at 1300 °C.

Based on the intensity profiles and order parameter studies on all four alloys, we believe there are two different structures in both stoichiometric and off-stoichiometric compositions. Further, no significant

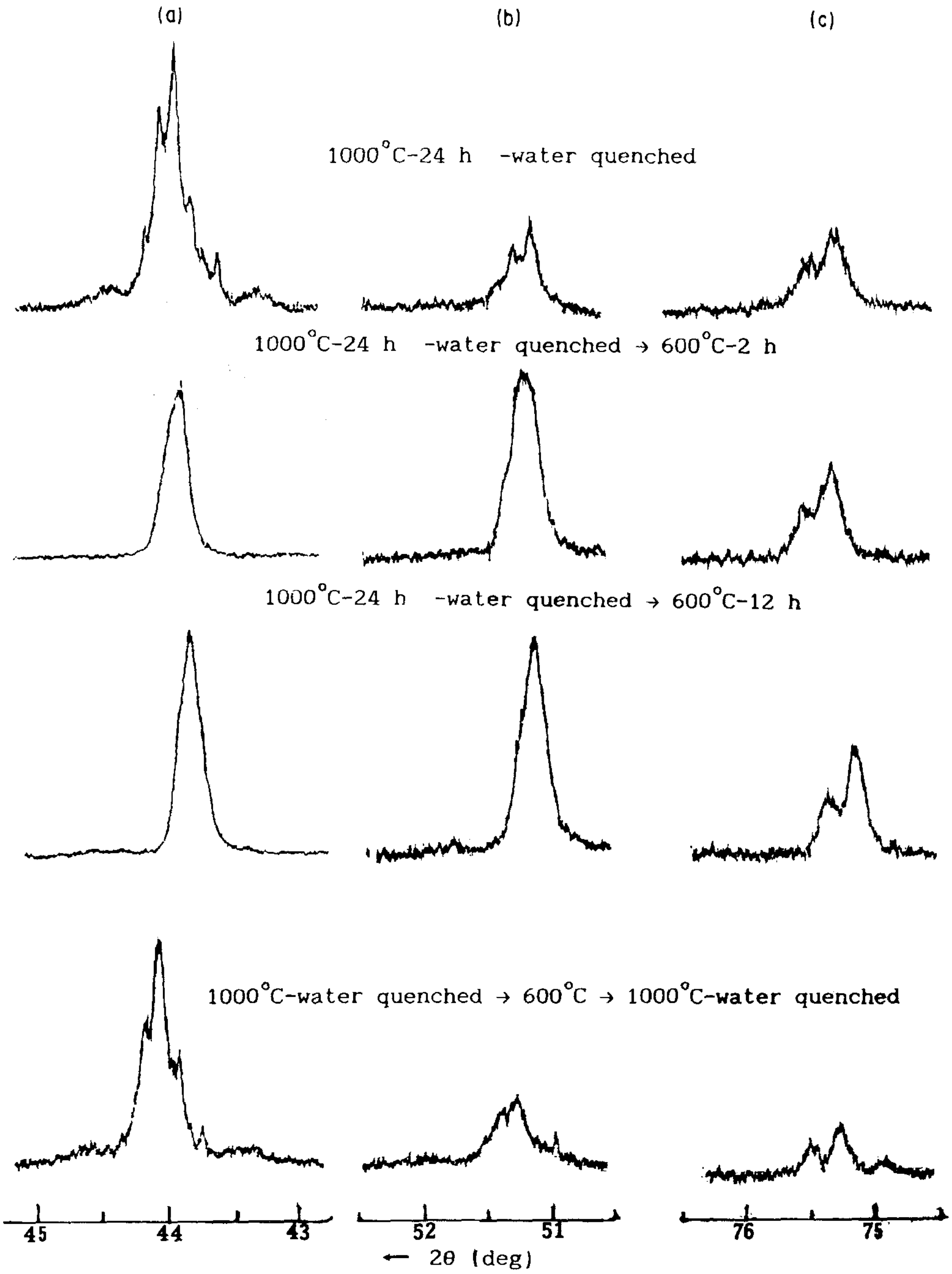

Figure 11 XRD intensity profiles of the alloy 7B providing evidence for structural transformation at higher temperatures. (a) (1 1 1); (b) (2 0 0); (c) (2 2 0) reflections.

difference was seen in the intensity profiles between the boron-doped and non-doped Ni_3Al alloys. The anomalies noticed in all the line profiles are clearly reproducible, confirming that the $L1_2$ structure in Ni_3Al alloys is not as uniquely stable at higher temperatures as is widely believed. In view of these observations, which suggest that the structure above 600 °C is not of the $L1_2$ type, the results of earlier work on lattice and order-parameter determinations at high temperatures, in which a $L1_2$ structure was assumed, may have to be revised. Flow stress studies are being carried out at present to examine the possibility that the anomalous strengthening behaviour of these alloys is related to the structural changes we noticed.

4. Conclusions

1. The $L1_2$ structure in Ni_3Al (homogeneity region) alloys is not stable up to its melting point, as has been widely believed to be the case.
2. The $L1_2$ structure attains a maximum stability at about 600 °C where the order parameter is near the theoretical value.
3. As the temperature exceeds 600 °C, the order parameter goes down and the $L1_2$ structure becomes unstable in relation to one or more other structures. These different structures appear to be thermodynamically stable at the respective temperatures, as revealed by thermal cycling studies. The exact crystal structures are difficult to ascertain at present.
4. The kinetics of such structural changes appears to be very slow.

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