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SPINODAL DECOMPOSITION IN NICKEL BASED NICKEL–TITANIUM ALLOYS

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Abstract—The early stages of the decomposition process in Ni based Ni–Ti alloys have been studied by means of transmission electron microscopy. It was found that the supersaturated solid solution of Ti in Ni decomposes by the spinodal mechanism into periodic and aligned regions which are Ti rich and Ti lean. After a critical amount of Ti enters the Ti rich regions, they order continuously to the Ll_2 (Cu_3Au) structure. The two processes then continue together until the fully ordered metastable γ' particles are formed.

Résumé—On a étudié par microscopie électronique en transmission les premiers stades de la décomposition des alliages Ni–Ti à base de nickel. On a trouvé que la solution solide sursaturée de titane se décompose selon le mécanisme de décomposition spinodale en régions périodiques et alignées, alternativement riches et pauvres en Ti. Lorsque la teneur en titane des régions riches en titane atteint une valeur critique, elles s'ordonnent continument selon la structure $L1_2$ (Cu_3Au). Les deux processus progressent simultanément jusqu'à la formation de particules γ' métastables parfaitement ordonnées.

Zusammenfassung—Das Anfangsstadium des Entmischungsprozesses in Ni–Ti Legierungen wurde mit Durchstrahlungselektronenmikroskopie untersucht. Die übersättigte feste Lösung von Ti in Ni entmischt sich durch einen spinodalan Mechanismus in periodische und ausgerichtete Bereiche, welche Ti-reich und Ti-arm sind. Die Ti-reichen Gebiete ordnen sich nach dem Uberschreiten eines kritischen Ti-Gehaltes kontinuierlich in die Ll_2 (Cu_3Au) Struktur um. Die beiden Prozesse laufen ab, bis die vollständig geordneten, metastabilen γ'-Teilchen gebildet sind.

1. INTRODUCTION

The sequence of the reactions which occur in Ni based Ni-Ti alloys (8–14 at.% Ti) has been studied by a number of investigators [1–10]. All have reported that the supersaturated solid solution of Ti in Ni decomposes into a metastable modulated two phase structure (one phase of which is ordered with the Ll_2, Cu_3Au structure) before the equilibrium mixture of the terminal solid solution (f.c.c.) and the ordered hexagonal phase η is formed. This paper will deal with the mechanism of formation of the metastable two phase mixture.

There are at least three ways that a supersaturated solid solution can decompose to form a two phase mixture of the terminal solid solution and an ordered phase [11]. One way is for the system first to decompose spinodally into solute enriched and solute lean disordered regions, followed by ordering within the solute rich regions. This is the case in the Cu–Ti system [12–14].

A second way is the well known nucleation of the ordered phase, exemplified in the case of the Ni-Al system [15]. In this system the ordered particles are originally randomly dispersed throughout the matrix. During coarsening, the particles apparently align themselves along the elastically soft directions.

The third method of decomposition has been termed continuous ordering [16]. In this case, the supersaturated solid solution continuously increases its order parameter with aging, and in time particles that are highly ordered appear. This mechanism appears to operate in the off-stoichiometric Ni_4Mo and Ni_3V systems. These alloys are currently being studied and initial results were recently reported [17].

To differentiate among these mechanisms, it is important to observe the early stages of the decomposition process. If the microstructure as seen by transmission electron microscopy is periodic and aligned along the elastically soft directions from the start of the process, spinodal decomposition is most likely the dominant mechanism. On the other hand if the alignment of particles occurs only during coarsening, the process is probably nucleation and growth (as in Ni–Al). It is also important to ascertain if ordering occurs during or after the initial decomposition process.

Previous electron microscopy studies on Ni–Ti alloys have failed to document in a consistent manner the microstructure and diffraction patterns of the earliest stages of the decomposition process. The as-quenched alloys have been reported to have a modulated structure, but the direction of the modulations were not given [6], and satellites around fundamental reflections were not reported to be present. If the modulations were due to composition fluctuations,

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satellites should be there. Also, no systematic variation of the operating $\boldsymbol{g}$ vectors were performed to indicate the type of contrast mechanism giving rise to the modulations. This investigation was initiated to clarify the types and sequence of the phase transformations which occur during the initial stages of the decomposition process in supersaturated Ni based Ni–Ti alloys.

2. EXPERIMENTAL

The nickel titanium alloys were prepared from high purity nickel and iodide titanium. Buttons of approx. 12 g were prepared in an atmosphere of high purity argon. Before melting, the system had been pumped to less than 30 μm and backfilled with high purity argon three times. To decrease the oxygen content in the system, a titanium getter button was melted before the alloy was melted. All alloys were melted three separate times. The buttons were pickled in acqua regia and rinsed in acetone after each melting.

The resulting buttons were slightly cold worked (less than 10% reduction), and then annealed at 1100°C for 4 hr and rapidly quenched in water. They were encapsulated in quartz tubing in a high purity argon atmosphere during the annealing process. After annealing they were rolled to 0·4 mm sheet and given an intermediate anneal at 1100°C for 2 hr. They were final rolled to 0·25 mm before being solution treated at 1100°C for four hours and quenched.

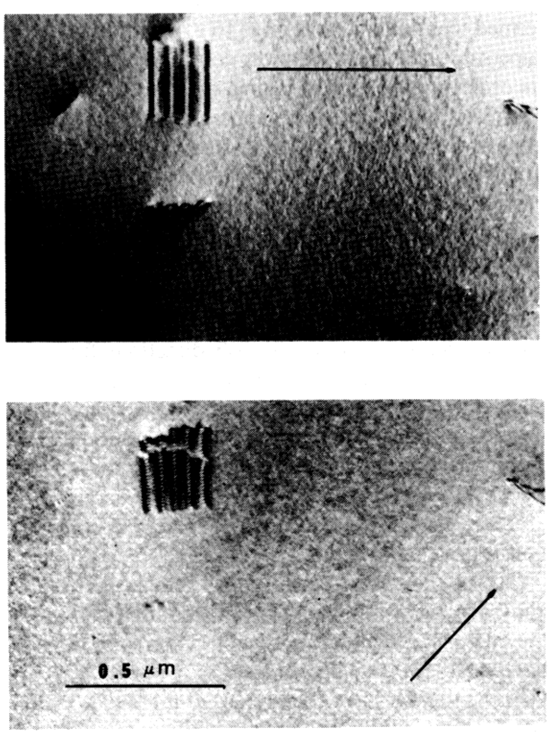

Fig. 1. Microstructure of a Ni–12 at.% Ti alloy in the as-quenched (helium) condition. The foil normal is near [110]; $\mathbf{g} = (002)$ in (a) and $\mathbf{g} = (1\bar{1}\bar{1})$ in (b).

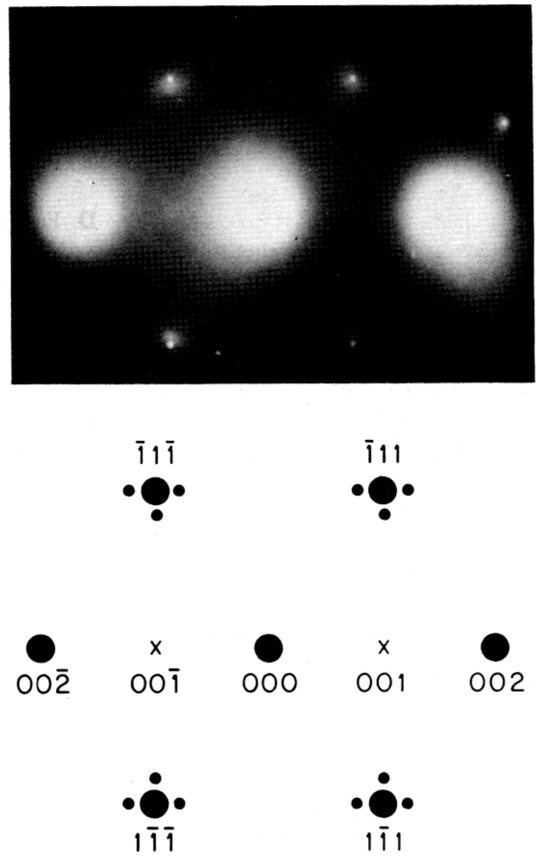

Fig. 2. Diffraction pattern and schematic thereof for the alloy shown in Fig. 1. A superlattice reflection can be best seen at the $(00\bar{1})$ position. The satellites on the low angle side of the {111} reflections are not in the [110] section. See text. Satellites also occur at the (002) and $(00\bar{2})$ reflections, but can not be seen because the reflections have been overexposed.

Two types of quenching methods were used. The most rapid method was done by withdrawing the quartz capsule from the tube furnace and breaking it by plunging in into an ice brine solution. A second, slightly slower quench was obtained by forcing high purity He gas into a vertical tube furnace in which the thin 0·25 mm strips were hanging. Both quenching methods yielded similar surface conditions with the oxidation being slight.

Short time aging experiments (less than 60 min) were performed in a salt bath, and longer time aging in an argon atmosphere.

Thin foils were prepared by double jet indenting, using a 1/3 nitric acid 2/3 methyl alcohol electrolyte solution at a temperature of −50°C. The electron microscope was operated at 100 kv and had a double-tilt stage.

3. RESULTS AND DISCUSSION

(A) As-quenched alloys

The electron microstructures and diffraction pattern of a helium quenched Ni–12 at.% Ti alloy are shown in Figs. 1 and 2, respectively. Figure 1(a) is the microstructure observed when $\mathbf{g} = (002)$ is satisfied, and 1(b) is that observed for $\mathbf{g} = (1\bar{1}\bar{1})$ satisfied. The contrast is very faint, but it can clearly be seen that the different diffracting conditions give distinct types of contrast. For the case of (002) satisfied, extremely faint modulations are visible perpendicular to the operating **g**. For $(1\bar{1}\bar{1})$ satisfied a more mottled 'salt and pepper' like contrast is observed.

The corresponding diffraction pattern, shown in Fig. 2(a), exhibits faint, diffuse satellites around the fundamental reflections (seen best at the $(1\bar{1}\bar{1})$ and $(\bar{1}1\bar{1})$ reflections) and a faint superlattice reflection at $(00\bar{1})$. (See Fig. 2(b) for complete indexing of the diffraction pattern.) The helium quenched Ni–10 at.% Ti alloys showed identical diffraction patterns and microstructures with the satellites, superlattice reflections and modulations being even fainter.

The faint modulations and diffuse satellites show that a periodic and aligned array of Ti-lean and Ti-enriched regions exists in these as quenched alloys. The direction of the modulation (viz. $\langle 100 \rangle$, best observed in the late stages of decomposition, see next section) is consistent with the known elastic anisotropy of Ni based alloys [18, 19]. Furthermore, as seen from the superlattice reflections, some ordering within the Ti enriched regions has occurred.

The most prominent wavelength of the modulations is not easily found, because of the broad spectrum in wavelengths that are present, as seen from the diffuse satellite reflections in Fig. 2(a). However, an estimate of the most prominent wavelength can be found from the bright field micrographs. Both the Ni–10 at.% Ti and 12 at.% alloys had a most prominent wavelength of *ca.* 12·0 nm.

The modulations are difficult to see this early in the decomposition process. However they are not to be considered artifacts or 'etching effects' since they do vary with operating **g** and since they also produce reciprocal space satellites. Furthermore, when the alloys are aged (see next section) the modulations increase in intensity. (Cf. Figs. 4 and 5 with 1 and 2.)

The diffraction pattern of a Ni–10 at.% Ti alloy that is brine quenched (i.e. at a faster rate; see experimental section) is shown in Fig. 3. Satellites were again observed in the diffraction pattern (see especially the $(00\bar{4})$ reflection). Also, the bright field

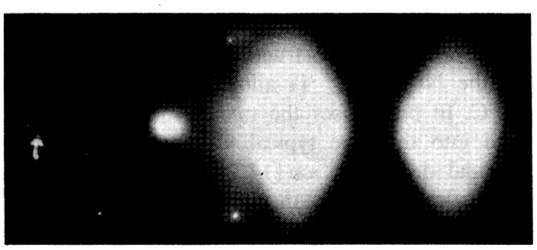

Fig. 3. Diffraction pattern of a Ni–10 at.% Ti alloy that was brine quenched. Satellites can be observed best near the $(00\bar{4})$ reflection. See arrow. Notice the absence of any {001} superlattice reflections.

micrographs exhibited faint modulations identical to those shown in Figs. 1(a) and (b). However, no superlattice reflections are observed in the diffraction pattern. Evidently the faster quench was sufficient to prevent the ordering reaction from progressing to an observable degree. It is therefore concluded that the segregation reaction precedes the ordering reaction in these alloys, just as it does in the similar Cu–Ti alloys [12–14].

It was not possible to perform the 'microstructural sequence method' [12, 14] on these alloys to prove that spinodal decomposition had occurred, because the satellites and modulations were so faint. However, periodicity and alignment along the elastically soft directions from the start of a phase transformation is strong evidence that spinodal decomposition has occurred. Moreover, the microstructure that evolves (see next section) is exactly that predicted for an alloy decomposing spinodally by continuous cooling from above the spinodal temperature [20]. Thus, since the only system that has been shown to attain alignment of second phase particles without the means of the spinodal mechanism did so during coarsening, it can be concluded that the 10 and 12 at.% Ti alloys decompose on the quench via the spinodal mechanism into Ti-enriched and Ti-lean regions. The ordering reaction then occurs within the Ti-enriched regions.

This conclusion is in apparent contradiction with the recent field ion microscopy results of Sinclair *et al.* [10]. They concluded that the ordering reaction occurred simultaneously with the spinodal reaction. However, the alloys studied here had less Ti than that of Sinclair *et al.* (they studied a Ni–14 at.% Ti alloy). The spinodal reaction in the brine quenched 10 at.% Ti alloys (Fig. 3) did not proceed as far as that in the more supersaturated as-quenched 14 at.% Ti alloy of Sinclair *et al.*, (or for that matter, those shown in Figs. 1 and 2) and hence the critical amount of Ti needed for the ordering reaction to occur did not exist in them. A similar result was found in the Cu–Ti case, where as-quenched Cu–5 wt.% Ti alloys undergo spinodal decomposition and ordering, whereas the as-quenched Cu-3 wt.% Ti alloys only undergo spinodal decomposition [12, 13]. Of course once the ordering begins, it occurs concurrently with the spinodal decomposition. There is a coupling between the two reactions. As the Ti-enriched regions continue to increase in Ti content (due to spinodal decomposition) they also increase in degree or order. This increase in order is dependent on the amount of Ti present, which depends on the extent of the spinodal reaction (see next section).

The observation of satellites in the as-quenched Ni–Ti alloys diffraction patterns has not been reported, even though composition modulations have been postulated to exist in the as-quenched condition [3]. Indeed, it has been stated that the satellites do not appear until 2–4 hr of aging at 600°C [6]. It must be emphasized that it was necessary in the present study to overexpose the diffraction patterns to observe the faint, diffuse satellites. This is probably because of the broad spectrum of composition wavelengths present in the alloy crystals. However, the existence of the satellites along the [001] direction of reciprocal space is consistent with the claim that ⟨100⟩ composition modulations exist in real space. Indeed, if the satellites were not observed one would have to postulate another source for the modulations, such as is done in the well known case of ⟨110⟩ tweed [16, 17].

Near the {111} reflections in the diffraction patterns shown in Figs. 2(a) and 3(a), diffuse satellites can be observed either on the low angle side of the reflections (Fig. 2(a), toward the {001} superlattice reflections) or the high angle side of the reflections (Fig. 3). These extra satellites appear because the tangent to the Ewald reflecting sphere was not exactly parallel to the (110)* reciprocal lattice plane. It therefore intersected one of the other satellites at each of the {111} reflections. For the case of satellites arising from 12 nm composition fluctuations, the angle α which the tangent to the reflecting sphere would have to make with the (110)* section is about $1{\cdot}75 \times 10^{-2}$ rad.

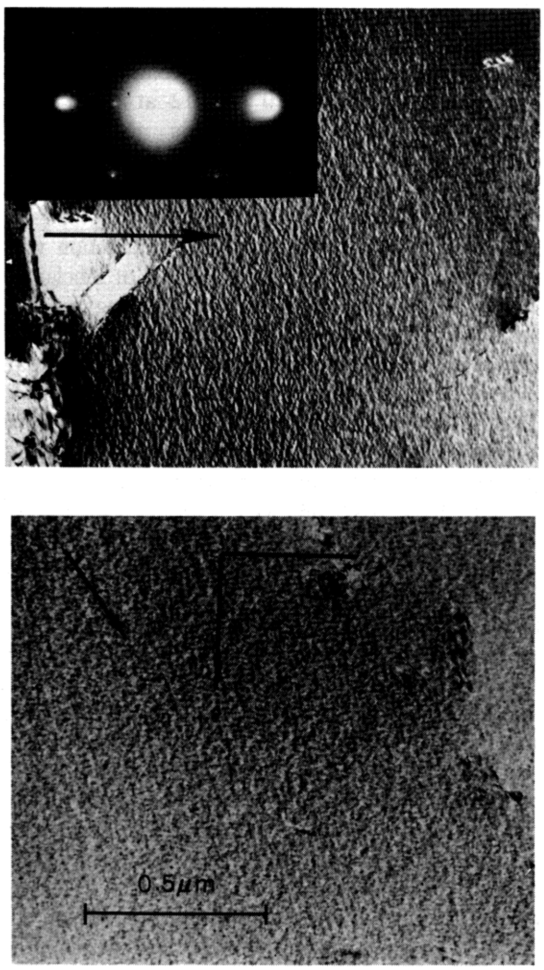

Fig. 4. Microstructures and diffraction pattern of a Ni–10 at.% Ti alloy aged for 60 min at 600°C. In (a), strong modulations exist perpendicular to the operating **g**, (002), while two sets of modulations exist in (b), both along traces of {200} planes (see b). Satellites and superlattice reflections are also quite prominent. Foil normal [110]; **g** = (002) for (a) and **g** = $(1\bar{1}1)$ for (b).

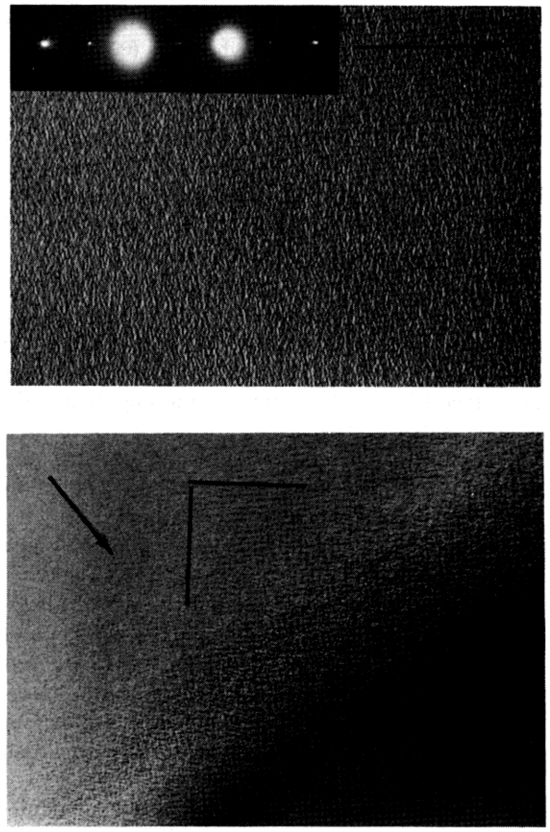

Fig. 5. Microstructures and diffraction pattern of a Ni–12 at.% Ti alloy aged for 15 min at 600°C. Again, the microstructure depends on the operating **g**, and the contrast of the microstructure and intensity of satellites and superlattice reflections are enhanced over that for the as-quenched condition of the alloy (Fig. 1). Foil normal [110]; **g** = (002) in (a) and **g** = (111) in (b). {200} traces shown in (b).

(B) Aged alloys

When the alloys were aged at a temperature of 600°C the two reactions continued to occur. Figure 4 shows the microstructure and diffraction pattern for the Ni–10 at.% Ti alloy aged 60 min at 600°C and Fig. 5 shows the microstructure and diffraction pattern for the Ni–12 at.% Ti alloys aged 15 minutes at 600°C. In both cases the microstructure has developed into the type typical for the early stages of spinodal decomposition [14, 21–23]. The net matrix strain clearly reveals the composition modulations which exist along the ⟨100⟩ directions. Furthermore, by comparing the two microstructures resulting from the different diffracting conditions (i.e. (a) and (b) of Figs. 4 or 5) it can be seen that if the operating **g** vector has only one non-zero component, only one set of composition modulations are present (Figs. 4a and 5a), whereas if the operating vector **g** has two non-zero components two sets of composition modulations appear (Figs 4b and 5b). This shows that the modulations are being observed via a strain contrast mechanism and not by the structure factor modulations. This is of course also true for the as-quenched condition, but the modulations are much fainter and hence it is harder to observe the differences (see Fig. 1).

The ordering reaction has progressed concurrently with the spinodal reaction, as evidenced by the increase in the intensity of the {001} superlattice reflections. Once the two reactions occur together it is possible to consider them to be only one reaction [10]. The degree of order in the Ti-enriched regions depends on the amount of Ti present in the regions and this in turn depends on the extent of the spinodal reaction. However it is important to remember that the continuous increase in order occurs after the basic microstructure (i.e. periodic and aligned array of regions) has been produced by the initial spinodal reaction. Thus the morphology and microstructure of the resulting two phase mixture depends only on the initial spinodal reaction.

It should be noted that the ordered $L1_2$ phase which forms within the Ti-enriched regions is a crystallographic derivative of the f.c.c. (A1) structure. Indeed for any transformation to occur continuously, the crystal structure of the newly formed phase must be so related to that of the parent phase. The original spinodal reaction yielded two disordered f.c.c. (A1) phases or regions, but once ordering began, two different crystal structures were present (A1 and $L1_2$). This means that the original spinodal reaction which occurred on the quench was the metastable coherent Ni–Ti spinodal reaction and not the metastable coherent Ni–Ni_3Ti spinodal reaction.

The sequence of the metastable reactions may be summarized as follows:

$$\alpha' \rightarrow \alpha_{Ni} + \alpha_{Ti} \tag{1}$$

$$\alpha_{Ti} \rightarrow \gamma' \tag{2}$$

where α' is the supersaturated solution of Ti in Ni (A1), α_{Ni} is the Ni-rich A1 phase, α_{Ti} is the Ti-enriched A1 phase and γ' is the ordered Ni_3Ti, $L1_2$ phase. Equation (1) represents the spinodal reaction, while equation (2) represents the ordering reaction within the Ti-enriched regions.

The overall metastable reaction can be written as:

$$\alpha' \rightarrow \alpha_{Ni} + \gamma', \tag{3}$$

which is just the general equation for the decomposition of a supersaturated solid solution (α') into the terminal solid solution (α_{Ni}) and an ordered precipitate (γ'). Equation (3) does not give any information concerning the mode of this decomposition, whereas equations (1) and (2) taken together do.

The similarity of Ni–Ti to Cu–Ti has been noted above. The sequence of reactions that occur in these

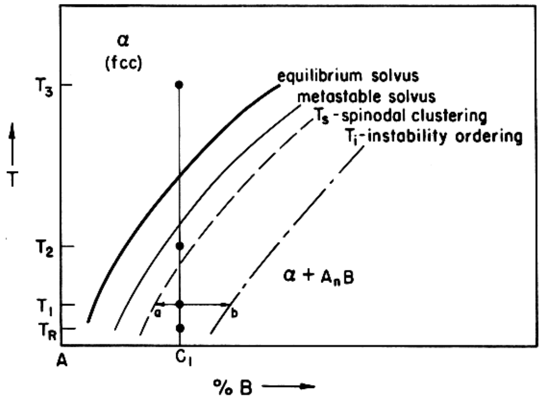

Fig. 6. A proposed phase diagram for systems like Ni–Ti and Cu–Ti, showing the relative positions of the equilibrium solvus, metastable solvus, spinodal and instability ordering curves. Spinodal decomposition should precede ordering in these systems if the temperature of the alloy does not drop below T_1.

systems can also be summarized by means of the hypothetical phase diagram shown in Fig. 6. In this A–B system, an alloy with overall composition C_1 is solution treated at T_3 and quenched to T_R, room temperature. It begins to spinodally decompose after passing through the spinodal temperature T_S, but at room temperature the reaction is effectively frozen (see Fig. 3). The alloy is then upquenched to an aging temperature T_1, where spinodal decomposition can resume because of increased thermal mobility. The composition of the B-enriched and B-lean regions approach points '*b*' and '*a*' respectively. Once the composition of the enriched regions reach '*b*', an *in situ* ordering process begins in them. Quenching from T_3 to T_2 would result in nucleation of the ordered A_nB phase, as discussed in Ref. 14.

Thus, in cases such as Cu–Ti and Ni–Ti, we may conclude that the instability ordering temperature curve lies below the spinodal curve, in the composition and temperature regions that have been studied.

With further aging, the metastable Ni_3Ti regions develop into cuboidal particles. These microstructures have been documented [5, 6] and will not be reproduced here. The contribution to the literature of this investigation has been the systematic documentation of the microstructure and diffraction patterns of as-quenched specimens as well as those for the early stages of aging.

4. SUMMARY

The following experimental observations have been made on the Ni–Ti alloys: (a) The periodic composition modulations in the as-quenched specimens have been shown to be present along the ⟨100⟩ directions; (b) Satellites around the fundamental reflections have been shown to exist from the start of the transformation; (c) The superlattice reflections appear after the segregation process has started.

From these observations it is concluded that:

1. The Ni–10 and –12 at.% Ti alloys decompose

spinodally during the quench from solutionizing temperatures.

2. The ordering reaction begins after the spinodal reaction has begun, showing that the instability ordering temperature lies below the spinodal curve in the regions studied in this alloy.

3. The two reactions then occur simultaneously, until fully ordered Ll_2 precipitates are formed.

The observations are consistent with and imply the conclusions and vice versa. This system transforms very similarly to the Cu–Ti system which has been reported on previously [12–14, 21].

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