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An electron-microscopical investigation on the martensitic transformation in TiNi

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An electron-microscopical investigation of the morphology of equiatomic TiNi martensite has revealed at least two types of martensite: the twinned plate martensite and a wavy martensite. To our knowledge the latter has never been reported in the literature before. In a thin foil, the plate martensite can be transformed into the wavy martensite within a few weeks at ambient temperature or by temperature cycling between +100°C and liquid nitrogen temperature.

The transformation into the wavy martensite has been studied dynamically with the aid of a video-recording system attached to the microscope. This revealed the step-wise migration of the irregular boundary between the wavy martensite and the high temperature phase. The transformation from the B2 phase to the wavy martensite is preceded by the formation of a superstructure having three times the lattice parameter of the CsCl (B2) structure. The transformation is very sensitive to the cooling rate during temperature cycling and can even be totally suppressed if the cooling rate is too high. The transformation characteristics are not affected by the thermal history of the sample.

1. Introduction

The intermetallic compound TiNi undergoes a martensitic transformation when the high temperature phase is cooled. The structure of the matrix has been established by most previous investigators as the B2 structure [1, 2, 5]. However, Wang *et al* [3] mentioned the co-existence of two structures: B2 and $P\bar{3}m1$. There are numerous and partly conflicting data available on the structure of the martensite. Chandra and Purdy [1] found, in their electron diffraction investigation at temperatures between 20 and 100°C, weak reflections emerging at half and one-third distances of the B2 reflections, indicating an intermediate phase. They explained these weak reflections as being streaks originating from instabilities in the crystal. The structure of this intermediate phase, based on X-ray measurements, was rhombohedral with a = 9.03 Å and $\alpha_{\min}$ = 89.3°. Moreover, they supposed the weak reflections to be unique to thin foils.

Marcinkowski *et al* [2] investigated only the low temperature martensite with the aid of electron diffraction and reported the existence of two closely related monoclinic structures. They also concluded that the martensite formed in bulk is identical to martensite formed in thin foils by cooling in the electron microscope. Wang *et al* [3], in their comprehensive work on powder specimens, calculated theoretically the possible martensitic structures from the two different high temperature structures mentioned above. They confirmed the existence of these structures mainly from X-ray measurements and concluded the resulting martensite structures to be triclinic and hexagonal.

Nagasawa [5] was able to index his diffraction patterns in a manner similar to that used by Sato *et al* [4] in their work on $AuMn_3$, Cu_3Al and AuCd alloys. A portion of these patterns could be explained on the basis of the existence of a high density of stacking faults, suggesting layer structures with stacking sequences of 4H, 2H, 3R, 12R and 18R and showing hexagonal and rhombohedral symmetry. Superlattice spots similar to those described by Chandra and Purdy were also observed and likewise interpreted as a 9 Å superlattice. These observations were explained in terms of a new phase transformation, always present next to the martensite and resulting merely from a release of stress induced by the formation of the martensite. Nagasawa also suggests that the formation of this new phase plays an important role in the "memory" effect in the TiNi alloy.

Otsuka *et al* [6] observed diffractions patterns of the martensitic phase formed in thin foils, and these are, in part, comparable with some of Nagasawa's as well as some observed in the present investigation. They interpreted their patterns as arising from a distorted B19 structure, leading to a monoclinic unit cell. At room temperature, they observed a B2 structure in which weak reflections emerged between the main diffraction spots and with $\frac{1}{3}$ the reciprocal spacing after cooling to liquid nitrogen temperatures.

The majority of papers on TiNi report the presence of the above-mentioned superlattice [1, 2, 5-7]. According to Wang *et al* [7], the superlattice transforms to the martensite, while Nagasawa [5], as well as Otsuka [6], found this superlattice co-existing with the martensite. Chandra and Purdy [1] report only the presence of the superlattice, probably because they did not cool the specimens below room temperature. These results suggest a tentative correlation

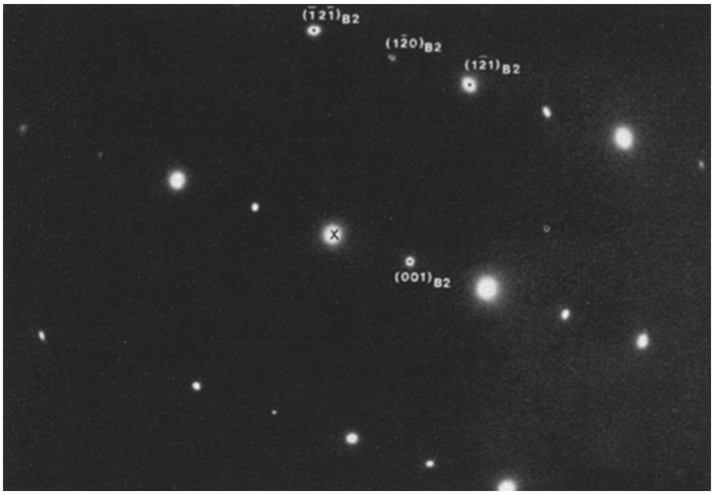

Figure 1 $(210)_{B2}$ reciprocal lattice plane, $T = 60°$ C. Alloy 3.

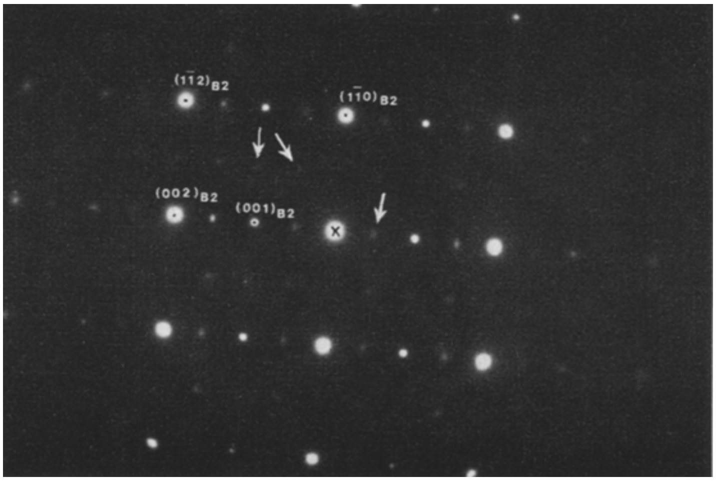

Figure 2 $(110)_{B2}$ reciprocal lattice with reflections at half distances indicated by the arrows, $T = -8°$ C. Alloy 3.

between the superlattice and the martensite. The object of the research reported in this paper was to investigate this correlation and to study the nature of the pre-martensitic phase and the different types of martensites in TiNi.

2. Experimental procedures

Four alloy melts of 25 g each were prepared by the arc-melting of high purity Ti (99.99 wt %) and Ni (99.99 wt %) in an argon atmosphere with 6 ppm O_2. After turning and remelting seven times, the buttons were sealed in a quartz capsule and heated to 1150°C in an argon atmosphere for 1 week in a porcelain crucible to ensure homogeneity. X-ray micro-analysis using Ti_2Ni and $TiNi_3$ as standards resulted in a variation of the Ni-content between 50.1 and 50.2 at. %. The oxygen content of the samples was 220 ppm or less.

To avoid decomposition, alloys 1, 2 and 3 were quenched from 1150°C in water followed immediately by quenching in liquid nitrogen and holding there for 15 min, after which the specimens were stored at ambient temperature until required. Alloy 4 was cooled in the furnace at a rate of 100°C h^{-1}. The buttons were then further treated as follows.

Alloy no. 1 was cut with a low-speed diamond saw to slices 0.25 to 0.4 mm thick, followed by spark-cutting, if necessary, to 0.25 mm. The

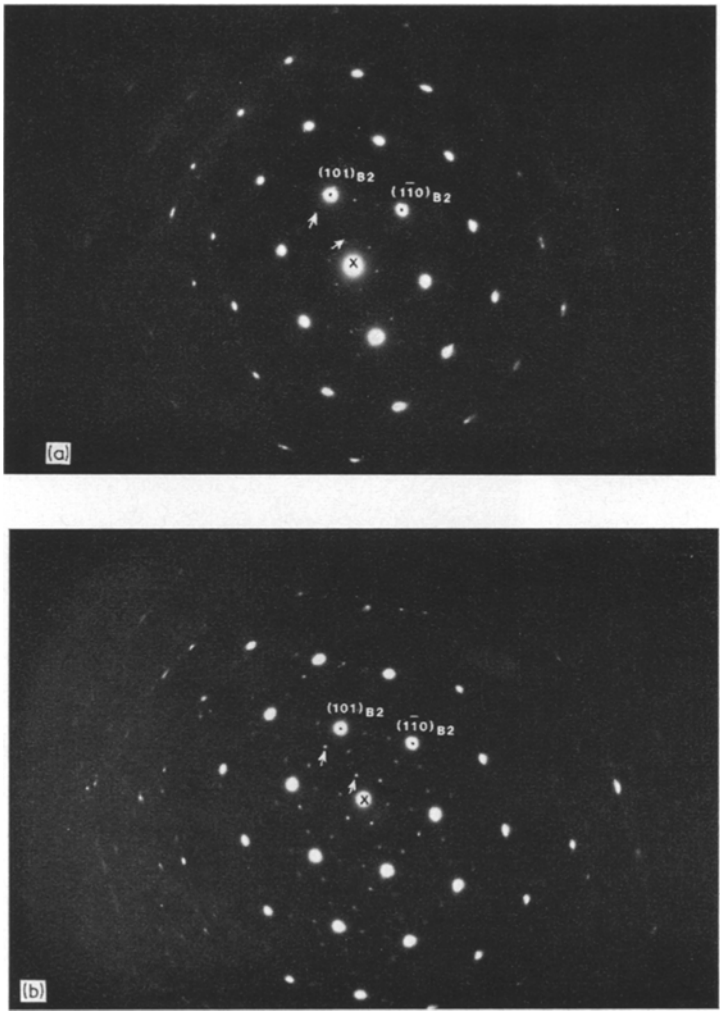

Figure 3 (a) $(1\,1\,1)_{B2}$ zone at $T = 5°C$ and $T = -120°C$, indicating (b) the increase in intensity of the super lattice spots. Alloy 3.

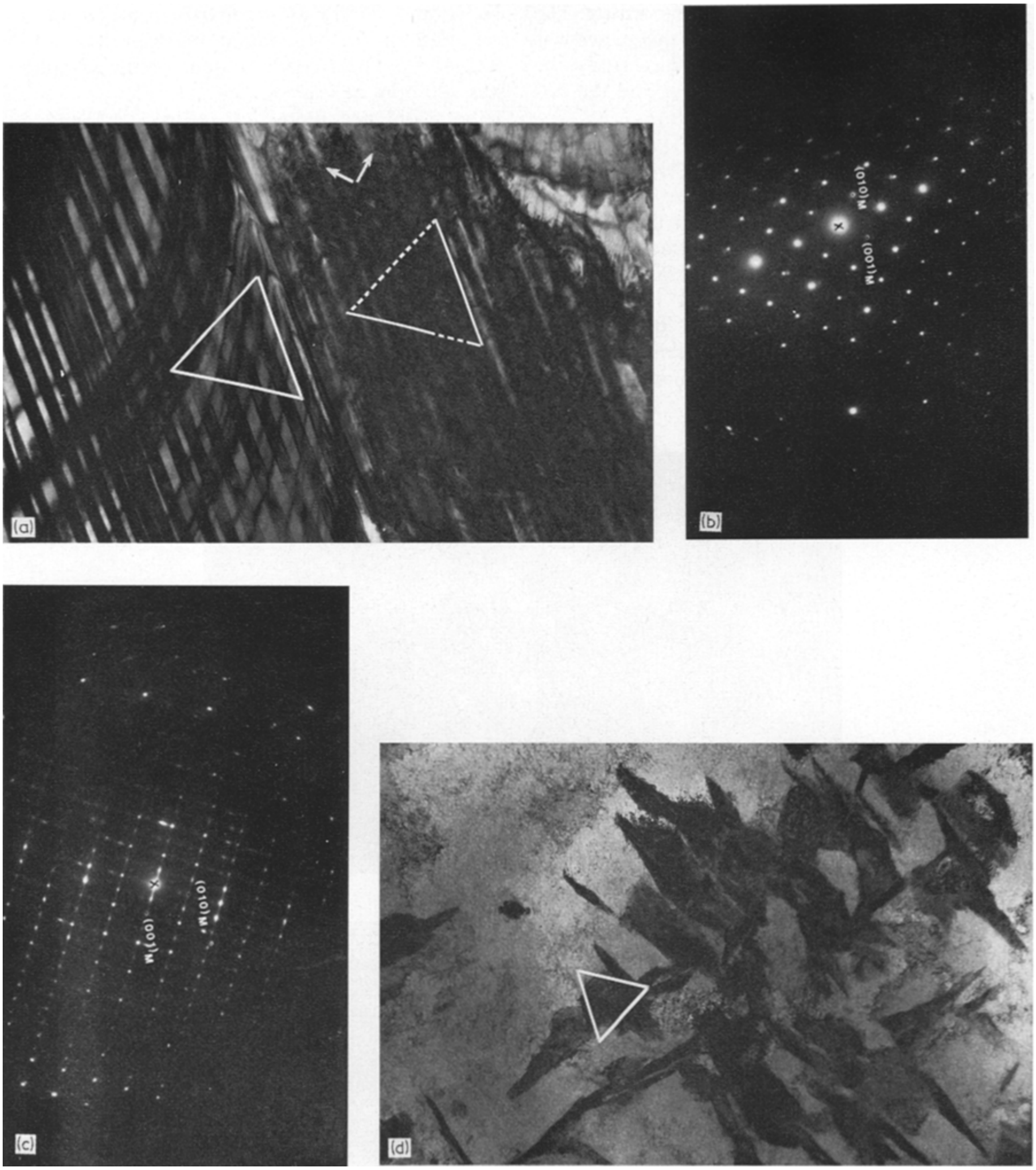

Figure 4 (a) (b) (c) and (d).

slices were further thinned by electrolytic polishing in 6% perchloric acid in methanol at 20 V and −60°C.

Alloys no. 2 and 4 were treated as alloy 1 except that the electrolytic polishing was performed in an 8% perchloric acid acetic acid solution at 12 V and 20°C.

Alloy no. 3 was cold-rolled to 0.2 mm in several steps. Between the rolling steps the alloy was heat-treated in a vacuum of 10^{-5} Torr at 750°C for 20 min and quenched in water. After the last heat-treatment the alloy was slowly cooled in the furnace.

All the thin foils proved to be in the martensitic

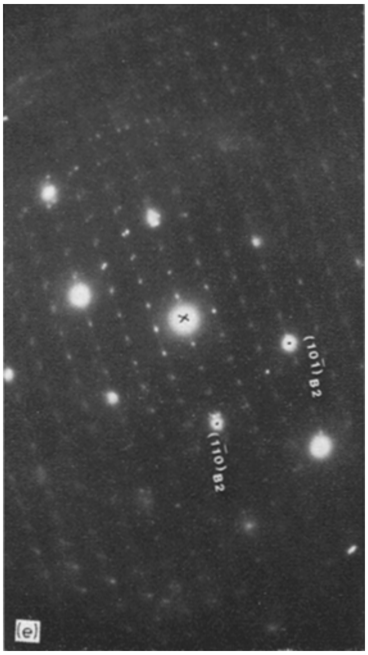

Figure 4(e).

Figure 4 (a) Electron micrograph of the plate martensite. Alloy 4 (× 23800). (b) Diffraction pattern of the area framed with solid lines (1 0 0) martensite reciprocal lattice. (c) Diffraction pattern of the area framed with dashed lines. Striations indicated in Fig. 4a by the arrows are perpendicular to the streaks in the (1 0 0) reciprocal lattice plane indicating stacking faults. (d) Massive martensite. (e) Its corresponding $(1\,1\,1)_{B2}$ diffraction pattern taken from the framed area. Alloy 3 (× 22000), $T = 20°$ C. Partly transformed back to B2.

state when inserted into the microscope. Different polishing temperatures were used below the M_S and near the M_S temperature to find the effect, if any, on the structure of the resulting martensite.

The thin foils were examined in a Philips EM 300G microscope operating at 100 kV which was equipped with a rotating heat- and cooling-holder and a TV camera for video-recording. The temperature of the sample in the cooling-holder could only be estimated; an exact temperature measurement was not possible.

3. Experimental results and discussions

3.1. Ordering phenomena

The photographs presented in the following sections are characteristic of all alloys studied independent of their thermal history. At 100°C, the structure of equiatomic TiNi is established to be the ordered CsCl (B2) structure by diffraction analysis (Fig. 1).

Sometimes weak reflections at half distances were added to the B2 reflections, as revealed in Fig. 2. The reason for the weak reflections is not yet known. They do no intensify during cooling. On cooling in the microscope from 100 to 50°C or lower temperatures, weak reflections emerge at $\frac{1}{3}$ distances in addition to the matrix reflections. In contrast with the reflections at half distances, these reflections do intensify on further cooling, as can be seen in Fig. 3. They could even be preserved at liquid nitrogen temperature by fast cooling. These patterns are in accordance with the patterns given by Nagasawa and Otsuka indicating a unit cell of $a = 9.0$ Å. It is emphasized that this superlattice has only been observed in combination with transformations to the wavy martensite described below.

3.2. Martensitic transformations

After electropolishing, all specimens from the four alloys contained both plate martensite and massive martensite (Fig. 4). The plate martensite is the most commonly observed type and appears with and without stacking faults as can be seen in Fig. 4a, b and c. The diffraction pattern (Fig. 4b) is in agreement with a (1 0 0) section of the reciprocal lattice of the monoclinic cell proposed by Otsuka [6].

The stacking-fault planes are parallel with the incident beam and perpendicular either to the [0 1 0] or the [0 0 1] direction. The stacking-fault separations are about 30 to 60 Å which is of the same order as that which led Nagasawa to describe the martensite as a layer structure. The massive martensite is always present to a lesser degree than the plate martensite and indicates a structure of large unit cell as can be seen from Fig. 4d and e. These two types of martensite will be investigated further.

In addition to the above mentioned martensites, however, we observed a new type of martensite with a wavy character. This wavy martensite (Fig. 5) has, to our knowledge, never before been mentioned or recognized as such in the literature. It consists of a very fine, irregular band and, as can be seen from the dark field photograph, there is an even finer substructure inside the band. Fig. 5d is a similar pattern to that found by Marcinkowski *et al* [2]. Their description of the growth of martensite indicates that they actually observed the same type of martensite without recognizing it as a distinct type with the wavy character.

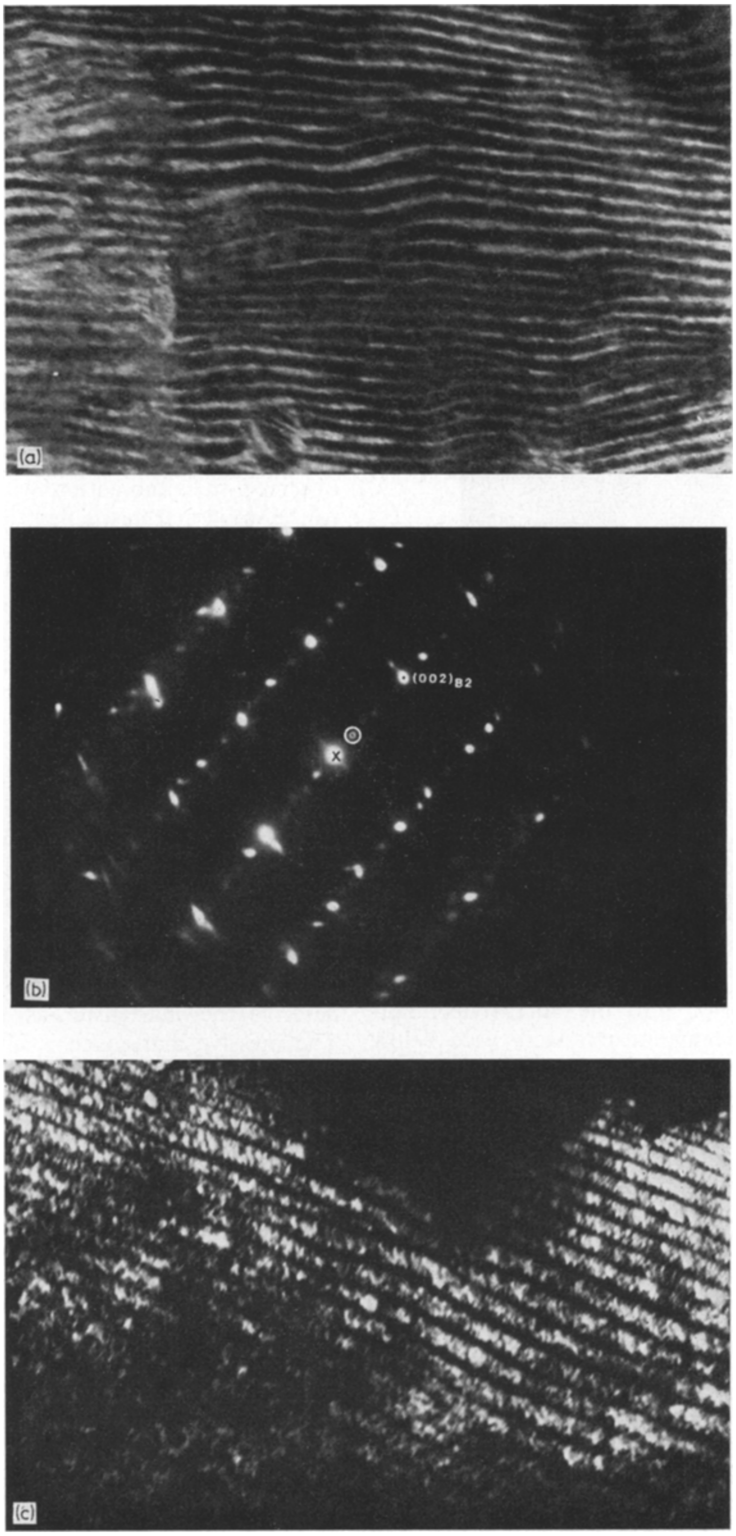

Figure 5(a) (b) and (c)

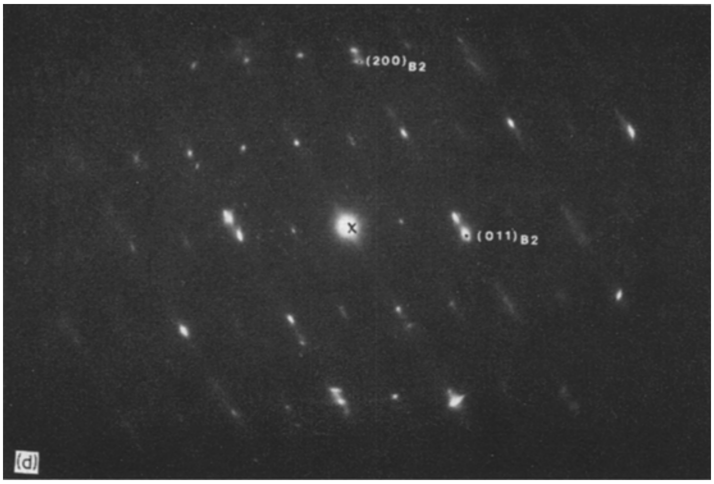

Figure 5(d)

Figure 5 (a) Substructure of the wavy martensite. $T = -120$°C, Alloy 1 (× 46750). (b) Diffraction pattern of wavy martensite. (c) Dark field photograph of wavy martensite. Diffraction spot encircled in (b) is used (× 57750). (d) A $(110)_{B2}$ pattern of the wavy martensite.

The formation of wavy martensite is, in thin foils anyway, perfectly reversible. On repeated heating above the A_f-temperature and subsequent cooling in the microscope, the martensite formed in exactly the same way as before. Estimated values for the A_f-temperature are 60°C for the plate martensite and between 0 and 30°C for the wavy martensite. The image on the screen of the electron microscope did not move during the transformation, which is an ideal situation for recording and, moreover, indicates a very small shape deformation. A few pictures of this film are shown in Fig. 6.

Starting from the B2-phase and cooling continuously down to -150°C first a change in contrast is observed owing to the rearrangement of dislocations preceding the transformation, resulting in the appearance of the ordered phase with $a = 9.0$ Å (Fig. 7), and this superstructure is the same as mentioned above [1, 5, 6].

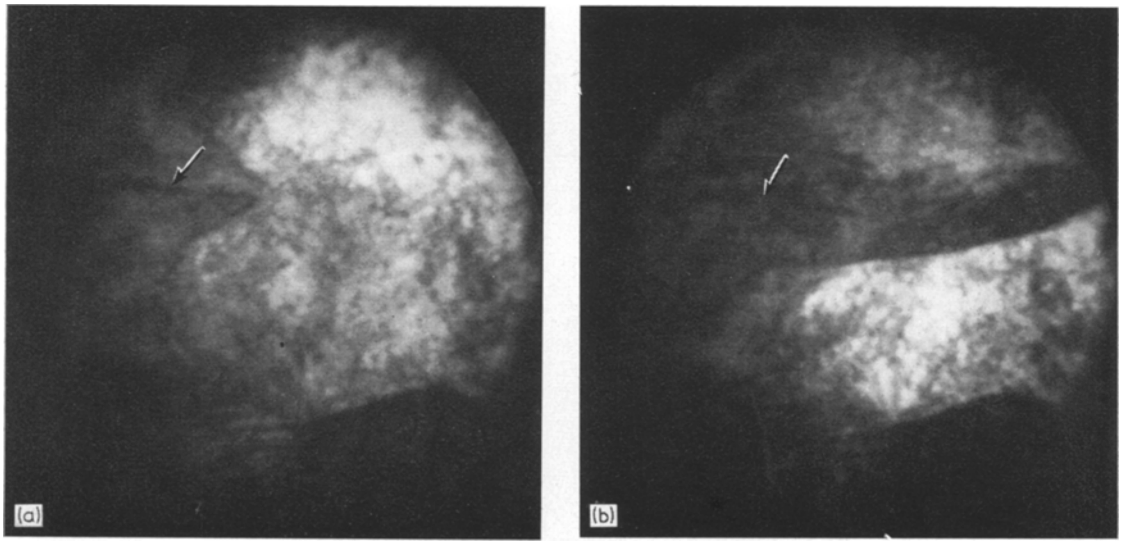

Figure 6(a) and (b)

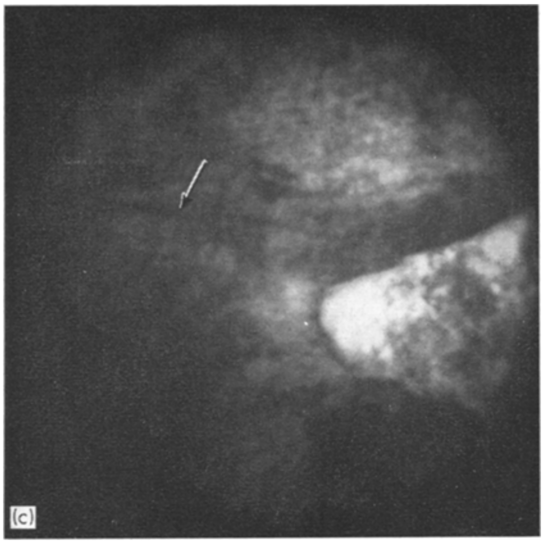

Figure 6(c)

Figure 6 Video photographs from the same area showing the growth of wavy martensite. Pictures taken from monitor at temperatures $T_1 = -5°C$, $T_2 = -15°C$ and $T_3 = -45°C$. Alloy 2 (× 42920), arrow indicates reference point.

This transition is followed by the martensitic transformation which starts from the thicker parts of the specimen moving discontinuously to the edge. The M_S temperature could vary from 0°C to liquid nitrogen temperature depending on cooling rate. On heating, the reverse transformation takes place in the same way (Fig. 8). This transformation could be repeated in each of the four alloys irrespective of their different thermal histories.

From an observation which, at first, seemed to be accidental, a remarkable connection between the two types of martensites was

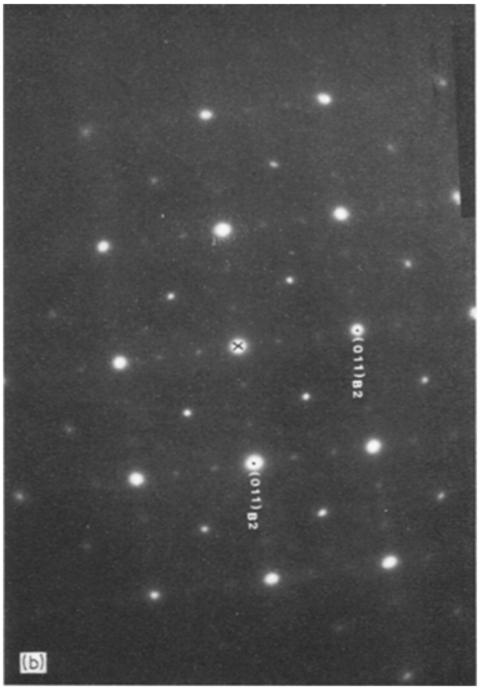

Figure 7(b)

Figure 7 Electron micrograph of the B2 phase and its corresponding diffraction pattern (100). Reciprocal lattice showing the appearance of superlattice spots. Alloy 2 (× 39050), $T = -80°C$.

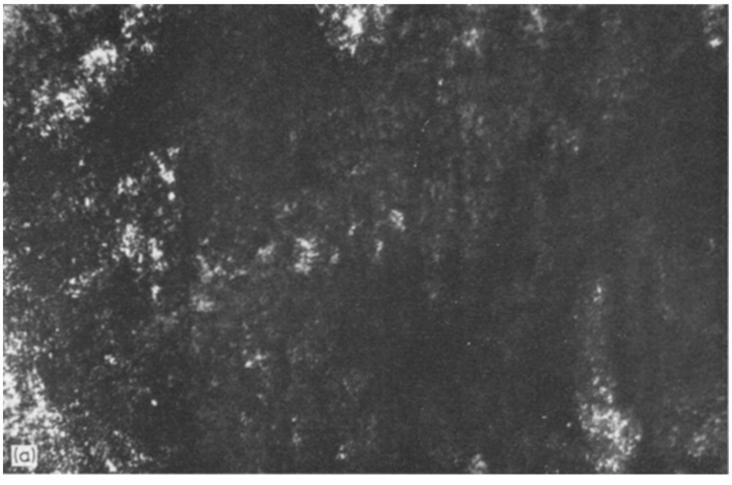

Figure 7(a)

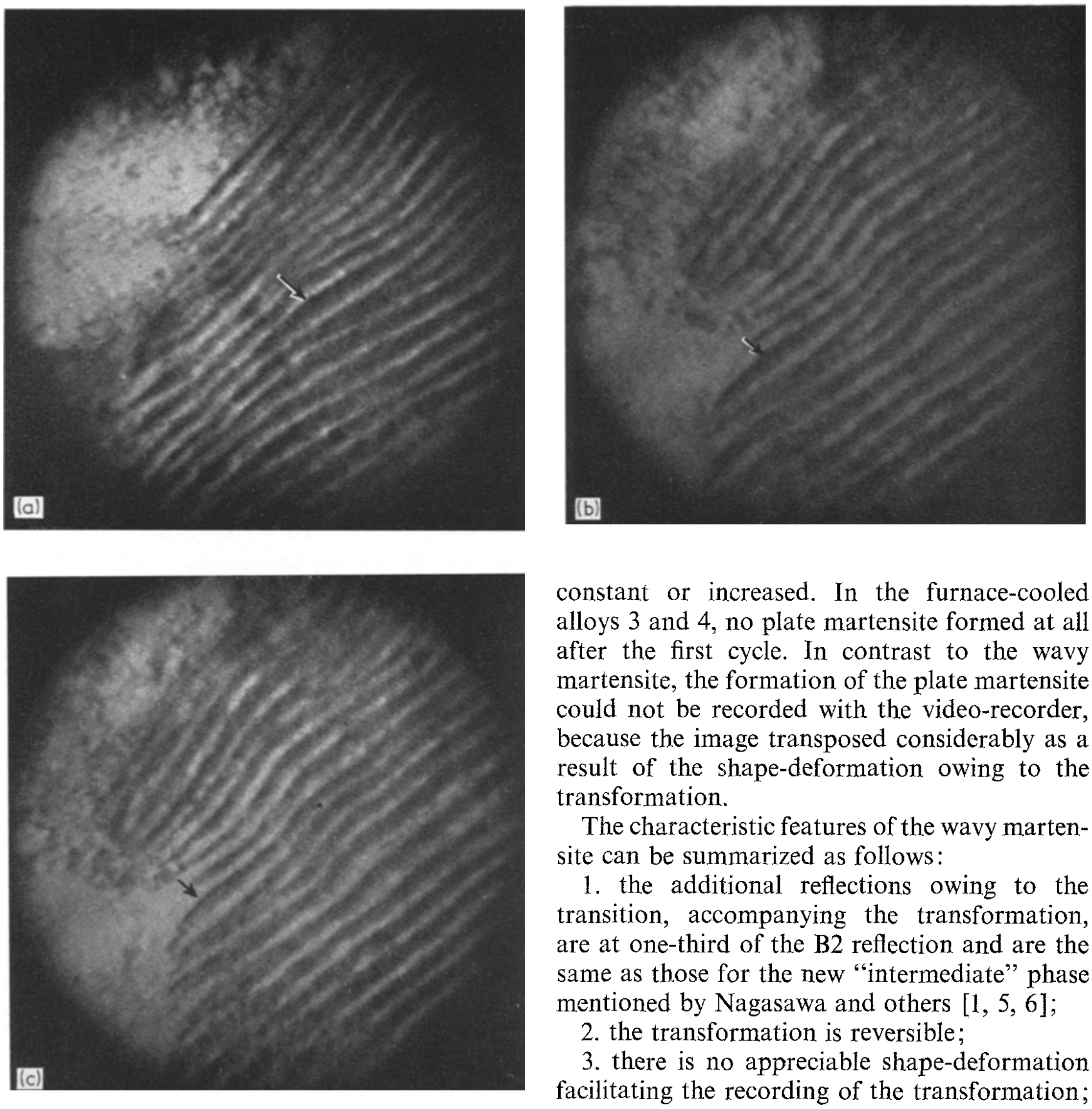

Figure 8 The reverse transformation of the wavy martensite to the B2 phase. Temperatures: $T_1 = +0°\mathrm{C}$ and $T_2 = +20°\mathrm{C}$ and $T_3 = +25°\mathrm{C}$. Alloy 3 (× 51 620), arrow indicates reference point.

revealed. The plate martensite in the thin foils of alloys 1 and 2, stored at 25° C, after a period of a few weeks, transformed partly into the wavy martensite. This has been checked with several thin foils of different alloys and proved to be reproducible. After heating to 120° C and subsequent cooling in the microscope, a smaller amount of plate martensite was formed, whereas the amount of the wavy martensite remained constant or increased. In the furnace-cooled alloys 3 and 4, no plate martensite formed at all after the first cycle. In contrast to the wavy martensite, the formation of the plate martensite could not be recorded with the video-recorder, because the image transposed considerably as a result of the shape-deformation owing to the transformation.

The characteristic features of the wavy martensite can be summarized as follows:

1. the additional reflections owing to the transition, accompanying the transformation, are at one-third of the B2 reflection and are the same as those for the new "intermediate" phase mentioned by Nagasawa and others [1, 5, 6];
2. the transformation is reversible;
3. there is no appreciable shape-deformation facilitating the recording of the transformation;
4. the interface is irregular and can propagate continuously and slowly as well as discontinuously and rapidly, depending on cooling rate;
5. transformation starts in the thicker parts of the foil growing outwards;
6. the wavy martensite has been found in all the specimens on temperature cycling between +120° C and liquid nitrogen temperature. It is, therefore, concluded that there is a small dependence on the thermal history of the specimen. It is more easily formed in furnace cooled specimens than in quenched specimens;
7. there is a large dependence on cooling rate during temperature cycling for the M_S temperature of the wavy martensite. High cooling rates can totally depress the transformation.

These observations on wavy martensite and the intermediate phase are in close agreement with those of Marcinkowski and Otsuka, although these authors did not recognize this as a separate type of martensite. Several investigators also found the superlattice reflections at one-third distances of the B2 reflections in bulk material. As concluded above, these reflections are coupled with the formation of the wavy martensite, which would indicate that the latter is also present in bulk material and that it is not a phenomenon peculiar to thin foils.

Although several problems regarding the crystal structure of the various types of martensite still have to be solved, in view of the work of Marcinkowski *et al*, and Wang and Otsuka, this study shows that the conflicting results of different investigations can partly be explained by the presence of at least three different types of martensite in TiNi.

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