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Mechanically alloyed $Ni_{50}Ti_{50}$ and its transformation by thermal treatments

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Amorphous powders have been obtained by mechanical alloying (MA) equiatomic powder mixtures of nickel and titanium. The amorphous phase thus formed decomposes upon heating first into the cubic B2 NiTi intermetallic compound; however, further heating promotes the precipitation of the intermetallics Ni_3Ti and $NiTi_2$. These transformations are shown to occur also in mechanically ground (MG) NiTi wire, but not in this same material exempted from ball-milling processing. It is suggested that this unique behaviour is brought about by the particular structural features of the MA or MG powders, which promote the otherwise sluggish decomposition of B2 NiTi.

1. Introduction

The equiatomic intermetallic compound NiTi has been extensively studied, especially in relation to its interesting shape-memory characteristics (e.g. [1, 2]). Phase transformations occurring in material with near equiatomic composition, as a function of temperature, composition, thermal treatment, deformation, etc., are of great diversity [1–5], and many of them remain partly unexplained and controversial [5].

One example of these transformations is given by eutectoid reaction first suggested by the work of Duwez and Taylor [6], namely

$$NiTi \rightarrow Ni_3Ti + NiTi_2 \qquad (1)$$

which has been tentatively set at 903 K in the equilibrium Ni–Ti phase diagram proposed by Murray [5]. Several arguments in favour of and against the occurrence of the decomposition of NiTi appeared in the technical literature of the period 1960–1980 [3, 4, 6–12], many of them also reporting the formation of several "metastable" phases which either preceded or actually took the place of the products in Reaction 1. Significantly, however, to the extent of our knowledge, the vast literature of later years on the intermetallic NiTi, dealing mainly with martensitic transformations and shape-memory effects, does not mention specifically the occurrence of the eutectoid Reaction 1 (see, for example, [13, 14]). In any case, it is recognized [3–8] that at best the kinetics of the eutectoid reaction are rather sluggish, although they can be enhanced somewhat by cold deformation [5].

In the present work, we report the formation of the intermetallic NiTi (with the B2 crystal structure) by crystallization from the amorphous material obtained in mechanically alloyed (MA) powder mixtures of the elemental components, as well as the subsequent decomposition of B2-NiTi into the intermetallic compounds Ni_3Ti and $NiTi_2$. We suggest that the occurrence of these transformations is closely related to the unique features of the microstructure in the MA products. In addition, we believe that these characteristics could become of great advantage in the study of those phase transformations which are known to be kinetically constrained by diffusional and/or nucleation aspects in the solid state.

2. Experimental procedure

Elemental powders of nickel (99.9% purity, < 63 μm) and titanium (99.9%, < 150 μm) were subjected to mechanical alloying (MA) in laboratory ball mills, using stainless steel vials and balls, and under an atmosphere of argon gas. The vials were 1700 ml in volume and the balls were 9.6 mm in diameter. The mill was rotated at 95 r.p.m. The powder charge was 36 g, with a ball to powder weight ratio of 100:1. Milling was performed with the addition of 2 wt % methyl alcohol.

The elements nickel and titanium were mixed in equiatomic proportions. These products of MA processing will be designated $Ni_{50}Ti_{50}$. Consolidation of these MA powder mixtures was carried out by means of the following procedure: cold compaction to produce discs of 13 mm diameter and 1 mm height, which were subsequently hot-compacted under vacuum at 1173 K/100 MPa for 600 s. Further detail of the processing conditions will be published elsewhere [15].

For reasons that will become apparent later, samples of mechanically ground (MG) NiTi intermetallic compound (equiatomic composition) were prepared by ball milling powders (< 150 μm) obtained from as-drawn NiTi wire, using the same experimental conditions described above. The NiTi powders were produced with the use of a vibratory mill, in which small

0022–2461

pieces of NiTi wire were fed and milled for a time only long enough to produce the powder size of $< 150\ \mu m$. The ball-milled samples of NiTi will subsequently be referred to as MG NiTi in order to avoid confusion with the (MA) $Ni_{50}Ti_{50}$ material.

The powders obtained both by MA or MG processing, as well as the consolidated material derived from them, were characterized by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The X-ray work was performed in MacScience MXP18, using CuK_α radiation. The DSC measurements were done on 10 mg powder samples, at a heating rate of $0.33\ K\,s^{-1}$ and under a continuous flow of argon gas. Some limited TEM work was also carried out in a Hitachi-800 electron microscope; in this case, only well-consolidated, hot-compacted MA samples were suitable for TEM examination after dimpling and ion milling.

3. Results and discussion

3.1. The effect of MA processing

Under the conditions of our experiments, the $Ni_{50}Ti_{50}$ powder mixtures gradually became true alloys and structurally amorphous as the milling time increased. This is shown by the XRD results in Fig. 1. It can be observed that the Bragg peaks of the original, elemental powders are shifted from their initial positions and their width increased appreciably as the MA time reached 72 ks. Longer MA times eventually produced the amorphization of the mixture, as the Bragg peaks disappeared and a single broad peak (with a maximum at about 42°) became the only distinguished feature of the diffractometer trace. This is the case of the specimens subjected to 1800 and 3600 ks MA time, as shown at the bottom of Fig. 1. In general terms, a similar behaviour during MA of nickel and titanium powder mixtures has been reported by other workers [16–19].

The XRD results pertaining to MG NiTi are shown in Fig. 2. Notice that both the as-drawn material and the powders obtained from it in the vibratory mill (MG 0 ks) had a crystal structure heavily distorted (and probably texturized) by plastic deformation, and that the application of MG processing promoted amorphization, until practically all the powder became amorphous. This state seems to have been reached in the specimen with only 72 ks MG processing time in Fig. 2. In this same figure we have included the XRD results from a sample of as-drawn NiTi wire which was given an annealing treatment (no MG) at 1273 K for 3.6 ks. Such a treatment restored the crystallinity of the material, producing a mixture of cubic (B2) NiTi phase and monoclinic NiTi martensite. The latter is expected to originate from the equilibrium (at 1273 K) B2 phase on cooling to room temperature (RT) [5].

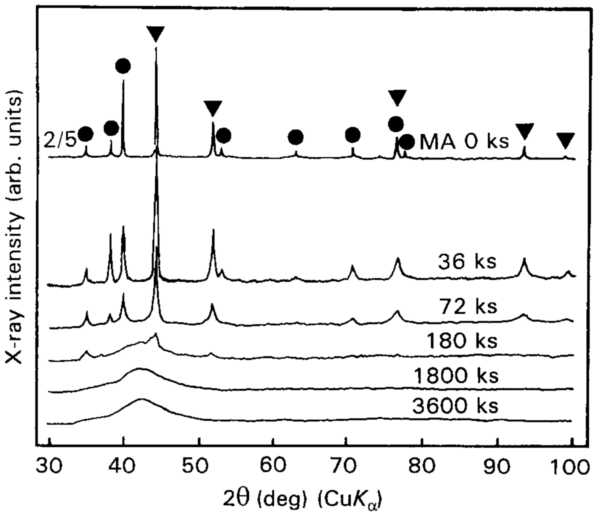

Figure 1 X-ray diffraction patterns of $Ni_{50}Ti_{50}$ powders milled for various times. (▼) Ni, (●) Ti.

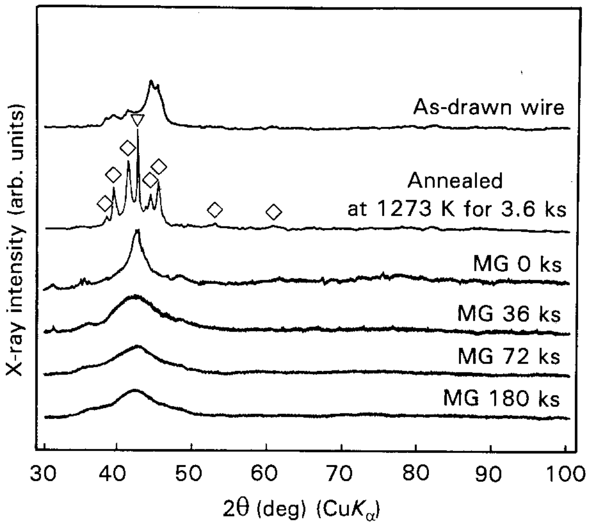

Figure 2 X-ray diffraction patterns of NiTi wire and its powder milled for various times. (◇) NiTi (M), (▽) NiTi (B2).

On the other hand, the phases found in the samples of MA $Ni_{50}Ti_{50}$ after the hot-compacting treatment are indicated by the XRD results in Fig. 3. In this case, the phases existing at room temperature are the intermetallic compounds NiTi, Ni_3Ti and $NiTi_2$. This is the case for MA samples either with a fully amorphized structure (MA time of 3600 ks) or with a seemingly partial degree of amorphization structure (MA time of 180 ks). Therefore, at this point it is clear that the response of the material obtained by MA to the thermal treatment is different from that observed in the "bulk" (wire) NiTi intermetallic.

Battezzati *et al.* [16] reported briefly the existence at room temperature of only the B2 NiTi phase in fully amorphized MA mixtures of $Ni_{50}Ti_{50}$, after being heated to 790 K (at the rate of $0.5\ K\,s^{-1}$ in a DSC); however, they did find the phases B2-NiTi, Ni_3Ti and (traces of) $NiTi_2$ when heating partially amorphized material to the same temperature. Furthermore, they argued that the Ni_3Ti intermetallic was formed at a lower temperature (during heating in the DSC) than the B2-NiTi phase. In turn, Morris and Morris [20] reported the existence at room temperature of the above three intermetallic compounds in MA material of equiatomic composition, which was first partially amorphized by MA and then annealed at 1223 K for 3.6 ks; but in the case of (apparently) fully amorphized MA material, which was subsequently hot-compacted

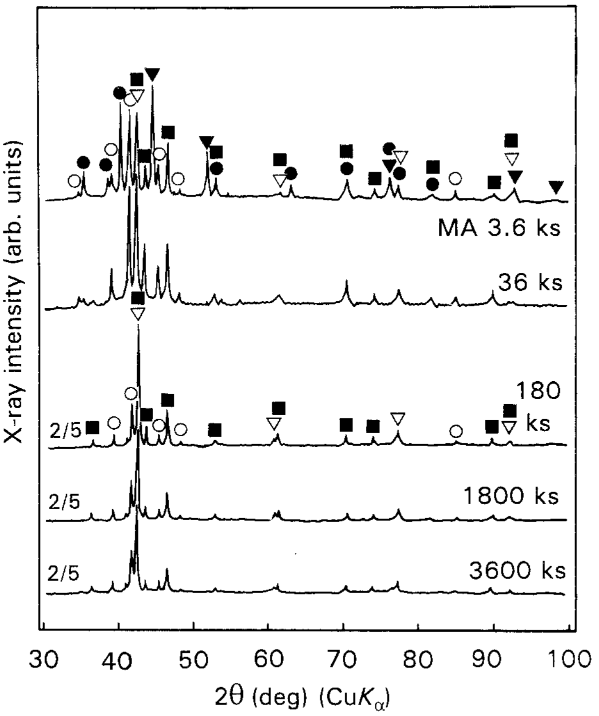

Figure 3 X-ray diffraction patterns of sintered specimens prepared from $Ni_{50}Ti_{50}$ powders milled for various times. 1173 K, 100 MPa, 600 s. (▼) Ni, (●) Ti, (▽) NiTi (B2), (○) $NiTi_2$, (■) Ni_3Ti.

(925 K, 1.5 GPa, 60 s) and annealed at 1073 K, the same authors reported the existence of the monoclinic (martensitic) NiTi phase. Clearly, the results of the present work, and especially those concerning the fully amorphized MA $Ni_{50}Ti_{50}$, are at variance with those quoted above.

3.2. DSC of mechanically alloyed material

In order to elucidate in more detail the transformations which occurred in our hot-compacted MA material, additional work by DSC and XRD was performed. Fig. 4a presents the background-subtracted DSC curves obtained from $Ni_{50}Ti_{50}$ powder samples subjected previously to different MA processing times. These curves are very similar to those obtained from samples of the intermetallic MG wire, shown by Fig. 4b. Because we are mainly interested in the transformation products, a detailed analysis of the DSC curves is not pursued here. However, we notice that the DSC curves from both the MA $Ni_{50}Ti_{50}$ and the MG NiTi materials reveal, for short MA/MG times, two broad exothermic peaks, with maxima at about 560–600 and 800 K, respectively; these peaks tend to change into at least four narrower peaks (with perhaps one of them of endothermic nature) as the MA/MG times become longer.

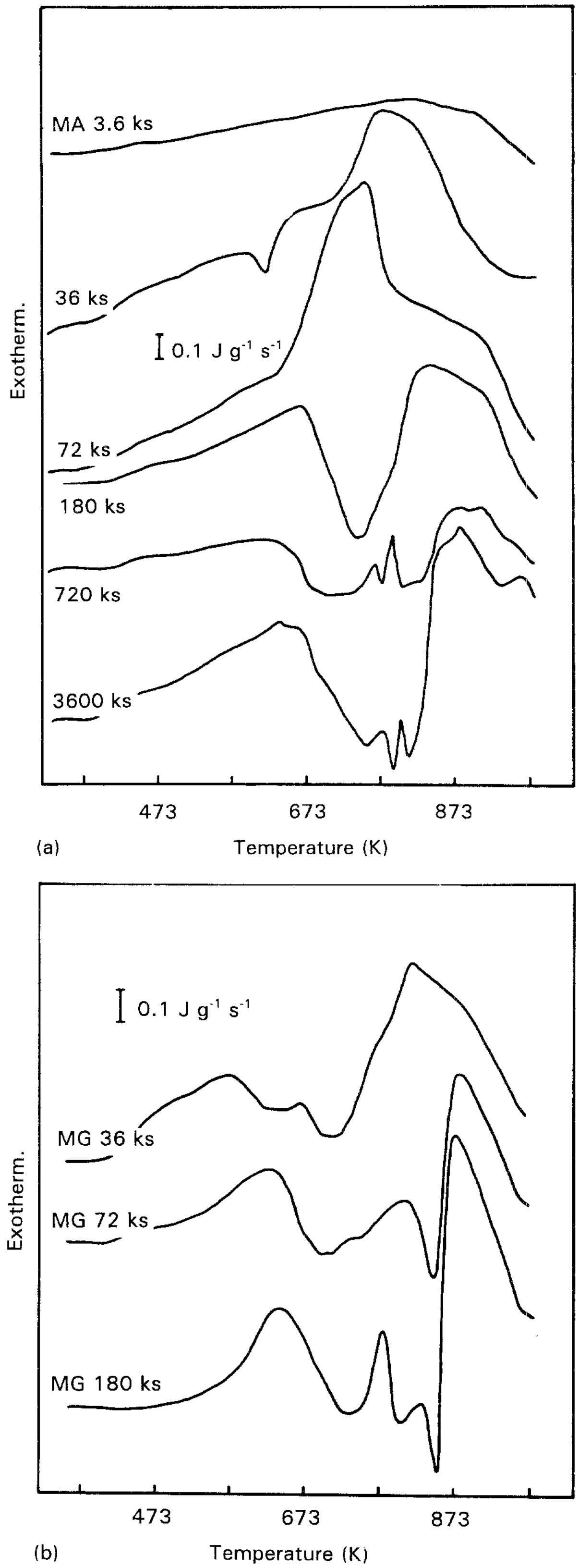

Figure 4 DSC traces of (a) $Ni_{50}Ti_{50}$ powders and (b) NiTi powders milled for various times at a heating rate of 0.33 K s^{-1}.

Next, Fig. 5a–c present the results of phase determination performed on samples which were heated up in the DSC apparatus to diverse "stages" on the DSC curves (see insets in Fig. 5a–c). In a sample with 36 ks MA time (Fig. 5a), the phases found at room temperature, after heating up to the end of the first broad peak, are fcc nickel (most probably with some titanium in solid solution) and hcp titanium; after the second broad peak, they are basically fcc nickel (solid solution), Ni_3Ti and $NiTi_2$. On the other hand, in the sample with 180 ks of MA time (i.e. partially amorphized), shown in Fig. 5b, heating to the end of the first broad peak produces the cubic B2 NiTi phase as the only existing phase; however, after the second broad peak, the XRD data reveal the presence of

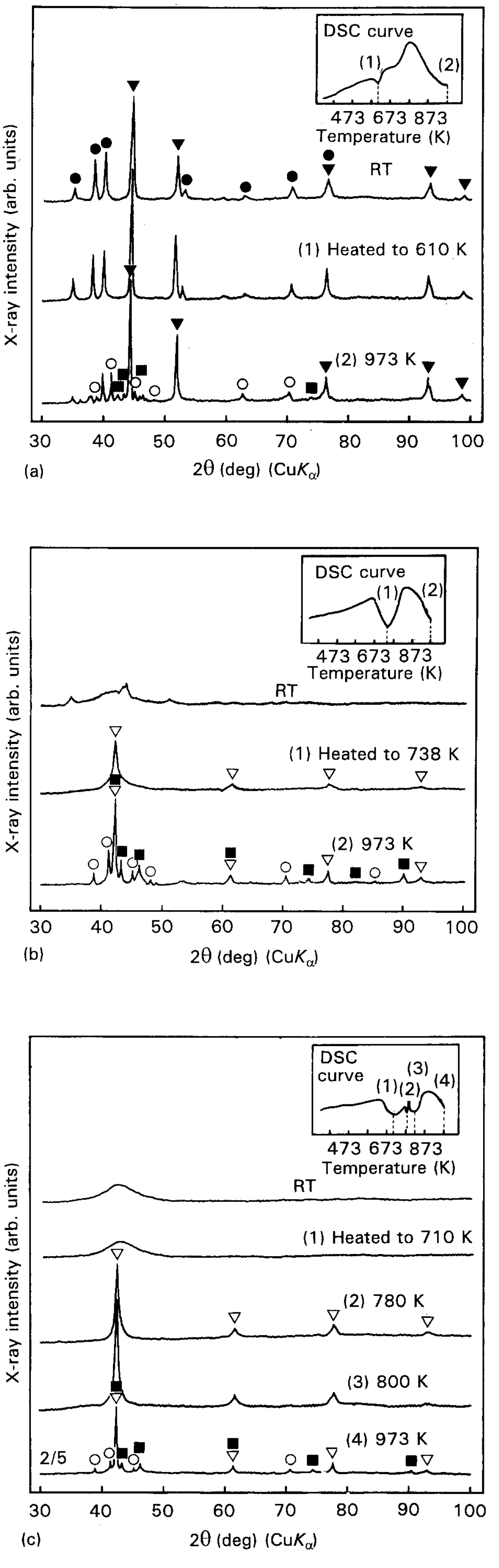

Figure 5 X-ray diffraction patterns of $Ni_{50}Ti_{50}$ powders milled for (a) 36 ks, (b) 180 ks, and (c) 720 ks after being heated to various temperatures. (▼) Ni, (●) Ti, (○) $NiTi_2$, (■) Ni_3Ti, (▽) NiTi (B2).

B2–NiTi, Ni_3Ti and $NiTi_2$. At last, the sample with fully amorphized structure (Fig. 5c, 720 ks MA time) shows no apparent phase change when heated to the end of the first broad peak; but after a slight increase (70 K) in temperature over the second (narrow) peak, the material has transformed completely to the B2 NiTi phase. Fig. 5c indicates next that on further heating up to the end of the last (broad) peak, the B2 NiTi phase has partially decomposed into Ni_3Ti and $NiTi_2$.

Conceivably, the formation of the intermetallic phases Ni_3Ti and $NiTi_2$ could be a consequence of the inhomogeneity in local chemical composition of the MA $Ni_{50}Ti_{50}$ powder mixtures [16–19, 21]. This is probably the explanation for the formation of these phases in the sample with 36 ks MA time; in these powders, the regions richer in nickel would transform into Ni_3Ti, while those richer in titanium would change into $NiTi_2$. But because the mixing in these powders would be still rather coarse, the whole sample could not transform in the time permitted by the heating rate during the DSC run. Nevertheless, this reasoning does not seem to apply to the transformation of the highly amorphized MA material; in this instance, the B2 NiTi phase is formed first (i.e. at a lower temperature in the DSC run), and the Ni_3Ti and $NiTi_2$ phases appear after the MA material has become fully B2 NiTi (Fig. 5b, c). This series of events involves the transformation (directly or indirectly – at this point it is not known) of B2 NiTi into $Ni_3Ti + NiTi_2$, that is, the controversial eutectoid transformation suggested in the equilibrium Ni–Ti phase diagram [5]. Evidently, much faster reaction kinetics for this transformation in the material produced by MA, as compared to conventionally produced material, are implicit in our results.

Additional evidence in support that the above behaviour is brought about specifically by the MA processing is given by the results shown in Fig. 6. In this case, the similarity observed between the DSC curves of fully amorphized MA($Ni_{50}Ti_{50}$) and MG(NiTi) – as shown in Fig. 4a and b – extends also to the transformation products obtained at several stages during the DSC runs; Fig. 6 illustrates that the amorphous MG NiTi transforms first to B2 NiTi, and then, at a higher temperature, to a mixture of B2 NiTi, Ni_3Ti and $NiTi_2$, precisely the behaviour indicated in Fig. 5c for the MA $Ni_{50}Ti_{50}$ material, but quite different from the results obtained by annealing the original, as-drawn NiTi wire (Fig. 2).

3.3. TEM observations of hot-compacted MA $Ni_{50}Ti_{50}$

The results of TEM examination of fully consolidated samples of MA $Ni_{50}Ti_{50}$ material tend to confirm the existence of the phases identified by XRD. Fig. 7 shows a TEM bright-field micrograph of a specimen taken from material which was first fully amorphized by MA and then hot-compacted (at 1173 K). The largest grains seen in this figure (and some of the smaller ones) correspond to the Ni_3Ti phase, with its typical heavily faulted structure [3, 4]; in turn, the smaller featureless grains correspond to the B2–NiTi

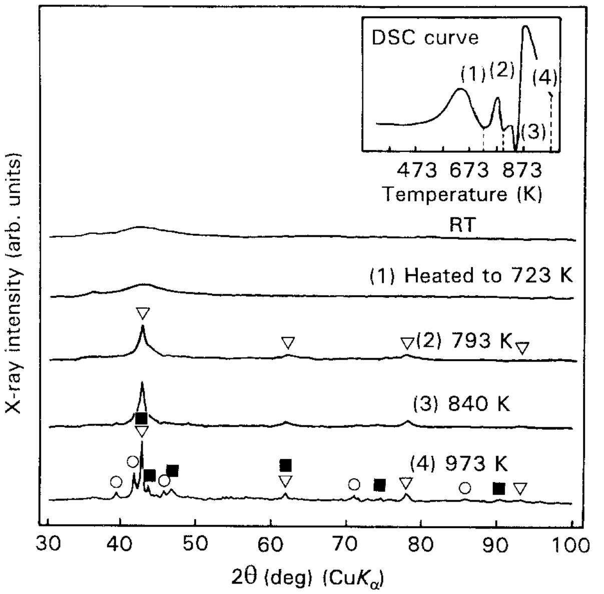

Figure 6 X-ray diffraction patterns of NiTi powders milled for 180 ks after being heated to various temperatures. (▽) NiTi (B2), (○) $NiTi_2$, (■) Ni_3Ti.

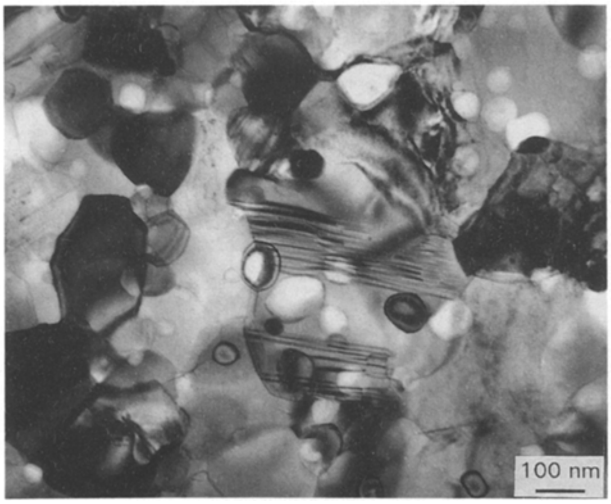

Figure 7 Transmission electron micrograph of mechanically alloyed and sintered $Ni_{50}Ti_{50}$ specimen.

and $NiTi_2$ phases, their appearance also agreeing with that reported in earlier works [3, 4]. In addition, some limited work with selected-area diffraction and microdiffraction has been used to confirm the crystal structure and lattice parameters of the three intermetallic compounds, as illustrated by Fig. 8a–c. However, we have not yet identified with certainty the smallest, rounded "particles" seen scattered throughout the grain structure in Fig. 7.

Although the XRD and TEM work confirms the existence of the three intermetallic phases in the consolidated MA material, the grain structure observed by TEM is not the typical one expected as a result of a eutectoid transformation. In actuality, we have found no such structure reported in the literature of the transformations of B2 NiTi, and several authors have suggested that the decomposition of this phase into $Ni_3Ti + NiTi_2$ occurs by way of the formation of

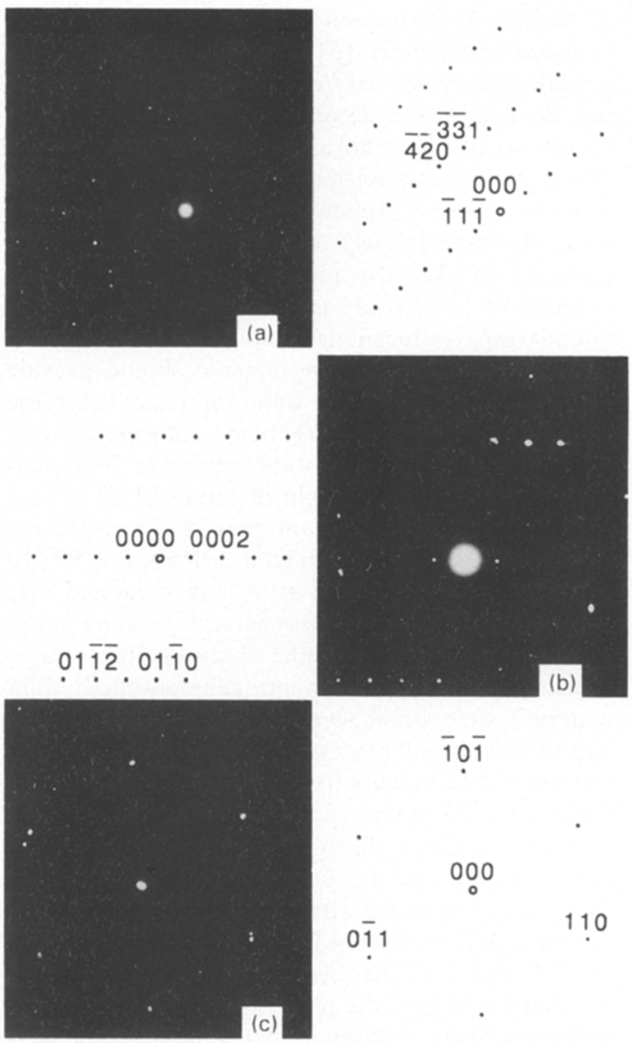

Figure 8 Diffraction patterns of (a) $NiTi_2$ [$\bar{1}23$] zone, (b) Ni_3Ti [$10\bar{1}0$] zone, and (c) NiTi (B2) [$\bar{1}11$] zone, in sintered $Ni_{50}Ti_{50}$ specimen.

intermediate (metastable) phases [3, 4]. Yet another interesting point resides in the fact that we have found the Ni_3Ti and $NiTi_2$ phases in MA material heated up to temperatures more than 270 K higher than the equilibrium eutectoid temperature suggested in the phase diagram of Murray [5], which would seem to raise the question of whether the B2 NiTi phase is at all an equilibrium phase. Thus, many questions are still open in relation to this topic.

It would seem necessary to clarify the discrepancies between the results of the present work, the work of Battezzati *et al.* [16] and that of Morris and Morris [20]. However, at this point we feel that a fruitful discussion is not guaranteed because of lack of detailed information in those two references concerning phase identification in their respective materials.

3.4. Phase transformations in MA materials

The results of the present study on $Ni_{50}Ti_{50}$ powder mixtures subjected to MA processing, as well as the preliminary work on MG NiTi wire, seem to indicate that decomposition of the B2 NiTi phase (usually regarded as a very "stable" phase, at least in materials produced by conventional methods) into the mixture of $Ni_3Ti + NiTi_2$ (considered the equilibrium phases at room temperature [5]), is greatly accelerated as a result directly derived from the MA or MG processing. Because such a decomposition must involve the occurrence of diffusional and nucleation processes, the first factor directly related to MA which comes forward in order to explain their accelerating effect is evidently the extremely fine and distorted structure observed in the MA products (Fig. 7). The large amount of interfacial area (grain and interphase boundaries), dislocations and, presumably, point defects created in the MA material should provide enhanced nucleation and diffusion kinetics for the transformation of the B2 NiTi phase, reducing substantially the quoted periods of weeks needed in the decomposition of cast and wrought materials [3–5].

If the above considerations proved to be accurate, there would be no reason to limit their applicability to the subject of this report. It is here suggested that mechanical alloying and mechanical grinding could become a useful tool for the study of phase transformations which, in conventionally-produced solid materials, were somehow constrained by nucleational and/or diffusional processes, by the acceleration of transformation kinetics to a point amenable for practical characterization.

A second factor directly related to the MA/MG processing involves the possible contamination of the MA powder mixtures with gaseous or solid elements during actual processing [17]. In this case, it is conceivable that both the thermodynamics (phase stability) and kinetics of the phase transformations could suffer significant changes in the contaminated material, in comparison to that which is not. This represents, however, an entirely new topic of research which has just recently started to be explored [22, 23]. In the case of the phase transformations in our MA $Ni_{50}Ti_{50}$ powder mixtures, we do not think it useful at present to speculate on the possible role of this second factor, as its understanding is yet quite limited.

4. Conclusions

1. Mechanical alloying of equiatomic mixtures of elemental powders of nickel and titanium produces eventually true alloyed, amorphous powders. The same product is obtained by mechanical grinding of bulk NiTi intermetallic wire.

2. Heating of the amorphous product up to temperatures into the range 730–800 K brings about its transformation into the cubic, B2 NiTi intermetallic compound.

3. Further heating of the B2 NiTi phase thus produced, has resulted in its partial decomposition into the intermetallics Ni_3Ti and $NiTi_2$. The resulting microstructure consists of very fine equiaxial grains, and does not resemble the typical microstructure of a direct eutectoid transformation.

4. The rapid decomposition of the B2 NiTi phase is a peculiar feature of the mechanically alloyed and mechanically ground materials. It is presumed that the fine-grained and disordered structure found in these materials is responsible for the observed acceleration in transformation kinetics.

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