Graded phase structure in the surface layer of NiTi alloy processed by surface severe plastic deformation

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The graded phase structure and its evolution in the surface of NiTi alloy after surface mechanical attrition treatment are studied using transmission electron microscopy. The initial B2–B19\textsuperscript{0} phase transformation occurs at low strain level. As the deformation strain increases, the B19\textsuperscript{0} martensite phase transforms back to B2 phase giving rise to graded phases. Our study reveals that stress induced martensite transformation and deformation heating play important roles in the formation of this graded phase structure.

Keywords: Graded phase; Nanocrystalline; NiTi alloy; Deformation heating; Surface mechanical attrition treatment

Severe plastic deformation (SPD) is an effective method to produce surface nanocrystalline structures [1,2]. After undergoing SPD, nanocrystalline materials have extraordinary properties, including high strength, enhanced hardness and diffusion coefficients superior to those of their coarse-grained counterparts [3–6]. To further improve the mechanical properties, recent research has been focussed on the grain size and its distribution, the underlying mechanism of grain refinement, as well as the compromise between strength and ductility [5,7,8]. Systematic studies have been mainly performed on pure metals, e.g. Cu, Fe, Ti, Co and Zr [5,9–11]; however, most engineering materials have dual/multiple phases or are intermetallic compounds. The mechanical properties of these materials are determined not only by the grain size, but also by the phase constituents and their evolution during processing. However, few investigations have been performed on the phase transformation and evolution in alloys or intermetallic compounds with nanocrystalline structures and refined grains. In order to obtain engineering nanocrystalline materials, it is imperative that the phase transformation behavior in multiphase alloys or intermetallic compounds is better understood.

NiTi shape memory alloys (SMAs) constitute a class of smart materials possessing the unique shape memory effect and pseudoelasticity [12,13]. The shape memory effect is based on the thermally elastic and reversible martensite transformation. The high-temperature B2 (austenite) phase transforms to B19\textsuperscript{0} (martensite) phase upon cooling below a specific temperature, producing a distorted monoclinic martensite structure. The B19\textsuperscript{0} phase is generated by stressing the metal in the B2 state and this B19\textsuperscript{0} phase is capable of large strain, yielding the pseudoelasticity. When the load is removed, the B19\textsuperscript{0} phase transforms back to the B2 phase, resuming its original shape. Therefore, NiTi SMA provides a suitable platform to study the phase transformation behavior under deformation and/or thermal treatment. In this study, NiTi SMA is subjected to SPD by surface mechanical attrition treatment (SMAT) to produce a graded phase structure on the surface. Microscopic studies disclose that the stress-induced martensite (SIM) transformation as well as deformation heating play important roles in the phase transformation behavior.

Commercial NiTi alloy plates containing 50.8 at.% Ni and 49.2 at.% Ti were supplied by Nitinol Device Company. The initiate phase was B2 austenite with transformation points $A_s = 234.5$ K and $A_f = 257$ K.

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The materials were first annealed to obtain homogeneous coarse grains ranging from 40 to 80 \( \mu \)m. Prior to SMAT, the NiTi plates were polished with sandpapers to grade 800 and then electrochemically polished to reduce residual stress resulting from mechanical polishing. The SMAT experiments were conducted at room temperature for different time durations at a vibration frequency of 20 kHz. Stainless steel balls 2 mm in diameter were employed in this study; the details of the apparatus and procedures can be found elsewhere [9,14,15]. After SMAT, the microstructure of the NiTi specimens treated for 60 min was examined by transmission electron microscopy (TEM) using a Philips CM20 microscope operated at 200 kV. High-resolution TEM (HR-TEM) was also conducted on JEOL 2100F and JEOL 3011 microscopes at 200 and 300 kV, respectively. Both plain-view and cross-sectional thin foils were prepared for TEM observation. The plan-view samples were prepared by slicing a thin sample parallel to the plane of the impacted surface, followed by polishing from the non-impacted side and thinning to perforation using a twin-jet polisher after a thin coating of transparent loc-tite had been applied to the impacted surface to prevent thinning of the impacted surface. After perforation, the loc-tite was dissolved by acetone and rinsing with ethanol. The twin-jet electropolishing process was conducted at \(-20^\circ\text{C}\) using a mixture of 15\% HNO\(_3\) and 85\% CH\(_3\)OH. The cross-sectioned samples were prepared by the following procedures. Two thin samples were bonded with the impacted surfaces facing each other using M-Bond 610 glue (Allied High Tech Products, CA). The sample was sliced perpendicularly along the plane of the impacted surface and the thin foil was mechanically ground down to a thickness of about 20 \( \mu \)m. Finally, the sample was ion milled near the bonding line using a Gatan PIPS at a small incident angle and room temperature. X-ray diffraction (XRD) was carried out on a Philips X’pert diffractometer with Cu K\(_\alpha\) radiation (\( \lambda = 0.154056 \) nm) at room temperature.

The deformed structure in the NiTi is first studied at low strain. Figure 1 shows the highly dense dislocations due to dislocation slipping at a depth of about 230 \( \mu \)m below the treated surface. The selected-area electron diffraction (SAED) pattern displays the typical B2 lattice in the NiTi alloy. This B2 phase undergoes reverse martensite transformation and reverse transformation during SMAT. According to Jiang et al.’s study, dislocation would be generated in NiTi matrix to reduce the strain field during the reverse martensite transformation [16]. Therefore, it is inferred that these observed highly dense dislocations are formed during the reverse martensite transformation. The formation of highly dense dislocations constitutes strain accommodation in the NiTi alloy deformed at low strain.

As the depth decreases, deformation strains increase. Figure 2 shows the phase structure at different strain levels after SMAT. At a depth of about 150 \( \mu \)m, martensite bands can be clearly seen (Fig. 2a1). These martensite bands are well oriented with widths of 40–200 nm and lengths of up to several micrometers. The results acquired by SAED show the B19\(^0\) phase (Fig. 2a2). The black and white bands originate from the B19\(^0\) phase, suggesting complete formation of the martensite phase at this depth, and the strain here is larger than that at the depth of 230 \( \mu \)m. The onset of the B2 \rightarrow B19\(^0\) transformation at this depth is due to the SIM transformation during deformation.

Figure 2b1 shows the microstructure at a depth of 30 \( \mu \)m after SMAT. The specimen contains heterogeneous distributed and refined grains with nano and sub-micrometer sizes. The corresponding SAED pattern in Figure 2b2 shows the diffraction rings superimposed by diffraction spots. These diffraction rings stem from electron diffraction in the nanocrystalline and ultrafine grains. The diffraction pattern also shows traces of both the B2 and B19\(^0\) phases at this strain level. The results show that the B2 and B19\(^0\) phases coexist at a depth of about 30 \( \mu \)m, suggesting the occurrence of incomplete reverse martensite transformation (B19\(^0\) \rightarrow B2) at high strain.

![Figure 1](image1.jpg)  
**Figure 1.** TEM image showing the high density of dislocations at a depth of about 230 \( \mu \)m in the SMAT NiTi specimen with the inset displaying the corresponding SAED pattern showing the B2 phase.

![Figure 2](image2.jpg)  
**Figure 2.** (a1) TEM image showing the martensite bands of SMAT NiTi at a depth of about 150 \( \mu \)m; (a2) SAED pattern taken from the TEM image in (a1); (b1) TEM image showing the microstructure of SMAT NiTi at a depth of about 30 \( \mu \)m; (b2) SAED pattern taken from TEM image in (b1) indicating the coexistence of the B19\(^0\) and B2 phases.
Figure 3 shows the microstructure of the SMAT NiTi specimen near the top surface (~7 μm deep) at which the deformation strain is significantly higher than that in the substrate. SPD results in the formation of nanocrystalline grains with an average size of about 20 nm in the top layer. Fast Fourier transform (FFT) from the high-resolution lattice image conducted to index the crystal lattice in area B indicates that the nanocrystalline grains have the B2 phase. Plastic deformation also causes lattice distortion, finally transforming it into an amorphous phase. The FFT pattern shows traces of the amorphous phase in area C and no B19′ martensite phase is found in the top layer. This provides evidence that the B19′ phase totally transforms into the B2 phase in the nanocrystallines. When NiTi grains with the B2 phase are refined to the nanometer scale or nanocrystals, martensite transformation is suppressed by the size effect [17,18]. Therefore, the nanocrystallines in the surface after SMAT have the B2 austenite phase. The results reveal that a graded phase structure is formed on the surface of NiTi alloy by SMAT but the bulk retains the B2 phase. Plastic deformation becomes more severe closer to the surface, and thereafter B19′ phase emerges due to SIM transformation. With further plastic deformation, a transient phase layer containing the B19′ and B2 phases is formed due to the reverse martensite transformation. In the surface layer, the deformation strain is significant high and only the B2 phase exists.

XRD is used to investigate the B19′ phase variation with deformation strain. The longer the SMAT treatment time, the higher is the strain imposed on the specimen. As shown in Figure 4a, the raw materials show only the B2 (1 1 0) diffraction peak, but after SMAT for 1 min, a B19′ peak emerges and the intensity increases with treatment time up to 5 min. However, the intensity of the B19′ peak decreases with further treatment time. This suggests that sufficient deformation strain can induce the reduction of martensite in the NiTi alloy, probably due to the reverse martensite transformation. The variations in the B19′ phase revealed by XRD exhibit similar trends as those observed by TEM. The schematic diagram in Figure 4b illustrates the graded phase structure in the surface layer after SMAT. The B2 phase exits in the top surface and there is a transient layer containing both the B2 and B19′ phases underneath. Below this transient layer, only the B19′ phase is present. Close to the substrate, the B2 phase exists, suggesting that there is no B2 → B19′ phase transformation when the strain is small.

The formation of the graded phase structure in NiTi after plastic deformation can be interpreted by the martensite transformation as well as reverse transformation. Since the Ms (martensite transformation starting temperature) of the raw materials is lower than As = 234.5 K and the thermal transformation can be excluded, the B2 → B19′ martensite transformation in the NiTi during SMAT arises from the SIM transformation which occurs at a depth of about 230 μm, corresponding to a low strain. The subsequent reverse martensite transformation leads to a recovered B2 phase and dislocations in the matrix. As soon as the B19′ martensite phase forms via SIM at the depth of about 150 μm, plastic deformation further deforms the martensite bands. Thereafter, highly dense dislocations inside these martensite bands are produced. The highly dense dislocations hinder the reverse martensite transformation (B19′ → B2) by imposing a friction stress among the phase interfaces [19]. Therefore, even after unloading, the SIM still remains at a depth of about 150 μm. To conduct reverse transformation (B19′ → B2), a relatively high temperature is needed to overcome the energy barrier due to friction stress. As the strain is increased, the transient layer containing the B19′ and B2 phases appears, and finally only the B2 phase can be observed in the top layer. This is due to the reverse martensite transformation (B19′ → B2) and there are two possible mechanisms. The first one is that SPD in the deformed B19′ results in the B2 phase in the presence of mechanical twinning [20]. However, in the present study, no mechanical twinning is found in the martensite bands, and hence the deformation-induced B19′ → B2 transformation can be excluded. The second possible reason is deformation heating when the stainless steel balls impact the sample surface at high velocity. The kinetic energy of the flying stainless steel balls fuels plastic deformation and heats up the sample. Considering that the process is adiabatic and frictionless, the temperature change can be calculated by [21,22]:

\[
\Delta T = \frac{\Delta Q}{\rho C_p} = \frac{\xi}{\rho C_p} \int_0^c \sigma ds,
\]

Figure 3. (a) HR-TEM image taken from the top surface layer of SMAT NiTi sample showing the nanocrystalline and amorphous region; (b) corresponding FFT of area B; (c) corresponding FFT of area C.
in which $\Delta Q$ is the energy contributing to the temperature rise, $\xi = 0.9$ (assuming 90% of the work of deformation is converted to heat), $\rho$ is the density of the materials (6.5 g cm$^{-3}$ for NiTi), and $C_p$ is the specific heat capacity (0.32 kJ kg$^{-1}$ K$^{-1}$). In the SMAT process, the velocity of the flying ball is about 20 m s$^{-1}$ [5]. Our calculation shows that each impact by a single flying stainless steel ball results in a temperature rise of about 166 K (see Supporting Information). In fact, the thermal process is not entirely adiabatic and the temperature rise is lower than the calculated one. Lu et al. have reported that SMAT results in an increase of 50–100 K on the surface of Fe [5]. The elevated temperature in reality is adequate for the reverse martensite transformation (B$_{19}^0$ → B$_2$). Thereafter, more B$_2$ phase appears to form the transient B$_{19}^0$ + B$_2$ phase layer and the B$_2$ phase layer. According to Eq. (1), the temperature induced by deformation heating is a function of strain. As shown in Figure 4c, the strain imposed by SMAT decreases with depths. Thus, the high strain in the top surface results in a large temperature rise inducing sufficient B$_{19}^0$ → B$_2$ transformation and finally formation of a complete B$_2$ phase layer. The deformation strain and temperature rise decrease with depth and then cause an incomplete reverse transformation. As a result, only the partial B$_{19}^0$ phase is transformed into the B$_2$ phase. As soon as that happens, subsequent plastic deformation produces grains with submicrometer sizes as well as nanocrystallines. Afterwards, martensite transformation is suppressed in the nanocrystallines and only the B$_2$ phase is present on the surface of the SMAT NiTi alloy.

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