Microstructural evolution in NiTi alloy subjected to surface mechanical attrition treatment and mechanism

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Both nanocrystalline and amorphous phases are observed from the near surface of nickel titanium shape memory alloy (NiTi SMA) with the B2 austenite phase after surface mechanical attrition treatment (SMAT). The microstructure and phase changes are systematically studied by cross-sectional and plane-view transmission electron microscopy. The strain induces grain refinement and it is accompanied by increased strain in the surface layer triggering the onset of highly dense dislocations and dislocation tangles (DTs), formation of the martensite plate via stress-induced martensite (SIM) transformation (B2 to B19', and dislocation lines (DLs) as well as dense dislocation walls (DDWs) inside the martensite plate leading to the subdivision of the martensite plate. In addition, reverse martensite transformation (B19' to B2) and amorphization take place concurrently in the surface region, and successive subdivision and amorphization finally result in the formation of well separated nanocrystalline and amorphous phases in the near surface. The average grain size of the nanocrystallites is about 20 nm. Owing to the almost complete reverse martensite transformation as well as thermal stability, the strain-induced nanocrystalline structure has the B2 austenite phase in the surface layer and no transformation occurs.

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1. Introduction

Nanocrystalline (nc) metals and alloys produced by severe plastic deformation (SPD) processes have been studied recently. There are several variations of SPD-based techniques such as high pressure torsion (HPT) [1,2], equal channel angular pressing (ECAP) [3], cold rolling [4,5], sliding wear [6], high energy milling [7] and surface mechanical attrition treatment (SMAT) [8,9]. The formation mechanism of nanocrystalline structures in a variety of materials during SPD has also been investigated and it is generally recognized that the dislocation activities and mechanical twinning dominate the grain refinement mechanism in many nc metals. For example, in bcc metals such as Fe [10], SPD-induced dislocation multiplication and interaction result in dense dislocation walls and dislocation tangles before they further transform into subboundaries. These sub-boundaries with small misorientations eventually evolve into highly misoriented grain boundaries and finally refine the original coarse grains. In some fcc or bcc metals with low stacking fault energies (SFEs) or some hcp metals [7,11–14], mechanical twinning becomes the main mode of grain refinement where the critical shear stress for twinning is lower than that of dislocation slip. It should be pointed out that studies on the grain refinement mechanism have mainly focused on pure metals and single-phase alloys. However, most engineering metals are multi-phase alloys and intermetallic compounds and the microstructural evolution, grain refinement, and related phase transformation have been seldom studied in comparison with those in pure metals and single-phase alloys. Therefore, it is both scientifically and technically important to investigate the grain refinement phenomenon and mechanism in multi-phase alloys and intermetallic compounds.

Intermetallic NiTi alloys are widely used in a myriad of engineering applications [15]. The intermetallic NiTi shape memory alloy has a cubic B2 phase at high temperature and upon cooling, the cubic B2 phase transforms into the monoclinic B19' martensite. This phase transformation can also occur due to applied stress. Owing to this extraordinary phase transformation behavior, NiTi
alloy possesses the unique shape memory effect and super-elasticity. Therefore, this material provides a suitable platform to investigate the grain refinement mechanism involving multiple phase transformation during SPD. In 1990, J. Koike found that cold rolling led to amorphization of the NiTi alloy [16]. Later investigations confirm that amorphization is always accompanied by the formation of nanocrystalline structures in the NiTi alloy when subjected to SPD [17–21]. Hence, a thorough understanding of the underlying grain refinement mechanism in NiTi alloy is difficult due to the amorphous phase. New SPD techniques such as ECAP and HPT have recently been adopted to process intermetallic NiTi alloys. Karaman et al. [22,23] produced NiTi with ultrafine grains by ECAP and studied the associated dislocation slip, twinning mode, and phase transformation. Waitz et al. [24,25] used HPT to prepare bulk amorphous NiTi and by subsequent devitrification of the amorphous phase, bulk nanocrystalline NiTi was produced. Since amorphization is always accompanied by grain refinement in NiTi, the microstructural evolution and mechanism should account for both issues. However, to our knowledge, no systematical work has been conducted. In order to elucidate the underlying mechanism associated with NiTi amorphization and grain refinement, systematic examination of the microstructures on both the macro- and nano-scales should be conducted.

Surface mechanical attrition treatment (SMAT) is an effective technique to generate severe plastic deformation in the surface region of the treated sample at a high strain rate (as high as $10^2$–$10^3$ s$^{-1}$) [9]. In the SMAT process, graded strain and strain rate are achieved from the surface to the bulk. As a result, a gradient microstructure spanning a large depth from the surface to the bulk is obtained due to the different strain rates and/or different degrees of plastic strain. This provides a unique opportunity to characterize the microstructure and mechanism of a metal over a wide range of strain rate or strain and to investigate the corresponding grain refinement mechanism in NiTi alloy.

2. Material and methods

2.1. Sample preparation

Commercial NiTi alloy plates (25.4 mm in diameter and 1.5 mm thick) with 50.8 at.% Ni and 49.2 at.% Ti were used as raw materials. The materials were annealed to obtain homogeneous coarse grains. The size of the coarse grains ranged from 40 to 80 μm as shown in Fig. 1(a). The initiate phase was B2 austenite with transformation points of $A_f = 234.5$ K and $A_r = 257$ K, respectively. Prior to SMAT, the NiTi plates were polished with silicon carbide sand papers to grade 800 and then electrochemically polished to reduce the residual stress resulting from mechanical polishing.

2.2. Surface mechanical attrition treatment (SMAT)

The NiTi plates underwent SMAT and the details of the apparatus and procedures can be found elsewhere [8,9,26]. During SMAT, the stainless steel balls were placed in a cylindrical chamber agitated by an ultrasonic generator. When the balls were resonated, the entire surface of the sample was impacted by a large number of flying balls in a short period of time. Each impact by the balls resulted in plastic deformation in the surface layer and repeated multidirectional impacts at high strain rates led to severe plastic deformation in the surface layer. In this work, the NiTi specimens were treated by SMAT at room temperature for 60 min at a vibration frequency of 20 kHz. Stainless steel balls 2 mm in diameter and 0.327 g in weight were used.

2.3. Microstructure characterization

The cross-sectional microstructure was examined using an Olympus BH2 optical microscope. TEM observations were carried out on the Philips CM20 and JEOL-2010 transmission electron microscope operated at 200 kV, and high-resolution TEM (HR-TEM) was performed on the JEOL-2100F at 200 kV. Both plane-view and cross-sectioned thin foils were prepared for TEM. 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 instrument after a thin coating of transparent loctite was applied to the impacted surface to prevent thinning of the impacted surface. After perforation, the loctite was removed by dissolution in acetone, followed by rinsing with ethanol. The twin-jet electro-polishing process was conducted at ~20 °C using a mixture of 15% HNO$_3$ and 85% CH$_3$OH. The cross-sectioned samples were prepared by the following procedures: (i) bonding two thin samples with the impacted surfaces facing each other using M-Bond 610 glue (Allied High Tech Products, CA); (ii) slicing the sample perpendicularly along the plane of the impacted surface; (iii) mechanically grinding the thin foil down to a thickness of about 20 μm, and (iv) ion-milling the foil near the bonding line using a Gatan PIPS with a small incident angle at room temperature.

Fig. 1. Cross-sectional metallographic observation of: (a) untreated and (b) SMAT NiTi specimens.
3. Results

3.1. Optical microscopy observation

Fig. 1 displays the cross-sectional microstructure of the NiTi specimens before and after SMAT processing. Fig. 1(a) shows that the annealed NiTi before SMAT is composed of coarse grains with an average grain size of ~50 μm. After undergoing SMAT for 60 min, an obvious deformed layer containing fine lamellae is observed in the top 200 μm as shown in Fig. 1(b). In this surface layer, large grains disappear and microstructure identification becomes very difficult under optical microscopy (OM). The thickness of the plastic deformed surface layer is estimated to be more than 200 μm.

Fig. 2(a) depicts the XRD patterns of the NiTi after SMAT and the untreated one (bare NiTi). A single B2 phase is observed after annealing and no obvious peaks corresponding to B19' and other precipitate phases can be observed. After undergoing SMAT for 60 min, the intensity of the Bragg reflection peaks B2 (110) and B2 (211) decreases and the peaks broaden significantly. It is possibly due to grain refinement [27] and will be demonstrated by TEM in subsequent sections.

3.2. TEM investigation

3.2.1. 200–250 μm below the treated surface

Fig. 3(a) depicts a representative cross-sectional bright-field TEM micrograph of the microstructure at about 200 μm below the surface in the SMAT NiTi specimen. The areas labeled 1, 2, 3, and 4 have high contrast due to the dislocation tangles (DTs) and dense dislocations, while other areas have a low dislocation density. Fig. 3(b) shows the selected area electron diffraction (SAED) pattern taken along the [111] zone axis from the area 3. This SAED pattern reveals that the crystal structure of the NiTi grains at this depth is the typical B2 lattice, which is similar to that in the area far from the treated surface. Areas with similar DTs and highly dense dislocations are consistently observed at various depths ranging from about 180 to 250 μm adjacent to the strain-free matrix. Besides the DTs, elongated bands with widths from 100 to 300 nm are also characteristic of the microstructure at this depth. SAED reveals that these elongated bands still have the B2 lattice. The boundaries of the elongated band located between the DTs are visible as indicated by the arrows in Fig. 3(a). These distinct boundaries suggest the presence of large misorientation between the elongated bands and DTs. The formation of the boundaries is closely related to the dislocation activities during plastic deformation and it will be discussed later in Section 4. That is to say, the DTs and high density of dislocations constitute the main mode of strain accommodation at the low strain level during SMAT.

3.2.2. About 150 μm beneath the treated surface

At a smaller depth, the strain increases. The martensite bands appear more frequently and become the dominant microstructure. Fig. 4 shows the martensite bands of the SMAT NiTi alloy at a depth of about 150 μm. The microstructure is characterized by well-orientated martensite bands having widths from 40 to 200 nm and lengths up to several micrometers. Fig. 4(b) depicts the detailed structure of the martensite bands. The contrast inside the martensite band arises from the trapped dislocations. The dislocation lines (DLs) and dense dislocation walls (DDWs) can be observed as indicated by the white triangles and yellow triangles, respectively. According to the TEM micrographs, the martensite bands are separated by evident boundaries which are highlighted by arrows. These boundaries are obviously sharper and thinner than the dislocation cells and the misorientation across them are much larger (usually a few degrees). It is believed that these boundaries are developed by accumulation and annihilation of dislocations. Similar dislocation activity has also been observed from nanostructured Fe [10]. Fig. 4(c) exhibits the SAED pattern obtained from the “black band” along the [100]₀₀₀ zone axis and Fig. 4(d) is acquired from the “white band”. Both SAED patterns indicate that the NiTi alloy has fully transformed from cubic B2 to monoclinic B19’ at the strain level at this depth. The plausible interpretation of this phase transformation is stress-induced martensite (SIM) transformation of NiTi alloy due to plastic deformation during SMAT. However, the SAED patterns do not indicate
the presence of twinning, which is the main deformation mechanism in the NiTi shape memory alloy with the martensite phase. This is probably associated with de-twinning as well as dislocation activities in the NiTi and this issue will be discussed in more details later. Formation of the martensite bands via SIM transformation and the relevant dislocation activities are believed to be the mechanism of strain accommodation at about 150 μm deep in the SMAT NiTi alloy.

3.2.3. About 50 μm beneath the treated surface

As the strain increases, the long martensite bands are refined into fine grains. Fig. 5 shows the microstructure of the SMAT NiTi alloy at a depth of about 50 μm and the corresponding SAED pattern and several important features are observed. First of all, although some long martensite bands about 200 nm wide can still be observed, several martensite bands have been refined into ultrafine grains. As indicated by the scale bar, at least one of their dimensions is in the nanometer regime. Secondly, the corresponding SAED pattern shows the co-existence of the B19′ martensite and B2 austenite phases, indicating that a reverse martensite transformation from B19′ martensite to B2 austenite occurs during SMAT at this high strain level. The reverse martensite transformation in the heavily deformed martensite is believed to result from severe plastic deformation. In fact, a similar reverse martensite transformation has also been observed from NiTi processed by ECAP reported by Karaman et al. [23]. Thirdly, as shown in Fig. 5(b), a broad diffraction ring is observed from the amorphous phase superimposed on diffraction spots indicated by the arrow. This broad diffraction ring has a radius corresponding to the length of the diffraction vector <110> in the B2 lattice. This phenomenon suggests that partial amorphization occurs when the strain is at a certain level during SMAT. Amorphization of NiTi has been

Fig. 4. (a) Cross-sectional TEM images acquired at a depth of about 150 μm from the treated surface in the NiTi alloy; (b) Magnified TEM image showing the martensite bands with DLs, DDWs and boundaries inside (white angles for DLs, yellow angles for DDWs and arrows for boundaries); (c) SAED pattern taken from the circle C in (b), electron beam//[100]A; (d) SAED pattern taken from the circle D in (b).
reported using various methods due to severe plastic deformation, e.g. cold rolling and HPT\cite{16,24}. Fourthly, grain refinement, reverse martensite transformation under severe plastic deformation, and partial amorphization are believed to jointly contribute to the strain accommodation at this depth.

3.2.4. About 25 \(\mu\)m beneath the treated surface

As a result of severe plastic deformation during SMAT, amorphization of the NiTi alloy becomes more apparent with increasing strain. Fig. 6 shows the microstructure at around 25 \(\mu\)m deep in the SMAT NiTi alloy. As shown in Fig. 6(a), the specimen contains heterogeneously distributed nanocrystallines and sub-micrometer grains mixed with the amorphous phase. The contrast is reversed in the dark-field TEM image in Fig. 6(b) and the distribution of the fine grains can be observed. Fig. 6(c) depicts the corresponding SAED pattern, in which the amorphous phase gives rise to diffuse rings superimposed by rather sharp diffraction spots from the nanocrystallines as well as micrometer grains. The diffuse diffraction ring has a radius corresponding to the \(<110>\) of the B\(2\) lattice. Inside the diffused diffraction ring, diffraction spots corresponding to B2 and B\(19^0\) grains can also be observed. Therefore, the microstructure in the SMAT NiTi alloy at a depth of 25 \(\mu\)m is shown to consist of a mixture of amorphous phase and fine grains.

3.2.5. Microstructure at the top surface

Fig. 7 shows the TEM micrographs and SAED patterns revealing the planar microstructures in the top layer (about 10 \(\mu\)m deep) which is subjected to high strain and strain rate during SMAT. As a result, the microstructure at this depth consists of separate nanocrystalline and amorphous regions as shown in Fig. 7(a). The corresponding SAED pattern (identified as the B2 lattice structure) shows fairly uniform rings, indicating a continuous and wide distribution of misorientations among the nanograins. In comparison with the nanocrystalline NiTi alloy produced by cold rolling or HPT, SMAT results in complete nanocrystallization of the NiTi, whereas the nanocrystalline structure produced by cold rolling or HPT is frequently mixed with the amorphous phase \cite{17,18,24}. According to the diffraction pattern in Fig. 7(c), the amorphous phase gives rise to diffuse rings having radii corresponding to the
length of the diffraction vectors \(<110>\) and \(<211>\) of the B2 lattice. It should be noted that the glass transition temperature of the amorphous phase is hard to obtain in this case due to the difficulty in the DSC measurement.

The nanocrystalline structure shown in Fig. 7 is further examined by TEM and HR-TEM. Equiaxial nanocrystallines with random orientation are observed from Fig. 8. The microstructure is characterized by nanometer-sized, equiaxial grains and the average grain size is about 20 nm. A closer examination of the nanostructure in the surface layer is conducted by HR-TEM and the micrograph is depicted in Fig. 8(c) which clearly discloses nanocrystallines with different misorientation.

4. Discussion

Based on the TEM and other results, the microstructural evolution and phase transformation occurring at various depths in the deformed layer in the NiTi alloy can be summarized in Table 1. The process and mechanism governing grain refinement and amorphization in the NiTi alloy at different levels of strain is discussed in the following sections.

4.1. Strain accommodation

4.1.1. Dislocations at depths far from the treated surface

Generally, deformation-induced strain yields dislocations in metals. In order to accommodate further strain, dislocation activities including accumulation, interaction, tangling, and rearrangement of dislocations are involved. As indicated in Fig. 3, plastic deformation leads to the formation of high density dislocations and DTs in the original grains after SMAT at depths from 180 to 220 \(\mu\)m. While moving in some slip planes, dislocations will curve when encountering obstacles such as forest dislocations and the dislocation density there will increase accordingly producing DTs. In these DTs, the dislocations interact with each other in a complex manner and are randomly arranged without preferred sliding orientations. When the strain attains a certain level, these dislocations will be annihilated and rearranged into ordered arrays but still tangled. Therefore, the formation of dense dislocations and DTs is believed to be the main strain accommodation mechanism. As the local elastic strain further increases, the dislocations evolve into subboundaries through accumulation, interaction, and spatial rearrangement. Similar dislocation activities have been observed in severely plastic deformed Ti alloy [28], Cu [29], and Fe-0.89C alloy [30].

4.1.2. Stress-induced martensite \(B19'\) phase

As the depth decreases (200–150 \(\mu\)m), the deformation strain and strain rate in the SMAT NiTi increase. Simultaneously, the dislocation activities become more acute. To minimize the total energy state, dislocations undergo accumulation and rearrangement. As observed from many metals with severe plastic deformation, the dislocation activities lead to the formation of dislocation lines (DLs), dense dislocation walls (DDWs), as well as sub-boundaries sequentially, although the dislocation activities depend on the crystal structure of the materials and deformation conditions [31]. Eventually, the sub-boundaries further develop into boundaries with high misorientation and refine the coarse grains into ultrafine grains or nanocrystallines. However, no obvious subdivision is found inside the original grains in the SMAT NiTi specimen within a wide depth ranging from 200 to 150 \(\mu\)m, in which the strain level is much higher. Instead, martensite bands as
shown in Fig. 4 are observed at about 150 μm deep. At this strain level, stress-induced martensite (SIM) transformation is believed to be the main strain accommodation mechanism. As shown in Fig. 4, those martensite plates result from SIM which is a unique transformation behavior in shape memory alloys [15]. It is known that SIM induces the transformation of austenite with cubic B2 into martensite with monoclinic B19° in NiTi. The crystallographic change associated with the phase transformation compensates the stored elastic energy resulting from the SPD process [32]. Meanwhile, in polycrystalline NiTi alloys, an irreversible energy component is unavoidable during deformation due to the necessity for plastic deformation as an accommodation mechanism between neighboring grains with mismatched orientations [33]. Furthermore, an internal elastic energy in the reoriented martensite that opposes its reverse transformation is created during SMAT [34]. Therefore, the energy consumption contributes to the main strain accommodation by SIM transformation in SMAT NiTi at a depth of about 150 μm.

Fig. 8. Plane-view TEM images taken from the nanocrystalline region at a depth of about 5 μm (a) bright-field TEM image; (b) dark-field TEM images corresponding to (110)B2 diffraction as circled in the SAED pattern, and (c) HR-TEM image of the nanocrystalline phase.

<table>
<thead>
<tr>
<th>Depth below surface (μm)</th>
<th>Phase composition</th>
<th>Microstructural characters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top surface (5–15)</td>
<td>B2</td>
<td>Distinct areas of the nanocrystalline and amorphous phases</td>
</tr>
<tr>
<td>20–40</td>
<td>B2 + B19°</td>
<td>Mixture of nanoscale grains and amorphous phase</td>
</tr>
<tr>
<td>50–100</td>
<td>B2 + B19°</td>
<td>Lamellar grain refined into ultrafine grains and appearance of the amorphous phase</td>
</tr>
<tr>
<td>120–160</td>
<td>Main B19°</td>
<td>Martensite bands with widths from 40 to 200 nm</td>
</tr>
<tr>
<td>180–220</td>
<td>B2</td>
<td>Coarse grains with a high density of dislocations</td>
</tr>
</tbody>
</table>
4.2. Microstructure evolution inside the stress-induced martensite plates

TEM reveals that the DLs, DDWs, and sub-boundaries constitute the main strain accommodation inside the martensite plates as shown in Fig. 4(b). In other words, after the formation of stress-induced martensite in the SMAT NiTi alloy, further plastic deformation spurs acute dislocations activities such as the formation of DLs, DDWs, and sub-boundaries inside the martensite plates. They are expected to inhibit the reverse martensite transformation (from B19\(^+\) to B2) by imposing a friction stress [35]. Thereafter, stress-induced martensite plates can be stabilized in the SMAT NiTi specimen rather than reverting back to the parent B2 phase while the applied stress is released after SMAT. These DLs, DDWs, and sub-boundaries hinder the migration of the interfaces, decrease the mobility of the corresponding SIM, and raise the critical driving force for the reverse transformation. This point has also been inferred based on in situ observation of the reverse martensitic transformation [36].

With respect to the martensite evolution in the NiTi alloy, twins, especially \(<011\>\) type II, are always important to the accommodation and coalescence of martensite variants [37]. However, no twins are observed from the martensite plates or between two adjacent martensite plates in the present investigation (see Fig. 4). It is proposed that localized severe plastic deformation leads to detwinning of the martensite twins. The (100) compound twins are believed to exist at lower strain in the NiTi alloy and as the strain increases, the martensite twins rearrange into coherent and parallel bands in the martensite plates [38]. Afterwards, reorientation and detwinning of the \(<011\>\) type II twins take place sequentially as the deformation strain goes up. By further deformation especially beyond the stress-plateau of the NiTi alloy, reorientation and detwinning of the martensite twins become less favorable to applied force [33,38]. After detwinning, the martensite twins disappear and a high density of dislocations is generated in the martensite plate. When the SMAT process imposes further strain, dense dislocations are developed into DLs and DDWs inside the martensite plates as shown in Fig. 4(b). This is believed to be the reason why dislocations rather than twins are observed inside the martensite plates here. However, there may be another explanation that twinning cannot accommodate a huge amount of deformation because the atomic displacement by twins is less than one inter-atomic distance. For instance, Chichili et al. have found that plastic deformation due to twinning is less than 0.2% in titanium at low strain and strain rates [39].

4.3. Phase transformation under severe plastic deformation

According to the summary shown in Table 1, it can be concluded that phase transformation in the SMAT NiTi alloy is dictated by the levels of strain and strain rates. The as-received NiTi specimen has the B2 austenite phase. As SMAT introduces plastic strain, a high density of dislocations is observed from the NiTi grains. Nevertheless, the phase is still B2 austenite \(\text{albeit the high density of dislocations generated in the substrate as shown in Fig. 3. As the strain and strain rate increase, transformation from B2 austenite to B19\(^+\) martensite occurs due to the stress-induced martensite transformation (see Fig. 4). As the depth decreases to 50 \(\mu\)m from the impact surface, a reverse martensite transformation (B19\(^+\) to B2) takes place and both B2 \(-\) B19 can be observed (see Figs. 5 and 6). Moreover, in the top layer in the SMAT NiTi alloy, the microstructure is composed of a nanocrystalline structure with the B2 austenite phase. This implies that the heavily deformed B19\(^+\) martensite recovers to B2 austenite under further severe plastic deformation. There are two possible mechanisms to explain this unusual back transformation from deformed B19\(^+\) to B2 observed here. The first one is deformation heating due to the high strain rate in the surface of the NiTi during SMAT. Another possible reason is that severe plastic deformation of the deformed B19\(^+\) in the NiTi transform it into B2. In fact, similar results have been obtained from NiTi alloys with ECP [23]. When the NiTi grains with the B2 phase are refined to the nanometer scale, martensite transformation is suppressed by the size effect. T. Waitz et al. have revealed that B2 austenite does not transform into B19\(^+\) martensite thermally when the grain size is less than about 50 \(\mu\)m [24]. In this work, the average size of the nanocrystallines in the surface of the SMAT NiTi is about 20 \(\mu\)m and they therefore are thermally stable and exhibit the B2 austenite phase.

4.4. Amorphization of NiTi under severe plastic deformation

NiTi is an intermetallic metal that can easily undergo bulk amorphization when bombarded by energetic particles/beams [40] or subjected to severe plastic deformation under a mechanical force [16–21,24,25]. On the ground of the experimental results, we only discuss the amorphization of NiTi driven by mechanical force here. In the case of amorphization under mechanical driving forces, plastic deformation-induced defects such as point defects, dislocations, twins, sub-boundaries, etc. are responsible for raising the free energy of the crystalline alloy to above that of the amorphous counterpart [41]. Huang et al. have used HR-TEM to investigate amorphization in NiTi processed by HPT [42]. Deformation-induced amorphization is observed to initiate from the dislocation core regions in the grain interior. In other words, deformation-induced amorphization in NiTi is closely related to the dislocation density yield during deformation. However, even in the 60% cold rolled NiTi, the dislocation density determined by HR-TEM is \(10^{11} - 10^{14} \text{ cm}^{-2}\). The elastic energy associated with a dislocation density of \(10^{14} \text{ cm}^{-2}\) is estimated to be 2.2 kJ mol\(^{-1}\), which is lower than the crystallization enthalpy reported for NiTi of 3.03–3.55 kJ mol\(^{-1}\). The stored energy only contributes to partial amorphization of the NiTi alloy. At the same time, grain refinement during SMAT provides a large volume of nanocrystalline and ultrafine grains, in which the grain boundaries significantly increase the stored energy. Yamada and Koch [43] have reported that the energy stored in grain boundaries can drive the crystalline-to-amorphous transformation. Therefore, it is inferred that both the dislocations and grain boundaries contribute significantly to the crystalline-to-amorphous transformation in NiTi. In most cases, the amorphous matrix in the NiTi shows diffraction rings superimposed by diffraction spots corresponding to the B2 lattice in SAED patterns but B19\(^+\) martensite is seldom observed. Hence, it can be concluded that the B2 austenite phase is more stable against amorphization than the B19\(^+\) martensite phase.

4.5. Grain refinement in the surface layer and lattice distortion inside the nanograin

Close to the treated surface, i.e. at a depth of about 50 \(\mu\)m (cf. Fig. 5), the microstructure consists of narrow lamellae subordinated into ultrafine grains. Furthermore, the formation of equiaxed nanograins is observed from close to the top surface as shown in Fig. 8. These two processes clearly show the evolution of grain refinement in the SMAT NiTi. Grain refinement is associated with dislocations movements during severe plastic deformation. In order to accommodate the plastic strain in polycrystalline materials, various dislocation activities are normally triggered and they include sliding, accumulation, interaction, tangling, and spatial rearrangement. As stated in Section 3.2.2, the dislocation activities lead to the formation of DLs and DDWs in the stress-induced martensite plates in the SMAT NiTi at a depth of around 150 \(\mu\)m. These dislocations gradually result in the subdivision of the coarse martensite plates by forming individual dislocation cells primarily separated by DDWs and DTs. Moreover, the multi-directional impacts in SMAT may
change the slip systems with the strain path even inside the same grain. The dislocations not only interact with other dislocations in the current active slip systems, but also interact with inactive dislocations generated in previous deformation. Therefore, the grains can be subdivided more efficiently by the DDWs and DTs during the SMAT process. With increased misorientation, DDWs and DTs will further be converted into subboundaries. With further increase in strain, the orientation of the grain with respect to their neighboring grains becomes completely random and the highly misoriented grain boundaries are formed. In order to accommodate the increasing strain, subdivision occurs inside the refined grains or subgrains thereby leading to much finer grains or subgrains. In other words, the additional strain accommodation is achieved by successive grain subdivision. The surface layer NiTi alloy is subjected to a very high strain rate estimated to be about $10^7 - 10^9 \text{s}^{-1}$. On account of the high strain rate and strain, the deformation-induced dislocation density is extremely high and the dislocation activities result in the formation of dislocation cells or subgrains on the nanometer scale and they eventually evolve into equiaxed nano-sized grains.

5. Conclusion

NiTi shape memory alloy samples with the B2 austenite phase are subjected to surface mechanical attrition treatment (SMAT). Severe plastic deformation during SMAT produces nanocrystalline and amorphous phases in the surface region of the alloy. The microstructural evolution and phase changes with depth are investigated by electron microscopy and other characterization techniques. SMAT results in a deformed layer more than 200 $\mu$m thick in the surface region of NiTi alloy. The high density dislocations and DDWs are found in the plastic zone. The nanocrystalline phase exhibits the B2 lattice structure and residual stress of a nickel-base alloy subjected to surface severe plastic deformation. Mater Sci Eng A 2006;440:531-5. The top surface has the B2 austenite phase due to the almost random orientation and the average grain size is about 20 nm. The top surface has the B2 austenite phase due to the almost random orientation and the average grain size is about 20 nm. The top surface has the B2 austenite phase due to the almost random orientation and the average grain size is about 20 nm. The top surface has the B2 austenite phase due to the almost random orientation and the average grain size is about 20 nm. The top surface has the B2 austenite phase due to the almost random orientation and the average grain size is about 20 nm.

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