Surface Nanocrystallization by Surface Mechanical Attrition Treatment

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**Abstract.** Based on strain-induced grain refinement, a novel surface mechanical attrition treatment (SMAT) technique has been developed to synthesize a nanostructured surface layer on metallic materials in order to upgrade their overall properties and performance without changing their chemical compositions. In recent several years, the microstructures and properties of surface layer were systematically investigated in various SMAT metals and alloys, including b.c.c., f.c.c. and h.c.p. crystal structures. Different grain refinement approaches and nanocrystalline formation mechanisms were identified in these deformed materials, involving dislocation activities, mechanical twinning and interaction of dislocations with mechanical twins. The properties of the surface layer were measured by means of hardness, tensile, fatigue and wear tests. The enhanced properties of the surface layer are mainly attributed to the strain-induced grain refinement. In this work, we reviewed the microstructures and properties of surface layer in the SMAT materials.

1. Introduction

Nanocrystalline materials, which are structurally characterized by nanometer-sized grains with a large number of grain boundaries, have been found to exhibit many novel properties relative to their coarse-grained counterparts [1, 2]. For example, most nanocrystalline metals and alloys possess high strength and hardness [3], enhanced chemical reactivity [4] and excellent tribological properties [5]. These properties and performance enable nanocrystalline materials to be potentially very useful in developing new material families with much enhanced properties for engineering applications. The previous investigations on nanocrystalline materials mainly focused on their synthesizing and processing techniques, microstructural characterization, thermal stability, properties and performance. Although various kinds of synthesis techniques have been developed to produce bulk nanocrystalline materials, such as consolidation of ultra-fine powders prepared by various kinds of techniques [6], ball-milling and consolidation [7], severe plastic deformation of bulk metals [8], crystallization of amorphous solids [9] and electrodeposition [10], difficulties still exist in synthesizing the required 3-dimensional bulk nanocrystalline samples without porosity, contamination or other defects. Hence, the research and industrial application of bulk nanocrystalline materials are hindered, to some extent, by various difficulties in synthesis techniques.

In most cases, material failures occur on their surfaces, such as fatigue fracture, wear and friction, fretting fatigue and corrosion. These failures are very sensitive to the structure and properties of the material surface. Optimization of the surface structure and properties may effective enhance the global behaviors of a material and its service lifetime. With increasing evidences of novel properties in nanostructured materials, it is reasonable to propose to achieve surface modification by the generation of nanostructured surface layer so that the overall properties and behaviors of the material are significantly improved. Conventionally, a nanostructured surface layer can be obtained on a bulk material by mean of various coating and deposition technologies, such as PVD, CVD, sputtering and electrodeposition. One of the disadvantages for these techniques is that the bonding of the coated
layer with the matrix and bonding between the particles of surface layer is not strong enough, which eliminate these techniques from some industrial applications.

By means of surface severe plastic deformation, the size of the coarse grains in the surface layer of a conventional bulk material can be reduced down to the nanometer scale while its overall composition and/or phases keep unchanged. Gradient variations in microstructures from nano-sized, submicro-sized grains/subgrains of the surface layer to dislocation structures of deformation layer adjacent to strain-free matrix were obtained. We refer this kind of formation approach of surface nanostructured layer as to surface nanocrystallization of bulk materials [11-13]. This kind of surface modification will greatly enhance the surface properties without changing the chemical composition. It is also a flexible approach that makes it possible to meet specific structure-property requirements on surface of metallic materials.

The surface nanocrystallization in metallic materials can be achieved by means of various kinds of surface severe plastic deformation technique, including repeatedly impacts on metallic materials with high-speed balls driven by ultrasonic generator [12, 14], mechanical vibration [15-18] and air blast [19-22], high speed drilling [23], deep rolling [24], stirring wire-brushing on metallic materials [25, 26] and ball drop [27, 28]. The reported results mainly focus on the microstructures and mechanical properties of surface nanostructured layer.

In recent several years, pioneered by K. Lu and J. Lu, the investigations on microstructural evolution and mechanical properties of strain-induced surface nanostructured layer in various kinds of materials, including b.c.c. [12, 16], f.c.c. [14-15, 17, 29-31] and h.c.p. [32-34] metals and alloys, have been systematically carried out. Different grain refinement approaches and nanocrystalline formation mechanisms were identified in these deformed materials due to their different intrinsic nature and deformation modes. The grain refinement process involves dislocation activities, mechanical twinning and interaction of dislocations with mechanical twins. The properties of the surface layer were measured by means of hardness, tensile, fatigue and wear tests. The enhanced properties of the surface layer are mainly attributed to the strain-induced grain refinement. In the present work, we reviewed the investigations on the microstructures and properties of surface nanostructured layer.

2. Surface mechanical attrition treatment (SMAT)

Various surface plastic deformation processes have been developed to achieve a nanostructured surface layer in bulk coarse-grained materials [11-28]. Now we generally referred the techniques that achieve surface severe plastic deformation via mechanical attrition as to surface mechanical attrition treatment (SMAT) [11-17, 29-45]. These processes are based on surface dynamic plastic deformation induced by repeated impacts with high-velocity balls. The impacted balls are accelerated by collision between balls and a vibrating chamber. When the vibrating chamber is driven by an electric motor, the SMAT process is named as I-type SMAT. The research results on microstructures and properties of the surface layer treated by I-type SMAT can be found in [15-17, 29, 33-39]. When the vibrating chamber is driven by an ultrasonic generator, the SMAT process is named as II-type SMAT, for example ultrasonic shot peening (USSP) [12, 14, 30-32, 40-45]. For these processes, different devices were used to accelerate impacted balls and a wide range of kinetic energies was generated, which can induce different levels of surface plastic deformation on metallic materials.
Figure 1 shows a schematic illustration of the SMAT set-up. Spherical steel balls with smooth surface (or other materials such as tungsten carbide, glass and ceramics) are placed in a reflecting chamber that is vibrated by a vibration generator (electrical motor or ultrasonic generator), with which the balls are resonated. Typical ball sizes are usually selected to be 1-10 mm in diameter. The vibration frequency of the chamber is 50 Hz and 20000 Hz for I-type and II-type SMAT, respectively. The sample surface to be treated is impacted by a large number of flying balls over a short period of time. The velocity of the balls is 1-20 m/s, depending upon the vibration frequency, the distance between the sample surface and the balls. The impact directions of the balls onto the sample surface are rather random, which facilitate grain refinement of surface layer. Each impact induces high strain rate deformation in the surface layer of the sample, as schematically shown in Fig. 1b. The temperature rise on the impacted surface was measured to be between 50\(^\circ\)C and 100\(^\circ\)C for SMAT Fe sample, which varies with the intensity of impacts and the materials treated.

3. Microstructures of surface layer

A nanostructured surface layer in various pure metals (Fe [12, 16], Cu [29], Ti [32], Co [33]) and alloys (Al-alloy [15], Ni-alloy [40-41], Mg-alloy [34], stainless steel [17, 30], intermetallic compound [35]) have been achieved by means of SMAT. The grain size and thickness of nanostructured layer are dependent upon the processing conditions (such as the size of balls, velocity of balls, treatment duration, etc.) and the nature of treated materials (crystal structure, stacking fault energy and mechanical properties). Table 1 summarizes the minimum grain size of the top surface layer and the thickness of nanostructured layer for some typical SMAT samples. The minimum grain size of the top surface is about 10 nanometers and the thickness of nanostructured layer is several decade micrometers for most of SMAT samples tested. Due to the variations of SMAT-induced strains and strain rates along the depth, a gradient microstructure was usually obtained in the treated surface layer. Beneath the nanostructured layer, various deformation structures were induced in the SMAT samples due to the difference in their deformation modes. For the b.c.c. and f.c.c. metals with high stacking fault energies (SFEs), plastic deformation was mainly accommodated by dislocation glide, so that
various dislocation structures and subgrains/grains were formed during SMAT. With the increase in depth from the top surface, the size of refined structure (grains/subgrains/dislocation cells) gradually increases from nanometer to micrometer scale, for example the SMAT Fe [16] and Al alloy [15]. While for low SFE f.c.c. metals [17, 40-41] or h.c.p. metals [32], strain-induced mechanical twins play an important role in plastic deformation. Therefore, parallel twin/matrix lamellae or regular blocks derived form the intersection of mechanical twins were usually found in the SMAT Ni-alloy [40-41], stainless steel [17] and pure Ti [32]. The following section will introduce typical gradient microstructures of the SMAT samples in detail.

Table 1. The minimum grain sizes ($D_{\text{min}}$) in the top surface layer and the thickness of nanostructured layer (grain size < 100 nm) in some typical materials subjected to SMAT.

<table>
<thead>
<tr>
<th>SMAT Material</th>
<th>Frequency</th>
<th>Time</th>
<th>$D_{\text{min}}$</th>
<th>Thickness</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>50 Hz</td>
<td>60 min</td>
<td>7 nm</td>
<td>15 μm</td>
<td>[16]</td>
</tr>
<tr>
<td>Cu</td>
<td>50 Hz</td>
<td>30 min</td>
<td>10 nm</td>
<td>25 μm</td>
<td>[29]</td>
</tr>
<tr>
<td>Ti</td>
<td>20000 Hz</td>
<td>60 min</td>
<td>50 nm</td>
<td>50 μm</td>
<td>[32]</td>
</tr>
<tr>
<td>AISI 304 Stainless steel</td>
<td>50 Hz</td>
<td>15 min</td>
<td>8 nm</td>
<td>30 μm</td>
<td>[17]</td>
</tr>
<tr>
<td>7075 Al alloy</td>
<td>50 Hz</td>
<td>15 min</td>
<td>20 nm</td>
<td>22 μm</td>
<td>[15]</td>
</tr>
<tr>
<td>AZ91D alloy</td>
<td>50 Hz</td>
<td>20 min</td>
<td>30 nm</td>
<td>100 μm</td>
<td>[34]</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>20000 Hz</td>
<td>12 min</td>
<td>10 nm</td>
<td>12 μm</td>
<td>[41]</td>
</tr>
</tbody>
</table>

3.1 Gradient structures with grains/subgrains and dislocation structures. Iron is a typical b.c.c. metal with a high SFE of about 200 mJ/m². Nanostructured grains were obtained in the surface layer of bulk Fe samples subjected to SMAT [12, 16]. Figure 2 shows the TEM images and statistical grain size distribution for the SMAT-Fe sample treated for 60 min. The microstructure of the top surface is characterized by ultra-fine equiaxed grains with random orientations, as indicated by the SAED pattern. The histogram of grain size distribution obtained from the dark-field images was characterized by a normal logarithmic distribution with a narrow size distribution. The average grain size of top surface layer is as small as 10 nm. The measured average grain (cell) size and the mean microstrain as a function of depth in the SMAT Fe sample by means of different analysis techniques (XRD, SEM and TEM) are summarized in Fig. 3. The microstrain determined from XRD analysis decreases significantly along the depth in the surface layer and gradually drops to zero at about 60 μm deep. Although no change in grain size and atomic-level micro-strain is detected, cross-sectional TEM and SEM observations showed the evidences of strain induced dislocation activities in even deep matrix (up to 110 μm deep). The size of the refined structures (grains, subgrains and dislocation cells) increases gradually from about 10 nm of top surface to several microns in the span adjacent to matrix. It is noted that the grains/subgrains in the span of 8-35 μm are elongated. In the deformation layer at low strains (60-80 μm deep from the top surface), typical strain-induced dislocation structures, such as dense dislocation walls and dislocation tangles, were formed. The dislocation walls are parallel to each other along main glide planes and separated with a uniform spacing. The misorientations across dislocation walls are usually smaller than 1°. In terms of the grain (or cell) size, the SMAT surface layer can be divided into four sections along the depth from the top surface: (1) nanostructured regime (0-15 μm); (2) submicro-sized regime (15-40 μm); (iii) micro-sized regime...
(40-60 µm); (iv) matrix with plastic deformation evidence (60-110 µm). The nanoscale grains, submicro-sized grains/subgrains and dislocation cell structures in sequences along the depth were also observed in other SMAT metals with a high SFE, such as Al-based alloy [15].

Fig. 2 Bright-field (a) and dark-field (b) TEM images, selected area electron diffraction (c) and statistic grain size distribution derived from TEM observations (d) of the top surface layer of SMAT Fe sample.
Fig. 3 Variations of the grain/cell size with the depth from the top surface of the SMAT Fe sample determined by means of XRD analysis, TEM and SEM observations.

3.2 Gradient structures with nanostructured grains and mechanical twins. For the Ni-based alloy with a low SFE, Inconel 600, cross-sectional TEM observations of the SMAT sample showed various types of microstructures in the surface layer, including randomly-oriented equiaxed nanocrystallites, mechanical nano-sized twins and planar dislocation arrays with the depth increasing [40, 41], as shown in Fig. 4. Below the nanostructured surface layer, the prominent feather of microstructure is mechanical twins instead of submicro and micro-sized subgrains as observed in the SMAT-Fe and Al-based alloys. These mechanical twins are parallel to each other, and their thicknesses are usually several to decades nanometers. The length of these twins is several hundred nanometers. High density of dislocations exists at twin boundaries and inside their inner, typical of deformation twins. Planar dislocation arrays instead of dislocation cells are formed in the plastic deformation regime adjacent to the strain-free matrix.

Fig. 4 Variation of grain size with the depth from the top surface for the SMAT Inconel 600 sample (NC presents nanocrystallites).
For the SMAT AISI 304 stainless steel, strain-induced grain refinement and martensite transformation take place in the top surface layer during SMAT, of which the microstructure is totally composed of $\alpha'$ martensite phase nano-sized grains with random orientations. The grain size is in the range from 8 to 60 nm with a mean value of about 30 nm. With increasing the depth, the grain size obviously increases and the grain orientations between adjacent grains become less random. In addition to $\alpha'$ martensite phase, the austenite phase could also be detected in the deep surface layer. At the depth of 30-40 $\mu$m deep from the treated surface, lamellar structures, typically less than 100 nm in width, are formed, which is derived from the evolution of nano-sized mechanical twin. At the depth of 100 $\mu$m, submicro-sized regular-shaped blocks with straight boundaries were obtained, resulting from intersection of mechanical twins. Some of these blocks are b.c.c. martensite phase. The intersection of two sets of mechanical twins induces the transformation of austenite phase into martensite phase. The size of martensite phase grains is dependent upon the thickness of intersecting twins. Different from SMAT Fe and Inconel 600, intersection of mechanical twins in two directions is usually observed in the deformation layer adjacent to matrix, as shown in Fig. 5.

![Cross-sectional TEM image of the microstructure at the depth of about 150 $\mu$m in the AISI 304 sample.](image)

**Fig. 5** Cross-sectional TEM image of the microstructure at the depth of about 150 $\mu$m in the AISI 304 sample.

### 4. Grain refinement mechanism

In order to understand the grain refinement process of the SMAT samples during the treatment, systematic investigations on the microstructure of the surface layer at different levels of straining are performed. As the strain decreases from maximum at the top surface layer to zero in the matrix, the structural evolution during the SMAT could be signed by the microstructure characteristics (with different stains) at different depths from the top surface to deep matrix. The microstructural evolution and formation mechanism of nanostructured materials were systematically investigated in [12-17, 29, 32-34]. Different grain refinement approaches and nanocrystalline formation mechanisms were identified in these deformed materials due to different material natures. Among these deformed materials, typical mechanisms for grain refinement will be introduced in the following section.

#### 4.1 Deformation via dislocation slip

Detailed cross-sectional TEM observations of the SMAT-Fe showed that the grain refinement process involves the following elemental process [16]:

1. Development of dense dislocation walls (DDWs) and dislocation tangles (DTs). Plastic deformation in the SMAT-Fe is accommodated by dislocation slip. In order to accommodate plastic deformation, various dislocation activities are normally motivated, including generation, accumulation, annihilation and rearrangement. Strain-induced numerous dislocations would form DDWs along (110) slip planes and DTs in original coarse grains depending on the grain orientations.
so that the original grains were divided into structure blocks separated by DDWs and DTs. DDWs are believed to result from dislocation accumulation and rearrangement for minimizing the total energy state. The repeated multi-directional impacts on the treated surface may lead to a change of slip systems with the strain path even inside the same grain. The induced 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 original coarse grains could be divided more efficiently by the DDWs and DTs during SMAT.

Fig.6 A schematic illustration of grain refinement for SMAT Fe.

(2) Transformation of DDWs and DTs into sub-boundaries with small misorientations. When the dislocation density is up to a certain value, dislocation annihilation and rearrangement occur in DDWs and DTs for decreasing the total system energy. This process transforms DDWs and DTs into subboundaries with sharp boundaries and increasing misorientations, which separate individual cells.

(3) Evolution of subboundaries to highly-misoriented grain boundaries. The misorientations of the subgrains with respect to their neighboring subgrains become gradually larger with further increasing strain. Subgrain boundaries evolve into highly-misoriented grain boundaries. The increment of misorientations between neighboring grains can be realized by accumulating and annihilating more dislocations in grain boundaries, or alternatively, by rotation of grains and/or grain boundary sliding with respect to each other when strain are enough large. The grain rotation process would be facilitated when the grain size is reduced due to the obvious size effect.
With further increasing strain, DDWs and DTs could form inside the inner of the refined subgrains or grains. These refined grains could be further subdivided following the similar refinement process. With strain increasing, the grain subdivision carries out on a finer and finer scale. When dislocation multiplication rate is balanced by the annihilation rate, the further increment of strain could not reduce the subgrain size any longer so that a stabilized grain size is obtained. The grain refinement process in SMAT Fe can be schematically illustrated in Fig. 6.

For the SMAT Cu (SFE 78 mJ/m\(^2\)), two different grain refinement approaches were identified in the surface layer due to different levels of deformation strain rate [29]. In the deformation layer with low strain rates, grain refinement is primarily achieved via formation and evolution of dislocation cells. Figure 7 shows typical cross-sectional bright-field TEM images and corresponding selected area electron diffraction (SAED) patterns at different depths from the topmost surface of the Cu sample treated for 5 minutes (SMAT-5 Cu). Adjacent to the strain-free matrix, high-density dislocations are generated by plastic deformation and these dislocation are arrayed in tangles. With the strain increasing, dislocation cells were formed in original grains. From the corresponding SAED pattern, it can be found that the misorientations between the adjacent dislocation cells are negligible. With the strain further increasing, dislocation cell walls become thinner and the cell size gradually decreases. Meanwhile, small misorientations between the adjacent dislocation cells were induced. The minimum size of dislocation cells is usually between 200 and 100 nm. Formation of dislocation cells in deformed structures is driven by minimizing the total free energy of high density of dislocations when the level of dislocation density increases to a certain value. Formation of equiaxed or elongated dislocation cells in copper during plastic deformation, such as cold rolling and ECAP, is commonly seen [46, 47], and the final size of dislocation cells are in the submicrometer scale. With the treatment time increasing, the spans of the DCs and grains in SMAT-30 are much larger than those in the SMAT-5 sample. Compared with SMAT-5 Cu at the same depth, the sizes of DCs and grains in SMAT-30 obviously decrease, and the boundaries are better developed. The steady-state size of refined grains evolved from dislocation cells is usually larger than 100 nm.

Fig. 7 Typical TEM images (A) and the corresponding SAED patterns (B) showing the microstructures at different depths from the topmost surface in SMAT Cu sample treated for 5 min.
4.2 Deformation via dislocation slip and mechanical twinning. For the top surface layer of SMAT Cu with high strain rates, mechanical twinning becomes main deformation mode. Nano-sized thick mechanical twins were formed in the SMAT-5 Cu. Dislocations and steps are seen at twin boundaries. The lengths of mechanical twins are about several hundred nanometers. Within initial coarse grains, multiple twins are formed and their density varies from grain to grain due to different crystallographic orientations of the grains. Apparently, formation of these high-density nanoscale twins induces a large number of twin boundaries subdividing the original coarse grains into lamellar nanocrystallites with special crystallographic orientations. High-density dislocations are found inside these twins and matrix, but dislocation cell structures could not be identified in this regime. Dislocation walls formed inside some twins are found to perpendicular to twin boundaries with a spacing of several decades of nanometers, as seen in Fig. 8. An obvious change in orientation of the twin boundary is identified at the section of twin boundaries and dislocation walls.

Fig. 8 A TEM image showing formation of dislocation walls (as indicated by arrows) inside twin lamellae in SMAT Cu.

A cobalt sample with a dual phase structure of h.c.p. and f.c.c. is subjected to SMAT, in which different grain refinement processes for both crystal structures were found [33]. For h.c.p. phase at a low strain, the deformation is accommodated mainly by \{10\bar{1}1\} deformation twinning. The \(\{\bar{1}120\}\) \{1\bar{1}00\} prismatic and \(\{11\bar{2}0\}\) (0001) basal slip starts to operate with increasing strain, which leads to the formation of low-angle dislocation grain subboundaries. Simultaneously, the misorientations between subgrains increase with strain. The process of grain subdivision may proceed successively to a finer and finer scale with strain, resulting in the formation of ultra-fine crystallites and nanocrystallites. Moreover, nanocrystalline grains could nucleate directly at the grain boundaries or triple junctions by dynamic recrystallization mechanism. For f.c.c. phase at low strains, the deformation was accommodated by the slip of dislocation, forming intersecting planar arrays of dislocation. With increasing strain, mechanical twins play an important role in plastic deformation. With further increased strain, the \(\gamma\rightarrow\varepsilon\) transformation occurred with orientation relationship: \((0001)_\varepsilon/\langle111\rangle_\gamma\) and \((11\bar{2}0)_\varepsilon/\langle110\rangle_\gamma\). The h.c.p. platelets developed on the \{111\} planes of the f.c.c.
AISI 304 stainless steel is a widely used engineering material with an f.c.c. austenite structure and a low SFE of about 17 mJ/m$^2$. Due to less slip systems, plastic deformation is mainly dominated by deformation twinning. The grain refinement process obviously differs from the SMAT-Fe sample. The grain refinement involves in the following process [17]:

1. Formation of planar dislocation arrays and mechanical twins. The strain-induced dislocations in the austenite phase slip mainly on their respective \{111\} planes, forming regular planar dislocation arrays, instead of dislocation cells (as in f.c.c. Al-based alloys and copper) or dense dislocation walls (as in b.c.c. Fe). A large separation between the partial dislocations in a 304 stainless steel due to a low SFE make it difficult for partial dislocations to cross-slip, which cause dislocations to arrange themselves into planar arrays on their primary slip planes.

2. Grain subdivision by mechanical twins and martensite transformation. The formation of mechanical twins introduces twin boundaries to subdivide the deformed grains. Parallel twins in one direction divide the grains lamellar twin-matrix alternative blocks separated by twin boundaries. Obviously, two sets of mechanical twins are activated to accommodate the plastic deformation, and the interactions of twins become natural, which will produce rhombic blocks. A strain-induced martensite transformation is a prevailing phenomenon in the plastic deformed AISI-304 stainless steel. In the SMAT-304 stainless steel, the formation of martensite phase was found at interactions of the twins, of which the size is in the range from several nanometers to submicrometers. XRD and TEM experimental results showed that nearly 100% volume martensite phase was produced in the top surface layer.

3. Formation of nanocrystallites. In the top surface layer, the high strain and strain rate may activate a high density of multi-system mechanical twins to accommodate the extremely deformation. The induced twin thickness is much reduced down to the nanometer scale. These nano-scale thick twin-twin intersections could subdivide the original grains into nano-scale blocks with a special shape. Analogous to other metals and alloys, randomly-oriented nanocrystallites are formed through grain rotation and/or grain boundary sliding with plastic deformation processing.

Titanium is a typical h.c.p. metal, in which only four independent slip systems make mechanical twinning prevalent in SMAT Ti sample [32]. Repeated multidirectional loading and increasing strain facilitate the initiation of different twin system, leading to the intersection of twins. Twin intersections rapidly reduce the microstructure scale. The presence of a large number of twins and their intersections hinder dislocation activities, and more dislocations exist at twin boundaries across which small misorientations were induced. With increasing strain, the microstructure of twin/matrix lamellae could be subdivided into dislocation cells or low angle disoriented blocks. The subsequent rotation recrystallization may play an important role in the final grain refinement mechanism.

Generally, dislocation slip dominates deformation process in a wide range of plastically deformed materials with high SFEs. As described above, for the SMAT b.c.c. and f.c.c. metals with high SFEs, such as Fe and Al alloy, coarse grains are refined upon continuous straining by various dislocation activities. The grain refinement process includes [16, 29]: (i) manipulation of lattice dislocations; (ii) formation of dislocation cells and/or dense dislocation walls that subdivide the original coarse grains into refined blocks; (iii) transformation of the dense dislocation walls or cell walls into sub-boundaries; (iv) evolution of sub-boundaries into conventional grain boundaries with large misorientations (or sharpening of grain boundaries).

The materials with low SFEs favor mechanical twinning, especially at high strain rates and/or at low temperatures. For the SMAT h.c.p. and f.c.c. metals with low stacking fault energies, such as Ti [32], Inconel 600 [40] and stainless steel [17], mechanical twinning and dislocation slip dominate the deformation process. The basic processes of grain refinement can be schematically illustrated in Fig. 9. As shown in step 1, formation of high-density parallel twins with a single direction introduce a large amount of twin boundaries to divide the original coarse grains into lamellar twin/matrix alternate blocks. In SMAT Inconel 600 [40], dislocation activities become functional inside twin/matrix
alternate blocks for accommodating further plastic deformation when formation of mechanical twins becomes more difficult within the thin lamellae. For minimizing the strain energy, dislocations in the thin twin-matrix lamellae arrange themselves into dislocation walls (Step 2A). With increasing strain, dislocation walls evolve into subgrain boundaries, which subdivide lamellar twin/matrix alternate blocks into equiaxed nanometer-sized blocks with misorientations (Step 3). In SMAT Ti, Co and stainless steel, twin-twin intersections could divide the initial coarse grains into rhombic blocks with changed orientations and bordered by large-angle boundaries (step 2B and 3).

Fig. 9 A schematic illustration of grain refinement in the materials with plastic deformation accommodated by mechanical twins and dislocations during SMAT.

Formation of randomly orientated nanocrystallites requires substantial variations of misorientations in the adjacent subgrains and in those regular oriented nanometer-sized blocks (Step 4 in Fig. 9). Possible mechanism responsible for the formation of random orientations may involve in grain boundary sliding and/or grain rotation. When the grain size is reduced down to the nanometer...
scale, the grain rotation and grain boundary sliding will be much easier with respect to their coarse grains, which results in the formation of randomly oriented nanocrystallites [48, 49].

5. Properties and performance

5.1 Hardness and tensile strength. Mechanical property measurements of the SMAT samples showed a significant increment in hardness and tensile strength for the surface layer with nanostructures [36-38, 42-45]. Figure 10 shows a variation of hardness along the depth from the treated surface as obtained from nanoindentation tests in the SMAT Fe sample [36]. Obviously, the maximum hardness of 3.8 GPa is obtained at the top surface in the sample, which is nearly twice that for the coarse-grained matrix. The hardness gradually decreases and tends to a stable value of 2.0 GPa at the depth of 60 µm. In the matrix with coarse grains, the hardness value obtained from the nanoindentation with the same measurement parameters is about 2.0 GPa. There is no change in hardness profile after the sample was annealed 593 K for 60 min for removing residual stress effect, which indicated that the high hardness in the surface layer is not resulted from the induced residual stress during SMAT. After annealing at 923 K for 60 min for crystallization of the nanostructures and formation of coarse grains, the hardness of surface layer drops down to that of coarse-grained matrix. These results showed that the hardness increment results from grain refinement into the nanometer scale, instead of the alloying (contamination) effect during the SMAT.

![Fig. 10 Measured hardness values as a function of depth from the treated surface for the SMAT and subsequent annealing (at 923K for 120 min) Fe samples.](image)

The tensile results of the SMAT-Cu surface layer showed that nanostructured Cu exhibits a yield strength as high as 760 MPa and the stress peaks at 790 MPa [37]. Nevertheless, its ductility is very low, less than 3% total strain. The high strength is consistent with the small nanocrystalline grain size with high-angle grain boundaries, and its yield strength is in fact close to the Hall-Petch relationship prediction for Cu. Unstable tensile deformation and fracture occurred at small strains due to little work hardening.
Uniaxial tensile true stress-strain curves of the nanostructured surface layer and the coarse-grained 316L stainless steel are shown in Fig. 11 [42]. It is obvious that nanostructured sample exhibits a much higher strength compared with its coarse-grained counterpart. The yield strength (0.2% offset) is as high as 1450 MPa, being about 6 times that of coarse grained sample, and the ultimate tensile strength is 1550 MPa. The plasticity is much decreased for the nanostructured sample with an elongation-to-failure of about 3.4%. The strain hardening exponent (n) for samples can be derived by fitting the equation $\sigma = K \varepsilon^n$ to the uniform plastic deformation stage of the true stress-strain curve well beyond the yield point. The $n$ value of the nanostructured sample is fitted to be 0.072, much smaller than that of the coarse-grained sample ($n = 0.385$). The surface layer of SMAT sample with nanostructured grains tends to lose work hardening during deformation due to their very low dislocation storage efficiency inside tiny grains. At the same time, the weak strain hardening also indicated that some lattice dislocation accumulation occurred during plastic straining before fracture.

![Fig. 11 Tensile true stress-strain curves for the nanocrystalline and the coarse grain 316L stainless steel sample. Insert shows the geometry of the tensile specimen.](image)

The tensile test of the SMAT 316 stainless steel with a coarse grained matrix was also performed, of which the top surface is a nanostructured layer of about 10 µm and the total thickness of tensile sample is 1 mm. The SMAT sample exhibits a very high tensile strength: the yield strength is as high as 550 MPa. Compared with the untreated sample (280 MPa), the yield strength of the SMAT sample rises by 96%. The reason may be that the strain-induced nanostructured layer enhances the strength and rigidity of the surface so that the initiation and propagation of cracks and defects are prevented. In addition, the top surface layer with high rigidity and strength could block the movement of the dislocations out of the material surface during plastic deformation, which inhibits the formation of slip bands on materials surface [43].

5.2 Fatigue properties. The fatigue tests of the SMAT stainless steel showed that the fatigue strength of the nanostructured stainless steel is considerably increased compared with the untreated sample [44]. The SMAT process with 3 mm diameter shots improved the fatigue endurance limit by 21%, which larger than that with 2 mm diameter shots. The increment of the fatigue strength for the SMAT samples treated with 3 mm shots is obvious for both low and high amplitude stress regimes, which is due to high yield strength and good ductility induced by SMAT. The localized plastic...
deformation in the surface layer results in the formation of high compressive residual stress and grain refinement of the microstructure, which enables the surface layer to resist against fatigue ignition and propagation. The consequent annealing of the SMAT stainless steel further improves the fatigue strength by about 5% compared with the SMAT sample. This may be due to the enhanced ductility from annealing induced recovery.

5.3 Wear and friction. The experimental results showed that the wear and friction properties of the SMAT samples are obviously improved compared with their coarse-grained bulk counterparts [36, 38-39]. Considering the thin nanostructured layer, the tribological behavior of the SMAT Fe was investigated by means of nanoscratch tests. One nanoscratch includes three steps in the experiment. Firstly, the initial surface profile of the tested sample was prescanned by the indenter with very low load to record the initial surface profile. Then, nanoscratching was performed with a constant normal load on the indenter. During the scratching, the indenter depth could be detected and recorded by the depth sensing system. Finally, post-scanning was carried out by the indenter with very low load in order to record the indenter surface profile after elastic recovery of the plowing indentation. Figure 12 shows the scratching depth profile after 10 runs scratching as a function of scratching distance in the SMAT and original Fe samples. The negative displacements presented the scratching depth after 10 runs scratching and the positive displacements between 600 - 700 µm resulted from the accumulation of debris during the scratching. The maximum (about 6 µm) of scratching depth in the SMAT sample was within the thickness of nanostructured layer (15 µm). With the constant normal load of 400 mN, the scratching depth of the original sample was larger than that of the SMAT sample. Due to the wear loss being directly proportional to the square value of scratching depth, the wear volume loss caused by plowing for the original sample was much larger than that of the SMAT sample, which was also qualitatively indicated by the phenomenon that the height of debris accumulation in the original sample was larger than that in the SMAT sample. These results showed that the wear resistance of the SMAT sample was better than that of the original sample. The friction coefficient of the SMAT sample was lower than that of the original sample. The average value of friction efficiencies for the SMAT and original Fe samples are 0.47 and 0.53, respectively. The improvement of wear resistance and the decrease of friction coefficient for the SMAT sample may result from the increase of hardness in the nanostructured surface layer. In the harder surface layer of the SMAT Fe sample, the depth that the indenter indented into sample was smaller, which caused the scratching depth smaller. Meanwhile, smaller indenting depth reduced the friction force used to plow the sample. As a result, the friction coefficient of the SMAT sample was smaller than that of the original sample.

Fig. 12 Scratching depth profiles after 10 runs scratching as a function of scratching distance in the SMAT and annealed Fe samples.
The unlubricated friction and wear properties of the SMAT low carbon steel with a gradient variation in the grain size from nanometer to micrometer were investigated under room temperature [38]. Experimental results show that the load-bearing ability of the SMAT low carbon steel is obviously enhanced compared with that of its coarse-grained material. The friction coefficient and the wear volume loss of SMAT sample are evidently smaller than those of coarse-grained one. The enhanced wear and friction properties could be attributed to the hardening surface layer which reduces the degree of plowing and micro-cutting under the lower load and the degree of plastic removal and surface fatigue fracture under the high load, respectively. Similar results were also obtained in the SMAT pure copper [39].

6. Summary

A gradient microstructure on conventional coarse-grained matrix is obtained in metallic materials by means of SMAT technique, on which a nanostructured surface layer is formed. This kind of gradient microstructure provides a unique advantage to investigate strain-induced grain refinement process in a rather wide grain size range from micrometer to nanometer. In the previous studies, different grain refinement approaches and mechanisms for nanocrystalline formation were identified in those SMAT materials due to the difference in their intrinsic nature and deformation modes. They involve formation of dislocation cells or mechanical twinning, interaction of dislocations with mechanical twins. The SMAT samples facilitate the studies on the structure-property relationship of solid, especially grain size dependence of various properties in metals and alloys in the micro-nanometer regime. Enhancements in properties such as hardness, tensile strength, fatigue and wear resistance for the SMAT surface layer, especially nanostructured layer, provide a potential advantage in engineering application.

SMAT processing is simple and low-cost technique to produce a nanostructured surface layer. With the further development of this new technique and increasing evidences of enhanced properties in SMAT materials, formation of surface nanostructures via SMAT technique is expecting to upgrade conventional engineering materials in industrial applications.

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Reference