Formation of nanostructured surface layer on AISI 304 stainless steel by means of surface mechanical attrition treatment

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Abstract

A nanostructured surface layer was formed on an AISI 304 stainless steel with low stacking-fault energy by means of the surface mechanical attrition treatment (SMAT). The microstructure of the surface layer of the SMATed sample was characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and cross-sectional TEM observation was performed to reveal the deformation-driven grain refinement mechanism for the f.c.c. materials with very low stacking-fault energy during SMAT. The grain refinement process in the surface layer involves formation of planar dislocation arrays and twins in deformed grains, twin–twin intersections leading to grain subdivision and a martensite transformation as well, and formation of randomly orientated refined crystallites. The formation of nanocrystallites in the top surface layer was ascribed to the much large strain and strain rate, as well as the multidirectional repetitive loading.

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1. Introduction

Surface mechanical attrition treatment (SMAT) is a recently developed technique that can induce grain refinement into the nanometer regime in the surface layer of bulk materials [1]. This technique has been successfully applied in achieving surface nanocrystallization (SNC) in a variety of materials including pure metals, alloys and steels [2–6]. Preliminary experimental measurements indicated that the mechanical and tribological properties and performance of the materials could be significantly enhanced by means of the SMAT-induced SNC. The SMAT shows an alternative approach to effectively upgrade the global properties of engineering
materials without change of the chemical constitution. As the SMAT is simple and flexible, and therefore low-cost, this new technique is potentially very useful in industrial applications. Meanwhile, the SMAT also provides a unique opportunity to investigate the plastic deformation induced grain refinement process. Due to a gradient variation of the strain and strain rate from the treated top surface (both are extremely large) to the deep matrix (essentially zero), a gradient grain size distribution from a few nanometers (in the top surface layer) to several micron (in the deep matrix) are developed in the SMATed sample. One may examine the microstructure characteristics at different levels of strain and strain rate to reveal the underlying mechanism for grain refinement in the nanometer regime.

Understanding of the grain refinement mechanism is crucial for development of the SMAT. In our previous work, grain refinement mechanisms in a pure Fe [5] and an Al-alloy [6] subjected to the SMAT were examined. In those systems with relatively high stacking fault energy (SFE), obvious dislocation activities were found to dominate the grain subdivision process. As plastic deformation mode may change from dislocation slip to mechanical twins (especially under high strain rate and/or low temperature) for metals with a low SFE [7], different types of grain refinement mechanisms may be involved for materials with different SFEs.

In this work, we will study the grain refinement process in an AISI 304 stainless steel, of which the SFE is very low, being 16.8 mJ/m^2, which is much smaller than that for other f.c.c. metals such as Al (166 mJ/m^2), Ni (128 mJ/m^2), and Cu (78 mJ/m^2) [8]. The objective of this work is to reveal the grain refinement mechanism for the low-SFE metals. In addition, AISI 304 stainless steel is a widely used engineering material. The grain refinement mechanism plays an important role in development of the SMAT for the materials that is of technologically importance.

2. Experimental procedure

The material used in this investigation was an AISI 304 stainless steel plate (100 × 100 mm^2) with chemical compositions of (in wt%): 0.049 C, 18.20 Cr, 8.66 Ni, 0.58 Si, 1.04 Mn, 0.021 P, 0.007 S and balance Fe. Prior to the SMAT, the sample was annealed in vacuum at 1080 °C for 1 h. The typical microstructure of the as-annealed sample is shown in Fig. 1, in which the grain size is in a range of 100–200 μm, and annealing twins are visible in some grains.

The set-up and procedures of the SMAT were described in our previous paper [5]. In the present investigation, the SMAT to the AISI 304 stainless steel was performed under vacuum at room temperature for 15 min with a vibrating frequency of 50 Hz.

A Rigaku D/max-2400 X-ray diffractometer (12 kW) with Cu Kα radiation (λ_Kα1 = 0.154056 nm and λ_Kα2 = 0.154439 nm were reflected by a graphite crystal using the (0002) reflection) was used to determine the phase constitution and the mean grain size at room temperature. A standard SiO₂ sample was employed to calibrate the instrument line broadening, and the grain size and microstrain were calculated from line broadening of Bragg diffraction peaks by using Scherrer and Wilson method [9].

Scanning electron microscopy (SEM) observations were performed on a JSM-6301 field emission scanning electron microscope. The cross-sectional SEM specimen was first mechanically polished using diamond paste, and then electro-etched at room temperature in a solution of 10 g
oxalic acid and 100 ml refined water with a voltage of 10 V. The treatment makes it possible to observe the mechanical twins in the steel sample [10].

Transmission electron microscopy (TEM) observations were carried out on a Hitachi-800 transmission electron microscope with operating voltage of 200 kV. The plane-view TEM foils of the layers from different depths were obtained first by polishing the corresponding surface layer and then mechanically polishing the sample from the untreated side until the sample reaches about 30 μm thickness; and finally thinning by electrochemical polishing (in a solution of 10% perchloric acid and alcohol at room temperature) so that it is suitable for TEM observations. The cross-sectional TEM specimen was prepared as follows: (1) cutoff two pieces (1.1 × 1.1 × 10 mm³ in size) of the treated sample and bonded them face-to-face together; (2) put it into a 3 mm diameter copper tube and bonded them together; (3) slice the tube with the sample inside into thin sheets (0.5 mm thick) perpendicular to the axial-direction and mechanically thinned them carefully down to about 30 μm thick; (4) pre-thin the TEM discs near the bonding line by means of a dimple grinder; (5) finally thin the foil by means of ion-thinning with proper incident angles.

3. Results

3.1. Microstructure characterization of the nanostructured surface layer

Fig. 2 shows X-ray diffraction (XRD) profiles of the annealed and the SMATed samples. It can be found that the annealed sample consists of austenite (f.c.c. structure with a lattice parameter of 0.361 nm), while the as-treated one is composed of α' martensite only (b.c.c. structure with a lattice parameter of 0.2865 nm [11]). Clearly, a martensite transformation took place in the surface layer during SMAT. The Bragg-diffractional peak broadening in the SMATed sample may be attributed to grain refinement and/or an increase in the atomic-level lattice strain. Quantitative XRD measurements indicate that the average grain size in the top surface layer of the treated sample is about 11 nm, and the microstrain is neglectable.

Fig. 3 shows typical plane-view TEM observations of the top surface layer and layers at different depths from the treated surface. The microstructure of the top surface layer (Fig. 3(a)) is characterized by uniformly distributed nanometer-scale grains. The corresponding selected-area electron diffraction (SAED) pattern shows that these grains are martensites with random orientations, and no austenite is detected. The histogram of grain size distribution obtained from the dark field images is characterized by a normal logarithmic distribution with a narrow size distribution of 8–60 nm. The mean grain size is approximately 10 nm, which is very close to XRD measurement result. Shown in Fig. 3(b) is the microstructure of the subsurface layer at 15 μm deep. It can be seen that fairly larger grains are visible relative to the top surface. The corresponding SAED pattern illustrates that the orientations of these grains are random, but an austenite phase can be indexed in addition to the martensite phase. The histogram shows a rather broad grain size distribution of 8–140 nm with an average value of ~30 nm. In the subsurface layer at about 30 μm deep (Fig. 3(c)), large irregular-shaped grains are seen, of which the average size is about 60 nm. The diffusive diffraction spots in the SAED pattern are identified as both the martensite and the austenite, but with apparently small misorientations.
The above experimental results clearly illustrate that a nanostructured surface layer was developed in the AISI 304 stainless steel by means of SMAT. With an increasing depth, the grain size increases and the grain orientations become less random. A matensite transformation occurs in the SMATed AISI 304 stainless steel.

3.2. Microstructural evolution

3.2.1. SEM observations

Fig. 4 shows a cross-sectional SEM observation of the treated sample. Profuse mechanical twins are identified in the surface layer (about 300 µm thick), which is evidently different from that of the orig-
3.2. Cross-sectional TEM observations

Fig. 5 shows the microstructure at about 300 µm deep from the treated surface. The microstructure is characterized by planar dislocation arrays and stacking faults. The planar dislocation arrays in two directions intersect with each other by an angle of about 70.5° (the angle between two {111} crystallographic planes), forming dislocation grids. The spacing between dislocation arrays is in the range 200 nm–1 µm, depending upon the orientation of original grains. This configuration differs from the dislocation cells separated by dense dislocation walls observed in Fe sample [5] and dislocation cells in the Al-alloy [6] after the SMAT.

Fig. 6 shows a typical microstructure observed at roughly 150 µm from the treated surface. The SAED pattern shows well-defined diffraction spots, from which the direction of the incident electron beam is determined to be close to $\langle 011 \rangle$. This pattern is evidently a superposition of two sets of $\langle 011 \rangle$ diffraction patterns that are symmetrical with each other with respect to the {111} plane.
i.e., a typical f.c.c. twin system is identified. Intersections of mechanical twins in two directions result in submicron rhombic blocks, of which the size is close to the SEM observations. High densities of dislocations are still visible in the grains beside the mechanical twins. The density of twin was found to relate to the depth and grain orientations.

Fig. 7 shows a TEM observation at about 100 µm deep, showing regular-shaped blocks (submicron-sized) with straight boundaries, which are obviously resulted from intersection of mechanical twins. The corresponding SAED pattern shows that some of these blocks are of b.c.c. martensite phase. It means the α′ martensite phase is formed at intersections of two sets of mechanical twins, analogy to those observed in the AISI 304 stainless steel during the shock deformation [12] and balanced biaxial straining [13]. The size of martensite is dependent upon the size of twins operated, small mechanical twins may result in fine martensite, and here typical submicron-sized martensites are identified as indicated by the arrows.

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Fig. 8. The cross-sectional TEM observations ((a) bright field and (b and c) dark field images) with SAED patterns of the microstructure at about 30–40 µm deep from the top treated surface, showing ultrafine grains of austenite and martensite.

Fig. 9. The cross-sectional TEM observation of the typical microstructure at about several microns deep from the top surface of the SMATed sample.

refinement processes in other materials, such as pure Fe [5] and Al-alloy [6], we noticed several characteristic features in the present sample.

1. Formation of planar dislocation arrays and twins.
2. Grain subdivision and martensite transformation.
3. Formation of nanocrystallites.

4.1. Formation of planar dislocation arrays and twins

Apparently, strain-induced dislocations in the austenite phase (f.c.c.) slip mainly on their respective \{111\} planes, forming regular dislocation grids, instead of irregular dislocation cells (as in f.c.c. Al-alloy, Cu) or dense dislocation walls (as in b.c.c. Fe). This observation may be attributed to the low-SFE value of the present sample. Formation of dislocation cell structures needs dislocation slipping on intersecting planes, i.e., cross-slip. For a f.c.c. metal cross-slip is believed to perform by pinching of partial dislocations in their original slip planes and their subsequent extension on the cross-slip planes [14]. In other words, formation of dislocation cells require pinching of partial dislocation for cross-slip. For those metals with high SFE values, separation of dislocations is small, which facilitates partial dislocation pinching. So that a
large tendency for cross-slip of partial dislocations is resulted and dislocation cells are favorable in which the majority of dislocation resides in the cell walls and the interior of cell lacked dislocations [15]. On the contrary, a small SFE results in a large separation between the partials, which inhibits dislocation to cross-slip and causes dislocations to arrange themselves into planar arrays on their primary slip planes ([111] planes in the present sample), as shown in Fig. 5.

Additionally, twinning is another deformation process that is believed to compete with dislocation slip. Generally, slip dominates the deformation process as in a wide range of plastic deformed materials with medium-high SFE values. However, the critical shear stress for twinning decreases with the SFE value, i.e. materials with a low SFE favor mechanical twinning, especially, at high strain rates and/or at low temperatures [16]. In the present investigation, mechanical twins are the decisive feature of the SMATed AISI 304 stainless steel (Figs. 4 and 6). Owing to the increase of strain and strain rate at smaller depths, the density of twinning increases, which is similar to the observations in other low SFE materials [17,18].

4.2. Grain subdivision and martensite transformation

The formation of mechanical twins introduces twin boundaries in the deformed grains. A twin boundary is particularly simple case of periodic boundary or a ‘special’ boundary with a very high degree of coincidence, i.e., a low coincidence index $\Sigma = 3$, which can be viewed as a $60^\circ$ (111) twist boundary or a $70.5^\circ$ (110) tilt boundary. So, formation of mechanical twins introduces large-angle boundary to subdivide the deformed grains. Parallel twins in one direction results in lamellar twin-matrix alternative blocks separated by twin boundaries. When two sets of mechanical twins are activated to accommodate the deformation, twin–twin intersection will be inevitable to produce rhombic blocks (Fig. 6), and other shaped blocks with different sets of twin intersections.

Twin–twin intersection is a crucial point for grain subdivision process in the present sample. One of the mechanisms proposed to interpret the twin–twin intersection [19] is that the intersection is accomplished by the occurrence of secondary twinning (bordered by twin boundaries but with changed orientation) in the crossed twins, and the accommodation of the strain by the secondary twinning. Another type of model devoted to twin–twin intersections is based on a propagating disclination dipole [20,21], in which movement of the crossing twin before and after intersecting with an obstacle twin was represented by migration of a partial dislocation wall normal to itself, and the propagation of the crossing twin within the obstacle twin was represented by motion of the oppositely signed dislocation from the mid-plane of the dipole arms to the two limiting planes. During these processes, the intersected volume underwent a combined rotation of $38.9^\circ$ normal to the (111) shear plane and pseudo-shear of $2^{1/2}$. As a result, asymmetrical $\Sigma 9$ boundaries between the intersected volume and the obstacle twin were produced. Apparently, the mechanism mentioned above implies that the twin–twin intersection produces rhombic blocks with changed orientations and bordered by large-angle boundaries. These boundaries are quite different from the dislocation boundaries developed in other plastic deformed materials with medium-high SFEs [22], they are large-angle boundaries ($\Sigma 3$ and $\Sigma 9$ etc.) when they are formed, and not as dislocation boundaries need absorption of accommodation dislocations to increase their boundary misorientations.

A martensite transformation is a prevailing phenomenon in the plastic deformed AISI 304 stainless steel, and the transformation is believed to be a strain-induced process instead of stress-assisted [23]. Under such a circumstance, plastic deformation of the parent phase creates proper defect structures, which may act as embryos for the transformation product. Specifically, in austenitic stainless steels embryos of martensite were found to be formed at some of the intersections of microscopic shear bands including stacking faults, twins, and $\varepsilon$ martensites [24–26]. The martensite formation in AISI 304 stainless steel is strongly influenced by the strain state, strain rate and grain size. As reported in Ref. [27], the amount of martensite was found to increase with degree of deformation and a reduction of grain size of AISI 304 stainless
steel during rolling at room temperature. Hecker et al. [28] observed that at low strains, martensite formed more readily at high strain rates ($10^3$ s$^{-1}$) than at low ones ($10^{-3}$ s$^{-1}$). However, at true strains higher than 0.25, they noted an opposite situation that was attributed to adiabatic heating, which inhibits martensite formation.

In the present case of the AISI 304 stainless steel under SMAT, the martensite phases are formed at intersections of twins (Fig. 7). With a decrease of depth from the top surface, strain amplitude and strain rate increase accompanied by a significant reduction of grain size. All of these factors will, in terms of the previous studies, enhance the martensite transformation. In the top surface layer, nearly 100% volume martensite phase was produced as detected by XRD and TEM experiments. This observation is similar to that reported in the ball-milled AISI 304 stainless steel, in which nearly 100% volume martensite phase was formed after a longer milling time [29]. The similarity implies a comparable strain, strain rate and grain size in the top surface layer of SMAT-ed sample and the ball-milled powders.

Apparently, twin–twin intersections not only subdivide the original grains efficiently through introducing different boundaries ($\Sigma 3$, $\Sigma 9$, and other boundaries), but also induces a martensite transformation (introducing phase boundaries) leading to the formation of refined microstructures.

### 4.3. Formation of nanocrystalline

In the top treated surface layer of the AISI 304 stainless steel, nanometer-sized martensite grains with random orientations are formed. Formation of the nanocrystallites may be attributed to three distinct effects in the top layer: (1) a very large strain; (2) an extremely large strain rate (estimated to be about $10^3$–$10^4$ s$^{-1}$); and (3) multidirectional repetitive loading by shots. The remarkably increased strain and strain rate may activate a high density of multisystem mechanical twins to accommodate the straining. The thickness of the twins will be much reduced with the extremely high strain and strain rate, feasibly in the nanometer regime. These ultrafine twin–twin intersections may result in grain subdivision as well as a martensite transformation in the nanometer scale. The multidirectional repetitive loading may also facilitate formation of different twin systems, leading to mechanical twins intersecting not only with the current cooperative twin systems, but also with the previously generated mechanical twins. Obviously, these three effects in the top surface layer contribute cooperatively to the refinement of the original grains into the nanometer regime.

Formation of randomly orientated nanocrystallites from the refined blocks with related orientations require a substantial variation in orientations of the crystallites. Possible mechanism responsible for this process may include grain boundary sliding and/or grain rotation, as well as recrystallization via nucleation and subsequent growth in some cases. In situ TEM investigations on nanocrystalline thin film Au or Ag specimens [30] indicated the deformation occurred by grain boundary sliding that is similar to the behavior observed in coarse-grained materials at elevated temperature. Grain rotation is an alternative process upon straining that may effectively lead to high angle grain boundaries and randomly orientated crystallites [31]. It is noted that both processes (grain boundary sliding and grain rotation) will become much easier when crystallite size is reduced into the nanoscale. A very recent experimental investigation by means of the atomic-level observation of a b.c.c. Fe underwent mechanical milling [32] indicated a rotation mechanism, i.e., motion of a disclination dipole along grain boundaries that causes plastic flow accompanied by crystal lattice rotation behind the disclinations.

Recrystallization of heavily deformed crystalline structure with a high density of dislocations is possible via copious nucleation and subsequent growth, especially with adiabatic heating induced by high strain rates, resulting in formation of nanograins with random crystallographic orientations. Such a recrystallization process was supposed to be responsible for formation of nanograins in ball-milled Zn sample [33]. Nanocrystallization of amorphous alloys was also observed when the samples were subjected to mechanical working [34] or straining using controlled nanoindentation at room temperature [35]. These facts indicated that nucleation (and growth) of nanocrystals is
feasible in amorphous alloys when a mechanical straining is applied at certain conditions (even at room temperature). In the present case, formation of randomly oriented nanograins in the low SFE stainless steel via recrystallization process cannot be ruled out as both the strain and strain rate are very high at the sample surface. Nevertheless, no solid evidence is available so far for the support of any of the before-mentioned mechanisms in the present nanostructured sample. Intensive investigations are needed to clarify this important point that are in progress.

5. Summary

A nanostructured surface layer was synthesized on an AISI 304 stainless steel with a low SFE by means of the SMAT. Microstructure examinations indicated that the grain refinement process in this material involves: (1) formation of planar dislocation arrays and twins; (2) intersection of multidirectional twins leading to grain subdivision and a martensite transformation; and (3) formation of randomly oriented crystallites. Formation of nanocrystallites in the top surface layer may be attributed to the much large strain and strain rate, as well as the multidirectional repetitive loading.

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