A Comparison of Strengthening Mechanisms of Austenitic Fe-13Mn-1.3C Steel in Warm and Cold High-Pressure Torsion

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Abstract: A study on the role of deformation temperature on a twin-assisted refinement of austenitic structure and phase transformations in high-pressure torsion of high-Mn Hadfield steel single crystals (Fe-13Mn-1.3C, in mass. %) has been carried out. In high pressure-torsion, twinning has been experimentally confirmed as a high-temperature deformation mechanism and has been observed at the temperature 400 °C. An increase in deformation temperature of up to 400 °C decreases the activity of mechanical twinning but does not fully suppress it. A dense net of twin boundaries, which has been produced in cold deformation by high-pressure torsion at room temperature, possesses high thermal stability and stays untransformed after post-deformation annealing at a temperature of 400 °C. In high-pressure torsion at a temperature of 400 °C, the complex effect of high temperature and severe plastic deformation on the strengthening of high-carbon Fe-13Mn-1.3C steel has been observed. A synergetic effect of severe plastic deformation and elevated temperature stimulates a nucleation of nanoscale precipitates (carbides and ferrite) along with deformation-induced defects in austenitic structure. These fine precipitates are homogeneously distributed in the bulk of the material and assist high values of microhardness in high-pressure torsion-processed specimens, which is similar to twin-assisted microstructure.

Keywords: austenitic steel; high-pressure torsion; annealing; grain boundary; twinning; shear bands; particle strengthening

1. Introduction

Grain boundary engineering (GBE) proposed by T. Watanabe [1] is one of the most promising ways to increase constructional and functional properties of different metals and alloys by modifying their grain boundary assemble—distribution and characteristics of grain boundaries [2–5]. The grain boundary engineering of materials’ microstructure, including steels, could be effectively realized through a combination of severe plastic deformation (SPD) and post-deformation thermal treatments [1,6–8]. To date, a high-pressure torsion (HPT) has been successfully applied for obtaining ultrafine-grained and nanograin structures in a variety of metallic materials [9–11]. In this way, ultrafine-grained materials look very attractive due to superior strength properties but, having a high-volume fraction of intergranular boundaries, they simultaneously possess limited plasticity and thermal stability compared to coarse-grained counterparts [8,9,12].

GBE could be the possible way to make the ultrafine-grained materials more stable against recrystallization during post-deformation heat treatment, via producing of low-energy coherent special boundaries, for instance, twin-assisted Σ3n boundaries [13–16]. For nanotwinned 330SS (stainless steel), Zhang and Misra [13] demonstrated a superior thermal stability of coherent twin boundaries, as
compared to ordinary high-angle boundaries (general type). For deformation-induced nano-twins, an extremely high thermal stability up to 800 °C in 316SS [14] and to 625 °C in TWIP steel [7] was reported. An accumulation of low-energy Σ3n twin-assisted boundaries can give rise to remarkable properties, such as high strength, low rates of grain boundary sliding during creep, resistance to high temperature fracture, high resistance to corrosion and stress corrosion [17].

Twinning is one of the major deformation mechanisms, along with dislocation slip and phase transformations ($\gamma \rightarrow \epsilon$, $\gamma \rightarrow \alpha'$), which all contribute a work hardening of TWIP/TRIP austenitic steels (TWIP—twinning induced plasticity, TRIP—transformation induced plasticity) during plastic deformation, including HPT-processing [1,12]. Plastic deformation by twinning can play a crucial role in structural refinement of the materials [15]. The realization and activity of mechanical twinning in austenitic steels depend on their stacking fault energy (SFE), deformation temperature, strain rate, amount of pre-strain, grain size, crystal orientation or specimen texture, precipitates or dispersed phases, etc. [18–22] Although the formation of deformation twins enhances the strength properties of TWIP-steels, it usually greatly reduces their ductility [23–25].

The influence of HPT (6 GPa, up to 10 revolutions) on microstructure of a high-manganese Fe-24Mn-3Al-2Si-1Ni-0.06 C steel was performed by Matoso et al. [26] They noted the pronounced twinning in the early stages of deformation, but after one full revolution of HPT-deformation, the mechanical twinning was exhausted and other deformation mechanisms was responsible for further refinement of the microstructure. Limited data exist about microstructural characterization of HPT-processed high-interstitial austenitic TWIP-steels, in which mechanical twinning is the dominating deformation mechanism [26–30]. Previous investigations of Fe-10Mn-0.71C, Fe-4.3Mn-1.12C TWIP-steels, including Hadfield steel (Fe-13.44%Mn-1.2C), have demonstrated that their HPT-assisted microstructure contains high dislocation density, twins and stacking faults, which all contribute high values of microhardness of 6–11 GPa [29]. For Fe-17Mn-1.8Al-0.65C steel [31], HPT (6 GPa, 0.125, 0.5, 1 revolutions) results in formation of the ultrafine-grained microstructure with a high density of twin boundaries, which provides high yield strength of 1700 MPa. Astafurova et al. [27] have demonstrated that cold deformation by rolling and high-pressure torsion (5 GPa) of Fe-13Mn-1.0C single crystals causes a high strengthening effect due to intensive mechanical twinning (700 HV after rolling (ε ~ 1.4) and 780 HV after HPT for 3 revolutions, deformation at room temperature) [27]. Later, Astafurova et al. investigated the single-crystalline Fe-13Mn-1.3C (Hadfield steel), Fe-13Mn-2.7Al-1.3C, and Fe-28Mn-2.7Al-1.3C (in %) austenitic steels with different SFEs after cold high-pressure torsion (5–6 GPa, up to 5 revolutions, room temperature). They have reported that, independently of SFE, mechanical twinning is the basic deformation mechanism responsible for the high strengthening (640–780 HV) and rapid generation of an ultrafine-grained microstructure with high volume fraction of twin boundaries in these steels with high interstitial content.

Despite the high hardening effect of twin-assisted ‘special boundaries’, the influence of processing temperature and post-deformation anneal on twinning-assisted microstructure and mechanical properties of high-Mn TWIP steels has not been studied in sufficient detail. Recently, researchers use several approaches to find the best combination between strength and ductility, based on the thermal stability of SPD-induced twins in TWIP steels. Bouaziz [23] has reported that the combination of plastic deformation (rolling) and annealing at 500 °C (to reduce a dislocation density between deformation-induced twin boundaries) is an effective way to obtain the excellent combination of an yield stress and a work-hardening rate in Fe-22Mn-0.6C TWIP steel. For Fe-25Mn-2.91Si-3.58Al-0.091C TWIP steel, Wang [17] has shown that partially recrystallized nanostructured samples of austenitic steel, of which the microstructure contains nanotwinned grains, exhibit an enhanced strength-ductility synergy, as compared to the samples with deformation-assisted microstructure. The same strategy was performed for cold-rolled Fe-31Mn-3Al-3Si TWIP steel by Son with co-authors in [4]. Another possibility to achieve a better combination of the yield strength and ductility in TWIP steels in SPD is to elevate the deformation temperature and, consequently, vary the ratio of twinning and dislocation glide activities. With this method, the balance between strength and ductility was reached in an ultrafine-grained
microstructure of a Fe-22.3Mn-0.19Si-0.14Ni-0.27Cr-0.61C TWIP steel, due to formation of deformation microbands and twins during equal channel angular pressing at elevated temperatures (200 °C, 300 °C, and 400 °C) [32].

In the work presented herein, we have pursued an experimental study on the role of deformation temperature on twin-assisted deformation, microstructure, phase composition and microhardness of high-Mn Hadfield steel and have evaluated the complex and separate effects of a high temperature and severe plastic deformation (HPT) on the strengthening of high-carbon TWIP-steel. We utilized single crystals to avoid the effect of pre-deformation grain boundaries to the strain hardening and microstructure of the steel.

2. Materials and Methods

A high manganese Fe-13.4Mn-0.6Cr-0.2Ni-0.8Si-1.3C (in mass. %) steel, also known as Hadfield steel, was chosen as an object of investigation. Steel single crystals were grown in an inert gas atmosphere using a Bridgman technique (by Professor Yu.I. Chumlyakov, Tomsk, Russia) [33]. A single crystalline bullet in the form of a cylinder with a diameter of 40 mm and height of 20 mm was homogenized in an argon atmosphere at 1100 °C K for 24 h, solution-treated at 1100 °C for 1 h-exposure and quenched into water at room temperature.

Disks with a diameter of 10 mm and a thickness of 0.7 mm were cut from the central part of the solution-treated single crystalline billet using an electrical discharged machine EDM DR 7750 (JIANGZHOU CNC MACHINE TOOL MANUFACTURE Co., LTD., Taizhou, China). The surfaces of the disks were cut parallel to the [001]-type and [335]-type planes of austenite. To avoid any processing-affected surface layers, discs were mechanically grinded and electrolytically polished in a supersaturated solution of chromium anhydride (CrO$_3$) in phosphoric acid (H$_3$PO$_4$). Then, the discs were subjected to HPT at different temperatures: one portion was processed at room temperature (HPT$_{23}$) and another one at a temperature of 400 °C (HPT$_{400}$). Independently on deformation temperature, HPT-processing was performed for five full revolutions using a pressure of 6 GPa and anvil rotation rate of 1 rotation per minute. Five specimens were obtained for each deformation temperature. Additionally, some specimens were HPT-processed at temperature 400 °C for 1, 2 and 3 full revolutions for study a microstructure evolution (two specimens for each treatment). After HPT$_{23}$ and HPT$_{400}$ processing, part of the specimens was additionally annealed in a helium environment at a temperature of 400 °C for 1 h. The temperature 400 °C for HPT-deformation and for anneal was chosen to avoid any phase transformations associated with a heating of the specimens [34].

A standard procedure was followed to prepare the surfaces of the specimens for investigation of microstructure, phase composition and microhardness. It included the mechanical grinding and electrolytical polishing in a supersaturated solution of chromium anhydride (CrO$_3$) in phosphoric acid (H$_3$PO$_4$). For a microstructural analysis, a transmission electron microscopy (TEM) was performed using a JEM 2100 microscope (Tokyo Boeki Ltd., Tokyo, Japan), with an accelerating voltage of 200 kV. The foils for TEM study were cut from the HPT-processed disks and electrochemically polished using a Tenupol-5 (Struers GmbH, Ballerup, Denmark) unit (in the supersaturated solution of chromium anhydride (CrO$_3$) in phosphoric acid (H$_3$PO$_4$), U = 20 V, 60 °C). TEM observation areas were located next to the middle of the HPT-disks’ radius. The average sizes and volume fraction of the microstructural elements (fragments, twins, shear bands, particles) were determined using dark-field TEM images. The microstructure of the specimens was also analyzed using a Quanta 600 FEG scanning electron microscope (FEI, Hillsboro, OR, USA), equipped with an electron back scattered diffraction (EBSD) unit. The step size was 0.4 µm, three phases (austenite, ferrite, iron carbide) were included for identification during data collection. The visualization of EBSD data was performed with a TSL OIM Analysis 6.2 software (EDAX, Draper, UT, USA); no cleaning of the EBSD-maps was used. A Shimadzu XRD-6000 X-ray diffractometer (SHIMADZU Corp., Tokyo, Japan) with Cu-K$_\alpha$ radiation was utilized for the X-ray diffraction (XRD) studies. A 2θ angle range from 40° to 100° was selected.
The Vickers microhardness of the steel was measured using a Duramin 5 tester (Struers GmbH, Ballerup, Denmark) at a load of 200 g, in accordance with ASTM E384-11. The microhardness values of 50 measurements made on the middle radius of the disk for each sample were averaged. The radial distributions of microhardness were also constructed for each processing regime (HPT and post-deformation annealing).

3. Results

3.1. A Comparison of the Microstructures Produced by HPT-Processing at Room Temperature and 400 °C

Figure 1 represents a typical TEM microstructure of the HPT23-deformed specimens. Under cold HPT, single crystals of Hadfield steel undergo fragmentation, due to formation of a high dislocation density, twins and localized shear bands (SB). The detailed description of strain-dependent evolution of the microstructure in this steel in cold HPT was previously described in [28].

TEM data testify to the high density of twin boundaries ($\rho_{tw} = 25 \times 10^{13} \text{ m}^{-2}$ [28]), which are homogeneously distributed in the specimens. Typically, at least three active twin systems with the thickness of lamellae 10–100 nm are observed in TEM images (two of them are interpreted in Figure 1). The formation of a coarse net of twin bands (each consisted from thin twin lamellae in one
system) leads to fragmentation of initial single crystalline microstructure by \( \Sigma 3^n \) ‘special’ boundaries. The areas between twin boundaries are filled with thin secondary twins and perfect dislocations (Figure 1). Complex TEM contrast in intertwin regions does not allow one to quantitatively estimate the dislocation density. According to previous research [28], it is of the order \( \rho_{\text{dis}} \approx 10^{15} \text{ m}^{-2} \) after a full five revolutions of cold HPT. Spot reflections and their low azimuthal diffusions on selected area electron diffraction (SAED) patterns obtained from the regions A and B in Figure 1 indicate a prevalence of initial single crystalline orientation of the specimens. For such regions, a combined point SAED patterns arise due to multiple twinning-assisted transformation of the crystal lattice during HPT, but they are not associated with deformation-induced low- or high-angle (general) boundaries typically arising in HPT deformation [7–10]. High dislocation density is accumulated in fragments bounded by twin boundaries and causes the azimuthal diffusions of both matrix and twin reflections (Figure 1). Much higher diffusions of the reflections are peculiar for region C in Figure 1, which corresponds to the microband produced by complex effect of dislocation slip and twinning in primary and secondary systems. These microbands are characteristic for the twin-assisted deformation of Hadfield steel, but they are obviously produced by the same deformation mechanisms as other parts of the material. In some TEM SAED patterns, weak reflections corresponded to \( \varepsilon \)-phase have been observed, as has been previously shown in detail [28]. Thus, the cold HPT of Fe-13Mn-1.3C steel is accompanied with the formation of high density of special type boundaries (twinning), which prevent austenitic structure against formation of misoriented grain structure typical for HPT deformation of fcc materials.

Representative TEM images of a microstructure in specimens processed by warm HPT are shown in Figure 2. Increases in HPT-processing temperature vary the main deformation mechanisms in Fe-13Mn-1.3C steel. HPT is accompanied with dislocation slip and formation of microscopical shear bands. Twinning activity is notably reduced as compared to cold deformation, but typical twinning-associated diffusions of austenitic reflections are still observed in SAED patterns (Figure 2b,f). Several twinning systems are seen in steel structure deformed by HPT at strain corresponded to 2 to 3 revolutions of HPT (Figure 3), but the density of twin boundaries, \( \rho_{\text{dis}} = 3 \times 10^{13} \text{ m}^{-2} \), is much lower than that for HPT-processed specimens. The distribution of twin boundaries is inhomogeneous; they are grouped in bands. A distance between the groups of twins varies in the range 0.2–20 \( \mu \text{m} \) and twin lamellae in bands are very thin—several nanometers in width.

Figure 2. TEM bright-field (a), dark-field (d, e) images of microstructure in Fe-13Mn-1.3C steel after HPT (N = 5) and corresponded to the SAED patterns (b, f) with interpretation (c). Dark-field images (d, e) were obtained in combined reflections of \( \gamma \)-Fe, \( \alpha' \)-Fe, and M\(_2\)C. Image (e) is a magnified area in image (d) corresponded to the yellow oval. SAED patterns probed area is 1.4 \( \mu \text{m}^2 \).
According to TEM research, twinning acts as a secondary deformation mechanism and does not
govern the fragmentation and refinement of austenitic phase in warm deformation at temperature
400 °C. In HPT \(400\) slip and the formation of localized shear bands are the dominating mechanisms
of deformation. After HPT \(400\)-deformation for one full rotation, high dislocation density is observed,
and mechanical twins are rarely seen in TEM images (Figure 3a,b). After two HPT \(400\) revolutions,
a spotty contrast in bright-field TEM images and radial diffusions of austenitic reflections testify
to initial stage of phase decompositon and depletion of austenite in carbon atoms (Figure 3c,d).
At this deformation stage, the weak reflections corresponded to \(\varepsilon\)-phase appear on SAED patterns
and shear bands form (Figure 3d). Shear bands divide the austenitic matrix into regular regions
of several micrometers in width and the microstructure in them has complex characteristics, with
both high- and low-angle misorientations (Figure 2a). Typical SAED patterns have combined point
and ring characteristics; it includes reflections for austenitic, ferritic and carbide (\(M_2\)C) phases
(Figure 2b,c). Several bright symmetric reflections with large azimuthal diffusions are clearly seen
in rings corresponded to austenitic phase. These reflections testify the preferred orientation of the
austenitic phase. They are more pronounced in SAED patterns obtained for the regions between shear
bands (Figure 2f). Contrarily, fine point reflections which produce the ideal ring pattern are typical for
the microstructure in shear bands (Figure 2b,c).

According to TEM dark-field analysis, the average sizes of structural elements (austenite) between
bands is about 50 nm and the TEM contrast testifies to the presence of low-angle misorientations inside of
them (Figure 2a,d). Such elements possess irregular shape and their boundaries are not clearly identified.
Additionally to these, fine regular shaped particles with homogeneous contrast and clearly identified
boundaries are observed, which are ultrafine precipitates of ferrite and carbide phases with size of

Figure 3. Typical TEM bright-field images of the microstructure and SAED patterns with interpretations
(inserts in (a,c,d)) in HPT \(400\)-processed specimens: (a,b)—\(N = 1\), (c)—\(N = 2\), (d)—\(N = 3\). SB—shear
band, ZA—zone axis. Image (b) is a magnified area in image (a) which show thin mechanical twins.
The microstructure inside of shear bands is rather homogeneous, it is composed with ultrafine austenitic, ferritic and carbide phases with the mean size of 10 nm (Figure 2d,e). Thus, the inhomogeneous multiphase microstructure is formed during HPT$_{400}$-processing, which includes sub-boundaries and boundaries of dislocation nature, shear bands and twins, all additionally stabilized by ultrafine carbide particles and ferrite.

### 3.2. The Effect of Post-Deformation Anneal at Temperature 400 °C on Microstructure of the HPT-Processed Specimens

Irrespective of HPT-processing temperature, a partial relaxation of HPT-produced microstructure occurs during annealing at 400 °C, but any changes of phase composition have not been detected by TEM analysis. After HPT$_{23}$-processing and annealing at temperature 400 °C, twins are observed both in TEM images (Figure 4) and in EBSD maps (Figure 5a–c). EBSD method could not be applied for as-deformed HPT$_{23}$-specimens, due to the low identification of the deformation-assisted microstructure. Despite a rather good identification quality of most of the points in the EBSD analysis of the annealed specimens (Figure 5c), thin twin lamellae in twin packets and between them have not been visualized. Nevertheless, they are clearly seen in TEM images (Figure 4). TEM analysis testifies to the fact that post-deformation anneal does not influence deformation-assisted twin boundaries and does not cause the precipitate hardening, any phase decomposition of austenite or recrystallization. According to EBSD analysis, specimen has one preferred orientation of the crystal lattice in direction normal to the viewing plane, which is very close to the initial crystal orientation of the single crystalline specimen (close to <001> direction), normal to the rotational plane of the plunger in HPT. The elongated regions colored in green in Figure 5a obviously correspond to twin packs, which have been identified in the TEM study (<127> zone axis of the matrix transforms into <011> zone axis of the twin, region B in Figure 1).

![Figure 4](image_url)

**Figure 4.** Bright-field (a) and dark-field (b) TEM images of the microstructure in specimens subjected to HPT$_{23}$-processing followed by annealing at temperature 400 °C. SAED pattern in (a) corresponds to the area 1.4 µm$^2$. Dark-field image (b) is obtained in (002) twin reflection (insert in image (a)).

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Figure 5. Typical electron back scattered diffraction (EBSD) orientation imaging maps for being annealed at 400 °C specimens of Fe-13Mn-1.3C steel pre-deformed in HPT23 (a–c) and HPT400 (d–f) regimes (N = 5): (a,d)—crystal orientation maps combined with color-coded triangles for austenite; (b,e)—Kernel average misorientation maps combined with color-coded bar; (c,f)—CI (confidence index) maps combined with color-coded bar. All maps and color-coded triangles in (b), (e) correspond to austenitic phase. EBSD maps correspond to the rotational plane of the plunger in HPT.

In specimens processed via regime HPT400 + annealing at 400 °C, the quality of identification in EBSD study is much lower than that for (HPT23 + 400 °C)-specimens (Figure 5c,f). This arises due to the high dispersion of the structural elements after HPT400-processing. Nevertheless, the preferred crystallographic orientation of the crystal lattice in austenite is obvious (Figure 5e) and it is several degrees tilted from the <335> direction, which corresponds to the initial orientation of the single crystal, relative to the external loading during HPT. No recrystallization is realized during annealing at 400 °C.

3.3. X-Rays Observations

After HPT-processing, the XRD patterns for Hadfield steel indicate the formation of a misoriented austenitic structure (Figure 6). The ratios of the austenitic reflections in XRD patterns in Figure 6 demonstrate the existence of the preferred orientations of the austenitic planes in the plane of specimen rotation in HPT—(001) planes in HPT23-processed specimens and (111) planes in HPT400-processed specimens. This result confirms the data of the EBSD analysis about the inheritance of the initial
The initial microhardness of the single crystalline specimens prior to deformation by HPT is 250 HV. The high-pressure torsion for five revolutions causes a hardening of the austenitic Fe-13Mn-1.3C steel, which depends on deformation temperature. In the regions corresponding to the center of radius in HPT-processed specimens, the microhardness values reach 780 HV (HPT23) and 820 HV (HPT400). Detailed Vickers microhardness measurements reveal a scattering of HV-values through the diameter of the disks, but there was no typical decrease in microhardness value next to the center of the HPT-processed disks (Figure 7). The distributions of the microhardness across the HPT-processed discs are rather homogeneous for both deformation temperatures.
Post-deformation annealing causes negligible variations in the distribution of microhardness for HPT$_{400}$-specimens, but is accompanied with some softening in HPT$_{23}$-specimens (Figure 7), because of the recovery of the microstructure and the decrease in dislocation density.

4. Discussion

Hadfield steel possesses high strain hardening, which is attributed mainly to the mechanical twinning and dynamic strain aging mechanisms under uniaxial tension and compression at room temperature and in low-temperature tests [21,35,36]. This steel possesses low SFE, allowing the occurrence of deformation twinning at low strain in a temperature range from $-196 \, ^\circ\text{C}$ to room temperature [21,35,36]. Along with dislocation slip, both deformation mechanisms, dynamic strain aging and twinning, significantly contribute to strain hardening during deformation in tension and compression. As for HPT$_{23}$ deformation, similar strain hardening mechanisms are responsible for the refinement of austenitic structure as it was previously described in [27,28].

During the HPT deformation of single-crystalline Fe-13Mn-1.3C steel (in the absence of grain or interphase boundaries) at room temperature, multiple twinning is realized in defective structure saturated by local barriers, which prevent separate twin lamellae to grow both in width and length—substitutional and interstitial atoms, Mn–C pairs in the early stages of the plastic flow, slip and twinning dislocations, twin boundaries and dislocation-assisted complexes, etc. in the stages of developed plastic deformation. Therefore, the refinement of the initially boundary-free crystal into micro- and nanoareas is attributed to the formation of thin micro- and nanotwins in several active twinning systems (Figure 1, scheme in Figure 8). High-angle $\Sigma 3$ special boundaries restrict the dislocation glide and provoke high strain hardening because a direct dislocation transmission through a $\Sigma 3$ boundary is always accompanied with an emission of other dislocations or decomposition of the boundary [37]. The consequence of the activation of the mechanical twinning in the early stages of HPT process and high density of twin-assisted boundaries is a preservation of the preferred orientation of...
the crystal lattice in the matrix, close to the initial orientation of the single crystal. This peculiarity arises from the fact that the distances between twin boundaries are very short to produce a well-developed misoriented microstructure with dislocation cells or random subboundaries. Due to the development of mechanical twinning in Hadfield steel under cold HPT, the high homogeneity of the structure of the samples across the disk has been revealed, which is not usually observed in materials subjected to deformation by HPT. As a rule, there is a non-uniform distribution of microhardness values across the diameter of a sample—with significantly lower microhardness values in the center of the disks for metals and alloys with slow recovery rate and low SFE [9].

![Figure 8](image_url)

**Figure 8.** A schematic illustration of the differences in microstructure of HPT23 and HPT400 specimens. TW—twin boundaries, SB—shear bands, LAB—low-angle boundaries.

Increasing the deformation temperature is one of the ways to suppress twinning and to change a dominating deformation mechanism and grain boundary assembly in as-deformed specimens. The main variations in microstructural characteristics and phase composition for HPT23 and HPT400-processed specimens are summarized in Table 2.

**Table 2.** Phase composition, deformation mechanisms and twinned volume ($V_{TW}$) of Fe-13Mn-1.3C steel after HPT and post-deformation annealing at 400 °C.

| State       | Phase Composition * | Mechanism of Deformation *                | $V_{TW}$, % |
|-------------|---------------------|------------------------------------------|-------------|
| HPT23       | austenite, ε-phase  | twinning, dislocation slip, shear bands, γ-ε transformation | ≈40         |
| HPT23 + 400 °C | austenite, ε-phase | -                                       | ≈40         |
| HPT400      | austenite, α'-phase, ε-phaseM₃C | slip, shear bands, twinning, γ-ε transformation, γ-α transformation, particle strengthening | ≈20         |
| HPT400 + 400 °C | austenite, α'-phase, ε-phaseM₃C | -                                       | ≈20         |

*dominating deformation mechanisms and phases are marked in bold.*
Increase in deformation temperature partially suppresses mechanical twinning in Hadfield steel. Nevertheless, our experimental data reveal the activation of this deformation mechanism in high-temperature tests (400 °C). Therefore, in the severe plastic deformation of high-strength Hadfield steel with low SFE and high level of solid-solution strengthening of austenite by carbon, mechanical twinning is confirmed as a high-temperature deformation mechanism (Figures 2 and 3).

Under HPT_{400} deformation, twinning is a secondary deformation mechanism and the warm deformation of single crystals promotes the formation of a misoriented multiphase structure with deformation-assisted subboundaries in austenite, shear bands and twins, ultrafine ferrite and carbide phases (Figure 2, scheme in Figure 8). High-pressure torsion accelerates mass-transfer and could drive phase transformations and promote the precipitation of carbide phase and ferrite at a temperature of 400 °C. According to a study of Zuidema [34], polycrystalline specimens of Hadfield steel with 1.25 mass % of carbon do not undergo any phase transformations during static annealing at temperature 400 °C for time period comparable and even much higher with one needed for heating of the specimens prior to deformation and further HPT processing. Two-phase “austenite+carbide” composition can be produced by short-time static anneal at 500 °C, but for multiphase “austenite + carbide + ferrite” composition, a long-term (longer than 10^5 s) anneal at 500 °C is necessary [34]. The successive action of HPT_{23} and anneal at 400 °C does not provide any phase transformations in Fe-13Mn-1.3C steel (Figures 4 and 5). Therefore, the precipitation of carbide and ferrite during HPT_{400} deformation is obviously attributed to the synergetic effect of severe plastic deformation and elevated temperature (400 °C). For different HPT-assisted microstructures in Cu-Ni, Al-Zn, Co-Cu alloys, Straumal B. has revealed that atomic movements driven by an external stress/strain during SPD are higher than those driven by conventional thermal diffusion [38]. Authors have proposed a concept of “an effective temperature” of SPD which does not coincide with the experimentally adjusted value, but rather indicates the temperature of decomposition of solid solution as it would appear in material in static long-term anneal. According to the diagram of Zuidema [34] and phase composition of the specimens (Table 2), the “effective temperature”, during which, the HPT_{400} deformation of Hadfield steel could be as high as 550–650 °C.

The different deformation mechanisms are responsible for the strain hardening of Hadfield steel in cold and warm HPT. Nevertheless, the values of microhardness produced by HPT are similar for both deformation temperatures (Figure 7). The contributions of various mechanisms revealed in TEM and XRD study on a yield strength of the steel can be estimated and summarized assuming their strengthening effect:

\[ \sigma_{0.2} = \sigma_{GB} + \sigma_{TB} + \sigma_{\rho} + \sigma_{SS} + \sigma_{PS}, \]  

(1)

where \( \sigma_{GB} \) (\( \sigma_{TB} \)) and \( \sigma_{\rho} \) are a grain boundary (twin boundary) strengthening and dislocation-assisted hardening, \( \sigma_{SS} \) and \( \sigma_{PS} \) are solid solution and precipitation strengthening.

The solid-solution hardening effect in fcc-Fe alloys could be estimated using equation for the lattice friction stress, which includes the solid solution hardening effect of C and Mn in Fe-Mn-C austenite [39–41]:

\[ \sigma_{SS} = 223 + 187\text{wt.} \% C - 2\text{wt.} \% \text{Mn}. \]  

(2)

The variations in carbon concentration due to an increase in temperature of HPT can be estimated by a change in the lattice parameter \( a \) (Table 1). According to [42], the variations in \( a \)-value caused by Mn and C are \( \Delta a_C = 2.72 \times 10^{-3} \) (nm/\%C) and \( \Delta a_{\text{Mn}} = 1.25 \times 10^{-4} \) (nm/\% Mn), respectively. The strengthening efficiency of carbon is much higher in comparison with manganese and the solid solution strengthening is primarily attributed to carbon atoms. Therefore, the partial decarburization of the austenite due to an increase in HPT temperature acts as a softening factor (Table 3).
Table 3. Contributions of strengthening factors for Fe-13Mn-1.3C steel in cold and warm HPT: solid solution strengthening $\sigma_{SS}$ (Equation (2)), twin boundary factor $\sigma_{TB}$ (Equation (4)), grain boundary factor $\sigma_{GB}$ (Equation (5)), dislocation density $\rho$ (Equation (6)), precipitate strengthening $\sigma_{PS}$ (Equation (7)).

| State     | $\sigma_{SS}$, MPa | $\sigma_{GB}$, MPa | $\sigma_{TB}$, MPa | $\rho$, MPa | $\sigma_{PS}$, MPa | HV Experiment | $\sigma^*$*, GPa |
|-----------|---------------------|--------------------|--------------------|-------------|--------------------|---------------|-----------------|
| HPT$_{23}$ | 450                 | -                  | 420                | 480–1080    | -                  | 780           | 2600            |
| HPT$_{23}$+ 400 $^\circ$C | 450                | -                  | 420                | 430–980     | -                  | 760           | 2530            |
| HPT$_{400}$ | 290                 | 1400               | 100                | 390–870     | 130               | 820           | 2730            |

* $\sigma = \frac{HV}{3}$ [26].

The hardening effect of grain boundaries is well described by the Hall-Petch relation [39]:

\[ \sigma_{GB} = k_{GB}d^{-1/2}, \]  

where $k_{GB}$ is a constant; $d$—average grain size. Single crystals have not contained any boundaries prior to deformation. After HPT$_{23}$, the structural elements are bounded by twin boundaries mainly and no grain boundaries form during deformation (Figure 8). Therefore, there is no typical grain boundary effect in HPT$_{23}$-deformed specimens. Instead, the microstructure of steel after HPT$_{23}$ processing contains (1) rough twin packets (bands consisted from thin twin lamellae) and (2) thin twins located between these packets. The strengthening effect from the twin boundaries with the average twin spacing $t$ (30 nm HPT$_{23}$-deformation [28]) can be evaluated using an extended Hall-Petch relation [40]:

\[ \sigma_{TB} = k_{TB}t^{-1/2}, \]  

where $k_{TB}$ is a constant, which has not been clearly defined because of the absence of the materials showing the mechanical twinning independently on other deformation mechanisms. We used the data of Zhou with coauthors [40], who reported the value $k_{TB} = 72.78 \text{ MPa} \cdot \mu\text{m}^{-1/2}$ for a microstructure with high density of twin boundaries. After HPT$_{400}$, the spacings between twin boundaries are increased drastically and the twinning-assisted barrier effect is much weaker than that for HPT$_{23}$ specimens (Table 3).

After HPT$_{400}$ deformation, the typical microstructure includes twin packets with the mean distance of 20 $\mu$m between them, shear bands with nanoscale crystallites of different phases (austenite, ferrite, carbide) inside of them and deformation-induced fragments of austenite (50 nm in size with ferrite and carbide phases) between shear bands (Figure 8). Authors [43] investigated the strengthening mechanisms in Fe-23Mn-0.3C-1.5Al TWIP steel during cold rolling. They demonstrated that strengthening associated with shear bands, which include nanoscale crystallites, in TWIN-assisted microstructure could be reasonably described by the modified Hall–Petch equation:

\[ \sigma_{GB} = k_{GB}(1 - f)d^{-1/2} + fd_{SB}^{-1/2}, \]  

where $f$ is a volume fraction of the shear bands ($f = 0.27$ in our case); $d$ is a distance between bands (2 $\mu$m), $d_{SB}$ is a size of nanoscale crystallites within the shear bands (10 nm). In case of microstructure of Hadfield steel processed via HPT$_{400}$ deformation, this factor gives the most valuable strengthening effect (Table 3).

The dislocation-assisted hardening can be calculated with the Taylor equation [44]:

\[ \sigma_{\rho} = \alpha M G B \sqrt{\rho}, \]  

where $\alpha$ is a constant ($\alpha = 0.21$ [43], $\alpha = 0.475$ [40]); $M$ is a Taylor factor ($M = 3.06$), $G$ is a shear modulus ($G = 70$ GPa for Hadfield steel [45]), and $b$ is the Burgers vector ($b = 0.2567$ nm). As summarized in Table 3, the deformation-assisted dislocation accumulation strongly influences the strength properties of Hadfield steel processed by HPT at both temperatures. The decrease in dislocation density is
obviously responsible for the decrease in microhardness of the HPT\textsubscript{23} specimens after annealing at 400 °C (Table 3).

The contribution of dispersion strengthening in the steel subjected to HPT\textsubscript{400}-deformation was estimated using the Orowan–Ashby equation [46].

\[ \sigma_{PS} = 0.538G\left(\frac{f^{1/2}}{d}\right)\ln\left(\frac{d}{2b}\right), \]  

(7)

where \( f \) is a volume fraction of precipitates, \( d \) is the mean particle diameter. According to TEM dark-field analysis, the volume fraction of fine precipitates in austenite \( f \) is 0.21% and the mean diameter of these phases is 10 nm for steel processed in HPT\textsubscript{400} deformation. Therefore, precipitate hardening is also important strengthening factor for HPT\textsubscript{400}-specimens and this factor could partially compensate the decrease in twinning-assisted hardening of the Hadfield steel in the high-temperature deformation regime (Table 3).

The data in Table 3 represent just a relative importance of strengthening factors in strength properties of Fe-13Mn-1.3C steel in HPT at different temperatures and post-deformation annealing. The direct comparison and totalization of different contributions could be speculative, because the constants in Equations (2) and (4)–(6) have been determined for Mn-steels with another carbon content and other microstructures (distribution and densities of dislocations and twins). The solid-solution hardening, strengthening effect from twin boundaries and dislocations all provide high values of the microhardness in cold HPT\textsubscript{23}. Despite the dynamic strain aging effect, stimulating the accumulation of perfect dislocations in Hadfield steel, the high dislocation density is also attributed to the high density of twin boundaries, as was previously described by Wang [47]. Under warm HPT (HPT\textsubscript{400}), the contribution of twinning has become weaker and values of \( \sigma_{\rho} \) and \( \sigma_{TB} \) possess lower values in comparison with HPT\textsubscript{23} regime. Nevertheless, an increase in deformation temperature is accompanied by appearance of the additional strengthening mechanisms: shear band formation, \( \gamma\rightarrow\alpha' \) transformation and dispersion strengthening. All these factors give a cumulative strengthening effect similar to the multiple twinning in HPT\textsubscript{23} deformation.

5. Conclusions

The role of deformation temperature (23 °C and 400 °C) on the twin-assisted deformation, microstructure, phase composition and microhardness of high-Mn Fe-13Mn-1.3C steel (Hadfield steel) has been studied. We have evaluated the complex and separate effects of high temperature and severe plastic deformation in HPT on the microstructure and strengthening of Hadfield steel. The following novel points were concluded.

1. Twin boundaries induced by cold HPT possess high thermal stability. HPT deformation at room temperature is associated with the formation of a dense net of twinning-assisted boundaries and high dislocation density and is not accompanied with any phase transformations. These twin boundaries stay untransformed after post-deformation annealing at temperature 400 °C.

2. In high pressure-torsion, twinning for the first time has been experimentally confirmed as a high-temperature deformation mechanism. The increase in deformation temperature from 23 °C up to 400 °C decreases the activity of mechanical twinning, but twin lamellae are experimentally observed even at a deformation temperature of 400 °C.

3. In high-pressure torsion at 400 °C, the synergetic effect of high temperature and severe plastic deformation on microstructure and phase composition of Hadfield steel has been confirmed for the first time. High-temperature severe plastic deformation drives austenite decomposition and provides a formation of multiphase (austenite, ferrite, carbides) microstructure, whilst separate effects of high temperature anneal (400 °C), high pressure torsion or their gradual application (cold HPT + annealing at 400 °C) is not accompanied with any phase transformations.
4. A complex effect of the HPT-driven nucleation of the nanoscale precipitates (carbides and ferrite), along with deformation-induced defects (dislocations, twin boundaries, low-angle boundaries, shear bands) in high-temperature deformation provides high microhardness values, which are similar to twin-assisted hardening in cold HPT.

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References
1. Watanabe, T. Grain boundary engineering: Historical perspective and future prospects. *J. Mater. Sci.* 2011, 46, 4095–4115. [CrossRef]
2. Liu, T.; Xia, S.; Du, D.; Bai, Q.; Zhang, L.; Lu, Y. Grain boundary engineering of large-size 316 stainless steel via warm-rolling for improving resistance to intergranular attack. *Mater. Lett.* 2019, 234, 201–204. [CrossRef]
3. Glezer, A.M.; Shurygina, N.A.; Binova, E.N.; Perymyakova, I.E.; Firstov, S.A. Approach to the theoretical strength of Ti-Ni-Cu alloy nanocrystals by grain boundary design. *J. Mater. Sci. Technol.* 2015, 31, 91–96. [CrossRef]
4. Song, S.-H.; Zhao, Y.; Cui, Y.; Sun, J.; Si, H.; Li, J.-Q. Effect of grain boundary character distribution and grain boundary phosphorus segregation on the brittleness of an interstitial-free steel. *Mater. Lett.* 2016, 182, 328–331. [CrossRef]
5. Randle, V. Grain boundary engineering: An overview after 25 years. *Mater. Sci. Technol.* 2010, 26, 253–261. [CrossRef]
6. Emeis, F.; Peterlechner, M.; Divinski, S.V.; Wilde, G. Grain boundary engineering parameters for ultrafine grained microstructures: Proof of principles by a systematic composition variation in the Cu-Ni system. *Acta Mater.* 2018, 150, 262–272. [CrossRef]
7. Sauvage, X.; Wilde, G.; Divinski, S.V.; Horita, Z.; Valiev, R.Z. Grain boundaries in ultrafine grained materials processed by severe plastic deformation and related phenomena. *Mater. Sci. Eng. A* 2012, 540, 1–12. [CrossRef]
8. Langdon, T.G. Twenty-five years of ultrafine-grained materials: Achieving exceptional properties through grain refinement. *Acta Mater.* 2013, 61, 7035–7059. [CrossRef]
9. Zhilyaev, A.P.; Langdon, T.G. Using high-pressure torsion for metal processing: Fundamentals and applications. *Prog. Mater. Sci.* 2008, 53, 893–979. [CrossRef]
10. Ivanisenko, Y.; Valiev, R.Z.; Fecht, H.-J. Grain boundary statistics in nano-structured iron produced by high pressure torsion. *Mater. Sci. Eng. A* 2005, 390, 159–165. [CrossRef]
11. Astafurova, E.G.; Dobatkin, S.V.; Naydenkin, E.V.; Shagalina, S.V.; Zakharova, G.G.; Ivanov, Y.F. Structural and phase transformations in nanostructured 0.1% C-Mn-V-Ti steel during cold deformation by high pressure torsion and subsequent heating. *Nanotechnol. Russ.* 2009, 4, 109–120. [CrossRef]
12. Valiev, R.Z.; Estrin, Y.; Horita, Z.; Langdon, T.G.; Zehetbauer, M.J. Producing bulk ultrafine-grained materials by severe plastic deformation. *J. Mater. 2006, 58, 33–39. [CrossRef]*
13. Zhang, X.; Misra, A. Superior thermal stability of coherent twin boundaries in nanotwinned metals. *Scr. Mater.* 2012, 66, 860–865. [CrossRef]
14. Wang, S.J.; Jozaghi, T.; Karaman, I.; Arroyave, R.; Chumlyakov, Y.I. Hierarchical evolution and thermal stability of microstructure with deformation twins in 316 stainless steel. *Mater. Sci. Eng. A* 2017, 694, 121–131. [CrossRef]
15. De Cooman, B.C.; Estrin, Y.; Kim, S.K. Twinning-induced plasticity (TWIP) steels. *Acta Mater.* 2018, 142, 283–362. [CrossRef]
16. Randle, V. Twinning-related grain boundary engineering. *Acta Mater.* 2004, 52, 4067–4081. [CrossRef]
17. Wang, H.T.; Tao, N.R.; Lu, K. Strengthening an austenitic Fe–Mn steel using nanotwinned austenitic grains. *Acta Mater.* **2012**, *60*, 4027–4040. [CrossRef]

18. Vercammen, S.; Blanpain, B.; De Cooman, B.C.; Wollants, P. Cold rolling behaviour of an austenitic Fe–30Mn–3Al–3Si TWIP-steel: The importance of deformation twinning. *Acta Mater.* **2004**, *52*, 2005–2012. [CrossRef]

19. Christian, J.W.; Mahajan, S. Deformation twinning. *Prog. Mater. Sci.* **1995**, *39*, 1–157. [CrossRef]

20. Niewczas, M. Dislocations and twinning in face centered cubic crystals. In *Dislocations in Solids*; Nabarro, F., Hirth, J., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; pp. 263–364.

21. Astafurova, E.G.; Kireeva, I.V.; Chumlyakov, Y.I.; Maier, H.J.; Sehitoglu, H. The influence of orientation and aluminium content on the deformation mechanisms of Hadfield steel single crystals. *Int. J. Mat. Res.* **2007**, *98*, 144–149. [CrossRef]

22. Chumlyakov, Y.I.; Kireeva, I.V.; Sehitoglu, H.; Litvinova, E.I.; Zaharova, E.G.; Luzginova, N.V. High-strength single crystals of austenitic stainless steel with nitrogen content: Mechanisms of deformation and fracture. *Mater. Sci. Forum* **1999**, *318*, 395–400. [CrossRef]

23. Bouaziz, O.; Scott, C.P.; Petitgand, G. Nanostructured steel with high work-hardening by the exploitation of the thermal stability of mechanically induced twins. *Scr. Mater.* **2009**, *60*, 714–716. [CrossRef]

24. Kim, J.G.; Enikeev, N.A.; Abramova, M.M.; Park, B.H.; Valiev, R.Z.; Kim, H.S. Effect of initial grain size on the microstructure and mechanical properties of high-pressure torsion processed twinning-induced plasticity steels. *Mater. Sci. Eng. A* **2017**, *682*, 164–167. [CrossRef]

25. Kim, J.G.; Enikeev, N.A.; Seol, J.B.; Abramova, M.M.; Park, C.G.; Kim, H.S. Superior strength and multiple strengthening mechanisms in nanocrystalline TWIP steel. *Sci. Rep.* **2018**, *8*, 11200. [CrossRef] [PubMed]

26. Matoso, M.; Figueiredo, R.B.; Kawasaki, M.; Santos, D.B.; Langdon, T.G. Processing a twinning-induced plasticity steel by high-pressure torsion. *Scr. Mater.* **2012**, *67*, 649–652. [CrossRef]

27. Astafurova, E.G.; Tukeeva, M.S.; Zakhurova, G.G.; Melnikov, E.V.; Maier, H.J. The role of twinning on microstructure and mechanical response of severely deformed single crystals of high-manganese austenitic steel. *Mater. Charact.* **2011**, *62*, 588–592. [CrossRef]

28. Astafurova, E.G.; Tukeeva, M.S.; Maier, G.G.; Melnikov, E.V.; Maier, H.J. Microstructure and mechanical response of single-crystalline high-manganese austenitic steels under high-pressure torsion: The effect of stacking-fault energy. *Mater. Sci. Eng. A* **2014**, *604*, 166–175. [CrossRef]

29. Teplov, V.A.; Korshunov, L.G.; Shabashov, V.A.; Kuznetsov, R.I.; Pilyugin, V.P.; Tupitsa, D.I. Structure transformations in high-manganese austenite steels upon deformation by shear under pressure. *Phys. Met. Metall.* **1986**, *66*, 563–571. (In Russian)

30. Abramova, M.M.; Enikeev, N.A.; Kim, J.G.; Valiev, R.Z.; Karavaeva, M.V.; Kim, H.S. Structural and phase transformation in a TWIP steel subjected to high pressure torsion. *Mater. Lett.* **2016**, *166*, 321–324. [CrossRef]

31. Park, B.H.; Um, H.Y.; Kim, J.G.; Jeong, H.Y.; Lee, S.; Kim, H.S. Large deformation of twin-induced plasticity steels under high-pressure torsion. *Met. Mater. Int.* **2016**, *22*, 1003–1008. [CrossRef]

32. Timokhina, I.B.; Medvedev, A.; Lapovok, R. Severe plastic deformation of a TWIP steel. *Mat. Sci. Eng. A* **2014**, *593*, 163–169. [CrossRef]

33. Derby, J.J.; Yeckel, A. Heat transfer analysis and design for bulk crystal growth: Perspectives of the Bridgman method. In *Bulk Growth: Growth Mechanisms and Dynamics*; Rudolph, P., Ed.; Elsevier: Amsterdam, The Netherlands, 2015; pp. 793–843.

34. Zuidema, B.K.; Subramanyam, D.K.; Leslie, W.C. Effect of aluminium on the work hardening and wear resistance of Hadfield manganese steel. *Metall. Trans. A* **1987**, *18*, 1629–1639. [CrossRef]

35. Chumlyakov, Y.I.; Kireeva, I.V.; Litvinova, E.I.; Zaharova, E.G.; Luzginova, N.V.; Sehitoglu, H.; Karaman, I. Strain hardening in single crystals of Hadfield steel. *Phys. Met. Metall.* **2000**, *90*, S1–S17.

36. Karaman, I.; Sehitoglu, H.; Gall, K.; Chumlyakov, Y.I.; Maier, H.J. Deformation of single crystal Hadfield steel by twinning and slip. *Acta Mater.* **2000**, *48*, 1345–1359. [CrossRef]

37. Randle, V. Mechanism of twinning-induced grain boundary engineering in low stacking-fault energy materials. *Acta Mater.* **1999**, *47*, 4187–4196. [CrossRef]

38. Straumal, B.B.; Mazilkin, A.A.; Baretzky, B.; Schütz, G.; Rabkin, E.; Valiev, R.Z. Accelerated diffusion and phase transformations in CoCu alloys driven by the severe plastic deformation. *Mater. Trans.* **2012**, *53*, 63–71. [CrossRef]
39. Bouaziz, O.; Allain, S.; Scott, C.P.; Cugy, P.; Barbier, D. High manganese austenitic twinning induced plasticity steels: A review of the microstructure properties relationships. *Curr. Opin. Solid State Mater. Sci.* **2011**, *15*, 141–168. [CrossRef]

40. Zhou, P.; Liang, Z.Y.; Liu, R.D.; Huang, M.X. Evolution of dislocations and twins in a strong and ductile nanotwinned steel. *Acta Mater.* **2016**, *111*, 96–107. [CrossRef]

41. De Cooman, B.C. High Mn TWIP steel and medium Mn steel. In *Automotive Steels: Design, Metallurgy, Processing and Applications*; Rana, R., Singh, S.B., Eds.; Elsevier: Amsterdam, The Netherlands, 2017; pp. 317–385.

42. Kim, H.-S.; Suh, D.-W.; Kim, N.-J. Fe–Al–Mn–C lightweight structural alloys: A review on the microstructures and mechanical properties. *Sci. Technol. Adv. Mater.* **2013**, *14*, 14205:1–14205:11. [CrossRef]

43. Kusakin, P.; Belyakov, A.; Haase, C.; Kaibyshev, R. Molodov, D.A. Microstructure evolution and strengthening mechanisms of Fe–23Mn–0.3C–1.5Al TWIP steel during cold rolling. *Mater. Sci. Eng. A* **2014**, *617*, 52–60. [CrossRef]

44. Bouaziz, O.; Allain, S.; Scott, C. Effect of grain and twin boundaries on the hardening mechanisms of twinning-induced plasticity steels. *Scr. Mater.* **2008**, *58*, 484–487. [CrossRef]

45. Rittel, D.; Roman, I. Tensile deformation of coarse-grained cast austenitic manganese steels. *Mater. Sci. Eng. A* **1989**, *110*, 77–87. [CrossRef]

46. Gladman, T. Precipitation hardening in metals. *Mater. Sci. Technol.* **1999**, *15*, 30–36. [CrossRef]

47. Wang, Z.W.; Wang, Y.B.; Liao, X.Z.; Zhao, Y.H. Influence of stacking fault energy on deformation mechanism and dislocation storage capacity in ultrafine-grained materials. *Scr. Mater.* **2009**, *60*, 52–55. [CrossRef]