The significance of phase reversion-induced nanograined/ultrafine-grained (NG/UFG) structure on the strain hardening behavior and deformation mechanism in copper-bearing antimicrobial austenitic stainless steel

H. Dong[1], Z.C. Li[2] M.C. Somani[3], R.D.K. Misra[1]
[1]Laboratory for Excellence in Advanced Steel Research,
Department of Metallurgical, Materials and Biomedical Engineering,
500 W. University Avenue,
University of Texas at El Paso, El Paso, TX 79968, USA
[2]School of Materials Science and Engineering
Shandong University of Science and Technology, Qingdao 266590, China
[3] Materials and Mechanical Engineering,
Centre for Advanced Steels Research,
University of Oulu, FI-90014 Oulu, Finland

***** Corresponding author: dmisra2@utep.edu (R.D.K. Misra); mahesh.somani@oulu.fi (M.C. Somani)

Abstract

The unique concept of phase reversion involving severe deformation of parent austenite into martensite, followed by annealing for a short duration, whereby the strain-induced martensite reverts to austenite, was adopted to obtain nano-grained/ultrafine-grained (NG/UFG) structure in a Cu-bearing biomedical austenitic stainless steel resulting in high strength-high ductility combination. Work hardening and accompanying deformation mechanism are two important aspects that govern the mechanical behavior of biomedical devices. Thus, post-mortem electron microscopy of the strained region was carried out to explore the differences in the deformation mechanisms induced by grain refinement, while the strain hardening behavior was analyzed by Crussard-Jaoul (C-J) analysis of the tensile stress-strain data. The strain hardening behavior consisted of four stages and was strongly affected by grain structure. Twinning-induced plasticity (TWIP) was the governing deformation mechanism in the NG/UFG structure and contributed to good ductility. In striking contrast, transformation-induced plasticity (TRIP) contributed to high ductility in the coarse-grained (CG) counterpart and was the governing strain hardening mechanism. When the grain size is less than ~1 μm, the increase in the strain energy and the austenite stability significantly reduce the possibility of strain-induced martensite transformation such that there is a distinct transition in deformation mechanism from nanoscale twinning in the NG/UFG structure to strain-induced martensite in CG structure. The differences in the deformation mechanisms are explained in terms of austenite stability – strain energy relationship.

Keywords: Antimicrobial Stainless Steel, Grain refinement, Strain Hardening, Deformation Mechanism

1. Introduction

Austenitic stainless steels are commonly used materials, besides titanium alloys for biomedical applications, such as in joint replacement, bone fixation, and coronary stents [1-3]. Biomedical devices manufactured from stainless steels are expected to have a life span of 20-25 years, but unfortunately, they tend to fail prematurely because of the inadequate build-up of bone mass around the implants. Furthermore, the debris generated with time due to wear may be absorbed in the surrounding areas of biomedical implants and may induce inflammation, tissue death, and even failure of the biomedical device. Stainless steel is also used as a biomedical device in Parkinson's disease and neurological problems [4].

In order to increase the long-term stability of metallic implants, significant efforts have been made to decrease the grain size and induce nanostructured features to favorably tune protein-material and cell-material interactions [4-6]. Moreover, grain refinement and alloying with copper address the challenge of microbial infections induced by microorganisms, thereby thwarting the risk of infection through the inhibition of bacterial colonization and biofilm formation on biomedical implants [7-10]. Copper has been considered as an antimicrobial element for a long time [11]. The release of Cu^{2+} ions damages the bacteria and is envisaged to destroy the permeability of the bacterial membranes, which helps in reducing sugars and proteins from the cells. Furthermore, they promote the formation of bacteria-killing reactive oxygen species (ROS). Thus, the antibacterial role of Cu encourages its potential use in inhibiting bacterial infection and materials containing copper are now being increasingly considered as antimicrobial biomaterials [8].

The ingenious concept of phase reversion has gained significance attention in recent years since it provides a route to enhance mechanical properties through extensive grain refinement [12-14]. In austenitic stainless steels, the strain induced martensitic transformation is categorized into two types: the body centered cubic (bcc) or body centered tetragonal (bct) α'-martensite and the hexagonal close packed (hcp) ε-martensite [15, 16]. It is generally noted that ε-martensite forms as a transition phase and assist in the formation of bcc α'-martensite by providing

favorable conditions [16]. According to Lagneborg [15], α'-martensite forms at the intersection of ε-martensite sheet, as it is observed in contact with the ε-martensite. In AISI 304 steel, ε-martensite is observed for even small strains at room temperature and then it transforms completely to α'-martensite with continued deformation. According to one study, ε-martensite forms in steels with relatively low stacking fault energy (SFE), much lower than when only α'-martensite forms in austenitic stainless steels (SFE < 20 mJ/m2) [17]. In essence, the SFE controls the possibility of strain induced martensite transformation and the rate of work hardening of austenite. The reversion concept involves severe cold deformation of parent austenite to strain-induced martensite followed by short duration annealing and has been adopted to obtain nano-grained/ultrafine-grained (NG/UFG) structure in austenitic stainless steels including a Cu-bearing biomedical steel, resulting in high strength-high ductility combination [18-27]. The concept was effectively used to critically analyze the interplay between the load-controlled deformation response and strain-rate sensitivity of NG/UFG austenitic stainless steel via nanoscale deformation experiments and compare with its coarse-grained (CG) counterpart. The study demonstrated that the strain-rate sensitivity of NG/UFG was ~1.5 times that of the CG structure [19]. While a study on biological functions indicated the occurrence of favorable modulation of osteoblast cellular activity on Cu-containing austenitic stainless steel in relation to the Cu-free counterpart [20].

Strain-induced hardening (also known as work hardening) is an important property for biomedical devices from the perspective of restricting deformation and providing wear resistance. Thus, in sequel to our recent studies on Cu-containing austenitic stainless steels [18-20], the objective of the present study is to fundamentally explore the strain hardening behavior of tensile strained NG/UFG Cu-containing austenitic stainless steel by combining the tensile data and post-mortem electron microscopy and to compare the behavior with the coarse-grained (CG) counterpart.

2. Experimental procedure

The investigated austenitic stainless steel was received as a hot-rolled sheet of ~3 mm thickness. It was made using standard melting process in a laboratory, and its chemical composition is presented in Table 1, showing alloying with 3.15 wt.% Cu. The typical features of this steel composition are its low C content (0.023% C) and high stability as estimated using the stability index, M_{d30} = -11.2 °C (for grain size ASTM #7). M_{d30} is the temperature at which an amount of 50 % austenite will be transformed to martensite through cold-deformation of 0.3 true strain (corresponding ca. 0.35 engineering strain) and is estimated using the following equation [28]:

$$M_{d30}\ (°C) = 552-462(C+N)-9.2Si-8.1Mn-13.7Cr-29(Ni+Cu)-18.5Mo-68Nb-1.42(GS-8) \quad (1)$$

Table 1. Chemical composition (wt.%) of the experimental Cu-bearing austenitic stainless steel.

C	Si	Mn	Cr	Ni	Cu	S	P	Fe
0.023	0.55	0.85	17.40	7.43	3.15	0.011	0.025	Balance

As regards the SFE, none of the empirical equations in literature can precisely estimate the SFE. However, the Brofman and Ansell equation for SFE calculation is somewhat better than the other ones. The SFE value of the investigated austenitic stainless steel computed using the Brofman and Ansell equation [29] as well as a more recent equation proposed by de Bellefon et al. [30], is estimated to be about 17 mJ/m^2 at room temperature. Since both the equations do not show any influence of copper, the actual SFE can be relatively higher, as Cu is one of the elements that increases the SFE of the austenitic stainless steel and increases the stability of the steel and decreases the M_{d30} temperature.

The as-received steel sheet was further cold-rolled in a laboratory rolling mill to 1 mm thickness (66.7% reduction) and subsequently annealed in a Gleeble 3800 thermo-mechanical simulator. The optimized reversion annealing temperature and holding time to obtain NG/UFG structures were 800°C and 10 s, respectively, and the corresponding values were 950°C and 100 s for CG structures.

According to Schaeffler diagram, the steel is in the austenitic-ferritic-martensitic region corresponding to the % Ni equivalent (Ni_{eq} = 9.7) and % Cr equivalent (Cr_{eq} = 18.6) given by the following equations [31]:

Ni_{eq} (in wt. %) = Ni + Co + 30C + 25N + 0.5Mn + 0.3Cu (2)

Cr_{eq} (in wt. %) = Cr + 2Si + 1.5Mo + 5V + 5.5Al + 1.75Nb + 1.5Ti + 0.75 W (3)

In annealed condition, the 2.95 mm thick sheet used in this study had about 1.5% ferrite. The α′-martensite fraction after reversion annealing at 950 °C for 100 s was 2.3 % and the corresponding strain induced α′-martensite fraction after tensile deformation was about 65.5% estimated near the fractured ends.

The measurement of grain size involved two different methods. In the first approach, the grain size of at least 50 grains in the micrographs were estimated by Image J software and subsequently, mean linear intercept grain size ($\bar{d}$) was determined. The second method considered the grain size distribution to measure the weighted average grain size ($\bar{d}_w$) [32]. An optimum bin size of 200 nm was selected for a statistically relevant distribution of 100 detected grains in the micrographs. Denoting the number of grains in the i-th bin as n_i and dividing it by the total number of grains, N, the weight of the i-th bin is [32]:

$$w_i = \frac{n_i}{N} \quad (4)$$

Moreover, the square root of the areal mean of n_i grains in the i-th bin provides the average grain size ($\bar{d}_i$) in the i-th bin. The weighted average grain size was calculated by the following formula [32].

$$\bar{d}_w = \sum_{i=1}^{N} w_i \bar{d}_i \quad (5)$$

Uniaxial tensile tests were carried out at room temperature using a Zwick Z100 machine on sheet specimens cut along rolling direction, with the gage dimensions of 15 × 5 × 1 mm at a strain rate of 0.008 s^{-1} according to the ASTM E8/E8M-16a standard. Generally, tests were repeated twice. After the tensile tests, the area close to the fractured end was cut from different

samples to prepare the thin foils for transmission electron microscopy (TEM). The samples were first thinned to 50 μm thickness and then 3 mm disks were punched to conduct twin-jet electropolishing. The electrolyte consisted of 10% perchloric acid and 90% acetic acid. The foils were examined in a Hitachi H7600 TEM operated at 120 kV.

3. Results

3.1 Microstructure

The optical and TEM micrographs of NG/UFG and CG steels are displayed in Fig. 1. The weighted average grain size of NG/UFG and CG steels after cold rolling and annealing are presented in Table 2. The NG/UFG steel consisted of nanograins (less than 100 nm) and a few ultrafine grains (~100-500 nm) with a weighted average grain size of 350 nm, whereas the CG steel was composed of uniform coarse grains with a weighted average grain size of 22 μm. The samples did not show formation of any ε-Cu particles under these conditions of reversion. However, in another study by Somani et al. showed formation of ε-Cu precipitates following reversion annealing treatments at 650-700 °C for long holding times of 1-1.5 h [18].

Table 2. Weighted average grain size and tensile properties of NG/UFG and CG copper-bearing antimicrobial austenitic stainless steels.

	Weighted average grain size	Average yield strength, MPa	Average elongation, %
NG/UFG	350 nm	769	38
CG	22 μm	297	68

3.2 Tensile properties and strain hardening behavior

The tensile properties of NG/UFG and CG steels are presented in Table 2. The yield strength and elongation of the NG/UFG steel were 769 MPa and 38 % respectively, whereas the values for the CG steel were 297 MPa and 68 %, respectively. The yield strength of NG/UFG steel was ~ 2.5 times higher than that of the CG steel, and the elongation was also reasonably good. The true stress-true strain (σ_T-ε_T) curves of NG/UFG and CG Cu-bearing steels obtained from the tensile data are presented in Fig 2.

The strain-hardening rates (SHR = $d\sigma_T/d\varepsilon_T$) of the two steels with remarkably different grain sizes are obtained from the true stress-true strain plots in Fig. 2 are presented as a function of true strain in Fig. 3. In the early stage, the SHR of NG/UFG steel decreased sharply and attained a small plateau of ~1858 MPa in the range ε=0.02-0.05. This was followed by a very slow decrease of SHR in the strain range of ε=0.05-0.22, and finally a sharp drop until the onset of necking. The SHR of CG steel also decreased rapidly in the initial stage, but in contrast to NG/UFG steel at $\varepsilon_T<0.02$, the SHR of CG steel decreased at a relatively higher rate and attained a plateau of ~ 1089 MPa in the strain range ε=0.26-0.40, and finally, decreased sharply with the onset of necking to fracture.

The strain-hardening behavior of the two steels was further analyzed by the Crussard-Jaoul (C-J) method ($\ln(d\sigma_T/d\varepsilon_T)$ vs. $\ln(\varepsilon_T)$) and is presented in Fig. 4. The differential C-J plot assumes the Ludwik power relation and can describe changes in the slope of a line segment, facilitating further insight into the differences in deformation mechanisms [33, 34]. Though limited in applicability, the C-J analysis of the tensile deformation was employed to show the changes in the strain hardening behavior of the two materials with widely different grain structures. The idea was to identify and reveal different stages characterized by by the decrease or increase in $\ln(d\sigma_T/d\varepsilon_T)$ with $\ln(\varepsilon_T)$, including plateaus and valleys. These stages are marked by the occurrences of mechanisms that are characteristic of NG/UFG and CG structures. In earlier studies on the C-J analysis [35-39], the natural logarithmic values of SHR (i.e., $\ln(d\sigma_T/d\varepsilon_T)$) was divided into various stages characterized by the decrease or increase in $\ln(d\sigma_T/d\varepsilon_T)$ with true strain, including plateaus, valleys and peak positions. It is evident from the C-J plot in Fig. 4 that the strain hardening behavior can be divided into three stages (A, B, D) for the NG/UFG steel and four stages (A, B, C, D) for the CG counterpart. The characteristic data points corresponding to these stages are summarized in Table 3. For the NG/UFG structure, the logarithmic value of SHR ($\ln(d\sigma_T/d\varepsilon_T)$) decreased rapidly in stage A ($\varepsilon<0.030$), followed by a period of slow decrease in stage B ($0.030<\varepsilon<0.172$) and then a rapid decrease corresponding to the necking region in stage D ($0.172<\varepsilon<0.268$). The $\ln(d\sigma_T/d\varepsilon_T)$ of the CG structure decreased relatively slowly

compared to the NG/UFG structure in stage A ($\varepsilon<0.022$), but maintained a near similar rate of decrement before reaching the valley level of stage B ($\varepsilon=0.195$). This was followed by a small but gradual increase of $\ln(d\sigma_T/d\varepsilon_T)$ to attain the minor peak of stage C ($\varepsilon=0.339$). This behavior was not observed in the NG/UFG structure. Lastly, the onset of necking in CG steel until fracture was characterized by stage D ($0.339<\varepsilon<0.461$). The main differences in the strain hardening behavior of NG/UFG and CG steels are summarized below:

(a) In stage A, the SHR decreased rapidly in the case of NG/UFG steel compared to the CG steel. Also, the NG/UFG steel had a wider SHR ($\ln(d\sigma_T/d\varepsilon_T)$) range and considerable strain in stage A; the corresponding decrease in SHR was gradual and characterized by a slower decrease with strain.

(b) Both structures experienced a small decrease in SHR in stage B at nearly similar $\ln(d\sigma_T/d\varepsilon_T)$.

(c) Stage C was absent in NG/UFG steel, whereas there was presence of a small stage C in CG steel.

(d) Stage D in the CG structure occurred at a higher strain, obviously as a result of greater elongation.

The plastic strain range for NG/UFG and CG steels based on C-J analysis is presented in Table 3 and the maximum and minimum SHR for the different stages are presented in Table 4.

Table 3. Plastic strain for different stages observed in NG/UFG and CG steels based on the C-J analysis.

Sample	Stage A	Stage B	Stage C	Stage D
NG/UFG	$\varepsilon < 0.030$	$0.030 < \varepsilon < 0.172$	-	$0.172 < \varepsilon < 0.268$
CG	$\varepsilon < 0.022$	$0.022 < \varepsilon < 0.195$	$0.195 < \varepsilon < 0.339$	$0.339 < \varepsilon < 0.461$

Table 4. Maximum and minimum strain hardening rates for different stages observed in NG/UFG and CG steels.

Sample	SHR in stage B, MPa		SHR in stage C, MPa		SHR in stage D, MPa	
	Max	Min	Max	Min	Max	Min
NG/UFG	1858	1464	-	-	1464	0
CG	2510	1089	1134	1089	1134	0

3.3 Deformation structure

Illustrations of post mortem electron microscopy of the tensile deformed region in the vicinity of the fracture surface are presented in Figs. 5 and 6 for the NG/UFG and CG steels, respectively. For the NG/UFG structure, a number of representative electron micrographs are presented, which clearly depict formation of stacking faults (SF) and nanoscale twins during tensile deformation (Fig. 5). A number of intersecting nanoscale twins were detected along with the stacking faults in various regions. The formation of stacking faults is contemplated as a precursor to the occurrence of twinning. In striking contrast, strain-induced martensite was observed in the case of CG steel (Fig. 6). Prior to tensile deformation, the fraction of martensite in the steel was very small (~2.3 %). However, a significant strain induced martensite (65.5 %) formed in the microstructure following tensile testing, measured near the fracture end. Thus, we can unambiguously conclude that there was a distinct change in the deformation mechanism, when the grain structure was refined from CG to NG/UFG structure.

Figures 5 and 6 confirm that the deformation mechanism was altered from stacking faults and nanoscale twinning in the NG/UFG structure (Figure 5) to strain-induced martensitic transformation in the CG structure (Figure 6). In the NG/UFG structure, twinning contributed to good ductility, while in the CG counterpart, the high ductility was associated with the formation of strain-induced martensite.

4. Discussion

The deformation-induced martensite is achieved by the cooperative shear movement of atoms, where the applied stress aids the transformation and the role of plastic strain on the martensitic transformation is significantly more complicated [40]. It is clear from Figs. 5 and 6 that the

deformation mechanism changed from nanoscale twinning in the NG/UFG structure to strain-induced martensitic transformation in the CG structure, and this transition was closely associated with the increase of strain energy and stability of austenite with the decrease of the grain size, as discussed below..

Stage A in C-J analysis plots (Figs. 3 and 4) can be characterized as the elastic deformation stage with dislocation nucleation [38, 41]. It is pertinent to indicate that slip or dislocation glide is precursor to any deformation mechanism (twinning or strain induced martensite) and is a major mechanism accommodating the strain. In stage A, the logarithmic value of SHR ($\ln(d\sigma_T/d\varepsilon_T)$) of NG/UFG steel was significantly greater than CG steel.

Stage B was characterized by a continuous decrease in SHR from 1858 to 1464 MPa (Table 4), and is attributed to the nucleation of stacking faults and twins in the NG/UFG steel. In the NG/UFG structure, emission of multiple partial dislocations promotes twin nucleation from grain boundaries. During this process, when a perfect dislocation in the matrix is stopped by an obstacle, such as a twin boundary, it dissociates into Frank sessile and Shockley partial dislocations ($\frac{1}{2}[\bar{1}01] \rightarrow \frac{1}{3}[\bar{1}\bar{1}1] + \frac{1}{6}[\bar{1}21]$) [42]. Stage B in the CG structure compromised of two sub-regions (I and II) of different slopes. The decrease of SHR in region I is slower, while in region II, the decrease occurs relatively rapidly, [38, 39, 41-45]. The SHR dropped from a maximum of 2510 MPa to about 1089 MPa in stage B for the CG steel, see Table 4. The accumulation of strain energy leads to an increase in the transformation of austenite to martensite with consequent increase in dislocation density, which consequently provides more nucleation sites for the new strain induced martensite and increases the strain hardening effect. Moreover, a high density of dislocations hinder the movement of partial Shockley dislocations.

In stage C, both the strain-induced transformation as well as generation of high dislocation density slightly increased the SHR of the CG structure from 1089 to 1134 MPa (Table 4). In contrast, stage C did not exist in the NG/UFG structure, because it just corresponded to nucleation rather than the growth of twins with increasing strain. Generally, twins tend to nucleate in the high-stress concentration regions, and the stress required for twins to nucleate is

far greater than the growth of twins. During the plastic deformation stage for the NG/UFG structure ($0.030<\varepsilon<0.172$), the formation of different twin configurations resulted in a significant increase in the twin density, thus hindering the glide of dislocations and providing the strain hardening effect [45]. Finally, necking (stage D) occurred beyond the endurance limit of the steel, resulting in a rapid decrease of SHR leading to fracture.

Considering that both mechanical twinning and strain-induced martensite formation contributed to the strain hardening effect, it can be inferred that the strain hardening characteristics associated with twinning and strain-induced martensite formation were similar. However, subtle differences were noticed between these two strain hardening mechanisms, due to the significant weighted average grain size difference between NG/UFG (350 nm) and CG structures (22 μm).

Although it is considered that grain size greatly controls the thermal stability of austenite, the impact of grain size on the mechanical stability of austenite continues to be unclear [46,47] and is revisited here. It is generally believed that the transformation of γ-austenite to α'-martensite leads to anisotropic strains in the neighboring untransformed austenite. Matsuoka et al. [46] suggested that when the grain size was large, 24 variants were equally obtained to minimize the total strain energy. However, when the grain size was equal to or smaller than the martensite lath width, for instance, in the case of NG/UFG structure, a majority of the variants of martensite are restricted to operate within an austenite grain because of the spatial restriction effect. Thus, during tensile straining, only a particular variant is selected for strain-induced martensitic transformation in the NG/UFG structure, where $<101>_{\alpha'}$ direction is parallel to the tensile direction [46]. In view of this reason, austenite is envisaged to transform to strain-induced martensite via a single variant. But the strain energy generated by martensitic transformation cannot be minimized by the limited variant transformation, leading to suppression of martensitic transformation in the NG/UFG structure.

In a recent study, different initial microstructures with various bimodal grain size distributions (BGSD) were obtained in a high Mn austenitic steel (TRIP/TWIP) through rolling at different

temperatures [48,49]. The corresponding room temperature mechanical properties and the related strain hardening behavior was assessed via tensile testing. The results indicated that in the microstructure with high grain size bimodality, the length and amplitude of rapid strain hardening region were greater, a behavior attributed to the higher capability to α'-martensite formation. Furthermore, different transformation paths were identified as the BGSD changed [50]. The austenite directly transformed to α'-martensite ($\gamma \rightarrow \alpha'$) in the case of the microstructure with lower BGSD. In contrast, nucleation occurred at the intersections of ε-martensite platelets in the case of the microstructure with higher BGSD. The co-existence of these transformation paths provided an extended transformation induced plasticity effect leading to higher elongation. In summary, the higher possibility of strain-induced transformation and twinning in coarser grains as compared to finer grains was observed to dictate the material work hardening potential during tensile deformation. The material characterized by more homogeneous grain size and low level of BGSD showed austenite to martensite transformation as the primary mechanism during tensile deformation at room temperature. In contrast, materials with bimodal grain size largely depicted the occurrence of mechanical twinning, which induced rapid hardening region and prompted work hardening behavior. The aforementioned effects were correlated to the length of work hardening region (dictated by twinning), and the magnitude of hardening rate (controlled by transformation of austenite to α' martensite.

In this study, the texture effect has not been determined, but a separate recent study carried out to understand the microstructure and properties of this Cu-bearing austenitic stainless steel revealed that the fully reverted CG structure had fully random orientation suggesting a very weak texture, though the grain size varied slightly due to a mixture of reversion-refined fine grains formed from deformation induced martensite and recrystallized grains formed from deformed austenite [18]. With lower reversion temperatures corresponding to NG structure, similar features were present with weak to very weak textures, but some large grains with numerous low angle grain boundaries were also present. However, no attempt has been made to exclude the effect of these features on the mechanical properties.

The mechanism of austenite stabilization induced by grain refinement can be discussed in terms of physical energy (equations 3-5) [50]. If austenite is transformed to martensite through a single variant mode, the increase of the elastic strain energy can be described by equation 6 [50].

$$\Delta E_v = \left(\frac{1}{2}\right) E_{\mathrm{I}} {\varepsilon_{\mathrm{I}}}^2 + \left(\frac{1}{2}\right) E_{\mathrm{II}} {\varepsilon_{\mathrm{II}}}^2 + \left(\frac{1}{2}\right) E_{\mathrm{III}} {\varepsilon_{\mathrm{III}}}^2 \quad (6)$$

where E and ε are Young's modulus and elastic strain in each lattice, respectively. The transformation of fcc γ-austenite into bcc α'-martensite experiences lattice displacement consisting of two types of atomic movement: (I) ~36% shear deformation along the $[\bar{1}10]$ direction and (II) anisotropic deformation with a volume expansion of ~4.5%. This volume expansion includes ~13.9% (ε_1) expansion along the $[001]$ direction, ~7.0% (ε_2) contraction along the $[\bar{1}10]$ direction and ~1.4% (ε_3) contraction along with the $[\bar{1}\bar{1}0]$ direction, and the corresponding Young's moduli are 132.1 GPa (E_{I}), 220.8 GPa (E_{II}), and 220.8 GPa (E_{III}), respectively [50]. The increase of elastic strain energy calculated using equation 3 is ~1839 MJ/m^3. Given that the maximum displacement occurs along the $[001]_{\mathrm{bcc}}$ direction, it can be assumed that the nucleation of thin-plate martensite would minimize the elastic strain energy. Moreover, lattice strain is controlled by austenitic grain size. Thus, equation 6 can be modified to:

$$\Delta E_v = \left(\frac{1}{2}\right) E_{\mathrm{I}} {\varepsilon_{\mathrm{I}}}^2 (\frac{x}{d})^2 + \left(\frac{1}{2}\right) E_{\mathrm{II}} {\varepsilon_{\mathrm{II}}}^2 (\frac{x}{d}) + \left(\frac{1}{2}\right) E_{\mathrm{III}} {\varepsilon_{\mathrm{III}}}^2 (\frac{x}{d}) \quad (7)$$

where x is the thickness of thin-plate martensite, and d is austenitic grain size. Substituting the value of Young's modulus and strain in equation 7, the increase of elastic strain can be obtained as [50]:

$$\Delta E_v = 1276.1 \left(\frac{x}{d}\right)^2 + 562.6 \left(\frac{x}{d}\right) \quad (8)$$

The elastic strain energy (ΔE_v) as a function of grain size (d) for martensite nucleation is plotted in Fig. 7 for the martensite lath thickness of 0.2 μm. It is noted that when the grain size is smaller than ~1 μm, the elastic strain energy increases rapidly. For the NG/UFG structure, the weighted average grain size of 350 nm results in a significantly high elastic strain energy of ~850 MJ/m^3.

In contrast, the CG structure had a relatively low elastic strain energy of ~5 MJ/m^3 because of larger weighted average grain size (22 μm). Thus, the possibility of multi-variant transformation to occur is restricted and the transformation of strain-induced martensite was significantly suppressed in the NG/UFG structure.

5. Conclusions

The significance of grain refinement on the strain hardening behavior and TWIP/TRIP deformation mechanisms in Cu-bearing NG/UFG and CG antimicrobial stainless steels was eluciadeted on the basis of Crussard-Jaoul analysis of tensile deformation data of the steels and post-mortem electron microscopy of the strained region near the fractured ends. The plastic deformation process can be divided into four stages based on the change in SHR. Grain refinement strongly affected the strain hardening ability. The good ductility and high SHR of the NG/UFG structure is attributed to the occurrence of mechanical twinning, whereas the strain-induced martensite transformation was the underlying reason for the excellent strain hardening ability and ductility of the CG structure. Both mechanisms were effective in inhibiting the movement of dislocations. In nano-grained austenitic stainless steel with grain size less than ~1 μm, the high strain energy and austenitic stability significantly reduced the possibility of multi-variant transformation and led to the suppression of strain-induced martensitic transformation. Extensive grain refinement due to reversion annealing was responsible for the transition of the deformation mechanism from a strain-induced martensitic transformation in the CG structure to mechanical twinning in the NG/UFG structure, besides manifestation of a large number of stacking faults, a precursor to the occurrence of twinning.

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